IONIC EQUILIBRIUM (ADVANCED)
CONTENTS

JEE (Advanced) Syllabus

Solubility product, common ion effect, pH and buffer solutions; Acids and bases (Bronsted and Lewis concepts); Hydrolysis of salts.

JEE (Main) Syllabus

Ionic equilibrium: Weak and strong electrolytes, ionization of electrolytes, various concepts of acids and bases (Arrhenius, Bronsted – Lowry and Lewis) and their ionization, acid – base equilibria (including multistage ionization) and ionization constants, ionization of water, pH scale, common ion effect, hydrolysis of salts and pH of their solutions, solubility of sparingly soluble salts and solubility products, buffer solutions.

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.

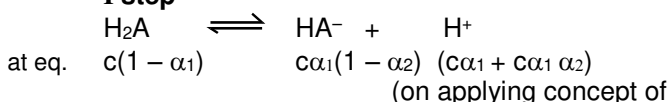In aqueous solution, following equilbria exist :

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

	I step				**II step**		
	H_2A $\rightleftharpoons$	HA^- +	H^+		HA^- $\rightleftharpoons$	A^{2-} +	H^+
at eq.	$c(1-\alpha_1)$	$c\alpha_1(1-\alpha_2)$	$(c\alpha_1 + c\alpha_1\alpha_2)$		$c\alpha_1(1-\alpha_2)$	$c\alpha_1\alpha_2$	$(c\alpha_1 + c\alpha_1\alpha_2)$

(on applying concept of siultaneous equilibrium)
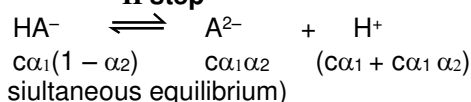
$$K_{a_1} = \frac{[H^+]\ [HA^-]}{[H_2A]} \qquad\qquad K_{a_2} = \frac{[H^+]\ [A^{2-}]}{[HA^-]}$$

$\therefore$

$$K_{a_1} = \frac{(c\alpha_1 + c\alpha_1\alpha_2)[c\alpha_1(1-\alpha_2)]}{c(1-\alpha_1)} \qquad K_{a_2} = \frac{(c\alpha_1 + c\alpha_1\alpha_2)(c\alpha_1 c\alpha_2)}{c\alpha_1\ (1-\alpha_2)}$$

$$= \frac{[c\alpha_1(1+\alpha_2)][\alpha_1(1-\alpha_2)]}{1-\alpha_1} \quad ....(i) \qquad = \frac{[c\alpha_1(1+\alpha_2)]\ \alpha_2}{1-\alpha_2} \quad ....(ii)$$

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 .

$\therefore$ $1 - \alpha_2 \approx 1$ and $1 + \alpha_2 \approx 1$

Thus, equation (i) can be reduced to $$K_{a_1} = \frac{C\alpha_1 \times \alpha_1}{1-\alpha_1}$$
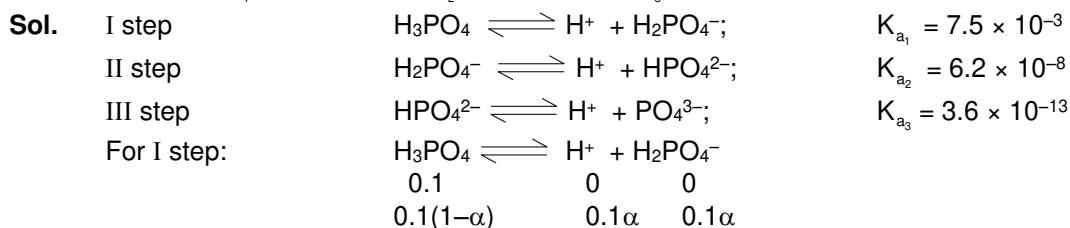
This is an expression similar to the expression for a weak monoprotic acid.

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

F1 : $\therefore$ **pH = $\frac{1}{2}$ (pK_{a_1} – log C)**   **[if $\alpha_1 \leq 0.1$ 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 $0.075 \times 4.075 = (0.555)^2$

Sol. I step $H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$; $K_{a_1} = 7.5 \times 10^{-3}$

II step $H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-}$; $K_{a_2} = 6.2 \times 10^{-8}$

III step $HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-}$; $K_{a_3} = 3.6 \times 10^{-13}$

For I step: $H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$

                        0.1   0   0

                        $0.1(1-\alpha)$ 0.1α 0.1α

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

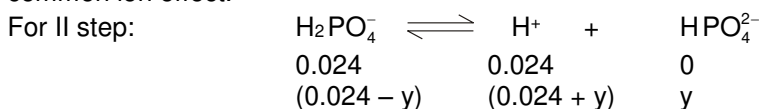Expecting $\alpha \ll 1$, $\alpha^2 = 7.5 \times 10^{-2}$ $\therefore$ $\alpha = 0.274$ (not negligible)

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

$\therefore$ $\qquad$ [H$^+$] = **0.024 M** $\Rightarrow$ $\qquad$ [OH$^-$] = $\dfrac{10^{-14}}{0.024}$ = 4.17 × 10^{-13} M (insignificant)

$\qquad$ & $\qquad$ [H$_2$PO$_4^-$] = **0.024 M**

$\qquad$ Also, [H$_3$PO$_4$] = 0.1 − 0.024 = **0.076 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.

For II step: $\qquad$ H$_2$PO$_4^-$ $\rightleftharpoons$ $\qquad$ H$^+$ $\quad$ + $\qquad$ HPO$_4^{2-}$

$\qquad\qquad\qquad$ 0.024 $\qquad\qquad$ 0.024 $\qquad\qquad$ 0

$\qquad\qquad\qquad$ (0.024 − y) $\qquad$ (0.024 + y) $\qquad$ y

The dissociation of H$_2$PO$_4^-$ occurs in presence of [H$^+$] furnished in step I.

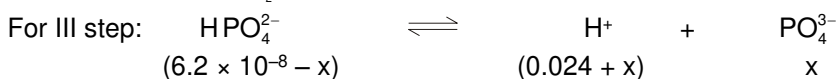Thus, $\qquad$ $K_{a_2} = \dfrac{[H^+][HPO_4^{2-}]}{[H_2PO_4^-]}$ $\qquad$ or $\qquad$ $6.2 \times 10^{-8} = \dfrac{(0.024 + y)y}{(0.024 - y)}$

$\because$ $\qquad$ y is small $\therefore$ 0.024 − y $\approx$ 0.024 and neglecting y^2.

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

$\therefore$ $\qquad$ y = 6.2 × 10^{-8} M

or $\qquad$ [HPO$_4^{2-}$] = K_{a_2} = 6.2 × 10^{-8} M $\qquad$ (Insignificant)

For III step: $\qquad$ HPO$_4^{2-}$ $\qquad\qquad$ $\rightleftharpoons$ $\qquad\qquad$ H$^+$ $\quad$ + $\qquad$ PO$_4^{3-}$

$\qquad\qquad$ (6.2 × 10^{-8} − x) $\qquad\qquad$ (0.024 + x) $\qquad\qquad$ x

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

$\because$ $\qquad$ x is small $\therefore$ Again neglecting x^2 and assuming 6.2 × 10^{-8} − x $\approx$ 6.2 × 10^{-8}

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

$\therefore$ $\qquad$ $x = \dfrac{3.6 \times 10^{-13} \times 6.2 \times 10^{-8}}{0.024}$ = 9.3 × 10^{-19} M

or $\qquad$ [PO$_4^{3-}$] = 9.3 × 10^{-19} 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.
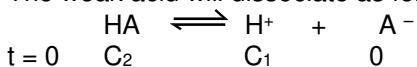

(B) pH Calculation : Solutions containing mixture of weak monoprotic acid and strong acid, solutions containing mixture of weak monoacidic base and strong base

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 :

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

t = 0 $\quad$ C$_2$ $\qquad\qquad$ C$_1$ $\qquad\qquad$ 0

t = eq. $\quad$ C$_2$(1−α) $\quad$ C$_2$α + C$_1$ $\qquad$ C$_2$α $\qquad\qquad$ $K_a = \dfrac{(C_2\alpha + C_1)\,C_2\alpha}{C_2(1-\alpha)}$ $\qquad$ ...(1)

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

$$K_a = C_1\alpha \qquad \qquad ...(2)$$

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 $\quad$ $C(1 - \alpha)$ $\qquad\qquad$ $C\alpha$ $\qquad\qquad$ $10^{-1} + C\alpha$

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

From above equilibrium, $2 \times 10^{-5} = \dfrac{C\alpha \times 10^{-1}}{C}$
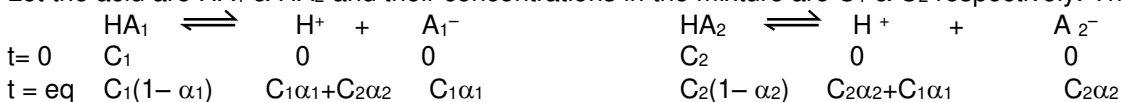
$\alpha = 2 \times 10^{-4}$

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

$$HA_1 \rightleftharpoons H^+ + A_1^- \qquad\qquad HA_2 \rightleftharpoons H^+ + A_2^-$$

t= 0 $\quad$ C_1 $\qquad$ 0 $\qquad$ 0 $\qquad\qquad\qquad$ C_2 $\qquad$ 0 $\qquad$ 0

t = eq $\quad$ $C_1(1- \alpha_1)$ $\quad$ $C_1\alpha_1+C_2\alpha_2$ $\quad$ $C_1\alpha_1$ $\qquad$ $C_2(1- \alpha_2)$ $\quad$ $C_2\alpha_2+C_1\alpha_1$ $\quad$ $C_2\alpha_2$

(On applying concept of simultaneous equilibrium)

$$K_{a_1} = \frac{C_1\alpha(C_1\alpha_1 + C_2\alpha_2)}{C_1(1-\alpha_1)} \quad ...(1) \qquad K_{a_2} = \frac{(C_2\alpha_2 + C_1\alpha_1)C_2\alpha_2}{C_2(1-\alpha_2)} \qquad\qquad ...(2)$$

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

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

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

- 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, concetration become half. So, after mixing :

$C_1 = 0.01$ M, $\quad$ $C_2 = 0.1$ M

$$[H^+] = \sqrt{C_1 K_{a_1} + C_2 K_{a_2}} = \sqrt{2\times 10^{-4} \times 0.01 + 2 \times 10^{-5} \times 0.1} = \sqrt{2\times 10^{-6} + 2\times 10^{-6}} = 2 \times 10^{-3}$$ M

$\therefore$ pH = 3 – log2 = 2.7

$[OCl^-] = \dfrac{0.01 \times 2 \times 10^{-4}}{2 \times 10^{-3}} = 1 \times 10^{-3}$ M ; $[CH_3COO^-] = \dfrac{0.1 \times 2 \times 10^{-4}}{2 \times 10^{-3}} = 1 \times 10^{-3}$ M ;

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

pH of a mixture of two weak acids (one monoprotic and one polyprotic) :
[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, $[H^+]$, $[OH^-]$, $[CH_3COO^-]$, $[CH_3COOH]$, $[SH^-]$, $[H_2S]$, $[S^{2-}]$ in a solution obtained by mixing equal volume of 0.2 M H_2S & 0.02 M acetic acid. Given that

$K_a(CH_3COOH) = 2 \times 10^{-5}$, K_{a_1} $(H_2S) = 10^{-7}$, K_{a_2} $(H_2S) = 10^{-14}$. Take log 21 = 1.32, $\dfrac{1}{\sqrt{21}} = 0.218$.

Sol. Now, $[H_2S] = 0.1$ M, $[CH_3COOH] = 0.01$ M after mixing.
For pH calculation, considering only first [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).

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

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

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

For acetic acid, $K_a = \dfrac{[H^+] \ [CH_3COO^-]}{[CH_3COOH]} = \dfrac{\sqrt{21} \times 10^{-4} \times [CH_3COO^-]}{0.01}$

$\Rightarrow$ $[CH_3COO^-] = 4.36 \times 10^{-4}$ M
$\Rightarrow$ $[CH_3COOH] = 0.01$ M

For H_2S, $K_{a_1} = \dfrac{[H^+] \ [HS^-]}{[H_2S]} = \dfrac{\sqrt{21} \times 10^{-4} \times [HS^-]}{0.1}$ $\Rightarrow$ $[HS^-] = 2.18 \times 10^{-5}$ M

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

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

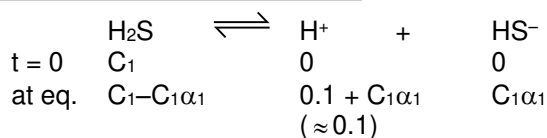**Mixture of a polyprotic weak acid and a strong acid :**
❍ pH can be calculated by taking the concentration of strong acid only.
❍ For other calculations, we should consider the dissociation equilibria of the weak polyprotic acid, as done in the following example.

——— *Solved Examples* ———

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

Sol.   HCl + H_2S
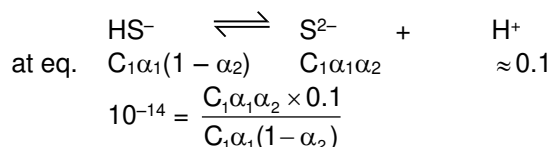   0.1 M 0.1 M
$\therefore$ pH = 1 (most of [H⁺] comes from HCl) & $[Cl^-] = 0.1$ M.

$$H_2S \rightleftharpoons H^+ + HS^-$$

t = 0	C_1	0	0
at eq.	$C_1 - C_1\alpha_1$	$0.1 + C_1\alpha_1$	$C_1\alpha_1$
		(≈ 0.1)	

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

degree of dissociation of $H_2S = \alpha_1 = \dfrac{10^{-7}}{10^{-1}} = 10^{-6}$

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

at eq.	$C_1\alpha_1(1-\alpha_2)$	$C_1\alpha_1\alpha_2$	≈ 0.1

$$10^{-14} = \frac{C_1\alpha_1\alpha_2 \times 0.1}{C_1\alpha_1(1-\alpha_2)}$$

$\Rightarrow$ degree of dissociation of $HS^- = \alpha_2 = 10^{-13}$

$[S^{2-}] = C_1\alpha_1\alpha_2 = 10^{-1} \times 10^{-6} \times 10^{-13} = 10^{-20}$ M

$[HS^-]$ $C_1\alpha_1 = 10^{-1} \times 10^{-6} = 10^{-7}$ M.

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, $H_2C_2O_4$), we already know that the disscociation always takes place in steps. Example : for H_3PO_4,

$$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^- \qquad\qquad K_{a_1} = \frac{[H^+]\ [H_2PO_4^-]}{[H_3PO_4]} \qquad ...(1)$$

$$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-} \qquad\qquad K_{a_2} = \frac{[H^+][HPO_4^{2-}]}{[H_2PO_4^-]} \qquad ...(2)$$

$$H_2PO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-} \qquad\qquad K_{a_3} = \frac{[H^+][PO_4^{3-}]}{[HPO_4^{2-}]} \qquad ...(3)$$

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

pH of the solution can be caculated from Ist step only because $[H^+]$ from IInd & IIIrd step can be neglected as
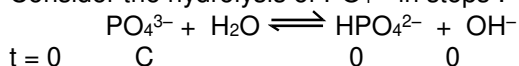(a) $K_{a_1} \gg K_{a_2} \gg K_{a_3}$
(b) $[H^+]$ from Ist dissociation will suppress the dissociation of IInd & IIIrd step.

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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 :

$$PO_4^{3-} + H_2O \rightleftharpoons HPO_4^{2-} + OH^-$$

$t = 0$ C   0   0

$t = eq$ $C(1-h)$ Ch Ch $K_{h_1} = \dfrac{[OH^-][HPO_4^{2-}]}{[PO_4^{3-}]}$ ...(4)

$$HPO_4^{2-} + H_2O \rightleftharpoons H_2PO_4^- + OH^- \qquad K_{h_2} = \dfrac{[OH^-][H_2PO_4^-]}{[HPO_4^{2-}]} \qquad ...(5)$$

$$H_2PO_4^- + H_2O \rightleftharpoons H_3PO_4 + OH^- \qquad K_{h_3} = \dfrac{[OH^-][H_3PO_4]}{[H_2PO_4^-]} \qquad ...(6)$$

$$H_2O \rightleftharpoons H^+ + OH^-, \qquad K_w = [H^+][OH^-] \qquad ...(7)$$

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

Genarally, pH is calculated only using the first step hydrolysis

$$K_{h_1} = \dfrac{Ch.Ch}{C(1-h)} = \dfrac{Ch^2}{1-h} \qquad ...(8)$$

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

F4 : $h = \sqrt{\dfrac{K_{h_1}}{C}}$ ...(9)

$\Rightarrow$ $[OH^-] = Ch = \sqrt{K_{h_1} \times C} \Rightarrow [H^+] = \dfrac{K_w}{[OH^-]} = K_w \sqrt{\dfrac{K_{a_3}}{K_w C}} = \sqrt{\dfrac{K_w \times K_{a_3}}{C}}$
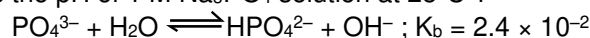
F5 :   So, **pH** $= \dfrac{1}{2}[pK_w + pK_{a_3} + \log C]$

NOTE : If h value from (9) comes ≥ 0.1, then its exact value should be obtained by solving quadratic (equation (8)) Then, $[OH^-] = Ch$ & $[H^+] = \dfrac{K_w}{[OH^-]}$

Solved Examples

Ex-6. What is the pH of 1 M Na_3PO_4 solution at 25ºC ?

$$PO_4^{3-} + H_2O \rightleftharpoons HPO_4^{2-} + OH^- \text{ ; } K_b = 2.4 \times 10^{-2}$$

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

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

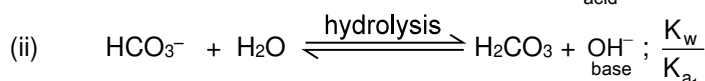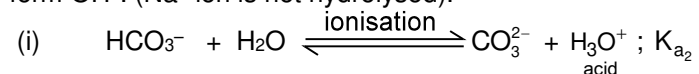$x^2 + (2.4 \times 10^{-2}) x - 2.4 \times 10^{-2} = 0$

$x = 0.143 = [OH^-]$

$[H^+] = \dfrac{K_w}{[OH^-]} = 7 \times 10^{-14}$ 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).

(i) $HCO_3^- + H_2O \xrightleftharpoons{\text{ionisation}} \underset{\text{acid}}{CO_3^{2-}} + H_3O^+$; K_{a_2}

(ii) $HCO_3^- + H_2O \xrightleftharpoons{\text{hydrolysis}} H_2CO_3 + \underset{\text{base}}{OH^-}$; $\dfrac{K_w}{K_{a_1}}$

Taking the assumption: Degree of ionisation (α) = Degree of hydrolysis (h) or $[CO_3^{2-}] = [H_2CO_3]$, an approximate calculation of pH can be done by the relation :

F6 : $\quad pH(HCO_3^-) = \left(\dfrac{pK_{a_1} + pK_{a_2}}{2} \right)$

$\qquad\qquad$ = 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,

F7 : $\quad pH(H_2PO_4^-) = \left(\dfrac{pK_{a_1} + pK_{a_2}}{2} \right) \quad$ and $\quad pH(HPO_4^{2-}) = \left(\dfrac{pK_{a_2} + pK_{a_3}}{2} \right)$

(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.

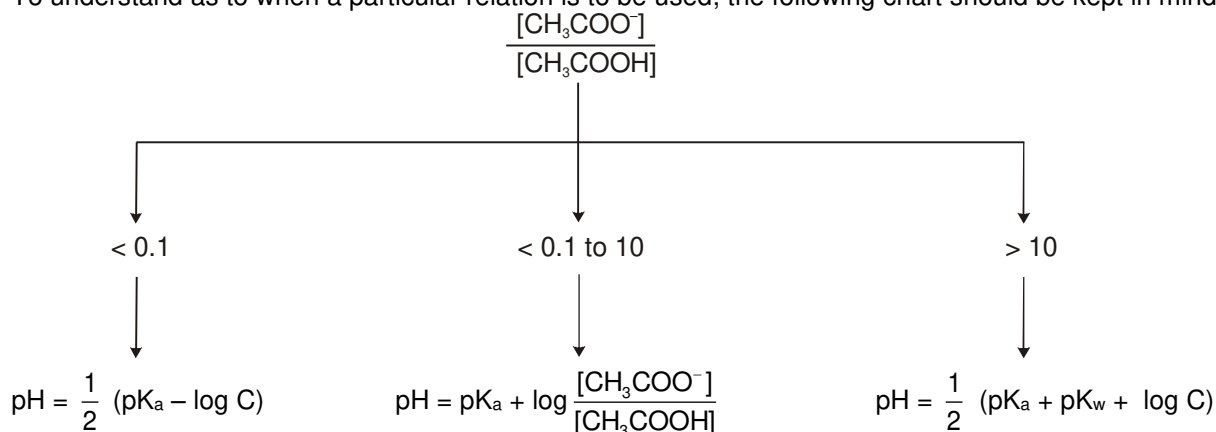# Ionic Equilibrium-II

(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 : pH = ½ (pK_a – log C) ; for (ii) the relation used is : $\dfrac{1}{2}$ (pK_w + pK_a + log C) and for (iii), the relation used is pH

= pK_a + log $\dfrac{[\text{Anion of Salt}]}{[\text{Acid}]}$.

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

$$\frac{[CH_3COO^-]}{[CH_3COOH]}$$

< 0.1	< 0.1 to 10	> 10
pH = $\dfrac{1}{2}$ (pK_a – log C)	pH = pK_a + log $\dfrac{[CH_3COO^-]}{[CH_3COOH]}$	pH = $\dfrac{1}{2}$ (pK_a + pK_w + log C)

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 [Salt]/[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 (pK_a ± 1) or (pK_b ± 1). This is called pH range of buffer.** For example, acetic acid (pK_a = 4.75 at 25^0C) 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.

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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 H_2CO_3 = 6.7, log 2 = 0.3)

Sol. $$pH = pK_{a_1} + \log \frac{[HCO_3^-]}{[H_2CO_3]}$$

$\Rightarrow$ $\quad 7.4 = 6.7 + \log \dfrac{[HCO_3^-]}{[H_2CO_3]}$ $\qquad \Rightarrow \dfrac{[HCO_3^-]}{[H_2CO_3]} = 5$

$\therefore$ $\quad$ 5 × moles of H2CO3 = Moles of HCO_3^- (since both are components of same solution, volume of solution would be same for both)

$\Rightarrow$ $\quad 5 \times 2.5 \times 10 \times 10^{-3} = 5 \times V$ $\qquad \Rightarrow$ required volume = 0.025 L = 25 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 :

$$pH = pK_a + \log \frac{b}{a}$$

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

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

Differentiating with respect to x we get

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

Taking the inverse

F8 : $\dfrac{\mathbf{dx}}{\mathbf{d\Delta pH}} = \mathbf{2.303} \dfrac{\mathbf{(a+x)(b-x)}}{\mathbf{a+b}} \approx \mathbf{2.303} \dfrac{\mathbf{ab}}{\mathbf{a+b}}$. 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

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

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

a – b = 0

F9 : $\therefore$ $\quad$ b = a $\quad \Rightarrow \quad$ [Acid] = [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 $\qquad$ (ii) 0.2M CH_3COOH and 0.2M CH_3COONa
Given : pK_a (CH_3COOH) = 4.74
Which will be a better buffer ?

