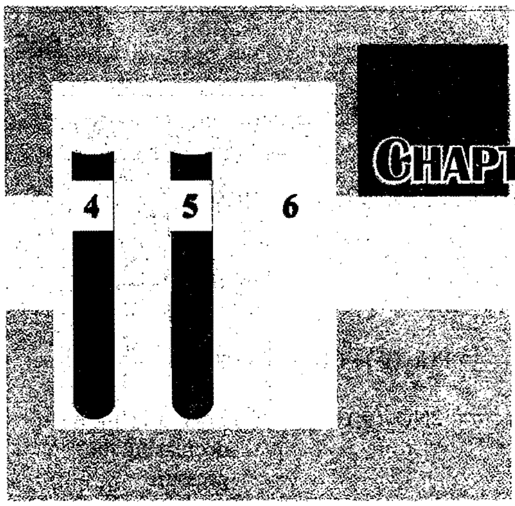


CHAPTER 10

IONIC EQUILIBRIUM

10.1 INTRODUCTION

The compounds which give ions either in molten state or in solution are called electrolytes. In the solid state they are bad conductors, but become good conductors either in the molten state or in solution.

There are two types of electrolytes:

(1) Strong electrolytes: These electrolytes are almost completely ionised when dissolved in a polar medium like water. In solution they are excellent conductors, *e.g.*, HNO_3, HCl, KOH, NaOH, etc. Their degree of ionization is high and approaches unity.

(2) Weak electrolytes: These are not completely ionized when dissolved in a polar solvent and they behave as poor conductors of electricity, *e.g.*, CH_3COOH, H_3PO_4, H_3BO_3, NH_4OH, etc. Equilibrium between ions and unionised molecules is established in solution; *e.g.*,

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

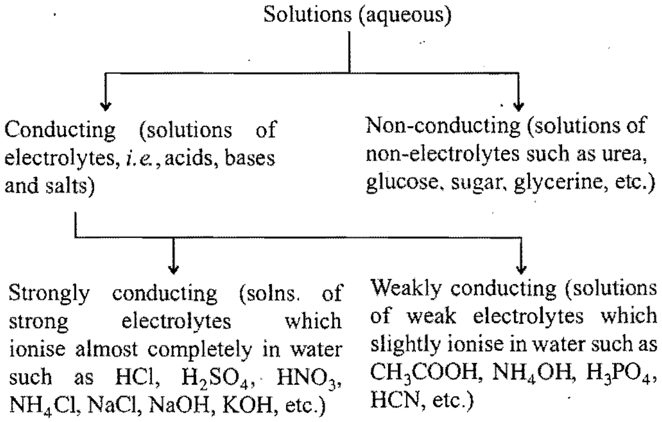
The above equilibrium is termed as ionic equilibrium. Degree of ionization of weak electrolytes is much less than unity.

Degree of ionization 'α' may be defined as a fraction of total number of molecules of an electrolyte which dissociate into ions.

$$\alpha = \frac{\%\text{ ionization}}{100}$$

$$= \frac{\text{Number of molecules dissociated as ions}}{\text{Total number of molecules of electrolyte dissolved}}$$

The following classification of electrolytes is based on their behaviour in a particular solvent, *i.e.*, water.



Solutions (aqueous)

Conducting (solutions of electrolytes, *i.e.*, acids, bases and salts)

Non-conducting (solutions of non-electrolytes such as urea, glucose, sugar, glycerine, etc.)

Strongly conducting (solns. of strong electrolytes which ionise almost completely in water such as HCl, H_2SO_4, HNO_3, NH_4Cl, NaCl, NaOH, KOH, etc.)

Weakly conducting (solutions of weak electrolytes which slightly ionise in water such as CH_3COOH, NH_4OH, H_3PO_4, HCN, etc.)

However, an electrolyte may behave as a strong one in aqueous solution, but it may behave as a weak one in another solvent. For example, sodium chloride behaves as a strong electrolyte and acetic acid as a weak electrolyte when dissolved in water but their conducting abilities are comparable in liquid ammonia solvent.

10.2 OSTWALD'S DILUTION LAW

According to Arrhenius theory of electrolytic dissociation, the molecules of an electrolyte in solution are constantly splitting up into ions and the ions are constantly reuniting to form unionized molecules. Therefore, a dynamic equilibrium exists between ions and unionized molecules of the electrolyte in solution. It was pointed out by Ostwald that like chemical equilibrium, **law of mass action** can be applied to such systems also.

Consider a binary electrolyte AB which dissociates into A^+ and B^- ions and the equilibrium state is represented by the equation:

	AB	$\rightleftharpoons$	A^+	$+$	B^-
Initially $t = 0$	C		0		0
At equilibrium	$C(1-\alpha)$		$C\alpha$		$C\alpha$

So, dissociation constant may be given as:

$$K = \frac{[A^+][B^-]}{[AB]} = \frac{C\alpha \times C\alpha}{C(1-\alpha)}$$

$$= \frac{C\alpha^2}{(1-\alpha)} \qquad \dots \text{(i)}$$

For very weak electrolytes,

$$\alpha <<< 1, (1-\alpha) \approx 1$$

$$\therefore \qquad K = C\alpha^2$$

$$\alpha = \sqrt{K/C} \qquad \dots \text{(ii)}$$

Concentration of any ion $= C\alpha = \sqrt{CK}$.

From equation (ii), it is clear that degree of ionization increases on dilution.

Thus, **degree of dissociation of a weak electrolyte is proportional to the square root of dilution.**

Limitations of Ostwald's dilution law: The law holds good only for weak electrolytes and fails completely in the case of strong electrolytes. The value of 'α' is determined by conductivity measurements by applying the formula Λ/Λ_∞. The value of 'α' determined at various dilutions of an electrolyte when substituted in eq. (i) gives a constant value of K only in the case of weak electrolytes like CH_3COOH, NH_4OH, etc. The cause of failure of Ostwald's dilution law in the case of strong electrolytes is due to the following factors:

(i) The law is based on the fact that only a portion of the electrolyte is dissociated into ions at ordinary dilution and completely at infinite dilution. Strong electrolytes are almost completely ionised at all dilutions and Λ/Λ_∞ does not give accurate value of 'α'.

(ii) When concentration of the ions is very high, the presence of charges on the ions appreciably affects the equilibrium. Hence, law of mass action in its simple form cannot be strictly applied in the case of strong electrolytes.

SOME SOLVED EXAMPLES

Example 1. *A 0.01 M solution of acetic acid is 5% ionised at 25° C. Calculate its dissociation constant.*

Solution: According to Ostwald's dilution law,

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

$$\alpha = 0.05, \quad V = \frac{1}{0.01} = 100 \text{ litre}$$

Hence,
$$K_a = \frac{0.05 \times 0.05}{(1-0.05)100} = 2.63 \times 10^{-5}$$

Example 2. *Calculate the H^+ ion concentration of a 0.01 N weak monobasic acid. The value of dissociation constant is 4.0×10^{-10}.*

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

Applying Ostwald's dilution law for a weak acid,

$$\alpha = \sqrt{K_a V}$$

$$K_a = 4.0 \times 10^{-10}, \quad V = \frac{1}{0.01} = 100 \text{ litre}$$

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

Concentration of hydrogen ions

$$= \frac{\alpha}{V} = \frac{2 \times 10^{-4}}{100} = 2 \times 10^{-6} \text{ mol L}^{-1}$$

or concentration of hydrogen ions

$$= \sqrt{CK} = \sqrt{0.01 \times 4 \times 10^{-10}} = 2 \times 10^{-6} \text{ mol L}^{-1}$$

Example 3. *The concentration of H^+ ions in 0.10 M solution of a weak acid is 1.0×10^{-5} mol L^{-1}. Calculate the dissociation constant of the acid.*

Solution:	HA	$\rightleftharpoons$	H^+	$+$	A^-
Initial concentration	0.1		0		0
Equilibrium concentration (mol L^{-1})	$0.1 - 1.0 \times 10^{-5}$		1.0×10^{-5}		1.0×10^{-5}

$[HA]$ can be taken as 0.1 M as 1.0×10^{-5} is very small.

Applying law of mass action,

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{1.0 \times 10^{-5} \times 1.0 \times 10^{-5}}{0.10}$$

$$= 1 \times 10^{-9}$$

Example 4. *What will be the dissociation constant of 0.1N aqueous ammonia solution in terms of degree of dissociation 'α'? What will be the value if the concentration is 0.01N?*

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

At equilibrium	$(1-\alpha)$	α	α

Since, the solution is 0.1 N,

$$V = \frac{1}{0.1} = 10 \text{ litre}$$

$$[NH_4OH] = \frac{(1-\alpha)}{10}, \; [NH_4^+] = \frac{\alpha}{10} \text{ and } [OH^-] = \frac{\alpha}{10}$$

Applying law of mass action,

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_4OH]} = \frac{\frac{\alpha}{10} \times \frac{\alpha}{10}}{\frac{1-\alpha}{10}} = \frac{\alpha^2}{10(1-\alpha)}$$

For 0.01 N solution, K_b remains the same at the same temperature but degree of dissociation value becomes different.

Example 5. *A 0.0128 N solution of acetic acid has $\Lambda = 14$ mho equiv^{-1} and $\Lambda_\infty = 391$ mho eq^{-1} at 25°C. Calculate the dissociation constant of the acid.*

Solution: Degree of dissociation,

$$\alpha = \frac{\Lambda}{\Lambda_\infty} = \frac{14}{391} = 3.58\times10^{-2}$$

$$[1-\alpha \longrightarrow 1 \text{ as } \alpha \text{ is very small}]$$

Now applying Ostwald's dilution law,

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

$$\alpha = 3.58\times10^{-2} \quad \text{and} \quad V = \frac{1}{0.0128}\ \text{litre}$$

So, $K_a = 3.58\times10^{-2}\times3.58\times10^{-2}\times0.0128 = 1.64\times10^{-5}$

10.3 COMMON ION EFFECT

Let AB be the weak electrolyte. Considering its dissociation,

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

and applying law of mass action, we have

$$K = \frac{[A^+][B^-]}{[AB]}$$

The equilibrium constant, K, has a definite value at any given temperature. If now another electrolyte furnishing the A^+ and B^- ions be added to the above solution, it will increase the concentration of either A^+ ions or B^- ions (whichever has been added) and in order that K may remain constant, the concentration of AB must increase, *i.e.*, the equilibrium will shift to the left hand side.

In other words, **the degree of dissociation of an electrolyte (weak) is suppressed by the addition of another electrolyte (strong) containing a common ion.** This is termed as **common ion effect.** Acetic acid is a weak electrolyte and its ionisation is suppressed in presence of a strong acid (H^+ ion as common ion) or a strong salt like sodium acetate (acetate ion as common ion). Similarly, the addition of NH_4Cl or NaOH to NH_4OH solution will suppress the dissociation of NH_4OH due to common ion either NH_4^+ or OH^-.

As a result of common ion effect, the concentration of the ion not in common in two electrolytes, is decreased. The use of this phenomenon is made in qualitative analysis to adjust concentration of S^{2-} ions in second group and OH^- ion concentration in third group of analysis.

SOME SOLVED EXAMPLES

Example 6. *The ionisation constant of HCN is* 4×10^{-10}. *Calculate the concentration of hydrogen ions in* 0.2 *M solution of HCN containing* 1 *mol* L^{-1} *of KCN.*

Solution: The dissociation of HCN is represented as

$$HCN \rightleftharpoons H^+ + CN^-$$

Applying law of mass action,

$$K_a = \frac{[H^+][CN^-]}{[HCN]} \quad \text{or} \quad [H^+] = \frac{K_a[HCN]}{[CN^-]}$$

In presence of strong electrolyte, the total CN^- concentration comes from KCN which undergoes complete dissociation. It is further assumed that dissociation of HCN is very-very small and the concentration of HCN can be taken as the concentration of undissociated HCN.

Thus, $[HCN] = 0.2\,M$ and $[CN^-] = 1\,M$

Putting these values in the expression

$$[H^+] = \frac{K_b[HCN]}{[CN^-]} = \frac{4\times10^{-10}\times0.2}{1} = 8\times10^{-11}\ \text{mol L}^{-1}$$

Note: When KCN is not present, the $[H^+]$ concentration is equal to $\sqrt{CK}$, *i.e.*, $\sqrt{0.2\times4\times10^{-10}} = 8.94\times10^{-6}$ mol L^{-1}. This shows that concentration of H^+ ions falls considerably when KCN is added to HCN solution.

Example 7. *Determine the concentration of hydroxyl ions in* 0.4 *M* NH_4OH *solution having* (*i*) *no ammonium chloride and* (*ii*) 5.35 *g of* NH_4Cl *in a litre of the solution. Ionisation constant of* NH_4OH *is* 1.8×10^{-5}.

Solution: (i) Let 'α' be the degree of dissociation of NH_4OH in absence of NH_4Cl.

$$\alpha = \sqrt{\frac{K_b}{C}}$$

So, $$[OH^-] = C\alpha = \sqrt{K_bC} = \sqrt{1.8\times10^{-5}\times0.4}$$
$$= 2.68\times10^{-3}\ \text{mol L}^{-1}$$

(ii) In presence of NH_4Cl,

$$[NH_4^+] = \frac{5.35}{53.5} = 0.1M \quad \text{and} \quad [NH_4OH] = 0.4\,M$$

So, $$[OH^-] = \frac{K_b[NH_4OH]}{[NH_4^+]} = \frac{1.8\times10^{-5}\times0.4}{0.1}$$
$$= 7.2\times10^{-5}\ \text{mol L}^{-1}$$

Example 8. *When* 0.100 *mole of ammonia,* NH_3, *is dissolved in sufficient water to make* 1.0 *L of solution, the solution is found to have a hydroxide ion concentration of* 1.34×10^{-3} *M. Calculate* K_b *for ammonia.*

Solution:

$$\begin{array}{lccc} & NH_3 & + H_2O \rightleftharpoons & NH_4^+ & + OH^- \\ \text{At equilibrium} & (0.100 - 1.34\times10^{-3})\,M & & 1.34\times10^{-3}\,M & 1.34\times10^{-3}\,M \\ & = 0.09866\,M & & & \end{array}$$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{1.34\times10^{-3}\times1.34\times10^{-3}}{0.09866} = 1.8199\times10^{-5}$$

Example 9. K_a *for HA is* 4.9×10^{-8}. *After making the necessary approximation, calculate for its decimolar solution*

(*a*) % *dissociation*

(*b*) H^+ *ion concentration.*

Solution: (a) For a weak electrolyte,

$$\alpha = \sqrt{\frac{K_a}{C}} = \sqrt{\frac{4.9\times10^{-8}}{0.1}} = 7\times10^{-4}$$

$$\%\,\text{dissociation} = 100 \times \alpha = 100 \times 7 \times 10^{-4}$$
$$= 7 \times 10^{-2}$$

(b)
$$\begin{array}{cccc} HA & \rightleftharpoons & H^+ & + & A^- \\ C\,(1-\alpha) & & C\alpha & & C\alpha \end{array}$$
$$[\mathrm{H^+}] = C \times \alpha = 0.1 \times 7 \times 10^{-4} = 7 \times 10^{-5}\ \text{mol L}^{-1}$$

Example 10. *Nicotinic acid* ($K_a = 1.4 \times 10^{-5}$) *is represented by the formula HNiC. Calculate its per cent dissociation in a solution which contains* 0.10 *mole of nicotinic acid per* 2 *litre of solution.* **(IIT 1993)**

Solution: Initial concentration of the nicotinic acid $= \frac{0.10}{2} = 0.05\ \text{mol L}^{-1}$

$$\begin{array}{lccccc} & \mathrm{HNiC} & \rightleftharpoons & \mathrm{H^+} & + & \mathrm{NiC^-} \\ \text{Equilibrium conc.} & (0.05-x) & & x & & x \end{array}$$

As x is very small, $(0.05-x)$ can be taken as 0.05

$$K_a = \frac{[\mathrm{H^+}][\mathrm{NiC^-}]}{[\mathrm{HNiC}]} = \frac{x \times x}{0.05}$$

or $$x^2 = (0.05) \times (1.4 \times 10^{-5})$$

or $$x = 0.83 \times 10^{-3}\ \text{mol L}^{-1}$$

$$\%\,\text{dissociation} = \frac{0.83 \times 10^{-3}}{0.05} \times 100 = 1.66$$

Alternative method: Let α be the degree of dissociation

$$\begin{array}{lccccc} & \mathrm{HNiC} & \rightleftharpoons & \mathrm{H^+} & + & \mathrm{NiC^-} \\ \text{At equilibrium} & 0.05\,(1-\alpha) & & 0.05\alpha & & 0.05\alpha \end{array}$$

$$K_a = \frac{0.05\alpha \times 0.05\alpha}{0.05\,(1-\alpha)}$$

As α is very small, $(1-\alpha) \longrightarrow 1$.

So, $$1.4 \times 10^{-5} = 0.05\alpha^2$$

or $$\alpha = \sqrt{\frac{1.4 \times 10^{-5}}{0.05}} = 1.67 \times 10^{-2}$$

$$\text{Per cent dissociation} = 100 \times \alpha = 100 \times 1.67 \times 10^{-2}$$
$$= 1.67$$

Example 11. *At 30°C, the degree of dissociation of* $0.066\,M$ *HA is* 0.0145. *What would be the degree of dissociation of* $0.02\,M$ *solution of the acid at the same temperature?*

Solution: Let the ionisation constant of the acid be K_a. Degree of dissociation at $0.066\,M$ concentration = 0.0145.

Applying $$\alpha = \sqrt{\frac{K_a}{C}}$$

$$0.0145 = \sqrt{\frac{K_a}{0.066}} \quad \text{... (i)}$$

Let the degree of dissociation of the acid at 0.02 M concentration be α_1.

$$\alpha_1 = \sqrt{\frac{K_a}{0.02}} \quad \text{... (ii)}$$

Dividing eq. (ii) by eq. (i),

$$\frac{\alpha_1}{0.0145} = \sqrt{\frac{0.066}{0.02}} = 1.8166$$

or $$\alpha_1 = 0.0145 \times 1.8166 = 0.0263$$

Example 12. *A solution contains* $0.1\,M$ H_2S *and* $0.3\,M$ *HCl. Calculate the concentration of* S^{2-} *and* HS^- *ions in solution. Given* K_{a_1} *and* K_{a_2} *for* H_2S *are* 10^{-7} *and* 1.3×10^{-13} *respectively.* **(IIT 1992)**

Solution: $$\mathrm{H_2S} \rightleftharpoons \mathrm{H^+} + \mathrm{HS^-}$$

$$K_{a_1} = \frac{[\mathrm{H^+}][\mathrm{HS^-}]}{[\mathrm{H_2S}]} \quad \text{... (i)}$$

Further $$\mathrm{HS^-} = \mathrm{H^+} + \mathrm{S^{2-}}$$

$$K_{a_2} = \frac{[\mathrm{H^+}][\mathrm{S^{2-}}]}{[\mathrm{HS^-}]} \quad \text{... (ii)}$$

Multiplying both the equations

$$K_{a_1} \times K_{a_2} = \frac{[\mathrm{H^+}]^2[\mathrm{S^{2-}}]}{[\mathrm{H_2S}]}$$

Due to common ion, the ionisation of H_2S is suppressed and the $[H^+]$ in solution is due to the presence of 0.3 M HCl.

$$[\mathrm{S^{2-}}] = \frac{K_{a_1} \times K_{a_2}[\mathrm{H_2S}]}{[\mathrm{H^+}]^2} = \frac{1.0 \times 10^{-7} \times 1.3 \times 10^{-13} \times (0.1)}{(0.3)^2}$$
$$= 1.44 \times 10^{-20}\ M$$

Putting the value of $[S^{2-}]$ in eq. (ii),

$$1.3 \times 10^{-13} = \frac{0.3 \times 1.44 \times 10^{-20}}{[\mathrm{HS^-}]}$$

or $$[\mathrm{HS^-}] = \frac{0.3 \times 1.44 \times 10^{-20}}{1.3 \times 10^{-13}} = 3.3 \times 10^{-8}\ M$$

Example 13. *What is the* H^+ *ion concentration of a solution known to contain* 0.1*g mole of* CH_3COONH_4 *in one litre of* $0.1\,M$ CH_3COOH*? Assume effective ionisation of ammonium acetate is* 80%. K_a *for acetic acid is* 1.8×10^{-5}.

Solution: $$\begin{array}{ccccc} \mathrm{CH_3COOH} & \rightleftharpoons & \mathrm{CH_3COO^-} & + & \mathrm{H^+} \\ (0.1-x) & & x & & x \end{array}$$

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

The solution also contains CH_3COONH_4 which is 80% dissociated, *i.e.*, α = 0.8. Thus, the acetate concentration provided by $0.1\,M$ $CH_3COONH_4 = 0.1 \times 0.8 = 0.08\,M$

Total $$[\mathrm{CH_3COO^-}] = (0.08 + x)\,M$$

So, $$K_a = \frac{(0.08 + x)x}{(0.1 - x)}$$

As x is very small, $(0.1 - x) \longrightarrow 0.1$ and neglecting x^2,

$$K_a = \frac{0.08x}{0.1}$$

or $$1.8\times10^{-5}\times0.1=0.08x$$

or $$x=[\mathrm{H}^+]=\frac{1.8\times10^{-5}\times0.1}{0.08}=2.25\times10^{-5}\ \text{mol L}^{-1}$$

Example 14. *Ostwald obtained the following table by determining the equivalent conductivities containing one gram equivalent of acetic acid in V litre. If the equivalent conductivity of acetic acid at infinite dilution be* 364, *show that the results are in agreement with Ostwald's law.*

Volume in litre (V)	*Equivalent conductivity*
8	4.34
64	12.09
128	16.99

Solution: Degree of dissociation, $\alpha=\frac{\Lambda_V}{\Lambda_\infty}$

(i) $$\alpha_1=\frac{4.34}{364}=0.0119$$

(ii) $$\alpha_2=\frac{12.09}{364}=0.0332$$

(iii) $$\alpha_3=\frac{16.99}{364}=0.0467$$

Now applying Ostwald's dilution law,

(i) $$K_a=\frac{\alpha_1^2}{V_1}=\frac{0.0119\times0.0119}{8}=1.77\times10^{-5}$$

(ii) $$K_a=\frac{\alpha_2^2}{V_2}=\frac{0.0332\times0.0332}{64}=1.72\times10^{-5}$$

(iii) $$K_a=\frac{\alpha_3^2}{V_3}=\frac{0.0467\times0.0467}{128}=1.70\times10^{-5}$$

The values of K_a are nearly the same which show the validity of Ostwald's dilution law.

Example 15. *Calculate the dissociation constant of* $H_2C_2O_4$ *(oxalic acid) if* 0.02 *M solution is* 2% *dissociated.*

Solution:
$$\underset{C(1-\alpha)}{\mathrm{H_2C_2O_4}} \rightleftharpoons \underset{2C\alpha}{2\mathrm{H}^+} + \underset{C\alpha}{\mathrm{C_2O_4^{2-}}}$$

$$K_a=\frac{[\mathrm{H}^+]^2[\mathrm{C_2O_4^{2-}}]}{[\mathrm{H_2C_2O_4}]}$$
$$=\frac{(2C\alpha)^2\times(C\alpha)}{C(1-\alpha)}$$
$$=\frac{4C^2\alpha^3}{1-\alpha}\quad[1-\alpha\to1\text{ as }\alpha\text{ is small}]$$
$$=4C^2\alpha^3$$
$$=4\times0.02\times0.02\times(0.02)^3$$
$$=1.28\times10^{-8}$$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

1. A monoprotic acid in 0.1 M solution ionizes to 0.001%. Its ionisation constant is:
(a) 1×10^{-3} (b) 1×10^{-6} (c) 1×10^{-8} (d) 1×10^{-11}
[Ans. (d)]
[Hint: $\alpha=\sqrt{\frac{K_a}{C}}$ or $K_a=C\alpha^2=0.1\times\left(\frac{0.001}{100}\right)^2$
$=1\times10^{-11}$]

2. The hydrogen ion concentration in mol/dm^3 in 0.2 M solution of weak acid, HA ($K_a=2\times10^{-5}$) is close to:
(a) 2×10^{-5} (b) 2×10^{-4} (c) 2×10^{-3} (d) 2×10^{-2}
[Ans. (c)]
[Hint: $[\mathrm{H_3O^+}]=\sqrt{CK_a}=\sqrt{0.2\times2\times10^{-5}}=2\times10^{-3}$]

3. Autoprotolysis constant of NH_3 is:
(a) $[\mathrm{NH_4^+}][\mathrm{NH_3}]$ (b) $[\mathrm{NH_2^-}][\mathrm{NH_3}]$
(c) $[\mathrm{NH_4^+}][\mathrm{NH_2^-}]$ (d) $\frac{[\mathrm{NH_4^+}]}{[\mathrm{NH_2^-}]}$
[Ans. (c)]
[Hint: Autoprotolysis of NH_3 takes place as:
$$2\mathrm{NH_3}\rightleftharpoons\mathrm{NH_4^+}+\mathrm{NH_2^-}$$
∴ Autoprotolysis constant = $[\mathrm{NH_4^+}][\mathrm{NH_2^-}]$]

4. The degree of ionization of an acid HA is 0.00001 at 0.1 M concentration. Its dissociation constant will be:
(a) 10^{-9} (b) 10^{-8} (c) 10^{-11} (d) 10^{-7}
[Ans. (c)]
[Hint: For monoprotic acid HA:
$K_a=C\alpha^2=0.1\times(10^{-5})^2=10^{-11}$]

5. The first and second dissociation constants of an acid, H$_2A$, are 1.0×10^{-5} and 5.0×10^{-10} respectively. The overall dissociation constant of the acid will be: **(AIEEE 2007)**
(a) 0.2×10^5 (b) 5.0×10^{-5}
(c) 5.0×10^{-15} (d) 5.0×10^{15}
[Ans. (c)]
[Hint: $K_a=K_{a_1}\times K_{a_2}$
$=1\times10^{-5}\times5\times10^{-10}$
$=5\times10^{-15}$]

10.4 SOLUBILITY PRODUCT

If to a given amount of solvent at a particular temperature, a solute is added gradually in increasing amounts, a stage is reached when some of the solute remains undissolved, no matter how long we wait or how vigorously we stir. The solution is then said to be saturated. **A solution which remains in contact with undissolved solute is said to be saturated.** At saturated stage, the quantity of the solute dissolved is always constant for the given amount of a particular solvent at a definite temperature.

In case, the solute is an electrolyte, its ionisation occurs in solution and degree of dissociation depends on the concentration of dissolved electrolyte at a particular temperature. Thus, in a saturated solution of an electrolyte two equilibria exist and can be represented as:

$$\underset{\text{Solid}}{AB}\rightleftharpoons\underset{\substack{\text{Unionised}\\\text{(Dissolved)}}}{AB}\rightleftharpoons\underbrace{A^++B^-}_{\text{Ions}}$$

Applying the law of mass action to the ionic equilibrium,

$$\frac{[A^+][B^-]}{[AB]} = K$$

Since, the solution is saturated, the concentration of unionised molecules of the electrolyte is constant at a particular temperature, *i.e.*, $[AB] = K' =$ constant.

Hence, $[A^+][B^-] = K[AB] = KK' = K_s$ (constant)

K_s is termed as the solubility product. It is defined as **the product of the concentration of ions in a saturated solution of an electrolyte at a given temperature.**

Consider, in general, the electrolyte of the type A_xB_y which is dissociated as:

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

Applying law of mass action,

$$\frac{[A^{y+}]^x[B^{x-}]^y}{[A_xB_y]} = K$$

When the solution is saturated,

$$[A_xB_y] = K' \text{ (constant)}$$

or $$[A^{y+}]^x[B^{x-}]^y = K[A_xB_y] = KK' = K_s \text{ (constant)}$$

Thus, solubility product is defined as **the product of concentrations of the ions raised to a power equal to the number of times the ions occur in the equation representing the dissociation of the electrolyte at a given temperature when the solution is saturated.**

[**Note:** Solubility product is not the ionic product under all conditions but only when the solution is saturated.]

Different Expressions for Solubility Products

(i) Electrolyte of the type AB: Its ionisation is represented as:

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

Thus, $K_s = [A^+][B^-]$

$$AgCl \rightleftharpoons Ag^+ + Cl^-; \quad K_s = [Ag^+][Cl^-]$$

$$BaSO_4 \rightleftharpoons Ba^{2+} + SO_4^{2-}; \quad K_s = [Ba^{2+}][SO_4^{2-}]$$

(ii) Electrolyte of the type AB_2: Its ionisation is represented as:

$$AB_2 \rightleftharpoons A^{2+} + 2B^-$$

Thus, $K_s = [A^{2+}][B^-]^2$

$$PbCl_2 \rightleftharpoons Pb^{2+} + 2Cl^-; \quad K_s = [Pb^{2+}][Cl^-]^2$$

$$CaF_2 \rightleftharpoons Ca^{2+} + 2F^-; \quad K_s = [Ca^{2+}][F^-]^2$$

(iii) Electrolyte of the type A_2B: Its ionisation is represented as:

$$A_2B \rightleftharpoons 2A^+ + B^{2-}$$

Thus, $K_s = [A^+]^2[B^{2-}]$

$$Ag_2CrO_4 \rightleftharpoons 2Ag^+ + CrO_4^{2-}; \quad K_s = [Ag^+]^2[CrO_4^{2-}]$$

$$H_2S \rightleftharpoons 2H^+ + S^{2-}; \quad K_s = [H^+]^2[S^{2-}]$$

(iv) Electrolyte of the type A_2B_3: Its ionisation is represented as:

$$A_2B_3 \rightleftharpoons 2A^{3+} + 3B^{2-}$$

Thus, $K_s = [A^{3+}]^2[B^{2-}]^3$

$$As_2S_3 \rightleftharpoons 2As^{3+} + 3S^{2-}; \quad K_s = [As^{3+}]^2[S^{2-}]^3$$

$$Sb_2S_3 \rightleftharpoons 2Sb^{3+} + 3S^{2-}; \quad K_s = [Sb^{3+}]^2[S^{2-}]^3$$

(v) Electrolyte of the type AB_3: Its ionisation is represented as:

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

Thus, $K_s = [A^{3+}][B^-]^3$

$$Fe(OH)_3 \rightleftharpoons Fe^{3+} + 3OH^-; \quad K_s = [Fe^{3+}][OH^-]^3$$

$$AlI_3 \rightleftharpoons Al^{3+} + 3I^-; \quad K_s = [Al^{3+}][I^-]^3$$

Solubility product of a weak electrolyte: Let degree of ionisation of weak electrolyte A_mB_n be 'α'.

$$\begin{array}{llll} & A_mB_n & \rightleftharpoons mA^{n+} & + nB^{m-} \\ t = 0 & S & 0 & 0 \\ t_{eq} & S - S\alpha & mS\alpha & nS\alpha \end{array}$$

$$K_{sp} = [A^{n+}]^m[B^{m-}]^n$$

$$= [mS\alpha]^m[nS\alpha]^n$$

$$K_{sp} = m^m n^n (S\alpha)^{m+n}$$

Criteria of precipitation of an electrolyte: A very useful conclusion is derived from the solubility product concept. No precipitation of the electrolyte occurs if the ionic product is less than the solubility product, *i.e.*, the solution has not reached the saturation stage.

Case I: When $K_{ip} < K_{sp}$, then solution is unsaturated in which more solute can be dissolved.

Case II: When $K_{ip} = K_{sp}$, then solution is saturated in which no more solute can be dissolved.

Case III: When $K_{ip} > K_{sp}$, then solution is supersaturated and precipitation takes place.

When the ionic product exceeds the solubility product, the equilibrium shifts towards left hand side, *i.e.*, increasing the concentration of undissociated molecules of the electrolyte. As the solvent can hold a fixed amount of electrolyte at a definite temperature, the excess of the electrolyte is thrown out from the solution as precipitate.

Thus, for the precipitation of an electrolyte, it is necessary that the ionic product must exceed its solubility product. For example, if equal volumes of 0.02 M $AgNO_3$ solution and 0.02 M K_2CrO_4 solution are mixed, the precipitation of Ag_2CrO_4 occurs as the ionic product exceeds the solubility product of Ag_2CrO_4 which is 2×10^{-12}.

In the resulting solution,

$$[Ag^+] = \frac{0.02}{2} = 0.01 = 1 \times 10^{-2}\ M$$

and $$[CrO_4^{2-}] = \frac{0.02}{2} = 0.01 = 1 \times 10^{-2}\ M$$

$$\text{Ionic product of } Ag_2CrO_4 = [Ag^+]^2[CrO_4^{2-}]$$
$$= (1\times10^{-2})^2\,(1\times10^{-2})$$
$$= 1\times10^{-6}$$

1×10^{-6} is higher than 2×10^{-12} and thus precipitation of Ag_2CrO_4 occurs.

Relationship between Solubility and Solubility Product

Salts like AgI, $BaSO_4$, $PbSO_4$, PbI_2, etc., are ordinarily considered insoluble but they do possess some solubility. These are sparingly soluble electrolytes. A saturated solution of sparingly soluble electrolyte contains a very small amount of the dissolved electrolyte. It is assumed that whole of the dissolved electrolyte is present in the form of ions, *i.e.*, it is completely dissociated.

The equilibrium for a saturated solution of any sparingly soluble salt may be expressed as:

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

Thus, solubility product, $K_s = [A^{y+}]^x[B^{x-}]^y$

Let 'S' mol litre^{-1} be the solubility of the salt; then

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

So, $$K_s = [xS]^x[yS]^y$$
$$= x^x \cdot y^y (S)^{x+y}$$

(i) 1 : 1 type salts: Examples: AgCl, AgI, $BaSO_4$, $PbSO_4$, etc.

Binary electrolyte: $AB \rightleftharpoons \underset{S}{A^+} + \underset{S}{B^-}$

Let solubility of AB be S mol litre^{-1}.

So, $$K_s = [A^+][B^-] = S\times S = S^2$$

or $$S = \sqrt{K_s}$$

(ii) 1 : 2 or 2 : 1 type salts: Examples: Ag_2CO_3, Ag_2CrO_4, $PbCl_2$, CaF_2, etc.

Ternary electrolyte: $AB_2 \rightleftharpoons \underset{S}{A^{2+}} + \underset{2S}{2B^-}$

Let solubility of AB_2 be S mol litre^{-1}.

So, $$K_s = [A^{2+}][B^-]^2 = S\times(2S)^2 = 4S^3$$

or $$S = \sqrt[3]{K_s/4}$$

$$A_2B \rightleftharpoons \underset{2S}{2A^+} + \underset{S}{B^{2-}}$$

Let S be the solubility of A_2B.

$$K_s = [A^+]^2[B^{2-}]$$
$$= (2S)^2(S) = 4S^3$$

or $$S = \sqrt[3]{K_s/4}$$

(iii) 1 : 3 type salts: Examples: AlI_3, $Fe(OH)_3$, $Cr(OH)_3$, $Al(OH)_3$, etc.

Quarternary electrolyte: $AB_3 \rightleftharpoons \underset{S}{A^{3+}} + \underset{3S}{3B^-}$

Let S mol litre^{-1} be the solubility of AB_3.

$$K_s = [A^{3+}][B^-]^3 = S\times(3S)^3 = 27S^4$$

or $$S = \sqrt[4]{K_s/27}$$

The presence of common ion affects the solubility of a salt. Let AB be a sparingly soluble salt in solution and $A'B$ be added to it. Let S and S' be the solubilities of the salt AB before and after addition of the electrolyte $A'B$. Let c be the concentration of $A'B$.

Before addition of $A'B$, $K_s = S^2$ ... (i)

After addition of $A'B$, the concentration of A^+ and B^- ions become S' and $(S'+c)$, respectively.

So, $$K_s = S'(S'+c) \quad \text{... (ii)}$$

Equating eqs. (i) and (ii),

$$S^2 = S'(S'+c)$$

Calculation of remaining concentration after precipitation: Sometimes an ion remains after precipitation if it is in excess. Remaining concentration can be determined, *e.g.*,

(i) $$[A^+]_{\text{left}} = \frac{K_{sp}[AB]}{[B^-]}$$

(ii) $$[Ca^{2+}]_{\text{left}} = \frac{K_{sp}[Ca(OH)_2]}{[OH^-]^2}$$

(iii) $$[A^{n+}]^m_{\text{left}} = \frac{K_{sp}[A_mB_n]}{[B^{m-}]^n}$$

Percentage precipitation of an ion

$$= \left[\frac{\text{Initial conc.} - \text{Left conc.}}{\text{Initial conc.}}\right]\times100$$

Simultaneous Solubility

Solubility of two electrolytes having common ion; when they are dissolved in the same solution, is called **simultaneous solubility**, *e.g.*,

(i) Solubility of AgBr and AgSCN, when dissolved together.
(ii) Solubility of CaF_2 and SrF_2, when dissolved together.
(iii) Solubility of MgF_2 and CaF_2, when dissolved together.

Calculation of simultaneous solubility is divided into two cases:

Case I: When the two electrolytes are almost equally strong (having close solubility product), *e.g.*,

$$AgBr\ (K_{sp} = 5\times10^{-13});\quad AgSCN\ (K_{sp} = 10^{-12})$$

(See example 26.)

Here, charge balancing concept is applied.

Charge of Ag^+ = Charge of Br^- + Charge of SCN^-

$$[Ag^+] = [Br^-] + [SCN^-]$$
$$(a+b) = a \qquad b$$

Case II: When solubility products of two electrolytes are not close, *i.e.*, they are not equally strong, *e.g.*,

CaF_2 ($K_{sp} = 3.4 \times 10^{-11}$); SrF_2 ($K_{sp} = 2.9 \times 10^{-9}$)

Most of fluoride ions come of stronger electrolyte.

SOME SOLVED EXAMPLES

Example 16. *The solubility product of silver chloride is 1.5625×10^{-10} at 25°C. Find its solubility in g L^{-1}.*

Solution: Let the solubility of AgCl be S mol litre^{-1}.

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

Hence, $S^2 = 1.5625 \times 10^{-10}$

or $S = 1.25 \times 10^{-5}$ mol L^{-1}

Molecular mass of AgCl = (108 + 35.5) = 143.5

So, Solubility in g litre^{-1} = Mol. mass × S

$$= 143.5 \times 1.25 \times 10^{-5}$$

$$= 1.79 \times 10^{-3} \text{ g L}^{-1}$$

Example 17. *The solubility of $PbSO_4$ in water is 0.038 g L^{-1} at 25°C. Calculate its solubility product at the same temperature.*

Solution: Solubility (S) of $PbSO_4$ in mol L^{-1},

$$= \frac{0.038}{\text{Mol. mass of } PbSO_4} = \frac{0.038}{303} = 1.254 \times 10^{-4}$$

The equilibrium is

$$PbSO_4 \rightleftharpoons \underset{S}{Pb^{2+}} + \underset{S}{SO_4^{2-}}$$

So, $K_s = [Pb^{2+}][SO_4^{2-}] = S \times S = S^2$

or $K_s = 1.254 \times 10^{-4} \times 1.254 \times 10^{-4} = 1.573 \times 10^{-8}$

Example 18. *The concentration of Ag^+ ion in a saturated solution of Ag_2CrO_4 at 20°C is 1.5×10^{-4} mol L^{-1}. Determine the solubility product of Ag_2CrO_4 at 20°C.*

Solution: The equilibrium is:

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

On the basis of this equation, the concentration of CrO_4^{2-} ions will be half of the concentration of Ag^+ ions.

Thus, $[Ag^+] = 1.5 \times 10^{-4}$ M and $[CrO_4^{2-}] = 0.75 \times 10^{-4}$ M

$$K_s = [Ag^+]^2[CrO_4^{2-}] = (1.5 \times 10^{-4})^2 \, (0.75 \times 10^{-4})$$

$$= 1.6875 \times 10^{-12}$$

Example 19. *The solubility product of $BaSO_4$ is 1.5×10^{-9}. Find out the solubility in (i) pure water and (ii) 0.1 M $BaCl_2$ solution.*

Solution: The equilibrium is:

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

Let S be the solubility in mol litre^{-1}; then

$$K_s = [Ba^{2+}][SO_4^{2-}] = S^2$$

or $1.5 \times 10^{-9} = S^2$

So, $S = 3.87 \times 10^{-5}$ mol L^{-1}

(ii) Let S' be the solubility of $BaSO_4$ in 0.1 M $BaCl_2$ solution.

Total Ba^{2+} ions concentration = $(S' + c)$ mol L^{-1}

and SO_4^{2-} ions concentration = S' mol L^{-1}

So, $K_s = (S' + c)S' \approx (S' + 0.1)S'$

or $1.5 \times 10^{-9} = (S' + 0.1)S'$

or $(S')^2 + 0.1S' = 1.5 \times 10^{-9}$

Neglecting $(S')^2$,

$$0.1S' = 1.5 \times 10^{-9}$$

or $S' = 1.5 \times 10^{-8}$ mol L^{-1}

Example 20. *The solubility of $Mg(OH)_2$ in pure water is 9.57×10^{-3} g L^{-1}. Calculate its solubility in g L^{-1} in 0.02 M $Mg(NO_3)_2$ solution.*

Solution: Solubility of $Mg(OH)_2$ in pure water

$$= 9.57 \times 10^{-3} \text{ g L}^{-1}$$

$$= \frac{9.57 \times 10^{-3}}{\text{Mol. mass}} \text{ mol L}^{-1}$$

$$= \frac{9.57 \times 10^{-3}}{58} = 1.65 \times 10^{-4} \text{ mol L}^{-1}$$

Further, $$Mg(OH)_2 \rightleftharpoons \underset{S}{Mg^{2+}} + \underset{2S}{2OH^-}$$

$$K_s = [Mg^{2+}][OH^-]^2 = S \times (2S)^2 = 4S^3 = 4 \times (1.65 \times 10^{-4})^3$$

$$= 17.9685 \times 10^{-12}$$

Let S' be solubility of $Mg(OH)_2$ in presence of $Mg(NO_3)_2$

$$[Mg^{2+}] = (S' + c) = (S' + 0.02)$$

$$[OH'] = 2S'$$

So, $K_S = (S' + 0.02)(2S')^2$

$$17.9685 \times 10^{-12} = 4(S')^2(S' + 0.02)$$

$$\frac{17.9685 \times 10^{-12}}{4} = (S')^3 + 0.02(S')^2$$

[neglecting $(S')^3$]

$$4.4921 \times 10^{-12} = 0.02(S')^2$$

or $(S')^2 = \frac{4.4921}{0.02} \times 10^{-12}$

or $S' = 14.9868 \times 10^{-6}$ mol L^{-1}

Solubility of $Mg(OH)_2$ in g litre^{-1} = $S' \times M$

$$= 14.9868 \times 10^{-6} \times 58$$

$$= 8.69 \times 10^{-4} \text{ g L}^{-1}$$

Example 21. *The solubility product of lead iodide is 1.4×10^{-8}. Calculate its molar solubility in 0.1 M KI solution.*

Solution: Let the solubility of PbI_2 be S. Then,

$$\underset{S}{PbI_2} \rightleftharpoons \underset{S}{Pb^{2+}} + \underset{2S}{2I^-}$$

Potassium iodide is a strong electrolyte and is completely ionised. It shall provide I^- ion concentration = 0.1 M.

$$[\mathrm{Pb}^{2+}] = S$$

$$[\mathrm{I}^-] = (2S + 0.1)M$$

$$K_{sp} = [\mathrm{Pb}^{2+}][\mathrm{I}^-]^2$$

$$= S \times (2S + 0.1)^2$$

$$= S \times (4S^2 + 0.01 + 0.4S)$$

$$= 4S^3 + 0.01S + 0.4S^2$$

Neglecting S^3 and S^2,

$$1.4 \times 10^{-8} = 0.01S$$

or $$S = \frac{1.4 \times 10^{-8}}{0.01} = 1.4 \times 10^{-6} \text{ mol L}^{-1}$$

Example 22. *The solubility product of lead bromide is 8×10^{-5}. If the salt is 80% dissociated in saturated solution, find the solubility of the salt.*

Solution: Let S be the solubility of the salt.

Degree of dissociation of the salt = 0.8.

$$\underset{}{\mathrm{PbBr_2}} \rightleftharpoons \underset{0.8S}{\mathrm{Pb}^{2+}} + \underset{2 \times 0.8S}{2\mathrm{Br}^-}$$

$$K_{sp} = [\mathrm{Pb}^{2+}][\mathrm{Br}^-]^2$$

$$= (0.8S) \times (1.6S)^2$$

$$= 2.048S^3$$

or $$S^3 = \frac{8 \times 10^{-5}}{2.048} = 3.906 \times 10^{-5}$$

$$S = \sqrt[3]{3.906 \times 10^{-5}} = 3.39 \times 10^{-2} \text{ mol L}^{-1}$$

Mol. mass of $\mathrm{PbBr_2} = 367$

Solubility of $\mathrm{PbBr_2} = 3.39 \times 10^{-2} \times 367 = 12.44 \text{ g L}^{-1}$

Example 23. *A solution has 0.05 M Mg^{2+} and 0.05 M NH_3. Calculate the concentration of NH_4Cl required to prevent the formation of $Mg(OH)_2$ in this solution. K_{sp} of $Mg(OH)_2$ = 9.0×10^{-12} and ionisation constant of NH_3 = 1.8×10^{-5}.* **(IIT 1993)**

Solution: The maximum concentration of $[\mathrm{OH}^-]$ ions that will precipitate $\mathrm{Mg(OH)_2}$ is calculated by applying the equation

$$K_{sp} = [\mathrm{Mg}^{2+}][\mathrm{OH}^-]^2$$

$$[\mathrm{OH}^-]^2 = \frac{K_{sp}}{[\mathrm{Mg}^{2+}]} = \frac{9.0 \times 10^{-12}}{0.05} = 1.8 \times 10^{-10}$$

or $$[\mathrm{OH}^-] = 1.34 \times 10^{-5} M$$

$\mathrm{NH_3}$ is present in solution in the form of $\mathrm{NH_4OH}$

$$\underset{0.05}{\mathrm{NH_3}} + \mathrm{H_2O} \rightleftharpoons \underset{0.05}{\mathrm{NH_4OH}} \rightleftharpoons \mathrm{NH_4^+} + \mathrm{OH^-}$$

The ionisation of $\mathrm{NH_4OH}$ is suppressed by the addition of $\mathrm{NH_4Cl}$ (Strong electrolyte).

$$K_{\mathrm{NH_3}} = K_{\mathrm{NH_4OH}} = \frac{[\mathrm{NH_4^+}][\mathrm{OH}^-]}{[\mathrm{NH_4OH}]}$$

Whole of the concentration of $\mathrm{NH_4^+}$ ions is provided by $\mathrm{NH_4Cl}$.

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

$$= \frac{1.8 \times 10^{-5} \times 0.05}{1.34 \times 10^{-5}} = 0.067 M$$

i.e., $$[\mathrm{NH_4Cl}] = 0.067 M$$

Example 24. *The solubility product of $Ag_2C_2O_4$ at 25°C is 1.29×10^{-11} mol^3 L^{-3}. A solution of $K_2C_2O_4$ containing 0.1520 mole in 500 mL of water is shaken with excess of Ag_2CO_3 till the following equilibrium is reached.*

$$Ag_2CO_3 + K_2C_2O_4 \rightleftharpoons Ag_2C_2O_4 + K_2CO_3$$

At equilibrium, the solution contains 0.0358 mole of K_2CO_3. Assuming the degree of dissociation of $K_2C_2O_4$ and K_2CO_3 to be equal, calculate the solubility product of Ag_2CO_3. **(IIT 1991)**

Solution:

	$\mathrm{Ag_2CO_3}$ +	$\mathrm{K_2C_2O_4}$	$\rightleftharpoons$ $\mathrm{Ag_2C_2O_4}$ +	$\mathrm{K_2CO_3}$
Initial		0.1520 mole		0
At equilibrium		(0.1520 – 0.0358) = 0.1162 mole		0.0358 mole
Concentration		2 × 0.1162 = 0.2324 M		2 × 0.0358 = 0.0716 M

$$K_{sp}\ \mathrm{Ag_2C_2O_4} = [\mathrm{Ag}^+]^2[\mathrm{C_2O_4^{2-}}]$$

$$[\mathrm{Ag}^+] = \left[\frac{K_{sp}\ \mathrm{Ag_2C_2O_4}}{[\mathrm{C_2O_4^{2-}}]}\right]^{1/2}$$

$$K_{sp}\mathrm{Ag_2CO_3} = [\mathrm{Ag}^+]^2[\mathrm{CO_3^{2-}}]$$

$$[\mathrm{Ag}^+] = \left[\frac{K_{sp}\ \mathrm{Ag_2CO_3}}{[\mathrm{CO_3^{2-}}]}\right]^{1/2}$$

So, $$\left[\frac{K_{sp}\ \mathrm{Ag_2C_2O_4}}{[\mathrm{C_2O_4^{2-}}]}\right]^{1/2} = \left[\frac{K_{sp}\ \mathrm{Ag_2CO_3}}{[\mathrm{CO_3^{2-}}]}\right]^{1/2}$$

or $$K_{sp}\ \mathrm{Ag_2CO_3} = \frac{K_{sp}\ \mathrm{Ag_2C_2O_4} \times [\mathrm{CO_3^{2-}}]}{[\mathrm{C_2O_4^{2-}}]}$$

$$= K_{sp}\ \mathrm{Ag_2C_2O_4} \frac{[\mathrm{K_2CO_3}]}{[\mathrm{K_2C_2O_4}]}$$

$$= 1.29 \times 10^{-11} \times \frac{0.0716}{0.2324} = 3.97 \times 10^{-12} \text{ mol}^3 \text{ L}^{-3}$$

Example 25. *20 mL of 0.001 M $AgNO_3$ solution is added to 1 litre of 0.002 M K_2CrO_4 solution. Will there be any precipitation? K_{sp} of Ag_2CrO_4 is 2.4×10^{-12}.*

Solution: No. of moles of Ag^+ in 20 mL

$$= \frac{20}{1000} \times 0.001 = 2 \times 10^{-5}$$

No. of moles $\mathrm{CrO_4^{2-}}$ in one litre $= 0.002 = 2 \times 10^{-3}$

After mixing, total volume of the solution

$$= 1000 + 20 = 1020 \text{ mL} = 1.02 \text{ L}$$

$$[Ag^+] = \frac{2\times10^{-5}}{1.02} = 1.96\times10^{-5}$$

$$[CrO_4^{2-}] = \frac{2\times10^{-3}}{1.02} = 1.96\times10^{-3}$$

$$\text{Ionic product} = [Ag^+]^2[CrO_4^{2-}]$$

$$= (1.96\times10^{-5})^2\,(1.96\times10^{-3})$$

$$= 7.53\times10^{-13}$$

There will be no precipitation of Ag_2CrO_4 as ionic product is less than solubility product.

Example 26. *Calculate simultaneous solubility of AgCNS and AgBr in a solution of water.* K_{sp} *of AgCNS* $= 1\times10^{-12}$, K_{sp} *of AgBr* $= 5\times10^{-13}$.

Solution: Let the solubility of AgCNS and AgBr in water be a and b respectively.

$$AgCNS \rightleftharpoons \underset{a}{Ag^+} + \underset{a}{CNS^-}$$

$$AgBr \rightleftharpoons \underset{b}{Ag^+} + \underset{b}{Br^-}$$

$$[Ag^+] = a+b, [CNS^-] = a \quad \text{and} \quad [Br^-] = b$$

$$K_{sp}AgCNS = [Ag^+][CNS^-] = a(a+b)$$

$$1\times10^{-12} = a(a+b) \qquad \text{... (i)}$$

$$K_{sp}\ AgBr = [Ag^+][Br^-] = b(a+b)$$

$$5\times10^{-13} = b(a+b) \qquad \text{... (ii)}$$

Dividing eq. (i) by (ii),

$$\frac{1\times10^{-12}}{5\times10^{-13}} = \frac{a}{b}$$

$$2 = \frac{a}{b} \quad \text{or} \quad a = 2b$$

Putting the value of a in eq. (i),

$$6b^2 = 1\times10^{-12}$$

$$b^2 = \frac{1}{6}\times10^{-12}$$

$$b = 4.08\times10^{-7}\ \text{mol L}^{-1}$$

$$a = 2\times4.08\times10^{-7}$$

$$= 8.16\times10^{-7}\ \text{mol L}^{-1}$$

Example 27. *The* K_{sp} *of* $Ca(OH)_2$ *is* 4.42×10^{-5} *at 25° C. 500 mL of saturated solution of* $Ca(OH)_2$ *is mixed with equal volume of 0.4 M NaOH. How much* $Ca(OH)_2$ *in mg is precipitated?* (IIT 1992)

Solution: Let S be the solubility of $Ca(OH)_2$ in saturated solution.

$$Ca(OH)_2 \rightleftharpoons \underset{S}{Ca^{2+}} + \underset{2S}{2OH^-}$$

$$K_{sp}\ Ca(OH)_2 = [Ca^{2+}][OH^-]^2$$

$$4.42\times10^{-5} = S\times4S^2 = 4S^3$$

$$S = 0.0223\ \text{mol L}^{-1}$$

After mixing the two solutions, the total volume becomes 1 litre.

$$[Ca^{2+}] = \frac{0.0223}{1000}\times500 = 0.01115\ \text{mol L}^{-1}$$

$$[OH^-] = \underset{[\text{From } Ca(OH)_2]}{\frac{0.0223\times2\times500}{1000}} + \underset{(\text{From NaOH})}{\frac{0.4\times500}{1000}} = 0.2223\ \text{mol L}^{-1}$$

Under the high concentration of OH^- ions, some $Ca(OH)_2$ will be precipitated.

$$[Ca^{2+}]_{left}[OH^-]^2 = K_{sp}$$

$$[Ca^{2+}]_{left} = \frac{4.42\times10^{-5}}{(0.2223)^2} = 8.94\times10^{-4}\ \text{mol L}^{-1}$$

Moles of $Ca(OH)_2$ precipitated = Moles of Ca^{2+} precipitated

$$= [Ca^{2+}]_{initial} - [Ca^{2+}]_{left}$$

$$= 0.01115 - 8.94\times10^{-4}$$

$$= 111.5\times10^{-4} - 8.94\times10^{-4}$$

$$= 102.56\times10^{-4}\ M = 102.56\times10^{-4}\times74\ \text{g}$$

$$= 7589.44\times10^{-4}\ \text{g} = 758.944\ \text{mg}$$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

6. The solubility product of sparingly soluble salt Ag_2CrO_4 is 4×10^{-12}. The molar solubility of the salt is:

   (a) 1×10^{-4} mol L^{-1} (b) 2×10^{-6} mol L^{-1}

   (c) 1×10^{-5} mol L^{-1} (d) 2×10^{-12} mol L^{-1}

   [Ans. (a)]

   [Hint: $K_{sp} = [Ag^+]^2[CrO_4^{2-}]$

   If solubility of Ag_2CrO_4 is 'S', then $[Ag^+] = 2S$ and $[CrO_4^{2-}] = S$.

   $$K_{sp} = 4S^3$$

   $$4\times10^{-12} = 4S^3$$

   $$S = 1\times10^{-4}\ M]$$

7. The solubility of $PbSO_4$ at 25°C is 1.1×10^{-4} mol/L. Then its K_{sp} is:

   (a) 1.21×10^{-8} (b) 12.1×10^{-6}

   (c) 121×10^{-11} (d) 1.21×10^{-10}

   [Ans. (a)]

   [Hint: $PbSO_4$ is a binary electrolyte, hence its K_{sp} can be calculated as:

   $$K_{sp} = S^2 = [1.1\times10^{-4}]^2 = 1.21\times10^{-8}\,]$$

8. The solubility of CaF_2 ($K_{sp} = 3.4\times10^{-11}$) in 0.1 M solution of NaF would be:

   (a) $3.4\times10^{-12}\ M$ (b) $3.4\times10^{-10}\ M$

   (c) $3.4\times10^{-9}\ M$ (d) $3.4\times10^{-13}\ M$

   [Ans. (c)]

   [Hint: $CaF_2 \rightleftharpoons \underset{x}{Ca^{2+}} + \underset{2x}{2F^-}$

$$\mathrm{NaF} \longrightarrow \underset{0.1}{\mathrm{Na}^+} + \underset{0.1}{\mathrm{F}^-}$$

$$[\mathrm{Ca}^{2+}] = x, \quad [\mathrm{F}^-] = [2x + 0.1] \approx 0.1\,M$$

$$K_{\mathrm{sp}} = [\mathrm{Ca}^{2+}][\mathrm{F}^-]^2$$

$$3.4 \times 10^{-11} = x(0.1)^2$$

$$x = 3.4 \times 10^{-9}\ M]$$

9. The solubility product of AgCl is 1.8×10^{-10}. Precipitation of AgCl will occur only when equal volumes of which of the following solutions are mixed ?

