



Ionic Equilibrium (Advanced)

Ionic Equilibrium-I

(A) pH Calculation : Solutions of polyprotic weak acids, solutions of polyacidic weak bases

Solution of a polyprotic weak acid :

Der1 : Let us take a weak diprotic acid (H_2A) in water whose concentration is C M.

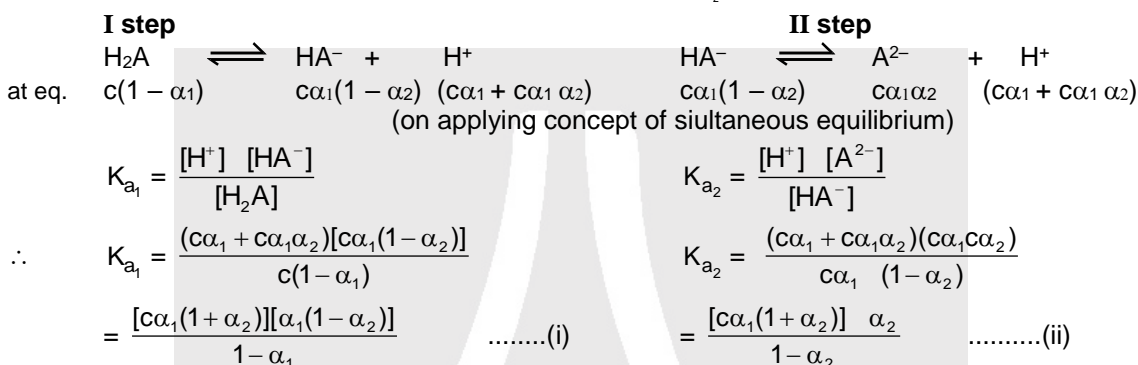
In aqueous solution, following equilibria exist :

α_1 = degree of ionization of H_2A in presence of HA^-

K_{a_1} = first ionisation constant of H_2A .

α_2 = degree of ionisation of HA^- in presence of H_2A

K_{a_2} = second ionisation constant of H_2A



Knowing the values of K_{a_1} , K_{a_2} and c , the values of α_1 and α_2 can be calculated using equations (i) & (ii).

After getting the values of α_1 and α_2 , $[H_3O^+]$ can be calculated as.

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

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

Approximation

For diprotic acids, $K_{a_2} < K_{a_1}$ and α_2 would be even smaller than α_1 .

$$\therefore 1 - \alpha_2 \approx 1 \text{ and } 1 + \alpha_2 \approx 1$$

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

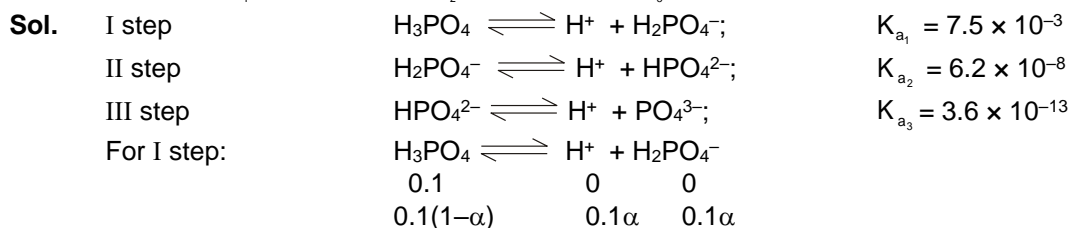
This is an expression similar to the expression for a weak monoprotic acid.

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

F1 : $\therefore \text{pH} = \frac{1}{2} (\text{p}K_{a_1} - \log C) \quad [\text{if } \alpha_1 \leq 0.1 \text{ or } 10\%]$

Solved Examples

Ex-1. Calculate the concentrations of all species of significant concentrations present in 0.1 M H_3PO_4 solution. $K_{a_1} = 7.5 \times 10^{-3}$, $K_{a_2} = 6.2 \times 10^{-8}$, $K_{a_3} = 3.6 \times 10^{-13}$. Take $0.075 \times 4.075 = (0.555)^2$





$$K_{a_1} = \frac{[H^+][H_2PO_4^-]}{[H_3PO_4]} \Rightarrow \frac{0.1\alpha^2}{(1-\alpha)} = 7.5 \times 10^{-3} \quad \dots(1)$$

Expecting $\alpha \ll 1$, $\alpha^2 = 7.5 \times 10^{-2} \therefore \alpha = 0.274$ (not negligible)

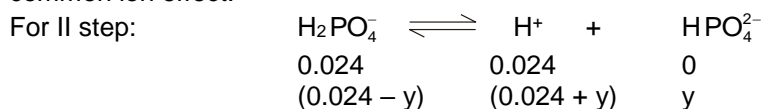
So, solve quadratic equation (1) & get $\alpha = 0.24$.

$$\therefore [H^+] = 0.024 \text{ M} \Rightarrow [OH^-] = \frac{10^{-14}}{0.024} = 4.17 \times 10^{-13} \text{ M (insignificant)}$$

$$\& [H_2PO_4^-] = 0.024 \text{ M}$$

$$\text{Also, } [H_3PO_4] = 0.1 - 0.024 = 0.076 \text{ M}$$

The value of K_{a_1} is much larger than K_{a_2} and K_{a_3} . Also dissociations of II and III steps occur in presence of H^+ furnished in I step and thus, dissociations of II and III steps are further suppressed due to common ion effect.



The dissociation of $H_2PO_4^-$ occurs in presence of $[H^+]$ furnished in step I.

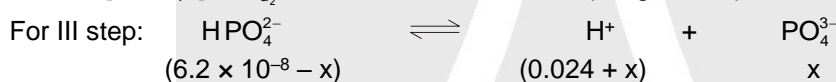
$$\text{Thus, } K_{a_2} = \frac{[H^+][HPO_4^{2-}]}{[H_2PO_4^-]} \quad \text{or} \quad 6.2 \times 10^{-8} = \frac{(0.024 + y)y}{(0.024 - y)}$$

\therefore y is small $\therefore 0.024 - y \approx 0.024$ and neglecting y^2 .

$$\therefore 6.2 \times 10^{-8} = \frac{0.024y}{0.024}$$

$$\therefore y = 6.2 \times 10^{-8} \text{ M}$$

$$\text{or } [HPO_4^{2-}] = K_{a_2} = 6.2 \times 10^{-8} \text{ M} \quad (\text{Insignificant})$$



$$\therefore K_3 = \frac{[H^+][PO_4^{3-}]}{[HPO_4^{2-}]} = \frac{(0.024 + x)x}{(6.2 \times 10^{-8} - x)}$$

\therefore x is small \therefore Again neglecting x^2 and assuming $6.2 \times 10^{-8} - x \approx 6.2 \times 10^{-8}$

$$\therefore 3.6 \times 10^{-13} = \frac{0.024x}{6.2 \times 10^{-8}}$$

$$\therefore x = \frac{3.6 \times 10^{-13} \times 6.2 \times 10^{-8}}{0.024} = 9.3 \times 10^{-19} \text{ M}$$

$$\text{or } [PO_4^{3-}] = 9.3 \times 10^{-19} \text{ M (insignificant)}$$

NOTE : For weak polyprotic acid solution having no other electrolyte, the anion concentration produced in II step of dissociation is always equal to K_{a_2} if concentration is reasonable.

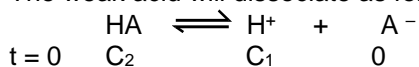
(B) pH Calculation : Solutions containing mixture of weak monoprotic acid and strong acid, solutions containing mixture of weak monoacidic base and strong base

Mixture of weak acid (monoprotic) and a strong acid :

- Weak acid and Strong acid both will contribute H^+ ion.
- We have to take the effect of presence of strong acid on the dissociation equilibrium of the weak acid.

Der2 : Let upon mixing $[H^+]_{SA} = C_1$ and $[WA] = C_2$

The weak acid will dissociate as follows :



$$t = \text{eq.} \quad C_2(1-\alpha) \quad C_2\alpha + C_1 \quad C_2\alpha$$

$$K_a = \frac{(C_2\alpha + C_1)C_2\alpha}{C_2(1-\alpha)} \quad \dots(1)$$



The weak acid's dissociation will be further suppressed because of presence of strong acid (common ion effect). So, expecting α to be $\ll 1$, $C_2\alpha + C_1 \approx C_1$ & $1 - \alpha \approx 1$.

$$K_a = C_1\alpha \quad \dots(2)$$

F2 : If α from (2) comes < 0.1 , then expectation gets correct & $[H^+]_f = C_1$ (just not considering the H^+ ions from WA).

- If α from (2) comes ≥ 0.1 , then solve quadratic equation in α (eq. (1)) to get exact α . Then,
Total H^+ ion concentration = $C_1 + C_2\alpha$

Solved Examples

Ex-2. Calculate pH of a solution which is 10^{-1} M in HCl & 10^{-3} M in CH_3COOH [$K_a = 2 \times 10^{-5}$]. Also calculate $[H^+]$ from CH_3COOH .

Sol. $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$
 $t = eq \quad C(1 - \alpha) \quad C\alpha \quad 10^{-1} + C\alpha$
 H^+ ion can be considered completely from HCl, due to less dissociation of CH_3COOH (because of common ion effect by H^+ of HCl, $\alpha \ll 1$) and its low conc. So, $[H^+] = 10^{-1}$ M $\therefore pH = 1$.

$$\text{From above equilibrium, } 2 \times 10^{-5} = \frac{C\alpha \times 10^{-1}}{C}$$

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

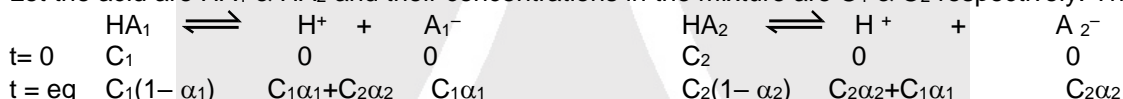
$$[H^+] \text{ from } CH_3COOH = C\alpha = 10^{-3} \times 2 \times 10^{-4} = 2 \times 10^{-7} \text{ M.}$$

(C) pH Calculation : Solutions containing mixture of weak acids, solutions containing mixture of weak bases

Mixture of two weak acids (both monoprotic) :

- Both acids will dissociate partially.

Der3 : Let the acid are HA_1 & HA_2 and their concentrations in the mixture are C_1 & C_2 respectively. Then :



(On applying concept of simultaneous equilibrium)

$$K_{a_1} = \frac{C_1\alpha_1(C_1\alpha_1 + C_2\alpha_2)}{C_1(1 - \alpha_1)} \quad \dots(1)$$

$$K_{a_2} = \frac{(C_2\alpha_2 + C_1\alpha_1)C_2\alpha_2}{C_2(1 - \alpha_2)} \quad \dots(2)$$

Since α_1, α_2 both are small in comparison to unity, putting $1 - \alpha_1 \approx 1$ & $1 - \alpha_2 \approx 1$ in above expressions & adding we get :

$$(C_1\alpha_1 + C_2\alpha_2)^2 = C_1K_{a_1} + C_2K_{a_2}$$

F3 : $[H^+] = C_1\alpha_1 + C_2\alpha_2 = \sqrt{C_1K_{a_1} + C_2K_{a_2}}$

- Both acids will dissociate less than in their individual aqueous solutions of same concentration because of common ion effect exerted by H^+ ions of one on other.
- If the dissociation constant of one of the acid is very much greater than that of the second acid then contribution from the second acid can be neglected.

So, $[H^+] = C_1\alpha_1 + C_2\alpha_2 \approx C_1\alpha_1$ (where C_2 is the concentration of weaker acid)

Solved Examples

Ex-3. Calculate the pH of a solution obtained by mixing equal volume of 0.02 M HOCl & 0.2 M CH_3COOH solutions.

Given that $K_a(HOCl) = 2 \times 10^{-4}$; $K_a(CH_3COOH) = 2 \times 10^{-5}$

Also calculate $[OH^-]$, $[OCl^-]$, $[CH_3COO^-]$ at equilibrium. Take $\log 2 = 0.3$.

Sol. Volume of final solution becomes double.

So, concentration become half. So, after mixing :

$$C_1 = 0.01 \text{ M, } C_2 = 0.1 \text{ M}$$

$$[H^+] = \sqrt{C_1K_{a_1} + C_2K_{a_2}} = \sqrt{2 \times 10^{-4} \times 0.01 + 2 \times 10^{-5} \times 0.1} = \sqrt{2 \times 10^{-6} + 2 \times 10^{-6}} = 2 \times 10^{-3} \text{ M}$$



$$\therefore \text{pH} = 3 - \log 2 = 2.7$$

$$[\text{OCl}^-] = \frac{0.01 \times 2 \times 10^{-4}}{2 \times 10^{-3}} = 1 \times 10^{-3} \text{ M} \quad ; \quad [\text{CH}_3\text{COO}^-] = \frac{0.1 \times 2 \times 10^{-4}}{2 \times 10^{-3}} = 1 \times 10^{-3} \text{ M} ;$$

$$[\text{OH}^-] = \frac{K_w}{[\text{H}^+]} = \frac{10^{-14}}{2 \times 10^{-3}} = 5 \times 10^{-12} \text{ M}.$$

pH of a mixture of two weak acids (one monoprotic and one polyprotic) :

$[\text{H}^+]$ calculation can be done similar to the case of mixture of two weak monoprotic acids.

Refer to the following example :

Solved Examples

Ex-4. Calculate pH, $[\text{H}^+]$, $[\text{OH}^-]$, $[\text{CH}_3\text{COO}^-]$, $[\text{CH}_3\text{COOH}]$, $[\text{SH}^-]$, $[\text{H}_2\text{S}]$, $[\text{S}^{2-}]$ in a solution obtained by mixing equal volume of 0.2 M H_2S & 0.02 M acetic acid. Given that

$$K_a(\text{CH}_3\text{COOH}) = 2 \times 10^{-5}, K_{a_1}(\text{H}_2\text{S}) = 10^{-7}, K_{a_2}(\text{H}_2\text{S}) = 10^{-14}. \text{ Take } \log 21 = 1.32, \frac{1}{\sqrt{21}} = 0.218.$$

Sol. Now, $[\text{H}_2\text{S}] = 0.1 \text{ M}$, $[\text{CH}_3\text{COOH}] = 0.01 \text{ M}$ after mixing.

For pH calculation, considering only first $[\text{H}^+]$ of H_2S , the system becomes similar to a mixture of two weak monoprotic acids.

(2nd H^+ coming from H_2S would be negligible because of very low value of K_{a_2} & also because of common ion effect exerted by H^+ from CH_3COOH).

$$[\text{H}^+] = \sqrt{(10^{-1} \times 10^{-7}) + (10^{-2} \times 2 \times 10^{-5})} = \sqrt{(0.1 + 2) \times 10^{-7}} = \sqrt{21} \times 10^{-4} \text{ M}$$

$$\text{pH} = 4 - \frac{1}{2} \log 21 = 3.34$$

$$[\text{OH}^-] = \frac{K_w}{[\text{H}^+]} = 2.18 \times 10^{-11} \text{ M}$$

$$\text{For acetic acid, } K_a = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = \frac{\sqrt{21} \times 10^{-4} \times [\text{CH}_3\text{COO}^-]}{0.01}$$

$$\Rightarrow [\text{CH}_3\text{COO}^-] = 4.36 \times 10^{-4} \text{ M}$$

$$\Rightarrow [\text{CH}_3\text{COOH}] = 0.01 \text{ M}$$

$$\text{For } \text{H}_2\text{S}, K_{a_1} = \frac{[\text{H}^+][\text{HS}^-]}{[\text{H}_2\text{S}]} = \frac{\sqrt{21} \times 10^{-4} \times [\text{HS}^-]}{0.1} \Rightarrow [\text{HS}^-] = 2.18 \times 10^{-5} \text{ M}$$

$$\text{For } \text{HS}^-, K_{a_2} = \frac{[\text{H}^+][\text{S}^{2-}]}{[\text{HS}^-]} = \frac{\sqrt{21} \times 10^{-4} \times [\text{S}^{2-}]}{2.18 \times 10^{-5}} \Rightarrow [\text{S}^{2-}] = 4.76 \times 10^{-16} \text{ M}$$

(D) pH Calculation : Solutions containing mixture of weak polyprotic acid and strong acid, solutions containing mixture of weak polyacidic base and strong base

Mixture of a polyprotic weak acid and a strong acid :

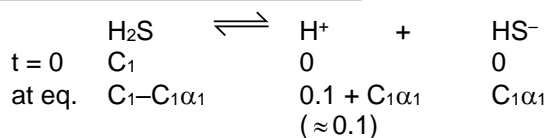
- pH can be calculated by taking the concentration of strong acid only.
- For other calculations, we should consider the dissociation equilibria of the weak polyprotic acid, as done in the following example.

Solved Examples

Ex-5. Calculate pH, $[\text{HS}^-]$, $[\text{S}^{2-}]$, $[\text{Cl}^-]$ in a solution which is 0.1 M in HCl & 0.1 M in H_2S . Given that $K_{a_1}(\text{H}_2\text{S}) = 10^{-7}$, $K_{a_2}(\text{H}_2\text{S}) = 10^{-14}$. Also calculate degree of dissociation of H_2S & HS^- in solution.

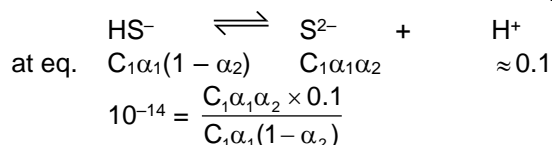
Sol. $\text{HCl} + \text{H}_2\text{S}$
0.1 M 0.1 M

$$\therefore \text{pH} = 1 \text{ (most of } [\text{H}^+] \text{ comes from HCl) \& } [\text{Cl}^-] = 0.1 \text{ M}.$$



$$K_{a_1} = \frac{C_1\alpha_1 \times 10^{-1}}{C_1(1-\alpha_1)}$$

$$\text{degree of dissociation of H}_2\text{S} = \alpha_1 = \frac{10^{-7}}{10^{-1}} = 10^{-6}$$



$$\begin{aligned}
 \Rightarrow \text{degree of dissociation of HS}^- &= \alpha_2 = 10^{-13} \\
 [\text{S}^{2-}] &= C_1\alpha_1\alpha_2 = 10^{-1} \times 10^{-6} \times 10^{-13} = 10^{-20} \text{ M} \\
 [\text{HS}^-] &= C_1\alpha_1 = 10^{-1} \times 10^{-6} = 10^{-7} \text{ M}
 \end{aligned}$$

Note : Analogous to cases (D), (E), (F), (G) & (H), we can have cases for weak bases also. There, pOH can be calculated similarly.

Mixture of a weak acid/ weak base with weak/strong base/acid respectively.

For this type, there can be two cases in general :

- (i) if the acids and bases are mixed in such amounts that they get exactly neutralized.
- (ii) if the acids and bases are mixed in such amounts that they don't get exactly neutralized.

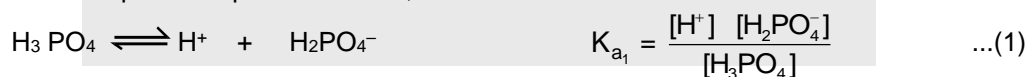
First case will lead to formation of **SALT SOLUTIONS** and second case may lead to formation of **BUFFER SOLUTIONS** (would be discussed later).

(E) pH Calculation : Solutions of salt of weak polyprotic acid and strong base, solutions of salt of weak polyacidic base and strong acid, solutions of amphiprotic species

Solutions containing polyvalent anions (or cations) of weak polyprotic acids (or bases).

- The hydrolysis of these species will take place in steps (just like dissociation of weak polyprotic acids).
- Out of different steps, generally first step hydrolysis dominates mainly because of two reasons :
 - The hydrolysis constant of second and further steps is generally negligible in comparison to first step hydrolysis constant.
 - The second and further step hydrolysis will be suppressed in presence of ions produced due to first step hydrolysis (common ion effect).

For polyprotic acids like (H_2S , H_3PO_4 , H_2CO_3 , $\text{H}_2\text{C}_2\text{O}_4$), we already know that the dissociation always takes place in steps. Example : for H_3PO_4 ,



For all acids we always have $K_{a_1} \gg K_{a_2} \gg K_{a_3}$

pH of the solution can be calculated from 1st step only because $[\text{H}^+]$ from IInd & IIIrd step can be neglected as

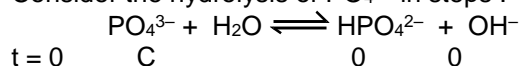
$$(a) \quad K_{a_1} \gg K_{a_2} \gg K_{a_3}$$

(b) $[\text{H}^+]$ from 1st dissociation will suppress the dissociation of IInd & IIIrd step.



Now, for the hydrolysis of polyvalent ions (from salts like K_3PO_4 , Na_2CO_3 , $ZnSO_4$, $FeCl_3$, $(NH_4)_2C_2O_4$ or ions like PO_4^{3-} , CO_3^{2-} , Zn^{2+} , Fe^{3+} etc.) :

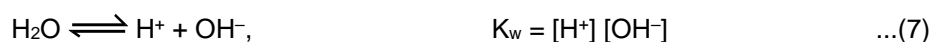
Der4 : Consider the hydrolysis of PO_4^{3-} in steps :



$$t = 0 \quad C \quad 0 \quad 0$$

$$t = eq \quad C(1-h) \quad Ch \quad Ch$$

$$K_{h_1} = \frac{[OH^-][HPO_4^{2-}]}{[PO_4^{3-}]} \quad \dots(4)$$



From above equations, we get : $K_{a_1} \times K_{h_3} = K_w$; $K_{a_2} \times K_{h_2} = K_w$; $K_{a_3} \times K_{h_1} = K_w$

Numerically, $K_{h_1} \gg K_{h_2} \gg K_{h_3}$.

Generally, pH is calculated only using the first step hydrolysis

$$K_{h_1} = \frac{Ch \cdot Ch}{C(1-h)} = \frac{Ch^2}{1-h} \quad \dots(8)$$

$$\approx Ch^2 \quad (\text{expecting } h \ll 1)$$

$$F4 : \quad h = \sqrt{\frac{K_{h_1}}{C}} \quad \dots(9)$$

$$\Rightarrow [OH^-] = Ch = \sqrt{K_{h_1} \times C} \Rightarrow [H^+] = \frac{K_w}{[OH^-]} = K_w \sqrt{\frac{K_{a_3}}{K_w C}} = \sqrt{\frac{K_w \times K_{a_3}}{C}}$$

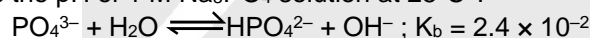
$$F5 : \quad \text{So, } pH = \frac{1}{2}[pK_w + pK_{a_3} + \log C]$$

NOTE : If h value from (9) comes ≥ 0.1 , then its exact value should be obtained by solving quadratic (equation

$$(8)) \text{ Then, } [OH^-] = Ch \text{ \& } [H^+] = \frac{K_w}{[OH^-]}$$

Solved Examples

Ex-6. What is the pH of 1 M Na_3PO_4 solution at $25^\circ C$?



Assume no hydrolysis of HPO_4^{2-} ions.

$$\text{Sol.} \quad K_b = \frac{x^2}{1-x} = 2.4 \times 10^{-2}$$

$$x^2 + (2.4 \times 10^{-2})x - 2.4 \times 10^{-2} = 0$$

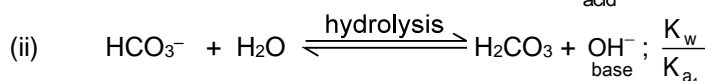
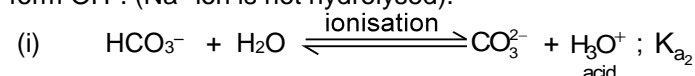
$$x = 0.143 = [OH^-]$$

$$[H^+] = \frac{K_w}{[OH^-]} = 7 \times 10^{-14} \text{ M}$$

$$\therefore pH = 13.15.$$

Solutions containing amphiprotic anion (or cation) :

Anions of $NaHCO_3$, $NaHS$, etc. can undergo ionisation to form H^+ and can also undergo hydrolysis to form OH^- . (Na^+ ion is not hydrolysed).





Taking the assumption: Degree of ionisation (α) = Degree of hydrolysis (h) or $[\text{CO}_3^{2-}] = [\text{H}_2\text{CO}_3]$, an approximate calculation of pH can be done by the relation :

$$\text{F6 : } \text{pH}(\text{HCO}_3^-) = \left(\frac{\text{pK}_{a_1} + \text{pK}_{a_2}}{2} \right)$$

= Average of pK_a values of parent acid (here H_2CO_3) involved in ionisation & hydrolysis reactions.

Similarly for H_2PO_4^- and HPO_4^{2-} amphiprotic anions,

$$\text{F7 : } \text{pH}(\text{H}_2\text{PO}_4^-) = \left(\frac{\text{pK}_{a_1} + \text{pK}_{a_2}}{2} \right) \quad \text{and} \quad \text{pH}(\text{HPO}_4^{2-}) = \left(\frac{\text{pK}_{a_2} + \text{pK}_{a_3}}{2} \right)$$

(Where K_{a_1} , K_{a_2} & K_{a_3} are dissociation constants of H_3PO_4)

NOTE : Exact calculation of pH is complicated and not relevant with respect to JEE.

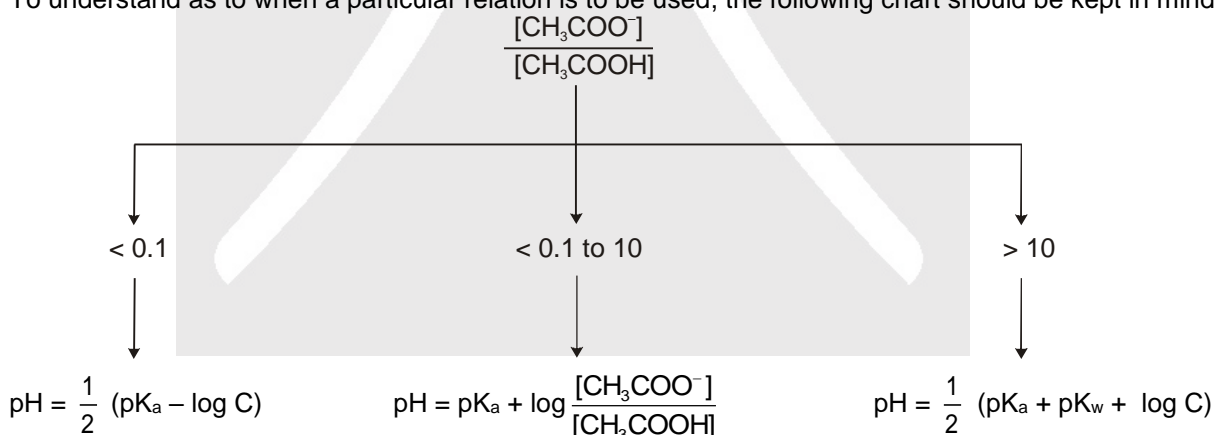
Ionic Equilibrium-II

(A) pH range of buffer, pH Calculation : Buffer solutions generated from polybases acid / polyacidic base, buffer capacity

Use of various relations :

Let us consider three situations, (i) a solution of CH_3COOH (ii) a solution of CH_3COONa and (iii) a solution of CH_3COOH and CH_3COONa (buffer). In all the three solutions, there will be some CH_3COO^- and CH_3COOH . But the relations used for calculating the pH differs. For (i), the relation used is : $\text{pH} = \frac{1}{2} (\text{pK}_a - \log C)$; for (ii) the relation used is : $\frac{1}{2} (\text{pK}_w + \text{pK}_a + \log C)$ and for (iii), the relation used is $\text{pH} = \text{pK}_a + \log \frac{[\text{Anion of Salt}]}{[\text{Acid}]}$.

To understand as to when a particular relation is to be used, the following chart should be kept in mind :



Although it is difficult to give an exact limit up to which a buffer can be used, it is generally accepted that a buffer solution can be used for practical purposes when its $[\text{Salt}]/[\text{Acid}]$ lies within the range of 0.1 to 10 (as shown above).

D2 : Therefore, it can be concluded that **a particular weak acid (or base) can be employed for making useful buffer solution of pH (or pOH) lying within the range of $(\text{pK}_a \pm 1)$ or $(\text{pK}_b \pm 1)$. This is called pH range of buffer.** For example, acetic acid ($\text{pK}_a = 4.75$ at 25°C) and sodium acetate mixture can be used for preparing buffer solutions whose pH values are roughly in the range of 3.75 to 5.75. Outside this range, the buffer capacity of acetic acid–sodium acetate solution is too small to be used for any practical purpose.



Solved Examples

Ex-7. The pH of a blood stream is maintained by a proper balance of H_2CO_3 and NaHCO_3 . What volume of 5 M NaHCO_3 solution should be mixed with 10 ml of a sample of solution which is 2.5 M in H_2CO_3 , in order to maintain a pH = 7.4. (Take pK_{a_1} for $\text{H}_2\text{CO}_3 = 6.7$, $\log 2 = 0.3$)

Sol. $\text{pH} = \text{pK}_{a_1} + \log \frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]}$

$$\Rightarrow 7.4 = 6.7 + \log \frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} \Rightarrow \frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = 5$$

$\therefore 5 \times \text{moles of } \text{H}_2\text{CO}_3 = \text{Moles of } \text{HCO}_3^-$ (since both are components of same solution, volume of solution would be same for both)

$$\Rightarrow 5 \times 2.5 \times 10 \times 10^{-3} = 5 \times V \Rightarrow \text{required volume} = 0.025 \text{ L} = 25 \text{ mL.}$$

Buffer Capacity :

D3 : It is defined as the moles of a strong acid or strong base required to change the pH of 1 L of a buffer by one unit.

Der5 : Let there be a buffer solution of volume 1 L with 'b' mole of anion (coming from salt) and 'a' mole of weak acid. The pH of the buffer would be given by :

$$\text{pH} = \text{pK}_a + \log \frac{b}{a}$$

On adding x mole of a strong acid (monobasic), the pH changes to $\text{pH} = \text{pK}_a + \log \frac{b-x}{(a+x)}$.

$$\therefore \Delta \text{pH} = \log \frac{b}{a} - \log \frac{b-x}{(a+x)}$$

Differentiating with respect to x we get

$$\frac{d\Delta \text{pH}}{dx} = \frac{1}{2.303} \left[\frac{1}{\frac{b}{a} \times \left(\frac{a+x}{b-x} \right)} \times \frac{b(a+b)}{a} \times \frac{1}{(b-x)^2} \right] = \frac{1}{2.303} \frac{a+b}{(a+x)(b-x)}$$

Taking the inverse

F8 : $\frac{dx}{d\Delta \text{pH}} = 2.303 \frac{(a+x)(b-x)}{a+b} \approx 2.303 \frac{ab}{a+b}$. This is defined as buffer capacity. It is the ratio of the small amount of acid or base added to the change in pH caused in the buffer.

Maximum buffer capacity :

Der6 : Differentiating buffer capacity with respect to 'b', the amount of salt present in the solution and equating it to zero, we get

$$\frac{d}{db} \left(\frac{dx}{d\Delta \text{pH}} \right) = 2.303 \frac{[-1 \times (b-x)] + [1 \times (a-b+x)]}{a} = 0$$

$a - b + 2x = 0$; Since x is very small we ignore 2x and we get

$$a - b = 0$$

F9 : $\therefore b = a \Rightarrow [\text{Acid}] = [\text{Anion of salt}]$

The buffer shows maximum buffer capacity when the amounts of acid (or base) and the anion (or cation) from salt are same.

Solved Examples

Ex-8. Calculate the buffer capacity of 1 L solution of :

(i) 0.1M CH_3COOH and 0.1M CH_3COONa

(ii) 0.2M CH_3COOH and 0.2M CH_3COONa

Given : $\text{pK}_a (\text{CH}_3\text{COOH}) = 4.74$

Which will be a better buffer ?



Sol. Buffer capacity = $\frac{2.303(a+x)(b-x)}{a+b} \approx \frac{2.303 ab}{a+b}$ $x \ll a, b$

(i) Buffer capacity = $\frac{0.1 \times 0.1 \times 2.303}{0.1 + 0.1} = 0.11515$

(ii) Buffer capacity = $\frac{0.2 \times 0.2 \times 2.303}{0.2 + 0.2} = 0.2303$

Second buffer solution (having greater buffer capacity) can be called better buffer.

(B) pH Calculation : Monobasic acid-monoacidic base titrations

(A) Titration of SA with SB :

Ex. 40 mL, 0.1 M HCl Vs 0.1 M NaOH

Volume of NaOH added

pH of solution

0 mL

1

10 mL

1.22 ($\therefore [H^+] = \frac{40 \times 0.1 - 10 \times 0.1}{50} = 6 \times 10^{-2}$)

20 mL

1.48

30 mL

1.84

39 mL

2.90

39.9 mL

3.90

40.0 mL

7

(Equivalence point : complete neutralization)

40.1 mL

10.1

41 mL

11.1

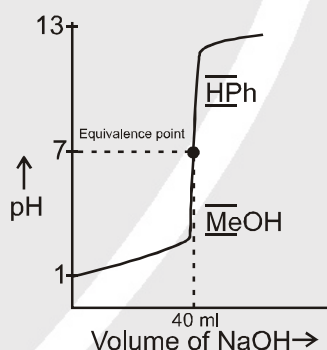
50 mL

12.05

60 mL

12.30 ($\therefore [OH^-] = \frac{60 \times 0.1 - 40 \times 0.1}{100} = 2 \times 10^{-2}$)

Figure-1



- pH values corresponding to different amounts of NaOH added can be calculated using the concept of : Mixture of strong acid & strong base. (Hint for 2 values has been given ; rest values can be obtained similarly) Using these values, a titration curve can be plotted as above.

D4 : pH range of titration : sharp change in pH about equivalence point for very small volume added (almost vertical portion of graph about equivalence point).

According to our data, it is 4 – 10.

- At equivalence point, slope of titration curve is maximum (almost vertical graph).
- An indicator can be considered suitable for detecting the end-point of a particular titration if some part of pH range of indicator lies within the pH range of titration. However, best indicator of a given titration (one giving least experimental error) is the one whose pH range contains pH at equivalence point.
- Almost all common indicators (Phenolphthalein, Methyl orange, Phenol red & Methyl red) can be used for endpoint detection here. However, best will be Phenol red.

NOTE : (1) In genral, endpoint & equivalence point are not the same. But during numerical solving, they should be considered same.

(2) Litmus indicator is generally not used for endpoint detection because of its large pH range. So, there are large experimental errors numerically, if it is used.

**(B) Titration of SB with WA :**

Ex. 20 mL, 0.5 M CH_3COOH ($\text{pK}_a = 4.7$) Vs 0.5 M NaOH
Volume of NaOH added

pH value

0 mL

$$2.5 \quad [\text{pH} = \frac{1}{2} (\text{pK}_a - \log C)]$$

5 mL

4.23

10 mL

$$4.7 \quad [\text{pH} = \text{pK}_a]$$

Half equivalence point

(both components of buffer in equal amounts)

15 mL

$$4.7 + \log 3 = 5.17$$

19 mL

$$4.7 + \log 19/1 = 6$$

20 mL

$$7 + \frac{1}{2} (4.7) + \frac{1}{2} \log (1/4) = 9.05$$

(Equivalence point : complete neutralization)

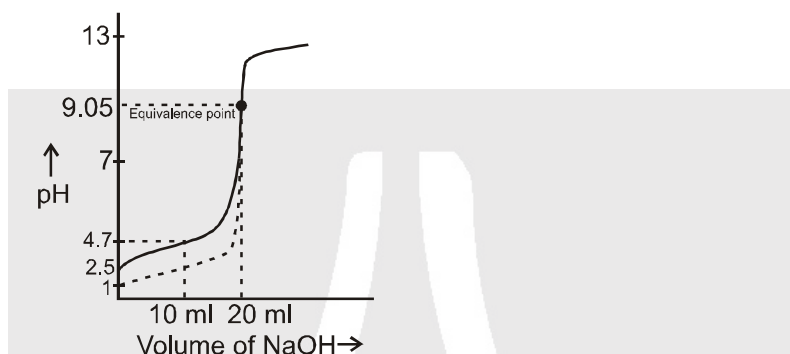
Salt of WA & SB ($\text{CH}_3\text{COONa} = 0.25 \text{ M}$)

21 mL

12.09

30 mL

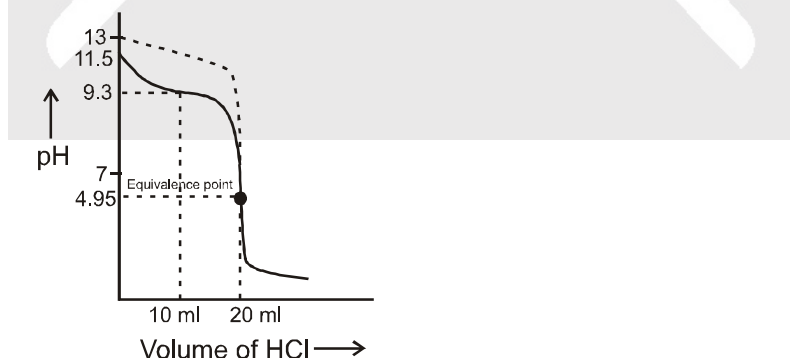
13

Figure-2

- pH calculation at all volumes of NaOH in between 0 mL & 20 mL can be done by concept of buffer of WA & its salt with SB & further data by excess NaOH.
- Initially, fast change in pH is due to free ions available from weak acid.
- Slow down of pH change thereafter is due to buffer formation. Least pH change is seen about half equivalence point (almost horizontal graph), which is point of maximum buffer capacity (at $\text{pH} = \text{pK}_a$).
- Near equivalence point, pH again increases fastly due to salt formation.
- After equivalent point, pH changes very sharply due to presence of strong base.
- pH range of titration : 7 – 10
- Common indicator that can be used : Phenolphthalein & Phenol red.
- Best indicator : Phenolphthalein.

(C) Titration of SA with WB

Ex. 20 mL of 0.5 M $\text{NH}_3 \cdot \text{H}_2\text{O}$ ($\text{pK}_b = 4.7$) Vs 0.5 M HCl

Figure-3

- Proceed similar to as done above with 0 mL data corresponding to weak base, between 0 to 20 mL data corresponding to buffer of WB & its salt with SA, 20 mL data corresponding to salt of WB & SA (NH_4Cl) & further data corresponding to excess HCl.
- pH range of titration : 4 – 7
- Common indicators that can be used : Methyl orange, Methyl red & Phenol red.
- Best indicator : Methyl red.



NOTE : Titration of WA & WB is generally not carried out in laboratory because of very small pH range of this titration (6.5 – 7.5). No common indicator can perform appropriately in this small pH range. However, if this titration is carried out, then Phenol red would be the best indicator.

(C) pH Calculation : Titration of salts, polyprotic acid, polyacidic base

(D) Titration of WA SB salt with SA

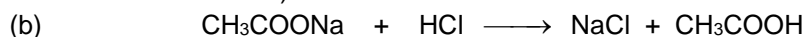
50 mL of 0.1 M CH_3COONa is titrated with 0.1 M HCl . Calculate pH when volume of HCl added is :

(a) 0 mL (b) 10 mL (c) 25 mL (d) 40 mL (e) 50 mL (f) 60 mL (g) 75 mL

Given : pK_a of $\text{CH}_3\text{COOH} = 4.74$

(a) $\text{pH} = 1/2 (\text{pK}_w + \text{pK}_a + \log c) = 1/2 (14 + 4.74 - 1) = 8.87$

(On calculating h by approximation, it comes negligible (< 0.1). That's why direct formula has been used).



t = 0 5 millimole 1 millimole 0 0

finally 4 millimole 0 – 1 millimole \Rightarrow Buffer

$\text{pH} = \text{pK}_a + \log 4 = 4.74 + 0.6 = 5.34$

(c) $\text{pH} = \text{pK}_a = 4.74$ (Half equivalence point : Both components of buffer in equal amount)

(d) $\text{pH} = \text{pK}_a + \log 1/4 = 4.14$ (Similar to as in (b) part)

(e) At equivalent point, weak acid solution (CH_3COOH) will be obtained from above reaction.

$[\text{CH}_3\text{COOH}] = 5/100 = 1/20 \text{ M}$

$\text{pH} = 1/2 (\text{pK}_a - \log C) = 1/2 (4.74 + 2 - 0.7) = \frac{6.04}{2} = 3.02$

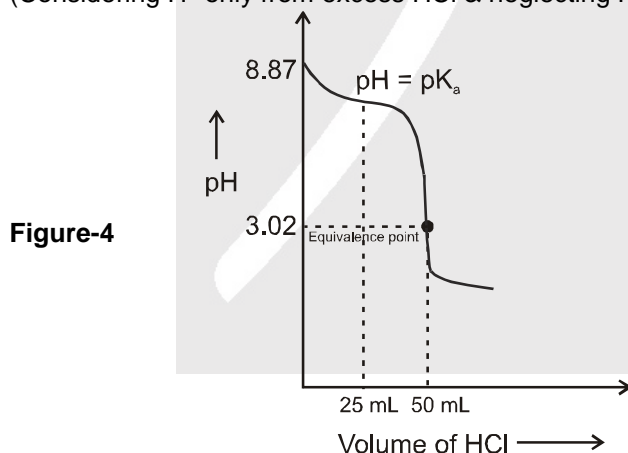
(On calculating by approximation, it comes negligible (< 0.1). That's why direct formula has been used)

(f) $[\text{HCl}] = 1/100 \text{ M}$; $\text{pH} = 2.1$

(Considering H^+ only from excess HCl & neglecting H^+ from CH_3COOH due to common ion effect)

(g) $[\text{HCl}] = \frac{2.5}{125} \text{ M}$; $\text{pH} = 1.7$

(Considering H^+ only from excess HCl & neglecting H^+ from CH_3COOH due to common ion effect)



(E) Titration of WB SA salt with SB

50 mL of 0.1 M NH_4Cl is titrated with 0.1 M NaOH . Calculate pH when volume of NaOH added is :

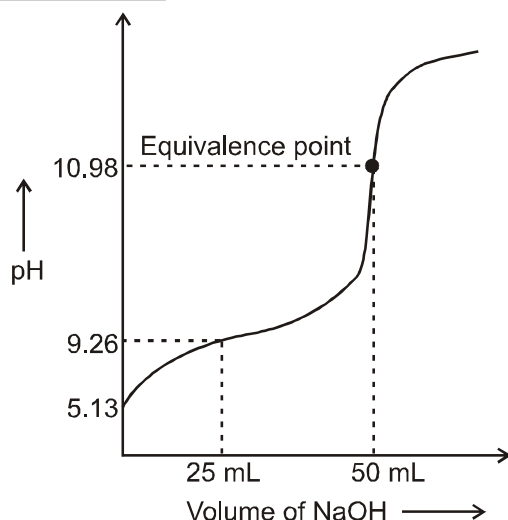
(a) 0 mL (b) 25 mL (c) 50 mL

Given : pK_b of $\text{NH}_3 \cdot \text{H}_2\text{O} = 4.74$

Proceed similar to above (a, c, e) keeping in mind that we have WB SA salt in (a) part, half equivalence point : both components of buffer (WB & its salt with SA) in equal amount in (b) part & equivalence point : weak base in (c) part.



Figure-5



Ionic Equilibrium-III

(A) Simultaneous solubility, complex formation

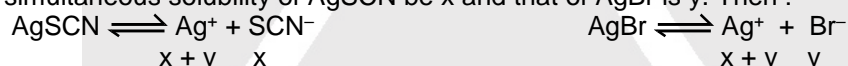
Simultaneous solubility

- When two sparingly soluble salts are added in water simultaneously, there will be simultaneous equilibrium in the solution.
- Simultaneous solubility of each salt will be less than its individual solubility because of common ion effect exerted by ion coming from other salt.

Solved Examples

Ex-9. Calculate simultaneous solubility of silver thiocyanate and silver bromide in water. Given that K_{sp} of silver thiocyanate = 10^{-12} and K_{sp} of silver bromide = 5×10^{-13} respectively.

Sol. Let the simultaneous solubility of AgSCN be x and that of AgBr be y . Then :



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

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

On solving, we get $x = 2y$

So, $y = 4.08 \times 10^{-7} \text{ M}$ and $x = 8.16 \times 10^{-7} \text{ M}$.

(B) Selective precipitation, solubility exchange

Selective precipitation

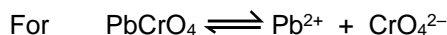
- If a single solution has two or more ions both having tendency to precipitate with an ion of a reagent, then the ion which require less concentration of ion of reagent for precipitation will form precipitate first.
- The ion whose salt has lesser solubility i.e. less K_{sp} value will form precipitate first, if the chemical formulae of the precipitates expected are similar (containing same number of cations & anions) as well as the concentrations of both the ions expected to precipitate with the ion of reagent are same.

Solved Examples

Ex-10. 100 mL of a clear saturated solution of Ag_2SO_4 is added to 250 mL of a clear saturated solution of PbCrO_4 . Will any precipitate form and if so what? Given, K_{sp} values for Ag_2SO_4 , Ag_2CrO_4 , PbCrO_4 & PbSO_4 are 1.4×10^{-5} , 2.4×10^{-12} , 2.8×10^{-13} and 1.6×10^{-8} respectively.

Sol. For $\text{Ag}_2\text{SO}_4 \rightleftharpoons 2\text{Ag}^+ + \text{SO}_4^{2-}$

$$K_{sp} = 4s^3 \quad \text{or} \quad s = \sqrt[3]{\frac{K_{sp}}{4}} = \sqrt[3]{\frac{1.4 \times 10^{-5}}{4}} = 1.52 \times 10^{-2} \text{ M}$$



$$K_{sp} = s_1^2 \quad \text{or} \quad s_1 = \sqrt{K_{sp}} = \sqrt{2.8 \times 10^{-13}} = 5.29 \times 10^{-7} \text{ M}$$

In solution, concentration of each ion can be given as :

Thus, $[\text{Ag}^+] = \frac{2s \times 100}{350} = \frac{2 \times 1.52 \times 10^{-2} \times 100}{350} = 0.869 \times 10^{-2} \text{ M}$

$$[\text{SO}_4^{2-}] = \frac{s \times 100}{350} = \frac{1.52 \times 10^{-2} \times 100}{350} = 0.43 \times 10^{-2} \text{ M}$$

$$[\text{Pb}^{2+}] = \frac{s_1 \times 250}{350} = \frac{5.29 \times 10^{-7} \times 250}{350} = 3.78 \times 10^{-7} \text{ M}$$

$$[\text{CrO}_4^{2-}] = \frac{s_1 \times 250}{350} = \frac{5.29 \times 10^{-7} \times 250}{350} = 3.78 \times 10^{-7} \text{ M}$$

It is thus evident that,

$$[\text{Ag}^+]^2 [\text{CrO}_4^{2-}] = (0.869 \times 10^{-2})^2 \times (3.78 \times 10^{-7}) = 2.85 \times 10^{-11} (> K_{sp} \text{ Ag}_2\text{CrO}_4)$$

Thus Ag_2CrO_4 will precipitate.

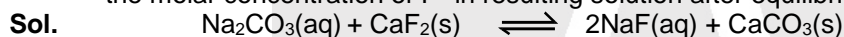
Precipitate Exchange :



One precipitate is mixed with solution of an ion to get another precipitate and another ion in solution.

Solved Examples

Ex-11. 2M solution of Na_2CO_3 is boiled in a closed container with excess of CaF_2 . Very little amount of CaCO_3 and NaF are formed. If the solubility product (K_{sp}) of CaCO_3 is x and molar solubility of CaF_2 is y , find the molar concentration of F^- in resulting solution after equilibrium is attained.



$$t = 0 \quad \begin{array}{ccc} 2 & - & 0 \end{array}$$

$$t = \text{eq} \quad \begin{array}{ccc} 2 - a & - & 2a \end{array}$$

where a is very small

For CaCO_3 , $K_{sp} = x = [\text{Ca}^{2+}] [\text{CO}_3^{2-}] = [\text{Ca}^{2+}] \times 2$ ($\because \text{CO}_3^{2-}$ mainly coming from Na_2CO_3)

$$\therefore [\text{Ca}^{2+}] = \frac{x}{2}$$

$$\text{For } \text{CaF}_2, K_{sp} = 4y^3 = \left(\frac{x}{2}\right) [\text{F}^-]^2 \Rightarrow [\text{F}^-] = \sqrt{\frac{8y^3}{x}}$$

Check List

Definitions (D)

- D1** pH range of buffer
D2 Buffer capacity
D3 pH range of titration

Formulae (F)

- F1** pH of a solution of a weak polyprotic acid
F2 $[\text{H}^+]$ in a solution containing mixture of weak monoprotic acid & strong acid
F3 $[\text{H}^+]$ in a solution containing mixture of two weak acids
F4 Degree of hydrolysis (h) of polyvalent anion (or cation) of weak acid (or base)
F5 $\text{pH}(\text{PO}_4^{3-})$ [$h < 0.1$]
F6 $\text{pH}(\text{HCO}_3^-)$ [$h < 0.1$]
F7 $\text{pH}(\text{H}_2\text{PO}_4^-)$ & $\text{pH}(\text{HPO}_4^{2-})$
F8 Buffer capacity

- F9** Condition for maximum buffer capacity

Derivation (Der)

- Der1** Equilibrium of a weak polyprotic acid
Der2 Equilibrium of a mixture of weak monoprotic acid & SA
Der3 Equilibrium of a mixture of two weak monoprotic acids
Der4 Hydrolysis of polyvalent anion PO_4^{3-}
Der5 Buffer capacity
Der6 Maximum buffer capacity



Table-1

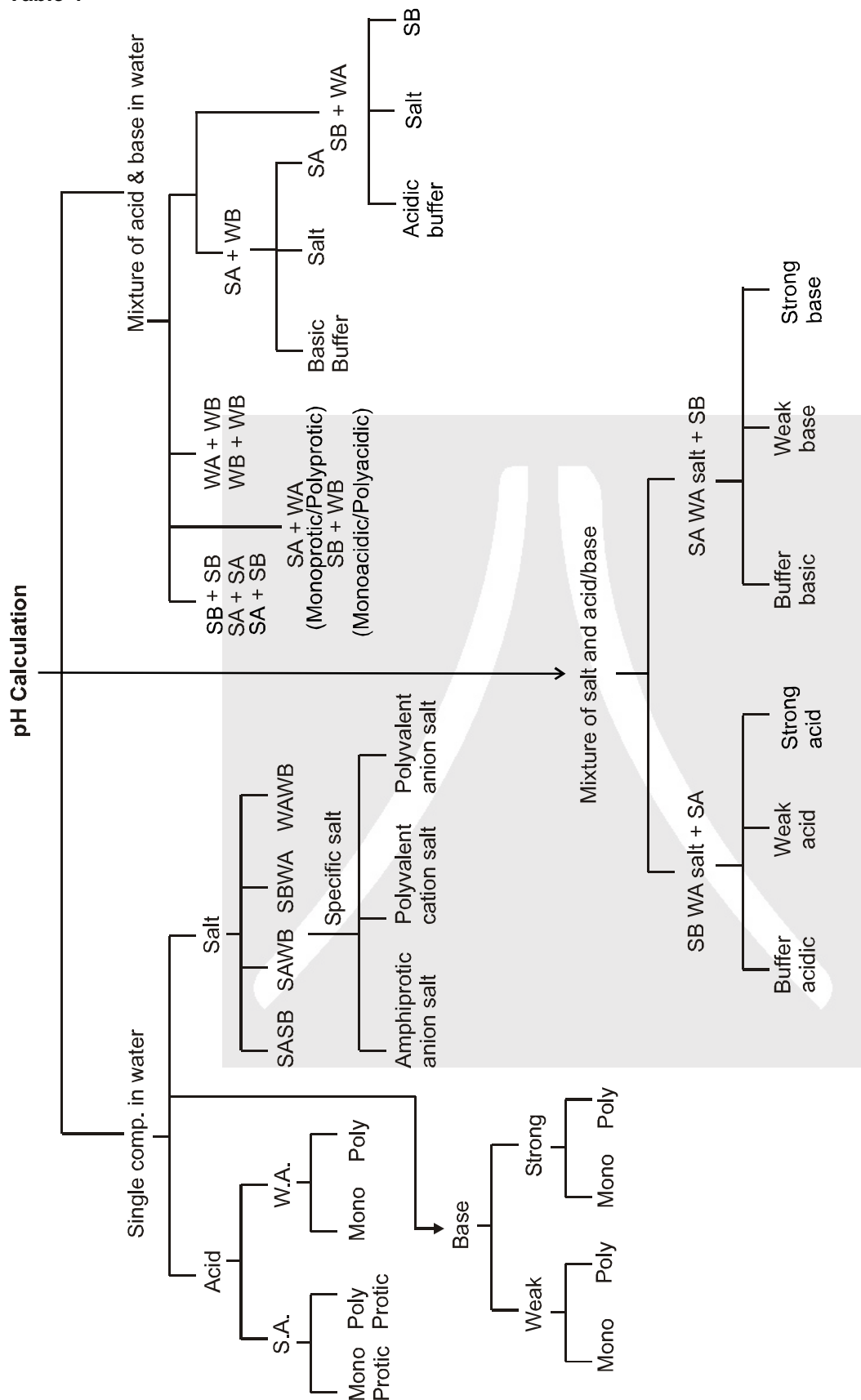
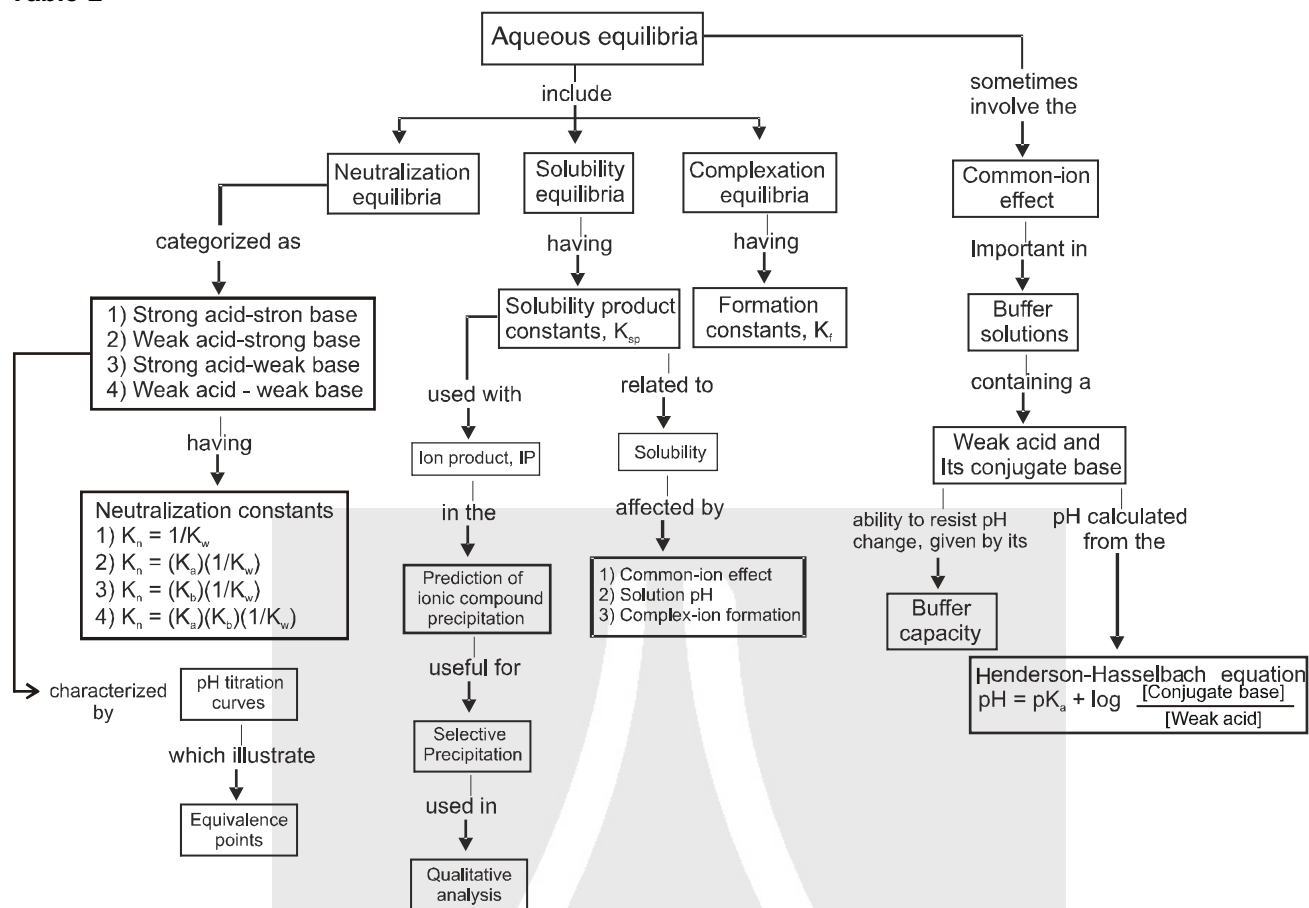




Table-2



MISCELLANEOUS SOLVED PROBLEMS (MSPs)

1. Calculate the pH of solution obtained by mixing 10 mL of 0.1 M HCl and 40 mL of 0.2 M H_2SO_4 .
Take $\log 3.4 = 0.53$

Sol. Given is the case of a mixture of 2 strong acids.

Milli moles of H^+ from HCl = $10 \times 0.1 = 1$

Milli moles of H^+ from $H_2SO_4 = 40 \times 0.2 \times 2 = 16$

\therefore Total millimoles of H^+ in solution = $1 + 16 = 17$

$$\therefore [H^+] = \frac{17}{50} = 3.4 \times 10^{-1} \quad \left(\because [H^+]_f = \frac{\text{Millimoles}_{\text{Total}}}{V_{f \text{ in mL}}} \right)$$

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

$$pH = \mathbf{0.47}$$

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

$$\text{Take } \frac{1}{1099} = 9.1 \times 10^{-4} \text{ \& log 9.1 = 0.96}$$

Sol. Given is the case of a mixture of a strong acid and a strong base.

	HCl	+	NaOH	\rightarrow	NaCl	+	H_2O
Millimoles before reaction	100×0.1		9.9×1		0		0
	= 10		= 9.9				
Millimoles after reaction	0.1		0		9.9		9.9

$$\therefore [H^+] = \text{from left HCl} = \frac{0.1}{109.9} = 9.1 \times 10^{-4} \text{ M}$$

$$\therefore pH = -\log H^+ = -\log 9.1 \times 10^{-4} \Rightarrow pH = \mathbf{3.04}$$

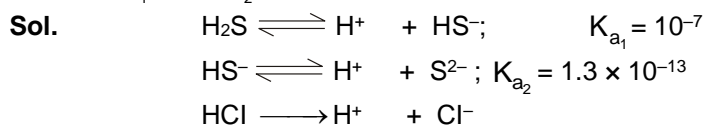


3. Calculate $[H^+]$ in a solution containing 0.1 M $HCOOH$ and 0.1 M $HOCN$. K_a for $HCOOH$ and $HOCN$ are 1.8×10^{-4} and 3.3×10^{-4} . Take $\sqrt{51} = 7.14$.

Sol. Given is the case of a mixture of two weak monoprotic acids.
So, applying direct relation :

$$[H^+] = \sqrt{C_1 K_{a_1} + C_2 K_{a_2}} = \sqrt{0.1 \times 1.8 \times 10^{-4} + 0.1 \times 3.3 \times 10^{-4}} = 7.14 \times 10^{-3} \text{ M}$$

4. A solution contains 0.1 M H_2S and 0.3 M HCl . Calculate the conc. of S^{2-} and HS^- ions in solution. Given K_{a_1} and K_{a_2} for H_2S are 10^{-7} and 1.3×10^{-13} respectively.



Due to common ion effect exerted by H^+ of HCl , the dissociations of H_2S are suppressed and the $[H^+]$ in solution is mainly due to HCl .

$$\therefore K_{a_1} = \frac{[H^+][HS^-]}{[H_2S]}$$

$$\Rightarrow 10^{-7} = \frac{[0.3][HS^-]}{[0.1]} \quad [\because [H^+] \text{ from } HCl = 0.3 \text{ \& } H_2S \text{ would have dissociated negligibly}]$$

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

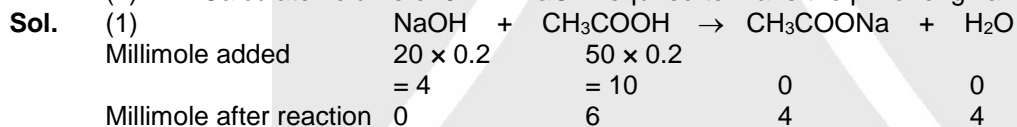
Further $K_{a_2} = \frac{[H^+][S^{2-}]}{[HS^-]} \Rightarrow 1.3 \times 10^{-13} = \frac{[0.3][S^{2-}]}{3.3 \times 10^{-8}}$

$$\therefore [S^{2-}] = \frac{1.3 \times 10^{-13} \times 3.3 \times 10^{-8}}{0.03} = 1.43 \times 10^{-19} \text{ M}$$

5. 20 mL of 0.2 M $NaOH$ are added to 50 mL of 0.2 M acetic acid ($K_a = 1.8 \times 10^{-5}$).
Take $\log 2 = 0.3$, $\log 3 = 0.48$

(1) What is pH of solution ?

(2) Calculate volume of 0.2 M $NaOH$ required to make the pH of original acetic acid solution 4.74.



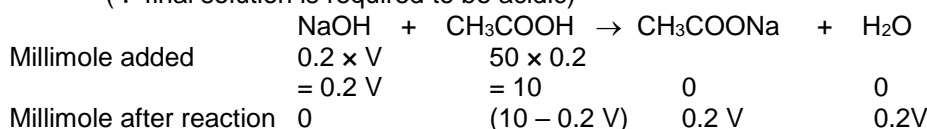
$$\therefore [\text{Molarity}] = \frac{\text{millimole}}{\text{Total volume}}$$

$$\therefore [CH_3COOH] = \frac{6}{70} \quad \& \quad [CH_3COONa] = \frac{4}{70}$$

\Rightarrow Buffer solution consisting of a weak acid & its salt with a strong base.

$$\therefore pH = -\log 1.8 \times 10^{-5} + \log \frac{4/70}{6/70} = 4.56$$

(2) Let V mL of 0.2 M $NaOH$ is required to make pH 4.74. Then, $NaOH$ should be completely used up
 (\because final solution is required to be acidic)



$$\therefore [\text{Acid}] = \frac{10 - 0.2V}{50 + V}; \quad [\text{Salt}] = \frac{0.2V}{50 + V}$$

$$\therefore 4.74 = -\log 1.8 \times 10^{-5} + \log \frac{(0.2V)/(50 + V)}{(10 - 0.2V)/(50 + V)} \quad \therefore V = 25 \text{ mL}$$



6. Calculate the concentration of NH_3 and NH_4Cl presenting a buffer solution of $\text{pH} = 9$, when total concentration of buffering reagents is $0.6 \text{ mol litre}^{-1}$. Take pK_b for $\text{NH}_3 = 4.7$, $\log 2 = 0.3$

Sol. $\text{pOH} = -\log K_b + \log \frac{[\text{Salt}]}{[\text{Base}]} \Rightarrow 5 = 4.7 + \log \frac{a}{b}$

$$\frac{a}{b} = 2 \quad \therefore a = 2b$$

Given $a + b = 0.6$; $2b + b = 0.6$

$\therefore 3b = 0.6$ or $b = 0.2 \text{ mole}$ and $a = 0.4 \text{ mole}$

Thus, $[\text{Salt}] = 0.4 \text{ M}$ and $[\text{Base}] = 0.2 \text{ M}$

7. A solution contains a mixture of Ag^+ (0.10 M) and Hg_2^{2+} (0.10 M) which are to be separated by selective precipitation. Calculate the maximum concentration of iodide ion at which one of them gets precipitated almost completely. What % of that metal ion is precipitated?

K_{sp} of $\text{AgI} = 8.5 \times 10^{-17}$ and K_{sp} of $\text{Hg}_2\text{I}_2 = 2.5 \times 10^{-26}$

- Sol.** The $[\text{I}^-]$ needed for precipitation of Ag^+ and Hg_2^{2+} and are derived as :

For AgI : $[\text{Ag}^+][\text{I}^-] = K_{\text{spAgI}}$

$(0.1)[\text{I}^-] = 8.5 \times 10^{-17}$

$\therefore [\text{I}^-] = 8.5 \times 10^{-16} \text{ M}$ (1)

For Hg_2I_2 : $[\text{Hg}_2^{2+}][\text{I}^-]^2 = 2.5 \times 10^{-26}$

$(0.1)[\text{I}^-]^2 = 2.5 \times 10^{-26}$

$\therefore [\text{I}^-] = 5 \times 10^{-13} \text{ M}$ (2)

Since $[\text{I}^-]$ required for precipitation of AgI is less and thus AgI begins to precipitate first. Also it will continue upto addition of $[\text{I}^-] = 5 \times 10^{-13}$ when Hg_2I_2 begins to precipitate and thus,

Maximum $[\text{I}^-]$ for AgI precipitation $= 5 \times 10^{-13} \text{ M}$

Now at this concentration of I^- , $[\text{Ag}^+]_{\text{left}}$ in solution is $[\text{Ag}^+]_{\text{left}}[\text{I}^-] = (K_{\text{sp}})_{\text{AgI}}$

$\therefore [\text{Ag}^+]_{\text{left}} = \frac{8.5 \times 10^{-17}}{5.0 \times 10^{-13}} = 1.7 \times 10^{-4} \text{ M}$

$\therefore 0.1 \text{ M Ag}^+$ will leave $= 1.7 \times 10^{-4} \text{ M Ag}^+$ in solution

$\therefore \% \text{ of Ag}^+ \text{ precipitated} = \frac{0.1 - 1.7 \times 10^{-4}}{0.1} \times 100 = 99.83\%$

8. Calculate solubility of BaSO_4 when CaSO_4 and BaSO_4 are dissolved in water simultaneously K_{sp} of $\text{CaSO}_4 = p$, K_{sp} of $\text{BaSO}_4 = q$ and simultaneous solubility of CaSO_4 is 'b' mol/litre.

Ans. bq/p

Sol. For BaSO_4 , $[\text{Ba}^{2+}][\text{SO}_4^{2-}] = K_{\text{sp}}$ of $\text{BaSO}_4 = q$

For CaSO_4 , $[\text{Ca}^{2+}][\text{SO}_4^{2-}] = K_{\text{sp}}$ of $\text{CaSO}_4 = p$

$\frac{[\text{Ba}^{2+}]}{[\text{Ca}^{2+}]} = \frac{q}{p} \Rightarrow [\text{Ba}^{2+}] = \frac{bq}{p}$

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

$K_{\text{sp}}(\text{CdS}) = 8 \times 10^{-27}$; $K_{\text{sp}}(\text{ZnS}) = 1 \times 10^{-21}$; $K_a(\text{H}_2\text{S}) = 1.1 \times 10^{-21}$

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

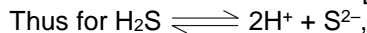
$[\text{Zn}^{2+}][\text{S}^{2-}] < K_{\text{sp}}(\text{ZnS}) = 1 \times 10^{-21}$

(Ionic product)

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

or $[\text{S}^{2-}] < 1 \times 10^{-20} \text{ M}$

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



$K_a = \frac{[\text{H}^+]^2[\text{S}^{2-}]}{[\text{H}_2\text{S}]} = \frac{x^2(1 \times 10^{-20})}{0.1} = 1.1 \times 10^{-21}$

Or $x = [\text{H}^+] = 0.105 \text{ M}$

\therefore No ZnS will precipitate at a concentration of H^+ greater than 0.105 M .



IONIC EQUILIBRIUM-I

आयनिक साम्य-I

Exercise-1

Marked questions are recommended for Revision.

चिन्हित प्रश्न दोहराने योग्य प्रश्न है।

PART - I : SUBJECTIVE QUESTIONS

भाग - I : विषयात्मक प्रश्न (SUBJECTIVE QUESTIONS)

Section (A) : pH calculation : Solutions of polyprotic weak acids, Solutions of Polyacidic weak bases

खण्ड (A) : pH गणना : बहुप्रोटिक दुर्बल अम्ल के विलयन, बहुअम्लीय दुर्बल क्षार के विलयन

Commit to memory :

Solution of a polyprotic weak acid (H_xA) : $pH = \frac{1}{2} (pK_{a_1} - \log C)$ [if $\alpha_1 \leq 0.1$ or 10%] ; $[H_{x-2}A^{2-}] = K_{a2}$

Solution of a polyprotic weak base (B) : $pOH = \frac{1}{2} (pK_{b_1} - \log C)$ [if $\alpha_1 \leq 0.1$ or 10%] ; $[BH_2^{2+}] = K_{b2}$

याद रखने योग्य तथ्य :

बहुप्रोटिक दुर्बल अम्ल (H_xA) का विलयन : $pH = \frac{1}{2} (pK_{a_1} - \log C)$ [यदि $\alpha_1 \leq 0.1$ या 10%] ; $[H_{x-2}A^{2-}] = K_{a2}$

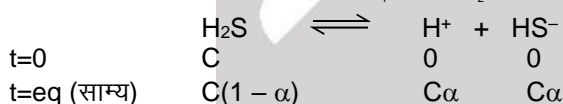
बहुप्रोटिक दुर्बल क्षार (B) का विलयन : $pOH = \frac{1}{2} (pK_{b_1} - \log C)$ [यदि $\alpha_1 \leq 0.1$ या 10%] ; $[BH_2^{2+}] = K_{b2}$

A-1. What is the pH of 0.01 M H_2S solution ? Also determine $[HS^-]$ & $[S^{2-}]$. Given: For H_2S , $K_{a_1} = 9 \times 10^{-8}$, $K_{a_2} = 1.2 \times 10^{-13}$.

H_2S के 0.01 M विलयन का pH क्या है ? $[HS^-]$ और $[S^{2-}]$ भी ज्ञात कीजिए। दिया है: H_2S के लिए, $K_{a_1} = 9 \times 10^{-8}$, $K_{a_2} = 1.2 \times 10^{-13}$.

Ans. $pH = 4.52$, $3 \times 10^{-5} M$, $1.2 \times 10^{-13} M$

Sol. Assuming (मानते हुए) $K_{a_1} \ll K_{a_2}$



$$\alpha = \sqrt{\frac{K_{a_1}}{C}} = \sqrt{\frac{9 \times 10^{-8}}{10^{-2}}} = 3 \times 10^{-3} \quad \Rightarrow \quad [H^+] = C\alpha = 10^{-2} \times 3 \times 10^{-3} = 3 \times 10^{-5} M.$$

$$pH = 5 - \log 3 = 4.52$$

A-2. Calculate the pH of 0.74 g/L aqueous solution of propane-1,2-diamine. Given : pK_{b_1} & pK_{b_2} for base is 4.18 & 7.39 respectively.

प्रोपेन-1,2-डाइएमीन के 0.74 g/L जलीय विलयन का pH परिकलित कीजिए। दिया है कि क्षार के लिये : pK_{b_1} तथा pK_{b_2} क्रमशः 4.18 तथा 7.39 हैं।

Ans. 10.91



Sol. $pOH = \frac{1}{2} (pK_{b_1} - \log C)$; $C = 0.74/74 = 0.01$ M

$$pOH = \frac{1}{2} (4.18 + 2) = 3.09$$

$$pH = 14 - 3.09 = 10.91.$$

Section (B) : pH calculation : Solutions containing mixture of weak monoprotic acid and strong acid, Solutions containing mixture of weak monoacidic base and strong base

खण्ड (B) : pH गणना : दुर्बल एकलप्रोटिक अम्ल व प्रबल अम्ल का मिश्रण रखने वाले विलयन, दुर्बल एकलअम्लीय क्षार व प्रबल क्षार का मिश्रण रखने वाले विलयन

Commit to memory :

Mixture of weak acid (monoprotic) and a strong acid: $[H^+]_f = C_1$ (just not considering the H^+ ions from WA).

Mixture of weak base (monoacidic) and a strong base: $[OH^-]_f = C_1$ (just not considering the H^+ ions from WB).

याद रखने योग्य तथ्य :

दुर्बल अम्ल (एकलप्रोटिक) तथा प्रबल अम्ल का मिश्रण: $[H^+]_f = C_1$ (WA से आने वाले H^+ आयनों को नहीं मानते हुए)।

दुर्बल क्षार (एकलअम्लीय) तथा प्रबल क्षार का मिश्रण: $[OH^-]_f = C_1$ (WB से आने वाले H^+ आयनों को नहीं मानते हुए)।

B-1. Upon passing 0.01 mole HCl gas through 100 mL of 0.05 M Formic acid solution ($K_a = 1.8 \times 10^{-4}$), determine change in pH of solution and $[HCOO^-]$ in resulting solution.

0.05 M फॉर्मिक अम्ल ($K_a = 1.8 \times 10^{-4}$) के 100 mL विलयन में 0.01 मोल HCl गैस प्रवाहित करने पर परिणामी विलयन में विलयन के pH में अन्तर तथा $[HCOO^-]$ का निर्धारण कीजिए।

Ans. $-1.52, 9 \times 10^{-5}$ M.

Sol. Initial (प्रारम्भ में) pH : $\alpha = \sqrt{\frac{K_a}{C}} = 0.06 (< 0.1)$

So, (अतः,) $[H^+] = C\alpha = 0.06 \times 0.05 = 0.003$ M

\therefore pH = 2.52

Final (अन्तिम) pH = $-\log \frac{0.01}{0.1} = 1$ \therefore Change (परिवर्तन) = $1 - 2.52 = -1.52$.

Now, (अब,) $K_a = \frac{[H^+][HCOO^-]}{[HCOOH]} \Rightarrow 1.8 \times 10^{-4} = \frac{0.1 \times [HCOO^-]}{0.05}$

$\Rightarrow [HCOO^-] = 9 \times 10^{-5}$ M

B-2. Determine pH & $[NH_4^+]$ in a solution obtained by mixing equal volumes of 0.02 M KOH solution and 0.2 M $NH_3 \cdot H_2O$ solution ($K_b = 2 \times 10^{-5}$). Also calculate % dissociation of $NH_3 \cdot H_2O$ in the final solution.

0.02 M KOH विलयन तथा 0.2 M $NH_3 \cdot H_2O$ विलयन ($K_b = 2 \times 10^{-5}$) के समान आयतनों को मिलाने पर प्राप्त विलयन में pH तथा $[NH_4^+]$ का निर्धारण कीजिए। अन्तिम विलयन में $NH_3 \cdot H_2O$ का % वियोजन भी परिकलित कीजिए।

Ans. 12, 2×10^{-4} M, 0.2 %

Sol. $pOH = -\log \left(\frac{0.02V}{V+V} \right) = 2$ So, (अतः,) pH = 12 ;

$2 \times 10^{-5} = \frac{10^{-2} \times [NH_4^+]}{0.1} \Rightarrow [NH_4^+] = 2 \times 10^{-4}$ M

$C\alpha = 2 \times 10^{-4} \Rightarrow \alpha = \frac{10^{-4} \times 2}{0.1} = 2 \times 10^{-3} = 0.2 \%$



Section (C) : pH calculation : Solutions containing mixture of weak acids, Solutions containing mixture of weak bases

खण्ड (C) : pH गणना : दुर्बल अम्लों का मिश्रण रखने वाले विलयन, दुर्बल क्षारों का मिश्रण रखने वाले विलयन

Commit to memory :

Mixture of two weak acids (both monoprotic) : $[H^+] = C_1\alpha_1 + C_2\alpha_2 = \sqrt{C_1K_{a_1} + C_2K_{a_2}}$

Mixture of two weak bases (both monoacidic) : $[OH^-] = C_1\alpha_1 + C_2\alpha_2 = \sqrt{C_1K_{b_1} + C_2K_{b_2}}$

याद रखने योग्य तथ्य :

दो दुर्बल अम्लों (दोनों एकलप्रोटिक) का मिश्रण : $[H^+] = C_1\alpha_1 + C_2\alpha_2 = \sqrt{C_1K_{a_1} + C_2K_{a_2}}$

दो दुर्बल क्षारों (दोनों एकलअम्लीय) का मिश्रण : $[OH^-] = C_1\alpha_1 + C_2\alpha_2 = \sqrt{C_1K_{b_1} + C_2K_{b_2}}$

C-1. Calculate $[H^+]$, $[HCOO^-]$ and $[OCN^-]$ in a solution that contains 0.1 M $HCOOH$ ($K_a = 2.4 \times 10^{-4}$) and 0.1 M $HOCN$ ($K_a = 4 \times 10^{-4}$).

