Many simple cations can act as Lewis acids:

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

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

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

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

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

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

BASICS OF IONIC EQUILIBRIUM Section - 2

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

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

Ions in solution arise mainly in two ways :

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

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

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

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

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

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

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

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

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

Weak Electrolytes are categorized into three types for easy understanding :

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

Weak Acids (HA) and Weak Bases (BOH)

Weak Acids :

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

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

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

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

[ ] = concentration in mol/L

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

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

$\Rightarrow$ Conjugate base of CH_3COOH is CH_3COO^- ; of H_3PO_4 is $H_2PO_4^-$ and so on.

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

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

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

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

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

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

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

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

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

Weak Bases :

Let BOH be the weak base, its aqueous solution is represented as : $BOH(aq) \rightleftharpoons B^+(aq) + OH^-(aq)$

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

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

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

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

- $H_2PO_4^-$: Its conjugate base is HPO_4^{2-} and its conjugate acid is H_3PO_4
- H_2O : Its Conjugate base is OH^- and its conjugate acid is H_3O^+

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

Now, if ‘c’ be the molar concentration of BOH and ‘α’ be its degree of dissociation, then :

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

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

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

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

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

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

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

For example in case of bases :

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

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

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

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

Self Ionisation of Water

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

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

$\Rightarrow \quad K_w = [H^+][OH^-]$ where $K_w = K_a[H_2O]$

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

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

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

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

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

pH Scale :

Sorensen, a French chemist developed a scale to measure the acidity in terms of concentrations of H^+ in a solution. *pH of a solution* is the negative logarithm to the base 10 of the concentration of H^+ ions which it contains.

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

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

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

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

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

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

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

			Acidic Solution				**H_2O**		**Basic Solution**				
At 25°C (298K)	1	2	3	4	5	6	7	8	9	10	11	12	13
							pH						
	⟵ acidity increases ---------⟵						(Neutral)	⟶--------- basicity increases					

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

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

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

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

Note : "p" operator is generally applied on any variable whose value is < 1. In most of the cases, we will use pK_w, pK_a, pK_b etc. Also, we can see that as temperature increases, both pH and pOH of pure water will decrease since there will be an increase in $[H^+]$ and $[OH^-]$ due to increased dissociation.

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

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

Dissociation equilibrium of HA :

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

Dissociation equilibrium of conjugate base A^- :

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

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

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

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

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

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

$$K_{b_{weak\ base}} \times K_{a_{conjugate\ acid}} = K_W \qquad \Rightarrow \qquad pK_{b(BOH)} + pK_{a(B^+)} = pK_W$$

pH of a Weak Acid and Weak Base :

Weak acid (HA) :

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

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

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

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

Weak base (BOH) :

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

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

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

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

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

SOLUTION :

$$\begin{array}{lll} HCN(aq) & \rightleftharpoons & H^+(aq) + CN^-(aq) \\ c & 0 & 0 \\ c - c\alpha & \alpha & c\alpha \end{array}$$

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

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

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

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

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

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

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

Thus, the answer obtained above is correct.

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

SOLUTION :

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

$\Rightarrow \quad K_a = \dfrac{[H^+]^2}{c - [H^+]} \approx \dfrac{[H^+]^2}{c} \quad$ (as K_a is too Low)

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

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

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

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

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

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

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

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

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

Check yourself that new degree of dissociation of acetic acid = $\alpha_{new} = \dfrac{[H^+]_{new}}{c_{new}} = 0.83$ which clearly suggests that using approximations would have generated poor/wrong results.

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

$4.8 \times 10^{-6} \times V = 0.2 \times 1 \qquad (C_1V_1 = C_2V_2)$

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

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

SOLUTION :

$$\begin{array}{lccc} & NH_4OH(aq) & \rightleftharpoons & NH_4^+(aq) + OH^-(aq) \\ & c & & 0 \qquad\quad 0 \\ & c - c\alpha & & c\alpha \qquad c\alpha \end{array}$$

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

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

$$\Rightarrow \quad \alpha = \sqrt{\frac{K_b}{c}} = \sqrt{2 \times 10^{-4}} = 1.41 \times 10^{-2} = 1.41\,\%$$

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

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

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

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

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

SOLUTION :

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

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

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

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

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

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

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

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

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

Solve the above quadratic equation to get :

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

Now, $\quad [H^+]_{total} = 10^{-8} + 9.52 \times 10^{-8} = 1.05 \times 10^{-7}\,M$

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

IN-CHAPTER EXERCISE - A

1. *Calculate the hydrogen and hydroxyl ion concentration in a solution of 0.0315 g of HNO_3 in 500 cc of water.*

2. *Find the dissociation constant, K_a of a weak monobasic acid (HA) which is 3.5% dissociated in an M/20 solution.*

3. *Calculate the pH of following solutions.*

(i) *0.1N HCl* **(ii)** *N/50 HCl* **(iii)** *N/100 H_2SO_4* **(iv)** *N/10 NaOH*

(v) *Find $[H^+]$ in a solution whose pH is 3.69.*

4. *Calculate the pH of a solution:*

(i) *containing 20 gm of NaOH per litre water*

(ii) *made by mixing 50mL of 0.01M $Ba(OH)_2$ with 50 mL water.*

5. *The dissociation constant of acetic acid is 1.8×10^{-5} at 25°C. Find the pH of:*

(i) *M/10* **(ii)** *M/100 solutions of the acetic acid.*

6. *Find the pH of a mixture containing 50mL of 1.0 M HCl and 30 mL of a 1.0 M NaOH. Both HCl and NaOH are 100% ionised.*

7. *The dissociation constant of a weak acid HA is* 4.9×10^{-8}. *Calculate for a decimolar solution of acid:*

(i) *% of ionisation* **(ii)** *pH* **(iii)** OH^- *concentration*

8. **(i)** *Calculate pH value of decinormal solution of acetic acid which is 1.3% ionised.* (use $\log_{10}13 = 1.11$)

(ii) *Calculate the pH value of N/1000 solution of acetic acid having ionisation constant as* 2.0×10^{-5}.