(a) $10^{-4}\,M\,\mathrm{Ag}^+$ and $10^{-4}\,M\,\mathrm{Cl}^-$

(b) $10^{-7}\,M\,\mathrm{Ag}^+$ and $10^{-7}\,M\,\mathrm{Cl}^-$

(c) $10^{-5}\,M\,\mathrm{Ag}^+$ and $10^{-5}\,M\,\mathrm{Cl}^-$

(d) $10^{-10}\,M\,\mathrm{Ag}^+$ and $10^{-10}\,M\,\mathrm{Cl}^-$

[**Ans.** (a)]

[**Hint:** After mixing,

$$[\mathrm{Ag}^+] = \frac{1}{2} \times 10^{-4} = 5 \times 10^{-5}\,M$$

$$[\mathrm{Cl}^-] = \frac{1}{2} \times 10^{-4} = 5 \times 10^{-5}\,M$$

$$K_{\mathrm{ip}} = [\mathrm{Ag}^+][\mathrm{Cl}^-] = (5 \times 10^{-5})^2 = 2.5 \times 10^{-9}$$

Since, ionic product is greater than solubility product, hence precipitation will take place.]

10. If x mol L^{-1} is the solubility of $\mathrm{KAl(SO_4)_2}$, then K_{sp} is equal to:

(a) x^3 (b) $4x^4$ (c) x^4 (d) $4x^3$

[**Ans.** (b)]

[**Hint:** $\mathrm{KAl(SO_4)_2} \longrightarrow \underset{x}{\mathrm{K}^+} + \underset{x}{\mathrm{Al}^{3+}} + \underset{2x}{2\mathrm{SO}_4^{2-}}$

$$K_{\mathrm{sp}} = [\mathrm{K}^+][\mathrm{Al}^{3+}][\mathrm{SO}_4^{2-}]^2$$

$$= x \times x \times (2x)^2 = 4x^4]$$

11. For which of the following sparingly soluble salt, the solubility (S) and solubility product (K_{sp}) are related by the expression:

$$S = \left[\frac{K_{\mathrm{sp}}}{4}\right]^{1/3}$$ [PET (Kerala) 2006]

(a) $\mathrm{BaSO_4}$ (b) $\mathrm{Ca_3(PO_4)_2}$ (c) $\mathrm{Hg_2Cl_2}$ (d) $\mathrm{Ag_3PO_4}$

(e) CuS

[**Ans.** (c)]

[**Hint:** $\mathrm{Hg_2Cl_2} \longrightarrow \underset{S}{\mathrm{Hg}_2^{2+}} + \underset{2S}{2\mathrm{Cl}^-}$, with S under $\mathrm{Hg_2Cl_2}$

$$K_{\mathrm{sp}} = [\mathrm{Hg}_2^{2+}][\mathrm{Cl}^-]^2 = [S][2S]^2 = 4S^3$$

$$S = \left[\frac{K_{\mathrm{sp}}}{4}\right]^{1/3}]$$

12. The solubility of $\mathrm{Sb_2S_3}$ in water is 1×10^{-5} mol/L at 298 K. What will be its solubility product? [PMT (Raj.) 2006]

(a) 108×10^{-25} (b) 1.0×10^{-25}

(c) 144×10^{-25} (d) 126×10^{-24}

[**Ans.** (a)]

[**Hint:** $\underset{S}{\mathrm{Sb_2S_3}} \longrightarrow \underset{2S}{2\mathrm{Sb}^{3+}} + \underset{3S}{3\mathrm{S}^{2-}}$

$$K_{\mathrm{sp}} = [\mathrm{Sb}^{3+}]^2[\mathrm{S}^{2-}]^3 = [2S]^2[3S]^3 = 108\,S^5$$

$$= 108 \times (10^{-5})^5 = 108 \times 10^{-25}]$$

Applications of Solubility Product

(i) Purification of common salt

Natural common salt consists of many insoluble and soluble impurities. Saturated solution of common salt is prepared and insoluble impurities are filtered off. Hydrogen chloride gas (HCl) is circulated through the saturated solution. HCl and NaCl dissociate into their respective ions as:

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

$$\mathrm{HCl} \rightleftharpoons \mathrm{H}^+ + \mathrm{Cl}^-$$

The concentration of Cl^- ions increases considerably in solution due to ionisation of HCl. Hence, the ionic product $[\mathrm{Na}^+][\mathrm{Cl}^-]$ exceeds the solubility product of sodium chloride and, therefore, pure sodium chloride precipitates out from solution.

(ii) Salting out of soap

Soap is a sodium salt of higher fatty acids. From the solution, soap is precipitated by the addition of concentrated solution of sodium chloride. Soap and sodium chloride are present in the form of ions.

$$\underset{\text{Soap}}{\mathrm{C}_n\mathrm{H}_{2n+1}\,\mathrm{COONa}} \rightleftharpoons \mathrm{C}_n\mathrm{H}_{2n+1}\mathrm{COO}^- + \mathrm{Na}^+$$

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

Thus, the concentration of Na^+ ions increases considerably on addition of NaCl solution. Hence, the ionic product $[\mathrm{C}_n\mathrm{H}_{2n+1}\mathrm{COO}^-][\mathrm{Na}^+]$ exceeds the solubility product of soap and, therefore, soap precipitates out from the solution.

(iii) Manufacture of sodium bicarbonate (baking soda)

In Solvay's soda process, $\mathrm{CO_2}$ gas is passed through ammonical brine to precipitate out $\mathrm{NaHCO_3}$.

$$\mathrm{NH_4OH + CO_2 \longrightarrow NH_4HCO_3}$$

$$\mathrm{NH_4HCO_3 + NaCl \longrightarrow NaHCO_3 + NH_4Cl}$$

$\mathrm{NaHCO_3}$ is precipitated first because of its lower solubility product as compared to those of $\mathrm{NH_4Cl}$, $\mathrm{NH_4HCO_3}$ and NaCl.

Thus, baking soda ($\mathrm{NaHCO_3}$) can be quantitatively estimated.

(iv) Application of solubility product in quantitative analysis

1. Estimation of barium as barium sulphate: $\mathrm{H_2SO_4}$ as precipitating agent is added to the aqueous solution of $\mathrm{BaCl_2}$.

$$\mathrm{BaCl_2 + H_2SO_4 \longrightarrow BaSO_4 + 2HCl}$$

Precipitation of $\mathrm{BaSO_4}$ takes place when its ionic product exceeds solubility product. $\mathrm{H_2SO_4}$ is added in slight excess to ensure complete precipitation. Large excess of $\mathrm{H_2SO_4}$ is harmful for complex formation.

2. Estimation of silver as silver chloride: NaCl solution is added to the silver nitrate solution; slight excess of NaCl is added to ensure complete precipitation.

$$\mathrm{AgNO_3 + NaCl \longrightarrow AgCl + NaNO_3}$$

Again, precipitation of AgCl takes place when ionic product of AgCl exceeds its solubility product.

3. In a similar manner, we estimate lead as lead chromate, calcium as calcium oxalate, etc.

(v) Precipitation of the sulphides of group II and IV

Hydrogen sulphide is a weak electrolyte and is used for the precipitation of various sulphides of group II and IV in qualitative analysis.

It ionises to a small extent in water:

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

Applying law of mass action,

$$K = \frac{[H^+]^2[S^{2-}]}{[H_2S]}$$

The concentration of S^{2-} ions can be decreased by increasing concentration of H^+ ions and it can be increased by decreasing concentration of H^+ ions. In group II, lower concentration of sulphide ions is required as the solubility products of the sulphides of group II are low while higher concentration of sulphide ions is required in group IV as the solubility products of the sulphides of group IV are high. The values of solubility products of various sulphides are given below:

	Metal sulphide	**Solubility product**
Group II	Bi_2S_3	1.6×10^{-72}
	HgS	4×10^{-54}
	CuS	1×10^{-44}
	PbS	5×10^{-29}
	CdS	1.4×10^{-28}
Group IV	CoS	3×10^{-26}
	NiS	1.4×10^{-24}
	ZnS	1.0×10^{-22}
	MnS	1.4×10^{-15}

The concentration of S^{2-} ions in group II is lowered by maintaining acidic medium. In the presence of HCl, the ionisation of H_2S is suppressed due to common ion effect. The concentration is so adjusted that only ionic products of the sulphides of group II exceed their solubility products and, therefore, get precipitated. However, CdS has somewhat higher value. For its precipitation, dilution of the solution is done which increases ionisation of H_2S and thereby increasing concentration of S^{2-} ions.

In group IV, higher concentration of S^{2-} ions is needed. This is done by changing the medium from acidic to alkaline. Ammonium hydroxide is added, the OH^- ions furnished by NH_4OH remove H^+ ions from solution in the form of water molecules as,

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

More of the ionisation of H_2S occurs and, thus, concentration of S^{2-} ions increases. It becomes so high that ionic products of the sulphides of group IV exceed their solubility products and they get precipitated.

(vi) Precipitation of III group hydroxides

When NH_4OH is added in presence of NH_4Cl then precipitation of III group hydroxides takes place, *i.e.*, $Al(OH)_3$, $Fe(OH)_3$ and $Cr(OH)_3$ are precipitated. Solubility product of III group hydroxides is less than those of higher group hydroxides.

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

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

NH_4^+ ion furnished by NH_4Cl lowers the ionisation of NH_4OH and hence the concentration of hydroxide ion OH^-. At low concentration of hydroxide ion only III group hydroxides precipitate.

Fractional Precipitation

It is a technique of separating two or more ions from a solution by adding a reagent that precipitates first one ion and then the second.

Let us suppose 0.1 *M* Ba^{2+} and 0.1 *M* Sr^{2+} in aqueous solution. K_2CrO_4 is added as precipitating agent. K_{sp} of $BaCrO_4$ is 1.2×10^{-10} and K_{sp} of $SrCrO_4$ is 3.5×10^{-5}.

$[CrO_4^{2-}]$ concentration required to precipitate $BaCrO_4$

$$= \frac{K_{sp}}{[Ba^{2+}]} = \frac{1.2 \times 10^{-10}}{0.1} = 1.2 \times 10^{-9}$$

$BaCrO_4$ will precipitate first because it requires low concentration of CrO_4^{2-} ions. On addition of chromate ions, $BaCrO_4$ starts precipitating when chromate ion concentration reaches 1.2×10^{-9} *M*. When CrO_4^{2-} ion concentration reaches up to 3.5×10^{-4} *M*, then $SrCrO_4$ also starts precipitating.

Remaining concentration of Ba^{2+} when $SrCrO_4$ starts precipitation

$$= \frac{K_{sp}BaCrO_4}{[CrO_4^{2-}]} = \frac{1.2 \times 10^{-10}}{3.5 \times 10^{-4}} = 3.4 \times 10^{-7}\ M$$

$$\%\ \text{remaining concentration} = \frac{3.4 \times 10^{-7}}{0.1} \times 100$$

$$= 0.00034\%$$

Stability Constant

Let us consider dissociation of the ion $FeBr^+$.

$$FeBr^+ \rightleftharpoons Fe^{2+} + Br^-$$

Dissociation constant for above equilibria may be given as:

$$K_d = \frac{[Fe^{2+}][Br^-]}{[FeBr^+]}$$

Reciprocal of dissociation constant is called stability constant.

$$K_s = \frac{[FeBr^+]}{[Fe^{2+}][Br^-]}$$

Let us consider the formation of complex $K_2Cd(CN)_4$. Complex ion is $Cd(CN)_4^{2-}$ where oxidation state of central metal Cd^{2+} is (+2). Complexing process proceeds in four steps as:

$$Cd^{2+} + CN^- \rightleftharpoons CdCN^+; \qquad K_1 = \frac{[CdCN^+]}{[Cd^{2+}][CN^-]}$$

$$CdCN^+ + CN^- \rightleftharpoons Cd(CN)_2; \qquad K_2 = \frac{[Cd(CN)_2]}{[CdCN^+][CN^-]}$$

$$Cd(CN)_2 + CN^- \rightleftharpoons Cd(CN)_3^-; \qquad K_3 = \frac{[Cd(CN)_3^-]}{[Cd(CN)_2][CN^-]}$$

$$Cd(CN)_3^- + CN^- \rightleftharpoons Cd(CN)_4^{2-}; \qquad K_4 = \frac{[Cd(CN)_4^{2-}]}{[Cd(CN)_3^-][CN^-]}$$

Overall reaction may be given as:

$$Cd^{2+} + 4CN^- \rightleftharpoons [Cd(CN)_4^{2-}]; \qquad K_s = \frac{[Cd(CN)_4^{2-}]}{[Cd^{2+}][CN^-]^4}$$

Here, $K_s = K_1 K_2 K_3 K_4$

Significance of stability constant: Greater will be the value of stability constant more stable will be the complex.

Note: (a) If on addition of a common ion in a salt solution (sparingly soluble), formation of complex ion takes place, then ionisation increases, *i.e.*, equilibrium shifts towards right hand direction to maintain the value of K_{sp} constant. It means, addition of common ion in the case of complex formation increases the solubility of the sparingly soluble salt which is against the concept of common ion effect.

(b) When we add an electrolyte to another electrolyte solution having no common ion, then ionisation of the latter increases.

(c) For a given electrolyte solubility product is always constant at a particular temperature.

Solubility of Metal Hydroxides in Acid Medium

H^+ ion furnished by the medium affects the solubility of metal hydroxide, say $M(OH)_2$, because of neutralization of OH^- ion by H^+ ion.

$$M(OH)_2 \rightleftharpoons M^{2+} + 2OH^-$$

$$K_{sp} \text{ of } M(OH)_2 = [M^{2+}][OH^-]^2$$

$$[M^{2+}] = \frac{K_{sp}}{[OH^-]^2} \qquad \text{... (i)}$$

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

$$[OH^-]^2 = \frac{10^{-28}}{[H^+]^2} \qquad \text{... (ii)}$$

From eqs. (i) and (ii), we have

$$[M^{2+}] = \frac{K_{sp}[H^+]^2}{10^{-28}}$$

10.5 ACIDS AND BASES

The earliest criteria for the characterisation of acids and bases were the experimentally observed properties of aqueous solutions. An acid* was defined as a substance whose water solution tastes sour, turns blue litmus red, neutralises bases and so on. A substance was a base if its aqueous solution tasted bitter, turns red litmus blue, neutralises acids and so on. **Faraday** termed acids, bases and salts as electrolytes and **Liebig** proposed that acids are compounds containing hydrogen that can be replaced by metals.

Different concepts have been put forth by different investigators to characterise acids and bases but the following are the three important modern concepts of acids and bases:

(1) Arrhenius concept

According to Arrhenius concept, **all substances which give H^+ ions when dissolved in water are called acids while those which ionise in water to furnish OH^- ions are called bases.**

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

$$BOH \rightleftharpoons B^+ + OH^- \qquad \text{(Base)}$$

Thus, HCl is an acid because it gives H^+ ions in water. Similarly, NaOH is a base as it yields OH^- ions in water.

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

$$NaOH \rightleftharpoons Na^+ + OH^-$$

Some acids and bases ionise almost completely in solutions and are called strong acids and bases. Others are dissociated to a limited extent in solutions and are termed weak acids and bases. HCl, HNO_3, H_2SO_4, $HClO_4$, etc., are examples of strong acids and NaOH, KOH, $(CH_3)_4NOH$ are strong bases. Every hydrogen compound cannot be regarded as an acid, *e.g.*, CH_4 is not an acid. Similarly, CH_3OH, C_2H_5OH, etc., have OH groups but they are not bases.

Actually free H^+ ions do not exist in water. They combine with solvent molecules, *i.e.*, have strong tendency to get hydrated.

$$HX + H_2O \rightleftharpoons \underset{\text{(Hydronium ion)}}{H_3O^+} + X^-$$

The proton in aqueous solution is generally represented as $H^+(aq.)$. It is now known that almost all the ions are hydrated to more or less extent and it is customary to put $(aq.)$ after each ion.

The oxides of many non-metals react with water to form acids and are called acidic oxides or acid anhydrides.

$$CO_2 + H_2O \longrightarrow H_2CO_3 \rightleftharpoons 2H^+(aq.) + CO_3^{2-}(aq.)$$

$$N_2O_5 + H_2O \longrightarrow 2HNO_3 \rightleftharpoons 2H^+(aq.) + 2NO_3^-(aq.)$$

Many oxides of metals dissolve in water to form hydroxides. Such oxides are termed basic oxides.

$$Na_2O + H_2O \longrightarrow 2NaOH \rightleftharpoons 2Na^+(aq.) + 2OH^-(aq.)$$

The substance like NH_3 and N_2H_4 act as bases as they react with water to produce OH^- ions.

$$NH_3 + H_2O \longrightarrow NH_4OH \rightleftharpoons NH_4^+(aq.) + OH^-(aq.)$$

The reaction between an acid and a base is termed neutralisation. According to Arrhenius concept, the neutralisation in aqueous solution involves the reaction between H^+ and OH^- ions or hydronium and OH^- ions. This can be represented as

$$H_3O^+ + OH^- \rightleftharpoons 2H_2O$$

Limitations: (i) For the acidic or basic properties, the presence of water is absolutely necessary. Dry HCl shall not act as an acid. HCl is regarded as an acid only when dissolved in water and not in any other solvent.

(ii) The concept does not explain acidic and basic character of substances in non-aqueous solvents.

(iii) The neutralisation process is limited to those reactions which can occur in aqueous solutions only, although reactions involving salt formation do occur in the absence of solvent.

(iv) It cannot explain the acidic character of certain salts such as $AlCl_3$ in aqueous solution.

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* Acid is a Latin word—*acidus*, meaning sour.

(v) An artificial explanation is required to explain the basic nature of NH_3 and metallic oxides and acidic nature of non-metal oxides.

(2) Bronsted-Lowry concept—The proton-donor-acceptor concept

In 1923, Bronsted and Lowry independently proposed a broader concept of acids and bases. According to Bronsted-Lowry concept **an acid is a substance (molecule or ion) that can donate proton, *i.e.,* a hydrogen ion, H^+, to some other substance and a base is a substance that can accept a proton from an acid.** More simply, an acid is a proton-donor (protogenic) and a base is a proton acceptor (protophilic). Consider the reaction,

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

In this reaction, HCl acts as an acid because it donates a proton to the water molecule. Water, on the other hand, behaves as a base by accepting a proton from the acid.

The dissolution of ammonia in water may be represented as

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

In this reaction, H_2O acts as an acid as it donates a proton to NH_3 molecule and NH_3 molecule behaves as a base as it accepts a proton.

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

$$\text{Acid} \rightleftharpoons H^+ + \text{Base}$$

The acid and base which differ by a proton are known to form a **conjugate pair.** Consider the following reaction:

$$CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^-$$

It involves two conjugate pairs. The acid-base pairs are:

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

Such pairs of substances which can be formed from one another by loss or gain of a proton are known as **conjugate acid-base pairs.**

If in the above reaction, the acid CH_3COOH is labelled acid_1 and its conjugate base, CH_3COO^- as base_1. H_2O is labelled as base_2 and its conjugate acid H_3O^+ as acid_2, the reaction can be written as:

$$\text{Acid}_1 + \text{Base}_2 \rightleftharpoons \text{Base}_1 + \text{Acid}_2$$

Thus, any acid-base reaction involves two conjugate pairs, *i.e.*, when an acid reacts with a base, another acid and base are formed. Some more examples are given below:

$$\text{Acid}_1 + \text{Base}_2 \rightleftharpoons \text{Acid}_2 + \text{Base}_1$$

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

$$HCN + H_2O \rightleftharpoons H_3O^+ + CN^-$$

$$HF + CH_3COOH \rightleftharpoons CH_3COOH_2^+ + F^-$$

$$CH_3COOH + NH_3 \rightleftharpoons NH_4^+ + CH_3COO^-$$

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

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$

$$HCO_3^- + H_2O \rightleftharpoons H_3O^+ + CO_3^{2-}$$

$$NH_4^+ + H_2O \rightleftharpoons H_3O^+ + NH_3$$

Thus, every acid has its conjugate base and every base has its conjugate acid. It is further observed that strong acids have weak conjugate bases while weak acids have strong conjugate bases.

$\underset{\text{Strong acid}}{HCl}$	$\underset{\text{Weak base}}{Cl^-}$	$\underset{\text{Weak acid}}{CH_3COOH}$	$\underset{\text{Strong base}}{CH_3COO^-}$

There are certain molecules which have dual character of an acid and a base. These are called **amphiprotic** or **amphoteric.**

Examples are NH_3, H_2O, CH_3COOH, etc.

$$\underset{\text{Acid}}{H_2O} \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} \underset{\text{Base}}{OH^-} \qquad \underset{\text{Acid}}{NH_3} \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} \underset{\text{Base}}{NH_2^-}$$

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

The strength of an acid depends upon its tendency to lose its proton and the strength of the base depends upon its tendency to gain the proton.

Acid-base chart containing some common conjugate acid-base pairs

Acid			Conjugate base		
$HClO_4$	(Perchloric acid)	↑ Increasing order of acid strength	ClO_4^-	(Perchlorate ion)	Increasing order of basic strength ↓
H_2SO_4	(Sulphuric acid)		HSO_4^-	(Hydrogen sulphate ion)	
HCl	(Hydrogen chloride)		Cl^-	(Chloride ion)	
HNO_3	(Nitric acid)		NO_3^-	(Nitrate ion)	
H_3O^+	(Hydronium ion)		H_2O	(Water)	
HSO_4^-	(Hydrogen sulphate ion)		SO_4^{2-}	(Sulphate ion)	
H_3PO_4	(Ortho-phosphoric acid)		$H_2PO_4^-$	(Dihydrogen phosphate ion)	
CH_3COOH	(Acetic acid)		CH_3COO^-	(Acetate ion)	
H_2CO_3	(Carbonic acid)		HCO_3^-	(Hydrogen carbonate ion)	
H_2S	(Hydrogen sulphide)		HS^-	(Hydrosulphide ion)	
NH_4^+	(Ammonium ion)		NH_3	(Ammonia)	
HCN	(Hydrogen cyanide)		CN^-	(Cyanide ion)	
C_6H_5OH	(Phenol)		$C_6H_5O^-$	(Phenoxide ion)	
H_2O	(Water)		OH^-	(Hydroxide ion)	
C_2H_5OH	(Ethyl alcohol)		$C_2H_5O^-$	(Ethoxide ion)	
NH_3	(Ammonia)		NH_2^-	(Amide ion)	
CH_4	(Methane)		CH_3^-	(Methide ion)	

In acid-base strength series, all acids above H_3O^+ in aqueous solution fall to the strength of H_3O^+. Similarly, the basic strength of bases below OH^- fall to the strength of OH^- in aqueous solution. This is known as **levelling effect.**

The strength of an acid also depends upon the solvent. The acids $HClO_4$, H_2SO_4, HCl and HNO_3 which have nearly the same strength in water will be in the order of $HClO_4 > H_2SO_4 > HCl > HNO_3$ in acetic acid, since, the proton accepting tendency of acetic acid is much weaker than water. So, the real strength of acids can be judged by solvents. On the basis of proton interaction, solvents can be classified into four types:

(i) Protophilic solvents: Solvents which have greater tendency to accept protons, *i.e.*, water, alcohol, liquid ammonia, etc.

(ii) Protogenic solvents: Solvents which have the tendency to produce protons, *i.e.*, water, liquid hydrogen chloride, glacial acetic acid, etc.

(iii) Amphiprotic solvents: Solvents which act both as protophilic or protogenic, *e.g.*, water, ammonia, ethyl alcohol, etc.

(iv) Aprotic solvents: Solvents which neither donate nor accept protons, *e.g.*, benzene, carbon tetrachloride, carbon disulphide, etc.

HCl acts as acid in H_2O, stronger acid in NH_3, weak acid in CH_3COOH, neutral in C_6H_6 and a weak base in HF.

$$\underset{\text{Base}}{HCl} + \underset{\text{Acid}}{HF} \longrightarrow \underset{\text{Acid}}{H_2Cl^+} + \underset{\text{Base}}{F^-}$$

Periodic Variations of Acidic and Basic Properties

(a) Hydracids of the elements of the same period: Consider the hydracids of the elements of II period, *viz.*, CH_4, NH_3, H_2O and HF. These hydrides become increasingly acidic as we move from CH_4 to HF. CH_4 has negligible acidic properties while HF is a fairly stronger acid. The increase in acidic nature is due to the fact that the stability of their conjugate bases increases in the order

$$CH_3^- < NH_2^- < OH^- < F^-$$

The increase in acidic properties is supported by the successive increase in the dissociation constant.

$$CH_4\ (=10^{-58}) < NH_3\ (=10^{-35}) < H_2O\ (=10^{-14}) < HF\ (=10^{-4})$$

(b) Hydracids of the elements of same group: (i) Hydrides of V group elements (NH_3, PH_3, AsH_3, SbH_3 and BiH_3) show basic character which decreases due to increase in size and decrease in electronegativity from N to Bi. There is a decrease in electron density in sp^3-hybrid orbital and thus electron donor capacity decreases.

(ii) Hydracids of VI group elements (H_2O, H_2S, H_2Se and H_2Te) act as weak acids. The strength increases in the order

$$H_2O < H_2S < H_2Se < H_2Te$$

The increasing acidic character reflects decreasing trend in the electron donor capacity of OH^-, HS^-, HSe^- or HTe^- ions.

(iii) Hydracids of VII group elements (HF, HCl, HBr and HI) show acidic nature which increases from HF to HI. This is explained by the fact that bond energies decrease. (H—F = 135 kcal/mol, HCl = 103, HBr = 88 and HI = 71 kcal/mol)

(c) Oxyacids: (i) The acidic character of oxyacids of the same element which is in different oxidation states increases with increase in oxidation number.

$$\overset{+1}{HClO} < \overset{+3}{HClO_2} < \overset{+5}{HClO_3} < \overset{+7}{HClO_4}$$

$$\overset{+4}{H_2SO_3} < \overset{+6}{H_2SO_4};\ \overset{+3}{HNO_2} < \overset{+5}{HNO_3}$$

But this rule fails in oxyacids of phosphorus.

$$H_3PO_2 > H_3PO_3 > H_3PO_4$$

(ii) The acidic character of the oxyacids of different elements which are in the same oxidation state decreases as the atomic number increases. This is due to increase in size and decrease in electronegativity.

$$HClO_4 > HBrO_4 > HIO_4$$

$$H_2SO_3 > H_2SeO_3$$

Limitations: There are number of acid-base reactions in which no proton transfer takes place, *e.g.*,

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

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

(3) Lewis concept

This concept was proposed by G.N. Lewis, in 1939. According to this concept, **a base is defined as a substance which can furnish a pair of electrons to form a coordinate bond whereas an acid is a substance which can accept a pair of electrons.** The acid is also known as electron acceptor or **electrophile** while the base is electron donor or **nucleophile.**

A simple example of an acid-base is the reaction of a proton with hydroxyl ion.

$$\underset{\text{Acid}}{H^+} + \underset{\text{Base}}{:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:H^-} = H:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:H$$

Some other examples are:

$$\underset{\text{Base}}{H_3N:} + \underset{\text{Acid}}{BF_3} = H_3N \rightarrow BF_3$$

$$\underset{\text{Acid}}{H^+} + \underset{\text{Base}}{:NH_3} = [H \leftarrow NH_3]^+$$

$$\underset{\text{Acid}}{BF_3} + \underset{\text{Base}}{[F]^-} = [F \rightarrow BF_3]^+$$

Lewis concept is more general than the Bronsted Lowry concept.

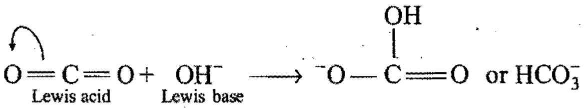
According to Lewis concept, the following species can act as Lewis acids:

(i) Molecules in which the central atom has incomplete octet: All compounds having central atom with less than 8 electrons are Lewis acids, *e.g.*, BF_3, BCl_3, $AlCl_3$, $MgCl_2$, $BeCl_2$, etc.

(ii) Simple cations: All cations are expected to act as Lewis acids since they are deficient in electrons. However, cations such as Na^+, K^+, Ca^{2+}, etc., have a very little tendency to accept electrons, while the cations like H^+, Ag^+, etc., have greater tendency to accept electrons and, therefore, act as Lewis acids.

(iii) Molecules in which the central atom has empty *d*-orbitals: The central atom of the halides such as SiX_4, GeX_4, $TiCl_4$, SnX_4, PX_3, PF_5, SF_4, SeF_4, $TeCl_4$, etc., have vacant *d*-orbitals. These can, therefore, accept an electron pair and act as Lewis acids.

(iv) Molecules having a multiple bond between atoms of dissimilar electronegativity: Typical examples of molecules falling in this class of Lewis acids are CO_2, SO_2 and SO_3. Under the influence of attacking Lewis base, one π-electron pair will be shifted towards the more negative atom.



$$\underset{\text{Lewis acid}}{O{=}C{=}O} + \underset{\text{Lewis base}}{OH^-} \longrightarrow {}^-O-\overset{\displaystyle OH}{\overset{|}{C}}{=}O \text{ or } HCO_3^-$$

The following species can act as Lewis bases:

(i) Neutral species having at least one lone pair of electrons: For example, ammonia, amines, alcohols, etc., act as Lewis bases because they contain a pair of electrons.

$$:NH_3,\quad -\ddot{N}H_2,\quad R-\underset{\cdot\cdot}{\ddot{O}}-H$$

(ii) Negatively charged species or anions: For example, chloride, cyanide, hydroxide ions, etc., act as Lewis bases.

$$CN^-,\quad Cl^-,\quad OH^-$$

It may be noted that all Bronsted bases are also Lewis bases but all Bronsted acids are not Lewis acids.

Limitations: Since, the strength of the Lewis acids and bases is found to depend on the type of reaction, it is not possible to arrange them in any order of their relative strength.

The choice of which definition of acids and bases one wishes to use in a particular instance depends largely on the sort of chemistry that is studied. But Arrhenius concept is perfectly satisfactory and simplest for dealing with reactions in aqueous solutions. It explains satisfactorily the strength of acids and bases in aqueous solutions, neutralisation, salt hydrolysis, etc.

10.6 RELATIVE STRENGTH OF ACIDS AND BASES

According to Arrhenius concept, an acid is a substance which furnishes H^+ ions when dissolved in water. All the acid properties on an acid are due to H^+ ions present in the solution.

The extent to which an acid property is given by an acid is a measure of its strength. The strength of the acid solution does not depend on its concentration but on the number of H^+ ions present. The concentration of H^+ ions depends on the ionisation of an acid in solution. On dilution, the ionisation increases and more of H^+ ions come to solution with the result that the strength of the acid increases. **Thus, strength of the acid increases on dilution while its concentration decreases.** At infinite dilution the dissociation of an acid is nearly complete and all acids are equally strong at infinite dilution.

The concentration of H^+ ions at all other dilutions of equimolar solutions of the acids may not be equal and depends on their degree of dissociation. Thus, to measure the relative strength of the two acids, the measurements of hydrogen ion concentration, *i.e.*, degree of dissociation is made of equinormal solutions of the two acids. Various methods are used for this purpose. Some are described below.

(i) The conductivity method: The degree of dissociation of a weak acid is equal to conductivity ratio $\frac{\Lambda}{\Lambda_\infty}$. Thus, the degrees of dissociation α_1 and α_2 for two equinormal acids are given by:

$$\text{For acid I,}\qquad \alpha_1 = \frac{\Lambda_1}{\Lambda_{\infty_1}}$$

$$\text{and}\qquad \text{For acid II,}\qquad \alpha_2 = \frac{\Lambda_2}{\Lambda_{\infty_2}}$$

At infinite dilution, all weak electrolytes have almost the same value of Λ_∞; hence,

$$\Lambda_{\infty_1} = \Lambda_{\infty_2}$$

$$\frac{\text{Strength of acid I}}{\text{Strength of acid II}} = \frac{\alpha_1}{\alpha_2} = \frac{\Lambda_1}{\Lambda_2} = \frac{\dfrac{1000 \times \text{sp. cond. acid I}}{C}}{\dfrac{1000 \times \text{sp. cond. acid II}}{C}}$$

$$= \frac{\text{Sp. cond. acid I}}{\text{Sp. cond. acid II}}$$

The relative strength of two acids is, thus, equal to the ratio of their equivalent conductance or specific conductance of equinormal solutions which can be determined experimentally.

(ii) Comparing dissociation constants: Let K_1 and K_2 be the dissociation constants of two acids and let α_1 and α_2 be their degree of dissociation in equinormal solutions.

Applying Ostwald's dilution law, $\alpha_1 = \sqrt{\frac{K_1}{C}}$ and $\alpha_2 = \sqrt{\frac{K_2}{C}}$

$$\text{Thus,}\qquad \frac{\text{Strength of acid I}}{\text{Strength of acid II}} = \frac{\alpha_1}{\alpha_2} = \sqrt{\frac{K_1}{K_2}}$$

Dissociation constants of some weak acids are given in the table:

Acid-ionization constants at 25°C

Substance	Formula	K_a
Acetic acid	$HC_2H_3O_2$	1.7×10^{-5}
Benzoic acid	$HC_7H_5O_2$	6.3×10^{-5}
Boric acid	H_3BO_3	5.9×10^{-10}
Carbonic acid	H_2CO_3 HCO_3^-	4.3×10^{-7} 4.8×10^{-11}
Cyanic acid	HOCN	3.5×10^{-4}

Substance	Formula	K_a
Formic acid	$HCHO_2$	1.7×10^{-4}
Hydrocyanic acid	HCN	4.9×10^{-10}
Hydrofluoric acid	HF	6.8×10^{-4}
Hydrogen sulphate ion	HSO_4^-	1.1×10^{-2}
Hydrogen sulphide	H_2S	8.9×10^{-8}
	HS^-	1.2×10^{-13}
Hypochlorous acid	HClO	3.5×10^{-8}
Nitrous acid	HNO_2	4.5×10^{-4}
Oxalic acid	$H_2C_2O_4$	5.6×10^{-2}
	$HC_2O_4^-$	5.1×10^{-5}
Phosphoric acid	H_3PO_4	6.9×10^{-3}
	$H_2PO_4^-$	6.2×10^{-8}
	HPO_4^{2-}	4.8×10^{-13}
Phosphorous acid	H_2PHO_3	1.6×10^{-2}
	$HPHO_3^-$	7.0×10^{-7}
Propionic acid	$HC_3H_5O_2$	1.3×10^{-5}
Pyruvic acid	$HC_3H_3O_3$	1.4×10^{-4}
Sulphurous acid	H_2SO_3	1.3×10^{-2}
	HSO_3^-	6.3×10^{-8}

(iii) Thomson thermal method: In this method, heat of neutralisation of two acids is first determined separately with NaOH. Let it be 'x' and 'y' calorie. The one gram equivalent of each of the two acids is mixed and one gram equivalent of NaOH is added. Let the heat evolved in this case be 'z' calorie. The two acids will neutralise a fraction of the base proportional to their relative strength. Suppose n gram equivalent of NaOH is neutralised by acid I and the rest $(1-n)$ by acid II.

$$\text{Total heat evolved, } z = nx + (1-n)y$$
$$= nx + y - ny$$

or
$$z - y = n(x-y)$$

or
$$n = \frac{(z-y)}{(x-y)}$$

So,
$$\frac{\text{Strength of acid I}}{\text{Strength of acid II}} = \frac{n}{(1-n)} = \frac{\frac{(z-y)}{(x-y)}}{1-\frac{(z-y)}{(x-y)}} = \frac{(z-y)}{(x-z)}$$

Relative strength of bases: A base is a substance which gives OH^- ions when dissolved in water. The strength of the base depends on OH^- ion concentration. The above methods can be used for measuring relative strengths of bases also. In the Thomson thermal method, the two bases and their mixtures will be neutralised by strong acid, say HCl.

The relative strengths of some of the acids are as follows:

(i) $HClO_4 > HBr > HCl > HNO_3 > H_2SO_4 > H_3O^+ > H_2SO_3 > H_2CO_3 > CH_3COOH$

(ii) $HClO_4 > HClO_3 > HClO_2 > HClO$

(iii) $HI > HBr > HCl > HF$

(iv) $HClO_3 > HBrO_3 > HIO_3$

(v) $CCl_3COOH > CHCl_2COOH > CH_2ClCOOH > CH_3COOH$

(vi) $HCOOH > CH_3COOH > C_2H_5COOH$

The relative strengths of some of the bases are as follows:

(i) $KOH > NaOH > Ca(OH)_2 > NH_4OH$

(ii) $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$

(iii) $(C_2H_5)_2NH > C_2H_5NH_2 > NH_3 > (C_2H_5)_3N$

(iv) $NaOH > NH_3 > H_2O$

(v) $NH_3 > NH_2 \cdot NH_2 > NH_2OH$

(vi) $NH_3 > C_5H_5N > C_6H_5NH_2$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

13. Which one is correct statement? **(DCE 2007)**

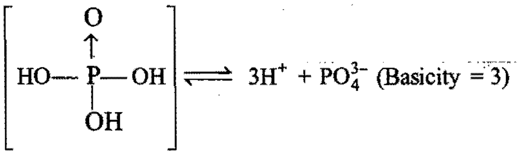
(a) Basicity of H_3PO_4 and H_3PO_3 are 3 and 3 respectively

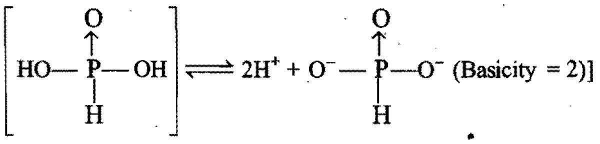
(b) Acidity of H_3PO_4 and H_3PO_3 are 3 and 3 respectively

(c) Acidity of H_3PO_4 and H_3PO_3 are 3 and 2 respectively

(d) Basicity of H_3PO_4 and H_3PO_3 are 3 and 2 respectively

[**Ans.** (d)]

[**Hint:**

$$\left[HO-\overset{\overset{O}{\uparrow}}{\underset{\underset{OH}{|}}{P}}-OH\right] \rightleftharpoons 3H^+ + PO_4^{3-} \text{ (Basicity = 3)}$$


$$\left[HO-\overset{\overset{O}{\uparrow}}{\underset{\underset{H}{|}}{P}}-OH\right] \rightleftharpoons 2H^+ + O^- - \overset{\overset{O}{\uparrow}}{\underset{\underset{H}{|}}{P}}-O^- \text{ (Basicity = 2)}$$
]

14. In the reaction,

$$HC_2O_4^- + PO_4^{3-} \rightleftharpoons HPO_4^{2-} + C_2O_4^{2-}$$

the Bronsted base are: **[PET (Raj.) 2004]**

(a) $PO_4^{3-}, C_2O_4^{2-}$
(b) PO_4^{3-}, HPO_4^{2-}
(c) $HC_2O_4^-, HPO_4^{2-}$
(d) $HC_2O_4^-, C_2O_4^{2-}$

[**Ans.** (a)]

[**Hint:** Acid $-$ H^+ = Conjugate base]

15. Conjugate base of HCO_3^- is: **[PET (Raj.) 2005]**

(a) CO_2 (b) H_2CO_3 (c) H_2O (d) CO_3^{2-}

[**Ans.** (d)]

[**Hint:** Acid $-$ H^+ = Conjugate base, $HCO_3^- - H^+ = CO_3^{2-}$]

16. Four species are listed below :

(i) HCO_3^- (ii) $H_3\overset{+}{O}$ (iii) HSO_4^- (iv) HSO_3F

Which one of the following is the correct sequence of their acid strength ? **(AIEEE 2008)**

(a) (iii) < (i) < (iv) < (ii)
(b) (iv) < (ii) < (iii) < (i)
(c) (ii) < (iii) < (i) < (iv)
(d) (i) < (iii) < (ii) < (iv)

[**Ans.** (d)]

[**Hint:** $HCO_3^- < HSO_4^- < H_3\overset{+}{O} < HSO_3F$

HSO_3F is super acid and it is most acidic. $H_3\overset{+}{O}$ is more acidic than anions because anions (HCO_3^-, HSO_4^-) do not release H^+ ion easily. HSO_4^- is more acidic than HCO_3^- because sulphur is more electronegative than carbon.]

17. Identify Bronsted-Lowry acids in the reaction given:

$$\underset{(A)}{[Al(H_2O)_6]^{3+}} + \underset{(B)}{HCO_3^-} \rightleftharpoons \underset{(C)}{[Al(H_2O)_5(OH^-)]^{2+}} + \underset{(D)}{H_2CO_3}$$

The correct answer is: [EAMCET (Med.) 2008]

(a) *A*, *C* (b) *B*, *D* (c) *A*, *D* (d) *B*, *C*

[**Ans.** (c)]

[**Hint :** $[Al(H_2O)_6]^{3+}$ and H_2CO_3 are proton donor or Bronsted acids]

18. Conjugate base of $H_2PO_4^-$ is: [Comed (Karnataka) 2008]

(a) HPO_4^{2-} (b) PO_4^{3-} (c) H_3PO_4 (d) HPO_4^-

[**Ans.** (a)]

[**Hint :** Acid − H^+ = Conjugate base

$H_2PO_4^- - H^+ = HPO_4^{2-}$]

10.7 ACID-BASE NEUTRALISATION—SALTS

When aqueous solutions of hydrochloric acid and sodium hydroxide are mixed in the proper proportion, a reaction takes place to form sodium chloride and water.

$$HCl(aq.) + NaOH(aq.) \rightleftharpoons \underset{\text{Sodium chloride}}{NaCl(aq.)} + H_2O(l)$$

Such a reaction is termed neutralisation because both acidic (H^+) and basic (OH^-) properties are eliminated during the reaction. The hydrogen ion, which is responsible for the acidic properties, has reacted with the hydroxyl ion which is responsible for the basic properties, producing neutral water. The Na^+ and Cl^- ions have undergone no chemical change and appear in the form of crystalline sodium chloride upon evaporation of the solution. Sodium chloride is an example of the class of compounds called **salts.**

$$H^+(aq.) + Cl^-(aq.) + Na^+(aq.) + OH^-(aq.) \rightleftharpoons H_2O(l) + Na^+(aq.) + Cl^-(aq.)$$

or $$H^+(aq.) + OH^-(aq.) \rightleftharpoons H_2O(l)$$

Thus, the neutralisation of a base with an acid involves the interaction between OH^- and H^+ ions.

Or

The reaction between an acid and a base to form salt and water is termed neutralisation.

The process of neutralisation does not produce the resulting solution always neutral; no doubt it involves the interaction of H^+ and OH^- ions. The nature of the resulting solution depends on the particular acid and a particular base involved in the reaction. The following examples illustrate this point when equivalent amounts of acids and bases are reacted in aqueous solution.

(i) A strong acid plus a strong base gives a neutral solution because both are completely ionised and the reaction goes to completion.

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

(ii) A strong acid plus a weak base gives an acidic solution as the weak base is not completely ionised. The reaction does not go to completion and there is an excess of hydrogen ions in solution.

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

(iii) A weak acid plus a strong base gives a basic solution as the weak acid is not completely ionised. The reaction does not go to completion and there is an excess of hydroxyl ions in solution.

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

(iv) A weak acid plus a weak base gives an acidic or a basic or a neutral solution depending on the relative strength of acid and base. In case, both have equal strength, the resulting solution is neutral in nature.

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

Salts: 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. Salts may taste salty, sour, bitter, astringent or sweet or tasteless. Solutions of salts may be acidic, basic or neutral. Fused salts and aqueous solutions of salts conduct electricity and undergo electrolysis. The properties of salts in aqueous solutions are the properties of ions. The salts are generally crystalline solids.

The salts are classified into the following classes:

(i) Simple salts: The salt formed by the neutralisation process, *i.e.*, interaction between acid and base, is termed as simple salt. These are of three types:

(a) Normal salts: The salts formed by the loss of all possible protons (replaceable hydrogen atoms as H^+) are called normal salts. Such a salt does not contain either a replaceable hydrogen or a hydroxyl group.

Examples are: NaCl, $NaNO_3$, K_2SO_4, $Ca_3(PO_4)_2$, Na_3BO_3, Na_2HPO_3 (one H atom is not replaceable as H_3PO_3 is a dibasic acid), NaH_2PO_2 (both H atoms are not replaceable as H_3PO_2 is a monobasic acid), 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 atoms. These salts when neutralised by bases form normal salts.

Examples are: $NaHCO_3$, $NaHSO_4$, NaH_2PO_4, Na_2HPO_4, etc.

(c) Basic salts: Salts formed by incomplete neutralisation of polyacidic bases are called basic salts. Such salts still contain one or more hydroxyl groups. These salts when neutralised by acids form normal salts.

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

(ii) 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.

Examples are: Ferrous ammonium sulphate, $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$, Potash alum, $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$ and other alums.

Properties: (a) When dissolved in water, it furnishes all the ions present in the simple salts from which it has been constituted.

(b) The solution of double salt shows the properties of the simple salts from which it has been constituted.

(iii) Complex salts: These are formed by combination of simple salts or molecular compounds. These are stable in solid state as well as in solutions.

$$\underbrace{FeSO_4 + 6KCN}_{\text{Simple salt}} \longrightarrow \underset{\text{Complex salt}}{K_4Fe(CN)_6} + K_2SO_4$$

$$\underset{\text{Simple salt}}{CoSO_4} + \underset{\text{Molecular compound}}{6NH_3} \longrightarrow \underset{\text{Complex salt}}{Co(NH_3)_6SO_4}$$

Properties: (a) On dissolving in water, it furnishes a complex ion.

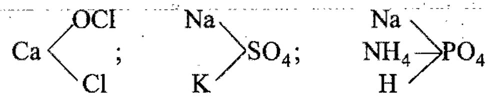
$$K_4Fe(CN)_6 \rightleftharpoons 4K^+ + \underset{\text{Complex ion}}{[Fe(CN)_6]^{4-}}$$

$$Cu(NH_3)_4SO_4 \rightleftharpoons \underset{\text{Complex ion}}{[Cu(NH_3)_4]^{2+}} + SO_4^{2-}$$

(b) The properties of the solution are different from the properties of the substances from which it has been constituted.

(iv) Mixed salts: The salt which furnishes more than one cation or more than one anion when dissolved in water is called a mixed salt.

Examples are:



$Ca(OCl)Cl$; $NaKSO_4$; $Na(NH_4)HPO_4$

Acidic, Basic and Amphoteric oxides

(i) Non-metal oxides are acidic, they dissolve in water to form acid. These oxides form salt with bases.

e.g., $\left.\begin{matrix} SO_2, SO_3, P_4O_{10}, CO_2, NO_2, N_2O_5 \\ SiO_2, B_2O_3 \end{matrix}\right\}$ Non-metal oxides

Some Transition metal oxides are also acidic.

e.g., $CrO_3, MoO_3, WO_3, Mn_2O_7$

$$CO_2 + H_2O \longrightarrow H_2CO_3 \text{ (Carbonic acid)}$$

$$2NO_2 + H_2O \longrightarrow HNO_2 + HNO_3 \text{ (Nitrous and nitric acid)}$$

$$P_2O_5 + 3H_2O \longrightarrow \underset{\text{(Phosphoric acid)}}{2H_3PO_4}$$

$$NaOH + SO_3 \longrightarrow \underset{\text{Salt}}{NaHSO_4}$$

$$2KOH + CO_2 \longrightarrow \underset{\text{Salt}}{K_2CO_3} + H_2O$$

(ii) Usually, oxides of highly electropositive metals are basic. These oxides dissolve in water to form base and they form salt with acids.

e.g., $Na_2O, K_2O, MgO, CaO, Sc_2O_3, TiO_2, ZrO_2$

$$Na_2O + H_2O \longrightarrow \underset{\text{(Sodium hydroxide, a base)}}{2NaOH}$$

$$CaO + 2HCl \longrightarrow \underset{\text{Salt}}{CaCl_2} + H_2O$$

$$Mg + H_2SO_4 \longrightarrow \underset{\text{Salt}}{MgSO_4} + H_2O$$

(iii) Oxides of metalloids and less electropositive metals are amphoteric. These oxides form salt with both acids and bases.

e.g., $BeO, Al_2O_3, GeO, SnO, Sb_2O_3, PbO$

ZnO, Cr_2O_3

$$Al_2O_3 + 6HCl \longrightarrow 2AlCl_3 + 3H_2O$$

$$Al_2O_3 + 2NaOH \longrightarrow 2NaAlO_2 + H_2O$$

10.8 IONIC PRODUCT OF WATER

Pure water is a very weak electrolyte and ionises according to the equation,

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

Applying law of mass action at equilibrium, the value of dissociation constant, K comes to

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

or $$[H^+][OH^-] = K[H_2O]$$

Since, dissociation takes place to a very small extent, the concentration of undissociated water molecules, $[H_2O]$, may be regarded as constant. Thus, the product $K[H_2O]$ gives another constant which is designated as K_w. So,

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

The constant, K_w, is termed as **ionic product of water.**

The product of concentrations of H^+ and OH^- ions in water at a particular temperature is known as ionic product of water. The value of K_w increases with the increase of temperature, *i.e.*, the concentration of H^+ and OH^- ions increases with increase in temperature.

Temperature (°C)	Value of K_w
0	0.11×10^{-14}
10	0.31×10^{-14}
25	1.00×10^{-14}
100	7.50×10^{-14}

The value of K_w at 25°C is 1×10^{-14}. Since, pure water is neutral in nature, H^+ ion concentration must be equal to OH^- ion concentration.

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

or $$[H^+][OH^-] = x^2 = 1 \times 10^{-14}$$

or $$x = 1 \times 10^{-7}\ M$$

or $$[H^+] = [OH^-] = 1 \times 10^{-7} \text{ mol litre}^{-1}$$

This shows that at 25°C, in 1 litre only 10^{-7} mole of water is in ionic form out of a total of approximately 55.5 moles.

When an acid or a base is added to water, the ionic concentration product, $[H^+][OH^-]$, remains constant, *i.e.*, equal to K_w but concentrations of H^+ and OH^- ions do not remain equal. The addition of acid increases the hydrogen ion concentration while that of hydroxyl ion concentration decreases, *i.e.*,

$[H^+] > [OH^-]$; (Acidic solution)

Similarly, when a base is added, the OH^- ion concentration increases while H^+ ion concentration decreases,

i.e., $[OH^-] > [H^+]$; (Alkaline or basic solution)

In neutral solution, $[H^+] = [OH^-] = 1 \times 10^{-7}\ M$

In acidic solution, $[H^+] > [OH^-]$

or $$[H^+] > 1 \times 10^{-7}\ M$$

and $$[OH^-] < 1 \times 10^{-7}\ M$$

In alkaline solution, $$[OH^-] > [H^+]$$

or $$[OH^-] > 1 \times 10^{-7}\ M$$

and $$[H^+] < 1 \times 10^{-7}\ M$$

Thus, if the hydrogen ion concentration is more than $1 \times 10^{-7}\ M$, the solution will be acidic in nature and if less than $1 \times 10^{-7}\ M$, the solution will be alkaline.

$[H^+] = 10^{-0}$ 10^{-1} 10^{-2} 10^{-3} 10^{-4} 10^{-5} 10^{-6} (Acidic)
$[H^+] =$ 10^{-7} (Neutral)
$[H^+] = 10^{-14}$ 10^{-13} 10^{-12} 10^{-11} 10^{-10} 10^{-9} 10^{-8} (Alkaline)

We shall have the following table if OH^- ion concentration is taken into account:

$[OH^-] = 10^{-14}$ 10^{-13} 10^{-12} 10^{-11} 10^{-10} 10^{-9} 10^{-8} (Acidic)
$[OH^-] =$ 10^{-7} (Neutral)
$[OH^-] = 10^{-0}$ 10^{-1} 10^{-2} 10^{-3} 10^{-4} 10^{-5} 10^{-6} (Alkaline)

It is, thus, concluded that every aqueous solution, whether acidic, neutral or alkaline contains both H^+ and OH^- ions. The product of their concentrations is always constant, equal to 1×10^{-14} at 25° C. If one increases, the other decreases accordingly so that the product remains 1×10^{-14} at 25° C.

If $[H^+] = 10^{-2}\ M$, then $[OH^-] = 10^{-12}\ M$; the product, $[H^+][OH^-] = 10^{-2} \times 10^{-12} = 10^{-14}$; the solution is acidic.

If $[H^+] = 10^{-10}\ M$, then $[OH^-] = 10^{-4}\ M$; the product, $[H^+][OH^-] = 10^{-10} \times 10^{-4} = 10^{-14}$; the solution is alkaline.

10.9 HYDROGEN ION CONCENTRATION—pH SCALE

It is clear from the above discussion that nature of the solution (acidic, alkaline or neutral) can be represented in terms of either hydrogen ion concentration or hydroxyl ion concentration but it is convenient to express acidity or alkalinity of a solution by referring to the concentration of hydrogen ions only. Since, H^+ ion concentration can vary within a wide range from 1 mol per litre to about 1.0×10^{-14} mol per litre, a logarithmic notation has been devised by **Sorensen,** in 1909, to simplify the expression of these quantities. The notation used is termed as the pH scale.

The hydrogen ion concentrations are expressed in terms of the numerical value of negative power to which 10 must be raised. This numerical value of negative power was termed as pH, *i.e.*,

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

or $$\log [H^+] = \log 10^{-pH} = -pH \log 10 = -pH$$

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

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

pH of a solution is, thus, defined as **the negative logarithm of the concentration (in mol per litre) of hydrogen ions which it contains** or pH of the solution is the **logarithm of the reciprocal of H^+ ion concentration.**

Just as pH indicates the hydrogen ion concentration, the pOH represents the hydroxyl ion concentration, *i.e.*,

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

Considering the relationship,

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

Taking log on both sides, we have

$$\log [H^+] + \log [OH^-] = \log K_w = \log (1 \times 10^{-14})$$

or $$-\log [H^+] - \log [OH^-] = -\log K_w = -\log (1 \times 10^{-14})$$

or $$pH + pOH = pK_w^* = 14$$

i.e., sum of pH and pOH is equal to 14 in any aqueous solution at 25° C. The above discussion can be summarised in the following manner:

	$[H^+]$	$[OH^-]$	pH	pOH
Acidic solution	$> 10^{-7}$	$< 10^{-7}$	< 7	> 7
Neutral solution	10^{-7}	10^{-7}	7	7
Basic solution	$< 10^{-7}$	$> 10^{-7}$	> 7	< 7

$[H^+]$	$[OH^-]$	pH	pOH	Nature of solution
10^0	10^{-14}	0	14	Strongly acidic
10^{-2}	10^{-12}	2	12	Acidic
10^{-5}	10^{-9}	5	9	Weakly acidic
10^{-7}	10^{-7}	7	7	Neutral
10^{-9}	10^{-5}	9	5	Weakly basic
10^{-11}	10^{-3}	11	3	Basic
10^{-14}	10^0	14	0	Strongly basic

The following table shows the pH range for a few common substances:

Substance	pH range	Substance	pH range
Gastric contents	1.0 – 3.0	Milk (cow)	6.3 – 6.6
Soft drinks	2.0 – 4.0	Saliva (human)	6.5 – 7.5
Lemons	2.2 – 2.4	Blood plasma (human)	7.3 – 7.5
Vinegar	2.4 – 3.4	Milk of magnesia	10.5
Apples	2.9 – 3.3	Seawater	8.5
Urine (human)	4.8 – 8.4		

***pK* value:** *p* stands for negative logarithm. Just as H^+ and OH^- ion concentrations range over many negative powers of 10, it is convenient to express them as pH or pOH, the dissociation constant (K) values also range over many negative powers of 10 and it is convenient to write them as pK. Thus, pK is the negative logarithm of dissociation constant.

$$pK_a = -\log K_a \quad \text{and} \quad pK_b = -\log K_b$$

Weak acids have higher pK_a values. Similarly, weak bases have higher pK_b values.