0.1 M $HCOOH$ ($K_a = 2.4 \times 10^{-4}$) तथा 0.1 M $HOCN$ ($K_a = 4 \times 10^{-4}$) युक्त विलयन है, इसमें $[H^+]$, $[HCOO^-]$ तथा $[OCN^-]$ की गणना कीजिए।

Ans. $[H^+] = 8 \times 10^{-3} M$, $[HCOO^-] = 3 \times 10^{-3} M$, $[OCN^-] = 5 \times 10^{-3} M$

Sol. $[H^+] = \sqrt{(0.1 \times 2.4 \times 10^{-4}) + (0.1 \times 4 \times 10^{-4})} = 8 \times 10^{-3} M$

For $HCOOH$, ($HCOOH$ के लिये) $K_a = 2.4 \times 10^{-4} = \frac{[H^+][HCOO^-]}{[HCOOH]}$

$\therefore [HCOO^-] = 3 \times 10^{-3} M$

for $HOCN$, ($HOCN$ के लिये) $K_a = 4 \times 10^{-4} = \frac{[H^+][OCN^-]}{[HOCN]}$

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

Section (D) : pH calculation : Solutions containing mixture of weak polyprotic acid and strong acid, Solutions containing mixture of weak Polyacidic base and strong base

खण्ड (D) : pH गणना : दुर्बल बहुप्रोटिक अम्ल व प्रबल अम्ल का मिश्रण रखने वाले विलयन, दुर्बल बहुअम्लीय क्षार व प्रबल क्षार का मिश्रण रखने वाले विलयन

Commit to memory :

Mixture of a polyprotic weak acid and a strong acid : $[H^+] = [H^+]$ from SA

Mixture of a polyprotic weak base and a strong base : $[OH^-] = [OH^-]$ from SB

याद रखने योग्य तथ्य :

बहुप्रोटिक दुर्बल अम्ल तथा प्रबल अम्ल का मिश्रण : $[H^+] = [H^+]$ SA से

बहुप्रोटिक दुर्बल क्षार तथा प्रबल क्षार का मिश्रण : $[OH^-] = [OH^-]$ SB से

D-1. What is $[HS^-]$ & $[S^{2-}]$ in solution of 0.01 M HCl and 0.1 M H_2S ? (Given that for H_2S : $K_{a_1} = 10^{-7}$ and $K_{a_2} = 10^{-14}$)

0.01 M HCl तथा 0.1 M H_2S के विलयन में $[HS^-]$ तथा $[S^{2-}]$ सान्द्रता ज्ञात कीजिए। (दिया गया है कि H_2S के लिए, $K_{a_1} = 10^{-7}$ तथा $K_{a_2} = 10^{-14}$)

Ans. $10^{-6} M$, $10^{-18} M$

Sol. $K_{a_1} = \frac{[H^+][HS^-]}{[H_2S]} = 10^{-7} \Rightarrow 10^{-7} \frac{0.01[HS^-]}{0.1} \Rightarrow [HS^-] = 10^{-6} M.$

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



$$[S^{2-}] = \frac{10^{-21} \times 0.1}{(0.01)^2} = 10^{-18} \text{ M.}$$

Section (E) : pH calculation : Solutions of salt of weak polyprotic acid and strong base, Solutions of salt of weak Polyacidic base and strong acid, Solutions of amphiprotic species.

खण्ड (E) : pH गणना : दुर्बल बहुप्रोटिक अम्ल व प्रबल क्षार के लवण के विलयन, दुर्बल बहुअम्लीय क्षार व प्रबल अम्ल के लवण के विलयन, उभयप्रोटिक स्पीशीज के विलयन

Commit to memory :

Solution containing polyvalent anion (A^{x-}) of weak polyprotic acid (H_xA) :

$$K_{h_1} = \frac{K_w}{K_{a_x}}; h = \sqrt{\frac{K_{h_1}}{C}}; pH = \frac{1}{2}[pK_w + pK_{a_x} + \log C]$$

Solution containing polyvalent cation (BH_y^{y+}) of weak polyprotic base (B) :

$$K_{h_1} = \frac{K_w}{K_{b_y}}; h = \sqrt{\frac{K_{h_1}}{C}}; pH = \frac{1}{2}[pK_w - pK_{b_y} - \log C]$$

$$\text{Solution containing amphiprotic anion of acid } H_xA : pH(H_{x-1}A^-) = \left(\frac{pK_{a_1} + pK_{a_2}}{2} \right); pH(H_{x-2}A^{2-}) = \left(\frac{pK_{a_2} + pK_{a_3}}{2} \right)$$

याद रखने योग्य तथ्य :

दुर्बल बहुप्रोटिक अम्ल (H_xA) का बहुसंयोजी ऋणायन (A^{x-}) युक्त विलयन :

$$K_{h_1} = \frac{K_w}{K_{a_x}}; h = \sqrt{\frac{K_{h_1}}{C}}; pH = \frac{1}{2}[pK_w + pK_{a_x} + \log C]$$

दुर्बल बहुप्रोटिक क्षार (B) का बहुसंयोजी धनायन (BH_y^{y+}) युक्त विलयन :

$$K_{h_1} = \frac{K_w}{K_{b_y}}; h = \sqrt{\frac{K_{h_1}}{C}}; pH = \frac{1}{2}[pK_w - pK_{b_y} - \log C]$$

$$\text{अम्ल } H_xA \text{ का उभयप्रोटिक ऋणायन युक्त विलयन : } pH(H_{x-1}A^-) = \left(\frac{pK_{a_1} + pK_{a_2}}{2} \right); pH(H_{x-2}A^{2-}) = \left(\frac{pK_{a_2} + pK_{a_3}}{2} \right)$$

E-1. Calculate the pH of 0.1 M Na_3A of solution (salt of a tribasic acid H_3A). Assume only first step hydrolysis to be significant. Given : K_{a_1} , K_{a_2} & K_{a_3} for H_3A are 10^{-4} , 10^{-7} & 10^{-9} respectively.

0.1 M Na_3A विलयन (त्रिक्षारीय अम्ल H_3A का लवण) का pH परिकलित कीजिए। माना कि केवल प्रथम पद जलअपघटन सार्थक है। दिया है : H_3A के लिए K_{a_1} , K_{a_2} & K_{a_3} क्रमशः 10^{-4} , 10^{-7} व 10^{-9} हैं।

Ans. 11

Sol. $pH = \frac{1}{2}(14 + pK_{a_3} + \log 0.1) = 7 + \frac{1}{2}(9 - 1) = 11$

E-2. What is the pH of M/20 $KHC_8H_4O_4$ solution ? Given : $H_2C_8H_4O_4$ is a dibasic acid with pK_{a_1} & pK_{a_2} as 2.94 & 5.44 respectively.

M/20 $KHC_8H_4O_4$ विलयन का pH क्या है ? दिया है : $H_2C_8H_4O_4$, pK_{a_1} तथा pK_{a_2} क्रमशः 2.94 व 5.44 के साथ एक द्विक्षारीय अम्ल है।

Ans. $pH = 4.19$

Sol. $NaHCO_3$ [C] = 0.1 M

$$pH = \frac{pK_{a_1} + pK_{a_2}}{2} = \frac{2.94 + 5.44}{2} = 4.19$$



PART - II : ONLY ONE OPTION CORRECT TYPE

भाग - II : केवल एक सही विकल्प प्रकार (ONLY ONE OPTION CORRECT TYPE)

Section (A) : pH calculation : Solutions of polyprotic weak acids, Solutions of Polyacidic weak bases

खण्ड (A) : pH गणना : बहुप्रोटिक दुर्बल अम्ल के विलयन, बहुप्रोटिक दुर्बल क्षार के विलयन

Commit to memory :

Solution of a polyprotic weak acid (H_xA) : $pH = \frac{1}{2} (pK_{a_1} - \log C)$ [if $\alpha_1 \leq 0.1$ or 10%] ; $[H_{x-2}A^{2-}] = K_{a_2}$

Solution of a polyprotic weak base (B) : $pOH = \frac{1}{2} (pK_{b_1} - \log C)$ [if $\alpha_1 \leq 0.1$ or 10%] ; $[BH_2^{2+}] = K_{b_2}$

याद रखने योग्य तथ्य :

बहुप्रोटिक दुर्बल अम्ल (H_xA) का विलयन : $pH = \frac{1}{2} (pK_{a_1} - \log C)$ [यदि $\alpha_1 \leq 0.1$ या 10%] ; $[H_{x-2}A^{2-}] = K_{a_2}$

बहुप्रोटिक दुर्बल क्षार (B) का विलयन : $pOH = \frac{1}{2} (pK_{b_1} - \log C)$ [यदि $\alpha_1 \leq 0.1$ या 10%] ; $[BH_2^{2+}] = K_{b_2}$

A-1. K_{b_1} of N_2H_4 is 4×10^{-6} . Then, what is the acid dissociation constant of $N_2H_5^+$ and $N_2H_6^{2+}$ respectively ?

(A) data insufficient, 4×10^{-6}

(B) data insufficient, 2.5×10^{-8}

(C*) 2.5×10^{-9} , data insufficient

(D) 2.5×10^{-9} , 4×10^{-6}

N_2H_4 का K_{b_1} 4×10^{-6} है। तब, $N_2H_5^+$ तथा $N_2H_6^{2+}$ के अम्ल वियोजन स्थिरांक क्रमशः क्या होंगे ?

(A) आंकड़े अपर्याप्त, 4×10^{-6}

(B) आंकड़े अपर्याप्त, 2.5×10^{-8}

(C*) 2.5×10^{-9} , आंकड़े अपर्याप्त

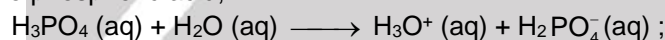
(D) 2.5×10^{-9} , 4×10^{-6}

Sol. $K_{a_1} = \frac{K_w}{K_{b_1}} = \frac{10^{-14}}{4 \times 10^{-6}} = 2.5 \times 10^{-9}$

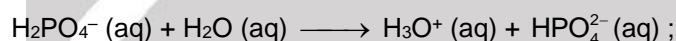
K_{b_2} data not given, so K_{a_2} cannot be determined.

K_{b_2} आंकड़े दिये गये नहीं हैं। अतः K_{a_2} का निर्धारण नहीं हो सकता है।

A-2. For ortho phosphoric acid,



K_{a_1}



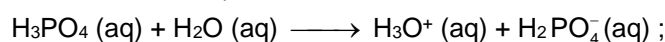
K_{a_2}



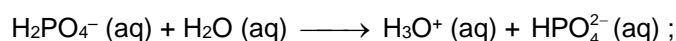
K_{a_3}

The correct order of K_a values is :

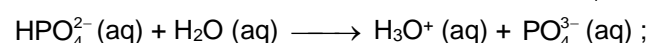
ऑर्थो फॉस्फोरिक अम्ल के लिए,



K_{a_1}



K_{a_2}



K_{a_3}

K_a के मान का सही क्रम है :

(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) $K_{a_1} < K_{a_2} > K_{a_3}$

Sol. For each weak polyprotic acid,

$K_{a_1} > K_{a_2} > K_{a_3}$

हल. प्रत्येक दुर्बल बहुप्रोटिक अम्ल

$K_{a_1} > K_{a_2} > K_{a_3}$



A-3. In a solution of 0.1 M H_3PO_4 acid : (Given $K_{a_1} = 10^{-3}$, $K_{a_2} = 10^{-7}$, $K_{a_3} = 10^{-12}$)

0.1 M H_3PO_4 के एक विलयन में : (दिया गया है, $K_{a_1} = 10^{-3}$, $K_{a_2} = 10^{-7}$, $K_{a_3} = 10^{-12}$)

- (i) Concentration of H_3PO_4 is :
 H_3PO_4 की सांद्रता है :
 (A) 0.01 M (B*) 0.09 M (C) 0.05 M (D) 0.1 M
- (ii) Concentration of H_2PO_4^- is :
 H_2PO_4^- की सांद्रता है :
 (A*) 0.01 M (B) 0.09 M (C) 0.02 M (D) 0.04 M
- (iii) Concentration of HPO_4^{2-} is :
 HPO_4^{2-} की सांद्रता है :
 (A*) 10^{-7} M (B) 10^{-8} M (C) 10^{-3} M (D) 10^{-4} M
- (iv) Concentration of PO_4^{3-} is :
 PO_4^{3-} की सांद्रता है :
 (A) 10^{-20} M (B*) 10^{-17} M (C) 10^{-15} M (D) 10^{-12} M
- (v) pH of solution is :
 विलयन का pH है :
 (A) 1 (B*) 2 (C) 4 (D) 5

Sol. $\text{H}_3\text{PO}_4 \rightleftharpoons \text{H}_2\text{PO}_4^- + \text{H}^+$
 0.1 - x x x

$$K_{a_1} = \frac{x^2}{0.1 - x} = 10^{-3}$$

$x = 0.01 = [\text{H}^+] = [\text{H}_2\text{PO}_4^-]$
 and (तथा) $[\text{HPO}_4^{2-}] = 10^{-7}$ M

$$K_{a_3} = \frac{[\text{H}^+][\text{PO}_4^{3-}]}{[\text{HPO}_4^{2-}]} \Rightarrow 10^{-12} = \frac{(0.01)[\text{PO}_4^{3-}]}{10^{-7}}$$

$$[\text{PO}_4^{3-}] = 10^{-17} \text{ M}$$

$$[\text{OH}^-] = 10^{-12} \text{ M}$$

A-4. Generally, in aqueous solutions of weak polyacidic bases, OH^- ions produced from 2nd ionisation are negligible because of :

- (A) $K_{b_2} \ll K_{b_1}$
 (B) Common ion effect exerted by OH^- ions produced from 1st ionisation.
 (C*) Both (A) & (B)
 (D) None of these

सामान्यतः दुर्बल बहुअम्लीय क्षारों के जलीय विलयनों में दूसरे आयनन से उत्पन्न OH^- आयन निम्न के कारण नगण्य होते हैं :

- (A) $K_{b_2} \ll K_{b_1}$
 (B) प्रथम आयनन से उत्पन्न OH^- आयनों द्वारा आरोपित समआयन प्रभाव
 (C*) दोनों (A) तथा (B)
 (D) इनमें से कोई नहीं

Sol. It is factual. (यह तथ्यात्मक है)



Section (B) : pH calculation : Solutions containing mixture of weak monoprotic acid and strong acid, Solutions containing mixture of weak monoacidic base and strong base

खण्ड (B) : pH गणना : दुर्बल एकलप्रोटिक अम्ल व प्रबल अम्ल का मिश्रण रखने वाले विलयन, दुर्बल एकलअम्लीय क्षार व प्रबल क्षार का मिश्रण रखने वाले विलयन

Commit to memory :

Mixture of weak acid (monoprotic) and a strong acid : $[H^+]_f = C_1$ (just not considering the H^+ ions from WA).

Mixture of weak base (monoacidic) and a strong base : $[OH^-]_f = C_1$ (just not considering the H^+ ions from WB).

याद रखने योग्य तथ्य :

दुर्बल अम्ल (एकलप्रोटिक) तथा प्रबल अम्ल का मिश्रण : $[H^+]_f = C_1$ (WA से आने वाले H^+ आयनों को नहीं मानते हुए)।

दुर्बल क्षार (एकलअम्लीय) तथा प्रबल क्षार का मिश्रण : $[OH^-]_f = C_1$ (WB से आने वाले H^+ आयनों को नहीं मानते हुए)।

B-1. The dissociation constant of acetic acid at a given temperature is 1.69×10^{-5} . The degree of dissociation of 0.01 M acetic acid in the presence of 0.01 M HCl is :
 किसी दिये गये ताप पर एसिटिक अम्ल का वियोजन नियतांक 1.69×10^{-5} है। 0.01 M HCl की उपस्थिति में 0.01 M एसिटिक अम्ल के वियोजन की मात्रा है :

- (A) 1.69×10^{-7} (B) 1.69×10^{-5} (C*) 1.69×10^{-3} (D) 2.9×10^{-2}

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

$t = 0$ 0.01

$t = eq$ 0.01 - x x x

$[H^+] = 0.01 \approx 0.01 M$

$$\therefore K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} \Rightarrow 1.69 \times 10^{-5} = \frac{0.01 \times [CH_3COO^-]}{0.01}$$

$$\therefore [CH_3COO^-] = 1.69 \times 10^{-5} M$$

So, degree of dissociation of CH_3COOH (इसलिए, CH_3COOH के वियोजन की मात्रा) = $\frac{1.69 \times 10^{-5}}{0.01} = 1.69 \times 10^{-3}$

B-2. On adding 100 mL of $10^{-2} M$ NaOH solution to 100 mL of 0.01 M Triethyl amine solution ($K_b = 6.4 \times 10^{-5}$), change in pH of solution with respect to triethylamine solution will be :
 0.01 M ट्राईएथिल एमीन विलयन ($K_b = 6.4 \times 10^{-5}$) के 100 mL में $10^{-2} M$ NaOH विलयन का 100 mL मिलाने पर ट्राईएथिल एमीन विलयन के pH में परिवर्तन होगा :

- (A) - 0.8 (B*) + 0.8 (C) + 1.1 (D) - 1.1

Sol. Initial (प्रारम्भ में) $\Rightarrow [OH^-] = \sqrt{6.4 \times 10^{-5} \times 0.01} = 8 \times 10^{-4} \therefore pH = 10.9$

Final (अन्त में) $\Rightarrow [OH^-] = \frac{10^{-2}}{2} \therefore pH = 11.7$; So, change (अतः परिवर्तन) = + 0.8

B-3. In above question, concentration of Triethyl ammonium ion ($[C_6NH_{16}^+]$) in resulting solution will be :
 उपरोक्त प्रश्न में, परिणामी विलयन में ट्राईएथिल अमोनियम आयन ($[C_6NH_{16}^+]$) की सान्द्रता होगी :

- (A) 100 K_b (B) 200 K_b (C) 10 K_b (D*) K_b

$$\text{Sol. } K_b = \frac{[OH^-][C_6NH_{16}^+]}{[C_6NH_{15}]} \Rightarrow \frac{\frac{10^{-2}}{2}[C_6NH_{16}^+]}{\frac{10^{-2}}{2}} \Rightarrow [C_6NH_{16}^+] = K_b$$



Section (C) : pH calculation : Solutions containing mixture of weak acids, Solutions containing mixture of weak bases

खण्ड (C) : pH गणना : दुर्बल अम्लों का मिश्रण रखने वाले विलयन, दुर्बल क्षारों का मिश्रण रखने वाले विलयन

Commit to memory :

Mixture of two weak acids (both monoprotic) : $[H^+] = C_1\alpha_1 + C_2\alpha_2 = \sqrt{C_1K_{a_1} + C_2K_{a_2}}$

Mixture of two weak bases (both monoacidic) : $[OH^-] = C_1\alpha_1 + C_2\alpha_2 = \sqrt{C_1K_{b_1} + C_2K_{b_2}}$

याद रखने योग्य तथ्य :

दो दुर्बल अम्लों (दोनों एकलप्रोटिक) का मिश्रण : $[H^+] = C_1\alpha_1 + C_2\alpha_2 = \sqrt{C_1K_{a_1} + C_2K_{a_2}}$

दो दुर्बल क्षारों (दोनों एकलअम्लीय) का मिश्रण : $[OH^-] = C_1\alpha_1 + C_2\alpha_2 = \sqrt{C_1K_{b_1} + C_2K_{b_2}}$

C-1. Consider an aqueous solution, 0.1 M each in HOCN, HCOOH, (COOH)₂ and H₃PO₄. For HOCN, we can write : $K_a(\text{HOCN}) = \frac{[H^+][\text{OCN}^-]}{[\text{HOCN}]}$. $[H^+]$ in this equation is :

- (A) H⁺ ions released by HOCN
- (B) Sum of H⁺ ions released by all monoprotic acids
- (C) Sum of H⁺ ions released only the first dissociation of all the acids.
- (D*) Overall H⁺ ion concentration in the solution.

एक जलीय विलयन, HOCN, HCOOH, (COOH)₂ तथा H₃PO₄ प्रत्येक में 0.1 M है।

HOCN के लिए, $K_a(\text{HOCN}) = \frac{[H^+][\text{OCN}^-]}{[\text{HOCN}]}$ लिख सकते हैं। इस समीकरण में $[H^+]$ है :

- (A) HOCN द्वारा मुक्त किये गये H⁺ आयन
- (B) सभी मोनोप्रोटिक अम्लों द्वारा मुक्त H⁺ आयनों का योग
- (C) सभी अम्लों के केवल प्रथम वियोजन से मुक्त H⁺ आयनों का योग
- (D*) विलयन में सम्पूर्ण H⁺ आयन सान्द्रता

Sol. For HOCN⁻, $K_a = \frac{[H^+][\text{OCN}^-]}{[\text{HOCN}]}$; Here $[H^+] = \text{total } H^+ \text{ concentration of solution.}$

हल. HOCN⁻ के लिए, $K_a = \frac{[H^+][\text{OCN}^-]}{[\text{HOCN}]}$; यहाँ $[H^+] = \text{विलयन में कुल } H^+ \text{ सान्द्रता}$

C-2. What are $[H^+]$, $[A^-]$ and $[B^-]$ in a solution that contains 0.03 M HA and 0.1 M HB. K_a for HA and HB are 3.0×10^{-4} and 1.0×10^{-10} respectively.

- (A) $[H^+] = 3 \times 10^{-3} \text{ M}$
- (B) $[A^-] = 3 \times 10^{-3} \text{ M}$
- (C) $[B^-] = 3.33 \times 10^{-9} \text{ M}$
- (D*) All of these

0.03 M HA एवं 0.1 M HB के एक विलयन में $[H^+]$, $[A^-]$ तथा $[B^-]$ क्या हैं ? HA एवं HB के लिए K_a क्रमशः 3.0×10^{-4} तथा 1.0×10^{-10} हैं।

- (A) $[H^+] = 3 \times 10^{-3} \text{ M}$
- (B) $[A^-] = 3 \times 10^{-3} \text{ M}$
- (C) $[B^-] = 3.33 \times 10^{-9} \text{ M}$
- (D*) उपरोक्त सभी

Sol. $[H^+] = \sqrt{K_{a_1} \times C} = \sqrt{3 \times 10^{-4} \times 3 \times 10^{-2}} = 3 \times 10^{-3} \text{ M}$

C-3. pH of a solution obtained by mixing equal volumes of 0.1 M Triethyl amine ($K_b = 6.4 \times 10^{-5}$) & $\frac{4}{45} \text{ M}$ NH₄OH ($K_b = 1.8 \times 10^{-5}$) will be :

NH₄OH ($K_b = 1.8 \times 10^{-5}$) will be :

0.1 M ट्राईएथिल एमीन ($K_b = 6.4 \times 10^{-5}$) तथा $\frac{4}{45} \text{ M}$ NH₄OH ($K_b = 1.8 \times 10^{-5}$) के बराबर आयतनों को मिलाने पर

प्राप्त विलयन की pH होगी :

- (A*) 11.3
- (B) 10.3
- (C) 12.3
- (D) 11.45



Sol. $[\text{OH}^-] = \sqrt{\left(0.1 \times 6.4 + \frac{4 \times 1.8}{45}\right)} \times 10^{-5} = 0.002 \text{ M} \therefore \text{pH} = 11.3$

C-4. At 25°C, K_b for BOH = 1.0×10^{-12} . A 0.01 M solution of BOH has what value of $[\text{OH}^-]$? [16JC110289]
 25°C पर BOH के लिए $K_b = 1.0 \times 10^{-12}$ है। BOH का एक 0.01 M विलयन, $[\text{OH}^-]$ का क्या मान रखता है ?

- (A) $1.0 \times 10^{-6} \text{ M}$ (B*) $\sqrt{2} \times 10^{-7} \text{ M}$ (C) $1.0 \times 10^{-5} \text{ M}$ (D) $2.0 \times 10^{-6} \text{ M}$



$$X_1 \quad X_1 + X_2$$



$$X_2 \quad X_1 + X_2$$

$$X_1 (X_1 + X_2) = 10^{-14}$$

$$\frac{X_2 (X_1 + X_2)}{10^{-2}} = 10^{-12} \Rightarrow X_2 (X_1 + X_2) = 10^{-14}$$

$$\frac{X_1}{X_2} = 1 \Rightarrow X_1 = X_2$$

$$X_1 (X_1 + X_1) = 10^{-14}$$

$$2X_1^2 = 10^{-14} \Rightarrow X_1 = \frac{1}{\sqrt{2}} \times 10^{-7}$$

$$[\text{OH}^-] = 2X_1 = \sqrt{2} \times 10^{-7}$$

Section (D) : pH calculation : Solutions containing mixture of weak polyprotic acid and strong acid, Solutions containing mixture of weak Polyacidic base and strong base

खण्ड (D) : pH गणना : दुर्बल बहुप्रोटिक अम्ल व प्रबल अम्ल का मिश्रण रखने वाले विलयन, दुर्बल बहुअम्लीय क्षार व प्रबल क्षार का मिश्रण रखने वाले विलयन

Commit to memory :

Mixture of a polyprotic weak acid and a strong acid : $[\text{H}^+] = [\text{H}^+]$ from SA

Mixture of a polyprotic weak base and a strong base : $[\text{OH}^-] = [\text{OH}^-]$ from SB

याद रखने योग्य तथ्य :

बहुप्रोटिक दुर्बल अम्ल तथा प्रबल अम्ल का मिश्रण : $[\text{H}^+] = [\text{H}^+]$ SA से

बहुप्रोटिक दुर्बल क्षार तथा प्रबल क्षार का मिश्रण : $[\text{OH}^-] = [\text{OH}^-]$ SB से

D-1. For a solution obtained by mixing equal volumes of 0.02 M KOH solution & 0.2 M B (weak diacidic base; $K_{b1} = 10^{-7}$ & $K_{b2} = 10^{-14}$) solution :

- (A) pH = 12 (B) $[\text{BH}^+] = 10^{-6} \text{ M}$ (C) $[\text{BH}_2^{2+}] = 10^{-18} \text{ M}$ (D*) All of these

0.02 M KOH विलयन तथा 0.2 M B (दुर्बल द्विअम्लीय क्षार ; $K_{b1} = 10^{-7}$ तथा $K_{b2} = 10^{-14}$) विलयन के बराबर आयतनों को मिलाने से प्राप्त विलयन के लिये :

- (A) pH = 12 (B) $[\text{BH}^+] = 10^{-6} \text{ M}$ (C) $[\text{BH}_2^{2+}] = 10^{-18} \text{ M}$ (D*) उपरोक्त सभी

Sol. $[\text{OH}^-] = \frac{0.02}{2} = 0.01 \text{ M} \therefore \text{pH} = 12$

$$10^{-7} = \frac{0.01 [\text{BH}^+]}{0.1} \Rightarrow [\text{BH}^+] = 10^{-6} \text{ M}$$

$$10^{-7} \times 10^{-14} = \frac{(0.01)^2 [\text{BH}_2^{2+}]}{0.1} \Rightarrow [\text{BH}_2^{2+}] = 10^{-18} \text{ M}$$


Section (E) : Salt hydrolysis, pH calculation : Solutions of salt of monoprotic acid and monoacidic base.
खण्ड (E) : लवण जलअपघटन, pH गणना : एकलप्रोटिक अम्ल व एकलअम्लीय क्षार के लवण के विलयन
Commit to memory :

 Salt of strong acid and weak base : $K_h \times K_b = K_w$; $h = \sqrt{\frac{K_h}{c}}$; $\text{pH} = \frac{1}{2} [\text{p}K_w - \text{p}K_b - \log c]$ (valid if $h < 0.1$ or 10%)

 Salt of strong base and weak acid : $K_h \times K_a = K_w$; $h = \sqrt{\frac{K_h}{c}}$; $\text{pH} = \frac{1}{2} [\text{p}K_w + \text{p}K_a + \log c]$ (valid if $h < 0.1$ or 10%)

 Salt of weak acid and weak base : $K_h \times K_a \times K_b = K_w$; $\left(\frac{h}{1-h}\right) = \sqrt{K_h}$; $\text{pH} = \frac{1}{2} [\text{p}K_w + \text{p}K_a - \text{p}K_b]$
याद रखने योग्य तथ्य :

 प्रबल अम्ल तथा दुर्बल क्षार का लवण : $K_h \times K_b = K_w$; $h = \sqrt{\frac{K_h}{c}}$; $\text{pH} = \frac{1}{2} [\text{p}K_w - \text{p}K_b - \log c]$ (मान्य यदि $h < 0.1$ या 10%)

 प्रबल क्षार तथा दुर्बल अम्ल का लवण : $K_h \times K_a = K_w$; $h = \sqrt{\frac{K_h}{c}}$; $\text{pH} = \frac{1}{2} [\text{p}K_w + \text{p}K_a + \log c]$ (मान्य यदि $h < 0.1$ या 10%)

 दुर्बल अम्ल तथा दुर्बल क्षार का लवण : $K_h \times K_a \times K_b = K_w$; $\left(\frac{h}{1-h}\right) = \sqrt{K_h}$; $\text{pH} = \frac{1}{2} [\text{p}K_w + \text{p}K_a - \text{p}K_b]$
E-1. 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 : ($\text{p}K_a$ for $\text{CH}_3\text{COOH} = 4.74$)

 0.2 M NaOH के 100 mL के साथ 0.2 M CH_3COOH के 100 mL को मिश्रित करने पर प्राप्त विलयन का pH होगा :

 (CH_3COOH के लिए $\text{p}K_a = 4.74$)

(A) 4.74

(B*) 8.87

(C) 9.10

(D) 8.57

Sol. $\text{CH}_3\text{COOH} + \text{OH}^- \longrightarrow \text{CH}_3\text{COO}^- + \text{H}_2\text{O}$

t = 0	20	20	
t = eq	—	—	20

 So, $[\text{CH}_3\text{COO}^-] = \frac{20}{200} = 0.1 \text{ M}$
 $\text{pH} = 7 + \frac{1}{2} \text{p}K_a + \frac{1}{2} \log C = 7 + 2.37 + \frac{1}{2} \log 10^{-1} = 7 + 2.37 - 0.5 = 8.87$
Sol. $\text{CH}_3\text{COOH} + \text{OH}^- \longrightarrow \text{CH}_3\text{COO}^- + \text{H}_2\text{O}$

t = 0	20	20	
t = साम्य	—	—	20

 इसलिए, $[\text{CH}_3\text{COO}^-] = \frac{20}{200} = 0.1 \text{ M}$
 $\text{pH} = 7 + \frac{1}{2} \text{p}K_a + \frac{1}{2} \log C = 7 + 2.37 + \frac{1}{2} \log 10^{-1} = 7 + 2.37 - 0.5 = 8.87$
Section (F) : pH calculation : Solutions of salt of weak polyprotic acid and strong base, Solutions of salt of weak Polyacidic base and strong acid, Solutions of amphiprotic species.
खण्ड (F) : pH गणना : दुर्बल बहुप्रोटिक अम्ल व प्रबल क्षार के लवण के विलयन, दुर्बल बहुअम्लीय क्षार व प्रबल अम्ल के लवण के विलयन, उभयप्रोटिक स्पीशीज के विलयन

**Commit to memory :**

Solution containing polyvalent anion (A^{x-}) of weak polyprotic acid (H_xA) :

$$K_{h_1} = \frac{K_w}{K_{a_x}}; h = \sqrt{\frac{K_{h_1}}{C}}; pH = \frac{1}{2}[pK_w + pK_{a_x} + \log C]$$

Solution containing polyvalent cation (BH_y^{y+}) of weak polyprotic base (B) :

$$K_{h_1} = \frac{K_w}{K_{b_y}}; h = \sqrt{\frac{K_{h_1}}{C}}; pH = \frac{1}{2}[pK_w - pK_{b_y} - \log C]$$

Solution containing amphiprotic anion of acid H_xA :

$$pH(H_{x-1}A^-) = \left(\frac{pK_{a_1} + pK_{a_2}}{2} \right); pH(H_{x-2}A^{2-}) = \left(\frac{pK_{a_2} + pK_{a_3}}{2} \right)$$

याद रखने योग्य तथ्य :

दुर्बल बहुप्रोटिक अम्ल (H_xA) का बहुसंयोजी ऋणायन (A^{x-}) युक्त विलयन

$$K_{h_1} = \frac{K_w}{K_{a_x}}; h = \sqrt{\frac{K_{h_1}}{C}}; pH = \frac{1}{2}[pK_w + pK_{a_x} + \log C]$$

दुर्बल बहुप्रोटिक क्षार (B) का बहुसंयोजी धनायन (BH_y^{y+}) युक्त विलयन :

$$K_{h_1} = \frac{K_w}{K_{b_y}}; h = \sqrt{\frac{K_{h_1}}{C}}; pH = \frac{1}{2}[pK_w - pK_{b_y} - \log C]$$

अम्ल H_xA का उभयप्रोटिक ऋणायन युक्त विलयन :

$$pH(H_{x-1}A^-) = \left(\frac{pK_{a_1} + pK_{a_2}}{2} \right); pH(H_{x-2}A^{2-}) = \left(\frac{pK_{a_2} + pK_{a_3}}{2} \right)$$

F-1. For a BH_2Cl_2 solution (chloride salt of a diacidic base B): (Dissociation constants of base are K_{b_1} & K_{b_2}) BH_2Cl_2 विलयन (द्विअम्लीय क्षार B का क्लोराइड लवण) के लिये : (क्षार के वियोजन नियतांक K_{b_1} तथा K_{b_2} हैं) :

- (A) $K_{h_1} \ll K_{h_2}$ (B) $K_{h_1} = \frac{K_w}{K_{b_1}}$ (C*) $K_{h_1} = \frac{K_w}{K_{b_2}}$ (D) $K_{h_2} = \frac{K_{b_1}}{K_w}$

Sol. (A) $K_{h_2} \ll K_{h_1}$ (B) $K_{h_1} = \frac{K_w}{K_{b_2}}$ (D) $K_{h_2} = \frac{K_w}{K_{b_1}}$

F-2. Select the correct statement regarding above solution :

- (A) Anion will undergo hydrolysis producing OH^- & solution is expected to be basic.
 (B) Anion will not undergo hydrolysis & solution is expected to be basic.
 (C*) Cation will undergo hydrolysis producing H_3O^+ & solution is expected to be acidic.
 (D) Cation will undergo hydrolysis producing OH^- & solution is expected to be acidic.

उपरोक्त विलयन के संदर्भ में सही कथन का चयन कीजिए :

- (A) ऋणायन जल अपघटन कर OH^- उत्पन्न करेगा तथा विलयन क्षारीय अपेक्षित है।
 (B) ऋणायन जल अपघटन नहीं देगा तथा विलयन क्षारीय अपेक्षित है।
 (C*) धनायन जल अपघटन कर H_3O^+ उत्पन्न करेगा तथा विलयन अम्लीय अपेक्षित है।
 (D) धनायन जल अपघटन कर OH^- उत्पन्न करेगा तथा विलयन अम्लीय अपेक्षित है।

Sol. $BH_2^{2+} + H_2O \rightarrow BH_2^+ + H_3O^+$

F-3. pH of 0.1 M Na_2HPO_4 and 0.2 M NaH_2PO_4 are respectively: (pK_a for H_3PO_4 are 2.2, 7.2 and 12)
 0.1 M Na_2HPO_4 तथा 0.2 M NaH_2PO_4 का pH क्रमशः निम्न है : (H_3PO_4 के वियोजन के लिये pK_a क्रमशः 2.2, 7.2 तथा 12 हैं।)

- (A) 4.7, 9.6 (B*) 9.6, 4.7 (C) 9.3, 4.4 (D) 4.4, 9.3



Sol. For Na_2HPO_4 , $\text{pH} = \frac{\text{pK}_{a_2} + \text{pK}_{a_3}}{2} = \frac{7.28 + 12}{2} = 9.6$.

For Na_2HPO_4 , $\text{pH} = \frac{\text{pK}_{a_1} + \text{pK}_{a_2}}{2} = \frac{2.2 + 7.2}{2} = 4.7$.

हल. Na_2HPO_4 के लिए, $\text{pH} = \frac{\text{pK}_{a_2} + \text{pK}_{a_3}}{2} = \frac{7.28 + 12}{2} = 9.6$.

Na_2HPO_4 के लिए, $\text{pH} = \frac{\text{pK}_{a_1} + \text{pK}_{a_2}}{2} = \frac{2.2 + 7.2}{2} = 4.7$.

F-4. The pH of which salt solution is independent of its concentration ?

किस लवण विलयन का pH, इसकी सांद्रता से स्वतन्त्र है ?

1. $(\text{CH}_3\text{COO})\text{C}_5\text{H}_5\text{NH}$ 2. NaH_2PO_4 3. Na_2HPO_4 4. NH_4CN

(A*) 1, 2, 3, 4 (B) 1, 4 (C) 2, 3 (D) 1, 2, 3

Sol. pH of amphiprotic salt solutions and weak acid-weak base salt solutions is independent of their concentration.

हल. उभयप्रोटिक लवणों व दुर्बल अम्ल दुर्बल क्षार के लवणों के विलयनों का pH, इनकी सांद्रता पर निर्भर नहीं करता है।

Exercise-2

Marked questions are recommended for Revision.

चिह्नित प्रश्न दोहराने योग्य प्रश्न हैं।

PART - I : ONLY ONE OPTION CORRECT TYPE

भाग-I : केवल एक सही विकल्प प्रकार (ONLY ONE OPTION CORRECT TYPE)

1. In a solution obtained by mixing 100 mL of 0.25 M Triethylamine ($K_b = 6.4 \times 10^{-5}$) & 400 mL of $\frac{M}{18} \text{NH}_4\text{OH}$ ($K_b = 1.8 \times 10^{-5}$) :
- (A) $[\text{NH}_4^+] = 4 \times 10^{-4} \text{ M}$ (B) $[\text{C}_6\text{NH}_{16}^+] = 1.6 \times 10^{-3} \text{ M}$
 (C*) Both (A) & (B) (D) None of these

0.25 M ट्राईएथिलामीन ($K_b = 6.4 \times 10^{-5}$) के 100 mL विलयन तथा $\frac{M}{18} \text{NH}_4\text{OH}$ ($K_b = 1.8 \times 10^{-5}$) के 400 mL

विलयन को मिलाने से प्राप्त एक विलयन में :

- (A) $[\text{NH}_4^+] = 4 \times 10^{-4} \text{ M}$ (B) $[\text{C}_6\text{NH}_{16}^+] = 1.6 \times 10^{-3} \text{ M}$
 (C*) दोनों (A) व (B) (D) इनमें से कोई नहीं

Sol. $[\text{OH}^-] = \sqrt{\frac{0.25}{5} \times 6.4 \times 10^{-5} + \frac{4}{5} \left(\frac{1}{18} \right) \times 1.8 \times 10^{-5}} = 2 \times 10^{-3} \text{ M}$

Now अब, $6.4 \times 10^{-5} = \frac{2 \times 10^{-3} [\text{C}_6\text{NH}_{16}^+]}{\frac{0.25}{5}} \Rightarrow [\text{C}_6\text{NH}_{16}^+] = 1.6 \times 10^{-3} \text{ M}$

and तथा, $1.8 \times 10^{-5} = \frac{2 \times 10^{-3} [\text{NH}_4^+]}{\frac{4}{5} \left(\frac{1}{18} \right)} \Rightarrow [\text{NH}_4^+] = 4 \times 10^{-4} \text{ M}$

2. Ratio of $[\text{HA}^{2-}]$ in 1 L of 0.1 M H_3A solution ($K_{a_1} = 10^{-5}$; $K_{a_2} = 10^{-8}$ & $K_{a_3} = 10^{-11}$) & upon addition of 0.1 mole HCl to it will be :
- 0.1 M H_3A विलयन ($K_{a_1} = 10^{-5}$; $K_{a_2} = 10^{-8}$ तथा $K_{a_3} = 10^{-11}$) के 1 L में तथा इसमें 0.1 मोल HCl मिलाने पर $[\text{HA}^{2-}]$ अनुपात होगा :
- (A) 10 (B) 100 (C) 1000 (D*) 10,000



Sol. Initial प्रारम्भिक : $[HA^{2-}] = 10^{-8} M = K_{a2}$

$$\text{Final अन्तिम : } K_{a1} \times K_{a2} = \frac{[H^+]^2 [HA^{2-}]}{[H_3A]} \quad \therefore 10^{-8} \times 10^{-5} = \frac{[H^+]^2 [HA^{2-}]}{[H_3A]} \Rightarrow [HA^{2-}] = 10^{-12} M$$

$$\text{So, ratio अतः अनुपात} = \frac{10^{-8}}{10^{-12}} = 10^4$$

3. Calculate the degree of hydrolysis and pH of 0.005 M K_2CrO_4 . $K_{a2} = 5 \times 10^{-7}$ for H_2CrO_4 . (It is essentially strong for first ionization)

0.005 M K_2CrO_4 के जल-अपघटन की मात्रा व pH परिकलित कीजिए। H_2CrO_4 के लिए $K_{a2} = 5 \times 10^{-7}$ (यह प्रथम आयनन के लिए अनिवार्य रूप से प्रबल है)

$$(A^*) h = 2 \times 10^{-3}$$

$$(B) h = 0.01$$

$$(C) pH = 5$$

$$(D) pH = 9.7$$

Sol. $CrO_4^{2-} + H_2O \rightleftharpoons HCrO_4^- + OH^-$

$$K_h = \frac{K_w}{K_a} = 2 \times 10^{-8} \quad \text{and तथा} \quad K_h = Ch^2 = 2 \times 10^{-8}$$

$$\Rightarrow h^2 = \frac{2 \times 10^{-8}}{0.005} \quad \therefore h = 2 \times 10^{-3}$$

$$\therefore [OH^-] = Ch = 0.005 \times 2 \times 10^{-3} = 10^{-5} M \quad \therefore pOH = 5 \text{ \& व } pH = 9$$

PART - II : SINGLE AND DOUBLE VALUE INTEGER TYPE

भाग - II : एकल एवं द्वि-पूर्णांक मान प्रकार (SINGLE AND DOUBLE VALUE INTEGER TYPE)

1. For a solution of weak triprotic acid H_3A ($K_{a1} \gg K_{a2}, K_{a3}$; $K_{a2} = 10^{-8}$; $K_{a3} = 10^{-13}$), $[A^{3-}] = 10^{-17} M$. Determine pH of solution. Report your answer as '0', if you find data insufficient.

दुर्बल त्रिप्रोटिक अम्ल H_3A ($K_{a1} \gg K_{a2}, K_{a3}$; $K_{a2} = 10^{-8}$; $K_{a3} = 10^{-13}$), के विलयन के लिए $[A^{3-}] = 10^{-17} M$ है। विलयन के pH का निर्धारण कीजिए। अपना उत्तर 0 के रूप में दीजिए, यदि आपको आंकड़े अपर्याप्त लगते हैं।

Ans. 4

Sol. $HA^{2-} \rightleftharpoons H^+ + A^{3-}; \quad K_{a3} = 10^{-13}$

$$t = \text{eqसाम्य } 10^{-8} \quad 10^{-17}$$

$$\frac{[H^+] \times 10^{-17}}{10^{-8}} = 10^{-13}$$

$$\text{So अतः, } [H^+] = 10^{-4} M \quad \therefore pH = 4$$

2. Calculate $[H^+]$ in a 0.2 M solution of dichloroacetic acid ($K_a = 5 \times 10^{-2}$) that also contains 0.05 M H_2SO_4 . Report your answer after multiplying it by 400.

0.05 M H_2SO_4 युक्त डाइक्लोरोएसिटिक अम्ल ($K_a = 5 \times 10^{-2}$) के 0.2 M विलयन में $[H^+]$ की गणना कीजिए। अपना उत्तर 400 से गुणा करके दीजिए।

Ans. 60

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

t = 0	0.2		0.1
t = eq	$0.2(1 - \alpha)$	0.2α	$0.1 + 0.2\alpha$

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{0.2\alpha(0.1 + 0.2\alpha)}{0.2(1 - \alpha)} \quad \dots(1)$$

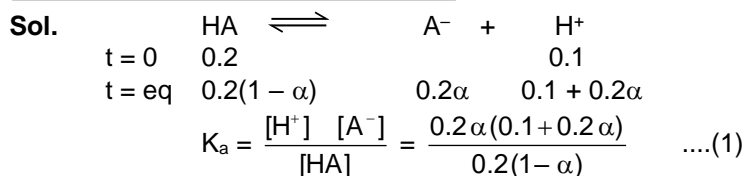
$$\text{Expecting } \alpha \ll 1, 5 \times 10^{-2} = \frac{0.2\alpha \times 0.1}{0.2}$$

$$\therefore \alpha = 0.5 \text{ (not negligible)}$$

So, solve quadratic (1) & get $\alpha = 0.25$

$$\therefore [H^+] = 0.1 + 0.2 \times 0.25 = 0.15 M$$

$$\text{Ans. } 0.15 \times 400 = 60$$



आपेक्षिक रूप से $\alpha \ll 1$, $5 \times 10^{-2} = \frac{0.2\alpha \times 0.1}{0.2}$

$\therefore \alpha = 0.5$ (नगण्य नहीं)

अतः द्विघात समीकरण (1) को हल करने पर हमें प्राप्त होता है $\alpha = 0.25$

$\therefore [H^+] = 0.1 + 0.2 \times 0.25 = 0.15 \text{ M}$

Ans. $0.15 \times 400 = 60$

- 3.** Calculate the ratio of concentrations of HCOO⁻ & OCN⁻ ions in a solution containing 0.1 M HCOOH ($K_a = 1.8 \times 10^{-4}$) and 0.1 M HOCN ($K_a = 4 \times 10^{-4}$). If simplest ratio is a : b, report your answer as (a + b).
0.1 M HCOOH ($K_a = 1.8 \times 10^{-4}$) तथा 0.1 M HOCN ($K_a = 4 \times 10^{-4}$) युक्त एक विलयन में HCOO⁻ तथा OCN⁻ की सान्द्रताओं का अनुपात परिकलित कीजिए। यदि सरलतम अनुपात a : b है, तो अपना उत्तर (a + b) के रूप में दीजिए।

Ans. 29 (actual answer = 9 : 20)

Sol. $[H^+]$ is the same for equilibria of both acids.

Now, let $[HCOO^-] = a \text{ M}$ and $[OCN^-] = b \text{ M}$

$$\therefore \frac{[H^+] \times a}{0.1} = 1.8 \times 10^{-4} \quad \& \quad \frac{[H^+] \times b}{0.1} = 4 \times 10^{-4} \Rightarrow \frac{a}{b} = \frac{9}{20}$$

So, (a + b) = 29

$[H^+]$ दोनों अम्लों के साम्यों के लिए समान है

अब माना $[HCOO^-] = a \text{ M}$ तथा $[OCN^-] = b \text{ M}$

$$\therefore \frac{[H^+] \times a}{0.1} = 1.8 \times 10^{-4} \quad \text{तथा} \quad \frac{[H^+] \times b}{0.1} = 4 \times 10^{-4} \Rightarrow \frac{a}{b} = \frac{9}{20}$$

अतः, (a + b) = 29

- 4.** In a solution containing 0.01 M HCl and 0.1 M H₂CO₃, ratio of $[H^+]$ produced from strong acid & weak acid respectively is: 1. Report your answer as x/500. Given : K_{a_1} & K_{a_2} of H₂CO₃ are 4×10^{-7} & 4×10^{-11} respectively.

0.01 M HCl तथा 0.1 M H₂CO₃ युक्त एक विलयन में प्रबल अम्ल तथा दुर्बल अम्ल से उत्पन्न $[H^+]$ का अनुपात क्रमशः 1 है। अपना उत्तर x/500 के रूप में दीजिए। दिया है : H₂CO₃ के लिए K_{a_1} & K_{a_2} क्रमशः 4×10^{-7} व 4×10^{-11} है।

Ans. 5

Sol. $4 \times 10^{-7} = \frac{0.01 \times [HCO_3^-]}{0.1} \Rightarrow [H^+]_{\text{from weak acid}} = [HCO_3^-] = 4 \times 10^{-6} \text{ M}$

$$\therefore \text{Ratio} = \frac{0.01}{4 \times 10^{-6}} = \frac{2500}{1} = x$$

So, answer = $\frac{x}{500} = 5$.

Sol. $4 \times 10^{-7} = \frac{0.01 \times [HCO_3^-]}{0.1} \Rightarrow [H^+]_{\text{दुर्बल अम्ल से}} = [HCO_3^-] = 4 \times 10^{-6} \text{ M}$

$$\therefore \text{अनुपात} = \frac{0.01}{4 \times 10^{-6}} = \frac{2500}{1} = x$$

अतः, उत्तर = $\frac{x}{500} = 5$.



5. Calculate the change in pH of 0.1 M Na_2HA solution after diluting it to ten times the original volume. (Given that for H_3A : $K_{a_1} = 10^{-4}$, $K_{a_2} = 10^{-7}$, $K_{a_3} = 10^{-11}$)

0.1 M Na_2HA विलयन के pH में अन्तर, वास्तविक विलयन की अपेक्षा दस गुना तनु करने के पश्चात् परिकलित कीजिए।
(दिया है कि H_3A के लिए : $K_{a_1} = 10^{-4}$, $K_{a_2} = 10^{-7}$, $K_{a_3} = 10^{-11}$)

Ans. 0

Sol. pH of solutions of amphiprotic species is independent of concentration of solution.

उभयप्रोटिक स्पीशीज के विलयनों की pH विलयन की सान्द्रता से स्वतन्त्र होती है।

6. What is the pOH of a 0.5 M Na_3PO_4 solution ? Report your answer as $10 \times \text{pOH}$.

($K_{a_1} = 7.5 \times 10^{-3}$, $K_{a_2} = 6.2 \times 10^{-8}$, $K_{a_3} = 4 \times 10^{-13}$)

0.5 M Na_3PO_4 विलयन का pOH क्या है ? अपना उत्तर $10 \times \text{pOH}$ के रूप में दीजिए।

($K_{a_1} = 7.5 \times 10^{-3}$, $K_{a_2} = 6.2 \times 10^{-8}$, $K_{a_3} = 4 \times 10^{-13}$)

Ans. 10

Sol. $\text{PO}_4^{3-} + \text{H}_2\text{O} \rightleftharpoons \text{HPO}_4^{2-} + \text{OH}^-$; $K_{h_1} = \frac{K_w}{K_{a_3}} = \frac{1}{40}$

t = eq $0.5(1-h)$ $0.5h$ $0.5h$

$$\frac{0.5h^2}{1-h} = \frac{1}{40} \quad \therefore h = 0.2.$$

$\therefore [\text{OH}^-] = 0.5h = 0.5 \times 0.2 = 0.1 \text{ M}.$

$\therefore \text{pOH} = -\log_{10}(0.1) = 1.$

PART - III : ONE OR MORE THAN ONE OPTIONS CORRECT TYPE

भाग - III : एक या एक से अधिक सही विकल्प प्रकार

1. If K_{a_1} and K_{a_2} of H_2SO_4 are 10^{-2} and 10^{-6} respectively at a certain temperature, then :
(A*) $K_{a_1} > K_{a_2}$ because it is easy to abstract H^+ from H_2SO_4 and less easy to abstract H^+ from HSO_4^- .
(B*) K_{a_1} and K_{a_2} may be measured in acetic acid.
(C) K_{a_1} and K_{a_2} are measured in H_2O .
(D*) the H^+ ion conc. of 0.01 M H_2SO_4 will be less than 0.02 M.
यदि एक निश्चित ताप पर H_2SO_4 के K_{a_1} तथा K_{a_2} क्रमशः 10^{-2} तथा 10^{-6} हैं, तब :
(A*) $K_{a_1} > K_{a_2}$ क्योंकि H_2SO_4 से H^+ का हटना आसान है तथा HSO_4^- से H^+ का हटना कम आसान है।
(B*) K_{a_1} तथा K_{a_2} के ये मान एसीटिक अम्ल में मापे जा सकते हैं।
(C) जल में K_{a_1} तथा K_{a_2} को मापते हैं।
(D*) 0.01 M H_2SO_4 के H^+ आयन की सान्द्रता 0.02 M की अपेक्षा कम होती है।
- Sol. H_2SO_4 is a strong acid and it completely dissociated in H_2O . Hence its K_{a_1} and K_{a_2} are determined in CH_3COOH .
Also H_2SO_4 is neutral while HSO_4^- because the $-ve$ charge has more affinity towards H^+ ion. Hence choices (A) and (B) are correct while (C) is incorrect.
- हल. H_2SO_4 एक प्रबल अम्ल हैं तथा H_2O में यह पूर्ण रूप से वियोजित हो जाता है। अतः CH_3COOH में K_{a_1} तथा K_{a_2} ज्ञात किये जाते हैं। साथ ही H_2SO_4 उदासीन है व जबकि HSO_4^- क्योंकि H^+ आयन की ओर $-ve$ आवेश अधिक बंधुता रखता हैं। अतः विकल्प (A) व (B) सही हैं जबकि (C) गलत हैं।
2. When 0.1 mole solid NaOH is added in 1 L of 0.1 M $\text{NH}_3(\text{aq})$ ($K_b = 2 \times 10^{-5}$), then select the correct statement(s) :
(A*) degree of dissociation of NH_3 approaches to zero.
(B*) change in pH by adding NaOH would be 1.85.
(C) In solution, $[\text{Na}^+] = 0.1 \text{ M}$, $[\text{NH}_3] = 0.1 \text{ M}$, $[\text{OH}^-] = 0.2 \text{ M}$.
(D*) on addition of OH^- , K_b of NH_3 does not changes.



जब 0.1 मोल ठोस NaOH को 0.1 M जलीय NH_3 ($K_b = 2 \times 10^{-5}$) के 1 लीटर में मिलाया जाता है, तब सही कथन(नों) का चयन कीजिए :

- (A*) NH_3 के वियोजन की मात्रा लगभग शून्य हो जाती है।
 (B*) NaOH मिलाने पर pH में परिवर्तन 1.85 होगा।
 (C) विलयन में, $[\text{Na}^+] = 0.1 \text{ M}$, $[\text{NH}_3] = 0.1 \text{ M}$, $[\text{OH}^-] = 0.2 \text{ M}$.
 (D*) OH^- के मिलाने से NH_3 के K_b के मान में कोई परिवर्तन नहीं होता है।

Sol. Initial $\text{pOH} = \frac{1}{2} (\text{p}K_b - \log C) = \frac{1}{2} (5 - \log 2 - \log 0.1) = 2.85$

After adding NaOH, pOH of solution = 1
 Change in $\text{pOH} = 1.85$

हल. प्रारम्भिक $\text{pOH} = \frac{1}{2} (\text{p}K_b - \log C) = \frac{1}{2} (5 - \log 2 - \log 0.1) = 2.85$

NaOH मिलाने के बाद, pOH का विलयन = 1
 pOH में परिवर्तन = 1.85

3. Which of the following solutions when added to 1L of a 0.01 M CH_3COOH solution will cause no change in the degree of dissociation of CH_3COOH and pH of the solution ? $K_a = 1.6 \times 10^{-5}$ for CH_3COOH ?
 निम्न में से किस विलयन को 0.01 M CH_3COOH के 1 L विलयन में मिलाने पर CH_3COOH के वियोजन की मात्रा में तथा विलयन के pH में कोई परिवर्तन नहीं आता है ? (CH_3COOH के लिए $K_a = 1.6 \times 10^{-5}$)

- (A*) 0.6 mM HCOOH ($K_a = 8 \times 10^{-4}$) (B) 0.1 M CH_3COONa
 (C*) 0.4 mM HCl (D*) 0.01 M CH_3COOH

Sol. (A) In 0.6 m M HCOOH solution

$$K_a = \frac{[\text{H}^+]^2}{C - [\text{H}^+]} \Rightarrow 8 \times 10^{-4} = \frac{[\text{H}^+]^2}{6 \times 10^{-4} - [\text{H}^+]}$$

$\therefore [\text{H}^+] = 4 \times 10^{-4} \text{ M.}$

So solution in (A), (C) & (D) are ISOHYDRIC.

हल. (A) 0.6 m M HCOOH विलयन में

$$K_a = \frac{[\text{H}^+]^2}{C - [\text{H}^+]} \Rightarrow 8 \times 10^{-4} = \frac{[\text{H}^+]^2}{6 \times 10^{-4} - [\text{H}^+]}$$

$\therefore [\text{H}^+] = 4 \times 10^{-4} \text{ M.}$

अतः (A), (C) तथा (D) के विलयन समअम्लीय (ISOHYDRIC) हैं।

Exercise-3

PART - I : JEE (ADVANCED) / IIT-JEE PROBLEMS (PREVIOUS YEARS)

भाग - I : JEE (ADVANCED) / IIT-JEE (पिछले वर्षों) के प्रश्न

* Marked questions may have more than one correct option.

* चिह्नित प्रश्नों के एक से अधिक सही विकल्प हो सकते हैं।

1. Will the pH of water be same at 4°C and 25°C ? Explain.
 क्या 4°C तथा 25°C पर जल का pH समान है ? वर्णन कीजिए।

[JEE-2003, 2/60]

[JEE-2003, 2/60]

Ans. It will not be same at two different temperatures.
 दो भिन्न तापमानों पर यह समान नहीं होगा।

Sol. At 25°C , Ionic product of water (K_w) = 1×10^{-14}

$\therefore [\text{H}^+] \times [\text{OH}^-] = 1 \times 10^{-14}$ or $-\log [\text{H}^+] - \log [\text{OH}^-] = 14$

$\therefore \text{pH} + \text{pOH} = 14$

It is neutral compound, so in it $\text{pH} = \text{pOH} = 7$ at 25°C . On decreasing the temperature, K_w decreases (since dissociation of water into H^+ and OH^- ions is endothermic; according to Van't Hoff equation), so $\text{p}K_w$ increases. Hence at 4°C $\text{p}K_w$ is greater than at 25°C and at greater $\text{p}K_w$, pH will be greater, i.e. at 4°C , pH of water is greater than 7.



हल. 25°C पर, जल का आयनिक गुणनफल (K_w) = 1×10^{-14}

$$\therefore [H^+] \times [OH^-] = 1 \times 10^{-14} \quad \text{या} \quad -\log [H^+] - \log [OH^-] = 14$$

$$\therefore \text{pH} + \text{pOH} = 14$$

यह उदासीन यौगिक है, अतः इसमें 25°C पर $\text{pH} = \text{pOH} = 7$ है। तापमान घटाने पर K_w घटता है (चूंकि जल का H^+ व OH^- में वियोजन ऊष्माशोषी होता है; वॉण्ट हॉफ समीकरण से), अतः $\text{p}K_w$ बढ़ता है। अतः 4°C पर $\text{p}K_w$; 25°C की तुलना में अधिक होता है तथा उच्च $\text{p}K_w$ पर, pH उच्च होगी अतः 4°C पर जल की $\text{pH} = 7$ से अधिक होती है।

2. A weak acid HX at 25°C has the dissociation constant 1×10^{-5} . It forms a salt NaX on reaction with caustic soda. The percentage hydrolysis of 0.1 M solution of NaX is : [JEE-2004(S), 3/84]

एक दुर्बल अम्ल का वियोजन नियतांक 25°C पर 1×10^{-5} M है। यह कास्टिक सोडा के साथ अभिक्रिया कर एक लवण NaX बनाता है। NaX के 0.1 M विलयन का प्रतिशत जल-अपघटन है : [JEE-2004(S), 3/84]

- (A) 0.0001% (B*) 0.01% (C) 0.1% (D) 0.15%

Sol. NaX is a salt of weak acid and strong base.

$$\therefore \text{Hydrolysis constant of NaX is } K_h = \frac{K_w}{K_a} = \frac{1 \times 10^{-14}}{10^{-5}} = 1 \times 10^{-9}$$

For this type of salt, $K_h = Ch^2$

C = molar concentration

h = degree of hydrolysis

$$\therefore 1 \times 10^{-9} = 0.1 \times h^2$$

$$\text{or } h^2 = \frac{1 \times 10^{-9}}{0.1} = 1 \times 10^{-8} \quad h = 1 \times 10^{-4}$$

$$\therefore \text{Percentage hydrolysis of NaX salt} = 1 \times 10^{-4} \times 100 = 1 \times 10^{-2} = 0.01\%$$

हल. NaX दुर्बल अम्ल तथा प्रबल क्षार का लवण है।

$$\therefore \text{NaX का जल अपघटन नियतांक } K_h = \frac{K_w}{K_a} = \frac{1 \times 10^{-14}}{10^{-5}} = 1 \times 10^{-9}$$

इस प्रकार के लवण के लिए $K_h = Ch^2$

C = मोलर सान्द्रता

h = जल अपघटन की कोटि

$$\therefore 1 \times 10^{-9} = 0.1 \times h^2$$

$$\text{या } h^2 = \frac{1 \times 10^{-9}}{0.1} = 1 \times 10^{-8} \quad h = 1 \times 10^{-4}$$

$$\therefore \text{NaX लवण का प्रतिशत में जल अपघटन} = 1 \times 10^{-4} \times 100 = 1 \times 10^{-2} = 0.01\%$$

3. The dissociation constant of a substituted benzoic acid at 25°C is 1.0×10^{-4} . The pH of 0.01 M solution of its sodium salt is : [JEE-2009, 4/160]

एक प्रतिस्थापित बेन्जोइक अम्ल (substituted benzoic acid) के 25°C पर वियोजन स्थिरांक (dissociation constant) का मान 1.0×10^{-4} है। इसके 0.01 M सोडियम लवण के विलयन का pH है : [JEE-2009, 4/160]

Ans. 8

Sol. Given (दिया गया है) $K_a = 10^{-4}$

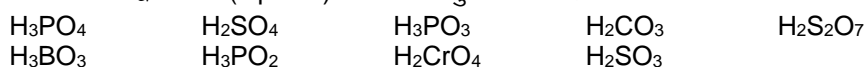
$$\text{p}K_a = 4$$

$$C = 0.01 \text{ M}$$

$$\text{pH} = 7 + \frac{1}{2} \text{p}K_a + \frac{1}{2} \log C = 7 + \frac{1}{2} (4) + \frac{1}{2} (-2) = 8 \quad \text{Ans.}$$

4. The total number of diprotic acids among the following is : [JEE 2010, 3/163]

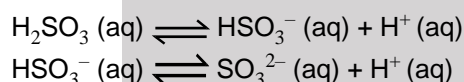
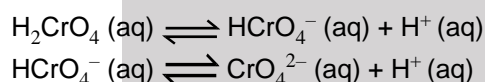
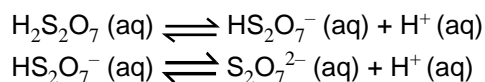
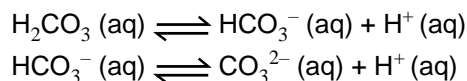
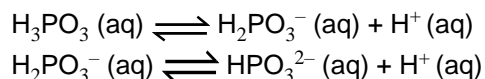
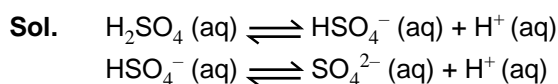
निम्न में से द्विप्रोटिक (diprotic) अम्लों की कुल संख्या है :



Ans. 6

Hint : Acid having two ionizable hydrogen atoms are diprotic acids.

संकेत : अम्ल जो दो आयनित होने वाले हाइड्रोजन परमाणु रखते हैं, वे द्विप्रोटिक अम्ल होते हैं।



So, H_2SO_4 , H_3PO_3 , H_2CO_3 , $\text{H}_2\text{S}_2\text{O}_7$, H_2CrO_4 and H_2SO_3 are diprotic acids.

अतः H_2SO_4 , H_3PO_3 , H_2CO_3 , $\text{H}_2\text{S}_2\text{O}_7$, H_2CrO_4 तथा H_2SO_3 द्विप्रोटिक अम्ल हैं।

5. Amongst the following, the total number of compounds whose aqueous solution turns red litmus paper blue is : [JEE-2010, 3/163]

निम्न के बीच में वे यौगिक, जिनके जलीय विलयन लाल लिटमस को नीला करते हैं, उनकी कुल संख्या है :

[JEE-2010, 3/163]

KCN	K_2SO_4	$(\text{NH}_4)_2\text{C}_2\text{O}_4$	NaCl	$\text{Zn}(\text{NO}_3)_2$
FeCl_3	K_2CO_3	NH_4NO_3	LiCN	

Ans.

3

Sol.

Basic solutions will convert red litmus blue.

$\left. \begin{array}{l} \text{KCN} \\ \text{K}_2\text{CO}_3 \\ \text{LiCN} \end{array} \right\}$ their aqueous solution will be basic due to anionic hydrolysis.

हल.

क्षारीय विलयन, लाल लिटमस को नीला करते हैं।

$\left. \begin{array}{l} \text{KCN} \\ \text{K}_2\text{CO}_3 \\ \text{LiCN} \end{array} \right\}$ इन लवणों का जलीय विलयन, ऋणायनिक जलअपघटन के कारण क्षारीय होगा।

PART - II : JEE (MAIN) (PREVIOUS YEARS)

भाग - II : JEE (MAIN) (पिछले वर्षों) के प्रश्न

JEE(MAIN) OFFLINE PROBLEMS

1. In aqueous solution, the ionization constants for carbonic acid are : [AIEEE-2010, 4/144]

$$K_1 = 4.2 \times 10^{-7} \text{ and } K_2 = 4.8 \times 10^{-11}$$

Select the correct statement for a saturated 0.034 M solution of the carbonic acid.

- (1) The concentration of CO_3^{2-} is 0.034 M.
- (2) The concentration of CO_3^{2-} is greater than that of HCO_3^- .
- (3*) The concentration of H^+ and HCO_3^- are approximately equal.
- (4) The concentration of H^+ is double that of CO_3^{2-} .



कार्बोनिक अम्ल के लिए जलीय विलयन में आयनन स्थिरांक हैं :

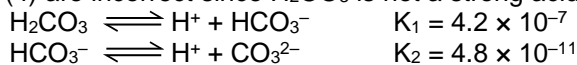
[AIEEE-2010, 4/144]

$$K_1 = 4.2 \times 10^{-7} \text{ तथा } K_2 = 4.8 \times 10^{-11}$$

कार्बोनिक अम्ल के एक संतृप्त 0.034 M विलयन के लिए सही कथन का चुनाव कीजिए।

- (1) CO_3^{2-} की सान्द्रता 0.034 M है। (2) CO_3^{2-} की सान्द्रता, HCO_3^- की सान्द्रता से अधिक है।
 (3*) H^+ तथा HCO_3^- की सान्द्रताएँ लगभग बराबर हैं। (4) H^+ की सान्द्रता, CO_3^{2-} की सान्द्रता से दुगुनी है।

Sol. (1) and (4) are incorrect since H_2CO_3 is not a strong acid.

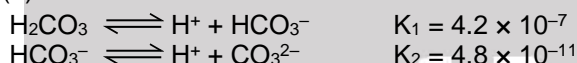


$\therefore K_1 \gg K_2$, so H^+ produced from IInd ionisation can be neglected as compared to those produced in Ist ionisation.

$\therefore [\text{H}^+] = [\text{HCO}_3^-]$ (from Ist ionisation)

Also, $[\text{CO}_3^{2-}] \ll [\text{HCO}_3^-]$ (\therefore IInd ionisation will occur upto negligible extent).

Sol. (1) तथा (4) विकल्प गलत है क्योंकि H_2CO_3 प्रबल अम्ल नहीं है।



$\therefore K_1 \gg K_2$, अतः IInd आयनन से उत्पन्न H^+ आयन Ist आयनन से उत्पन्न H^+ आयनों की तुलना में नगण्य हो सकते हैं।

$\therefore [\text{H}^+] = [\text{HCO}_3^-]$ (Ist आयनन से)

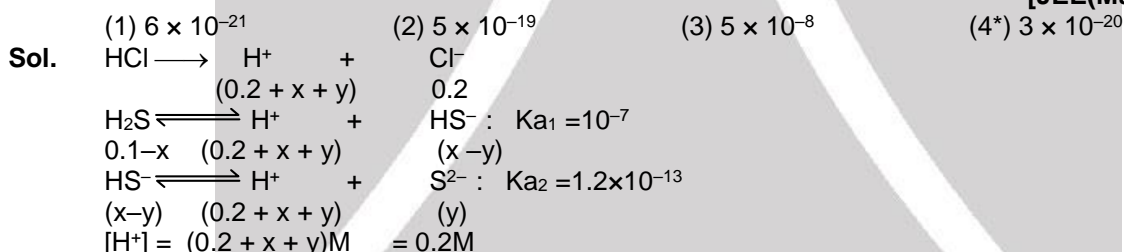
यह भी, $[\text{CO}_3^{2-}] \ll [\text{HCO}_3^-]$ (\therefore IInd आयनन नगण्य प्रसार तक प्राप्त होगा।)

2. An aqueous solution contains 0.10 M H_2S and 0.20 M HCl . If the equilibrium constant for the formation of HS^- from H_2S is 1.0×10^{-7} and that of S^{2-} from HS^- ions is 1.2×10^{-13} then the concentration of S^{2-} ions in aqueous solution is :

[JEE(Main)-2018, 4/120]

एक जलीय विलयन में 0.10 M H_2S तथा 0.20 M HCl हैं। यदि H_2S से HS^- बनने का साम्य स्थिरांक 1.0×10^{-7} हो तथा HS^- से S^{2-} बनने का साम्य स्थिरांक 1.2×10^{-13} हो तो जलीय विलयन में S^{2-} आयनों की सान्द्रता होगी -

[JEE(Main)-2018, 4/120]



$$K_{a1} = \frac{[\text{H}^+][\text{HS}^-]}{[\text{H}_2\text{S}]} = \frac{0.2 \times [\text{HS}^-]}{0.1 - x} = \frac{0.2[\text{HS}^-]}{0.1} \quad (x = \text{negligible}) \quad (x = \text{नगण्य})$$

$$[\text{HS}^-] = \frac{K_{a1} \times 0.1}{0.2} = \frac{1}{2} \times 10^{-7}$$

$$K_{a2} = \frac{[\text{H}^+][\text{S}^{2-}]}{[\text{HS}^-]} = \frac{[0.2\text{M}][\text{S}^{2-}]}{\frac{1}{2} \times 10^{-7}}$$

$$[\text{S}^{2-}] = \frac{K_{a2} \times \frac{1}{2} \times 10^{-7}}{0.2} = \frac{1.2 \times 10^{-13} \times \frac{1}{2} \times 10^{-7}}{0.2} = 3 \times 10^{-20} \text{ M}$$





IONIC EQUILIBRIUM-II

आयनिक साम्य-II

Exercise-1

Marked Questions may have for Revision Questions.

चिह्नित प्रश्न दोहराने योग्य प्रश्न है।

PART - I : SUBJECTIVE QUESTIONS

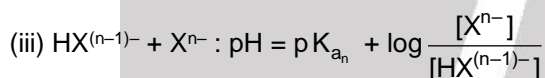
भाग - I : विषयात्मक प्रश्न (SUBJECTIVE QUESTIONS)

Section (A) : pH calculation : Buffer solutions generated from Polybasic acid / Polyacidic base, Buffer capacity

खण्ड (A) : pH गणना : बहुक्षारीय अम्ल / बहुअम्लीय क्षार से प्राप्त बफर विलयन, बफर क्षमता

Commit to memory :

pH calculation : Buffer solutions generated from Polybasic acid (H_nX) :



Buffer capacity : Moles of a strong acid or strong base required to change the pH of 1 L of a buffer by one unit.

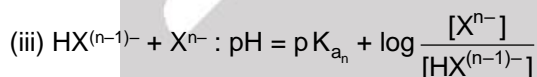
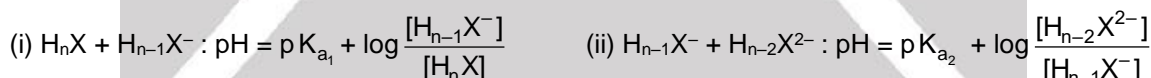
Let there be a buffer solution of volume 1 L with 'b' mole of anion (coming from salt) and 'a' mole of weak acid.

$$B.C. = \frac{dx}{d\Delta pH} = 2.303 \frac{(a+x)(b-x)}{a+b} \approx 2.303 \frac{ab}{a+b}$$

Condition for maximum buffer capacity : [Acid] = [Anion of salt]

याद रखने योग्य तथ्य :

pH गणना : बहुक्षारीय अम्ल (H_nX) से उत्पन्न बफर विलयन :



बफर क्षमता : एक इकाई से 1 L बफर विलयन की pH को परिवर्तित करने के लिए प्रबल अम्ल या प्रबल क्षार के मोलों की आवश्यकता होती है।

माना यहाँ ऋणायन (लवण से आने वाले) के 'b' मोल तथा दुर्बल अम्ल के 'a' मोल युक्त 1 L आयतन का एक बफर विलयन है।

$$B.C. = \frac{dx}{d\Delta pH} = 2.303 \frac{(a+x)(b-x)}{a+b} \approx 2.303 \frac{ab}{a+b}$$

अधिकतम बफर क्षमता के लिए शर्त : [अम्ल] = [लवण का ऋणायन]

- A-1.** An environmental chemist needs a carbonate buffer of pH 10 to study the effects of the acidification of limestone-rich soils. How many grams of Na_2CO_3 must be added to 1.5 L of freshly prepared 0.2 M $NaHCO_3$ to make the buffer ? For H_2CO_3 , $K_{a_1} = 4.7 \times 10^{-7}$; $K_{a_2} = 4.7 \times 10^{-11}$.





चूना पत्थर युक्त मिट्टी में अम्लीकरण के प्रभाव के अध्ययन के लिए एक पर्यावरण रसायनज्ञ को pH 10 के एक कार्बोनेट बफर की आवश्यकता है। बफर बनाने के लिए ताजे बने 0.2 M NaHCO₃ के 1.5 L के साथ Na₂CO₃ के कितने ग्राम मिलाने चाहिए ? H₂CO₃ के लिए, K_{a1} = 4.7 × 10⁻⁷ ; K_{a2} = 4.7 × 10⁻¹¹.

Ans. 15 g Na₂CO₃

Sol. pK_a = 11 – log 4.7

$$\text{pH} = \text{pK}_a + \log \left(\frac{n_{\text{Na}_2\text{CO}_3}}{0.3} \right) \quad \therefore \quad 10 = 11 - \log 4.7 + \log \left(\frac{n_{\text{Na}_2\text{CO}_3}}{0.3} \right)$$

$$\log \frac{4.7 \times 0.3}{n_{\text{Na}_2\text{CO}_3}} = 1 \quad \Rightarrow \quad n_{\text{Na}_2\text{CO}_3} = 0.141$$

$$W_{\text{Na}_2\text{CO}_3} = 0.141 \times 106 = 14.946 \approx 15 \text{ gram}$$

Section (B) : pH calculation : Monobasic acid - Monoacidic base Titrations

खण्ड (B) : pH गणना : एकलक्षारीय अम्ल-एकलअम्लीय क्षार अनुमापन

Commit to memory :

pH calculation : Monobasic acid-Monoacidic base Titrations :

Carry out chemical reaction between the two components, apply mole concept, observe the final composition of the mixture and then calculate pH accordingly (using different cases dealt in Ionic Equilibrium-I).

In titration of WA by SB :

$$\text{At half equivalence point : pH} = \text{pK}_a ; \text{pH}_{x\% \text{ neutralisation}} = \text{pK}_a + \frac{x}{100 - x}$$

In titration of WB and SA :

$$\text{At half equivalence point : pOH} = \text{pK}_b ; \text{pOH}_{x\% \text{ neutralisation}} = \text{pK}_b + \frac{x}{100 - x}$$

याद रखने योग्य तथ्य :

pH गणना : एकलक्षारीय अम्ल-एकलअम्लीय क्षार अनुमापन :

दो घटकों के मध्य रासायनिक अभिक्रिया करने के लिए मोल सिद्धांत का अनुप्रयोग करते हैं, मिश्रण के अन्तिम घटक का प्रेक्षण करते हैं तथा बाद में (आयनिक साम्य-I में विभिन्न परिस्थितियों का उपयोग करते हुए) नियमानुसार pH की गणना करते हैं। SB द्वारा WA के अनुमापन में :

$$\text{अर्द्ध तुल्यांक बिन्दु पर : pH} = \text{pK}_a ; \text{pH}_{x\% \text{ उदासीनीकरण}} = \text{pK}_a + \frac{x}{100 - x}$$

WB तथा SA के अनुमापन में :

$$\text{अर्द्ध तुल्यांक बिन्दु पर : pOH} = \text{pK}_b ; \text{pOH}_{x\% \text{ उदासीनीकरण}} = \text{pK}_b + \frac{x}{100 - x}$$

B-1. Calculate pH of the following mixtures. Given : K_a of CH₃COOH = 2 × 10⁻⁵ and K_b of NH₄OH = 2 × 10⁻⁵.

(a) 50 mL of 0.10 M NaOH + 50 mL of 0.10 M HCl.

(b) 50 mL of 0.10 M NaOH + 50 mL of 0.05 M CH₃COOH.

(c) 50 mL of 0.05 M NaOH + 50 mL of 0.10 M CH₃COOH.

(d) 50 mL of 0.10 M NH₄OH + 50 mL of 0.05 M HCl.

(e) 50 mL of 0.10 M NH₄OH + 50 mL of 0.10 M HCl.

(f) 50 mL of 0.05 M NH₄OH + 50 mL of 0.05 M CH₃COOH.

निम्न मिश्रणों के pH की गणना कीजिए। दिया गया है: CH₃COOH का K_a = 2 × 10⁻⁵ तथा NH₄OH का K_b = 2 × 10⁻⁵

(a) 0.10 M NaOH का 50 mL + 0.10 M HCl का 50 mL.

(b) 0.10 M NaOH का 50 mL + 0.05 M CH₃COOH का 50 mL.

(c) 0.05 M NaOH का 50 mL + 0.10 M CH₃COOH का 50 mL.

(d) 0.10 M NH₄OH का 50 mL + 0.05 M HCl का 50 mL.




 (e) 0.10 M NH_4OH का 50 mL + 0.10 M HCl का 50 mL.

 (f) 0.05 M NH_4OH का 50 mL + 0.05 M CH_3COOH का 50 mL.

Ans. (a) 7 (b) 12.4, (c) 4.7, (d) 9.3, (e) 5.3, (f) 7

Sol. (a) $\text{H}^+ + \text{OH}^- \longrightarrow \text{H}_2\text{O}$

t = 0 5 mmol 5 mmol

so pH of resulting solution = 7.