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

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

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

$\qquad$ 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

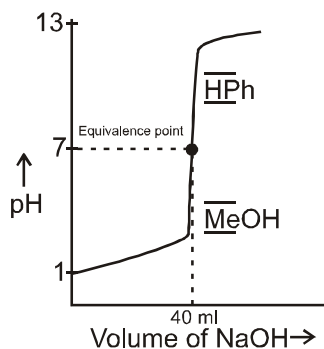| Volume of NaOH added	pH of solution
0 mL	1
10 mL	1.22 ($\because$ $[H^+]$ = $\dfrac{40 \times 0.1 - 10 \times 0.1}{50}$ = 6×10^{-2})
20 mL	1.48
30 mL	1.84
39 mL	2.90
39.9 mL	3.90
40.0 mL	7
(Equivalence point : complete neutralization)	
40.1 mL	10.1
41 mL	11.1
50 mL	12.05
60 mL	12.30 ($\because$ $[OH^-]$ = $\dfrac{60 \times 0.1 - 40 \times 0.1}{100}$ = 2×10^{-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)**.
$\qquad$ 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 rnage. So, there are large experimental errors numerically, if it is used.
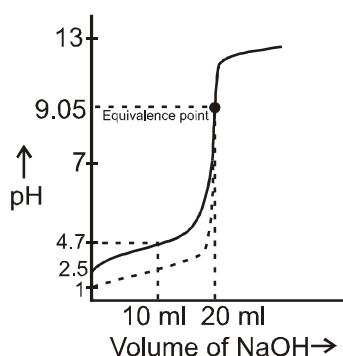

(B)   Titration of SB with WA :
Ex.   20 mL, 0.5 M CH_3COOH (pK_a = 4.7) Vs 0.5 M NaOH

Volume of NaOH added	pH value
0 mL	2.5 [pH = $\frac{1}{2}$ (pK_a – log C)]
5 mL	4.23
10 mL	4.7 [pH = 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 + 1/2 (4.7) + 1/2 log (1/4) = 9.05
(Equivalence point : complete neutralization)	Salt of WA & SB (CH_3COONa = 0.25 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 horzontal graph), which is point of maximum buffer capacity (at pH = 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 $NH_3.H_2O$ (pK_b = 4.7) Vs 0.5 M HCl

Figure-3
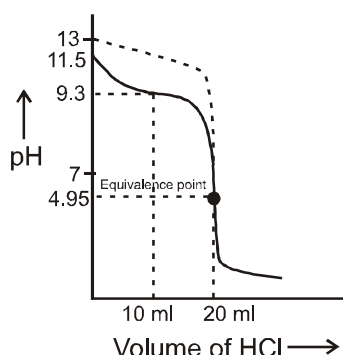
○   Proceed similar to as done above with 0 mL data corresponding to weak base, between 0 to 20 mL data corresponding to buffer of WB & its salt with SA, 20 mL data corresponding to salt of WB & SA (NH_4Cl) & further data corresponding to excess HCl.
○   pH range of titration : 4 – 7
○   Common indicators that can be used : Methyl orange, Methyl red & Phenol red.
○   Best indicator : Methyl red.

NOTE : Titration of WA & WB is genrally 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 CH_3COOH = 4.74

- (a)   pH = 1/2 (pK_w + pK_a + log c) = 1/2 (14 + 4.74 – 1) = 8.87
  (On calculating h by approximantion, it comes negligible (< 0.1). That's why direct formula has been used).

- (b)

  $$CH_3COONa \ + \ HCl \longrightarrow NaCl \ + \ CH_3COOH$$

t = 0	5 millimole	1 millimole	0	0
finally	4 millimole	0	–	1 millimole $\Rightarrow$ Buffer

  pH = pK_a + log 4 = 4.74 + 0.6 = 5.34

- (c)   pH = pK_a = 4.74 (Half equivalence point : Both components of buffer in equal amount)
- (d)   pH = 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.
  $[CH_3COOH] = 5/100 = 1/20$ M

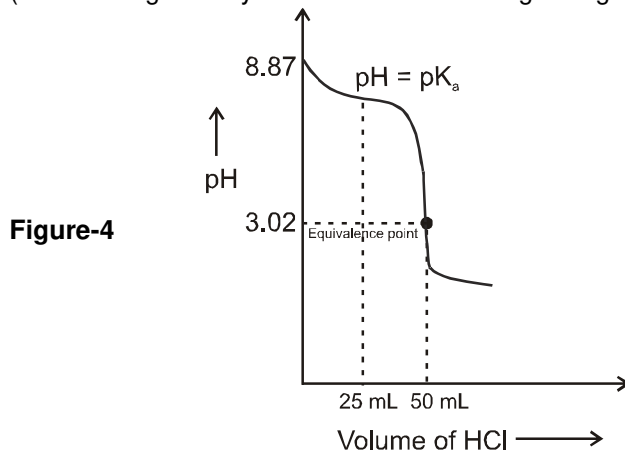 $$pH = 1/2 \ (pK_a - \log C) = 1/2 \ (4.74 + 2 - 0.7) = \frac{6.04}{2} = 3.02$$

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

- (f)   [HCl] = 1/100 M ; pH = 2.1
  (Considering H^+ only from excess HCl & neglecting H^+ from CH_3COOH due to common ion effect)

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

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

Figure-4

(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 :
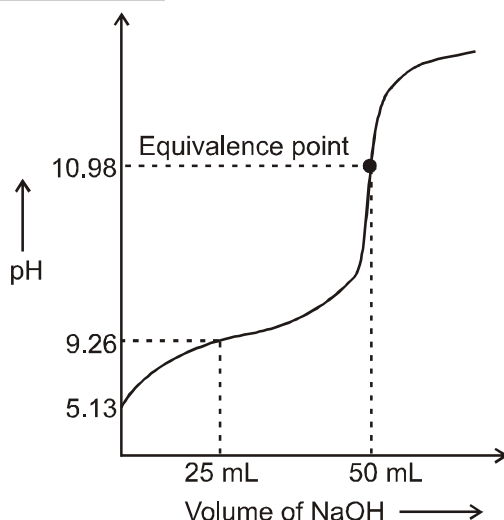(a) 0 mL   (b) 25 mL   (c) 50 mL
Given : pK_b of $NH_3.H_2O$ = 4.74
Proceed similar to above (a, c, e) keeping in mind that we have WB SA salt in (a) part, half equivalence point : both components of buffer (WB & its salt with SA) in equal amount in (b) part & equivalence point : weak base in (c) part.

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 is y. Then :

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

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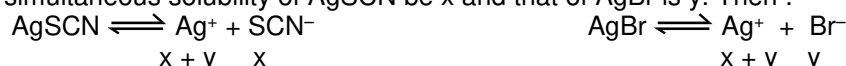
$10^{-12} = x (x + y)$ -------(i)

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

On solving, we get x = 2y

So, y = 4.08×10^{-7} M and x = 8.16×10^{-7} 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 excepted to precipate with the ion of reagent are same.
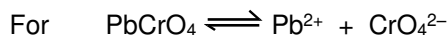
Solved Examples

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 $Ag_2SO_4 \rightleftharpoons 2Ag^+ + SO_4^{2-}$

                      2s   s

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

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For $PbCrO_4 \rightleftharpoons Pb^{2+} + CrO_4^{2-}$

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

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

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

$[SO_4^{2-}] = \dfrac{s \times 100}{350} = \dfrac{1.52 \times 10^{-2} \times 100}{350} = 0.43 \times 10^{-2}\,M$

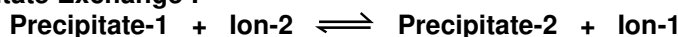$[Pb^{2+}] = \dfrac{s_1 \times 250}{350} = \dfrac{5.29 \times 10^{-7} \times 250}{350} = 3.78 \times 10^{-7}\,M$

$[CrO_4^{2-}] = \dfrac{s_1 \times 250}{350} = \dfrac{5.29 \times 10^{-7} \times 250}{350} = 3.78 \times 10^{-7}\,M$

It is thus evident that,
$[Ag^+]^2[CrO_4^{2-}] = (0.869 \times 10^{-2})^2 \times (3.78 \times 10^{-7}) = 2.85 \times 10^{-11}$ (> K_{sp} Ag$_2$ CrO$_4$)
Thus Ag$_2$CrO$_4$ will precipitate.

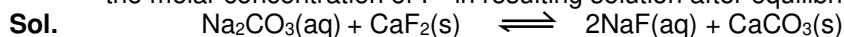## Precipitate Exchange :
Precipitate-1 + Ion-2 $\rightleftharpoons$ Precipitate-2 + Ion-1
One precipitate is mixed with solution of an ion to get another precipitate and another ion in solution.

Solved Examples

Ex-11. 2M solution of Na$_2$CO$_3$ 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.

Sol. $Na_2CO_3(aq) + CaF_2(s) \rightleftharpoons 2NaF(aq) + CaCO_3(s)$

t = 0   2   –   0   –
t = eq   2 – a   –   2a   –
where a is very small

For CaCO$_3$, $K_{sp} = x = [Ca^{2+}][CO_3^{2-}] = [Ca^{2+}] \times 2$ (∵ CO_3^{2-} mainly coming from Na$_2$CO$_3$)

∴ $[Ca^{2+}] = \dfrac{x}{2}$

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

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   [H$^+$] in a solution containing mixture of weak
      monoprotic acid & strong acid

F3   [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   pH(PO$_4^{3-}$) [h < 0.1]

F6   pH(HCO$_3^-$) [h < 0.1]

F7   pH(H$_2$PO$_4^-$) & pH(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 monoptoric acid & SA

Der3   Equilibrium of a mixture of two weak monoptoric acids

Der4   Hydrolysis of polyvalent anion PO$_4^{3-}$

Der5   Buffer capacity

Der6   Maximum buffer capacity

Table-1

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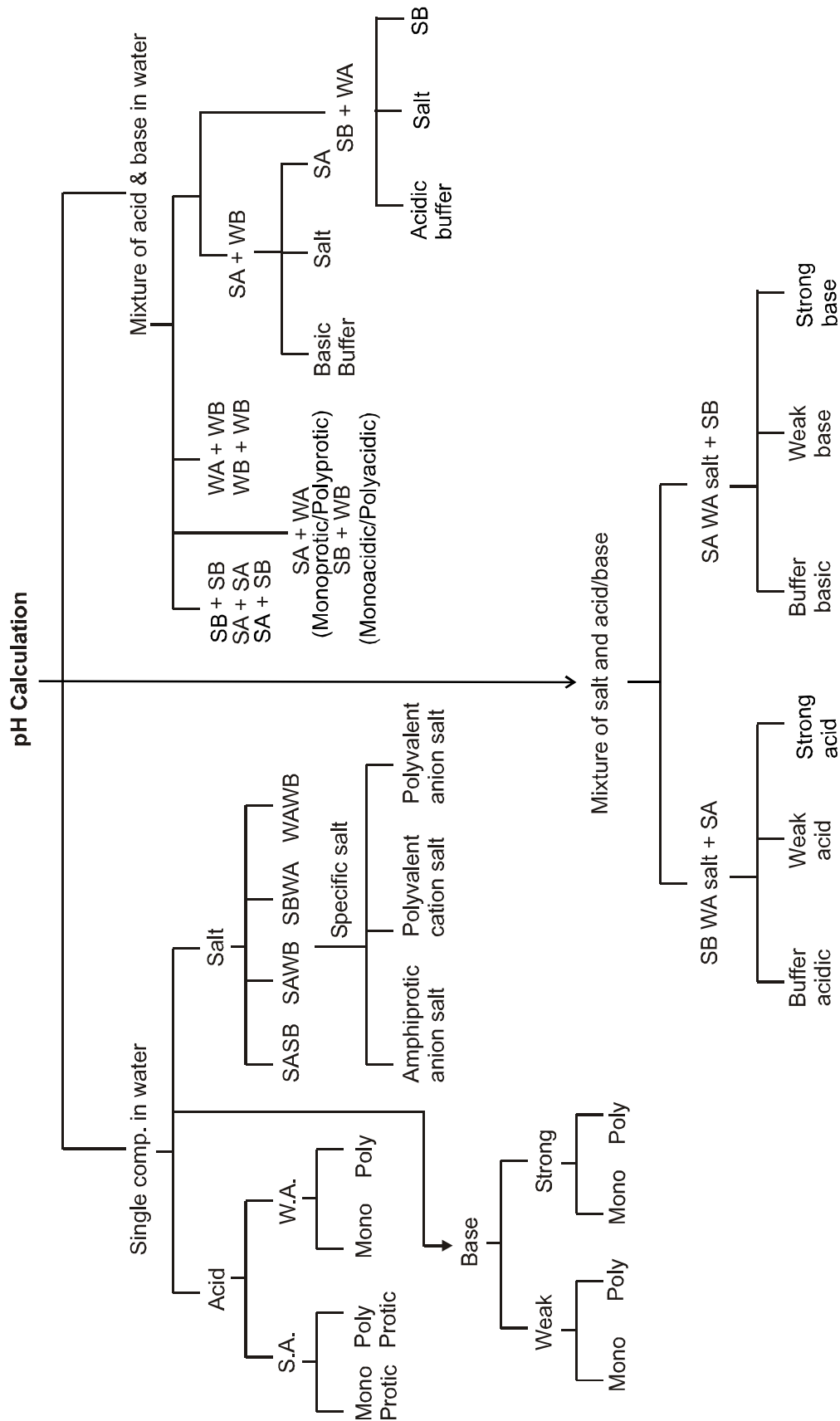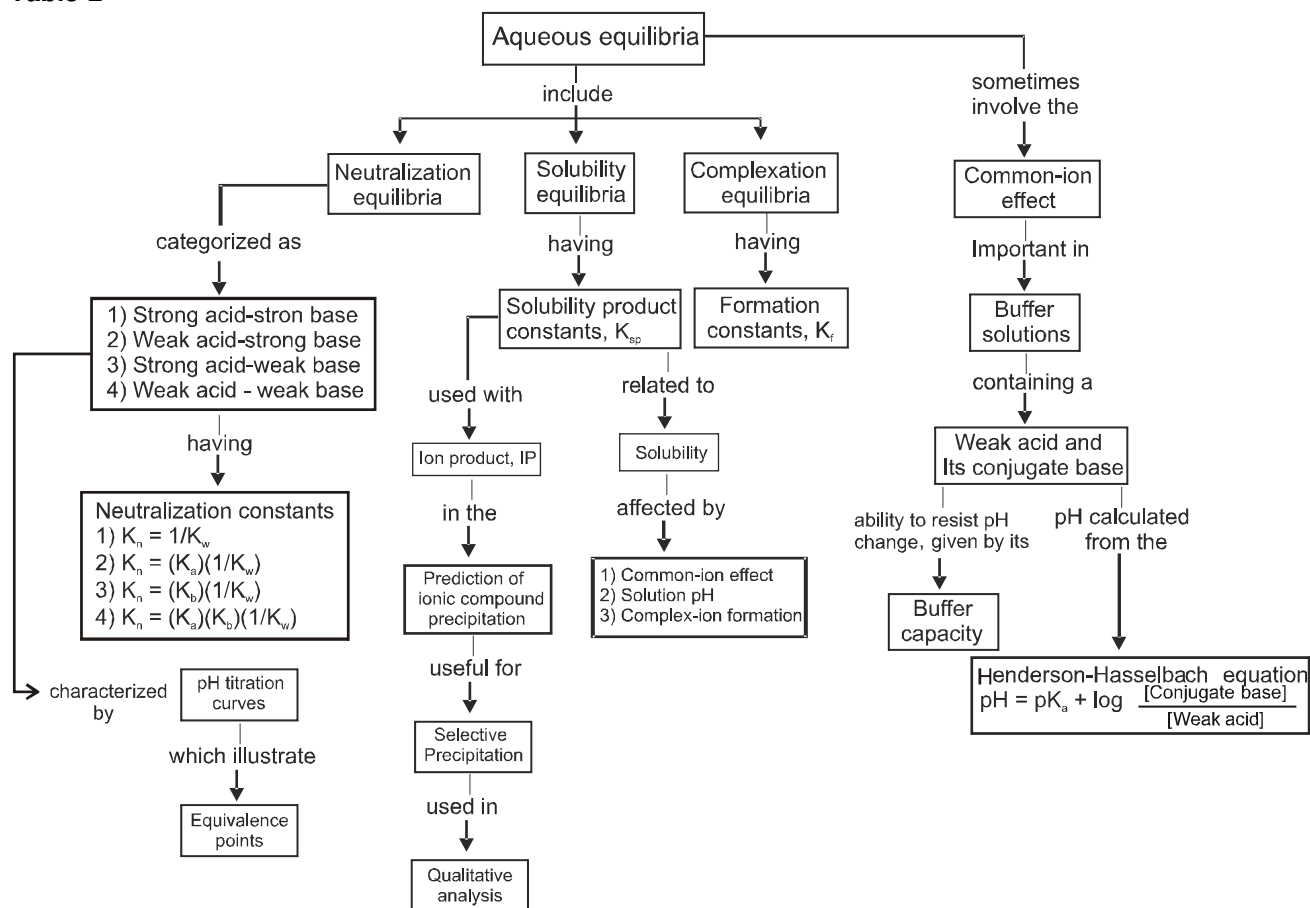
ADVIEQ(A)- 14

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 × 0.1 = 1
Milli moles of H^+ from H_2SO_4 = 40 × 0.2 × 2 = 16

∴ Total millimoles of H^+ in solution = 1 + 16 = 17

∴ $[H^+] = \dfrac{17}{50} = 3.4 \times 10^{-1}$ $\left(\because [H^+]_f = \dfrac{Millimoles_{Total}}{V_{f\ in\ mL}} \right)$

∴ pH = – log $[H^+]$ = – log 0.34
pH = **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.

Take $\dfrac{1}{1099}$ = 9.1 × 10 × 10^{-4} & log 9.1 = 0.96

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

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

∴ $[H^+]$ = from left HCl = $\dfrac{0.1}{109.9}$ = 9.1 × 10^{-4} M

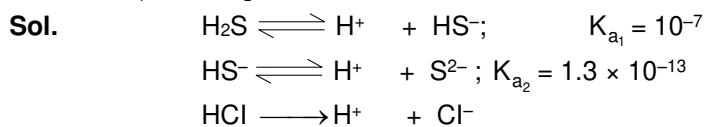∴ pH = – log H^+ = – log 9.1 × 10^{-4} ⇒ pH = **3.04**

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.

Sol.
$$H_2S \rightleftharpoons H^+ + HS^-; \qquad K_{a_1} = 10^{-7}$$
$$HS^- \rightleftharpoons H^+ + S^{2-}; \quad K_{a_2} = 1.3 \times 10^{-13}$$
$$HCl \longrightarrow H^+ + Cl^-$$

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.

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

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

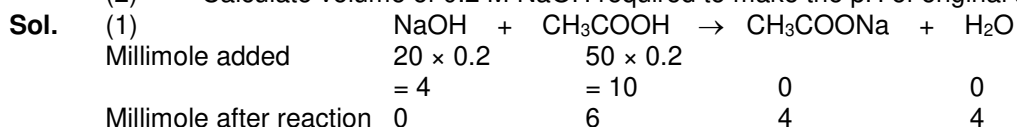$$\therefore \qquad [HS^-] = \frac{10^{-7} \times 0.1}{0.3} = \mathbf{3.3 \times 10^{-8} \text{ M}}$$

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

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

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.

Sol. (1)

	NaOH	+	CH₃COOH	→	CH₃COONa	+	H₂O
Millimole added	20 × 0.2		50 × 0.2				
	= 4		= 10		0		0
Millimole after reaction	0		6		4		4

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

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

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

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

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

(∵ final solution is required to be acidic)

	NaOH	+	CH₃COOH	→	CH₃COONa	+	H₂O
Millimole added	0.2 × V		50 × 0.2				
	= 0.2 V		= 10		0		0
Millimole after reaction	0		(10 − 0.2 V)		0.2 V		0.2V
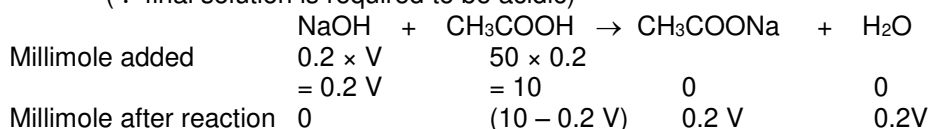
$$\therefore \qquad [\text{Acid}] = \frac{10 - 1.2V}{50 + V} ; \qquad [\text{Salt}] = \frac{0.2V}{50 + V}$$

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

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

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

$\dfrac{a}{b} = 2$ $\therefore$ a = 2b

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

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

Thus, [Salt] = **0.4 M** and [Base] = **0.2 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 AgI = 8.5×10^{-17} and K_{sp} of Hg_2I_2 = 2.5×10^{-26}

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

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

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

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

For Hg_2I_2: $[Hg_2^{2+}][I^-]^2 = 2.5 \times 10^{-26}$

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

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

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

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

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

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

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

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

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

Ans. bq / p

Sol. For $BaSO_4$, $[Ba^{2+}][SO_4^{2-}] = K_{sp}$ of $BaSO_4$ = q

For $CaSO_4$, $[Ca^{2+}][SO_4^{2-}] = K_{sp}$ of $CaSO_4$ = p

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

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

K_{sp} (CdS) = 8×10^{-27} ; K_{sp} (ZnS) = 1×10^{-21} ; K_a (H_2S) = 1.1×10^{-21}

Sol. In order to prevent precipitation of ZnS,

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

(Ionic product)

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

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

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

Thus for $H_2S \rightleftharpoons 2H^+ + S^{2-}$,
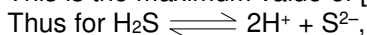
$K_a = \dfrac{[H^+]^2[S^{2-}]}{[H_2S]} = \dfrac{x^2(1 \times 10^{-20})}{0.1} = 1.1 \times 10^{-21}$

Or x = [H$^+$] = 0.105 M

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

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ADVIEQ(A)- 17

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) : $pH = \dfrac{1}{2} (pK_{a_1} - \log C)$ [if $\alpha_1 \le 0.1$ or 10%] ; $[H_{x-2}A^{2-}] = K_{a2}$

Solution of a polyprotic weak base (B) : $pOH = \dfrac{1}{2} (pK_{b_1} - \log C)$[if $\alpha_1 \le 0.1$ or 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, $K_{a_1} = 9 \times 10^{-8}$, $K_{a_2} = 1.2 \times 10^{-13}$.

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 $NH_3.H_2O$ solution ($K_b = 2 \times 10^{-5}$). Also calculate % dissociation of $NH_3.H_2O$ 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) : $[H^+] = C_1\alpha_1 + C_2\alpha_2 = \sqrt{C_1 K_{a_1} + C_2 K_{a_2}}$

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

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) :

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

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

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 $\alpha_1 \le 0.1$ 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 $\alpha_1 \le 0.1$ 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}
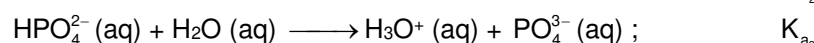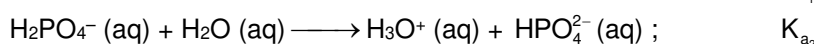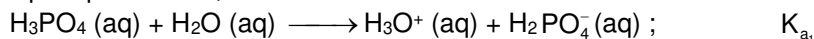
The correct order of K_a values is :
(A) $K_{a_1} > K_{a_2} < K_{a_3}$ (B) $K_{a_1} < K_{a_2} < K_{a_3}$ (C) $K_{a_1} > K_{a_2} > K_{a_3}$ (D) $K_{a_1} < K_{a_2} > K_{a_3}$

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 fron 2nd ionisation are negligible because of :
(A) $K_{b_2} << K_{b_1}$
(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 : $[H^+]_f = C_1$ (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. 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 ($[C_6NH_{16}^+]$) 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) : $[H^+] = C_1\alpha_1 + C_2\alpha_2 = \sqrt{C_1 K_{a_1} + C_2 K_{a_2}}$
> Mixture of two weak bases (both monoacidic) : $[OH^-] = C_1\alpha_1 + C_2\alpha_2 = \sqrt{C_1 K_{b_1} + C_2 K_{b_2}}$

C-1. Consider an aqueous solution, 0.1 M each in HOCN, HCOOH, $(COOH)_2$ and H_3PO_4. For HOCN, we can write : $K_a(HOCN) = \dfrac{[H^+][OCN^-]}{[HOCN]}$. $[H^+]$ 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.