Any method which can measure the concentration of H^+ ions or OH^- ions in a solution can serve for finding pH value.

Limitations of pH Scale: (i) pH values of the solutions do not give us immediate idea of the relative strengths of the solutions. A solution of pH = 1 has a hydrogen ion concentration 100 times that of a solution of pH = 3 (not three times). A 4×10^{-5} N HCl is twice concentrated of a 2×10^{-5} N HCl solution, but the pH values of these solutions are 4.40 and 4.70 (not double).

(ii) pH value of zero is obtained in 1 N solution of strong acid. In case the concentration is 2 N, 3 N, 10 N, etc. The respective pH values will be negative.

(iii) A solution of an acid having very low concentration, say 10^{-8} N, cannot have pH 8, as shown by pH formula, but the actual pH value will be less than 7.

[**Note:** (i) Normality of strong acid $= [H_3O^+]$

Normality of strong base $= [OH^-]$

$$\therefore \quad pH = -\log [N] \quad \text{for strong acids}$$

$$pOH = -\log [N] \quad \text{for strong bases}$$

(ii) Sometimes, pH of acid comes more than 7 and that of base comes less than 7. It shows that the solution is very dilute; in such cases, H^+ or OH^- contribution from water is also considered, *e.g.*, in 10^{-8} N HCl,

$$[H^+]_{\text{Total}} = [10^{-8}]_{\text{Acid}} + [10^{-7}]_{\text{Water}}$$

$$= 11 \times 10^{-8}\ M = 1.1 \times 10^{-7}\ M$$

(iii) **pH of mixture:** Let one litre of an acidic solution of pH 2 be mixed with two litre of other acidic solution of pH 3. The resultant pH of the mixture can be evaluated in the following way:

Sample-1	**Sample-2**
$pH = 2$	$pH = 3$
$[H^+] = 10^{-2}\ M$	$[H^+] = 10^{-3}\ M$
$V = 1$ litre	$V = 2$ litre

$$M_1V_1 + M_2V_2 = M_R(V_1 + V_2)$$

$$10^{-2} \times 1 + 10^{-3} \times 2 = M_R(1 + 2)$$

$$\frac{12 \times 10^{-3}}{3} = M_R$$

$4 \times 10^{-3} = M_R$ (Here, M_R = **Resultant molarity**)

$$pH = -\log (4 \times 10^{-3})$$

(iv) Total concentration of $[H^+]$ or $[H_3^+O]$ in a mixture of **weak acid** and a **strong acid**

$$= \frac{C_2 + \sqrt{C_2^2 + 4K_aC_1}}{2}$$

where, C_1 is the concentration of weak acid (in mol litre^{-1}) having dissociation constant K_a and C_2 is the concentration of strong acid.

(v) Let us consider mixture of two weak acids HA and HB.

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

$$HB \rightleftharpoons H^+ + B^-$$

On applying charge balance

$$[H^+] = [A^-] + [B^-] + [OH^-]$$

$$= \frac{K_a[HA]}{[H^+]} + \frac{K_b[HB]}{[H^+]} + \frac{K_w}{[H^+]}$$

$$[H^+] = \sqrt{K_a[HA] + K_b[HB] + K_w}$$

$$= \sqrt{CK_a + CK_b + K_w}$$

(vi) Let us consider mixture of two weak bases AOH and BOH with dissociation constant K_1, K_2 and concentration C_1, C_2 respectively

$$[OH^-] = \sqrt{C_1K_1 + C_2K_2 + K_w}$$

10.10 pH OF WEAK ACIDS AND BASES

Weak acids and bases are not completely ionised; an equilibrium is found to have been established between ions and unionised molecules. Let us consider a weak acid of basicity 'n'.

$$\begin{array}{cccc} & AH_n & \rightleftharpoons A^{n-} & + \ nH^+ \\ t = 0 & C & 0 & 0 \\ t_{eq} & C(1-\alpha) & C\alpha & nC\alpha \end{array}$$

$$[H^+] = nC\alpha; \qquad \therefore \qquad pH = -\log_{10}[nC\alpha] \qquad \text{... (i)}$$

For monobasic acid, $n = 1$

$$pH = -\log_{10}[C\alpha] \qquad \text{... (ii)}$$

Dissociation constant of acid K_a may be calculated as:

$$K_a = \frac{[A^{n-}][H^+]^n}{[AH_n]} = \frac{[C\alpha][nC\alpha]^n}{C(1-\alpha)}$$

$$= \frac{\alpha[nC\alpha]^n}{(1-\alpha)} \qquad [\text{for weak acids, } \alpha << 1$$

$$\therefore (1-\alpha) \approx 1]$$

$$= \alpha[nC\alpha]^n$$

$$nCK_a = nC\alpha[nC\alpha]^n = [nC\alpha]^{(n+1)}$$

$$[nC\alpha] = [nCK_a]^{1/(n+1)}$$

$$[H^+] = [nCK_a]^{1/(n+1)}$$

$$\therefore \qquad pH = -\frac{1}{(n+1)}\log_{10}(nCK_a) \qquad \text{... (iii)}$$

For monobasic acid, $n = 1$

$$pH = -\log_{10}\sqrt{CK_a} \qquad \text{... (iv)}$$

Since, $K_a = \alpha[nC\alpha]^n$

$$\frac{K_a}{\alpha} = (nC\alpha)^n$$

$$[nC\alpha] = \left[\frac{K_a}{\alpha}\right]^{1/n} = [H^+]$$

$$pH = -\frac{1}{n}\log_{10}\left(\frac{K_a}{\alpha}\right) \qquad \text{... (v)}$$

For $n = 1$,

$$pH = -\log_{10}\left(\frac{K_a}{\alpha}\right) \qquad \text{... (vi)}$$

SOME SOLVED EXAMPLES

Example 28. *The hydrogen ion concentration of a solution is 0.001 M. What will be the hydroxyl ion concentration of solution?*

Solution: We know that, $[H^+][OH^-] = 1.0 \times 10^{-14}$

Given that, $[H^+] = 0.001\,M = 10^{-3}\,M$

So, $$[OH^-] = \frac{1.0 \times 10^{-14}}{[H^+]} = \frac{1 \times 10^{-14}}{10^{-3}} = 10^{-11}\,M$$

Example 29. *What is the pH of the following solutions?*

(a) 10^{-3} *M HCl (b)* 0.0001 *M NaOH (c)* 0.0001 *M* H_2SO_4

Solution: HCl is a strong electrolyte and is completely ionised.

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

So, $$[H^+] = 10^{-3}\,M$$

$$pH = -\log[H^+] = -\log(10^{-3}) = 3$$

(b) NaOH is a strong electrolyte and is completely ionised.

$$NaOH \rightleftharpoons Na^+ + OH^-$$

So, $$[OH^+] = 0.0001\,M = 10^{-4}\,M$$

$$pOH = -\log(10^{-4}) = 4$$

As $pH + pOH = 14$

So, $pH + 4 = 14$ or $pH = 10$

Alternative method: $[OH^-] = 10^{-4}\,M$

We know that, $[H^+][OH^-] = 1.0 \times 10^{-14}$

So, $$[H^+] = \frac{1.0 \times 10^{-14}}{10^{-4}} = 10^{-10}\,M$$

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

(c) H_2SO_4 is a strong electrolyte and is ionised completely.

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

One molecule of H_2SO_4 furnishes $2H^+$ ions.

So, $$[H^+] = 2 \times 10^{-4}\,M$$

$$pH = -\log[H^+]$$
$$= -\log(2 \times 10^{-4}) = 3.70$$

Example 30. *Calculate the pH of the following solutions assuming complete dissociation:*

(a) 0.365 *g* L^{-1} *HCl solution*

(b) 0.001 *M* $Ba(OH)_2$ *solution.*

Solution: (a) Mole. mass of HCl = 36.5

Concentration of HCl $= \frac{0.365}{36.5} = 1.0 \times 10^{-2}$ mol L^{-1}

HCl is a strong electrolyte and is completely ionised.

So, $[H^+] = 1 \times 10^{-2}$ mol L^{-1}

$$pH = -\log[H^+] = -\log(1 \times 10^{-2}) = 2$$

(b) $Ba(OH)_2$ is a strong electrolyte and is completely ionised

$$Ba(OH)_2 \rightleftharpoons Ba^{2+} + 2OH^-$$

One molecule on dissociation furnishes 2 OH^- ions.

So, $$[OH^-] = 2 \times 10^{-3}\,M$$

$$pOH = -\log[OH^-]$$
$$= -\log(2 \times 10^{-3}) = 2.7$$

We know that, $pH + pOH = 14$

So, $$pH = (14 - 2.7) = 11.3$$

Example 31. *Find the pH of a 0.002 N acetic acid solution, if it is 2.3% ionised at a given dilution.*

Solution: Degree of dissociation, $\alpha = \frac{2.3}{100} = 0.023$

Concentration of acetic acid, $C = 0.002\,M$

The equilibrium is,

$$\underset{C(1-\alpha)}{CH_3COOH} \rightleftharpoons \underset{C\alpha}{CH_3COO^-} + \underset{C\alpha}{H^+}$$

So, $$[H^+] = C\alpha = 0.002 \times 0.023$$
$$= 4.6 \times 10^{-5}\,M$$
$$pH = -\log[H^+]$$
$$= -\log(4.6 \times 10^{-5}) = 4.3372$$

Example 32. *Calculate the pH value of a solution obtained by mixing 50 mL of 0.2 N HCl with 50 mL of 0.1 N NaOH.*

Solution: Number of milli-equivalents of the acid

$= 50 \times 0.2 = 10$

Number of milli-equivalents of the base

$= 50 \times 0.1 = 5$

Number of milli-equivalents of the acid left after the addition of base

$= (10 - 5) = 5$

Total volume of the solution $= 50 + 50 = 100$ mL

Thus, 5 milli-equivalents of the acid are present in 100 mL of solution.

or 50 milli-equivalents of the acid are present in one litre of solution.

or 0.05 equivalents of the acid are present in one litre of solution.

The acid is monobasic and completely ionised in solution.

0.05 *N* HCl = 0.05 *M* HCl

So, $$[H^+] = 0.05\,M$$

$$pH = -\log[H^+] = -\log 5 \times 10^{-2} = -[\log 5.0 + \log 10^{-2}]$$
$$= -[0.70 - 2] = 1.3$$

Example 33. *What will be the pH of a solution obtained by mixing 800 mL of 0.05 N sodium hydroxide and 200 mL of 0.1 N HCl, assuming the complete ionisation of the acid and the base?*

Solution: Number of milli-equivalents of NaOH

$= 800 \times 0.05 = 40$

Number of milli-equivalents of HCl $= 200 \times 0.1 = 20$

Number of milli-equivalents of NaOH left after the addition of HCl

$= (40 - 20) = 20$

Total volume $= (200 + 800)$ mL $= 1000$ mL $= 1$ litre

20 milli-equivalents or 0.02 equivalents of NaOH are present in one litre, *i.e.*,

0.02 *N* NaOH = 0.02 *M* NaOH (Mono-acidic) and the base is completely ionised.

So, $[OH^-] = 0.02\,M$

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

$$pOH = -\log\,(2 \times 10^{-2}) = 1.7$$

We know that, $pH + pOH = 14$

So, $pH = (14 - 1.7) = 12.3$

Example 34. *What is the hydrogen ion concentration of a solution (i) whose pH is* 12, *(ii) whose pH is* 5.6*?*

Solution:

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

or $\log\,[H^+] = -pH = -12$

$$[H^+] = 10^{-12}\ M$$

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

or $\log\,[H^+] = -5.6$

or $[H^+] = 10^{-5.6} = 10^{-6} \times 10^{0.4} = 2.5 \times 10^{-6}\ M$

Example 35. *How many moles of calcium hydroxide must be dissolved to produce* 250 *mL of an aqueous solution of pH* 10.65*? Assume the complete ionisation.*

Solution: We know that,

$$pH + pOH = 14$$

So, $pOH = (14 - 10.65) = 3.35$

$$[OH^-] = 10^{-3.35} = 10^{-4} \times 10^{0.65}$$

$$= 4.47 \times 10^{-4}\ M$$

One molecule of $Ca(OH)_2$ furnishes $2\,OH^-$ ions.

Hence, concentration of

$$Ca(OH)_2 = \frac{4.47 \times 10^{-4}}{2} = 2.235 \times 10^{-4}\ M$$

$$\text{No. of moles in 250 mL} = \frac{2.235 \times 10^{-4}}{4} = 5.58 \times 10^{-5}$$

Example 36. *The pH of* $0.1\,M$ *hydrocyanic acid solution is* 5.2. *What is the value of* K_a *for hydrocyanic acid?*

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

or $\log\,[H^+] = -pH = -5.2$

$$[H^+] = 10^{-5.2} = 10^{-6} \times 10^{0.8}$$

$$= 6.3 \times 10^{-6}\ M$$

$$\text{'}\alpha\text{', degree of dissociation} = \frac{[H^+]}{C} = \frac{6.3 \times 10^{-6}}{0.1} = 6.3 \times 10^{-5}$$

According to Ostwald's formula for weak electrolyte,

$$K_a = \alpha^2 C = 6.3 \times 10^{-5} \times 6.3 \times 10^{-5} \times 0.1$$

$$= 3.69 \times 10^{-10}$$

Example 37. *Calculate the pH of the following solutions:*

(*i*) 1.0×10^{-8} *M HCl*, (*ii*) 1.0×10^{-8} *M NaOH*

Solution: (i) The neutral water has $[H^+] = 1 \times 10^{-7}\ M$

By adding $1.0 \times 10^{-8}\ M$ HCl, a concentration of $1.0 \times 10^{-8}\ M$ H^+ ions has increased in solution.

Thus, total $[H^+] = (1 \times 10^{-7} + 1 \times 10^{-8})\,M$

$$= (1 \times 10^{-7} + 0.1 \times 10^{-7})\,M$$

$$= 1.1 \times 10^{-7}\ M$$

$$pH = -\log\,(1.1 \times 10^{-7}) = -[\log 1.1 + \log 10^{-7}]$$

$$= -[0.0414 - 7.0] = 6.9586$$

(i) The neutral water has $[OH^-] = 1 \times 10^{-7}\ M$

By adding $1.0 \times 10^{-8}\ M$ NaOH, a concentration of $1.0 \times 10^{-8}\ M$ OH^- ions has increased in solution.

Thus, total $[OH^-] = (1 \times 10^{-7} + 1.0 \times 10^{-8})\,M$

$$= 1.1 \times 10^{-7}\ M$$

$$pOH = -\log 1.1 \times 10^{-7}$$

$$= 6.9586$$

$$pH = (14 - pOH) = (14 - 6.9586) = 7.0414$$

Example 38. *Calculate the* S^{2-} *ion concentration in a saturated solution* $(0.1\,M)$ *of* H_2S *whose pH was adjusted to* 2 *by the addition of HCl.* $(K_a = 1.1 \times 10^{-21})$

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

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

or $$[S^{2-}] = \frac{K_a\,[H_2S]}{[H^+]^2}$$

$pH = 2$; So, $[H^+] = 1 \times 10^{-2}\ M$

H_2S is a weak electrolyte, So, $[H_2S] = 0.1\,M$

So, $$[S^{2-}] = \frac{1.1 \times 10^{-21} \times 0.1}{1 \times 10^{-2} \times 1 \times 10^{-2}} = 1.1 \times 10^{-18}\ M$$

Example 39. *What is the hydrogen ion concentration of* 0.1 *N* CH_3COOH *solution? The ionisation constant of* CH_3COOH *is* 1.8×10^{-5}. *What is the pH of the solution?*

(IIT 1993)

Solution: Let the degree of dissociation be 'α'.

CH_3COOH is a weak electrolyte; thus,

$$\alpha^2 C = K_a$$

$$\alpha^2 \times 0.1 = 1.8 \times 10^{-5}$$

or $$\alpha = 1.34 \times 10^{-2}$$

$$[H^+] = \alpha \cdot C = 1.34 \times 10^{-2} \times 0.1 = 1.34 \times 10^{-3}\ M$$

$$pH = -\log\,[H^+] = -\log 1.34 \times 10^{-3} = 2.8729$$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

19. At 90°C, pure water has $[H_3O^+] = 10^{-6}\ M$. What is the value of K_w at this temperature? **[CBSE (Med.) 2006]**

(a) 10^{-6} (b) 10^{-12} (c) 10^{-13} (d) 10^{-14}

[Ans. (b)]

[Hint: $[H_3O^+] = [OH^-] = 10^{-6}\ M$

$\therefore\quad K_w = [H_3O^+][OH^-] = 10^{-12}$]

20. The pH of 0.5 M aqueous solution of HF ($K_a = 2 \times 10^{-4}$) is:

(a) 2 (b) 4 (c) 6 (d) 10

[Ans. (a)]

[Hint: $[H^+] = \sqrt{CK_a} = \sqrt{0.5 \times 2 \times 10^{-4}} = 10^{-2}\ M$

$pH = -\log_{10}[H^+] = -\log 10^{-2} = 2$]

21. The hydroxyl ion concentration in a solution having pH value 3 will be:

(a) $10^{-11}\ M$ (b) $10^{-7}\ M$ (c) $10^{-3}\ M$ (d) $10^{-14}\ M$

[Ans. (a)]

[Hint: pH + pOH = 14

pOH = 14 − pH = 14 − 3 = 11

$[OH^-] = 10^{-pOH} = 10^{-11}\ M$]

22. A 50 mL solution of pH = 1 is mixed with a 50 mL solution of pH = 2. The pH of the mixture will be nearly:

(a) 0.76 (b) 1.26 (c) 1.76 (d) 2.26

[Ans. (b)]

[Hint: pH = 1, $[H^+] = 10^{-1}\ M$

pH = 2, $[H^+] = 10^{-2}\ M$

$$M_1V_1 + M_2V_2 = M_R(V_1 + V_2)$$

$$10^{-1} \times 50 + 10^{-2} \times 50 = M_R \times 100$$

$$M_R = 5.5 \times 10^{-2}\ M$$

(Resultant molarity of H^+ ions)

$pH = -\log 5.5 \times 10^{-2} = 1.26$]

23. The pH of a solution obtained by mixing 50 mL of 0.4 N HCl and 50 mL of 0.2 N NaOH is:

(a) −log 2 (b) − log 0.2 (c) 1 (d) 2

[Ans. (c)]

[Hint: $N_1V_{1\,\text{acid}} - N_2V_{2\,\text{base}} = N_R(V_1 + V_2)$

$$0.4 \times 50 - 0.2 \times 50 = N_R \times 100$$

$$N_R = 0.1$$

$\therefore\quad [H^+] = 0.1\ M$

$pH = -\log[H^+] = -\log 0.1 = 1$]

24. What will be the pH value of 0.05 M $Ba(OH)_2$ solution? **[PMT (Raj.) 2006]**

(a) 12 (b) 13 (c) 1 (d) 12.96

[Ans. (b)]

[Hint: $\underset{0.05\ M}{Ba(OH)_2} \longrightarrow Ba^{2+} + \underset{\substack{2 \times 0.05\ M \\ = 0.1\ M}}{2OH^-}$

$pOH = -\log[OH^-] = -\log 0.1 = 1$

$pH = 14 - 1 = 13$]

25. 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 (PMT) 2008]**

(a) $3.7 \times 10^{-3} M$ (b) $1.11 \times 10^{-3} M$

(c) $1.11 \times 10^{-4} M$ (d) $3.7 \times 10^{-4} M$

[Ans. (d)]

[Hint: $[H^+] = 10^{-3} M$, $[H^+] = 10^{-4}\ M$, $[H^+] = 10^{-5}\ M$ for the given acids.

$$M_{mix}V_{mix} = M_1V_1 + M_2V_2 + M_3V_3$$

$$M_{mix} \times 3 = 10^{-3} \times 1 + 10^{-4} \times 1 + 10^{-5} \times 1$$

$$M_{mix} = \frac{10^{-5}[100 + 10 + 1]}{3} = \frac{111 \times 10^{-5}}{3} = 37 \times 10^{-5}\ M$$

$= 3.7 \times 10^{-4}\ M$]

10.11 BUFFER SOLUTIONS

For several purposes, we need solutions which should have constant pH. Many reactions, particularly the biochemical reactions, are to be carried out at a constant pH. But it is observed that solutions and even pure water (pH = 7) cannot retain the constant pH for long. If the solution comes in contact with air, it will absorb CO_2 and becomes more acidic. If the solution is stored in a glass bottle, alkaline impurities dissolve from glass and the solution becomes alkaline.

A solution whose pH is not altered to any great extent by the addition of small quantities of either an acid (H^+ ions) or a base (OH^- ions) is called the **buffer solution.** It can also be defined as a solution of **reserve acidity** or **alkalinity** which resists change of pH upon the addition of small amount of acid or alkali.

General Characteristics of a Buffer Solution

(i) It has a definite pH, *i.e.*, it has reserve acidity or alkalinity.

(ii) Its pH does not change on standing for long.

(iii) Its pH does not change on dilution.

(iv) Its pH is slightly changed by the addition of small quantity of an acid or a base.

Buffer solutions can be obtained:

(i) by mixing a weak acid with its salt with a strong base, *e.g.*,
  (a) $CH_3COOH + CH_3COONa$
  (b) Boric acid + Borax
  (c) Phthalic acid + Potassium acid phthalate

(ii) by mixing a weak base with its salt with a strong acid, *e.g.*,
  (a) $NH_4OH + NH_4Cl$
  (b) Glycine + Glycine hydrochloride

(iii) by a solution of ampholyte. The ampholytes or amphoteric electrolytes are the substances which show properties of both an acid and a base. Proteins and amino acids are the examples of such electrolytes.

(iv) by a mixture of an acid salt and a normal salt of a polybasic acid, *e.g.*, $Na_2HPO_4 + Na_3PO_4$ or a salt of weak acid and a weak base, such as CH_3COONH_4.

The first and second type are also called acidic and basic buffers respectively.

Explanation of Buffer Action

(i) Acidic buffer: Consider the case of the solution of acetic acid containing sodium acetate. Acetic acid is feebly ionised while sodium acetate is almost completely ionised. The mixture thus contains CH_3COOH molecules, CH_3COO^- ions, Na^+ ions, H^+ ions and OH^- ions. Thus, we have the following equilibria in solution:

$$CH_3COOH \rightleftharpoons H^+ + CH_3COO^- \qquad \text{(Feebly ionised)}$$

$$CH_3COONa \rightleftharpoons Na^+ + CH_3COO^- \qquad \text{(Completely ionised)}$$

$$H_2O \rightleftharpoons H^+ + OH^- \qquad \text{(Very feebly ionised)}$$

When a drop of strong acid, say HCl, is added, the H^+ ions furnished by HCl combine with CH_3COO^- ions to form feebly ionised CH_3COOH whose ionisation is further suppressed due to common ion effect. Thus, there will be a very slight effect in the overall H^+ ion concentration or pH value.

When a drop of NaOH is added, it will react with free acid to form undissociated water molecules.

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

Thus, OH^- ions furnished by a base are removed and pH of the solution is practically unaltered.

(ii) Basic buffer: Consider the case of the solution containing NH_4OH and its salt NH_4Cl. The solution will have NH_4OH molecule, NH_4^+ ions, Cl^- ions, OH^- ions and H^+ ions.

$$NH_4OH \rightleftharpoons NH_4^+ + OH^- \qquad \text{(Feebly ionised)}$$

$$NH_4Cl \rightleftharpoons NH_4^+ + Cl^- \qquad \text{(Completely ionised)}$$

$$H_2O \rightleftharpoons H^+ + OH^- \qquad \text{(Very feebly ionised)}$$

When a drop of NaOH is added, the added OH^- ions combine with NH_4^+ ions to form feebly ionised NH_4OH whose ionisation is further suppressed due to common ion effect. Thus, pH is not disturbed considerably.

$$NH_4^+ + \underset{\substack{\uparrow \\ \text{(From strong base)}}}{OH^-} \rightleftharpoons NH_4OH$$

When a drop of HCl is added, the added H^+ ions combine with NH_4OH to form undissociated water molecules.

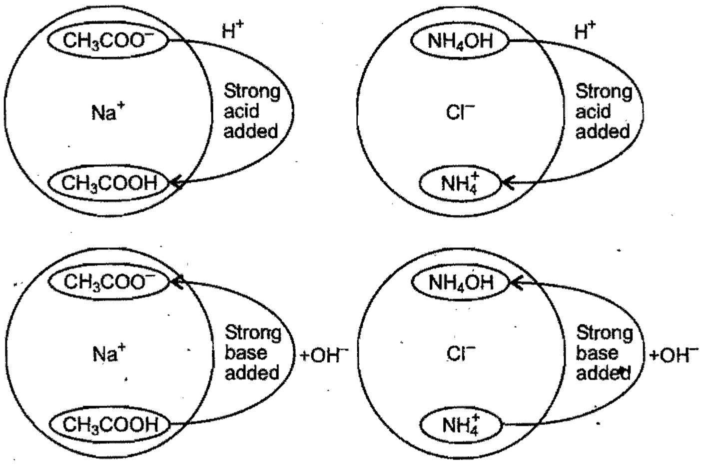
$$NH_4OH + \underset{\substack{\uparrow \\ \text{(From strong acid)}}}{H^+} \rightleftharpoons NH_4^+ + H_2O$$

Thus, pH of the buffer is practically unaffected.

Diagramatic Representation of Buffer Action

Acid Buffer $(CH_3COOH + CH_3COONa)$

Base Buffer $(NH_4OH + NH_4Cl)$



Henderson's Equation (pH of a buffer)

(i) Acidic buffer: It consists of a mixture of weak acid and its salt (strong electrolyte). The ionisation of the weak acid, *HA*, can be shown by the equation,

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

Applying law of mass action,

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

or

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

It can be assumed that concentration of A^- ions from complete ionisation of the salt *BA* is too large to be compared with concentration of A^- ions from the acid *HA*.

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

Thus, $[HA]$ = Initial concentration of the acid as it is feebly ionised in presence of common ion

and $[A^-]$ = Initial concentration of the salt as it is completely ionised.

So,

$$[H^+] = K_a \cdot \frac{[\text{Acid}]}{[\text{Salt}]} \qquad \text{... (iii)}$$

Taking logarithm and reversing sign,

$$-\log [H^+] = -\log K_a - \log \frac{[\text{Acid}]}{[\text{Salt}]}$$

or

$$pH = \log \frac{[\text{Salt}]}{[\text{Acid}]} - \log K_a$$

or

$$pH = pK_a + \log \frac{[\text{Salt}]}{[\text{Acid}]} \qquad \text{... (iv)}$$

This is known as **Henderson's equation.**

When $\frac{[\text{Salt}]}{[\text{Acid}]} = 10$, then

$$pH = 1 + pK_a$$

and when $\frac{[\text{Salt}]}{[\text{Acid}]} = \frac{1}{10}$, then

$$pH = pK_a - 1$$

So, weak acid may be used for preparing buffer solutions having pH values lying within the ranges $pK_a + 1$ and $pK_a - 1$. The acetic acid has a pK_a of about 4.8; it may, therefore, be used for making buffer solutions with pH values lying roughly within the range 3.8 to 5.8.

(ii) Basic buffer: It consists of a weak base and its salt with strong acid. Ionisation of a weak base, BOH, can be represented by the equation,

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

Applying law of mass action,

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

or

$$[OH^-] = K_b \frac{[BOH]}{[B^+]} \quad \text{... (ii)}$$

As the salt is completely ionised, it can be assumed that whole of B^+ ion concentration comes from the salt and contribution of weak base to B^+ ions can be ignored.

$$BA \rightleftharpoons B^+ + A^- \quad \text{(Completely ionised)}$$

So,

$$[OH^-] = K_b \frac{[\text{Base}]}{[\text{Salt}]} \quad \text{... (iii)}$$

or

$$pOH = \log \frac{[\text{Salt}]}{[\text{Base}]} - \log K_b$$

or

$$pOH = pK_b + \log \frac{[\text{Salt}]}{[\text{Base}]} \quad \text{... (iv)}$$

Knowing pOH, pH can be calculated by the application of the formula,

$$pH + pOH = 14$$

Buffer capacity: The property of a buffer solution to resist alteration in its pH value is known as **buffer capacity.** It has been found that if the ratio $\frac{[\text{Salt}]}{[\text{Acid}]}$ or $\frac{[\text{Salt}]}{[\text{Base}]}$ is unity, the pH of a particular buffer does not change at all. Buffer capacity is defined quantitatively as **number of moles of acid or base added in one litre of solution as to change the pH by unity,** *i.e.*,

Buffer capacity

$$(\phi) = \frac{\text{No. of moles of acid or base added to 1 litre}}{\text{Change in pH}}$$

or

$$\phi = \frac{\partial b}{\partial(pH)}$$

where, $\partial b \longrightarrow$ number of moles of acid or base added to 1 litre solution and $\partial(pH) \longrightarrow$ change in pH.

Buffer capacity is maximum:

(i) When [Salt] = [Acid], *i.e.*, $pH = pK_a$ for acid buffer

(ii) When [Salt] = [Base], *i.e.*, $pOH = pK_b$ for base buffer under above conditions, the buffer is called efficient.

Utility of Buffer Solutions in Analytical Chemistry

Buffers are used:

(i) To determine the pH with the help of indicators.

(ii) For the removal of phosphate ion in the qualitative inorganic analysis after second group using $CH_3COOH + CH_3COONa$ buffer.

(iii) For the precipitation of lead chromate quantitatively in gravimetric analysis, the buffer, $CH_3COOH + CH_3COONa$, is used.

(iv) For precipitation of hydroxides of third group of qualitative analysis, a buffer, $NH_4Cl + NH_4OH$, is used.

(v) A buffer solution of NH_4Cl, NH_4OH and $(NH_4)_2CO_3$ is used for precipitation of carbonates of fifth group in qualitative inorganic analysis.

(vi) The pH of intracellular fluid, blood is naturally maintained. This maintenance of pH is essential to sustain life because, enzyme catalysis is pH sensitive process. The normal pH of blood plasma is 7.4. Following two buffers in the blood help to maintain pH (7.4):

(a) Buffer of carbonic acid (H_2CO_3 and $NaHCO_3$)

(b) Buffer of phosphoric acid ($H_2PO_4^-$, HPO_4^{2-})

Buffers are used in industrial processes such as manufacture of paper, dyes, inks, paints, drugs, etc. Buffers are also employed in agriculture, dairy products and preservation of various types of foods and fruits.

SOME SOLVED EXAMPLES

Example 40. *The pH of a buffer is 4.745. When 0.01 mole of NaOH is added to 1 litre of it, the pH changes to 4.832, calculate its buffer capacity.*

Solution: From definition,

$$\text{Buffer capacity } (\phi) = \frac{\partial b}{\partial[pH]}$$

$$\partial(pH) = (4.832 - 4.745) = 0.087; \quad \partial b = 0.01$$

Substituting given values,

$$\phi = \frac{0.01}{0.087} = 0.115$$

Example 41. *Suppose it is required to make a buffer solution of pH = 4, using acetic acid and sodium acetate. How much of sodium acetate is to be added to 1 litre of N/10 acetic acid?*

Dissociation constant of acetic acid $= 1.8 \times 10^{-5}$.

Solution: Applying Henderson's equation,

$$pH = \log \frac{[\text{Salt}]}{[\text{Acid}]} - \log K_a$$

$$4 = \log[\text{Salt}] - \log(0.1) - \log 1.8 \times 10^{-5}$$

So, $\log[\text{Salt}] = (4 - 1 - 5 + 0.2552) = \bar{2}.2552$

$$[\text{Salt}] = 0.018 \text{ g mol L}^{-1}$$

The molecular mass of $CH_3COONa = 82$

$$\text{Amount of salt} = 0.018 \times 82 = 1.476 \text{ g}$$

Example 42. *What is the pH of the solution when 0.2 mole of hydrochloric acid is added to one litre of a solution containing 1 M acetic acid and acetate ion? Assume that the total volume is one litre.* (K_a *for* $CH_3COOH = 1.8 \times 10^{-5}$)

Solution: On adding HCl, the free hydrogen ions will combine with CH_3COO^- ions to form CH_3COOH. Thus, the concentration of acetic acid increases while that of CH_3COO^- ions decreases.

$$[CH_3COOH] = (0.2 + 1) = 1.2 \text{ mol litre}^{-1}$$

$$[\text{Salt}] = (1 - 0.2) = 0.8 \text{ mol litre}^{-1}$$

Applying Henderson's equation,

$$\text{pH} = \log \frac{[\text{Salt}]}{[\text{Acid}]} - \log K_a$$

$$= \log \frac{0.8}{1.2} - \log 1.8 \times 10^{-5}$$

$$= \log 2 - \log 3 - \log 1.8 \times 10^{-5} = 4.5687$$

Example 43. *20 mL of 0.2 M sodium hydroxide is added to 50 mL of 0.2 M acetic acid to give 70 mL of the solution. What is the pH of the solution? Calculate the additional volume of 0.2 M NaOH required to make the pH of solution 4.74. The ionisation constant of acetic acid is* 1.8×10^{-5}.

Solution: No. of moles of NaOH in

$$20 \text{ mL} = \frac{0.2}{1000} \times 20 = 0.004$$

$$\text{No. of moles of acetic acid in } 50 \text{ mL} = \frac{0.2}{1000} \times 50 = 0.01$$

When NaOH is added, CH_3COONa is formed.

$$\underset{1 \text{ mole}}{CH_3COOH} + \underset{1 \text{ mole}}{NaOH} \rightleftharpoons \underset{1 \text{ mole}}{CH_3COONa} + \underset{1 \text{ mole}}{H_2O}$$

No. of moles of CH_3COONa in 70 mL solution $= 0.004$

No. of moles of CH_3COOH in 70 mL solution

$$= (0.01 - 0.004) = 0.006$$

Applying Henderson's equation,

$$\text{pH} = \log \frac{[\text{Salt}]}{[\text{Acid}]} - \log K_a$$

$$= \log \frac{0.004}{0.006} - \log 1.8 \times 10^{-5} = 4.5687$$

On further addition of NaOH, the pH becomes 4.74.

$$\text{pH} = \log \frac{[\text{Salt}]}{[\text{Acid}]} - \log K_a$$

$$= \log \frac{[\text{Salt}]}{[\text{Acid}]} - \log 1.8 \times 10^{-5}$$

$$\text{or } \log \frac{[\text{Salt}]}{[\text{Acid}]} = \text{pH} + \log 1.8 \times 10^{-5} = (4.74 - 4.7448) = -0.0048$$

So, $$\log \frac{[\text{Salt}]}{[\text{Acid}]} = \bar{1}.9952$$

$$\frac{[\text{Salt}]}{[\text{Acid}]} = 0.9891$$

Let 'x' moles of NaOH be added.

$$[\text{Salt}] = (0.004 + x) \text{ mole}$$

$$[\text{Acid}] = (0.006 - x) \text{ mole}$$

$$\frac{[\text{Salt}]}{[\text{Acid}]} = \frac{0.004 + x}{0.006 - x} = 0.9891$$

or $$0.004 + x = 0.9891 \times 0.006 - 0.9891x$$

$$x = 0.000972 \text{ mole}$$

Volume of 0.2 M NaOH solution having 0.000972 mole

$$= \frac{1000}{0.2} \times 0.000972 = 4.86 \text{ mL}$$

Example 44. *Calculate the pH of the buffer solution containing 0.15 mole of NH_4OH and 0.25 mole of NH_4Cl. K_b for NH_4OH is* 1.98×10^{-5}.

Solution: Applying the equation,

$$\text{pOH} = \log \frac{[\text{Salt}]}{[\text{Base}]} - \log K_b$$

$$= \log \frac{0.25}{0.15} - \log 1.8 \times 10^{-5}$$

$$= \log 5 - \log 3 - \log 1.8 \times 10^{-5}$$

$$= 0.6989 - 0.4771 + 4.7448 = 4.966$$

$$\text{pH} = (14 - 4.966) = 9.034$$

Example 45. *What volume of 0.10 M sodium formate solution should be added to 50 mL of 0.05 M formic acid to produce a buffer solution of pH 4.0? pK_a for formic acid is 3.80.* (IIT 1990)

Solution: Let x mL of 0.10 M sodium formate be added.

$$\text{No. of moles in } x \text{ mL of } 0.10\,M \text{ sodium formate} = \frac{0.10}{1000} \times x$$

$$\text{No. of moles in } 50 \text{ mL of } 0.05\,M \text{ formic acid} = \frac{0.05}{1000} \times 50$$

$$\frac{[\text{Sod. formate}]}{[\text{Formic acid}]} = \frac{\frac{0.10 \times x}{1000}}{\frac{0.05 \times 50}{1000}} = \frac{0.10x}{2.5} = 0.04x$$

Applying the equation,

$$\text{pH} = \log \frac{[\text{Salt}]}{[\text{Acid}]} + \text{p}K_a$$

$$4.0 = \log 0.04x + 3.8$$

or $$x = 39.6 \text{ mL}$$

Example 46. *How many gram moles of HCl will be required to prepare one litre of a buffer solution (containing NaCN and HCN) of pH 8.5 using 0.01 g formula mass of NaCN? K_a for HCN* $= 4.1 \times 10^{-10}$.

Solution: Let a mole of HCl be added. It will combine with NaCN to form HCN.

$$\underset{a}{NaCN} + \underset{a}{HCl} \longrightarrow NaCl + \underset{a}{HCN}$$

$$[NaCN] = (0.01 - a)$$

$$[HCN] = a$$

Applying the equation,

$$\text{pH} = \log \frac{[NaCN]}{[HCN]} - \log K_a$$

$$8.5 = \log \frac{0.01 - a}{a} - \log 4.1 \times 10^{-10}$$

So, $$\log \frac{(0.01 - a)}{a} = 8.5 + 0.6127 - 10.0 = \bar{1}.1127$$

$$\frac{(0.01 - a)}{a} = 0.1296$$

or $$a = \frac{0.01}{1.1296} = 0.0089 \text{ mole}$$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

26. The pH of a solution that is 0.1 M NaA and 0.1 M HA $(K_a = 1 \times 10^{-6})$ would be:

(a) 5 (b) 6 (c) 3 (d) 7

[Ans. (b)]

[Hint: $\text{pH} = \text{p}K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]} = -\log K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$

$$= -\log 10^{-6} + \log \frac{0.1}{0.1} = 6]$$

27. pK_a for acetic acid is 4.74. What should be the ratio of concentrations of acetic acid and acetate ions to have a solution with pH 5.74?

(a) 1 : 10 (b) 10 : 1 (c) 1 : 1 (d) 2 : 1

[Ans. (a)]

[Hint: $$\text{pH} = \text{p}K_a + \log \frac{[\text{Acetate ion}]}{[\text{Acetic acid}]}$$

$$5.74 = 4.74 + \log \frac{[\text{Acetate ion}]}{[\text{Acetic acid}]}$$

$$[\text{Acetic acid}] : [\text{Acetate}] = 1 : 10]$$

28. What is the pH of the buffer solution containing 0.15 mol of NH_4OH and 0.25 mol of NH_4Cl? K_b for NH_4OH is 1.98×10^{-5}:

(a) 10 (b) 9 (c) 9.2 (d) 10.2

[Ans. (b)]

[Hint: $14 - \text{pH} = \text{p}K_b + \log \frac{[\text{Salt}]}{[\text{Base}]}$

$$= -\log (1.98 \times 10^{-5}) + \log \left(\frac{0.25}{0.15}\right)$$

$$\text{pH} \approx 9]$$

29. The pH of a buffer solution of 0.1 M CH_3COOH and 0.1 M CH_3COONa is .... (pK_a = 4.745).

(a) 4.745 (b) 3.745 (c) 5.745 (d) 3.255

[Ans. (a)]

[Hint: $\text{pH} = \text{p}K_a + \log \frac{[CH_3COONa]}{[CH_3COOH]}$

$$= 4.745 + \log \frac{0.1}{0.1} = 4.745]$$

30. The pH of a buffer solution prepared by adding 10 mL of 0.1 M CH_3COOH and 20 mL of 0.1 M sodium acetate will be: (Given: pK_a of CH_3COOH = 4.74)

(a) 4.05 (b) 3.04 (c) 5.04 (d) 3.05

[Ans. (c)]

[Hint:

$$\text{Number of moles of } CH_3COOH = \frac{MV}{1000} = \frac{0.1 \times 10}{1000} = 0.001$$

$$\text{Number of moles of } CH_3COONa = \frac{MV}{1000} = \frac{0.1 \times 20}{1000} = 0.002$$

$$\text{pH} = \text{p}K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

$$= 4.74 + \log \left[\frac{0.002}{0.001}\right] = 5.04]$$

31. 40 mL of 0.1 M ammonium hydroxide is mixed with 20 mL of 0.1 M HCl. What is the pH of the mixture? (pK_b of ammonia solution is 4.74.) (AIIMS 2006)

(a) 4.74 (b) 2.26 (c) 9.26 (d) 5

[Ans. (c)]

[Hint: Since, ammonium hydroxide is 50% neutralised, hence

$$[\text{Salt}] = [\text{Base}]$$

$$\text{pOH} = \text{p}K_b + \log_{10} \frac{[\text{Salt}]}{[\text{Base}]} = 4.74 + \log_{10} 1 = 4.74$$

$$\text{pH} = 14 - 4.74 = 9.26]$$

32. The pK_a of a weak acid (HA) is 4.5. The pOH of an aqueous buffered solution of HA, in which 50% of the acid is ionised, is: (AIEEE 2007)

(a) 7.0 (b) 4.5 (c) 2.5 (d) 9.5

[Ans. (d)]

[Hint: $\text{pH} = \text{p}K_a + \log_{10} \frac{[A^-]}{[HA]}$

Since, acid is 50% ionised, hence $[A^-] = [HA]$

or $$\text{pH} = \text{p}K_a + \log 1$$

$$= 4.5$$

$$\text{pOH} = 14 - 4.5 = 9.5]$$

33. pK_a value of acetic acid is 4.75. If the buffer solution contains 0.125 M acetic acid and 0.25 M sodium acetate, the pH of buffer solution is : [Comed (Karnataka) 2008]

(a) 5.05 (b) 5.5 (c) 4.9 (d) 5.75

[Ans. (a)]

[Hint : $\text{pH} = \text{p}K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$

$$= 4.75 + \log \frac{0.25}{0.125}$$

$$= 5.05]$$

Example 47. *The dissociation constants for HCOOH and CH_3COOH are 2.1×10^{-4} and 1.8×10^{-5} respectively. Calculate the relative strengths of the acids.*

Solution: The strength of the acid is directly proportional to the square root of the dissociation constant.

$$\text{Strength of the acid} \propto \sqrt{\text{dissociation constant}}$$

Hence, $$\frac{\text{Strength of HCOOH}}{\text{Strength of } CH_3COOH} = \sqrt{\frac{K_{HCOOH}}{K_{CH_3COOH}}}$$

$$= \sqrt{\frac{2.1 \times 10^{-4}}{1.8 \times 10^{-5}}} = 3.415$$

Example 48. *Freshly precipitated aluminium and magnesium hydroxides are stirred vigorously in a buffer solution containing* 0.05 *mol* L^{-1} *of* NH_4OH *and* 0.25 *mol* L^{-1} *of* NH_4Cl*. Calculate the concentration of aluminium and magnesium ions in solution.*

$K_{sp}\ Al(OH)_3 = 6\times 10^{-32}$; $K_b\ NH_4OH = 1.8\times 10^{-5}$

$K_{sp}\ Mg(OH)_2 = 6\times 10^{-10}$

Solution: $$\text{pOH} = \log\frac{[\text{Salt}]}{[\text{Base}]} - \log K_b$$

$$-\log[\text{OH}^-] = \log\frac{0.25}{0.05} - \log 1.8\times 10^{-5}$$

or $$\log[\text{OH}^-] = \log\frac{1.8\times 10^{-5}}{5}$$

$$[\text{OH}^-] = 0.36\times 10^{-5}\ \text{mol L}^{-1}$$

$$[\text{Al}^{3+}] = \frac{K_{sp}\ \text{Al(OH)}_3}{[\text{OH}^-]^3} = \frac{6\times 10^{-32}}{(0.36\times 10^{-5})^3} = 1.29\times 10^{-10}\ \text{mol L}^{-1}$$

$$[\text{Mg}^{2+}] = \frac{K_{sp}\ \text{Mg(OH)}_2}{[\text{OH}^-]^2} = \frac{6\times 10^{-10}}{(0.36\times 10^{-5})^2} = 46.3\ \text{mol L}^{-1}$$

Example 49. *Calculate the pH at which* $Mg(OH)_2$ *begins to precipitate from a solution containing* $0.10\ M\ Mg^{2+}$ *ions.*
($K_{sp}\ Mg(OH)_2 = 1.0\times 10^{-11}$) **(IIT 1992)**

Solution: $K_{sp}\ \text{Mg(OH)}_2 = 1.0\times 10^{-11} = [\text{Mg}^{2+}][\text{OH}^-]^2$

$$= (0.10)[\text{OH}^-]^2$$

or $$[\text{OH}^-]^2 = \frac{1.0\times 10^{-11}}{0.10} = 1\times 10^{-10}$$

or $$[\text{OH}^-] = 1\times 10^{-5}$$

$$[\text{H}^+] = \frac{1\times 10^{-14}}{1\times 10^{-5}} = 1\times 10^{-9}$$

$$\text{pH} = -\log[\text{H}^+] = -\log(1\times 10^{-9}) = 9.0$$

Example 50. *An aqueous solution of metal bromide,* MBr_2 ($0.05\,M$) *is saturated with* H_2S*. What is the minimum pH at which MS will precipitate?* K_{sp} *for* $MS = 6.0\times 10^{-21}$*, conc. of saturated* $H_2S = 0.1\,M$*.*
$K_1 = 10^{-7}$ *and* $K_2 = 1.3\times 10^{-13}$ *for* H_2S **(IIT 1993)**

Solution: The minimum concentration of S^{2-} ions required to precipitate MS is,

$$[\text{S}^{2-}] = \frac{K_{sp}\ M\text{S}}{[M^{2+}]} = \frac{6.0\times 10^{-21}}{0.05} = 1.2\times 10^{-19}\ M$$

H_2S ionises in solution in two steps:

$$\text{H}_2\text{S} \rightleftharpoons \text{H}^+ + \text{HS}^-;\quad K_1 = 10^{-7}$$

$$\text{HS}^- \rightleftharpoons \text{H}^+ + \text{S}^{2-};\quad K_2 = 1.3\times 10^{-13}$$

$$\frac{[\text{H}^+][\text{HS}^-]}{[\text{H}_2\text{S}]} = K_1 \quad\text{and}\quad \frac{[\text{H}^+][\text{S}^{2-}]}{[\text{HS}^-]} = K_2$$

Hence, $$K_1K_2 = \frac{[\text{H}^+]^2[\text{S}^{2-}]}{[\text{H}_2\text{S}]}$$

or $$[\text{H}^+]^2 = \frac{K_1K_2[\text{H}_2\text{S}]}{[\text{S}^{2-}]} = \frac{10^{-7}\times 1.3\times 10^{-13}\times 0.1}{1.2\times 10^{-19}}$$

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

So, $$[\text{H}^+] = 1.04\times 10^{-1}$$

$$\text{pH} = -\log[\text{H}^+] = -\log(1.04\times 10^{-1}) = 0.98$$

Example 51. *The pH of blood stream is maintained by a proper balance of* H_2CO_3 *and* $NaHCO_3$ *concentrations. What volume of* $5\,M\ NaHCO_3$ *solution should be mixed with a* $10\,mL$ *sample of blood which is* $2\,M$ *in* H_2CO_3*, in order to maintain a pH of 7.47 ?* K_a *for* H_2CO_3 *in blood is* 7.8×10^{-7}*.* **(IIT 1993)**

Solution: Let V mL of 5 M NaHCO_3 solution be mixed.

Total volume = $(V + 10)$ mL

Conc. of H_2CO_3 and NaHCO_3 in the solution becomes

$$[\text{NaHCO}_3] = \frac{5\times V}{(V+10)}\,M$$

and $$[\text{H}_2\text{CO}_3] = \frac{2\times 10}{(V+10)}\,M$$

Now applying Henderson's equation,

$$\text{pH} = -\log K_a + \log\frac{[\text{NaHCO}_3]}{[\text{H}_2\text{CO}_3]}$$

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

$$= -\log 7.8\times 10^{-7} + \log\frac{V}{4}$$

or $$\log\frac{V}{4} = 7.4 + \log 7.8\times 10^{-7}$$

$$V = 78.32\ \text{mL}$$

Example 52. *The pH of* $0.05\ M$ *aqueous solution of diethylamine is 12. Calculate its* K_b*.* **(IIT 1993)**

Solution: We know that, $\text{pH} + \text{pOH} = 14$

or $$\text{pOH} = 14 - \text{pH} = 14 - 12 = 2$$

So, $$[\text{OH}^-] = 10^{-2}$$

$$\begin{array}{lcccc} & (\text{C}_2\text{H}_5)_2\text{NH} + \text{H}_2\text{O} & \rightleftharpoons & (\text{C}_2\text{H}_5)_2\text{NH}_2^+ & + \ \text{OH}^- \\ \text{At equilibrium} & (0.05 - x) & & x & x \\ & (0.05 - 0.01) & & 0.01 & 0.01 \end{array}$$

$$K_b = \frac{[(\text{C}_2\text{H}_5)_2\text{NH}_2^+][\text{OH}^-]}{[(\text{C}_2\text{H}_5)_2\text{NH}]} = \frac{0.01\times 0.01}{0.04} = 2.5\times 10^{-3}$$

Example 53. *100 mL of HCl gas at 25°C and 740 mm pressure were dissolved in one litre of water. Calculate the pH of solution. Given, vapour pressure of* H_2O *at 25° C is 23.7 mm.*

Solution: Given, $V = 100\ \text{mL} = 0.1\ \text{L}$

$$P = \left(\frac{740 - 23.7}{760}\right)\text{atm} = 0.9425\ \text{atm}$$

$$R = 0.0821$$

$$T = (25 + 273)\ \text{K} = 298\ \text{K}$$

Applying, $$PV = nRT$$

or $$n = \frac{PV}{RT} = \frac{0.9425 \times 0.1}{0.0821 \times 298} = 3.85 \times 10^{-3} \text{ mol}$$

$$\text{Molarity} = \frac{n}{V} = \frac{3.85 \times 10^{-3}}{1} = 3.85 \times 10^{-3}\ M$$

HCl is a strong electrolyte. It is completely dissociated.