 (b) $\text{CH}_3\text{COOH} + \text{OH}^- \longrightarrow \text{CH}_3\text{COO}^- + \text{H}_2\text{O}$
 t = 0 2.5 mmol 5 mmol 2.5 2.5 -

$$[\text{OH}^-] = \frac{2.5}{100} \text{ M} = 2.5 \times 10^{-2} \text{ M}$$

$$\text{pOH} = 3 - \log(2.5) = 1.6$$

 $\therefore \text{pH} = 12.4$

 (c) $\text{CH}_3\text{COOH} + \text{OH}^- \longrightarrow \text{CH}_3\text{COO}^- + \text{H}_2\text{O}$
 t = 0 5 mmol 2.5 mmol 2.5

$$\text{pH} = \text{pK}_a + \log \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = \text{pK}_a = 4.7$$

 (d) $\text{NH}_4\text{OH} + \text{H}^+ \longrightarrow \text{NH}_4^+ + \text{H}_2\text{O}$
 t = 0 5 mmol 2.5 mmol 2.5

$$\text{pOH} = \text{pK}_b + \log \frac{[\text{NH}_4^+]}{[\text{NH}_3]} = 4.7$$

 $\therefore \text{pH} = 9.3$

 (e) $\text{NH}_4\text{OH} + \text{H}^+ \longrightarrow \text{NH}_4^+ + \text{H}_2\text{O}$
 t = 0 5 mmol 5 mmol 0 5

$$\text{pH} = \frac{1}{2} [14 - 4.7 - \log 0.05]$$

$$\text{pH} = 5.3$$

 (f) $\text{NH}_4\text{OH} + \text{CH}_3\text{COOH} \longrightarrow \text{CH}_3\text{COONH}_4 + \text{H}_2\text{O}$
 t = 0 2.5 mmol 2.5 mmol 2.5

$$\text{pH} = 7 + \frac{1}{2} \text{pK}_a - \frac{1}{2} \text{pK}_b = 7$$

हल. (a) $\text{H}^+ + \text{OH}^- \longrightarrow \text{H}_2\text{O}$
 t = 0 5 मिलीमोल 5 मिलीमोल

 अतः परिणामी विलयन की $\text{pH} = 7$.

 (b) $\text{CH}_3\text{COOH} + \text{OH}^- \longrightarrow \text{CH}_3\text{COO}^- + \text{H}_2\text{O}$
 t = 0 2.5 मिलीमोल 5 मिलीमोल 2.5 2.5 -

$$[\text{OH}^-] = \frac{2.5}{100} \text{ M} = 2.5 \times 10^{-2} \text{ M}$$

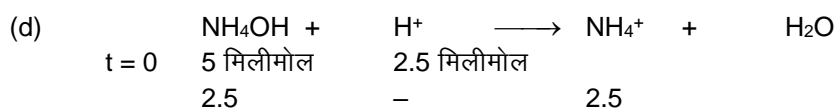
$$\text{pOH} = 3 - \log(2.5) = 1.6$$

 $\therefore \text{pH} = 12.4$

 (c) $\text{CH}_3\text{COOH} + \text{OH}^- \longrightarrow \text{CH}_3\text{COO}^- + \text{H}_2\text{O}$
 t = 0 5 मिलीमोल 2.5 मिलीमोल 2.5

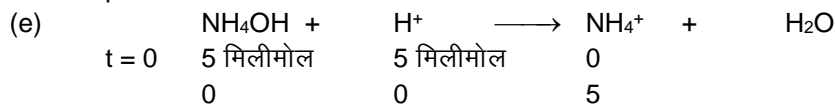


$$\text{pH} = \text{pK}_a + \log \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = \text{pK}_a = 4.7$$



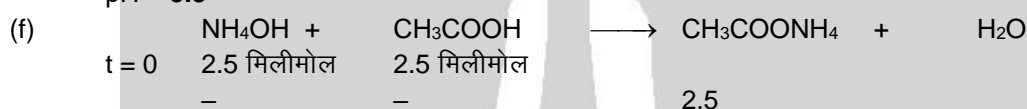
$$\text{pOH} = \text{pK}_b + \log \frac{[\text{NH}_4^+]}{[\text{NH}_3]} = 4.7$$

$$\therefore \text{pH} = 9.3$$



$$\text{pH} = \frac{1}{2} [14 - 4.7 - \log 0.05]$$

$$\text{pH} = 5.3$$



$$\text{pH} = 7 + \frac{1}{2} \text{pK}_a - \frac{1}{2} \text{pK}_b = 7$$

B-2. 0.1 M CH_3COOH solution is titrated against 0.05 M NaOH solution. Calculate pH at 1/4th and 3/4th stages of neutralization of acid. Given : pH of 0.1 M CH_3COOH solution is 3. **[16JC110323]**

0.1 M CH_3COOH विलयन को 0.05 M NaOH विलयन से अनुमापित करते हैं। अम्ल के 1/4 स्तर तथा 3/4 स्तर पर उदासीनीकरण के pH की गणना कीजिए। दिया है : 0.1 M CH_3COOH विलयन के लिए pH 3 है।

Ans. 4.52, 5.48

Sol. pH of $\text{CH}_3\text{COOH} = \frac{1}{2} (\text{pK}_a - \log c)$

$$3 = \frac{1}{2} (\text{pK}_a - \log 0.1) \quad \therefore \text{pK}_a = 5$$

$$\frac{1}{4} \text{ stage of neutralisation : } \text{pH} = 5 + \log \frac{1/4}{3/4} = 4.52$$

$$\frac{3}{4} \text{ stage of neutralisation : } \text{pH} = 5 + \log \frac{3/4}{1/4} = 5.48$$

हल. CH_3COOH का $\text{pH} = \frac{1}{2} (\text{pK}_a - \log c)$

$$3 = \frac{1}{2} (\text{pK}_a - \log 0.1) \quad \therefore \text{pK}_a = 5$$

$$\text{उदासीनीकरण का } \frac{1}{4} \text{ स्तर : } \text{pH} = 5 + \log \frac{1/4}{3/4} = 4.52$$

$$\text{उदासीनीकरण का } \frac{3}{4} \text{ स्तर : } \text{pH} = 5 + \log \frac{3/4}{1/4} = 5.48$$

Section (C) : pH calculation : Titration of Salts, Polyprotic acid, Polyacidic base

खण्ड (C) : pH गणना : लवण, बहुप्रोटिक अम्ल, बहुअम्लीय क्षार का अनुमापन

Commit to memory :

pH calculation : Titration of Polyprotic acid, Polyacidic base :

Carry out chemical reaction between the two components, apply mole concept, observe the final composition of the mixture and then calculate pH accordingly (using different cases dealt in Ionic Equilibrium-I).



In titration of H_nX by strong base :

At half equivalence point w.r.t 1st neutralisation : $pH = pK_{a_1}$;

At equivalence point w.r.t 1st neutralisation : $pH = \frac{pK_{a_2} + pK_{a_1}}{2}$;

At half equivalence point w.r.t 2nd neutralisation : $pH = pK_{a_2}$;

At equivalence point w.r.t 2nd neutralisation : $pH = \frac{pK_{a_3} + pK_{a_2}}{2}$;

At equivalence point w.r.t last neutralisation : $pH = \frac{1}{2}(pK_w + pK_{a_n} + \log C)$.

In titration of Polyacidic base B by strong acid :

At half equivalence point w.r.t 1st neutralisation : $pOH = pK_{b_1}$;

At equivalence point w.r.t 1st neutralisation : $pOH = \frac{pK_{b_2} + pK_{b_1}}{2}$;

At half equivalence point w.r.t 2nd neutralisation : $pOH = pK_{b_2}$;

At equivalence point w.r.t 2nd neutralisation : $pH = \frac{pK_{b_3} + pK_{b_2}}{2}$;

At equivalence point w.r.t last neutralisation : $pH = \frac{1}{2}(pK_w - pK_{b_n} - \log C)$.

याद रखने योग्य तथ्य :

pH गणना : बहुप्रोटिक अम्ल, बहुअम्लीय क्षार का अनुमापन :

दो घटकों के मध्य रासायनिक अभिक्रिया करने के लिए मोल सिद्धांत का अनुप्रयोग करते हैं, मिश्रण के अन्तिम घटक का प्रेक्षण करते हैं तथा बाद में (आयनिक साम्य-I) में विभिन्न परिस्थितियों का उपयोग करते हुए नियमानुसार pH की गणना करते हैं।

प्रबल क्षार द्वारा H_nX के अनुमापन में :

1st उदासीनीकरण के संदर्भ में अर्द्ध तुल्यांकी बिन्दु पर : $pH = pK_{a_1}$;

1st उदासीनीकरण के संदर्भ में तुल्यांकी बिन्दु पर : $pH = \frac{pK_{a_2} + pK_{a_1}}{2}$;

2nd उदासीनीकरण के संदर्भ में अर्द्ध तुल्यांकी बिन्दु पर : $pH = pK_{a_2}$;

2nd उदासीनीकरण के संदर्भ में तुल्यांकी बिन्दु पर : $pH = \frac{pK_{a_3} + pK_{a_2}}{2}$;

अन्तिम उदासीनीकरण के संदर्भ में तुल्यांकी बिन्दु पर : $pH = \frac{1}{2}(pK_w + pK_{a_n} + \log C)$.

प्रबल अम्ल द्वारा बहुअम्लीय क्षार B के अनुमापन में :

1st उदासीनीकरण के संदर्भ में अर्द्ध तुल्यांकी बिन्दु पर : $pOH = pK_{b_1}$;

1st उदासीनीकरण के संदर्भ में तुल्यांकी बिन्दु पर : $pOH = \frac{pK_{b_2} + pK_{b_1}}{2}$;

2nd उदासीनीकरण के संदर्भ में अर्द्ध तुल्यांकी बिन्दु पर : $pOH = pK_{b_2}$;

2nd उदासीनीकरण के संदर्भ में तुल्यांकी बिन्दु पर : $pH = \frac{pK_{b_3} + pK_{b_2}}{2}$;

अन्तिम उदासीनीकरण के संदर्भ में तुल्यांकी बिन्दु पर : $pH = \frac{1}{2}(pK_w - pK_{b_n} - \log C)$.





C-1. 50 mL of 0.05 M Propane-1,2-diamine solution is titrated with 0.1 M HCl solution at 25°C. Determine the pH of solutions obtained by adding following volumes of HCl solution :

(a) 12.5 mL (b) 25 mL (c) 30 mL

Given : pK_{b_1} and pK_{b_2} of weak base are 4.18 and 7.39 respectively.

25°C पर 50 mL, 0.05 M प्रोपेन-1,2-डाइएमीन विलयन को 0.1 M HCl के साथ अनुमापित करते हैं। HCl विलयन के निम्न आयतनों को मिलाने से प्राप्त विलयनों के pH का निर्धारण कीजिए।

(a) 12.5 mL (b) 25 mL (c) 30 mL

दिया है : दुर्बल क्षार के pK_{b_1} तथा pK_{b_2} क्रमशः 4.18 तथा 7.39 है।

Ans. (a) 9.82 (b) 8.215 (c) 7.21

Sol. (a) Half neutralisation : $pH = pK_{a_1} = 14 - 4.18 = 9.82$

$$(b) pH = \frac{pK_{a_1} + pK_{a_2}}{2} = \frac{14 - 4.18 + 14 - 7.39}{2} = 8.215$$

$$(c) \text{ Buffer : } pH = 14 - 7.39 + \log \left(\frac{2.5 - 0.5}{0.5} \right) = 7.21$$

हल. (a) अर्द्ध उदासीनीकरण : $pH = pK_{a_1} = 14 - 4.18 = 9.82$

$$(b) pH = \frac{pK_{a_1} + pK_{a_2}}{2} = \frac{14 - 4.18 + 14 - 7.39}{2} = 8.215$$

$$(c) \text{ बफर : } pH = 14 - 7.39 + \log \left(\frac{2.5 - 0.5}{0.5} \right) = 7.21$$

C-2. Determine the $[H^+]$ at half-equivalence point and pH at equivalence point during the titration of a 50 mL, 0.1 M NH_4Cl solution with 0.1 M NaOH solution at 25°C. Given : K_b of $NH_3 = 2 \times 10^{-5}$.

25°C पर 50 mL, 0.1 M NH_4Cl विलयन को 0.1 M NaOH विलयन के साथ अनुमापित करने के दौरान अर्द्ध तुल्यांकी बिन्दु पर $[H^+]$ तथा तुल्यांकी बिन्दु पर pH का निर्धारण कीजिए। दिया है : NH_3 का $K_b = 2 \times 10^{-5}$.

Ans. 5×10^{-10} M; 11

Sol. $[H^+] = \frac{K_w}{K_b} = 5 \times 10^{-10}$: At half equivalence point.

$$[OH^-] = \sqrt{2 \times 10^{-5} \times \frac{0.1}{2}} = 10^{-3}$$

$\therefore pH = 11$: Equivalence point.

हल. $[H^+] = \frac{K_w}{K_b} = 5 \times 10^{-10}$: अर्द्ध तुल्यांकी बिन्दु पर

$$[OH^-] = \sqrt{2 \times 10^{-5} \times \frac{0.1}{2}} = 10^{-3}$$

$\therefore pH = 11$: तुल्यांकी बिन्दु

PART - II : ONLY ONE OPTION CORRECT TYPE

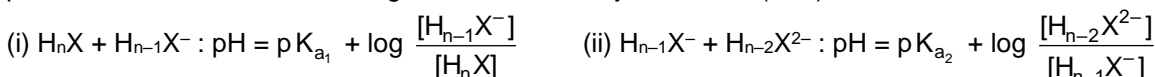
भाग - II : केवल एक सही विकल्प प्रकार (ONLY ONE OPTION CORRECT TYPE)

Section (A) : pH calculation : Buffer solutions generated from Polybasic acid / Polyacidic base, Buffer capacity

खण्ड (A) : pH गणना : बहुक्षारीय अम्ल / बहुअम्लीय क्षार से प्राप्त बफर विलयन, बफर क्षमता

Commit to memory :

pH calculation : Buffer solutions generated from Polybasic acid (H_nX) :



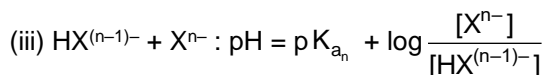
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ADVIEQ(A)- 6



Buffer capacity : Moles of a strong acid or strong base required to change the pH of 1 L of a buffer by one unit.

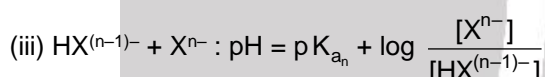
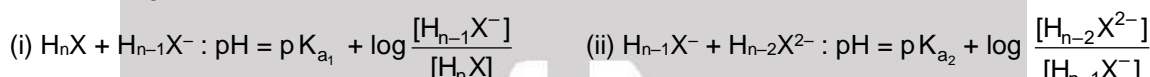
Let there be a buffer solution of volume 1 L with 'b' mole of anion (coming from salt) and 'a' mole of weak acid.

$$\text{B.C.} = \frac{dx}{d\text{pH}} = 2.303 \frac{(a+x)(b-x)}{a+b} \approx 2.303 \frac{ab}{a+b}$$

Condition for maximum buffer capacity : [Acid] = [Anion of salt]

याद रखने योग्य तथ्य :

pH गणना : बहुक्षारीय अम्ल (H_nX) से उत्पन्न बफर विलयन :



बफर क्षमता : एक इकाई से 1 L बफर विलयन की pH को परिवर्तित करने के लिए प्रबल अम्ल या प्रबल क्षार के मोलों की आवश्यकता होती है।

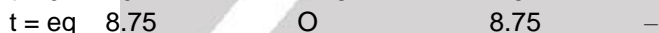
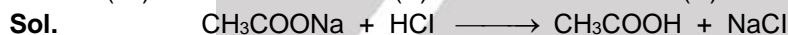
माना यहाँ ऋणायन (लवण से आने वाले) के 'b' मोल तथा दुर्बल अम्ल के 'a' मोल युक्त 1 L आयतन का एक बफर विलयन है।

$$\text{B.C.} = \frac{dx}{d\text{pH}} = 2.303 \frac{(a+x)(b-x)}{a+b} \approx 2.303 \frac{ab}{a+b}$$

अधिकतम बफर क्षमता के लिए शर्त : [अम्ल] = [लवण का ऋणायन]

- A-1.** The pH of a solution resulting from the addition of 12.5 ml of 0.1 M HCl to 50 ml of a solution containing 0.15 M CH_3COOH & 0.2 M CH_3COONa will be : (Given : pK_a of $\text{CH}_3\text{COOH} = 4.74$)
 0.1 M HCl के 12.5 mL को 0.15 M CH_3COOH व 0.2 M CH_3COONa रखने वाले विलयन के 50 mL में मिलाने पर प्राप्त होने वाले विलयन का pH होगा : (दिया है : CH_3COOH का $\text{pK}_a = 4.74$)

- (A*) 4.74 (B) < 4.74 (C) > 4.74 (D) > 9.26



pH = $\text{pK}_a = 4.74$

- A-2.** What % of the carbon in the $\text{H}_2\text{CO}_3 - \text{HCO}_3^-$ buffer should be in the form of HCO_3^- , so as to have a neutral solution ? (K_{a_1} of $\text{H}_2\text{CO}_3 = 4 \times 10^{-7}$)

- (A) 20 % (B) 40 % (C) 60 % (D*) 80 %

$\text{H}_2\text{CO}_3 - \text{HCO}_3^-$ के बफर में उदासीन विलयन प्राप्त करने के लिए कितना प्रतिशत कार्बन, HCO_3^- के रूप में उपस्थित है ? (H_2CO_3 का $\text{K}_{a_1} = 4 \times 10^{-7}$)

- (A) 20 % (B) 40 % (C) 60 % (D*) 80 %

Sol. $\text{pH} = \text{pK}_a + \log \frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} \Rightarrow 7 = 7 - \log 4 + \log \frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} \Rightarrow \frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = 4$

% of Carbon in the form of $\text{HCO}_3^- = \frac{[\text{HCO}_3^-]}{[\text{HCO}_3^-] + [\text{H}_2\text{CO}_3]} \times 100 = \frac{4}{1+4} \times 100 = 80\%$

Sol. $\text{pH} = \text{pK}_a + \log \frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} \Rightarrow 7 = 7 - \log 4 + \log \frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} \Rightarrow \frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = 4$

HCO_3^- के रूप में उपस्थित कार्बन का प्रतिशत = $\frac{[\text{HCO}_3^-]}{[\text{HCO}_3^-] + [\text{H}_2\text{CO}_3]} \times 100 = \frac{4}{1+4} \times 100 = 80\%$



A-3. Buffer capacity of a buffer solution is x . The volume of 1 M NaOH solution added to 100 mL of this solution if change the pH by 1 is :

एक बफर विलयन की बफर क्षमता x है। इसकी pH में इकाई से परिवर्तन करने के लिए इस विलयन के 100 mL में 1 M NaOH का कितना आयतन मिलाना पड़ेगा ?

- (A) $0.1x$ mL (B) $10x$ mL (C*) $100x$ mL (D) x mL

Sol. Mole of NaOH is required for 1 lit solution = x
 \therefore Mole of NaOH is required for 100 ml of solution = $0.1x$
 Now, $0.1x = 1 \times V \Rightarrow V = 0.1x \text{ lt} = 100x \text{ mL}$.

हल. 1 लीटर विलयन के लिए आवश्यक NaOH के मोल = x
 \therefore 100 मिली विलयन के लिए आवश्यक NaOH के मोल = $0.1x$
 अब, $0.1x = 1 \times V \Rightarrow V = 0.1x \text{ lt} = 100x \text{ mL}$.

Section (B) : pH calculation : Monobasic acid - Monoacidic base Titrations

खण्ड (B) : pH गणना : एकलक्षारीय अम्ल-एकलक्षारीय क्षार अनुमापन

Commit to memory :

pH calculation : Monobasic acid - Monoacidic base Titrations :

Carry out chemical reaction between the two components, apply mole concept, observe the final composition of the mixture and then calculate pH accordingly (using different cases dealt in Ionic Equilibrium-I).

In titration of WA by SB :

At half equivalence point : $\text{pH} = \text{pK}_a$; $\text{pH}_{x\% \text{ neutralisation}} = \text{pK}_a + \frac{x}{100 - x}$

In titration of WB and SA :

At half equivalence point : $\text{pOH} = \text{pK}_b$; $\text{pOH}_{x\% \text{ neutralisation}} = \text{pK}_b + \frac{x}{100 - x}$

याद रखने योग्य तथ्य :

pH गणना : एकलक्षारीय अम्ल - एकलक्षारीय क्षार अनुमापन :

दो घटकों के मध्य रासायनिक अभिक्रिया करने के लिए मोल सिद्धांत का अनुप्रयोग करते हैं, मिश्रण के अन्तिम घटक का प्रेक्षण करते हैं तथा बाद में (आयनिक साम्य-I में विभिन्न परिस्थितियों का उपयोग करते हुए) नियमानुसार pH की गणना करते हैं। SB द्वारा WA के अनुमापन में :

अर्द्ध तुल्यांक बिन्दु पर : $\text{pH} = \text{pK}_a$; $\text{pH}_{x\% \text{ उदासीनीकरण}} = \text{pK}_a + \frac{x}{100 - x}$

WB तथा SA के अनुमापन में :

अर्द्ध तुल्यांक बिन्दु पर : $\text{pOH} = \text{pK}_b$; $\text{pOH}_{x\% \text{ उदासीनीकरण}} = \text{pK}_b + \frac{x}{100 - x}$

B-1. Upon titrating 50 mL of 1.96% (w/v) H_2SO_4 with a KOH solution (containing 11.2 g KOH per litre of solution), on adding 50 mL KOH solution :

(A) Equivalence point has been just reached. (B) Equivalence point has been crossed.

(C*) pH of resulting solution = 1 (D) pH of resulting solution = 7

KOH विलयन (11.2 ग्राम KOH प्रति लीटर विलयन युक्त) के साथ 50 mL, 1.96% (w/v) H_2SO_4 के अनुमापन के दौरान 50 mL KOH विलयन मिलाने पर :

(A) तुल्यांकी बिन्दु बस प्राप्त ही हुआ है। (B) तुल्यांकी बिन्दु क्रॉस हो जाता है।

(C*) परिणामी विलयन का pH = 1 (D) परिणामी विलयन का pH = 7

Sol. $[\text{H}_2\text{SO}_4] = \frac{19.6}{98} = 0.2 \text{ M}$ and $\text{KOH} = \frac{11.2}{56} = 0.2 \text{ M}$

So, for equivalence point, $\frac{0.2 \times 50 \times 2}{0.2} = 100 \text{ mL}$ of KOH solution should be added.





$$[H^+] = \frac{0.2 \times 2 - 0.2}{2} = 0.1 \text{ M} \quad \text{So, pH} = 1.$$

हल. $[H_2SO_4] = \frac{19.6}{98} = 0.2 \text{ M}$ तथा $KOH = \frac{11.2}{56} = 0.2 \text{ M}$

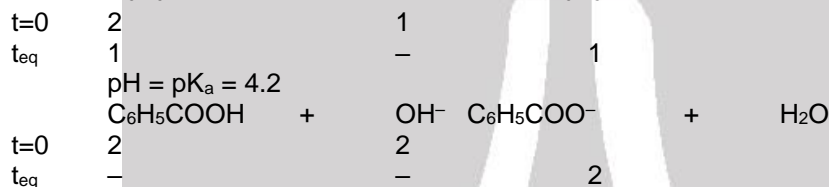
अतः, तुल्यांकी बिन्दु के लिए, $\frac{0.2 \times 50 \times 2}{0.2} = 100 \text{ mL}$, KOH विलयन मिलाया जाना चाहिए।

$$[H^+] = \frac{0.2 \times 2 - 0.2}{2} = 0.1 \text{ M} \quad \text{अतः, pH} = 1.$$

B-2. 100 mL of 0.02 M benzoic acid ($pK_a = 4.2$) is titrated using 0.02 M NaOH. pH after 50 mL and 100 mL of NaOH have been added are :

0.02 M बेन्जोइक अम्ल ($pK_a = 4.2$) के 100 mL के अनुमापन के लिए 0.02 M NaOH को काम में लिया जाता है। NaOH के 50 mL तथा 100 mL मिलाने के पश्चात pH निम्न हैं :

- (A) 2.1, 8.1 (B) 4.2, 7 (C*) 4.2, 8.1 (D) 4.2, 8.25



$$[C_6H_5COO^-] = \frac{2}{200} = 0.01 \text{ M}$$

$$\therefore \text{pH} = 7 + pK_a + \frac{1}{2} \log C = 7 + \frac{4.2}{2} + \frac{1}{2} \log (0.01) = 8.1$$

B-3. In the above question, upon 75% neutralisation of Benzoic acid, select the INCORRECT statement :

- (A) Resulting solution will be a buffer solution. (B) pH = $4.2 + \log 3$
(C) Both (A) & (B) (D*) None of these

उपरोक्त प्रश्न में, बेन्जोइक अम्ल के 75% उदासीनीकरण पर गलत कथन का चयन कीजिए :

- (A) परिणामी विलयन बफर विलयन होगा। (B) pH = $4.2 + \log 3$
(C) दोनों (A) तथा (B) (D*) इनमें से कोई नहीं

B-4. Which of the following solutions have different pH ?

- (i) 100 mL of 0.2 M HCl + 100 mL of 0.4 M NH_3
(ii) 50 mL of 0.1 M HCl + 50 mL of 0.2 M NH_3
(iii) 100 mL of 0.3 M HCl + 100 mL of 0.6 M NH_3

- (A) i & ii (B) ii & iii (C) i & iii

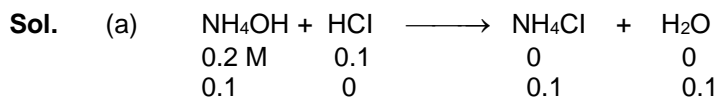
(D*) All will have same pH.

निम्न विलयनों में से कौन भिन्न pH रखते हैं ?

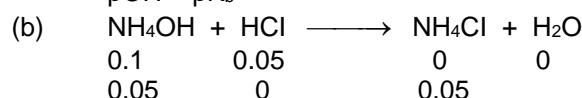
- (i) 0.2 M HCl का 100 mL + 0.4 M NH_3 का 100 mL
(ii) 0.1 M HCl को 50 mL + 0.2 M NH_3 का 50 mL
(iii) 0.3 M HCl का 100 mL + 0.6 M NH_3 का 100 mL

- (A) i तथा ii (B) ii तथा iii (C) i तथा iii

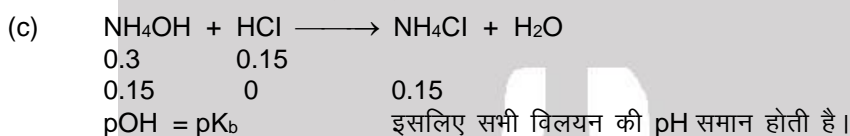
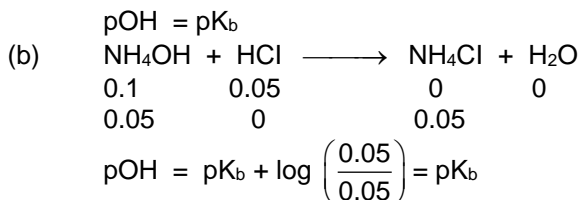
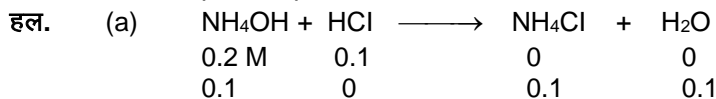
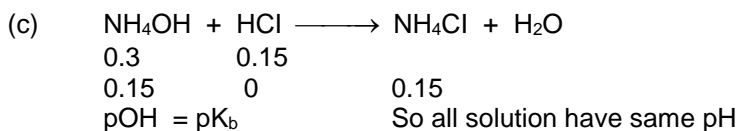
(D*) सभी का pH समान है।



$$pOH = pK_b$$



$$pOH = pK_b + \log \left(\frac{0.05}{0.05} \right) = pK_b$$



B-5. Upon titrating a solution of weak monoprotic acid with a weak monoacidic base solution, at equivalence point :

(A) pH in general would increase if both solutions are first diluted to 10 times the original volume & then titration is carried out.

(B) pH in general would decrease if both solutions are first diluted to 10 times the original volume & then titration is carried out.

(C) pH in general would remain same (= 7) if both solutions are first diluted to 10 times the original volume & then titration is carried out.

(D*) pH in general could be less than, greater than or equal to 7 if both solutions are first diluted to 10 times the original volume & then titration is carried out.

तुल्यांकी बिन्दु पर दुर्बल एकल अम्लीय क्षार के एक विलयन के साथ दुर्बल एकल प्रोटिक अम्ल के विलयन के अनुमापन पर :

(A) सामान्यतः pH बढ़ेगा यदि दोनों विलयनों को सर्वप्रथम वास्तविक विलयन से 10 गुना तनु करते हैं तथा बाद में अनुमापन करते हैं।

(B) सामान्यतः pH घटेगा यदि दोनों विलयनों को सर्वप्रथम वास्तविक विलयन से 10 गुना तनु करते हैं तथा बाद में अनुमापन करते हैं।

(C) सामान्यतः pH समान (= 7) रहेगा यदि दोनों विलयनों को सर्वप्रथम वास्तविक विलयन से 10 गुना तनु करते हैं तथा बाद में अनुमापन करते हैं।

(D*) सामान्यतः pH 7 से कम, अधिक अथवा बराबर होगा यदि दोनों विलयनों को सर्वप्रथम वास्तविक विलयन से 10 गुना तनु करते हैं तथा बाद में अनुमापन करते हैं।

Sol. Salt of WA-WB formed at equivalence point has pH independent of concentration and depends on pK_a and pK_b of WA and WB respectively.

हल. तुल्यांकी बिन्दु पर निर्मित WA-WB का लवण सान्द्रता की स्वतंत्र pH रखता है तथा WA तथा WB के क्रमशः pK_a तथा pK_b पर निर्भर करता है।

Section (C) : pH calculation : Titration of Salts, Polyprotic acid, Polyacidic base

खण्ड (C) : pH गणना : लवण, बहुप्रोटिक अम्ल, बहुअम्लीय क्षार का अनुमापन

Commit to memory :

pH calculation : Titration of Polyprotic acid, Polyacidic base :

Carry out chemical reaction between the two components, apply mole concept, observe the final composition of the mixture and then calculate pH accordingly (using different cases dealt in Ionic Equilibrium-I).

In titration of H_nX by strong base :



At half equivalence point w.r.t 1st neutralisation : $\text{pH} = \text{p}K_{a_1}$;

At equivalence point w.r.t 1st neutralisation : $\text{pH} = \frac{\text{p}K_{a_2} + \text{p}K_{a_1}}{2}$;

At half equivalence point w.r.t 2nd neutralisation : $\text{pH} = \text{p}K_{a_2}$;

At equivalence point w.r.t 2nd neutralisation : $\text{pH} = \frac{\text{p}K_{a_3} + \text{p}K_{a_2}}{2}$;

At equivalence point w.r.t last neutralisation : $\text{pH} = \frac{1}{2}(\text{p}K_w + \text{p}K_{a_n} + \log C)$.

In titration of Polyacidic base B by strong acid:

At half equivalence point w.r.t 1st neutralisation : $\text{pOH} = \text{p}K_{b_1}$;

At equivalence point w.r.t 1st neutralisation : $\text{pOH} = \frac{\text{p}K_{b_2} + \text{p}K_{b_1}}{2}$;

At half equivalence point w.r.t 2nd neutralisation : $\text{pOH} = \text{p}K_{b_2}$;

At equivalence point w.r.t 2nd neutralisation : $\text{pH} = \frac{\text{p}K_{b_3} + \text{p}K_{b_2}}{2}$;

At equivalence point w.r.t last neutralisation : $\text{pH} = \frac{1}{2}(\text{p}K_w - \text{p}K_{b_n} - \log C)$.

याद रखने योग्य तथ्य :

pH गणना : बहुप्रोटिक अम्ल, बहुअम्लीय क्षार का अनुमापन :

दो घटकों के मध्य रासायनिक अभिक्रिया करने के लिए मोल सिद्धांत का अनुप्रयोग करते हैं, मिश्रण के अन्तिम घटक का प्रेक्षण करते हैं तथा बाद में (आयनिक साम्य-I में विभिन्न परिस्थितियों का उपयोग करते हुए) नियमानुसार pH की गणना करते हैं।

प्रबल क्षार द्वारा H_nX के अनुमापन में :

1st उदासीनीकरण के संदर्भ में अर्द्ध तुल्यांकी बिन्दु पर : $\text{pH} = \text{p}K_{a_1}$;

1st उदासीनीकरण के संदर्भ में तुल्यांकी बिन्दु पर : $\text{pH} = \frac{\text{p}K_{a_2} + \text{p}K_{a_1}}{2}$;

2nd उदासीनीकरण के संदर्भ में अर्द्ध तुल्यांकी बिन्दु पर : $\text{pH} = \text{p}K_{a_2}$;

2nd उदासीनीकरण के संदर्भ में तुल्यांकी बिन्दु पर : $\text{pH} = \frac{\text{p}K_{a_3} + \text{p}K_{a_2}}{2}$;

अन्तिम उदासीनीकरण के संदर्भ में तुल्यांकी बिन्दु पर : $\text{pH} = \frac{1}{2}(\text{p}K_w + \text{p}K_{a_n} + \log C)$.

प्रबल अम्ल द्वारा बहुअम्लीय क्षार B के अनुमापन में :

1st उदासीनीकरण के संदर्भ में अर्द्ध तुल्यांकी बिन्दु पर : $\text{pOH} = \text{p}K_{b_1}$;

1st उदासीनीकरण के संदर्भ में तुल्यांकी बिन्दु पर : $\text{pOH} = \frac{\text{p}K_{b_2} + \text{p}K_{b_1}}{2}$;

2nd उदासीनीकरण के संदर्भ में अर्द्ध तुल्यांकी बिन्दु पर : $\text{pOH} = \text{p}K_{b_2}$;

2nd उदासीनीकरण के संदर्भ में तुल्यांकी बिन्दु पर : $\text{pH} = \frac{\text{p}K_{b_3} + \text{p}K_{b_2}}{2}$;

अन्तिम उदासीनीकरण के संदर्भ में तुल्यांकी बिन्दु पर : $\text{pH} = \frac{1}{2}(\text{p}K_w - \text{p}K_{b_n} - \log C)$.

C-1. The total number of different kind of buffers obtained during the titration of H_3PO_4 with NaOH are :
 NaOH के साथ H_3PO_4 के अनुमापन के दौरान प्रकार के बफर प्राप्त होते हैं।

(A*) 3

(B) 1

(C) 2

(D) Zero (शून्य)

Sol. $\text{NaH}_2\text{PO}_4 + \text{H}_3\text{PO}_4$; $\text{NaH}_2\text{PO}_4 + \text{Na}_2\text{HPO}_4$; $\text{Na}_2\text{HPO}_4 + \text{Na}_3\text{PO}_4$.



C-2 Upon titration a solution of Ethylene diamine ($K_{b_1} = 8 \times 10^{-5}$; $K_{b_2} = 2.7 \times 10^{-8}$) with HCl solution, pH value of solution at 1st equivalence point depends upon :

- (A) Initial concentration of weak base solution (B) Initial concentration of strong acid solution
(C) Both (A) & (B) (D*) None of these

HCl विलयन के साथ एथाइलीन डाइएमीन ($K_{b_1} = 8 \times 10^{-5}$; $K_{b_2} = 2.7 \times 10^{-8}$) के विलयन के अनुमापन के दौरान प्रथम तुल्यांकी बिन्दु पर विलयन के pH का मान निम्न पर निर्भर करता है :

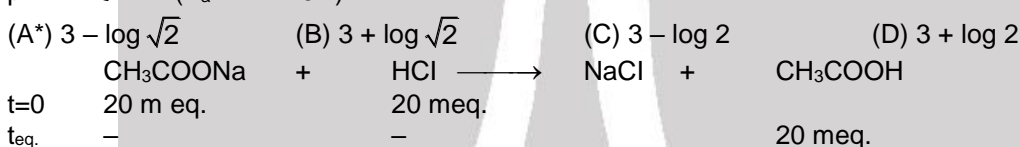
- (A) दुर्बल क्षार विलयन की प्रारम्भिक सान्द्रता (B) प्रबल अम्ल विलयन की प्रारम्भिक सान्द्रता
(C) दोनों (A) तथा (B) (D*) इनमें से कोई नहीं

Sol. An ampholyte will be formed ($C_2N_2H_9^+Cl^-$).

हल. एक एम्फोलाइट (ampholyte) ($C_2N_2H_9^+Cl^-$) बनेगा।

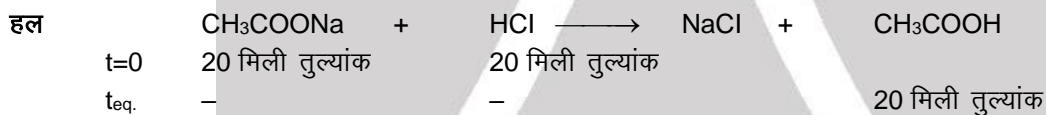
C-3. What will be the pH at the equivalence point during the titration of a 100 mL 0.2 M solution of CH_3COONa with 0.2 M solution of HCl ? $K_a = 2 \times 10^{-5}$.

HCl के 0.2 M विलयन के साथ CH_3COONa के 0.2 M वाले 100 mL विलयन के अनुमापन के दौरान तुल्यांक बिन्दु पर pH क्या होगा ? ($K_a = 2 \times 10^{-5}$)



$$[CH_3COOH] = \frac{20}{200} = 0.1 \text{ M}$$

$$pH = \frac{1}{2} [pK_a - \log C] = \frac{1}{2} [5 - \log 2 + 1] = \frac{1}{2} [6 - \log 2] = 3 - \log \sqrt{2}$$



$$[CH_3COOH] = \frac{20}{200} = 0.1 \text{ M}$$

$$pH = \frac{1}{2} [pK_a - \log C] = \frac{1}{2} [5 - \log 2 + 1] = \frac{1}{2} [6 - \log 2] = 3 - \log \sqrt{2}$$

Exercise-2

☞ Marked Questions may have for Revision Questions.

☞ चिन्हित प्रश्न दोहराने योग्य प्रश्न है।

PART - I : SINGLE AND DOUBLE VALUE INTEGER TYPE

भाग - I : एकल एवं द्वि-पूर्णांक मान प्रकार (SINGLE AND DOUBLE VALUE INTEGER TYPE)

1.☞ 15 mL sample of 0.15 M $NH_3(aq)$ is titrated against 0.1M $HCl(aq)$. What is the pH at the end point ? K_b of $NH_3(aq) = 1.8 \times 10^{-5}$. Report the answer rounding it off to the nearest whole number.
0.15 M NH_3 (जलीय) के 15 mL प्रादर्श को 0.1 M HCl (जलीय) के साथ अनुमापित किया जाता है। अन्तिम बिन्दु पर pH क्या है ? NH_3 (जलीय) का $K_b = 1.8 \times 10^{-5}$. अपने उत्तर को निकटतम पूर्णांक के रूप में दें।

Ans. 5 (exact answer यथार्थ उत्तर = 5.24)

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

Milimole	2.25	2.25	0
at end point	0	0	2.25

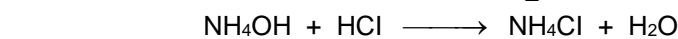
$$\text{Milimole} = N_1 \times V_{HCl} = 2.25 \quad V_{HCl} = \frac{2.25}{0.1} = 22.5$$



$$[\text{NH}_4\text{Cl}] = \left[\frac{2.25}{37.5} \right] = 0.06\text{M} \quad \text{and} \quad \text{pK}_b = 5 - \log 1.8 = 4.74$$

$$\therefore \text{pH} = 7 - \frac{1}{2} \text{pK}_b - \frac{1}{2} \log C = 7 - \frac{4.74}{2} - \frac{1}{2} \log 0.06 = 5.24$$

हल



अन्तिम बिन्दु

2.25 2.25 0

पर मिलीमोल

0 0 2.25

$$\text{मिलीमोल} = N_1 \times V_{\text{HCl}} = 2.25$$

$$V_{\text{HCl}} = \frac{2.25}{0.1} = 22.5$$

$$[\text{NH}_4\text{Cl}] = \left[\frac{2.25}{37.5} \right] = 0.06\text{M} \quad \text{तथा} \quad \text{pK}_b = 5 - \log 1.8 = 4.74$$

$$\therefore \text{pH} = 7 - \frac{1}{2} \text{pK}_b - \frac{1}{2} \log C = 7 - \frac{4.74}{2} - \frac{1}{2} \log 0.06 = 5.24$$

2.25

A 0.252 g sample of unknown organic base is dissolved in water and titrated with a 0.14 M HCl solution. After the addition of 20 mL of acid, a pH of 10.7 is recorded. The equivalence point is reached when a total of 40 mL of HCl is added. If the base and acid combine in a 1 : 1 molar ratio, then 'a' g is the molar mass of the organic base and 'b' is the ionisation constant of base. Report your answer as

$$\left(\frac{a}{1000b} \right)$$

एक अज्ञात कार्बनिक क्षार के 0.252 ग्राम प्रादर्श को जल में घोला जाता है तथा 0.14 M HCl विलयन के साथ अनुमापित किया जाता है। 20 mL अम्ल के मिलाने के पश्चात् विलयन का pH 10.7 मापा गया। जब HCl के कुल 40 mL मिलाये जाते हैं, तब तुल्यांक बिन्दु प्राप्त होता है। अम्ल तथा क्षार 1 : 1 मोलर अनुपात में संयोजित होते हैं, तो कार्बनिक क्षार का

मोलर द्रव्यमान 'a' ग्राम है तथा क्षार का आयनन नियतांक 'b' है। अपना उत्तर $\left(\frac{a}{1000b} \right)$ के रूप में दीजिए।

Ans.

90 (a = 45 & b = 5 × 10⁻⁴)

Sol.

At eq. point

No. of millieq. of Base = No. of millieq. of HCl

$$\frac{0.252 \times 1000}{\text{Molarmass}} = 0.14 \times 40$$

$$\therefore \text{Molar mass of base} = 45$$

हल.

तुल्यांकी बिन्दु पर

क्षार के मिली तुल्यांकों की संख्या = HCl के मिली तुल्यांक

$$\frac{0.252 \times 1000}{\text{मोलर द्रव्यमान}} = 0.14 \times 40$$

$$\therefore \text{क्षार का मोलर द्रव्यमान} = 45$$

PART - II : ONE OR MORE THAN ONE OPTIONS CORRECT TYPE

भाग - III : एक या एक से अधिक सही विकल्प प्रकार

- Aniline behaves as a weak base. When 0.1 M, 50 mL solution sample of aniline was mixed with 0.2 M, 12.5 mL solution of HCl, the pH of resulting solution was 8. Then :
 (A*) pH of 0.01 M solution of anilinium chloride is 5.
 (B) pH of original solution of aniline is 3.5.
 (C*) Upon adding the same aniline sample to the above mixture, pH of resulting solution becomes 8.48.
 (D*) Upon adding the same HCl sample to the above mixture, pH of resulting solution becomes 4.59.



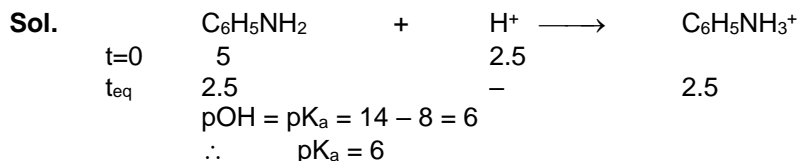
एनीलीन एक दुर्बल क्षार के समान व्यवहार करता है। जब एनीलीन के 0.1 M, 50 mL विलयन प्रादर्श को 0.2 M, 12.5 mL HCl विलयन के साथ मिश्रित करते हैं, तब परिणामी विलयन का pH 8 प्राप्त हुआ। अतः,

(A*) एनीलिनीयम क्लोराइड के 0.01 M विलयन का pH 5 है।

(B) एनीलीन के वास्तविक विलयन का pH 3.5 है।

(C*) उपरोक्त मिश्रण में समान एनीलीन प्रादर्श को मिलाने पर परिणामी विलयन का pH 8.48 हो जाती है।

(D*) उपरोक्त मिश्रण में समान HCl प्रादर्श को मिलाने पर परिणामी विलयन का pH 4.59 हो जाती है।



Now for the solution of $[\text{C}_6\text{H}_5\text{NH}_3^+]$ (अब $[\text{C}_6\text{H}_5\text{NH}_3^+]$ के विलयन के लिए) = 0.01 M

$$\text{pH} = 7 - \frac{1}{2} \text{pK}_a - \frac{1}{2} \log C = 7 - \frac{6}{2} - \frac{1}{2} \log (0.01) = 5$$

2. Which of the following mixtures will act as buffer ?

(A*) $\text{H}_2\text{CO}_3 + \text{NaOH}$ (1.5 : 1 molar ratio)

(B*) $\text{H}_2\text{CO}_3 + \text{NaOH}$ (1.5 : 2 molar ratio)

(C*) $\text{NH}_4\text{OH} + \text{HCl}$ (5 : 4 molar ratio)

(D) $\text{NH}_4\text{OH} + \text{HCl}$ (4 : 5 molar ratio)

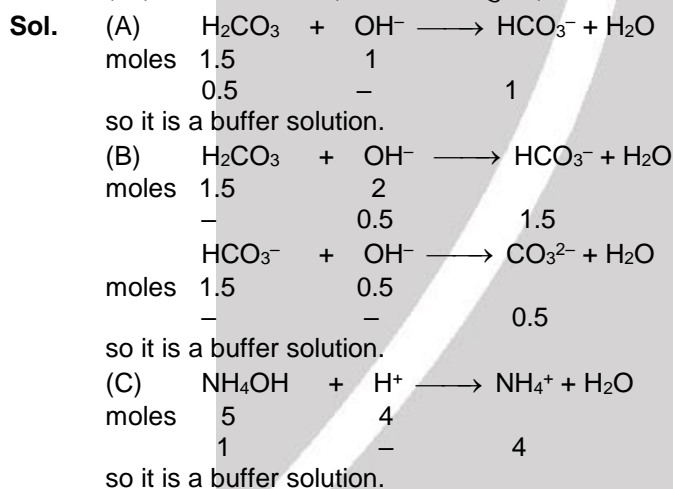
निम्न में से कौनसा(से) मिश्रण बफर के समान व्यवहार प्रदर्शित करेगा/करेंगे ?

(A*) $\text{H}_2\text{CO}_3 + \text{NaOH}$ (1.5 : 1 मोलर अनुपात)

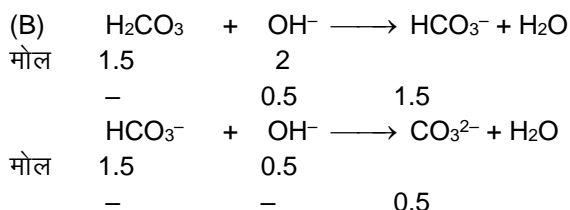
(B*) $\text{H}_2\text{CO}_3 + \text{NaOH}$ (1.5 : 2 मोलर अनुपात)

(C*) $\text{NH}_4\text{OH} + \text{HCl}$ (5 : 4 मोलर अनुपात)

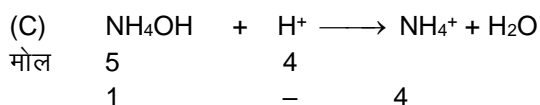
(D) $\text{NH}_4\text{OH} + \text{HCl}$ (4 : 5 मोलर अनुपात)



अतः यह विलयन बफर है।



अतः यह विलयन बफर है।

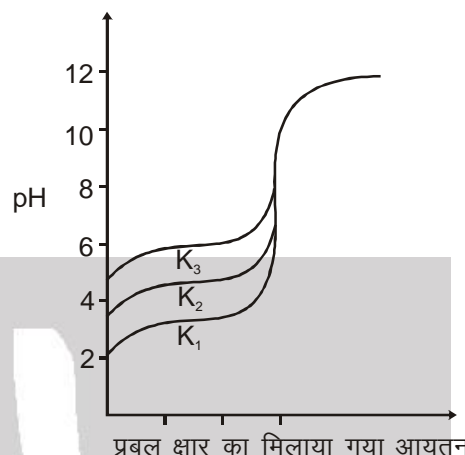
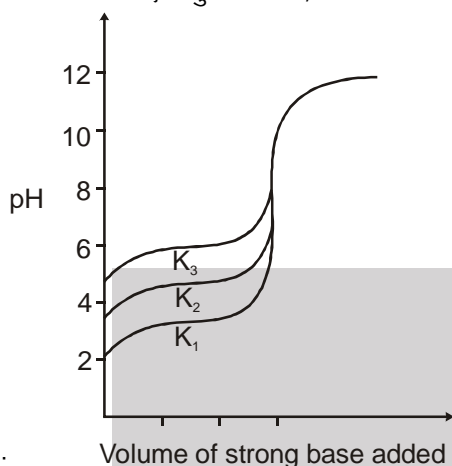


अतः यह विलयन बफर है।



3. Titration curves for 0.1M solutions of three weak acids HA_1 , HA_2 and HA_3 with ionization constants K_1 , K_2 and K_3 respectively with a strong base are plotted as shown in the figure. Which of the following options is/are true ?

प्रबल क्षार के साथ आयनन नियतांक K_1 , K_2 तथा K_3 के साथ तीन दुर्बल अम्ल क्रमशः HA_1 , HA_2 व HA_3 के 0.1 M विलयन के लिए अनुमापन वक्र, चित्र में दिखाये अनुसार आरेखित किये गये हैं। निम्न में से कौनसा(से) विकल्प सत्य है/हैं



- (A) $K_2 = (K_1 + K_3)/2$ (B*) $pK_1 < pK_3$ (C*) $K_1 > K_2$ (D*) $K_2 > K_3$
Sol. Higher the K_a of acid lower is the pH of acid for same concentration.
Sol. समान सान्द्रता के लिए, किसी अम्ल का K_a जितना अधिक होगा pH उतनी ही कम होगी।

PART - III : COMPREHENSION

भाग - III : अनुच्छेद (COMPREHENSION)

Read the following passage carefully and answer the questions.

निम्न अनुच्छेद को ध्यानपूर्वक पढ़िये तथा प्रश्नों के उत्तर दीजिए।

Comprehension # 1

The pH of basic buffer mixtures is given by : $pH = pK_a + \log \frac{[Base]}{[Salt]}$, whereas pH of acidic buffer mixtures is given by : $pH = pK_a + \log \frac{[Salt]}{[Acid]}$. Addition of little acid or base although shows no appreciable change in pH for all practical purposes, but since the ratio $\frac{[Base]}{[Salt]}$ for $\frac{[Salt]}{[Acid]}$ changes, a slight decrease or increase in pH results.

अनुच्छेद # 1

क्षारीय बफर मिश्रण का pH निम्न सूत्र से दिया जाता है : $pH = pK_a + \log \frac{[क्षार]}{[लवण]}$, तथा अम्लीय बफर मिश्रण का pH निम्न सूत्र से दिया जाता है : $pH = pK_a + \log \frac{[लवण]}{[अम्ल]}$ । अल्प मात्रा में अम्ल या क्षार को मिलाने पर प्रायोगिक उद्देश्य में pH में कोई सार्थक परिवर्तन नहीं दिखाई देता है, परन्तु $\frac{[क्षार]}{[लवण]}$ व $\frac{[लवण]}{[अम्ल]}$ के अनुपात में परिवर्तन होने से pH के परिणाम में अल्प कमी या वृद्धि होती है।

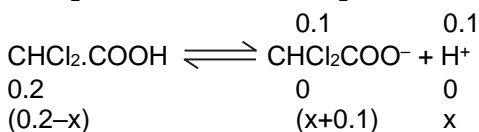
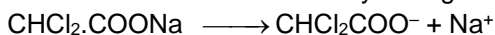




1. A solution containing 0.2 mole of dichloroacetic acid ($K_a = 5 \times 10^{-2}$) and 0.1 mole sodium dichloroacetate in one litre solution has $[H^+]$:
 एक लीटर विलयन में 0.2 मोल डाइक्लोरोएसीटिक अम्ल ($K_a = 5 \times 10^{-2}$) तथा 0.1 मोल सोडियम डाइक्लोरोएसीटेट उपस्थित हैं। विलयन में $[H^+]$ है :

(A*) 0.05 M (B) 0.025 M (C) 0.10 M (D) 0.005 M

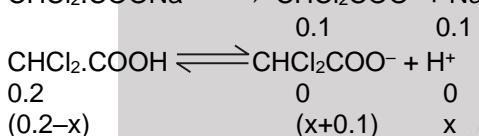
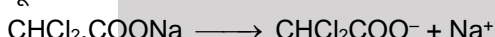
Sol. Since $CHCl_2COOH$ is relatively strong acid having more K_a .



$$\therefore K_a = \frac{[CHCl_2COO^-][H^+]}{[CHCl_2COOH]} \quad \text{or} \quad 5 \times 10^{-2} = \frac{[0.1+x][x]}{[0.2-x]}$$

$$\therefore x = 0.05.$$

हल. चूंकि $CHCl_2COOH$ आपेक्षिक रूप से प्रबल अम्ल है तथा इसलिए K_a अधिक होता है



$$\therefore K_a = \frac{[CHCl_2COO^-][H^+]}{[CHCl_2COOH]} \quad \text{या} \quad 5 \times 10^{-2} = \frac{[0.1+x][x]}{[0.2-x]}$$

$$\therefore x = 0.05.$$

2. The volume of 0.2 M NaOH needed to prepare a buffer of pH 4.74 with 50 mL of 0.2 M acetic acid is :
 (pK_b of $CH_3COO^- = 9.26$)

0.2 M एसीटिक अम्ल के 50 mL के साथ 0.2 M NaOH का आयतन मिलाकर तैयार किया जाये, कि बने हुए विलयन का pH 4.74 हो जाये : (CH_3COO^- का pK_b = 9.26)

(A) 50 mL (B*) 25 mL (C) 20 mL (D) 10 mL

Sol. Let V mL of NaOH be needed to give CH_3COONa .



$$\therefore pH = pK_a + \log \frac{[Salt]}{[Acid]} = pK_w - pK_b + \log \frac{[Salt]}{[Acid]} = 14 - 9.26 + \log \frac{[Salt]}{[Acid]}$$

$$= 14 - 9.26 + \log \frac{\left[\frac{0.2V}{50 + V} \right]}{\left[\frac{10 - 0.2V}{50 + V} \right]}$$

$$4.74 = 4.74 + \log \left[\frac{0.2V}{10 - 0.2V} \right] \quad \therefore V = \frac{10}{0.4} = 25 \text{ mL.}$$

हल. माना NaOH का V mL CH_3COONa को देने के लिए आवश्यक है।



$$\therefore pH = pK_a + \log \frac{[\text{लवण}]}{[\text{अम्ल}]} = pK_w - pK_b + \log \frac{[\text{लवण}]}{[\text{अम्ल}]} = 14 - 9.26 + \log \frac{[\text{लवण}]}{[\text{अम्ल}]}$$



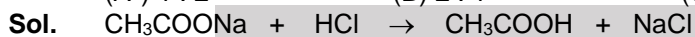
$$= 14 - 9.26 + \log \frac{\left[\frac{0.2V}{50+V} \right]}{\left[\frac{10-0.2V}{50+V} \right]}$$

$$4.74 = 4.74 + \log \left[\frac{0.2V}{10-0.2V} \right] \quad \therefore V = \frac{10}{0.4} = 25 \text{ mL.}$$

3. The ratio of pH of solution (I) containing 1 mole of CH_3COONa and 1 mole of HCl and solution (II) containing 1 mole of CH_3COONa and 1 mole of acetic acid in one litre is :

विलयन (I) जिसमें CH_3COONa तथा HCl प्रत्येक का 1 मोल तथा विलयन (II) में CH_3COONa का 1 मोल तथा एसिटिक अम्ल का 1 मोल, एक लीटर में उपस्थित है। इन विलयनों के pH का अनुपात है :

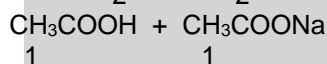
(A*) 1 : 2 (B) 2 : 1 (C) 1 : 3 (D) 3 : 1



$$\therefore [\text{CH}_3\text{COOH}] = \frac{1}{1} = 1.$$

$$\therefore [\text{H}^+] = C\alpha = C \sqrt{\frac{K_a}{C}} = \sqrt{K_a \cdot C} = \sqrt{K_a}$$

or (या) $\text{pH}_1 = -\frac{1}{2} \log K_a = \frac{1}{2} \text{p}K_a.$



$$\therefore \text{pH} = \text{p}K_a + \log \frac{1}{1}.$$

$$\text{pH}_2 = \text{p}K_a.$$

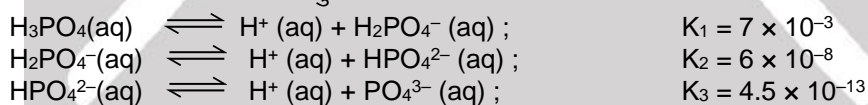
$$\therefore \frac{\text{pH}_1}{\text{pH}_2} = \frac{1}{2}.$$

Comprehension # 2

अनुच्छेद # 2

Phosphoric acid ionizes according to the following equations :

फॉस्फोरिक अम्ल निम्न समीकरणों के अनुसार आयनित होता है :



4. If you are asked to prepare a buffer with a $\text{pH} = 7.00$, what may be the molar ratio of the species that should be used in the solution ?

यदि आप से कहा जाये कि $\text{pH} = 7.00$ का बफर विलयन बनाइये, तब उन स्पीशीज का मोलर अनुपात क्या हो सकता है, जो विलयन में प्रयुक्त होनी चाहिए ?

(A*) 0.6 (B) 0.8 (C) 2 (D) 4

Sol. $\text{pH} = \text{p}K_{a_2} + \log \frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} = 7$

$$\Rightarrow \log \frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} = -0.22 \quad \Rightarrow \quad \frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} = 0.6$$





5. Assume 50 mL of the buffer prepared in the previous part is available in which more abundant species has a concentration of 0.1 M. If to this solution, 20 mL 0.1 M NaOH is added further, what will be the new pH ?

(A) 6.56 (B*) 7.44 (C) 7.78 (D) Same as before as it's a buffer
 माना कि पूर्ववर्ती भाग में बने बफर विलयन का 50 mL उपलब्ध है, जिसमें कि अधिक बाहुल्य स्पीशीज की सान्द्रता 0.1 M है। यदि इस विलयन में 0.1 M NaOH का 20 mL विलयन मिलाया जाये, तब विलयन का नया pH क्या होगा ?
 (A) 6.56 (B*) 7.44 (C) 7.78 (D) पूर्व के समान क्योंकि यह एक बफर है।

Sol. A buffer solution show best buffering action when the pH of solution is near to K_a of acid component of buffer solution

There for the above buffer can be best prepared by taking $H_2PO_4^-$ and HPO_4^{2-} .

In 50 ml buffer solution

$[H_2PO_4^-] = 0.1 \text{ M} = 5 \text{ milimole}$, $[HPO_4^{2-}] = 0.06 = 3 \text{ milimole}$
 milimole of NaOH added = $20 \times 0.01 = 2$



$$pH = pK_{a2} + \log\left(\frac{5}{3}\right) = 7.44.$$

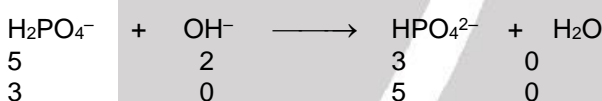
हल जब विलयन की pH बफर के अम्लीय अवयव के K_a के आसपास होती है तो बफर विलयन सबसे अच्छा बफर गुण प्रदर्शित करता है।

इसलिए $H_2PO_4^-$ और HPO_4^{2-} को लेकर उपर्युक्त में सबसे अच्छा बफर बनाया जा सकता है।

50 मिली लीटर बफर विलयन में

$[H_2PO_4^-] = 0.1 \text{ M} = 5 \text{ मिलीमोल}$, $[HPO_4^{2-}] = 0.06 = 3 \text{ मिलीमोल}$

मिलाये गये NaOH के मिलीमोल = $20 \times 0.01 = 2$



$$pH = pK_{a2} + \log\left(\frac{5}{3}\right) = 7.44.$$

Exercise-3

* Marked questions may have more than one correct option.

* चिन्हित प्रश्नों के एक से अधिक सही विकल्प हो सकते हैं।

PART - I : JEE (ADVANCED) / IIT-JEE PROBLEMS (PREVIOUS YEARS)

भाग - I : JEE (ADVANCED) / IIT-JEE (पिछले वर्षों) के प्रश्न

1. 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 of acetic acid is 1.75×10^{-5} . [JEE-2002, 5/60]
 25°C पर एसिटिक अम्ल के 0.2 M जलीय विलयन के 500 ml को 0.2 M HCl के 500 mL के साथ मिलाया जाता है।
 (a) परिणामी विलयन में एसिटिक अम्ल के वियोजन की मात्रा तथा विलयन का pH परिकलित कीजिए।
 (b) यदि उपरोक्त विलयन के साथ NaOH के 6 ग्राम मिलाये जाते हों, तो अंतिम pH ज्ञात कीजिए। यह मानकर कि मिश्रित करने पर आयतन में कोई परिवर्तन नहीं होता है। एसिटिक अम्ल का $K_a = 1.75 \times 10^{-5}$. [JEE-2002, 5/60]

Ans. (a) 0.0175%, 1 (b) 4.757

Sol. (a) $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$
 conc. 0.1 (1- α) 0.1 α (0.1+0.1 α)
 approximations



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ADVIEQ(A)- 18



Let $1-\alpha \approx 1$
and $1+\alpha \approx 1$

$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]}$$

or $1.75 \times 10^{-5} = \frac{[\text{CH}_3\text{COO}^-] \times 0.1}{0.1}$

or $[\text{CH}_3\text{COO}^-] = 1.75 \times 10^{-5}$;

or $0.1 \alpha = 1.75 \times 10^{-5}$;

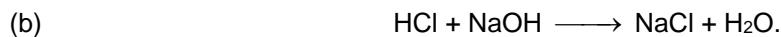
or $\alpha = 0.0175\%$

or $\text{pH} = -\log[\text{H}^+] = -\log(0.1)$;

or $C\alpha = 1.75 \times 10^{-5}$.

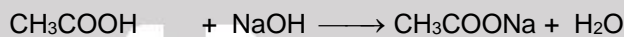
or $\alpha = 1.75 \times 10^{-4}$.

or **pH = 1.**



m mole before reaction 100 150

m mole after reaction 0 50 100

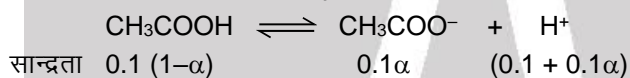


m mole before reaction 100 50

m mole after reaction 50 0 50 (buffer sol.)

$\text{pH} = \text{pK}_a + \log \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = -\log(1.75 \times 10^{-5}) = 4.757 \text{ Ans.}$

हल. (a)



माना कि $1-\alpha \approx 1$

तथा $1+\alpha \approx 1$

$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]}$$

या $1.75 \times 10^{-5} = \frac{[\text{CH}_3\text{COO}^-] \times 0.1}{0.1}$

या $[\text{CH}_3\text{COO}^-] = 1.75 \times 10^{-5}$;

या $0.1 \alpha = 1.75 \times 10^{-5}$;

या $\alpha = 0.0175\%$

या $\text{pH} = -\log[\text{H}^+] = -\log(0.1)$;

या $C\alpha = 1.75 \times 10^{-5}$.

या $\alpha = 1.75 \times 10^{-4}$.

या **pH = 1.**



अभिक्रिया के पहले मिली मोल 100 150

अभिक्रिया के बाद मिली मोल 0 50 100



अभिक्रिया के पहले मिली मोल 100 50

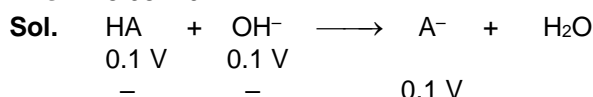
अभिक्रिया के बाद मिली मोल 50 0 50 (बफर विलयन)

$\text{pH} = \text{pK}_a + \log \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = -\log(1.75 \times 10^{-5}) = 4.757 \text{ Ans.}$

2. 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. [JEE-2004, 2/60]

0.1 M NaOH को 0.1 M HA के साथ अन्तिम बिन्दु तक अनुमापित किया जाता है। HA के लिए $K_a = 5.6 \times 10^{-6}$ है तथा वियोजन की कोटि 1 से कम है। अन्तिम बिन्दु पर परिणामी विलयन का pH परिकलित कीजिए। [JEE-2004, 2/60]

Ans. $8.98 \approx 9$



m. moles



$$[A^-] = \frac{0.1}{2} \frac{V}{V} = \frac{0.1}{2} M,$$

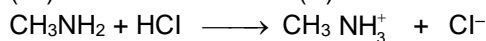
$$pH = 7 + \frac{1}{2} (pK_a + \log c) = 7 + \frac{1}{2} (6 - \log 5.6) + \frac{1}{2} \log \left(\frac{0.1}{2} \right) = 8.98 \approx 9$$

3. 0.1 mole of CH_3NH_2 ($K_b = 5 \times 10^{-4}$) is mixed with 0.08 mole of HCl and diluted to one litre. What will be the H^+ concentration in the solution ? **[JEE-2005, 3/84]**

CH_3NH_2 ($K_b = 5 \times 10^{-4}$) के 0.1 mole को HCl के 0.08 mole के साथ मिश्रित किया गया तथा 1 लीटर तक तनु किया गया। विलयन में H^+ की सांद्रता क्या होगी ? **[JEE-2005, 3/84]**

- (A) $8 \times 10^{-2} M$ (B*) $8 \times 10^{-11} M$ (C) $1.6 \times 10^{-11} M$ (D) $8 \times 10^{-5} M$

Sol.



Initial moles 0.1 0.08
moles after reaction 0.02 0 0.08 mole (in 1 L solution) \Rightarrow buffer

$$K_b = \frac{[OH^-][CH_3NH_3^+]}{[CH_3NH_2]}$$

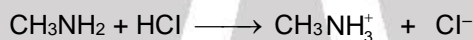
$$\text{or, } 5 \times 10^{-4} = \frac{[OH^-] \times 0.08}{0.02}$$

$$\text{or, } [OH^-] = \frac{5}{4} \times 10^{-4}$$

$$\therefore [H^+] = \frac{K_w}{[OH^-]}$$

$$\text{or, } [H^+] = \frac{10^{-14} \times 4}{5 \times 10^{-4}} = 8 \times 10^{-11} M.$$

Sol.



प्रारम्भिक मोल 0.1 0.08
अभिक्रिया के बाद मोल 0.02 0 0.08 mole (1 L विलयन में) \Rightarrow बफर

$$K_b = \frac{[OH^-][CH_3NH_3^+]}{[CH_3NH_2]}$$

$$\text{या, } 5 \times 10^{-4} = \frac{[OH^-] \times 0.08}{0.02}$$

$$\text{या, } [OH^-] = \frac{5}{4} \times 10^{-4}$$

$$\therefore [H^+] = \frac{K_w}{[OH^-]}$$

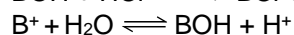
$$\text{या, } [H^+] = \frac{10^{-14} \times 4}{5 \times 10^{-4}} = 8 \times 10^{-11} M.$$

4. 2.5 mL of $\frac{2}{5} M$ weak monoacidic base ($K_b = 1 \times 10^{-12}$ at $25^\circ C$) is titrated with $\frac{2}{15} M$ HCl in water at $25^\circ C$. The concentration of H^+ at equivalence point is : ($K_w = 1 \times 10^{-14}$ at $25^\circ C$) **[JEE-2008, 3/163]**

$\frac{2}{5} M$ दुर्बल एक अम्लीय क्षार ($K_b = 1 \times 10^{-12}$, $25^\circ C$ पर) के 2.5 मिली लीटर का अनुमापन (titration) जलीय $\frac{2}{15} M$ HCl के साथ $25^\circ C$ पर किया जाता है। तुल्यांक बिन्दु (equivalence point) पर H^+ की सांद्रता है : ($K_w = 1 \times 10^{-14}$, $25^\circ C$ पर) **[JEE-2008, 3/163]**

- (A) $3.7 \times 10^{-14} M$ (B) $3.2 \times 10^{-7} M$ (C) $3.2 \times 10^{-2} M$ (D*) $2.7 \times 10^{-2} M$

Sol.



For titration :

$$M_{\text{acid}} V_{\text{acid}} = M_{\text{base}} V_{\text{base}} \text{ (since both are monoacidic and monobasic)}$$

$$\frac{2}{15} \times V = 2.5 \times \frac{2}{5}$$

$$V = 3 \times 2.5 = 7.5 \text{ mL}$$

In resulting solution,

$$[B^+] = \frac{\frac{2}{5} \times 2.5}{10} = \frac{2}{20} = 0.1 M$$

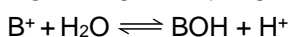


$$K_h = \frac{K_w}{K_b} = \frac{10^{-14}}{10^{-12}} = 10^{-2} \quad \text{or} \quad K_h = \frac{0.1h^2}{(1-h)} = 10^{-2}$$

(solve quadratic equation to get 'h', as we can't write $1-h \approx 1$, since $h > 0.1$)

$$\therefore h = 0.27 \quad \& \quad [H^+] = 0.1 \times 0.27 = 2.7 \times 10^{-2} \text{ M}$$

हल $\text{BOH} + \text{HCl} \longrightarrow \text{BCl} + \text{H}_2\text{O}$ (अनुमापन में)



अनुमापन के लिये :

$$M_{\text{अम्ल}} V_{\text{अम्ल}} = M_{\text{क्षार}} V_{\text{क्षार}} \quad (\text{चूँकि दोनों एकअम्लीय व एकक्षारीय हैं})$$

$$\frac{2}{15} \times V = 2.5 \times \frac{2}{5}$$

$$V = 3 \times 2.5 = 7.5 \text{ mL}$$

परिणामी विलयन में,

$$[B^+] = \frac{\frac{2}{5} \times 2.5}{10} = \frac{2}{20} = 0.1 \text{ M}$$

$$K_h = \frac{K_w}{K_b} = \frac{10^{-14}}{10^{-12}} = 10^{-2} \quad \text{या} \quad K_h = \frac{0.1h^2}{(1-h)} = 10^{-2}$$

(द्विघात समीकरण को हल कर 'h' प्राप्त करें क्योंकि हम $1-h \approx 1$ नहीं लिख सकते हैं, चूँकि $h > 0.1$ है)

$$\therefore h = 0.27 \quad \text{तथा} \quad [H^+] = 0.1 \times 0.27 = 2.7 \times 10^{-2} \text{ M}$$

5.* Aqueous solutions 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) : [JEE-2010, 3/163]

(A) HNO_3 and CH_3COOH

(B) KOH and CH_3COONa

(C*) HNO_3 and CH_3COONa

(D*) CH_3COOH and CH_3COONa

HNO_3 , KOH , CH_3COOH और CH_3COONa के समान सान्द्रताओं वाले जलीय घोल दिये गये हैं। जोड़ा/जोड़ियाँ, जो मिश्रण करने पर बफ़र बनाता/बनाते है/हैं :

[JEE-2010, 3/163]

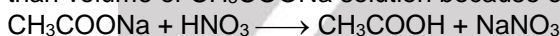
(A) HNO_3 और CH_3COOH

(B) KOH और CH_3COONa

(C*) HNO_3 और CH_3COONa

(D*) CH_3COOH और CH_3COONa

Sol. (C) $\text{HNO}_3 + \text{CH}_3\text{COONa}$ mixture can act as buffer solution if volume of HNO_3 solution taken is lesser than volume of CH_3COONa solution because of following reaction :



(D) $\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}$ - mixture will act as buffer.

Sol. (C) $\text{HNO}_3 + \text{CH}_3\text{COONa}$ मिश्रण, बफ़र विलयन की तरह कार्य कर सकता है यदि HNO_3 विलयन का आयतन CH_3COONa विलयन के आयतन की तुलना में कम लिया जाये।

अभिक्रिया निम्न प्रकार से होगी :



(D) $\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}$ - मिश्रण बफ़र की भाँति कार्य करेगा।

Comprehension

When 100 mL of 1.0 M HCl was mixed with 100 mL of 1.0 M NaOH in an insulated beaker at constant pressure, a temperature increase of 5.7°C was measured for the beaker and its contents (**Expt. 1**). Because the enthalpy of neutralization of a strong acid with a strong base is a constant ($-57.0 \text{ kJ mol}^{-1}$), this experiment could be used to measure the calorimeter constant. In a second experiment (**Expt. 2**), 100 mL of 2.0 M acetic acid ($K_a = 2.0 \times 10^{-5}$) was mixed with 100 mL of 1.0 M NaOH (under identical conditions to **Expt. 1**) where a temperature rise of 5.6°C was measured. (Consider heat capacity of all solutions as $4.2 \text{ J g}^{-1} \text{ K}^{-1}$ and density of all solutions as 1.0 g mL^{-1})



अनुच्छेद

स्थिर दाब पर एक ऊष्मारोधी बीकर (insulated beaker) में 100 mL HCl (1.0 M) को 100 mL NaOH (1.0 M) के साथ मिश्रित करने पर बीकर तथा उसकी अन्तर्वस्तुओं का तापमान 5.7°C बढ़ जाता है (प्रयोग 1)। प्रबल अम्ल के साथ प्रबल क्षारक की उदासीनीकरण (neutralization) ऐन्थैल्पी एक नियतांक ($-57.0 \text{ kJ mol}^{-1}$) होने के कारण इस प्रयोग का उपयोग कैलोरीमीटर स्थिरांक (calorimeter constant) को मापने में किया जा सकता है। एक दूसरे प्रयोग (प्रयोग 2) में 100 mL ऐसीटिक अम्ल (2.0 M , $K_a = 2.0 \times 10^{-5}$) को 100 mL NaOH (1.0 M) के साथ मिश्रित करने पर (प्रयोग 1 की समरूप अवस्था में) 5.6°C तापमान वृद्धि मापित की गयी।
(सभी विलयनों की ऊष्मा धारिता $4.2 \text{ J g}^{-1} \text{ K}^{-1}$ तथा सभी विलयनों का घनत्व 1.0 g mL^{-1} है)

6. Enthalpy of dissociation (in kJ mol^{-1}) of acetic acid obtained from the Expt. 2 is :

[JEE (Advance)2015, 4/168]

प्रयोग 2 से प्राप्त ऐसीटिक अम्ल की वियोजन ऐन्थैल्पी (dissociation enthalpy) (kJ mol^{-1} में) है : [JP/JP*]

- (A*) 1.0 (B) 10.0 (C) 24.5 (D) 51.4

Sol. Let the heat capacity of insulated beaker be C.

Mass of aqueous content in expt. 1 = $(100 + 100) \times 1 = 200 \text{ g}$

\Rightarrow Total heat capacity = $(C + 200 \times 4.2) \text{ J/K}$

Moles of acid, base neutralised in expt. 1 = $0.1 \times 1 = 0.1$

\Rightarrow Heat released in expt. 1 = $0.1 \times 57 = 5.7 \text{ KJ}$

$\Rightarrow 5.7 \times 1000 = (C + 200 \times 4.2) \times \Delta T.$

$5.7 \times 1000 = (C + 200 + 4.2) \times 5.7$

$\Rightarrow (C + 200 \times 4.2) = 1000$

In second experiment, $n_{\text{CH}_3\text{COOH}} = 0.2$, $n_{\text{NaOH}} = 0.1$

Total mass of aqueous content = 200 g

\Rightarrow Total heat capacity = $(C + 200 \times 4.2) = 1000$

\Rightarrow Heat released = $1000 \times 5.6 = 5600 \text{ J.}$

Overall, only 0.1 mol of CH_3COOH undergo neutralization.

$\Rightarrow \Delta H_{\text{neutralization}}$ of $\text{CH}_3\text{COOH} = \frac{-5600}{0.1} = -56000 \text{ J/mol} = -56 \text{ KJ/mol.}$

$\Rightarrow \Delta H_{\text{ionization}}$ of $\text{CH}_3\text{COOH} = 57 - 56 = 1 \text{ KJ/mol}$

हल : माना कि ऊष्मारोधी बीकर की ऊष्माधारिता C है।

प्रयोग प्रथम में जलीय घटक का द्रव्यमान = $(100 + 100) \times 1 = 200 \text{ g}$

\Rightarrow कुल ऊष्मा धारिता = $(C + 200 \times 4.2) \text{ J/K}$

प्रयोग प्रथम में उदासीनीकरण होने वाले अम्ल, क्षार के मोलों की संख्या = $0.1 \times 1 = 0.1$

\Rightarrow प्रयोग प्रथम में मुक्त ऊष्मा = $0.1 \times 57 = 5.7 \text{ KJ}$

$\Rightarrow 5.7 \times 1000 = (C + 200 \times 4.2) \times \Delta T.$

$5.7 \times 1000 = (C + 200 + 4.2) \times 5.7$

$\Rightarrow (C + 200 \times 4.2) = 1000$

द्वितीय प्रयोग में, $n_{\text{CH}_3\text{COOH}} = 0.2$, $n_{\text{NaOH}} = 0.1$

जलीय घटक का कुल द्रव्यमान = 200 g

\Rightarrow कुल ऊष्मा धारिता = $(C + 200 \times 4.2) = 1000$

\Rightarrow मुक्त ऊष्मा = $1000 \times 5.6 = 5600 \text{ J.}$

केवल CH_3COOH के 0.1 मोल का उदासीनीकरण होता है।

$\Rightarrow \Delta H_{\text{उदासीनीकरण}}$ $\text{CH}_3\text{COOH} = \frac{-5600}{0.1} = -56000 \text{ J/mol} = -56 \text{ KJ/mol.}$

$\Rightarrow \Delta H_{\text{आयनन}}$ $\text{CH}_3\text{COOH} = 57 - 56 = 1 \text{ KJ/mol}$

7. The pH of the solution after Expt. 2 is

प्रयोग 2 के पश्चात विलयन का pH है

- (A) 2.8 (B*) 4.7 (C) 5.0 (D) 7.0

[JEE (Advance)2015, 4/168]

[JEE (Advance)2015, 4/168]

(D) 7.0



Sol. Final solution contain 0.1 mole of CH_3COOH and CH_3COONa each.
Hence it is a buffer solution.

$$\text{pH} = \text{pK}_a + \log \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = 5 - \log 2 + \log \frac{0.1}{0.1} = 4.7$$

Sol. अन्तिम विलयन CH_3COOH तथा CH_3COONa प्रत्येक के 0.1 मोल युक्त है।
अतः यह एक बफर विलयन है

$$\text{pH} = \text{pK}_a + \log \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = 5 - \log 2 + \log \frac{0.1}{0.1} = 4.7$$

8. Dilution processes of different aqueous solutions, with water, are given in LIST-I. The effects of dilution of the solution on $[\text{H}^+]$ are given in LIST-II.