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

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

NH$_4$OH ($K_b = 1.8 \times 10^{-5}$) will be :

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

C-4. At 25ºC, K_b for BOH = 1.0×10^{-12}. A 0.01 M solution of BOH has what value of [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 : $K_h \times K_b = K_w$; $h = \sqrt{\dfrac{K_h}{c}}$; pH = $\dfrac{1}{2}$ [pK$_w$–pK$_b$–log c] (valid if h < 0.1 or 10%)

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

Salt of weak acid and weak base : $K_h \times K_a \times K_b = K_w$; $\left(\dfrac{h}{1-h}\right) = \sqrt{K_h}$; pH = $\dfrac{1}{2}$ [pK$_w$+pK$_a$ – pK$_b$]

E-1. The pH of a solution obtained by mixing 100 mL of 0.2 M CH$_3$COOH with 100 mL of 0.2 M NaOH would be : (pK$_a$ for CH$_3$COOH = 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$_x$A) :

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

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

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

Solution containing amphiprotic anion of acid H$_x$A :

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

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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) $K_{h_1} << K_{h_2}$ (B) $K_{h_1} = \dfrac{K_w}{K_{b_1}}$ (C) $K_{h_1} = \dfrac{K_w}{K_{b_2}}$ (D) $K_{h_2} = \dfrac{K_{b_1}}{K_w}$

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. $(CH_3COO)C_5H_5NH$ 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

1. In a solution obtained by mixing 100 mL of 0.25 M Triethylamine ($K_b = 6.4 \times 10^{-5}$) & 400 mL of $\dfrac{M}{18}$ NH_4 OH ($K_b = 1.8 \times 10^{-5}$) :
(A) $[NH_4^+] = 4 \times 10^{-4}$ M (B) $[C_6NH_{16}^+] = 1.6 \times 10^{-3}$ M
(C) Both (A) & (B) (D) None of these

2. Ratio of $[HA^{2-}]$ 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

3. 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 = 2×10^{-3} (B) h = 0.01 (C) pH = 5 (D) pH = 9.7

PART - II : SINGLE AND DOUBLE VALUE INTEGER TYPE

1. For a solution of weak triprotic acid H_3A ($K_{a_1} >> K_{a_2}$, K_{a_3} ; $K_{a_2} = 10^{-8}$; $K_{a_3} = 10^{-13}$), $[A^{3-}] = 10^{-17}$ M. Determine pH of solution. Report your answer as '0', if you find data insufficient.

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.

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).

4. In a solution containing 0.01 M HCl and 0.1 M H_2CO_3, 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 H_2CO_3 are 4×10^{-7} & 4×10^{-11} respectively.

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 : $K_{a_1} = 10^{-4}$, $K_{a_2} = 10^{-7}$, $K_{a_3} = 10^{-11}$)

6. What is the pOH of a 0.5 M Na_3PO_4 solution ? Report your answer as 10 × pOH.
($K_{a_1} = 7.5 \times 10^{-3}$, $K_{a_2} = 6.2 \times 10^{-8}$, $K_{a_3} = 4 \times 10^{-13}$)

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

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.

2. When 0.1 mole solid NaOH is added in 1 L of 0.1 M NH_3(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, $[Na^+] = 0.1$ M, $[NH_3] = 0.1$ M, $[OH^-] = 0.2$ 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 4ºC and 25ºC ? Explain.   **[JEE-2003, 2/60]**

2. A weak acid HX at 25ºC 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 25ºC is 1.0×10^{-4}. The pH of 0.01 M solution of its sodium salt is :   **[JEE-2009, 4/160]**

4. 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	$(NH_4)_2C_2O_4$	NaCl	$Zn(NO_3)_2$
$FeCl_3$	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. pH = 4.52, 3×10^{-5} M, 1.2×10^{-13} M **A-2.** 10.91

B-1. -1.52, 9×10^{-5} M. **B-2.** 12, 2×10^{-4} M, 0.2 %

C-1. $[H^+] = 8 \times 10^{-3}$ M, $[HCOO^-] = 3 \times 10^{-3}$ M, $[OCN^-] = 5 \times 10^{-3}$ M

D-1. 10^{-6} M, 10^{-18} M **E-1.** 11 **E-2.** 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-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.** 3

PART – II

JEE(MAIN) OFFLINE PROBLEMS

1. (3) **2.** (4)
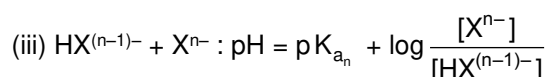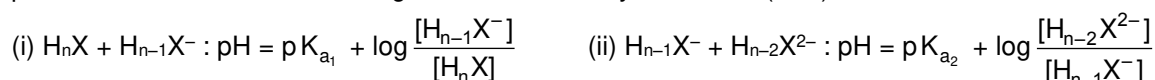
IONIC EQUILIBRIUM-II

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) :

(i) $H_nX + H_{n-1}X^-$: $pH = pK_{a_1} + \log \dfrac{[H_{n-1}X^-]}{[H_nX]}$ (ii) $H_{n-1}X^- + H_{n-2}X^{2-}$: $pH = pK_{a_2} + \log \dfrac{[H_{n-2}X^{2-}]}{[H_{n-1}X^-]}$

(iii) $HX^{(n-1)-} + X^{n-}$: $pH = pK_{a_n} + \log \dfrac{[X^{n-}]}{[HX^{(n-1)-}]}$

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.

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

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

A-1. An enviromental 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 :

At half equivalence point : $pH = pK_a$; $pH_{x \% \text{ neutralisation}} = pK_a + \dfrac{x}{100-x}$

In titration of WB and SA :

At half equivalence point : $pOH = pK_b$; $pOH_{x \% \text{ neutralisation}} = pK_b + \dfrac{x}{100-x}$

B-1. Calculate pH of the following mixtures. Given : K_a of $CH_3COOH = 2 \times 10^{-5}$ and K_b of $NH_4OH = 2 \times 10^{-5}$.
(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 CH_3COOH.
(c) 50 mL of 0.05 M NaOH + 50 mL of 0.10 M CH_3COOH.
(d) 50 mL of 0.10 M NH_4OH + 50 mL of 0.05 M HCl.
(e) 50 mL of 0.10 M NH_4OH + 50 mL of 0.10 M HCl.
(f) 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.

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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 : $pH = \dfrac{pK_{a_2} + pK_{a_1}}{2}$;

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

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

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

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 : $pOH = \dfrac{pK_{b_2} + pK_{b_1}}{2}$;

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

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

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

C-1. 50 mL of 0.05 M Propane-1,2-diamine solution is titrated with 0.1 M HCl solution at 25ºC. 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 25ºC. 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) $H_nX + H_{n-1}X^-$: $pH = pK_{a_1} + \log \dfrac{[H_{n-1}X^-]}{[H_nX]}$ (ii) $H_{n-1}X^- + H_{n-2}X^{2-}$: $pH = pK_{a_2} + \log \dfrac{[H_{n-2}X^{2-}]}{[H_{n-1}X^-]}$

(iii) $HX^{(n-1)-} + X^{n-}$: $pH = pK_{a_n} + \log \dfrac{[X^{n-}]}{[HX^{(n-1)-}]}$

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

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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. = $\dfrac{dx}{d\Delta pH}$ = $2.303\dfrac{(a+x)(b-x)}{a+b}$ ≈ $2.303\dfrac{ab}{a+b}$

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 H_2CO_3 – HCO_3^- buffer should be in the form of HCO_3^-, so as to have a neutral solution ? (K_{a_1} 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) 0.1 x mL (B) 10 x mL (C) 100 x 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 : pH = pK_a ; $pH_{x\% \text{ neutralisation}}$ = pK_a + $\dfrac{x}{100 - x}$

In titration of WB and SA :

At half equivalence point : pOH = pK_b ; $pOH_{x\% \text{ neutralisation}}$ = pK_b + $\dfrac{x}{100 - x}$

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 (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) 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 : $pH = \dfrac{pK_{a_2} + pK_{a_1}}{2}$;

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

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

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

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 : $pOH = \dfrac{pK_{b_2} + pK_{b_1}}{2}$;

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

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

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

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 $\left(K_{b_1} = 8 \times 10^{-5}; K_{b_2} = 2.7 \times 10^{-8}\right)$ with HCl solution, pH value of solution at Ist 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) $3 + \log 2$

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Exercise-2

✎ **Marked questions are recommended for Revision.**

PART - I : 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) = 1.8×10^{-5}. Report the answer rounding it off to the nearest whole number.

2.✎ 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 $\left(\dfrac{a}{1000\ b}\right)$.

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

1. 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.

2. Which of the following mixtures will act as buffer ?
(A) H_2CO_3 + NaOH (1.5 : 1 molar ratio)   (B) H_2CO_3 + NaOH (1.5 : 2 molar ratio)
(C) NH_4OH + HCl (5 : 4 molar ratio)   (D) NH_4OH + HCl (4 : 5 molar ratio)

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 ?
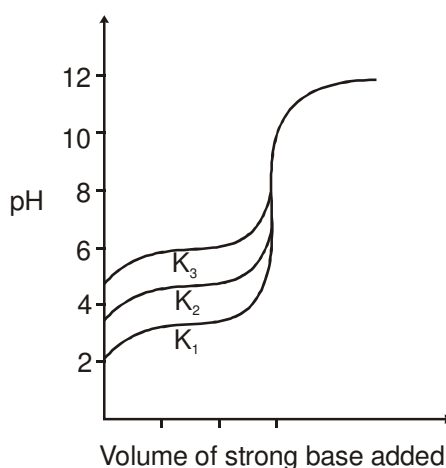
(A) $K_2 = (K_1 + K_3)/2$ (B) $pK_1 < pK_3$ (C) $K_1 > K_2$ (D) $K_2 > K_3$

PART - III : COMPREHENSION

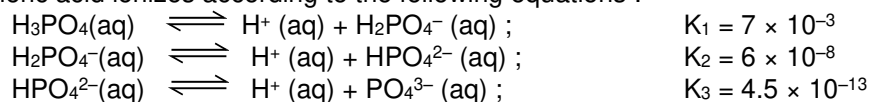**Read the following passage carefully and answer the questions.**

Comprehension # 1

The pH of basic buffer mixtures is given by : $pH = pK_a + \log \frac{[Base]}{[Salt]}$, 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.

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$^+$] :
   (A) 0.05 M   (B) 0.025 M   (C) 0.10 M   (D) 0.005 M

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$_3$COO$^-$ = 9.26)
   (A) 50 mL   (B) 25 mL   (C) 20 mL   (D) 10 mL

3. The ratio of pH of solution (I) containing 1 mole of CH$_3$COONa and 1 mole of HCl and solution (II) containing 1 mole of CH$_3$COONa 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 :

$$H_3PO_4(aq) \rightleftharpoons H^+ (aq) + H_2PO_4^- (aq) ; \qquad K_1 = 7 \times 10^{-3}$$
$$H_2PO_4^-(aq) \rightleftharpoons H^+ (aq) + HPO_4^{2-} (aq) ; \qquad K_2 = 6 \times 10^{-8}$$
$$HPO_4^{2-}(aq) \rightleftharpoons H^+ (aq) + PO_4^{3-} (aq) ; \qquad K_3 = 4.5 \times 10^{-13}$$

4. 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

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

Exercise-3

* Marked questions may have more than one correct option.

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

1. 500 ml of 0.2 M aqueous solution of acetic acid is mixed with 500 mL of 0.2 M HCl at 25ºC.
   (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]**

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]**

3. 0.1 mole of CH$_3$NH$_2$ ($K_b = 5 \times 10^{-4}$) 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]**
   (A) 8×10^{-2} M   (B) 8×10^{-11} M   (C) 1.6×10^{-11} M   (D) 8×10^{-5} M

4. 2.5 mL of $\dfrac{2}{5}$ M weak monoacidic base ($K_b = 1 \times 10^{-12}$ at 25°C) is titrated with $\dfrac{2}{15}$ 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 5.7ºC 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 5.6ºC was measured.

(Consider heat capacity of all solutions as 4.2 J g^{-1} 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 $[H^+]$ are given in LIST-II.

(Note : degree of dissociation (α) of weak acid and weak base is <<1; degree of hydrolysis of salt <<1; $[H^+]$ 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 $Ni(OH)_2$ in equilibrium with excess solid $Ni(OH)_2$ is diluted to 20 mL (solid $Ni(OH)_2$ is still present after dilution).

LIST-II

(1) the value of $[H^+]$ does not change on dilution

(2) the value of $[H^+]$ changes to half of its initial value on dilution

(3) the value of $[H^+]$ changes to two times of its initial value on dilution

(4) the value of $[H^+]$ changes to $\dfrac{1}{\sqrt{2}}$ times of its initial value on dilution

(5) the value of $[H^+]$ 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 → 4 ; Q → 2 ; R → 3 ; S → 1   (B) P → 4 ; Q → 3 ; R → 2 ; S → 3

(C) P → 1 ; Q → 4 ; R → 5 ; S → 3   (D) P → 1 ; Q → 5 ; R → 4 ; S → 1

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

JEE(MAIN) OFFLINE PROBLEMS

1. An alkali is titrated against an acid with methyl orange as indictor, 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

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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 = 5×10^{-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 ≈ 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 : $K_{sp} = x^x.y^y.(s)^{x+y}$

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 ?

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 $K_{IP} > K_{sp}$; $[A^{y+}]^x [B^{x-}]^y > K_{sp}$ 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' = **.....**

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) :

$$\frac{K_{sp}(A_xB_y)}{K_{sp}(A_xC_y)} = \frac{[B^{x-}]^y}{[C^{x-}]^y} = \frac{(ys_1)^y}{(ys_2)^y} = \left(\frac{s_1}{s_2}\right)^y$$

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.

C-1.✍   Calculate the simultaneous solubility of AgCl and AgI. Assume no hydrolysis of Ag^+ ion.
K_{sp} (AgCl) = 1×10^{-10}, K_{sp} (AgI) = 8.5×10^{-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.

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Section (D) : Selective Precipitation, Solubility exchange

Commit to memory :

Selective precipitation: On gradually adding $A_pB_q(s$; readily soluble) to a solution containing $C_1 M\ X^{w-}$ & $C_2 M\ Y^{z-}$

$[A^{q+}]$ req. for A_wX_q pptn = $\sqrt[w]{\dfrac{K_{sp}(A_wX_q)}{(C_1)^q}}$; $[A^{q+}]$ req. for A_zY_q pptn = $\sqrt[z]{\dfrac{K_{sp}(A_zY_q)}{(C_2)^q}}$

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 :

$$\sqrt[x]{\dfrac{K_{sp}(A_xB_y)}{[B^{x-}]_f^y}} = \sqrt[p]{\dfrac{K_{sp}(A_pD_y)}{[D^{p-}]_f^y}}$$

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_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' = **.....**

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_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.

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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-}
>
> $[A^{q+}]$ req. for A_wX_q pptn = $\sqrt[w]{\dfrac{K_{sp}(A_wX_q)}{(C_1)^q}}$; $[A^{q+}]$ req. for A_zY_q pptn = $\sqrt[z]{\dfrac{K_{sp}(A_zY_q)}{(C_2)^q}}$
>
> 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 :
>
> $\sqrt[x]{\dfrac{K_{sp}(A_xB_y)}{[B^{x-}]_f^y}} = \sqrt[p]{\dfrac{K_{sp}(A_pD_y)}{[D^{p-}]_f^y}}$

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

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Exercise-2

✎ **Marked questions are recommended for Revision.**

PART - I : ONLY ONE OPTION CORRECT TYPE

1. A solution contains $[NaCl] = [Na_2CO_3] = C$ 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, $\sqrt{\dfrac{K_{sp}(Ag_2CO_3)}{C}} < \dfrac{K_{sp}(AgCl)}{C}$ then Ag_2CO_3 will start precipitating first.

(D) If, $\sqrt{\dfrac{K_{sp}(Ag_2CO_3)}{C}} < \dfrac{K_{sp}(AgCl)}{C}$ then AgCl will start precipitating first.

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.

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.

PART - II : 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.

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 $[Ag(CN)_2]^- = 10^{-18}$. 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 $MgCl_2$(s) are added in 1 litre volume of a solution (S), already containing 0.2 mole of NaOH(s). Now answer the following questions :

1. Calculate pH of obtained solution. K_{sp} of $Mg(OH)_2$ is 1.6×10^{-12}.

(A) 8.6   (B) 8.5   (C) 8.65   (D) 8.56

2. What would be the new pH when 0.04 mole of NaOH(s) are added in the solution (S) ?

(A) 8.6   (B) 8.5   (C) 8.65   (D) 8.56

3.✎ Find the pH of the solution obtained after adding 0.04 mole of HCl(g) to the solution .

(A) 8.6   (B) 8.5   (C) 8.65   (D) 8.56

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Comprehension # 2

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 25ºC.

	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 $< \left(\dfrac{K_{sp}}{27}\right)^{1/4}$	(ii)	Solubility decreases because of presence of common cation in solution	(Q)	Solubility increases in basic solution as pH increases above 11
(III)	Solubility $= \left(\dfrac{K_{sp}}{27}\right)^{1/4}$	(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$_3$X 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$_3$X   (B) M$_3$X > MX$_2$ > MX   (C) MX$_2$ > M$_3$X > MX   (D) MX > M$_3$X > MX$_2$

4. In 1 L saturated solution of AgCl [K_{sp}(AgCl) = 1.6×10^{-10}], 0.1 mole of CuCl [K_{sp}(CuCl) = 1.0×10^{-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 solubility of a salt of weak acid **(AB)** at pH 3 is **Y**×10^{-3} 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]**

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

JEE(MAIN) ONLINE PROBLEMS

1. Zirconium phosphate $[Zr_3(PO_4)_4]$ dissociates into three zirconium cations of charge +4 and four phosphate anions of charge –3. If molar solubility of ziroconium 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) $S = \{K^{sp}/6912\}^7$

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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. $PbSO_4$, 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.** 4.47

PART - II

JEE(MAIN) ONLINE PROBLEMS

1. (2)

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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
1. The test is of **1 hour** duration.
2. The Test Booklet consists of **30** questions. The maximum marks are **120.**
3. Each question is allotted **4 (four)** marks for correct response.
4. Candidates will be awarded marks as stated above in Instructions No. 3 for correct response of each question.
   ¼ (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.
5. 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.

1. Which of the following is not a Lewis acid ?
   (1) $SiCl_4$ (2) SO_3 (3) Zn^{2+} (4) CO

2. 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}

3. An aqueous solution whose pH = 0 is :
   (1) Alkaline   (2) Acidic   (3) Neutral   (4) Not possible

4. 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

5. A 100 mL solution of a strong acid of pH = 1 is mixed with a 100 mL solution of another strong acid of pH = 2. The resulting pH will be nearly : (log 11 = 1.04)
   (1) 1.74   (2) 0.96   (3) 1.26   (4) 1.5

6. V_1 mL of 0.1 M HNO_3 is mixed with V_2 mL of 0.1 M $Sr(OH)_2$. 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 $V_1 = 2V_2$

7. 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

8. 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 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.

9. The pH of the solution of 0.2 M acetic acid and 0.1 M benzoic acid is :
   ($K_a(C_6H_5COOH) = 6.5 \times 10^{-5}$, $K_a(CH_3COOH) = 1.75 \times 10^{-5}$)
   (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 $X = \dfrac{[A^{3-}]}{[HA^{2-}]}$

(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 25ºC respectively are :
(1) 4, 10^{-8} (2) 10, 10^{-6} (3) 10, 10^{-8} (4) 4, 10^{-6}

13. 10 mL of $\dfrac{M}{5}$ CH_3COOH solution is mixed with 10 mL of $\dfrac{M}{5}$ 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 $K_{a_1} = 0^{-7}$ 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 × 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) $\dfrac{2}{3}$ (2) $\dfrac{1}{3}$ (3) $\dfrac{1}{2}$ (4) $\dfrac{1}{11}$

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

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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 :
(pK_a(CH_3COOH) = 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_{sp} = 2.5 × 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 certian 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) 10   (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 :

27. $SrCO_3$ (K_{sp} = 10^{-10}) and $ZnCO_3$ (K_{sp} = 1.5 × 10^{-11}) are dissolved together in a solution. The ratio of [Sr^{2+}]/[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 $Fe(OH)_3$ 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 KCN(aq) is greater than in pure water.
Statement-2 : When AgCN dissolve in KCN(aq), complex ion [$Ag(CN)_2$]$^-$ 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 $M(CN)_2$? (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) 1.73×10^{-5} mol dm^{-3} (B) 6.9×10^{-10} mol dm^{-3}
   (C) 9×10^{-20} mol dm^{-3} (D) 1.73×10^{-10} 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 ?
   (A) 10 (B) 8 (C) 5 (D) 12 **[NSEC-2000]**

4. The concentration of H_3O^+ ions in pure water is 10^{-6} mol dm^{-3}. The corresponding concentration of OH^- ions will be : **[NSEC-2000]**
   (A) 10^{-14} mol dm^{-3} (B) 10^{-8} mol dm^{-3} (C) 10^{-6} mol dm^{-3} (D) 10^{-7} mol dm^{-3}

5. In a reaction, $HCO_3^- + H_2O \rightarrow CO_3^{-2} + H_3O^+$
   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 0.1M solution of NH_4^+ ?
   [NSEC-2000]
   (A) NH_3 (B) NH_4Cl (C) both (D) none of these

7. The solubility of AgCl is 1.56×10^{-5} 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) $K_a = \left(\dfrac{\alpha^2}{1-\alpha}\right)V$ (B) $K_a = \left(\dfrac{\alpha^2}{1-\alpha}\right)\dfrac{1}{V}$ (C) $K_a = \dfrac{\alpha}{V}$ (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 0.1M CH_3COOH (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) $pH = pK_a + \log \dfrac{[acid]}{[salt]}$ (B) $pH = pK_a + \log \dfrac{[salt]}{[acid]}$

    (C) $pK_w = pK_a + \log \dfrac{[salt]}{[acid]}$ (D) $pH = pK_a + \log (salt) . (acid)$

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16. For the salt of strong acid and weak base, the hydrolysis constant is given by :   **[NSEC-2002]**

(A) $K_h = \dfrac{K_w}{K_b}$ (B) $K_h = \dfrac{K_w}{K_a}$ (C) $K_h = \dfrac{K_w}{K_a.K_b}$ (D) $K_h = \sqrt{\dfrac{K_w}{K_a.K_b}}$

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 :
(A) K_{sp} of ZnS is not exceeded   (B) K_{sp} of ZnS is decreases   **[NSEC-2002]**
(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) 1.62×10^{-2} mol dm^{-3} (B) 4.123×10^{-3} mol dm^{-3}
(C) 4.123×10^{-6} mol dm^{-3} (D) 5.1×10^{-3} 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^oC 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 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.