So, $$[H^+] = 3.85 \times 10^{-3}\ M$$

$$pH = -\log [H^+] = -\log 3.85 \times 10^{-3} = 2.4146$$

Example 54. *Calculate the $[Cl^-]$, $[Na^+]$, $[H^+]$, $[OH^-]$ and pH of the resulting solution obtained by mixing 50 mL of 0.6 N HCl and 50 mL of 0.3 N NaOH.*

Solution:	HCl +	NaOH	$\longrightarrow$ NaCl +	H_2O
Milli-equivalents before reaction	50×0.6 = 30	50×0.3 = 15	0	0
Milli-equivalents after reaction	(30 − 15) = 15	0	15	15

$$\text{Total volume} = 50 + 50 = 100 \text{ mL}$$

$$[Cl^-] = \frac{15 + 15}{100} = 0.3\ M$$

$$[Na^+] = \frac{15}{100} = 0.15\ M$$

$$[H^+] = \frac{15}{100} = 0.15\ M$$

$$[OH^-] = \frac{10^{-14}}{0.15} = 6.6 \times 10^{-14}$$

$$pH = -\log [H^+] = -\log 0.15 = 0.8239$$

Example 55. *What is the pH of a 1.0 M solution of acetic acid? To what volume of one litre of this solution be diluted so that the pH of the resulting solution will be twice the original value? Given, $K_a = 1.8 \times 10^{-5}$.* **(IIT 1990)**

Solution: We know that degree of dissociation,

$$\alpha = \sqrt{\frac{K_a}{C}}$$

$$= \sqrt{\frac{1.8 \times 10^{-5}}{1}}$$

$$= 4.2426 \times 10^{-3}$$

$$[H^+] = C \times \alpha = 1 \times 4.2426 \times 10^{-3}$$

$$= 4.2426 \times 10^{-3} \text{ mol L}^{-1}$$

$$pH = -\log [H^+] = -\log 4.2426 \times 10^{-3} = 2.3724$$

So, pH of the acetic acid solution after dilution = 2 × 2.3724

= 4.7448

$$\text{New } [H^+] = 10^{-4.7448} = 1.8 \times 10^{-5}$$

Let the new concentration be C_0.

$$\underset{\text{At equilibrium } C_0 - 1.8 \times 10^{-5}}{CH_3COOH} \rightleftharpoons \underset{1.8 \times 10^{-5}}{H^+} + \underset{1.8 \times 10^{-5}}{CH_3COO^-}$$

$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} = \frac{1.8 \times 10^{-5} \times 1.8 \times 10^{-5}}{(C_0 - 1.8 \times 10^{-5})} = 1.8 \times 10^{-5}$$

So, $$C_0 = 3.6 \times 10^{-5}$$

Let the new volume be V litre

$$1 \times 1 = 3.6 \times 10^{-5} \times V$$

$$V = \frac{1}{3.6 \times 10^{-5}} = 2.78 \times 10^4 \text{ litre}$$

Example 56. *Calculate the change in pH of one litre buffer solution containing 0.10 mole each of NH_3 and NH_4Cl upon addition of* (i) 0.02 *mole of dissolved gaseous HCl,* (ii) 0.02 *mole of dissolved NaOH.*
Assume no change in volume (K_b for $NH_3 = 1.8 \times 10^{-5}$). **(IIT 1992)**

Solution: pOH of NH_3 and NH_4Cl buffer

$$= -\log K_b + \log \frac{[\text{Salt}]}{[\text{Base}]}$$

$$= -\log 1.8 \times 10^{-5} + \log \frac{0.1}{0.1} = 4.75$$

$$pH = (14 - 4.75) = 9.25$$

First case: $NH_3 + HCl \longrightarrow NH_4Cl$

$$[\text{Salt}] = (0.1 + 0.02) = 0.12\ M$$

$$[\text{Base}] = (0.1 - 0.02) = 0.08\ M$$

$$pOH = -\log K_b + \log \frac{0.12}{0.08}$$

$$= 4.75 + 0.176 = 4.926$$

$$pH = (14 - 4.926) = 9.074$$

$$\Delta pH = (9.25 - 9.074) = 0.176 \text{ pH unit}$$

Second case: $NH_4Cl + NaOH \longrightarrow NH_3 + NaCl$

$$[\text{Salt}] = (0.1 - 0.02) = 0.08\ M$$

$$[\text{Base}] = (0.1 + 0.02) = 0.12\ M$$

$$pOH = -\log K_b + \log \frac{0.08}{0.12}$$

$$= (4.75 - 0.176) = 4.576$$

$$pH = (14 - 4.574) = 9.426$$

$$\Delta pH = (9.426 - 9.25) = 0.176 \text{ pH unit}$$

Example 57. *Saccharin ($K_a = 2 \times 10^{-12}$) is a weak acid represented by formula HSac. A 4×10^{-4} mole amount of saccharin is dissolved in 200 cm³ water of pH = 3. Assuming no change in volume, calculate the concentration of Sac⁻ ions in the resulting solution at equilibrium.* **(IIT 1994)**

Solution: Concentration of saccharin

$$= \frac{4 \times 10^{-4}}{200} \times 1000 = 2 \times 10^{-3} \text{ mol L}^{-1}$$

$$[H^+] = 10^{-pH} = 10^{-3} \text{ mol L}^{-1}$$

$$\underset{[(2\times10^{-3})-x]}{\text{HSac}} \rightleftharpoons \underset{(10^{-3}+x)}{\text{H}^+} + \text{Sac}^-$$

$$K_a = \frac{[\text{H}^+][\text{Sac}^-]}{[\text{HSac}]} = \frac{(10^{-3}+x)[\text{Sac}^-]}{[2\times10^{-3}-x]}$$

$$[\text{Sac}^-] = \frac{2\times10^{-12}\times(2\times10^{-3}-x)}{(10^{-3}+x)}$$

Since, x is very small, it can be neglected.

$$[\text{Sac}^-] = \frac{2\times10^{-12}\times2\times10^{-3}}{10^{-3}} = 4\times10^{-12}\ \text{mol L}^{-1}$$

Example 58. *An aqueous solution contains 10% ammonia by mass and has a density 0.99 g cm^{-3}. Calculate hydroxyl and hydrogen ion concentration in this solution. (K_a for $NH_4^+ \approx 5.0\times10^{-10}\ M$)* (IIT 1995)

Solution: Mass of 1 litre solution $= 1000\times0.99$ g

$= 990$ g

NH_3 present in 990 g solution $= 99$ g

1 litre solution contains $= \frac{99}{17} = 5.8$ mole

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

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{x\times x}{(5.8-x)} \approx \frac{x^2}{5.8}$$

$$K_b = \frac{K_w}{K_a} = \frac{10^{-14}}{5.0\times10^{-10}} = 2\times10^{-5}$$

So, $$2\times10^{-5} = \frac{x^2}{5.8}$$

$$x^2 = 2\times10^{-5}\times5.8$$

$$x = 1.078\times10^{-2}\ \text{mol L}^{-1}$$

$$[OH^-] = x = 1.078\times10^{-2}\ M$$

$$[H^+] = \frac{10^{-14}}{1.078\times10^{-2}} = 9.27\times10^{-13}\ M$$

Example 59. 0.15 *mole of pyridium chloride has been added into 500 cm^3 of 0.2 M pyridine solution. Calculate pH and hydroxyl ion concentration in the resulting solution assuming no change in volume.*

(K_b for pyridine $= 1.5\times10^{-9}\ M$) (IIT 1995)

Solution: Concentration of pyridium chloride

$= 0.15\times2 = 0.3\ M$

$$\text{pOH} = \log\frac{[\text{Salt}]}{[\text{Base}]} - \log K_b$$

$$= \log\frac{0.3}{0.2} - \log 1.5\times10^{-9}$$

$$= 9$$

$$[OH^-] = 10^{-\text{pOH}} = 10^{-9}$$

$$\text{pH} = (14-\text{pOH}) = (14-9) = 5$$

Example 60. *How many moles of acetic acid and sodium acetate each should be dissolved to prepare one litre of 0.063 molar buffer solution of pH 4.5?*

(K_a for $CH_3COOH = 1.8\times10^{-5}$)

Solution: Applying Henderson's equation,

$$\text{pH} = \log\frac{[\text{Salt}]}{[\text{Acid}]} - \log K_a$$

$$\log\frac{[\text{Salt}]}{[\text{Acid}]} = 4.5 + \log 1.8\times10^{-5} = -0.2447$$

$$\frac{[\text{Salt}]}{[\text{Acid}]} = \text{antilog}\ (-0.2447) = 0.5692$$

$$[\text{Salt}] = 0.5692\times[\text{Acid}]$$

Given: $[\text{Acid}] + [\text{Salt}] = 0.063$

$$[\text{Acid}] = \frac{0.063}{1.5692} = 0.040\ \text{mol L}^{-1}$$

$$[\text{Salt}] = (0.063-0.040) = 0.023\ \text{mol L}^{-1}$$

10.12 SALT HYDROLYSIS

Pure water is a weak electrolyte and neutral in nature, *i.e.*, H^+ ion concentration is exactly equal to OH^- ion concentration

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

When this condition is disturbed by decreasing the concentration of either of the two ions, the neutral nature changes into acidic or basic. When $[H^+] > [OH^-]$, the water becomes acidic and when $[H^+] < [OH^-]$, the water acquires basic nature. This is exactly the change which occurs during the phenomenon known as **salt hydrolysis.** It is defined as **a reaction in which the cation or anion or both of a salt react with water to produce acidity or alkalinity.**

Salts are strong electrolytes. When dissolved in water, they dissociate almost completely into ions. In some salts, cations are more reactive in comparison to anions and these react with water to produce H^+ ions. Thus, the solution acquires acidic nature.

$$M^+ + H_2O \rightleftharpoons \underset{\text{Weak base}}{MOH} + H^+$$

In other salts, anions may be more reactive in comparison to cations and these react with water to produce OH^- ions. Thus, the solution becomes basic.

$$A^- + H_2O \rightleftharpoons \underset{\text{Weak acid}}{HA} + OH^-$$

The process of hydrolysis is actually the reverse of neutralisation.

$$\text{Salt} + \text{Water} \rightleftharpoons \text{Acid} + \text{Base}$$

If acid is stronger than base, the solution is acidic and in case base is stronger than acid, the solution is alkaline. When both the acid and the base are either strong or weak, the solution is generally neutral in nature.

As the nature of the cation or the anion of the salt determines whether its solution will be acidic or basic, it is proper to divide the salts into four categories.

(i) Salt of a strong acid and a weak base.
Examples: $FeCl_3$, $CuCl_2$, $AlCl_3$, NH_4Cl, $CuSO_4$, etc.

(ii) Salt of a strong base and a weak acid.
Examples: CH_3COONa, $NaCN$, $NaHCO_3$, Na_2CO_3, etc.

(iii) Salt of a weak acid and a weak base.
Examples: CH_3COONH_4, $(NH_4)_2CO_3$, NH_4HCO_3, etc.

(iv) Salt of a strong acid and a strong base.
Examples: $NaCl$, K_2SO_4, $NaNO_3$, $NaBr$, etc.

1. Salt of a strong acid and a weak base

The solution of such a salt is acidic in nature. The cation of the salt which has come from weak base is reactive. It reacts with water to form a weak base and H^+ ions.

$$B^+ + H_2O \rightleftharpoons \underset{\text{Weak base}}{BOH} + H^+$$

Consider, for example, NH_4Cl. It ionises in water completely into NH_4^+ and Cl^- ions. NH_4^+ ions react with water to form a weak base (NH_4OH) and H^+ ions.

$$\underset{C(1-x)}{NH_4^+} + H_2O \rightleftharpoons \underset{Cx}{NH_4OH} + \underset{Cx}{H^+}$$

Thus, hydrogen ion concentration increases and the solution becomes acidic.

Applying law of mass action,

$$K_h = \frac{[H^+][NH_4OH]}{[NH_4^+]} = \frac{Cx \cdot Cx}{C(1-x)} = \frac{x^2C}{(1-x)} \qquad \text{... (i)}$$

where, C is the concentration of salt and x the degree of hydrolysis.

Other equilibria which exist in solution are

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-,\ K_b = \frac{[NH_4^+][OH^-]}{[NH_4OH]} \qquad \text{... (ii)}$$

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

From eqs. (ii) and (iii),

$$\frac{K_w}{K_b} = \frac{[H^+][NH_4OH]}{[NH_4^+]} = K_h \qquad \text{... (iv)}$$

$$[H^+] = \frac{K_h[NH_4^+]}{[NH_4OH]} = \frac{K_w}{K_b} \times \frac{[NH_4^+]}{[NH_4OH]}$$

$$\log[H^+] = \log K_w - \log K_b + \log\frac{[\text{Salt}]}{[\text{Base}]}$$

$$-\text{pH} = -\text{p}K_w + \text{p}K_b + \log\frac{[\text{Salt}]}{[\text{Base}]}$$

$$\text{p}K_w - \text{pH} = \text{p}K_b + \log\frac{[\text{Salt}]}{[\text{Base}]}$$

$$\text{pOH} = \text{p}K_b + \log\frac{[\text{Salt}]}{[\text{Base}]}$$

Relation between Hydrolysis Constant and Degree of Hydrolysis

The extent to which hydrolysis proceeds is expressed as degree of hydrolysis and is defined as the fraction of one mole of the salt that is hydrolysed when the equilibrium has been attained. It is generally expressed as h or x.

$$h = \frac{\text{Amount of salt hydrolysed}}{\text{Total salt taken}}$$

Considering again eq. (i),

$$K_h = \frac{x^2C}{(1-x)} \quad \text{or} \quad K_h = \frac{h^2C}{(1-h)}$$

When h is very small $(1-h) \longrightarrow 1$,

$$h^2 = K_h \times \frac{1}{C}$$

or

$$h = \sqrt{\frac{K_h}{C}}$$

$$= \sqrt{\frac{K_w}{K_b \times C}}$$

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

$$\log[H^+] = \frac{1}{2}\log K_w + \frac{1}{2}\log C - \frac{1}{2}\log K_b$$

$$\text{pH} = \frac{1}{2}\text{p}K_w - \frac{1}{2}\log C - \frac{1}{2}\text{p}K_b$$

$$= 7 - \frac{1}{2}\text{p}K_b - \frac{1}{2}\log C$$

2. Salt of a weak acid and a strong base

The solution of such a salt is basic in nature. The anion of the salt is reactive. It reacts with water to form a weak acid and OH^- ions.

$$A^- + H_2O \rightleftharpoons \underset{\text{Weak acid}}{HA} + OH^-$$

Consider, for example, the salt CH_3COONa. It ionises in water completely to give CH_3COO^- and Na^+ ions. CH_3COO^- ions react with water to form a weak acid, CH_3COOH and OH^- ions.

$$\underset{C(1-x)}{CH_3COO^-} + H_2O \rightleftharpoons \underset{Cx}{CH_3COOH} + \underset{Cx}{OH^-}$$

Thus, OH^- ion concentration increases, the solution becomes alkaline.

Applying law of mass action,

$$K_h = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]} = \frac{Cx \times Cx}{C(1-x)} = \frac{Cx^2}{(1-x)} \qquad \text{... (i)}$$

Other equilibria present in the solution are:

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

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

From eqs. (ii) and (iii),

$$\frac{K_w}{K_a} = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]} = K_h \qquad \text{... (iv)}$$

$$[OH^-] = \frac{K_h[CH_3COO^-]}{[CH_3COOH]} = \frac{K_w}{K_a}\frac{[CH_3COO^-]}{[CH_3COOH]}$$

$$\log [OH^-] = \log K_w - \log K_a + \log \frac{[Salt]}{[Acid]}$$

$$-pOH = -pK_w + pK_a + \log \frac{[Salt]}{[Acid]}$$

$$pK_w - pOH = pK_a + \log \frac{[Salt]}{[Acid]}$$

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

Considering eq. (i) again,

$$K_h = \frac{Cx^2}{(1-x)} \text{ or } K_h = \frac{Ch^2}{(1-h)}$$

When h is very small, $(1-h) \longrightarrow 1$

or $$h^2 = \frac{K_h}{C}$$

or $$h = \sqrt{\frac{K_h}{C}}$$

$$[OH^-] = h \times C = \sqrt{CK_h} = \sqrt{\frac{C \times K_w}{K_a}}$$

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

$$= \frac{K_w}{\sqrt{\frac{C \times K_w}{K_a}}} = \sqrt{\frac{K_a \times K_w}{C}}$$

$$-\log [H^+] = -\frac{1}{2}\log K_w - \frac{1}{2}\log K_a + \frac{1}{2}\log C$$

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

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

3. Salt of a weak acid and a weak base

Maximum hydrolysis occurs in the case of such a salt as both the cation and anion are reactive and react with water to produce H^+ and OH^- ions. The solution is generally neutral but it can be either slightly acidic or slightly alkaline if both the reactions take place with slightly different rates. Consider, for example, the salt CH_3COONH_4. It gives CH_3COO^- and NH_4^+ ions in solution. Both react with water.

$$\left.\begin{array}{l} NH_4^+ + H_2O \rightleftharpoons \underset{\text{Weak base}}{NH_4OH} + H^+ \\ CH_3COO^- + H_2O \rightleftharpoons \underset{\text{Weak acid}}{CH_3COOH} + OH^- \end{array}\right\}$$

Both the reactions occur with same speeds. The solution is neutral.

$$\text{or } \underset{C(1-h)}{CH_3COO^-} + \underset{C(1-h)}{NH_4^+} + H_2O \rightleftharpoons \underset{Ch}{CH_3COOH} + \underset{Ch}{NH_4OH}$$

$$K_h = \frac{[CH_3COOH][NH_4OH]}{[CH_3COO^-][NH_4^+]}$$

Other equilibria which exist in solution are:

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

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-, \quad K_b = \frac{[NH_4^+][OH^-]}{[NH_4OH]} \qquad \text{... (ii)}$$

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

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

$$K_h = \frac{K_w}{K_a \cdot K_b} = \frac{[CH_3COOH][NH_4OH]}{[CH_3COO^-][NH_4^+]} \qquad \text{... (iv)}$$

Let C be the concentration and h be the degree of hydrolysis

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

When h is small, $(1-h) \longrightarrow 1$,

$$K_h = h^2$$

$$h = \sqrt{K_h} = \sqrt{\frac{K_w}{K_a \times K_b}}$$

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

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

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

$$-\log [H^+] = -\frac{1}{2}\log K_a - \frac{1}{2}\log K_w + \frac{1}{2}\log K_b$$

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

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

When $pK_a = pK_b$, pH = 7, *i.e.*, solution will be neutral in nature.

When $pK_a > pK_b$, the solution will be alkaline as the acid will be slightly weaker than base and pH value will be more than 7. In case $pK_a < pK_b$, the solution will be acidic as the acid is relatively stronger than base and pH will be less than 7.

4. Salt of a strong acid and a strong base

Such a salt, say NaCl, does not undergo hydrolysis as both the ions are not reactive. The solution is thus, neutral in nature.

5. Hydrolysis of amphiprotic anion

Let us consider hydrolysis of amphiprotic anion only, *i.e.*, when counter cation is not hydrolysed example of some salts of this category are $NaHCO_3$, NaHS, Na_2HPO_4, NaH_2PO_4.

$$\text{(i) } H_3PO_4 \rightleftharpoons H_2PO_4^- + H^+; \quad K_{a_1} = \frac{[H_2PO_4^-][H^+]}{[H_3PO_4]}$$

$$\text{(ii) } H_2PO_4^- \rightleftharpoons HPO_4^{2-} + H^+; \quad K_{a_2} = \frac{[HPO_4^{2-}][H^+]}{[H_2PO_4^-]}$$

$$\text{(iii) } HPO_4^{2-} \rightleftharpoons PO_4^{3-} + H^+; \quad K_{a_3} = \frac{[PO_4^{3-}][H^+]}{[HPO_4^{2-}]}$$

Here, $H_2PO_4^-$ and HPO_4^{2-} are amphiprotic anions, pH after their hydrolysis can be calculated as,

$$\text{pH of } H_2PO_4^- \text{ in aqueous medium} = \frac{pK_{a_1} + pK_{a_2}}{2}$$

$$\text{pH of } HPO_4^{2-} \text{ in aqueous medium} = \frac{pK_{a_2} + pK_{a_3}}{2}$$

Here, $\mathbf{HPO_4^{2-}}$ is conjugate base of $\mathbf{H_2PO_4^-}$ and $\mathbf{H_3PO_4}$ is conjugate acid of $\mathbf{H_2PO_4^-}$.

Similarly, $\mathbf{PO_4^{3-}}$ is conjugate base of $\mathbf{HPO_4^{2-}}$ and $\mathbf{HPO_4^{2-}}$ is conjugate acid of $\mathbf{PO_4^{3-}}$.

(iv) Let us consider amphiprotic bicarbonate anion.

$$\underset{\text{Acid}}{HCO_3^{2-}} + H_2O \rightleftharpoons \underset{\text{Conjugate base}}{CO_3^{2-}} + H_3^+O \quad \text{(Ionization)}$$

$$\underset{\text{Base}}{HCO_3^-} + H_2O \rightleftharpoons \underset{\text{Conjugate acid}}{H_2CO_3} + OH^- \quad \text{(Hydrolysis)}$$

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-; \quad K_{a_1} = \frac{[H^+][HCO_3^-]}{[H_2CO_3]}$$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}; \quad K_{a_2} = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]}$$

pH of HCO_3^- ion after hydrolysis in aqueous medium

$$= \frac{pK_{a_1} + pK_{a_2}}{2}$$

(v) Let us consider the hydrolysis of amphiprotic anion along with cation, *e.g.*, NH_4HCO_3, NH_4HS.

In above examples both cations and anions are derived from weak base and weak acids respectively, hence both will undergo hydrolysis in aqueous medium.

When these salts are dissolved in water, $[H_3O^+]$ concentration can be determined as,

$$[H_3O^+] = \sqrt{K_{a_1}\left[\frac{K_w}{K_b} + K_{a_2}\right]}$$

$$pH = -\log\sqrt{K_{a_1}\left[\frac{K_w}{K_b} + K_{a_2}\right]}$$

Table 10.1 Hydrolysis at a Glance

Salt	Nature	Degree	Hydrolysis Constant	pH
1. NaCl (Strong acid + Strong base)	Neutral	No hydrolysis	—	—
2. CH_3COONa (Weak acid + Strong base)	Basic	$h = \sqrt{\frac{K_w}{CK_a}}$	$K_h = \frac{K_w}{K_a}$	$pH = \frac{1}{2}[pK_w + pK_a + \log C]$
3. NH_4Cl (Strong acid + Weak base)	Acidic	$h = \sqrt{\frac{K_w}{CK_b}}$	$K_h = \frac{K_w}{K_b}$	$pH = \frac{1}{2}[pK_w - pK_b - \log C]$
4. CH_3COONH_4 (Weak acid + Weak base)	*	$h = \sqrt{\frac{K_w}{K_a \times K_b}}$	$K_h = \frac{K_w}{K_a \times K_b}$	$pH = \frac{1}{2}[pK_w + pK_a - pK_b]$

*In the case of salt of weak acid and weak base, nature of medium after hydrolysis is decided in the following manner:

(i) If $K_a = K_b$, the medium will be neutral.
(ii) If $K_a > K_b$, the medium will be acidic.
(iii) If $K_a < K_b$, the medium will be basic.

The degree of hydrolysis of salts of weak acids and weak bases is unaffected by dilution because there is no concentration term in the expression of degree of hydrolysis.

[**Note:** Degree of hydrolysis always increases with increase in temperature because at elevated temperature increase in K_w is greater as compared to K_a and K_b.]

SOME SOLVED EXAMPLES

Example 61. *Calculate the degree of hydrolysis and pH of* 0.1 *M sodium acetate solution. Hydrolysis constant of sodium acetate is* 5.6×10^{-10}.

Solution: $\underset{0.1(1-h)}{CH_3COO^-} + H_2O \rightleftharpoons \underset{(0.1 \times h)}{CH_3COOH} + \underset{(0.1 \times h)}{OH^-}$

$$K_h = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]} = \frac{(0.1 \times h)(0.1 \times h)}{0.1(1-h)};$$

$$\because h \text{ is small } (1-h) \longrightarrow 1$$

$$5.6 \times 10^{-10} = 0.1 \times h^2$$

or $$h^2 = \frac{5.6 \times 10^{-10}}{0.1} = 56 \times 10^{-10}$$

$$h = 7.48 \times 10^{-5}$$

$$[OH^-] = Ch = 0.1 \times 7.48 \times 10^{-5} = 7.48 \times 10^{-6}\ M$$

$$[H^+] = \frac{K_w}{[OH^-]} = \frac{10^{-14}}{7.48 \times 10^{-6}} = 1.33 \times 10^{-9}\ M$$

$$pH = -\log[H^+] = -\log(1.33 \times 10^{-9}) = 8.88$$

Example 62. *When* 0.2 *M acetic acid is neutralised with* 0.2 *M NaOH in* 0.5 *litre of water the resulting solution is slightly alkaline. Calculate the pH of the resulting solution.* K_a *for* $CH_3COOH = 1.8 \times 10^{-5}$.

Solution: 0.2 M acetic acid will form 0.2 M CH_3COONa in 0.5 litre of water. Hence, concentration of sodium acetate, $[CH_3COONa] = 0.1\,\text{mol L}^{-1}$.

$$\underset{C(1-x)}{CH_3COO^-} + H_2O \rightleftharpoons \underset{Cx}{CH_3COOH} + \underset{Cx}{OH^-}$$

$$K_h = \frac{Cx^2}{(1-x)} = Cx^2 \qquad (1-x) \longrightarrow 1$$

$$K_h = \frac{K_w}{K_a} = \frac{1\times 10^{-14}}{1.8\times 10^{-5}} = 5.5\times 10^{-10}$$

So, $K_h = Cx^2 = 5.5\times 10^{-10}$

or $x^2 = \dfrac{5.5\times 10^{-10}}{0.1} = 55\times 10^{-10}$

or $x = 7.42\times 10^{-5}$

$$[OH^-] = Cx = 7.42\times 10^{-5}\times 0.1 = 7.42\times 10^{-6}\ M$$

$$[H^+] = \frac{K_w}{[OH^-]} = \frac{1\times 10^{-14}}{7.42\times 10^{-6}} = 1.3477\times 10^{-9}\ M$$

$$pH = -\log[H^+] = -\log(1.3477\times 10^{-9}) = 8.87$$

Example 63. *Calculate the hydrolysis constant for NH_4Cl, pH value and $[OH^-]$ in 0.1 M NH_4Cl solution.*
$(K_{NH_4OH} = 1.75\times 10^{-5}, K_w = 1\times 10^{-14})$

Solution: We know that, $K_h = \dfrac{K_w}{K_b}$

So, $K_h = \dfrac{1\times 10^{-14}}{1.75\times 10^{-5}} = 5.7\times 10^{-10}$

Hydrolysis of NH_4Cl can be represented as,

$$\underset{C(1-x)}{NH_4^+} + H_2O \rightleftharpoons \underset{Cx}{NH_4OH} + \underset{Cx}{H^+}$$

Thus, $K_h = \dfrac{Cx^2}{(1-x)}$

Neglecting 'x' in denominator,

$$x^2 = \frac{K_h}{C} = \frac{5.7\times 10^{-10}}{0.1} = 57\times 10^{-10}$$

or $x = 7.55\times 10^{-5}$

$$[H^+] = Cx = 0.1\times 7.55\times 10^{-5} = 7.55\times 10^{-6}\ M$$

$$pH = -\log[H^+] = -\log(7.55\times 10^{-6}) = 5.12$$

Again, $[OH^-] = \dfrac{K_w}{[H^+]} = \dfrac{1\times 10^{-14}}{7.55\times 10^{-6}} = 1.32\times 10^{-9}\ M$

Example 64. *Calculate the pH at the equivalence point when a solution of 0.1 M acetic acid is titrated with a solution of 0.1 M sodium hydroxide.*
K_a for acetic acid $= 1.9\times 10^{-5}$ **(IIT 1990)**

Solution: Concentration of sodium acetate $= \dfrac{0.1}{2} = 0.05\ M$ as equal volumes of the acid and the base will be used.

The equilibrium is,

$$\underset{C(1-x)}{CH_3COO^-} + H_2O \rightleftharpoons \underset{Cx}{CH_3COOH} + \underset{Cx}{OH^-}$$

where, x is the degree of hydrolysis, and

$$K_h = \frac{Cx^2}{(1-x)}$$

We know that,

$$K_h = \frac{K_w}{K_a} = \frac{1\times 10^{-14}}{1.9\times 10^{-5}} = 5.26\times 10^{-10}$$

So, $K_h = Cx^2$ as $(1-x) \longrightarrow 1$

$5.26\times 10^{-10} = 0.05\times x^2$

or $x^2 = \dfrac{5.26\times 10^{-10}}{0.05} = 1.05\times 10^{-8}$

or $x = 1.025\times 10^{-4}$

$$[OH^-] = Cx = 1.025\times 10^{-4}\times 0.05 = 5.125\times 10^{-6}\ M$$

$$[H^+] = \frac{1\times 10^{-14}}{5.125\times 10^{-6}} = 1.95\times 10^{-9}\ M$$

$$pH = -\log[H^+] = -\log(1.95\times 10^{-9}) = 8.71$$

Example 65. *Calculate the amount of ammonium chloride required to dissolve in 500 mL water to have pH = 4.5. (K_b for NH_4OH is 1.8×10^{-5})*

Solution: $[H^+] = 10^{-pH} = 10^{-4.5} = 10^{-5}$ antilog 0.5
$= 3.162\times 10^{-5}\ M$

Let C be the concentration of NH_4Cl

$$\underset{C(1-h)}{NH_4^+} + H_2O \rightleftharpoons \underset{Ch}{NH_4OH} + \underset{Ch}{H^+}$$

If h is small, then

$$K_h = Ch^2 \qquad \left[K_h = \frac{K_w}{K_b} = \frac{10^{-14}}{1.8\times 10^{-5}} = 5.5\times 10^{-10}\right]$$

$$h = \frac{K_h}{Ch} = \frac{K_h}{[H^+]}$$

$$= \frac{5.5\times 10^{-10}}{3.162\times 10^{-5}} = 1.739\times 10^{-5}$$

$$Ch = [H^+]$$

$$C = \frac{[H^+]}{h} = \frac{3.162\times 10^{-5}}{1.739\times 10^{-5}} = 1.8\ \text{mol L}^{-1}$$

500 mL of water contains $= \dfrac{1.8}{2} = 0.9$ mole

Mass in g $= 0.9\times 53.5 = 48.15$ g

Example 66. *Calcium lactate is a salt of a weak organic acid and represented as $Ca(Lac)_2$. A saturated solution of*

$Ca(Lac)_2$ contains 0.13 *mole of this salt in* 0.50 *litre solution. The pOH of this solution is* 5.60. *Assuming a complete dissociation of salt, calculate K_a of the lactic acid.* **(IIT 1991)**

Solution: $$\underset{0.13\times 2\,M}{Ca(Lac)_2} \rightleftharpoons Ca^{2+} + \underset{2\times 2\times 0.13\,M}{2Lac^-}$$

$$\text{At equilibrium}\quad \underset{(0.52-x)}{Lac^-} + H_2O \rightleftharpoons \underset{x}{HLac} + \underset{x}{OH^-}$$

$$K_h = \frac{x^2}{(0.52-x)} = \frac{x^2}{0.52} \text{ as } x \text{ is small}$$

$$[OH^-] = 10^{-5.6} = 2.51\times 10^{-6} = x$$

$$K_h = \frac{2.51\times 10^{-6}\times 2.51\times 10^{-6}}{0.52} = 12.12\times 10^{-12}$$

$$K_a = \frac{K_w}{K_h} = \frac{10^{-14}}{12.12\times 10^{-12}} = 8.26\times 10^{-4}$$

Example 67. *K_a for butyric acid is 2×10^{-5}. Calculate pH and hydroxyl ion concentration of 0.2 M aqueous solution of sodium butyrate.* **(IIT 1994)**

Solution: Butyrate ion hydrolysis in solution into butyric acid and OH^- ions. Let x mole of butyrate ion be hydrolysed.

$$\underset{(0.2-x)}{C_3H_7COO^-} + H_2O \rightleftharpoons \underset{x}{C_3H_7COOH} + \underset{x}{OH^-}$$

$$K_h = \frac{x^2}{(0.2-x)} = \frac{x^2}{0.2} \quad (x \text{ being small is neglected as compared to } 0.2)$$

So, $$K_h = \frac{K_w}{K_a}$$

$$\frac{K_w}{K_a} = \frac{x^2}{0.2}$$

$$\frac{10^{-14}}{2\times 10^{-5}} = \frac{x^2}{0.2}$$

or $$x^2 = 10^{-10} \text{ or } x = 10^{-5} \text{ mol L}^{-1}$$

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

$$[H^+] = \frac{10^{-14}}{10^{-5}} = 10^{-9}\,M$$

$$pH = -\log[10^{-9}] = 9$$

Example 68. *Calculate the pH of an aqueous solution of 1.0M ammonium formate assuming complete dissociation. pK_a for formic acid = 3.8 and pK_b of ammonia = 4.8.* **(IIT 1995)**

Solution: Ammonium formate is a salt of weak acid and weak base. Hence,

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

$$= 7 + (1/2)\times 3.8 - (1/2)\times 4.8$$

$$= 7 + 1.9 - 2.4$$

$$= 6.5$$

Example 69. *A certain weak acid has $K_a = 1.0\times 10^{-4}$. Calculate the equilibrium constant for its reaction with a strong base.* **(IIT 1991)**

Solution: $$\underset{\text{Weak}}{HA} + \underset{\text{Strong}}{BOH} \rightleftharpoons BA + H_2O$$

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

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

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

In the above reaction,

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

So, $$K = \frac{1}{K_h}$$

We know that, $$K_h = \frac{K_w}{K_a} = \frac{10^{-14}}{1.0\times 10^{-4}} = 10^{-10}$$

$$K = \frac{1}{10^{-10}} = 10^{10}$$

Example 70. *Calculate for 0.01 N solution of sodium acetate:*

(a) Hydrolysis constant, (b) degree of hydrolysis, (c) pH.
(Given, $K_a = 1.9\times 10^{-5}$) **(MLNR 1991)**

Solution: $$K_h = \frac{K_w}{K_a} = \frac{10^{-14}}{1.9\times 10^{-5}} = 5.26\times 10^{-10}$$

$$h = \sqrt{\frac{K_h}{C}} = \sqrt{\frac{5.26\times 10^{-10}}{0.01}} = 2.29\times 10^{-4}$$

$$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + \underset{Ch}{OH^-}$$

$$[OH^-] = C\times h = 0.01\times 2.29\times 10^{-4}$$

$$= 2.29\times 10^{-6}\,M$$

$$[H^+] = \frac{K_w}{[OH^-]} = \frac{10^{-14}}{2.29\times 10^{-6}} = 4.37\times 10^{-9}\,M$$

$$pH = -\log[H^+] = -\log(4.37\times 10^{-9}) = 8.36$$

Example 71. *H_2CO_3 ionises as,*

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-;\quad K_1 = 4.3\times 10^{-7}$$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-};\quad K_2 = 5.6\times 10^{-11}$$

Calculate the degree of hydrolysis and pH value of 0.12 M Na_2CO_3 solution.

Solution: Na_2CO_3 is a salt of strong base and weak acid. Thus, CO_3^{2-} ion is hydrolysed.

$$\underset{0.12(1-h)}{CO_3^{2-}} + H_2O \rightleftharpoons \underset{0.12h}{HCO_3^-} + \underset{0.12h}{OH^-}$$

$$K_h = h^2C$$

or $$h^2 = \frac{K_h}{C} = \frac{K_h}{0.12}$$

We know that, $$K_h = \frac{K_w}{K_a} = \frac{K_w}{K_2} = \frac{10^{-14}}{5.6 \times 10^{-11}} = 1.7857 \times 10^{-4}$$

So, $$h^2 = \frac{1.7857 \times 10^{-4}}{0.12} = 14.88 \times 10^{-4}$$

$$h = 3.85 \times 10^{-2}$$

$$[OH^-] = C \times h = 0.12 \times 3.85 \times 10^{-2}$$

$$= 0.462 \times 10^{-2} = 4.62 \times 10^{-3}$$

$$[H^+] = \frac{10^{-14}}{4.62 \times 10^{-3}} = 2.164 \times 10^{-12}\ M$$

$$pH = -\log [H^+] = -\log (2.164 \times 10^{-12}) = 11.665$$

Example 72. *How much must a 0.2 M solution of sodium acetate be diluted at 25°C in order to double the degree of hydrolysis?*

Solution: Let h be the initial degree of hydrolysis

$$K_h = Ch^2 = 0.2 \times h^2 \quad \text{... (i)}$$

Let the concentration be C_1 when degree of hydrolysis is $2h$.

$$K_h = C_1 (2h)^2 \quad \text{... (ii)}$$

Dividing both the equations,

$$1 = \frac{0.2 \times (h^2)}{4C_1 \times (h)^2}$$

$$C_1 = \frac{0.2}{4} = 0.05\,M$$

Applying, $$M_1V_1 = M_2V_2$$

$$0.2V_1 = 0.05 \times V_2$$

$$V_2 = \frac{0.2}{0.05} V_1 = 4V_1$$

The solution be diluted four times.

Example 73. *Calculate change in pH upon ten-fold dilution of the following solutions:*

(a) 0.1 HCl (b) 0.1 M acetic acid (c) 0.1 M NH_4Cl

K_a $CH_3COOH = 1.8 \times 10^{-5}$, K_b $NH_3 = 1.8 \times 10^{-5}$

Solution: (a) HCl is a strong acid. It is completely ionised in solution.

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

$$[H^+] = 0.1 = 10^{-1}$$

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

After dilution, $$[H^+] = 0.01 = 10^{-2}\ M$$

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

pH change from 1 to 2.

(b) $$\underset{(0.1-x)}{CH_3COOH} \rightleftharpoons \underset{x}{CH_3COO^-} + \underset{x}{H^+}$$

(CH_3COOH is a weak acid)

$$\frac{x^2}{0.1} = 1.8 \times 10^{-5} \text{ or } x^2 = 1.8 \times 10^{-6} \text{ or } x = 1.34 \times 10^{-3}$$

$$pH = -\log x = -\log (1.34 \times 10^{-3}) = 2.87$$

After dilution,

$$\frac{x_1^2}{0.01} = 1.8 \times 10^{-5} \text{ or } x_1^2 = 18 \times 10^{-8} \text{ or } x_1 = 4.24 \times 10^{-4}\ M$$

$$pH = -\log x = -\log 4.24 \times 10^{-4} = 3.37$$

pH change from 2.87 to 3.37.

(c) NH_4Cl is a salt of weak base and strong acid.

$$\underset{(0.1-h)}{NH_4^+} + H_2O \rightleftharpoons \underset{h}{NH_4OH} + \underset{h}{H^+}$$

$$\frac{h^2}{0.1} = K_h \quad \text{or} \quad h^2 = 0.1 \times K_h$$

$$\left[K_h = \frac{K_w}{K_b} = \frac{10^{-14}}{1.8 \times 10^{-5}} = 5.55 \times 10^{-10}\right]$$

$$= 0.1 \times 5.55 \times 10^{-10}$$

$$h = 7.45 \times 10^{-6} = [H^+]$$

$$pH = -\log (7.45 \times 10^{-6}) = 5.128$$

After dilution, $$h^2 = 0.01 \times K_h = 0.01 \times 5.55 \times 10^{-10}$$

$$h = 2.35 \times 10^{-6}$$

$$pH = -\log 2.35 \times 10^{-6} = 5.627$$

pH change from 5.128 to 5.627.

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

34. The pH of a solution obtained by mixing 100 mL of 0.2 *M* CH_3COOH with 100 mL of 0.2 *M* NaOH would be: (Given: pK_a for $CH_3COOH = 4.74$)

(a) 4.74 (b) 8.87 (c) 9.10 (d) 8.57

[**Ans.** (b)]

[**Hint:** Concentration of salt formed will be 0.1 *M*.

$$CH_3COOH + NaOH \rightleftharpoons CH_3COONa + H_2O$$

$$pH = \frac{1}{2}[pK_w + pK_a + \log C]$$

$$= \frac{1}{2}[14 + 4.74 - 1] = 8.87\ ]$$

35. The pH of 0.02 *M* $NH_4Cl(aq.)$ ($pK_b = 4.73$) is equal to:

(a) 3.78 (b) 4.73 (c) 5.48 (d) 7.00

[**Ans.** (c)]

[**Hint:** $$pH = \frac{1}{2}[pK_w - pK_b - \log C]$$

$$= \frac{1}{2}[14 - 4.73 - \log 0.02]$$

$$= \frac{1}{2}[14 - 4.73 + 1.698] = 5.48\ ]$$

36. pH of 0.05 *M* $(CH_3COO)_2Ca$ ($pK_a = 4.74$) is:

(a) 8.72 (b) 8.87 (c) 7 (d) 1.30

[**Ans.** (b)]

[**Hint:** $[CH_3COO^-] = 2 \times 0.05 = 0.1$

$$pH = \frac{1}{2}[pK_w + pK_a + \log C]$$

$$= \frac{1}{2}[14 + 4.74 + \log 0.1]$$

$$=\frac{1}{2}[14+4.74-1]=8.87\,]$$

37. The degree of hydrolysis of which of the following salt is independent of the concentration of salt solution?

(a) CH_3COONa (b) NH_4Cl

(c) CH_3COONH_4 (d) NaCl

[**Ans.** (c)]

[**Hint:** It is the salt of weak acid and weak base, hence its degree of hydrolysis will be independent of concentration.

$$h=\sqrt{\frac{K_w}{K_a\times K_b}}\,]$$

38. The pH of 1 M $PO_4^{3-}(aq.)$ solution will be: (given pK_b of $PO_4^{3-}=1.62$)

(a) 1.62 (b) 12.38 (c) 13.19 (d) 7

[**Ans.** (c)]

[**Hint:** $pK_a=14-pK_b=14-1.62=12.38$

$$pH=\frac{1}{2}[\,pK_w+pK_a+\log C\,]$$

$$=\frac{1}{2}[14+12.38+0]=13.19\,]$$

39. For the following equilibrium:

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

calculate the equilibrium constant, if for the equilibrium,

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

the equilibrium constant is 5.5×10^{-10}.

(a) 1.8×10^{-4} (b) 1.8×10^{-5} (c) 1.8×10^{-6} (d) 1.8×10^{-7}

[**Ans.** (b)]

[**Hint:** $K_w=K_a\times K_b$

$$10^{-14}=5.5\times10^{-10}\times K_b$$

$$K_b=1.8\times10^{-5}\,]$$

40. Which of the following expressions is not applicable on the hydrolysis equilibrium? [PET (Raj.) 2004]

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

(a) $K_h=\dfrac{K_w}{K_a(\text{HCN})}$ (b) $h=\sqrt{\dfrac{K_h}{C}}$

(c) $pH=\dfrac{1}{2}pK_a(\text{HCN})$ (d) $(H^+)=\sqrt{\dfrac{K_w\times K_a}{C}}$

[**Ans.** (c)]

[**Hint:** For the salt of weak acid and strong base:

$$pH=\frac{1}{2}[pK_w+pK_a-\log C\,]$$

41. The pK_a of weak acid HA is 4.80 and the pK_b of a weak base BOH is 4.78. The pH of an aqueous solution of corresponding salt BA will be : (AIEEE 2008)

(a) 9.22 (b) 9.58 (c) 4.79 (d) 7.01

[**Ans.** (d)]

[**Hint:** $pH=\dfrac{1}{2}[pK_w+pK_a-pK_b]$

$$=\frac{1}{2}[14+4.8-4.78]=7.01\,]$$

10.13 THEORY OF INDICATORS

An indicator is a substance which is used to determine the end point in a titration. In acid-base titrations, organic substances (weak acids or weak bases) are generally used as indicators. They change their colour within a certain pH range. The colour change and the pH range of some common indicators are tabulated below:

Indicator	pH range	Colour change
Methyl orange	3.2 – 4.5	Pink to yellow
Methyl red	4.4 – 6.5	Red to yellow
Litmus	5.5 – 7.5	Red to blue
Phenol red	6.8 – 8.4	Yellow to red
Phenolphthalein	8.3 – 10.5	Colourless to pink

Theory of acid-base indicators: Two theories have been proposed to explain the change of colour of acid-base indicators with change in pH.

1. Ostwald's theory: According to this theory:

(a) The colour change is due to ionisation of the acid-base indicator. The unionised form has different colour than the ionised form.

(b) The ionisation of the indicator is largely affected in acids and bases as it is either a weak acid or a weak base. In case, the indicator is a weak acid, its ionisation is very much low in acids due to common H^+ ions while it is fairly ionised in alkalies. Similarly, if the indicator is a weak base, its ionisation is large in acids and low in alkalies due to common OH^- ions.

Considering two important indicators phenolphthalein (a weak acid) and methyl orange (a weak base), Ostwald's theory can be illustrated as follows:

Phenolphthalein: It can be represented as HPh. It ionises in solution to a small extent as:

$$\underset{\text{Colourless}}{HPh}\rightleftharpoons H^++\underset{\text{Pink}}{Ph^-}$$

Applying law of mass action,

$$K=\frac{[H^+][Ph^-]}{[HPh]}$$

The undissociated molecules of phenolphthalein are colourless while Ph^- ions are pink in colour. In presence of an acid, the ionisation of HPh is practically negligible as the equilibrium shifts to left hand side due to high concentration of H^+ ions. Thus, the solution would remain colourless. On addition of alkali, hydrogen ions are removed by OH^- ions in the form of water molecules and the equilibrium shifts to right hand side. Thus, the concentration of Ph^- ions increases in solution and they impart pink colour to the solution.

Let us derive Henderson's equation for an indicator

$$\underset{\text{'Acid form'}}{HIn}+H_2O\rightleftharpoons H_3^+O+\underset{\text{'Base form'}}{In^-}$$

Conjugate acid-base pair

$$K_{In}=\frac{[In^-][H_3^+O]}{[HIn]};(K_{In}=\text{Ionization constant of indicator})$$

$$[H_3^+O] = K_{In} \times \frac{[HIn]}{[In^-]}$$

$$pH = -\log_{10}[H_3^+O] = -\log_{10}[K_{In}] - \log_{10}\frac{[HIn]}{[In^-]}$$

$$pH = pK_{In} + \log_{10}\frac{[In^-]}{[HIn]}$$ (Henderson's equation for indicator)

At equivalence point;

$$[In^-] = [HIn] \quad \text{and} \quad pH = pK_{In}$$

Methyl orange: It is a very weak base and can be represented as MeOH. It is ionised in solution to give Me^+ and OH^- ions.

$$\underset{\text{Yellow}}{MeOH} \rightleftharpoons \underset{\text{Red}}{Me^+} + OH^-$$

Applying law of mass action,

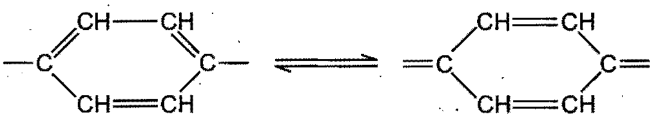
$$K = \frac{[Me^+][OH^-]}{[MeOH]}$$

In presence of an acid, OH^- ions are removed in the form of water molecules and the above equilibrium shifts to right hand side. Thus, sufficient Me^+ ions are produced which impart red colour to the solution. On addition of alkali, the concentration of OH^- ions increases in the solution and the equilibrium shifts to left hand side, *i.e.*, the ionisation of MeOH is practically negligible. Thus, the solution acquires the colour of unionised methyl orange molecules, *i.e.*, yellow.

This theory also explains the reason why phenolphthalein is not a suitable indicator for titrating a weak base against strong acid. The OH^- ions furnished by a weak base are not sufficient to shift the equilibrium towards right hand side considerably, *i.e.*, pH is not reached to 8.3. Thus, the solution does not attain pink colour. Similarly, it can be explained why methyl orange is not a suitable indicator for the titration of weak acid with strong base.

2. Quinonoid theory: According to this theory:

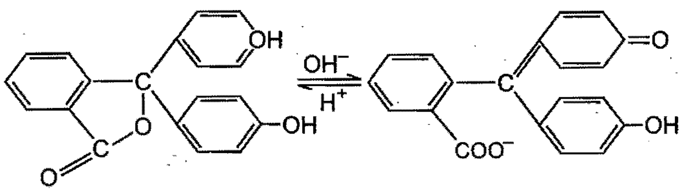
(a) The acid-base indicators exist in two tautomeric forms having different structures. Two forms are in equilibrium. One form is termed **benzenoid form** and the other **quinonoid form.**



(b) The two forms have different colours. The colour change is due to the interconversion of one tautomeric form into other.

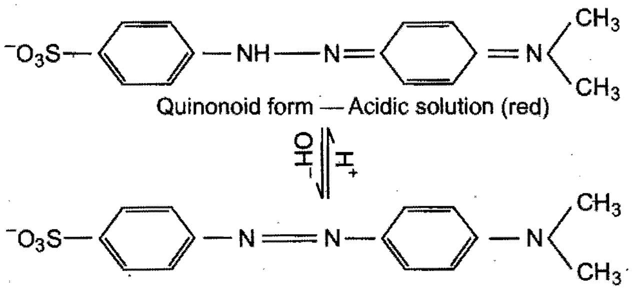
(c) One form mainly exists in acidic medium and the other in alkaline medium.

Thus, during titration the medium changes from acidic to alkaline or *vice-versa*. The change in pH converts one tautomeric form into other and thus, the colour change occurs.



Phenolphthalein has benzenoid form in acidic medium and thus, it is colourless while it has quinonoid form in alkaline medium which has pink colour.

Methyl orange has quinonoid form in acidic solution and benzenoid form in alkaline solution. The colour of benzenoid form is yellow while that of quinonoid form is red.



Selection of suitable indicator or choice of indicator

The neutralisation reactions are of the following four types:

(i) A strong acid *versus* a strong base. [Fig. 10.1 (a)]
(ii) A weak acid *versus* a strong base. [Fig. 10.1 (b)]
(iii) A strong acid *versus* a weak base. [Fig. 10.1 (c)]
(iv) A weak acid *versus* a weak base. [Fig. 10.1 (d)]

In order to choose a suitable indicator, it is necessary to understand the pH changes in the above four types of titrations. The change in pH in the vicinity of the equivalence point is most important for this purpose. The curve obtained by plotting pH as ordinate against the volume of alkali added as abscissa is known as neutralisation or titration curve. The titration curves of the above four types of neutralisation reactions are shown in Fig. 10.1 (a), 10.1 (b), 10.1 (c) and 10.1 (d).

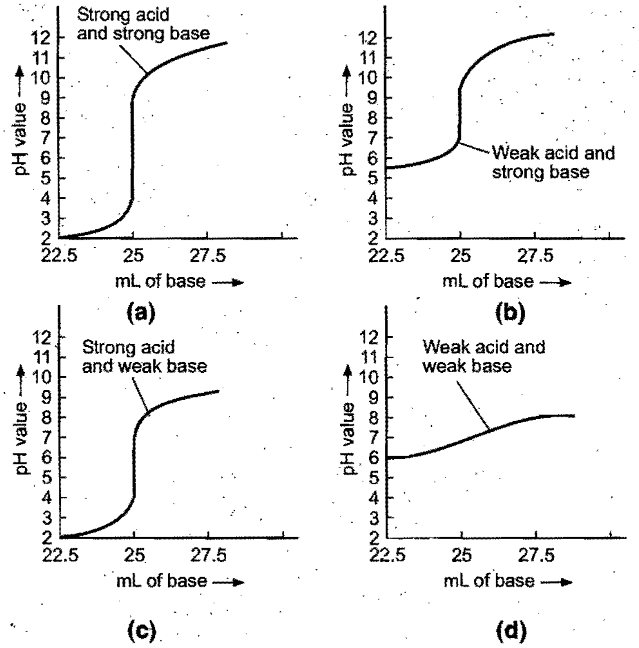


Fig. 10.1

In each case 25 mL of the acid (*N*/10) has been titrated against a standard solution of a base (*N*/10). Each curve becomes almost vertical for some distance [except curve Fig. 10.1 (d)] and then bends away again. This region of abrupt change in pH indicates the equivalence point. For a particular titration, the indicator should be so selected that it changes its colour within vertical distance of the curve.

(i) Strong acid *vs.* strong base: pH curve of strong acid (say HCl) and strong base (say NaOH) is vertical over almost the pH range 4–10. So, the indicators phenolphthalein (pH range 8.3 to 10.5), methyl red (pH range 4.4–6.5) and methyl orange (pH range 3.2–4.5) are suitable for such a titration.

(ii) Weak acid *vs.* strong base: pH curve of weak acid (say CH_3COOH or oxalic acid) and strong base (say NaOH) is vertical over the approximate pH range 7 to 11. So, phenolphthalein is the suitable indicator for such a titration.

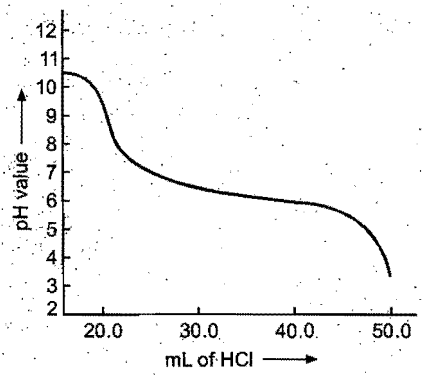


Fig. 10.2

(iii) Strong acid *vs.* weak base: pH curve of strong acid (say HCl or H_2SO_4 or HNO_3) with a weak base (say NH_4OH) is vertical over the pH range of 4 to 7. So, the indicators methyl red and methyl orange are suitable for such a titration.

(iv) Weak acid *vs.* weak base: pH curve of weak acid and weak base indicates that there is no vertical part and hence, no suitable indicator can be used for such a titration.

Titration of soluble carbonate with strong acid.

pH curve of sodium carbonate with HCl shows two inflection points (Fig. 10.2). First inflection point (pH = 8.5) indicates conversion of carbonate into bicarbonate.

$$Na_2CO_3 + HCl \longrightarrow NaHCO_3 + NaCl$$

As the inflection point lies in the pH range 8 to 10, phenolphthalein can be used to indicate the above conversion. The second inflection point (pH = 4.3) indicates the following reaction:

$$NaHCO_3 + HCl \longrightarrow NaCl + CO_2 + H_2O$$

As the point lies between 3 to 5, methyl orange can be used.

MISCELLANEOUS NUMERICAL EXAMPLES

Example 1. *Ionisation constant of* NH_4^+ *in water is* 5.6×10^{-10} *at* $25°C$. *The rate constant for reaction of* NH_4^+ *and* OH^- *to form* NH_3 *and* H_2O *at* $25°C$ *is* 3.4×10^{10} *litre mol*$^{-1}$ *sec*$^{-1}$. *Calculate rate constant for proton transfer from water to* NH_3. **(IIT 1996)**

Solution: $NH_3 + H_2O \underset{k_b}{\overset{k_f}{\rightleftharpoons}} NH_4^+ + OH^- ; k_b = 3.4 \times 10^{10}$

$$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+ ; k_a = 5.6 \times 10^{-10}$$

$$K_{Base} = \frac{k_f}{k_b} = \frac{K_w}{K_{Acid}} \quad \text{... (i)}$$

$$K_{Acid} \times K_{Base} = K_w \quad \text{... (ii)}$$

$$\therefore \quad \frac{k_f}{3.4 \times 10^{10}} = \frac{10^{-14}}{5.6 \times 10^{-10}}$$

$$k_f = 6.07 \times 10^5$$

Example 2. K_a *for the acid ionisation constant of* Fe^{3+} *to* $Fe(OH)_2^{2+}$ *and* H^+ *is* 6.5×10^{-3}. *What is the maximum pH value which could be used so that at least 95% of total* Fe^{3+} *ion in solution exists free?*

Solution: $Fe^{3+} + H_2O \rightleftharpoons Fe(OH)^{2+} + H^+$

$$K = \frac{[Fe(OH)_2]^{2+}[H^+]}{[Fe^{3+}]} = \frac{\frac{5}{100} \times [H^+]}{95/100} = 6.5 \times 10^{-3}$$

$$[H^+] = 0.12\,M$$

$$pH = -\log 0.12 = 0.91$$

Example 3. K_a *for ascorbic acid (HAsc) is* 5×10^{-5}. *Calculate the hydrogen ion concentration and percentage hydrolysis in an aqueous solution in which the concentration of* Asc^- *ions is* $0.02\,M$. **(IIT 1997)**

Solution:

$$\text{Degree of hydrolysis 'h'} = \sqrt{\frac{K_w}{CK_a}}$$

$$= \sqrt{\frac{10^{-14}}{0.02 \times 5 \times 10^{-5}}} = 10^{-4}$$

$$\% \text{ hydrolysis} = 0.01$$

$$pH = \frac{1}{2}[pK_w + pK_a + \log C]$$

$$= \frac{1}{2}[14 + (-\log 5 \times 10^{-5}) + \log 0.02]$$

$$pH = 8.3$$

$$[H^+] = 5 \times 10^{-9}\,M$$

Example 4. *Determine the number of moles of AgI which may be dissolved in 1 litre of 1 M* CN^- *solution* K_{sp} *for AgI and* K_c *for* $Ag(CN)_2^-$ *are* $1.2 \times 10^{-17}\,M^2$ *and* $7.1 \times 10^{19}\,M^{-2}$ *respectively.* **(IIT 1998)**

Solution: $AgI(s) \rightleftharpoons Ag^+ + I^-$

$$K_{sp} = [Ag^+][I^-] = 1.2 \times 10^{-17}$$

$$Ag^+ + 2CN^- \rightleftharpoons [Ag(CN)_2]^-$$

$$K_f = \frac{[Ag(CN)_2^-]}{[Ag^+][CN^-]^2} = 7.1 \times 10^{19}$$

$$K_{eq} = K_{sp} \times K_f$$

$$= \frac{[Ag(CN)_2^-][I^-]}{[CN^-]^2} = 1.2 \times 10^{-7} \times 7.1 \times 10^{19}$$

$$= 8.52 \times 10^2$$

Let us consider the following equilibrium:

$$\begin{array}{lcccc} & AgI(s) + 2CN^- & \rightleftharpoons & [Ag(CN)_2^-] & + I^- \\ t=0 & 1 & & 0 & 0 \\ t_{eq} & 1-2x & & x & x \end{array}$$

Let 'x' moles of AgI be dissolved in CN^- solution.

Then,

$$AgI + 2CN^- \rightleftharpoons Ag(CN)_2^- + I^-$$

$$K_{eq} = 8.5 \times 10^2 = \frac{x \times x}{(1-2x)^2}$$

$$\frac{x}{1-2x} = 29.2$$

$$x = 0.49 \text{ mole}$$

Example 5. *Given* $Ag(NH_3)_2^+ \rightleftharpoons Ag^+ + 2NH_3$, $K_c = 6.2 \times 10^{-8}$ *and* K_{sp} *of AgCl is* 1.8×10^{-10} *at* 298 *K. Calculate concentration of the complex in* 1 *M aqueous ammonia.* (IIT 1998)

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

On adding ammonia solution, complex formation takes place.

$$\underset{(x-y)}{Ag^+} + \underset{1}{2NH_3} \rightleftharpoons \underset{y}{[Ag(NH_3)_2]^+} \quad \ldots \text{(i)}$$

where, x = solubility of AgCl in NH_3

y = amount of complex formed

$$K_{sp} \text{ of AgCl} = [Ag^+][Cl^-]$$

$$1.8 \times 10^{-10} = (x-y) \times x \quad \ldots \text{(ii)}$$

$$K_c \text{ for equation (i)} = \frac{[Ag(NH_3)_2]^+}{[Ag^+][NH_3]^2}$$

$$\frac{1}{6.2 \times 10^{-8}} = \frac{y}{(x-y)1} \quad \ldots \text{(iii)}$$

On solving equations (ii) and (iii), we get

$$y = 0.0539\,M$$

Example 6. *An aqueous solution of aniline of concentration* 0.24 *is prepared. What concentration of sodium hydroxide is needed in this solution so that anilinium ion concentration remains at* 1×10^{-8} *M?* K_a *for* $C_6H_5NH_3^+$ *is* 2.4×10^{-5} *M.* (IIT 1996)

Solution: $C_6H_5NH_2 + H_2O \rightleftharpoons C_6H_5NH_3^+ + OH^-$

Thus, $$K_b = \frac{[C_6H_5NH_3^+][OH^-]}{[C_6H_5NH_2]} \quad \ldots \text{(i)}$$

Also K_b for

$$C_6H_5NH_2 = \frac{K_w}{K_a \text{ for } C_6H_5NH_3^+} = \frac{10^{-14}}{2.4 \times 10^{-5}} \quad \ldots \text{(ii)}$$

Since, dissociation of $C_6H_5NH_2$ occurs in presence of NaOH and thus dissociation of $C_6H_5NH_2$ will be suppressed.