(Note : degree of dissociation (α) of weak acid and weak base is $\ll 1$; degree of hydrolysis of salt $\ll 1$; $[\text{H}^+]$ represents the concentration of H^+ ions)

[JEE (Advance) 2018, 3/120]

LIST-I

- (P) (10 mL of 0.1 M NaOH + 20 mL of 0.1 M acetic acid) diluted to 60 mL
(Q) (20 mL of 0.1 M NaOH + 20 mL of 0.1 M acetic acid) diluted to 80 mL
(R) (20 mL of 0.1 M HCl + 20 mL of 0.1 M ammonia solution) diluted to 80 mL
(S) 10 mL saturated solution of $\text{Ni}(\text{OH})_2$ in equilibrium with excess solid $\text{Ni}(\text{OH})_2$ is diluted to 20 mL (solid $\text{Ni}(\text{OH})_2$ is still present after dilution).

LIST-II

- (1) the value of $[\text{H}^+]$ does not change on dilution
(2) the value of $[\text{H}^+]$ changes to half of its initial value on dilution
(3) the value of $[\text{H}^+]$ changes to two times of its initial value on dilution
(4) the value of $[\text{H}^+]$ changes to $\frac{1}{\sqrt{2}}$ times of its initial value on dilution
(5) the value of $[\text{H}^+]$ changes to $\sqrt{2}$ times of its initial value on dilution

Match each process given in LIST-I with one or more effect(s) in LIST-II. the correct option is

- (A) $P \rightarrow 4$; $Q \rightarrow 2$; $R \rightarrow 3$; $S \rightarrow 1$
(C) $P \rightarrow 1$; $Q \rightarrow 4$; $R \rightarrow 5$; $S \rightarrow 3$

- (B) $P \rightarrow 4$; $Q \rightarrow 3$; $R \rightarrow 2$; $S \rightarrow 3$
(D) $P \rightarrow 1$; $Q \rightarrow 5$; $R \rightarrow 4$; $S \rightarrow 1$

सूची-I (LIST-I) में अलग अलग जलीय विलयनों का जल के साथ तनुकरण करने में प्रक्रम दिए गए हैं। विलयन के तनुकरण से $[\text{H}^+]$ पर हुए प्रभाव सूची-II (LIST-II) में दिए गए हैं।

[JEE (Advance) 2018, 3/120]

(ध्यान दें, दुर्बल अम्ल और दुर्बल क्षार की वियोजन मात्रा (α) (degree of dissociation) $\ll 1$ है; लवण के जल-अपघटन की मात्रा (degree of hydrolysis of salt) $\ll 1$ है; $[\text{H}^+]$, H^+ आयनों की सांद्रता को निरूपित करता है)

LIST-I

- (P) (0.1 M NaOH का 10 mL + 0.1 M एसिटिक अम्ल का 20 mL) का 60 mL तक तनुकरण
(Q) (0.1 M NaOH का 20 mL + 0.1 M एसिटिक अम्ल का 20 mL) का 80 mL तक तनुकरण
(R) (0.1 M HCl का 20 mL + 0.1 M अमोनिया विलयन का 20 mL) का 80 mL तक तनुकरण
(S) 10 mL $\text{Ni}(\text{OH})_2$ का संतृप्त विलयन (saturated solution) जो आधिक्य ठोस

$\text{Ni}(\text{OH})_2$ के साथ साम्यावस्था में है, उसका 20 mL तक तनुकरण किया गया (ठोस $\text{Ni}(\text{OH})_2$ तनुकरण के पश्चात भी उपस्थित है)।

LIST-II

- (1) तनुकरण करने पर $[\text{H}^+]$ के मान में कोई बदलाव नहीं होता है
(2) तनुकरण करने पर $[\text{H}^+]$ का मान बदलकर इसके प्रारंभिक मान का आधा होता है
(3) तनुकरण करने पर $[\text{H}^+]$ का मान बदलकर इसके प्रारंभिक मान का दो गुणा होता है
(4) तनुकरण करने पर $[\text{H}^+]$ का मान बदलकर इसके प्रारंभिक मान का $\frac{1}{\sqrt{2}}$ गुणा होता है
(5) तनुकरण करने पर $[\text{H}^+]$ का मान बदलकर इसके प्रारंभिक मान का $\sqrt{2}$ गुणा होता है





सूची-I में दिए गये प्रत्येक प्रक्रम को सूची-II में दिए गए एक या अनेक प्रभाव (प्रभावों) के साथ सुमेल करें। सही विकल्प है

(A) $P \rightarrow 4$; $Q \rightarrow 2$; $R \rightarrow 3$; $S \rightarrow 1$

(B) $P \rightarrow 4$; $Q \rightarrow 3$; $R \rightarrow 2$; $S \rightarrow 3$

(C) $P \rightarrow 1$; $Q \rightarrow 4$; $R \rightarrow 5$; $S \rightarrow 3$

(D) $P \rightarrow 1$; $Q \rightarrow 5$; $R \rightarrow 4$; $S \rightarrow 1$

Ans. (D) ($P \rightarrow 1$) ; ($Q \rightarrow 5$) ; ($R \rightarrow 4$) ; ($S \rightarrow 1$)

Sol.

(P) $\text{NaOH} + \text{CH}_3\text{COOH} \longrightarrow \text{CH}_3\text{COONa} + \text{H}_2\text{O}$

M.Mole 1 2

Now solution contains 1 m. mole CH_3COOH & 1 m.mole CH_3COONa in 30 ml solution.
It is a Buffer solution

$\therefore [\text{H}^+]$ does not change with dilution.

(Q) $\text{NaOH} + \text{CH}_3\text{COOH} \longrightarrow \text{CH}_3\text{COONa} + \text{H}_2\text{O}$

M.Mole 2 2

Now solution contain 2 m.mole of CH_3COONa in 40 ml solution (salt of weak acid strong base)

$$[\text{H}^+]_{\text{initial}} = \sqrt{\frac{K_w K_a}{C}}$$

Now on dilution upto 80 ml, now conc. Becomes $\frac{C}{2}$.

$$\therefore [\text{H}^+]_{\text{new}} = \sqrt{\frac{K_w K_a}{C/2}} = [\text{H}^+]_{\text{initial}} \times \sqrt{2}$$

(R) $\text{HCl} + \text{NH}_3 \longrightarrow \text{NH}_4\text{Cl}$

M.Mole 2 2

Now solution contain 2 m.mole of NH_4Cl in 40 ml solution (salt of SA & WB)

$$[\text{H}^+]_{\text{initial}} = \sqrt{\frac{K_w}{K_b C}}$$

Now on dilution upto 80 ml, new conc. becomes $\frac{C}{2}$.

$$\therefore [\text{H}^+]_{\text{new}} = \sqrt{\frac{K_w}{K_b \frac{C}{2}}} = \frac{[\text{H}^+]_{\text{initial}}}{\sqrt{2}}$$

(S) $\text{Ni}(\text{OH})_2 (\text{s}) \longrightarrow \text{Ni}^{2+} + 2\text{OH}^-$

\therefore it is sparingly soluble salt

\therefore on dilution $[\text{OH}^-]$ conc. in saturated solution of $\text{Ni}(\text{OH})_2$ remains const.

$\therefore [\text{H}^+]_{\text{new}} = [\text{H}^+]_{\text{initial}}$

Sol.

(P) $\text{NaOH} + \text{CH}_3\text{COOH} \longrightarrow \text{CH}_3\text{COONa} + \text{H}_2\text{O}$

M.Mole 1 2

अब विलयन में 1 मिलीमोल CH_3COOH तथा 1 मिलिमोल CH_3COONa 30 ml विलयन में उपस्थित है।
यह एक बफर विलयन है।

$\therefore [\text{H}^+]$ तनुता के साथ परिवर्तित नहीं होता है।

(Q) $\text{NaOH} + \text{CH}_3\text{COOH} \longrightarrow \text{CH}_3\text{COONa} + \text{H}_2\text{O}$

M.Mole 2 2

अब विलयन में 2 m. मिलिमोल CH_3COONa 40 ml विलयन (दुर्बल अम्ल प्रबल क्षार का लवण) में उपस्थित है।

$$[\text{H}^+]_{\text{initial}} = \sqrt{\frac{K_w K_a}{C}}$$

अब 80 ml तक तनुता पर सांद्रता $\frac{C}{2}$ हो जाती है।



$$\therefore [H^+]_{\text{new}} = \sqrt{\frac{K_w K_a}{C/2}} = [H^+]_{\text{initial}} \times \sqrt{2}$$



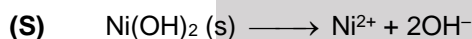
M.Mole 2 2

अब विलयन में 2 m. मिलिमोल NH_4Cl 40 ml विलयन (SA तथा WB का लवण) में उपस्थित है।

$$[H^+]_{\text{initial}} = \sqrt{\frac{K_w C}{K_b}}$$

अब 80 ml तक तनुता पर सांद्रता $\frac{C}{2}$ हो जाती है।

$$\therefore [H^+]_{\text{new}} = \sqrt{\frac{K_w C}{K_b \cdot 2}} = \frac{[H^+]_{\text{initial}}}{\sqrt{2}}$$



\therefore यह अल्प विलयशील लवण है।

\therefore तनुता पर $[OH^-]$ सांद्रता $Ni(OH)_2$ के संतृप्त विलयन में नियत रखती है।

$$\therefore [H^+]_{\text{new}} = [H^+]_{\text{initial}}$$

PART - II : JEE (MAIN) (PREVIOUS YEARS)

भाग - II : JEE (MAIN) (पिछले वर्षों) के प्रश्न

JEE(MAIN) OFFLINE PROBLEMS

1. An alkali is titrated against an acid with methyl orange as indicator, which of the following is a correct combination? [JEE(Main)-2018, 4/120]

Base	Acid	End point
(1*) Weak	Strong	Yellow to pinkish red
(2) Strong	Strong	Pink to colourless
(3) Weak	Strong	Colourless to pink
(4) Strong	Strong	Pinkish red to yellow

मेथिल ऑरेंज को एक सूचक के रूप में प्रयोग करके, एक क्षार को एक अम्ल के विरुद्ध अनुमापित किया जाता है। निम्न में से कौन सा एक सही संयोग है? [JEE(Main)-2018, 4/120]

क्षार	अम्ल	अन्त्य बिन्दु
(1*) दुर्बल	प्रबल	पीले से गुलाबी लाल
(2) प्रबल	प्रबल	गुलाबी से रंगहीन
(3) दुर्बल	प्रबल	रंगहीन से गुलाबी
(4) प्रबल	प्रबल	गुलाबी लाल से पीला



Weak base Strong acid

At end point pH will be less than 7

$$\text{as strong acid weak base salt have } pH = 7 - \frac{(pK_b + \log c)}{2}$$

\therefore Methyl orange will change colour from yellow to pinkish red at the end point.



दुर्बल क्षार प्रबल अम्ल

अन्तिम बिन्दु पर pH, 7 से कम होगी

$$\text{चुकि प्रबल अम्ल तथा दुर्बल क्षार वाले लवण की } pH = 7 - \frac{(pK_b + \log c)}{2}$$

\therefore अन्तिम बिन्दु पर मेथिल ऑरेंज का रंग पीले से गुलाबी लाल हो जाता है।



IONIC EQUILIBRIUM-III

आयनिक साम्य-III

Exercise-1

Marked Questions may have for Revision Questions.

चिह्नित प्रश्न दोहराने योग्य प्रश्न है।

PART - I : SUBJECTIVE QUESTIONS

भाग - I : विषयात्मक प्रश्न (SUBJECTIVE QUESTIONS)

Section (A) : Solubility, Solubility product and Simple solubility calculations

खण्ड (A) : विलेयता, विलेयता गुणनफल तथा विलेयता की सरल गणनाएँ

Commit to memory :

Solubility (s; in mol/L) of a sparingly soluble salt A_xB_y : $K_{sp} = x^x \cdot y^y \cdot (s)^{x+y}$

याद रखने योग्य तथ्य :

एक कम विलयशील लवण A_xB_y की विलेयता (s; mol/L में) : $K_{sp} = x^x \cdot y^y \cdot (s)^{x+y}$

A-1. Although it is a violent poison if swallowed, Mercury(II) cyanide $Hg(CN)_2$, has been used as a typical skin antiseptic. (K_{sp} of $Hg(CN)_2 = 1.35 \times 10^{-23}$, Atomic mass of Hg = 200 u). Assume no ion to be undergoing hydrolysis.

(a) What is the molar solubility of this salt in pure water ?

(b) How many milligrams of $Hg(CN)_2$ dissolve per litre of pure water ?

(c) How many milliliters of water are required to dissolve 1.134 g of the salt ?

मर्करी(II) सायनाइड $Hg(CN)_2$ निगलने पर यद्यपि तीव्र विष है, लेकिन त्वचा-प्रतिरोधी के रूप में प्रयुक्त किया जाता है।

($Hg(CN)_2$ का $K_{sp} = 1.35 \times 10^{-23}$, Hg का परमाणु द्रव्यमान = 200 u) किसी भी आयन को जल-अपघटन करता हुआ न मानें।

(a) शुद्ध जल में इस लवण की मोलर विलेयता क्या होगी ?

(b) कितने मिलीग्राम $Hg(CN)_2$ प्रति लीटर शुद्ध जल में विलेय हैं ?

(c) इस लवण के 1.134 ग्राम को घोलने के लिए कितने मिलीलीटर जल की आवश्यकता होगी ?

Ans. (a) 1.5×10^{-8} M

(b) 3.78×10^{-3} mg

(c) 3×10^5 mL

Sol. (a) $Hg(CN)_2 \longrightarrow Hg^{+2} + 2CN^-$

$$K_{sp} = 4s^3 = 1.35 \times 10^{-23} \Rightarrow s = 1.5 \times 10^{-8} \text{ M}$$

$$(b) \text{ Milligram of } Hg(CN)_2 = [1.5 \times 10^{-8}] \times 252 \times 10^3 = 3.78 \times 10^{-3} \text{ mg/L}$$

$$(c) \therefore 3.78 \times 10^{-6} \text{ g dissolve in 1 L water,}$$

$$\therefore 1.134 \text{ gram dissolve in } = \frac{1 \times 1.134}{3.78 \times 10^{-6}} \text{ L} = \frac{11.34 \times 10^5}{3.78} \text{ L} = 3 \times 10^5 \text{ L} = 3 \times 10^8 \text{ mL}$$

हल (a) $Hg(CN)_2 \longrightarrow Hg^{+2} + 2CN^-$

$$K_{sp} = 4s^3 = 1.35 \times 10^{-23} \Rightarrow s = 1.5 \times 10^{-8} \text{ M}$$

$$(b) Hg(CN)_2 \text{ के मिलीग्राम } = [1.5 \times 10^{-8}] \times 252 \times 10^3 = 3.78 \times 10^{-3} \text{ मिलीग्राम/लीटर}$$

$$(c) \therefore 3.78 \times 10^{-6} \text{ ग्राम, 1 लीटर जल में घुलते हैं,}$$

$$\therefore 1.134 \text{ ग्राम को घोलने के लिए जल का आवश्यक आयतन } = \frac{1 \times 1.134}{3.78 \times 10^{-6}} \text{ लीटर } = \frac{11.34 \times 10^5}{3.78} \text{ लीटर } = 3 \times 10^5$$

$$\text{लीटर } = 3 \times 10^8 \text{ मिलीलीटर}$$





- A-2.** How many milligrams of gold(III) ion are there per litre of solution in a saturated aqueous solution of gold (III) iodide ? $\text{AuI}_3(\text{s}) \rightleftharpoons \text{Au}^{3+}(\text{aq}) + 3\text{I}^{-}(\text{aq})$. K_{sp} of $\text{AuI}_3 = 2.7 \times 10^{-47}$, atomic mass of Au = 197 u. Assume no hydrolysis of Au^{3+} ion.

गोल्ड (III) आयोडाइड के सतृप्त जलीय विलयन में प्रतिलीटर गोल्ड (III) आयन के कितने मिलीग्राम उपस्थित हैं ? $\text{AuI}_3(\text{s}) \rightleftharpoons \text{Au}^{3+}(\text{aq}) + 3\text{I}^{-}(\text{aq})$. AuI_3 का $K_{\text{sp}} = 2.7 \times 10^{-47}$, Au का परमाणु द्रव्यमान = 197 u. Au^{3+} का जल-अपघटन न मानें।

Ans. 1.97×10^{-7} mg

Sol. $\text{AuI}_3 \rightleftharpoons \text{Au}^{3+}(\text{aq}) + 3\text{I}^{-}(\text{aq})$

$$K_{\text{sp}} = 27(s)^4 = 2.7 \times 10^{-47} \Rightarrow s = 10^{-12} \text{ mole/L} = 1.97 \times 10^{-7} \text{ mg/L}$$

हल $\text{AuI}_3 \rightleftharpoons \text{Au}^{3+}(\text{जलीय}) + 3\text{I}^{-}(\text{जलीय})$

$$K_{\text{sp}} = 27(s)^4 = 2.7 \times 10^{-47} \Rightarrow s = 10^{-12} \text{ मोल/लीटर} = 1.97 \times 10^{-7} \text{ मिलीग्राम/लीटर}$$

Section (B) : Condition for precipitation, Common ion effect on solubility

खण्ड (B) : अवक्षेपण के लिए आवश्यक स्थिति तथा विलेयता पर समआयन प्रभाव

Commit to memory :

Condition for precipitation of A_xB_y : Ionic product or $K_{\text{IP}} > K_{\text{sp}}$; $[\text{A}^{y+}]^x [\text{B}^{x-}]^y > K_{\text{sp}}$ of A_xB_y

Common ion effect on solubility : Solubility (s') of A_xB_y (sparingly soluble ; K_{sp}) in a solution of ' c ' M $\text{A}_p\text{D}_q/\text{E}_r\text{B}_p$ (both readily soluble) : $(pc)^x(ys')^y = K_{\text{sp}}$; $s' = \dots$

याद रखने योग्य तथ्य :

A_xB_y के अवक्षेपण की शर्त : आयनिक गुणनफल या $K_{\text{IP}} > K_{\text{sp}}$; $[\text{A}^{y+}]^x [\text{B}^{x-}]^y > K_{\text{sp}}$ का K_{sp}

विलेयता पर समआयन प्रभाव : ' c ' M $\text{A}_p\text{D}_q/\text{E}_r\text{B}_p$ (दोनों तीव्र विलयशील) के विलयन में A_xB_y (कम विलयशील ; K_{sp}) की विलेयता (s') : $(pc)^x(ys')^y = K_{\text{sp}}$; $s' = \dots$

- B-1.** What can be the maximum concentration of equimolar solutions of ferrous sulphate (FeSO_4) and sodium sulphide (Na_2S), so that when mixed in equal volumes, there is no precipitation of iron sulphide (FeS) ? (For iron sulphide, $K_{\text{sp}} = 6.25 \times 10^{-18}$) Assume no ion to be undergoing hydrolysis.

फेरस सल्फेट (FeSO_4) तथा सोडियम सल्फाइड (Na_2S) के सममोलर विलयनों की सान्द्रता अधिकतम क्या हो सकती है, कि इन्हें समान आयतन में मिश्रित करने पर आयरन सल्फाइड (FeS) का अवक्षेप प्राप्त नहीं होता हो ? (आयरन सल्फाइड के लिए, $K_{\text{sp}} = 6.25 \times 10^{-18}$) किसी भी आयन को जल-अपघटन करता हुआ न मानें।

Ans. 5×10^{-9} M

Sol. $\text{FeSO}_4 + \text{Na}_2\text{S} \longrightarrow \text{FeS} + \text{Na}_2\text{SO}_4$

a M a M

$$K_{\text{sp}} = \left[\frac{a}{2} \right] \left[\frac{a}{2} \right] = 6.25 \times 10^{-18}$$

$$a^2 = 4 \times 6.25 \times 10^{-18} = 4 \times 625 \times 10^{-20}$$

$$a = 2 \times 25 \times 10^{-10} = 5 \times 10^{-9} \text{ M}$$

- B-2.** Calculate the solubility of silver phosphate (Ag_3PO_4) in mg/mL (a) in pure water and (b) in a solution that is 0.03 M in AgNO_3 . [$K_{\text{sp}}(\text{Ag}_3\text{PO}_4) = 2.7 \times 10^{-23}$]. Assume no ion to be undergoing hydrolysis. Atomic mass of Ag = 108 u.

सिल्वर फॉस्फेट, Ag_3PO_4 की mg/mL में विलेयता (a) शुद्ध जल में (b) 0.03 M AgNO_3 के विलयन में परिकलित कीजिए। [$K_{\text{sp}}(\text{Ag}_3\text{PO}_4) = 2.7 \times 10^{-23}$] किसी भी आयन को जल-अपघटन करता हुआ न मानें। Ag का परमाणु द्रव्यमान = 108 u.

Ans. (a) 4.19×10^{-4} mg/mL (b) 4.19×10^{-16} mg/mL

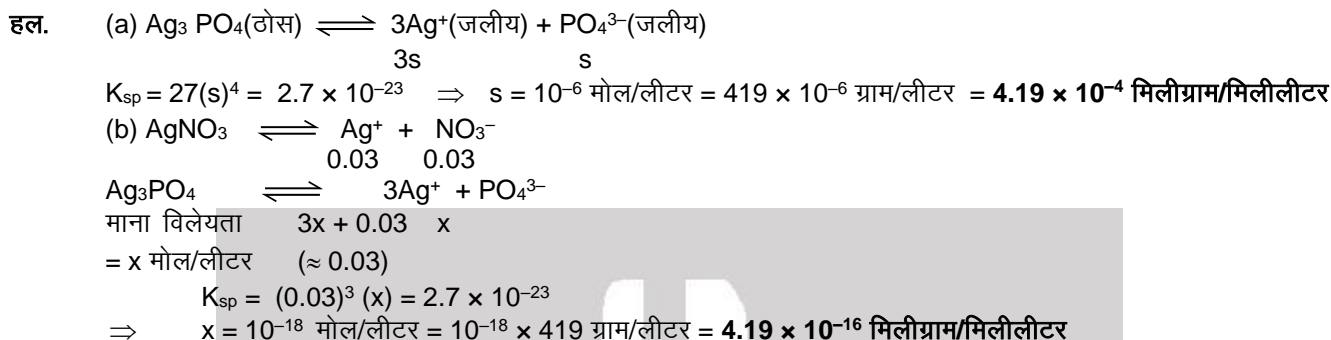
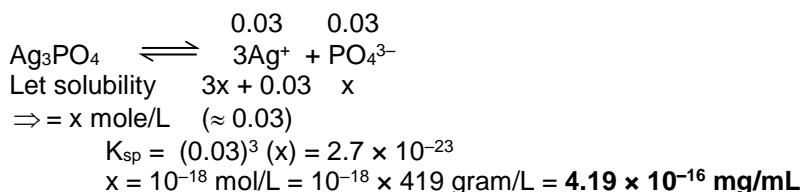
Sol. (a) $\text{Ag}_3\text{PO}_4(\text{s}) \rightleftharpoons 3\text{Ag}^{+}(\text{aq}) + \text{PO}_4^{3-}(\text{aq})$

3s s

$$K_{\text{sp}} = 27(s)^4 = 2.7 \times 10^{-23} \Rightarrow s = 10^{-6} \text{ mole/L} = 419 \times 10^{-6} \text{ gram/L} = 4.19 \times 10^{-4} \text{ mg/mL}$$

(b) $\text{AgNO}_3 \rightleftharpoons \text{Ag}^{+} + \text{NO}_3^{-}$





Section (C) : Simultaneous Solubility, Complex Formation

खण्ड (C) : समकालिक विलेयता, संकुल निर्माण

Commit to memory :

Simultaneous solubility (s_1 & s_2) of A_xB_y & A_xC_y (both sparingly soluble) :

$$\frac{K_{sp}(\text{A}_x\text{B}_y)}{K_{sp}(\text{A}_x\text{C}_y)} = \frac{[\text{B}^{x-}]^y}{[\text{C}^{x-}]^y} = \frac{(ys_1)^y}{(ys_2)^y} = \left(\frac{s_1}{s_2}\right)^y$$

Further, $(xs_1 + xs_2)^x (ys_1)^y = K_{sp}(\text{A}_x\text{B}_y)$ & $(xs_2 + xs_1)^x (ys_2)^y = K_{sp}(\text{A}_x\text{C}_y)$. Put s_1 in terms of s_2 from eq.1 in eq.2 or eq.3 to obtain s_2 & then obtain s_1 .

Complex formation : Upon mixing M^{n+} & L and analyzing the reaction $\text{M}^{n+} + x\text{L} \rightleftharpoons [\text{ML}_x]^{n+}$ through chemical equilibrium (assuming M^{n+} to be completely consumed), concentrations of L and $[\text{ML}_x]^{n+}$ can be obtained. When they are put in expression of K_c , $[\text{M}^{n+}]_{\text{eq}}$ can be obtained.

याद रखने योग्य तथ्य :

A_xB_y तथा A_xC_y (दोनों कम विलयशील) की समकालिक विलेयता (s_1 तथा s_2) :

$$\frac{K_{sp}(\text{A}_x\text{B}_y)}{K_{sp}(\text{A}_x\text{C}_y)} = \frac{[\text{B}^{x-}]^y}{[\text{C}^{x-}]^y} = \frac{(ys_1)^y}{(ys_2)^y} = \left(\frac{s_1}{s_2}\right)^y$$

आगे, $(xs_1 + xs_2)^x (ys_1)^y = K_{sp}(\text{A}_x\text{B}_y)$ तथा $(xs_2 + xs_1)^x (ys_2)^y = K_{sp}(\text{A}_x\text{C}_y)$ समीकरण-2 या समीकरण-3 में समीकरण-1 से s_2 के पदों में s_1 का मान रखने पर s_2 प्राप्त होता है तथा बाद में s_1 प्राप्त होता है :

संकुल निर्माण : M^{n+} तथा L को मिश्रित करने पर तथा रासायनिक साम्य (माना M^{n+} पूर्णतः प्रयुक्त होता है) के द्वारा अभिक्रिया $\text{M}^{n+} + x\text{L} \rightleftharpoons [\text{ML}_x]^{n+}$ का विश्लेषण करने पर L तथा $[\text{ML}_x]^{n+}$ की सान्द्रता प्राप्त हो सकती है। जब इनको K_c के व्यंजक में रखते हैं तो $[\text{M}^{n+}]_{\text{eq}}$ प्राप्त हो सकता है।

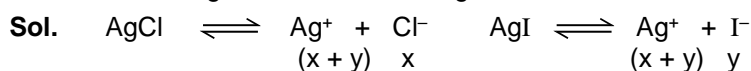
C-1. Calculate the simultaneous solubility of AgCl and AgI. Assume no hydrolysis of Ag^+ ion.

$$K_{sp}(\text{AgCl}) = 1 \times 10^{-10}, K_{sp}(\text{AgI}) = 8.5 \times 10^{-17}$$

AgCl तथा AgI की समकालिक (एक-साथ) विलेयता परिकलित कीजिए। Ag^+ का जल-अपघटन न मानें।

$$K_{sp}(\text{AgCl}) = 1 \times 10^{-10}, K_{sp}(\text{AgI}) = 8.5 \times 10^{-17}$$

Ans. $10^{-5} \text{ M AgCl}, 8.5 \times 10^{-12} \text{ M AgI}$.





$$\frac{K_{sp}(\text{AgCl})}{K_{sp}(\text{AgI})} = \frac{x}{y} = \frac{1 \times 10^{-10}}{8.5 \times 10^{-17}} = \frac{10}{8.5} \times 10^6$$

$$x = 1.8 \times 10^6 y$$

$$x + y \approx x$$

$$(x + y) \times x \approx x^2 = 10^{-10} \quad \&$$

$$(x + y) \times y \approx xy = 8.5 \times 10^{-17} \quad \&$$

$$x = 10^{-5}$$

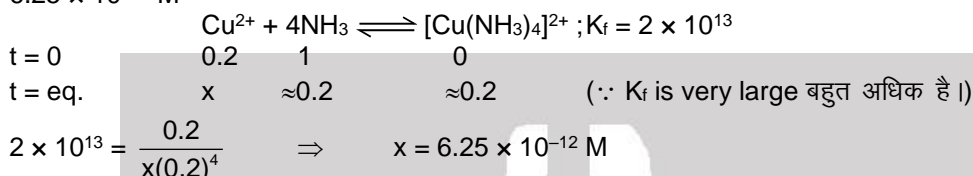
$$\&$$

$$y = 8.5 \times 10^{-12}$$

- C-2.** On passing 1 mole NH_3 gas through 1 L of 0.2 M CuSO_4 solution, determine $[\text{Cu}^{2+}]$ in the resulting solution. Given : K_f of $[\text{Cu}(\text{NH}_3)_4]^{2+} = 2 \times 10^{13}$. Assume no hydrolysis of Cu^{2+} ion.
 1 मोल NH_3 गैस को 1 L, 0.2 M CuSO_4 विलयन में प्रवाहित करने पर परिणामी विलयन में $[\text{Cu}^{2+}]$ का निर्धारण कीजिए।
 दिया गया है : $[\text{Cu}(\text{NH}_3)_4]^{2+}$ का $K_f = 2 \times 10^{13}$ माना Cu^{2+} आयन का जलअपघटन नहीं होता है।

Ans. 6.25×10^{-12} M

Sol.



Section (D) : Selective Precipitation, Solubility exchange

खण्ड (D) : चयनात्मक अवक्षेपण तथा विलेयता विनिमय

Commit to memory :

Selective precipitation: On gradually adding $\text{A}_p\text{B}_q(\text{s})$; readily soluble) to a solution containing $\text{C}_1\text{M X}^{w-}$ & $\text{C}_2\text{M Y}^{z-}$

$$[\text{A}^{q+}] \text{ req. for } \text{A}_w\text{X}_q \text{ pptn} = \sqrt[q]{\frac{K_{sp}(\text{A}_w\text{X}_q)}{(\text{C}_1)^q}}; [\text{A}^{q+}] \text{ req. for } \text{A}_z\text{Y}_q \text{ pptn} = \sqrt[q]{\frac{K_{sp}(\text{A}_z\text{Y}_q)}{(\text{C}_2)^q}}$$

Minimum value of $[\text{A}^{q+}]$ req. will tell which salt will precipitate first.

Solubility exchange: Upon treating a solution of $\text{C}_p\text{D}_q / \text{C}_p\text{D}_q(\text{s})$ (readily soluble) with $\text{A}_x\text{B}_y(\text{s})$ / saturated solution of A_xB_y (sparingly soluble) such that some A_xB_y gets converted to A_pD_y (sparingly soluble), then :

$$\sqrt[q]{\frac{K_{sp}(\text{A}_x\text{B}_y)}{[\text{B}^{x-}]_f^y}} = \sqrt[p]{\frac{K_{sp}(\text{A}_p\text{D}_y)}{[\text{D}^{p-}]_f^y}}$$

याद रखने योग्य तथ्य :

चयनात्मक अवक्षेपण : $\text{C}_1\text{M X}^{w-}$ तथा $\text{C}_2\text{M Y}^{z-}$ वाले एक विलयन में $\text{A}_p\text{B}_q(\text{s})$; तीव्र विलयशील) धीरे-धीरे मिलाने पर

$$\text{A}_w\text{X}_q \text{ के अवक्षेपण के लिए आवश्यक } [\text{A}^{q+}] = \sqrt[q]{\frac{K_{sp}(\text{A}_w\text{X}_q)}{(\text{C}_1)^q}};$$

$$\text{A}_z\text{Y}_q \text{ के अवक्षेपण के लिए आवश्यक } [\text{A}^{q+}] = \sqrt[q]{\frac{K_{sp}(\text{A}_z\text{Y}_q)}{(\text{C}_2)^q}}$$

आवश्यक $[\text{A}^{q+}]$ का न्यूनतम मान बताता है कि कौनसा लवण पहले अवक्षेपित होगा।

विलेयता विनिमय : $\text{A}_x\text{B}_y(\text{s})$ के साथ A_xB_y (कम विलयशील) के संतृप्त विलयन के साथ $\text{C}_p\text{D}_q / \text{C}_p\text{D}_q(\text{s})$ (तीव्र विलयशील) के विलयन को उपचारित करने पर कुछ A_xB_y कम विलयशील A_pD_y में परिवर्तित होता है, तब :

$$\sqrt[q]{\frac{K_{sp}(\text{A}_x\text{B}_y)}{[\text{B}^{x-}]_f^y}} = \sqrt[p]{\frac{K_{sp}(\text{A}_p\text{D}_y)}{[\text{D}^{p-}]_f^y}}$$

- D-1.** A solution which is 0.1 M in NaI and also 0.1 M in Na_2SO_4 is treated with solid $\text{Pb}(\text{NO}_3)_2$. Which compound, PbI_2 or PbSO_4 , will precipitate first ? What is the concentration of anion of the least soluble compound when the more soluble one starts precipitating ? $K_{sp}(\text{PbI}_2) = 9 \times 10^{-9}$, $K_{sp}(\text{PbSO}_4) = 1.8 \times 10^{-8}$. Assume no hydrolysis of Pb^{2+} ion.



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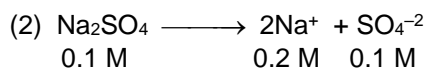
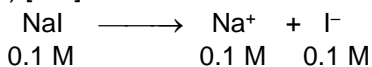
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एक विलयन, जो NaI से 0.1 M तथा Na_2SO_4 में 0.1 M है, को ठोस $\text{Pb}(\text{NO}_3)_2$ के साथ उपचारित किया जाता है। PbI_2 अथवा PbSO_4 में से कौनसा यौगिक पहले अवक्षेपित होगा ? जब अधिक विलेय पदार्थ अवक्षेपित होना प्रारम्भ होता है, तब अल्प विलेय पदार्थ के ऋणायन की सान्द्रता क्या होगी ? $K_{\text{sp}}(\text{PbI}_2) = 9 \times 10^{-9}$, $K_{\text{sp}}(\text{PbSO}_4) = 1.8 \times 10^{-8}$. Pb^{2+} का जल-अपघटन न मानें।

Ans. PbSO_4 , 0.02 M

Sol. (1) $[\text{NaI}] = 0.1 \text{ M}$



For precipitation of PbI_2 ,

$$K_{\text{sp}}(\text{PbI}_2) = [\text{Pb}^{2+}] [\text{I}^-]^2 = 9 \times 10^{-9} \quad \Rightarrow \quad [\text{Pb}^{2+}] \times (0.1)^2 = 9 \times 10^{-9}$$

$$\Rightarrow [\text{Pb}^{2+}]_{\text{req}} = 9 \times 10^{-7} \text{ M}$$

For precipitation of PbSO_4 ,

$$K_{\text{sp}}(\text{PbSO}_4) = [\text{Pb}^{2+}] [\text{SO}_4^{2-}] = 1.8 \times 10^{-8} \quad \Rightarrow \quad [\text{Pb}^{2+}] \times 0.1 = 1.8 \times 10^{-8}$$

$$\Rightarrow [\text{Pb}^{2+}]_{\text{req}} = 1.8 \times 10^{-7} \text{ M}$$

For precipitation of PbSO_4 , required conc. of Pb^{2+} is less. **So, PbSO_4 precipitates first.**

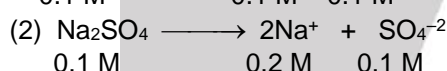
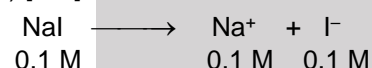
When PbI_2 (more soluble compound) starts precipitating, $[\text{Pb}^{2+}] = 9 \times 10^{-7} \text{ M}$.

Then, conc. of anion of less soluble salt can be obtained as follows :

$$K_{\text{sp}}(\text{PbSO}_4) = [\text{Pb}^{2+}] [\text{SO}_4^{2-}] = 1.8 \times 10^{-8} \Rightarrow (9 \times 10^{-7}) [\text{SO}_4^{2-}] = 1.8 \times 10^{-8}$$

$$[\text{SO}_4^{2-}] = \mathbf{0.02 \text{ M}}$$

हल (1) $[\text{NaI}] = 0.1 \text{ M}$



PbI_2 के अवक्षेपण के लिए,

$$K_{\text{sp}}(\text{PbI}_2) = [\text{Pb}^{2+}] [\text{I}^-]^2 = 9 \times 10^{-9} \quad \Rightarrow \quad [\text{Pb}^{2+}] \times (0.1)^2 = 9 \times 10^{-9}$$

$$\Rightarrow [\text{Pb}^{2+}]_{\text{आवश्यक}} = 9 \times 10^{-7} \text{ M}$$

PbSO_4 के अवक्षेपण के लिए,

$$K_{\text{sp}}(\text{PbSO}_4) = [\text{Pb}^{2+}] [\text{SO}_4^{2-}] = 1.8 \times 10^{-8} \quad \Rightarrow \quad [\text{Pb}^{2+}] \times 0.1 = 1.8 \times 10^{-8}$$

$$\Rightarrow [\text{Pb}^{2+}]_{\text{आवश्यक}} = 1.8 \times 10^{-7} \text{ M}$$

PbSO_4 के अवक्षेपण के लिए Pb^{2+} की आवश्यक सान्द्रता कम है, **इसलिए PbSO_4 पहले अवक्षेपित होता है।**

PbI_2 का अवक्षेपण तब शुरू होता है, जब $[\text{Pb}^{2+}]$ की सान्द्रता $= 9 \times 10^{-7} \text{ M}$

तब, कम विलेय लवण के ऋणायन की सान्द्रता निम्न प्रकार से प्राप्त की जा सकती है :

$$K_{\text{sp}}(\text{PbSO}_4) = [\text{Pb}^{2+}] [\text{SO}_4^{2-}] = 1.8 \times 10^{-8} \Rightarrow (9 \times 10^{-7}) [\text{SO}_4^{2-}] = 1.8 \times 10^{-8}$$

$$[\text{SO}_4^{2-}] = \mathbf{0.02 \text{ M}}$$

D-2. 0.1 mole $\text{AgCl}(\text{s})$ is added to 1 litre H_2O . Next, crystals of NaBr are added until 75% of the AgCl is converted to $\text{AgBr}(\text{s})$, the less soluble silver halide. What is $[\text{Br}^-]$ in the resulting solution ? K_{sp} of AgCl is 1.75×10^{-10} and K_{sp} of AgBr is 5.25×10^{-13} . Assume no hydrolysis of Ag^+ ion.

0.1 मोल $\text{AgCl}(\text{s})$ को 1 लीटर H_2O में मिलाया जाता है। अब NaBr के क्रिस्टल को मिलाने पर 75% AgCl , कम विलेय सिल्वर हैलाइड $\text{AgBr}(\text{s})$, में परिवर्तित होता है। परिणामी विलयन में $[\text{Br}^-]$ क्या होगी ? AgCl का $K_{\text{sp}} = 1.75 \times 10^{-10}$ तथा AgBr का $K_{\text{sp}} = 5.25 \times 10^{-13}$ है। Ag^+ का जल-अपघटन न मानें।

Ans. $2.25 \times 10^{-4} \text{ M}$

Sol. $[\text{Ag}^+] [\text{Cl}^-] = 1.75 \times 10^{-10}$

$$[\text{Ag}^+] [\text{Br}^-] = 5.25 \times 10^{-13}$$

$$\Rightarrow [\text{Br}^-] = \frac{5.25 \times 10^{-13}}{1.75 \times 10^{-10}} \times [\text{Cl}^-] = \frac{5.25 \times 10^{-13}}{1.75 \times 10^{-10}} \times (0.075) = 2.25 \times 10^{-4} \text{ M}.$$





PART - II : ONLY ONE OPTION CORRECT TYPE

भाग - II : केवल एक सही विकल्प प्रकार (ONLY ONE OPTION CORRECT TYPE)

Section (A) : Condition for precipitation, Common ion effect on solubility

खण्ड (A) : अवक्षेपण के लिए आवश्यक स्थिति तथा विलेयता पर समआयन प्रभाव

Commit to memory :

Condition for precipitation of A_xB_y : Ionic product or $K_{IP} > K_{sp}$; $[A^{y+}]^x [B^{x-}]^y > K_{sp}$ of A_xB_y

Common ion effect on solubility : Solubility (s') of A_xB_y (sparingly soluble; K_{sp}) in a solution of ' c ' M A_pD_q/E_rB_p (both readily soluble) : $(pc)^x(ys')^y = K_{sp}$; $s' = \dots$

याद रखने योग्य तथ्य :

A_xB_y के अवक्षेपण की शर्त : आयनिक गुणनफल या $K_{IP} > K_{sp}$; $[A^{y+}]^x [B^{x-}]^y > K_{sp}$ का K_{sp}

विलेयता पर समआयन प्रभाव : ' c ' M A_pD_q/E_rB_p (दोनों तीव्र विलयशील) के विलयन में A_xB_y (कम विलयशील; K_{sp}) की विलेयता (s') : $(pc)^x(ys')^y = K_{sp}$; $s' = \dots$

A-1. What is the minimum pH at which $Mg(OH)_2$ starts precipitating from a solution containing 0.02 M $MgCl_2$? K_{sp} of $Mg(OH)_2 = 1.8 \times 10^{-11}$.

0.02 M $MgCl_2$ युक्त एक विलयन से जब $Mg(OH)_2$ का अवक्षेपण प्रारम्भ होता है, तब विलयन की न्यूनतम pH क्या है ?

$Mg(OH)_2$ का $K_{sp} = 1.8 \times 10^{-11}$.

(A) 4.52 (B) 9.04 (C*) 9.48 (D) 8.48

Sol. $[Fe^{3+}][OH^-]^3 \geq K_{sp}$

$[OH^-] \geq 10^{-4.52} \Rightarrow pOH \leq 4.52 \Rightarrow pH \geq 9.48.$

Section (B) : Simultaneous solubility and Complex formation

खण्ड (B) : समकालिक विलेयता तथा संकुल निर्माण

Commit to memory :

Simultaneous solubility (s_1 & s_2) of A_xB_y & A_xC_y (both sparingly soluble) :

$$\frac{K_{sp}(A_xB_y)}{K_{sp}(A_xC_y)} = \frac{[B^{x-}]^y}{[C^{x-}]^y} = \frac{(ys_1)^y}{(ys_2)^y} = \left(\frac{s_1}{s_2}\right)^y$$

Further, $(xs_1 + xs_2)^x (ys_1)^y = K_{sp}(A_xB_y)$ & $(xs_2 + xs_1)^x (ys_2)^y = K_{sp}(A_xC_y)$. Put s_1 in terms of s_2 from eq.1 in eq.2 or

eq.3 to obtain s_2 & then obtain s_1 .

Complex formation : Upon mixing M^{n+} & L and analyzing the reaction $M^{n+} + xL \rightleftharpoons [ML_x]^{n+}$ through chemical equilibrium (assuming M^{n+} to be completely consumed), concentrations of L and $[ML_x]^{n+}$ can be obtained. When they are put in expression of K_c , $[M^{n+}]_{eq}$ can be obtained.

याद रखने योग्य तथ्य :

A_xB_y तथा A_xC_y (दोनों कम विलयशील) की समकालिक विलेयता (s_1 तथा s_2) :

$$\frac{K_{sp}(A_xB_y)}{K_{sp}(A_xC_y)} = \frac{[B^{x-}]^y}{[C^{x-}]^y} = \frac{(ys_1)^y}{(ys_2)^y} = \left(\frac{s_1}{s_2}\right)^y$$

आगे, $(xs_1 + xs_2)^x (ys_1)^y = K_{sp}(A_xB_y)$ तथा $(xs_2 + xs_1)^x (ys_2)^y = K_{sp}(A_xC_y)$ समीकरण-2 या समीकरण-3 में समीकरण-1 से s_2 के पदों में s_1 का मान रखने पर s_2 प्राप्त होता है तथा बाद में s_1 प्राप्त होता है :

संकुल निर्माण : M^{n+} तथा L को मिश्रित करने पर तथा रासायनिक साम्य (माना M^{n+} पूर्णतः प्रयुक्त होता है) के द्वारा अभिक्रिया

$M^{n+} + xL \rightleftharpoons [ML_x]^{n+}$ का विश्लेषण करने पर L तथा $[ML_x]^{n+}$ की सान्द्रता प्राप्त हो सकती है। जब इनको K_c के व्यंजक में रखते हैं तो $[M^{n+}]_{eq}$ प्राप्त हो सकता है।



- B-1.** Simultaneous solubility of two sparingly soluble salts A & B having some common ion :
 (A) is greater than their respective solubilities in separate solutions.
 (B) lies in between their solubilities in separate solutions.
 (C) is less than its solubility in separate solutions for more soluble salt, but is greater than its solubility in separate solution for less soluble salt.
 (D*) is less than their respective solubilities in separate solutions.
 कोई समान आयन रखने वाले दो कम विलयशील लवण A व B की समकालिक विलेयता :
 (A) पृथक् विलयनों में इनकी संगत विलेयताओं से अधिक होती है।
 (B) पृथक् विलयनों में इनकी विलेयताओं के मध्य में स्थित होती है।
 (C) अधिक विलयशील लवण के लिए पृथक् विलयनों में इसकी विलेयता से कम होती है, लेकिन कम विलयशील लवण के लिए पृथक् विलयनों में इसकी विलेयता से अधिक होती है।
 (D*) पृथक् विलयनों में इनकी संगत विलेयताओं से कम होती है।

Sol. Ion produced from one salt will exert common ion effect on the solubility of other salt. As a result, solubility of both salts will decrease.
 एक लवण से उत्पन्न आयन अन्य लवण की विलेयता पर समआयन प्रभाव आरोपित करेंगे इसके परिणामस्वरूप दोनों लवणों की विलेयता घटेगी।

- B-2.** The solubility product values of AgCl and AgCNS are 1.8×10^{-10} and 1.6×10^{-11} respectively. When a solution is saturated with both solids, calculate the ratio $[Cl^-]/[CNS^-]$ and also $[Ag^+]$ in the solution : Assume no reaction of cation/anion.
 AgCl एवं AgCNS के विलेयता गुणनफल के मान, क्रमशः 1.8×10^{-10} तथा 1.6×10^{-11} हैं। जब एक विलयन दोनों ठोसों से संतृप्त है, तो विलयन में $[Cl^-]/[CNS^-]$ अनुपात तथा $[Ag^+]$ परिकलित कीजिए :
 (A) 1.125, $4 \times 10^{-6} M$ (B*) 11.25, $1.4 \times 10^{-6} M$ (C) 1.25, $4 \times 10^{-5} M$ (D) 1.25, $4 \times 10^{-6} M$

Sol. $AgCl \rightleftharpoons Ag^+ + Cl^-$ $AgCNS \rightleftharpoons Ag^+ + CNS^-$
 $(x+y) \quad x \quad (x+y) \quad y$
 $\frac{K_{sp}(AgCl)}{K_{sp}(AgCNS)} = \frac{x}{y} = \frac{[Cl^-]}{[CNS^-]}$
 So, $\frac{[Cl^-]}{[CNS^-]} = \frac{x}{y} = \frac{1.8 \times 10^{-10}}{1.6 \times 10^{-11}} = 1.125 \times 10 = 11.25$
 $\Rightarrow \frac{x}{y} = 11.25 \quad \text{or } x = 11.25 y.$
 $K_{sp}(AgCl) = [Ag^+][Cl^-] = (x+y)x = 1.8 \times 10^{-10}$
 $11.25 y \times 11.25 y = 1.8 \times 10^{-10}$
 $y^2 = \frac{1.8 \times 10^{-10}}{12.25 \times 11.25}$
 So अतः, $y = 1.14 \times 10^{-6}$
 & तथा $x = 11.25 \times 1.14 \times 10^{-6} = 12.83 \times 10^{-6}$
 So अतः, $[Ag^+] = [x+y] = 12.83 \times 10^{-6} + 1.14 \times 10^{-6} = 13.97 \times 10^{-6} = 1.4 \times 10^{-5} M.$

- B-3.** Which of the following options is true for a solution saturated with AgCl and AgBr, if their solubilities in mole per litre in separate water samples are x and y respectively ? Given : $x > y$. Assume no hydrolysis of Ag^+ ion.

AgCl तथा AgBr के साथ संतृप्त एक विलयन के लिए निम्न में से कौनसा विकल्प सत्य है, यदि पृथक् जल प्रादर्शों में इनकी विलेयता मोल/लीटर में क्रमशः x तथा y है ? दिया है : $x > y$ । Ag^+ आयन का जल अपघटन न मानें।

- (A) $[Ag^+] < [Br^-] + [Cl^-]$ (B*) $x > [Cl^-] > [Br^-]$ (C) $[Br^-] > y$ (D) $[Ag^+] = x + y$

Sol. $AgCl \rightleftharpoons Ag^+ + Cl^-$; $AgBr \rightleftharpoons Ag^+ + Br^-$
 $x' + y' \quad x' \quad x' + y' \quad y'$
 (both equilibria are established simultaneously in a solution saturated with AgCl and AgBr)
 (A) $[Ag^+] = [Br^-] + [Cl^-]$
 (B, C, D)





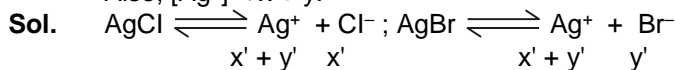
$$x > y \Rightarrow x^2 > y^2 \Rightarrow K_{sp}(\text{AgCl}) > K_{sp}(\text{AgBr})$$

$$\text{Now, for simultaneous equilibrium, } \frac{K_{sp}(\text{AgCl})}{K_{sp}(\text{AgBr})} = \frac{[\text{Cl}^-]}{[\text{Br}^-]} (> 1).$$

Also, Ag^+ produced from each salt will exert common ion effect on the equilibrium of other.

$$\therefore x > [\text{Cl}^-] \text{ \& } y > [\text{Br}^-].$$

$$\text{Also, } [\text{Ag}^+] < x + y.$$



(दोनों साम्य AgCl तथा AgBr के साथ एक संतृप्त विलयन में एक साथ स्थापित होते हैं।)

$$(A) [\text{Ag}^+] = [\text{Br}^-] + [\text{Cl}^-]$$

(B, C, D)

$$x > y \Rightarrow x^2 > y^2 \Rightarrow K_{sp}(\text{AgCl}) > K_{sp}(\text{AgBr})$$

$$\text{अब, समकालीक साम्य के लिये, } \frac{K_{sp}(\text{AgCl})}{K_{sp}(\text{AgBr})} = \frac{[\text{Cl}^-]}{[\text{Br}^-]} (> 1).$$

प्रत्येक लवण से उत्पन्न Ag^+ भी अन्य साम्य पर समआयन प्रभाव आरोपित करेंगे।

$$\therefore x > [\text{Cl}^-] \text{ \& } y > [\text{Br}^-].$$

$$\text{यह भी, } [\text{Ag}^+] < x + y.$$

B-4. Upon mixing equal volumes of 0.02 M AgNO_3 & 0.16 M KCN solutions : (Assume no hydrolysis of any ion).



$$(A) [\text{NO}_3^-] = 0.01 \text{ M} ; [\text{K}^+] = 0.08 \text{ M}$$

$$(B) [\text{CN}^-] = 0.06 \text{ M}$$

$$(C) [\text{Ag}(\text{CN})_2^-] = 0.01 \text{ M}$$

(D*) All of these

0.02 M AgNO_3 तथा 0.16 M KCN विलयनों के समान आयतनों को मिश्रित करने पर : (माना कि किसी भी आयन का जल अपघटन नहीं होता है।)

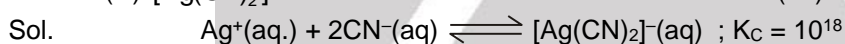


$$(A) [\text{NO}_3^-] = 0.01 \text{ M} ; [\text{K}^+] = 0.08 \text{ M}$$

$$(B) [\text{CN}^-] = 0.06 \text{ M}$$

$$(C) [\text{Ag}(\text{CN})_2^-] = 0.01 \text{ M}$$

(D*) यह सभी

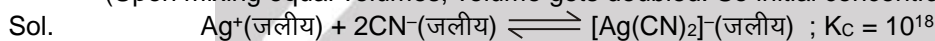


$$t = 0 \quad 0.01 \quad 0.08 \quad 0$$

$$t = \text{eq} \quad x \quad \approx 0.06 \quad \approx 0.01 \quad (\text{Assuming nearly all } \text{Ag}^+ \text{ ions to form complex } K_C \text{ very large})$$

$$(\approx 0)$$

(Upon mixing equal volumes, volume gets doubled. So initial concentrations get halved).



$$t = 0 \quad 0.01 \quad 0.08 \quad 0$$

$$t = \text{eq} \quad x \quad \approx 0.06 \quad \approx 0.01 \quad (\text{माना लगभग सभी } \text{Ag}^+ \text{ आयन संकुल बनाते हैं } K_C \text{ बहुत अधिक है।})$$

$$(\approx 0)$$

(समान आयतनों को मिश्रित करने पर आयतन दुगुना प्राप्त होता है। इसलिए प्रारम्भिक सांद्रता आधी प्राप्त होती है।)

B-5. In the above question (B-4), $[\text{Ag}^+]$ is about :

$$(A^*) 2.78 \times 10^{-18} \text{ M}$$

$$(B) 1.67 \times 10^{-19} \text{ M}$$

(C) No free Ag^+ ions will be left in the solution

(D) Cannot be determined

उपरोक्त प्रश्न (B-4) में, $[\text{Ag}^+]$ लगभग है :

$$(A^*) 2.78 \times 10^{-18} \text{ M}$$

$$(B) 1.67 \times 10^{-19} \text{ M}$$

(C) विलयन में कोई भी मुक्त Ag^+ आयन शेष नहीं रहेंगे।

(D) निर्धारण नहीं कर सकते

Sol. $10^{18} = \frac{0.01}{(0.06)^2(x)} \Rightarrow x = 2.78 \times 10^{-18} \text{ M}.$





Section (C) : Selective Precipitation, Solubility exchange

खण्ड (C) : चयनात्मक अवक्षेपण तथा विलेयता विनिमय

Commit to memory :

Selective Precipitation : On gradually adding $A_p B_q(s)$; readily soluble) to a solution containing $C_1 M X^{w-}$ & $C_2 M Y^{z-}$

$$[A^{q+}] \text{ req. for } A_w X_q \text{ pptn} = \sqrt[q]{\frac{K_{sp}(A_w X_q)}{(C_1)^q}} ; [A^{q+}] \text{ req. for } A_z Y_q \text{ pptn} = \sqrt[q]{\frac{K_{sp}(A_z Y_q)}{(C_2)^q}}$$

Minimum value of $[A^{q+}]$ req. will tell which salt will precipitate first.

Solubility exchange : Upon treating a solution of $C_p D_q / C_p D_q(s)$ (readily soluble) with $A_x B_y(s)$ / saturated solution of $A_x B_y$ (sparingly soluble) such that some $A_x B_y$ gets converted to $A_p D_y$ (sparingly soluble), then :

$$\sqrt[x]{\frac{K_{sp}(A_x B_y)}{[B^{x-}]^y}} = \sqrt[p]{\frac{K_{sp}(A_p D_y)}{[D^{p-}]^y}}$$

याद रखने योग्य तथ्य :

चयनात्मक अवक्षेपण : $C_1 M X^{w-}$ तथा $C_2 M Y^{z-}$ वाले एक विलयन में $A_p B_q(s)$; तीव्र विलयशील) धीरे-धीरे मिलाने पर

$A_w X_q$ के अवक्षेपण के लिए आवश्यक $[A^{q+}] = \sqrt[q]{\frac{K_{sp}(A_w X_q)}{(C_1)^q}} ; A_z Y_q$ के अवक्षेपण के लिए आवश्यक $[A^{q+}] =$

$$\sqrt[q]{\frac{K_{sp}(A_z Y_q)}{(C_2)^q}}$$

आवश्यक $[A^{q+}]$ का न्यूनतम मान बताता है कि कौनसा लवण पहले अवक्षेपित होगा।

विलेयता विनिमय : $A_x B_y(s)$ के साथ $A_x B_y$ (कम विलयशील) के संतृप्त विलयन के साथ $C_p D_q / C_p D_q(s)$ (तीव्र विलयशील) के विलयन को उपचारित करने पर कुछ $A_x B_y$ कम विलयशील $A_p D_y$ में परिवर्तित होता है, तब :

$$\sqrt[x]{\frac{K_{sp}(A_x B_y)}{[B^{x-}]^y}} = \sqrt[p]{\frac{K_{sp}(A_p D_y)}{[D^{p-}]^y}}$$

C-1. In a solution containing equal concentrations of X^- , Y^- & Z^- , $MCl(s)$ (a readily soluble salt) is gradually added. If $K_{sp}(MX) > K_{sp}(MY) > K_{sp}(MZ)$, then : (Assume no hydrolysis of any ion).

(A) MX will precipitate first.

(B) MY will precipitate first.

(C*) MZ will precipitate first.

(D) Nothing can be said about which salt will precipitate first, as numerical data is not given.

X^- , Y^- तथा Z^- की समान सान्द्रता वाले विलयन में, $MCl(s)$ (अत्यधिक विलयशील लवण) को धीरे-धीरे मिलाते हैं। यदि $K_{sp}(MX) > K_{sp}(MY) > K_{sp}(MZ)$, तब : (माना कि किसी भी आयन का जल अपघटन नहीं होता है।)

(A) MX सर्वप्रथम अवक्षेपित होगा।

(B) MY सर्वप्रथम अवक्षेपित होगा।

(C*) MZ सर्वप्रथम अवक्षेपित होगा।

(D) कुछ भी नहीं कहा जा सकता है कि कौनसा लवण सर्वप्रथम अवक्षेपित होगा, क्योंकि संख्यात्मक आँकड़े नहीं दिये गये हैं।

Sol. The salt with least K_{sp} is precipitated first (in this case).

न्यूनतम K_{sp} युक्त लवण सर्वप्रथम अवक्षेपित होता है। (इस स्थिति में)।

C-2. In above question, If $[X^-] : [Y^-] : [Z^-] = 100 : 10 : 1$ & $K_{sp}[MX] : K_{sp}[MY] : K_{sp}[MZ] = 10 : 0.1 : 1$, order of precipitation will be :

(A) MZ, then MX & MY at last

(B*) MY, then MX & MZ at last

(C) MX, then MY & MZ at last

(D) MY, then MZ & MX at last





उपरोक्त प्रश्न में यदि $[X^-]_i : [Y^-]_i : [Z^-]_i = 100 : 10 : 1$ तथा $K_{sp}[MX] : K_{sp}[MY] : K_{sp}[MZ] = 10 : 0.1 : 1$, तो अवक्षेपण का क्रम होगा :

- (A) MZ, बाद में MX व अन्त में MY (B*) MY, बाद में MX व अन्त में MZ
(C) MX, बाद में MY व अन्त में MZ (D) MY, बाद में MZ व अन्त में MX

Sol. Calculation of concentration of M^+ required for precipitation ($K_{sp}(\text{salt}) = [\text{Anion}] [M^+]_{\text{min. req. for salt's pptn.}}$)
अवक्षेपण के लिए आवश्यक M^+ की सान्द्रता की गणना ($K_{sp}(\text{लवण}) = [\text{ऋणायन}] [M^+]_{\text{लवण अवक्षेपण के लिए न्यूनतम आवश्यक}}$)

$$MX : [M^+]_{MX} = \frac{10}{100} = 0.1 \text{ M}$$

$$MY : [M^+]_{MY} = \frac{0.1}{10} = 0.01 \text{ M}$$

$$MZ : [M^+]_{MZ} = \frac{1}{1} = 1 \text{ M}$$

Order for precipitation is increasing order of $[M^+]_{\text{salt}}$, so, first MY, then MX and then MZ.
अवक्षेपण के लिए क्रम $[M^+]_{\text{लवण}}$ का बढ़ता हुए क्रम है अतः सर्वप्रथम MY बाद में MX तथा MZ.

Exercise-2

Marked Questions may have for Revision Questions.

चिह्नित प्रश्न दोहराने योग्य प्रश्न है।

PART - I : ONLY ONE OPTION CORRECT TYPE

भाग-I : केवल एक सही विकल्प प्रकार (ONLY ONE OPTION CORRECT TYPE)

1. A solution contains $[NaCl] = [Na_2CO_3] = C \text{ M}$. Upon gradually adding $AgNO_3(s)$: (Assume no hydrolysis of any ion).

- (A) Out of $AgCl$ & Ag_2CO_3 , one having lesser K_{sp} will start precipitating first.
(B) Out of $AgCl$ & Ag_2CO_3 , one having greater K_{sp} will start precipitating first.

(C*) If, $\sqrt{\frac{K_{sp}(Ag_2CO_3)}{C}} < \frac{K_{sp}(AgCl)}{C}$ then Ag_2CO_3 will start precipitating first.

(D) If, $\sqrt{\frac{K_{sp}(Ag_2CO_3)}{C}} > \frac{K_{sp}(AgCl)}{C}$ then $AgCl$ will start precipitating first.

एक विलयन में $[NaCl] = [Na_2CO_3] = C \text{ M}$ है। $AgNO_3(s)$ धीरे-धीरे मिलाने पर : (माना कि किसी भी आयन का जलअपघटन नहीं होता है।)

- (A) $AgCl$ तथा Ag_2CO_3 में से कम K_{sp} रखने वाला एक यौगिक सर्वप्रथम अवक्षेपित होना प्रारम्भ करेगा।
(B) $AgCl$ तथा Ag_2CO_3 में से अधिक K_{sp} रखने वाला एक यौगिक सर्वप्रथम अवक्षेपित होना प्रारम्भ करेगा।

(C*) यदि $\sqrt{\frac{K_{sp}(Ag_2CO_3)}{C}} < \frac{K_{sp}(AgCl)}{C}$ तब Ag_2CO_3 सर्वप्रथम अवक्षेपित होना प्रारम्भ करेगा।

(D) यदि $\sqrt{\frac{K_{sp}(Ag_2CO_3)}{C}} > \frac{K_{sp}(AgCl)}{C}$, तब $AgCl$ सर्वप्रथम अवक्षेपित होना प्रारम्भ करेगा।

Sol. (A) & (B) : when number of ions being produced per salt molecule is different, K_{sp} alone cant judge which salt precipitates first.

(C) & (D) : $[Ag^+]_{\text{min. req. for first salt's pptn.}} = \frac{K_{sp}(AgCl)}{C}$ & $[Ag^+]_{\text{min. req. for second salt's pptn.}} = \sqrt{\frac{K_{sp}(Ag_2CO_3)}{C}}$

So, whichever is minimum, will precipitate first.

(A) व (B) : जब प्रति लवण अणु उत्पन्न होने वाले आयनों की संख्या भिन्न होती है तो केवल K_{sp} के द्वारा यह निर्धारित नहीं कर सकते कि कौनसा लवण सर्वप्रथम अवक्षेपित होता है।





(C) व (D) : $[Ag^+]$ सर्वप्रथम लवण अवक्षेपण के लिए न्यूनतम आवश्यक = $\frac{K_{sp}(AgCl)}{C}$ तथा $[Ag^+]$ द्वितीय लवण अवक्षेपण के लिए न्यूनतम आवश्यक =

$$\sqrt{\frac{K_{sp}(Ag_2CO_3)}{C}}$$

इस प्रकार जो न्यूनतम है वह सर्वप्रथम अवक्षेपित होगा।

2. For the reaction : $[Ag(CN)_2]^{-}(aq) \rightleftharpoons Ag^{+}(aq) + 2CN^{-}(aq)$, K_c at $25^{\circ}C$ is 4×10^{-19} . Calculate $[Ag^+]$ in solution which was originally 0.1 M in KCN and 0.03 M in $AgNO_3$.

(A) 1.5×10^{-17} M

(B*) 7.5×10^{-18} M

(C) 4.6875×10^{-19} M

(D) Value cannot be determined due to mathematical complications.

$25^{\circ}C$ पर अभिक्रिया : $[Ag(CN)_2]^{-}(aq) \rightleftharpoons Ag^{+}(aq) + 2CN^{-}(aq)$ के लिए K_c , 4×10^{-19} है। विलयन, जो वास्तव में 0.1 KCN तथा 0.03 M $AgNO_3$ युक्त है, में $[Ag^+]$ परिकलित कीजिए।

(A) 1.5×10^{-17} M

(B*) 7.5×10^{-18} M

(C) 4.6875×10^{-19} M

(D) गणितीय जटिलताओं के कारण मान का निर्धारण नहीं हो सकता है।

Sol. $4 \times 10^{-19} = \frac{[Ag^+](0.04)^2}{0.03} \Rightarrow [Ag^+] = 7.5 \times 10^{-18}$ M

3. A solution of Na_2CO_3 is added drop by drop to one litre of a solution containing 10^{-4} mole of Ba^{2+} and 10^{-5} mole of Ag^+ . If K_{sp} for $BaCO_3$ is 8.1×10^{-9} and K_{sp} for Ag_2CO_3 is 6.9×10^{-12} , then which is not true ? Assume no hydrolysis of CO_3^{2-} ion.

(A) No precipitate of $BaCO_3$ will appear until $[CO_3^{2-}]$ reaches 8.1×10^{-5} mol per litre.

(B*) A precipitate of Ag_2CO_3 will appear when $[CO_3^{2-}]$ reaches 6.9×10^{-5} mol per litre.

(C) No precipitate of Ag_2CO_3 will appear until $[CO_3^{2-}]$ reaches 6.9×10^{-2} mole per litre.

(D) $BaCO_3$ will be precipitated first.

Ba^{2+} के 10^{-4} मोल तथा Ag^+ के 10^{-5} मोल युक्त एक विलयन के एक लीटर में बून्द-बून्द करके Na_2CO_3 के एक विलयन को मिलाया जाता है। यदि $BaCO_3$ के लिए $K_{sp} = 8.1 \times 10^{-9}$ तथा Ag_2CO_3 के लिए $K_{sp} = 6.9 \times 10^{-12}$ है, तब कौनसा सही नहीं है ? यह मानें कि CO_3^{2-} आयन का जल अपघटन नहीं होता है।

(A) जब तक $[CO_3^{2-}]$ 8.1×10^{-9} मोल/लीटर नहीं पहुँचता है, तब तक $BaCO_3$ का अवक्षेप नहीं बनेगा।

(B*) जब $[CO_3^{2-}]$ 6.9×10^{-5} मोल/लीटर पहुँचता है, तब Ag_2CO_3 के एक अवक्षेप प्रकट होगा।

(C) जब तक $[CO_3^{2-}]$ 6.9×10^{-2} मोल/लीटर नहीं पहुँचता है, तब तक Ag_2CO_3 का अवक्षेप नहीं बनेगा।

(D) $BaCO_3$ सबसे पहले अवक्षेपित होगा।

Sol. For precipitation of Ag_2CO_3 . $[CO_3^{2-}] = \frac{K_{sp}}{[Ag^+]^2} = \frac{6.9 \times 10^{-12}}{[10^{-5}]^2} = 6.9 \times 10^{-2}$

and for precipitation of $BaCO_3$. $[CO_3^{2-}] = \frac{K_{sp}}{[Ba^{2+}]} = \frac{8.1 \times 10^{-9}}{10^{-4}} = 8.1 \times 10^{-5}$

हल. Ag_2CO_3 के अवक्षेपण के लिए $[CO_3^{2-}] = \frac{K_{sp}}{[Ag^+]^2} = \frac{6.9 \times 10^{-12}}{[10^{-5}]^2} = 6.9 \times 10^{-2}$

तथा $BaCO_3$ के अवक्षेपण के लिए $[CO_3^{2-}] = \frac{K_{sp}}{[Ba^{2+}]} = \frac{8.1 \times 10^{-9}}{10^{-4}} = 8.1 \times 10^{-5}$

PART - II : SINGLE AND DOUBLE VALUE INTEGER TYPE

भाग - II : एकल एवं द्वि-पूर्णांक मान प्रकार (SINGLE AND DOUBLE VALUE INTEGER TYPE)

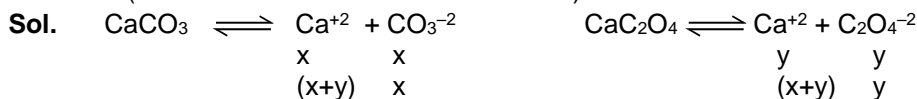
1. When pure water is saturated with both $CaCO_3$ and CaC_2O_4 , the concentration of calcium ion in the solution under equilibrium is 8×10^{-5} M. If the ratio of the solubility product of $CaCO_3$ to that of CaC_2O_4 is 3, what is the solubility product of $CaCO_3$ in pure water ? Report your answer after multiplying by 10^9 and rounding it off to nearest whole number.





जब CaCO_3 एवं CaC_2O_4 दोनों के साथ शुद्ध जल को संतृप्त किया जाता है, तो साम्य पर विलयन में कैल्शियम आयनों की सांद्रता $8 \times 10^{-5} \text{ M}$ है। यदि CaCO_3 एवं CaC_2O_4 के विलेयता गुणनफलों का अनुपात 3 है, तो शुद्ध जल में CaCO_3 का विलेयता गुणनफल क्या है ? अपना उत्तर 10^9 से गुणा करने के पश्चात् निकटतम पूर्णांक के मान में दीजिए।

Ans. 5 (actual answer यथार्थ उत्तर = 4.8×10^{-9})



$$\frac{K_{\text{SP}}(\text{CaCO}_3)}{K_{\text{SP}}(\text{CaC}_2\text{O}_4)} = \frac{x}{y} = 3 \Rightarrow x = 3y$$

$$(x + y) = 8 \times 10^{-5}$$

$$(3y + y) = 8 \times 10^{-5} \Rightarrow y = 2 \times 10^{-5}; x = 6 \times 10^{-5}$$

$$K_{\text{SP}}(\text{CaCO}_3) = [\text{Ca}^{+2}][\text{CO}_3^{-2}]$$

$$= 8 \times 10^{-5} \times 6 \times 10^{-5}$$

$$= 48 \times 10^{-10}$$

$$K_{\text{SP}}(\text{CaCO}_3) = 4.8 \times 10^{-9}$$

2. On mixing equal volumes of 0.1 M AgNO_3 & 0.8 M KCN solutions, what % of original Ag^+ is in the form of free Ag^+ ions ? Given : K_d of $[\text{Ag}(\text{CN})_2]^- = 10^{-18}$. Report your answer after multiplying it by 4.5×10^{16} . (Assume no hydrolysis of any ion)

0.1 M AgNO_3 तथा 0.8 M KCN विलयनों के समान आयतनों को मिश्रित करने पर मुक्त Ag^+ आयनों के रूप में कितना प्रतिशत वास्तविक Ag^+ होता है ? दिया है : $[\text{Ag}(\text{CN})_2]^-$ का $K_d = 10^{-18}$ अपना उत्तर इसे 4.5×10^{16} से गुणा करने के पश्चात् दीजिए। (माना कि किसी भी आयन का जलअपघटन नहीं होता है।)

Ans. 50

Sol. $10^{-18} = \frac{[\text{Ag}^+]_{\text{free}}(0.3)^2}{(0.05)} \Rightarrow [\text{Ag}^+]_{\text{free}} = \frac{5}{9} \times 10^{-18} \text{ M}$

$$\% \text{ of } \text{Ag}^+ (\text{Ag}^+ \text{ का } \%) = \frac{\frac{5}{9} \times 10^{-18}}{0.05} \times 100 \times 4.5 \times 10^{16} = 50\%$$

PART - III : COMPREHENSION

भाग - III : अनुच्छेद (COMPREHENSION)

Comprehension # 1

0.2 mole of $\text{MgCl}_2(\text{s})$ are added in 1 litre volume of a solution, already containing 0.2 mole of $\text{NaOH}(\text{s})$. Now answer the following questions :

अनुच्छेद # 1

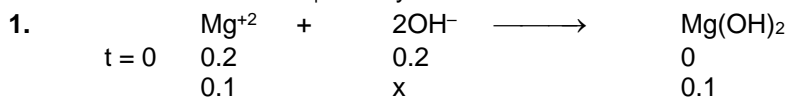
$\text{MgCl}_2(\text{s})$ के 0.2 मोल, $\text{NaOH}(\text{s})$ के 0.2 मोल युक्त 1 लीटर विलयन में मिलाये गये। अब निम्न प्रश्नों के उत्तर दीजिए :

- Calculate pH of obtained solution. K_{sp} of $\text{Mg}(\text{OH})_2$ is 1.6×10^{-12} .
प्राप्त विलयन के pH की गणना कीजिये। $\text{Mg}(\text{OH})_2$ का K_{sp} 1.6×10^{-12} है।
(A*) 8.6 (B) 8.5 (C) 8.65 (D) 8.56
- What would be the new pH when 0.04 mole of $\text{NaOH}(\text{s})$ are added in the solution obtained from comprehension ?
अनुच्छेद से प्राप्त विलयन में $\text{NaOH}(\text{s})$ के 0.04 मोल मिलाने के पश्चात् नया pH क्या होगा ?
(A) 8.6 (B) 8.5 (C*) 8.65 (D) 8.56
- Find the pH of the solution obtained after adding 0.04 mole of $\text{HCl}(\text{g})$ to the solution obtained from comprehension ?
अनुच्छेद से प्राप्त विलयन में $\text{HCl}(\text{g})$ के 0.04 मोल मिलाने के पश्चात् प्राप्त विलयन का pH ज्ञात कीजिये।
(A) 8.6 (B) 8.5 (C) 8.65 (D*) 8.56





Sol. As the value of K_{sp} is very low so we can assume that almost all the $Mg(OH)_2$ will Present in solid state.

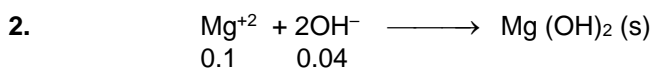


At the end of reaction $[Mg^{+2}] = 0.1$

$$K_{sp} [Mg (OH)_2] = [Mg^{+2}] [OH^-]^2 = 1.6 \times 10^{-12}$$

$$\Rightarrow [OH^-]^2 = \frac{1.6 \times 10^{-12}}{0.1} \Rightarrow [OH^-] = 4 \times 10^{-6} M$$

$$\Rightarrow pOH = 6 - \log 4 \Rightarrow pH = 14 - 6 + 0.6 = 8.6$$



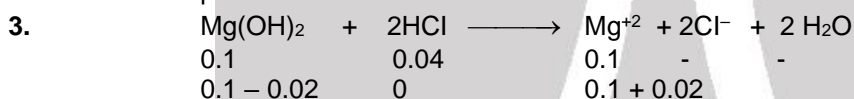
At the end of reaction $[Mg^{+2}] = 0.1 - \frac{0.04}{2} = 0.08$

$$K_{sp} (Mg(OH)_2) = [Mg^{+2}] [OH^-]^2 = 1.6 \times 10^{-12}$$

$$[OH^-]^2 = \frac{1.6 \times 10^{-12}}{0.08} \Rightarrow [OH^-] = 4.47 \times 10^{-6}$$

$$\therefore pOH = 6 - \log 4.47 = 5.35$$

$$pH = 14 - 5.35 = 8.65$$



$$[Mg^{+2}] = 0.12 M$$

$$K_{sp} [Mg (OH)_2] = [Mg^{+2}] [OH^-]^2 = 1.6 \times 10^{-12}$$

$$[OH^-]^2 = \frac{1.6 \times 10^{-12}}{0.12} = \frac{4}{3} \times 10^{-11} M^2 \Rightarrow [OH^-] = \sqrt{\frac{4}{3} \times 10^{-11}} M$$

$$\Rightarrow pOH = 5.44 \Rightarrow pH = 14 - 5.44 = 8.56$$

हल K_{sp} का मान बहुत कम है इसलिए हम मान सकते हैं कि लगभग सम्पूर्ण $Mg(OH)_2$ ठोस अवस्था में उपस्थित है।



अभिक्रिया के अन्त पर $[Mg^{+2}] = 0.1$

$$K_{sp} [Mg (OH)_2] = [Mg^{+2}] [OH^-]^2 = 1.6 \times 10^{-12}$$

$$\Rightarrow [OH^-]^2 = \frac{1.6 \times 10^{-12}}{0.1} \Rightarrow [OH^-] = 4 \times 10^{-6} M$$

$$\Rightarrow pOH = 6 - \log 4 \Rightarrow pH = 14 - 6 + 0.6 = 8.6$$



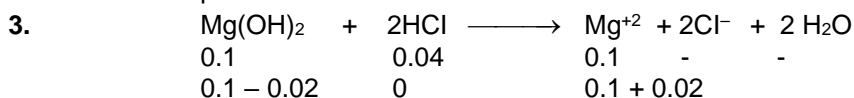
अभिक्रिया के अन्त पर $[Mg^{+2}] = 0.1 - \frac{0.04}{2} = 0.08$

$$K_{sp} (Mg(OH)_2) = [Mg^{+2}] [OH^-]^2 = 1.6 \times 10^{-12}$$

$$[OH^-]^2 = \frac{1.6 \times 10^{-12}}{0.08} \Rightarrow [OH^-] = 4.47 \times 10^{-6}$$

$$\therefore pOH = 6 - \log 4.47 = 5.35$$

$$pH = 14 - 5.35 = 8.65$$



$$[Mg^{+2}] = 0.12 M$$

$$K_{sp} [Mg (OH)_2] = [Mg^{+2}] [OH^-]^2 = 1.6 \times 10^{-12}$$



$$[\text{OH}^-]^2 = \frac{1.6 \times 10^{-12}}{0.12} = \frac{4}{3} \times 10^{-11} \text{ M}^2 \Rightarrow [\text{OH}^-] = \sqrt{\frac{4}{3} \times 10^{-11}} \text{ M}$$

$$\Rightarrow \text{pOH} = 5.44 \Rightarrow \text{pH} = 14 - 5.44 = 8.56$$

Comprehension # 2

Answer Q.4, Q.5 and Q.6 by appropriately matching the information given in the three columns of the following table.