9. *If the pH of 0.26 M* HNO_2 *is 2.5, what will be its dissociation constant ?*

10. 25.0 *mL of* 0.10 *M NaOH is titrated with* 0.10 *M HCl. Calculate the pH when :*

(i) 20 *mL* **(ii)** 24 *mL of acid have been added.*

11. **Choose the correct alternative for each of the following. Only one choice is correct.**

(i) *The conjugate acid of* NH_2^- *is :*

(A) NH_4^+ **(B)** NH_2OH **(C)** NH_3 **(D)** N_2H_4

(ii) *An acid solution of pH = 6 is diluted hundred times. The pH of the solution becomes :*

(A) 6.95 **(B)** 6 **(C)** 4 **(D)** 8

(iii) *Which of the following mixture will have the pH close to 1 ?*

(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*

(iv) *At 90°C, pure water has* $[H_3O^+] = 10^{-6}$ *mole litre*$^{-1}$. *What is the value of* K_w *at* $90^\circ C$?

(A) 10^{-6} **(B)** 10^{-12} **(C)** 10^{-14} **(D)** 10^{-8}

(v) *HCOOH and* CH_3COOH *solutions have equal pH. If* K_1/K_2 *(ratio of acid dissociation constants) is 4, ratio of their molar concentration will be :*

(A) 2 **(B)** 0.5 **(C)** 4 **(D)** 0.25

(vi) $2H_2O \rightleftharpoons H_3O^+ + OH^-,\ K_w = 1 \times 10^{-14}$ *at 25°C hence* K_a *is :*

(A) 1×10^{-14} **(B)** 5.55×10^{-13} **(C)** 18×10^{-17} **(D)** 1.00×10^{-7}

(vii) *The number of* H^+ *ions present in 1 mL of a solution having pH = 13 is :*

(A) 10^{13} **(B)** 6.023×10^{13} **(C)** 6.023×10^{7} **(D)** 6.023×10^{10}

(viii) *Which of the following expressions is not true ?*

(A) $\left[H^+\right] = \left[OH^-\right] = \sqrt{K_w}$ *for a neutral solution*

(B) $\left[H^+\right] > \sqrt{K_w}$ *and* $\left[OH^-\right] < \sqrt{K_w}$ *for an acidic solution*

(C) $\left[H^+\right] < \sqrt{K_w}$ *and* $\left[OH^-\right] > \sqrt{K_w}$ *for an alkaline solution*

(D) $[H^+] = [OH^-] = 10^{-7}$ *M for a neutral solution at all temperature*

(ix) *For pure water,*

(A) *pH increases and pOH decreases with increase in temperature*

(B) *pH decreases and pOH increases with increase in temperature*

(C) *both pH and pOH increase with increase in temperature*

(D) *both pH and pOH decrease with increase in temperature*

(x) *For a "c molar" concentrated solution of a weak electrolyte* A_xB_y, *the degree of dissociation is given as :*

(A) $\alpha = \sqrt{K_{eq}/c(x+y)}$ **(B)** $\alpha = \sqrt{K_{eq}c/(xy)}$

(C) $\alpha = \left(K_{eq}/c^{x+y-1}x^x y^y\right)^{1/(x+y)}$ **(D)** $\sqrt{K_{eq}/xyc}$

(xi) *Equal volumes of two solutions of hydrochloric acid are mixed. One solution has a pH* 1 *while the other has a pH* 5. *The pH of the resulting solution is :*

(A) *less than* 1 **(B)** *Between* 1 *and* 2 **(C)** 3 **(D)** *Between* 4 *and* 5

(xii) *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)** *None of these*

(xiii) *The dissociation constant of* NH_4OH *is* 1.8×10^{-5}. *The concentration of* OH^- *ions in moles per litre of* 0.1 *molar* NH_4OH solution *is :*

(A) 1.8×10^{-6} **(B)** 1.34×10^{-3} **(C)** 4.20×10^{-3} **(D)** 5.00×10^{-2}

(xiv) *The pH of a solution is increased from* 3 *to* 6 ; *its* H^+ *ion concentration will be :*

(A) reduced to half **(B)** *doubled*

(C) *reduced by* 1000 *times* **(D)** *increased by* 1000 *times*

(xv) *The following equilibrium is established when hydrogen chloride is dissolved in acetic acid.*

$$HCl + CH_3COOH \rightleftharpoons Cl^- + CH_3COOH_2^+$$

The set that characterizes the conjugate acid-base pairs is :

(A) (HCl, CH_3COOH) *and* $(CH_2COOH_2^+, Cl^-)$

(B) $(HCl, CH_3COOH_2^+)$ *and* (CH_3COOH, Cl^-)

(C) $(CH_3COOH_2^+, HCl)$ *and* (Cl^-, CH_3COOH)

(D) (HCl, Cl^-) *and* $(CH_3COOH_2^+, CH_3COOH)$