Thus, $[OH^-] = ?$; $[C_6H_5NH_2] = 0.24$; $[C_6H_5NH_3^+] = 10^{-8}$

Therefore, $$\frac{10^{-14}}{2.4 \times 10^{-5}} = \frac{10^{-8} \times [OH^-]}{0.24}$$

$$\therefore \quad [OH^-] = \frac{0.24 \times 10^{-14}}{2.4 \times 10^{-5} \times 10^{-8}} = 0.01$$

$$\therefore \quad [NaOH] = 0.01\,M$$

Example 7. *A solution contains* 0.05 *mol litre*$^{-1}$ *of* Ba^{2+} *ions and* 0.002 *mol litre*$^{-1}$ *of* Ag^+ *ions. The metals are to be precipitated by addition of chromate ions,* CrO_4^{2-}*. Which ion precipitates first? What percentage of this ion remain in the solution when the second ion begins to precipitate?*

$$K_{sp}\ Ag_2CrO_4 = 3 \times 10^{-12}, \qquad K_{sp}\ BaCrO_4 = 1 \times 10^{-10}$$

Solution: CrO_4^{2-} ion concentration required for precipitation:

For $BaCrO_4$:

$$[CrO_4^{2-}] = \frac{K_{sp}\ BaCrO_4}{[Ba^{2+}]} = \frac{10^{-10}}{0.05} = 20 \times 10^{-10}\ M$$

For Ag_2CrO_4:

$$[CrO_4^{2-}] = \frac{K_{sp}\ Ag_2CrO_4}{[Ag^+]^2} = \frac{3 \times 10^{-12}}{[0.002]^2} = 0.75 \times 10^{-6}\ M$$

Ba^{2+} will be precipitated first because it requires low concentration of CrO_4^{2-}. Remaining conc. of Ba^{2+} when Ag^+ will start precipitation.

$$[Ba^{2+}]_{\text{Remaining}} = \frac{K_{sp}\ BaCrO_4}{[CrO_4^{2-}]} = \frac{10^{-10}}{0.75 \times 10^{-6}} = 1.33 \times 10^{-4}\ M$$

$$\%\text{ of remaining } Ba^{2+} = \frac{1.33 \times 10^{-4}}{0.05} \times 100 = 0.26\%$$

Example 8. *Calculate pH change which results when* 50 *mL of* 0.1 *M* HNO_3 *is added to each of the following at* 25° *C:*

(*a*) 1.00 *litre of pure water.*

(*b*) 1.00 *litre of a solution containing acetic acid and sodium acetate each of* 0.1 *M concentration.*

Solution:

(a) Molarity after dilution = M_2

$$M_1V_1 = M_2V_2$$

$$0.1 \times 50 = M_2 \times 1050$$

$$M_2 = 0.00476$$

$$\text{pH} = -\log(0.00476) = 2.322$$

Change in pH of water = 7 − 2.322 = 4.68

(b) $$\text{pH} = \text{p}K_a + \log\frac{[\text{Salt}]}{[\text{Acid}]}$$

$$= 4.7447 + \log\frac{0.1}{0.1} = 4.7447$$

Moles of HNO_3 added $= \frac{0.1}{1000} \times 50 = 5 \times 10^{-3}$; it will convert sodium acetate to acetic acid.

$$\text{pH} = 4.7447 + \log\left[\frac{0.1 - 5\times10^{-3}}{0.1 + 5\times10^{-3}}\right] = 4.70123$$

Change in pH = 4.7447 − 4.70123 = 0.043

Example 9. *A certain monoprotic acid (weak) serves as indicator. Assuming that colour change is seen when 1/3rd of the indicator has been converted to ions and that at end point the pH of solution is 6, what is the value of* pK_{In}*?*

Solution: $HIn \rightleftharpoons H^+ + In^-$ (Ionization equilibrium of indicator)

$$\text{pH} = \text{p}K_{\text{In}} + \log_{10}\frac{[\text{In}^-]}{[\text{HIn}]}$$

$$6 = \text{p}K_{\text{In}} + \log_{10}\left[\frac{0.33}{0.67}\right] \quad \text{(1/3rd conversion)}$$

$$\text{p}K_{\text{In}} = 6.307$$

Example 10. *What is the minimum pH of a solution 0.10 M in* Mg^{2+} *from which* $Mg(OH)_2$ *will not precipitate?* K_{sp} $Mg(OH)_2 = 1.2 \times 10^{-11}\ M^3$.

Solution: Given that,

$$K_{\text{sp}}\ \text{Mg(OH)}_2 = [\text{Mg}^{2+}][\text{OH}^-]^2$$

$$1.2 \times 10^{-11} = [0.1][\text{OH}^-]^2$$

$$[\text{OH}^-]^2 = 1.2 \times 10^{-10}$$

$$[\text{OH}^-] = 1.0954 \times 10^{-5}\ M$$

$$\text{pOH} = -\log_{10}(1.0954 \times 10^{-5}) = 4.96$$

$$\text{pH} = 14 - 4.96 = 9.04$$

Thus, at 9.04 pH, precipitation will not take place.

Example 11. *What is the pH of* 10^{-7} *mol litre*$^{-1}$ *HCl at 25° C?*

Solution: $$[\text{H}^+] = [\text{H}^+]_{\text{Acid}} + [\text{H}^+]_{\text{Water}}$$

$$= 10^{-7} + 10^{-7} = 2 \times 10^{-7}\ M$$

$$\text{pH} = -\log(2 \times 10^{-7}) = 6.70$$

Example 12. *A solution contains 0.1 M* Cl^- *and 0.001 M* CrO_4^{2-}*. If solid* $AgNO_3$ *is gradually added to this solution, which will precipitate first, AgCl or* Ag_2CrO_4*? Assume that the addition causes no change in volume. Given* $K_{sp}\ AgCl = 1.7 \times 10^{-10} M^2$ *and* $K_{sp} Ag_2CrO_4 = 1.79 \times 10^{-12} M^3$.

What per cent of Cl^- *remains in the solution when* CrO_4^{2-} *starts precipitating?*

Solution: Ag^+ ion concentration required for precipitation:

For AgCl:

$$[\text{Ag}^+] = \frac{K_{\text{sp}}\ \text{AgCl}}{[\text{Cl}^-]} = \frac{1.7 \times 10^{-10}}{0.1} = 1.7 \times 10^{-9} M$$

For Ag_2CrO_4:

$$[\text{Ag}^+]^2 = \frac{K_{\text{sp}}\ \text{Ag}_2\text{CrO}_4}{[\text{CrO}_4^{2-}]} = \frac{1.79 \times 10^{-12}}{[0.001]}$$

$$[\text{Ag}^+] = [1.79 \times 10^{-9}\ \text{M}^2]^{1/2}$$

$$= 4.23 \times 10^{-5} M$$

AgCl will precipitate first because it requires low conc. of Ag^+.

$$\text{Remaining conc. of } [\text{Cl}^-] = \frac{K_{\text{sp}} \text{ of AgCl}}{[\text{Ag}^+]}$$

$$= \frac{1.7 \times 10^{-10}}{4.23 \times 10^{-5}} = 4.01 \times 10^{-6} M$$

$$\%\ \text{Remaining conc. of } [\text{Cl}^-] = \frac{4.01 \times 10^{-6}}{0.1} \times 100 = 4 \times 10^{-3}\%$$

Example 13. *25 mL of 0.1 mol* dm^{-3} *aqueous pyridine* ($K_b = 1.7 \times 10^{-9}$ *mol* dm^{-3}) *is titrated with 0.1 mol* dm^{-3} *hydrochloric acid. Calculate the pH initially, at equivalence and after 30* cm^3 *hydrochloric acid have been added.*

Solution: For salt of weak base and strong acid:

$$\text{pH} = \frac{1}{2}[\text{p}K_w - \text{p}K_b - \log C]$$

$$\text{p}K_w = 14;\quad \text{p}K_b = -\log_{10} 1.7 \times 10^{-9} = 8.769;\quad C = 0.05$$

$$\text{pH} = \frac{1}{2}[14 - 8.769 + 1.30102] = 3.27 \quad \text{(pH at equivalence)}$$

5 cc 0.1 *M* HCl will be considered for pH.

$$\text{Mole of HCl remaining} = \frac{0.1}{1000} \times 5 = 5 \times 10^{-4}$$

$$\text{New molarity} = \frac{5 \times 10^{-4}}{55} \times 1000 = 0.00909\,M$$

$$\text{pH} = -\log[0.00909] = 2.04$$

Example 14. *If very small amount of phenolphthalein is added to 0.15 mol litre*$^{-1}$ *solution of sodium benzoate, what fraction of the indicator will exist in the coloured form? State any assumption that you make.*

K_a *(Benzoic acid)* $= 6.2 \times 10^{-5}$, K_w $(H_2O) = 1 \times 10^{-14}$,

K_{In} *(Phenolphthalein)* $= 3.16 \times 10^{-10}$

Solution: Formula for pH of salt hydrolysis:

$$\mathrm{pH} = \frac{1}{2}[\mathrm{p}K_w + \mathrm{p}K_a + \log C]$$

$$= \frac{1}{2}[14 - \log_{10} 6.2\times10^{-5} + \log 0.15]$$

$$= 8.6918$$

Formula for pH of indicator:

$$\mathrm{pH} = \mathrm{p}K_{\mathrm{In}} + \log_{10}\frac{[\mathrm{In}^-]}{[\mathrm{HIn}]}$$

$$8.6918 = -\log_{10}(3.16\times10^{-10}) + \log_{10}\frac{[\mathrm{In}^-]}{[\mathrm{HIn}]}$$

$0.16 = [\mathrm{In}^-]/[\mathrm{HIn}] =$ Fraction of indicator in coloured form.

Example 15. *How much NH_3 must be added to 0.004 M Ag^+ solution to prevent the precipitation of AgCl when (Cl^-) reaches 0.001 M? K_{sp} for AgCl is 1.8×10^{-10} and K for $Ag(NH_3)_2^+$ is 5.9×10^{-8}.*

Solution:

$$[\mathrm{Ag}^+] = \frac{K_{\mathrm{sp}}}{[\mathrm{Cl}^-]} = \frac{1.8\times10^{-10}}{0.001} = 1.8\times10^{-7}\ M$$

NH_3 is added to keep the conc. of Ag^+ below $1.8\times10^{-7}\ M$ to prevent precipitation.

$[Ag(NH_3)_2]^+$ at above limiting condition

$$= 0.004 - 1.8\times10^{-7} \approx 0.004\ M$$

$$[\mathrm{Ag(NH_3)_2}]^+ \rightleftharpoons \mathrm{Ag}^+ + 2\mathrm{NH_3}$$

$$K_d = \frac{[\mathrm{Ag}^+][\mathrm{NH_3}]^2}{[\mathrm{Ag(NH_3)_2}]^+}$$

$$5.9\times10^{-8} = \frac{[1.8\times10^{-7}][\mathrm{NH_3}]^2}{[0.004]}$$

$$[\mathrm{NH_3}] = 0.036\ M$$

$$[\mathrm{NH_3}]_{\mathrm{Total}} = [\mathrm{NH_3}]_{\mathrm{Free}} + [\mathrm{NH_3}]_{\mathrm{Complexed}}$$

$$= 0.036 + 2\times0.004 = 0.044\ \text{mol/litre}$$

Example 16. *Calculate the percentage error in hydronium ion concentration made by neglecting ionization of water in 10^{-6} M NaOH.*

Solution: $[\mathrm{H_3O^+}] = \dfrac{K_w}{[\mathrm{OH}^-]} = \dfrac{10^{-14}}{10^{-6}} = 10^{-8}\ M$

[Neglecting ionization of water]

Consider ionization of water.

$$[\mathrm{H_3O^+}] = y \quad [\mathrm{OH}^-] = (y + 10^{-6})$$

$$[\mathrm{H_3O^+}][\mathrm{OH}^-] = K_w = 10^{-14}$$

$$y[y + 10^{-6}] = 10^{-14}$$

$$y^2 + 10^{-6}y - 10^{-14} = 0$$

On solving for y, $\quad y = 9.9\times10^{-9}$

$$\%\,\text{error} = \frac{10^{-8} - 9.9\times10^{-9}}{9.9\times10^{-9}}\times100 = 1\%$$

Example 17. *Determine the silver ion concentration in a 0.2 M solution of $[Ag(NH_3)_2]NO_3$.*

$$Ag(NH_3)_2^+ \rightleftharpoons Ag^+ + 2NH_3$$

$$K_{diss.} = \frac{[Ag^+][NH_3]^2}{[Ag(NH_3)_2^+]} = 6.8\times10^{-8}$$

Solution: Let concentration of Ag^+ at equilibrium be 'C' M.

$\therefore \quad [\mathrm{NH_3}] = 2C\ M$

$$K = \frac{[\mathrm{Ag}^+][\mathrm{NH_3}]^2}{[\mathrm{Ag(NH_3)_2^+}]}$$

$$6.8\times10^{-8} = \frac{C\times4C^2}{0.2}$$

$$C = 0.0015\ M$$

Example 18. *The solubility of silver acetate in pure water at 25° C is 8.35 g litre^{-1} and 61.8 g litre^{-1} in an acid solution of pH = 3. Calculate:*

(*i*) *K_{sp} of silver acetate and*

(*ii*) *dissociation constant of acetic acid.*

Solution: (i) CH_3COOAg (mw) = 167

$$S = \frac{8.35}{167}\ \text{mol/litre} = 0.05\ M$$

$$K_{\mathrm{sp}} = S^2 = (0.05)^2 = 2.5\times10^{-4}\ M$$

(ii) Use expression of salt hydrolysis to calculate K_a.

$$\mathrm{pH} = \frac{1}{2}[\mathrm{p}K_w + \mathrm{p}K_a + \log C]$$

$$K_a = 1.8\times10^{-5}$$

Example 19. *How many moles of NH_3 must be added to 1 litre of a 0.1 M $AgNO_3$ to reduce Ag^+ concentration to 2×10^{-7} M?*

$$Ag(NH_3)_2^+ \rightleftharpoons Ag^+ + 2NH_3$$

$$K_{diss.} = \frac{[Ag^+][NH_3]^2}{[Ag(NH_3)_2^+]} = 6.8\times10^{-8}$$

Solution: $[\mathrm{Ag(NH_3)_2}]^+ \approx 0.1\ M$

$$[\mathrm{Ag}^+] = 2\times10^{-7}$$

$$K = \frac{[\mathrm{Ag}^+][\mathrm{NH_3}]^2}{[\mathrm{Ag(NH_3)_2}]^+}$$

$$6.8\times10^{-8} = \frac{2\times10^{-7}[\mathrm{NH_3}]^2}{0.1}$$

$$[\mathrm{NH_3}] = 0.184\ M$$

It is the concentration of free NH_3.

$$[\mathrm{NH_3}]_{\mathrm{Total}} = [\mathrm{NH_3}]_{\mathrm{Free}} + [\mathrm{NH_3}]_{\mathrm{Complexed}}$$

$$= 0.184 + 2\times0.1 = 0.384\ M$$

Example 20. *A buffer of pH 8.50 is prepared from 0.02 mole of KCN. The desired volume of buffer solution is to be 1* *litre. How will you make this buffer by using HCl? What is the change after addition of* 0.5×10^{-4} *mole HCl to* $100\ cm^3$ *and same amount of NaOH in* $100\ cm^3$ *of buffer?* (K_a *HCN* $= 6.2 \times 10^{-10}$)

Solution:
$$\underset{(0.02-x)}{\text{KCN}} + \underset{x}{\text{HCl}} \longrightarrow \underset{x}{\text{KCl}} + \underset{x}{\text{HCN}}$$

$$\text{pH} = \text{p}K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

$$8.50 = -\log(6.2 \times 10^{-10}) + \log_{10}\left[\frac{0.02 - x}{x}\right]$$

$$8.50 = 9.2076 + \log_{10}\left[\frac{0.02 - x}{x}\right]$$

$$x = 0.01672$$

(Buffer is prepared by adding 0.01672 mole of HCl in salt KCN.)

Calculation of pH change when HCl is added:

Moles of HCl added in 1 litre buffer $= 0.5 \times 10^{-3}$

HCl will convert more salt into acid.

$$\text{pH} = 9.2076 + \log_{10}\frac{0.00382 - 0.5 \times 10^{-3}}{0.01672 + 0.5 \times 10^{-3}} = 9.4156$$

pH change $= 9.4156 - 8.50 = 0.9156$

Example 21. *What* (H_3O^+) *must be maintained in a saturated* H_2S *solution to precipitate* Pb^{2+}*, but not* Zn^{2+} *from a solution in which each ion is present at a concentration of* $0.01M$? ($K_{sp}\ H_2S = 1.1 \times 10^{-22}$ *and* $K_{sp}\ ZnS = 1.0 \times 10^{-21}$) **(IIT 2000)**

Solution:

$$K_{sp}\ \text{ZnS} = [\text{Zn}^{2+}][\text{S}^{2-}] = 1.0 \times 10^{-21}$$

or $$0.01 \times [\text{S}^{2-}] = 1.0 \times 10^{-21}$$

or $$[\text{S}^{2-}] = 1.0 \times 10^{-19}$$

To start precipitation of ZnS, the required concentration of sulphide ions is 1.0×10^{-19}.

$$K_{sp}\ \text{H}_2\text{S} = [\text{H}^+]^2[\text{S}^{2-}] = 1.1 \times 10^{-22}$$

or $$[\text{H}^+]^2 = \frac{1.1 \times 10^{-22}}{1.0 \times 10^{-19}} = 1.1 \times 10^{-3}$$

or $$[\text{H}^+] = 0.0331M$$

Thus, the hydrogen ion concentration higher than 0.0331 M will reduce the concentration of sulphide ions which will not allow the precipitation of Zn^{2+} ions as ZnS and under this condition only PbS precipitation occurs.

Example 22. *The average concentration of* SO_2 *in the atmosphere over a city on a certain day is 10 ppm, when the average temperature is 298 K. Given that the solubility of* SO_2 *in water at 298 K is 1.3653 mol litre*$^{-1}$ *and the* pK_a *of* H_2SO_3 *is 1.92, estimate the pH of rain on that day.* **(IIT 2000)**

Solution:
$$\text{p}K_a = 1.92$$

$$K_a = \text{antilog}(-1.92) = 0.012$$

$$\begin{array}{lccc} & \text{H}_2\text{SO}_3 & \rightleftharpoons & 2\text{H}^+ + \text{SO}_3^{2-} \\ t=0 & C & & 0 \qquad 0 \\ t_{eq} & C - C\alpha & & 2C\alpha \qquad C\alpha \end{array}$$

$$K_a = \frac{[\text{H}^+]^2[\text{SO}_3^{2-}]}{[\text{H}_2\text{SO}_3]}$$

$$0.012 = \frac{(2C\alpha)^2 \times C\alpha}{C(1-\alpha)} = \frac{4C^2\alpha^3}{(1-\alpha)} \approx 4C^2\alpha^3$$

$$0.012 = 4 \times (1.3653)^2 \times \alpha^3$$

or $$\alpha = 0.117$$

$$[\text{H}^+] = 2C\alpha = 2 \times 1.3653 \times 0.117 = 0.3194$$

$$\text{pH} = -\log_{10}(0.3194) = 0.495$$

Example 23. 0.16 *g of* N_2H_4 *are dissolved in water and the total volume made up to* 500 *mL. Calculate the percentage of* N_2H_4 *that has reacted with water at this dilution. The* K_b *for* N_2H_4 *is* 4.0×10^{-6} *M.* **(IIT 1998)**

Solution: Concentration of N_2H_4,

$$[\text{N}_2\text{H}_4] = \frac{0.16}{32} \times \frac{1000}{500} = 0.01M$$

$$\begin{array}{lccc} & \text{N}_2\text{H}_4 + \text{H}_2\text{O} & \rightleftharpoons & \text{N}_2\text{H}_5^+ + \text{OH}^- \\ \text{At equilibrium} & 1-\alpha & & \alpha \qquad \alpha \end{array}$$

$$K_b = C\alpha^2 \text{ or } \alpha^2 = \frac{K_b}{C} = \frac{4.0 \times 10^{-6}}{0.01} = 4 \times 10^{-4}$$

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

i.e., 2%

Example 24. *What will be the resultant pH when* 200 *mL of an aqueous solution of HCl (pH* = 2) *is mixed with* 300 *mL of an aqueous solution of NaOH (pH* = 12)? **(IIT 1998)**

Solution: pH of HCl = 2 $\quad \therefore [\text{HCl}] = 10^{-2}\ M$

pH of NaOH = 12 $\quad \therefore [\text{NaOH}] = 10^{-2}\ M$

$$\begin{array}{lcccc} & \text{HCl} & + \text{NaOH} & \rightleftharpoons & \text{NaCl} + \text{H}_2\text{O} \\ \text{meq after reaction} & 0 & 100 \times 10^{-2} & & \\ & & = 1 & & \end{array}$$

$$[\text{OH}^-] \text{ after reaction} = \frac{1}{500} = 2 \times 10^{-3}\ M$$

$$\text{pOH} = -\log[\text{OH}^-] = -\log 2 \times 10^{-3} = 2.7$$

$$\therefore \quad \text{pH} = 14 - 2.7 = 11.3$$

Example 25. 500 *mL of* 0.2 *M aqueous solution of acetic acid is mixed with* 500 *mL of* 0.2 *M HCl at* 25°C.

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

(*b*) *If* 6 *g of NaOH is added to the above solution, determine final pH. Assume there is no change in volume on mixing.* K_a *for acetic acid is* 1.75×10^{-5} *M.* **(IIT 2002)**

Solution: (a) Conc. of HCl and CH_3COOH after mixing will be 0.1 M.

$$\begin{array}{lcccc} & \text{CH}_3\text{COOH} & \rightleftharpoons & \text{CH}_3\text{COO}^- & + \text{H}^+ \\ t=0 & 0.1 & & 0 & 0.1 \quad \text{(from HCl)} \\ t_{eq} & 0.1 - x & & x & (0.1 + x) \end{array}$$

$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]}$$

$$1.75\times10^{-5}=\frac{x\times(0.1+x)}{(0.1-x)}$$

On approximation, $x\approx1.75\times10^{-5}$

$$[H^+]=0.1+x\approx0.1\,M$$

$$pH=-\log[0.1]=1$$

Degree of dissociation of acetic acid $=\dfrac{1.75\times10^{-5}}{0.1}=1.75\times10^{-4}$

(b) Number of moles of NaOH added $=\dfrac{6}{40}=0.15$

$$\begin{array}{lcccccc} & CH_3COOH & + HCl & + NaOH & \rightleftharpoons CH_3COONa & + NaCl & + H_2O \\ t=0 & 0.1 & 0.1 & 0.15 & 0 & 0 & 0 \\ t_{eq} & 0.05 & 0 & 0 & 0.05 & 0 & 0 \end{array}$$

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

$$=-\log1.75\times10^{-5}+\log\frac{0.05}{0.05}=4.757$$

Example 26. *Will the pH of water be same at 4°C and 25°C? Explain.* (IIT 2003)

Solution: We know that,

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

At 25°C, $[H^+]=[OH^-]=1.01\times10^{-7}\,M$

$$pH=-\log_{10}[H^+]=-\log_{10}[10^{-7}]=7$$

At 4°C, ionization of water will be less than that at 25°C.

∴ at 25°C $K_w=[H^+][OH^-]$ will be less than 10^{-14}. Thus, pH of water will be more than 7 at 4°C.

Example 27. *0.1 M NaOH is titrated with 0.1 M HA till the end point; K_a for HA is 5.6×10^{-6} and degree of hydrolysis is less compared to 1. Calculate pH of the resulting solution at the end point.* (IIT 2004)

Solution: Neutralization of HA with NaOH may be given as,

$$HA+NaOH\longrightarrow NaA+H_2O$$

Concentration of salt will be $\frac{0.1}{2}M$, *i.e.*, 0.05 *M*, since volume will be double. pH of the salt after hydrolysis may be calculated as,

$$pH=\frac{1}{2}[pK_w+pK_a+\log C] \qquad \ldots\text{(i)}$$

$$pK_w=14$$

$$pK_a=-\log K_a=-\log(5.6\times10^{-6})=5.2518$$

$$\log C=\log0.05=-1.3010$$

Substituting the values of pK_w, pK_a and log *C* in eq. (i) we get,

$$pH=\frac{1}{2}[14+5.2518-1.3010]=8.9754$$

Example 28. *A solution of acetic acid is 1% ionised. Determine the molar concentration of acetic acid. (ionization constant for acetic acid $=1.8\times10^{-5}$)* [BCECE (Mains) 2006]

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

$$\begin{array}{lccc} t_0 & C & 0 & 0 \\ t_{eq.} & C-C\alpha & C\alpha & C\alpha \end{array}$$

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

$$=\frac{C\alpha^2}{1-\alpha} \qquad (\alpha=\frac{1}{100}=0.01)$$

$$1.8\times10^{-5}=\frac{C\times(0.01)^2}{1-0.01}$$

$$1.8\times10^{-5}\approx C\times10^{-4}$$

$$C=0.18\,M$$

Example 29. *A mixture of H_2O and solid AgCl shaken to obtain saturated solution. The solid is filtered and to 100 mL of filtrate, 100 mL of 0.03 M NaBr is added, will a precipitate be formed?* [BCECE (Mains) 2006]

K_{sp} *AgCl* $=10^{-10}$, K_{sp} *AgBr* $=5\times10^{-13}$

Solution: Let solubility of AgCl is '*S*'

∴ $K_{sp}\,\text{AgCl}=S^2$

$$S=\sqrt{K_{sp}}$$

$$=\sqrt{10^{-10}}=10^{-5}$$

When, 100 mL of both AgCl and NaBr are mixed then, concentration of Ag^+ and Br^- will be:

$$[Ag^+]=\frac{100\times10^{-5}}{200}=0.5\times10^{-5}M$$

$$[Br^-]=\frac{100\times0.03}{200}=0.015\,M$$

Ionic product of AgBr $=0.5\times10^{-5}\times0.015$

$$=7.5\times10^{-8}$$

Since, ionic product of AgBr is greater than its solubility product, hence AgBr will be precipitated.

SUMMARY AND IMPORTANT POINTS TO REMEMBER

1. Strong and weak electrolytes: Electrolytes which ionise almost completely when dissolved in water are termed strong electrolytes while those electrolytes which ionise to small extent are termed as weak electrolytes. The degree of ionisation and electrical conductivity of strong electrolytes have high values while weak electrolytes possess small values. NaOH, HCl, H_2SO_4, $BaCl_2$, KCl, etc., are strong electrolytes while NH_4OH, CH_3COOH, $(NH_4)_2CO_3$, HCN, etc., are weak electrolytes.

Degree of ionisation

$$= \frac{\text{Number of molecules of the electrolyte dissociated into ions}}{\text{Total number of molecules of the electrolyte dissolved}}$$

2. Ostwald's dilution law: A dynamic equilibrium exists between ions and unionised molecules of the electrolyte in solution and law of mass action can be applied to this equilibrium also. Consider a binary electrolyte AB.

$$\begin{array}{lccc} & AB & \rightleftharpoons & A^+ + B^- \\ \text{Initial concentration} & C & & 0 \quad 0 \\ \text{Conc. at equilibrium} & C(1-\alpha) & & C\alpha \quad C\alpha \end{array}$$

where, α is the degree of dissociation

$$K = \frac{[A^+][B^-]}{[AB]} = \frac{C\alpha \times C\alpha}{C(1-\alpha)} = \frac{C \times \alpha^2}{(1-\alpha)}$$

K is termed ionisation constant. For a weak electrolyte, the value of α is very small in comparison to 1. Thus, $1-\alpha \rightarrow 1$.

$$K = C\alpha^2 \quad \text{or} \quad \alpha = \sqrt{\frac{K}{C}} \quad \text{or} \quad \alpha = \sqrt{KV}$$

Where, V is the volume containing one mole of electrolyte.

The degree of dissociation of a weak electrolyte is proportional to the square root of dilution. It increases as V increases and approaches to one at high dilution.

This law holds good for weak electrolytes. In the case of acids, ionisation constant is represented as K_a and in case of bases K_b. Polybasic acids ionise stepwise and each step has its own ionisation constant.

For example, H_3PO_4 ionises in three steps:

Step I: $H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$; $K_1 = \frac{[H^+][H_2PO_4^-]}{[H_3PO_4]}$

Step II: $H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-}$; $K_2 = \frac{[H^+][HPO_4^{2-}]}{[H_2PO_4^-]}$

Step III: $HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-}$; $K_3 = \frac{[H^+][PO_4^{3-}]}{[HPO_4^{2-}]}$

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

$$K = K_1 \times K_2 \times K_3$$

Generally, $K_1 > K_2 > K_3$

3. Common ion effect: The degree of dissociation of a weak electrolyte is suppressed by the presence of another electrolyte (strong) containing a common ion. As a result of common ion effect, the concentration of the ion not in common in two electrolytes decreases.

4. Solubility product: In a saturated solution of an electrolyte, two equilibria exist in solution. It can be represented as:

$$\underset{\text{Solid}}{AB} \rightleftharpoons \underset{\substack{\text{Unionised} \\ \text{(dissolved)}}}{AB} \rightleftharpoons \underbrace{A^+ + B^-}_{\text{Ions}}$$

$$K = \frac{[A^+][B^-]}{[AB]}$$

In saturated solution, the value of $[AB]$ is fixed at a definite temperature.

Thus, $K[AB] = [A^+][B^-] = K_s$ (constant)

K_s is termed solubility product. For a general equation,

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

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

Thus, solubility product is defined as the product of concentrations of ions raised to a power equal to the number of times the ions occur in the equation representing the dissociation of the electrolyte at a given temperature when the solution is saturated.

For the precipitation of an electrolyte, it is necessary that the ionic product must exceed its solubility product.

Relationship between solubility and solubility product: Salts like AgI, $PbSO_4$, $BaSO_4$, PbI_2, etc., which are considered to be insoluble do possess solubility. It is assumed that whole of the dissolved electrolyte is present in the form of ions.

$$A_x \times B_y = \underset{xS}{xA^{y+}} + \underset{yS}{yB^{x-}}$$

Let 'S' mol per litre be solubility of the salt; then

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

$$= (xS)^x(yS)^y$$

$$= x^x y^y (S)^{x+y}$$

(a) 1 : 1 type salts such as AgCl, AgI, $BaSO_4$, $PbSO_4$, etc.

$$K_s = S^2 \quad \text{or} \quad S = \sqrt{K_s}$$

(b) 1 : 2 or 2 : 1 type salts such as Ag_2CO_3, Ag_2CrO_4, PbI_2, CaF_2, etc.

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

$$S = \sqrt[3]{\frac{K_s}{4}}$$

(c) 1 : 3 type salts such as AlI_3, $Fe(OH)_3$, etc.

$$K_s = S \times (3S)^3 = 27S^4$$

$$S = \sqrt[4]{\frac{K_s}{27}}$$

The presence of common ion affects the solubility of salt. Let C be the concentration of strong electrolyte containing common ion and new solubility of salt be S'. For an electrolyte, AB,

$$S^2 = K_s = S'(S' + C)$$

Applications of Solubility Product and Common ion Effect

(i) Purification of common salt.
(ii) Salting out of soap.
(iii) Precipitation of the sulphides of group (II) and (IV).
(iv) Precipitation of the hydroxides of group (III).
(v) Using excess of precipitating agent in gravimetric estimations.
(vi) Predicting precipitation in ionic reactions.

5. Acids and Bases: Three important concepts are:

(i) Arrhenius concept: All substances which furnish H^+ ions when dissolved in water are called acids while those which ionise in water to furnish OH^- ions are called bases. Actually free H^+ ions do not exist in water. They combine with water to form hydronium ions (H_3O^+). The reaction between an acid and a base is termed as neutralisation.

All aqueous solutions contain both H^+ and OH^- ions. However, their relative amounts are different in different solutions.

$H^+ > OH^-$ —solution will be acidic
$H^+ < OH^-$ —solution will be basic
$H^+ = OH^-$ —solution will be neutral

(ii) Bronsted-Lowry concept: Any molecule, cation or anion, which provides proton to any other substance is known as an acid and any molecule, cation or anion, which can accept proton from any other substance is known as base. Conjugate acid-base pairs are formed by the loss or gain of a proton.

$$\underset{\text{Acid}}{CH_3COOH} \xrightleftharpoons[+H^+]{-H^+} \underset{\text{Base}}{CH_3COO^-}$$

$$\underset{\text{Base}}{NH_3} \xrightleftharpoons[-H^+]{+H^+} \underset{\text{Acid}}{NH_4^+}$$

In a conjugate pair, if acid is strong, the base will be weak and *vice-versa*. The substances which possess dual nature are termed amphiprotic such as H_2O and NH_3. The acid-base reaction involves two conjugate pairs.

$$\text{Acid}_1 + \underbrace{\text{Base}_2 \rightleftharpoons \text{Acid}_2}_{\text{Conjugate pair}} + \text{Base}_1$$

Conjugate pair

This concept fails to explain reactions between non-protic acids and bases.

(iii) Lewis concept: A base is defined as a substance which can furnish a pair of electrons to form a coordinate bond whereas an acid is a substance which can accept a pair of electrons, *i.e.*, base is a **nucleophile** and acid is an **electrophile.** All Lewis bases are Bronsted bases but all Lewis acids are not Bronsted acids. All simple cations, molecules whose central atom has incomplete octet, the molecules in which central atom can expand its valence cell and molecules having multiple bonds between atoms of different electronegativities can act as Lewis acids. All simple anions and molecules having one or more lone pairs of electrons can act as Lewis bases.

Arrhenius concept is most simple and explains satisfactorily reactions in aqueous solutions.

6. Relative strength of acids and bases: The extent to which an acid property is given by an acid is a measure of its strength. The strength of the acid solution does not depend on its concentration but on the number of H^+ ions present. On dilution, as the number of H^+ ions increases, the strength of an acid also increases. At infinite dilution, all acids are almost completely ionised and, therefore, tend to be equally strong. The concentration of H^+ ions at all other dilutions of equimolar solutions of the acids may not be equal and depends on their degree of dissociation. The relative strength is generally compared in terms of degree of dissociation of equimolar solutions.

$$\frac{\text{Strength of acid I}}{\text{Strength of acid II}} = \frac{\alpha_1}{\alpha_2} = \sqrt{\frac{K_{a_1}}{K_{a_2}}}$$

The strength of the base depends upon OH^- ion concentration.

$$\frac{\text{Strength of base I}}{\text{Strength of base II}} = \frac{\alpha_1}{\alpha_2} = \sqrt{\frac{K_{b_1}}{K_{b_2}}}$$

7. Neutralisation: The neutralisation is the interaction of H^+ ions furnished by an acid and OH^- ions furnished by a base or a reaction between acid and base to form salt and water is termed neutralisation.

Salts are regarded as compounds made up of positive and negative ions. The positive part comes from a base and negative part comes from an acid. The salts are generally crystalline solids. These are classified into the following classes:

(i) Simple salts: The salts formed by neutralisation process are of three types:

(a) **Normal salts** are salts formed by the replacement of all replaceable hydrogen atoms at H^+ ions. Examples are NaCl, KNO_3, $CuSO_4$, $FeSO_4$, etc.

(b) **Acid salts** are formed by incomplete neutralisation of polybasic acids. Examples are $NaHCO_3$, $NaHSO_4$, Na_2HPO_4, etc.

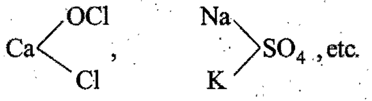
(c) **Basic salts** are salts formed by incomplete neutralisation of polyacidic bases. Examples are: Zn(OH)Cl, Mg(OH)Cl, $Fe(OH)_2Cl$, etc.

(ii) Double salts are the addition compounds formed by combination of two or more simple salts. Such salts are stable in solid state only. Examples are $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$, $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$, etc. These salts when dissolved in water furnish all the ions present in simple salts.

(iii) Complex salts are the salts formed by combination of simple salts or molecular compounds. These are stable in solid state. On dissolving in water, they furnish at least one complex ion.

Examples are $K_4Fe(CN)_6$, $[Cu(NH_3)_4]SO_4$, etc.

(iv) Mixed salts furnish more than one cation or more than one anion when dissolved in water. Examples are:



8. Ionic product of water: Pure water is a weak electrolyte and is very slightly dissociated into hydrogen and hydroxyl ions.

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

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

$[H_2O]$ can be taken as constant.

$$K[H_2O] = [H^+][OH^-] = K_w$$

K_w is constant and known as ionic product of water. Its value is 1×10^{-14} at 25°C. The value increases with increases of temperature. Since, water is neutral, $[H^+]=[OH^-]$

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

When $[H^+]>[OH^-]$, the solution is acidic.

Similarly, when $[H^+]<[OH^-]$, the solution is basic in nature. Every aqueous solution, whether acidic, neutral or basic, contains both H^+ and OH^- ions. The product of their concentrations is always 1×10^{-14} at 25°C. If one increases, the other decreases.

$$[H^+]=\frac{K_w}{[OH^-]} \quad \text{and} \quad [OH^-]=\frac{K_w}{[H^+]}$$

9. pH scale: This has been devised by Sorensen in 1909. The negative logarithm of the concentration of hydrogen ions is termed the pH of the solution.

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

pH is thus logarithm of the reciprocal of hydrogen ion concentration.

Similarly, $$pOH=-\log[OH^-]=\log\frac{1}{[OH^-]}$$

$$pH+pOH=14$$

Limitations of pH scale: pH values do not give any immediate idea about the relative strengths of the solution. pH value is zero for 1 *N* solution of strong acid. In case of 2 *N*, 3 *N*, 4 *N*, etc., solutions, pH values are negative. A solution of an acid having very low concentration, say 10^{-8} *N*, cannot have pH 8 as shown by pH formula but the actual pH value will be less than 7.

10. Hydrolysis: It is the interaction of ions of a salt with water to give acidic, basic or neutral solution. It is found in the salts of weak acids and strong bases, in salts of strong acids and weak bases and in salts of weak acids and weak bases. The process of hydrolysis is actually the reverse of neutralisation.

$$\text{Salt} + \text{Water} \rightleftharpoons \text{Acid} + \text{Base}$$

If acid is stronger than base, the solution is acidic and in case base is stronger than acid, the solution is alkaline. When both acid and base are either strong or weak, the solution is generally neutral in nature.

Salt of a strong acid and a weak base: The solution of such a salt is acidic in nature. The cation of the salt is reactive and reacts with water.

$$\underset{C(1-h)}{B^+} + H_2O \rightleftharpoons \underset{\substack{Ch\\ \text{Weak base}}}{BOH} + \underset{Ch}{H^+}$$

The extent to which hydrolysis proceeds is expressed as degree of hydrolysis. It is denoted as *h* or *x*.

$$h=\frac{\text{Amount of salt hydrolysed}}{\text{Total salt taken}}$$

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

$$K_h=\frac{[BOH][H^+]}{[B^+]}=\frac{Ch\times Ch}{C(1-h)}=\frac{Ch^2}{(1-h)}\approx Ch^2 \quad (\text{if } h \text{ is small})$$

$$K_h=\frac{K_w}{K_b}$$

$$h=\sqrt{\frac{K_h}{C}}=\sqrt{\frac{K_w}{C\times K_b}}$$

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

$$pH=\tfrac{1}{2}pK_w-\tfrac{1}{2}pK_b-\tfrac{1}{2}\log C$$

11. Summary pH of mixtures of acids and bases:

Let '*x*' meq of acid (*HA*) and '*y*' meq of base (*B*OH) be mixed.

$$\text{meq}=NV\text{ mL};\ N=M\times\text{acidity or basicity}$$

Case I. Strong acid and strong base

(a) When $x=y$, then there will be complete neutralisation; the solution will then be neutral with pH = 7.

(b) When $x>y$, then acid will remain after neutralisation.

$$\text{meq of remaining acid}=(x-y)$$

$$N_a=\frac{(x-y)}{V\text{ mL}}$$

$$[H^+]_{\text{Strong acid}}=N_a=\frac{(x-y)}{V\text{ mL}}$$

$$pH=-\log_{10}\left[\frac{x-y}{V\text{ mL}}\right]$$

(c) When $y>x$, then base will remain after neutralization.

$$\text{meq of remaining base}=(y-x)$$

$$N_b=\frac{(y-x)}{V\text{ mL}}$$

$$[OH^-]_{\text{Strong base}}=N_b=\frac{(y-x)}{V\text{ mL}}$$

$$pOH=-\log_{10}\left[\frac{(y-x)}{V\text{ mL}}\right]; \qquad pH=14-pOH$$

Case II. Strong base and weak acid

(a) If $x=y$, then after complete neutralisation there will be salt of weak acid and strong base. There will be hydrolysis; pH after hydrolysis may be calculated as:

$$pH=\frac{1}{2}[pK_w+pK_a+\log_{10}C]$$

C = Conc. of salt in mol litre^{-1}.

(b) If $x>y$, then weak acid will be in excess.

$$\text{Weak acid}=(x-y)\text{ meq}$$

$$\text{Salt}=y\text{ meq}$$

The resultant solution will be acid buffer; its pH may be calculated as:

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

Conc. should be taken in mol litre^{-1}.

(c) When $y > x$, then excess of strong base will remain after neutralisation. Remaining base $= (y - x)$ meq

$$\underset{\text{Strong}}{N_b} = \frac{(y-x)}{V\text{ mL}} = [\text{OH}^-]$$

$$\text{pOH} = -\log_{10}\left[\frac{y-x}{V\text{ mL}}\right]$$

Case III. Strong acid and weak base

(a) When $x = y$, there will be salt formation after complete neutralisation. Salt of weak base and strong base will undergo hydrolysis. pH after hydrolysis may be calculated as:

$$\text{pH} = \frac{1}{2}[\text{p}K_w - \text{p}K_a - \log_{10} C]$$

$$C = \text{Conc. of salt in mol litre}^{-1}.$$

(b) When $x > y$, then strong acid will remain after neutralisation.

Remaining acid $= (x - y)$ meq

$$\underset{\text{Strong}}{N_a} = \frac{(x-y)}{V\text{ mL}} = [\text{H}^+]$$

$$\text{pH} = -\log_{10}\left[\frac{x-y}{V\text{ mL}}\right]$$

(c) When $y > x$, then weak base will remain after salt formation; the resultant mixture will be, therefore, base buffer.

$$14 - \text{pH} = \text{pOH} = \text{p}K_b + \log_{10}\frac{[\text{Salt}]}{[\text{Base}]}$$

Remaining base $= (y - x)$ meq

Salt $= x$ meq

Salt and base conc. should be taken in mol litre^{-1}.

Case IV. Weak acid and weak base

(a) When $x = y$, there will complete neutralisation forming salt of weak acid and weak base. pH after salt hydrolysis may be calculated as:

$$\text{pH} = \frac{1}{2}[\text{p}K_w + \text{p}K_a - \text{p}K_b]$$

(b) When $x > y$, weak acid will remain after neutralisation; the mixture of weak acid and salt behaves as acid buffer.

(c) When $y > x$, then weak base will remain after salt formation; the mixture thus behaves as base buffer.

12. Acid-base indicators: In acid-base titrations, organic substances (weak acids or weak bases) are generally used as indicators. They change their colours within a certain pH range.

Methyl orange	pH range 3.2 – 4.5	Pink to yellow
Methyl red	pH range 4.4 – 6.5	Red to yellow
Phenolphthalein	pH range 8.3 – 10.5	Colourless to pink

Two theories have been proposed to explain the change of colour of these acid-base indicators. These theories are:

(a) Ostwald's theory (b) Quinonoid theory

The suitable indicators for the following titrations are:

(i) Strong acid *versus* strong base—Phenolphthalein, methyl red and methyl orange.

(ii) Weak acid *versus* strong base—Phenolphthalein.

(iii) Strong acid *versus* weak base—Methyl red and methyl orange.

Questions

1. (a) Mention conjugate base of each of the following:
HS^-, H_3O^+, $H_2PO_4^-$, HSO_4^-, HF, CH_3COOH, C_6H_5OH, $HClO_4$, NH_4^+

(b) Mention the conjugate acid of each of the following:
OH^-, CH_3COO^-, Cl^-, CO_3^{2-}, $H_2PO_4^-$, CH_3NH_2, CH_3COOH, NH_2^-

(c) Which of the following behave both as Bronsted acids as well as Bronsted bases?

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

(d) Which is stronger acid in each of the following pairs?
HCl, HI; H_2CO_3, H_2SO_4; H_2O, H_2S; C_6H_5OH, C_2H_5OH; Na^+, K^+

(e) Which is stronger base in each of the following pairs?
OH^-, Cl^-; OH^-, NH_2^-; OH^-, CH_3COO^-; CH_3COO^-, Cl^-; NH_3, CH_3NH_2

(f) Classify the following into acids and bases according to Lewis concept:
S^{2-}, H^+, OH^-, BF_3, Ni^{2+}, NF_3, $AlCl_3$, $SnCl_4$, NH_3, $(CH_3)_2O$

2. Predict whether the following substances will give acidic, basic or neutral solution?

(i) K_2CO_3 (ii) NaCl (iii) $FeCl_3$
(iv) $CuSO_4$ (v) $AlCl_3$ (vi) NH_4Cl
(vii) CH_3COONH_4 (viii) NaCN (ix) Na_2S
(x) $Na_2B_4O_7$

3. [A] Match the List-I with List-II:

List-I (Salt)	**List-II (pH)**
(a) Salt of strong acid and strong base	(p) $\frac{1}{2}[pK_w + pK_a - pK_b]$
(b) Salt of weak acid and strong base	(q) $\frac{1}{2}[pK_w + pK_a + \log C]$
(c) Salt of weak base and strong acid	(r) $\frac{1}{2}[pK_w - pK_b - \log C]$
(d) Salt of weak acid and weak base	(s) $\frac{1}{2}pK_w$

[B] Match the List-I with List-II:

List-I (Indicator)	**List-II (pH range)**
(a) Phenolphthalein	(p) 4.2 – 6.3
(b) Litmus	(q) 3.1 – 4.4
(c) Methyl red	(r) 8.3–10.0
(d) Methyl orange	(s) 5.0–8.0

[C] Match the List-I with List-II:

List-I	**List-II**
(a) Lewis acid	(p) PH_3
(b) Lewis base	(q) $[Al(H_2O)_5OH]^{2+}$
(c) Conjugate acid	(r) $(CH_3)_3B$
(d) Conjugate base	(s) H_3O^+

4. **Matrix-Matching Problems (For IIT Aspirants):**

[A] Match the List-I with List-II:

List-I	**List-II**
(a) H_3PO_4	(p) Monobasic
(b) H_3PO_3	(q) Dibasic
(c) H_3PO_2	(r) Tribasic
(d) H_3BO_3	(s) sp^3-hybrid state

[B] Match the List-I with List-II:

List-I (Indicator)	**List-II (Types of titration)**
(a) Phenolphthalein	(p) NaOH + HCl
(b) Phenol red	(q) $H_2SO_4 + NH_4OH$
(c) Bromo cresol green	(r) $CH_3COOH + NH_4OH$
(d) Methyl orange	(s) $KOH + H_2SO_4$

[C] Match the acid/base in List-I with their nature in List-II:

List-I	**List-II**
(a) HSO_4^-	(p) Lewis acid
(b) BF_3	(q) Lewis base
(c) NH_3	(r) Bronsted acid
(d) OH^-	(s) Bronsted base

[**Note:** Consider the normal behaviour of species.]

[D] Match the Column-I with Column-II:

Column -I (Salt)	**Column-II (Solubility product)**
(a) Zirconium phosphate	(p) $27S^4$
(b) Aluminium phosphate	(q) $108S^5$
(c) Calcium phosphate	(r) $6912S^7$
(d) Sodium phosphate	(s) S^2

[E] Match the Column-I with Column-II:

Column-I (Salt)	**Column-II (Nature of hydrolysis)**
(a) NH_4CN	(p) Only cation hydrolysis
(b) CH_3COONa	(q) Only anion hydrolysis
(c) $NaClO_4$	(r) Both cation and anion hydrolysis
(d) $Fe(NO_3)_2$	(s) No hydrolysis

[F] Match the Column-I with Column-II:

Column-I (Titration)	**Column-II (Indicator used)**
(a) Strong acid versus strong base	(p) Methyl orange (3 – 4.4)
(b) Weak acid versus strong base	(q) Methyl red (4.3 – 6.3)
(c) Strong acid versus weak base	(r) Phenolphthalein (8–10)
(d) Weak acid versus weak base.	(s) No suitable indicator

Answers

1. (a) $S^{2-}, H_2O, HPO_4^{2-}, SO_4^{2-}, F^-, CH_3COO^-, C_6H_5O^-, ClO_4^-, NH_3$
   (b) $H_2O, CH_3COOH, HCl, HCO_3^-, H_3PO_4, CH_3NH_3^+, CH_3COOH_2^+, NH_3$
   (c) H_2O, HCO_3^-, HS^- and NH_3 behave both as acids and bases.
   (d) $HI > HCl$; $H_2SO_4 > H_2CO_3$; $H_2S > H_2O$; $C_6H_5OH > C_2H_5OH$; $Na^+ > K^+$
   (e) $OH^- > Cl$; $NH_2^- > OH^-$; $OH^- > CH_3COO^-$; $CH_3COO^- > Cl^-$; $CH_3NH_2 > NH_3$
   (f) Lewis acids: $H^+, BF_3, Ni^{2+}, AlCl_3, SnCl_4$
   Lewis bases: $S^{2-}, OH^-, NF_3, NH_3, (CH_3)_2O$
2. Acidic: $FeCl_3, CuSO_4, AlCl_3, NH_4Cl$
   Basic: $K_2CO_3, NaCN, Na_2S, Na_2B_4O_7$
   Neutral: $NaCl, CH_3COONH_4$
3. [A] (a–s), (b–q), (c–r), (d–p)
   [B] (a–r), (b–s), (c–p), (d–q)
   [C] (a–r), (b–p), (c–s), (d–q)
4. [A] (a–r, s), (b–q, s), (c–p, s), (d–p)
   [B] (a—p, s), (b–r), (c–q), (d–p, s, q)
   [C] (a–r, s), (b–p), (c–q, s), (d–q, s)
   [D] (a–r), (b–s), (c–q), (d–p)
   [E] (a–r), (b–q), (c–s), (d–p)
   [F] (a–p, q, r), (b–r), (c–p, q), (d–s)

• PRACTICE PROBLEMS •

1. Calculate the degree of ionisation of 0.1 *M* acetic acid. The dissociation constant of acetic acid is 1.8×10^{-5}.
   [Ans. $\alpha = 1.34 \times 10^{-2}$]
2. Calculate the concentration of OH^- ions of 0.01 *M* NH_4OH solution. The equilibrium constant of NH_4OH is 1.8×10^{-5}.
   [Ans. 4.24×10^{-4} mol L^{-1}]
3. At 15° C, 0.05 *N* solution of a weak monobasic acid is 3.5% ionised. Calculate the ionisation constant of acid.
   [Ans. 6.125×10^{-5}]
4. 0.02 *M* solution of NH_4OH is 3% dissociated. Calculate the dissociation constant of NH_4OH.
   [Ans. 1.8×10^{-5}]
5. A solution contains 0.4 *M* CH_3COOH and 0.2 *M* CH_3COONa. Calculate the concentration of H^+ ions. The ionisation constant of acetic acid is 1.8×10^{-5}.
   [Ans. 3.6×10^{-5} mol L^{-1}]
6. The dissociation constant of hydrocyanic acid (HCN) is 4×10^{-8}. Calculate the H^+ ion concentration of 0.01 *M* HCN solution.
   [2×10^{-5} mol L^{-1}]
7. The degree of dissociation of a weak electrolyte in 0.1 *M* aqueous solution is 0.0114 at 298 K. Calculate the degree of dissociation of the same electrolyte at 298 K in 0.001 *M* solution.
   [Ans. 0.114]
8. Calculate K_a for a dibasic acid if its concentration is 0.05 *N* and hydrogen ion concentration is 1×10^{-3} mol L^{-1}.
   [Ans. 2×10^{-8}]
   [Hint: Conc.= 0.025 *M*, $[H^+] = 2C \times \alpha = 1 \times 10^{-3}$, *i.e.*, $\alpha = 0.02, K_a = 4 \times C^2 \times \alpha^3$]
9. K_a for $HC_2H_3O_2$ is 1.8×10^{-5}. What concentration of the acid must be taken so that it is 1% dissociated?
   [Ans. 0.18 mol L^{-1}]
10. Calculate the degree of ionisation and hydroxyl ion concentration in 0.2 *M* NH_3 solution. ($K_b = 1.85 \times 10^{-5}$ at 298 K)
    [Ans. $\alpha = 0.962 \times 10^{-2}, [OH^-] = 1.924 \times 10^{-3}$ *M*]
11. The dissociation constant of acetic acid at 18° C is 1.8×10^{-5}. Calculate the pH of 0.1 *N* and 0.001 *N* solution of acetic acid.
    [Ans. 2.873, 3.726]

12. Calculate the approximate pH of 0.1 M aqueous H_2S solution. K_1 and K_2 for H_2S are 1.0×10^{-7} and 1.3×10^{-13} respectively at 25° C.

[**Ans.** pH = 4]

[**Hint:** Second dissociation constant is very small. H^+ ion concentration mainly depends on the first dissociation constant.

$$H_2S \xrightleftharpoons{K_1} H^+ + HS^-\ ]$$

13. The pH of a soft drink is 4.4. Calculate $[H_3O^+]$ and $[OH^-]$ of the drink.

[**Ans.** 3.98×10^{-5} mol L^{-1}, 2.5×10^{-10} mol L^{-1}]

14. Calculate the pH of a 0.001 M solution of $Sr(OH)_2$ assuming it to be completely ionised.

[**Ans.** 11.301]

[**Hint:** $Sr(OH)_2 \rightleftharpoons Sr^{2+} + 2OH^-$;

$[OH^-] = 2 \times 0.001 = 0.002\ M$]

15. The value of K_w is 9.55×10^{-14} at a certain temperature. Calculate the pH of water at this temperature.

[**Ans.** 6.51]

[**Hint:** $K_w = [H^+][OH^-]$, So, $[H^+] = \sqrt{K_w}$]

16. 9.8 g of H_2SO_4 is present in 500 mL of the solution. Calculate the pH of the solution.

[**Ans.** 0.3979]

17. The pH of a 0.1 M solution of an organic acid is 4.0. Calculate the dissociation constant of the acid.

[**Ans.** 1×10^{-7}]

18. Calculate $[H_3O^+]$, $[OH^-]$ and pH of 0.2 M solution of HCN. $(K_a = 7.2 \times 10^{-10})$

[**Ans.** $[H_3O^+] = 1.2 \times 10^{-5}$ mol L^{-1}, $[OH^-] = 8.33 \times 10^{-10}$ mol L^{-1}, pH = 4.92]

19. Calculate pH of 0.002 M CH_3COOH if it is 2.3% ionised at this concentration.

[**Ans.** 4.34]

20. Calculate the pH of the solution obtained by mixing 150 mL of 0.2 M HCl and 150 mL of 0.1 M NaOH.

[**Ans.** 1.30]

21. pH of a 0.1 M HCN solution is 5.2. What is the value of K_a for the acid?