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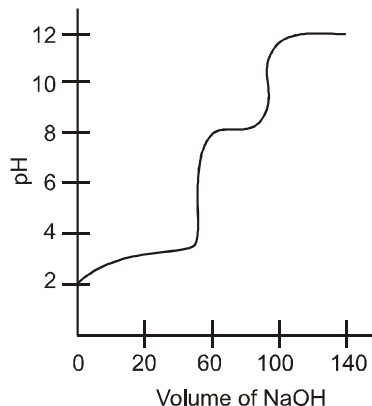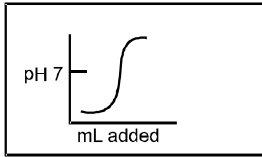Toll Free : 1800 258 5555 | CIN: U80302RJ2007PLC024029

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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°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 3.4×10^{-11} mol^3 L^{-3}. What will be is its solubiliy in gL^{-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 KNO_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_3 COONa and 250 cm^3 of 0.10 M CH_3COOH. [K_a of CH_3COOH = 1.8×10^{-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}

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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 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/dm^3 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]**
$[C_6H_5COOH$, Molar Mass = 122.1 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 $\dfrac{[HCO_3^-]}{[CO_2]}$ 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

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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 I2.0 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 1.00×10^{-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 3.60×10^{-5} 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 $moldm^{-3}$. 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 : ($pK_a = 4.74$) **[NSEC-2011]**
(A) 2.37 (B) 4.74 (C) 1.34 (D) 5.74

70. A 0.056 M solution of benzoic acid, C_6H_5COOH, is titrated with a strong base. $[H^+]$ 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) 6.3×10^{-5} M (B) 1.8×10^{-3} M (C) 7.9×10^{-3} M (D) 2.6×10^{-2} 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
$HOCl(aq) \rightleftharpoons H^+(aq) + OCl^-(aq)$, $OCl^-(aq) + H_2O(l) \rightleftharpoons HOCl(aq) + OH^-(aq)$
K_a for this reaction at 25ºC is 3.0×10^{-8} ($K_w = 1.0 \times 10^{-14}$ at 25º C)
Hence, K_h 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^-

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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 9.55×10^{-5} 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, acetric 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) $Al(CN)_3$ (B) $KC_2H_3O_2$ (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) 1.58×10^{-4} mol L^{-1} (B) 1.58×10^{-11} mol L^{-1} (C) 3.16×10^{-4} mol L^{-1} (D) 9.98×10^{-8} 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 $AgCl(s) + CNS^{-}(aq) \rightleftharpoons AgCNS(s) + Cl^{-}(aq)$ 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_wK_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 > 0.04M

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) $Mx > MY_2 > MZ_3$ (B) $MZ_3 > MY_2 > MX$ (C) $MZ_3 > MX > MY_2$ (D) $MY_2 > MX > MZ_3$

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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 1.0×10^{-3} mol L^{-1} solution of weak acid HA is 3.60. The dissociation constant of the acid is:
(A) 8.4×10^{-8} (B) 8.4×10^{-6} (C) 8.4×10^{-5} (D) 8.4×10^{-2} **[NSEC-2016]**

90. The colour changes of an indicator HIn in acid base titrations is given below
HIn (aq) $\rightleftharpoons$ H$^+$ (aq) + In$^-$ (aq)
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$_{NaOH\ moldm^{-3}}$
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 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$^+$, (C$_2$H$_5$)$_2$O   (B) H$_2$O, 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 pH = pK$_a$ of a monoprotic acid, 50% of the acid is ionised
II. If pH = pKa$_2$ of a diprotic acid, the average charge of all the ionised species is 0.5
III. When pH = pKa + 1, 10% of the acid is ionised
IV. When 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, pH = pK$_a$ + 2 at 25ºC, 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 [H$_3$O$^+$] and [OH$^-$] in an aqueous solution at a constant temperature ? **[NSEC-2018]**
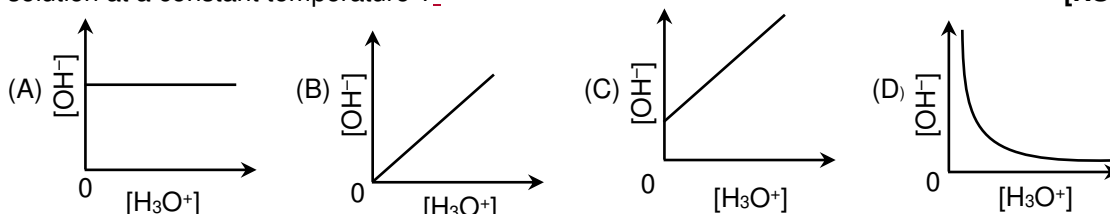
PART - III : HIGH LEVEL PROBLEMS (HLP)
THEORY

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 unionsed form of an acid indicator (HIn)
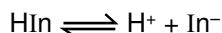
$$HIn \rightleftharpoons H^+ + In^-$$

$\therefore$ $K_{In} = \dfrac{[H^+][In^-]}{[HIn]}$ [K_{In} = indicator constant or dissociation constant of indicator]

or $[H^+] = K_{In} \times \dfrac{[HIn]}{[In^-]}$

Taking negative logarithm of both sides,

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

$\therefore$ **$pH = pK_{In} + \log \dfrac{[In^{''}]}{[HIn]}$** $\Rightarrow$ $pH = pK_{In} + \log \dfrac{[Ionised\ \ form]}{[Unionised\ \ form]}$

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 $\dfrac{[In^-]}{[HIn]}$ should be 10.

$\therefore$ $pH = pK_{In} + \log 10 = pK_{In} + 1$

At this stage, the percentage of the indicator in In$^-$ form would be given by :

$$\dfrac{[In^-]}{[In^-]+[HIn]} \times 100 = \dfrac{10}{10+1} \times 100 \ \ 91\%$$

Thus, nearly 91% of the indicator has been present in the ionised form (In$^-$). In fact, pH = pK$_{In}$ + 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 pH $\geq$ pK$_{In}$ + 1, the solution has a colour characteristic of In$^-$.

Case – II : For the solution to show colour due to HIn, the minimum ratio of $\dfrac{[In^-]}{[HIn]}$ should be $\dfrac{1}{10}$.

$\therefore$ $pH = pK_{In} + \log \dfrac{1}{10} = pK_{In} - 1$.

At this stage, the percentage of the indicator in In$^-$ form would be given by :

$$\dfrac{[In^-]}{[In^-]+[HIn]} \times 100 = \dfrac{1}{10+1} \times 100 \approx 9\%$$

Thus, nearly 9% of the indicator has been present in the ionised from (In⁻) and ≈ 91% of the indicator is present in the unionzed from (HIn). In fact, pH = pK_{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 pH ≤ pK_{In} – 1, the solution has a colour characteristic of HIn.

∴　　　　General pH range of an indicator : pK_{In} – 1 to pK_{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 pH$_{solution}$ < Minimum value of pH range	If pH$_{solution}$ > 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
	$NaOH + HCl \rightarrow NaCl + H_2O$	$NaOH + HCl \rightarrow NaCl + H_2O$
Na_2CO_3	50% reaction upto $NaHCO_3$ stage is indicated	100% reaction is indicated
	$Na_2CO_3 + HCl \rightarrow NaHCO_3 + NaCl$	$Na_2CO_3 + 2HCl \rightarrow 2NaCl + H_2O + CO_2$
$NaHCO_3$	No reaction is indicated	100% reaction is indicated
		$NaHCO_3 + HCl \rightarrow NaCl + H_2O + CO_2$

Solved Examples

Ex-1. pH of 0.1 M solution of NaA (sodium salt of a weak acid HA) is 8.92. Caculate 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 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.　　　$pH = \dfrac{1}{2}$ ($pK_a + pK_w + \log c$)

$8.92 = 7 + \dfrac{1}{2} pK_a + \dfrac{1}{2}$ (−1)

$\dfrac{1}{2} pK_a = 8.92 – 6.5 = 2.42$

∴　pK_a of HA = 4.84

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

$8.92 = 9.52 + \log \dfrac{[In^-]}{[HIn]}$

$\dfrac{[In^-]}{[HIn]} = \dfrac{\text{ionised}}{\text{unionised}} = \dfrac{1}{4}$

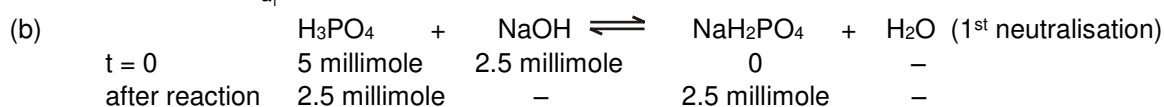Since ionised form % = $\dfrac{1}{1+4}$ × 100 = 20%, pink colour will not be visible.

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

(b)

$$H_3PO_4 \quad + \quad NaOH \rightleftharpoons \quad NaH_2PO_4 \quad + \quad H_2O \text{ (1}^{st}\text{ neutralisation)}$$

t = 0   5 millimole   2.5 millimole   0   –

after reaction   2.5 millimole   –   2.5 millimole   –

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 jsut sufficient to complete 1st neutralisation of H_3PO_4.

$$pH = \frac{pK_{a_1} + pK_{a_2}}{2} = \frac{3+7}{2} = 5 \text{ (1}^{st}\text{ eq pt)}$$

(d)   50 ml NaOH solution will be consumed in 1st neutralisation & remaining 25 mL (2.5 millimole) will participate in 2nd neutralisation.

$$NaH_2PO_4 \quad + \quad NaOH \longrightarrow \quad Na_2HPO_4 + \quad H_2O \text{ (2}^{nd}\text{ neutralisation)}$$

t = 0   5 millimole   2.5 millimole   0   –

after reaction   2.5 millimole   –   2.5 millimole   –
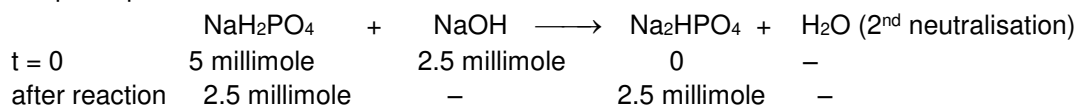
Buffer with equal amounts of $H_2PO_4^-$ & HPO_4^{2-} $\Rightarrow$ Half equivalence point with respect to 2nd neutralisation.

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.

$$pH = \frac{pK_{a_2} + pK_{a_3}}{2} = 9 \text{ (2}^{nd}\text{ eq pt)}$$

(f)   100 ml NaOH solution will be consumed in 2 neutralisations & remaining 25 mL (2.5 millimole) will participate in 3rd neutralisation.

$$Na_2HPO_4 \quad + \quad NaOH \longrightarrow \quad Na_3PO_4 \quad + \quad H_2O \text{ (3}^{rd}\text{ neutralisation)}$$

t = 0   5 millimole   2.5 millimole   0   –

after reaction   2.5 millimole   –   2.5 millimole   –
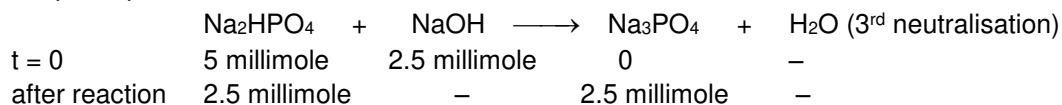
Buffer with equal amounts of HPO_4^{2-} & PO_4^{3-} $\Rightarrow$ Half equivalence point with respect to 3rd neutralisation.

pH = 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.

$$[Na_3PO_4] = \frac{\text{Millimole}}{\text{Total volume in mL}} = 5/200 = 1/40 \text{ M}$$

Assuming h to be negligible

$$h = \sqrt{\frac{K_w / K_{a_3}}{C}} = \sqrt{\frac{10^{-14}/10^{-11}}{1/40}} = 0.2 \text{ (not negligible)}$$

$$\therefore \quad \frac{1}{40} = \frac{h^2}{1-h} = \frac{10^{-14}}{10^{-11}}$$

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On solving this quadratic, h = 0.18

∴ $[OH^-] = ch = 4.5 \times 10^{-3}$ M

∴   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.

$[OH^-] = \dfrac{Millimole}{Total\ volume\ in\ mL} = 5/250 = 1/50$ M   ∴ pOH = 1.7 & pH = 12.3

(i)   50 mL NaOH will be consumed in 1st neutralisation & remaining 40 mL (4 millimole) will participate in 2nd neutralisation

	NaH_2PO_4 +	NaOH	⟶	Na_2HPO_4	+	H_2O
t = 0	5 millimole	4 millimole		0		–
after reaction	1 millimole	0		4 millimole		– ⟹ Buffer

$pH = pK_{a_2} + \log 4 = 7.6.$
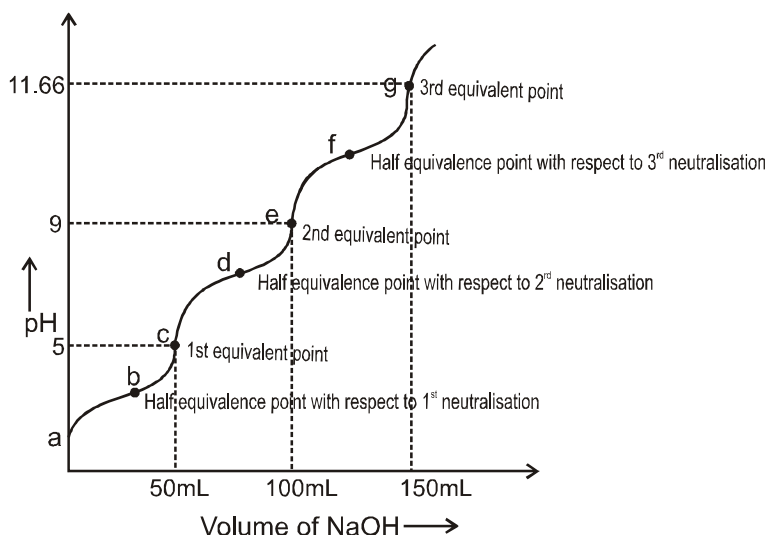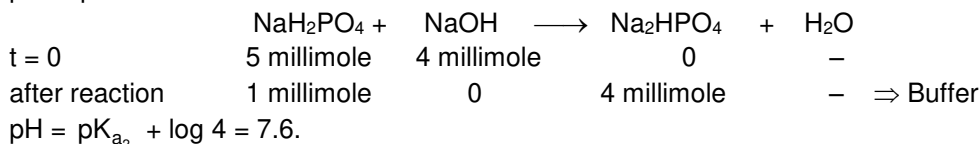
Solved Examples

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.

$$M_{base}\ V_{base} = M_{acid}\ V_{acid} \Rightarrow V_{acid} = \frac{0.3}{0.1} V_{base} = 3\ V_{base}$$

$$[CH_3COONa]_{Equivalence\ point} = \frac{Total\ \ moles}{Total\ \ volume} = \frac{0.3 \times V_{base}}{V_{acid} + V_{base}} = \frac{0.3}{4}\ \frac{V_{base}}{V_{base}} = 0.075$$

$$[OH^-] = \sqrt{\frac{K_w}{K_a} \times C} = \sqrt{\frac{10^{-14}}{7.5 \times 10^{-6}} \times 0.075} = 10^{-5} \qquad \Rightarrow \qquad pOH = 5$$

∴   pH = 9

Ex-3.   Predict titration curve for titration of Na_2CO_3 & HCl.

Sol. $Na_2CO_3 + HCl \longrightarrow NaHCO_3 + NaCl$

pH_1 = Half equivalence point with respect to 1st neutralisation = pK_{a_2} (∵ solution will be a buffer consisting of equal amount of CO_3^{2-} & HCO_3^-)

$$pH_{1^{st}\ eq\ pt} = \frac{pK_{a_1} + pK_{a_2}}{2} \ (\because amphiprotic\ anion)$$

$$NaHCO_3 + NaCl \longrightarrow H_2CO_3 + NaCl$$
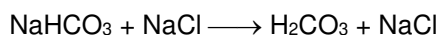
pH_2 = Half equivalence point with respect to 2nd neutralisation = pK_{a_1} ($\because$ solution will be a buffer consisting of equal amount of HCO_3^- & H_2CO_3)
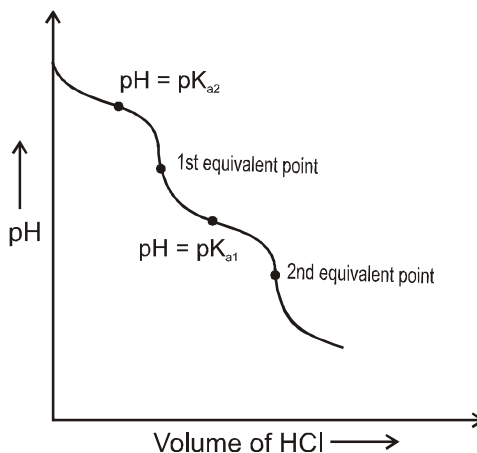
Figure-9

$pH_{2^{nd} \, eq \, pt} = 1/2 \, (pK_{a_1} - \log C)$ ($\because$ 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 4×10^{-3} M Ag^+ and 0.001 M NaCl, to prevent the precipitation of AgCl.

Given that $K_{sp}(AgCl) = 1.8 \times 10^{-10}$ and the formation constant of $[Ag(NH_3)_2]^+$ is $K_{formation} = \dfrac{10^8}{6}$.

Sol. Silver ion concentration which can be allowed to remain in the solution,

$1.8 \times 10^{-10} = [Ag^+] [Cl^-]$

$[Ag^+] = \dfrac{1.8 \times 10^{-10}}{0.001} = 1.8 \times 10^{-7}$ M,

This quantity is so small that almost all the Ag^+ ion will be consumed by NH_3 in complex formation.

	Ag^+	+	$2NH_3$	$\rightleftharpoons$	$[Ag(NH_3)_2]^+$	$K = \dfrac{10^8}{6}$
t = 0	4×10^{-3}		b		0	
at eq.	1.8×10^{-7}		$(b - 8 \times 10^{-3})$		4×10^{-3}	

$K = \dfrac{10^8}{6} = \dfrac{4 \times 10^{-3}}{1.8 \times 10^{-7} \times (b - 8 \times 10^{-3})^2} \Rightarrow b = 0.0445$ M.
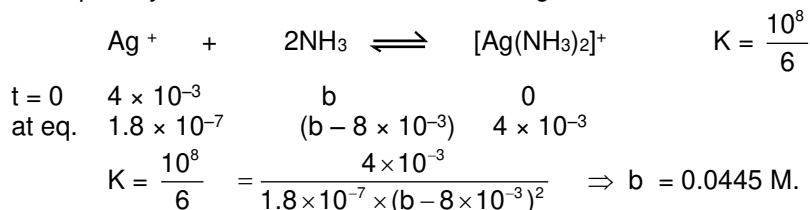
(B)   Solubility in appropriate buffer solutions

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.

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Solved Examples

Ex-5. The solubility of $Pb(OH)_2$ in water is 6.7×10^{-6} M. Calculate the solubility of $Pb(OH)_2$ in a buffer solution of pH = 8. Take $(6.7)^3 = 301$

Sol. $K_{sp} = 4 \times (6.7 \times 10^{-6})^3 = 1.204 \times 10^{-15}$

$s \times (10^{-6})^2 = 1.204 \times 10^{-15}$ $\Rightarrow$ $s = 1.204 \times 10^{-3}$ M

**Ex-6.** Caculate 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 MnS = x

$\therefore$ $[Mn^{2+}]$ = x = Initial concentration of S^{2-} ions, but free S^{2-} ions will be less because some of the S^{2-} ions will react with H^+ from buffer to form HS^- and H_2S.

$[Mn^{2+}]$ = x = $[S^{2-}]$ + $[HS^-]$ + $[H_2S]$ .....(1)
     free

Let us calculate the value of $[HS^-]$ & $[H_2S]$, in terms of free $[S^{2-}]$ ion. For that, consider :
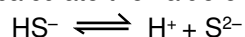
$HS^- \rightleftharpoons H^+ + S^{2-}$ $H_2S \rightleftharpoons H^+ + HS^-$
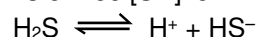
$K_2 = \dfrac{[H^+][S^{2-}]}{[HS^-]}$ $K_1 = \dfrac{[H^+][HS^-]}{[H_2S]}$

$\therefore$ $[HS^-] = \dfrac{[H^+]\ [S^{2-}]}{K_2}$ ....(2)

and $[H_2S] = \dfrac{[H^+]\ [HS^-]}{K_1} = \dfrac{[H^+]^2[S^{2-}]}{K_1\ K_2}$ ....(3)

Put (2) & (3) in (1)

$x = [S^{2-}]\left(1 + \dfrac{[H^+]}{K_2} + \dfrac{[H^+]^2}{K_1\ K_2}\right)$

$x = \dfrac{K_{sp}}{[Mn^{2+}]}\left(1 + \dfrac{[H^+]}{K_2} + \dfrac{[H^+]^2}{K_1\ K_2}\right)$ $\Rightarrow$ $x = \sqrt{K_{sp}\left(1 + \dfrac{[H^+]}{K_2} + \dfrac{[H^+]^2}{K_1 K_2}\right)}$

(C) **Solubility Exchange :**
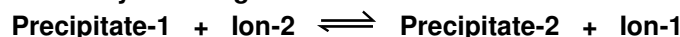
Precipitate-1 + Ion-2 $\rightleftharpoons$ Precipitate-2 + Ion-1

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.

Sol. $Na_2CO_3(aq) + CaF_2(s) \rightleftharpoons 2NaF(aq) + CaCO_3(s)$

t = 0   2   –   0   –
t = eq   2 – a   –   2a   –

where a is very small

For $CaCO_3$, $K_{sp} = x = [Ca^{2+}]\ [CO_3^{2-}] = [Ca^{2+}] \times 2$ ($\because CO_3^{2-}$ mainly coming from Na_2CO_3)

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

For CaF_2, $K_{sp} = 4y^3 = \left(\dfrac{x}{2}\right)[F^-]^2 \Rightarrow [F^-] = \sqrt{\dfrac{8y^3}{x}}$

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(D)   Solubility related to H_2S

The sulphide ion concentration in a solution that has been saturated with H_2S is given by :

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

Solved Examples

Ex-8. What $[H_3O^+]$ must be maintained in a saturated H_2S solution to precipitate Pb^{2+}, but not Zn^{2+} from a solution in which each ion is present at a concentration of 0.01 M ?
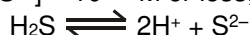
(K$_{sp}$ of H_2S = 1.1 × 10^{-22} ; K$_{sp}$ of ZnS = 1.0 × 10^{-21} ; $\sqrt{11}$ = 3.3)

Sol. For ZnS not to be precipitated from a solution of Zn^{2+} and Pb^{2+}, $IP_{ZnS} < K_{sp(ZnS)}$

$[Zn^{2+}][S^{2-}] < K_{sp}$ of ZnS

$[10^{-2}][S^{2-}] < 1.0 × 10^{-21}$ ∴ $[S^{2-}] < 10^{-19}$ M

So, at $[S^{2-}]$ = 10^{-19} M or less, no precipitation of ZnS will occur.

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

∴ $[H^+]^2[S^{2-}] = K_{sp(H_2S)} = 1.1 × 10^{-22}$ ∴ $[H^+]_{min}^2 [10^{-19}] = 1.1 × 10^{-22}$

$[H^+]_{min}^2 = 11 × 10^{-4}$ ∴ $[H^+]_{min} = 3.3 × 10^{-2}$ M

Thus, if $[H^+]$ = 3.3 × 10^{-2} M or more, the precipitation of ZnS will not take place and only PbS will precipitate.

SUBJECTIVE QUESTIONS

1.   (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.

2.   Calculate pOH, $[CH_3NH_3^+]$, $[C_4H_{13}N_2^+]$ & $[C_4H_{14}N_2^{2+}]$ in an aqueous solution consisting of 0.2 M Methyl amine (K$_b$ = 4.1 × 10^{-4}) & 0.1 M Butane-1, 4-diamine (K$_{b1}$= 6.2 × 10^{-4} M ; K$_{b2}$= 2.25 × 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 × 10^{-5} ; K$_{b2}$ = 2.7 × 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_{b_1} & K_{b_2} 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 x 10^{-5}, K for the indicator = 3.075 x 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 × 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 $\dfrac{a}{b}$ or more. However, red colour can be sensed by human eye distinctly when ratio of red form concentration to blue form concentration is $\dfrac{c}{d}$ 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$_{eq}$.

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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 $MgF_2 = \dfrac{9}{14} \times 10^{-8}$ and K_a of HF = 3.5×10^{-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 $\sqrt[4]{\dfrac{1000}{2.8}} = 4.4$. 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 (H_2S) = 1.2×10^{-13}, K_{sp} for MS = 6×10^{-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 $\alpha << 1$ for H_3PO_4 :
(A) pH = 1   (B) $\alpha_{H_3PO_4} = 10 K_{a_1}$ (C) $[HPO_4^{2-}] = 10 K_{a_1} K_{a_2}$ (D) All of these

16. (b) In above question
(A) $[PO_4^{3-}] = 100 K_{a_1} K_{a_2} K_{a_3}$ (B) $[PO_4^{3-}] = 10 K_{a_1} K_{a_2} K_{a_3}$
(C) $[PO_4^{3-}] = 1000 K_{a_1} K_{a_2} K_{a_3}$ (D) $[PO_4^{3-}] = K_{a_1} K_{a_2} K_{a_3}$

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 : HF > HOCl > HOBr > 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 << 1)

(A) pH = $\dfrac{1}{2}$ ($pK_w + pK_{a_3} + \log c$)   (B) pH = $\dfrac{1}{2}$ ($pK_w + pK_{a_2} + \log c$)

(C) pH = $\dfrac{1}{2}$ ($pK_w + pK_{a_1} + \log c$)   (D) pH = $\dfrac{1}{2}$ ($pK_w - pK_{a_3} - \log c$)

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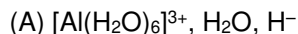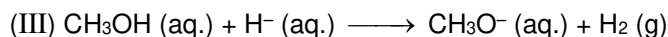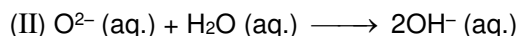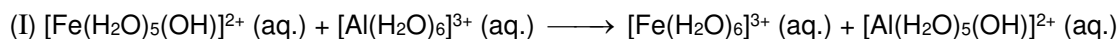**ADVIEQ(A)- 57**

18. (b) In above solution,

(A) $[HA^{2-}] = \sqrt{\dfrac{cK_w}{K_{a_3}}}$

(B) $[H_2A^-] = \dfrac{K_w}{K_{a_2}}$

(C) $[H_3A] = \dfrac{K_w}{K_{a_1}K_{a_2}}\sqrt{\dfrac{K_wK_{a_3}}{c}}$

(D) All of these

19. Identify acids in the following reactions according to Bronsted - Lowry concept :

(I) $[Fe(H_2O)_5(OH)]^{2+}$ (aq.) + $[Al(H_2O)_6]^{3+}$ (aq.) $\longrightarrow$ $[Fe(H_2O)_6]^{3+}$ (aq.) + $[Al(H_2O)_5(OH)]^{2+}$ (aq.)