Following 3 columns contain informations regarding water solubility of some sparingly soluble salts and its relation with their solubility product constants (K_{sp}).

Take temperature as 25°C .

Column-1		Column-2		Column-3	
(I)	Solubility $> \sqrt{K_{sp}}$	(i)	Solubility increases because of presence of common anion in solution	(P)	Solubility increases in acidic solution as pH decreases below 3
(II)	Solubility $< \left(\frac{K_{sp}}{27}\right)^{1/4}$	(ii)	Solubility decreases because of presence of common cation in solution	(Q)	Solubility increases in basic solution as pH increases above 11
(III)	Solubility $= \left(\frac{K_{sp}}{27}\right)^{1/4}$	(iii)	Solubility decreases because of presence of common anion in solution	(R)	Solubility is unaffected by pH of solution
(IV)	Solubility $= \sqrt{K_{sp}}$	(iv)	Solubility increases because of presence of common cation in solution	(S)	Anionic hydrolysis will make solubility in water greater than expected

अनुच्छेद # 2

निम्न सारणी के तीन स्तम्भों में दी गयी सूचना के उचित मिलान द्वारा Q.4, Q.5 तथा Q.6 के उत्तर दीजिए।

निम्न 3 कॉलम में कुछ कम विलयशील लवणों की जल विलेयता से सम्बन्धित सूचनायें हैं तथा इनका सम्बन्ध इनके विलेयता गुणनफल नियतांकों (K_{sp}) से है।

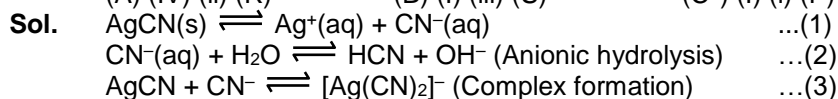
तापमान 25°C लीजिए।

कॉलम -1		कॉलम -2		कॉलम -3	
(I)	विलेयता $> \sqrt{K_{sp}}$	(i)	विलेयता विलयन में उभयनिष्ठ ऋणायन की उपस्थिति के कारण बढ़ती है।	(P)	विलेयता अम्लीय विलयन में बढ़ती है क्योंकि 3 से कम हो जाती है।
(II)	विलेयता $< \left(\frac{K_{sp}}{27}\right)^{1/4}$	(ii)	विलेयता विलयन में उभयनिष्ठ धनायन की उपस्थिति के कारण घटती है।	(Q)	विलेयता क्षारीय विलयन में बढ़ती है क्योंकि pH 11 से अधिक हो जाती है।
(III)	विलेयता $= \left(\frac{K_{sp}}{27}\right)^{1/4}$	(iii)	विलेयता विलयन में उभयनिष्ठ ऋणायन की उपस्थिति के कारण घटती है।	(R)	विलेयता विलयन की pH द्वारा अप्रभावित होती है।
(IV)	विलेयता $= \sqrt{K_{sp}}$	(iv)	विलेयता विलयन में उभयनिष्ठ धनायन की उपस्थिति के कारण बढ़ती है।	(S)	ऋणायनिक जलअपघटन से जल में विलेयता अपेक्षा से अधिक हो जाती है।

4. For AgCN, the only correct combination is :

AgCN के लिए, केवल सही संयोजन है—

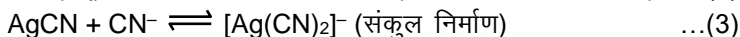
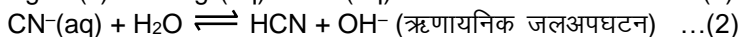
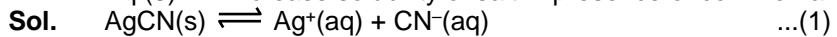
(A) (IV) (ii) (R) (B) (I) (iii) (S) (C*) (I) (i) (P) (D) (I) (iii) (P)



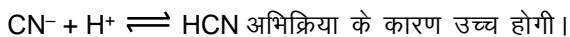
Equation (2) will make Eq.(1) shift forward. So, solubility $> \sqrt{K_{sp}}$. Solubility in acidic solution would be high because of reaction : $\text{CN}^- + \text{H}^+ \rightleftharpoons \text{HCN}$



Eq.(3) will increase solubility of salt in presence of common anion (CN⁻).



समीकरण (2), समीकरण (1) को अग्र दिशा में विस्थापित करेगा, अतः विलेयता $> \sqrt{K_{sp}}$. अम्लीय विलयन में विलेयता:

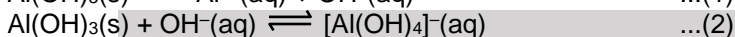
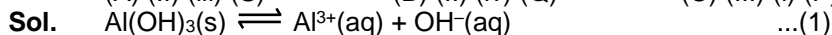


समीकरण (3) उभयनिष्ठ ऋणायन (CN⁻) की उपस्थिति में लवण की विलेयता को बढ़ायेगी।

5. For Al(OH)₃, the only correct combination is :

Al(OH)₃ के लिए, केवल सही संयोजन है—

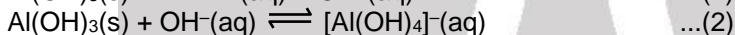
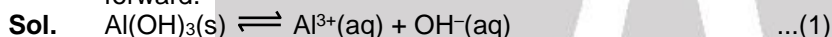
(A) (II) (iii) (S) (B) (II) (iv) (Q) (C) (III) (i) (P) (D*) (II) (ii) (Q)



Al(OH)₃, expected to be having very less K_{sp} value, will face common ion effect by OH⁻ ions present in water. So, solubility $< \sqrt[4]{\frac{K_{sp}}{27}}$.

Acidic medium will making Eq.(1) shift forward by consuming OH⁻ ions leading to greater solubility.

OH⁻ ions (basic medium as well as common anion) will increase solubility by making Eq.(2) shift forward.



Al(OH)₃ अपेक्षित रूप से बहुत कम K_{sp} मान रखता है, यह जल में उपस्थित OH⁻ आयनों द्वारा उभयनिष्ठ आयन प्रभाव

का सामना करता है। अतः विलेयता $< \sqrt[4]{\frac{K_{sp}}{27}}$.

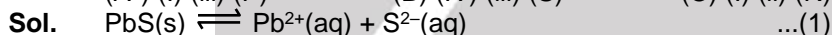
अम्लीय माध्यम समीकरण (1) को OH⁻ आयनों के खर्च द्वारा अग्र दिशा में विस्थापित करता है, जिससे विलेयता बढ़ती है।

OH⁻ आयन (क्षारीय माध्यम तथा उभयनिष्ठ ऋणायन) समीकरण (2) के अग्र विस्थापन द्वारा विलेयता को बढ़ायेगा।

6. For PbS, the only correct combination is :

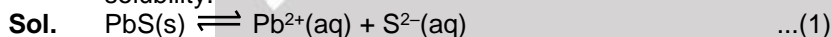
PbS के लिए, केवल सही संयोजन है—

(A*) (I) (iii) (P) (B) (IV) (iii) (S) (C) (I) (ii) (R) (D) (IV) (ii) (P)



Eq.(2) will make Eq.(1) shift forward. So, solubility $> \sqrt{K_{sp}}$. Solubility in acidic solutions would be higher because of reaction : $\text{S}^{2-} + \text{H}^+ \rightleftharpoons \text{HS}^-$

Presence of common cation or anion will both make Eq.(1) shift backward leading to decrease in solubility.



समीकरण (2), समीकरण (1) को अग्र दिशा में विस्थापित करेगी। अतः विलेयता $> \sqrt{K_{sp}}$. अम्लीय विलयनों में विलेयता

अभिक्रिया : $\text{S}^{2-} + \text{H}^+ \rightleftharpoons \text{HS}^-$ के कारण उच्च होगी।

समीकरण (1) को पश्च दिशा में विस्थापित करेगी जिससे विलेयता में कमी होती है।





Exercise-3

* Marked questions may have more than one correct option.

* चिन्हित प्रश्नों के एक से अधिक सही विकल्प हो सकते हैं।

PART - I : JEE (ADVANCED) / IIT-JEE PROBLEMS (PREVIOUS YEARS)

भाग - I : JEE (ADVANCED) / IIT-JEE (पिछले वर्षों) के प्रश्न

1. For a sparingly soluble salt A_pB_q , the relationship of its solubility product (L_s) with its solubility (S) is :
[JEE-2001(S), 1/35]

एक अल्प विलेयी लवण A_pB_q के लिए, इसके विलेयता गुणनफल (L_s) का इसकी विलेयता (S) के साथ संबंध है :

[JEE-2001(S), 1/35]

- (A*) $L_s = S^{p+q} \cdot p^p \cdot q^q$ (B) $L_s = S^{p+q} \cdot p^q \cdot q^p$ (C) $L_s = S^{pq} \cdot p^p \cdot q^q$ (D) $L_s = S^{pq} \cdot (pq)^{p+q}$
Sol. (A) $A_pB_q(s) \rightleftharpoons pA^{+q} + qB^{-p}$
 $pS \quad qS$
 $L_s = (pS)^p \cdot (qS)^q = p^p \cdot q^q \cdot S^{(p+q)}$

2. A solution which is 10^{-3} M each in Mn^{2+} , Fe^{2+} , Zn^{2+} and Hg^{2+} is treated with 10^{-16} M sulphide ion. If K_{sp} values of MnS , FeS , ZnS and HgS are 10^{-15} , 10^{-23} , 10^{-20} and 10^{-54} respectively, which one will precipitate first ?
[JEE-2003, 3/84]

एक विलयन Mn^{2+} , Fe^{2+} , Zn^{2+} तथा Hg^{2+} प्रत्येक से 10^{-3} M है। इस विलयन को 10^{-16} M सल्फाइड आयन के साथ उपचारित किया जाता है। यदि MnS , FeS , ZnS तथा HgS के K_{sp} के मान क्रमशः 10^{-15} , 10^{-23} , 10^{-20} तथा 10^{-54} हैं, तो उक्त में से कौन सर्वप्रथम अवक्षेपित होगा ?

[JEE-2003, 3/84]

- (A) FeS (B) MgS (C*) HgS (D) ZnS
Sol. Lesser the K_{sp} , earlier is the precipitation (if the formula type of precipitation & concentrations of various precipitating ions is same).

K_{sp} का मान जितना कम होगा, अवक्षेपण उतना ही पहले होगा। (यदि अवक्षेपण का सूत्र प्रकार तथा विभिन्न अवक्षेपित होने वाले आयनों की सान्द्रता समान है।)

3. Solubility product constant (K_{sp}) of salts of types MX , MX_2 and M_3X at temperature T are 4.0×10^{-8} , 3.2×10^{-14} and 2.7×10^{-15} , respectively. Solubilities (in mol dm^{-3}) of the salts at temperature T are in the order :
[JEE-2008, 3/163]

लवण MX , MX_2 तथा M_3X के विलेयता गुणनफल स्थिरांक (K_{sp}), तापमान T पर क्रमशः 4.0×10^{-8} , 3.2×10^{-14} तथा 2.7×10^{-15} हैं। तापमान T पर लवणों की विलेयता (mol dm^{-3} में) का क्रम है :

[JEE-2008, 3/163]

- (A) $MX > MX_2 > M_3X$ (B) $M_3X > MX_2 > MX$ (C) $MX_2 > M_3X > MX$ (D*) $MX > M_3X > MX_2$
Sol. MX MX_2 M_3X
 $s_1^2 = 4 \times 10^{-8}$ $4s_2^3 = 3.2 \times 10^{-14}$ $27s_3^4 = 2.7 \times 10^{-15}$
 $s_1 = 2 \times 10^{-4}$ $s_2^3 = 8 \times 10^{-15}$ $s_3^4 = 10^{-16}$
 $s_2 = 2 \times 10^{-5}$ $s_3 = 10^{-4}$
 $\Rightarrow s_1 > s_3 > s_2$
 $\Rightarrow MX > M_3X > MX_2$

4. In 1 L saturated solution of $AgCl$ [$K_{sp}(AgCl) = 1.6 \times 10^{-10}$], 0.1 mole of $CuCl$ [$K_{sp}(CuCl) = 1.0 \times 10^{-6}$] is added. The resultant concentration of Ag^+ in the solution is 1.6×10^{-x} . The value of "x" is :
[JEE-2011, 4/180]

$AgCl$ [$K_{sp}(AgCl) = 1.6 \times 10^{-10}$] के 1 लीटर संतृप्त विलयन में 0.1 मोल $CuCl$ [$K_{sp}(CuCl) = 1.0 \times 10^{-6}$] मिलाया जाता है। इस विलयन में Ag^+ की परिणामी सान्द्रता 1.6×10^{-x} है। "x" का मान है :

[JEE-2011, 4/180]

Ans. 7

- Sol. $AgCl(s) \rightleftharpoons Ag^+ + Cl^-$ $K_{sp}(AgCl) = 1.6 \times 10^{-10}$
 $Z \quad Z + Y$
 $CuCl(s) \rightleftharpoons Cu^+ + Cl^-$ $K_{sp}(CuCl) = 10^{-6}$
 $Y \quad Z + Y$
 $Z(Z + Y) = 1.6 \times 10^{-10}$ and तथा $Y(Z + Y) = 10^{-6}$



$$\begin{aligned} \Rightarrow (Z + Y)^2 &= 1.6 \times 10^{-10} + 10^{-6} \\ \Rightarrow (Z + Y)^2 &\approx 10^{-6} \\ \Rightarrow Z + Y &= 10^{-3} \\ \text{We know हम जानते हैं,} \\ \Rightarrow Z(Z + Y) &= 1.6 \times 10^{-10} \\ \Rightarrow Z \times 10^{-3} &= 1.6 \times 10^{-10} \\ \Rightarrow Z &= 1.6 \times 10^{-7} \\ \Rightarrow 1.6 \times 10^{-x} &= 1.6 \times 10^{-7} \\ \Rightarrow x &= 7 \end{aligned}$$

5. The K_{sp} of Ag_2CrO_4 is 1.1×10^{-12} at 298 K. The solubility (in mol/L) of Ag_2CrO_4 in a 0.1 M AgNO_3 solution is **[JEE (Advanced)-2013, 3/120]**

$K_{sp}(\text{Ag}_2\text{CrO}_4)$ का मान 298 K पर 1.1×10^{-12} है। 0.1 M AgNO_3 के विलयन में Ag_2CrO_4 की विलेयता मोल/लीटर में है

(A) 1.1×10^{-11} (B*) 1.1×10^{-10} (C) 1.1×10^{-12} (D) 1.1×10^{-9}

Sol. $\text{Ag}_2\text{CrO}_4 \rightleftharpoons 2\text{Ag}^+ + \text{CrO}_4^{2-}$

s 0.1 + 2s s

≈ 0.1

$1.1 \times 10^{-12} = (0.1)^2 s$

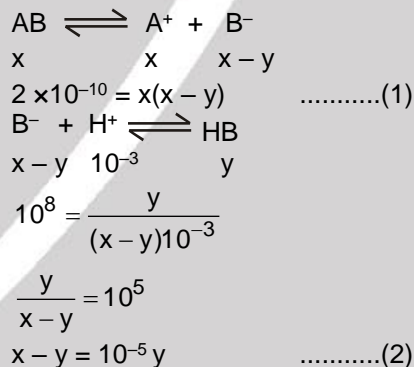
$s = 1.1 \times 10^{-10}$

6. The solubility of a salt of weak acid (AB) at pH 3 is $Y \times 10^{-3} \text{ mol L}^{-1}$. The value of Y is _____.
(Given that the value of solubility product of AB (K_{sp}) = 2×10^{-10} and the value of ionization constant of HB (K_a) = 1×10^{-8}) **[JEE(Advanced)-2018, 3/120]**
- pH 3 पर दुर्बल अम्ल (AB) के लवण की विलेयता $Y \times 10^{-3} \text{ mol L}^{-1}$ है। Y का मान _____ है।
(दिया गया है AB के विलेयता गुणनफल का मान (K_{sp}) = 2×10^{-10} और HB के आयनन स्थिरांक का मान (K_a) = 1×10^{-8}) **[JEE(Advanced)-2018, 3/120]**

Ans. 4.47

Sol.

solubility विलेयता



From (1) & (2)

(1) तथा (2) से

$$\begin{aligned} 2 \times 10^{-10} &= x^2 - 2 \times 10^{-5} \\ x^2 &= 2 \times 10^{-5} \\ x &= \sqrt{20} \times 10^{-3} = 4.47 \times 10^{-3} \end{aligned}$$





PART - II : JEE (MAIN) (PREVIOUS YEARS)

भाग - II : JEE (MAIN) (पिछले वर्षों) के प्रश्न

JEE(MAIN) ONLINE PROBLEMS

1. Zirconium phosphate $[\text{Zr}_3(\text{PO}_4)_4]$ dissociates into three zirconium cations of charge +4 and four phosphate anions of charge -3. If molar solubility of zirconium phosphate is denoted by S and its solubility product by K_{sp} then which of the following relationship between S and K_{sp} is correct ?

[JEE(Main) 2016 Online (19-04-14), 4/120]

जिरकोनियम फास्फेट $[\text{Zr}_3(\text{PO}_4)_4]$ वियोजित होकर +4 आवेश प्रति केटायन के तीन जिरकोनियम केटायन और -3 आवेश प्रति: एनायन के चार फास्फेट एनायन देता है। यदि जिरकोनियम फास्फेट की मोलर विलेयता को S से और इसके विलेयता गुणनफल को K_{sp} से सूचित किया जाये तो निम्न सम्बन्धों से कौनसा S तथा K_{sp} का सम्बन्ध सही माना जावेगा ?

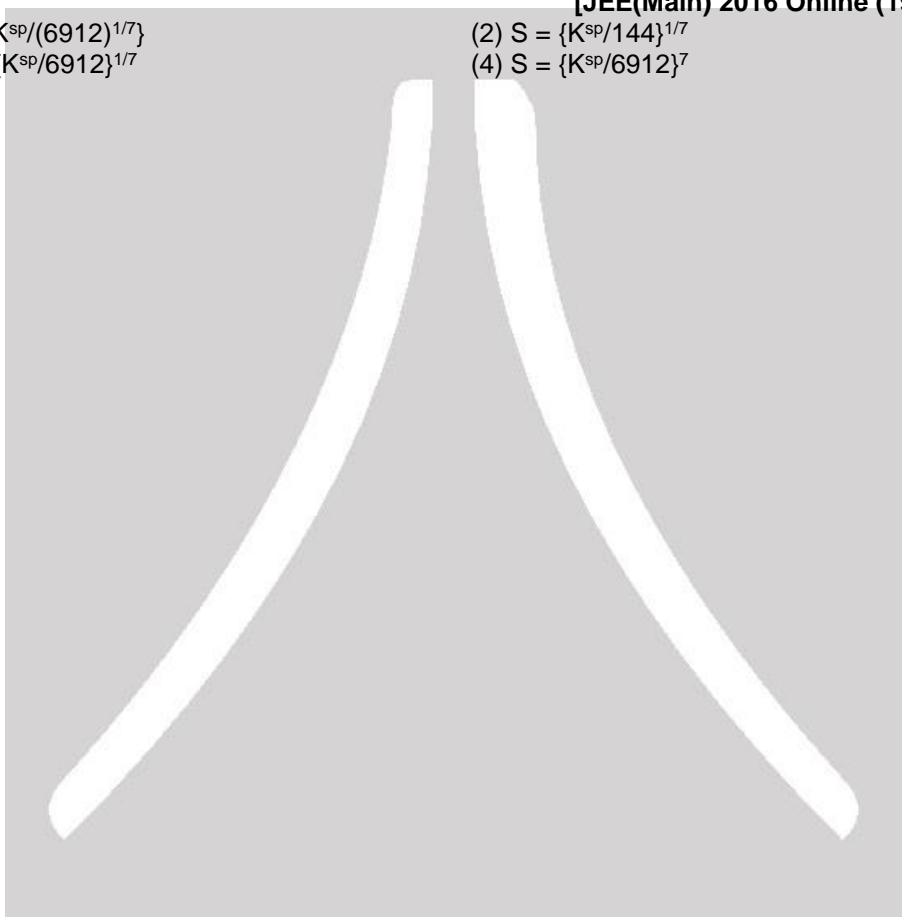
[JEE(Main) 2016 Online (19-04-14), 4/120]

(1) $S = \{K_{sp}/(6912)^{1/7}\}$

(2) $S = \{K_{sp}/144\}^{1/7}$

(3*) $S = \{K_{sp}/6912\}^{1/7}$

(4) $S = \{K_{sp}/6912\}^7$





IONIC EQUILIBRIUM-I

Exercise-1

Marked questions are recommended for Revision.

PART - I : SUBJECTIVE QUESTIONS

Section (A) : pH calculation : Solutions of polyprotic weak acids, Solutions of Polyacidic weak bases

Commit to memory :

Solution of a polyprotic weak acid (H_xA) : $pH = \frac{1}{2} (pK_{a_1} - \log C)$ [if $\alpha_1 \leq 0.1$ or 10%] ; $[H_{x-2}A^{2-}] = K_{a_2}$

Solution of a polyprotic weak base (B) : $pOH = \frac{1}{2} (pK_{b_1} - \log C)$ [if $\alpha_1 \leq 0.1$ or 10%] ; $[BH_2^{2+}] = K_{b_2}$

A-1. What is the pH of 0.01 M H_2S solution ? Also determine $[HS^-]$ & $[S^{2-}]$. Given: For H_2S , $K_{a_1} = 9 \times 10^{-8}$, $K_{a_2} = 1.2 \times 10^{-13}$.

A-2. Calculate the pH of 0.74 g/L aqueous solution of propane-1,2-diamine. Given : pK_{b_1} & pK_{b_2} for base is 4.18 & 7.39 respectively.

Section (B) : pH calculation : Solutions containing mixture of weak monoprotic acid and strong acid, Solutions containing mixture of weak monoacidic base and strong base

Commit to memory :

Mixture of weak acid (monoprotic) and a strong acid: $[H^+]_f = C_1$ (just not considering the H^+ ions from WA).

Mixture of weak base (monoacidic) and a strong base: $[OH^-]_f = C_1$ (just not considering the H^+ ions from WB).

B-1. Upon passing 0.01 mole HCl gas through 100 mL of 0.05 M Formic acid solution ($K_a = 1.8 \times 10^{-4}$), determine change in pH of solution and $[HCOO^-]$ in resulting solution.

B-2. Determine pH & $[NH_4^+]$ in a solution obtained by mixing equal volumes of 0.02 M KOH solution and 0.2 M $NH_3 \cdot H_2O$ solution ($K_b = 2 \times 10^{-5}$). Also calculate % dissociation of $NH_3 \cdot H_2O$ in the final solution.

Section (C) : pH calculation : Solutions containing mixture of weak acids, Solutions containing mixture of weak bases

Commit to memory :

Mixture of two weak acids (both monoprotic) : $[H^+] = C_1\alpha_1 + C_2\alpha_2 = \sqrt{C_1K_{a_1} + C_2K_{a_2}}$

Mixture of two weak bases (both monoacidic) : $[OH^-] = C_1\alpha_1 + C_2\alpha_2 = \sqrt{C_1K_{b_1} + C_2K_{b_2}}$

C-1. Calculate $[H^+]$, $[HCOO^-]$ and $[OCN^-]$ in a solution that contains 0.1 M $HCOOH$ ($K_a = 2.4 \times 10^{-4}$) and 0.1 M $HOCN$ ($K_a = 4 \times 10^{-4}$).

Section (D) : pH calculation : Solutions containing mixture of weak polyprotic acid and strong acid, Solutions containing mixture of weak Polyacidic base and strong base

Commit to memory :

Mixture of a polyprotic weak acid and a strong acid : $[H^+] = [H^+]$ from SA

Mixture of a polyprotic weak base and a strong base : $[OH^-] = [OH^-]$ from SB

D-1. What is $[HS^-]$ & $[S^{2-}]$ in solution of 0.01 M HCl and 0.1 M H_2S ? (Given that for H_2S : $K_{a_1} = 10^{-7}$ and $K_{a_2} = 10^{-14}$)



Section (E) : pH calculation : Solutions of salt of weak polyprotic acid and strong base, Solutions of salt of weak Polyacidic base and strong acid, Solutions of amphiprotic species.

Commit to memory :

Solution containing polyvalent anion (A^{x-}) of weak polyprotic acid (H_xA) :

$$K_{h_1} = \frac{K_w}{K_{a_x}} ; h = \sqrt{\frac{K_{h_1}}{C}} ; pH = \frac{1}{2}[pK_w + pK_{a_x} + \log C]$$

Solution containing polyvalent cation (BH_y^{y+}) of weak polyprotic base (B) :

$$K_{h_1} = \frac{K_w}{K_{b_y}} ; h = \sqrt{\frac{K_{h_1}}{C}} ; pH = \frac{1}{2}[pK_w - pK_{b_y} - \log C]$$

$$\text{Solution containing amphiprotic anion of acid } H_xA : pH(H_{x-1}A^-) = \left(\frac{pK_{a_1} + pK_{a_2}}{2} \right) ; pH(H_{x-2}A^{2-}) = \left(\frac{pK_{a_2} + pK_{a_3}}{2} \right)$$

- E-1.** Calculate the pH of 0.1 M Na_3A of solution (salt of a tribasic acid H_3A). Assume only first step hydrolysis to be significant. Given : K_{a_1}, K_{a_2} & K_{a_3} for H_3A are $10^{-4}, 10^{-7}$ & 10^{-9} respectively.
- E-2.** What is the pH of M/20 $KHC_8H_4O_4$ solution ? Given : $H_2C_8H_4O_4$ is a dibasic acid with pK_{a_1} & pK_{a_2} as 2.94 & 5.44 respectively.

PART - II : ONLY ONE OPTION CORRECT TYPE

Section (A) : pH calculation : Solutions of polyprotic weak acids, Solutions of Polyacidic weak bases

Commit to memory :

Solution of a polyprotic weak acid (H_xA) : $pH = \frac{1}{2}(pK_{a_1} - \log C)$ [if $\alpha_1 \leq 0.1$ or 10%] ; $[H_{x-2}A^{2-}] = K_{a_2}$

Solution of a polyprotic weak base (B) : $pOH = \frac{1}{2}(pK_{b_1} - \log C)$ [if $\alpha_1 \leq 0.1$ or 10%] ; $[BH_2^{2+}] = K_{b_2}$

- A-1.** K_{b_1} of N_2H_4 is 4×10^{-6} . Then, what is the acid dissociation constant of $N_2H_5^+$ and $N_2H_6^{2+}$ respectively ?
 (A) data insufficient, 4×10^{-6} (B) data insufficient, 2.5×10^{-8}
 (C) 2.5×10^{-9} , data insufficient (D) 2.5×10^{-9} , 4×10^{-6}
- A-2.** For ortho phosphoric acid,
 $H_3PO_4(aq) + H_2O(aq) \longrightarrow H_3O^+(aq) + H_2PO_4^-(aq) ; K_{a_1}$
 $H_2PO_4^-(aq) + H_2O(aq) \longrightarrow H_3O^+(aq) + HPO_4^{2-}(aq) ; K_{a_2}$
 $HPO_4^{2-}(aq) + H_2O(aq) \longrightarrow H_3O^+(aq) + PO_4^{3-}(aq) ; K_{a_3}$
 The correct order of K_a values is :
 (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) $K_{a_1} < K_{a_2} > K_{a_3}$
- A-3.** In a solution of 0.1 M H_3PO_4 acid : (Given $K_{a_1} = 10^{-3}, K_{a_2} = 10^{-7}, K_{a_3} = 10^{-12}$)
 (i) Concentration of H_3PO_4 is :
 (A) 0.01 M (B) 0.09 M (C) 0.05 M (D) 0.1 M
 (ii) Concentration of $H_2PO_4^-$ is :
 (A) 0.01 M (B) 0.09 M (C) 0.02 M (D) 0.04 M
 (iii) Concentration of HPO_4^{2-} is :
 (A) 10^{-7} M (B) 10^{-8} M (C) 10^{-3} M (D) 10^{-4} M
 (iv) Concentration of PO_4^{3-} is :
 (A) 10^{-20} M (B) 10^{-17} M (C) 10^{-15} M (D) 10^{-12} M



- (v) pH of solution is :
 (A) 1 (B) 2 (C) 4 (D) 5
- A-4. Generally, in aqueous solutions of weak polyacidic bases, OH^- ions produced from 2nd ionisation are negligible because of :
 (A) $K_{b_2} \ll K_{b_1}$
 (B) Common ion effect exerted by OH^- ions produced from 1st ionisation.
 (C) Both (A) & (B)
 (D) None of these

Section (B) : pH calculation: Solutions containing mixture of weak monoprotic acid and strong acid, Solutions containing mixture of weak monoacidic base and strong base

Commit to memory :

Mixture of weak acid (monoprotic) and a strong acid : $[\text{H}^+]_f = C_1$ (just not considering the H^+ ions from WA).

Mixture of weak base (monoacidic) and a strong base : $[\text{OH}^-]_f = C_1$ (just not considering the H^+ ions from WB).

- B-1. The dissociation constant of acetic acid at a given temperature is 1.69×10^{-5} . The degree of dissociation of 0.01 M acetic acid in the presence of 0.01 M HCl is :
 (A) 1.69×10^{-7} (B) 1.69×10^{-5} (C) 1.69×10^{-3} (D) 2.9×10^{-2}
- B-2. On adding 100 mL of 10^{-2} M NaOH solution to 100 mL of 0.01 M Triethyl amine solution ($K_b = 6.4 \times 10^{-5}$), change in pH of solution with respect to triethylamine solution will be :
 (A) - 0.8 (B) + 0.8 (C) + 1.1 (D) - 1.1
- B-3. In above question, concentration of Triethyl ammonium ion ($[\text{C}_6\text{NH}_{16}^+]$) in resulting solution will be :
 (A) $100 K_b$ (B) $200 K_b$ (C) $10 K_b$ (D) K_b

Section (C) : pH calculation : Solutions containing mixture of weak acids, Solutions containing mixture of weak bases

Commit to memory :

Mixture of two weak acids (both monoprotic) : $[\text{H}^+] = C_1\alpha_1 + C_2\alpha_2 = \sqrt{C_1K_{a_1} + C_2K_{a_2}}$

Mixture of two weak bases (both monoacidic) : $[\text{OH}^-] = C_1\alpha_1 + C_2\alpha_2 = \sqrt{C_1K_{b_1} + C_2K_{b_2}}$

- C-1. Consider an aqueous solution, 0.1 M each in HOCN, HCOOH, $(\text{COOH})_2$ and H_3PO_4 . For HOCN, we can write : $K_a(\text{HOCN}) = \frac{[\text{H}^+][\text{OCN}^-]}{[\text{HOCN}]}$. $[\text{H}^+]$ in this equation is :
 (A) H^+ ions released by HOCN
 (B) Sum of H^+ ions released by all monoprotic acids
 (C) Sum of H^+ ions released only the first dissociation of all the acids.
 (D) Overall H^+ ion concentration in the solution.
- C-2. What are $[\text{H}^+]$, $[\text{A}^-]$ and $[\text{B}^-]$ in a solution that contains 0.03 M HA and 0.1 M HB. K_a for HA and HB are 3.0×10^{-4} and 1.0×10^{-10} respectively.
 (A) $[\text{H}^+] = 3 \times 10^{-3}$ M (B) $[\text{A}^-] = 3 \times 10^{-3}$ M
 (C) $[\text{B}^-] = 3.33 \times 10^{-9}$ M (D) All of these
- C-3. pH of a solution obtained by mixing equal volumes of 0.1 M Triethyl amine ($K_b = 6.4 \times 10^{-5}$) & $\frac{4}{45}$ M NH_4OH ($K_b = 1.8 \times 10^{-5}$) will be :
 (A) 11.3 (B) 10.3 (C) 12.3 (D) 11.45
- C-4. At 25°C, K_b for BOH = 1.0×10^{-12} . A 0.01 M solution of BOH has what value of $[\text{OH}^-]$?
 (A) 1.0×10^{-6} M (B) $\sqrt{2} \times 10^{-7}$ M (C) 1.0×10^{-5} M (D) 2.0×10^{-6} M


Section (D) : pH calculation : Solutions containing mixture of weak polyprotic acid and strong acid, Solutions containing mixture of weak Polyacidic base and strong base
Commit to memory :

 Mixture of a polyprotic weak acid and a strong acid : $[H^+] = [H^+]$ from SA

 Mixture of a polyprotic weak base and a strong base : $[OH^-] = [OH^-]$ from SB

D-1. For a solution obtained by mixing equal volumes of 0.02 M KOH solution & 0.2 M B (weak diacidic base; $K_{b_1} = 10^{-7}$ & $K_{b_2} = 10^{-14}$) solution :

- (A) pH = 12 (B)
- $[BH^+] = 10^{-6}$
- M (C)
- $[BH_2^{2+}] = 10^{-18}$
- M (D) All of these

Section (E) : Salt hydrolysis, pH calculation : Solutions of salt of monoprotic acid and monoacidic base.
Commit to memory :

 Salt of strong acid and weak base : $K_h \times K_b = K_w$; $h = \sqrt{\frac{K_h}{c}}$; $pH = \frac{1}{2} [pK_w - pK_b - \log c]$ (valid if $h < 0.1$ or 10%)

 Salt of strong base and weak acid : $K_h \times K_a = K_w$; $h = \sqrt{\frac{K_h}{c}}$; $pH = \frac{1}{2} [pK_w + pK_a + \log c]$ (valid if $h < 0.1$ or 10%)

 Salt of weak acid and weak base : $K_h \times K_a \times K_b = K_w$; $\left(\frac{h}{1-h}\right) = \sqrt{K_h}$; $pH = \frac{1}{2} [pK_w + pK_a - pK_b]$
E-1. 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 : (pK_a for $CH_3COOH = 4.74$)

- (A) 4.74 (B) 8.87 (C) 9.10 (D) 8.57

Section (F) : pH calculation : Solutions of salt of weak polyprotic acid and strong base, Solutions of salt of weak Polyacidic base and strong acid, Solutions of amphiprotic species.
Commit to memory :

 Solution containing polyvalent anion (A^{x-}) of weak polyprotic acid (H_xA) :

$$K_{h_1} = \frac{K_w}{K_{a_x}}; h = \sqrt{\frac{K_{h_1}}{C}}; pH = \frac{1}{2} [pK_w + pK_{a_x} + \log C]$$

 Solution containing polyvalent cation (BH_y^{y+}) of weak polyprotic base (B) :

$$K_{h_1} = \frac{K_w}{K_{b_y}}; h = \sqrt{\frac{K_{h_1}}{C}}; pH = \frac{1}{2} [pK_w - pK_{b_y} - \log C]$$

 Solution containing amphiprotic anion of acid H_xA :

$$pH(H_{x-1}A^-) = \left(\frac{pK_{a_1} + pK_{a_2}}{2}\right); pH(H_{x-2}A^{2-}) = \left(\frac{pK_{a_2} + pK_{a_3}}{2}\right)$$

F-1. For a BH_2Cl_2 solution (chloride salt of a diacidic base B): (Dissociation constants of base are K_{b_1} & K_{b_2})

- (A)
- $K_{h_1} \ll K_{h_2}$
- (B)
- $K_{h_1} = \frac{K_w}{K_{b_1}}$
- (C)
- $K_{h_1} = \frac{K_w}{K_{b_2}}$
- (D)
- $K_{h_2} = \frac{K_{b_1}}{K_w}$

F-2. Select the correct statement regarding above solution :

- (A) Anion will undergo hydrolysis producing
- OH^-
- & solution is expected to be basic.
-
- (B) Anion will not undergo hydrolysis & solution is expected to be basic.
-
- (C) Cation will undergo hydrolysis producing
- H_3O^+
- & solution is expected to be acidic.
-
- (D) Cation will undergo hydrolysis producing
- OH^-
- & solution is expected to be acidic.



- F-3.** pH of 0.1 M Na_2HPO_4 and 0.2 M NaH_2PO_4 are respectively: (pK_a for H_3PO_4 are 2.2, 7.2 and 12)
 (A) 4.7, 9.6 (B) 9.6, 4.7 (C) 9.3, 4.4 (D) 4.4, 9.3
- F-4.** The pH of which salt solution is independent of its concentration ?
 1. $(\text{CH}_3\text{COO})\text{C}_5\text{H}_5\text{NH}$ 2. NaH_2PO_4 3. Na_2HPO_4 4. NH_4CN
 (A) 1, 2, 3, 4 (B) 1, 4 (C) 2, 3 (D) 1, 2, 3

Exercise-2

Marked questions are recommended for Revision.

PART - I : ONLY ONE OPTION CORRECT TYPE

- In a solution obtained by mixing 100 mL of 0.25 M Triethylamine ($K_b = 6.4 \times 10^{-5}$) & 400 mL of $\frac{\text{M}}{18} \text{NH}_4\text{OH}$ ($K_b = 1.8 \times 10^{-5}$) :
 (A) $[\text{NH}_4^+] = 4 \times 10^{-4} \text{ M}$ (B) $[\text{C}_6\text{H}_{16}^+] = 1.6 \times 10^{-3} \text{ M}$
 (C) Both (A) & (B) (D) None of these
- Ratio of $[\text{HA}^{2-}]$ in 1 L of 0.1 M H_3A solution ($K_{a_1} = 10^{-5}$; $K_{a_2} = 10^{-8}$ & $K_{a_3} = 10^{-11}$) & upon addition of 0.1 mole HCl to it will be :
 (A) 10 (B) 100 (C) 1000 (D) 10,000
- Calculate the degree of hydrolysis and pH of 0.005 M K_2CrO_4 . $K_{a_2} = 5 \times 10^{-7}$ for H_2CrO_4 . (It is essentially strong for first ionization)
 (A) $h = 2 \times 10^{-3}$ (B) $h = 0.01$ (C) pH = 5 (D) pH = 9.7

PART - II : SINGLE AND DOUBLE VALUE INTEGER TYPE

- For a solution of weak triprotic acid H_3A ($K_{a_1} \gg K_{a_2}, K_{a_3}$; $K_{a_2} = 10^{-8}$; $K_{a_3} = 10^{-13}$), $[\text{A}^{3-}] = 10^{-17} \text{ M}$. Determine pH of solution. Report your answer as '0', if you find data insufficient.
- Calculate $[\text{H}^+]$ in a 0.2 M solution of dichloroacetic acid ($K_a = 5 \times 10^{-2}$) that also contains 0.05 M H_2SO_4 . Report your answer after multiplying it by 400.
- Calculate the ratio of concentrations of HCOO^- & OCN^- ions in a solution containing 0.1 M HCOOH ($K_a = 1.8 \times 10^{-4}$) and 0.1 M HOCN ($K_a = 4 \times 10^{-4}$). If simplest ratio is a : b, report your answer as (a + b).
- In a solution containing 0.01 M HCl and 0.1 M H_2CO_3 , ratio of $[\text{H}^+]$ produced from strong acid & weak acid respectively is: 1. Report your answer as x/500. Given: K_{a_1} & K_{a_2} of H_2CO_3 are 4×10^{-7} & 4×10^{-11} respectively.
- Calculate the change in pH of 0.1 M Na_2HA solution after diluting it to ten times the original volume. (Given that for H_3A : $K_{a_1} = 10^{-4}$, $K_{a_2} = 10^{-7}$, $K_{a_3} = 10^{-11}$)
- What is the pOH of a 0.5 M Na_3PO_4 solution ? Report your answer as $10 \times \text{pOH}$. ($K_{a_1} = 7.5 \times 10^{-3}$, $K_{a_2} = 6.2 \times 10^{-8}$, $K_{a_3} = 4 \times 10^{-13}$)

PART - III : ONE OR MORE THAN ONE OPTIONS CORRECT TYPE

- If K_{a_1} and K_{a_2} of H_2SO_4 are 10^{-2} and 10^{-6} respectively at a certain temperature, then :
 (A) $K_{a_1} > K_{a_2}$ because it is easy to abstract H^+ from H_2SO_4 and less easy to abstract H^+ from HSO_4^- .
 (B) K_{a_1} and K_{a_2} may be measured in acetic acid.
 (C) K_{a_1} and K_{a_2} are measured in H_2O .
 (D) the H^+ ion conc. of 0.01 M H_2SO_4 will be less than 0.02 M.



2. When 0.1 mole solid NaOH is added in 1 L of 0.1 M $\text{NH}_3(\text{aq})$ ($K_b = 2 \times 10^{-5}$), then select the correct statement(s) :
- (A) degree of dissociation of NH_3 approaches to zero.
 (B) change in pH by adding NaOH would be 1.85.
 (C) In solution, $[\text{Na}^+] = 0.1 \text{ M}$, $[\text{NH}_3] = 0.1 \text{ M}$, $[\text{OH}^-] = 0.2 \text{ M}$.
 (D) on addition of OH^- , K_b of NH_3 does not changes.
3. Which of the following solutions when added to 1L of a 0.01 M CH_3COOH solution will cause no change in the degree of dissociation of CH_3COOH and pH of the solution ? $K_a = 1.6 \times 10^{-5}$ for CH_3COOH
- (A) 0.6 mM HCOOH ($K_a = 8 \times 10^{-4}$) (B) 0.1 M CH_3COONa
 (C) 0.4 mM HCl (D) 0.01 M CH_3COOH

Exercise-3

* Marked questions may have more than one correct option.

PART - I : JEE (ADVANCED) / IIT-JEE PROBLEMS (PREVIOUS YEARS)

1. Will the pH of water be same at 4°C and 25°C ? Explain. [JEE-2003, 2/60]
2. A weak acid HX at 25°C has the dissociation constant 1×10^{-5} . It forms a salt NaX on reaction with caustic soda. The percentage hydrolysis of 0.1 M solution of NaX is : [JEE-2004(S), 3/84]
 (A) 0.0001% (B) 0.01 % (C) 0.1 % (D) 0.15 %
3. The dissociation constant of a substituted benzoic acid at 25°C is 1.0×10^{-4} . The pH of 0.01 M solution of its sodium salt is : [JEE-2009, 4/160]
4. The total number of diprotic acids among the following is : [JEE 2010, 3/163]
 H_3PO_4 H_2SO_4 H_3PO_3 H_2CO_3 $\text{H}_2\text{S}_2\text{O}_7$
 H_3BO_3 H_3PO_2 H_2CrO_4 H_2SO_3
5. Amongst the following, the total number of compounds whose aqueous solution turns red litmus paper blue is : [JEE-2010, 3/163]
 KCN K_2SO_4 $(\text{NH}_4)_2\text{C}_2\text{O}_4$ NaCl $\text{Zn}(\text{NO}_3)_2$
 FeCl_3 K_2CO_3 NH_4NO_3 LiCN

PART - II : JEE (MAIN) (PREVIOUS YEARS)

JEE(MAIN) OFFLINE PROBLEMS

1. In aqueous solution, the ionization constants for carbonic acid are : [AIEEE-2010, 4/144]
 $K_1 = 4.2 \times 10^{-7}$ and $K_2 = 4.8 \times 10^{-11}$
 Select the correct statement for a saturated 0.034 M solution of the carbonic acid.
 (1) The concentration of CO_3^{2-} is 0.034 M.
 (2) The concentration of CO_3^{2-} is greater than that of HCO_3^- .
 (3) The concentration of H^+ and HCO_3^- are approximately equal.
 (4) The concentration of H^+ is double that of CO_3^{2-} .
2. An aqueous solution contains 0.10 M H_2S and 0.20 M HCl . If the equilibrium constant for the formation of HS^- from H_2S is 1.0×10^{-7} and that of S^{2-} from HS^- ions is 1.2×10^{-13} then the concentration of S^{2-} ions in aqueous solution is : [JEE(Main)-2018, 4/120]
 (1) 6×10^{-21} (2) 5×10^{-19} (3) 5×10^{-8} (4) 3×10^{-20}



Answers

EXERCISE - 1

PART - I

- A-1. $\text{pH} = 4.52$, $3 \times 10^{-5} \text{ M}$, $1.2 \times 10^{-13} \text{ M}$ A-2. 10.91
 B-1. -1.52 , $9 \times 10^{-5} \text{ M}$. B-2. 12 , $2 \times 10^{-4} \text{ M}$, 0.2%
 C-1. $[\text{H}^+] = 8 \times 10^{-3} \text{ M}$, $[\text{HCOO}^-] = 3 \times 10^{-3} \text{ M}$, $[\text{OCN}^-] = 5 \times 10^{-3} \text{ M}$
 D-1. 10^{-6} M , 10^{-18} M E-1. 11 E-2. $\text{pH} = 4.19$

PART - II

- | | | |
|----------|----------|--|
| A-1. (C) | A-2. (C) | A-3. (i) (B) (ii) (A) (iii) (A) (iv) (B) (v) (B) |
| A-4. (C) | B-1. (C) | B-2. (B) B-3. (D) C-1. (D) |
| C-2. (D) | C-3. (A) | C-4. (B) D-1. (D) E-1. (B) |
| F-1. (C) | F-2. (C) | F-3. (B) F-4. (A) |

EXERCISE - 2

PART - I

1. (C) 2. (D) 3. (A)

PART - II

1. 4 2. 60 3. 29 (actual answer = 9 : 20) 4. 5
 5. 0 6. 10

PART - III

1. (ABD) 2. (ABD) 3. (ACD)

EXERCISE - 3

PART - I

1. It will not be same at two different temperatures.
 2. (B) 3. 8 4. 6 5. 3

PART - II

JEE(MAIN) OFFLINE PROBLEMS

1. (3) 2. (4)



IONIC EQUILIBRIUM-II

Exercise-1

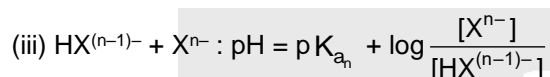
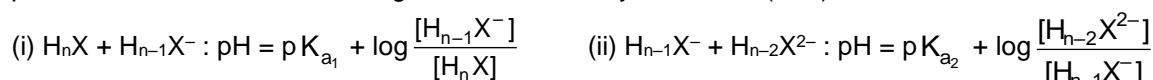
Marked questions are recommended for Revision.

PART - I : SUBJECTIVE QUESTIONS

Section (A) : pH calculation : Buffer solutions generated from Polybasic acid / Polyacidic base, Buffer capacity

Commit to memory :

pH calculation : Buffer solutions generated from Polybasic acid (H_nX) :



Buffer capacity : Moles of a strong acid or strong base required to change the pH of 1 L of a buffer by one unit.

Let there be a buffer solution of volume 1 L with 'b' mole of anion (coming from salt) and 'a' mole of weak acid.

$$B.C. = \frac{dx}{d\Delta pH} = 2.303 \frac{(a+x)(b-x)}{a+b} \approx 2.303 \frac{ab}{a+b}$$

Condition for maximum buffer capacity : [Acid] = [Anion of salt]

- A-1.** An environmental chemist needs a carbonate buffer of pH 10 to study the effects of the acidification of limestone-rich soils. How many grams of Na_2CO_3 must be added to 1.5 L of freshly prepared 0.2 M $NaHCO_3$ to make the buffer ? For H_2CO_3 , $K_{a_1} = 4.7 \times 10^{-7}$; $K_{a_2} = 4.7 \times 10^{-11}$.

Section (B) : pH calculation : Monobasic acid - Monoacidic base Titrations

Commit to memory :

pH calculation : Monobasic acid-Monoacidic base Titrations :

Carry out chemical reaction between the two components, apply mole concept, observe the final composition of the mixture and then calculate pH accordingly (using different cases dealt in Ionic Equilibrium-I).

In titration of WA by SB :

$$\text{At half equivalence point : } pH = pK_a ; pH_{x\% \text{ neutralisation}} = pK_a + \frac{x}{100-x}$$

In titration of WB and SA :

$$\text{At half equivalence point : } pOH = pK_b ; pOH_{x\% \text{ neutralisation}} = pK_b + \frac{x}{100-x}$$

- B-1.** Calculate pH of the following mixtures. Given : K_a of $CH_3COOH = 2 \times 10^{-5}$ and K_b of $NH_4OH = 2 \times 10^{-5}$.
- 50 mL of 0.10 M NaOH + 50 mL of 0.10 M HCl.
 - 50 mL of 0.10 M NaOH + 50 mL of 0.05 M CH_3COOH .
 - 50 mL of 0.05 M NaOH + 50 mL of 0.10 M CH_3COOH .
 - 50 mL of 0.10 M NH_4OH + 50 mL of 0.05 M HCl.
 - 50 mL of 0.10 M NH_4OH + 50 mL of 0.10 M HCl.
 - 50 mL of 0.05 M NH_4OH + 50 mL of 0.05 M CH_3COOH .
- B-2.** 0.1 M CH_3COOH solution is titrated against 0.05 M NaOH solution. Calculate pH at 1/4th and 3/4th stages of neutralization of acid. Given : pH of 0.1 M CH_3COOH solution is 3.


Section (C) : pH calculation : Titration of Salts, Polyprotic acid, Polyacidic base
Commit to memory :

pH calculation : Titration of Polyprotic acid, Polyacidic base :

Carry out chemical reaction between the two components, apply mole concept, observe the final composition of the mixture and then calculate pH accordingly (using different cases dealt in Ionic Equilibrium-I).

In titration of H_nX by strong base :

At half equivalence point w.r.t 1st neutralisation : $pH = pK_{a_1}$;

At equivalence point w.r.t 1st neutralisation : $pH = \frac{pK_{a_2} + pK_{a_1}}{2}$;

At half equivalence point w.r.t 2nd neutralisation : $pH = pK_{a_2}$;

At equivalence point w.r.t 2nd neutralisation : $pH = \frac{pK_{a_3} + pK_{a_2}}{2}$;

At equivalence point w.r.t last neutralisation : $pH = \frac{1}{2}(pK_w + pK_{a_n} + \log C)$.

In titration of Polyacidic base B by strong acid :

At half equivalence point w.r.t 1st neutralisation : $pOH = pK_{b_1}$;

At equivalence point w.r.t 1st neutralisation : $pOH = \frac{pK_{b_2} + pK_{b_1}}{2}$;

At half equivalence point w.r.t 2nd neutralisation : $pOH = pK_{b_2}$;

At equivalence point w.r.t 2nd neutralisation : $pH = \frac{pK_{b_3} + pK_{b_2}}{2}$;

At equivalence point w.r.t last neutralisation : $pH = \frac{1}{2}(pK_w - pK_{b_n} - \log C)$.

C-1. 50 mL of 0.05 M Propane-1,2-diamine solution is titrated with 0.1 M HCl solution at 25°C. Determine the pH of solutions obtained by adding following volumes of HCl solution :

(a) 12.5 mL (b) 25 mL (c) 30 mL

Given : pK_{b_1} and pK_{b_2} of weak base are 4.18 and 7.39 respectively.

C-2. Determine the $[H^+]$ at half-equivalence point and pH at equivalence point during the titration of a 50 mL, 0.1 M NH_4Cl solution with 0.1 M NaOH solution at 25°C. Given : K_b of $NH_3 = 2 \times 10^{-5}$.

PART - II : ONLY ONE OPTION CORRECT TYPE
Section (A) : pH calculation : Buffer solutions generated from Polybasic acid / Polyacidic base, Buffer capacity
Commit to memory :

pH calculation : Buffer solutions generated from Polybasic acid (H_nX) :

(i) $H_nX + H_{n-1}X^- : pH = pK_{a_1} + \log \frac{[H_{n-1}X^-]}{[H_nX]}$ (ii) $H_{n-1}X^- + H_{n-2}X^{2-} : pH = pK_{a_2} + \log \frac{[H_{n-2}X^{2-}]}{[H_{n-1}X^-]}$

(iii) $HX^{(n-1)-} + X^{n-} : pH = pK_{a_n} + \log \frac{[X^{n-}]}{[HX^{(n-1)-}]}$

Buffer capacity : Moles of a strong acid or strong base required to change the pH of 1 L of a buffer by one unit.



Let there be a buffer solution of volume 1 L with 'b' mole of anion (coming from salt) and 'a' mole of weak acid.

$$\text{B.C.} = \frac{dx}{d\text{pH}} = 2.303 \frac{(a+x)(b-x)}{a+b} \approx 2.303 \frac{ab}{a+b}$$

Condition for maximum buffer capacity : [Acid] = [Anion of salt]

- A-1.** The pH of a solution resulting from the addition of 12.5 ml of 0.1 M HCl to 50 ml of a solution containing 0.15 M CH_3COOH & 0.2 M CH_3COONa will be : (Given : pK_a of CH_3COOH = 4.74)
 (A) 4.74 (B) < 4.74 (C) > 4.74 (D) > 9.26
- A-2.** What % of the carbon in the $\text{H}_2\text{CO}_3 - \text{HCO}_3^-$ buffer should be in the form of HCO_3^- , so as to have a neutral solution ? (K_{a1} of H_2CO_3 = 4×10^{-7})
 (A) 20 % (B) 40 % (C) 60 % (D) 80 %
- A-3.** Buffer capacity of a buffer solution is x . The volume of 1 M NaOH solution added to 100 mL of this solution if change the pH by 1 is :
 (A) $0.1x$ mL (B) $10x$ mL (C) $100x$ mL (D) x mL

Section (B) : pH calculation : Monobasic acid - Monoacidic base Titrations

Commit to memory :

pH calculation : Monobasic acid - Monoacidic base Titrations :

Carry out chemical reaction between the two components, apply mole concept, observe the final composition of the mixture and then calculate pH accordingly (using different cases dealt in Ionic Equilibrium-I).

In titration of WA by SB :

At half equivalence point : $\text{pH} = \text{pK}_a$; $\text{pH}_{x\% \text{ neutralisation}} = \text{pK}_a + \frac{x}{100-x}$

In titration of WB and SA :

At half equivalence point : $\text{pOH} = \text{pK}_b$; $\text{pOH}_{x\% \text{ neutralisation}} = \text{pK}_b + \frac{x}{100-x}$

- B-1.** Upon titrating 50 mL of 1.96% (w/v) H_2SO_4 with a KOH solution (containing 11.2 g KOH per litre of solution), on adding 50 mL KOH solution :
 (A) Equivalence point has been just reached. (B) Equivalence point has been crossed.
 (C) pH of resulting solution = 1 (D) pH of resulting solution = 7
- B-2.** 100 mL of 0.02 M benzoic acid ($\text{pK}_a = 4.2$) is titrated using 0.02 M NaOH. pH after 50 mL and 100 mL of NaOH have been added are :
 (A) 2.1, 8.1 (B) 4.2, 7 (C) 4.2, 8.1 (D) 4.2, 8.25
- B-3.** In the above question, upon 75% neutralisation of Benzoic acid, select the INCORRECT statement :
 (A) Resulting solution will be a buffer solution. (B) $\text{pH} = 4.2 + \log 3$
 (C) Both (A) & (B) (D) None of these
- B-4.** Which of the following solutions have different pH ?
 (i) 100 mL of 0.2 M HCl + 100 mL of 0.4 M NH_3
 (ii) 50 mL of 0.1 M HCl + 50 mL of 0.2 M NH_3
 (iii) 100 mL of 0.3 M HCl + 100 mL of 0.6 M NH_3
 (A) i & ii (B) ii & iii (C) i & iii (D) All will have same pH.



- B-5.** Upon titrating a solution of weak monoprotic acid with a weak monoacidic base solution, at equivalence point :
- (A) pH in general would increase if both solutions are first diluted to 10 times the original volume & then titration is carried out.
- (B) pH in general would decrease if both solutions are first diluted to 10 times the original volume & then titration is carried out.
- (C) pH in general would remain same (= 7) if both solutions are first diluted to 10 times the original volume & then titration is carried out.
- (D) pH in general could be less than, greater than or equal to 7 if both solutions are first diluted to 10 times the original volume & then titration is carried out.

Section (C) : pH calculation : Titration of Salts, Polyprotic acid, Polyacidic base

Commit to memory :

pH calculation : Titration of Polyprotic acid, Polyacidic base :

Carry out chemical reaction between the two components, apply mole concept, observe the final composition of the mixture and then calculate pH accordingly (using different cases dealt in Ionic Equilibrium-I).

In titration of H_nX by strong base :

At half equivalence point w.r.t 1st neutralisation : $pH = pK_{a_1}$;

At equivalence point w.r.t 1st neutralisation : $pH = \frac{pK_{a_2} + pK_{a_1}}{2}$;

At half equivalence point w.r.t 2nd neutralisation : $pH = pK_{a_2}$;

At equivalence point w.r.t 2nd neutralisation : $pH = \frac{pK_{a_3} + pK_{a_2}}{2}$;

At equivalence point w.r.t last neutralisation : $pH = \frac{1}{2}(pK_w + pK_{a_n} + \log C)$.

In titration of Polyacidic base B by strong acid:

At half equivalence point w.r.t 1st neutralisation : $pOH = pK_{b_1}$;

At equivalence point w.r.t 1st neutralisation : $pOH = \frac{pK_{b_2} + pK_{b_1}}{2}$;

At half equivalence point w.r.t 2nd neutralisation : $pOH = pK_{b_2}$;

At equivalence point w.r.t 2nd neutralisation : $pH = \frac{pK_{b_3} + pK_{b_2}}{2}$;

At equivalence point w.r.t last neutralisation : $pH = \frac{1}{2}(pK_w - pK_{b_n} - \log C)$.

- C-1.** The total number of different kind of buffers obtained during the titration of H_3PO_4 with NaOH are :
 (A) 3 (B) 1 (C) 2 (D) Zero
- C-2.** Upon titration a solution of Ethylene diamine ($K_{b_1} = 8 \times 10^{-5}$; $K_{b_2} = 2.7 \times 10^{-8}$) with HCl solution, pH value of solution at 1st equivalence point depends upon :
 (A) Initial concentration of weak base solution (B) Initial concentration of strong acid solution
 (C) Both (A) & (B) (D) None of these
- C-3.** What will be the pH at the equivalence point during the titration of a 100 mL 0.2 M solution of CH_3COONa with 0.2 M solution of HCl ? $K_a = 2 \times 10^{-5}$.
 (A) $3 - \log \sqrt{2}$ (B) $3 + \log \sqrt{2}$ (C) $3 - \log 2$ (D) $3 + \log 2$



Exercise-2

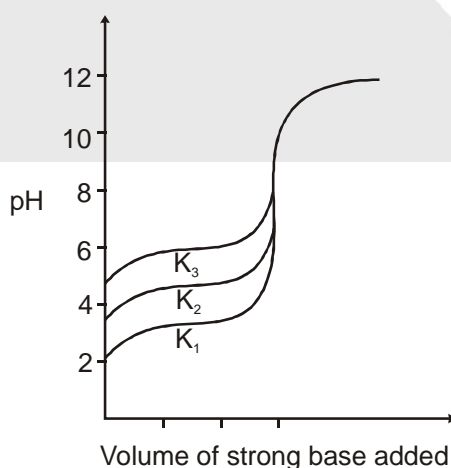
Marked questions are recommended for Revision.

PART - I : SINGLE AND DOUBLE VALUE INTEGER TYPE

- 15 mL sample of 0.15 M $\text{NH}_3(\text{aq})$ is titrated against 0.1M $\text{HCl}(\text{aq})$. What is the pH at the end point ? K_b of $\text{NH}_3(\text{aq}) = 1.8 \times 10^{-5}$. Report the answer rounding it off to the nearest whole number.
- A 0.252 g sample of unknown organic base is dissolved in water and titrated with a 0.14 M HCl solution. After the addition of 20 mL of acid, a pH of 10.7 is recorded. The equivalence point is reached when a total of 40 mL of HCl is added. If the base and acid combine in a 1 : 1 molar ratio, then 'a' g is the molar mass of the organic base and 'b' is the ionisation constant of base. Report your answer as $\left(\frac{a}{1000 b} \right)$.

PART - II : ONE OR MORE THAN ONE OPTIONS CORRECT TYPE

- Aniline behaves as a weak base. When 0.1 M, 50 mL solution sample of aniline was mixed with 0.2 M, 12.5 mL solution of HCl , the pH of resulting solution was 8. Then :
 (A) pH of 0.01 M solution of anilinium chloride is 5.
 (B) pH of original solution of aniline is 3.5.
 (C) Upon adding the same aniline sample to the above mixture, pH of resulting solution becomes 8.48.
 (D) Upon adding the same HCl sample to the above mixture, pH of resulting solution becomes 4.59.
- Which of the following mixtures will act as buffer ?
 (A) $\text{H}_2\text{CO}_3 + \text{NaOH}$ (1.5 : 1 molar ratio) (B) $\text{H}_2\text{CO}_3 + \text{NaOH}$ (1.5 : 2 molar ratio)
 (C) $\text{NH}_4\text{OH} + \text{HCl}$ (5 : 4 molar ratio) (D) $\text{NH}_4\text{OH} + \text{HCl}$ (4 : 5 molar ratio)
- Titration curves for 0.1M solutions of three weak acids HA_1 , HA_2 and HA_3 with ionization constants K_1 , K_2 and K_3 respectively with a strong base are plotted as shown in the figure. Which of the following options is/are true ?



- (A) $K_2 = (K_1 + K_3)/2$ (B) $\text{p}K_1 < \text{p}K_3$ (C) $K_1 > K_2$ (D) $K_2 > K_3$



PART - III : COMPREHENSION

Read the following passage carefully and answer the questions.

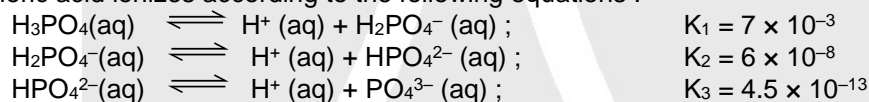
Comprehension # 1

The pH of basic buffer mixtures is given by : $\text{pH} = \text{pK}_a + \log \frac{[\text{Base}]}{[\text{Salt}]}$, whereas pH of acidic buffer mixtures is given by : $\text{pH} = \text{pK}_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$. Addition of little acid or base although shows no appreciable change in pH for all practical purposes, but since the ratio $\frac{[\text{Base}]}{[\text{Salt}]}$ for $\frac{[\text{Salt}]}{[\text{Acid}]}$ changes, a slight decrease or increase in pH results.

- A solution containing 0.2 mole of dichloroacetic acid ($K_a = 5 \times 10^{-2}$) and 0.1 mole sodium dichloroacetate in one litre solution has $[\text{H}^+]$:
(A) 0.05 M (B) 0.025 M (C) 0.10 M (D) 0.005 M
- The volume of 0.2 M NaOH needed to prepare a buffer of pH 4.74 with 50 mL of 0.2 M acetic acid is : (pK_b of $\text{CH}_3\text{COO}^- = 9.26$)
(A) 50 mL (B) 25 mL (C) 20 mL (D) 10 mL
- The ratio of pH of solution (I) containing 1 mole of CH_3COONa and 1 mole of HCl and solution (II) containing 1 mole of CH_3COONa and 1 mole of acetic acid in one litre is :
(A) 1 : 2 (B) 2 : 1 (C) 1 : 3 (D) 3 : 1

Comprehension # 2

Phosphoric acid ionizes according to the following equations :



- If you are asked to prepare a buffer with a pH = 7.00, what may be the molar ratio of the species that should be used in the solution ?
(A) 0.6 (B) 0.8 (C) 2 (D) 4
- Assume 50 mL of the buffer prepared in the previous part is available in which more abundant species has a concentration of 0.1 M. If to this solution, 20 mL 0.1 M NaOH is added further, what will be the new pH ?
(A) 6.56 (B) 7.44
(C) 7.78 (D) Same as before as it's a buffer

Exercise-3

* Marked questions may have more than one correct option.

PART - I : JEE (ADVANCED) / IIT-JEE PROBLEMS (PREVIOUS YEARS)

- 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 of acetic acid is 1.75×10^{-5} .
[JEE-2002, 5/60]
- 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.
[JEE-2004, 2/60]
- 0.1 mole of CH_3NH_2 ($K_b = 5 \times 10^{-4}$) is mixed with 0.08 mole of HCl and diluted to one litre. What will be the H^+ concentration in the solution ?
(A) 8×10^{-2} M (B) 8×10^{-11} M (C) 1.6×10^{-11} M (D) 8×10^{-5} M
[JEE-2005, 3/84]



4. 2.5 mL of $\frac{2}{5}$ M weak monoacidic base ($K_b = 1 \times 10^{-12}$ at 25°C) is titrated with $\frac{2}{15}$ M HCl in water at 25°C . The concentration of H^+ at equivalence point is : ($K_w = 1 \times 10^{-14}$ at 25°C) [JEE-2008, 3/163]
 (A) 3.7×10^{-14} M (B) 3.2×10^{-7} M (C) 3.2×10^{-2} M (D) 2.7×10^{-2} M
- 5.* Aqueous solutions 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) : [JEE-2010, 3/163]
 (A) HNO_3 and CH_3COOH (B) KOH and CH_3COONa
 (C) HNO_3 and CH_3COONa (D) CH_3COOH and CH_3COONa

Comprehension #

When 100 mL of 1.0 M HCl was mixed with 100 mL of 1.0 M NaOH in an insulated beaker at constant pressure, a temperature increase of 5.7°C was measured for the beaker and its contents (**Expt. 1**). Because the enthalpy of neutralization of a strong acid with a strong base is a constant (-57.0 kJ mol^{-1}), this experiment could be used to measure the calorimeter constant. In a second experiment (**Expt. 2**), 100 mL of 2.0 M acetic acid ($K_a = 2.0 \times 10^{-5}$) was mixed with 100 mL of 1.0 M NaOH (under identical conditions to **Expt. 1**) where a temperature rise of 5.6°C was measured. (Consider heat capacity of all solutions as 4.2 J $\text{g}^{-1} \text{K}^{-1}$ and density of all solutions as 1.0 g mL^{-1})

6. Enthalpy of dissociation (in kJ mol^{-1}) of acetic acid obtained from the **Expt. 2** is : [JEE (Advance)2015, 4/168]
 (A) 1.0 (B) 10.0 (C) 24.5 (D) 51.4
7. The pH of the solution after **Expt. 2** is [JEE (Advance)2015, 4/168]
 (A) 2.8 (B) 4.7 (C) 5.0 (D) 7.0
8. Dilution processes of different aqueous solutions, with water, are given in LIST-I. The effects of dilution of the solution on $[\text{H}^+]$ are given in LIST-II.
 (Note : degree of dissociation (α) of weak acid and weak base is $\ll 1$; degree of hydrolysis of salt $\ll 1$; $[\text{H}^+]$ represents the concentration of H^+ ions) [JEE (Advance)2018, 3/120]

LIST-I

- (P) (10 mL of 0.1 M NaOH + 20 mL of 0.1 M acetic acid) diluted to 60 mL
 (Q) (20 mL of 0.1 M NaOH + 20 mL of 0.1 M acetic acid) diluted to 80 mL
 (R) (20 mL of 0.1 M HCl + 20 mL of 0.1 M ammonia solution) diluted to 80 mL

(S) 10 mL saturated solution of $\text{Ni}(\text{OH})_2$ in equilibrium with excess solid $\text{Ni}(\text{OH})_2$ is diluted to 20 mL (solid $\text{Ni}(\text{OH})_2$ is still present after dilution).

LIST-II

- (1) the value of $[\text{H}^+]$ does not change on dilution
 (2) the value of $[\text{H}^+]$ changes to half of its initial value on dilution
 (3) the value of $[\text{H}^+]$ changes to two times of its initial value on dilution
 (4) the value of $[\text{H}^+]$ changes to $\frac{1}{\sqrt{2}}$ times of its initial value on dilution
 (5) the value of $[\text{H}^+]$ changes to $\sqrt{2}$ times of its initial value on dilution

Match each process given in LIST-I with one or more effect(s) in LIST-II. the correct option is

- (A) $P \rightarrow 4$; $Q \rightarrow 2$; $R \rightarrow 3$; $S \rightarrow 1$ (B) $P \rightarrow 4$; $Q \rightarrow 3$; $R \rightarrow 2$; $S \rightarrow 3$
 (C) $P \rightarrow 1$; $Q \rightarrow 4$; $R \rightarrow 5$; $S \rightarrow 3$ (D) $P \rightarrow 1$; $Q \rightarrow 5$; $R \rightarrow 4$; $S \rightarrow 1$

PART - II : JEE (MAIN) (PREVIOUS YEARS)

JEE(MAIN) OFFLINE PROBLEMS

1. An alkali is titrated against an acid with methyl orange as indicator, which of the following is a correct combination? [JEE(Main)-2018, 4/120]
- | Base | Acid | End point |
|------------|--------|-----------------------|
| (1) Weak | Strong | Yellow to pinkish red |
| (2) Strong | Strong | Pink to colourless |
| (3) Weak | Strong | Colourless to pink |
| (4) Strong | Strong | Pinkish red to yellow |





Answers

EXERCISE - 1

PART - I

- A-1. K A-2. 15 g Na_2CO_3 B-1. (a) 7, (b) 12.4, (c) 4.7, (d) 9.3, (e) 5.3, (f) 7
 B-2. 4.52, 5.48 C-1. (a) 9.82 (b) 8.215 (c) 7.21 C-2. 5×10^{-10} M; 11

PART - II

- A-1. (A) A-2. (D) A-3. (C) B-1. (C) B-2. (C)
 B-3. (D) B-4. (D) B-5. (D) C-1. (A) C-2. (D)
 C-3. (A)

EXERCISE - 2

PART - I

1. 5 (exact answer = 5.24) 2. 90 ($a = 45$ & $b = 5 \times 10^{-4}$)

PART - II

1. (ACD) 2. (ABC) 3. (BCD)

PART - III

1. (A) 2. (B) 3. (A) 4. (A) 5. (B)

EXERCISE - 3

PART - I

1. (a) 0.0175%, 1 (b) 4.757 2. $8.98 \approx 9$ 3. (B) 4. (D)
 5.* (CD) 6. (A) 7. (B) 8. (D)

PART - II

JEE(MAIN) OFFLINE PROBLEMS

1. (1)



IONIC EQUILIBRIUM-III

Exercise-1

✎ Marked questions are recommended for Revision.

PART - I : SUBJECTIVE QUESTIONS

Section (A) : Solubility, Solubility product and Simple solubility calculations

Commit to memory :

Solubility (s ; in mol/L) of a sparingly soluble salt A_xB_y : $K_{sp} = x^x \cdot y^y \cdot (s)^{x+y}$

- A-1.** Although it is a violent poison if swallowed, Mercury(II) cyanide $Hg(CN)_2$, has been used as a typical skin antiseptic. (K_{sp} of $Hg(CN)_2 = 1.35 \times 10^{-23}$, Atomic mass of $Hg = 200$ u). Assume no ion to be undergoing hydrolysis.
- What is the molar solubility of this salt in pure water ?
 - How many milligrams of $Hg(CN)_2$ dissolve per litre of pure water ?
 - How many milliliters of water are required to dissolve 1.134 g of the salt ?
- A-2.** How many milligrams of gold(III) ion are there per litre of solution in a saturated aqueous solution of gold (III) iodide ? $AuI_3(s) \rightleftharpoons Au^{3+}(aq) + 3I^-(aq)$. K_{sp} of $AuI_3 = 2.7 \times 10^{-47}$, atomic mass of $Au = 197$ u. Assume no hydrolysis of Au^{3+} ion.

Section (B) : Condition for precipitation, Common ion effect on solubility

Commit to memory :

Condition for precipitation of A_xB_y : Ionic product or $K_{IP} > K_{sp}$; $[A^{x+}]^x [B^{y-}]^y > K_{sp}$ of A_xB_y

Common ion effect on solubility : Solubility (s') of A_xB_y (sparingly soluble ; K_{sp}) in a solution of 'c' M A_pD_q/E_rB_p (both readily soluble) : $(pc)^x(ys')^y = K_{sp}$; $s' = \dots$

- B-1.** What can be the maximum concentration of equimolar solutions of ferrous sulphate ($FeSO_4$) and sodium sulphide (Na_2S), so that when mixed in equal volumes, there is no precipitation of iron sulphide (FeS) ? (For iron sulphide, $K_{sp} = 6.25 \times 10^{-18}$) Assume no ion to be undergoing hydrolysis.
- B-2.** ✎ Calculate the solubility of silver phosphate (Ag_3PO_4) in mg/mL (a) in pure water and (b) in a solution that is 0.03 M in $AgNO_3$. [$K_{sp}(Ag_3PO_4) = 2.7 \times 10^{-23}$]. Assume no ion to be undergoing hydrolysis. Atomic mass of $Ag = 108$ u.

Section (C) : Simultaneous Solubility, Complex Formation

Commit to memory :

Simultaneous solubility (s_1 & s_2) of A_xB_y & A_xC_y (both sparingly soluble) :

$$\frac{K_{sp}(A_xB_y)}{K_{sp}(A_xC_y)} = \frac{[B^{y-}]^y}{[C^{y-}]^y} = \frac{(ys_1)^y}{(ys_2)^y} = \left(\frac{s_1}{s_2}\right)^y$$

Further, $(xs_1 + xs_2)^x (ys_1)^y = K_{sp}(A_xB_y)$ & $(xs_2 + xs_1)^x (ys_2)^y = K_{sp}(A_xC_y)$. Put s_1 in terms of s_2 from eq.1 in eq.2 or eq.3 to obtain s_2 & then obtain s_1 .

Complex formation : Upon mixing M^{n+} & L and analyzing the reaction $M^{n+} + xL \rightleftharpoons [ML_x]^{n+}$ through chemical equilibrium (assuming M^{n+} to be completely consumed), concentrations of L and $[ML_x]^{n+}$ can be obtained. When they are put in expression of K_c , $[M^{n+}]_{eq}$ can be obtained.

- C-1.** ✎ Calculate the simultaneous solubility of $AgCl$ and AgI . Assume no hydrolysis of Ag^+ ion.
 $K_{sp}(AgCl) = 1 \times 10^{-10}$, $K_{sp}(AgI) = 8.5 \times 10^{-17}$
- C-2.** On passing 1 mole NH_3 gas through 1 L of 0.2 M $CuSO_4$ solution, determine $[Cu^{2+}]$ in the resulting solution. Given : K_f of $[Cu(NH_3)_4]^{2+} = 2 \times 10^{13}$. Assume no hydrolysis of Cu^{2+} ion.





Section (D) : Selective Precipitation, Solubility exchange

Commit to memory :

Selective precipitation: On gradually adding $A_p B_q(s)$ (readily soluble) to a solution containing $C_1 M X^{w-}$ & $C_2 M Y^{z-}$

$$[A^{q+}] \text{ req. for } A_w X_q \text{ pptn} = \sqrt[w]{\frac{K_{sp}(A_w X_q)}{(C_1)^q}}; [A^{q+}] \text{ req. for } A_z Y_q \text{ pptn} = \sqrt[z]{\frac{K_{sp}(A_z Y_q)}{(C_2)^q}}$$

Minimum value of $[A^{q+}]$ req. will tell which salt will precipitate first.

Solubility exchange: Upon treating a solution of $C_p D_q / C_p D_q(s)$ (readily soluble) with $A_x B_y(s)$ / saturated solution of $A_x B_y$ (sparingly soluble) such that some $A_x B_y$ gets converted to $A_p D_y$ (sparingly soluble), then :

$$\sqrt[x]{\frac{K_{sp}(A_x B_y)}{[B^{x-}]_f^y}} = \sqrt[p]{\frac{K_{sp}(A_p D_y)}{[D^{p-}]_f^y}}$$

D-1. A solution which is 0.1 M in NaI and also 0.1 M in Na_2SO_4 is treated with solid $Pb(NO_3)_2$. Which compound, PbI_2 or $PbSO_4$, will precipitate first? What is the concentration of anion of the least soluble compound when the more soluble one starts precipitating? $K_{sp}(PbI_2) = 9 \times 10^{-9}$, $K_{sp}(PbSO_4) = 1.8 \times 10^{-8}$. Assume no hydrolysis of Pb^{2+} ion.

D-2. 0.1 mole $AgCl(s)$ is added to 1 litre H_2O . Next, crystals of NaBr are added until 75% of the $AgCl$ is converted to $AgBr(s)$, the less soluble silver halide. What is $[Br^-]$ in the resulting solution? K_{sp} of $AgCl$ is 1.75×10^{-10} and K_{sp} of $AgBr$ is 5.25×10^{-13} . Assume no hydrolysis of Ag^+ ion.