[**Ans.** 3.97×10^{-10}]

22. The pH of a solution of $B(OH)_2$ is 10.6. Calculate the solubility and solubility product of hydroxide.

[**Hint:** pOH = 3.4, $[OH^-] = 3.98 \times 10^{-4}$ mol L^{-1}

$$\text{Solubility} = \tfrac{1}{2}[OH^-] = 1.99 \times 10^{-4} \text{ mol } L^{-1}$$

$$K_{sp} = [B^+][OH^-]^2 = 3.15 \times 10^{-11}\ ]$$

23. Calculate the pH of a solution:

(i) containing 2 g of sodium hydroxide in one litre;

(ii) made by mixing 50 mL of 0.01 M $Ba(OH)_2$ solution with 50 mL water.

[**Ans.** (i) pH = 12.7, (ii) pH = 12]

24. What happens to the pH of 500 mL of a solution that is 0.1 molar in sodium acetate and 0.1 molar in acetic acid when 10 mL of 0.1 M sodium hydroxide is added?

[**Ans.** pH = 4.7447 and pH will increase]

25. What ratio of acetic acid to sodium acetate concentration is needed to achieve a buffer whose pH is 5.70? The dissociation constant of acetic acid is 1.8×10^{-5}.

[**Ans.** 1 : 9]

26. Find the concentration of H^+, HCO_3^- and CO_3^{2-} in a 0.01 M solution of carbonic acid if the pH of the solution is 4.18, $K_1 = 4.45 \times 10^{-7}$, $K_2 = 4.69 \times 10^{-11}$.

[**Ans.** $[H^+] = 6.61 \times 10^{-5}\ M$, $[HCO_3^-] = 6.73 \times 10^{-5}\ M$,

$[CO_3^{2-}] = 4.78 \times 10^{-11}$ mol L^{-1}]

[**Hint.** $K_1 = \dfrac{[H^+][HCO_3^-]}{[H_2CO_3]} = 4.45 \times 10^{-7}$

$$K_2 = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} = 4.69 \times 10^{-11}$$

$$[H^+] = 6.61 \times 10^{-5}\ M, [H_2CO_3] = 0.01\ M$$

$$[HCO_3^-] = 6.73 \times 10^{-5}\ M, [CO_3^{2-}] = 4.78 \times 10^{-11} \text{ mol } L^{-1}\ ]$$

27. What will be the pH value of a solution of 500 mL containing 5 g acetic acid and 7.2 g of sodium acetate? $K_a = 1.8 \times 10^{-5}$ at 25° C.

[**Ans.** 4.82]

28. The concentration of HCN and NaCN in a solution is 0.01 M each. Calculate the concentration of hydrogen and hydroxyl ions if the dissociation constant of HCN is 7.2×10^{-10}. **(IIT 1991)**

[**Ans.** $[H^+] = 7.2 \times 10^{-10}\ M$; $[OH^-] = 1.4 \times 10^{-7}\ M$]

[**Hint:** $\text{pH} = \log \dfrac{[\text{Salt}]}{[\text{Acid}]} - \log K_a = -\log [H^+]$]

29. A buffer solution of pH = 9 is to be prepared by mixing NH_4Cl and NH_4OH. Calculate the number of moles of NH_4Cl that should be added to one litre of 1.0 M NH_4OH solution. $(K_b = 1.8 \times 10^{-5})$ **(MLNR 1991)**

[**Ans.** 1.8 mole]

30. Calculate the amount of $(NH_4)_2SO_4$ which must be added to 500 mL of 0.200 M NH_3 to yield a solution of pH 9.35. (K_b for $NH_3 = 1.78 \times 10^{-5}$) **(MLNR 1992)**

[**Ans.** 10.494 g]

31. Calculate the pH of the buffer containing 1.0 mol L^{-1} of weak acid HA and 0.1 mol L^{-1} of its sodium salt NaA assuming K_a to be 10^{-6}. **(Dhanbad 1993)**

[**Ans.** pH = 5]

32. Calculate K_b for a base whose 0.1 M solution has pH of 10.5.

[**Ans.** 10^{-6}]

33. What is the maximum pH of a solution 0.10 M in Mg^{2+} from which $Mg(OH)_2$ will not precipitate? Given, $K_{sp}[Mg(OH)_2] = 1.2 \times 10^{-11}$.

[**Ans.** pH = 9.4]

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

[**Ans.** pH = 6.9586]

[**Hint:** pH = 5, $[H^+] = 10^{-5}\ M$. After dilution $= \frac{10^{-5}}{1000} = 10^{-8} M$

$$[H^+] = 10^{-8} + 10^{-7}$$
$$= 1.1 \times 10^{-7}$$
$$pH = -\log[H^+] = -\log 1.1 \times 10^{-7} = 6.9586]$$

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

[**Ans.** pH = 0.4685]

[**Hint:** $[H^+] = \frac{10 \times 0.1 + 40 \times 0.4}{50} = 0.34$]

36. The degree of dissociation of a weak electrolyte in 0.1 M aqueous solution is 0.0114 at 298 K. Calculate the degree of dissociation of the same electrolyte at 298 K in 0.001 M solution.

[**Ans.** 0.114]

[**Hint:** α is proportional to $\sqrt{\frac{1}{C}}$.

$$\frac{\alpha}{\alpha'} = \sqrt{\frac{C'}{C}} = \sqrt{\frac{0.001}{0.1}} = 0.1$$
$$\alpha' = \frac{\alpha}{0.1} = \frac{0.0114}{0.1} = 0.114]$$

37. The degree of dissociation of water is 1.8×10^{-9} at 298 K. Calculate the ionisation constant and ionic product of water at 298 K.

[**Hint:** $H_2O \rightleftharpoons H^+ + OH^-$, $[H_2O] = \frac{1000}{18} = 55.56 \text{ mol L}^{-1}$,

$$[H^+] = [OH^-] = C \times \alpha = 55.56 \times 1.8 \times 10^{-9}$$
$$K_a = \frac{[H^+][OH^-]}{[H_2O]} = \frac{55.56 \times 1.8 \times 10^{-9} \times 55.56 \times 1.8 \times 10^{-9}}{55.56}$$
$$= 1.8 \times 10^{-16}$$
$$K_w = [H^+][OH^-] = (55.56 \times 1.8 \times 10^{-9})^2 = 1 \times 10^{-14}]$$

38. One litre of a buffer solution is prepared by dissolving 0.6 mole of NH_3 and 0.4 mole of NH_4Cl. What is the pH of the solution? For NH_3, $K_b = 1.8 \times 10^{-5}$.

(i) What is the pH of the buffer after addition of 0.1 mole of HCl?

(ii) What is the pH of the buffer after addition of 0.1 mole of NaOH?

[**Ans.** 9.4314 (i) 9.2553 (ii) 9.6233]

39. One litre of a buffer contains 40 g of NH_4Cl and 20 g of NH_3. Calculate the pH of the solution. $K_b(NH_3) = 1.8 \times 10^{-5}$ at 298 K.

[**Ans.** 9.452]

40. A buffer solution is prepared by mixing 50 mL of 0.5 molar ammonia solution, 40 mL of 0.4 molar NH_4Cl solution and 10 mL of distilled water. Calculate the pH of the buffer. $K_b(NH_3) = 1.8 \times 10^{-8}$ at 298 K.

[**Ans.** 9.45]

[**Hint:** Total volume = 50 + 40 + 10 = 100 mL

$$\text{Molarity of } NH_3 = \frac{0.5 \times 50}{100} = 0.25;$$
$$\text{Molarity of } NH_4Cl = \frac{0.4 \times 40}{100} = 0.16]$$

41. pK_a value of acetic acid is 4.76 at room temperature. How will you obtain buffers of 4.40 and 5.40 pH values from acetic acid and sodium acetate?

[**Ans.** $\frac{\text{Acetate}}{\text{Acid}} = 0.4365$ and $\frac{\text{Acetate}}{\text{Acid}} = 4.364$]

42. Calculate the ratio of pH of a solution containing 1 mole of CH_3COONa + 1 mole of HCl per litre and of the other solution containing 1 mole of CH_3COONa + 1 mole of CH_3COOH per litre.

[**Hint:** 1st case: $CH_3COONa + HCl \longrightarrow \underset{1\text{ mole}}{CH_3COOH} + NaCl$

$$pH_1 = -\frac{1}{2}\log K_a$$

2nd case: $pH_2 = -\log K_a + \log\frac{[\text{Salt}]}{[\text{Acid}]} = -\log K_a$

$$\frac{pH_1}{pH_2} = \frac{1}{2}]$$

43. Calculate the composition of an acidic buffer solution (HA + NaA) of total molarity 0.29 having pH = 4.4 and $K_a = 1.8 \times 10^{-5}$.

[**Ans.** [Salt] = 0.09 M; [Acid] = 0.20 M]

[**Hint:** $pH = -\log K_a + \log\frac{[\text{Salt}]}{[\text{Acid}]}$

$$= -\log K_a + \log\frac{a}{(0.29 - a)}]$$

44. Calculate the pH of a solution obtained by mixing 100 mL of an acid of pH = 3 and 400 mL solution of pH = 1.

[**Ans.** 1.096]

45. The solubility product of AgCl in water is 1.5×10^{-10}. Calculate its solubility in 0.01 M NaCl aqueous solution. (IIT 1995)

[**Ans.** 1.5×10^{-8} mol L^{-1}]

46. Calculate the pH of a 0.02 M aqueous solution of NH_4Cl? Given, $pK_{NH_4OH} = 4.73$.

[**Ans.** 3.78]

47. Determine the pH value of 0.1 M aqueous solution of ammonium cyanide (pK_a = 9.04, pK_b = 4.73).

[**Ans.** 9.15]

48. Calculate the pH of a 0.2 M solution of strychnine hydrochloride. ($K_b = 1 \times 10^{-7}$)

[**Ans.** 3.8494]

49. The dissociation constants of acetic acid and aniline are 1.8×10^{-5} and 4.2×10^{-10} respectively. What is the degree of hydrolysis of aqueous aniline acetate? What is the pH of the solution?

[**Ans.** 0.5348, pH = 4.684]

50. A weak acid HA after treatment with 12 mL of 0.1 M strong base has a pH of 5. At the end point, the volume of the same base required is 26.6 mL. Calculate the K_a of the acid.

[**Ans.** 8.219×10^{-6}]

[**Hint:** Applying $\underset{\text{Acid}}{M_1V_1} = \underset{\text{Base}}{M_2V_2}$

$$= 26.6 \times 0.1$$
$$= 2.66 \text{ meq.}$$

$$\begin{array}{lcccc} & HA & + BOH \rightleftharpoons & BA & + H_2O \\ & 2.66 & 1.2 & 0 & 0 \\ \text{After the reaction} & 1.46 & 0 & 1.2 & 1.2 \end{array}$$

Applying Henderson's equation,

$$\text{pH} = \log \frac{[\text{Salt}]}{[\text{Acid}]} - \text{p}K_a \;]$$

51. K_a for HCN is 1.4×10^{-9}. Calculate for 0.01 N KCN solution:

(a) degree of hydrolysis

(b) $[OH^-]$ and $[CN^-]$

(c) pH

[**Ans.** (a) 2.67×10^{-2} (b) $2.67 \times 10^{-4}, 9.73 \times 10^{-3}$ (c) 10.4265]

52. What is the H^+ ion concentration in ammonium acetate solution?

$K_a = 1.8 \times 10^{-5}, K_b = 1.8 \times 10^{-5}$ and $K_w = 1.0 \times 10^{-14}$

[**Ans.** 1.0×10^{-7}]

53. A 40 mL sample of 0.1 M solution of nitric acid is added to 20 mL of 0.3 M aqueous ammonia. What is the pH of the resulting solution? Given, K_b for ammonia $= 1.8 \times 10^{-5}$.

[**Ans.** 8.95]

54. Calculate the pH of 0.1 M solution of NH_4OCN. K_b for NH_3 is 1.75×10^{-5} and K_a for HOCN is 3.3×10^{-4}.

[**Ans.** 6.36]

55. Which of the two solutions 0.1 M HCN ($K_a = 4 \times 10^{-10}$) and 0.1 M HF ($K_a = 6.7 \times 10^{-4}$) will have greater degree of ionisation and to what extent?

[**Ans.** HF will have greater degree of dissociation.

$$\frac{\alpha\,(\text{HF})}{\alpha\,(\text{HCN})} = 1294\,]$$

56. Calculate the pH of a solution prepared by mixing 100.0 mL of 0.4 M HCl with 100.0 mL of 0.4 M NH_3. Hydrolysis constant of ammonium chloride is 5.6×10^{-10}.

[**Ans.** pH = 4.96]

57. Calculate the per cent hydrolysis in 0.003 M aqueous solution of NaOCN.

(K_a for HOCN $= 3.33 \times 10^{-4}$ M) (IIT 1996)

[**Ans.** 0.01%]

58. What is the $[OH^-]$ in a 0.01 M solution of aniline hydrochloride? K_b for aniline is 4.0×10^{-10}.

[**Ans.** 2.0×10^{-11} M]

[**Hint:** $\underset{(0.01-x)}{C_6H_5NH_3^+} + H_2O \rightleftharpoons \underset{x}{C_6H_5NH_2} + \underset{x}{H_3O^+}$]

59. Calculate the pH of 1.0×10^{-3} M sodium phenolate $NaOC_6H_5$. K_a for C_6H_5OH is 1×10^{-10}.

[**Ans.** pH = 10.43]

[**Hint:** $\underset{(0.001-x)}{C_6H_5O^-} + H_2O \rightleftharpoons \underset{x}{C_6H_5OH} + \underset{x}{OH^-}$

$$K_h = \frac{K_w}{K_a} = 1 \times 10^{-4} = \frac{x^2}{(0.001-x)}$$

$$x^2 + 1 \times 10^{-4}x - 1 \times 10^{-7} = 0, x = 2.7 \times 10^{-4}, \text{pOH} = 3.57]$$

60. The dissociation constants of *m*-nitrobenzoic acid and acetic acid are 36.0×10^{-5} and 1.8×10^{-5} respectively. What are their relative strengths?

[**Ans.** 4.47 : 1]

61. Calculate the degree of hydrolysis of 0.10 solution of KCN. Dissociation constant of HCN $= 7.2 \times 10^{-10}$ at 25°C and $K_w = 1.0 \times 10^{-14}$.

[**Ans.** 1.18×10^{-2}]

62. An aqueous solution of aniline of concentration 0.24 M is prepared. What concentration of sodium hydroxide is needed in this solution so that anilinium ion concentration remains at 1×10^{-8} M?

(K_a for $C_6H_5NH_3^+ = 2.4 \times 10^{-5}$ M) (IIT 1996)

[**Ans.** 0.01 M]

63. What is the pH of a 0.50 M aqueous NaCN solution? pK_b of CN^- is 4.70. (IIT 1996)

[**Ans.** pH = 11.5]

64. Calculate the pH of an aqueous solution of 1 M ammonium formate, assuming complete dissociation.

(pK_a = 3.8, pK_b = 4.8) (IIT 1995)

[**Ans.** 6.5]

[**Hint:** Use; $\text{pH} = \frac{1}{2}[\text{p}K_w - \text{p}K_b + \text{p}K_a]$]

65. Calculate the hydrolysis constant of the salt containing NO_2^- ions. Given, K_a for $HNO_2 = 4.5 \times 10^{-10}$. (MLNR 1996)

[**Ans.** 2.2×10^{-5}]

66. Aniline is an amine that is used to manufacture dyes. It is isolated as aniline hydrochloride $[C_6H_5NH_3]Cl$, a salt of aniline and HCl. Calculate the pH of 0.233 M solution of aniline.

[K_b = (aniline) $= 4.6 \times 10^{-10}$]

[**Ans.** 2.64]

67. Calculate the pH of a 0.1 M solution of $AlCl_3$ that dissolves to give hydrated aluminium ion $[Al(H_2O)_6]^{3+}$ in solution. ($K_a = 1.4 \times 10^{-5}$)

[**Ans.** 2.92]

[**Hint:** Consider the equilibrium:

$$[Al(H_2O)_6]^{3+} + H_2O \rightleftharpoons H_3O^+ + [Al(H_2O)_5(OH)]^{2+}\,]$$

68. Calculate the amount of NH_3 and NH_4Cl required to prepare a buffer solution of pH, when total concentration of buffering reagents is 0.6 mol litre^{-1}, pK_b for NH_3 = 4.7, $\log_{10} 2 = 0.30$. (IIT 1997)

[**Ans.** [Salt] = 0.4 M, [Base] = 0.2 M]

69. The solubility product of AgCl in water is 1.5×10^{-10} at 18°C. Calculate its solubility at the same temperature.

[**Ans.** 1.75×10^{-3} g L^{-1}]

70. The solubility product of AgBr is 4×10^{-13} and the concentration of Ag^+ ions in it is 1×10^{-6} mol L^{-1}. What is concentration of Br^- ions?

[**Ans.** 4×10^{-7} mol L^{-1}]

71. A sample of hard water contains 0.005 mole of $CaCl_2$ per litre. What is the minimum concentration of Na_2SO_4 which must be exceeded for removing calcium ions from this water solution? The solubility product of $CaSO_4$ is 2.4×10^{-5}.

[**Ans.** 4.8×10^{-3} mol L^{-1}]

72. Solubility of AgCl at 20° C is 1.435×10^{-5} g L^{-1}. Calculate the solubility product of AgCl.

[**Ans.** 1×10^{-14}]

73. Given, that the solubility product of radium sulphate ($RaSO_4$) is 4×10^{-11}. Calculate its solubility in:

(a) pure water.

(b) 0.10 M Na_2SO_4. **(Dhanbad 1992)**

[**Ans.** (a) 6.32×10^{-6} mol L^{-1} (b) 4×10^{-10} mol L^{-1}]

74. Calculate the solubility of AgCl in 0.20 M $AgNO_3$. K_{sp} AgCl is 1×10^{-10}.

[**Ans.** 5×10^{-10} mol L^{-1}]

75. The values of K_{sp} for sparingly soluble AB and MB_2 are each equal to 4.0×10^{-18}. Which salt is more soluble?

[**Ans.** Solubility $AB = 2 \times 10^{-9}$; Solubility $MB_2 = 1.0 \times 10^{-6}$; MB_2 is more soluble]

76. The solubility of $CaSO_4$ at 25° C is 2.036 g L^{-1} and degree of dissociation of the saturated solution at this temperature is 52.25%. Compute K_{sp} for $CaSO_4$. (Mol. mass of $CaSO_4$ = 136)

[**Ans.** 6.12×10^{-5}]

77. The concentration of the Ag^+ ion in a saturated solution of Ag_2CrO_4 at 20° C is 1.5×10^{-4} mol L^{-1}. Compute the solubility product constant of Ag_2CrO_4 at 20° C.

[**Ans.** 1.7×10^{-12}]

78. K_{sp} AgCl is 2.8×10^{-10} at 25° C. Calculate the solubility of AgCl in (a) pure water (b) 0.1 M $AgNO_3$ (c) 0.1 M KCl and (d) 0.1 M KNO_3. **(MLNR 1994)**

[**Ans.** (a) 1.673×10^{-3} mol L^{-1} (b) 2.8×10^{-9} mol L^{-1} (c) 2.8×10^{-9} mol L^{-1} (d) No common ion is present, so treat it like water 2.8×10^{-9} mol L^{-1}]

79. A solution is saturated with respect to strontium fluoride and strontium carbonate. The fluoride ion concentration in the solution is found to be 3.7×10^{-2} mol L^{-1}. What is the value of $[CO_3^{2-}]$?

K_{sp} $SrF_2 = 7.9 \times 10^{-10}$ and K_{sp} $SrCO_3 = 7.0 \times 10^{-10}$

[**Ans.** 1.2×10^{-3} mol L^{-1}]

[**Hint:** $\frac{K_{sp}\ SrCO_3}{K_{sp}\ SrF_2} = \frac{[Sr^{2+}][CO_3^{2-}]}{[Sr^{2+}][F^-]^2} = \frac{[CO_3^{2-}]}{[F^-]^2}$]

80. A solution contains 0.01 mol L^{-1} of each Pb^{2+} and Zn^{2+} ions. The solution is saturated with H_2S when $[S^{2-}]$ is 1.0×10^{-14} mol L^{-1}. Predict which one of the two ions will be precipitated from the solution? K_{sp} PbS = 2.4×10^{-27} and K_{sp} ZnS = 1.0×10^{-21}.

[**Ans.** Both the ions will be precipitated as ionic products exceed the solubility products of both the sulphides.]

81. An acid type indicator, HIn, differs in colour from its conjugate base In^-. The human eye is sensitive to colour differences only when the ratio $[In^-]/[HIn]$ is greater than 10 or smaller than 0.1. What should be the minimum change in pH of solution to observe a complete colour change? ($K_a = 10^{-5}$) **(IIT 1997)**

[**Ans.** 2]

[**Hint:** For calculation of pH we can use following relation:

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

(i) $pH = 5 + \log_{10} 10 = 6$

(ii) $pH = 5 + \log_{10} 0.1 = 4$

Thus, minimum pH change will be 2.]

82. A sample of AgCl was treated with 5 mL of 1.5 M Na_2CO_3 solution to give Ag_2CO_3. The remaining solution contained 0.0026 g Cl^- per litre. Calculate the solubility product of AgCl. (K_{sp} $Ag_2CO_3 = 8.2 \times 10^{-12}$) **(IIT 1997)**

[**Ans.** K_{sp} AgCl = 1.71×10^{-10}]

83. Calculate the simultaneous solubility of CaF_2 and SrF_2. K_{sp} for the two salts are 4×10^{-11} and 2.8×10^{-9} respectively.

[**Ans.** 1.25×10^{-5} and 8.75×10^{-4}]

84. The solubility product of $Fe(OH)_3$ is 1×10^{-36}. What is the minimum concentration of OH^- ions required to precipitate $Fe(OH)_3$ from 0.001 M solution of $FeCl_3$?

[**Ans.** 1×10^{-11} mol L^{-1}]

85. The solubility product of AgCl is 1.5×10^{-10}. Predict whether there will be any precipitation by mixing 50 mL of 0.01 M NaCl and 50 mL of 0.01 M $AgNO_3$ solution.

[**Ans.** Since, ionic product (2.5×10^{-5}) is greater than solubility product, precipitation will occur.]

86. A solution containing 0.1 M Zn^{2+} and 0.01 M Cu^{2+} is saturated with H_2S. The S^{2-} concentration is 8.1×10^{-31} M. Will ZnS or CuS precipitate?

K_{sp}ZnS = 3.0×10^{-23} and K_{sp}CuS = 8.0×10^{-34}

[**Ans.** CuS precipitates]

87. The precipitate of M_2S_3 is obtained on mixing equal volumes of solutions S_1 having $[M^{3+}] = 4 \times 10^{-5}$ M and S_2 having $[S^{2-}] = 2 \times 10^{-3}$ M. Calculate its solubility product.

[**Ans.** 4×10^{-17}]

[**Hint:** Let 1 litre of both S_1 and S_2 be mixed; then their concentration in mixture will become half ($M_1V_1 = M_2V_2$).

$$[M^{3+}] = 2 \times 10^{-4}\ M; [S^{2-}] = 1 \times 10^{-3}$$

$$K_{sp}M_2S_3 = [M^{3+}]^2[S^{2-}]^3$$

$$= [2 \times 10^{-4}]^2[1 \times 10^{-3}]^3 = 4 \times 10^{-17}\ M^5]$$

88. Solubility products (K_{sp}) of two salts AB and A_2C are same where, 'A' is mono cation and B and C are anions. Calculate the ratio of their solubilities.

[**Ans.** $(16\,K_{sp})^{1/3}$]

[**Hint:** Use; $K_{sp}\ AB = x^2$

$K_{sp}\ A_2C = 4y^3$]

89. Calculate the pH of a solution having 0.1 M formic acid and 0.2 M HCl. Also find the concentration of all the anions present in the solution.

[**Ans.** $\text{pH} = 0.6989, [\text{OH}^-] = 5 \times 10^{-14}$]

90. Calculate the accurate pH of 5×10^{-3} M formic acid solution. K_a (HCOOH) $= 2 \times 10^{-4}$.

[**Ans.** pH = 3.043]

[**Hint:** Use the quadratic equation:

$$[\text{H}^+]^2 + K_a[\text{H}^+] - CK_a = 0$$

$$[\text{H}^+] = \frac{-K_a + \sqrt{K_a^2 + 4CK_a}}{2} = 9.05 \times 10^{-4}$$

(On substituting the values of C and K_a)

$$\text{pH} = -\log_{10}[\text{H}^+]$$

$$= -\log_{10}[9.05 \times 10^{-4}]$$

$$= 3.043]$$

91. Calculate the accurate pH of 5×10^{-6} M pyridine solution. K_b(pyridine) $= 1.5 \times 10^{-9}$.

[**Ans.** 7.1215]

[**Hint:** Use; $[\text{OH}^-]^2 = CK_b + K_w$

$$[\text{OH}^-] = \sqrt{5 \times 10^{-6} \times 1.5 \times 10^{-9} + 10^{-14}}$$

$$= \sqrt{1.75 \times 10^{-14}}$$

$$\text{pOH} = -\log[\text{OH}^-]$$

$$= -\log\sqrt{1.75 \times 10^{-14}} = 6.8785$$

pH = 7.1215]

92. Ionic product of water (K_w) at two different temperatures 25° C and 50° C are 1.08×10^{-14} and 5.474×10^{-14} respectively. Assuming ΔH of any reaction to be independent of temperature, calculate enthalpy of neutralisation of strong acid with strong base.

[**Ans.** 12.5 kcal]

[**Hint:** Use $\log \frac{K_{w_2}}{K_{w_1}} = \frac{\Delta H}{2.303\,R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$]

93. The solubility product of PbI_2 is 7.47×10^{-9} at 15° C and 1.39×10^{-8} at 25 °C. Calculate the molar heat of solution of PbI_2.

[**Ans.** 44.318 kJ/mol]

[**Hint:**

$$\log \frac{(K_{sp})_2}{(K_{sp})_1} = \frac{\Delta H}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\log \frac{[1.39 \times 10^{-8}]}{[7.47 \times 10^{-9}]} = \frac{\Delta H}{2.303 \times 8.314}\left(\frac{1}{288} - \frac{1}{298}\right)$$

$$\Delta H = 44318.4 \text{ J} = 44.318 \text{ kJ/mol}]$$

94. Given, a solution of acetic acid. How many times of the acid concentration, acetate salt should be added to obtain a solution with pH = 7?

K_a for dissociation of $\text{CH}_3\text{COOH} = 1.8 \times 10^{-5}$.

[BCECE (Mains) 2007]

[**Ans.** 1.799×10^2]

OBJECTIVE QUESTIONS

Set–1: Questions with single correct answer

1. A certain weak acid has a dissociation constant of 1×10^{-4}. The equilibrium for its reaction with a strong base is:

(a) 1×10^{-4} (b) 1×10^{-10} (c) 1×10^{10} (d) 1×10^{14}

[**Hint:** $K_h = \frac{K_w}{K_a} = \frac{1 \times 10^{-14}}{1 \times 10^{-4}} = 1 \times 10^{-10}$;

$K_{eq} = \frac{1}{K_h} = 1 \times 10^{10}$]

2. Which one of the following formulae represents Ostwald's dilution law for a binary electrolyte whose degree of dissociation is 'α' and concentration C?

(a) $K = \frac{(1-\alpha)C}{\alpha}$ (b) $K = \frac{\alpha^2 C}{(1-\alpha)}$

(c) $K = \frac{(1-\alpha)C}{\alpha^2}$ (d) $K = \frac{\alpha^2}{(1-\alpha)C}$

3. Which of the following is the correct quadratic form of the Ostwald's dilution law equation? **[CET (J& 2009]**

(a) $\alpha^2 C + \alpha K - K = 0$ (b) $\alpha^2 C - \alpha K - K = 0$

(c) $\alpha^2 C - \alpha K + K = 0$ (d) $\alpha^2 C + \alpha K + K = 0$

[**Hint:** According to Ostwald's dilution law :

$$K = \frac{C\alpha^2}{1-\alpha}$$

or $C\alpha^2 + K\alpha - K = 0$]

4. A monoprotic acid in 1.00 M solution is 0.001% ionised. The dissociation constant of acid is:

(a) 1.0×10^{-3} (b) 1.0×10^{-6}

(c) 1.0×10^{-8} (d) 1.0×10^{-10}

5. Formic acid is 4.5% dissociated in a 0.1 N solution at 20° C. The ionisation constant of formic acid is:

(a) 21×10^{-4} (b) 21

(c) 0.21×10^{-4} (d) 2.1×10^{-4}

6. The fraction of total molecules which is ionised in a solution of an electrolyte is known as:

(a) molecular velocity

(b) order of reaction

(c) degree of ionisation

(d) mole fraction of the electrolyte

97. One litre of water contains 10^{-7} mole of H^+ ions. Degree of ionisation of water is:
(a) $1.8 \times 10^{-7}\%$ (b) $0.8 \times 10^{-9}\%$
(c) $3.6 \times 10^{-9}\%$ (d) $3.6 \times 10^{-7}\%$
[**Hint:** Since, 1 litre of water contains 1000/18 mole, degree of ionisation $= 10^{-7} / \frac{1000}{18}$]

98. The degree of dissociation in a weak electrolyte increases:
(a) on increasing pressure (b) on decreasing dilution
(c) on increasing dilution (d) on increasing concentration

99. Which of the following is the weakest base?
(a) NaOH (b) $Ca(OH)_2$
(c) NH_4OH (d) KOH

100. Acetic acid is a weak electrolyte because:
(a) its molecular mass is high
(b) it is a covalent compound
(c) it is highly unstable
(d) it does not dissociate much or its ionisation is very small

101. When NH_4Cl is added to NH_4OH solution, the dissociation of ammonium hydroxide is reduced. It is due to: [PMT (MP) 1993]
(a) common ion effect (b) hydrolysis
(c) oxidation (d) reduction

102. The addition of HCl will not suppress the ionisation of: [PMT (MP) 1993]
(a) acetic acid (b) sulphuric acid
(c) H_2S (d) benzoic acid

103. H_2S in presence of HCl precipitates second group radicals but not fourth group radicals because:
(a) HCl activates H_2S
(b) HCl decreases concentration of sulphide ions
(c) HCl increases concentration of sulphide ions
(d) sulphides of IV group are unstable in HCl

104. The solubility product of a salt *AB* is 1×10^{-8}. In a solution, in which concentration of *A* is 10^{-3} *M*, *AB* will precipitate when the concentration of *B* will be: [PET (MP) 1990]
(a) 10^{-7} *M* (b) 10^{-4} *M* (c) 10^{-5} *M* (d) 10^{-6} *M*

105. The solubility product of $BaSO_4$ is 1.5×10^{-9}. The precipitation in a 0.01 *M* Ba^{2+} ions solution will start on adding H_2SO_4 of concentration:
(a) 10^{-9} *M* (b) 10^{-8} *M*
(c) 10^{-7} *M* (d) 10^{-6} *M*

106. Solubility product of $BaCl_2$ is 4×10^{-9}. Its solubility would be: [UGET (Manipal) 2006]
(a) 1×10^{-27} (b) 1×10^{-3} (c) 1×10^{-7} (d) 1×10^{-2}

107. Which pair will show common ion effect? [PMT (MP) 1990]
(a) $BaCl_2 + Ba(NO_3)_2$ (b) NaCl + HCl
(c) $NH_4OH + NH_4Cl$ (d) AgCN + KCN

108. What is the correct representation of solubility product of Ag_2CrO_4?
(a) $[Ag^+]^2[CrO_4^{2-}]$ (b) $[Ag^+][CrO_4^{2-}]$
(c) $[2Ag^+][CrO_4^{2-}]$ (d) $[2Ag^+]^2[CrO_4^{2-}]$

109. Solubility product of silver bromide 5×10^{-13}. The quantity of potassium bromide (molar mass taken as 120 g mol^{-1}) to be added to 1 litre of 0.05 M solution of silver nitrate to start the precipitation of AgBr is : (AIEEE 2010)
(a) 6.2×10^{-5} g (b) 5.0×10^{-8} g
(c) 1.2×10^{-10} g (d) 1.2×10^{-9} g

110. When equal volumes of the following solutions are mixed, precipitation of AgCl ($K_{sp} = 1.8 \times 10^{-10}$) will occur only with: [AMU (PMT) 2009]
(a) 10^{-4} *M* $Ag^+ + 10^{-4}$ *M* Cl^-
(b) 10^{-5} *M* $Ag^+ + 10^{-5}$ *M* Cl^-
(c) 10^{-6} *M* $Ag^+ + 10^{-6}$ *M* Cl^-
(d) 10^{-10} *M* $Ag^+ + 10^{-10}$ *M* Cl^-

111. Buffering action of a mixture of CH_3COOH and CH_3COONa is maximum when the ratio of salt to acid is equal to:
(a) 1.0 (b) 100.0 (c) 10.0 (d) 0.1

112. Which hydroxide will have lowest value of solubility product at normal temperature (25°C)? (IIT 1990)
(a) $Mg(OH)_2$ (b) $Ca(OH)_2$
(c) $Ba(OH)_2$ (d) $Be(OH)_2$

113. The solubility of $Al(OH)_3$ is '*S*' g mol L^{-1}. Its solubility product is:
(a) S^2 (b) S^3 (c) $27S^4$ (d) $27S^3$

114. The solubility products of $Al(OH)_3$ and $Zn(OH)_2$ are 8.5×10^{-23} and 1.8×10^{-14} at room temperature. If the solution contains Al^{3+} and Zn^{2+} ions, the ion first precipitated by adding NH_4OH is:
(a) Al^{3+} (b) Zn^{2+}
(c) both (d) none of these

115. The solubility product of $CaSO_4$ is 2.4×10^{-5}. When 100 mL of 0.01 *M* $CaCl_2$ and 100 mL of 0.02 *M* Na_2SO_4 are mixed, then:
(a) Na_2SO_4 will precipitate (b) both will precipitate
(c) $CaSO_4$ will precipitate (d) none will precipitate

116. The solubility of AgCl in a solution of common salt is lower than in water. This is due to:
(a) salt effect (b) lowering of solubility effect
(c) common ion effect (d) complex formation

117. The solubility products of AgCl and AgI are 1.1×10^{-10} and 1.6×10^{-16} respectively. If $AgNO_3$ is added drop by drop to the solution containing both chloride and iodide ions, the salt precipitated first is:
(a) AgI (b) $AgNO_3$
(c) AgCl (d) both AgI and AgCl

118. Why is pure NaCl precipitated when HCl gas is passed in saturated solution of NaCl? [PET (MP) 1993]
(a) Impurities dissolve in HCl
(b) The value of $[Na^+]$ and $[Cl^-]$ product becomes smaller than K_{sp} of NaCl
(c) The value of $[Na^+]$ and $[Cl^-]$ product becomes higher than K_{sp} of NaCl
(d) HCl dissolves in water

119. On passing a current of HCl gas in saturated solution of NaCl, the solubility of NaCl:

(a) increases (b) decreases
(c) remains unchanged (d) NaCl decomposes

30. In a saturated solution of electrolytes, the ionic products of their concentration are constant at a particular temperature. This constant for an electrolyte is known as:
(a) ionic product (b) ionisation constant
(c) dissociation constant (d) solubility product

31. On addition of ammonium chloride to a solution of NH_4OH:
(a) dissociation of NH_4OH increases
(b) concentration of OH^- decreases
(c) concentration of OH^- increases
(d) concentration of both NH_4^+ and OH^- increases

32. The solubility product of a salt A_2B is 4×10^{-9}. Its solubility would be: (IIT 1990)
(a) $4 \times 10^{-2}\ M$ (b) $2 \times 10^{-4}\ M$
(c) $1 \times 10^{-4}\ M$ (d) $1 \times 10^{-3}\ M$

33. If the concentration of CrO_4^{2-} ions in a saturated solution of silver chromate is 2×10^{-4}, solubility product of silver chromate will be: [PET (MP) 1992]
(a) 4×10^{-8} (b) 8×10^{-12}
(c) 16×10^{-12} (d) 32×10^{-12}

34. 50% neutralisation of a solution of formic acid ($K_a = 2 \times 10^{-4}$) with NaOH would result in a solution having a hydrogen ion concentration of:
(a) 2×10^{-4} (b) 3.7 (c) 2.7 (d) 1.85

35. The solubility product of $BaCl_2$ is 4×10^{-9}. Its solubility in mol L^{-1} would be:
(a) 1×10^{-3} (b) 1×10^{-9}
(c) 4×10^{-27} (d) 1×10^{-27}

36. Addition of conc. HCl to saturated $BaCl_2$ solution precipitate $BaCl_2$ because: [BHU (Screening) 2010]
(a) at constant temperature the product $[Ba^{2+}][Cl^-]^2$ remains constant in a saturated solution
(b) ionic product of $[Ba^{2+}][Cl^-]$ remains constant in a saturated solution
(c) of common ion effect
(d) it follows Le-Chatelier's principle

37. How many grams of CaC_2O_4 will dissolve in distilled water to make one litre of saturated solution? ($K_{sp} = 2.5 \times 10^{-9}$ and its molecular mass is 128) [PMT (MP) 1993]
(a) 0.0064 g (b) 0.0128 g (c) 0.0032 g (d) 0.0640 g

38. On the addition of a solution containing CrO_4^{2-} ions to the solution of Ba^{2+}, Sr^{2+} and Ca^{2+} ions, the precipitate obtained first will be of: [PET (MP) 1993]
(a) $CaCrO_4$ (b) $SrCrO_4$
(c) $BaCrO_4$ (d) a mixture of all the three

39. Ostwald's dilution law is applicable in the case of the solution of:
(a) NaCl (b) NaOH (c) H_2SO_4 (d) CH_3COOH

40. What will be the solubility of AgCl in a 0.1 M NaCl solution? (K_{sp} AgCl $= 1.20 \times 10^{-10}$) [PMT (MP) 1992]
(a) $0.1\ M$ (b) $1.2 \times 10^{-4}\ M$
(c) $1.2 \times 10^{-9}\ M$ (d) $1.2 \times 10^{-10}\ M$

41. Which of the following metal sulphides has maximum solubility in water?
(a) CdS ($K_{sp} = 36 \times 10^{-30}$) (b) FeS ($K_{sp} = 11 \times 10^{-20}$)
(c) HgS ($K_{sp} = 32 \times 10^{-54}$) (d) ZnS ($K_{sp} = 11 \times 10^{-22}$)

42. The ionisation constant of acetic acid is 1.8×10^{-5}. The concentration at which it will be dissociated to 2%, is:
(a) $1\ M$ (b) $0.045\ M$ (c) $0.018\ M$ (d) $0.45\ M$

43. The solubility of $PbSO_4$ in 0.01 M Na_2SO_4 solution is: (K_{sp} for $PbSO_4 = 1.25 \times 10^{-9}$)
(a) 1.25×10^{-7} mol L^{-1} (b) 1.25×10^{-9} mol L^{-1}
(c) 1.25×10^{-10} mol L^{-1} (d) 1.25×10^{-18} mol L^{-1}

44. The value of K_{sp} for $HgCl_2$ is 4×10^{-15}. The concentration of Cl^- ion in its aqueous solution at saturation point is:
(a) $1 \times 10^{-5}\ M$ (b) $4 \times 10^{-15}\ M$
(c) $8 \times 10^{-15}\ M$ (d) $2 \times 10^{-5}\ M$

45. If the solubility of $PbBr_2$ is 'S' gram mol per litre, considering 80% ionisation, its ionic product is:
(a) $2S^3$ (b) $4S^2$ (c) $4S^3$ (d) $2S^4$

46. If the solubility of M_3N_2 is 'S' g mol L^{-1}, its solubility product is:
(a) $2S^3$ (b) $8S^4$ (c) $108S^5$ (d) $27S^3$

47. At 30 °C, the solubility of Ag_2CO_3 ($K_{sp} = 8 \times 10^{-12}$) would be greatest in one litre of:
(a) 0.05 M Na_2CO_3 (b) 0.05 M $AgNO_3$
(c) pure water (d) 0.05 M NH_3

48. The following equilibrium exists in aqueous solution;

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

If dilute HCl is added:
(a) the equilibrium constant will increase
(b) the equilibrium constant will decrease
(c) acetate ion concentration will increase
(d) acetate ion concentration will decrease

49. According to Arrhenius concept, base is a substance that:
(a) gives H^+ ions in solution
(b) gives OH^- ions in solution
(c) accepts electrons
(d) donates electrons

50. According to Bronsted-Lowry concept an acid is a substance which:
(a) accepts proton (b) gives an electron pair
(c) gives proton (d) combines with H_3O^+ ions

51. According to Lewis concept, a base is a substance which:
(a) donates an electron pair (b) accepts an electron pair
(c) produces hydronium ions (d) combines with OH^- ions

52. The strength of the acid depends on the:
(a) number of hydrogen atoms present in the molecule
(b) oxygen content
(c) density
(d) concentration of hydrogen ions furnished by ionisation

53. Cl^- ion is the conjugate base of:
(a) HCl (b) HOCl (c) $HClO_3$ (d) $HClO_4$

54. Which one of the following is the strongest acid?
(a) CH_3COOH (b) $CH_2ClCOOH$
(c) $CHCl_2COOH$ (d) CCl_3COOH

55. Number of H^+ ions present in 250 mL of lemon juice of pH = 3 is: **[PMT (Kerala) 2008]**
(a) 1.506×10^{22} (b) 1.506×10^{23}
(c) 1.506×10^{20} (d) 3.012×10^{21}
(e) 2.008×10^{23}

[**Hint:** $[H^+] = 10^{-3}\ M$

$$\text{Number of moles of } H^+ \text{ ions in 250 mL} = \frac{10^{-3}}{4} \times 6.023 \times 10^{23}$$
$$= 1.506 \times 10^{20}\ ]$$

56. Conjugate acid of OH^- base is:
(a) H_2 (b) H_2O (c) H^+ (d) H_3O^+

57. Which among the following qualifies as a Lewis acid?
(a) NaF (b) NaCl (c) BF_3 (d) $MgCl_2$

58. Which of the following will qualify as Lewis base?
(a) BCl_3 (b) CH_4 (c) Cl_2 (d) NH_3

59. NH_4^+ ion in an aqueous solution will behave as:
(a) a base (b) an acid
(c) both acid and base (d) neutral

60. In the dissociation of bicarbonate ion, the conjugate base involved is:
(a) CO_3^{2-} (b) CO_2 (c) H_2CO_3 (d) CO

61. Which one of the following is an acidic salt?
(a) $NaHSO_4$ (b) Na_2SO_4 (c) Na_2SO_3 (d) Na_2SO_4

62. The conjugate acid of NH_2^- is:
(a) NH_4^+ (b) NH_3 (c) NH_2OH (d) N_2H_4

63. The correct increasing order of strengths of following acids is:
(a) $H_2SO_4, CH_3COOH, H_2CO_3$
(b) $CH_3COOH, H_2SO_4, H_2CO_3$
(c) $H_2CO_3, CH_3COOH, H_2SO_4$
(d) $CH_3COOH, H_2CO_3, H_2SO_4$

64. The decreasing order of strength of following bases is:
(a) Cl^-, CH_3COO^-, NH_3 (b) CH_3COO^-, NH_3, Cl^-
(c) CH_3COO^-, Cl^-, NH_3 (d) NH_3, CH_3COO^-, Cl^-

65. Which one of the following does not act as a Bronsted acid?
(a) NH_4^+ (b) HCO_3^- (c) HSO_3^- (d) CH_3COO^-

66. Of the given anions, the strongest Bronsted base is:
(a) ClO^- (b) ClO_2^- (c) ClO_3^- (d) ClO_4^-

67. The compound that is not a Lewis acid is:
(a) $BaCl_2$ (b) $AlCl_3$ (c) BCl_3 (d) $SnCl_4$

68. The dissociation constants of two acids HA_1 and HA_2 are 3.0×10^{-4} and 1.8×10^{-5} respectively. The relative strengths of the acids will be:
(a) 1 : 4 (b) 4 : 1 (c) 1 : 16 (d) 16 : 1

69. In the acid-base relation;
$$HCl + CH_3COOH \rightleftharpoons Cl^- + CH_3COOH_2^+,$$
the conjugate acid of acetic acid is:
(a) Cl^- (b) HCl
(c) $CH_3COOH_2^+$ (d) H_3O^+

70. The numerical value of negative power to which 10 must be raised in order to express hydrogen ion concentration, is equal to:
(a) strength of the solution
(b) pH of the solution
(c) degree of hydrolysis
(d) solubility product of the electrolyte

71. Which one of the following solutions will have pH close to unity? **[IIT 1992; PMT(Kerala) 2008]**
(a) 100 mL of *M*/10 HCl + 100 mL of *M*/10 NaOH
(b) 55 mL of *M*/10 HCl + 45 mL of *M*/10 NaOH
(c) 10 mL of *M*/10 HCl + 90 mL of *M*/10 NaOH
(d) 75 mL of *M*/5 HCl + 25 mL of *M*/5 NaOH
(e) 50 mL of *M*/5 HCl + 50 mL of *M*/5 NaOH

[**Hint:** $M_{mix} V_{mix} = M_{HCl} V_{HCl} + M_{NaOH} V_{NaOH}$

$$M_{mix}(100) = \frac{1}{5} \times 75 + \frac{1}{5} \times 25 = 20$$
$$M_{mix} = 0.2$$
$$[H^+] = 0.2\ M$$
$$pH = -\log 0.2 = 0.7 \approx \text{close to unity}]$$

72. 0.1 *M* acetic acid solution is titrated against 0.1 *M* NaOH solution. What would be the difference in pH between 1/4 and 3/4 stages of neutralisation of acid?
(a) 2 log 3/4 (b) 2 log 1/4 (c) log 1/3 (d) 2 log 3

73. The pK_a of acetylsalicylic acid (aspirin) is 3.5. The pH of gastric juice in human stomach is about 2–3 and the pH in the small intestine is about 8. Aspirin will be:
(a) unionised in the small intestine and in the stomach
(b) completely ionised in the small intestine and in the stomach
(c) ionised in the stomach and almost unionised in the small intestine
(d) ionised in the small intestine and almost unionised in the stomach

74. When 10^{-6} mole of a monobasic strong acid is dissolved in one litre of solvent, the pH of the solution is:
(a) 6 (b) 7
(c) less than 6 (d) more than 7

75. When pH of a solution is 2, the hydrogen ion concentration in mol $litre^{-1}$ is:
(a) 1×10^{-12} (b) 1×10^{-2} (c) 1×10^{-7} (d) 1×10^{-4}

76. At 90°C, pure water has $[H_3O^+] = 10^{-6}$ mol $litre^{-1}$. The value of K_w at 90°C is: **(MLNR 1990)**
(a) 10^{-6} (b) 10^{-12} (c) 10^{-14} (d) 10^{-8}

77. The pH of 10^{-8} molar solution of HCl in water is: **(CPMT 1990; MLNR 1992)**
(a) 8 (b) –8
(c) between 7 and 8 (d) between 6 and 7

78. When pH of 0.001 *M* solution of HCl is:
(a) 1.0 (b) 3 (c) 4.0 (d) 5.0

79. The pH of a solution containing 0.1 *N* NaOH solution is:
(a) 1 (b) 10^{-1} (c) 13 (d) 10^{-13}

80. When 0.4 g of NaOH is dissolved in one litre of solution, the pH of the solution is:
(a) 12 (b) 2 (c) 6 (d) 10

81. The pH of an aqueous solution of a 0.1 M solution of a weak monoprotic acid which is 1% ionised is:
(a) 1 (b) 2 (c) 3 (d) 11

82. The pH of a 0.002 N acetic acid solution if it is 2.3% ionised at this dilution is: ($\log 4.6 = 0.6628$)
(a) 4.3372 (b) 0.4337 (c) 3.4337 (d) 0.6628

83. 0.1 M HCl and 0.1 M H_2SO_4 each of volume 2 mL are mixed and the volume is made up to 6 mL by adding 2 mL of 0.01 N NaCl solution. The pH of the resulting mixture is:
(a) 1.17 (b) 1.0
(c) 0.3 (d) $\log 2 - \log 3$

[**Hint:** Number of millimoles of $H^+ = 0.1 \times 2 + 0.1 \times 2 \times 2 = 0.6$

Concentration of $[H^+] = \frac{0.6}{6} = 0.1$ M

$$pH = -\log [H^+]$$
$$= -\log 0.1 = 1]$$

84. The pH and pOH of 0.1 M aqueous solution of HNO_3 are:
(a) 0, 14 (b) 14, 0 (c) 13, 1 (d) 1, 13

85. The pH of a neutral solution at 50° C is: ($K_w = 10^{-13.26}$ at 50° C)
(a) 7 (b) 6.0 (c) 7.23 (d) 6.63

86. The pH of 0.005 molar aqueous solution of sulphuric acid is approximately:
(a) 0.005 (b) 1 (c) 0.1 (d) 2.0

87. 20 mL of 0.1 N HCl is mixed with 20 mL of 0.1 N KOH solution; the pH of the solution will be:
(a) 0 (b) 2 (c) 7 (d) 9

88. When the pH changes from 4 to 2, the hydrogen ion concentration will increase by a factor:
(a) 2 (b) 1/2 (c) 10^2 (d) $10^{0.5}$

89. 100 mL of 0.2 N HCl is added to 100 mL of 0.18 N NaOH and the whole volume is made one litre. The pH of the resulting solution is:
(a) 1 (b) 2 (c) 3 (d) 4

90. 10 mL of 0.1 N HCl is added to 990 mL solution of NaCl. The pH of the resulting solution is:
(a) zero (b) 3 (c) 7 (d) 10

91. Solutions with reserve acidity and alkalinity are called:
(a) isohydric solutions (b) true solutions
(c) normal solutions (d) buffer solutions

92. A solution which is resistant to changes of pH on dilution, or addition of small amounts of an acid or a base is known as:
(a) buffer solution (b) true solution
(c) isohydric solution (d) ideal solution

93. Which of the following is a buffer solution?
(a) $CH_3COOH + CH_3COONa$
(b) NaCl + NaOH
(c) $HCl + NH_4Cl$
(d) $CH_3COOH + HCl$

94. The hydrogen ion concentration of a buffer solution consisting of a weak acid and its sodium salt is given by:
(a) $[H^+] = K_a \frac{[\text{Acid}]}{[\text{Salt}]}$ (b) $[H^+] = K_a [\text{Salt}]$
(c) $[H^+] = K_a [\text{Acid}]$ (d) $[H^+] = K_a \frac{[\text{Salt}]}{[\text{Acid}]}$

95. When a buffer solution of CH_3COOH and CH_3COONa is diluted with water:
(a) CH_3COO^- ion concentration increases
(b) $[H^+]$ ion concentration increases
(c) OH^- ion concentration increases
(d) H^+ ion concentration does not change

96. In a buffer solution consisting of a weak acid and its salt, the ratio of concentration of salt to acid is increased tenfold; then the pH of the solution will:
(a) increase by one (b) increase tenfold
(c) decrease by one (d) decrease tenfold

97. Acetic acid and propionic acid have K_a values 1.75×10^{-5} and 1.3×10^{-5} respectively at a certain temperature. An equimolar solution of a mixture of the two acids is partially neutralised by NaOH. How is the ratio of the contents of acetate and propionate ions related to the K_a values and the molarity?
(a) $\left[\frac{\alpha}{1-\alpha}\right] = \frac{1.75}{1.3} \times \left[\frac{\beta}{1-\beta}\right]$, where, α and β are ionised fractions of the acids
(b) The ratio is unrelated to the K_a values
(c) The ratio is unrelated to the molarity
(d) The ratio is unrelated to the pH of the solution

98. A weak acid of dissociation constant 10^{-5} is being titrated with aqueous NaOH solution. The pH at the point of one-third neutralisation of the acid will be: **[JEE (WB) 2010]**
(a) $5 + \log 2 - \log 3$ (b) $5 - \log 2$
(c) $5 - \log 3$ (d) $5 - \log 6$

[**Hint:** $pK_a = -\log 10^{-5} = 5$

$$pH = pK_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$
$$= 5 + \log \frac{1/3}{2/3} = 5 - \log 2]$$

99. Which of the following salts when dissolved in water will hydrolyse?
(a) NaCl (b) KCl (c) NH_4Cl (d) Na_2SO_4

100. The aqueous solution of $AlCl_3$ is acidic due to:
(a) cation hydrolysis
(b) anion hydrolysis
(c) hydrolysis of both the ions
(d) dissociation

101. A certain buffer solution contains equal concentration of X^- and H_X. The K_b for X^- is 10^{-10}. The pH of the buffer is:
(a) 4 (b) 7 (c) 10 (d) 14

102. An acidic buffer solution can be prepared by mixing the solutions of:
(a) sodium acetate and acetic acid
(b) ammonium chloride and ammonium hydroxide
(c) sulphuric acid and sodium hydroxide
(d) sodium chloride and sodium hydroxide

103. The compound whose aqueous solution has highest pH, is:
(a) NaCl (b) NH_4Cl
(c) CH_3COONH_4 (d) Na_2CO_3

104. The compound whose 0.1 M solution basic, is:
(a) ammonium chloride (b) ammonium acetate
(c) ammonium sulphate (d) sodium acetate

105. Aqueous solution of copper sulphate:
(a) turns blue litmus red
(b) turns red litmus blue
(c) does not affect litmus
(d) affects both red and blue litmus

106. When an equivalent of a strong acid is added to one equivalent of a weak base, the resulting solution will be:
(a) neutral (b) acidic
(c) alkaline (d) coloured

107. Indicators used in acid-base titrations are:
(a) strong organic acids
(b) strong organic bases
(c) weak organic acids or weak organic bases
(d) non-electrolytes

108. For the titration between oxalic acid and sodium hydroxide, the indicator used is:
(a) potassium permanganate (b) phenolphthalein
(c) litmus (d) methyl orange

109. Phenolphthalein gives a pink colour in alkaline medium due to the fact that:
(a) it is a coloured compound
(b) it ionises to give coloured ions
(c) it is decomposed by alkali
(d) it forms a complex compound with alkali

110. Which is the best choice for weak base-strong acid titration ? [JEE (Orissa) 2008]
(a) Methyl red (b) Litmus
(c) Phenol red (d) Phenolphthalein

111. Water is:
(a) a base (b) an acid
(c) non-electrolyte (d) an amphiprotic molecule

112. An aqueous solution, whose pH is zero, is:
(a) alkaline (b) neutral
(c) acidic (d) amphoteric

113. 0.1 N solution of Na_2CO_3 is being titrated with 0.1 N HCl. The best indicator to be used is:
(a) potassium ferricyanide (b) phenolphthalein
(c) methyl red (d) litmus

114. In the reaction, $AlCl_3 + Cl^- = AlCl_4^-$, $AlCl_3$ can be classified as:
(a) a base (b) an acid
(c) a salt (d) none of these

115. Sulphuric acid is a dibasic acid. Hence, it forms:
(a) acidic salt (b) basic and acidic salt
(c) acidic and normal salt (d) double salt

116. The buffer solutions play an important role in:
(a) increasing the pH value (b) decreasing the pH value
(c) keeping the pH constant (d) none of these

117. Which of the following will occur if 1.0 M solution of a weak acid is diluted to 0.01 M at constant temperature? (AIIMS 1993)
(a) $[H^+]$ will decrease to 0.01 M
(b) pH will decrease by 2 units
(c) K_a will increase
(d) Percentage ionisation will increase

118. Which one of the following indicators works in the pH range 8 – 9.8?
(a) Litmus (b) Phenolphthalein
(c) Methyl red (d) Methyl orange

119. What is $[OH^-]$ in the final solution prepared by mixing 20 mL of 0.05 M HCl with 30 mL of 0.10 M $Ba(OH)_2$? [CBSE (PMT) 2009]
(a) 0.12 M (b) 0.10 M
(c) 0.40 M (d) 0.005 M

[**Hint :** $n_{H^+} = \frac{MV}{1000} = \frac{0.05\times 20}{1000} = 10^{-3}$ mol

$$n_{OH^-} = 2\times n_{Ba(OH)_2}$$
$$= 2\times\frac{MV}{1000} = 2\times\frac{0.1\times 30}{1000} = 6\times 10^{-3}\text{ mol}$$