(II) O^{2-} (aq.) + H_2O (aq.) $\longrightarrow$ $2OH^-$ (aq.)

(III) CH_3OH (aq.) + H^- (aq.) $\longrightarrow$ CH_3O^- (aq.) + H_2 (g)

(A) $[Al(H_2O)_6]^{3+}$, H_2O, H^-

(B) $[Fe(H_2O)_5(OH)]^{2+}$, H_2O, CH_3OH

(C) $[Al(H_2O)_6]^{3+}$, H_2O, CH_3OH

(D) $[Fe(H_2O)_5(OH)]^{2+}$, O^{2-}, H^-
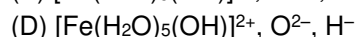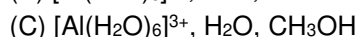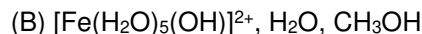
20. In aqueous solution, boric acid H_3BO_3 is a :

(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 (pK_{b1}= 3.7 & pK_{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}
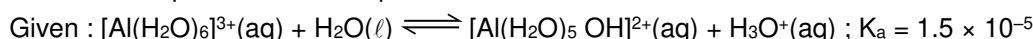
(A) 0.36 M   (B) 0.036 M   (C) 2×10^{-5} M   (D) None of these

23. Calculate the pH of a 0.15 M aqueous solution of $AlCl_3$.

Given : $[Al(H_2O)_6]^{3+}$(aq.) + $H_2O(\ell)$ $\rightleftharpoons$ $[Al(H_2O)_5 OH]^{2+}$(aq.) + H_3O^+(aq) ; $K_a = 1.5 \times 10^{-5}$

(A) 2.82   (B) 5   (C) 9   (D) 11.18

24. Calculate $[OH^-]$ & $[H_2C_2O_4]$ in a 0.005 M $Na_2C_2O_4$ solution. Given : K_{a_1} & K_{a_2} for oxalic acid are 5.6×10^{-2} & 5.4×10^{-5}. Take $\sqrt{\dfrac{1}{108}} = 0.096$

(A) $[OH^-] = 9.6 \times 10^{-7}$ M

(B) $[H_2C_2O_4] = \dfrac{5}{28} \times 10^{-12}$ 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 (C) OH^-

26. Which one of the following statements is not true ?

(A) The conjugate base of $H_2PO_4^-$ is HPO_4^{2-}.

(B) pH + pOH = 14 for all aqueous solutions at 25ºC.

(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.

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28. 100 mL of 0.05 M $C_3N_2H_{12}SO_4$ (salt of Propane-1,2-diamine & H_2SO_4) and some volume of 0.1 M $C_3N_2H_{11}$ 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 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 $(pK_a - 1)$ to $(pK_a + 1)$ and indicator shows its characteristic colours in this range.

(ii) In general, pH range of an indicator is $(pK_a - 1)$ to $(pK_a + 1)$ and indicator does not show its characteristic colours in this range.

(iii) In the relation : $pH = pK_{In} + \log_{10} \dfrac{\left[In^-\right]}{[HIn]}$, pH value represents pH of indicator solution.

(iv) In the relation : $pH = pK_{In} + \log_{10} \dfrac{\left[In^-\right]}{[HIn]}$, 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 $pK_a = 5$. 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 pH < 3.1, the indicator methyl red is coloured red, at 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 pK_b (NH_4OH) = 4.74.

(A) Red   (B) Yellow

(C) Orange   (D) 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) $\dfrac{9}{10}$ (B) $\dfrac{1}{11}$ (C) $\dfrac{10}{11}$ (D) $\dfrac{1}{10}$

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 :
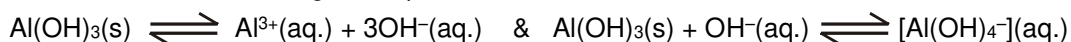
(A)

(B)

(C)

(D)
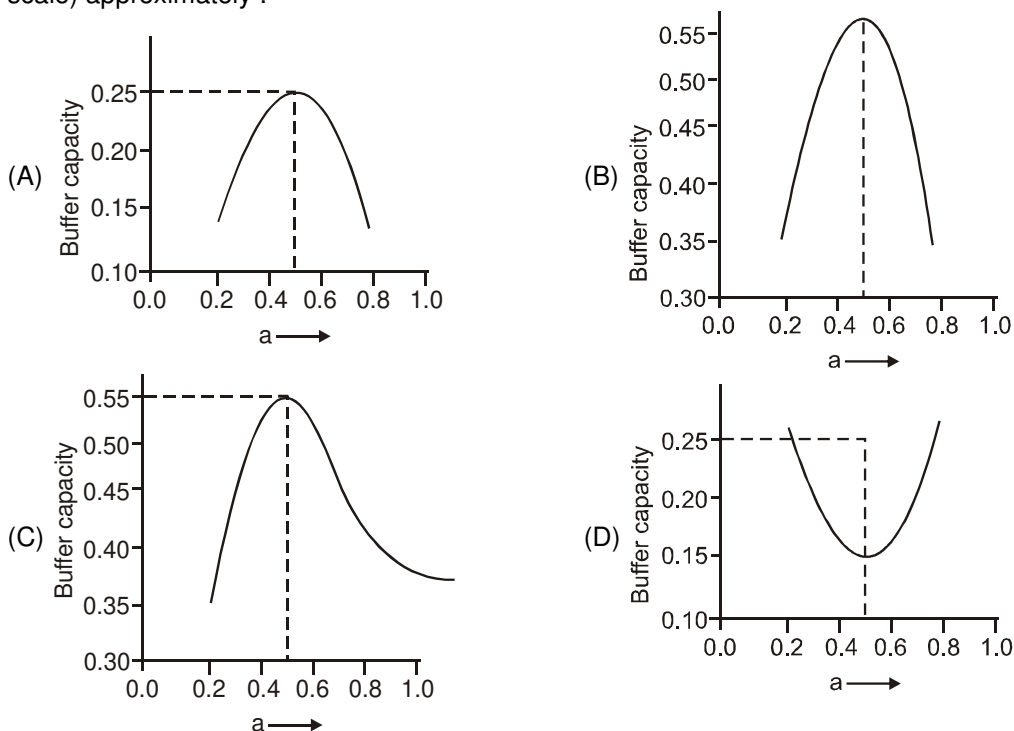
37. An acid-base indicator which is a weak acid has a pK_{In} value = 5.45. At what concentration ratio of sodium acetate to acetic acid would the indicator show a colour half-way between those of its acid and conjugate base forms? [pK_a of acetic acid = 4.75]
(A) 4 : 1   (B) 6 : 1   (C) 5 : 1   (D) 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) >> 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) $[N^+] \approx \dfrac{K_{sp}(NX)}{\sqrt{K_{sp}(MX)}}$ (<< $[M^+]$)
(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}

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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) $\left[X^-\right] = \dfrac{nx}{100}$

(C) $\left[Y^-\right] = \dfrac{K_{sp}(MY)}{K_{sp}(MX)} \times \dfrac{nx}{100}$

(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 $K_{sp}(AgCl)$, if $K_{sp}(Ag_2CO_3) = 8.1 \times 10^{-12}$. (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 $[NH_3]$ in its solution. K_{sp} of $Mg(OH)_2 = 1.62 \times 10^{-11}$ and K_b of $NH_4OH = 1.8 \times 10^{-5}$.

(A) 0.4 M   (B) 0.8 M   (C) 1.6 M   (D) 0.08 M

45. Solubility of $Fe(OH)_3$ ($K_{sp} = 10^{-38}$) :

(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 $H_2S = 9.6 \times 10^{-21}$; K_{sp} of MnS $= 2.5 \times 10^{-13}$; K_{sp} of 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 $H_2S = 9.6 \times 10^{-21}$; K_{sp} of MnS $= 2.5 \times 10^{-13}$; K_{sp} of 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 $[Cu^{2+}]$ ion that will saturate the above solution with CuS. Given K_{sp} of CuS $= 6.4 \times 10^{-36}$, K_a for $H_2S = 9.6 \times 10^{-21}$ and solubility of $H_2S = 0.1$ mole litre^{-1}.

(A) $\dfrac{2}{3} \times 10^{-16}$ M   (B) $\dfrac{2}{3} \times 10^{-14}$ M   (C) $\dfrac{2}{3} \times 10^{-18}$ M   (D) $\dfrac{3}{2} \times 10^{-16}$ M

49(a). The salt $Al(OH)_3$ is involved in the following two equilibria :

$Al(OH)_3(s) \rightleftharpoons Al^{3+}(aq) + 3OH^-(aq)$; K_{sp}

$Al(OH)_3(s) + OH^-(aq) \rightleftharpoons Al(OH)_4^-(aq)$; K_C

Which of the following relationship is correct when the solubility is minimum ?

(A) $[OH^-] = \left(\dfrac{K_{sp}}{K_C}\right)^{1/3}$ (B) $[OH^-] = \left(\dfrac{K_C}{K_{sp}}\right)^{1/4}$

(C) $[OH^-] = \sqrt{\left(\dfrac{K_{sp}}{K_C}\right)^{1/4}}$ (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)

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49(c). $Al(OH)_3$ is involved in the folllowing two equilibria :

$$Al(OH)_3(s) \rightleftharpoons Al^{3+}(aq.) + 3OH^-(aq.) \quad \& \quad Al(OH)_3(s) + OH^-(aq.) \rightleftharpoons [Al(OH)_4^-](aq.)$$

Then :

(A) Solubility of $Al(OH)_3$ will be more in acidic solutions & less in basic solution, both as compared to in water.

(B) Solubility of $Al(OH)_3$ will be less in acidic solutions & more in basic solution, both as compared to in water.

(C) Solubility of $Al(OH)_3$ will be more in acidic solutions & more in basic solution, both as compared to in water.

(D) Solubility of $Al(OH)_3$ 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 = $NH_3.H_2O$ solution of pH equal to 9.26	(q)	$[OH^-]$
(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 $Ba(OH)_2$ + 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 (pK_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 (pK_{a_1} = 4, pK_{a_2} = 7, pK_{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 $H_2C_2O_4$ (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 hydrolyisis
(D)	100 mL of NaOH	(s)	pH > 7

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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 (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 (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)	$[Mg^{2+}]_{min}$ required for precipitation of $Mg(OH)_2$ ($K_{sp} = 1.794 \times 10^{-11}$) from a solution containing 0.36 M NaOH.
(B)	1.38×10^{-10} M	(q)	Solubility of Hg_2Cl_2 ($K_{sp} = 1.296 \times 10^{-18}$) in 0.18 M $BaCl_2$ solution.
(C)	10^{-17} M	(r)	$[Ca^{2+}]$ in a solution saturated with respect to both $CaCO_3$ ($K_{sp} = 2.6 \times 10^{-9}$) & CaC_2O_4 ($K_{sp} = 3.8 \times 10^{-9}$).
(D)	7.5×10^{-18} M	(s)	Solubility of $Fe(OH)_3$ ($K_{sp} = 10^{-38}$) in pure water.
		(t)	$[Ag^+]$ in resulting solution obtained by mixing equal volumes of 0.06 M $AgNO_3$ solution & 0.2 M KCN solution (K_f of $[Ag(CN)_2]^-$ = 2.5×10^{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, $(COOH)_2$, $H_2S_2O_8$, H_2SO_4, H_2SO_3, H_2CO_3, H_2S and $H_4P_2O_5$?

56. 'A' solution of strong acid/strong base of pH = x is mixed with equal volume of 'B' solution of strong acid/strong base of pH = (14 – x), such that the resulting mixture has a 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 NH_4^+–NH_3 buffer is supposed to keep the pH of the solution constant within 0.3 pH unit during the reaction. $CH_3COOCH_3(aq) + 2H_2O(aq) \longrightarrow CH_3COO^-(aq) + H_3O^+(aq) + CH_3OH(aq)$
If this solution had initial concentrations : $[NH_4^+]_0$ = 0.1 M, $[NH_3]_0$ = 0.06 M, $[CH_3COOCH_3]_0$ = 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.
[$K_b(NH_3)$ = 1.8×10^{-5}]

58. 0.98 g H_3PO_4 is dissolved in 100 mL of a buffer solution (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 $pC_1 + pC_2 + pC_3 + pC_4$. ($pC_i$ = $-\log C_i$; where i = 1, 2, 3, 4) Given : For H_3PO_4, K_{a_1} = 10^{-3}, K_{a_2} = 10^{-8}, K_{a_3} = 10^{-12}.

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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_2PO_2 + H_2SO_4	InOH ($K_{In} = 3 \times 10^{-5}$)
(viii)	Pyridine + Benzoic acid	Phenol red (6.8 - 8.2)
(ix)	KH_2BO_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, $K_2C_2O_4$, KHC_2O_4, H_3PO_3, $\underset{COOH}{\overset{COOH}{|}}$, 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 $pH_{solution} = x$ (> 7), when it is titrated against 50 mL, 0.2 M H_2CO_3. (For H_2CO_3 : $K_{a_1} = 4.3 \times 10^{-6}$, $K_{a_2} = 5.6 \times 10^{-11}$)

Report your answer as (V + x) × 0.4, rounding it off to the nearest whole number.

62. The solubility product of $Ag_2C_2O_4$ at 25°C is 1.29×10^{-11} mol^3 L^{-3}. A solution of $K_2C_2O_4$ containing 0.152 mole in 500 mL water is shaken with excess of Ag_2CO_3 till the following equilibrium is reached :

$$Ag_2CO_3(s) + K_2C_2O_4(aq) \rightleftharpoons Ag_2C_2O_4(s) + K_2CO_3(aq)$$

At equilibrium, the solution contains 0.0358 mole of K_2CO_3. Assuming the degree of dissociation of $K_2C_2O_4$ and K_2CO_3 to be equal, if the solubility product of Ag_2CO_3 is 3.794×10^{-x} mol^3L^{-3}, find x.

63. Find out maximum number of moles of $PbCO_3$ soluble in 100 L buffer solution of pH = 3, rounding it off to the nearest whole number.

K_{a_1} (H_2CO_3) = $\dfrac{50}{11} \times 10^{-7}$

K_{a_2} (H_2CO_3) = 5.5×10^{-11}

K_{sp} ($PbCO_3$) = 7.5×10^{-14} ; (Take $\sqrt{0.3} = 0.55$)

64. 0.1 millimole of $CdSO_4$ are present in 10 mL acid solution of 0.08 M HCl. Now H_2S is passed to precipitate all the Cd^{2+} ions. Find the pOH of the solution after filtering off precipitate, boiling off H_2S and making the solution 100 mL by adding H_2O.

ONE OR MORE THAN ONE OPTIONS CORRECT TYPE

65. Select correct statement(s) :
(A) CH_3COOH (a weak acid) behaves as a strong acid in NH_3.
(B) HNO_3 (strong acid) behaves as a base in HF (anhydrous).
(C) H_2SO_4 dissociates to a very small extent in glacial CH_3COOH.
(D) HI is a stronger acid than HCl in H_2O.

66. C M fluoroacetic acid solution was found to contain $[H^+] = 1.5 \times 10^{-3}$ M. K_a of fluoroacetic acid = 2.5×10^{-3}. Then :
(A) C = 9×10^{-4} M
(B) $[FCH_2COOH] = 9 \times 10^{-4}$ M
(C) C = 2.4×10^{-3} 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 $Ba(OH)_2$ is added. Then :

(A) $pH_f - pH_i = 0.5$ (B) $\alpha_i - \alpha_f = 0.12$ (C) $\dfrac{[C_2N_2H_{10}^{2+}]_i}{[C_2N_2H_{10}^{2+}]_f} = 0.128$ (D) $\dfrac{[C_2N_2H_9^{+}]_i}{[C_2N_2H_9^{+}]_f} = 2.5$

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) $pH_1 > pH_2$ (B) $pH_2 < pH_4$ (C) $pH_2 < pH_3$ (D) $pH_3 > pH_4$

69. For a 0.072 M $NaHSO_4$ solution, select the incorrect option(s) : (K_{a_1} and K_{a_2} of $H_2SO_4 = \infty$ & 1.2×10^{-2})

(A) pH = 1.62   (B) pH = 7.39

(C) Degree of hydrolysis, $h = \dfrac{1}{\sqrt{6}}$ (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 replace by H_2SO_4 of equal $[H_3O^+]$.

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 ($pK_{In} = 9$) is added to a solution of 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 ?
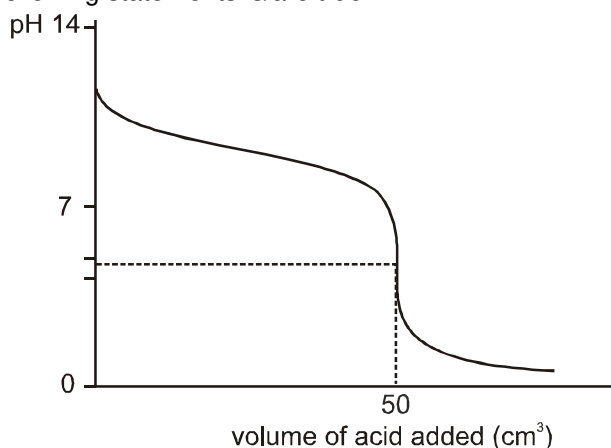
(A) The initial fast decrement in pH is due to fast consumption of free OH^- ions by HCl.
(B) The slow decrease of pH is due to formation of an acidic buffer solution after addition of some HCl.
(C) The slope of shown pH graph (magnitude only) will be minimum when 25 mL of 0.1 M HCl is added.
(D) The slow decrease of pH is due to formation of a basic buffer solution after addition of some HCl.

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ADVIEQ(A)- 65

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 :
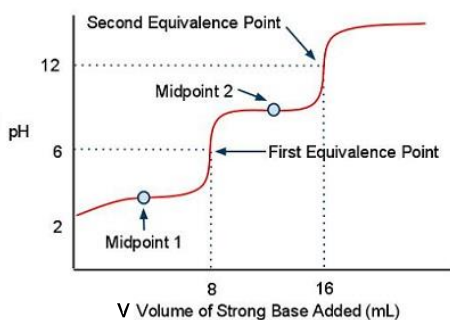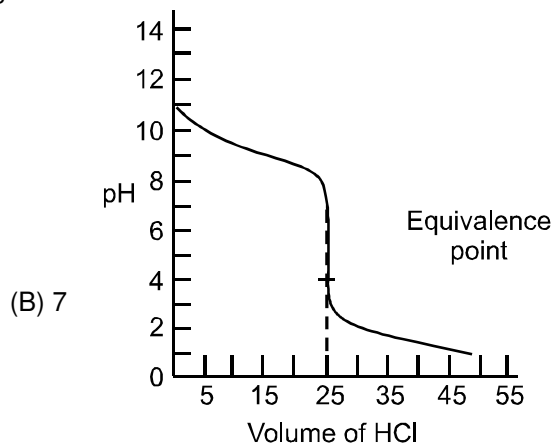

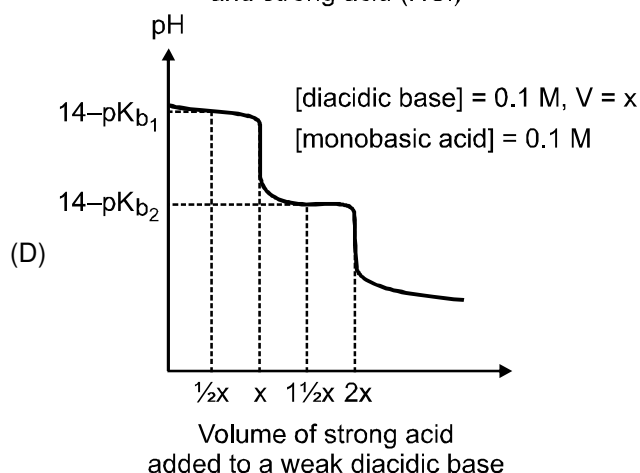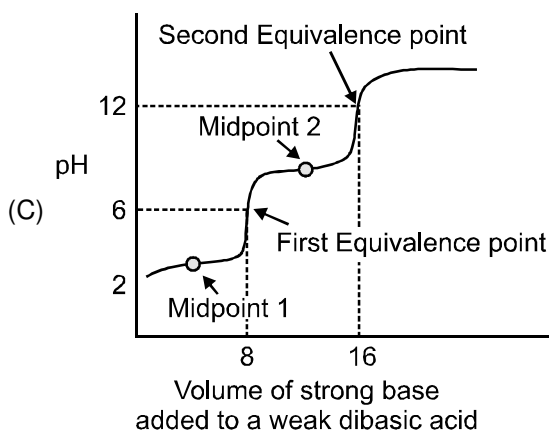(A) Na_2CO_3 (B) Ethylene diamine   (C) $H_2C_2O_4$ (D) $CH_2(COOH)_2$

75. Select the correct graph(s) for the corresponding acid-base titration :
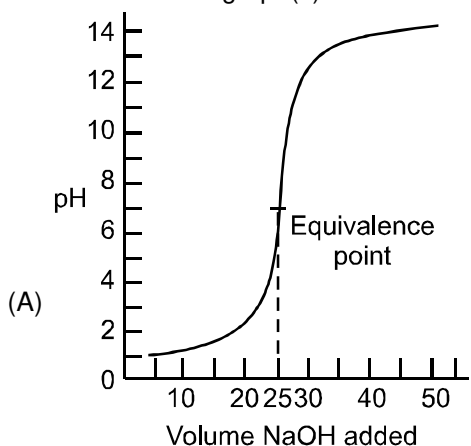
(A) Titration curve of strong acid (HCl) with a strong base (NaOH)

(B) The pH titration curve of weak base (NH_4OH) and strong acid (HCl)

(C) Volume of strong base added to a weak dibasic acid

(D) [diacidic base] = 0.1 M, V = x, [monobasic acid] = 0.1 M. 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) $[Ag^+]_{\text{Just after mixing}} = 3.038 \times 10^{-2}$ M.

(B) $[Pb^{2+}]_{\text{Just after mixing}} = 3.78 \times 10^{-7}$ M

(C) Only $PbSO_4$ will get precipitated.

(D) Both Ag_2CrO_4 and $PbSO_4$ will get precipitated.

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77. Calculate $[Ag^+]$, $[CO_3^{2-}]$ & $[CrO_4^{2-}]$ in a solution saturated with respect to both Ag_2CO_3 & Ag_2CrO_4.

Given: $K_{sp} (Ag_2CO_3) = 4 \times 10^{-12}$; $K_{sp} (Ag_2CrO_4) = 2.4 \times 10^{-12}$ & $\dfrac{1}{4\sqrt[3]{5}} = 0.146$

(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 Ag NO_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) $s_1 = \dfrac{1}{27}$ mol/L   (B) $s_2 = \dfrac{10^{-4}}{1728}$ mol/L   (C) $\dfrac{[Cl^-]}{[CN^-]} = 6.4 \times 10^5$

(D) Separate values of s_1 and s_2 cannot be determined, just their ratio $\dfrac{s_2}{s_1} = 1.5625 \times 10^{-6}$ can be known.