PART - II : ONLY ONE OPTION CORRECT TYPE

Section (A) : Condition for precipitation, Common ion effect on solubility

Commit to memory :

Condition for precipitation of $A_x B_y$: Ionic product or $K_{IP} > K_{sp}$; $[A^{x+}]^x [B^{y-}]^y > K_{sp}$ of $A_x B_y$

Common ion effect on solubility : Solubility (s') of $A_x B_y$ (sparingly soluble; K_{sp}) in a solution of 'c' M $A_p D_q / E_r B_p$ (both readily soluble) : $(pc)^x (ys')^y = K_{sp}$; $s' = \dots$

A-1. What is the minimum pH at which $Mg(OH)_2$ starts precipitating from a solution containing 0.02 M $MgCl_2$? K_{sp} of $Mg(OH)_2 = 1.8 \times 10^{-11}$.
(A) 4.52 (B) 9.04 (C) 9.48 (D) 8.48

Section (B) : Simultaneous solubility and Complex formation

Commit to memory :

Simultaneous solubility (s_1 & s_2) of $A_x B_y$ & $A_x C_y$ (both sparingly soluble) :

$$\frac{K_{sp}(A_x B_y)}{K_{sp}(A_x C_y)} = \frac{[B^{x-}]^y}{[C^{x-}]^y} = \frac{(ys_1)^y}{(ys_2)^y} = \left(\frac{s_1}{s_2}\right)^y$$

Further, $(xs_1 + xs_2)^x (ys_1)^y = K_{sp}(A_x B_y)$ & $(xs_2 + xs_1)^x (ys_2)^y = K_{sp}(A_x C_y)$. Put s_1 in terms of s_2 from eq.1 in eq.2 or

eq.3 to obtain s_2 & then obtain s_1 .

Complex formation : Upon mixing M^{n+} & L and analyzing the reaction $M^{n+} + xL \rightleftharpoons [ML_x]^{n+}$ through chemical equilibrium (assuming M^{n+} to be completely consumed), concentrations of L and $[ML_x]^{n+}$ can be obtained. When they are put in expression of K_c , $[M^{n+}]_{eq}$ can be obtained.



- B-1.** Simultaneous solubility of two sparingly soluble salts A & B having some common ion :
 (A) is greater than their respective solubilities in separate solutions.
 (B) lies in between their solubilities in separate solutions.
 (C) is less than its solubility in separate solutions for more soluble salt, but is greater than its solubility in separate solution for less soluble salt.
 (D) is less than their respective solubilities in separate solutions.
- B-2.** The solubility product values of AgCl and AgCNS are 1.8×10^{-10} and 1.6×10^{-11} respectively. When a solution is saturated with both solids, calculate the ratio $[Cl^-]/[CNS^-]$ and also $[Ag^+]$ in the solution : Assume no reaction of cation/anion.
 (A) 1.125, 4×10^{-6} M (B) 11.25, 1.4×10^{-5} M (C) 1.25, 4×10^{-5} M (D) 1.25, 4×10^{-6} M
- B-3.** Which of the following options is true for a solution saturated with AgCl and AgBr, if their solubilities in mole per litre in separate water samples are x and y respectively ? Given : $x > y$. Assume no hydrolysis of Ag^+ ion.
 (A) $[Ag^+] < [Br^-] + [Cl^-]$ (B) $x > [Cl^-] > [Br^-]$ (C) $[Br^-] > y$ (D) $[Ag^+] = x + y$
- B-4.** Upon mixing equal volumes of 0.02 M $AgNO_3$ & 0.16 M KCN solutions : (Assume no hydrolysis of any ion). Given : $Ag^+(aq.) + 2CN^-(aq) \rightleftharpoons [Ag(CN)_2]^-(aq)$; $K_c = 10^{18}$
 (A) $[NO_3^-] = 0.01$ M ; $[K^+] = 0.08$ M (B) $[CN^-] = 0.06$ M
 (C) $[Ag(CN)_2^-] = 0.01$ M (D) All of these
- B-5.** In the above question (B-4), $[Ag^+]$ is about :
 (A) 2.78×10^{-18} M (B) 1.67×10^{-19} M
 (C) No free Ag^+ ions will be left in the solution (D) Cannot be determined

Section (C) : Selective Precipitation, Solubility exchange

Commit to memory :

Selective Precipitation : On gradually adding $A_pB_q(s)$; readily soluble) to a solution containing C_1 M X^{w-} & C_2 M Y^{z-}

$$[A^{q+}] \text{ req. for } A_wX_q \text{ pptn} = \sqrt[q]{\frac{K_{sp}(A_wX_q)}{(C_1)^q}} ; [A^{q+}] \text{ req. for } A_zY_q \text{ pptn} = \sqrt[q]{\frac{K_{sp}(A_zY_q)}{(C_2)^q}}$$

Minimum value of $[A^{q+}]$ req. will tell which salt will precipitate first.

Solubility exchange : Upon treating a solution of $C_pD_q / C_pD_q(s)$ (readily soluble) with $A_xB_y(s)$ / saturated solution of A_xB_y (sparingly soluble) such that some A_xB_y gets converted to A_pD_y (sparingly soluble), then :

$$\sqrt[x]{\frac{K_{sp}(A_xB_y)}{[B^{x-}]_f^y}} = \sqrt[p]{\frac{K_{sp}(A_pD_y)}{[D^{p-}]_f^y}}$$

- C-1.** In a solution containing equal concentrations of X^- , Y^- & Z^- , $MCl(s)$ (a readily soluble salt) is gradually added. If $K_{sp}(MX) > K_{sp}(MY) > K_{sp}(MZ)$, then : (Assume no hydrolysis of any ion).
 (A) MX will precipitate first.
 (B) MY will precipitate first.
 (C) MZ will precipitate first.
 (D) Nothing can be said about which salt will precipitate first, as numerical data is not given.
- C-2.** In above question, If $[X^-]_i : [Y^-]_i : [Z^-]_i = 100 : 10 : 1$ & $K_{sp}[MX] : K_{sp}[MY] : K_{sp}[MZ] = 10 : 0.1 : 1$, order of precipitation will be :
 (A) MZ, then MX & MY at last (B) MY, then MX & MZ at last
 (C) MX, then MY & MZ at last (D) MY, then MZ & MX at last



Exercise-2

Marked questions are recommended for Revision.

PART - I : ONLY ONE OPTION CORRECT TYPE

- A solution contains $[\text{NaCl}] = [\text{Na}_2\text{CO}_3] = C$ M. Upon gradually adding $\text{AgNO}_3(\text{s})$: (Assume no hydrolysis of any ion).

(A) Out of AgCl & Ag_2CO_3 , one having lesser K_{sp} will start precipitating first.

(B) Out of AgCl & Ag_2CO_3 , one having greater K_{sp} will start precipitating first.

(C) If, $\sqrt{\frac{K_{\text{sp}}(\text{Ag}_2\text{CO}_3)}{C}} < \frac{K_{\text{sp}}(\text{AgCl})}{C}$ then Ag_2CO_3 will start precipitating first.

(D) If, $\sqrt{\frac{K_{\text{sp}}(\text{Ag}_2\text{CO}_3)}{C}} < \frac{K_{\text{sp}}(\text{AgCl})}{C}$ then AgCl will start precipitating first.
- For the reaction : $[\text{Ag}(\text{CN})_2]^{-}(\text{aq}) \rightleftharpoons \text{Ag}^{+}(\text{aq}) + 2\text{CN}^{-}(\text{aq})$, K_{c} at 25°C is 4×10^{-19} . Calculate $[\text{Ag}^{+}]$ in solution which was originally 0.1 M in KCN and 0.03 M in AgNO_3 .

(A) 1.5×10^{-17} M (B) 7.5×10^{-18} M

(C) 4.6875×10^{-19} M (D) Value cannot be determined due to mathematical complications.
- A solution of Na_2CO_3 is added drop by drop to one litre of a solution containing 10^{-4} mole of Ba^{2+} and 10^{-5} mole of Ag^{+} . If K_{sp} for BaCO_3 is 8.1×10^{-9} and K_{sp} for Ag_2CO_3 is 6.9×10^{-12} , then which is not true? Assume no hydrolysis of CO_3^{2-} ion.

(A) No precipitate of BaCO_3 will appear until $[\text{CO}_3^{2-}]$ reaches 8.1×10^{-5} mol per litre.

(B) A precipitate of Ag_2CO_3 will appear when $[\text{CO}_3^{2-}]$ reaches 6.9×10^{-5} mol per litre.

(C) No precipitate of Ag_2CO_3 will appear until $[\text{CO}_3^{2-}]$ reaches 6.9×10^{-2} mole per litre.

(D) BaCO_3 will be precipitated first.

PART - II : SINGLE AND DOUBLE VALUE INTEGER TYPE

- When pure water is saturated with both CaCO_3 and CaC_2O_4 , the concentration of calcium ion in the solution under equilibrium is 8×10^{-5} M. If the ratio of the solubility product of CaCO_3 to that of CaC_2O_4 is 3, what is the solubility product of CaCO_3 in pure water ? Report your answer after multiplying by 10^9 and rounding it off to nearest whole number.
- On mixing equal volumes of 0.1 M AgNO_3 & 0.8 M KCN solutions, what % of original Ag^{+} is in the form of free Ag^{+} ions ? Given : K_{d} of $[\text{Ag}(\text{CN})_2]^{-} = 10^{-18}$. Report your answer after multiplying it by 4.5×10^{16} . (Assume no hydrolysis of any ion)

PART - III : COMPREHENSION

Comprehension # 1

0.2 mole of $\text{MgCl}_2(\text{s})$ are added in 1 litre volume of a solution (S), already containing 0.2 mole of $\text{NaOH}(\text{s})$. Now answer the following questions :

- Calculate pH of obtained solution. K_{sp} of $\text{Mg}(\text{OH})_2$ is 1.6×10^{-12} .

(A) 8.6 (B) 8.5 (C) 8.65 (D) 8.56
- What would be the new pH when 0.04 mole of $\text{NaOH}(\text{s})$ are added in the solution obtained from comprehension ?

(A) 8.6 (B) 8.5 (C) 8.65 (D) 8.56
- Find the pH of the solution obtained after adding 0.04 mole of $\text{HCl}(\text{g})$ to the solution obtained from comprehension ?

(A) 8.6 (B) 8.5 (C) 8.65 (D) 8.56



**Comprehension # 2**

Answer Q.4, Q.5 and Q.6 by appropriately matching the information given in the three columns of the following table.

Following 3 columns contain informations regarding water solubility of some sparingly soluble salts and its relation with their solubility product constants (K_{sp}).

Take temperature as 25°C.

Column-1		Column-2		Column-3	
(I)	Solubility $> \sqrt{K_{sp}}$	(i)	Solubility increases because of presence of common anion in solution	(P)	Solubility increases in acidic solution as pH decreases below 3
(II)	Solubility $< \left(\frac{K_{sp}}{27}\right)^{1/4}$	(ii)	Solubility decreases because of presence of common cation in solution	(Q)	Solubility increases in basic solution as pH increases above 11
(III)	Solubility $= \left(\frac{K_{sp}}{27}\right)^{1/4}$	(iii)	Solubility decreases because of presence of common anion in solution	(R)	Solubility is unaffected by pH of solution
(IV)	Solubility $= \sqrt{K_{sp}}$	(iv)	Solubility increases because of presence of common cation in solution	(S)	Anionic hydrolysis will make solubility in water greater than expected

4. For AgCN, the only correct combination is :
 (A) (IV) (ii) (R) (B) (I) (iii) (S) (C) (I) (i) (P) (D) (I) (iii) (P)
5. For $Al(OH)_3$, the only correct combination is :
 (A) (II) (iii) (S) (B) (II) (iv) (Q) (C) (III) (i) (P) (D) (II) (ii) (Q)
6. For PbS, the only correct combination is :
 (A) (I) (iii) (P) (B) (IV) (iii) (S) (C) (I) (ii) (R) (D) (IV) (ii) (P)

Exercise-3

* Marked questions may have more than one correct option.

PART - I : JEE (ADVANCED) / IIT-JEE PROBLEMS (PREVIOUS YEARS)

1. For a sparingly soluble salt A_pB_q , the relationship of its solubility product (L_s) with its solubility (S) is :
[JEE-2001(S), 1/35]
 (A) $L_s = S^{p+q} \cdot p^p \cdot q^q$ (B) $L_s = S^{p+q} \cdot p^q \cdot q^p$ (C) $L_s = S^{pq} \cdot p^p \cdot q^q$ (D) $L_s = S^{pq} \cdot (pq)^{p+q}$
2. A solution which is 10^{-3} M each in Mn^{2+} , Fe^{2+} , Zn^{2+} and Hg^{2+} is treated with 10^{-16} M sulphide ion. If K_{sp} values of MnS, FeS, ZnS and HgS are 10^{-15} , 10^{-23} , 10^{-20} and 10^{-54} respectively, which one will precipitate first ?
[JEE-2003, 3/84]
 (A) FeS (B) MgS (C) HgS (D) ZnS
3. Solubility product constant (K_{sp}) of salts of types MX, MX_2 and M_3X at temperature T are 4.0×10^{-8} , 3.2×10^{-14} and 2.7×10^{-15} , respectively. Solubilities (in mol dm^{-3}) of the salts at temperature T are in the order :
[JEE-2008, 3/163]
 (A) $MX > MX_2 > M_3X$ (B) $M_3X > MX_2 > MX$ (C) $MX_2 > M_3X > MX$ (D) $MX > M_3X > MX_2$
4. In 1 L saturated solution of AgCl [$K_{sp}(AgCl) = 1.6 \times 10^{-10}$], 0.1 mole of CuCl [$K_{sp}(CuCl) = 1.0 \times 10^{-6}$] is added. The resultant concentration of Ag^+ in the solution is 1.6×10^{-x} . The value of "x" is :
[JEE-2011, 4/180]
5. The K_{sp} of Ag_2CrO_4 is 1.1×10^{-12} at 298 K. The solubility (in mol/L) of Ag_2CrO_4 in a 0.1 M $AgNO_3$ solution is
[JEE (Advanced)-2013, 3/120]
 (A) 1.1×10^{-11} (B) 1.1×10^{-10} (C) 1.1×10^{-12} (D) 1.1×10^{-9}



6. The solubility of a salt of weak acid (**AB**) at pH 3 is $Y \times 10^{-3} \text{ mol L}^{-1}$. The value of Y is _____.
 (Given that the value of solubility product of **AB** (K_{sp}) = 2×10^{-10} and the value of ionization constant of HB (K_a) = 1×10^{-8})
[JEE(Advanced)-2018, 3/120]

PART - II : JEE (MAIN) (PREVIOUS YEARS)

JEE(MAIN) ONLINE PROBLEMS

1. Zirconium phosphate [$\text{Zr}_3(\text{PO}_4)_4$] dissociates into three zirconium cations of charge +4 and four phosphate anions of charge -3. If molar solubility of zirconium phosphate is denoted by S and its solubility product by K_{sp} then which of the following relationship between S and K_{sp} is correct ?

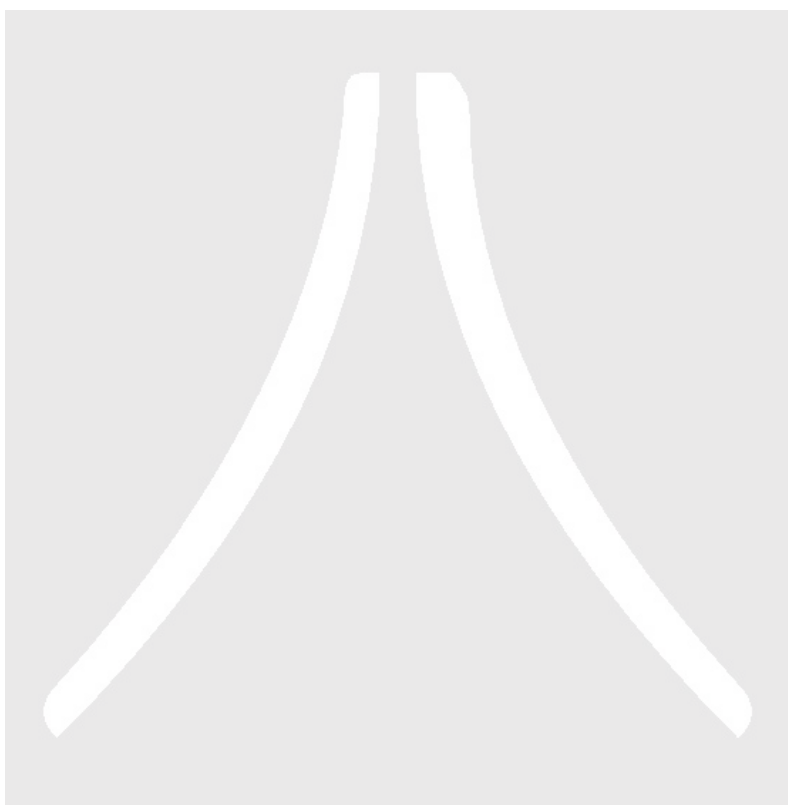
[JEE(Main) 2016 Online (19-04-14), 4/120]

(1) $S = \{K_{sp}/(6912)^{1/7}\}$

(2) $S = \{K_{sp}/144\}^{1/7}$

(3) $S = \{K_{sp}/6912\}^{1/7}$

(4) $S = \{K_{sp}/6912\}^7$





Answers

EXERCISE - 1

PART - I

- A-1.** (a) 1.5×10^{-8} M (b) 3.78×10^{-3} mg (c) 3×10^8 mL **A-2.** 1.97×10^{-7} mg
B-1. 5×10^{-9} M **B-2.** (a) 4.19×10^{-4} mg/mL (b) 4.19×10^{-16} mg/mL
C-1. 10^{-5} M AgCl, 8.5×10^{-12} M AgI. **C-2.** 6.25×10^{-12} M
D-1. PbSO₄, 0.02 M **D-2.** 2.25×10^{-4} M

PART - II

- A-1.** (C) **B-1.** (D) **B-2.** (B) **B-3.** (B) **B-4.** (D)
B-5. (A) **C-1.** (C) **C-2.** (B).

EXERCISE - 2

PART - I

1. (C) 2. (B) 3. (B)

PART - II

1. 5 (actual answer = 4.8×10^{-9}) 2. 50

PART - III

1. (A) 2. (C) 3. (D) 4. (C) 5. (D)
 6. (A)

EXERCISE - 3

PART - I

1. (A) 2. (C) 3. (D) 4. 7 5. (B)
 6. 4.47

PART - II

JEE(MAIN) ONLINE PROBLEMS

1. (3)



Additional Problems for Self Practice (APSP)

This Section is not meant for classroom discussion. It is being given to promote self-study and self testing amongst the Resonance students.

PART - I : PRACTICE TEST-1 (IIT-JEE (MAIN Pattern))

Max. Time : 1 Hr.

Max. Marks : 120

Important Instructions

- The test is of **1 hour** duration.
- The Test Booklet consists of **30** questions. The maximum marks are **120**.
- Each question is allotted **4 (four)** marks for correct response.
- Candidates will be awarded marks as stated above in Instructions No. 3 for correct response of each question.
 $\frac{1}{4}$ (**one fourth**) marks will be deducted for indicating incorrect response of each question. No deduction from the total score will be made if no response is indicated for an item in the answer sheet.
- There is only one correct response for each question. Filling up more than one response in any question will be treated as wrong response and marks for wrong response will be deducted accordingly as per instructions 4 above.

Note : Take water as solvent and temperature as 25°C , if not specified.
 Take $\log 2 = 0.3$, $\log 3 = 0.48$, $\log 5 = 0.7$, $\log 7 = 0.845$, if not specified.

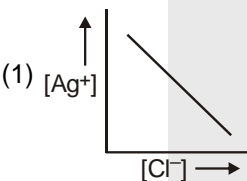
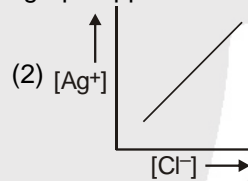
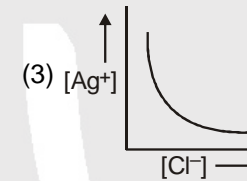
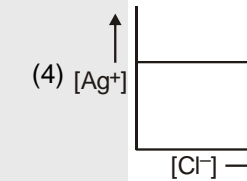
- Which of the following is not a Lewis acid ?
 (1) SiCl_4 (2) SO_3 (3) Zn^{2+} (4) CO
- If the degree of ionization of water at a particular temperature was found to be 1.8×10^{-9} , the K_a of water is:
 (1) 10^{-14} (2) 1.8×10^{-12} (3) 1.8×10^{-16} (4) 10^{-7}
- An aqueous solution whose $\text{pH} = 0$ is :
 (1) Alkaline (2) Acidic (3) Neutral (4) Not possible
- The pH , when 10^{-2} M H_2SO_4 solution is prepared in 10^{-3} M Na_2SO_4 solution, is :
 (1) 2 (2) 1.7 (3) 2.3 (4) 7
- A 100 mL solution of a strong acid of $\text{pH} = 1$ is mixed with a 100 mL solution of another strong acid of $\text{pH} = 2$. The resulting pH will be nearly : ($\log 11 = 1.04$)
 (1) 1.74 (2) 0.96 (3) 1.26 (4) 1.5
- V_1 mL of 0.1 M HNO_3 is mixed with V_2 mL of 0.1 M $\text{Sr}(\text{OH})_2$. The final solution :
 (1) is neutral, if $2V_1 = V_2$ (2) is acidic, if $V_1 > V_2$
 (3) is neutral, if $V_1 = V_2$ (4) is neutral, if $V_1 = 2V_2$
- The dissociation constants of two bases B_1OH and B_2OH are 2.56×10^{-4} and 1.6×10^{-5} respectively. The relative strength of the bases will be respectively :
 (1) 1 : 4 (2) 4 : 1 (3) 1 : 16 (4) 16 : 1
- What will be the effect of adding 10^{-3} M HCl solution to a solution of HA having concentration 0.1 M ? (K_a of $\text{HA} = 10^{-5}$)
 (1) Both degree of dissociation of HA and pH will decrease.
 (2) Degree of dissociation of HA will decrease but pH of solution will remain constant.
 (3) Effect on degree of dissociation of HA and pH of solution can be predicted only by knowing the volumes of both solutions.
 (4) Neither pH nor degree of dissociation of HA will change.
- The pH of the solution of 0.2 M acetic acid and 0.1 M benzoic acid is :
 ($K_a(\text{C}_6\text{H}_5\text{COOH}) = 6.5 \times 10^{-5}$, $K_a(\text{CH}_3\text{COOH}) = 1.75 \times 10^{-5}$)
 (1) 2.65 (2) 2.5 (3) 5.3 (4) 2.4





10. H_3A is a weak triprotic acid ($K_{a_1} = 10^{-5}$, $K_{a_2} = 10^{-9}$, $K_{a_3} = 10^{-13}$). What is the value of pX of 0.1 M H_3A (aq) solution ? Where $pX = -\log X$ and $X = \frac{[A^{3-}]}{[HA^{2-}]}$
- (1) 11 (2) 8 (3) 9 (4) 10
11. When $FeCl_3$ gets soluble in water, then its solution represents which of the following characteristics ?
- (1) Amphoteric (2) Acidic (3) Basic (4) Neutral
12. The salt NaA of weak acid HA is dissolved to form its 0.01 M solution. If the degree of hydrolysis is 0.01, the pH of solution and K_a of HA at $25^\circ C$ respectively are :
- (1) 4, 10^{-8} (2) 10, 10^{-6} (3) 10, 10^{-8} (4) 4, 10^{-6}
13. 10 mL of $\frac{M}{5}$ CH_3COOH solution is mixed with 10 mL of $\frac{M}{5}$ NH_4OH solution. The change in pH of solution upon diluting each solution to double volume will be : (pK_a of $CH_3COOH = 4.76$, pK_b of $NH_4OH = 4.74$)
- (1) - 0.3 (2) + 0.3 (3) + 1 (4) No change
14. H_2A is a diprotic acid for which $K_{a_1} = 10^{-7}$ and $K_{a_2} = 10^{-11}$. The solution which will have a pH closest to 9 is :
- (1) 0.1 M H_2A (2) 0.1 M Na_2A (3) 0.1 M $NaHA$ (4) 0.1 M $NaHA + 0.1$ M Na_2A
15. S_1 : The pH of solution made by dissolving 1 mole each of HCl, NaOH & CH_3COONH_4 in the same beaker is 7, if $pK_a(CH_3COOH) = pK_b(NH_3)$.
 S_2 : Methyl orange can be used as an indicator in the titration of CH_3COOH with NaOH.
 S_3 : Water act as an acid when ammonia is dissolved in water.
- (1) T F T (2) T F F (3) F T T (4) T T T
16. Which of following cannot act as buffer ?
- (1) NH_4CN (2) $NaHCO_3 + H_2CO_3$
 (3) $NaH_2PO_4 + Na_2HPO_4$ (4) None of these
17. 500 mL of 0.01 M $CH_3COOH + 500$ mL of 0.02 M CH_3COONa gives a pH equal to 5.3. The pK_b of CH_3COO^- is :
- (1) 10 (2) 9 (3) 4 (4) 5
18. HCl gas is passed through an aqueous solution of 0.1 M 1-aminopropane ($PrNH_2$) till the pH reaches 9.7. Calculate the ratio of $[PrNH_2]/[PrNH_3^+]$ in this solution. [$K_b(PrNH_2) = 5 \times 10^{-4}$]
- (1) 0.1 (2) 0.25 (3) 10 (4) 4
19. What fraction of indicator is in acidic form at a solution pH of 5, if pK_a of the indicator is 4.7 ?
- (1) $\frac{2}{3}$ (2) $\frac{1}{3}$ (3) $\frac{1}{2}$ (4) $\frac{1}{11}$
20. **Statement-1** : In a titration of weak monoacidic base with strong acid, the pOH at the half equivalent point is pK_b .
Statement-2 : At half equivalence point, it will form buffer at its maximum capacity where $[base] = [conjugate\ acid]$.
- (1) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
 (2) Statement-1 is true, statement-2 is true and statement-2 is not correct explanation for statement-1.
 (3) Statement-1 is true, statement-2 is false
 (4) Statement-1 is false, statement-2 is true
21. 8 g weak acid HX (molecular mass = 80 u ; $K_a = 10^{-4}$) is dissolved in 100 mL water. If it is titrated with 0.25 M NaOH, find pH at equivalence point :
- (1) 9.35 (2) 8.65 (3) 9 (4) 8.7



22. 10 mL of $\frac{M}{5}$ CH_3COONa solution is titrated with $\frac{M}{5}$ HCl solution. The pH value at equivalence point is :
($\text{pK}_a(\text{CH}_3\text{COOH}) = 4.76$)
(1) 0.7 (2) 1 (3) 1.88 (4) 2.88
23. The minimum volume of water required to dissolve 10 mg CaCO_3 ($K_{\text{sp}} = 2.5 \times 10^{-9}$) is : (neglect hydrolysis of Ca^{2+} and CO_3^{2-}).
(1) 2 L (2) 0.2 L (3) 20 L (4) 0.02 L
24. Which of the following sparingly soluble salts is most soluble in water, assuming all to have same K_{sp} values ?
(1) AB (ionising into A^+ & B^-) (2) CD_2 (ionising into C^{2+} & D^-)
(3) E_2F_2 (ionising into E_2^{2+} & F^-) (4) GH_3 (ionising into G^{3+} & H^-)
25. K_{sp} of Ag_2CrO_4 at a certain temperature is 8.64×10^{-13} . How many times is its solubility in water greater than in 0.6 M Na_2CrO_4 solution ?
(1) 100 (2) 10 (3) 1000 (4) ≈ 129
26. In a saturated solution of AgCl , NaCl is added gradually. The concentration of Ag^+ is plotted against the concentration of Cl^- . The graph appears as :
(1)  (2)  (3)  (4) 
27. SrCO_3 ($K_{\text{sp}} = 10^{-10}$) and ZnCO_3 ($K_{\text{sp}} = 1.5 \times 10^{-11}$) are dissolved together in a solution. The ratio of $[\text{Sr}^{2+}]/[\text{Zn}^{2+}]$ in the solution is :
(1) $\frac{10}{3}$ (2) $\frac{3}{10}$ (3) $\frac{20}{3}$ (4) $\frac{3}{20}$
28. The solubility of $\text{Fe}(\text{OH})_3$ would be maximum in :
(1) 0.1 M NaOH (2) 0.1 M HCl (3) 0.1 M KOH (4) 0.1 M H_2SO_4 .
29. **Statement-1** : Solubility of AgCN in $\text{KCN}(\text{aq})$ is greater than in pure water.
Statement-2 : When AgCN dissolve in $\text{KCN}(\text{aq})$, complex ion $[\text{Ag}(\text{CN})_2]^-$ formation takes place and solubility equilibrium of AgCN shifted in backward direction.
(1) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
(2) Statement-1 is true, statement-2 is true and statement-2 is not correct explanation for statement-1.
(3) Statement-1 is true, statement-2 is false. (4) Statement-1 is false, statement-2 is true.
30. What is the effect of pH on the solubility of $\text{M}(\text{CN})_2$? (neglect hydrolysis of M^{2+} ion)
(1) As pH decreases, solubility decreases.
(2) As pH decreases below 7 or increases above 7, solubility increases in both cases.
(3) As pH decreases, solubility increases. (4) No dependence on pH of solution.

Practice Test-1 (IIT-JEE (Main Pattern))

OBJECTIVE RESPONSE SHEET (ORS)

Que.	1	2	3	4	5	6	7	8	9	10
Ans.										
Que.	11	12	13	14	15	16	17	18	19	20
Ans.										
Que.	21	22	23	24	25	26	27	28	29	30
Ans.										


PART-II : NATIONAL STANDARD EXAMINATION IN CHEMISTRY (NSEC) STAGE-I

1. Which of the following is not a strong electrolyte ? [NSEC-2000]
 (A) fused NaCl (B) acetic acid
 (C) dilute perchloric acid (D) aqueous NaOH solution
2. If the solubility product of a salt MX is 3×10^{-10} at 0°C , its solubility is : [NSEC-2000]
 (A) $1.73 \times 10^{-5} \text{ mol dm}^{-3}$ (B) $6.9 \times 10^{-10} \text{ mol dm}^{-3}$
 (C) $9 \times 10^{-20} \text{ mol dm}^{-3}$ (D) $1.73 \times 10^{-10} \text{ mol dm}^{-3}$
3. 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 ? [NSEC-2000]
 (A) 10 (B) 8 (C) 5 (D) 12
4. The concentration of H_3O^+ ions in pure water is $10^{-6} \text{ mol dm}^{-3}$. The corresponding concentration of OH^- ions will be : [NSEC-2000]
 (A) $10^{-14} \text{ mol dm}^{-3}$ (B) $10^{-8} \text{ mol dm}^{-3}$ (C) $10^{-6} \text{ mol dm}^{-3}$ (D) $10^{-7} \text{ mol dm}^{-3}$
5. In a reaction, $\text{HCO}_3^- + \text{H}_2\text{O} \rightarrow \text{CO}_3^{2-} + \text{H}_3\text{O}^+$
 Which two substances are Bronsted bases ? [NSEC-2000]
 (A) CO_3^{2-} & H_3O^+ (B) HCO_3^- & H_3O^+ (C) HCO_3^- & CO_3^{2-} (D) CO_3^{2-} & H_2O
6. Which of the reagents listed below could be added to water to make 0.1 M solution of NH_4^+ ? [NSEC-2000]
 (A) NH_3 (B) NH_4Cl (C) both (D) none of these
7. The solubility of AgCl is $1.56 \times 10^{-5} \text{ mol m}^{-3}$ at 30°C . Its solubility product K_{sp} will be : [NSEC-2001]
 (A) 1.25×10^{-10} (B) 2.43×10^{-10} (C) 1.25×10^{-5} (D) 5.90×10^{-20}
8. The Ostwald's dilution law can be written as : [NSEC-2001]
 (A) $K_a = \left(\frac{\alpha^2}{1-\alpha} \right) V$ (B) $K_a = \left(\frac{\alpha^2}{1-\alpha} \right) \frac{1}{V}$ (C) $K_a = \frac{\alpha}{V}$ (D) $K_a = \alpha^2 \sqrt{V}$
9. Which of the alkali hydroxides is most basic ? [NSEC-2001]
 (A) KOH (B) NaOH (C) LiOH (D) CsOH
10. The pH of $0.1 \text{ M CH}_3\text{COOH}$ (dissociation constant of acetic acid is 1.80×10^{-5} at 25°C) will be : [NSEC-2001]
 (A) 5 (B) 2.873 (C) 1 (D) 0.18
11. Which of the following does not act as a buffer solution ? [NSEC-2001]
 (A) Sodium acetate and acetic acid (B) Boric acid and borax
 (C) Na_3PO_4 and Na_2HPO_4 (D) Sodium acetate and sodium citrate
12. The pH of a soft drink is 3.82. Its hydrogen ion concentration in mol.dm^{-3} will be : [NSEC-2001]
 (A) 1.5×10^{-4} (B) 1.96×10^{-3} (C) 1.96×10^{-2} (D) 1.96×10^{-1}
13. The colour change of an acid-base indicator is due to formation of : [NSEC-2002]
 (A) benzoic structure (B) quinoid structure (C) ionic structure (D) covalent bond.
14. The pK_a of aspirin is 3.5. The pH of gastric juice in human stomach is about 2 to 3, while in small intestine, the pH is 8. Aspirin will be : [NSEC-2002]
 (A) unionised in the small intestine and in the stomach
 (B) completely ionised in stomach and small intestine
 (C) ionised in stomach and almost unionised in small intestine
 (D) none of these
15. The Henderson equation for an acidic buffer is : [NSEC-2002]
 (A) $\text{pH} = \text{pK}_a + \log \frac{[\text{acid}]}{[\text{salt}]}$ (B) $\text{pH} = \text{pK}_a + \log \frac{[\text{salt}]}{[\text{acid}]}$
 (C) $\text{pK}_w = \text{pK}_a + \log \frac{[\text{salt}]}{[\text{acid}]}$ (D) $\text{pH} = \text{pK}_a + \log (\text{salt}) \cdot (\text{acid})$



16. For the salt of strong acid and weak base, the hydrolysis constant is given by : [NSEC-2002]
 (A) $K_h = \frac{K_w}{K_b}$ (B) $K_h = \frac{K_w}{K_a}$ (C) $K_h = \frac{K_w}{K_a \cdot K_b}$ (D) $K_h = \sqrt{\frac{K_w}{K_a \cdot K_b}}$
17. When a salt 'X' is dissolved in water at pH = 7, the resulting solution becomes alkaline in nature. Salt 'X' is made up of : [NSEC-2002]
 (A) strong acid and strong base (B) weak acid and weak base
 (C) weak acid and strong base (D) strong acid and weak base
18. The pH of 10^{-6} M KOH is [NSEC-2002]
 (A) 6.0 (B) 7.0 (C) 8.0 (D) 9.0
19. If H_2S gas is passed in a acidified $ZnSO_4$, the precipitation of ZnS does not take place because : [NSEC-2002]
 (A) K_{sp} of ZnS is not exceeded (B) K_{sp} of ZnS is decreases
 (C) K_{sp} of ZnS is increases (D) none of these
20. pH of circulating blood is maintained around 7.4 by the action of buffer system of : [NSEC-2002]
 (A) $H_2PO_4^-/HPO_4^{2-}$ (B) CO_2 / HCO_3^- (C) NH_4Cl/NH_4OH (D) CH_3COO^-/CH_3COONa .
21. Lead chloride has a solubility product of 1.7×10^{-5} at 300 K. Its solubility will be [NSEC-2002]
 (A) $1.62 \times 10^{-2} \text{ mol dm}^{-3}$ (B) $4.123 \times 10^{-3} \text{ mol dm}^{-3}$
 (C) $4.123 \times 10^{-6} \text{ mol dm}^{-3}$ (D) $5.1 \times 10^{-3} \text{ mol dm}^{-3}$
22. The pK_a of acetic acid is 4.74, which implies that : [NSEC-2003]
 (A) pH of 1 N acetic acid is 4.74.
 (B) at pH 4.74, the dissociation of acetic acid is maximum.
 (C) at pH 4.74, half of the acetic acid molecules are dissociated in the solution.
 (D) at pH 4.74, the dissociation of acetic acid is minimum.
23. Sodium hydroxide cannot be used as a primary standard for acid base titration because : [NSEC-2003]
 (A) it is corrosive and reacts with glass.
 (B) the dissolution of sodium hydroxide in water is highly exothermic, hence its concentration changes on dissolution.
 (C) it is hygroscopic and also reacts with atmospheric carbon dioxide.
 (D) hydroxides cannot be used as primary standards.
24. The molar concentration of pure water at 4°C and 1 atm pressure is [NSEC-2003]
 (A) 1 (B) 5.5 (C) 18 (D) 55.5
25. The solubility product of $AgCl$ is 1.8×10^{-10} . The minimum volume (in L) of water, required to dissolve 1.9 mg of $AgCl$ is approximately [NSEC-2003]
 (A) 10 (B) 2 (C) 1 (D) 20
26. In a titration experiment, 50.0 mL of 0.1 N HCl is being titrated against 0.1 N $NaOH$. The pH of the solution on addition of 49.9 mL of $NaOH$ is approximately : [NSEC-2003]
 (A) 7.0 (B) 6.0 (C) 4.0 (D) 3.0
27. The solubility product of Ag_2CrO_4 is 1.9×10^{-12} . The volume of water in mL that can just dissolve 4 mg of Ag_2CrO_4 is about : [NSEC-2004]
 (A) 150 mL (B) 1000 mL (C) 250 mL (D) 500 mL
28. The precipitate of $AgCl$ dissolves in : [NSEC-2004]
 (A) conc. HNO_3 (B) excess of HCl (C) dilute H_2SO_4 (D) aq. ammonia.
- 29.* In its 0.20 M solution, methanoic acid has degree of dissociation 0.032. Hence, its dissociation constant would be : [NSEC-2004]
 (A) 2.1×10^{-2} (B) 2.1×10^{-4} (C) 1.1×10^{-6} (D) 1.6×10^{-8}
30. A pair that forms a buffer system is : [NSEC-2004]
 (A) $BaCl_2 + Ba(NO_3)_2$ (B) $NaCl + HCl$
 (C) $Na_3PO_4 + Na_2HPO_4$ (D) $AgCN + KCN$.



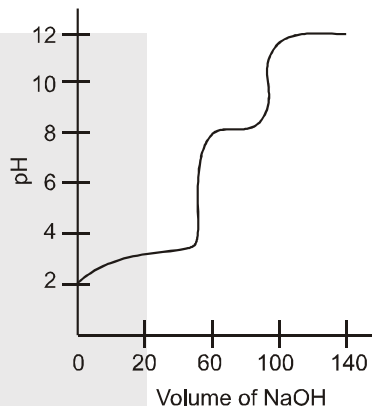
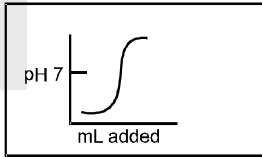
31. A buffer solution is prepared by mixing 0.050 moles of a weak acid HA and 0.20 moles of NaA in sufficient amount of water to give 500 mL of solution (K_a for HA is 4.5×10^{-4}). The pH of this solution is: [NSEC-2004]
 (A) 1.97 (B) 2.17 (C) 2.74 (D) 3.95
- 32.* Consider various species generated when H_3PO_4 dissolved in water. Among these, the conjugate acid of HPO_4^{2-} is : [NSEC-2004]
 (A) H_3PO_4 (B) $H_2PO_4^-$ (C) PO_4^{3-} (D) H_3O^+
33. If a weak base has the dissociation constant K_b , then the value of the dissociation constant, K_a of its conjugate acid is given by : [NSEC-2004]
 (A) $1/K_b$ (B) K_w/K_b (C) K_b/K_w (D) $K_w K_b$
34. The salt that when added to water will not change its pH is : [NSEC-2004]
 (A) Na_2CO_3 (B) NaCl (C) KCN (D) NH_4Cl
35. What is the pH of 10^{-3} (N) CH_3COOH solution? (Dissociation constant of CH_3COOH is 1.74×10^{-5}) [NSEC-2005]
 (A) 3.88 (B) 4.76 (C) 5.55 (D) 3.0
36. The ionic product of water at $25^\circ C$ is 10^{-14} . The corresponding dissociation constant is : [NSEC-2005]
 (A) 2.0×10^{-16} (B) 3.6×10^{-16} (C) 1.5×10^{-16} (D) 1.8×10^{-16}
37. The solubility product of $Mg(OH)_2$ is $3.4 \times 10^{-11} \text{ mol}^3 \text{ L}^{-3}$. What will be its solubility in g L^{-1} (molecular weight of $Mg(OH)_2$ is 58.3) [NSEC-2005]
 (A) 2.0×10^{-4} (B) 1.2×10^{-2} (C) 1.6×10^{-3} (D) 3.5×10^{-4}
38. pH of the blood in the body is maintained by : [NSEC-2005]
 (A) glucose and salt concentration (B) protein and salt concentration
 (C) carbonate and bicarbonate concentration (D) salt and carbonate
39. Which indicator will be suitable for the titration of acetic acid vs NaOH ? [NSEC-2005]
 (A) methyl orange [$pK_{in} = 3.7$] (B) bromocresol green [$pK_{in} = 4.7$]
 (C) chlorophenol red [$pK_{in} = 6.1$] (D) phenolphthalein [$pK_{in} = 9.6$]
40. The compound that may be added to water to increase its pH from 7 to a higher value is : [NSEC-2006]
 (A) Na_2CO_3 (B) $AlCl_3$ (C) NaCl (D) HCl
41. The most acidic aqueous solution is : [NSEC-2006]
 (A) CH_3COONa (B) Na_2CO_3 (C) NH_4Cl (D) Na_2HPO_4
42. The slightly soluble Ag_2CrO_4 is expected to be more soluble in : [NSEC-2006]
 (A) 0.1 M HNO_3 (B) 0.01 M K_2CrO_4 (C) pure water (D) 0.1 M $AgNO_3$.
43. Pure water is saturated with a sparingly soluble salt, PbI_2 which has a solubility product K_{sp} . In this saturated solution : [NSEC-2006]
 (A) $[Pb^{2+}] = [I^-]$ (B) $[Pb^{2+}] = K_{sp}$ (C) $[Pb^{2+}] = (K_{sp})^{1/2}$ (D) $2[Pb^{2+}] = [I^-]$
44. Which of the following metal sulphides has maximum solubility in water? (K_{sp} values are indicated in parentheses). [NSEC-2006]
 (A) HgS (10^{-54}) (B) CdS (10^{-30}) (C) FeS (10^{-20}) (D) ZnS (10^{-22}) .
45. If 25 mL of 0.01 N NaOH is added to 50 mL of 0.01 N acetic acid, the pH of the resultant solution will be: (pK_a of $CH_3COOH = 4.76$) [NSEC-2006]
 (A) 5.5 (B) 4.5 (C) 4.76 (D) 2.48
46. Calculate the pH of a solution made by mixing 150 cm^3 of 0.10 M CH_3COONa and 250 cm^3 of 0.10 M CH_3COOH . [K_a of $CH_3COOH = 1.8 \times 10^{-5}$] [NSEC-2007]
 (A) 237 (B) 4.52 (C) 4.74 (D) 4.97
47. The solubility product constant, K_{sp} of Ag_3PO_4 is 1.8×10^{-18} . What is the molar solubility of Ag_3PO_4 in water? (Neglect any hydrolysis) [NSEC-2007]
 (A) 1.6×10^{-5} (B) 8.4×10^{-7} (C) 1.3×10^{-9} (D) 4.5×10^{-19}



48. If each of the following salts has $K_{sp} = 1 \times 10^{-9}$, which of them is the least soluble in water? [NSEC-2007]
 (A) XY (B) XY_2 (C) X_2Y (D) X_3Y
49. The pH of a 0.01 M solution of ammonium acetate can be changed by changing : [NSEC-2007]
 (A) the temperature (B) the volume of solution
 (C) the concentration (D) the pressure on solution
50. The pH of 0.1 M NH_4OH ($K_b = 1.8 \times 10^{-5}$) is : [NSEC-2008]
 (A) 1 (B) 13 (C) 5.7 (D) 11.1
51. The pH of mixture of 100 mL of 0.25 N HCl and 100 mL of 0.125 N NaOH is : [NSEC-2008]
 (A) 1.20 (B) 0.90 (C) 0.70 (D) 0.42
52. CaF_2 (Mol. Wt. = 78) has a solubility of 1.6×10^{-2} g/dm³ at 293 K. The solubility product of CaF_2 is : [NSEC-2008]
 (A) 3.45×10^{-11} (B) 4.20×10^{-8} (C) 2.56×10^{-4} (D) 4.69×10^{-9}
53. Which of these mixtures constitute buffer solutions ? [NSEC-2008]
Mixture 1 : 25 mL of 0.10 M HNO_3 and 25 mL of 0.10 M $NaNO_3$
Mixture 2 : 25 mL of 0.10 M $HC_2H_3O_2$ and 25 mL of 0.10 M NaOH
 (A) 1 only (B) 2 only (C) both 1 and 2 (D) neither 1 nor 2
54. A 0.200 g sample of benzoic acid, C_6H_5COOH , is titrated with a 0.120 M $Ba(OH)_2$ solution. What volume of the $Ba(OH)_2$ solution is required to reach the equivalence point ? [NSEC-2008]
 $[C_6H_5COOH, \text{Molar Mass} = 122.1 \text{ g mol}^{-1}]$
 (A) 6.82 mL (B) 13.6 mL (C) 17.6 mL (D) 35.2 mL
55. The amount of sodium hydrogen carbonate, $NaHCO_3$, in an antacid tablet is to be determined by dissolving the tablet in water and then titrating the resulting solution with hydrochloric acid. Which indicator is the most appropriate for this titration ? [NSEC-2008]
- | Acid | K_a |
|-----------|----------------------|
| H_2CO_3 | 2.5×10^{-4} |
| HCO_3^- | 2.4×10^{-8} |
- (A) methyl orange, $pK_{in} = 3.7$ (B) bromothymol blue, $pK_{in} = 7.0$
 (C) phenolphthalein, $pK_{in} = 9.3$ (D) alizarin yellow, $pK_{in} = 12.5$
56. The hydrolysis constant of 0.5 M ammonium benzoate is 6.25×10^{-6} . The percentage hydrolysis of the salt is : [NSEC-2009]
 (A) 0.25 (B) 0.177 (C) 0.125 (D) 0.50
57. When CO_2 dissolves in water, the following equilibrium is established – [NSEC-2009]
 $CO_2 + 2H_2O \rightleftharpoons H_3O^+ + HCO_3^{1-}$
- If the equilibrium constant for the reaction is 3.8×10^{-7} and pH = 6, the ratio $\frac{[HCO_3^-]}{[CO_2]}$ will be:
 (A) 3.8×10^{-13} (B) 3.8×10^{-1} (C) 6.0 (D) 3.0
58. Carbonic acid, H_2CO_3 , is a diprotic acid for which $K_1 = 4.2 \times 10^{-7}$, and $K_2 = 4.7 \times 10^{-11}$. The solution which will have a pH closest to 9 is : [NSEC-2009]
 (A) 0.1 M H_2CO_3 (B) 0.1 M Na_2CO_3
 (C) 0.1 M $NaHCO_3$ (D) 0.1 M $NaHCO_3$ + 0.1 M Na_2CO_3
59. The strongest Bronsted base among the following compounds is – [NSEC-2009]
 (A) $NaCH_3$ (B) NaOH (C) NaF (D) $NaNH_2$
60. The ionization of benzoic acid is represented by the equation : [NSEC-2009]
 $C_6H_5COOH(aq) \rightleftharpoons H^+(aq) + C_6H_5COO^-(aq)$
 If a 0.045 M solution of benzoic acid has an $[H^+] = 1.7 \times 10^{-3}$ M, then, the K_a of benzoic acid is :
 (A) 7.7×10^{-5} (B) 6.4×10^{-5} (C) 3.8×10^{-2} (D) 8.4×10^{-1}
61. If the K_{sp} of CaF_2 at 25°C is 1.6×10^{-10} , then the number of moles of the salt must be dissolved in 2.0 L of water at 25°C to form a saturated solution is : [NSEC-2009]
 (A) 2.6×10^{-2} mol (B) 1.3×10^{-3} mol (C) 6.8×10^{-4} mol (D) 3.4×10^{-4} mol





62. A solution of 0.10 M NaZ has pH = 8.90. The K_a of HZ is : [NSEC-2010]
 (A) 1.6×10^{-4} (B) 1.6×10^{-5} (C) 6.3×10^{-10} (D) 6.3×10^{-11}
63. The pH of a solution made of mixing 200 mL of 0.0657 M NaOH, 140 mL of 0.107 M HCl and 150 mL of water would be : [NSEC-2010]
 (A) 3.04 (B) 2.43 (C) 2.74 (D) 2.27
64. The molarity of NH_3 solution of pH 12.0 at 25°C is (K_b of NH_3 at 25°C is 1.8×10^{-5}) [NSEC-2010]
 (A) 0.55 M (B) 5.5 M (C) 0.01 M (D) 11.7 M
65. A weak acid HA has $K_a = 1.00 \times 10^{-5}$ at 25°C . If 0.100 mole of this acid are dissolved in 1 L water, the percentage of the acid dissociated at equilibrium will be closest to : [NSEC-2010]
 (A) 0.100% (B) 99.0% (C) 1.00% (D) 99.9%
66. The solubility of a salt MX is $3.60 \times 10^{-5} \text{ mol dm}^{-3}$. The K_{sp} MX is: [NSEC-2010]
 (A) 3.60×10^{-5} (B) 12.96×10^{-10} (C) 7.20×10^{-5} (D) 1.80×10^{-10}
67. The following curve represents the titration of : [NSEC-2010]
 (A) a diprotic acid
 (B) two monoprotic acids with the same K_a , but different concentrations
 (C) two monoprotic acids with the different K_a , but the same concentration
 (D) two monoprotic acids with the different K_a , and different concentrations
- 
68. The solubility of calcium phosphate is $S \text{ moldm}^{-3}$. Hence, the solubility product is : [NSEC-2011]
 (A) S^5 (B) $27S^3$ (C) $54S^4$ (D) $108S^5$
69. 0.1 dm^3 of 0.1 M acetic acid is titrated against 0.1 M NaOH. When 50 cm^3 of 0.1 M NaOH are added, the pH of the solution will be : ($\text{p}K_a = 4.74$) [NSEC-2011]
 (A) 2.37 (B) 4.74 (C) 1.34 (D) 5.74
70. A 0.056 M solution of benzoic acid, $\text{C}_6\text{H}_5\text{COOH}$, is titrated with a strong base. $[\text{H}^+]$ of the solution when half of the solution is titrated before the equivalence point is : (K_a of benzoic acid = 6.3×10^{-5})
 (A) $6.3 \times 10^{-5} \text{ M}$ (B) $1.8 \times 10^{-3} \text{ M}$ (C) $7.9 \times 10^{-3} \text{ M}$ (D) $2.6 \times 10^{-2} \text{ M}$
71. The following titration curve represents the titration of a _____ acid with a _____ base. [NSEC-2011]
 (A) strong, strong
 (B) weak, strong
 (C) strong, weak
 (D) weak, weak
- 
72. Hypochlorous acid ionizes as
 $\text{HOCl(aq)} \rightleftharpoons \text{H}^+(\text{aq}) + \text{OCl}^-(\text{aq})$, $\text{OCl}^-(\text{aq}) + \text{H}_2\text{O(l)} \rightleftharpoons \text{HOCl(aq)} + \text{OH}^-(\text{aq})$
 K_a for this reaction at 25°C is 3.0×10^{-8} ($K_w = 1.0 \times 10^{-14}$ at 25°C)
 Hence, K_b for OCl^- is : [NSEC-2011]
 (A) 3.3×10^{-7} (B) 3.0×10^{-8} (C) 3.0×10^6 (D) 3.3×10^7
73. When equal volumes of the following solutions are mixed, precipitation of AgCl ($K_{sp} = 1.8 \times 10^{-10}$) will occur only with : [NSEC-2012]
 (A) 10^{-4} M Ag^+ and 10^{-4} M Cl^- (B) 10^{-5} M Ag^+ and 10^{-5} M Cl^-
 (C) 10^{-6} M Ag^+ and 10^{-6} M Cl^- (D) 10^{-10} M Ag^+ and 10^{-10} M Cl^-



74. Equal volumes of two solutions of pH = 2 and pH = 4 are mixed together. The pH of the resulting solution will be : **[NSEC-2012]**
 (A) 2.0 (B) 3.1 (C) 4.2 (D) 2.3
75. The solubility of SrF_2 in water at 303 K is $9.55 \times 10^{-5} \text{ mol dm}^{-3}$. The solubility product of the salt is : **[NSEC-2012]**
 (A) 8.7×10^{-17} (B) 9.1×10^{-11} (C) 9.55×10^{-5} (D) 3.48×10^{-12}
76. The pKa value of picric acid, acetic acid and phenol are in the order : **[NSEC-2012]**
 (A) Picric acid 0.4, acetic acid 4.75, phenol 10.0
 (B) Acetic acid 0.4, picric acid 4.75, phenol 10.0
 (C) picric acid 0.4, phenol 4.75, acetic acid 10.0
 (D) phenol 0.4, acetic acid 4.75, picric acid 10.0
77. If each of the following salts has solubility product $K_{sp} = 1 \times 10^{-9}$, which of them is least soluble in water? **[NSEC-2013]**
 (A) XY (B) X_2Y (C) XY_2 (D) X_3Y
78. Which of the following salts produces the most basic solution ? **[NSEC-2013]**
 (A) $\text{Al}(\text{CN})_3$ (B) $\text{KC}_2\text{H}_3\text{O}_2$ (C) FeCl_3 (D) KCl
79. The pH of 0.1 M NH_4OH , ($K_b = 1.8 \times 10^{-5}$, $K_w = 10^{-14}$), is : **[NSEC-2013]**
 (A) 1.0 (B) 5.7 (C) 11.1 (D) 13.0
80. Which solution has the highest pH ? **[NSEC-2013]**
 (A) 0.01 M CaCl_2 (B) 0.01 M KNO_2 (C) 0.01 M CH_3COOH (D) 0.01 M CH_3COCH_3
81. pH of a saturated solution of magnesium hydroxide in water at 298 K is 10.5. The solubility of the hydroxide in water at 298 K is **[NSEC-2014]**
 (A) $1.58 \times 10^{-4} \text{ mol L}^{-1}$ (B) $1.58 \times 10^{-11} \text{ mol L}^{-1}$ (C) $3.16 \times 10^{-4} \text{ mol L}^{-1}$ (D) $9.98 \times 10^{-8} \text{ mol L}^{-1}$
82. Solubility product of silver chloride and silver thiocyanate are 1.2×10^{-10} and 7.1×10^{-13} respectively. The equilibrium constant for the reaction $\text{AgCl(s)} + \text{CNS}^{-1}(\text{aq}) \rightleftharpoons \text{AgCNS(s)} + \text{Cl}^{-1}(\text{aq})$ is **[NSEC-2014]**
 (A) 0.0625 (B) 169 (C) 13 (D) 1.40×10^{-4}
83. If a weak base has the dissociation constant, K_b , then the value of the dissociation constant, K_a , of its conjugate acid is given by **[NSEC-2014]**
 (A) $1/K_b$ (B) K_w/K_b (C) K_b/K_w (D) $K_w K_b$
84. When 1L of 0.1 M sulphuric acid solution is allowed to react with 1L of 0.1 M sodium hydroxide solution, the amount of sodium sulphate (anhydrous) that can be obtained from the solution formed and the concentration of H^+ in the solution respectively are **[NSEC-2015]**
 (A) 3.55 g, 0.1 M (B) 7.10 g, 0.025M (C) 3.55g, 0.025M. (D) 7.10g, 0.05 M
85. A water sample from a municipal water supply was found to have a pH = 7.0. On evaporating 2 L of this water, 2.016 g of white solid was left behind in the evaporation vessel, i.e., the total dissolved solid (TDS) content of this water was 1008 mg L^{-1} . However, addition of soap to a bucket of this water did not produce any visible scum. Based on these findings, one can conclude that **[NSEC-2015]**
 (A) There are no Ca^{2+} or Mg^{2+} ion in the water
 (B) There are no CO_3^{2-} or HCO_3^{-} ion in the water
 (C) concentration of any ion in the water is lower than 0.038M
 (D) water may be containing Na^+ ions in concentration $> 0.04\text{M}$
86. A 50 mL solution of pH = 1 is mixed with a 50 mL solution of pH = 2. The pH of the mixture is : **[NSEC-2015]**
 (A) 0.86 (B) 1.26 (C) 1.76 (D) 2.26
87. The solubility products (K_{sp}) of three salts MX , MY_2 and MZ_3 are 1×10^{-8} , 4×10^{-9} and 27×10^{-8} , respectively. The correct order for solubilities of these salts is **[NSEC-2015]**
 (A) $\text{Mx} > \text{MY}_2 > \text{MZ}_3$ (B) $\text{MZ}_3 > \text{MY}_2 > \text{MX}$ (C) $\text{MZ}_3 > \text{MX} > \text{MY}_2$ (D) $\text{MY}_2 > \text{MX} > \text{MZ}_3$

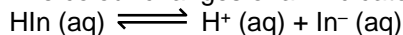




88. If the solubility product of iron(III) hydroxide is 1.8×10^{-37} , the pH of a saturated solution of iron(III) hydroxide in distilled water is close to : [NSEC-2016]
 (A) 4 (B) 5 (C) 7 (D) 9

89. The pH of a $1.0 \times 10^{-3} \text{ mol L}^{-1}$ solution of weak acid HA is 3.60. The dissociation constant of the acid is: [NSEC-2016]
 (A) 8.4×10^{-8} (B) 8.4×10^{-6} (C) 8.4×10^{-5} (D) 8.4×10^{-2}

90. The colour changes of an indicator HIn in acid base titrations is given below



Colour X

Colour Y

Which of the following statements is correct?

[NSEC-2017]

- (A) In a strong alkaline solution colour Y will be observed
 (B) In a strong acidic solution colour Y will be observed
 (C) Concentration of In^- is higher than that of HIn at the equivalence point
 (D) In a strong alkaline solution colour X is observed

91. The table below gives the results of three titrations carried out with 0.200 M HCl to determine the molarity of a given NaOH solution using phenolphthalein as indicator. NaOH was taken in the burette and HCl was taken in a conical flask for the titrations [NSEC-2017]

Titration No.	V _{HCl} (mL)	V _{NaOH} (mL)	M _{NaOH} mol dm ⁻³
I	21.4	19.3	0.222
II	18.6	16.8	0.221
III	22.2	21.1	0.210

The actual molarity of the prepared NaOH solution was $0.220 \text{ mol dm}^{-3}$. Which among the following could be the reason for the wrong value obtained in titration III?

- (A) Number of drops of phenolphthalein added to the titration flask was more in this titration
 (B) The concentration of HCl was wrongly used as 0.250 M for the calculation of M_{NaOH}
 (C) A few drops of NaOH solution were spilled outside the titration flask during titration
 (D) A few drops of the neutralized solution from titration II were left behind in the flask

92. The solution with pH value close to 1 is [NSEC-2017]

- (A) 10 mL, 0.1 M HCl + 90 mL, 0.1 M NaOH (B) 55 mL, 0.1 M HCl + 45 mL, 0.1 M NaOH
 (C) 75 mL, 0.2 M HCl + 25 mL, 0.2 M NaOH (D) 75 mL, 0.2 M HCl + 25 mL, 0.1 M NaOH

93. Which of the following is not a pair of a Lewis acid and a Lewis base ? [NSEC-2017]

- (A) H^+ , $(\text{C}_2\text{H}_5)_2\text{O}$ (B) H_2O , AlCl_3 (C) Fe^{3+} , CO (D) SiF_4 , BF_3

94. Which of the following statement/s is/are correct about weak acids in aqueous solutions? [NSEC-2017]

- I. When $\text{pH} = \text{pK}_a$ of a monoprotic acid, 50% of the acid is ionised
 II. If $\text{pH} = \text{pK}_{a2}$ of a diprotic acid, the average charge of all the ionised species is 0.5
 III. When $\text{pH} = \text{pK}_a + 1$, 10% of the acid is ionised
 IV. When $\text{pH} = 7$, 50% of a monibasic acid is ionized.

- (A) I and IV (B) I, II and IV (C) I, II and IV (D) I only

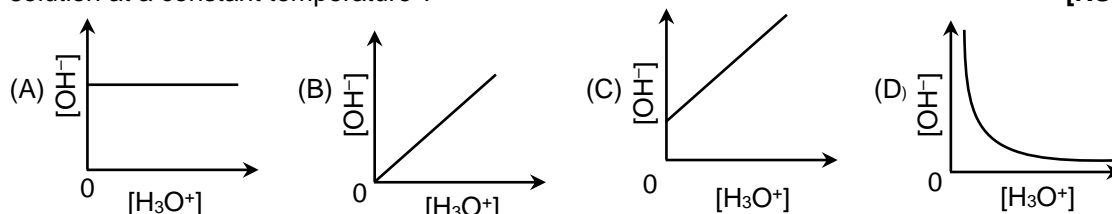
95. Solubility product of AgCl is 1.8×10^{-10} . The minimum volume (in L) of water required to dissolve 1 mg of AgCl is close to [NSEC-2018]

- (A) 0.5 (B) 7.5 (C) 50 (D) 0.75

96. If for an aqueous solution of a weak acid, $\text{pH} = \text{pK}_a + 2$ at 25°C , the approximate fraction of the acid in the dissociated form is [NSEC-2018]

- (A) 1.1 % (B) 0.99 % (C) 99.0 % (D) 9.9 %

97. Which of the following graphs describes the relationship between $[\text{H}_3\text{O}^+]$ and $[\text{OH}^-]$ in an aqueous solution at a constant temperature ? [NSEC-2018]





PART - III : HIGH LEVEL PROBLEMS (HLP)

THEORY

Levelling / Differentiating Effect of Solvent :

A solvent is said to be showing levelling effect if various electrolytes (generally acids and bases) get completely dissociated in it and thus have the same strength. For example, in water solvent, all strong acids (HClO_4 , H_2SO_4 , HI , HBr and HCl) are completely dissociated and are said to have the same strength. Similarly, all strong bases (CsOH , RbOH , KOH , NaOH and Ba(OH)_2) are also completely dissociated in water solvent. So, their relative strengths cannot be compared in water solvent.

However, a solvent is said to be showing differentiating effect if various acids and bases dissociate to different degrees in it and thus their relative strengths can be compared. For example, in water solvent, weak acids (like CH_3COOH , HCOOH etc.) dissociate to different extents and on comparing their degree of dissociation, their relative strengths can be compared. Same is the case with weak bases (like $\text{NH}_3 \cdot \text{H}_2\text{O}$, Aniline etc.). So, it can be concluded that water in general behaves as a levelling solvent for strong acids as well as strong bases, but it behaves as a differentiating solvent for weak acids as well as weak bases.

Considering other solvents, in glacial acetic acid solvent, strong acids dissociate to different degrees. So, strengths of strong acids can be compared in this solvent and in general, it behaves as differentiating solvent for strong acids. However, due to acidic nature of solvent, weak bases dissociate completely in it. So, in general, it behaves as a levelling solvent for weak bases.

Similarly, behaviour of ammonia solvent (basic in nature) can be thought of.

Note : In anhydrous HF solvent, only HClO_4 behaves like an acid because HF does not have a tendency to accept H^+ from other acids and form an unstable species H_2F^+ (positive charge on most electronegative atom F). So, rest all acids behave as bases in HF solvent.

INDICATORS :

Indicators are the substances, which indicate the end-point of a titration generally by changing their colour.

They are, in general, either weak organic acids or weak organic bases, having characteristically different colours in the ionised and unionised forms. For example, methyl orange is a weak base (having red colour in ionised form and yellow colour in the unionised form) and phenolphthalein is a weak acid (having pink colour in the ionized form while its unionised form is colourless)

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



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

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

Taking negative logarithm of both sides,

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

$$\therefore \text{pH} = \text{p}K_{\text{In}} + \log \frac{[\text{In}^-]}{[\text{HIn}]} \quad \Rightarrow \quad \text{pH} = \text{p}K_{\text{In}} + \log \frac{[\text{Ionised form}]}{[\text{Unionised form}]}$$

In general, the intensity of a coloured solution depends on the concentration of the colour imparting species. If the solution contains two coloured species, then the colour of the solution depends on the relative concentration of the colour imparting species. When the solution contains two coloured species as HIn and In^- , then it is a medical fact that the solution acquires a distinct colour of In^- for visibility by human eyes only when the concentration of In^- is approximately atleast 10 times greater than the concentration of HIn and vice versa. Actually, this numerical factor has different value for different colours, but if not specified, we take this factor as 10 in general.



Let us consider two cases :

Case-I : For the solution to show colour due to In^- , the minimum ratio $\frac{[\text{In}^-]}{[\text{HIn}]}$ should be 10.

$$\therefore \text{pH} = \text{pK}_{\text{In}} + \log 10 = \text{pK}_{\text{In}} + 1$$

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

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

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

Case – II : For the solution to show colour due to HIn , the minimum ratio of $\frac{[\text{In}^-]}{[\text{HIn}]}$ should be $\frac{1}{10}$.

$$\therefore \text{pH} = \text{pK}_{\text{In}} + \log \frac{1}{10} = \text{pK}_{\text{In}} - 1.$$

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

$$\frac{[\text{In}^-]}{[\text{In}^-] + [\text{HIn}]} \times 100 = \frac{1}{10 + 1} \times 100 \approx 9\%$$

Thus, nearly 9% of the indicator has been present in the ionised form (In^-) and $\approx 91\%$ of the indicator is present in the unionized form (HIn). In fact, $\text{pH} = \text{pK}_{\text{In}} - 1$ is the maximum pH upto which the solution has a distinct colour characteristic of HIn . At pH smaller than this value, some more indicator will be present in the unionised form. Thus, at $\text{pH} \leq \text{pK}_{\text{In}} - 1$, the solution has a colour characteristic of HIn .

\therefore General pH range of an indicator : $\text{pK}_{\text{In}} - 1$ to $\text{pK}_{\text{In}} + 1$.

SIGNIFICANCE OF INDICATORS :

Indicators work in specific pH range i.e. they change their colour distinctly once a specific pH range is crossed. For example, phenolphthalein works in pH range 8.3–10 while methyl orange in the range 3.1 to 4.4. Range of some common indicators is given below :

Table-1

Indicator	pH range	Colour	
		If $\text{pH}_{\text{solution}} < \text{Minimum value of pH range}$	If $\text{pH}_{\text{solution}} > \text{Maximum value of pH range}$
Methyl orange	3.1 – 4.4	Red	Yellow
Methyl red	4.2 – 6.3	Red	Yellow
Litmus	5.0 – 8.0	Red	Blue
Phenol red	6.4 – 8.2	Yellow	Red
Phenolphthalein	8.3 – 10.0	Colourless	Pink



Extent of reaction of different bases with acid (HCl) using two indicators Phenolphthalein & Methyl orange is summarised below :

	Phenolphthalein	Methyl Orange
NaOH	100% reaction is indicated	100% reaction is indicated
	$\text{NaOH} + \text{HCl} \rightarrow \text{NaCl} + \text{H}_2\text{O}$	$\text{NaOH} + \text{HCl} \rightarrow \text{NaCl} + \text{H}_2\text{O}$
Na_2CO_3	50% reaction upto NaHCO_3 stage is indicated	100% reaction is indicated
	$\text{Na}_2\text{CO}_3 + \text{HCl} \rightarrow \text{NaHCO}_3 + \text{NaCl}$	$\text{Na}_2\text{CO}_3 + 2\text{HCl} \rightarrow 2\text{NaCl} + \text{H}_2\text{O} + \text{CO}_2$
NaHCO_3	No reaction is indicated	100% reaction is indicated
		$\text{NaHCO}_3 + \text{HCl} \rightarrow \text{NaCl} + \text{H}_2\text{O} + \text{CO}_2$





Solved Examples

Ex-1. pH of 0.1 M solution of NaA (sodium salt of a weak acid HA) is 8.92. Calculate pK_a of HA. If a drop of HPh ($pK_{In} = 9.52$) be added to the above solution, predict whether the pink colour will be visible or not, under the medical fact that our eyes can see the pink color if the mole % of ionised form of indicator is 25% or more.

Sol.
$$pH = \frac{1}{2} (pK_a + pK_w + \log c)$$

$$8.92 = 7 + \frac{1}{2} pK_a + \frac{1}{2} (-1)$$

$$\frac{1}{2} pK_a = 8.92 - 6.5 = 2.42$$

$\therefore pK_a \text{ of HA} = 4.84$

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

$$8.92 = 9.52 + \log \frac{[In^-]}{[HIn]}$$

$$\frac{[In^-]}{[HIn]} = \frac{\text{ionised}}{\text{unionised}} = \frac{1}{4}$$

Since ionised form % = $\frac{1}{1+4} \times 100 = 20\%$, pink colour will not be visible.

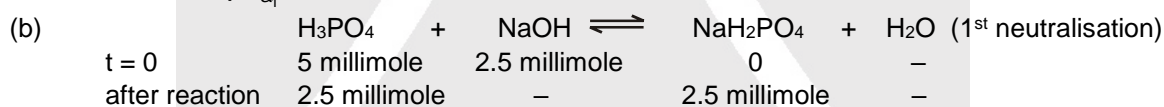
Titration of Poly protic acid with SB :

Ex. 50 mL of 0.1 M H_3PO_4 with 0.1 M NaOH. For plotting curve, calculate pH when volume of NaOH added is :

- (a) 0 mL (b) 25 mL (c) 50 mL (d) 75 mL (e) 100 mL
(f) 125 mL (g) 150 mL (h) 200 mL (i) 90 mL

For H_3PO_4 : $pK_{a_1} = 3$; $pK_{a_2} = 7$; $pK_{a_3} = 11$

(a) $pH = 1/2 (pK_{a_1} - \log C) = 1/2 (3 + 1) = 2$



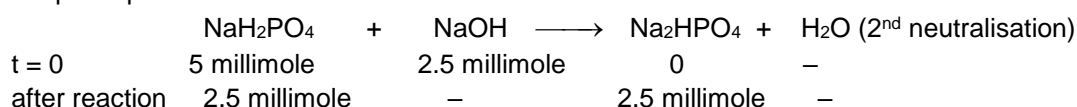
Buffer with equal amounts of H_3PO_4 & $H_2PO_4^- \Rightarrow$ Half equivalence point with respect to 1st neutralisation.

$$pH = pK_{a_1} = 3$$

(c) Solution of $H_2PO_4^-$ (amphiprotic species) will be obtained as amount of NaOH added is just sufficient to complete 1st neutralisation of H_3PO_4 .

$$pH = \frac{pK_{a_1} + pK_{a_2}}{2} = \frac{3+7}{2} = 5 \text{ (1st eq pt)}$$

(d) 50 ml NaOH solution will be consumed in 1st neutralisation & remaining 25 mL (2.5 millimole) will participate in 2nd neutralisation.



Buffer with equal amounts of $H_2PO_4^-$ & $HPO_4^{2-} \Rightarrow$ Half equivalence point with respect to 2nd neutralisation.

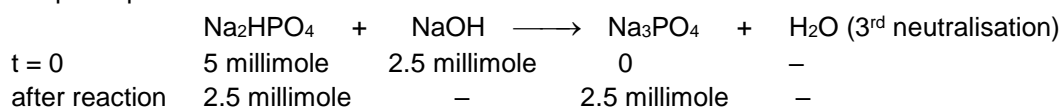
$$pH = pK_{a_2} = 7$$

(e) Solution of HPO_4^{2-} solution (amphiprotic species) will be obtained as amount of NaOH added is just sufficient to complete 2nd neutralisation of H_3PO_4 .



$$\text{pH} = \frac{\text{pK}_{a_2} + \text{pK}_{a_3}}{2} = 9 \text{ (2nd eq pt)}$$

- (f) 100 mL NaOH solution will be consumed in 2 neutralisations & remaining 25 mL (2.5 millimole) will participate in 3rd neutralisation.



Buffer with equal amounts of HPO_4^{2-} & $\text{PO}_4^{3-} \Rightarrow$ Half equivalence point with respect to 3rd neutralisation.

$$\text{pH} = \text{pK}_{a_3} = 11$$

- (g) Solution of PO_4^{3-} will be obtained as amount of NaOH added is just sufficient to complete 3rd neutralisation of H_3PO_4 .

$$[\text{Na}_3\text{PO}_4] = \frac{\text{Millimole}}{\text{Total volume in mL}} = 5/200 = 1/40 \text{ M}$$

Assuming h to be negligible

$$h = \sqrt{\frac{K_w/K_{a_3}}{C}} = \sqrt{\frac{10^{-14}/10^{-11}}{1/40}} = 0.2 \text{ (not negligible)}$$

$$\therefore \frac{1}{40} = \frac{h^2}{1-h} = \frac{10^{-14}}{10^{-11}}$$

On solving this quadratic, $h = 0.18$

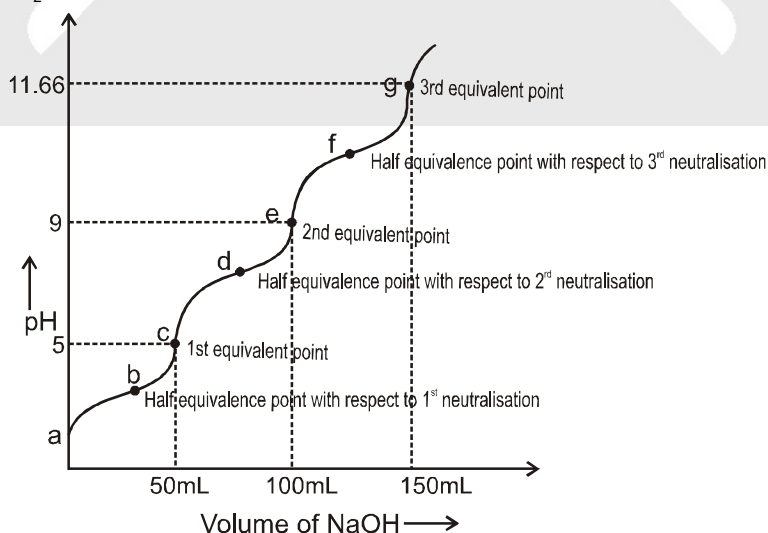
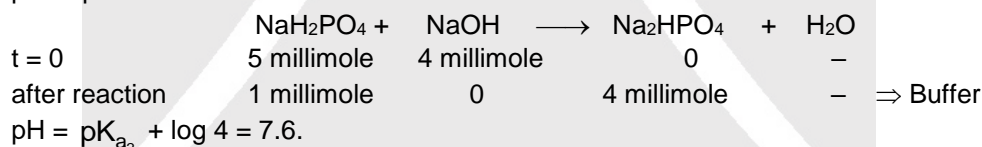
$$\therefore [\text{OH}^-] = ch = 4.5 \times 10^{-3} \text{ M}$$

$$\therefore \text{pH} = 11.66$$

- (h) 150 mL NaOH will be consumed in three neutralisations & 50 mL will be left unreacted. Also, hydrolysis of Na_3PO_4 can be neglected in presence of NaOH left.

$$[\text{OH}^-] = \frac{\text{Millimole}}{\text{Total volume in mL}} = 5/250 = 1/50 \text{ M} \quad \therefore \text{pOH} = 1.7 \text{ \& } \text{pH} = 12.3$$

- (i) 50 mL NaOH will be consumed in 1st neutralisation & remaining 40 mL (4 millimole) will participate in 2nd neutralisation





Solved Examples

Ex-2. Find the pH at equivalence point when a solution of 0.1 M acetic acid is titrated with a solution of 0.3 M NaOH. K_a for acetic acid = 7.5×10^{-6} .

Sol. At equivalence point CH_3COONa will be formed.

$$M_{\text{base}} V_{\text{base}} = M_{\text{acid}} V_{\text{acid}} \Rightarrow V_{\text{acid}} = \frac{0.3}{0.1} V_{\text{base}} = 3 V_{\text{base}}$$

$$[\text{CH}_3\text{COONa}]_{\text{Equivalence point}} = \frac{\text{Total moles}}{\text{Total volume}} = \frac{0.3 \times V_{\text{base}}}{V_{\text{acid}} + V_{\text{base}}} = \frac{0.3}{4} \frac{V_{\text{base}}}{V_{\text{base}}} = 0.075$$

$$[\text{OH}^-] = \sqrt{\frac{K_w}{K_a} \times C} = \sqrt{\frac{10^{-14}}{7.5 \times 10^{-6}} \times 0.075} = 10^{-5} \Rightarrow \text{pOH} = 5$$

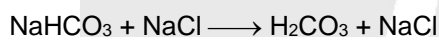
$$\therefore \text{pH} = 9$$

Ex-3. Predict titration curve for titration of Na_2CO_3 & HCl .