Remaining moles of OH^- after neutralization
$$= 6\times 10^{-3} - 10^{-3}$$
$$= 5\times 10^{-3}\text{ mol}$$

Conc. of $[OH^-] = \frac{n_{OH^-}}{V}\times 1000 = \frac{5\times 10^{-3}}{50}\times 1000 = 0.1 M$]

120. The following reaction is known to occur in the human body;
$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$
If CO_2 escapes from the system:
(a) pH will decrease
(b) H^+ ion concentration will decrease
(c) H_2CO_3 concentration will be unaltered
(d) the forward reaction will be promoted

121. The pH of human blood is about:
(a) 5.2 (b) 6.3 (c) 7.4 (d) 8.3

122. The dissociation constants of acids HA, HB, HC and HD are 2.6×10^{-3}, 5.3×10^{-9}, 1.1×10^{-2} and 7.5×10^{-5} respectively. The weakest acid amongst these acids is:
(a) HA (b) HB (c) HC (d) HD

123. The addition of sodium carbonate in pure water causes:
(a) an increase in the hydrogen ion concentration
(b) a decrease in hydroxyl ion concentration
(c) no change in pH
(d) an increase in pH

124. The best indicator for titrating HCl against NH_4OH is:
(a) litmus (b) phenolphthalein
(c) phenol red (d) methyl orange

125. A buffer solution is used in:
(a) preparation of potash alum
(b) the removal of PO_4^{3-} ions
(c) increasing the pH value of a solution
(d) precipitation of $Cr(OH)_3$ from $CrCl_3$

126. A certain weak acid has a dissociation constant of 1.0×10^{-4}. The equilibrium constant for its reaction with a strong base is:
(a) 1.0×10^{-4} (b) 1.0×10^{-10}
(c) 1.0×10^{10} (d) 1.0×10^{-14}

[**Hint:** $HA + BOH \rightleftharpoons BA + H_2O$. The equilibrium constt. $= 1/K_h$ and $K_h = K_w/K_a$]

127. Which one of the following statements is correct?
(a) CH_3COOH is a weak acid
(b) NH_4Cl gives an alkaline solution in water
(c) CH_3COONa gives an acidic solution in water
(d) NH_4OH is a strong base

128. In the hydrolytic equilibrium $A^- + H_2O \rightleftharpoons HA + OH^-$ $K_a = 1.0 \times 10^{-5}$. The degree of hydrolysis of 0.001 M solution of the salt is:
(a) 10^{-3} (b) 10^{-4} (c) 10^{-5} (d) 10^{-6}

129. The pH of an aqueous solution of 0.1 M solution of the salt of a weak base ($K_b = 1.0 \times 10^{-5}$) and a strong acid is:
(a) 4.5 (b) 5.0 (c) 5.5 (d) 6.0
[Hint: First calculate degree of hydrolysis;
$$\alpha^2 C = K_h, K_h = (K_w / K_b), [H^+] = \alpha C]$$

130. The pH of the solution obtained by mixing equal volumes of solution of pH = 5 and pH = 3 of the same electrolyte is:
(a) 3.3 (b) 4.0 (c) 4.5 (d) 2.0
[Hint: $[H^+] = \dfrac{10^{-3} + 10^{-5}}{2} = \dfrac{100 \times 10^{-5} + 10^{-5}}{2} = 50.5 \times 10^{-5}]$

131. pK_a values of four acids are given below at 25°C. The strongest acid is: [PMT (MP) 1990]
(a) 2.0 (b) 2.5 (c) 3.0 (d) 4.0

132. The ionisation constant of NH_4^+ in water is 5.6×10^{-10} at 25°C. The rate constant of the reaction of NH_4^+ and OH^- to form NH_3 and H_2O at 25°C is 3.4×10^{10} L mol^{-1} s^{-1}. The rate constant for proton transfer from water to NH_3 is:
(a) $6.07 \times 10^5\ s^{-1}$ (b) $6.07 \times 10^{-10}\ s^{-1}$
(c) $6.07 \times 10^{-5}\ s^{-1}$ (d) $6.07 \times 10^{10}\ s^{-1}$

133. The pH of a soft drink is 3.82. The hydrogen ion concentration will be: (given a antilog 0.18 = 1.5) [PET (MP) 1990]
(a) 1.96×10^{-2} mol lit^{-1} (b) 1.96×10^{-5} mol lit^{-1}
(c) 1.5×10^{-4} mol lit^{-1} (d) 1.5×10^{-2} mol lit^{-1}

134. 100 mL of 0.1 M HCl is mixed with 100 mL of 0.01 M HCl. The pH of the resulting solution is:
(a) 2.0 (b) 1.0
(c) 1.26 (d) none of these

135. How many times has a solution of pH 2 higher acidity than a solution of pH 6?
(a) 10,000 (b) 12
(c) 400 (d) 4

136. For a concentrated solution of a weak electrolyte A_xB_y of concentration 'C', the degree of dissociation 'α' is given as: [PET (Kerala) 2008]
(a) $\alpha = \sqrt{K_{eq.}/C(x + y)}$ (b) $\alpha = \sqrt{\dfrac{C\,K_{eq.}}{xy}}$
(c) $\alpha = \left[\dfrac{K_{eq.}}{(C^{x+y-1}\,x^x\,y^y)}\right]^{1/x+y}$
(d) $\alpha = \dfrac{K_{eq.}}{C\,xy}$, (e) $\alpha = \dfrac{K_{eq.}}{C^{xy}}$
[Hint: $A_xB_y \rightleftharpoons xA^{y+} + yB^{x-}$
$$\begin{array}{llll} t_0 & C & 0 & 0 \\ t_{eq.} & C(1-\alpha) & xC\alpha & yC\alpha \end{array}$$
$$K_{eq.} = \frac{(xC\alpha)^x (yC\alpha)^y}{C\,(1-\alpha)}$$
$$\approx \frac{(xC\alpha)^x (yC\alpha)^y}{C} \qquad \because (1-\alpha) \approx 1$$
$$\alpha = \left[\frac{K_{eq.}}{C^{x+y-1}\,x^x\,y^y}\right]^{1/x+y}\ ]$$

137. The following equilibrium is established when hydrogen chloride is dissolved in acetic acid;
$$HCl + CH_3COOH \rightleftharpoons Cl^- + CH_3COOH_2^+$$
The set that characterises the conjugate acid-base pairs is: (IIT 1992)
(a) (HCl, CH_3COOH) and ($CH_3COOH_2^+$, Cl^-)
(b) (HCl, $HC_3COOH_2^+$) and (CH_3COOH, Cl^-)
(c) ($CH_3COOH_2^+$, HCl) and (Cl^-, CH_3COOH)
(d) (HCl, Cl^-) and ($CH_3COOH_2^+$, CH_3COOH)

138. The pH of a 10^{-10} M NaOH solution is: [PMT (Uttarakhand) 2006]
(a) 10 (b) 7.01 (c) 6.99 (d) 4

139. Which of the following is strongest Lewis base?
(a) CH_3^- (b) Ag^+ (c) NH_3 (d) H_2

140. If the solubility of lithium sodium hexafluoro aluminate, $Li_3Na_3(AlF_6)_2$ is 'S' mol L^{-1}, its solubility product is equal to: (CPMT 1992)
(a) S^8 (b) $12S^3$ (c) $18S^3$ (d) $2916S^8$

141. Given that the dissociation constant for water is $K_w = 1 \times 10^{-14}$ mol^2 L^{-2}. The pH of a 0.001 molar KOH solution is: (MLNR 1991)
(a) 10^{-11} (b) 10^{-3} (c) 3 (d) 11

142. Which one of the following solutions will have the highest pH value? (CPMT 1992)
(a) 0.01 M NaOH (b) 0.02 M CH_3COONa
(c) 0.10 M $NaHCO_3$ (d) 0.10 M H_2SO_4

143. In the titration of NH_4OH with HCl, the indicator which cannot be used is:
(a) phenolphthalein
(b) methyl orange
(c) methyl red
(d) both methyl orange and methyl red

144. pH of the buffer containing 0.6 g of acetic acid and 8.2 g of sodium acetate in 1 litre of water is: (pK_a of acetic acid = 4.5)
(a) 7.5 (b) 4.5 (c) 5.5 (d) 6.5

145. At 25°C, the dissociation constants of CH_3COOH and NH_4OH in aqueous solution are almost the same. The pH of a solution of 0.01 N CH_3COOH is 4.0 at 25°C. The pH of 0.01 N NH_4OH solution at the same temperature would be: (IIT 1990)
(a) 3.0 (b) 4.0
(c) 10.0 (d) 10.5
[Hint: $[H^+]$ in CH_3COOH soln. = 10^{-4};
Similarly $[OH^-]$ in NH_4OH soln. = 10^{-4};
So, $[H^+] = \dfrac{K_w}{[OH^-]} = \dfrac{10^{-14}}{10^{-4}} = 10^{-10}]$

146. The dissociation constant of acetic acid is 1.8×10^{-5} and that of ammonium hydroxide is also 1.8×10^{-5} at 25°C. Hence, an aqueous solution of ammonium acetate is:
(a) acidic (b) basic
(c) neutral (d) slightly acidic

147. The concentration of OH^- ions in neutral solution is:
(a) 1×10^{-14} g ions/litre (b) 1×10^{14} g ions/litre
(c) 1×10^{7} g ions/litre (d) 1×10^{-7} g ions/litre

148. 10^{-6} M NaOH is diluted by 100 times. The pH of diluted base is: **[PMT (Pb.) 1993]**
(a) between 6 and 7 (b) between 10 and 11
(c) between 7 and 8 (d) between 5 and 6

149. Ionic dissociation of acetic acid is represented as:

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$

According to Lowry and Bronsted, the reaction possesses: **[CEE (Bihar) 1992]**
(a) an acid and three bases (b) two acids and two bases
(c) an acid and a base (d) three acids and a base

150. The concept of an acid as an acceptor of a pair of electrons was introduced by:
(a) Lowry (b) Bronsted (c) Arrhenius (d) Lewis

151. The ionic product of water will increase if:
(a) pressure is decreased (b) H^+ ions are added
(c) OH^- ions are added (d) temperature is increased

152. One litre of a buffer solution containing 0.01 M NH_4Cl and 0.1 M NH_4OH having pK_b of 5 has pH of:
(a) 10 (b) 9 (c) 4 (d) 6

153. An aqueous solution of ferric chloride would be:
(a) acidic (b) neutral (c) basic (d) amphoteric

154. An acid solution of pH 6 is diluted hundred times. The pH of the solution becomes:
(a) 6 (b) 6.95 (c) 4 (d) 8

155. The pH of a solution is 5.0. To this solution sufficient acid is added to decrease the pH to 2.0. The increase in hydrogen ion concentration is: **(CPMT 1990)**
(a) 100 times (b) 10 times (c) 1000 times (d) 2.5 times

156. Conjugate base of HPO_4^{2-} is: **[PMT (MP) 1991]**
(a) PO_4^{3-} (b) $H_2PO_4^-$
(c) H_3PO_4 (d) H_4PO_3

157. The pH of a solution is 2. Its pH is to be changed to 4. Then the H^+ ion concentration of original solution has to be:
(a) halved (b) doubled
(c) increased 100 times (d) decreased 100 times

158. The pH value of 0.1 mol/litre HCl is approximately 1. The approximate pH value of 0.05 mol/litre H_2SO_4 is most likely to be:
(a) 0.05 (b) 0.5
(c) 1 (d) 2

159. The aqueous solution of a salt is alkaline. This shows that the salt is made from: **[PMT (MP) 1991]**
(a) a weak acid and a weak base
(b) a weak acid and a strong base
(c) a strong acid and a strong base
(d) a strong acid and a weak base

160. A semi-normal solution of sodium acetate in water has $[H^+]$:
(a) less than 10^{-7} M (b) greater than 10^{-7} M
(c) equal to 10^{-7} M (d) none of these

161. The most important buffer in the blood consists of:
(a) HCl and Cl^- (b) H_2CO_3 and HCO_3^-
(c) H_2CO_3 and Cl^- (d) HCl and HCO_3^-

162. The pH of a buffer solution containing 25 mL of 1 M CH_3COONa and 25 mL of 1 M CH_3COOH will be appreciably affected by 5 mL of:
(a) 1 M CH_3COOH (b) 5 M HCl
(c) 5 M CH_3COOH (d) 1 M NH_4OH

163. 50 mL of 2 N acetic acid mixed with 10 mL of 1 N sodium acetate solution will have an approximate pH:
(a) 7 (b) 6 (c) 5 (d) 4

164. The solution of which salt in water is acidic?
(a) $Na_2B_4O_7$ (b) $NaHCO_3$ (c) KCl (d) $FeCl_3$

165. Which of the following expressions is not true?
(a) $[H^+] = [OH^-] = \sqrt{K_w}$ for a neutral solution
(b) $[H^+] > \sqrt{K_w}$ and $[OH^-] < \sqrt{K_w}$ for an acidic solution
(c) $[H^+] < \sqrt{K_w}$ and $[OH^-] > \sqrt{K_w}$ for an alkaline solution
(d) $[H^+] = [OH^-] = 10^{-7}$ M for a neutral solution at all temperatures

166. Ammonia gas dissolves in water to give NH_4OH. In this reaction water acts as: **[PMT (MP) 1990]**
(a) an acid (b) a base
(c) a salt (d) a conjugate base

167. What is the decreasing order of strength of the bases OH^-, NH_2^-, $H—C{\equiv}C^-$ and $CH_3CH_2^-$? **(IIT 1993)**
(a) $CH_3CH_2^- > NH_2^- > H—C{\equiv}C^- > OH^-$
(b) $H—C{\equiv}C^- > CH_3—CH_2^- > NH_2^- > OH^-$
(c) $OH^- > NH_2^- > H—C{\equiv}C^- > CH_3CH_2^-$
(d) $NH_2^- > H—C{\equiv}C^- > OH^- > CH_3CH_2^-$

168. The best explanation for the solubility of MnS in dil. HCl is that: **(MLNR 1993)**
(a) solubility product of $MnCl_2$ is less than that of MnS
(b) concentration of Mn^{2+} is lowered by the formation of complex ions
(c) concentration of sulphide ions is lowered by oxidation to free sulphur
(d) concentration of sulphide ions is lowered by the formation of weak acid H_2S

169. The correct order of increasing $[H_3O^+]$ in the following aqueous solution is: **(MLNR 1993; AFMC 2009)**
(a) 0.001 M $H_2S <$ 0.01 M $H_2SO_4 <$ 0.01 M NaCl $<$ 0.01 M $NaNO_2$
(b) 0.01 M NaCl $<$ 0.01 M $NaNO_2 <$ 0.01 M $H_2S <$ 0.01 M H_2SO_4
(c) 0.01 M $NaNO_2 <$ 0.01 M NaCl $<$ 0.01 M $H_2S <$ 0.01 M H_2SO_4
(d) 0.01 M $H_2S <$ 0.01 M NaCl $<$ 0.01 M $NaNO_2 <$ 0.01 M H_2SO_4

170. Which of the following statements/relationships is not correct?
(a) Upon hydrolysis salt of strong base and weak acid gives a solution with $pH > 7$
(b) $pH = \log \frac{1}{[H^+]}$
(c) Only at 25° C, the pH of pure water is 7
(d) The value of pK_w at 25°C is 7

171. Fear and excitement generally cause one to breathe rapidly and it results in the decrease of CO_2 concentration in blood. In what way will it change the pH of the blood? **(IIT 1993)**
(a) pH will decrease
(b) pH will increase
(c) No change
(d) pH will adjust to 7

172. Nucleophiles are:
(a) Lewis acids
(b) Lewis bases
(c) Bronsted acids
(d) none of these

173. Electrophiles are:
(a) Lewis acids
(b) Lewis bases
(c) Bronsted acids
(d) Bronsted bases

174. K_h (hydrolysis constant) of ammonium benzoate can be calculated by the formula:
(a) $\sqrt{\frac{K_w}{K_a C}}$ (b) $\sqrt{\frac{K_w}{K_a \times K_b}}$ (c) $\sqrt{\frac{K_w}{K_b \times C}}$ (d) $\sqrt{\frac{K_h}{C}}$

175. The pH of a neutral water is 6.5. Then the temperature of water: **[PET (Kerala) 2007]**
(a) is 25°C
(b) is more than 25°C
(c) is less than 25°C
(d) can be more or less than 25°C
(e) cannot be predicted

176. The buffer capacity of buffer containing acid with $pK_a = 4.0$ is highest when its pH is equal to:
(a) 6.0
(b) 5.0
(c) 4.0
(d) 3.0

177. K_{sp} (AgCl) > K_{sp} (AgBr) > K_{sp} (AgI). This means that:
(a) AgCl is more ionised than AgBr and AgI
(b) both AgBr and AgI are less soluble than AgCl
(c) AgI is most soluble
(d) AgBr is more soluble than AgCl but less soluble than AgI

178. In the hydrolytic equilibrium;

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

$K_b = 1 \times 10^{-5}$. The hydrolysis constant is:
(a) 10^{-5} (b) 10^{-19} (c) 10^{-10} (d) 10^{-9}

179. The solution of a salt of a weak acid and weak base will have pH: ($K_b = 1.0 \times 10^{-6}$ and $K_a = 1.0 \times 10^{-4}$)
(a) 7.0
(b) 8.0
(c) 6
(d) 4.0

180. 0.1 N solution of sodium acetate will have pH: ($pK_a = 4.57$)
(a) 8.78
(b) 11.57
(c) 4.57
(d) 7.0

181. The following acids have been arranged in the order of decreasing acid strength. Identify the correct order: **(IIT 1996)**

ClOH (I) BrOH (II) IOH (III)

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

182. Which of the following statements is correct?
(a) pK_w increases with increase of temperature
(b) pK_w decreases with increase of temperature
(c) $pK_w = 14$ at all temperatures
(d) $pK_w = pH$ at all temperatures

183. For a concentrated solution of a weak electrolyte A_x and B_y, the degree of dissociation is given as:
(a) $\alpha = \sqrt{K_{eq}/c(x+y)}$
(b) $\alpha = \sqrt{K_{eq}c/(xy)}$
(c) $\alpha = (K_{eq}/c^{x+y-1}\,x^x y^y)^{1/(x+y)}$
(d) $\alpha = \sqrt{K_{eq}/xyc}$

184. A solution is saturated with respect to $SrCO_3$ and SrF_2. The $[CO_3^{2-}]$ was found to be $1.2 \times 10^{-3}\ M$. The concentration of F^- in the solution would be:
(a) $1.3 \times 10^{-3}\ M$
(b) $2.6 \times 10^{-2}\ M$
(c) $3.7 \times 10^{-2}\ M$
(d) $5.8 \times 10^{-7}\ M$
(Given: K_{sp} $SrCO_3 = 7.0 \times 10^{-10}\ M^2$,
$K_{sp}(SrF_2) = 7.9 \times 10^{-10}\ M^3$)

185. The solubility of sparingly soluble electrolyte $M_m A_a$ in water is given by the expression:
(a) $S = \left[\frac{K_{sp}}{m^m a^a}\right]^{m+a}$
(b) $S = \left[\frac{K_{sp}}{m^m a^a}\right]^{1/(m+a)}$
(c) $S = \left[\frac{K_{sp}}{m^a a^m}\right]^{m+a}$
(d) $S = \left[\frac{K_{sp}}{m^a a^m}\right]^{1/(m+a)}$

186. The solubility of mercurous chloride in water will be given as:
(a) $S = K_{sp}$
(b) $S = K_{sp}/4$
(c) $S = (K_{sp}/4)^{1/2}$
(d) $S = (K_{sp}/4)^{1/3}$

187. In the titration of acetic acid *versus* sodium hydroxide, the pH of the solution at equivalence point (when temperature is 25°C) is:
(a) about 5.5
(b) about 6.5
(c) about 7
(d) about 8.5

188. When K_2O is added to water, the solution is basic because it contains a significant concentration of:
(a) K^+
(b) OH^-
(c) O^{3-}
(d) O_2^{2-}

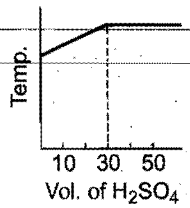
189. The blood buffers are most often involved in stabilizing the pH in presence of metabolically produced:
(a) acids
(b) bases
(c) salts
(d) none of these

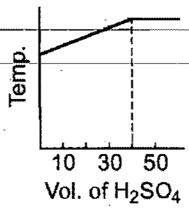
190. The colour of $CuCr_2O_7$ solution in water is green because:
(a) Cu^{2+} ion is green
(b) $Cr_2O_7^{2-}$ ions are green
(c) both the ions are green
(d) Cu^{2+} ion is blue and $Cr_2O_7^{2-}$ ion is yellow

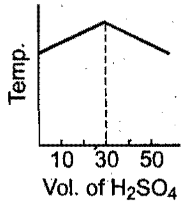
191. An acid with molecular formula $C_7H_6O_3$ forms three types of sodium salts, *i.e.*, $C_7H_5O_3Na$, $C_7H_4O_3Na_2$ and $C_7H_3O_3Na_3$. The basicity of the acid is:
(a) one (b) two (c) three (d) four

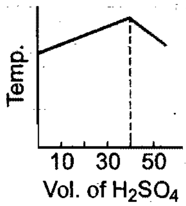
192. If the salts M_2X, QY_2 and PZ_3 have the same solubilities, their K_{sp} values are related as:
(a) $K_{sp}(M_2X) = K_{sp}(QY_2) < K_{sp}(PZ_3)$
(b) $K_{sp}(M_2X) > K_{sp}(QY_2) = K_{sp}(PZ_3)$
(c) $K_{sp}(M_2X) = K_{sp}(QY_2) = K_{sp}(PZ_3)$
(d) $K_{sp}(M_2X) > K_{sp}(QY_2) > K_{sp}(PZ_3)$

193. In an experiment to determine the enthalpy of neutralization of sodium hydroxide with sulphuric acid, 50 cm^3 of 0.4 M sodium hydroxide were titrated thermometrically with 0.25 M sulphuric acid. Which of the following plots gives the correct representation?

(a)


(b)


(c)


(d)


194. K_{sp} of CuS, Ag_2S and HgS are 10^{-31}, 10^{-44} and 10^{-54} respectively. Select the correct order for their solubility in water: (CBSE 1997)
(a) $Ag_2S > HgS > CuS$ (b) $HgS > CuS > Ag_2S$
(c) $HgS > Ag_2S > CuS$ (d) $Ag_2S > CuS > HgS$
[**Hint:** Solubility of Ag_2S $(4S^3 = K_{sp})$ and for CuS and HgS $(S^2 = K_{sp})$.]

195. If the K_b value in the hydrolysis reaction,

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

is 1.0×10^{-6}, then the hydrolysis constant of the salt would be: (IIT 1998)
(a) 1.0×10^{-6} (b) 1.0×10^{-7} (c) 1×10^{-8} (d) 1.0×10^{-9}

196. The concentration of $[H^+]$ and $[OH^-]$ of a 0.1 M aqueous solution of 2% ionised weak acid is: (ionic product of water $= 1 \times 10^{-14}$) (CBSE 1999)
(a) 0.2×10^{-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
[**Hint:** $[H^+] = C \times \alpha = 0.1 \times 0.02 = 2 \times 10^{-3}$ M;
$[OH^-] = \frac{K_w}{[H^+]}$]

197. The pH value of decinormal solution of NH_4OH, which is 20% ionised, is: (C[illegible])
(a) 13.30 (b) 14.70 (c) 12.30 (d) 12.95
[**Hint:** $[OH^-] = 0.1 \times 0.2 = 2 \times 10^{-3}$;
$pOH = 1.7 \; pH = 14 - pOH$]

198. The pH of 0.1 M solution of the following salts increases in the order of: (IIT 1999)
(a) $NaCl < NH_4Cl < NaCN < HCl$
(b) $HCl < NH_4Cl < NaCl < NaCN$
(c) $NaCN < NH_4Cl < NaCl < HCl$
(d) $HCl < NaCl < NaCN < NH_4Cl$

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

200. Which one does not give a buffer solution?
(a) Ammonia and sodium hydroxide in water
(b) Sodium acetate and acetic acid in water
(c) Ammonia and ammonium chloride in water
(d) Sodium acetate and hydrochloric acid in water

201. Conjugate base of $[Al(H_2O)_3(OH)_3]$ is:
(a) $[Al(H_2O)_3(OH)_2]^+$ (b) $[Al(H_2O)_3(OH)_2O]^-$
(c) $[Al(H_2O)_3(OH)_3]^-$ (d) $[Al(H_2O)_2(OH)_4]^-$

202. The solubility of calcium phosphate in water is x mol h^{-1} at 25°C. Its solubility product is equal to: [illegible] 1995
(a) $108x^2$ (b) $36x^3$
(c) $36x^5$ (d) $108x^5$

203. K_{sp} values for silver bromide, silver chloride and silver iodide are 5×10^{-13} mol^2 dm^{-6}, 2×10^{-10} mol^2 dm^{-6} and 8×10^{-17} mol^2 dm^{-6} respectively. The order of solubility of these silver salts is : (PET (R[illegible])
(a) AgCl > AgBr > AgI (b) AgI > AgBr > AgCl
(c) AgCl > AgI > AgBr (d) AgI > AgCl > AgBr

204. In the reaction,

$$I_2 + I^- \longrightarrow I_3^-$$

the Lewis base is: (A[illegible] 199[illegible])
(a) I_2 (b) I^-
(c) I_3^- (d) none of these

205. Which of the following on reaction with H_2S does not produce metallic sulphide? (AIIMS 199[illegible])
(a) $CdCl_2$ (b) $ZnCl_2$ (c) $CoCl_2$ (d) $CuCl_2$

206. A buffer solution of pH = 9 can be prepared by mixing: (CPMT 2000)
(a) CH_3COONa and CH_3COOH
(b) NaCl and NaOH
(c) NH_4Cl and NH_4OH
(d) KH_2PO_4 and K_2HPO_4

207. Which of the following is the strongest Lewis base? [PMT (MP) [illegible]]
(a) CH_3^- (b) NH_2^- (c) OH^- (d) F^-

208. The monobasic acid among the following is : **(ISAT 2010)**
(a) H_3PO_3 (b) $H_2S_2O_7$
(c) H_3PO_2 (d) $H_4P_2O_7$

209. To Ag_2CrO_4 solution over its own precipitate, CrO_4^{2-} ions are added. This results in: **[MEE (Kerala) 2000]**
(a) increase in Ag^+ concentration
(b) decrease in Ag^+ concentration
(c) increase in solubility product
(d) shifting of Ag^+ ions from the precipitate into the solution

210. Aluminium chloride is: **(KCET 2000)**
(a) Bronsted Lowry acid (b) Arrhenius acid
(c) Lewis acid (d) Lewis base

211. A 50 mL solution of pH = 1 is mixed with a 50 mL solution of pH = 2. The pH of the mixture will be nearly: **[IAS (Prelim.) 1995]**
(a) 0.76 (b) 1.26 (c) 1.76 (d) 2.26

212. The $[Ag^+]$ in a saturated solution of Ag_2CrO_4 is $1.5\times10^{-4}\,M$. What is the solubility product of Ag_2CrO_4? **(SCRA 2009)**
(a) $3.375\times10^{-12}M^3$ (b) $1.6875\times10^{-10}M^3$
(c) $1.6875\times10^{-11}M^3$ (d) $1.6875\times10^{-12}M^3$

[**Hint :** $Ag_2CrO_4 \longrightarrow 2Ag^+ + CrO_4^{2-}$

$[Ag^+] = 1.5\times10^{-4}\,M \quad \therefore\ [CrO_4^{2-}] = 0.75\times10^{-4}\,M$

$K_{sp} = [Ag^+]^2[CrO_4^{2-}]$

$= [1.5\times10^{-4}]^2[0.75\times10^{-4}]$

$= 1.6875\times10^{-12}M^3$]

213. The pH of a buffer containing equal molar concentrations of a weak base and its chloride (K_b for weak base $= 2\times10^{-5}$, log 2 = 0.3) is:
(a) 5 (b) 9 (c) 4.7 (d) 9.3

214. The solubility product (K_{sp}) of AgCl is 1.8×10^{-10}. Precipitation of AgCl will occur only when equal volumes of solutions of: **[IAS (Prelim.) 1997; PET (MP) 2007]**
(a) $10^{-4}\,M\,Ag^+$ and $10^{-4}\,M\,Cl^-$ are mixed
(b) $10^{-7}\,M\,Ag^+$ and $10^{-7}\,M\,Cl^-$ are mixed
(c) $10^{-5}\,M\,Ag^+$ and $10^{-5}\,M\,Cl^-$ are mixed
(d) $10^{-10}\,M\,Ag^+$ and $10^{-10}\,M\,Cl^-$ are mixed

215. Solid $Ba(NO_3)_2$ is gradually dissolved in a $1\times10^{-4}\,M\,Na_2CO_3$ solution. At what concentration of Ba^{2+} will a precipitate begin to form ? (K_{sp} for $BaCO_3 = 5.1\times10^{-9}$) **(AIEEE 2009)**
(a) $4.1\times10^{-5}\,M$ (b) $5.1\times10^{-5}\,M$
(c) $8.1\times10^{-8}\,M$ (d) $8.1\times10^{-7}\,M$

216. How many gram of CaC_2O_4 will dissolve in distilled water to make one litre of unsaturated solution of it? (K_{sp} for $CaC_2O_4 = 2.5\times10^{-9}\ mol^2\ lit^{-2}$) **[PMT (MP) [illegible]]**
(a) 0.0064 g (b) 0.1028 g (c) 0.1280 g (d) 0.2056 g

217. When CO_2 dissolves in water, the following equilibrium is established,

$$CO_2 + 2H_2O \rightleftharpoons H_3O^+ + HCO_3^-$$

for which the equilibrium constant is 3.8×10^{-7} and pH = 6.0. The ratio of $[HCO_3^-]$ to $[CO_2]$ would be:
(a) 3.8×10^{-13} (b) 3.8×10^{-1} (c) 6.0 (d) 13.4

218. pH of a buffer solution decreases by 0.02 units when 0.12 g of acetic acid is added to 250 mL of a buffer solution of acetic acid and potassium acetate at 27°C. The buffer capacity of the solution is: **(EAMCET 2009)**
(a) 0.1 (b) 10 (c) 1 (d) 0.4

219. The dissociation constants of monobasic acids A, B, C and D are 6×10^{-4}, 5×10^{-5}, 3.6×10^{-6} and 7×10^{-10} respectively. The pH values of their 0.1 molar aqueous solutions are in the order:
(a) $A<B<C<D$ (b) $A>B>C>D$
(c) $A=B=C=D$ (d) $A>B<C>D$

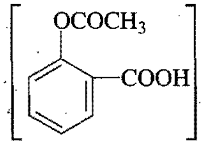
220. If the equilibrium constant of the reaction of weak acid HA with strong base is 10^9, then pH in 0.1 M NaA is:
(a) 5 (b) 9 (c) 7 (d) 8

221. If the freezing point of 0.1 molal HA (*aq.*) is – 0.2046°C, then pH of the solution is: [K_f (H_2O) = 1.86° mol^{-1} kg]
(a) 1 (b) 2 (c) 1.3 (d) 1.7

222. % ionisation of weak acid can be calculated as:
(a) $100\sqrt{\dfrac{K_a}{c}}$ (b) $\dfrac{100}{1+10^{(pK_a - pH)}}$
(c) both correct (d) none is correct

223. Assuming complete ionisation which will have maximum pH?
(a) 0.01 M NH_4Cl (b) 0.01 M $(NH_4)_2SO_4$
(c) 0.01 M $(NH_4)_3PO_4$ (d) equal

224. $H_2O + H_3PO_4 \rightleftharpoons H_3O^+ + H_2PO_4^-;\ pK_1 = 2.15$
$H_2O + H_2PO_4^- \rightleftharpoons H_3O^+ + HPO_4^{2-};\ pK_2 = 7.20$
Hence, pH of 0.01 M NaH_2PO_4 is:
(a) 9.35 (b) 4.675 (c) 2.675 (d) 7.350

225. Acetyl salicylic acid  called aspirin is a pain killer with pK_a = 2. If two tablets each of 0.09 g mass, containing aspirin are dissolved in 100 mL solution. Its pH will be:
(a) 0.5 (b) 1.0
(c) 0.0 (d) 2.0

226. If ionic product of water is $K_w = 10^{-16}$ at 4°C, then a solution with pH = 7.5 at 4°C will:
(a) turn blue litmus red (b) turn red litmus blue
(c) turn turmeric paper brown (d) be neutral to litmus

227. How do we differentiate between Fe^{3+} and Cr^{3+} in group III? **(AIEEE 2002)**
(a) By taking excess of NH_4OH
(b) By increasing NH_4^+ ion concentration
(c) By decreasing OH^- ion concentration
(d) Both (b) and (c)

228. Which has the highest pH? **[CBSE (PMT) 2002]**
(a) CH_3COOK (b) Na_2CO_3
(c) NH_4Cl (d) $NaNO_3$

229. Water is a: **(KCET 2002)**
(a) protophobic solvent (b) protophilic solvent
(c) amphiprotic solvent (d) aprotic solvent

230. 1 M NaCl and 1 M HCl are present in an aqueous solution. The solution is: **(AIEEE 2002)**
(a) not a buffer solution with pH < 7
(b) not a buffer solution with pH > 7
(c) a buffer solution with pH < 7
(d) a buffer solution with pH = 7

231. Solution of 0.1 M NH_4OH and 0.1 M NH_4Cl has pH 9.25. Then pK_b of NH_4OH is: **[CBSE (PMT) 2002]**
(a) 9.25 (b) 4.75
(c) 3.75 (d) 8.25

232. Solubility of an MX_2 type electrolyte is 0.5×10^{-4} mol/litre, then K_{sp} of electrolyte is: **[CBSE (PMT) 2002]**
(a) 5×10^{-12} (b) 25×10^{-10}
(c) 1×10^{-13} (d) 5×10^{-13}

233. The concentration of KI and KCl in a certain solution containing both is 0.001 M each. If 20 mL of this solution is added to 20 mL of a saturated solution of AgI in water. What will happen?
(K_{sp} AgCl $= 10^{-10}$; K_{sp} AgI $= 10^{-16}$). **[PET (MP) 2004]**
(a) AgI will be precipitated
(b) AgCl will be precipitated
(c) There will be no precipitate
(d) Both AgCl and AgI will be precipitated

234. Degree of dissociation of NH_4OH in water is 1.8×10^{-5}, then hydrolysis constant of NH_4OH is: **[CECE (Bihar) Pre. 2004]**
(a) 1.8×10^{-5} (b) 1.8×10^{-10}
(c) 5.55×10^{-5} (d) 5.55×10^{-10}

235. What is the pH of 0.01 M glycine solution? For glycine $K_{a_1} = 4.5 \times 10^{-3}$; $K_{a_2} = 1.7 \times 10^{-10}$ at 298 K: **(AIIMS 2004)**
(a) 3.02 (b) 6.94 (c) 7.06 (d) 10.02

236. 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 the ratio of the concentrations of the conjugate acid HIn and base In^- forms of the indicator by the expression: **[CBSE (PMT) 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) $\log \frac{[In^-]}{[HIn]} = pH - pK_{In}$

237. A weak acid HX has the dissociation constant 1×10^{-5} M. It forms a salt NaX on reaction with alkali. The degree of hydrolysis of 0.1 M solution of NaX is: **[IIT (S) 2004]**
(a) 0.0001% (b) 0.01% (c) 0.1% (d) 0.15%

238. The molar solubility (in mol litre^{-1}) of a sparingly soluble salt MX_4 is S. The corresponding solubility product K_{sp} is given by the relation: **(AIEEE 2004)**
(a) $S = (K_{sp}/128)^{1/4}$ (b) $S = (218\, K_{sp})^{1/4}$
(c) $S = (256\, K_{sp})^{1/5}$ (d) $S = (K_{sp}/256)^{1/5}$

239. The K_{sp} of $Mg(OH)_2$ is 1×10^{-12}. 0.01 M $Mg(OH)_2$ will precipitate at the limiting pH: **(DPMT 2005)**
(a) 3 (b) 9 (c) 5 (d) 8
[**Hint:** $[Mg^{2+}][OH^-]^2 = 10^{-12}$
$0.01 \times [OH^-]^2 = 10^{-12}$
$[OH^-] = 10^{-5}\, M$
$\therefore [H^+] = 10^{-9}\, M$ and $pH = -\log[10^{-9}] = 9$]

240. The correct expression for the solubility product of $Ca_3(PO_4)_2$ is: **[JEE (Orissa) 2005]**
(a) $108S^5$ (b) $27S^5$ (b) $16S^4$ (d) $81S^4$

241. The solubility product of a salt, having the general formula MX_2, in water is 4×10^{-12}. The concentration of M^{2+} ions in the aqueous solution of the salt is: **(AIEEE 2005)**
(a) $2 \times 10^{-6}\, M$ (b) $1 \times 10^{-4}\, M$
(c) $1.6 \times 10^{-4}\, M$ (d) $4 \times 10^{-10}\, M$
[**Hint:** It is ternary electrolyte.
$\therefore$ $K_{sp} = 4S^3$
$4 \times 10^{-12} = 4S^3$
$S = 10^{-4}\, M$
$\therefore$ $(M^{2+}) = 10^{-4}\, M$]

242. The ionization constant of ammonium hydroxide is 1.77×10^{-5} at 298 K. Hydrolysis constant of ammonium chloride is: **[CBSE (PMT) 2009]**
(a) 5.65×10^{-12} (b) 5.65×10^{-10}
(c) 6.50×10^{-12} (d) 5.65×10^{-13}
[**Hint:** $K_h = \frac{K_w}{K_b} = \frac{10^{-14}}{1.77 \times 10^{-5}}$
$= 5.65 \times 10^{-10}$]

243. The K_a values of formic acid and acetic acid are respectively 1.77×10^{-4} and 1.75×10^{-5}. The ratio of the acid strength of 0.1 M acid is: **[PMT (Kerala) 2005]**
(a) 10 (b) 3.178 (c) 0.3 (d) 0.1
(e) 100

244. Equal volumes of the following Ca^{2+} and F^- solutions are mixed. In which solution will the precipitation occur?

K_{sp} of $CaF_2 = 1.7 \times 10^{-10}$

1. $10^{-2}\, M\, Ca^{2+} + 10^{-5}\, M\, F^-$ 2. $10^{-3}\, M\, Ca^{2+} + 10^{-3}\, M\, F^-$
3. $10^{-4}\, M\, Ca^{2+} + 10^{-2}\, M\, F^-$ 4. $10^{-2}\, M\, Ca^{2+} + 10^{-3}\, M\, F^-$

Select the correct answer using the codes given below: **[PMT (Kerala) 2005]**
(a) in 4 only (b) in 1 and 2 (c) in 3 and 4 (d) in 2, 3 and 4
(e) in all of these

245. Given, pH of a solution A is 3 and it is mixed with another solution B having pH 2. If both are mixed, then the resultant pH of the solution will be: **[BHU (Pre.) 2005]**
(a) 3.2 (b) 1.9 (c) 3.4 (d) 3.5

246. When 10 mL of 0.1 M acetic acid ($pK_a = 5$) is titrated against 10 mL of 0.1 M ammonia solution ($pK_b = 5$), the equivalent point will occur at pH: **(AIIMS 2005)**
(a) 5 (b) 6 (c) 7 (d) 9

247. On adding 0.1 M solution each of Ag^+, Ba^{2+} and Ca^{2+} in an Na_2SO_4 solution, the species first precipitated is: **(DCE 2005)**
(K_{sp} $BaSO_4 = 10^{-11}$, K_{sp} $CaSO_4 = 10^{-6}$, K_{sp} $Ag_2SO_4 = 10^{-5}$)
(a) Ag_2SO_4 (b) $BaSO_4$
(c) $CaSO_4$ (d) all of these

248. When 0.1 mole of CH_3NH_2 (ionization constant, $K_b = 5 \times 10^{-4}$) is mixed with 0.08 mole HCl and the volume is made up to 1 litre, find the $[H^+]$ of resulting solution: **(IIT 2005)**

(a) 8×10^{-2} (b) 2×10^{-11}

(c) 1.23×10^{-4} (d) 8×10^{-11}

[**Hint:**
$$\begin{array}{cccc} CH_3NH_2 + & HCl & \longrightarrow & CH_3NH_3^+Cl^- \\ 0.1 \text{ mol} & 0.08 \text{ mol} & & 0 \\ 0.02 \text{ mol} & 0 & & 0.08 \end{array}$$

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

$$= -\log 5 \times 10^{-4} + \log \frac{0.08}{0.02} = 3.903$$

$$pH = 10.0967$$

$$[H^+] = \text{antilog}[-10.0967] = 8 \times 10^{-11}]$$

249. At 25°C, the dissociation constant of a base BOH is 1×10^{-12}. The concentration of hydroxyl ions in 0.01 M aqueous solution of the base would be: **[CBSE-PMT (Pre.) 2005]**

(a) 10^{-5} mol L^{-1} (b) 10^{-6} mol L^{-1}

(c) 2×10^{-6} mol L^{-1} (d) 10^{-7} mol L^{-1}

[**Hint:** $[OH^-] = \sqrt{CK_b} = \sqrt{0.01 \times 10^{-12}} = 10^{-7}$ mol L^{-1}]

250. Which of the following solutions has pH equal to 10? **[UGET (Manipal) 2006]**

(a) 10^{-4} M KOH (b) 10^{-10} M KOH

(c) 10^{-10} M HCl (d) 10^{-4} M HCl

251. A weak monobasic acid is half neutralised by a strong base. If the pH of the solution is 5.4, its pK_a is: **[JEE (Orissa) 2006]**

(a) 6.8 (b) 2.7 (c) 5.4 (d) 10.8

[**Hint:** [Acid] = [Salt]

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

$$5.4 = pK_a + \log_{10} 1$$

$$\therefore \; pK_a = 5.4]$$

252. ZnS is not precipitated by passing H_2S in acidic medium but CuS precipitated. The reason for it is: **[JEE (Orissa) 2006]**

(a) K_{sp} CuS << K_{sp} ZnS (b) K_{sp} CuS >> K_{sp} ZnS

(c) K_{sp} CuS = K_{sp} ZnS (d) none of these

253. Solubility product of salt AB is 1×10^{-8} M^2 in a solution, in which the concentration of A^+ ions is 10^{-3} M. The salt will precipitate when the concentration of B^- ions is kept: **(KCET 2006)**

(a) between 10^{-8} M to 10^{-7} M (b) between 10^{-7} M to 10^{-8} M

(c) $> 10^{-5}$ M (d) $< 10^{-8}$ M

254. NaOH(*aq*.), HCl(*aq*.) and NaCl(*aq*.) have concentration of 10^{-3} M each. Their pH will be respectively: **[PMT (Uttarakhand) 2006]**

(a) 10, 6, 2 (b) 11, 3, 7

(c) 10, 3, 7 (d) 10, 4, 7

255. The weak acid, HA, has a K_a of 1.00×10^{-5}. If 0.1 mol of this acid is dissolved in one litre of water, the percentage of acid dissociated at equilibrium is closest to: **[CBSE (Med.) 2007]**

(a) 1% (b) 99.9%

(c) 0.1% (d) 99%

[**Hint:**
$$\begin{array}{lccc} & HA & \rightleftharpoons & H^+ & + & A^- \\ t = 0 & C & & 0 & & 0 \\ t_{eq.} & C - C\alpha & & C\alpha & & C\alpha \end{array}$$

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

$$= \frac{C\alpha^2}{1-\alpha} \approx C\alpha^2$$

$$\alpha = \sqrt{\frac{K_a}{C}} = \sqrt{\frac{10^{-5}}{0.1}} = 10^{-2}$$

% ionisation = $\alpha \times 100 = 1$]

256. At 25° C, the value of pK_b (K_b being the dissociation constant as a base) for NH_3 in aqueous solution is 4.7. What is the pH of 0.1 M aqueous solution of NH_4Cl with 0.01 M NH_3 (approximately)? **(SCRA 2007)**

(a) 8.3 (b) 9 (c) 9.5 (d) 10

[**Hint:** $pOH = pK_b + \log_{10} \frac{[NH_4Cl]}{[NH_4OH]}$

$$= 4.7 + \log \left[\frac{0.1}{0.01}\right] = 5.7$$

$$pH = 14 - 5.7 = 8.3]$$

257. The ionisation of strong electrolytes in acetic acid compared to that in water is: **[CET (J&K) 2007]**

(a) weak, low (b) strong, more

(c) medium, the same (d) no ionisation, 100%

258. By adding a little of acid or base, the change in pH of blood is not significant, because blood: **[PET (Raj.) 2006]**

(a) has iron as a part of molecule

(b) is a body fluid

(c) has serum protein which works as buffer

(d) is easily coagulated

259. 2.5 mL of 2/5 M weak monoacidic base ($K_b = 1 \times 10^{-12}$ at 25°C) is titrated with 2/15 M HCl in water at 25°C. The concentration of H^+ ion at equivalence point is: ($K_w = 1 \times 10^{-14}$ at 25°C) **(IIT 2008)**

(a) $3.7 \times 10^{-13} M$ (b) $3.2 \times 10^{-7} M$

(c) $3.2 \times 10^{-2} M$ (d) $2.7 \times 10^{-2} M$

[**Hint:** $1\,BOH + 1HCl \longrightarrow BCl + H_2O$

$$\frac{M_1V_1}{1} \text{ (Base)} = \frac{M_2V_2}{1} \text{ (Acid)}$$

$$\frac{2}{5} \times 2.5 = \frac{2}{15} \times V_2$$

$$V_2 = 7.5 \text{ mL}$$

Total volume = 7.5 + 2.5 = 10 mL

Concentration of salt in the mixture :

$$M_1V_1 \text{ (Base)} = M_2V_2 \text{ (Salt)}$$

$$\frac{2}{5} \times 2.5 = M_2 \times 10$$

$$M_2 = 0.1$$

$$pH = \frac{1}{2}[pK_w - pK_b - \log C]$$

$$= \frac{1}{2}[14 - 12 - (-1)] = 1.5$$

$$[H^+] = \text{Antilog}(-1.5) = 0.032\,M]$$

260. Solubility product constants (K_{sp}) of salts of types MX, MX_2, M_3X at temperature T are 4×10^{-8}, 3.2×10^{-14} and 2.7×10^{-15} respectively. Solubility (mol dm^{-3}) of the salts at temperature T are in the order: **(IIT 2008)**

(a) $MX > MX_2 > M_3X$ (b) $M_3X > MX_2 > MX$

(c) $MX_2 > M_3X > MX$ (d) $MX > M_3X > MX_2$

[Hint:

Solubility (S_1) of $MX = \sqrt{K_{sp}} = \sqrt{4 \times 10^{-8}} = 2 \times 10^{-4} M$

Solubility (S_2) of

$$MX_2 = \left(\frac{K_{sp}}{4}\right)^{\frac{1}{3}} = \left(\frac{3.2 \times 10^{-14}}{4}\right)^{\frac{1}{3}} = 2 \times 10^{-5} M$$

Solubility (S_3) of

$$M_3X = \left(\frac{K_{sp}}{27}\right)^{\frac{1}{4}} = \left(\frac{2.7 \times 10^{-15}}{27}\right)^{\frac{1}{4}} = 10^{-4} M$$

$\therefore S_1 > S_3 > S_2$]

261. In aqueous solution, the ionization constants for carbonic acid are :

$$K_1 = 4.2 \times 10^{-7} \text{ and } K_2 = 4.8 \times 10^{-11}$$

Select the correct statement for a saturated 0.034 M solution of the carbonic acid : **(AIEEE 2010)**

(a) The concentrations of H^+ and HCO_3^- are approximately equal

(b) The concentration of H^+ is double that of CO_3^{2-}

(c) Concentration of CO_3^{2-} is 0.034 M

(d) The concentration of CO_3^{2-} is greater than that of HCO_3^-

Set-2: The Questions given below may have more than one correct answers

1. For dissociation constant (K) and ionic product (K_w) of water which is correct?

(a) $K > K_w$ (b) $K_w > K$

(c) $K_w = K$ (d) None of these

2. Which is an example of auto protolysis?

(a) $H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$

(b) $NH_3 + NH_3 \rightleftharpoons NH_4^+ + NH_2^-$

(c) $H_2SO_4 + H_2SO_4 \rightleftharpoons H_3SO_4^+ + HSO_4^-$

(d) All of the above

3. If concentrations of two acids are same, their relative strengths can be compared by:

(a) α_1/α_2 (b) K_1/K_2

(c) $[H^+]_1/[H^+]_2$ (d) $\sqrt{K_1/K_2}$

4. Three bases XOH, YOH and ZOH have pK_b values 2, 3 and 4 respectively; the strongest conjugate acid is:

(a) XOH_2^+ (b) YOH_2^+

(c) ZOH_2^+ (d) all are same

5. Aqueous solution of HNO_3, KOH, CH_3COOH and CH_3COONa of identical concentrations are provided. The pair(s) of solutions which form a buffer upon mixing is (are): **(IIT 2010)**

(a) HNO_3 and CH_3COOH

(b) KOH and CH_3COONa

(c) HNO_3 and CH_3COONa

(d) CH_3COOH and CH_3COONa

6. Four solutions of NH_4Cl are taken with concentrations 1 M, 0.1 M, 0.01 M and 0.001 M. Their degree of hydrolysis are h_1, h_2, h_3 and h_4. What is the graduation of degree of hydrolysis?

(a) $h_1 > h_2 > h_3 > h_4$ (b) $h_1 = h_2 = h_3 = h_4$

(c) $h_4 > h_3 > h_2 > h_1$ (d) None of these

7. Which has maximum solubility AB, AB_2, AB_3 and AB_4 if K_{sp} for all the salts are 10^{-10} ?

(a) AB (b) AB_2 (c) AB_3 (d) AB_4

8. Dissociation of an indicator can be considered as,

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

Colours of HIn and In^- are different. Which statement is correct?

(a) Solution assumes colours of HIn when pH = P_{K-1}

(b) Solution assumes colours of In^- when pH = P_{K+1}

(c) Solution assumes colours of HIn^- when pH = P_{K+1}

(d) Solution assumes colours of In^- when pH = P_{K-1}

9. The % error in $[H^+]$ made by neglecting the ionisation of water in 10^{-6} M NaOH is:

(a) 1% (b) 2% (c) 3% (d) 4%

10. 50 mL $N/10$ NaOH solution is mixed with 50 mL $N/20$ HCl solution. The resulting solution will:

(a) turn phenolphthalein solution pink

(b) turn blue litmus red

(c) turn methyl orange red

(d) $[H^+] < [OH^-]$

11. An acid indicator HIn has $K_a = 3 \times 10^{-5}$, the acid form is red and basic form is blue. Which is correct?

(a) pH = 5 when indicator is 75% red

(b) pH = 4.05 when indicator is 75% red

(c) pH = 5 when indicator is 75% blue

(d) pH = 4.05 when indicator is 75% blue

12. Which of the following will function as buffer? **[IAS (Pre.) 1997]**

(a) NaCl + NaOH (b) Borax + boric acid

(c) $NaH_2PO_4 + NaHPO_4$ (d) $NH_4Cl + NH_4OH$

13. Choose the correct statement(s):

(a) pH of an acidic buffer increases if more salt is added.

(b) pH of a basic buffer decreases if more salt is added.

(c) In a saturated solution, ionic product is equal to its solubility product.

(d) The term solubility product is only for sparingly soluble salts.

14. In the following reaction,

$$\underset{(A)}{[Cu(H_2O)_3(OH)]^+} + \underset{(B)}{[Al(H_2O)_6]^{3+}} \longrightarrow \underset{(C)}{[Cu(H_2O)_4]^{2+}} + \underset{(D)}{[Al(H_2O)_5(OH)]^{2+}} :$$

(a) (A) is an acid and (B) is a base

(b) (A) is a base and (B) is an acid

(c) (*C*) is the conjugate acid of (*A*) and (*D*) is the conjugate base of (*B*)

(d) (*C*) is the conjugate base of (*A*) and (*D*) is the conjugate acid of (*B*)

15. Which among the following will not react with NaOH or which is not acid salt?

(a) NaH_2PO_2 (b) Na_2HPO_3 (c) Na_2HPO_2 (d) $NaHCO_3$

Direction: In the following three questions, more than one of the answers given may be correct. Select the correct answers and mark it according to the codes. [BHU (Med.) 2007]

Codes:

(a) 1, 2 and 3 are correct (b) 1 and 2 are correct

(c) 2 and 4 are correct (d) 1 and 3 are correct

16. If equal volumes of 0.1 *M* HBr and 0.1 *M* KOH are mixed, then which of the following is/are correct about the resulting solution?

(1) $[H_3O^+] = 1.0 \times 10^{-7}$ mol L^{-1}

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

(3) $[K^+] = 0.05$ mol L^{-1}

(4) $[Br^-] = 0.10$ mol L^{-1}

17. Which of the following solutions will be acidic?

(1) 0.1 *M* $FeSO_4$ (2) 0.1 *M* $(NH_4)_2SO_4$

(3) 0.1 *M* CH_3COONa (4) 0.1 *M* NH_4OH

18. In a buffer solution consisting NaH_2PO_4 and Na_2HPO_4: [BHU (Mains, 2010]

(1) NaH_2PO_4 is acid and Na_2HPO_4 is salt

(2) The pH of solution can be calculated using the relation :

$$pH = pK_2 + \log_{10}\frac{[HPO_4^{2-}]}{[H_2PO_4^-]}$$

(3) The Na_2HPO_4 is acid and NaH_2PO_4 is salt

(4) The pH can not be calculated

Assertion-Reason TYPE QUESTIONS

The questions given below consist of two statements each printed as **'Assertion' (A)** and **'Reason' (R).** While answering these questions you are required to choose any one of the following four responses:

(a) If both (A) and (R) are correct and (R) is the correct explanation for (A).
(b) If both (A) and (R) are correct but (R) is not the correct explanation for (A).
(c) If (A) is correct, but (R) is incorrect.
(d) If both (A) and (R) are incorrect.

1. (A) A very dilute acidic solution of Cd^{2+} and Ni^{2+} gives yellow precipitate of CdS on passing hydrogen sulphide.
(R) Solubility product of CdS is more than that of NiS.

2. (A) In the titration of Na_2CO_3 with HCl using methyl orange indicator, the volume of the acid required at the equivalence point is twice that of the acid required using phenolphthalein as indicator.
(R) Two moles of HCl are required for the complete neutralisation of one mole of Na_2CO_3. **(IIT 1991)**

3. (A) The pH of an aqueous solution of acetic acid remains unchanged on the addition of sodium acetate.
(R) The ionisation of acetic acid is suppressed by the addition of sodium acetate.

4. (A) In acidic medium, Zn^{2+} is not precipitated by S^{2-} ions.
(R) Common ion effect reduces the concentration of S^{2-} ions to the minimum level.

5. (A) In the acid-base titration involving a strong base and a weak acid, methyl orange can be used as an indicator.
(R) Methyl orange changes its colour in pH range 3 to 5.

6. (A) A mixture of sodium acetate and sodium propionate forms a buffer solution.
(R) A buffer solution reacts with small quantities of hydrogen or hydroxyl ions and keeps the pH almost same.

7. (A) When small amount of an acid or base is added to pure water its pH undergoes a change.
(R) Addition of an acid or a base increases the degree of ionisation of water.

8. (A) At 25°C, the pH of 10^{-8} M HCl is 8.
(R) pH of acidic solution is always below 7 at 25° C.

9. (A) The addition of silver ions to a mixture of aqueous sodium chloride and sodium bromide solution, will first precipitate AgBr rather than AgCl.
(R) The value of K_{sp} of AgCl < K_{sp} of AgBr. **(AIIMS 2004)**

10. (A) Sb (III) is not precipitated as sulphide when in its alkaline solution H_2S is passed.
(R) Concentration of S^{2-} ions in alkaline medium is inadequate for precipitation. **(AIIMS 2004)**

11. (A) Sb_2S_3 is not soluble in yellow ammonium sulphide.
(R) The common ion effect due to S^{2-} ions reduces the solubility of Sb_2S_3. **(AIIMS 2006)**

12. (A) H_2SO_4 acts as a base in presence of $HClO_4$.
(R) Perchloric acid is stronger acid than H_2SO_4.