PART - IV : PRACTICE TEST-2 (IIT-JEE (ADVANCED Pattern))

Max. Time : 1 Hr.   **Max. Marks : 66**

Important Instructions
A.   General :
1.   The test is of 1 hour duration.
2.   The Test Booklet consists of 22 questions. The maximum marks are 66.
B.   Question Paper Format :
3.   Each part consists of five sections.
4.   Section 1 contains 7 multiple choice questions. Each question has four choices (A), (B), (C) and (D) out of which ONE is correct.
5.   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.
6.   Section 3 contains 6 questions. The answer to each of the questions is a single-digit integer, ranging from 0 to 9 (both inclusive).
7.   Section 4 contains 1 paragraph, describing theory, experiment and data etc. 3 questions relate to paragraph. Each question pertaining to a partcular passage should have only one correct answer among the four given choices (A), (B), (C) and (D).
8.   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 :
9.   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.
10.   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.

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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 25ºC, 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.

---

1. 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 :
   (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) $pH_I < pH_{II} < pH_{III}$
   (D) Solutions II and III cannot be used as standard solutions in a titration.

2. 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

3. A 0.01 M solution of $PuO_2(NO_3)_2$ was found to have a pH of 4. Then select the INCORRECT option :
   (A) % hydrolysis of PuO_2^{2+} = 1 %.   (B) K_b for $PuO_2(OH)^+$ = 10^{-8}.
   (C) Hydrolysis is expected to be endothermic.   (D) None of these

4. 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 NH_4^+ = 5×10^{-10})
   (A) $\dfrac{10}{4.7}$ % increase   (B) $\dfrac{10}{4.7}$ % decrease   (C) $\dfrac{10}{9.3}$ % increase   (D) $\dfrac{10}{9.3}$ % decrease

5. Select INCORRECT statement :
   (A) Phenolphthalein is not a suitable indicator for the titration of HCl(aq) with NH_4OH(aq).
   (B) An acid-type indicator in a buffer solution of pH = pK_{In} + 1 is ionized to the extent of $\dfrac{1000}{11}$ %.
   (C) In the titration of a monoacidic weak base with a strong acid, the pH at the equivalent point is always calculated by pH = $\dfrac{1}{2}$ [$pK_w - pK_b - \log C$].
   (D) When Na_3PO_4(aq) is titrated with HCl(aq), the pH of solution at second equivalent point is calculated by $\dfrac{1}{2}$ [$pK_{a_1} + pK_{a_2}$].

6. The solubility of SrF_2 ($K_{sp} = 2.5 \times 10^{-9}$) in 0.1 M $SrCl_2$ solution is : (neglect hydrolysis of F^-)
   (A) $\sqrt{\dfrac{5}{2}} \times 10^{-4}$ mol/L   (B) 5×10^{-3} mol/L   (C) $5\sqrt{\dfrac{5}{2}} \times 10^{-5}$ mol/L   (D) $\dfrac{5}{2} \times 10^{-3}$ mol/L

7. 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 AgA(s).
   Given : K_a(HA) = 10^{-10}
   (A) 1.1×10^{-11} (B) 1.1×10^{-10} (C) 10^{-12} (D) Data insufficient

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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) $pH > \dfrac{pK_w}{2}$ (B) $pH > pOH$ (C) $pOH < \dfrac{pK_w}{2}$ (D) $pH < pOH$

9.   pH of aqueous solution of which of the following salt(s) is/are independent of its concentration ?
   (A) CH_3COONa (B) $C_6H_5NH_3Cl$ (C) $KClO_4$ (D) CH_3COONH_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) $pH_1 = 7.9$ (B) $pH_1 = 6.5$ (C) $pH_2 = 7.3$ (D) $pH_2 = 7.1$

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 $\left(\dfrac{1}{5}\right)^{th}$ 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 $\{[H_2S] = 0.1\ M\}$ can be represented by :

   $$MS + 2H^+ \rightleftharpoons M^{2+} + H_2S\ ;\ K_{eq} = \dfrac{[M^{2+}][H_2S]}{[H^+]^2}$$

   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 precipated at total $[H^+] = 1$ 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 25ºC for reaction : $NH_3 + H_3O^+ \rightleftharpoons NH_4^+ + H_2O$ 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 0ºC :
   $$2Ag(s) + 2I^-(aq) + 2H_2O(\ell) \rightleftharpoons 2AgI(s) + H_2(g) + 2OH^-(aq)$$

   The equilibrium constant for the above reaction is 4×10^{-9}. At equilibrium, solution occupies $\left(\dfrac{1}{3.24}\right)^{th}$ 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 $[A^{2-}]/[H^+]$ 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(BOH) = 10^{-5}]

17. 3.29×10^{-3} mg AgBr(s) (K_{sp}= 4.9×10^{-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, [Mn^{2+}] = 0.015 M and is saturated with H_2S (0.1 M). Given : K_a (CH_3COOH) = 1.8×10^{-5}, $K_a(H_2S)$ = 9×10^{-21}, $K_{sp}(MnS)$ = 2.4×10^{-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.
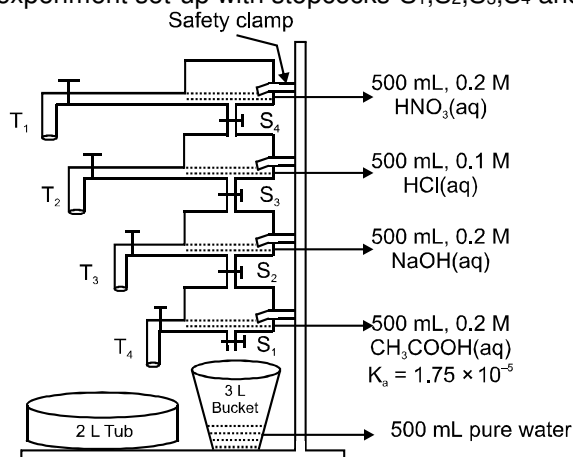
19. In which of the following cases will the solutions in tub have a pH different from others ?
(A) T_1 and T_4 are opened.   (B) Only T_2 is opened.
(C) T_1, T_2, T_3 and T_4 are all opened.   (D) T_1 is opened and the content of bucket is poured in the tub.

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 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/deacrease) 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   (B) I–Q, II–P, III–S, IV–R
(C) I–R, II–S, III–Q, IV–P   (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.***	(AB)	**30.**	(C)
31.	(C)	**32.***	(BC)	**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.**	(D)	**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 ; $\dfrac{41}{60} \times 10^{-2}\,M$; $\dfrac{31}{60} \times 10^{-2}\,M$; $\dfrac{1395}{144} \times 10^{-6}\,M$ **3.** $13, 5.4 \times 10^{-11}\,M$

4. 2.3 ; $5 \times 10^{-3}\,M$; $10^{-8}\,M$ **5.** 0.23 for first solution and 0.46 for second solution

6. 0.25   **7.** 28.57%   **8.** $14 - pK_{eq} - \log \dfrac{b}{a}$ to $14 - pK_{eq} - \log \dfrac{c}{d}$

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$_2$HPO$_4$, Na$_2$S, K$_2$C$_2$O$_4$, K$_2$CO$_3$, 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.** (ABCD   **74.** (CD)   **75.** (ABCD)

76. (ACD)   **77.** (ABC)   **78.** (AD)   **79.** (CD)   **80.** (ABC)

PART - IV

1. (A)   **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)

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APSP Solutions

PART - I

1. CO doesn't have a vacant orbital. Infact, due to the presence of lone pair on carbon, it behaves like a Lewis base.

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

   t = eq $C(1 - \alpha)$ $C\alpha$ $C\alpha$ (C = 55.55 M ; $\alpha = 1.8 \times 10^{-9}$)

   $K_a = \dfrac{C\alpha^2}{1 - \alpha} \approx C\alpha^2 = 1.8 \times 10^{-16}$

3. pH = 0 means $[H^+] = 10^0 = 1M$. Hence solution is strongly acidic.

4. Na_2SO_4 will not exert any common ion effect on H_2SO_4 (since strong electrolyte).

   So, $[H^+] = 2 \times [H_2SO_4] = 2 \times 10^{-2}$ M

   ∴   pH = 2 – log2 = 1.7.

5. $[H^+] = \dfrac{0.1 \times 100 + 0.01 \times 100}{200} = \dfrac{11}{200}$ M

   So,   pH = 2 – 0.74 = 1.26.

6. Millimole of $H^+ = V_1 \times 0.1 \times 1$

   & Millimole of $OH^- = V_2 \times 0.1 \times 2$

   If we put $V_1 = 2V_2$, the final solution will be neutral i.e.

   Millimole of $H^+ = 2V_2 \times 0.1$ = Millimole of OH^-

7. $\dfrac{\alpha_1}{\alpha_2} = \sqrt{\dfrac{K_{b_1}}{K_{b_2}}} = \sqrt{\dfrac{2.56 \times 10^{-4}}{1.6 \times 10^{-5}}} = 4 : 1$

8. $[H^+]$ from HCl = 10^{-3} M & $[H^+]$ from HA = $\sqrt{CK_a} = 10^{-3}$ M.

   So, addition of HCl will not exert common ion effect on HA.

   So, neither pH nor degree of dissociation of HA will change.

9. $[H^+] = \sqrt{K_{a_1}C_1 + K_{a_2}C_2} = \sqrt{10} \times 10^{-3}$ M

   ∴ $pH = 3 - \dfrac{1}{2}\log 10 = 2.5$.

10. α is negligible w.r.t. 1.

    $[H^+]$ mainly comes from first step ionisation.

    $[H^+] = \sqrt{K_{a_1} \times C} = \sqrt{10^{-5} \times 0.1} = 10^{-3}$ M

    ∴ $K_{a_3} = \dfrac{[H^+][A^{3-}]}{[HA^{2-}]} \Rightarrow 10^{-13} = \dfrac{10^{-3}[A^{3-}]}{[HA^{2-}]}$

    $X = \dfrac{[A^{3-}]}{[HA^{2-}]} = 10^{-10}$ ∴   pX = 10.

11. Hydrolysis of Fe^{3+} takes place :

    $Fe^{3+} + 3 H_2O \longrightarrow Fe(OH)_3 + 3 H^+$

12.
$$h = \sqrt{\frac{K_h}{C}} = \sqrt{\frac{K_W}{K_a.C}} = \sqrt{\frac{10^{-14}}{K_a \times (0.01)}}$$

$\Rightarrow \quad 0.01 = \sqrt{\frac{10^{-14}}{K_a \times (0.01)}} \quad \Rightarrow \quad 10^{-14} = \frac{10^{-14}}{K_a \times 10^{-2}} \quad \Rightarrow \quad K_a = 10^{-8}.$

Also, hydrolysis product of $A^- = [OH^-] = Ch = 10^{-4}$ M.

$\therefore \quad [H^+] = 10^{-10}$ M

$\therefore \quad$ pH = 10.

13. pH of a salt solution made from weak acid and weak base = $\frac{1}{2}$ ($pK_w + pK_a - pK_b$)

= independent of concentration of salt solution.

14. pH = $\frac{pK_{a_1} + pK_{a_2}}{2} = 9$ $\qquad$ (amphoteric species HA^-)

15. **S₁ :** Final solution will contain NaCl (salt of SA and SB) and CH_3COONH_4 (salt of WA and WB with $K_a = K_b$). So, final solution will be neutral (pH = 7 at 25ºC).

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.

S₃ : $\quad NH_3 \quad + \quad H_2O \quad \rightleftharpoons \quad NH_4^+ \quad + \quad OH^-$

$\qquad\qquad\qquad$ (proton donor)
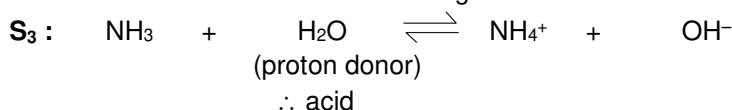
$\qquad\qquad\qquad\quad \therefore$ acid

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. Buffer solution $\Rightarrow$ pH = $pK_a + \log\frac{(0.02 \times 500)}{(0.01 \times 500)}$

$\Rightarrow 5.3 = pK_a + \log 2$

$\Rightarrow pK_a = 5 \qquad\qquad \therefore \quad pK_b = 14 - pK_a = 9$

18. pH = 9.7 = 10 – log2

$\therefore \quad [H^+] = 2 \times 10^{-10}$ M

$PrNH_2 + H_2O \rightleftharpoons PrNH_3^+ + OH^- \qquad ; \qquad K_b = 5 \times 10^{-4}$

and $H^+ + OH^- \rightleftharpoons H_2O \qquad\qquad ; \qquad K_{eq} = \frac{1}{K_w} = 10^{14}$

$\therefore \quad PrNH_2 + H^+ \rightleftharpoons PrNH_3^+ \qquad ; \qquad K_{eq} = \frac{K_b}{K_w} = 5 \times 10^{10}$

$5 \times 10^{10} = \frac{[PrNH_3^+]}{[PrNH_2] \times 2 \times 10^{-10}} \quad \therefore \quad \frac{[PrNH_2]}{[PrNH_3^+]} = \frac{1}{10} = 0.1.$

19. pH = $pK_{In} + \log\frac{[In^-]}{[HIn]} \qquad \Rightarrow \qquad 5 = 4.7 + \log\frac{[In^-]}{[HIn]}$

$\Rightarrow \quad 0.3 = \log\frac{[In^-]}{[HIn]} \qquad \Rightarrow \qquad \log 2 = \log\frac{[In^-]}{[HIn]}$

$\Rightarrow \quad 2 = \frac{[In^-]}{[HIn]}$

Fraction = $\frac{HIn}{In^- + HIn} = \frac{1}{3}$

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20. B $+$ H$^+$ $\longrightarrow$ BH$^+$

At the half equivalent point, [B] = [BH$^+$] $\Rightarrow$ pOH = pK$_b$ (from buffer formula)

21. $n_{HX} = n_{NaOH}$

$\therefore$ $\dfrac{8}{80} = 0.25 \times V_L$

$\therefore$ $V_L = 0.4$ L

[NaX] = $\dfrac{1}{5}$ = 0.2 M (Since volume of solution becomes 5 times, so concentration of salt will become 1/5 times the concentration of HX).

pH = $\dfrac{1}{2}$ (pK$_w$ + pK$_a$ + logC) = $\dfrac{1}{2}$ (14 + 4 − 0.7) = 8.65.

22. [CH$_3$COOH] = 0.1 M

$\therefore$ pH = $\dfrac{1}{2}$ (pK$_a$ − logC) = $\dfrac{1}{2}$ (4.76 + 1) = 2.88.

23. $s^2 = 2.5 \times 10^{-9}$

$\therefore$ s = 5×10^{-5} mol/L = $5 \times 10^{-5} \times 100 \times 1000$ mg/L = 5 mg/L.

So, for dissolving 10 mg CaCO$_3$, (V$_{min}$)$_{H2O}$ 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. $4s_1^3 = 8.64 \times 10^{-13}$

$\therefore$ $s_1 = 6 \times 10^{-5}$ mol/L (in water)

Ag$_2$CrO$_4$ $\rightleftharpoons$ 2 Ag$^+$ + CrO$_4^{2-}$

Let solubility $\quad$ 2s$_2$ $\quad$ s$_2$ + 0.6

= s$_2$ mol/L $\qquad\qquad \approx 0.6$

$(2s_2)^2 \times 0.6 = 8.64 \times 10^{-13}$

$\therefore$ $s_2 = 6 \times 10^{-7}$ mol/L (in Na$_2$CrO$_4$ solution)

$\therefore$ $\dfrac{s_1}{s_2} = 100$.

26. [Ag$^+$] [Cl$^-$] = K$_{sp}$ = constant

$\Rightarrow$ xy = constant

So, shape of graph should be a rectangular hyperbola.

27. SrCO$_3$ $\rightleftharpoons$ $\quad$ Sr^2 $\quad$ + $\quad$ CO$_3^{2-}$

$\qquad\qquad\qquad$ S$_1$ $\qquad\qquad$ S$_1$+S$_2$

ZnCO$_3$ $\rightleftharpoons$ $\quad$ Zn^{2+} $\quad$ + $\quad$ CO$_3^{2-}$

$\qquad\qquad\qquad$ S$_2$ $\qquad\qquad$ S$_1$+S$_2$

$\qquad$ S$_1$ × (S$_1$ + S$_2$) = 10^{-10}

$\qquad$ S$_2$ × (S$_1$ + S$_2$) = 1.5 × 10^{-11}

$\Rightarrow$ $\dfrac{S_1}{S_2} = \dfrac{[Sr^{2+}]}{[Zn^{2+}]} = \dfrac{10^{-10}}{1.5 \times 10^{-11}} = \dfrac{10}{1.5} = \dfrac{100}{15} = \dfrac{20}{3}$

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$_2$SO$_4$.

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 $\alpha_2 << \alpha_1$ & $\alpha_2 << \alpha$ 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 :

$[OH^-] = \sqrt{0.2 \times (4.1 \times 10^{-4}) + 0.1 \times (6.2 \times 10^{-4})} = \sqrt{(8.2 + 6.2) \times 10^{-5}} = \sqrt{144 \times 10^{-6}}$

$\therefore \quad pOH = -\log 0.012 \approx 1.92$

Now, $K_b = \dfrac{[OH^-][CH_3NH_3^+]}{[CH_3NH_2]} \Rightarrow 4.1 \times 10^{-4} = \dfrac{0.012}{0.2}[CH_3NH_3^+] \quad \Rightarrow \quad [CH_3NH_3^+] = \dfrac{41}{60} \times 10^{-2}$ M

Again :, $K_{b_1} = \dfrac{[OH^-][C_4H_{13}N_2^+]}{[C_4H_{12}N_2]} \Rightarrow 6.2 \times 10^{-4} = \dfrac{0.012}{0.1}[C_4H_{13}N_2^+] \Rightarrow [C_4H_{13}N_2^+] = \dfrac{31}{60} \times 10^{-2}$ M

And $K_{b_2} = \dfrac{[OH^-][C_4H_{14}N_2^{2+}]}{[C_4H_{13}N_2^+]} \Rightarrow 2.25 \times 10^{-5} = \dfrac{0.012[C_4H_{14}N_2^{2+}]}{\frac{31}{60} \times 10^{-2}} \Rightarrow [C_4H_{14}N_2^{2+}] = \dfrac{1395}{144} \times 10^{-6}$ M

3. $[OH^-] = \dfrac{0.2}{2} = 0.1$ M $\Rightarrow$ pH $= 14 - (-\log 0.1) = 13$.

$K_{b_1} \times K_{b_2} = \dfrac{[OH^-]^2[C_2N_2H_{10}^{2+}]}{[C_2N_2H_8]} \Rightarrow 8 \times 2.7 \times 10^{-13} = \dfrac{(0.1)^2[C_2N_2H_{10}^{2+}]}{(0.5/2)}$

$\Rightarrow [C_2N_2H_{10}^{2+}] = \dfrac{8 \times 2.7 \times 10^{-13}}{4 \times 10^{-2}}$ M $= 5.4 \times 10^{-11}$ M

4. pH $= \dfrac{1}{2}(14 - pK_{b_2} - \log \ 0.5) = 7 - 4.7 = 2.3$.

$[BH^+] = [H^+] = 10^{-2.3} = 5 \times 10^{-3}$ M.

$\dfrac{10^{-14} \times 10^{-14}}{2 \times 10^{-6} \times 10^{-10}} = \dfrac{(5 \times 10^{-3})^2[B]}{0.5} \Rightarrow [B] = 10^{-8}$ M.

5. (i) $\dfrac{dx}{d(\Delta pH)} = \dfrac{2.303 \ (a \ b)}{(a+b)} = \dfrac{2.303 \times 0.2 \times 0.2}{0.4} = \textbf{0.23}$

(ii) $\dfrac{dx}{d(\Delta pH)} = \dfrac{2.303(0.4 \times 0.4)}{0.8} = \textbf{0.46}$

6. For sodium butyrate

pH $= 7 + \dfrac{1}{2}pK_a + \dfrac{1}{2}\log C = 7 + \left(\dfrac{5 - \log 1.5}{2}\right) + \dfrac{1}{2}\log(0.1) = 7 + 2.41 - 0.5 = 8.91$

For Indicator

$K_{In} = \dfrac{[H^+] \ [In^-]}{[HIn]} \Rightarrow \dfrac{[In^-]}{[HIn]} = \dfrac{K_{In}}{[H^+]} = \dfrac{3.075 \times 10^{-10}}{10^{-8.91}} = 0.25$

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7. For this indicator, pH = pK_{In} = 2

Now, at $[H^+]$ = 4 × 10^{-3} M,

$$K_{In} = \frac{(4 \times 10^{-3})\ [In^-]}{[HIn]} \quad \Rightarrow \quad \frac{[HIn]}{[In^-]} = 0.4$$

$$\therefore \ \% \text{ of HIn} = \frac{[HIn]}{[In^-] + [HIn]} \times 100 = \frac{0.4}{1.4} \times 100 = \textbf{28.57 \%}.$$

8. $\because$ pOH = pK_{eq} + log $\dfrac{[\text{Acidic form}]}{[\text{Basic form}]}$ = pK_{eq} + log $\dfrac{[\text{Red}]}{[\text{Blue}]}$

$(pOH)_{blue}$ = pK_{eq} + log $\dfrac{b}{a}$ and $\quad$ $p(OH)_{red}$ = pK_{eq} + pK_{eq} + log $\dfrac{c}{d}$

So, range = pH_{blue} to pH_{red} = 14 – pK_{eq} – log $\dfrac{b}{a}$ to 14 – pK_{eq} – log $\dfrac{c}{d}$

9. K_{sp} = $[Mg^{2+}][F^-]^2$ $\qquad$ & $\qquad$ $K_a = \dfrac{[H^+][F^-]}{[HF]}$ $\quad \Rightarrow \quad$ 3.5[HF] = $[F^-]$

Now, $\quad \because [F^-] + [HF] = 2s \quad \Rightarrow \quad \dfrac{4.5}{3.5}\ [F^-] \qquad = 2s \qquad\qquad$ ...(1)

Since, K_{sp} = $s[F^-]^2$

$$\therefore \qquad \frac{9}{14} \times 10^{-8} = 4s^3 \times \left(\frac{3.5}{4.5}\right)^2 \qquad \text{from (1)}$$

$$\left(\frac{9}{14}\right)^3 \times 10^{-9} \times 10 = s^3$$

$\therefore \qquad$ s = 1.395 × 10^{-3} mole/L

So, for 1000 L : Moles = s × 10^3 = 1.395.

10(a). $\qquad$ $CuCO_3$ (s) + 4NH_3 $\rightleftharpoons$ CO_3^{2-} + $[Cu(NH_3)_4]^{2+}$ $\quad$; $\qquad$ $K_f \times K_{sp}$ = 2.8 × 10^3

t = 0 $\qquad$ 0.1 $\qquad$ c $\qquad\qquad$ 0 $\qquad\qquad$ 0

t = eq $\qquad$ 0 $\qquad$ c–0.4 $\qquad$ 0.1 $\qquad\quad$ 0.1

2.8 × 10^3 = $\dfrac{0.1 \times 0.1}{(c - 0.4)^4}$ $\quad \Rightarrow \quad$ c – 0.4 = $\sqrt[4]{\dfrac{1000}{2.8 \times 10^8}}$ = 0.044 $\quad \Rightarrow \quad$ c = 0.444 M.

10(b). For precipiatation of MS, K_{sp} of (MS) = $[M^{+2}]\,[S^{-2}]$ = 6 × 10^{-21}

$\Rightarrow \qquad [S^{2-}]_{req}$ = $\dfrac{100 \times 6 \times 10^{-21}}{5}$ = 120 × 10^{-21} = 1.2 × 10^{-19} M

Precipitation of MS will start when H_2S will provide atleast 1.2 × 10^{-19} M S^{-2}.

For H_2S, $\qquad$ H_2S $\rightleftharpoons$ 2 H^+ + S^{-2} $\qquad$; $\qquad$ K = $K_{a1}.K_{a2}$ = $\dfrac{[H^+]^2\ [S^{-2}]}{[H_2S]}$

10^{-7} × 1.2 × 10^{-13} = $\dfrac{[H^+]^2 \times 1.2 \times 10^{-19}}{0.1}$ $\qquad$; $\qquad$ $[H^+]^2$ = 10^{-2}

So, $[H^+]$ = 0.1 M $\qquad \therefore \qquad$ 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.