Sol. $\text{Na}_2\text{CO}_3 + \text{HCl} \longrightarrow \text{NaHCO}_3 + \text{NaCl}$

pH_1 = Half equivalence point with respect to 1st neutralisation = pK_{a_2} (\because solution will be a buffer consisting of equal amount of CO_3^{2-} & HCO_3^-)

$$\text{pH}_{1^{\text{st eq pt}}} = \frac{\text{pK}_{a_1} + \text{pK}_{a_2}}{2} (\because \text{amphiprotic anion})$$



pH_2 = Half equivalence point with respect to 2nd neutralisation = pK_{a_1} (\because solution will be a buffer consisting of equal amount of HCO_3^- & H_2CO_3)

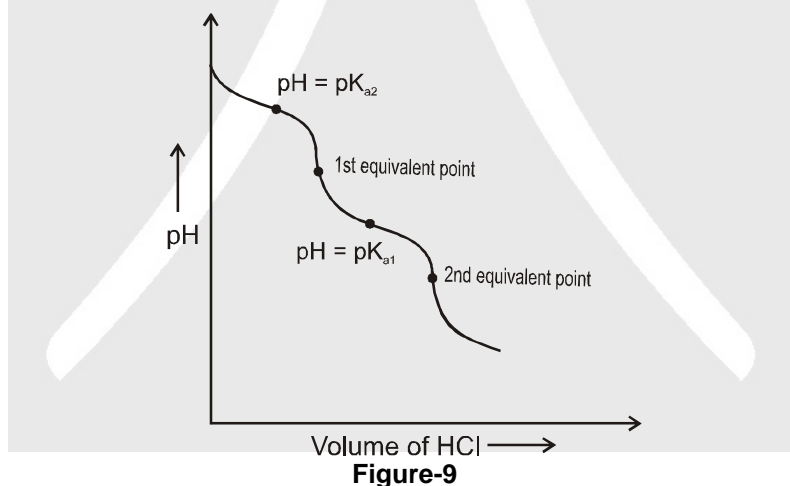


Figure-9

$$\text{pH}_{2^{\text{nd eq pt}}} = 1/2 (\text{pK}_{a_1} - \log C) (\because \text{weak acid})$$

Ionic Equilibrium-III

SOLUBILITY(s) AND SOLUBILITY PRODUCT (K_{sp})

Some complicated cases for solubility of sparingly soluble salts could be as follows :

(A) **Effect on solubility because of complex formation**

○ When ions of a salt form complex in the solution, then concentration of that ion decreases, so solubility equilibrium is shifted forward & solubility increases.



Solved Examples

Ex-4. What must be the concentration of aqueous NH_3 which must be added to a solution containing $4 \times 10^{-3} \text{ M Ag}^+$ and 0.001 M NaCl , to prevent the precipitation of AgCl .

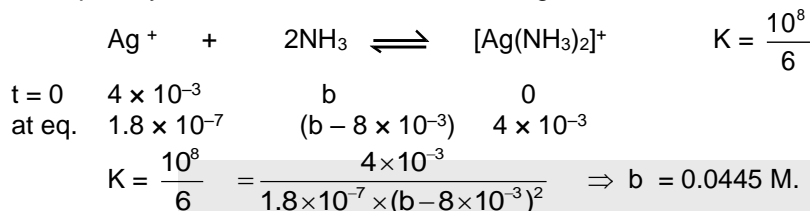
Given that $K_{\text{sp}}(\text{AgCl}) = 1.8 \times 10^{-10}$ and the formation constant of $[\text{Ag}(\text{NH}_3)_2]^+$ is $K_{\text{formation}} = \frac{10^8}{6}$.

Sol. Silver ion concentration which can be allowed to remain in the solution,

$$1.8 \times 10^{-10} = [\text{Ag}^+][\text{Cl}^-]$$

$$[\text{Ag}^+] = \frac{1.8 \times 10^{-10}}{0.001} = 1.8 \times 10^{-7} \text{ M},$$

This quantity is so small that almost all the Ag^+ ion will be consumed by NH_3 in complex formation.



(B) Solubility in appropriate buffer solutions

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

Solved Examples

Ex-5. The solubility of $\text{Pb}(\text{OH})_2$ in water is $6.7 \times 10^{-6} \text{ M}$. Calculate the solubility of $\text{Pb}(\text{OH})_2$ in a buffer solution of $\text{pH} = 8$. Take $(6.7)^3 = 301$

Sol. $K_{\text{sp}} = 4 \times (6.7 \times 10^{-6})^3 = 1.204 \times 10^{-15}$

$$s \times (10^{-6})^2 = 1.204 \times 10^{-15} \Rightarrow s = 1.204 \times 10^{-3} \text{ M}$$

Ex-6. Calculate solubility of MnS in a buffer solution of given pH. K_{sp} of MnS and K_{a_1} & K_{a_2} for H_2S are given.

Sol. Let the new solubility of $\text{MnS} = x$

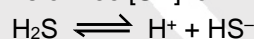
$\therefore [\text{Mn}^{2+}] = x = \text{Initial concentration of } \text{S}^{2-} \text{ ions, but free } \text{S}^{2-} \text{ ions will be less because some of the } \text{S}^{2-} \text{ ions will react with } \text{H}^+ \text{ from buffer to form } \text{HS}^- \text{ and } \text{H}_2\text{S}.$

$$[\text{Mn}^{2+}] = x = [\text{S}^{2-}] + [\text{HS}^-] + [\text{H}_2\text{S}] \quad \text{.....(1)}$$

Let us calculate the value of $[\text{HS}^-]$ & $[\text{H}_2\text{S}]$, in terms of free $[\text{S}^{2-}]$ ion. For that, consider :



$$K_2 = \frac{[\text{H}^+][\text{S}^{2-}]}{[\text{HS}^-]}$$



$$K_1 = \frac{[\text{H}^+][\text{HS}^-]}{[\text{H}_2\text{S}]}$$

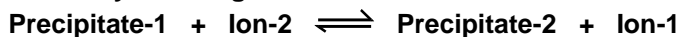
$$\therefore [\text{HS}^-] = \frac{[\text{H}^+][\text{S}^{2-}]}{K_2} \quad \text{....(2)}$$

$$\text{and } [\text{H}_2\text{S}] = \frac{[\text{H}^+][\text{HS}^-]}{K_1} = \frac{[\text{H}^+]^2[\text{S}^{2-}]}{K_1 K_2} \quad \text{....(3)}$$

Put (2) & (3) in (1)

$$x = [\text{S}^{2-}] \left(1 + \frac{[\text{H}^+]}{K_2} + \frac{[\text{H}^+]^2}{K_1 K_2} \right)$$

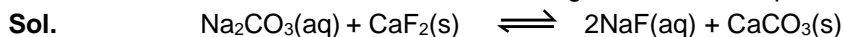
$$x = \frac{K_{\text{sp}}}{[\text{Mn}^{2+}]} \left(1 + \frac{[\text{H}^+]}{K_2} + \frac{[\text{H}^+]^2}{K_1 K_2} \right) \Rightarrow x = \sqrt{K_{\text{sp}} \left(1 + \frac{[\text{H}^+]}{K_2} + \frac{[\text{H}^+]^2}{K_1 K_2} \right)}$$

**(C) Solubility Exchange :**

One precipitate is mixed with solution of an ion to get another precipitate and another ion in solution.

Solved Examples

Ex-7. 2M solution of Na_2CO_3 is boiled in a closed container with excess of CaF_2 . Very little amount of CaCO_3 and NaF are formed. If the solubility product (K_{sp}) of CaCO_3 is x and molar solubility of CaF_2 is y , find the molar concentration of F^- in resulting solution after equilibrium is attained.



$$t = 0 \quad 2 \quad - \quad 0 \quad -$$

$$t = \text{eq} \quad 2 - a \quad - \quad 2a \quad -$$

where a is very small

For CaCO_3 , $K_{sp} = x = [\text{Ca}^{2+}][\text{CO}_3^{2-}] = [\text{Ca}^{2+}] \times 2$ ($\because \text{CO}_3^{2-}$ mainly coming from Na_2CO_3)

$$\therefore [\text{Ca}^{2+}] = \frac{x}{2}$$

$$\text{For } \text{CaF}_2, K_{sp} = 4y^3 = \left(\frac{x}{2}\right) [\text{F}^-]^2 \Rightarrow [\text{F}^-] = \sqrt{\frac{8y^3}{x}}$$

(D) Solubility related to H_2S

The sulphide ion concentration in a solution that has been saturated with H_2S is given by :

$$[\text{S}^{2-}] = \frac{K_{a1}K_{a2}[\text{H}_2\text{S}]}{[\text{H}^+]^2} = \frac{K_{sp(\text{H}_2\text{S})}}{[\text{H}^+]^2}$$

Solved Examples

Ex-8. What $[\text{H}_3\text{O}^+]$ 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 0.01 M ?

(K_{sp} of $\text{H}_2\text{S} = 1.1 \times 10^{-22}$; K_{sp} of $\text{ZnS} = 1.0 \times 10^{-21}$; $\sqrt{11} = 3.3$)

Sol. For ZnS not to be precipitated from a solution of Zn^{2+} and Pb^{2+} , $IP_{\text{ZnS}} < K_{sp}(\text{ZnS})$

$$[\text{Zn}^{2+}][\text{S}^{2-}] < K_{sp} \text{ of } \text{ZnS}$$

$$[10^{-2}][\text{S}^{2-}] < 1.0 \times 10^{-21} \therefore [\text{S}^{2-}] < 10^{-19} \text{ M}$$

So, at $[\text{S}^{2-}] = 10^{-19} \text{ M}$ or less, no precipitation of ZnS will occur.



$$\therefore [\text{H}^+]^2 [\text{S}^{2-}] = K_{sp(\text{H}_2\text{S})} = 1.1 \times 10^{-22} \quad \therefore [\text{H}^+]_{\min}^2 [10^{-19}] = 1.1 \times 10^{-22}$$

$$[\text{H}^+]_{\min}^2 = 11 \times 10^{-4}$$

$$\therefore [\text{H}^+]_{\min} = 3.3 \times 10^{-2} \text{ M}$$

Thus, if $[\text{H}^+] = 3.3 \times 10^{-2} \text{ M}$ or more, the precipitation of ZnS will not take place and only PbS will precipitate.

SUBJECTIVE QUESTIONS

- (a) For which of the following, water would behave as a levelling solvent and for which, it would behave as a differentiating solvent ?
Strong acids, weak acids, strong bases, weak bases.

(b) For which of the following, glacial acetic acid would behave as a levelling solvent and for which, it would behave as a differentiating solvent ?
Strong acids, weak acids, strong bases, weak bases.

(c) For which of the following, liquid ammonia would behave as a levelling solvent and for which, it would behave as a differentiating solvent ?
Strong acids, weak acids, strong bases, weak bases.
- Calculate pOH , $[\text{CH}_3\text{NH}_3^+]$, $[\text{C}_4\text{H}_{13}\text{N}_2^+]$ & $[\text{C}_4\text{H}_{14}\text{N}_2^{2+}]$ in an aqueous solution consisting of 0.2 M Methyl amine ($K_b = 4.1 \times 10^{-4}$) & 0.1 M Butane-1, 4-diamine ($K_{b1} = 6.2 \times 10^{-4} \text{ M}$; $K_{b2} = 2.25 \times 10^{-5}$).





3. Upon adding 50 mL of 0.2 M KOH solution to 50 mL of 0.5 M solution of Ethylene diamine ($K_{b1} = 8 \times 10^{-5}$; $K_{b2} = 2.7 \times 10^{-8}$), calculate pH of final solution and $[C_2N_2H_{10}^{2+}]$ in resulting solution.
4. Determine the pH of 0.5 M BH_2Cl_2 solution (salt of a diacidic base B). Also calculate $[BH^+]$ & $[B]$. Given : K_{b1} & K_{b2} for B are 10^{-6} & 2×10^{-10}
5. Prove that buffer capacity of 0.2 M CH_3COOH –0.2M CH_3COONa buffer is less than the 0.4 M CH_3COOH –0.4 M CH_3COONa .
6. A small quantity of phenolphthalein (an acid indicator) is added to a decimolar solution of Sodium butyrate. Calculate the ratio of the coloured to the colourless form of the indicator. K_a for butyric acid 1.5×10^{-5} , K for the indicator $= 3.075 \times 10^{-10}$ and $K_w = 10^{-14}$. Take $\log 1.23 = 0.09$
7. At pH = 2, half of the indicator, thymol blue (an acid type indicator) is in unionised form. Find the % of indicator in unionised form in the solution with $[H^+] = 4 \times 10^{-3}$ M.
8. A base type indicator B differs in colour from its conjugate acid (BH^+). Acidic form is red in colour while basic form is blue in colour. Human eye can sense blue colour distinctly when ratio of blue form concentration to red form concentration is $\frac{a}{b}$ or more. However, red colour can be sensed by human eye distinctly when ratio of red form concentration to blue form concentration is $\frac{c}{d}$ or more. Determine the pH range of solution in which human eyes will be unable to observe distinct red or distinct blue colour. Take ionisation constant of B as K_{eq} .
9. Determine the maximum number of moles of MgF_2 that can dissolve in 1000 L of a buffer solution of pH = 4. Given : K_{sp} of $MgF_2 = \frac{9}{14} \times 10^{-8}$ and K_a of HF $= 3.5 \times 10^{-4}$. Take $(2.17)^3 = 10$.
- 10(a). Determine the concentration of NH_3 solution whose 1 L can dissolve 0.1 mole $CuCO_3$.
Given : K_{sp} of $CuCO_3 = 1.4 \times 10^{-10}$ and K_f of $[Cu(NH_3)_4]^{2+} = 2 \times 10^{13}$. Take $\sqrt[4]{\frac{1000}{2.8}} = 4.4$. Assume no other reaction to take place.
- 10(b). An aqueous solution of a metal bromide, MBr_2 (0.05 M) is saturated with H_2S . Calculate the minimum pH at which the metal sulphide will be precipitated. Concentration of H_2S in a saturated solution = 0.1M. [K_{a1} of $(H_2S) = 10^{-7}$, K_{a2} of $(HS^-) = 1.2 \times 10^{-13}$, K_{sp} for MS $= 6 \times 10^{-21}$]

ONLY ONE OPTION CORRECT TYPE

11. In the reaction : $Ni^{2+} + 6H_2O \rightarrow [Ni(H_2O)_6]^{2+}$,
(A) Ni^{2+} behaves like a Lewis acid. (B) H_2O behaves like a Lewis base.
(C) Above cannot be called an acid-base reaction. (D) Both (A) and (B).
12. In water, the bases NaOH, KOH, RbOH, CsOH and $Ba(OH)_2$ exhibit the same strength as they are completely ionised in water (an acid). This is called of the solvent water.
(A) Strength (B) Capacity (C) Buffer effect (D) Levelling effect
13. The ratio of dissociation constant of two weak acids HA and HB is 4:1. At what initial molar concentration ratio of two acid solution, the two will have same pH in separate solutions ? Assume negligible dissociation of both acids in their solutions.
(A) 2 : 1 (B) 1 : 2 (C) 4 : 1 (D) 1 : 4
14. For 10^{-4} M BOH (weak base ; $K_b = 5 \times 10^{-5}$) :
(A) $\alpha = 0.707$ (B) $[OH^-] = 5 \times 10^{-5}$ M (C) pH = 9.85 (D) All of these
15. In a 0.2 M aqueous solution of Ethylene diamine ($H_2NCH_2CH_2NH_2$) :
Given : $K_{b1} = 8 \times 10^{-5}$ & $K_{b2} = 2.7 \times 10^{-8}$
(A) $[OH^-] = 2 \times 10^{-2}$ M (B) $[C_2N_2H_{10}^{2+}] = 2.7 \times 10^{-8}$ M
(C) Both (A) and (B) (D) none of these



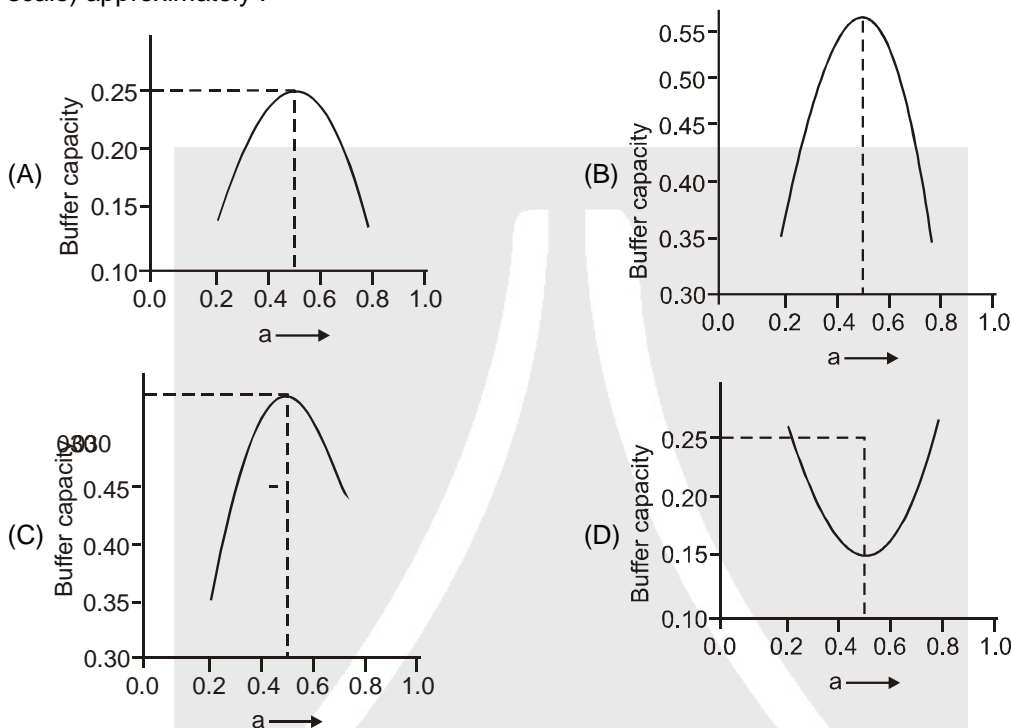
16. (a) In a solution containing 0.1 M HCl & 0.1 M H_3PO_4 (having dissociation constants K_{a_1} , K_{a_2} & K_{a_3}), assuming $\alpha \ll 1$ for H_3PO_4 :
- (A) $\text{pH} = 1$ (B) $\alpha_{\text{H}_3\text{PO}_4} = 10K_{a_1}$ (C) $[\text{HPO}_4^{2-}] = 10K_{a_1}K_{a_2}$ (D) All of these
16. (b) In above question
- (A) $[\text{PO}_4^{3-}] = 100K_{a_1}K_{a_2}K_{a_3}$ (B) $[\text{PO}_4^{3-}] = 10K_{a_1}K_{a_2}K_{a_3}$
 (C) $[\text{PO}_4^{3-}] = 1000K_{a_1}K_{a_2}K_{a_3}$ (D) $[\text{PO}_4^{3-}] = K_{a_1}K_{a_2}K_{a_3}$
17. A pair of salts are given in a solution each in 0.1M concentration. Which solution has highest pH ?
 Given : Order of acidic strength of acids is : $\text{HF} > \text{HOCl} > \text{HOBr} > \text{HCN}$
 (A) NaCN and NaOBr (B) NaF and NaOCl (C) NaF and NaOBr (D) NaCN and NaOCl
18. (a) For a c M K_3A (potassium salt of a tribasic acid H_3A) solution :
 (Dissociation constants of acid are K_{a_1} , K_{a_2} & K_{a_3} ; $h \ll 1$)
- (A) $\text{pH} = \frac{1}{2} (\text{p}K_w + \text{p}K_{a_3} + \log c)$ (B) $\text{pH} = \frac{1}{2} (\text{p}K_w + \text{p}K_{a_2} + \log c)$
 (C) $\text{pH} = \frac{1}{2} (\text{p}K_w + \text{p}K_{a_1} + \log c)$ (D) $\text{pH} = \frac{1}{2} (\text{p}K_w - \text{p}K_{a_3} - \log c)$
18. (b) In above solution,
- (A) $[\text{HA}^{2-}] = \sqrt{\frac{cK_w}{K_{a_3}}}$ (B) $[\text{H}_2\text{A}^-] = \frac{K_w}{K_{a_2}}$
 (C) $[\text{H}_3\text{A}] = \frac{K_w}{K_{a_1}K_{a_2}} \sqrt{\frac{K_wK_{a_3}}{c}}$ (D) All of these
19. Identify acids in the following reactions according to Bronsted - Lowry concept :
- (I) $[\text{Fe}(\text{H}_2\text{O})_5(\text{OH})]^{2+} (\text{aq.}) + [\text{Al}(\text{H}_2\text{O})_6]^{3+} (\text{aq.}) \longrightarrow [\text{Fe}(\text{H}_2\text{O})_6]^{3+} (\text{aq.}) + [\text{Al}(\text{H}_2\text{O})_5(\text{OH})]^{2+} (\text{aq.})$
 (II) $\text{O}^{2-} (\text{aq.}) + \text{H}_2\text{O} (\text{aq.}) \longrightarrow 2\text{OH}^- (\text{aq.})$
 (III) $\text{CH}_3\text{OH} (\text{aq.}) + \text{H}^+ (\text{aq.}) \longrightarrow \text{CH}_3\text{O}^- (\text{aq.}) + \text{H}_2 (\text{g})$
- (A) $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$, H_2O , H^+ (B) $[\text{Fe}(\text{H}_2\text{O})_5(\text{OH})]^{2+}$, H_2O , CH_3OH
 (C) $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$, H_2O , CH_3OH (D) $[\text{Fe}(\text{H}_2\text{O})_5(\text{OH})]^{2+}$, O^{2-} , H^+
20. In aqueous solution, boric acid H_3BO_3 is a :
 (A) Arrhenius acid (B) Bronsted acid (C) Lewis acid (D) Both (B) & (C)
21. pOH of a 0.004 M aqueous solution of a diacidic weak base B ($\text{p}K_{b1} = 3.7$ & $\text{p}K_{b2} = 7.3$) is :
 (A) 3.05 (B) 3.1 (C) 0.65 (D) 3.15
22. What concentration of OH^- ions will reduce NH_4^+ ion to 2×10^{-5} M in 0.4 M solution of NH_4OH ? K_b (NH_4OH) = 1.8×10^{-5}
 (A) 0.36 M (B) 0.036 M (C) 2×10^{-5} M (D) None of these
23. Calculate the pH of a 0.15 M aqueous solution of AlCl_3 .
 Given : $[\text{Al}(\text{H}_2\text{O})_6]^{3+} (\text{aq.}) + \text{H}_2\text{O} (\ell) \rightleftharpoons [\text{Al}(\text{H}_2\text{O})_5\text{OH}]^{2+} (\text{aq.}) + \text{H}_3\text{O}^+ (\text{aq.})$; $K_a = 1.5 \times 10^{-5}$
 (A) 2.82 (B) 5 (C) 9 (D) 11.18
24. Calculate $[\text{OH}^-]$ & $[\text{H}_2\text{C}_2\text{O}_4]$ in a 0.005 M $\text{Na}_2\text{C}_2\text{O}_4$ solution. Given : K_{a_1} & K_{a_2} for oxalic acid are 5.6×10^{-2} & 5.4×10^{-5} . Take $\sqrt{\frac{1}{108}} = 0.096$
- (A) $[\text{OH}^-] = 9.6 \times 10^{-7}$ M (B) $[\text{H}_2\text{C}_2\text{O}_4] = \frac{5}{28} \times 10^{-12}$ M
 (C) Both (A) & (B) (D) None of these



25. Species acting as both bronsted acid and base is :
 (A) HSO_4^- (B) Na_2CO_3 (C) NH_3 (D) OH^-
26. Which one of the following statements is not true ?
 (A) The conjugate base of H_2PO_4^- is HPO_4^{2-} .
 (B) $\text{pH} + \text{pOH} = 14$ for all aqueous solutions at 25°C .
 (C) The pH of 1×10^{-8} M HCl is 8.
 (D) 96, 500 coulombs of electricity when passed through a CuSO_4 solution deposits 1 gram equivalent of copper at the cathode.
27. When rain is accompanied by a thunderstorm, the collected rain water will have a pH value :
 (A) slightly lower than that of rain water without thunderstorm.
 (B) slightly higher than that when the thunderstorm is not there.
 (C) uninfluenced by occurrence of thunderstorm.
 (D) which depends on the amount of dust in air.
28. 100 mL of 0.05 M $\text{C}_3\text{N}_2\text{H}_{12}\text{SO}_4$ (salt of Propane-1,2-diamine & H_2SO_4) and some volume of 0.1 M $\text{C}_3\text{N}_2\text{H}_{11}\text{Cl}$ (salt of propane-1,2-diamine & HCl) are available. What volume (in mL) of 2nd salt solution should be taken to prepare a buffer solution of $\text{pH} = 6.31$? Given : pK_{b1} & pK_{b2} of propane-1, 2-diamine are 4.18 & 7.39 respectively.
 (A) 50 mL (B) 25 mL (C) 12.5 mL (D) 0.015 mL
29. Select the correct set of statements for an acid type indicator used in a titration :
 (i) In general, pH range of an indicator is $(\text{pK}_a - 1)$ to $(\text{pK}_a + 1)$ and indicator shows its characteristic colours in this range.
 (ii) In general, pH range of an indicator is $(\text{pK}_a - 1)$ to $(\text{pK}_a + 1)$ and indicator does not show its characteristic colours in this range.
 (iii) In the relation : $\text{pH} = \text{pK}_{\text{In}} + \log_{10} \frac{[\text{In}^-]}{[\text{HIn}]}$, pH value represents pH of indicator solution.
 (iv) In the relation : $\text{pH} = \text{pK}_{\text{In}} + \log_{10} \frac{[\text{In}^-]}{[\text{HIn}]}$, pH value represents pH of resulting solution containing indicator.
 (A) i & iii (B) ii & iv (C) ii & iii (D) i & iv
30. Methyl orange indicator (pH range = 3.1 – 4.4) cannot be used for end point detection of following titration(s) :
 (A) CH_3COOH vs NaOH (B) H_2O_2 vs KMnO_4 (in acidic medium)
 (C) Both (A) & (B) (D) None of these
31. A certain indicator (an organic dye) has $\text{pK}_a = 5$. For which of the following titrations may it be suitable ?
 (A) acetic acid against NaOH (B) aniline hydrochloride against NaOH
 (C) sodium carbonate against HCl (D) barium hydroxide against oxalic acid
32. The best indicator (with their pH range given) for the detection of end point in titration of a weak acid and a strong base is :
 (A) Methyl orange (3 to 4) (B) Methyl red (5 to 6)
 (C) Bromothymol blue (6 to 7.5) (D) Phenolphthalein (8 to 9.6)
33. At $\text{pH} < 3.1$, the indicator methyl red is coloured red, at $\text{pH} > 6.3$, it is yellow and at the intermediate values of the pH, it is orange. What will the colour of indicator be in a 0.1 M solution of NH_4Br ? Take $\text{pK}_b(\text{NH}_4\text{OH}) = 4.74$.
 (A) Red (B) Yellow
 (C) Orange (D) $\text{pH} = 3.1$ so colour cannot be predicted



34. What fraction of an indicator HIn is in basic form at a pH of 6 if the pK_a of the indicator is 5 ?
 (A) $\frac{9}{10}$ (B) $\frac{1}{11}$ (C) $\frac{10}{11}$ (D) $\frac{1}{10}$
35. 50 mL of 0.1 M NaOH is added to 60 mL of 0.15 M H_3PO_4 solution (K_1 , K_2 and K_3 for H_3PO_4 are 10^{-3} , 10^{-8} and 10^{-13} respectively). The pH of the mixture would be about :
 (A) 3.1 (B) 5.5 (C) 4.1 (D) 6.5
36. A buffer solution is prepared by mixing 'a' moles of CH_3COONa and 'b' moles of CH_3COOH such that **(a + b) = 1**, into water to make 1L buffer solution. If the instantaneous (differential) buffer capacity of this buffer solution is plotted against moles of salt CH_3COONa (a), then the plot obtained will be (to the scale) approximately :



37. An acid-base indicator which is a weak acid has a pK_{In} value = 5.45. At what concentration ratio of sodium acetate to acetic acid would the indicator show a colour half-way between those of its acid and conjugate base forms? [pK_a of acetic acid = 4.75]
 (A) 4 : 1 (B) 6 : 1 (C) 5 : 1 (D) 3 : 1
38. If the indicator is a weak acid with $K_{In} = 4 \times 10^{-4}$, for indication of equivalence point of which of the following neutralisation(s), would the indicator be useful ?
 (A) $HCl + NaOH$ (B) $HCl + NH_3$ (C) $NaOH + CH_3COOH$ (D) Both (A) and (B)
39. 50 mL of 0.05 M Na_2CO_3 is titrated against 0.1 M HCl. On adding 40 mL of HCl, pH of the solution will be : [Given : For H_2CO_3 , $pK_{a_1} = 6.35$, $pK_{a_2} = 10.33$]
 (A) 6.35 (B) 6.526 (C) 8.34 (D) 6.173
40. One mole of a sparingly soluble salt MX are added in 1 L saturated solution of another sparingly soluble salt NX. If $K_{sp}(MX) \gg K_{sp}(NX)$, then : (Assume no chemical reaction to be taking place).
 (A) Some MX & NX solid will get collected at the bottom of vessel.
 (B) $[X^-] \approx \sqrt{K_{sp}(MX)}$ (C) $[N^+] \approx \frac{K_{sp}(NX)}{\sqrt{K_{sp}(MX)}} (\ll [M^+])$ (D) All of these

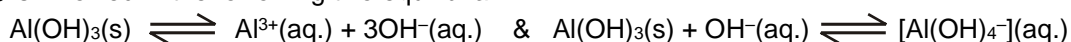


41. The solubility of CaCO_3 is 7 mg / litre. Calculate the solubility of BaCO_3 (in mol/L) from this information and from the fact that when Na_2CO_3 is added slowly to a solution containing equimolar concentration of Ca^{+2} and Ba^{+2} , no precipitate of CaCO_3 is formed until 90% of Ba^{+2} has been precipitated as BaCO_3 . (Assume no hydrolysis of CO_3^{2-} ion).
 (A) 4.9×10^{-10} (B) 7×10^{-6} (C) 2.21×10^{-5} (D) 4.9×10^{-11}
42. To a solution formed by adding n mole of sparingly soluble salt MX in 1 L water, NaY solid (a readily soluble salt) is added until x% of MX is converted to MY(s) (another sparingly soluble salt). Then :
 (Assume no hydrolysis of any ion).
 (A) Resulting solution can be called saturated with respect to both MX & MY.
 (B) $[X^-] = \frac{nx}{100}$
 (C) $[Y^-] = \frac{K_{sp}(\text{MY})}{K_{sp}(\text{MX})} \times \frac{nx}{100}$
 (D) All of these
43. A sample of AgCl was treated with 5 mL of 1.6 M Na_2CO_3 solution to give Ag_2CO_3 . The resulting solution contained 0.00284 g of Cl^- per litre. Determine $K_{sp}(\text{AgCl})$, if $K_{sp}(\text{Ag}_2\text{CO}_3) = 8.1 \times 10^{-12}$. (Assume no hydrolysis of any ion).
 (A) 1.8×10^{-10} (B) 10^{-10} (C) 10^{-5} (D) 1.34×10^{-5}
44. To a solution of 0.1 M Mg^{2+} and 0.8 M NH_4Cl , an equal volume of NH_3 is added which just gives precipitate. Calculate $[\text{NH}_3]$ in its solution. K_{sp} of $\text{Mg}(\text{OH})_2 = 1.62 \times 10^{-11}$ and K_b of $\text{NH}_4\text{OH} = 1.8 \times 10^{-5}$.
 (A) 0.4 M (B) 0.8 M (C) 1.6 M (D) 0.08 M
45. Solubility of $\text{Fe}(\text{OH})_3$ ($K_{sp} = 10^{-38}$) :
 (A) In a buffer solution of pH = 2 is 10^{-2} mol/L (B) In a buffer solution of pH = 11 is 10^{-29} mol/L
 (C) Both (A) & (B) (D) None of these
46. What maximum pH must be maintained in a saturated H_2S solution (0.1 M) to avoid precipitation of both Mn^{2+} & Fe^{2+} from a solution, in which each ion is present at a concentration of 0.01 M ?
 (K_a of $\text{H}_2\text{S} = 9.6 \times 10^{-21}$; K_{sp} of $\text{MnS} = 2.5 \times 10^{-13}$; K_{sp} of $\text{FeS} = 6.4 \times 10^{-18}$)
 (A) 5.2 (B) 2.91 (C) 4.7 (D) 2.41
47. What minimum pH must be maintained in a saturated H_2S solution (0.1 M) to cause precipitation of both Mn^{2+} & Fe^{2+} from a solution, in which each ion is present at a concentration of 0.01 M ?
 (K_a of $\text{H}_2\text{S} = 9.6 \times 10^{-21}$; K_{sp} of $\text{MnS} = 2.5 \times 10^{-13}$; K_{sp} of $\text{FeS} = 6.4 \times 10^{-18}$)
 (A) 5.21 (B) 2.91 (C) 4.7 (D) 2.41
48. A decimolar solution of HCl is saturated with H_2S gas. Calculate the minimum $[\text{Cu}^{2+}]$ ion that will saturate the above solution with CuS. Given K_{sp} of CuS = 6.4×10^{-36} , K_a for $\text{H}_2\text{S} = 9.6 \times 10^{-21}$ and solubility of $\text{H}_2\text{S} = 0.1$ mole litre $^{-1}$.
 (A) $\frac{2}{3} \times 10^{-16}$ M (B) $\frac{2}{3} \times 10^{-14}$ M (C) $\frac{2}{3} \times 10^{-18}$ M (D) $\frac{3}{2} \times 10^{-16}$ M
- 49(a). The salt $\text{Al}(\text{OH})_3$ is involved in the following two equilibria :
 $\text{Al}(\text{OH})_3(\text{s}) \rightleftharpoons \text{Al}^{3+}(\text{aq}) + 3\text{OH}^-(\text{aq}) ; K_{sp}$
 $\text{Al}(\text{OH})_3(\text{s}) + \text{OH}^-(\text{aq}) \rightleftharpoons \text{Al}(\text{OH})_4^-(\text{aq}) ; K_c$
 Which of the following relationship is correct when the solubility is minimum ?
 (A) $[\text{OH}^-] = \left(\frac{K_{sp}}{K_c} \right)^{1/3}$ (B) $[\text{OH}^-] = \left(\frac{K_c}{K_{sp}} \right)^{1/4}$
 (C) $[\text{OH}^-] = \sqrt{\left(\frac{K_{sp}}{K_c} \right)^{1/4}}$ (D) None of these



- 49(b). Arrange solubility of AgBr in the given solutions in increasing order : (consider no hydrolysis of Ag^+ ion)
- (i) 0.1 M NH_3 (ii) 0.1 M AgNO_3 (iii) 0.2 M NaBr (iv) pure water
- (A) (iii) < (ii) < (iv) < (i) (B) (iii) < (ii) < (i) < (iv) (C) (iii) < (ii) = (i) < (iv) (D) (ii) < (iii) < (iv) < (i)

- 49(c). $\text{Al}(\text{OH})_3$ is involved in the following two equilibria :



Then :

- (A) Solubility of $\text{Al}(\text{OH})_3$ will be more in acidic solutions & less in basic solution, both as compared to in water.
- (B) Solubility of $\text{Al}(\text{OH})_3$ will be less in acidic solutions & more in basic solution, both as compared to in water.
- (C) Solubility of $\text{Al}(\text{OH})_3$ will be more in acidic solutions & more in basic solution, both as compared to in water.
- (D) Solubility of $\text{Al}(\text{OH})_3$ will be less in acidic solutions & less in basic solution, both as compared to in water.

MATCH THE COLUMN

50. Match the entries of column II for which the equality or inequality given in the column I are satisfied. (Use $\log 1.8 = 0.26$, K_a of formic acid = 1.8×10^{-4} , K_a of acetic acid = 1.8×10^{-5} , K_b of ammonia = 1.8×10^{-5} , K_{a_1} of H_2S = 10^{-7} and K_{a_2} of H_2S = 10^{-14} , for the following matchings)

	Column I		Column II
(A)	10^{-5} M HCl solution > 0.1 M H_2S solution	(p)	α_{water} (degree of dissociation of water)
(B)	CH_3COOH solution of pH equal to 4.74 = $\text{NH}_3 \cdot \text{H}_2\text{O}$ solution of pH equal to 9.26	(q)	$[\text{OH}^-]$
(C)	0.1 M CH_3COOH solution = 1.0 M HCOOH solution	(r)	α (degree of dissociation)
(D)	0.1 M solution of a weak acid HA_1 ($K_a = 10^{-5}$) < 0.01 M solution of a weak acid HA_2 ($K_a = 10^{-6}$)	(s)	pH

51. Match the column:

	Column-I		Column-II
	Mixture of various solutions		pH of resulting solution
(A)	10 L of 0.015 M $\text{Ba}(\text{OH})_2$ + 5 L of 0.08 M HCl + 485 L of 0.05 M BaCl_2	(p)	5.5
(B)	100 mL of 0.15 M CH_3COOH ($\text{p}K_a = 4.74$) + 50 mL of 0.3 M NaOH	(q)	11.2
(C)	20 mL of 0.5 M RNH_3Cl ($K_h = 10^{-9}$) + 20 mL of 0.5 M KOH	(r)	8.87
(D)	10 mL of 0.1 M H_3A ($\text{p}K_{a_1} = 4$, $\text{p}K_{a_2} = 7$, $\text{p}K_{a_3} = 11$) + 10 mL of 0.1 M NaOH	(s)	3.7

52. Match the effect of addition of 1 M NaOH to 50 mL of 1 M $\text{H}_2\text{C}_2\text{O}_4$ (diprotic acid) in column I with column II (Given : $K_{a_1} = 10^{-4}$, $K_{a_2} = 10^{-9}$)

	Column-I		Column-II
(A)	25 mL of NaOH	(p)	Buffer solution
(B)	50 mL of NaOH	(q)	pH is independent of concentration of species present in the solution.
(C)	75 mL of NaOH	(r)	anionic hydrolysis
(D)	100 mL of NaOH	(s)	pH > 7



53. Match the column:

	Column-I		Column-II
	Titrations		Best Indicator (with its pH range) to detect end point
(A)	Titration of 0.1 M H_2SO_4 by adding 0.1 M KOH	(p)	Methyl red (4.2 – 6.3)
(B)	Titration of 0.5 M HCOOH ($\text{pK}_a = 3.74$) by adding 0.125 M NaOH	(q)	Phenol red (6.8 – 8.2)
(C)	Titration of 0.2 M NH_4OH ($\text{pK}_b = 4.74$) by adding 0.1 M H_2SO_4	(r)	Methyl orange (3.1 – 4.4)
(D)	Titration of 0.3 M Na_2CO_3 by adding 0.3 M HCl (K_{a_1} & K_{a_2} of H_2CO_3 are 4×10^{-7} & 5.6×10^{-11})	(s)	Phenolphthalein (8.3 – 10)

54. Match the column:

	Column-I		Column-II
	(Concentration/solubility)		(Solutions)
(A)	8×10^{-5} M	(p)	$[\text{Mg}^{2+}]_{\text{min}}$ required for precipitation of $\text{Mg}(\text{OH})_2$ ($\text{K}_{\text{sp}} = 1.794 \times 10^{-11}$) from a solution containing 0.36 M NaOH.
(B)	1.38×10^{-10} M	(q)	Solubility of Hg_2Cl_2 ($\text{K}_{\text{sp}} = 1.296 \times 10^{-18}$) in 0.18 M BaCl_2 solution.
(C)	10^{-17} M	(r)	$[\text{Ca}^{2+}]$ in a solution saturated with respect to both CaCO_3 ($\text{K}_{\text{sp}} = 2.6 \times 10^{-9}$) & CaC_2O_4 ($\text{K}_{\text{sp}} = 3.8 \times 10^{-9}$).
(D)	7.5×10^{-18} M	(s)	Solubility of $\text{Fe}(\text{OH})_3$ ($\text{K}_{\text{sp}} = 10^{-38}$) in pure water.
		(t)	$[\text{Ag}^+]$ in resulting solution obtained by mixing equal volumes of 0.06 M AgNO_3 solution & 0.2 M KCN solution (K_f of $[\text{Ag}(\text{CN})_2]^- = 2.5 \times 10^{18}$).

SINGLE AND DOUBLE VALUE INTEGER TYPE

55. What is the sum of basicity of H_3PO_4 , H_3PO_3 , H_3PO_2 , H_3BO_3 , $(\text{COOH})_2$, $\text{H}_2\text{S}_2\text{O}_8$, H_2SO_4 , H_2SO_3 , H_2CO_3 , H_2S and $\text{H}_4\text{P}_2\text{O}_5$?
56. 'A' solution of strong acid/strong base of $\text{pH} = x$ is mixed with equal volume of 'B' solution of strong acid/strong base of $\text{pH} = (14 - x)$, such that the resulting mixture has a $\text{pH} = 7$. If only natural number values of x are allowed, excluding $x = 7$, then how many possible values of x would be there? (Negative values of pH are not to be considered)
57. An $\text{NH}_4^+ - \text{NH}_3$ buffer is supposed to keep the pH of the solution constant within 0.3 pH unit during the reaction. $\text{CH}_3\text{COOCH}_3(\text{aq}) + 2\text{H}_2\text{O}(\text{aq}) \longrightarrow \text{CH}_3\text{COO}^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq}) + \text{CH}_3\text{OH}(\text{aq})$
If this solution had initial concentrations : $[\text{NH}_4^+]_0 = 0.1$ M, $[\text{NH}_3]_0 = 0.06$ M, $[\text{CH}_3\text{COOCH}_3]_0 = 0.02$ M, determine the magnitude of pH change as a result of reaction.
Multiply the magnitude by 10 & add 1 if it is a satisfactory buffer, otherwise subtract 1. Report the answer rounding it off to the nearest whole number.
 $[\text{K}_b(\text{NH}_3) = 1.8 \times 10^{-5}]$
58. 0.98 g H_3PO_4 is dissolved in 100 mL of a buffer solution ($\text{pH} = 5$). If the equilibrium concentrations of H_2PO_4^- , HPO_4^{2-} , PO_4^{3-} and H_3PO_4 are C_1 , C_2 , C_3 and C_4 respectively. Find $\text{pC}_1 + \text{pC}_2 + \text{pC}_3 + \text{pC}_4$.
($\text{pC}_i = -\log \text{C}_i$; where $i = 1, 2, 3, 4$) Given : For H_3PO_4 , $\text{K}_{a_1} = 10^{-3}$, $\text{K}_{a_2} = 10^{-8}$, $\text{K}_{a_3} = 10^{-12}$.



59. End point/equivalence point of how many of the following titrations cannot be detected with the indicators given against them ?

	Titration	Indicator with its pH range
(i)	KOH + HCN	Methyl orange (3.1 - 4.4)
(ii)	NaOH + HF	HIn ($K_{In} = 3 \times 10^{-4}$)
(iii)	HNO ₃ + Sr(OH) ₂	Phenol red (6.8 - 8.2)
(iv)	HClO ₄ + Aniline	Methyl red (4.2 - 6.3)
(v)	HCl + Dimethyl amine	HIn ($K_{In} = 5 \times 10^{-5}$)
(vi)	Ba(OH) ₂ + HNO ₂	Phenolphthalein (8.3 - 10)
(vii)	NaH ₂ PO ₂ + H ₂ SO ₄	InOH ($K_{In} = 3 \times 10^{-5}$)
(viii)	Pyridine + Benzoic acid	Phenol red (6.8 - 8.2)
(ix)	KH ₂ BO ₃ + HI	Methyl red

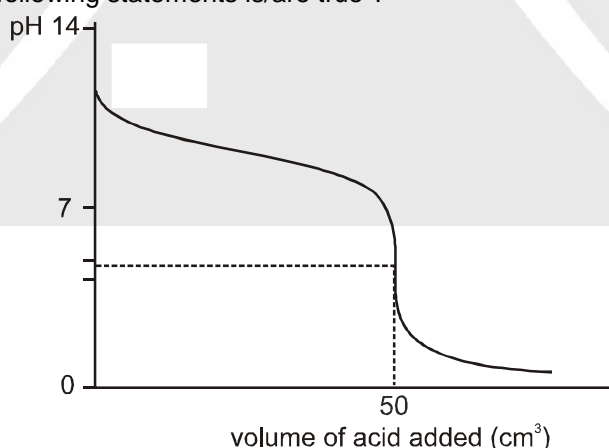
60. Number of compounds among following which give two end points when titrated with HCl is
 Na_2HPO_4 , Na_2S , $\text{K}_2\text{C}_2\text{O}_4$, KHC_2O_4 , H_3PO_3 , $\begin{matrix} \text{COOH} \\ | \\ \text{C} \\ | \\ \text{COOH} \end{matrix}$, K_2CO_3 , NaHCO_3 , Ethylene diamine
61. On addition of V mL volume of 0.1 M KOH, buffer capacity is found maximum at $\text{pH}_{\text{solution}} = x$ (> 7), when it is titrated against 50 mL, 0.2 M H₂CO₃. (For H₂CO₃: $K_{a1} = 4.3 \times 10^{-6}$, $K_{a2} = 5.6 \times 10^{-11}$)
 Report your answer as $(V + x) \times 0.4$, rounding it off to the nearest whole number.
62. The solubility product of Ag₂C₂O₄ at 25°C is $1.29 \times 10^{-11} \text{ mol}^3 \text{ L}^{-3}$. A solution of K₂C₂O₄ containing 0.152 mole in 500 mL water is shaken with excess of Ag₂CO₃ till the following equilibrium is reached :
 $\text{Ag}_2\text{CO}_3(\text{s}) + \text{K}_2\text{C}_2\text{O}_4(\text{aq}) \rightleftharpoons \text{Ag}_2\text{C}_2\text{O}_4(\text{s}) + \text{K}_2\text{CO}_3(\text{aq})$
 At equilibrium, the solution contains 0.0358 mole of K₂CO₃. Assuming the degree of dissociation of K₂C₂O₄ and K₂CO₃ to be equal, if the solubility product of Ag₂CO₃ is $3.794 \times 10^{-x} \text{ mol}^3 \text{ L}^{-3}$, find x.
63. Find out maximum number of moles of PbCO₃ soluble in 100 L buffer solution of pH = 3, rounding it off to the nearest whole number.
 $K_{a1}(\text{H}_2\text{CO}_3) = \frac{50}{11} \times 10^{-7}$
 $K_{a2}(\text{H}_2\text{CO}_3) = 5.5 \times 10^{-11}$
 $K_{sp}(\text{PbCO}_3) = 7.5 \times 10^{-14}$; (Take $\sqrt{0.3} = 0.55$)
64. 0.1 millimole of CdSO₄ are present in 10 mL acid solution of 0.08 M HCl. Now H₂S is passed to precipitate all the Cd²⁺ ions. Find the pOH of the solution after filtering off precipitate, boiling off H₂S and making the solution 100 mL by adding H₂O.

ONE OR MORE THAN ONE OPTIONS CORRECT TYPE

65. Select correct statement(s) :
 (A) CH₃COOH (a weak acid) behaves as a strong acid in NH₃.
 (B) HNO₃ (strong acid) behaves as a base in HF (anhydrous).
 (C) H₂SO₄ dissociates to a very small extent in glacial CH₃COOH.
 (D) HI is a stronger acid than HCl in H₂O.
66. C M fluoroacetic acid solution was found to contain $[\text{H}^+] = 1.5 \times 10^{-3} \text{ M}$. K_a of fluoroacetic acid = 2.5×10^{-3} . Then :
 (A) C = $9 \times 10^{-4} \text{ M}$ (B) $[\text{FCH}_2\text{COOH}] = 9 \times 10^{-4} \text{ M}$
 (C) C = $2.4 \times 10^{-3} \text{ M}$ (D) $\alpha = 0.625$



67. To 1 L of a 1.6×10^{-3} M aqueous solutions of ethylene diamine ($K_{b_1} = 8 \times 10^{-5}$, $K_{b_2} = 2.7 \times 10^{-8}$), 5×10^{-4} mole of $\text{Ba}(\text{OH})_2$ is added. Then :
- (A) $\text{pH}_f - \text{pH}_i = 0.5$ (B) $\alpha_i - \alpha_f = 0.12$ (C) $\frac{[\text{C}_2\text{N}_2\text{H}_{10}^{2+}]_i}{[\text{C}_2\text{N}_2\text{H}_{10}^{2+}]_f} = 0.128$ (D) $\frac{[\text{C}_2\text{N}_2\text{H}_9^+]_i}{[\text{C}_2\text{N}_2\text{H}_9^+]_f} = 2.5$
68. The correct relationship(s) between the pH of isomolar solutions of Na_2O (pH_1), Na_2S (pH_2), Na_2Se (pH_3) and Na_2Te (pH_4) is/are :
- (A) $\text{pH}_1 > \text{pH}_2$ (B) $\text{pH}_2 < \text{pH}_4$ (C) $\text{pH}_2 < \text{pH}_3$ (D) $\text{pH}_3 > \text{pH}_4$
69. For a 0.072 M NaHSO_4 solution, select the incorrect option(s) : (K_{a_1} and K_{a_2} of $\text{H}_2\text{SO}_4 = \infty$ & 1.2×10^{-2})
- (A) $\text{pH} = 1.62$ (B) $\text{pH} = 7.39$
 (C) Degree of hydrolysis, $h = \frac{1}{\sqrt{6}}$ (D) $h = 3.4 \times 10^{-6}$
70. Choose the correct statement(s) about buffer capacity during titration of NH_4OH with HCl :
- (A) Buffer capacity during titration first increases, then decreases.
 (B) Buffer capacity reaches to maximum at equivalence point.
 (C) Buffer capacity will increase if concentration of NH_4OH increases.
 (D) Buffer capacity value will remain same if strong acid HCl is replaced by H_2SO_4 of equal $[\text{H}_3\text{O}^+]$.
71. Which of the following statements is/are true for indicators ?
- (A) Indicators catalyse the acid base reactions by releasing or accepting H^+ ions.
 (B) Indicators do not significantly affect the pH of the solution to which they are added.
 (C) Acid-base reactions do not occur in absence of indicators.
 (D) Indicators have different colours in dissociated and undissociated forms.
72. Let the colour of the indicator HIn (colourless) will be visible only when its ionised form (pink) is 25% or more in a solution. Suppose HIn ($\text{pK}_{\text{In}} = 9$) is added to a solution of $\text{pH} = 9.6$. Predict what will happen :
- (A) pink colour will be visible. (B) pink colour will not be visible.
 (C) % of ionised form will be less than 25%. (D) % of ionised form will be more than 25%.
73. When a weak base solution (50 mL of 0.1 M NH_4OH) is titrated with a strong acid (0.1 M HCl), the pH of solution initially decreases fast and then decreases slowly till near equivalence point (as shown in the figure). Which of the following statements is/are true ?

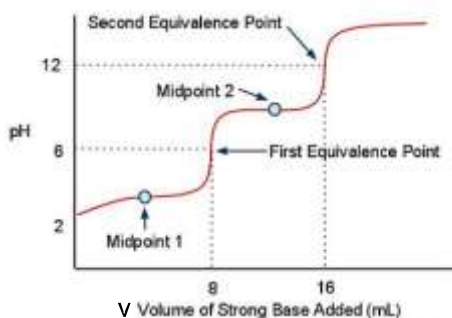


- (A) The initial fast decrement in pH is due to fast consumption of free OH^- ions by HCl .
 (B) The slow decrease of pH is due to formation of an acidic buffer solution after addition of some HCl .
 (C) The slope of shown pH graph (magnitude only) will be minimum when 25 mL of 0.1 M HCl is added.
 (D) The slow decrease of pH is due to formation of a basic buffer solution after addition of some HCl .



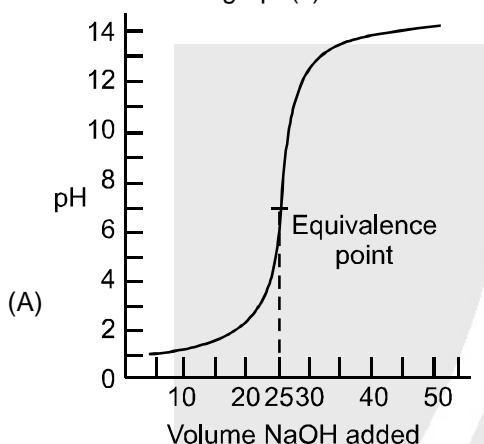


74. A solution of a substance is titrated against a strong base (or acid), volume V of strong base (or acid) is plotted against pH of the solution (as shown in figure). The substance could be :

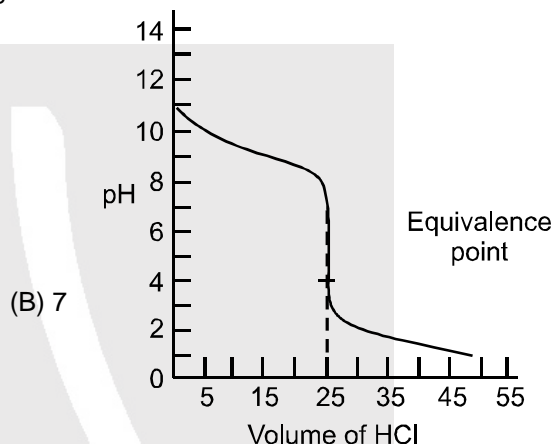


- (A) Na_2CO_3 (B) Ethylene diamine (C) $\text{H}_2\text{C}_2\text{O}_4$ (D) $\text{CH}_2(\text{COOH})_2$

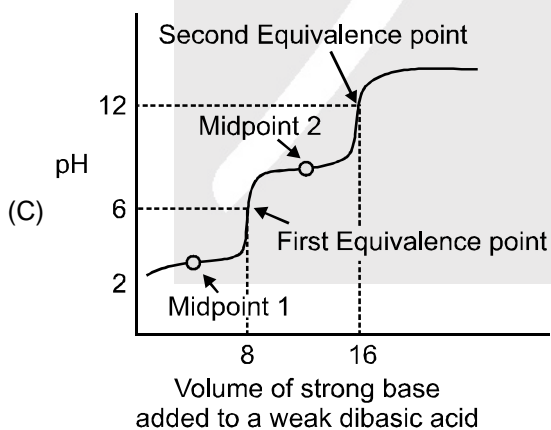
75. Select the correct graph(s) for the corresponding acid-base titration :



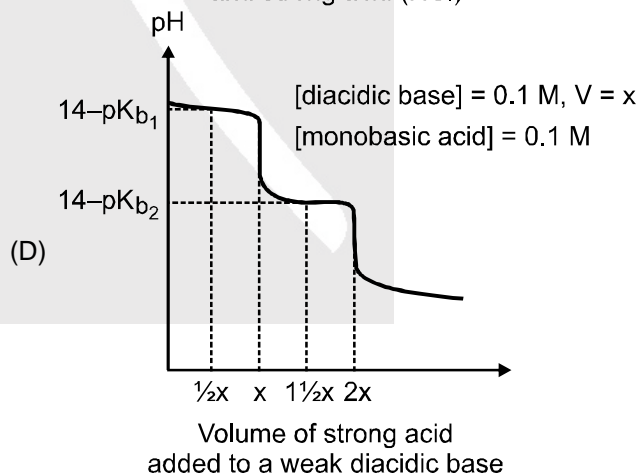
Titration curve of strong acid (HCl) with a strong base (NaOH)



The pH titration curve of weak base (NH_4OH) and strong acid (HCl)



Volume of strong base added to a weak dibasic acid



Volume of strong acid added to a weak diacidic base

76. 100 mL of a clear saturated solution of Ag_2SO_4 is added to 250 mL of a clear saturated solution of PbCrO_4 . Then select the incorrect option(s). Given K_{sp} values for Ag_2SO_4 , Ag_2CrO_4 , PbCrO_4 and PbSO_4 are 1.4×10^{-5} , 2.4×10^{-12} , 2.8×10^{-13} and 1.6×10^{-8} respectively.
- (A) $[\text{Ag}^+]_{\text{Just after mixing}} = 3.038 \times 10^{-2} \text{ M}$.
 (B) $[\text{Pb}^{2+}]_{\text{Just after mixing}} = 3.78 \times 10^{-7} \text{ M}$
 (C) Only PbSO_4 will get precipitated.
 (D) Both Ag_2CrO_4 and PbSO_4 will get precipitated.



77. Calculate $[Ag^+]$, $[CO_3^{2-}]$ & $[CrO_4^{2-}]$ in a solution saturated with respect to both Ag_2CO_3 & Ag_2CrO_4 .
 Given: $K_{sp}(Ag_2CO_3) = 4 \times 10^{-12}$; $K_{sp}(Ag_2CrO_4) = 2.4 \times 10^{-12}$ & $\frac{1}{4\sqrt[3]{5}} = 0.146$
- (A) $[Ag^+] = 2.336 \times 10^{-4} M$ (B) $[CO_3^{2-}] = 7.3 \times 10^{-5} M$
 (C) $[CrO_4^{2-}] = 4.35 \times 10^{-5} M$ (D) $2[Ag^+] = [CO_3^{2-}] + [CrO_4^{2-}]$
78. 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 of Cl^- per litre. Then : ($K_{sp}(Ag_2CO_3) = 8.2 \times 10^{-12}$)
- (A) $K_{sp}(AgCl) = 1.17 \times 10^{-10}$ (B) $K_{sp}(AgCl) = 1.17 \times 10^{-9}$
 (C) $[Ag^+] = 2.34 \times 10^{-7} M$ (D) $[Ag^+] = 2.34 \times 10^{-6} M$
79. In which of the following solutions, the solubility of $AgCN$ will be greater than that in pure water ?
 Given : $K_{sp}(AgCN) = 4 \times 10^{-16}$, $K_a(HCN) = 5 \times 10^{-10}$
- (A) 0.01 M $AgNO_3$ solution (B) A buffer solution of pH = 12
 (C) 0.2 M NH_3 solution (D) A buffer solution of pH = 5
80. The simultaneous solubility of $AgCN$ ($K_{sp} = 2.5 \times 10^{-16}$) and $AgCl$ ($K_{sp} = 1.6 \times 10^{-10}$) in 1 M $NH_3(aq)$ are s_1 and s_2 respectively. Then : [Given : $K_f[Ag(NH_3)_2^+] = 10^7$]
- (A) $s_1 = \frac{1}{27} \text{ mol/L}$ (B) $s_2 = \frac{10^{-4}}{1728} \text{ mol/L}$ (C) $\frac{[Cl^-]}{[CN^-]} = 6.4 \times 10^5$
 (D) Separate values of s_1 and s_2 cannot be determined, just their ratio $\frac{s_2}{s_1} = 1.5625 \times 10^{-6}$ can be known.

PART - IV : PRACTICE TEST-2 (IIT-JEE (ADVANCED Pattern))

Max. Time : 1 Hr.

Max. Marks : 66

Important Instructions

A. General :

- The test is of 1 hour duration.
- The Test Booklet consists of 22 questions. The maximum marks are 66.

B. Question Paper Format :

- Each part consists of five sections.
- Section 1 contains 7 multiple choice questions. Each question has four choices (A), (B), (C) and (D) out of which ONE is correct.
- Section 2 contains 5 multiple choice questions. Each question has four choices (A), (B), (C) and (D) out of which ONE OR MORE THAN ONE are correct.
- Section 3 contains 6 questions. The answer to each of the questions is a single-digit integer, ranging from 0 to 9 (both inclusive).
- Section 4 contains 1 paragraph, describing theory, experiment and data etc. 3 questions relate to paragraph. Each question pertaining to a particular passage should have only one correct answer among the four given choices (A), (B), (C) and (D).
- Section 5 contains 1 multiple choice questions. Question has two lists (list-1 : P, Q, R and S; List-2 : 1, 2, 3 and 4). The options for the correct match are provided as (A), (B), (C) and (D) out of which ONLY ONE is correct.

C. Marking Scheme :

- For each question in Section 1, 4 and 5 you will be awarded 3 marks if you darken the bubble corresponding to the correct answer and zero mark if no bubble is darkened. In all other cases, minus one (– 1) mark will be awarded.
- For each question in Section 2, you will be awarded 3 marks. If you darken all the bubble(s) corresponding to the correct answer(s) and zero mark. If no bubbles are darkened. No negative marks will be answered for incorrect answer in this section.



11. For each question in Section 3, you will be awarded 3 marks if you darken only the bubble corresponding to the correct answer and zero mark if no bubble is darkened. No negative marks will be awarded for incorrect answer in this section.

Note : Take water as solvent and temperature as 25°C, if not specified.
Take $\log 2 = 0.3$, $\log 3 = 0.48$, $\log 5 = 0.7$, $\log 7 = 0.845$, if not specified.

SECTION-1 : (Only One option correct Type)

This section contains 7 multiple choice questions. Each questions has four choices (A), (B), (C) and (D) out of which Only ONE option is correct.

- Azhar prepared three different solutions of HCl, NaOH and brine (NaCl) but forgot to label them. In order to identify he kept them on table and named them as solution I, solution II and solution III. When he added a sample from solution II or solution III to a sample from solution I, the pH of the solution I increased. However, when a sample from solution III was added to a sample from solution II, the pH of the solution II decreased. Identify the incorrect option(s) :

(A) Solution I, II and III contain HCl, NaOH and NaCl respectively.
(B) Solutions I and solution III can be mixed to get the pH of solution II.
(C) $\text{pH}_I < \text{pH}_{II} < \text{pH}_{III}$
(D) Both (B) & (C)
- An aqueous solution contains 0.01 M RNH_2 ($K_b = 2 \times 10^{-6}$) & 10^{-4} M NaOH. The concentration of OH^- is nearly :

(A) 1.414×10^{-4} M (B) 10^{-4} M (C) 3×10^{-4} M (D) 2×10^{-4} M
- A 0.01 M solution of $\text{PuO}_2(\text{NO}_3)_2$ was found to have a pH of 4. Then select the INCORRECT option :

(A) % hydrolysis of $\text{PuO}_2^{2+} = 1\%$. (B) K_b for $\text{PuO}_2(\text{OH})^+ = 10^{-8}$.
(C) Hydrolysis is expected to be endothermic. (D) None of these
- 10 mL of 0.1 M HCl solution is added in 90 mL of a buffer solution having 0.1 M NH_4OH and 0.1 M NH_4Cl . The percentage change in pH of solution is : (K_a of $\text{NH}_4^+ = 5 \times 10^{-10}$)

(A) $\frac{10}{4.7}$ % increase (B) $\frac{10}{4.7}$ % decrease (C) $\frac{10}{9.3}$ % increase (D) $\frac{10}{9.3}$ % decrease
- Select INCORRECT statement :

(A) Phenolphthalein is not a suitable indicator for the titration of $\text{HCl}(\text{aq})$ with $\text{NH}_4\text{OH}(\text{aq})$.
(B) An acid-type indicator in a buffer solution of $\text{pH} = \text{pK}_{\text{in}} + 1$ is ionized to the extent of $\frac{1000}{11}\%$.
(C) In the titration of a monoacidic weak base with a strong acid, the pH at the equivalent point is always calculated by $\text{pH} = \frac{1}{2} [\text{pK}_w - \text{pK}_b - \log C]$.
(D) When $\text{Na}_3\text{PO}_4(\text{aq})$ is titrated with $\text{HCl}(\text{aq})$, the pH of solution at second equivalent point is calculated by $\frac{1}{2} [\text{pK}_{a_1} + \text{pK}_{a_2}]$.
- The solubility of SrF_2 ($K_{\text{sp}} = 2.5 \times 10^{-9}$) in 0.1 M SrCl_2 solution is : (neglect hydrolysis of F^-)

(A) $\sqrt{\frac{5}{2}} \times 10^{-4}$ mol/L (B) 5×10^{-3} mol/L (C) $5\sqrt{\frac{5}{2}} \times 10^{-5}$ mol/L (D) $\frac{5}{2} \times 10^{-3}$ mol/L
- pH of a saturated solution of silver salt of monobasic acid HA is found to be 9. Find the K_{sp} of sparingly soluble salt $\text{AgA}(\text{s})$.
Given : $K_a(\text{HA}) = 10^{-10}$

(A) 1.1×10^{-11} (B) 1.1×10^{-10} (C) 10^{-12} (D) Data insufficient



**Section-2 : (One or More than one options correct Type)**

This section contains 5 multipole choice questions. Each questions has four choices (A), (B), (C) and (D) out of which ONE or MORE THAN ONE are correct.

8. Which of the following options is/are true for alkaline aqueous solution ?
 (A) $\text{pH} > \frac{\text{pK}_w}{2}$ (B) $\text{pH} > \text{pOH}$ (C) $\text{pOH} < \frac{\text{pK}_w}{2}$ (D) $\text{pH} < \text{pOH}$
9. pH of aqueous solution of which of the following salt(s) is/are independent of its concentration ?
 (A) CH_3COONa (B) $\text{C}_6\text{H}_5\text{NH}_3\text{Cl}$ (C) KClO_4 (D) $\text{CH}_3\text{COONH}_4$
10. A base type indicator is half in ionised form when pH is 7.2. If the ratio of unionised form to ionised form is 1 : 5, let pH of the solution is pH_1 . With the same pH of solution, indicator is altered (not its type) such that the ratio of unionised form to ionised form is 1 : 4. Let pH_2 be the pH of solution when 50% of new indicator is in ionised form. Then :
 (A) $\text{pH}_1 = 7.9$ (B) $\text{pH}_1 = 6.5$ (C) $\text{pH}_2 = 7.3$ (D) $\text{pH}_2 = 7.1$
11. A 2.5 g impure sample containing weak monoacidic base (Mol. wt. = 45 u) is dissolved in 100 mL water and titrated with 0.5 M HCl. When $\left(\frac{1}{5}\right)^{\text{th}}$ of the base was neutralised, the pH was found to be 9 and at equivalence point, pH of solution is 4.5. Select correct statement(s) :
 (A) K_b of base is less than 10^{-6} .
 (B) Concentration of salt (C) at equivalent point is 0.25 M.
 (C) Volume of HCl is used at equivalent point is 100 mL.
 (D) Weight percentage of a base in given sample is 80%.
12. The solubility of metal sulphides in saturated solution of H_2S $\{[\text{H}_2\text{S}] = 0.1 \text{ M}\}$ can be represented by :

$$\text{MS} + 2\text{H}^+ \rightleftharpoons \text{M}^{2+} + \text{H}_2\text{S} ; K_{\text{eq}} = \frac{[\text{M}^{2+}][\text{H}_2\text{S}]}{[\text{H}^+]^2}$$

 The value of K_{eq} is given for few metal sulphides. If concentration of each metal ion in solution is 0.01 M, which metal sulphide(s) is/are selectively precipitated at total $[\text{H}^+] = 1 \text{ M}$ in saturated H_2S solution ?

Metal sulphide :	MnS	ZnS	CoS	PbS
K_{eq} :	3×10^{10}	3×10^{-2}	3	3×10^{-7}

 (A) MnS (B) ZnS (C) CoS (D) PbS

Section-3 : (One Integer Value Correct Type.)

This section contains 6 questions. Each question, when worked out will result in one integer from 0 to 9 (both inclusive)

13. Value of K_{eq} at 25°C for reaction : $\text{NH}_3 + \text{H}_3\text{O}^+ \rightleftharpoons \text{NH}_4^+ + \text{H}_2\text{O}$ is 2×10^9 . Determine pK_b of NH_4OH , rounding it off to nearest whole number. Report your answer as '0' if value cannot be determined.
14. In a 3.24 L closed cylindrical container, the following equilibrium is established at 0°C :
 $2\text{Ag(s)} + 2\text{I}^-(\text{aq}) + 2\text{H}_2\text{O(l)} \rightleftharpoons 2\text{AgI(s)} + \text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq})$
 The equilibrium constant for the above reaction is 4×10^{-9} . At equilibrium, solution occupies $\left(\frac{1}{3.24}\right)^{\text{th}}$ height of the container and contains 0.5 M I^- and other species. If gaseous matter weighs 2 g, find pOH of solution. Neglect aqueous tension.
15. Calculate $[\text{A}^{2-}]/[\text{H}^+]$ in an aqueous solution of 0.1 M H_2A (dibasic weak acid).
 Given : For H_2A , $K_{a1} = 0.05$, $K_{a2} = 2 \times 10^{-6}$.
 Report your answer after multiplying by 1,00,000.



16. To a 200 mL of 0.1 M weak base BOH solution, 46 mL of 0.2 M solution of HCl are added. Now, what volume (in mL) of 0.1 M H_2SO_4 should be added into above solution, so that pH of resulting solution becomes 9? [$K_b(\text{BOH}) = 10^{-5}$]
17. 3.29×10^{-3} mg AgBr(s) ($K_{sp} = 4.9 \times 10^{-13}$) is added to 250 mL water. Determine the % saturation of solution. Report your answer after dividing by 10. (Report your answer as '0', if the given amount of salt cannot dissolve/just dissolves).
18. A buffer solution has 0.25 M CH_3COOH , 0.15 M CH_3COONa , $[\text{Mn}^{2+}] = 0.015$ M and is saturated with H_2S (0.1 M). Given: $K_a(\text{CH}_3\text{COOH}) = 1.8 \times 10^{-5}$, $K_a(\text{H}_2\text{S}) = 9 \times 10^{-21}$, $K_{sp}(\text{MnS}) = 2.4 \times 10^{-13}$. Concentration of a component of the buffer may have to be increased to start the precipitation of MnS. What would be its new concentration (in mole per litre)? Report your answer after multiplying by 10. (Report your answer as '0', if the concentration of any component need not be increased to start the precipitation).

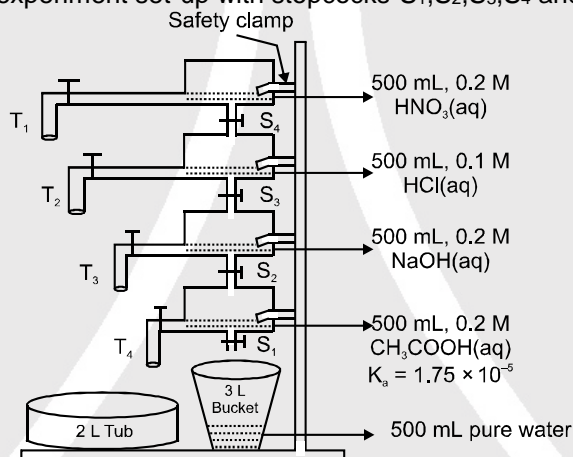
SECTION-4 : Comprehension Type (Only One options correct)

This section contains 1 paragraph, describing theory, experiments, data etc. 3 questions relate to the paragraph. Each question has only one correct answer among the four given options (A), (B), (C) and (D)

Paragraph for Questions 19 to 21

Read the following passage carefully and answer the questions.

Consider the following experiment set-up with stopcocks- S_1, S_2, S_3, S_4 and taps- T_1, T_2, T_3, T_4 .



19. In which of the following cases will the solutions in tub have a pH different from others?
- (A) T_1 and T_4 are opened. (B) Only T_2 is opened.
(C) T_1, T_2, T_3 and T_4 are all opened. (D) T_1 is opened and the content of bucket is poured in the tub.
20. A pH meter is immersed in the bucket of the original set-up shown. It shows a reading of 7. Now, S_1 is first opened and all content is allowed to drain out into the bucket. pH of the solution in the bucket is measured again. Similarly S_2, S_3 and S_4 are sequentially opened and the pH of the solution in the bucket is measured each time after complete drainage. Opening which stop cock would cause maximum pH change (increase/decrease) compared to the previous pH in bucket?
- (A) S_1 (B) S_2 (C) S_3 (D) S_4
21. The above apparatus was setup to study the functioning of the human stomach, where a low pH is maintained at a nearly constant value even when reactions take place in it. Following the same procedure as in the previous question, can a solution imitating stomach-like pH properties be generated in the bucket, and if so, by opening which stopcock? Would this solution have the lowest pH possible from this setup? If your answer is "No" for any of these questions, then after answering "No", choose the stopcock, opening of which will lead to solution in bucket with minimum pH, following the same procedure as above.
- (A) S_4 ; Yes (B) No; S_4 (C) S_3 ; No; S_1 (D) S_3 ; No; S_4

**SECTION-5 : Matching List Type (Only One options correct)**

This section contains 1 question, having two matching lists. Choices for the correct combination of elements from List-I and List-II are given as options (A), (B), (C) and (D) out of which one is correct

22. 0.01 mole of AgNO_3 are gradually added to 1 litre of a solution, which is 0.1 M in Na_2CrO_4 and 0.005 M in NaIO_3 . (K_{sp} values of Ag_2CrO_4 and AgIO_3 are 10^{-8} and 10^{-13} respectively) Now match the values in list II with list I.

	List-I		List-II
(I)	Mole of precipitate formed	(P)	0.0975
(II)	Equilibrium concentration of Ag^+ (in mol/L)	(Q)	0.00032
(III)	Equilibrium concentration of IO_3^- (in mol/L)	(R)	0.0075
(IV)	Equilibrium concentration of CrO_4^{2-} (in mol/L)	(S)	3.125×10^{-10}

Code :

- (A) I–Q, II–R, III–S, IV–P
(C) I–R, II–S, III–Q, IV–P

- (B) I–Q, II–P, III–S, IV–R
(D) I–R, II–Q, III–S, IV–P

Practice Test-2 (IIT-JEE (ADVANCED Pattern))**OBJECTIVE RESPONSE SHEET (ORS)**

Que.	1	2	3	4	5	6	7	8	9	10
Ans.										
Que.	11	12	13	14	15	16	17	18	19	20
Ans.										
Que.	21	22								
Ans.										



APSP Answers

PART - I

1. (4)	2. (3)	3. (2)	4. (2)	5. (3)
6. (4)	7. (2)	8. (4)	9. (2)	10. (4)
11. (2)	12. (3)	13. (4)	14. (3)	15. (1)
16. (4)	17. (2)	18. (1)	19. (2)	20. (1)
21. (2)	22. (4)	23. (1)	24. (4)	25. (1)
26. (3)	27. (3)	28. (4)	29. (3)	30. (3)

PART - II

1. (B)	2. (A)	3. (D)	4. (B)	5. (D)
6. (B)	7. (B)	8. (B)	9. (D)	10. (B)
11. (D)	12. (A)	13. (B)	14. (C)	15. (B)
16. (A)	17. (C)	18. (C)	19. (A)	20. (B)
21. (A)	22. (C)	23. (C)	24. (D)	25. (C)
26. (C)	27. (C)	28. (D)	29. (B)	30. (C)
31. (D)	32. (B)	33. (C)	34. (B)	35. (A)
36. (D)	37. (B)	38. (C)	39. (D)	40. (A)
41. (C)	42. (A)	43. (D)	44. (C)	45. (C)
46. (B)	47. (A)	48. (A)	49. (A)	50. (D)
51. (A)	52. (A)	53. (D)	54. (A)	55. (A)
56. (A)	57. (B)	58. (C)	59. (A)	60. (B)
61. (C)	62. (B)	63. (B)	64. (A)	65. (C)
66. (B)	67. (D)	68. (D)	69. (B)	70. (A)
71. (A)	72. (A)	73. (A)	74. (D)	75. (D)
76. (A)	77. (A)	78. (B)	79. (C)	80. (B)
81. (A)	82. (B)	83. (B)	84. (D)	85. (C)
86. (B)	87. (B)	88. (C)	89. (C)	90. (A)
91. (C)	92. (C)	93. (D)	94. (D)	95. (A)
96. (C)	97. (D)			





PART - III

1. (a) As levelling solvent : Strong acids, strong bases. As differentiating solvent : Weak acids, weak bases.
(b) As levelling solvent : Strong bases, weak bases. As differentiating solvent : Strong acids, weak acids.
(c) As levelling solvent : Strong acids, weak acids, As differentiating solvent : Strong bases, weak bases.
2. $1.92 ; \frac{41}{60} \times 10^{-2} \text{ M} ; \frac{31}{60} \times 10^{-2} \text{ M} ; \frac{1395}{144} \times 10^{-6} \text{ M}$
3. $13, 5.4 \times 10^{-11} \text{ M}$
4. $2.3 ; 5 \times 10^{-3} \text{ M} ; 10^{-8} \text{ M}$
5. 0.23 for first solution and 0.46 for second solution
6. 0.25
7. 28.57%
8. $14 - \text{pK}_{\text{eq}} - \log \frac{b}{a}$ to $14 - \text{pK}_{\text{eq}} - \log \frac{c}{d}$
9. 1.395
- 10(a). 0.444 M
- 10(b). 1
11. (D)
12. (D)
13. (D)
14. (B)
15. (B)
16. (a) (D)
16. (b) (A)
17. (A)
18. (a) (A)
18. (b) (D)
19. (C)
20. (C)
21. (B)
22. (A)
23. (A)
24. (C)
25. (A)
26. (C)
27. (A)
28. (B)
29. (B)
30. (C)
31. (C)
32. (D)
33. (C)
34. (C)
35. (A)
36. (B)
37. (C)
38. (D)
39. (D)
40. (D)
41. (C)
42. (D)
43. (A)
44. (B)
45. (C)
46. (B)
47. (A)
48. (A)
- 49(a). (D)
- 49(b). (A)
- 49(c). (C)
50. (A – p, q, r, s); (B – p, r); (C – r); (D – p, q, s)
51. (A – s); (B – r); (C – q); (D – p)
52. (A – p, q); (B – q, r); (C – p, q, s); (D – r, s)
53. (A – q); (B – s); (C – p); (D – r)
54. (A → r); (B → p); (C → q, s); (D → t)
55. 21
56. 13
57. 4
58. 19
59. 3 [(i), (ii) & (vii)]
60. 5 [Na_2HPO_4 , Na_2S , $\text{K}_2\text{C}_2\text{O}_4$, K_2CO_3 , Ethylene diamine]
61. 64
62. 12
63. 6 (actual answer = 5.5)
64. 12
65. (ABC)
66. (BCD)
67. (ABD)
68. (AD)
69. (BCD)
70. (ACD)
71. (BD)
72. (AD)
73. (ACD)
74. (CD)
75. (ABCD)
76. (ACD)
77. (ABC)
78. (AD)
79. (CD)
80. (ABC)

PART - IV

1. (D)
2. (D)
3. (D)
4. (D)
5. (C)
6. (C)
7. (A)
8. (ABC)
9. (CD)
10. (BD)
11. (BC)
12. (D)
13. 5 (exact answer = 4.7)
14. 5
15. 4
16. 4
17. 1
18. 6
19. (C)
20. (B)
21. (D)
22. (D)





APSP Solutions

PART - I

- CO doesn't have a vacant orbital. Infact, due to the presence of lone pair on carbon, it behaves like a Lewis base.
- $$\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$$

$$t = \text{eq} \quad \text{C}(1 - \alpha) \quad \text{C}\alpha \quad \text{C}\alpha \quad (\text{C} = 55.55 \text{ M} ; \alpha = 1.8 \times 10^{-9})$$

$$K_a = \frac{\text{C}\alpha^2}{1 - \alpha} \approx \text{C}\alpha^2 = 1.8 \times 10^{-16}$$
- pH = 0 means $[\text{H}^+] = 10^0 = 1\text{M}$. Hence solution is strongly acidic.
- Na_2SO_4 will not exert any common ion effect on H_2SO_4 (since strong electrolyte).
 So, $[\text{H}^+] = 2 \times [\text{H}_2\text{SO}_4] = 2 \times 10^{-2} \text{ M}$
 $\therefore \text{pH} = 2 - \log 2 = 1.7$.
- $$[\text{H}^+] = \frac{0.1 \times 100 + 0.01 \times 100}{200} = \frac{11}{200} \text{ M}$$
 So, $\text{pH} = 2 - 0.74 = 1.26$.
- Millimole of $\text{H}^+ = V_1 \times 0.1 \times 1$
 & Millimole of $\text{OH}^- = V_2 \times 0.1 \times 2$
 If we put $V_1 = 2V_2$, the final solution will be neutral i.e.
 Millimole of $\text{H}^+ = 2V_2 \times 0.1 = \text{Millimole of OH}^-$
- $$\frac{\alpha_1}{\alpha_2} = \sqrt{\frac{K_{b1}}{K_{b2}}} = \sqrt{\frac{2.56 \times 10^{-4}}{1.6 \times 10^{-5}}} = 4 : 1$$
- $[\text{H}^+]$ from $\text{HCl} = 10^{-3} \text{ M}$ & $[\text{H}^+]$ from $\text{HA} = \sqrt{\text{CK}_a} = 10^{-3} \text{ M}$.
 So, addition of HCl will not exert common ion effect on HA .
 So, neither pH nor degree of dissociation of HA will change.
- $$[\text{H}^+] = \sqrt{K_{a1}C_1 + K_{a2}C_2} = \sqrt{10} \times 10^{-3} \text{ M}$$

$$\therefore \text{pH} = 3 - \frac{1}{2} \log 10 = 2.5$$
- α is negligible w.r.t. 1.
 $[\text{H}^+]$ mainly comes from first step ionisation.

$$[\text{H}^+] = \sqrt{K_{a1} \times C} = \sqrt{10^{-5} \times 0.1} = 10^{-3} \text{ M}$$

$$\therefore K_{a3} = \frac{[\text{H}^+][\text{A}^{3-}]}{[\text{HA}^{2-}]} \Rightarrow 10^{-13} = \frac{10^{-3}[\text{A}^{3-}]}{[\text{HA}^{2-}]}$$

$$X = \frac{[\text{A}^{3-}]}{[\text{HA}^{2-}]} = 10^{-10} \quad \therefore \text{pX} = 10$$
- Hydrolysis of Fe^{3+} takes place :

$$\text{Fe}^{3+} + 3 \text{H}_2\text{O} \longrightarrow \text{Fe}(\text{OH})_3 + 3 \text{H}^+$$





$$12. \quad h = \sqrt{\frac{K_h}{C}} = \sqrt{\frac{K_w}{K_a \cdot C}} = \sqrt{\frac{10^{-14}}{K_a \times (0.01)}}$$

$$\Rightarrow 0.01 = \sqrt{\frac{10^{-14}}{K_a \times (0.01)}} \Rightarrow 10^{-14} = \frac{10^{-14}}{K_a \times 10^{-2}} \Rightarrow K_a = 10^{-8}.$$

Also, hydrolysis product of $A^- = [OH^-] = Ch = 10^{-4} \text{ M}$.

$$\therefore [H^+] = 10^{-10} \text{ M}$$

$$\therefore \text{pH} = 10.$$

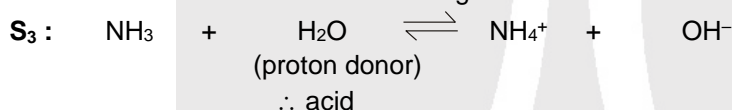
$$13. \quad \text{pH of a salt solution made from weak acid and weak base} = \frac{1}{2} (\text{p}K_w + \text{p}K_a - \text{p}K_b)$$

= independent of concentration of salt solution.

$$14. \quad \text{pH} = \frac{\text{p}K_{a_1} + \text{p}K_{a_2}}{2} = 9 \quad (\text{amphoteric species } HA^-)$$

15. **S₁** : Final solution will contain NaCl (salt of SA and SB) and $\text{CH}_3\text{COONH}_4$ (salt of WA and WB with $K_a = K_b$). So, final solution will be neutral ($\text{pH} = 7$ at 25°C).