13. (A) pH of a neutral solution is always 7.
(R) pH of a solution does not depend upon temperature.

14. (A) pH of 10^{-8} M HCl is not equal to 8.
(R) HCl does not dissociate properly in very dilute solution.

15. (A) If a solution with pH = 2 is diluted to double the volume, the pH of the solution will fall to 1.
(R) pH is inversely proportional to the volume of the solution.

16. (A) If HCl gas is passed through saturated NaCl solution, solid NaCl starts separating out.
(R) HCl decreases the solubility product of NaCl.

17. (A) pH of a buffer changes with temperature.
(R) Ionic product of water (K_w) changes with temperature.

18. (A) $I_2 + I^- \longrightarrow I_3^-$
In above reaction, I_2 is Lewis base.
(R) Electron pair acceptor is Lewis base.

19. (A) Phenolphthalein is used as indicator during the titration of oxalic acid against sodium hydroxide.
(R) The pH range of phenolphthalein is from 8 to 9.6.

20. (A) If K_{sp} is less than K_{ip}, the precipitate is formed.
(R) Solubility product (K_{sp}) is the highest limit of ionic product of electrolyte solutions.

21. (A) H_3PO_3 is a dibasic acid.
(R) There are two hydrogen atoms directly attached to phosphorus. **(AIIMS 2007)**

22. (A) NaCl is precipitated when HCl gas is passed in a saturated solution of NaCl.
(R) HCl is a strong acid. **(AIIMS 2007)**

23. (A) On mixing 500 mL of 10^{-6} M Ca^{2+} ion and 500 mL of 10^{-6} MF^- ion, the precipitate of CaF_2 will be obtained. $K_{sp}(CaF_2) = 10^{-18}$.
(R) If K_{sp} is greater than ionic product, precipitate will be obtained. **(AIIMS 2007)**

24. (A) The aqueous solution of CH_3COONa is alkaline in nature.
(R) Acetate ion undergoes an ionic hydrolysis. **(EAMCET 2008)**

25. (A) An aqueous solution of ammonium acetate can act as a buffer.
(R) Acetic acid is a weak acid and NH_4OH is a weak base. **(EAMCET 2010)**

26. (A) $[Al(H_2O)_6]^{3+}$ is a stronger acid than $[Mg(H_2O)_6]^{2+}$.
(R) Size of $[Al(H_2O)_6]^{3+}$ smaller than $[Mg(H_2O)_6]^{2+}$ and possesses more effective nuclear charge. **(AIIMS 2010)**

Answers : OBJECTIVE QUESTIONS

Set–1

1. (c) 2. (b) 3. (a) 4. (d) 5. (d) 6. (c) 7. (a) 8. (c)
9. (c) 10. (d) 11. (a) 12. (b) 13. (b) 14. (b) 15. (d) 16. (b)
17. (c) 18. (a) 19. (d) 20. (a) 21. (a) 22. (d) 23. (c) 24. (a)
25. (c) 26. (c) 27. (a) 28. (c) 29. (b) 30. (d) 31. (b) 32. (d)
33. (d) 34. (c) 35. (a) 36. (c) 37. (a) 38. (c) 39. (d) 40. (c)
41. (b) 42. (b) 43. (a) 44. (d) 45. (a) 46. (c) 47. (d) 48. (d)
49. (b) 50. (c) 51. (a) 52. (d) 53. (a) 54. (d) 55. (c) 56. (b)
57. (c) 58. (d) 59. (b) 60. (a) 61. (a) 62. (b) 63. (c) 64. (d)
65. (d) 66. (a) 67. (a) 68. (b) 69. (c) 70. (b) 71. (d) 72. (d)
73. (d) 74. (a) 75. (b) 76. (b) 77. (d) 78. (b) 79. (c) 80. (a)
81. (c) 82. (a) 83. (b) 84. (d) 85. (d) 86. (d) 87. (c) 88. (c)
89. (b) 90. (b) 91. (d) 92. (a) 93. (a) 94. (a) 95. (d) 96. (a)
97. (a) 98. (b) 99. (c) 100. (a) 101. (a) 102. (a) 103. (d) 104. (d)
105. (a) 106. (b) 107. (c) 108. (b) 109. (b) 110. (a) 111. (d) 112. (c)
113. (c) 114. (b) 115. (c) 116. (c) 117. (d) 118. (b) 119. (b) 120. (b)
121. (c) 122. (b) 123. (d) 124. (d) 125. (b) 126. (c) 127. (a) 128. (a)
129. (b) 130. (a) 131. (a) 132. (a) 133. (c) 134. (c) 135. (a) 136. (c)
137. (d) 138. (b) 139. (a) 140. (d) 141. (d) 142. (c) 143. (a) 144. (b)
145. (c) 146. (c) 147. (d) 148. (c) 149. (b) 150. (d) 151. (d) 152. (a)
153. (a) 154. (b) 155. (c) 156. (a) 157. (d) 158. (c) 159. (b) 160. (a)
161. (b) 162. (b) 163. (d) 164. (d) 165. (d) 166. (a) 167. (a) 168. (d)
169. (c) 170. (d) 171. (b) 172. (b) 173. (a) 174. (b) 175. (b) 176. (c)
177. (b) 178. (d) 179. (c) 180. (a) 181. (a) 182. (b) 183. (c) 184. (c)
185. (b) 186. (d) 187. (d) 188. (b) 189. (a) 190. (d) 191. (c) 192. (a)
193. (b) 194. (d) 195. (c) 196. (c) 197. (c) 198. (b) 199. (c) 200. (a)
201. (d) 202. (d) 203. (a) 204. (b) 205. (c) 206. (c) 207. (d) 208. (c)
209. (b) 210. (c) 211. (b) 212. (d) 213. (d) 214. (a) 215. (b) 216. (a)
217. (b) 218. (d) 219. (d) 220. (b) 221. (b) 222. (c) 223. (c) 224. (b)
225. (d) 226. (a) 227. (d) 228. (b) 229. (c) 230. (a) 231. (b) 232. (d)
233. (a) 234. (d) 235. (c) 236. (c) 237. (b) 238. (d) 239. (b) 240. (a)
241. (b) 242. (b) 243. (b) 244. (d) 245. (b) 246. (c) 247. (a) 248. (d)
249. (d) 250. (a) 251. (c) 252. (a) 253. (c) 254. (b) 255. (a) 256. (a)
257. (a) 258. (c) 259. (c) 260. (d) 261. (b)

Set–2

1. (b) 2. (d) 3. (a, c, d) 4. (c) 5. (c, d) 6. (c) 7. (d) 8. (a, b)
9. (a) 10. (a, d) 11. (b, c) 12. (b, d) 13. (a, b, c) 14. (b, c) 15. (a, b, c) 16. (a)
17. (b) 18. (a)

Answers : ASSERTION-REASON TYPE QUESTIONS

1. (c) 2. (b) 3. (d) 4. (a) 5. (d) 6. (b) 7. (c) 8. (d)
9. (c) 10. (c) 11. (d) 12. (a) 13. (d) 14. (c) 15. (d) 16. (c)
17. (a) 18. (d) 19. (a) 20. (b) 21. (c) 22. (b) 23. (d) 24. (a)
25. (c) 26. (a)

BRAIN STORMING PROBLEMS

OBJECTIVE QUESTIONS *for* IIT ASPIRANTS

The following questions contain single correct option:

1. The pH value of 10^{-3} M aqueous solution of NaCl is:
(a) 7 (b) 3 (c) 11 (d) 14
[**Hint:** NaCl is the salt of strong acid HCl and strong base NaOH. Its aqueous solution will be neutral with pH equal to seven.]

2. The acidic buffer solution can be prepared by mixing solutions of:
(a) sodium acetate and acetic acid
(b) ammonium chloride and ammonium hydroxide
(c) sulphuric acid and sodium sulphate
(d) sodium chloride and sodium hydroxide

3. Hydrolysis constants of two salts KA and KB of weak acids HA and HB are 10^{-8} and 10^{-6}. If the dissociation constant of third acid HC is 10^{-2}. The order of acidic strengths of three acids will be:
(a) $HA > HB > HC$ (b) $HB > HA > HC$
(c) $HC > HA > HB$ (d) $HA = HB = HC$

[**Hint:** $K_a(HA) = \frac{K_w}{K_h} = \frac{10^{-14}}{10^{-8}} = 10^{-6}$

$K_a(HB) = \frac{K_w}{K_h} = \frac{10^{-14}}{10^{-6}} = 10^{-8}$

$K_a(HC) = 10^{-2}$

Greater the value of dissociation constant K_a, more is the acidic strength.]

4. Three sparingly soluble salts that have same solubility products are given below:
I. A_2X II. AX III. AX_3
Their solubilities in a saturated solution will be such that:
(a) III > II > I (b) III > I > II (c) II > III > I (d) II > I > III

[**Hint:** $S = \sqrt{K_{sp}}$ for AX; $S = \left[\frac{K_{sp}}{4}\right]^{1/3}$ for A_2X;

$S = \left[\frac{K_{sp}}{27}\right]^{1/4}$ for AX_3

$\therefore \quad S_{II} > S_I > S_{III}$]

5. Consider the three solutions of 1 M concentration.
1. Sodium acetate (CH_3COONa)
2. Acetic acid + Sodium acetate ($CH_3COOH + CH_3COONa$)
3. Acetic acid (CH_3COOH)

The pH of these solutions will lie in the following sequence:
(a) 3 < 2 < 1 (b) 2 < 1 < 3 (c) 1 < 2 < 3 (d) 3 < 1 < 2

[**Hint:** $\underset{\text{pH} < 7}{CH_3COOH \text{ (Acetic acid)}} < \underset{\text{Buffer}}{(CH_3COOH + CH_3COONa)}$

$\underset{\substack{\text{pH} > 7 \\ \text{Salt of weak acid} \\ \text{with strong base}}}{CH_3COONa}$]

6. Glycine NH_2CH_2COOH behaves:
(a) as a Bronsted acid
(b) as a Bronsted base
(c) both as an acid and a base
(d) neither as an acid nor as a base

7. Solubility of Hg_2Cl_2 in a solvent is S moles/litre. Its solubility product will be:
(a) $16S^2$ (b) $8S^2$ (c) $16S^4$ (d) $4S^3$
[**Hint:** $Hg_2Cl_2 \longrightarrow Hg_2^{2+} + 2Cl^-$]

8. Arrange the following acids in increasing order of their acid strength:
I. $HClO_4$ II. H_2SO_4 III. H_3PO_4
(a) III < II < I (b) I < II < III (c) II < III < I (d) III < I < II

9. Select the anion which is the strongest bronsted base:
(a) ClO_4^- (b) ClO_3^- (c) ClO_2^- (d) ClO^-

[**Hint:** $HClO_4 > HClO_3 > HClO_2 > HClO$
(Decreasing acidic character)
$ClO_4^- < ClO_3^- < ClO_2^- < ClO^-$
(Increasing basic strength)
(Conjugate base of strong acid is weak base)]

10. $M(OH)_x$ has a K_{sp} of 4×10^{-9} and its solubility is 10^{-3} M. The value of x is:
(a) 4 (b) 1 (c) 3 (d) 2

11. What is the maximum possible concentration of Ni^{2+} ions in a solution containing 0.15 M HCl and 0.10 M H_2S? [Given that, $K_{sp}(NiS) = 2 \times 10^{-21}$ and $[S^{2-}]_{H_2S} = 4 \times 10^{-21}$]:
(a) 0.65 M (b) 0.45 M (c) 0.10 M (d) 0.15 M

12. The pH of 10^{-10} M H_2SO_4 will be almost:
(a) 4 (b) 7 (c) 6 (d) 0

13. Solubility of calcium phosphate (molecular mass, M) in water is W g per 100 mL at 25°C. Its solubility product at 25°C will be approximately:
(a) $10^9\left(\frac{W}{M}\right)^5$ (b) $10^7\left(\frac{W}{M}\right)^5$ (c) $10^5\left(\frac{W}{M}\right)^5$ (d) $10^3\left(\frac{W}{M}\right)^5$

[**Hint:** $S = \frac{10W}{M}$ mol litre

K_{sp} of $Ca_3(PO_4)_2 = 108S^5$

$= 108\left(\frac{10W}{M}\right)^5$

$= 10^7\left(\frac{W}{M}\right)^5$ (approximately)]

14. When some amount of sodium acetate is further added to a mixture of acetic acid and sodium acetate, then pH of the solution:

(a) increases
(b) decreases
(c) remains same
(d) none of these can be predicted from given information

[**Hint:** $\text{pH} = \text{p}K_a + \log \dfrac{[\text{Salt}]}{[\text{Acid}]}$

When the concentration of salt is increased, the value of pH will increase.]

15. When strong base (NaOH) is added to the weak acid (acetic acid, CH_3COOH), then dissociation of acetic acid increases; this effect is known as:
(a) common ion effect (b) reverse ion effect
(c) saltation effect (d) solubility effect

[**Hint:** $CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$

Ionization of acetic acid will increase with the progress of its neutralization. This effect is called reverse ion effect.]

16. In our body, carbon dioxide (CO_2) combines with water (H_2O) to form carbonic acid.

$$H_2O + CO_2 \longrightarrow H_2CO_3$$

Carbonic acid undergoes dissociation as,

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$

During the physical and mental stress, the rate of respiration increases, which results in the decrease in concentration of CO_2 in the blood. What will be the effect on pH of human blood during the stress?
(a) Decreases (b) Remains same
(c) Increases (d) Cannot be predicted

17. The correct order of basic strength is: **(AIIMS 2007)**
(a) $H_2O < OH^- < CH_3OH < CH_3O^-$
(b) $CH_3OH < H_2O < CH_3O^- < OH^-$
(c) $H_2O < CH_3OH < OH^- < CH_3O^-$
(d) $OH^- < H_2O < CH_3O^- < CH_3OH$

18. Which of the following orders is expected to be correct?
(a) $\text{p}K_a(ClCH_2COOH) > \text{p}K_a(CH_3COOH) > \text{p}K_a(CH_3CH_2COOH)$
(b) $\text{p}K_a(ClCH_2COOH) < \text{p}K_a(CH_3COOH) < \text{p}K_a(CH_3CH_2COOH)$ /
(c) $\text{p}K_a(ClCH_2COOH) > \text{p}K_a(CH_3COOH) < \text{p}K_a(CH_3CH_2COOH)$
(d) $\text{p}K_a(ClCH_2COOH) < \text{p}K_a(CH_3COOH) > \text{p}K_a(CH_3CH_2COOH)$

19. The concentration of H_3^+O ions in pure water is 10^{-6} mol dm^{-3}. The corresponding concentration of OH^- ions will be:
(a) 10^{-14} mol dm^{-3} (b) 10^{-8} mol dm^{-3}
(c) 10^{-6} mol dm^{-3} (d) 10^{-7} mol dm^{-3}

[**Hint:** In water, $[H^+] = [OH^-] = 10^{-6}$ mol dm^{-3}]

20. What will be the pH of a solution formed by mixing 40 cm^3 of 0.1 M HCl with 10 cm^3 of 0.45 M NaOH?
(a) 10 (b) 8 (c) 5 (d) 12

[**Hint:** Number of moles of HCl $= \dfrac{MV}{1000} = \dfrac{0.1 \times 40}{1000} = 0.004$

Number of moles of NaOH $= \dfrac{MV}{1000} = \dfrac{0.45 \times 10}{1000} = 0.0045$

Remaining moles of NaOH after neutralization = 0.0005

Molarity of $OH^- = \dfrac{0.0005}{50} \times 1000 = 0.01M$

$$\text{pOH} = 2 \quad \therefore \quad \text{pH} = 14 - 2 = 12]$$

21. In the following reaction:

$$HCO_3^- + H_2O \rightleftharpoons CO_3^{2-} + H_3O^+$$

which two substances are Bronsted bases?
(a) CO_3^{2-} and H_3O^+ (b) HCO_3^- and H_3O^+
(c) HCO_3^- and CO_3^{2-} (d) CO_3^{2-} and H_2O

22. Which are strong acids?
I. $HClO_3$ II. H_2SeO_3 III. H_3AsO_4
(a) I only (b) III only
(c) I and III only (d) II and III only

23. $HCOOH \rightleftharpoons HCOO^- + H^+$; $K_a = 1.7 \times 10^{-4}$
The ionization of formic acid is represented above. Calculate $[H^+]$ of a solution initially containing 0.1 M HCOOH and 0.05 M HCOONa:
(a) 8.5×10^{-5} M (b) 3.4×10^{-4} M
(c) 4.1×10^{-3} M (d) 1.8×10^{-2} M

24. Carbonic acid, H_2CO_3, is a diprotic acid for which $K_1 = 4.2 \times 10^{-7}$ and $K_2 = 4.7 \times 10^{-11}$. Which solution will produce a pH closest to 9?
(a) 0.1 M H_2CO_3
(b) 0.1 M Na_2CO_3
(c) 0.1 M $NaHCO_3$
(d) 0.1 M $NaHCO_3$ and 0.1 M Na_2CO_3

25. What is the conjugate acid of HPO_4^{2-}?
(a) H_3PO_4 (b) $H_2PO_4^-$ (c) H_3O^+ (d) PO_4^{3-}

26. What is the K_b of a weak base that produces one OH^- per molecule if a 0.05 M solution is 2.5% ionized?
(a) 7.8×10^{-8} (b) 1.6×10^{-6} (c) 3.2×10^{-5} (d) 1.2×10^{-3}

[**Hint:** $K_b = C\alpha^2$

$$= 0.05 \times \left(\frac{2.5}{100}\right)^2 = 3.1 \times 10^{-5}]$$

27. The amount of sodium hydrogen carbonate, $NaHCO_3$, in an antacid tablet is to be determined by dissolving the tablet in water and titrating the resulting solution with hydrochloric acid. Which indicator is the most appropriate for this titration?

Acid	K_a
H_2CO_3	2.5×10^{-4}
HCO_3^-	2.4×10^{-8}

(a) Methyl orange, $\text{p}K_{In} = 3.7$
(b) Bromothymol blue, $\text{p}K_{In} = 7.0$
(c) Phenolphthalein, $\text{p}K_{In} = 9.3$
(d) Alizarin yellow, $\text{p}K_{In} = 12.5$

28. If equal volumes of $BaCl_2$ and NaF solutions are mixed, which of these combinations will not give a precipitate?

Substance	K_{sp}
BaF_2	1.7×10^{-7}

(a) 0.004 M $BaCl_2$ and 0.02 M NaF
(b) 0.010 M $BaCl_2$ and 0.015 M NaF
(c) 0.015 M $BaCl_2$ and 0.010 M NaF
(d) 0.020 M $BaCl_2$ and 0.002 M NaF

[**Hint:** In the mixture of 0.02 M $BaCl_2$ and 0.002 M NaF, the ionic product is less than the solubility product, hence there will be no precipitation of BaF_2.]

29. HCN is a weak acid ($K_a = 6.2 \times 10^{-10}$). NH_4OH is a weak base ($K_b = 1.8 \times 10^{-5}$). A 1 M solution of NH_4CN would be:
(a) strongly acidic (b) weakly acidic
(c) neutral (d) weakly basic

[**Hint:** Since, $K_b > K_a$, hence the medium will be weakly basic.]

30. How many moles of HCOONa must be added to 1 L of 0.1 M HCOOH to prepare a buffer solution with a pH of 3.4? Given: K_a for HCOOH $= 2 \times 10^{-4}$
(a) 0.01 (b) 0.05 (c) 0.1 (d) 0.2

31. Silver ions are added to the solution with:

$$[Br^-] = [Cl^-] = [CO_3^{2-}] = [AsO_4^{3-}] = 0.1\,M$$

Which compound will precipitate at the lowest $[Ag^+]$?
(a) AgBr ($K_{sp} = 5 \times 10^{-13}$)
(b) AgCl ($K_{sp} = 1.8 \times 10^{-10}$)
(c) Ag_2CO_3 ($K_{sp} = 8.1 \times 10^{-12}$)
(d) Ag_3AsO_4 ($K_{sp} = 10^{-22}$)

[**Hint:** In case of AgBr, the ionic product will exceed the solubility product before AgCl, Ag_2CO_3 and Ag_3AsO_4. Thus, AgBr will start precipitation before other salts.]

32. The equilibrium constant for this reaction is approximately 10^{-3}.

$$HPO_4^{2-}(aq.) + HCO_3^-(aq.) \rightleftharpoons H_2PO_4^-(aq.) + CO_3^{2-}(aq.)$$

Which is the strongest conjugate base in this reaction?
(a) $HPO_4^{2-}(aq.)$ (b) $HCO_3^-(aq.)$
(c) $H_2PO_4^-(aq.)$ (d) $CO_3^{2-}(aq.)$

[**Hint:** Conjugate base of weak acid is strong base.]

33. Which mixture forms a buffer when dissolved in 1 L of water?
(a) 0.2 mol NaOH + 0.2 mol HBr
(b) 0.2 mol NaCl + 0.3 mol HCl
(c) 0.4 mol HNO_2 + 0.2 mol NaOH
(d) 0.5 mol NH_3 + 0.5 mol HCl

34. The equilibrium constant for this reaction is 3.6×10^{-7}.

$$OCl^-(aq.) + H_2O(l) \rightleftharpoons HOCl(aq.) + OH^-(aq.)$$

What is K_a for HOCl?
(a) 2.8×10^{-8} (b) 3.6×10^{-7} (c) 6×10^{-4} (d) 2.8×10^{-6}

35. What is the concentration of H^+ in a solution that is prepared by mixing 50 mL of 0.5 M HCl and 200 mL of 0.25 M HCl?
(a) 0.30 M (b) 0.35 M (c) 0.40 M (d) 0.45 M

36. K_a for hydrofluoric acid is 6.9×10^{-4}. What is the equilibrium constant K for the following reaction?

$$F^-(aq.) + H_2O(l) \rightleftharpoons HF(aq.) + OH^-(aq.)$$

(a) 6.9×10^{-11} (b) 1.4×10^{-11} (c) 2.6×10^{-9} (d) 8.3×10^{-6}

37. A solution of 2 M formic acid (HCOOH) is 0.95% ionized. What is the K_a of formic acid?
(a) 1.9×10^{-2} (b) 1.8×10^{-4} (c) 9×10^{-5} (d) 4.5×10^{-5}

[**Hint:** $K_a = C\alpha^2 = 2 \times \left(\frac{0.95}{100}\right)^2$]

38. If 0.1 mol of salt is added to 1 L water, which of these salts is expected to produce the most acidic solution?
(a) $NaC_2H_3O_2$ (b) NH_4NO_3
(c) $CuSO_4$ (d) $AlCl_3$

39. A sample of hard water contains 0.005 mole of calcium chloride per litre. What is the minimum concentration of sodium sulphate which must be added for removing the Ca^{2+} ions from this water sample? K_{sp} of $CaSO_4 = 2.4 \times 10^{-5}$.
(a) 4.8×10^{-2} (b) 4.8×10^{-3}
(c) 2.4×10^{-2} (d) 2.4×10^{-3}

40. Match the List-I and List-II:

List-I	**List-II**
(A) The limits of pH values of buffer solution	(i) 5×10^{-12}
(B) Concentration of $[H_3O^+]$ in 0.001 M $Ba(OH)_2$	(ii) Equal
(C) The buffer capacity of a solution is maximum when concentration of salt to that of acid is	(iii) 10^{-14}
(D) Ionic product of water is	(iv) $pK_a \pm 1$

Codes:	A	B	C	D
(a)	iv	ii	i	iii
(b)	iv	i	iii	ii
(c)	i	iv	ii	iii
(d)	iv	i	ii	iii

41. Match the List-I and List-II:

List-I	**List-II**
(A) Degree of ionization of weak electrolytes increases	(i) Common ion effect
(B) pH of water decreases on	(ii) pH = 4
(C) The solution has hydronium ion concentration of 0.0001 mol/litre	(iii) Heating
(D) The addition of NaOH to $Ca(OH)_2$ solution precipitates $Ca(OH)_2$	(iv) On dilution

Codes:	A	B	C	D
(a)	iv	iii	i	ii
(b)	iii	iv	ii	i
(c)	iv	iii	ii	i
(d)	iv	ii	iii	i

42. Which of the following is not correct about the percentage ionization of BOH ?
(a) $\frac{K_w[H^+]}{K_b + K_w}$ (b) $100 \times \sqrt{\frac{K_b}{C}}$
(c) $\frac{100}{1 + 10^{(pK_b - pOH)}}$ (d) $\frac{K_b \times 100}{K_b + OH^-}$

[**Hint:**

$$\begin{array}{llll} & BOH & \rightleftharpoons B^+ & + \; OH^- \\ t_0 & C & 0 & 0 \\ t_{eq.} & C - C\alpha & C\alpha & C\alpha \end{array}$$

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

$$\approx C\alpha^2 \qquad (\alpha <<< 1)$$

$$\alpha = \sqrt{\frac{K_b}{C}} \quad \% \text{ ionization} = 100 \times \sqrt{\frac{K_b}{C}} \quad ...(1)$$

$$\alpha = \frac{[B^+]}{[B^+]+[BOH]} = \frac{1}{1+\frac{[BOH]}{[B^+]}} = \frac{1}{1+\frac{[OH^-]}{[K_b]}}$$

$$\alpha = \frac{K_b}{K_b + OH^-} \quad ...(2)$$

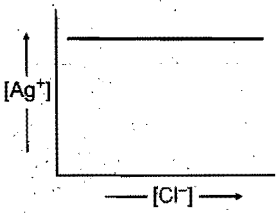
Percentage ionization = $\frac{100\,K_b}{K_b + OH^-}$

$$\alpha = \frac{1}{1+\frac{[OH^-]}{K_b}} = \frac{1}{1+\frac{10^{-pOH}}{10^{-pK_b}}}$$

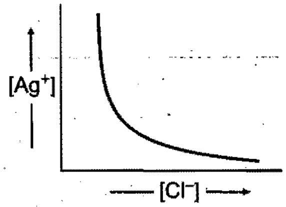
$$\alpha = \frac{1}{1+10^{(pK_b - pOH)}}$$

∴ Percentage ionization = $\frac{100}{1+10^{(pK_b - pOH)}}$]

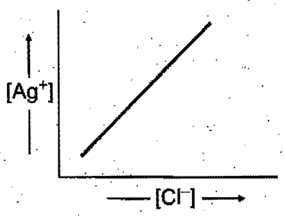
43. When NaCl is added gradually to the saturated solution of AgCl then which of the following plot is correct ?



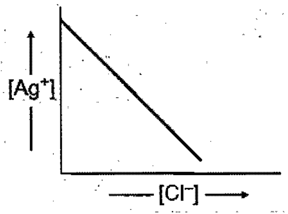
(a)



(b)



(c)



(d)

The following questions may have more than one correct options:

1. Which of the following statements is/are correct about the ionic product of water?
   (a) K (equilibrium constant of water) < K_w (ionic product of water)
   (b) $pK > pK_w$
   (c) At 300 K, K_w of water becomes 10^{-12}
   (d) Ionic product of water at 25°C is 10^{-14}

2. Which among the following statements is/are correct?
   (a) $pH = -\log_{10}(H_3O^+)$
   (b) pH decreases with increase of temperature
   (c) pH cannot be zero, negative or more than 14
   (d) If a solution is diluted ten times, its pH increases by 1

3. Which among the following statements is/are correct?
   (a) pH of $10^{-8}\,M$ HCl is equal to 8
   (b) Conjugate base of $H_2PO_4^-$ is HPO_4^{2-}
   (c) pH of 0.1 M NaCl (aqueous solution) = $\frac{1}{2}pK_w$
   (d) Ionization of water increases with decrease in temperature

4. Let us consider the ionization of HCl in the aqueous solution of CH_3COOH.
   $$CH_3COOH + HCl \rightleftharpoons CH_3COOH_2^+ + Cl^-$$
   Select the correct statement(s) among the following:
   (a) Cl^- is the conjugate base of HCl
   (b) CH_3COOH is the conjugate base of $CH_3COOH_2^+$
   (c) $CH_3COOH_2^+$ is the conjugate base of CH_3COOH
   (d) Cl^- is the conjugate base of CH_3COOH

5. Which among the following species act both as an acid as well as a base?
   (a) SO_4^{2-} (b) HSO_4^-
   (c) PO_4^{3-} (d) NH_3

6. Which among the following salts will give basic solution on hydrolysis? **[PET (MP) 2008]**
   (a) NaH_2PO_4 (b) NH_4Cl
   (c) NaCl (d) K_2CO_3

7. Which among the following represent the conjugate acid/base pairs?
   (a) H_3O^+/H_2O
   (b) H_2SO_4/SO_4^{2-}
   (c) HCO_3^-/CO_3^{2-}
   (d) All are conjugate acid/base pairs

8. If you have saturated solution of CaF_2 then:
   (a) $[Ca^{2+}] = \sqrt{K_{sp}}$ (b) $[Ca^{2+}] = 2[F^-]$
   (c) $2[Ca^{2+}] = [F^-]$ (d) $[Ca^{2+}] = [K_{sp/4}]^{1/3}$

9. The relative strength of two weak bases at same concentration may be given as:
   (a) $\frac{K_{b_1}}{K_{b_2}}$ (b) $\frac{[OH^-]_1}{[OH^-]_2}$
   (c) $\frac{\alpha_1}{\alpha_2}$ (d) $\frac{\sqrt{K_{b_1}}}{\sqrt{K_{b_2}}}$

Answers

- **Single correct option**

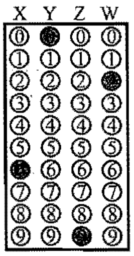
1. (a) **2.** (a) **3.** (c) **4.** (d) **5.** (a) **6.** (c) **7.** (d) **8.** (a)
9. (d) **10.** (d) **11.** (b) **12.** (b) **13.** (b) **14.** (a) **15.** (b) **16.** (c)
17. (c) **18.** (b) **19.** (c) **20.** (d) **21.** (d) **22.** (a) **23.** (b) **24.** (c)
25. (b) **26.** (c) **27.** (a) **28.** (d) **29.** (d) **30.** (b) **31.** (a) **32.** (d)
33. (c) **34.** (a) **35.** (a) **36.** (b) **37.** (b) **38.** (b) **39.** (b) **40.** (d)
41. (c) **42.** (c) **43.** (b)

- **One or more than one correct options**

1. (a, b, c, d) **2.** (a, b, d) **3.** (b, c) **4.** (a, b) **5.** (b, d) **6.** (a, d) **7.** (a, c) **8.** (c, d)
9. (b, c, d)

Integer Answer TYPE QUESTIONS

This section contains 13 questions. The answer to each of the questions is a single digit integer, ranging from 0 to 9. If the correct answers to question numbers X, Y, Z and W (say) are 6, 0, 9 and 2 respectively, then the correct darkening of bubbles will look like the given figure :



1. What will be the pH of 0.1 M CH_3COONH_4? Dissociation constants of CH_3COOH and NH_4OH are $K_a = 1.8 \times 10^{-5}$ and $K_b = 1.8 \times 10^{-5}$ respectively.
2. Ionic product of water is 1×10^{-12}. pH of water will be :
3. Calculate the pH at which an acid indicator HIn with concentration 0.1 M changes its colour. (K_a for HIn $= 1 \times 10^{-5}$)
4. Sum of basicity of H_3PO_4, H_3PO_3, H_3PO_2 is equal to :
5. A given weak acid ($0.01\,M$) has $pK_a = 6$. The pH of this solution is :
6. Solubility product of an electrolyte is $6912S^7$. How many ions will be obtained by the ionization of one molecule of electrolyte?
7. The solubility product of $Mg(OH)_2$ is 5×10^{-19} at 25°C. pH of saturated solution of $Mg(OH)_2$ will be :
8. pH of $10^{-x}\,M$ HCl is 6.9586. The value of x will be :
9. If the equilibrium constant of the reaction of weak acid HA with strong base is 10^9, then the pH of 0.1 M NaA solution will be :
10. Consider the titration of 50 mL of 0.1 M HBr with 0.1 M KOH. Calculate pH after 49 mL of the base has been added to the 50 mL of HBr.
11. The dissociation constant of a substituted benzoic acid at 25°C is 1×10^{-4}. The pH of a 0.01 M solution of its sodium salt is: **(IIT 2009)**

    [**Hint :** pH of salt after hydrolysis may be calculated as,
    $$pH = \frac{1}{2}[pK_w + pK_a + \log C]$$
    $$= \frac{1}{2}[14 + (-\log 10^{-4}) + \log 0.01]$$
    $$= \frac{1}{2}[14 + 4 - 2] = 8\ ]$$
12. The total number of diprotic acids among the following is: H_3PO_4, H_2SO_4, H_3PO_3, H_2CO_3, $H_2S_2O_7$, H_2BO_3, H_3PO_2, H_2CrO_4, H_2SO_3 **(IIT ~~2010)~~**

    [**Hint :** H_2SO_4, H_3PO_3, H_2CO_3, $H_2S_2O_7$, H_2CrO_4, H_2SO_3 are diprotic acid.]
13. Amongst the following, the total number of compounds whose aqueous solution turns red litmus paper blue is: KCN, K_2SO_4, $(NH_4)_2C_2O_4$, NaCl, $Zn(NO_3)_2$, $FeCl_3$, K_2CO_3, NH_4NO_3, LiCN **(IIT 2010)**

    [**Hint :** Salts of weak acid and strong base will give basic solution on hydrolysis and will turn red litmus to blue KCN, K_2CO_3 and LiCN are such type of salts.]

Answers

1. (7) **2.** (6) **3.** (5) **4.** (6) **5.** (4) **6.** (7) **7.** (8) **8.** (8)
9. (9) **10.** (3) **11.** (8) **12.** (6) **13.** (3)

LINKED COMPREHENSION TYPE QUESTIONS

Passage 1

Higher the amount of acid or base used to produce a definite change of pH in a buffer solution, higher will be its buffer capacity. Buffer capacity of solution is maximum under the following conditions:

$$[Salt] = [Acid] \ (in\ acid\ buffer)$$

$$[Salt] = [Base] \ (in\ base\ buffer)$$

pH of a buffer solution lies in the range given below:

$$pH = pK_a \neq 1$$

In other words, any buffer solution can be used as buffer up to two pH units only, depending upon the value of pK_a or pK_b. A buffer is said to be efficient when $pH = pK_a$ or $pOH = pK_b$.

Answer the following questions:

1. Any buffer can be used as a buffer up to:
   (a) 10 pH units (b) 5 pH units (c) 2 pH units (d) 1 pH unit
2. Which among the following solutions will be the most efficient buffer?
   (a) 0.1 M CH_3COONa + 0.01 M CH_3COOH
   (b) 0.1 M NH_4Cl + 0.1 M NH_4OH
   (c) 0.001 M HCOOH + 0.002 M HCOONa
   (d) All of the above
3. The buffer capacity is equal to:
   (a) $\frac{\Delta n}{\Delta pH}$ (b) $\frac{pH}{\Delta n}$ (c) $\pm$ 1pK_a (d) none of these
4. A buffer of acetic acid ($pK_a \approx 4.8$) with sodium acetate will be, when CH_3COOH and CH_3COONa are present in equivalent amounts has pH limits equal to:
   (a) 0 to 4.8 (b) 3.8 to 5.8 (c) 4.3 to 5.3 (d) 4.8
5. Buffer capacity is maximum when:
   (a) one mole of NH_4Cl is added to two moles of NH_4OH
   (b) one mole of NH_4Cl is added to one mole of NH_4OH
   (c) one mole of NH_4Cl is added to one mole of NaOH
   (d) one mole of NaCl is added to one mole of NaOH
6. A buffer solution is prepared by mixing equal concentration of acid (ionisation constant K_a) and a salt. The pH of buffer is: **[JEE (Orissa) 2008]**
   (a) $pK_a + 7$ (b) $14 - pK_a$ (c) pK_a (d) $pK_a + 1$

Passage 2

When a salt reacts with water to form acidic or basic solution, the process is called hydrolysis. The pH of salt solution can be calculated using the following relations:

$$pH = \frac{1}{2}[pK_w + pK_a + \log C]$$

(for salt of weak acid and strong base.)

$$pH = \frac{1}{2}[pK_w - pK_b - \log C]$$

(for salt of weak base and strong acid.)

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

(for salt of weak acid and weak base.)

where, 'C' represents the concentration of salt.

When a weak acid or a weak base is not completely neutralized by strong base or strong acid respectively, then formation of buffer takes place. The pH of buffer solution can be calculated using the following relation:

$$pH = pK_a + \log\frac{[Salt]}{[Acid]};\ pOH = pK_b + \log\frac{[Salt]}{[Base]}$$

Answer the following questions using the following data:

$$pK_a = 4.7447,\ pK_b = 4.7447,\ pK_w = 14$$

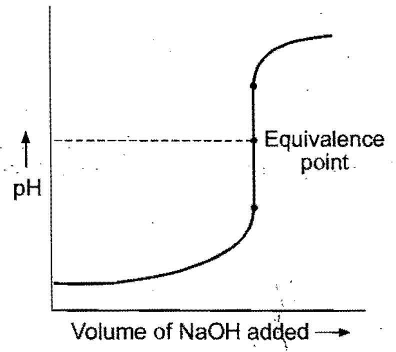
1. When 50 mL of 0.1 M NH_4OH is added to 50 mL of 0.05 M HCl solution, the pH is:
   (a) 1.6021 (b) 12.3979 (c) 4.7447 (d) 9.2553
2. 0.001 M NH_4Cl aqueous solution has pH:
   (a) 6.127 (b) 7.126 (c) 2.167 (d) 1.267
3. 50 mL 0.1 M NaOH is added to 50 mL of 0.1 M CH_3COOH solution, the pH will be:
   (a) 4.7447 (b) 9.2553 (c) 8.7218 (d) 1.6021
4. 1 mole CH_3COOH and 1 mole CH_3COONa are dissolved in water to form 1 litre aqueous solution. The pH of the resulting solution will be:
   (a) 9.2553 (b) 4.7447 (c) 14 (d) 7
5. When 50 mL of 0.1 M NaOH is added to 50 mL of 0.05 M CH_3COOH solution. The pH of the solution is:
   (a) 1.6021 (b) 12.3979 (c) 4.7447 (d) 8.7218

Passage 3

An acid-base titration consists of the controlled addition of a dissolved base to a dissolved acid (or the reverse). Acid-base react rapidly to neutralize each other. At the equivalence point, enough titrant, the solution being added, has gone into make the chemical amounts of the acid and base exactly equal. The pH of a titration changes every time a drop of titrant is added, but the rate of this change varies enormously. A titration curve, graph of pH as a function of the volume of titrant, displays in detail how the pH changes over the course of an acid-base titration. Significantly, the pH changes most rapidly near the equivalence point. The exact shape of a titration curve depends on the K_a and K_b acid and base.

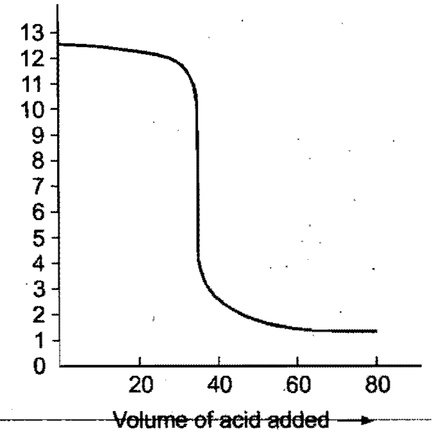
Answer the following questions:

1. The following figure represents titration curve of HCl against NaOH. The pH at equivalence point will be:



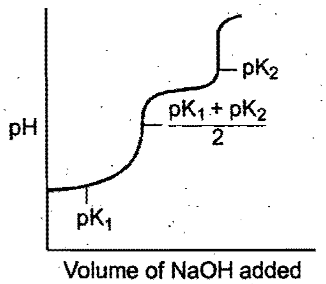
(a) 7 (b) 6 (c) 8 (d) 3

Examine the titration curve below:

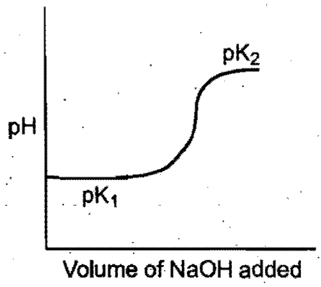


Answer the questions 2, 3 and 4 on the above curve.

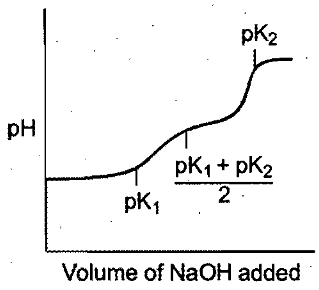
2. Which of the titrations could it represent?
   (a) HCl by KOH (b) RbOH by HBr
   (c) HCl by NaOH (d) NH_3 by HNO_3
3. The suitable indicator for this titration will be:
   (a) bromothymol blue (b) methyl orange
   (c) methyl red (d) all of these
4. The pH at equivalence point is:
   (a) 11 (b) 7 (c) 3 (d) 2
5. Which of the following curves indicates the titration of a weak diprotic acid by NaOH of equivalent strength?



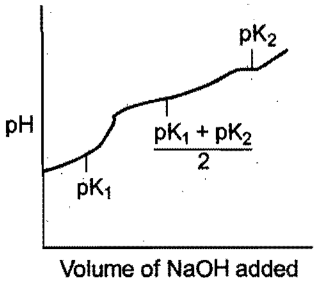
(a)



(b)



(c)



(d)

• Passage 4

Acid rain takes place due to combination of acidic oxides with water. In atmosphere, sulphur dioxide and nitrogen monoxide are oxidised to sulphur trioxide and nitrogen dioxide respectively, which react with water to give sulphuric and nitric acid. The resultant solution so called is acid rain. Sulphur dioxide dissolves in water to form diprotic acid in aqueous solution.

$$SO_2(g) + H_2O(l) \rightleftharpoons HSO_3^- + H^+; \; K_{a_1} = 10^{-2}\,M$$

$$HSO_3^- \rightleftharpoons SO_3^{2-} + H^+; \; K_{a_2} = 10^{-7}\,M$$

and for equilibrium,

$$SO_2(aq.) + H_2O(l) \rightleftharpoons SO_3^{2-}(aq.) + 2H^+(aq.);$$

$$K_a = K_{a_1} \times K_{a_2} = 10^{-9} \text{ at } 300\,K \text{ at } 27°C$$

Answer the following questions:

1. Which of the following reagents will give white precipitate with the aqueous solution of sulphurous acid?
   (a) NaCl (b) KCl (c) $BaCl_2$ (d) HCl
2. The pH of 0.01 *M* aqueous solution of sodium sulphite will be:
   (a) 8.5 (b) 9 (c) 4.5 (d) 9.5
3. The dominant equilibrium in an aqueous solution of sodium hydrogen sulphite is:
   $$2HSO_3^-(aq.) \rightleftharpoons SO_2(aq.) + SO_3^{2-}(aq.) + H_2O(l)$$
   The equilibrium constant for the above reaction is:
   (a) 10^{-6} (b) 10^{-9} (c) 10^{-5} (d) 10^{-3}
4. Which among the following statements is correct?
   (a) CO_2 gas develops more acidity in rain-water than SO_2
   (b) H_2SO_3 is less acidic than H_2SO_4
   (c) HNO_3 is less acidic than HNO_2
   (d) $SO_2(g)$ is reduced in the atmosphere during thunderstorm

• Passage 5

The product of the concentrations of the ions of an electrolyte raised to power of their coefficients in the balanced chemical equation in the solution at any concentration. Its value is not constant and varies with change in concentration. Ionic product of the saturated solution is called solubility product K_{sp}.

(*i*) *When $K_{ip} = K_{sp}$, the solution is just saturated and no precipitation takes place.*

(*ii*) *When $K_{ip} < K_{sp}$, the solution is unsaturated and precipitation will not take place.*

(*iii*) *When $K_{ip} > K_{sp}$, the solution is supersaturated and precipitation takes place.*

Answer the following questions:

1. The solubility product, K_{sp}, of sparingly soluble salt *MX* at 25°C is 2.5×10^{-9}. The solubility of the salt in mol L^{-1} at this temperature is:
   (a) 1×10^{-14} (b) 5×10^{-8} (c) 1.25×10^{-9} (d) 5×10^{-5}
2. Which of the following is most soluble?
   (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 ($K_{sp} = 6 \times 10^{-51}$)
3. The concentration of Ag^+ ions in a given saturated solution of AgCl at 25°C is 1.06×10^{-5} g ion per litre. The solubility product of AgCl is:
   (a) 0.353×10^{-10} (b) 0.530×10^{-10}
   (c) 1.12×10^{-10} (d) 2.12×10^{-10}
4. When equal volumes of the following solutions are mixed, precipitation of AgCl ($K_{sp} = 1.8 \times 10^{-10}$) will occur only with:

(a) $10^{-4}\,M\,Ag^+ + 10^{-4}\,M\,Cl^-$
(b) $10^{-5}\,M\,Ag^+ + 10^{-5}\,M\,Cl^-$
(c) $10^{-6}\,M\,Ag^+ + 10^{-6}\,M\,Cl^-$
(d) $10^{-10}\,M\,Ag^+ + 10^{-10}\,M\,Cl^-$

5. When HCl gas is passed through saturated NaCl solution, the ionic product of NaCl is exceeded because of:
(a) increase in Cl^- ion concentration
(b) increase in Na^+ ion concentration
(c) decrease in the NaCl concentration
(d) decrease in Cl^- ion concentration

6. If the solubility of $Li_3Na_3(AlF_6)_2$ is x mol L^{-1}, then its solubility product is equal to:
(a) $12x^3$ (b) $18x^3$ (c) x^8 (d) $2916x^8$

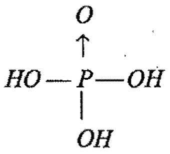
Passage 6

The dissociation of weak electrolyte (weak acid) is expressed in terms of Ostwald dilution law. Stronger is the acid, weaker is its conjugate base. The dissociation constants of an acid (K_a) and its conjugate base (K_b) are related by the given relation:

$$K_w = K_a \times K_b$$

At 25°C, K_w (Ionic product of water) = 10^{-14}.

Phosphoric acid is a weak acid. It is used in fertilizer, food, detergent and toothpaste. Structure of phosphoric acid is:



$HO-\overset{\overset{O}{\uparrow}}{P}-OH$ ($pK_{a_1} = 2.12$, $pK_{a_2} = 7.21$, $pK_{a_3} = 12.32$)
$\qquad\;\; \underset{OH}{|}$

Aqueous solution of phosphoric acid with a density of 1 g mL^{-1} containing 0.05% by weight of phosphoric acid is used to impart tart taste to many soft drinks.

Phosphate ion is an interfering radical in qualitative analysis. It should be removed for analysis beyond third group of qualitative analysis.

Answer the following questions:

1. The basicity of phosphoric acid is:
(a) 1 (b) 2 (c) 3 (d) 4

2. The state of hybridization of phosphorous in phosphoric acid is:
(a) sp (b) sp^2 (c) sp^3 (d) sp^3d

3. The removal of PO_4^{3-} in qualitative analysis of basic radicals is made by using a buffer solution of:
(a) HCO_3^- and CO_3^{2-} (b) CH_3COO^- and CH_3COOH
(c) NH_4^+ and NH_4OH (d) none of these

4. What is the molarity of phosphoric acid used in soft drinks?
(a) 5.1×10^{-3} (b) 1.5×10^{-3} (c) 3.1×10^{-3} (d) 2.1×10^{-3}

5. Which among the following relations is correct?
(a) $K_{a_1} < K_{a_2} < K_{a_3}$ (b) $K_{a_1} > K_{a_2} > K_{a_3}$
(c) $K_{a_1} = K_{a_2} = K_{a_3}$ (d) $K_{a_1} > K_{a_3} > K_{a_2}$

6. First ionization of phosphoric acid is:

$$H_3PO_4 \rightleftharpoons H_2PO_4^- + H^+$$
$$pK_{a_1} = 2.21$$

The dissociation constant of conjugate base of H_3PO_4 will be:
(a) 6.45×10^{-9} (b) 1.62×10^{-12}
(c) 3.48×10^{-11} (d) 4.62×10^{-2}

[Hint: $pK_{a_1} = 2.21$

$$K_{a_1} = \text{antilog}(-2.21) = 6.165 \times 10^{-3}$$

$$K_b \text{ (of conjugate base)} = \frac{K_w}{K_{a_1}} = \frac{10^{-14}}{6.165 \times 10^{-3}} = 1.62 \times 10^{-12}$$]

Answers

Passage 1.	1. (c)	2. (b)	3. (a)	4. (b)	5. (b)	6. (c)
Passage 2.	1. (d)	2. (a)	3. (c)	4. (b)	5. (b)	
Passage 3.	1. (a)	2. (b)	3. (d)	4. (b)	5. (a)	
Passage 4.	1. (c)	2. (d)	3. (c)	4. (b)		
Passage 5.	1. (d)	2. (b)	3. (c)	4. (a)	5. (a)	6. (d)
Passage 6.	1. (c)	2. (c)	3. (b)	4. (a)	5. (b)	6. (b)

SELF ASSESSMENT

ASSIGNMENT NO. 10

SECTION-I

Straight Objective Type Questions

This section contains 7 multiple choice questions. Each question has 4 choices (a), (b), (c) and (d), out of which only one is correct.

1. When 50 mL of 0.1 M NaOH is mixed with 50 mL of 0.05 M CH_3COOH solution, pH becomes:
(a) 1.602 (b) 12.39
(c) 4.74 (d) 8.72

2. If the degree of dissociation of water at 90°C is 1.28×10^{-8} then the ionisation constant of water at 90°C is:
(a) 7.52×10^{-12} M (b) 9.07×10^{-15} M
(c) 1.28×10^{-14} M (d) 1.38×10^{-14} M

3. How much water from 5 litre of 10^{-3} M HCl should be evaporated to change its pH by 2 units?
(a) 1.5 litre (b) 0.5 litre (c) 2.54 litre (d) 4.95 litre

4. Which among the following cannot exist in an aqueous solution?
(a) NH_4^+ (b) NO_3^-
(c) NO_2^- (d) NH_2^-

5. The pH of an HCl solution is 2. Sufficient water is added to make the pH of new solutions. The hydrogen ion concentration is reduced:
(a) ten fold (b) seven fold
(c) thousand fold (d) hundred fold

6. Consider the following statements:
I. HNO_3 (strong acid) behaves as a base in HF.
II. H_2SO_4 dissociates to a small extent in glacial acetic acid.
III. CH_3COOH (a weak acid) behaves as strong acid in $NH_3(l)$. Select the correct alternate for these statements:
(a) I, II, and III (b) I and III
(c) II and III (d) I and II

7. The solubility of A_2X_5 is x mol dm^{-3}. Its solubility product is:
(a) $36x^6$ (b) $64 \times 10^4 x^7$
(c) $126x^7$ (d) $1.25 \times 10^4 x^7$

SECTION-II

Multiple Answers Type Objective Questions

8. During the titration of mixture of NaOH, Na_2CO_3 and an inert substance against hydrochloric acid:
(a) phenolphthalein is used to detect the end point when NaOH is completely neutralized and half of Na_2CO_3 is neutralized
(b) methyl orange is used to detect the final end point
(c) methyl orange is used to detect the first end point
(d) phenolphthalein is used to detect the final end point

9. Solubility product of the hydroxide $M(OH)_2$ is 4×10^{-12}. Select the correct statement(s) among the following:
(a) the pH of its saturated solution will be 10.3
(b) its solubility will decrease in a buffer medium of pH = 9
(c) its solubility will increase in a buffer medium of pH = 1
(d) its solubility is unaffected by pH of the medium

10. Which of the following salt solutions will be basic?
(a) NaCl (b) NaCN (c) K_2CO_3 (d) NH_4NO_3

11. Which of the following salts will not undergo hydrolysis?
(a) NaCl (b) KCl (c) NH_4Cl (d) CH_3COONa

12. Which of the following mixtures will be buffer?
(a) $CH_3COOH + CH_3COONH_4$
(b) HCl + NaCl
(c) Borax + boric acid
(d) $CH_3COOH + CH_3COONa$

SECTION-III

Assertion-Reason Type Questions

This section contains 5 questions. Each question contains **Statement-1** (Assertion) and **Statement-2** (Reason). Each question has following 4 choices (a), (b), (c) and (d), out of which only one is correct.

(a) Statement-1 is true; statement-2 is true; statement-2 is a correct explanation for statement-1.
(b) Statement-1 is true; statement-2 is true; statement-2 is not a correct explanation for statement-1.
(c) Statement-1 is true; statement-2 is false.
(d) Statement-1 is false; statement-2 is true.

13. **Statement-1:** Mixture of CH_3COOH and CH_3COONH_4 is not a buffer solution.

Because

Statement-2: Acid buffer contains the mixture of weak acid and its salt with strong base.

14. **Statement-1:** Addition of NH_4OH to an aqueous solution of $BaCl_2$ in the presence of excess NH_4Cl, precipitates $Ba(OH)_2$.

Because

Statement-2: $Ba(OH)_2$ is soluble in water.

15. **Statement-1:** pH of blood does not change inspite of taking acidic foods.

Because

Statement-2: Blood behaves as buffer solution.

16. **Statement-1:** Borax forms alkaline aqueous solution.

Because

Statement-2: Borax is the salt of a weak acid (H_3BO_3) and a strong base (NaOH).

17. **Statement-1:** When the aqueous solution of CH_3COONH_4 is diluted, then its degree of hydrolysis does not change.

Because

Statement-2: It is the salt of a weak acid and a weak base hence its degree of hydrolysis does not depend on the concentration.

SECTION-IV

Matrix-Matching Type Questions

This section contains 3 questions. Each question contains statement given in two columns which have to be matched. Statements (a, b, c and d) in Column-I have to be matched with statements (p, q, r and s) in Column-II. The answers to these questions have to be appropriately bubbled as illustrated in the following examples:

If the correct matches are (a-p,s); (b-q,r); (c-p,q) and (d-s); then correct bubbled 4 × 4 matrix should be as given:

	p	q	r	s
a	●	○	○	●
b	○	●	●	○
c	●	●	○	○
d	○	○	○	●

18. Match the Column-I with Column-II:

Column-I (Salt solution in water)	**Column-II (Nature of hydrolysis)**
(a) NaCl	(p) Cationic hydrolysis
(b) CH_3COONa	(q) Anionic hydrolysis
(c) NH_4CN	(r) Both cationic and anionic hydrolysis
(d) NH_4Cl	(s) Does not undergo hydrolysis

19. Match the Column-I with Column-II:

Column-I	**Column-II**
(a) H_3PO_2	(p) Dibasic
(b) H_3PO_4	(q) Monobasic
(c) H_3PO_3	(r) Tribasic
(d) H_3BO_3	(s) Aprotic

20. Match the Column-I with Column-II:

Column-I (Salt)	**Column-II (Degree of hydrolysis)**
(a) NH_4Cl	(p) No hydrolysis
(b) NaCl	(q) $h = \sqrt{\frac{K_h}{C}}$
(c) CH_3COONa	(r) $h = \sqrt{\frac{K_w}{CK_b}}$
(d) CH_3COONH_4	(s) $h = \sqrt{K_h}$

Answers

1. (b) **2.** (a) **3.** (a) **4.** (d) **5.** (c) **6.** (a) **7.** (d) **8.** (a, b)
9. (a, b, c) **10.** (b, c) **11.** (a, b) **12.** (c, d) **13.** (d) **14.** (d) **15.** (a) **16.** (a)
17. (a) **18.** (a-s) (b-q) (c-r) (d-p) **19.** (a-q) (b-r) (c-p) (d-q, s) **20.** (a-q, r) (b-p) (c-q) (d-s)