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13. $K_a = \dfrac{[H^+][A^-]}{[HA]} = \dfrac{[H^+]^2}{[HA]}$ $(\because [H^+] = [A^-])$ and $K_b = \dfrac{[H^+][B^-]}{[HB]} = \dfrac{[H^+]^2}{[HB]}$ $(\because [H^+] = [B^-])$

Also H^+ are same $\therefore \dfrac{K_a}{K_b} = \dfrac{[HB]}{[HA]} = \dfrac{4}{1}$ $\dfrac{[HA]}{[HB]} = \dfrac{1}{4}$

14. $\alpha = \sqrt{\dfrac{5 \times 10^{-5}}{10^{-4}}} > 0.1$ So, $\dfrac{C\alpha^2}{1-\alpha} = K_b \Rightarrow 5 \times 10^{-5} = \dfrac{10^{-4}\alpha^2}{1-\alpha} \Rightarrow 2\alpha^2 + \alpha - 1 = 0 \Rightarrow \alpha = 0.5$

Hence, $[OH^-] = C\alpha = 5 \times 10^{-5}$ & (तथा) pH = 9.7

15. $[OH^-] = \sqrt{K_{b_1} \times C} = \sqrt{1.6 \times 10^{-5}} = 4 \times 10^{-3}$ M

$K_{b_1} \times K_{b_2} = \dfrac{[OH^-]^2[C_2H_{10}N_2^{2+}]}{[C_2N_2H_8]} \Rightarrow 8 \times 2.7 \times 10^{-13} = \dfrac{16 \times 10^{-3}[C_2H_{10}N_2^{2+}]}{0.2}$

$\therefore \quad [C_2H_{10}N_2^{2+}] = 2.7 \times 10^{-8}$ M

16. (a) $[H^+] = 0.1$ M & pH = 1

$K_{a_1} = \dfrac{0.1\ [H_2PO_4^-]}{0.1} \Rightarrow [H_2PO_4^-] = K_{a_1} \Rightarrow C\alpha = K_{a_1} \Rightarrow \alpha = \dfrac{K_{a_1}}{0.1} = 10 K_{a_1}$

$K_{a_2} = \dfrac{0.1\ [HPO_4^{2-}]}{K_{a_1}} \Rightarrow [HPO_4^{2-}] = K_{a_1} \times K_{a_2} \times 10$

16. (b) $K_{a_3} = \dfrac{0.1\ [PO_4^{3-}]}{10\ K_{a_1}K_{a_2}K_{a_3}} \Rightarrow [PO_4^{3-}] = 100 K_{a_1}K_{a_2}K_{a_3}$

17. Factual

18.(a) & 18(b) :

$$A^{3-} + H_2O \rightleftharpoons HA^{2-} + OH^- \ ; \quad K_{h_1} = \dfrac{K_w}{K_{a_3}}$$
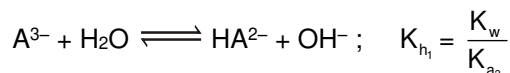
t = eq   c(1–h)   ch   ch

$\dfrac{K_w}{K_{a_3}} = \dfrac{ch^2}{1-h} \approx ch^2 \therefore h = \sqrt{\dfrac{K_w}{cK_{a_3}}}$

$\therefore \quad [OH^-] = [HA^{2-}] = ch = \sqrt{\dfrac{cK_w}{K_{a_3}}}$

$\therefore \quad [H^+] = \dfrac{K_w}{[OH^-]} = \sqrt{\dfrac{K_wK_{a_3}}{c}}$ & pH = $\dfrac{1}{2}$ (pK_w + pK_{a_3} + log c)

$$HA^{2-} + H_2O \rightleftharpoons H_2A^- + OH^- \ ; \quad K_{h_2} = \dfrac{K_w}{K_{a_2}}$$
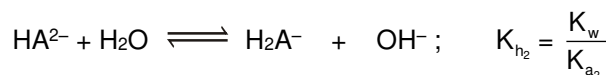
19. According to Bronsted-Lowry concept, acid gives H^+ ion and base accept H^+ ion.

20. $H_3BO_3 = $
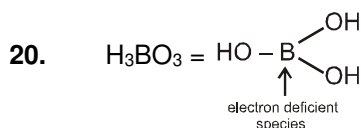
So it will behave as Lewis acid.

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21. $2 \times 10^{-4} = \dfrac{4 \times 10^{-3} \alpha^2}{1 - \alpha}$ $\Rightarrow$ $20\alpha^2 + \alpha - 1 = 0$ $\Rightarrow$ $\alpha = 0.2$

$\therefore$ $[OH^-] = C\alpha = 8 \times 10^{-4}\,M \Rightarrow$ pOH = 3.1

22. $\qquad\qquad NH_4OH \quad \rightleftharpoons \quad NH_4^+ \quad + \quad OH^-$

t = eq $\quad$ 0.4 (1 − α) $\qquad$ 2 × 10^{-5}

$\qquad\qquad\qquad\qquad\qquad\qquad$ (= 0.4 α)
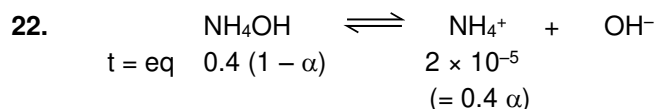
So, $\alpha = 5 \times 10^{-5}$ (<< 1) $\therefore$ 0.4 (1 − α) ≈ 0.4

$K_b = \dfrac{2 \times 10^{-5} \times [OH^-]}{0.4} = 1.8 \times 10^{-5}$ $\Rightarrow$ $[OH^-] = $ **0.36 M**

23. $\qquad\qquad\qquad\qquad AlCl_3 \qquad\qquad C = 0.15\,M \qquad (AlCl_3$ is SAWB salt)

$\qquad\qquad\qquad\qquad [Al\,(H_2O)_6]^{3+} + H_2O(\ell) \rightleftharpoons [Al\,(H_2O)_5\,OH]^{2+}{}_{(aq)} + H_3O^+{}_{(aq)} \qquad K_a = 1.5 \times 10^{-5}$

At t = 0 $\qquad\quad$ 0.15 $\qquad\qquad$ − $\qquad\qquad\qquad$ 0 $\qquad\qquad\qquad$ 0

At t = t_{eq} $\qquad$ 0.15 (1− α) $\qquad\qquad\qquad\qquad$ 0.15 α $\qquad\qquad$ 0.15 α

$\qquad\qquad K_a = \dfrac{0.15\ \alpha\ \times 0.15\ \alpha}{0.15\ [1 - \alpha]} = 1.5 \times 10^{-5}$
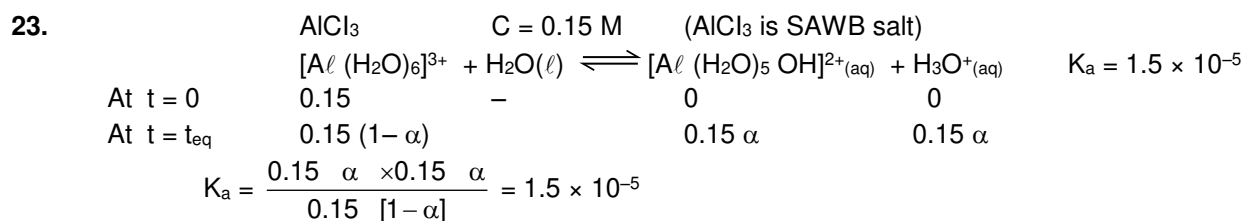
$\Rightarrow$ $\quad$ $1.5 \times 10^{-1}\,\alpha^2 = 1.5 \times 10^{-5}$ $\qquad$ $\Rightarrow$ $\qquad$ $\alpha^2 = 10^{-4}$ $\qquad$ $\Rightarrow$ $\qquad$ $\alpha = 10^{-2}$

$\qquad\qquad [H_3O^+] = 0.15 \times 10^{-2} = 1.5 \times 10^{-3}\,M$

$\Rightarrow$ $\qquad$ pH = 3 − log 1.5 = 3 − 0.18 = 2.82

24. $\qquad\qquad\qquad\qquad C_2O_4^{2-} + H_2O \rightleftharpoons HC_2O_4^- + OH^-$; $\quad K_{h_1} = \dfrac{K_w}{K_{a_2}} = \dfrac{10^{-9}}{5.4}$
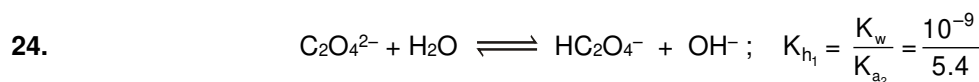
t = eq $\qquad\quad$ 0.005 (1−h) $\qquad$ 0.005h $\qquad$ 0.005h

$\qquad\qquad\qquad$ (≈ 0.005)

$\dfrac{(0.005h)(0.005h)}{(0.005)} = \dfrac{10^{-9}}{5.4}$ $\qquad$ $\therefore$ $\qquad h = 1.92 \times 10^{-4}$.

$[OH^-] = 0.005h = 9.6 \times 10^{-7}\,M$.

$\qquad\qquad\qquad HC_2O_4^- + H_2O \rightleftharpoons H_2C_2O_4 + OH^-$; $\qquad K_{h_2} = \dfrac{K_w}{K_{a_1}} = \dfrac{10^{-12}}{5.6}$
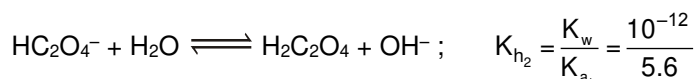
t = eq $\qquad\qquad$ ≈ 9.6 × 10^{-7} $\qquad\qquad\qquad$ ≈ 9.6 × 10^{-7}

$\qquad$ $\therefore$ $\qquad [H_2C_2O_4] = K_{h_2} = \dfrac{5}{28} \times 10^{-12}\,M$.

25. HSO_4^- – can accept and donate a proton. $\quad HSO_4^- + H^+ \to H_2SO_4$; $HSO_4^- \to H^+ + SO_4^{2-}$
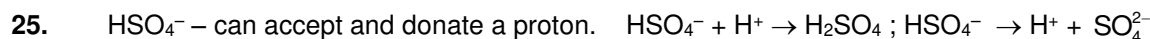
Note : Answer could also be NH_3 or OH^-.

26. We know that for acids at 25ºC, pH must be less than 7.

27. When rain is accompanied by a thunderstorm,

$\qquad\qquad N_2 + O_2 \longrightarrow NO \longrightarrow NO_2 \xrightarrow{\ H_2O\ } HNO_2 + HNO_3$

28. $6.31 = 6.61 + \log\left(\dfrac{M \times V}{100 \times 0.05}\right)$ $\Rightarrow$ $\quad -0.3 = \log\left(\dfrac{MV}{5}\right)$

$\Rightarrow$ $\qquad \dfrac{1}{2} = \dfrac{MV}{5}$ $\qquad\qquad\qquad$ $\Rightarrow$ $\quad 0.1\,V = \dfrac{5}{2}$ $\qquad$ $\Rightarrow$ $\qquad$ V = 25 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) Auiline 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

$$pH = 7 - \frac{1}{2}pK_b - \frac{1}{2}\log C = 7 - \frac{4.74}{2} - \frac{1}{2}\log 10^{-1} = 7 - 2.37 + \frac{1}{2} = \mathbf{5.13}$$

34. $pH = pK_a + \log \dfrac{[Ionised]}{[un\ Ionised]}$ $\Rightarrow$ $6 = 5 + \log \dfrac{[Ionised]}{[un\ Ionised]} \Rightarrow$ $1 = \log \dfrac{[Ionised]}{[un\ Ionised]}$

$\dfrac{[Ionised]}{[un\ Ionised]} = 10$ $\Rightarrow$ $\dfrac{[Ionised]}{[Ionised]\ +\ [un\ Ionised]} = \left[\dfrac{10}{11}\right]$

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 $= 2.303 \left(\dfrac{ab}{a+b}\right)$. Hence the result.

and $a = b = 0.5$, $BC = 2.303 \times \dfrac{(0.5)^2}{1} = 0.57$

37. $pK_a = 5.45$

$pH = pK_{HIn} + \log \dfrac{[Base\ form]}{[Acid\ form]}$ $\Rightarrow$ $pH = pK_{HIn} = 5.45$

For a Buffer solution

$pH = pK_a + \log \dfrac{[CH_3COONa]}{[CH_3COOH]}$ $\Rightarrow$ $5.45 = 4.75 + \log \dfrac{[CH_3COONa]}{[CH_3COOH]}$

$0.7 = \log \dfrac{[CH_3COONa]}{[CH_3COOH]}$ $\Rightarrow$ $\dfrac{5}{1} = \dfrac{[CH_3COONa]}{[CH_3COOH]}$

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.

(B) $MX \rightleftharpoons M^+ + X^-$; $K_{sp}(MX)$ $\qquad$ $NX \rightleftharpoons N^+ + X^-$; $K_{sp}(NX)$

$\qquad\qquad$ x $\quad$ x + y $\qquad\qquad\qquad\qquad\qquad$ y $\quad$ y + x
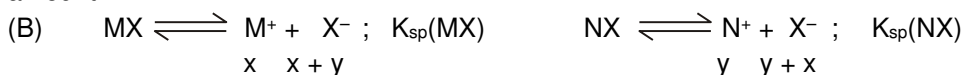
$K_{sp}(MX) + K_{sp}(NX) = (x + y)^2$

$\Rightarrow \qquad \sqrt{K_{sp}(MX)} \approx x + y = [X^-]$ ...(1) $\qquad (\because K_{sp}(MX) >> K_{sp}(NX))$

(C) $(y + x)y = K_{sp}(NX) \Rightarrow y = [N^+] \approx \dfrac{K_{sp}(NX)}{\sqrt{K_{sp}(MX)}}$ $\qquad\qquad$ ...(2)

Similarly, $[M^+] = x \approx \dfrac{K_{sp}(MX)}{\sqrt{K_{sp}(MX)}}$ $\qquad\qquad$ ...(3)

From (2) & (3) : $[M^+] >> [N^+]$

41. Solubility of $CaCO_3 = \left[\dfrac{7 \times 10^{-3}}{100}\right]$ mole/L $= 7 \times 10^{-5}$ mole/L = s

K_{sp} of $CaCO_3 = s^2 = 49 \times 10^{-10}$.

When $[Ba^{+2}]$ 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,

$[Ca^{+2}][CO_3^{-2}] = 49 \times 10^{-10}$, $\qquad [CO_3^{-2}] = \left[\dfrac{49 \times 10^{-10}}{a}\right]$ M.

Now for $BaCO_3$, $K_{sp} = [Ba^{+2}][CO_3^{-2}] = \dfrac{a \times 10}{100} \times \dfrac{49 \times 10^{-10}}{a} = 4.9 \times 10^{-10}$. ($\because$ 90% Ba^{2+} has precipitated,

so $[Ba^{+2}] = \dfrac{a \times 10}{100}$ M)

42. (A) As long an a solid-aqueous equilibrium exists, a salt solution is saturated.

(B) $\qquad\qquad\qquad$ $MX(s) + Y^-(aq.) \rightleftharpoons MY(s) + X^-(aq.)$; $\qquad K = \dfrac{K_{sp}(MX)}{K_{sp}(MY)}$
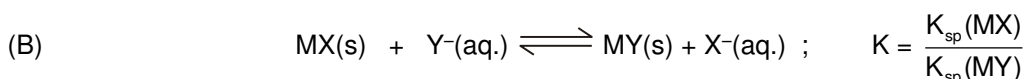
$\qquad$ t = 0 $\qquad\qquad$ n $\qquad\quad \dfrac{nx}{100}$ $\qquad\qquad$ 0 $\qquad\qquad$ 0

$\qquad$ t = eq $\qquad\quad n - \dfrac{nx}{100} \qquad y \qquad\qquad \dfrac{nx}{100} \qquad \dfrac{nx}{100} = [X^-]$

(C) $\dfrac{K_{sp}(MX)}{K_{sp}(MY)} = \dfrac{[X^-][M^+]}{[Y^-][M^+]} \Rightarrow [Y^-] = \dfrac{K_{sp}(MY)}{K_{sp}(MX)} \times [X^-] = \dfrac{K_{sp}(MY)}{K_{sp}(MX)} \times \dfrac{nx}{100}$.

43. The concerned chemical reaction is :

$2\,AgCl + Na_2CO_3 \longrightarrow Ag_2CO_3 + 2\,NaCl$
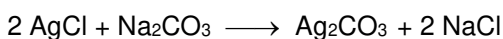
Calculation of $[Ag^+]$ left in the solution :

$K_{sp}(Ag_2CO_3) = [Ag^+][CO_3^{2-}]$

$[Ag^+] = \sqrt{\dfrac{8.1 \times 10^{-12}}{1.6}} = 2.25 \times 10^{-6}$ M

Concentration of Cl^- left = 0.00284 g/L = $\dfrac{0.00284}{35.5}$ mol/L = 8×10^{-5} M

$\therefore K_{sp}(AgCl) = [Ag^+][Cl^-] = (2.25 \times 10^{-6})(8 \times 10^{-5}) = 1.8 \times 10^{-10}$.

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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 $Mg(OH)_2$. Then :

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

$\left[\dfrac{0.1V}{2V}\right][OH^-]^2 = 1.62 \times 10^{-11}$ $\left([Mg^{2+}] = \dfrac{Millimole}{Total \;\; volume \; in \; mL}\right)$

$\therefore$ $[OH^-] = 1.8 \times 10^{-5}\,M$

Now, if the $[OH^-] = 1.8 \times 10^{-5}$ M, on addition of NH_3 in NH_4Cl, then $Mg(OH)_2$ will precipitate. For buffer solution of NH_3 and NH_4Cl :

$[OH^-] = K_b \times \dfrac{[NH_3]}{[NH_4^+]}$

$1.8 \times 10^{-5} = 1.8 \times 10^{-5} \times \dfrac{(0.8 \times V)/2V}{(a \times V)/2V}$

$\therefore$ a = 0.8 M.

45.   (A) $S_{pH \, = \, 2} = \dfrac{10^{-38}}{(10^{-12})^3} = 10^{-2}\,M$ (B) $S_{pH \, = \, 11} = \dfrac{10^{-38}}{(10^{-3})^3} = 10^{-29}\,M$

46. For FeS and MnS not to be precipitated from a solution of Fe^{2+} and Mn^{2+}, $IP_{FeS} < K_{sp(FeS)}$

$[Fe^{2+}][S^{2-}] < K_{sp}$ of FeS

$[10^{-2}][S^{2-}] < 6.4 \times 10^{-18}$ $\therefore$ $[S^{2-}] < 6.4 \times 10^{-16}$ M

So, at $[S^{2-}] = 6.4 \times 10^{-16}$ M or less, no precipitation of FeS and MnS will occur.

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

$\therefore [H^+]^2 [S^{2-}] = K_{a(H_2S)} \times [H_2S] = 9.6 \times 10^{-22}$

$\therefore$ $[H^+]^2_{min} [6.4 \times 10^{-16}] = 9.6 \times 10^{-22}$

$[H^+]^2_{min} = 3/2 \times 10^{-6}$ $\therefore$ $[H^+]_{min} = \sqrt{\dfrac{3}{2}} \times 10^{-3}$ M

Thus, if $[H^+] = \sqrt{\dfrac{3}{2}} \times 10^{-3}$ M or more, the precipitation of FeS and MnS will not take place.

Therefore, $pH_{(max.)} = 3 - \frac{1}{2} \log \dfrac{3}{2} = 2.91$ **Ans.**

47. For FeS and MnS to be precipitated from a solution of Fe^{2+} and Mn^{2+}, $IP_{MnS} > K_{sp(MnS)}$

$[Mn^{2+}][S^{2-}] > K_{sp}$ of MnS

$[10^{-2}][S^{2-}] > 2.5 \times 10^{-13}$ $\therefore$ $[S^{2-}] > 2.5 \times 10^{-11}$ M

So, at $[S^{2-}] = 2.5 \times 10^{-11}$ M or more, precipitation of FeS and MnS will occur.

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

$\therefore [H^+]^2 [S^{2-}] = K_{a(H_2S)} \times [H_2S] = 9.6 \times 10^{-22}$

$\therefore$ $[H^+]^2_{max} [2.5 \times 10^{-11}] = 9.6 \times 10^{-22}$

$[H^+]^2_{max} = 3.84 \times 10^{-11}$ $\therefore$ $[H^+]_{max} = 8\sqrt{\dfrac{3}{5}} \times 10^{-6}$ M

Thus, if $[H^+] = 8\sqrt{\dfrac{3}{5}}$ × 10^{-6} M or less, the precipitation of FeS and MnS will take place.

Therefore, $pH_{(min.)} = 6 - \frac{1}{2} \log \dfrac{192}{5} = 5.21$ **Ans.**

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48. $9.6 \times 10^{-21} = \dfrac{(0.1)^2 [S^{2-}]}{(0.1)} \Rightarrow [S^{2-}] = 9.6 \times 10^{-20}$ M

$9.6 \times 10^{-20} [Cu^{2+}]_{min} = 6.4 \times 10^{-36} \Rightarrow [Cu^{2+}]_{min} = \dfrac{2}{3} \times 10^{-16}$

49(a). Dissolved $Al(OH)_3$ present in solution as $Al^{3+}(aq)$ as well as $Al(OH)_4^-$ (aq)

$\therefore \quad S = [Al^{3+}(aq)] + [Al(OH)_4(aq)]$

$S = \dfrac{K_{sp}}{[OH^-]^3} + K_C[OH^-]$

for minimum solubility : $\dfrac{dS}{d(OH^-)} = 0$

or $\quad -\dfrac{K_{sp} \times 3}{[OH^-]^4} + K_C = 0$

$[OH^-] = \left(\dfrac{3K_{sp}}{K_C} \right)^{1/4}$

49(b). Order of solubility : Complex formation > Pure water > Common ion effect.
AgBr form complex $[Ag(NH_3)_2]^+$ in NH_3, so solubility is maximum in $NH_3(aq)$.

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) $\quad [H^+]$ in HCl solution = 10^{-5} M

$[H^+]$ in H_2S solution = $\sqrt{K_a \times C}$ = 10^{-4} M

so $\quad [H^+]$ in HCl solution < $[H^+]$ in H_2S solution

& $\quad [OH^-]$ in HCl solution > $[OH^-]$ in H_2S solution

& $\quad$ 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) $\quad$ At pH = 4.74 in CH_3COOH solution, $[CH_3COO^-] = [CH_3COOH]$

$\therefore \quad$ degree of dissociation of $CH_3COOH = \dfrac{1}{2}$

At pH = 9.26 i.e. pOH = 4.74 in $NH_3.H_2O$ solution, $[NH_4^+] = [NH_3.H_2O]$

$\therefore \quad$ degree of dissociation of CH_3COOH = degree of dissociation of $NH_3.H_2O$

degree of dissociation of water in CH_3COOH solution > degree of dissociation of water in $NH_3.H_2O$ solution.

(C) $\quad [H^+]$ in CH_3COOH solution = $\sqrt{1.8 \times 10^{-5} \times 0.1}$ = $\sqrt{1.8} \times 10^{-3}$ M

$[H^+]$ in HCOOH solution = $\sqrt{1.8 \times 10^{-4} \times 1}$ = $\sqrt{1.8} \times 10^{-2}$ M

so, degree of dissociation of CH_3COOH = degree dissociation of HCOOH.