S₂ : Equivalence point pH will be greater than 7, but MeOH indicator has pH range = 3.1 – 4.4. So, MeOH cannot be used as indicator in given titration.



16. (1) Salt of WA and WB.
 (2) Weak acid (H_2CO_3) + its conjugate base (HCO_3^-).
 (3) Weak acid (H_2PO_4^-) + its conjugate base (HPO_4^{2-}).

$$17. \quad \text{Buffer solution} \Rightarrow \text{pH} = \text{p}K_a + \log \frac{(0.02 \times 500)}{(0.01 \times 500)}$$

$$\Rightarrow 5.3 = \text{p}K_a + \log 2$$

$$\Rightarrow \text{p}K_a = 5 \quad \therefore \text{p}K_b = 14 - \text{p}K_a = 9$$

$$18. \quad \text{pH} = 9.7 = 10 - \log 2$$

$$\therefore [H^+] = 2 \times 10^{-10} \text{ M}$$

$$\text{PrNH}_2 + \text{H}_2\text{O} \rightleftharpoons \text{PrNH}_3^+ + \text{OH}^- \quad ; \quad K_b = 5 \times 10^{-4}$$

$$\text{and } H^+ + \text{OH}^- \rightleftharpoons \text{H}_2\text{O} \quad ; \quad K_{eq} = \frac{1}{K_w} = 10^{14}$$

$$\therefore \text{PrNH}_2 + H^+ \rightleftharpoons \text{PrNH}_3^+ \quad ; \quad K_{eq} = \frac{K_b}{K_w} = 5 \times 10^{10}$$

$$5 \times 10^{10} = \frac{[\text{PrNH}_3^+]}{[\text{PrNH}_2] \times 2 \times 10^{-10}} \quad \therefore \quad \frac{[\text{PrNH}_2]}{[\text{PrNH}_3^+]} = \frac{1}{10} = 0.1.$$

$$19. \quad \text{pH} = \text{p}K_{In} + \log \frac{[In^-]}{[HIn]} \Rightarrow 5 = 4.7 + \log \frac{[In^-]}{[HIn]}$$

$$\Rightarrow 0.3 = \log \frac{[In^-]}{[HIn]} \Rightarrow \log 2 = \log \frac{[In^-]}{[HIn]}$$

$$\Rightarrow 2 = \frac{[In^-]}{[HIn]}$$

$$\text{Fraction} = \frac{HIn}{In^- + HIn} = \frac{1}{3}$$



20. $B + H^+ \longrightarrow BH^+$
At the half equivalent point, $[B] = [BH^+] \Rightarrow pOH = pK_b$ (from buffer formula)
21. $n_{HX} = n_{NaOH}$
 $\therefore \frac{8}{80} = 0.25 \times V_L$
 $\therefore V_L = 0.4 \text{ L}$
 $[NaX] = \frac{1}{5} = 0.2 \text{ M}$ (Since volume of solution becomes 5 times, so concentration of salt will become 1/5 times the concentration of HX).
 $pH = \frac{1}{2} (pK_w + pK_a + \log C) = \frac{1}{2} (14 + 4 - 0.7) = 8.65.$
22. $[CH_3COOH] = 0.1 \text{ M}$
 $\therefore pH = \frac{1}{2} (pK_a - \log C) = \frac{1}{2} (4.76 + 1) = 2.88.$
23. $s^2 = 2.5 \times 10^{-9}$
 $\therefore s = 5 \times 10^{-5} \text{ mol/L} = 5 \times 10^{-5} \times 100 \times 1000 \text{ mg/L} = 5 \text{ mg/L}.$
So, for dissolving 10 mg $CaCO_3$, $(V_{min})_{H_2O}$ required = 2 L.
24. For sparingly soluble salts having same K_{sp} values, the one producing maximum number of ions per formula-unit will be most soluble.
25. $4s_1^3 = 8.64 \times 10^{-13}$
 $\therefore s_1 = 6 \times 10^{-5} \text{ mol/L (in water)}$
 $Ag_2CrO_4 \rightleftharpoons 2Ag^+ + CrO_4^{2-}$
Let solubility $2s_2 \quad s_2 + 0.6$
 $= s_2 \text{ mol/L} \quad \approx 0.6$
 $(2s_2)^2 \times 0.6 = 8.64 \times 10^{-13}$
 $\therefore s_2 = 6 \times 10^{-7} \text{ mol/L (in } Na_2CrO_4 \text{ solution)}$
 $\therefore \frac{s_1}{s_2} = 100.$
26. $[Ag^+][Cl^-] = K_{sp} = \text{constant}$
 $\Rightarrow xy = \text{constant}$
So, shape of graph should be a rectangular hyperbola.
27. $SrCO_3 \rightleftharpoons Sr^{2+} + CO_3^{2-}$
 $\quad \quad \quad S_1 \quad \quad \quad S_1 + S_2$
 $ZnCO_3 \rightleftharpoons Zn^{2+} + CO_3^{2-}$
 $\quad \quad \quad S_2 \quad \quad \quad S_1 + S_2$
 $S_1 \times (S_1 + S_2) = 10^{-10}$
 $S_2 \times (S_1 + S_2) = 1.5 \times 10^{-11}$
 $\Rightarrow \frac{S_1}{S_2} = \frac{[Sr^{2+}]}{[Zn^{2+}]} = \frac{10^{-10}}{1.5 \times 10^{-11}} = \frac{10}{1.5} = \frac{100}{15} = \frac{20}{3}$
28. Higher the concentration of H^+ , higher is the solubility of $Fe(OH)_3$. (H^+ ions will shift its solubility equilibrium in forward direction by consuming the OH^- ions produced). So, solubility of $Fe(OH)_3$ is maximum in 0.1 M H_2SO_4 .





29. Due to complex formation, solubility of sparingly soluble salt increases because of solubility equilibrium shifting in forward direction.
30. As pH decreases, $[H^+]$ increases. So, CN^- will combine with H^+ forming HCN making the solubility equilibrium shift in forward direction.

PART - III

1. Refer class notes / sheet theory.
2. Assuming $\alpha_2 \ll \alpha_1$ & $\alpha_2 \ll \alpha$ due to common ion effect of OH^- from first dissociation of same base (with α_1) & dissociation of CH_3NH_2 (with α) on second dissociation of base (with α_2), we have :

$$[OH^-] = \sqrt{0.2 \times (4.1 \times 10^{-4}) + 0.1 \times (6.2 \times 10^{-4})} = \sqrt{(8.2 + 6.2) \times 10^{-5}} = \sqrt{144 \times 10^{-6}}$$

$$\therefore pOH = -\log 0.012 \approx 1.92$$

$$\text{Now, } K_b = \frac{[OH^-][CH_3NH_3^+]}{[CH_3NH_2]} \Rightarrow 4.1 \times 10^{-4} = \frac{0.012}{0.2} [CH_3NH_3^+] \Rightarrow [CH_3NH_3^+] = \frac{41}{60} \times 10^{-2} M$$

$$\text{Again } \therefore, K_{b_1} = \frac{[OH^-][C_4H_{13}N_2^+]}{[C_4H_{12}N_2]} \Rightarrow 6.2 \times 10^{-4} = \frac{0.012}{0.1} [C_4H_{13}N_2^+] \Rightarrow [C_4H_{13}N_2^+] = \frac{31}{60} \times 10^{-2} M$$

$$\text{And } K_{b_2} = \frac{[OH^-][C_4H_{14}N_2^{2+}]}{[C_4H_{13}N_2^+]} \Rightarrow 2.25 \times 10^{-5} = \frac{0.012[C_4H_{14}N_2^{2+}]}{\frac{31}{60} \times 10^{-2}} \Rightarrow [C_4H_{14}N_2^{2+}] = \frac{1395}{144} \times 10^{-6} M$$

3. $[OH^-] = \frac{0.2}{2} = 0.1 M \Rightarrow pH = 14 - (-\log 0.1) = 13.$

$$K_{b_1} \times K_{b_2} = \frac{[OH^-]^2 [C_2N_2H_{10}^{2+}]}{[C_2N_2H_8]} \Rightarrow 8 \times 2.7 \times 10^{-13} = \frac{(0.1)^2 [C_2N_2H_{10}^{2+}]}{(0.5/2)}$$

$$\Rightarrow [C_2N_2H_{10}^{2+}] = \frac{8 \times 2.7 \times 10^{-13}}{4 \times 10^{-2}} M = 5.4 \times 10^{-11} M$$

4. $pH = \frac{1}{2}(14 - pK_{b_2} - \log 0.5) = 7 - 4.7 = 2.3.$

$$[BH^+] = [H^+] = 10^{-2.3} = 5 \times 10^{-3} M.$$

$$\frac{10^{-14} \times 10^{-14}}{2 \times 10^{-6} \times 10^{-10}} = \frac{(5 \times 10^{-3})^2 [B]}{0.5} \Rightarrow [B] = 10^{-8} M.$$

5. (i) $\frac{dx}{d(\Delta pH)} = \frac{2.303 (a-b)}{(a+b)} = \frac{2.303 \times 0.2 \times 0.2}{0.4} = 0.23$

(ii) $\frac{dx}{d(\Delta pH)} = \frac{2.303(0.4 \times 0.4)}{0.8} = 0.46$

6. For sodium butyrate

$$pH = 7 + \frac{1}{2} pK_a + \frac{1}{2} \log C = 7 + \left(\frac{5 - \log 1.5}{2} \right) + \frac{1}{2} \log (0.1) = 7 + 2.41 - 0.5 = 8.91$$

For Indicator

$$K_{In} = \frac{[H^+][In^-]}{[HIn]} \Rightarrow \frac{[In^-]}{[HIn]} = \frac{K_{In}}{[H^+]} = \frac{3.075 \times 10^{-10}}{10^{-8.91}} = 0.25$$



7. For this indicator, $\text{pH} = \text{pK}_{\text{In}} = 2$

Now, at $[\text{H}^+] = 4 \times 10^{-3} \text{ M}$,

$$K_{\text{In}} = \frac{(4 \times 10^{-3}) [\text{In}^-]}{[\text{HIn}]} \Rightarrow \frac{[\text{HIn}]}{[\text{In}^-]} = 0.4$$

$$\therefore \% \text{ of HIn} = \frac{[\text{HIn}]}{[\text{In}^-] + [\text{HIn}]} \times 100 = \frac{0.4}{1.4} \times 100 = \mathbf{28.57 \%}$$

8. $\therefore \text{pOH} = \text{pK}_{\text{eq}} + \log \frac{[\text{Acidic form}]}{[\text{Basic form}]} = \text{pK}_{\text{eq}} + \log \frac{[\text{Red}]}{[\text{Blue}]}$

$$(\text{pOH})_{\text{blue}} = \text{pK}_{\text{eq}} + \log \frac{b}{a} \quad \text{and} \quad (\text{pOH})_{\text{red}} = \text{pK}_{\text{eq}} + \log \frac{c}{d}$$

$$\text{So, range} = \text{pH}_{\text{blue}} \text{ to } \text{pH}_{\text{red}} = 14 - \text{pK}_{\text{eq}} - \log \frac{b}{a} \text{ to } 14 - \text{pK}_{\text{eq}} - \log \frac{c}{d}$$

9. $K_{\text{sp}} = [\text{Mg}^{2+}][\text{F}^-]^2$ & $K_{\text{a}} = \frac{[\text{H}^+][\text{F}^-]}{[\text{HF}]} \Rightarrow 3.5[\text{HF}] = [\text{F}^-]$

$$\text{Now, } \therefore [\text{F}^-] + [\text{HF}] = 2s \Rightarrow \frac{4.5}{3.5} [\text{F}^-] = 2s \quad \dots(1)$$

Since, $K_{\text{sp}} = s[\text{F}^-]^2$

$$\therefore \frac{9}{14} \times 10^{-8} = 4s^3 \times \left(\frac{3.5}{4.5}\right)^2 \quad \text{from (1)}$$

$$\left(\frac{9}{14}\right)^3 \times 10^{-9} \times 10 = s^3$$

$$\therefore s = 1.395 \times 10^{-3} \text{ mole/L}$$

$$\text{So, for } 1000 \text{ L : Moles} = s \times 10^3 = 1.395.$$

- 10(a). $\text{CuCO}_3 (\text{s}) + 4\text{NH}_3 \rightleftharpoons \text{CO}_3^{2-} + [\text{Cu}(\text{NH}_3)_4]^{2+}$; $K_{\text{f}} \times K_{\text{sp}} = 2.8 \times 10^3$

$$t = 0 \quad 0.1 \quad c \quad 0 \quad 0$$

$$t = \text{eq} \quad 0 \quad c-0.4 \quad 0.1 \quad 0.1$$

$$2.8 \times 10^3 = \frac{0.1 \times 0.1}{(c-0.4)^4} \Rightarrow c-0.4 = \sqrt[4]{\frac{1000}{2.8 \times 10^8}} = 0.044 \Rightarrow c = 0.444 \text{ M.}$$

- 10(b). For precipitation of MS, $K_{\text{sp}} \text{ of (MS)} = [\text{M}^{+2}] [\text{S}^{2-}] = 6 \times 10^{-21}$

$$\Rightarrow [\text{S}^{2-}]_{\text{req}} = \frac{100 \times 6 \times 10^{-21}}{5} = 120 \times 10^{-21} = 1.2 \times 10^{-19} \text{ M}$$

Precipitation of MS will start when H_2S will provide atleast $1.2 \times 10^{-19} \text{ M S}^{2-}$.

$$\text{For } \text{H}_2\text{S}, \quad \text{H}_2\text{S} \rightleftharpoons 2 \text{H}^+ + \text{S}^{2-} \quad ; \quad K = K_{\text{a1}}.K_{\text{a2}} = \frac{[\text{H}^+]^2 [\text{S}^{2-}]}{[\text{H}_2\text{S}]}$$

$$10^{-7} \times 1.2 \times 10^{-19} = \frac{[\text{H}^+]^2 \times 1.2 \times 10^{-19}}{0.1} \quad ; \quad [\text{H}^+]^2 = 10^{-2}$$

$$\text{So, } [\text{H}^+] = 0.1 \text{ M} \quad \therefore \text{pH} = 1$$

11. Ni^{2+} accepts a pair of electron and H_2O donates it. This an acid-base reaction.

12. It is definition of Levelling effect.



$$13. \quad K_a = \frac{[H^+][A^-]}{[HA]} = \frac{[H^+]^2}{[HA]} \quad (\because [H^+] = [A^-]) \quad \text{and} \quad K_b = \frac{[H^+][B^-]}{[HB]} = \frac{[H^+]^2}{[HB]} \quad (\because [H^+] = [B^-])$$

$$\text{Also } H^+ \text{ are same} \quad \therefore \frac{K_a}{K_b} = \frac{[HB]}{[HA]} = \frac{4}{1} \quad \frac{[HA]}{[HB]} = \frac{1}{4}$$

$$14. \quad \alpha = \sqrt{\frac{5 \times 10^{-5}}{10^{-4}}} > 0.1 \quad \text{So, } \frac{C\alpha^2}{1-\alpha} = K_b \Rightarrow 5 \times 10^{-5} = \frac{10^{-4}\alpha^2}{1-\alpha} \Rightarrow 2\alpha^2 + \alpha - 1 = 0 \Rightarrow \alpha = 0.5$$

$$\text{Hence, } [OH^-] = C\alpha = 5 \times 10^{-5} \quad \& \text{ (तथा) } pH = 9.7$$

$$15. \quad [OH^-] = \sqrt{K_{b1} \times C} = \sqrt{1.6 \times 10^{-5}} = 4 \times 10^{-3} M$$

$$K_{b1} \times K_{b2} = \frac{[OH^-]^2 [C_2H_{10}N_2^{2+}]}{[C_2N_2H_8]} \Rightarrow 8 \times 2.7 \times 10^{-13} = \frac{16 \times 10^{-3} [C_2H_{10}N_2^{2+}]}{0.2}$$

$$\therefore [C_2H_{10}N_2^{2+}] = 2.7 \times 10^{-8} M$$

$$16. (a) \quad [H^+] = 0.1 M \& pH = 1$$

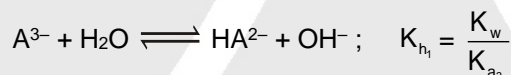
$$K_{a1} = \frac{0.1 [H_2PO_4^-]}{0.1} \Rightarrow [H_2PO_4^-] = K_{a1} \Rightarrow C\alpha = K_{a1} \Rightarrow \alpha = \frac{K_{a1}}{0.1} = 10 K_{a1}$$

$$K_{a2} = \frac{0.1 [HPO_4^{2-}]}{K_{a1}} \Rightarrow [HPO_4^{2-}] = K_{a1} \times K_{a2} \times 10$$

$$16. (b) \quad K_{a3} = \frac{0.1 [PO_4^{3-}]}{10 K_{a1} K_{a2} K_{a3}} \Rightarrow [PO_4^{3-}] = 100 K_{a1} K_{a2} K_{a3}$$

17. Factual

18.(a) & 18(b) :

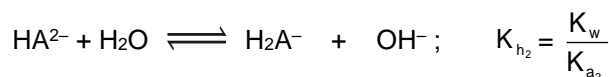


$$t = eq \quad c(1-h) \quad ch \quad ch$$

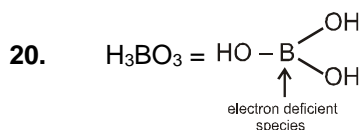
$$\frac{K_w}{K_{a3}} = \frac{ch^2}{1-h} \approx ch^2 \therefore h = \sqrt{\frac{K_w}{cK_{a3}}}$$

$$\therefore [OH^-] = [HA^{2-}] = ch = \sqrt{\frac{cK_w}{K_{a3}}}$$

$$\therefore [H^+] = \frac{K_w}{[OH^-]} = \sqrt{\frac{K_w K_{a3}}{c}} \& pH = \frac{1}{2} (pK_w + pK_{a3} + \log c)$$



19. According to Bronsted-Lowry concept, acid gives H^+ ion and base accept H^+ ion.

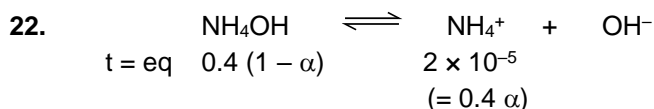


So it will behave as Lewis acid.



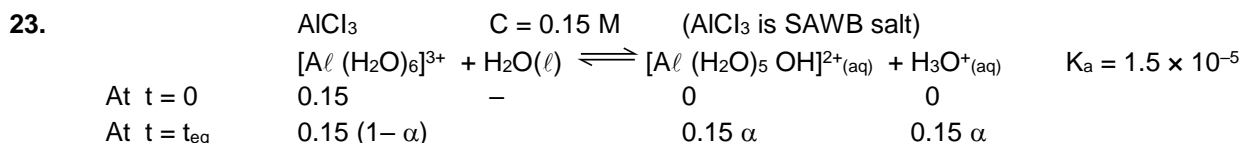
$$21. \quad 2 \times 10^{-4} = \frac{4 \times 10^{-3} \alpha^2}{1 - \alpha} \Rightarrow 20\alpha^2 + \alpha - 1 = 0 \Rightarrow \alpha = 0.2$$

$$\therefore [\text{OH}^-] = C\alpha = 8 \times 10^{-4} \text{ M} \Rightarrow \text{pOH} = 3.1$$



$$\text{So, } \alpha = 5 \times 10^{-5} (<< 1) \therefore 0.4(1 - \alpha) \approx 0.4$$

$$K_b = \frac{2 \times 10^{-5} \times [\text{OH}^-]}{0.4} = 1.8 \times 10^{-5} \Rightarrow [\text{OH}^-] = 0.36 \text{ M}$$

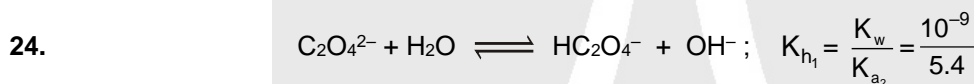


$$K_a = \frac{0.15\alpha \times 0.15\alpha}{0.15[1 - \alpha]} = 1.5 \times 10^{-5}$$

$$\Rightarrow 1.5 \times 10^{-1} \alpha^2 = 1.5 \times 10^{-5} \Rightarrow \alpha^2 = 10^{-4} \Rightarrow \alpha = 10^{-2}$$

$$[\text{H}_3\text{O}^+] = 0.15 \times 10^{-2} = 1.5 \times 10^{-3} \text{ M}$$

$$\Rightarrow \text{pH} = 3 - \log 1.5 = 3 - 0.18 = 2.82$$

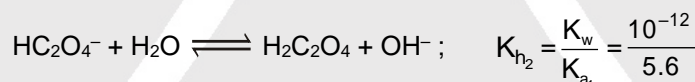


$$t = \text{eq} \quad 0.005(1 - h) \quad 0.005h \quad 0.005h$$

$$(\approx 0.005)$$

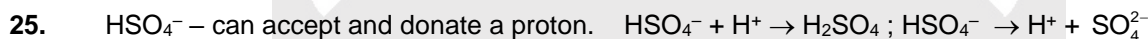
$$\frac{(0.005h)(0.005h)}{(0.005)} = \frac{10^{-9}}{5.4} \therefore h = 1.92 \times 10^{-4}$$

$$[\text{OH}^-] = 0.005h = 9.6 \times 10^{-7} \text{ M}$$



$$t = \text{eq} \quad \approx 9.6 \times 10^{-7} \quad \approx 9.6 \times 10^{-7}$$

$$\therefore [\text{H}_2\text{C}_2\text{O}_4] = K_{h_2} = \frac{5}{28} \times 10^{-12} \text{ M}$$



Note : Answer could also be NH_3 or OH^- .

26. We know that for acids at 25°C , pH must be less than 7.

27. When rain is accompanied by a thunderstorm,



$$28. \quad 6.31 = 6.61 + \log\left(\frac{M \times V}{100 \times 0.05}\right) \Rightarrow -0.3 = \log\left(\frac{MV}{5}\right)$$

$$\Rightarrow \frac{1}{2} = \frac{MV}{5} \Rightarrow 0.1V = \frac{5}{2} \Rightarrow V = 25 \text{ mL}$$

29. It is factual.



30. End points of both titrations will lie in acidic range.
31. $pK_{HIn} = 5$
 (a) $CH_3COOH + NaOH$, end point $pH > 7$ (b) Aniline hydrochloride + $NaOH$, end point $pH > 7$
 (c) $NaHCO_3 + HCl$, end point $pH < 7$ (d) $Ba(OH)_2 + H_2C_2O_4$, end point $pH > 7$
32. WA Vs SB end point > 7 Phenolphthalein
33. $NH_4Br \longrightarrow$ Salt of SA WB
 $pH = 7 - \frac{1}{2}pK_b - \frac{1}{2}\log C = 7 - \frac{4.74}{2} - \frac{1}{2}\log 10^{-1} = 7 - 2.37 + \frac{1}{2} = 5.13$
34. $pH = pK_a + \log \frac{[Ionised]}{[un\ Ionised]} \Rightarrow 6 = 5 + \log \frac{[Ionised]}{[un\ Ionised]} \Rightarrow 1 = \log \frac{[Ionised]}{[un\ Ionised]}$
 $\frac{[Ionised]}{[un\ Ionised]} = 10 \Rightarrow \frac{[Ionised]}{[Ionised] + [un\ Ionised]} = \left[\frac{10}{11} \right]$
35. $H_3PO_4 + NaOH \longrightarrow NaH_2PO_4$

9	5	0
4	0	5

 $pH = pK_a + \log \frac{5}{4} = 3 + 0.1 = 3.1$
36. Maximum buffer capacity of a solution is given by, buffer capacity $= 2.303 \left(\frac{ab}{a+b} \right)$. Hence the result.
 and $a = b = 0.5$, $BC = 2.303 \times \frac{(0.5)^2}{1} = 0.57$
37. $pK_a = 5.45$
 $pH = pK_{HIn} + \log \frac{[Base\ form]}{[Acid\ form]} \Rightarrow pH = pK_{HIn} = 5.45$
 For a Buffer solution
 $pH = pK_a + \log \frac{[CH_3COONa]}{[CH_3COOH]} \Rightarrow 5.45 = 4.75 + \log \frac{[CH_3COONa]}{[CH_3COOH]}$
 $0.7 = \log \frac{[CH_3COONa]}{[CH_3COOH]} \Rightarrow \frac{5}{1} = \frac{[CH_3COONa]}{[CH_3COOH]}$
38. The end points of all the titrations will lie in acidic range.
39. $CO_3^{2-} + H^+ \longrightarrow HCO_3^-$

Initial milli-moles	50×0.05	40×0.1	—
Final milli-moles	—	1.5	2.5

 $HCO_3^- + H^+ \longrightarrow H_2CO_3$

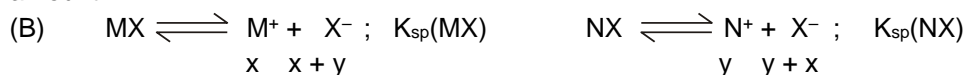
Initial milli-moles	2.5	1.5	—
Final milli-moles	1	—	1.5

 $pH = pK_{a_1} + \log \frac{[HCO_3^-]}{[H_2CO_3]} = 6.173$





40. (A) As both salts are sparingly soluble, due to common ion effect, both will be precipitated in some amount.



$$K_{sp}(MX) + K_{sp}(NX) = (x+y)^2$$

$$\Rightarrow \sqrt{K_{sp}(MX)} \approx x+y = [X^-] \dots (1) \quad (\because K_{sp}(MX) \gg K_{sp}(NX))$$

$$(C) \quad (y+x)y = K_{sp}(NX) \Rightarrow y = [N^+] \approx \frac{K_{sp}(NX)}{\sqrt{K_{sp}(MX)}} \dots (2)$$

$$\text{Similarly, } [M^+] = x \approx \frac{K_{sp}(MX)}{\sqrt{K_{sp}(MX)}} \dots (3)$$

From (2) & (3) : $[M^+] \gg [N^+]$

41. Solubility of $\text{CaCO}_3 = \left[\frac{7 \times 10^{-3}}{100} \right] \text{ mole/L} = 7 \times 10^{-5} \text{ mole/L} = s$

$$K_{sp} \text{ of } \text{CaCO}_3 = s^2 = 49 \times 10^{-10}.$$

When $[\text{Ba}^{+2}]$ is 90% precipitated, then only CaCO_3 starts precipitation.

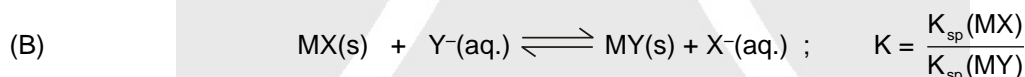
If original solution contain 'a' mole/L of Ca^{+2} & Ba^{+2} , then for CaCO_3 precipitation,

$$[\text{Ca}^{+2}][\text{CO}_3^{2-}] = 49 \times 10^{-10}, \quad [\text{CO}_3^{2-}] = \left[\frac{49 \times 10^{-10}}{a} \right] \text{ M.}$$

$$\text{Now for } \text{BaCO}_3, K_{sp} = [\text{Ba}^{+2}][\text{CO}_3^{2-}] = \frac{a \times 10}{100} \times \frac{49 \times 10^{-10}}{a} = 4.9 \times 10^{-10}. (\because 90\% \text{ Ba}^{2+} \text{ has precipitated,})$$

$$\text{so } [\text{Ba}^{+2}] = \frac{a \times 10}{100} \text{ M)}$$

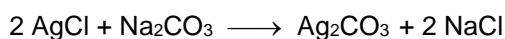
42. (A) As long as a solid-aqueous equilibrium exists, a salt solution is saturated.



$$\begin{array}{ccccc} t = 0 & n & \frac{nx}{100} & 0 & 0 \\ t = \text{eq} & n - \frac{nx}{100} & y & \frac{nx}{100} & \frac{nx}{100} = [X^-] \end{array}$$

$$(C) \quad \frac{K_{sp}(\text{MX})}{K_{sp}(\text{MY})} = \frac{[X^-][M^+]}{[Y^-][M^+]} \Rightarrow [Y^-] = \frac{K_{sp}(\text{MY})}{K_{sp}(\text{MX})} \times [X^-] = \frac{K_{sp}(\text{MY})}{K_{sp}(\text{MX})} \times \frac{nx}{100}.$$

43. The concerned chemical reaction is :



Calculation of $[\text{Ag}^+]$ left in the solution :

$$K_{sp}(\text{Ag}_2\text{CO}_3) = [\text{Ag}^+][\text{CO}_3^{2-}]$$

$$[\text{Ag}^+] = \sqrt{\frac{8.1 \times 10^{-12}}{1.6}} = 2.25 \times 10^{-6} \text{ M}$$

$$\text{Concentration of } \text{Cl}^- \text{ left} = 0.00284 \text{ g/L} = \frac{0.00284}{35.5} \text{ mol/L} = 8 \times 10^{-5} \text{ M}$$

$$\therefore K_{sp}(\text{AgCl}) = [\text{Ag}^+][\text{Cl}^-] = (2.25 \times 10^{-6})(8 \times 10^{-5}) = 1.8 \times 10^{-10}.$$



44. Suppose V mL of solution contains 0.1 M Mg^{2+} and 0.8 M NH_4Cl
 Now, V mL of 'a' M NH_3 is added, which just gives precipitate of $\text{Mg}(\text{OH})_2$. Then :
 $[\text{Mg}^{2+}][\text{OH}^-]^2 = K_{\text{sp}} \text{Mg}(\text{OH})_2$
 $\left[\frac{0.1V}{2V}\right][\text{OH}^-]^2 = 1.62 \times 10^{-11} \quad \left([\text{Mg}^{2+}] = \frac{\text{Millimole}}{\text{Total volume in mL}}\right)$
 $\therefore [\text{OH}^-] = 1.8 \times 10^{-5} \text{ M}$
 Now, if the $[\text{OH}^-] = 1.8 \times 10^{-5} \text{ M}$, on addition of NH_3 in NH_4Cl , then $\text{Mg}(\text{OH})_2$ will precipitate. For buffer solution of NH_3 and NH_4Cl :
 $[\text{OH}^-] = K_b \times \frac{[\text{NH}_3]}{[\text{NH}_4^+]}$
 $1.8 \times 10^{-5} = 1.8 \times 10^{-5} \times \frac{(0.8 \times V)/2V}{(a \times V)/2V}$
 $\therefore a = 0.8 \text{ M}.$
45. (A) $S_{\text{pH} = 2} = \frac{10^{-38}}{(10^{-12})^3} = 10^{-2} \text{ M}$ (B) $S_{\text{pH} = 11} = \frac{10^{-38}}{(10^{-3})^3} = 10^{-29} \text{ M}$
46. For FeS and MnS not to be precipitated from a solution of Fe^{2+} and Mn^{2+} , $\text{IP}_{\text{FeS}} < K_{\text{sp}}(\text{FeS})$
 $[\text{Fe}^{2+}][\text{S}^{2-}] < K_{\text{sp}} \text{ of FeS}$
 $[10^{-2}][\text{S}^{2-}] < 6.4 \times 10^{-18} \therefore [\text{S}^{2-}] < 6.4 \times 10^{-16} \text{ M}$
 So, at $[\text{S}^{2-}] = 6.4 \times 10^{-16} \text{ M}$ or less, no precipitation of FeS and MnS will occur.
 $\text{H}_2\text{S} \rightleftharpoons 2\text{H}^+ + \text{S}^{2-}$
 $\therefore [\text{H}^+]^2 [\text{S}^{2-}] = K_{\text{a}(\text{H}_2\text{S})} \times [\text{H}_2\text{S}] = 9.6 \times 10^{-22}$
 $\therefore [\text{H}^+]_{\text{min}}^2 [6.4 \times 10^{-16}] = 9.6 \times 10^{-22}$
 $[\text{H}^+]_{\text{min}}^2 = 3/2 \times 10^{-6} \therefore [\text{H}^+]_{\text{min}} = \sqrt{\frac{3}{2}} \times 10^{-3} \text{ M}$
 Thus, if $[\text{H}^+] = \sqrt{\frac{3}{2}} \times 10^{-3} \text{ M}$ or more, the precipitation of FeS and MnS will not take place.
 Therefore, $\text{pH}_{(\text{max.})} = 3 - \frac{1}{2} \log \frac{3}{2} = 2.91 \text{ Ans.}$
47. For FeS and MnS to be precipitated from a solution of Fe^{2+} and Mn^{2+} , $\text{IP}_{\text{MnS}} > K_{\text{sp}}(\text{MnS})$
 $[\text{Mn}^{2+}][\text{S}^{2-}] > K_{\text{sp}} \text{ of MnS}$
 $[10^{-2}][\text{S}^{2-}] > 2.5 \times 10^{-13} \therefore [\text{S}^{2-}] > 2.5 \times 10^{-11} \text{ M}$
 So, at $[\text{S}^{2-}] = 2.5 \times 10^{-11} \text{ M}$ or more, precipitation of FeS and MnS will occur.
 $\text{H}_2\text{S} \rightleftharpoons 2\text{H}^+ + \text{S}^{2-}$
 $\therefore [\text{H}^+]^2 [\text{S}^{2-}] = K_{\text{a}(\text{H}_2\text{S})} \times [\text{H}_2\text{S}] = 9.6 \times 10^{-22}$
 $\therefore [\text{H}^+]_{\text{max}}^2 [2.5 \times 10^{-11}] = 9.6 \times 10^{-22}$
 $[\text{H}^+]_{\text{max}}^2 = 3.84 \times 10^{-11} \therefore [\text{H}^+]_{\text{max}} = 8 \sqrt{\frac{3}{5}} \times 10^{-6} \text{ M}$
 Thus, if $[\text{H}^+] = 8 \sqrt{\frac{3}{5}} \times 10^{-6} \text{ M}$ or less, the precipitation of FeS and MnS will take place.
 Therefore, $\text{pH}_{(\text{min.})} = 6 - \frac{1}{2} \log \frac{192}{5} = 5.21 \text{ Ans.}$





$$48. \quad 9.6 \times 10^{-21} = \frac{(0.1)^2[S^{2-}]}{(0.1)} \Rightarrow [S^{2-}] = 9.6 \times 10^{-20} \text{ M}$$

$$9.6 \times 10^{-20}[\text{Cu}^{2+}]_{\min} = 6.4 \times 10^{-36} \Rightarrow [\text{Cu}^{2+}]_{\min} = \frac{2}{3} \times 10^{-16}$$

49(a). Dissolved $\text{Al}(\text{OH})_3$ present in solution as $\text{Al}^{3+}(\text{aq})$ as well as $\text{Al}(\text{OH})_4^- (\text{aq})$

$$\therefore S = [\text{Al}^{3+}(\text{aq})] + [\text{Al}(\text{OH})_4^-(\text{aq})]$$

$$S = \frac{K_{\text{sp}}}{[\text{OH}^-]^3} + K_c[\text{OH}^-]$$

$$\text{for minimum solubility : } \frac{dS}{d(\text{OH}^-)} = 0$$

$$\text{or } -\frac{K_{\text{sp}} \times 3}{[\text{OH}^-]^4} + K_c = 0$$

$$[\text{OH}^-] = \left(\frac{3K_{\text{sp}}}{K_c} \right)^{1/4}$$

49(b). Order of solubility : Complex formation > Pure water > Common ion effect.

AgBr form complex $[\text{Ag}(\text{NH}_3)_2]^+$ in NH_3 , so solubility is maximum in $\text{NH}_3(\text{aq})$.

49(c). In acidic medium, it behaves as a base & in basic medium, it behaves as an acid (accepting OH^-), driving the equilibrium forward in both cases.

50. (A) $[\text{H}^+]$ in HCl solution = 10^{-5} M

$$[\text{H}^+] \text{ in } \text{H}_2\text{S} \text{ solution} = \sqrt{K_a \times C} = 10^{-4} \text{ M}$$

so $[\text{H}^+]$ in HCl solution < $[\text{H}^+]$ in H_2S solution

& $[\text{OH}^-]$ in HCl solution > $[\text{OH}^-]$ in H_2S solution

& degree of dissociation of water in HCl solution > degree of dissociation of water in H_2S solution
pH of HCl solution > pH of H_2S solution.

(B) At pH = 4.74 in CH_3COOH solution, $[\text{CH}_3\text{COO}^-] = [\text{CH}_3\text{COOH}]$

$$\therefore \text{degree of dissociation of } \text{CH}_3\text{COOH} = \frac{1}{2}$$

At pH = 9.26 i.e. pOH = 4.74 in $\text{NH}_3 \cdot \text{H}_2\text{O}$ solution, $[\text{NH}_4^+] = [\text{NH}_3 \cdot \text{H}_2\text{O}]$

\therefore degree of dissociation of CH_3COOH = degree of dissociation of $\text{NH}_3 \cdot \text{H}_2\text{O}$

degree of dissociation of water in CH_3COOH solution > degree of dissociation of water in $\text{NH}_3 \cdot \text{H}_2\text{O}$ solution.

$$(C) \quad [\text{H}^+] \text{ in } \text{CH}_3\text{COOH} \text{ solution} = \sqrt{1.8 \times 10^{-5} \times 0.1} = \sqrt{1.8} \times 10^{-3} \text{ M}$$

$$[\text{H}^+] \text{ in } \text{HCOOH} \text{ solution} = \sqrt{1.8 \times 10^{-4} \times 1} = \sqrt{1.8} \times 10^{-2} \text{ M}$$

so, degree of dissociation of CH_3COOH = degree dissociation of HCOOH .

$$(D) \quad [\text{H}^+] \text{ in } \text{HA}_1 \text{ solution} = \sqrt{10^{-5} \times 0.1} = 10^{-3} \text{ M}$$

$$[\text{H}^+] \text{ in } \text{HA}_2 \text{ solution} = \sqrt{10^{-6} \times 0.01} = 10^{-4} \text{ M}$$

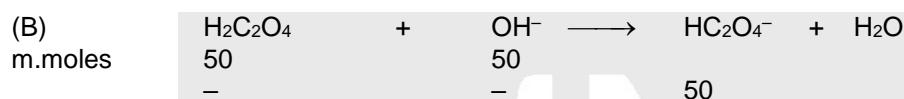
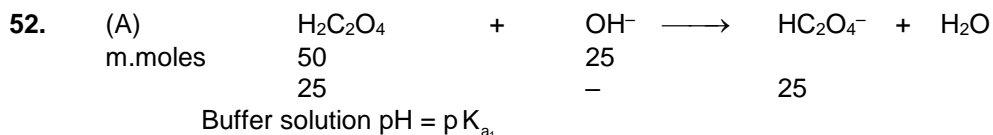
so $[\text{OH}^-]$ in solution of HA_1 < $[\text{OH}^-]$ in solution of HA_2

pH in solution of HA_1 < pH in solution of HA_2

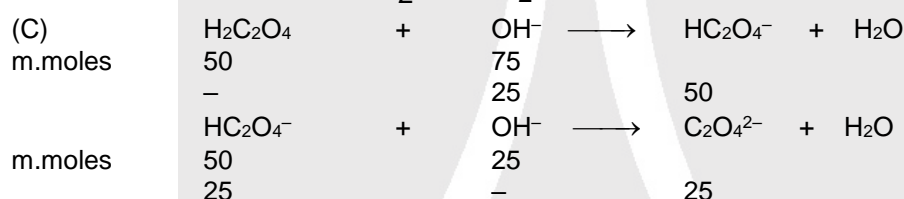
& degree of dissociation of water HA_1 < degree of dissociation of water HA_2 .



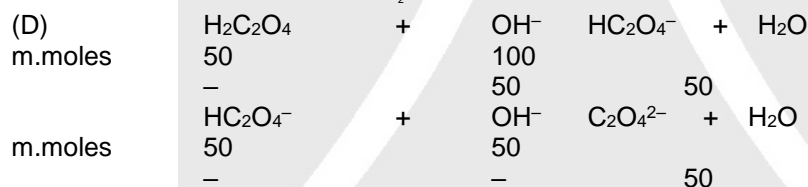
51. (A) $[H^+] = \frac{5 \times 0.08 - 10 \times 0.015 \times 2}{500} = 2 \times 10^{-4} \text{ M} \therefore \text{pH} = 3.7$
- (B) For salt CH_3COONa : $\text{pH} = \frac{1}{2} \left(14 + 4.74 + \log \left(\frac{15}{150} \right) \right) = 8.87$
- (C) For RNH_2 : $\text{pOH} = \frac{1}{2} (\text{p}K_b - \log 0.25)$ & $K_h = \frac{K_w}{K_b} \therefore K_b = 10^{-5}$
 $\text{pOH} = 2.8 \therefore \text{pH} = 11.2$
- (D) For NaH_2A : $\text{pH} = \frac{\text{p}K_{a_2} + \text{p}K_{a_1}}{2} = \frac{4+7}{2} = 5.5$



Amphiprotic, $\text{pH} = \frac{\text{p}K_{a_1} + \text{p}K_{a_2}}{2} = \frac{13}{2} = 6.5$.



Buffer solution $\text{pH} = \text{p}K_{a_2}$.



Salt hydrolysis, $\text{pH} > 7$.

54. (p) $1.794 \times 10^{-11} = [\text{Mg}^{2+}] (0.36)^2 \Rightarrow [\text{Mg}^{2+}] = 1.38 \times 10^{-10} \text{ M}$.
- (q) $[\text{Hg}_2^{2+}] [\text{Cl}^-]^2 = K_{sp} \Rightarrow s(2 \times 0.18)^2 = 1.296 \times 10^{-18} \Rightarrow s = 10^{-17} \text{ M}$.
- (r) $[\text{Ca}^{2+}] = \sqrt{K_{sp_1} + K_{sp_2}} = \sqrt{(2.6 \times 10^{-9}) + (3.8 \times 10^{-9})} = 8 \times 10^{-5} \text{ M}$. (simultaneous solubility)
- (s) $s = \frac{10^{-38}}{(10^{-7})^3} = 10^{-17} \text{ M}$
 (neglecting OH^- coming from $\text{Fe}(\text{OH})_3$ in terms of those coming from water).
- (t)
- | | | | | | | | |
|---------|---------------|---|----------------|----------------------|------------------------------|--|---|
| | Ag^+ | + | 2CN^- | \rightleftharpoons | $[\text{Ag}(\text{CN})_2]^-$ | | $K_f = 2.5 \times 10^{18}$ |
| t = 0 | 0.03 | | 0.1 | | 0 | | |
| t = eq. | x | | 0.04 | | 0.03 | | (Assuming nearly all Ag^+ ions to form complex K_f very large) |
- (≈ 0)

(Upon mixing equal volumes, volume gets doubled. So initial concentrations get halved).

$$2.5 \times 10^{18} = \frac{0.03}{x(0.04)^2} \Rightarrow x = 7.5 \times 10^{-18} \text{ M}$$

55. $\text{H}_3\text{PO}_4 = 3$, $\text{H}_3\text{BO}_3 = 1$, $\text{H}_3\text{PO}_2 = 1$, rest diprotic



56. $x = 1, 2, 3, 4, 5, 6, 8, 9, 10, 11, 12, 13, 14$
There are 13 possible values.

57. $K_b(\text{NH}_3) = 1.8 \times 10^{-5}$
 $\text{CH}_3\text{COOCH}_3(\text{aq}) + 2\text{H}_2\text{O}(\text{aq}) \longrightarrow \text{CH}_3\text{COO}^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq}) + \text{CH}_3\text{OH}(\text{aq})$
 $[\text{NH}_4^+]_0 = 0.1 \text{ M}, [\text{NH}_3] = 0.06 \text{ M}, [\text{CH}_3\text{COOCH}_3]_0 = 0.02 \text{ M}$

$$\text{pOH} = \text{p}K_b + \log \frac{[\text{NH}_4^+]}{[\text{NH}_3]} = 4.74 + \log \left(\frac{0.1}{0.06} \right)$$

$$(\text{pOH})_{\text{initial}} = 4.74 + 0.22 = 4.96 \quad \therefore (\text{pH})_{\text{initial}} = 9.04$$

$$\text{NH}_3(\text{aq}) + \text{H}^+(\text{aq}) \longrightarrow \text{NH}_4^+(\text{aq})$$

0.06	0.02	0.1	mole
0.04	–	0.12	mole

$$(\text{pOH})_{\text{final}} = 4.74 + \log \frac{0.12}{0.04} = 4.74 + \log \left(\frac{0.12}{0.04} \right) = 4.74 + \log 3 = 4.74 + 0.48 = 5.22$$

$$\therefore (\text{pH})_{\text{final}} = 8.78$$

$$\Delta \text{pH} = 9.04 - 8.78 = 0.26$$

Yes this is satisfactory buffer.

58. $\text{H}_3\text{PO}_4 = \frac{0.98}{98} = 10^{-2} \text{ Mole} \Rightarrow [\text{H}_3\text{PO}_4] = \frac{10^{-2}}{100} \times 10^3 = 0.1 \text{ M}$
 $\text{pH} = 5 \quad [\text{H}^+] = 10^{-5}$
 $\text{H}_3\text{PO}_4 \text{ \& } \text{H}_2\text{PO}_4^-$

$$\text{pH} = \text{p}K_{a1} + \log \frac{[\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{PO}_4]} \Rightarrow 5 = 3 + \log \frac{[\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{PO}_4]} \Rightarrow 10^2 = \frac{[\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{PO}_4]}$$

$$[\text{H}_2\text{PO}_4^-] = 10^2 [\text{H}_3\text{PO}_4] \Rightarrow \text{But } [\text{H}_3\text{PO}_4] + [\text{H}_2\text{PO}_4^-] = 0.1$$

$$\text{H}_3\text{PO}_4 + 10^2 [\text{H}_3\text{PO}_4] = 0.1 \Rightarrow [1 + 10^2] [\text{H}_3\text{PO}_4] = 0.1$$

$$[\text{H}_3\text{PO}_4] = 10^{-3} \text{ M} \Rightarrow [\text{H}_2\text{PO}_4^-] = 0.1 \text{ M}$$

For $\text{H}_2\text{PO}_4^- \text{ \& } \text{HPO}_4^{2-}$ $\Rightarrow \text{pH} = \text{p}K_{a2} + \log \frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]}$

$$5 = 8 + \log \frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} \Rightarrow -3 = \log \frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]}$$

$$\frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} = 10^{-3} \Rightarrow [\text{HPO}_4^{2-}] = 10^{-3} [\text{H}_2\text{PO}_4^-]$$

$$[\text{H}_2\text{PO}_4^-] + [\text{HPO}_4^{2-}] = 0.1 \Rightarrow [\text{H}_2\text{PO}_4^-] + 10^{-3} [\text{H}_2\text{PO}_4^-] = 0.1$$

$$[1 + 10^{-3}] [\text{H}_2\text{PO}_4^-] = 0.1 \Rightarrow [\text{H}_2\text{PO}_4^-] = 0.1 \text{ M} \Rightarrow [\text{HPO}_4^{2-}] = 10^{-4} \text{ M}$$

Again

$$\text{pH} = \text{p}K_{a3} + \log \frac{[\text{PO}_4^{3-}]}{[\text{HPO}_4^{2-}]} \Rightarrow 5 = 12 + \log \frac{[\text{PO}_4^{3-}]}{[\text{HPO}_4^{2-}]}$$

$$10^{-7} = \frac{[\text{PO}_4^{3-}]}{[\text{HPO}_4^{2-}]} \Rightarrow [\text{PO}_4^{3-}] = 10^{-7} [\text{HPO}_4^{2-}]$$

$$[\text{HPO}_4^{2-}] + [\text{PO}_4^{3-}] = 10^{-4} \Rightarrow [1 + 10^{-7}] [\text{HPO}_4^{2-}] = 10^{-4}$$

$$[\text{PO}_4^{3-}] = 10^{-7} \Rightarrow [\text{HPO}_4^{2-}] = 10^{-11} \text{ M}$$

$$\text{pC}_1 + \text{pC}_2 + \text{pC}_3 + \text{pC}_4 = 11 + 4 + 1 + 3 = 19$$

59. (i), (ii) & (vii) are not matched with suitable indicators as the end point of these titrations doesn't lie within the pH range of the indicator





60. Na_2HPO_4 , Na_2S , $\text{K}_2\text{C}_2\text{O}_4$, K_2CO_3 , Ethylene diamine

61. $\text{H}_2\text{CO}_3 + \text{KOH} \longrightarrow \text{KHCO}_3 + \text{H}_2\text{O}$ $V_{\text{KOH}} = 50 \text{ mL}$ needed
 0.2 M, 50 mL
 $\text{KOHCO}_3 + \text{KOH} \longrightarrow \text{K}_2\text{CO}_3 + \text{H}_2\text{O}$ $V_{\text{KOH}} = 25 \text{ mL}$ needed for mid point
 pH = 10.7 is is mid titration point of IInd reaction as pH = pK_{a_2} so it is possible at $V_{\text{KOH}} = 75 \text{ mL}$.

62.

	$\text{Ag}_2\text{CO}_3 + \text{K}_2\text{C}_2\text{O}_4 \rightleftharpoons \text{Ag}_2\text{C}_2\text{O}_4 + \text{K}_2\text{CO}_3$
Mole at start	Excess 0.1520 0 0
Mole after reaction	0.1520 - 0.0358 0.0358 0.0358
	= 0.1162

Molar concentration of $\text{K}_2\text{C}_2\text{O}_4$ or $\text{C}_2\text{O}_4^{2-}$ left unreacted = $\frac{0.1162}{0.5} = 0.2324 \text{ moles l}^{-1}$

$[\text{K}_2\text{CO}_3] = [\text{CO}_3^{2-}]$ at equilibrium = $\frac{0.0358}{0.5} = 0.07156 \text{ moles l}^{-1}$

Given that K_{sp} for $\text{Ag}_2\text{C}_2\text{O}_4 = 1.29 \times 10^{-11} \text{ mol}^3 \text{ l}^{-3}$ at 25°C

So $[\text{Ag}^+]^2 [\text{C}_2\text{O}_4^{2-}] = 1.29 \times 10^{-11}$
 or $[\text{Ag}^+]^2 \times 0.2324 = 1.29 \times 10^{-11}$

Hence $[\text{Ag}^+]^2 = \frac{1.29}{0.2324} \times 10^{-11}$

Then K_{sp} for $\text{Ag}_2\text{CO}_3 = [\text{Ag}^+]^2 [\text{CO}_3^{2-}] = \frac{1.29 \times 10^{-11}}{0.2324} \times 0.0716 = 3.794 \times 10^{-12} \text{ mol}^3 \text{ l}^{-3}$

63. $K_{\text{sp}} = \frac{S^2}{1 + \frac{[\text{H}^+]}{K_{a_2}} + \frac{[\text{H}^+]^2}{K_{a_1} \cdot K_{a_2}}}$

$$7.5 \times 10^{-14} = \frac{S^2}{1 + \frac{10^{-3}}{5.5 \times 10^{-11}} + \frac{10^{-6}}{25 \times 10^{-18}}}$$

$$7.5 \times 10^{-14} = \frac{S^2}{1 + \frac{10^8}{5.5} + \frac{10^{12}}{25}}$$

$$7.5 \times 10^{-14} = \frac{25 \times S^2}{10^{12}}$$

$$S^2 = 0.3 \times 10^{-14} \times 10^{12}$$

$$S^2 = 0.003$$

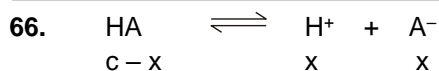
$$S = 0.055 \text{ M}$$

64.

	$\text{Cd}^{2+} + \text{H}_2\text{S} \longrightarrow \text{CdS} \downarrow + 2\text{H}^+$
m.moles	0.1 0.2

Total m.moles of H^+ in solution after the reaction = $0.2 + 0.8 = 1$

$\therefore [\text{H}^+] = \frac{1}{100} = 0.01 \text{ M} \Rightarrow \text{pH} = 2.$



$$[\text{H}^+] = x = 1.5 \times 10^{-3} \text{ M}$$

$$K_a = \frac{x^2}{c - x}$$

$$2.5 \times 10^{-3} = \frac{(1.5 \times 10^{-3})^2}{c - 1.5 \times 10^{-3}}$$

$$C = 2.4 \times 10^{-3} \text{ M.}$$

67. Initial: $8 \times 10^{-5} = \frac{1.6 \times 10^{-3} \alpha^2}{1 - \alpha} \Rightarrow \alpha = \frac{1}{5}$

$$\therefore [\text{OH}^-] = 3.2 \times 10^{-4} \Rightarrow \text{pH} = 10.5$$

$$8 \times 10^{-5} \times 2.7 \times 10^{-8} = \frac{(3.2 \times 10^{-4})^2 [\text{C}_2\text{N}_2\text{H}_{10}^{2+}]_i}{1.28 \times 10^{-3}}$$

$$\Rightarrow 2.7 \times 10^{-8} = [\text{C}_2\text{N}_2\text{H}_{10}^{2+}]_i$$

Final $\text{pH} = 11$; $8 \times 10^{-5} = 10^{-3} \times \alpha \Rightarrow \alpha = 0.08$
 $[\text{C}_2\text{N}_2\text{H}_9^+] = 1.28 \times 10^{-4}$

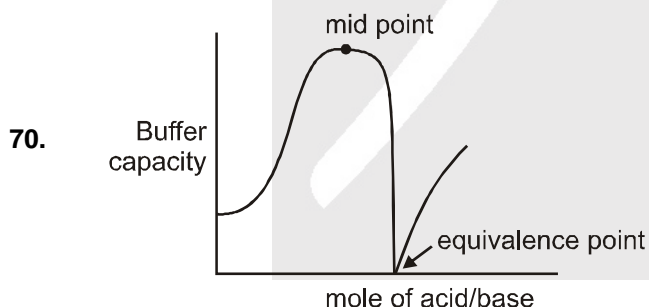
$$2.7 \times 8 \times 10^{-13} = \frac{(10^{-6}) [\text{C}_2\text{N}_2\text{H}_{10}^{2+}]_f}{1.6 \times 10^{-3}} \Rightarrow [\text{C}_2\text{N}_2\text{H}_{10}^{2+}]_f = 1.28 \times 2.7 \times 10^{-9} \text{ M}$$

So, (A), (B) and (D) are correct but $\frac{[\text{C}_2\text{N}_2\text{H}_{10}^{2+}]_i}{[\text{C}_2\text{N}_2\text{H}_{10}^{2+}]_f} = \frac{1}{0.128}$

68. Order of basic strength $\text{O}^{2-} > \text{S}^{2-} > \text{Se}^{2-} > \text{Te}^{2-}$

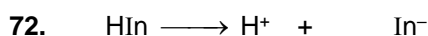
69. $1.2 \times 10^{-7} = \frac{7.2 \times 10^{-2} \alpha^2}{1 - \alpha} \Rightarrow 6\alpha^2 + \alpha - 1 = 0 \Rightarrow \alpha = \frac{1}{3}$

So, $\text{pH} = -\log \frac{0.072}{3} = 1.62$



When conc. of base or acid increases buffer capacity increases.

71. Facutal



$$K_{\text{In}} = \frac{[\text{H}^+][\text{In}^-]}{[\text{HIn}]} \Rightarrow \frac{[\text{In}^-]}{[\text{HIn}]} = \frac{K_{\text{In}}}{[\text{H}^+]} = \frac{10^{-9}}{10^{-9.6}} = 10^{0.6} = 4$$

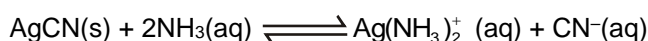
$$\therefore \% \text{ of } [\text{In}^-] \text{ in solution} = \frac{4}{5} \times 100 = 80\%$$

so pink colour will be visible.



$$K_1 = 1.6 \times 10^{-10} \times 10^7 = 1.6 \times 10^{-3}$$

$$= \frac{[\text{Ag}(\text{NH}_3)_2^+][\text{Cl}^-]}{[\text{NH}_3]^2}$$



$$K_2 = 2.5 \times 10^{-16} \times 10^7 = 2.5 \times 10^{-9}$$

$$\frac{[\text{Cl}^-]}{[\text{CN}^-]} = \frac{1.6 \times 10^{-3}}{2.5 \times 10^{-9}} = 6.4 \times 10^5$$

$$K_1 = \frac{x^2}{(1-2x)^2} \Rightarrow \frac{x}{1-2x} = 0.04$$

$$x = 0.037$$

$$\therefore [\text{CN}^-] = \frac{0.037}{6.4 \times 10^5} = 5.78 \times 10^{-8} \text{ M}$$

PART - IV

1. Upon adding two of the above solutions to an original solution, pH increase in both cases can take place only if original solution is of HCl (since NaCl solution addition will cause its dilution, thus increasing its pH while NaOH solution addition will cause its neutralization, thus increasing its pH upto 7). Further, pH of NaOH solution will decrease upon addition of NaCl solution (because of dilution). So, solutions I, II and III contain HCl, NaCl and NaOH respectively.
 $\text{HCl} + \text{NaOH} \longrightarrow \text{NaCl} + \text{H}_2\text{O}$
 Only HCl and NaOH solutions can be used as standard solutions in an acid-base titration.

2.
$$\begin{array}{ccccccc} \text{RNH}_2 & + & \text{H}_2\text{O} & \rightleftharpoons & \text{RNH}_3^+ & + & \text{OH}^- \\ t = \text{eq} & 0.01(1-\alpha) & & & 0.01\alpha & & 0.01\alpha + 10^{-4} \\ & 0.01 & \alpha & (0.01 & \alpha + 10^{-4}) & & \\ & 0.01 & (1-\alpha) & & & & \end{array} = 2 \times 10^{-6}$$

 $\therefore \alpha \approx 0.01$
 $\therefore [\text{OH}^-] = 0.01(0.01) + 10^{-4}$
 $= 2 \times 10^{-4} \text{ M.}$

3.
$$\begin{array}{ccccccc} \text{PuO}_2^{2+} & + & \text{H}_2\text{O} & \rightleftharpoons & \text{PuO}_2(\text{OH})^+ & + & \text{H}^+ \\ t = 0 & 0.01 & & & 0 & & 0 \\ t = \text{eq} & 0.01(1-h) & & & 0.01 h & & 0.01 h \\ & & & & & & (=10^{-4}) \end{array}$$

Therefore, $h = 0.01 = 1\%$. So, $1-h \approx 1$.

$$K_b \text{ of } \text{PuO}_2(\text{OH})^+ = \frac{[\text{PuO}_2^{2+}][\text{OH}^-]}{[\text{PuO}_2(\text{OH})^+]} = \frac{0.01 \times 10^{-10}}{0.01 h} = \frac{10^{-10}}{0.01} = 10^{-8}.$$

Hydrolysis is expected to be endothermic because it is reverse of neutralization (exothermic process).

4. $\text{pOH}_i = \text{pK}_b + \log_{10} \frac{[\text{NH}_4^+]_i}{[\text{NH}_4\text{OH}]_i} = 4.7$. Therefore, $\text{pH}_i = 9.3$.
 and $\text{pOH}_f = \text{pK}_b + \log_{10} \left(\frac{90 \times 0.1 + 10 \times 0.1}{90 \times 0.1 - 10 \times 0.1} \right) = 4.7 + \log \frac{5}{4} = 4.8$. Therefore, $\text{pH}_f = 9.2$
 $\% \text{ decrease} = \frac{9.3 - 9.2}{9.3} \times 100 = \frac{10}{9.3} \%$



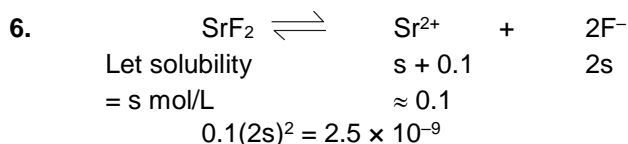
5. (A) Equivalence point pH will be less than 7, but HPh indicator has pH range = 8.3 – 10. So, HPh cannot be used as indicator in given titration.

$$(B) \text{p}K_{\text{In}} + 1 = \text{p}K_{\text{In}} + \log_{10} \frac{[\text{In}^-]}{[\text{HIn}]}$$

$$\frac{[\text{In}^-]}{[\text{HIn}]} = 10. \text{ So, \% ionisation } \frac{10}{10+1} \times 100 = \frac{1000}{11} \%$$

(C) Above formula is valid only when degree of hydrolysis is negligible.

(D) At second equivalent point, NaH_2PO_4 (amphiprotic species) is produced. So, $\text{pH} = \frac{1}{2} [\text{p}K_{a_1} + \text{p}K_{a_2}]$.



$$\therefore s = 5 \sqrt{\frac{5}{2}} \times 10^{-5} \text{ mol/L.}$$



$$\begin{array}{lclcl} t=0 & c & & 0 & 0 \\ t=\text{eq} & c(1-h) & & ch & ch \\ \frac{ch^2}{1-h} = 10^{-4}. & \text{But } [\text{OH}^-] = ch = 10^{-5} \text{ M. (} \because \text{pH} = 9) \end{array}$$

$$\text{So, } \frac{10^{-5} h}{1-h} = 10^{-4}. \text{ Therefore, } h = \frac{10}{11}.$$

$$\text{So, } c = 1.1 \times 10^{-5} \text{ M.}$$

$$\begin{aligned} K_{sp} &= [\text{Ag}^+][\text{A}^-] = c \times c(1-h) \\ &= 1.1 \times 10^{-5} \times 10^{-6} \\ &= 1.1 \times 10^{-11}. \end{aligned}$$

8. In an alkaline aqueous solution, $[\text{H}^+] < [\text{OH}^-]$.

$$\therefore \text{pH} > \text{pOH}.$$

$$\text{Also, } \text{pH} + \text{pOH} = \text{p}K_w \text{ and for pure water, } \text{pH} = \text{pOH} = \frac{\text{p}K_w}{2}.$$

In an alkaline solution, $[\text{H}^+] < [\text{H}^+]_{\text{H}_2\text{O}}$ and $[\text{OH}^-] > [\text{OH}^-]_{\text{H}_2\text{O}}$.

$$\therefore \text{pH} > \frac{\text{p}K_w}{2} \text{ and } \text{pOH} < \frac{\text{p}K_w}{2}.$$

9. pH of the salt solutions of SA-SB and WA-WB is independent of concentration of solution.

10. As indicator (InOH) is base type indicator, so $\text{p}K_{\text{InOH}} = \text{pOH}$ at half ionisation point = 6.8.

$$\text{pOH}_1 = \text{p}K_{\text{InOH}} + \log_{10} \frac{5}{1} = 7.5. \quad \therefore \text{pH}_1 = 6.5$$

$$\text{and } \text{pOH}_1 = \text{p}K_{\text{In}^+\text{OH}} + \log_{10} \frac{4}{1} \quad \therefore \text{p}K_{\text{In}^+\text{OH}} = 6.9 = \text{pOH}_2$$

$$\therefore \text{pH}_2 = 7.1.$$



11. At 20% neutralisation, $\text{pOH} = \text{pK}_b + \log_{10} \frac{20}{80} = 5$.

$$\therefore \text{pK}_b = 5 - \log \frac{1}{4} \quad \therefore \text{K}_b = 2.5 \times 10^{-6}$$

At equivalence point, $\text{pH} = \frac{1}{2} (\text{pK}_w - \text{pK}_b - \log C)$

$$\therefore 4.5 = \frac{1}{2} (14 - 5.6 - \log C) \quad \therefore C = 0.25 \text{ M}$$

$$\text{Now, } C = \frac{n_{\text{HCl}}}{V_f(\text{L})} \quad \therefore 0.25 = \frac{0.5 \times V_L}{V_L + 0.1} \quad \therefore V_L = 0.1 \text{ L} = 100 \text{ mL}$$

At equivalence point, $n_{\text{WB}} = n_{\text{HCl}}$

$$\frac{m}{45} = 0.5 \times 0.1 \quad \therefore m = 2.25 \text{ g}$$

$$\therefore \text{Weight \% of base in sample} = \frac{2.25}{2.5} \times 100 = 90\%$$

12. For getting selectively precipitated, $\text{IP} > K_{\text{sp}}$.

$$[\text{M}^{2+}] [\text{S}^{2-}] > K_{\text{sp}}$$

$$[\text{M}^{2+}] \frac{K_{a_1} K_{a_2} [\text{H}_2\text{S}]}{[\text{H}^+]^2} > K_{\text{sp}}$$

$$\frac{[\text{M}^{2+}][\text{H}_2\text{S}]}{[\text{H}^+]^2} > K_{\text{eq}} \therefore \frac{0.01 \times 0.1}{1^2} > K_{\text{eq}}$$

$$\therefore K_{\text{eq}} < 10^{-3}$$

For PbS, above condition is satisfied.

13. $K_a(\text{NH}_4^+) = \frac{1}{K_{\text{eq}}} = 5 \times 10^{-10}$

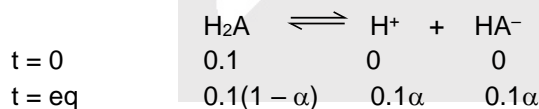
$$\text{Now, } K_b(\text{NH}_3) \times K_a(\text{NH}_4^+) = K_w = 10^{-14}$$

$$\text{So, } \text{pK}_b(\text{NH}_4\text{OH}) = -\log_{10} (K_b(\text{NH}_3)) = -\log_{10} (2 \times 10^{-5}) = 4.7$$

14. $\text{p}_{\text{H}_2} = 10 \text{ atm}$ (as 1 mole H_2 in 2.24 L at 0°C) & $[\text{I}^-] = 0.5 \text{ M}$

$$K = \frac{[\text{OH}^-]^2 \text{p}_{\text{H}_2}}{[\text{I}^-]^2} \Rightarrow [\text{OH}^-]^2 = \frac{4 \times (0.5)^2 \times 10^{-9}}{10} \Rightarrow [\text{OH}^-] = 10^{-5} \text{ M} \quad \therefore \text{pOH} = 5$$

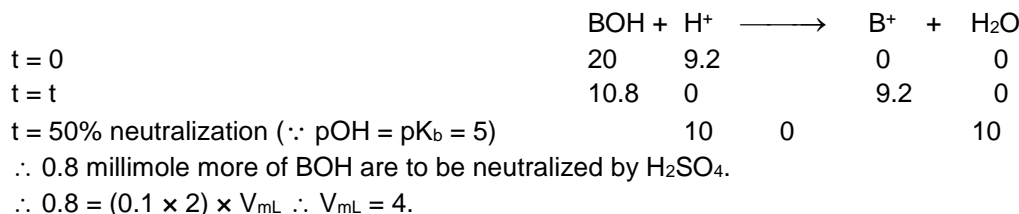
15.



$$K_{a1} = 0.05 = \frac{0.1 \alpha^2}{1 - \alpha} \quad \therefore \alpha = 0.5$$

$$\text{Now, } [\text{A}^{2-}]/[\text{H}^+] = K_{a_2}/[\text{H}^+] = \frac{2 \times 10^{-6}}{0.05} = 4 \times 10^{-5}$$

16.





$$17. \quad s = \sqrt{K_{sp}} = 7 \times 10^{-7} \text{ mol/L} = \frac{7 \times 10^{-7} \times 188 \times 10^3}{4} \text{ mg / 250 mL.}$$

$$= 3.29 \times 10^{-2} \text{ mg / 250 mL.}$$

$$\therefore \text{Percentage saturation} = \frac{3.29 \times 10^{-3}}{3.29 \times 10^{-2}} \times 100 = 10\%.$$

$$18. \quad pK_a (\text{CH}_3\text{COOH}) = 4.74$$

$$[\text{CH}_3\text{COOH}] = 0.25 \text{ M}, \quad [\text{CH}_3\text{COONa}] = 0.15 \text{ M}$$

$$[\text{H}^+] = \frac{K_a [\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]} = \frac{1.8 \times 10^{-5} \times 0.25}{0.15} = 3 \times 10^{-5} \text{ M}$$



$$[\text{S}^{2-}] = \frac{9 \times 10^{-21} \times 0.1}{9 \times 10^{-10}} = 10^{-12} \text{ M}$$

$$\text{IP} (\text{MnS}) = [\text{Mn}^{2+}] [\text{S}^{2-}] = 1.5 \times 10^{-2} \times 10^{-12} = 1.5 \times 10^{-14}$$

$$\text{IP} < K_{sp} \quad \Rightarrow \quad \text{No ppt is formed.}$$

For precipitation of MnS, the minimum concentration of $[\text{S}^{2-}]$ can be obtained as follows :

$$[\text{Mn}^{2+}] [\text{S}^{2-}] = K_{sp}$$

$$1.5 \times 10^{-2} \times [\text{S}^{2-}] = 2.4 \times 10^{-13} \quad \Rightarrow \quad [\text{S}^{2-}] = 1.6 \times 10^{-11} \text{ M}$$

For this $[\text{S}^{2-}]$,

$$[\text{H}^+]^2 = \frac{K_a [\text{H}_2\text{S}]}{[\text{S}^{2-}]} = \frac{9 \times 10^{-21} \times 0.10}{1.6 \times 10^{-11}} = 7.5 \times 10^{-6} \text{ M}$$

$$[\text{H}^+] = \frac{K_a [\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]} \Rightarrow 7.5 \times 10^{-6} = \frac{1.8 \times 10^{-5} \times 0.25}{[\text{CH}_3\text{COO}^-]}$$

$$[\text{CH}_3\text{COONa}] = 0.6 \text{ M}$$

$$19. \quad \text{In all the other cases, pH} = 1.$$

When all taps are opened,

Millimoles of H^+ = 100

Volume of solution = 2000 mL

$$\therefore [\text{H}^+] = \frac{100}{2000} = 0.05 \text{ M.}$$

$$\text{pH} = -\log[\text{H}^+] = -\log(5 \times 10^{-2}) = 2 - \log 5 \neq 1.$$

$$20. \quad \text{pH}_i = 7.$$

After opening S_1 , solution in bucket would contain $[\text{CH}_3\text{COOH}] = 0.1 \text{ M}$. So, pH after opening

$$S_1 = \frac{1}{2} (pK_a - \log C) = 2.8775.$$

After opening S_2 , solution in bucket would contain $[\text{CH}_3\text{COONa}] = \frac{1}{15} \text{ M}$. So, pH after opening

$$S_2 = \frac{1}{2} (pK_w + pK_a + \log C) = 8.7875.$$

After opening S_3 , solution in bucket would contain $[\text{CH}_3\text{COONa}] = \frac{1}{40} \text{ M}$ & $[\text{CH}_3\text{COOH}] = \frac{1}{40} \text{ M}$. So, pH

$$\text{after opening } S_3 = pK_a + \log \left(\frac{1/40}{1/40} \right) = pK_a = 4.755. \text{ (Buffer properties)}$$



After opening S_4 , solution in bucket would contain $[\text{CH}_3\text{COOH}] = \frac{1}{25} \text{ M}$ & $[\text{HNO}_3] = \frac{1}{50} \text{ M}$. So, pH after

opening $S_4 = -\log \frac{1}{50} = 1.7$. (Minimum pH)

Clearly, opening S_2 stop cock would cause maximum pH change compared to the previous pH in bucket.

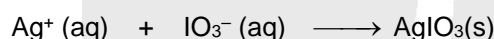
21. Refer solution of previous question.

22. Total added moles of $\text{Ag}^+ = 0.01$; Initial moles of $\text{IO}_3^- = 0.005$
Initial moles of $\text{CrO}_4^{2-} = 0.1$

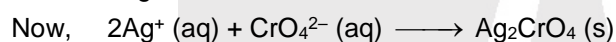
$$[\text{Ag}^+] \text{ required for } \text{AgIO}_3 \text{ precipitation} = \frac{K_{\text{sp}}(\text{AgIO}_3)}{[\text{IO}_3^-]} = \frac{10^{-13}}{0.005} = 2 \times 10^{-11} \text{ M}$$

$$\text{and } [\text{Ag}^+] \text{ required for } \text{Ag}_2\text{CrO}_4 \text{ precipitation} = \sqrt{\frac{K_{\text{sp}}(\text{Ag}_2\text{CrO}_4)}{[\text{CrO}_4^{2-}]}} = \sqrt{\frac{10^{-8}}{0.1}} = 3.162 \times 10^{-4} \text{ M}$$

So, Ag^+ first combines with IO_3^- , almost whole of Ag^+ gets precipitated out, then precipitation of Ag_2CrO_4 starts.



Moles of Ag^+ left after the above reaction = $0.01 - 0.005 = 0.005$.



Moles 0.005 0.1

Moles of CrO_4^{2-} left after the above reaction = $0.1 - 0.0025 = 0.0975$.

At equilibrium,

$[\text{CrO}_4^{2-}] = 0.0975 \text{ M}$

$$[\text{Ag}^+] = \sqrt{\frac{K_{\text{sp}}(\text{Ag}_2\text{CrO}_4)}{[\text{CrO}_4^{2-}]}} = \sqrt{\frac{10^{-8}}{0.0975}} = 3.2 \times 10^{-4} \text{ M.}$$

$$[\text{IO}_3^-] = \frac{K_{\text{sp}}(\text{AgIO}_3)}{[\text{Ag}^+]} = \frac{10^{-13}}{3.2 \times 10^{-4}} = 3.125 \times 10^{-10} \text{ M.}$$

Total moles of precipitate formed = $0.005 + 0.0025 = 0.0075$.