(D) $\quad [H^+]$ in HA_1 solution = $\sqrt{10^{-5} \times 0.1} = 10^{-3}$ M

$[H^+]$ in HA_2 solution = $\sqrt{10^{-6} \times 0.01} = 10^{-4}$ M

so $\quad [OH^-]$ in solution of HA_1 < $[OH^-]$ in solution of HA_2

pH in solution of HA_1 < pH in solution of HA_2

& $\quad$ degree of dissociation of water HA_1 < degree of dissociation of water HA_2.
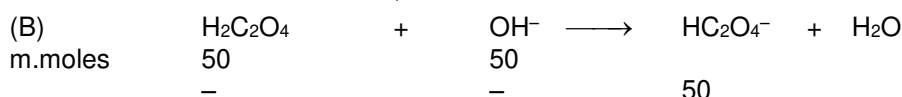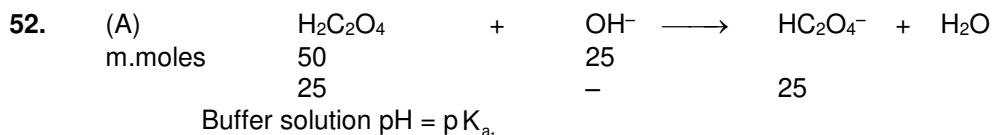
51. (A) $[H^+] = \dfrac{5 \times 0.08 - 10 \times 0.015 \times 2}{500} = 2 \times 10^{-4}\,M$ $\therefore$ pH = 3.7

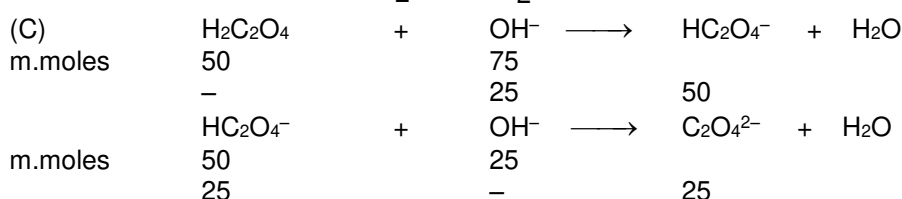(B) For salt CH_3COONa : pH = $\dfrac{1}{2}\left(14 + 4.74 + \log\left(\dfrac{15}{150}\right)\right) = 8.87$

(C) For RNH_2 : pOH = $\dfrac{1}{2}$ ($pK_b - \log 0.25$)   & $K_h = \dfrac{K_w}{K_b}$ $\therefore$ $K_b = 10^{-5}$

     pOH = 2.8 $\therefore$ pH = 11.2
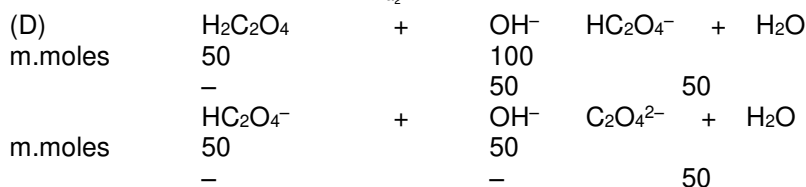
(D) For NaH_2A : pH = $\dfrac{pK_{a_2} + pK_{a_1}}{2} = \dfrac{4+7}{2} = 5.5$

52. (A)

	$H_2C_2O_4$	+	OH^-	$\longrightarrow$	$HC_2O_4^-$	+	H_2O
m.moles	50		25				
	25		–		25		

Buffer solution pH = pK_{a_1}

(B)

	$H_2C_2O_4$	+	OH^-	$\longrightarrow$	$HC_2O_4^-$	+	H_2O
m.moles	50		50				
	–		–		50		

Amphiprotic, pH = $\dfrac{pK_{a_1} + pK_{a2}}{2} = \dfrac{13}{2} = 6.5$.

(C)

	$H_2C_2O_4$	+	OH^-	$\longrightarrow$	$HC_2O_4^-$	+	H_2O
m.moles	50		75				
	–		25		50		

	$HC_2O_4^-$	+	OH^-	$\longrightarrow$	$C_2O_4^{2-}$	+	H_2O
m.moles	50		25				
	25		–		25		

Buffer solution pH = pK_{a_2}.

(D)

	$H_2C_2O_4$	+	OH^-	$HC_2O_4^-$	+	H_2O
m.moles	50		100			
	–		50	50		

	$HC_2O_4^-$	+	OH^-	$C_2O_4^{2-}$	+	H_2O
m.moles	50		50			
	–		–	50		

Salt hydrolysis, pH > 7.

54. (p) $1.794 \times 10^{-11} = [Mg^{2+}] (0.36)^2 \Rightarrow [Mg^{2+}] = 1.38 \times 10^{-10}\,M$.

(q) $[Hg_2^{2+}][Cl^-]^2 = K_{sp} \Rightarrow s(2 \times 0.18)^2 = 1.296 \times 10^{-18} \Rightarrow s = 10^{-17}\,M$.

(r) $[Ca^{2+}] = \sqrt{K_{sp_1} + K_{sp_2}} = \sqrt{(2.6 \times 10^{-9}) + (3.8 \times 10^{-9})} = 8 \times 10^{-5}\,M$. (simultaneous solubility)

(s) $s = \dfrac{10^{-38}}{(10^{-7})^3} = 10^{-17}\,M$

(neglecting OH^- coming from $Fe(OH)_3$ in terms of those coming from water).

(t) $Ag^+ + 2CN^- \rightleftharpoons [Ag(CN)_2]^-$; $K_f = 2.5 \times 10^{18}$

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)
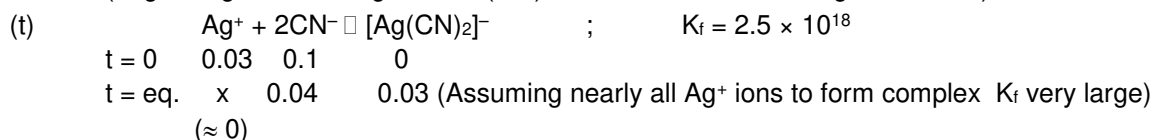
(Upon mixing equal volumes, volume gets doubled. So initial concentrations get halved).

$2.5 \times 10^{18} = \dfrac{0.03}{x(0.04)^2}$ $\Rightarrow x = 7.5 \times 10^{-18}\,M$.

55. $H_3PO_4 = 3$, $H_3BO_3 = 1$, $H_3PO_2 = 1$, rest diprotic

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56. $x = 1, 2, 3, 4, 5, 6, 8, 9, 10, 11, 12, 13, 14$
There are 13 possible values.

57. $K_b (NH_3) = 1.8 \times 10^{-5}$
$CH_3COOCH_3 (aq) + 2H_2O (aq) \longrightarrow CH_3COO^- (aq) + H_3O^+ (aq) + CH_3OH(aq)$
$[NH_4^+]_0 = 0.1$ M, $[NH_3] = 0.06$ M, $[CH_3COOCH_3]_0 = 0.02$ M

$pOH = pK_b + \log \dfrac{[NH_4^+]}{[NH_3]} = 4.74 + \log \left(\dfrac{0.1}{0.06} \right)$

$(pOH)_{initial} = 4.74 + 0.22 = 4.96 \qquad \therefore \qquad (pH)_{initial} = \mathbf{9.04}$

$NH_3 (aq) + H^+ (aq) \longrightarrow NH_4^+ (aq)$

0.06	0.02	0.1	mole
0.04	–	0.12	mole

$(pOH)_{final} = 4.74 + \log \dfrac{0.12}{0.04} = 4.74 + \log \left(\dfrac{0.12}{0.04} \right) = 4.74 + \log 3 = 4.74 + 0.48 \qquad = 5.22$

$\therefore \qquad (pH)_{final} = \mathbf{8.78}$
$\Delta pH = 9.04 - 8.78 = 0.26$
Yes this is satisfactory buffer.

58. $H_3PO_4 = \dfrac{0.98}{98} = 10^{-2}$ Mole $\Rightarrow \qquad [H_3PO_4] = \dfrac{10^{-2}}{100} \times 10^3 = 0.1$ M

$pH = 5 \quad [H^+] = 10^{-5}$
H_3PO_4 & $H_2PO_4^-$

$pH = pK_{a1} + \log \dfrac{[H_2PO_4^-]}{[H_3PO_4]} \qquad \Rightarrow \qquad 5 = 3 + \log \dfrac{[H_2PO_4^-]}{[H_3PO_4]} \qquad \Rightarrow \qquad 10^2 = \dfrac{[H_2PO_4^-]}{[H_3PO_4]}$

$[H_2PO_4^-] = 10^2 [H_3PO_4] \qquad \Rightarrow \qquad$ But $[H_3PO_4] + [H_2PO_4^-] = 0.1$
$H_3PO_4 + 10^2 [H_3PO_4] = 0.1 \qquad \Rightarrow \qquad [1 + 10^2] [H_3PO_4] = 0.1$
$[H_3PO_4] = \mathbf{10^{-3}}$ **M** $\qquad \Rightarrow \qquad [H_2PO_4^-] = 0.1$ M

For $\quad H_2PO_4^-$ & $HPO_4^{2-} \qquad \Rightarrow \qquad pH = pK_{a2} + \log \dfrac{[HPO_4^{2-}]}{[H_2PO_4^-]}$

$5 = 8 + \log \dfrac{[HPO_4^{2-}]}{[H_2PO_4^{-1}]} \qquad \Rightarrow \qquad -3 = \log \dfrac{[HPO_4^{2-}]}{[H_2PO_4^-]}$

$\dfrac{[HPO_4^{2-}]}{[H_2PO_4^1]} = 10^{-3} \qquad \Rightarrow \qquad [HPO_4^{2-}] = 10^{-3} [H_2PO_2^-]$

$[H_2PO_4^-] + [HPO_4^{2-}] = 0.1 \qquad \Rightarrow \qquad [H_2PO_4^-] + 10^{-3} [H_2PO_4^-] = 0.1$

$[1 + 10^{-3}] [H_2PO_4^-] = 0.1 \Rightarrow \quad [H_2PO_4^-] = \mathbf{0.1}$ **M** $\qquad \Rightarrow \qquad [HPO_4^{2-}] = \mathbf{10^{-4}}$ **M**

Again

$pH = pK_{a3} + \log \dfrac{[PO_4^{-3}]}{[HPO_4^{-2}]} \qquad \Rightarrow \qquad 5 = 12 + \log \dfrac{[PO_4^{-3}]}{[HPO_4^{-2}]}$

$10^{-7} = \dfrac{[PO_4^{-3}]}{[HPO_4^{-2}]} \qquad \Rightarrow \qquad [PO_4^{-3}] = 10^{-7} [HPO_4^{-2}]$

$[HPO_4^{-2}] + [PO_4^{-3}] = 10^{-4} \qquad \Rightarrow \qquad [1 + 10^{-7}] [HPO_4^{-2}] = 10^{-4}$

$[PO_4^{-3}] = 10^{-7} \Rightarrow [HPO_4^{-2}] = \mathbf{10^{-11}}$ **M**
$pC_1 + pC_2 + pC_3 + pC_4 = 11 + 4 + 1 + 3 = 19$

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

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ADVIEQ(A)- 86

60. Na_2HPO_4, Na_2S, $K_2C_2O_4$, K_2CO_3, Ethylene diamine

61. $H_2CO_3 + KOH \longrightarrow KHCO_3 + H_2O$ $\qquad V_{KOH} = 50$ mL needed

0.2 M, 50 mL

$KOHCO_3 + KOH \longrightarrow K_2CO_3 + H_2O$ $\qquad V_{KOH} = 25$ 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_{KOH} = 75 mL.

62. $\qquad\qquad\qquad\qquad Ag_2CO_3 + K_2C_2O_4 \rightleftharpoons Ag_2C_2O_4 + K_2CO_3$

Mole at start $\qquad\qquad$ Excess $\quad$ 0.1520 $\qquad\qquad$ 0 $\qquad\qquad$ 0

Mole after reaction $\qquad\qquad\qquad$ 0.1520-0.0358 $\quad$ 0.0358 $\quad\quad$ 0.0358

$\qquad\qquad\qquad\qquad\qquad\qquad\quad$ = 0.1162

Molar concentration of $K_2C_2O_4$ or $C_2O_4^{2-}$ left unreacted = $\dfrac{0.1162}{0.5}$ $\qquad$ = 0.2324 moles l^{-1}

$[K_2CO_3] = [CO_3^{2-}]$ at equilibrium = $\dfrac{0.0358}{0.5}$ = 0.07156 moles l^-

Given that K_{sp} for $Ag_2C_2O_4 = 1.29 \times 10^{-11}$ mol^3 l^{-3} at 25°C

So $\qquad [Ag^+]^2[C_2O_4^{2-}] = 1.29 \times 10^{-11}$

or $\qquad [Ag^+]^2 \times 0.2324 = 1.29 \times 10^{-11}$

Hence $[Ag^+]^2 = \dfrac{1.29}{0.2324} \times 10^{-11}$

Then K_{sp} for $Ag_2CO_3 = [Ag^+]^2[CO_3^{2-}] = \dfrac{1.29 \times 10^{-11}}{0.2324} \times 0.0716 = 3.794 \times 10^{-12}$ mol^3 l^{-3}

63. $K_{sp} = \dfrac{S^2}{1 + \dfrac{[H^+]}{K_{a_2}} + \dfrac{[H^+]^2}{K_{a_1} \cdot K_{a_2}}}$

$7.5 \times 10^{-14} = \dfrac{S^2}{1 + \dfrac{10^{-3}}{5.5 \times 10^{-11}} + \dfrac{10^{-6}}{25 \times 10^{-18}}}$

$7.5 \times 10^{-14} = \dfrac{S^2}{1 + \dfrac{10^8}{5.5} + \dfrac{10^{12}}{25}}$

$7.5 \times 10^{-14} = \dfrac{25 \times S^2}{10^{12}}$

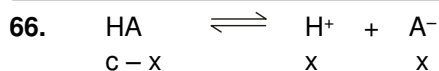$S^2 = 0.3 \times 10^{-14} \times 10^{12}$

$S^2 = 0.003$

$S = 0.055$ M

64. $\qquad\qquad\qquad Cd^{2+} \quad + \quad H_2S \longrightarrow CdS \downarrow \quad + \quad 2H^+$

m.moles $\qquad\quad$ 0.1

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ 0.2

Total m.moles of H^+ in solution after the reaction = 0.2 + 0.8 = 1

$\therefore \qquad [H^+] = \dfrac{1}{100} = 0.01$ M $\qquad\qquad \Rightarrow \qquad$ pH = **2.**

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ADVIEQ(A)- 87

66. $\quad$ HA $\quad\rightleftharpoons\quad$ H$^+$ $\quad+\quad$ A$^-$

$\qquad$ c $-$ x $\qquad\qquad$ x $\qquad\quad$ x

$\qquad$ [H$^+$] = x = 1.5 × 10^{-3} M

$\qquad$ $K_a = \dfrac{x^2}{c-x}$

$\qquad$ $2.5 \times 10^{-3} = \dfrac{(1.5 \times 10^{-3})^2}{c - 1.5 \times 10^{-3}}$.

$\qquad$ **C = 2.4 × 10^{-3} M.**

67. $\quad$ Initial: $8 \times 10^{-5} = \dfrac{1.6 \times 10^{-3}\alpha^2}{1-\alpha}$ $\qquad\qquad\Rightarrow\qquad \alpha = \dfrac{1}{5}$

$\qquad$ ∴ $\quad$ [OH$^-$] = 3.2 × 10^{-4} $\qquad\qquad\qquad\qquad\Rightarrow\qquad$ pH = 10.5

$\qquad\qquad 8 \times 10^{-5} \times 2.7 \times 10^{-8} = \dfrac{(3.2 \times 10^{-4})^2 [C_2N_2H_{10}^{2+}]_i}{1.28 \times 10^{-3}}$

$\qquad\Rightarrow\qquad$ 2.7 × 10^{-8} = [C$_2$N$_2$H$_{10}^{2+}$]$_i$

$\qquad$ Final $\quad$ pH = 11 ; $\qquad$ 8 × 10^{-5} = 10^{-3} × α $\qquad\Rightarrow\qquad$ α = 0.08

$\qquad\qquad$ [C$_2$N$_2$H$_9^+$] = 1.28 × 10^{-4}.

$\qquad\qquad 2.7 \times 8 \times 10^{-13} = \dfrac{(10^{-6})[C_2N_2H_{10}^{2+}]_f}{1.6 \times 10^{-3}}$ $\qquad\qquad\Rightarrow\qquad$ [C$_2$N$_2$H$_{10}^{2+}$]$_f$ = 1.28 × 2.7 × 10^{-9} M

$\qquad$ So, (A), (B) and (D) are correct but $\dfrac{[C_2N_2H_{10}^{2+}]_i}{[C_2N_2H_{10}^{2+}]_f} = \dfrac{1}{0.128}$

68. $\quad$ Order of basic strength O^{2-} > S^{2-} > Se^{2-} > Te^{2-}

69. $\quad$ $1.2 \times 10^{-7} = \dfrac{7.2 \times 10^{-2}\alpha^2}{1-\alpha}$ $\qquad\Rightarrow\qquad 6\alpha^2 + \alpha - 1 = 0$ $\qquad\Rightarrow\qquad \alpha = \dfrac{1}{3}$

$\qquad$ So, pH = $-$ log $\dfrac{0.072}{3}$ = 1.62

70.
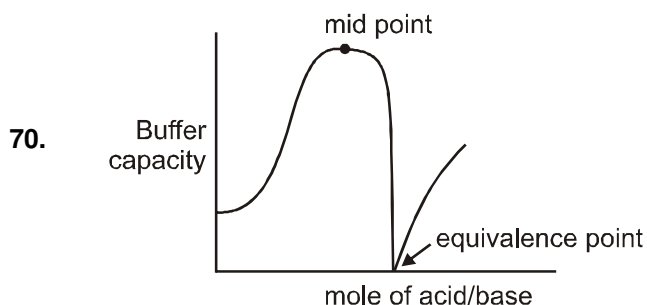
$\qquad$ When conc. of base or acid increases buffer capacity increases.

71. $\quad$ Facutal
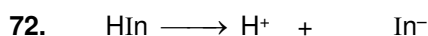
72. $\quad$ HIn $\longrightarrow$ H$^+$ $\quad+\quad$ In$^-$

$\qquad$ $K_{In} = \dfrac{[H^+]\ [In^-]}{[H\ In]}$ $\qquad\Rightarrow\qquad$ $\dfrac{[In^-]}{[H\ In]} = \dfrac{K_{In}}{[H^+]} = \dfrac{10^{-9}}{10^{-9.6}} = 10^{0.6} = 4$

$\qquad$ ∴ % of [In$^-$] in solution $= \dfrac{4}{5} \times 100$ = 80%

$\qquad$ so $\quad$ pink colour will be visible.

73. Initial decrement is due to consumption of free OH^- ions, then slow decrement in pH is due to basic buffer solution and minimum slope will be there when there is best buffer action ([salt] / [base] = 1)

74. Given graph is plotted for the titration of weak diprotic acid with base.

75. Factual

76. $[Ag^+]$ concentration = $\dfrac{100}{350} \times 2 \times \sqrt[3]{\dfrac{1.4 \times 10^{-5}}{4}}$ = 8.68 × 10^{-3}.

$[SO_4^{2-}]$ concentration = $\dfrac{100}{350} \times \sqrt[3]{\dfrac{1.4 \times 10^{-5}}{4}}$ = 4.34 × 10^{-3}.

$[Pb^{2+}]$ = $\dfrac{250}{350} \times \sqrt{2.8 \times 10^{-13}}$ = 3.78 × 10^{-7}.

$[CrO_4^{2-}]$ = 3.78 × 10^{-7}.

$[Ag^+]^2 [CrO_4^{2-}]$ = 2.85 × 10^{-11} > K_{sp} of Ag_2CrO_4.

$[Pb^{2+}] [SO_4^{2-}]$ = 1.64 × 10^{-9} < K_{sp} of $PbSO_4$.

Only Ag_2CrO_4 will precipitate.

77. (A) $Ag_2CO_3 \rightarrow 2Ag^+ + CO_3^{2-}$ $\qquad\qquad\qquad\qquad$ $Ag_2CrO_4 \rightarrow 2Ag^+ + CrO_4^{2-}$

$\qquad\qquad\qquad$ (2x + 2y) x $\qquad\qquad\qquad\qquad\qquad\qquad$ (2y + 2x) y

$\qquad\qquad$ $4(x + y)^2(x + y) = (4 + 2.4) \times 10^{-12} \Rightarrow (x + y)^3 = 1.6 \times 10^{-12} = \dfrac{8^3 \times 10^{-12}}{4^3 \times 5}$

$\Rightarrow$ $\qquad$ (x + y) = 1.168 M $\qquad \therefore$ $[Ag^+] = 2(x + y)$ = 2.336 × 10^{-4} M

(B) $\qquad [CO_3^{2-}] = \dfrac{4 \times 10^{-12}}{(2.336)^2 \times 10^{-8}}$ = 7.3 × 10^{-5} M

(C) $\qquad [CrO_4^{2-}] = \dfrac{2.4 \times 10^{-12}}{(2.336)^2 \times 10^{-8}}$ = 4.35 × 10^{-5} M

(D) $\qquad [Ag^+] = 2([CO_3^{2-}] + [CrO_4^{2-}])$

78. The concerned chemical reaction is :

$2\,AgCl + Na_2CO_3 \longrightarrow Ag_2CO_3 + 2\,NaCl$

Calculation of $[Ag^+]$ left in the solution :

$K_{sp}(Ag_2CO_3) = [Ag^+] [CO_3^{2-}]$

$[Ag^+] = \sqrt{\dfrac{8.2 \times 10^{-12}}{1.5}}$ = 2.34 × 10^{-6} M

Concentration of Cl^- left = 0.0026 g/L = $\dfrac{0.0026}{35.5}$ mol/L = 7.33 × 10^{-5} M

$\therefore K_{sp}(AgCl) = [Ag^+] [Cl^-] = (2.34 \times 10^{-6}) (7.33 \times 10^{-5})$ = 1.17 × 10^{-10}

79. In $AgNO_3$ solution, the solubility of $AgCN$ will decrease as compared to pure water because of common ion effect of Ag^+ ion.

In NH_3 solution and buffer of pH = 5, the solubility of $AgCN$ will increase due to complex formation in case of NH_3 solution and hydrolysis of CN^- ions in case of buffer of pH = 5.

80. $AgCl(s) + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+ (aq) + Cl^-(aq)$

$K_1 = 1.6 \times 10^{-10} \times 10^7 = 1.6 \times 10^{-3}$

$$= \frac{[Ag(NH_3)_2^+][Cl^-]}{[NH_3]^2}$$

$AgCN(s) + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+ (aq) + CN^-(aq)$
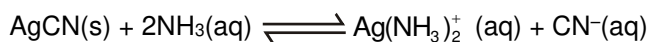
$K_2 = 2.5 \times 10^{-16} \times 10^7 = 2.5 \times 10^{-9}$

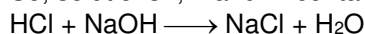$$\frac{[Cl^-]}{[CN^-]} = \frac{1.6 \times 10^{-3}}{2.5 \times 10^{-9}} = 6.4 \times 10^5$$

$K_1 = \dfrac{x^2}{(1-2x)^2} \quad \Rightarrow \quad \dfrac{x}{1-2x} = 0.04$

$x = 0.037$

$\therefore \quad [CN^-] = \dfrac{0.037}{6.4 \times 10^5} = 5.78 \times 10^{-8}\,M$

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.
$HCl + NaOH \longrightarrow NaCl + H_2O$
Only HCl and NaOH solutions can be used as standard solutions in an acid-base titration.

2.
$$RNH_2 \quad + \quad H_2O \quad \rightleftharpoons \quad RNH_3^+ \quad + \quad OH^-$$
$t = eq \quad 0.01(1-\alpha) \quad\quad\quad 0.01\alpha \quad\quad 0.01\alpha + 10^{-4}$

$\dfrac{0.01\ \alpha\ (0.01\ \alpha + 10^{-4})}{0.01\ (1-\alpha)} = 2 \times 10^{-6}$

$\therefore \alpha \approx 0.01$
$\therefore [OH^-] = 0.01(0.01) + 10^{-4}$
$\quad\quad = 2 \times 10^{-4}\,M.$

3.
$$PuO_2^{2+} \quad + \quad H_2O \quad \rightleftharpoons \quad PuO_2(OH)^+ \quad + \quad H^+$$
$t = 0 \quad 0.01 \quad\quad\quad\quad\quad\quad 0 \quad\quad\quad\quad 0$
$t = eq \quad 0.01(1-h) \quad\quad\quad\quad 0.01\,h \quad\quad\quad 0.01\,h$
$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad (=10^{-4})$

Therefore, $h = 0.01 = 1\,\%$. So, $1 - h \approx 1$.

K_b of $PuO_2(OH)^+ = \dfrac{[PuO_2^{2+}][OH^-]}{[PuO_2(OH)^+]} = \dfrac{0.01 \times 10^{-10}}{0.01\ h} = \dfrac{10^{-10}}{0.01} = 10^{-8}.$

Hydrolysis is expected to be endothermic because it is reverse of neutralization (exothermic process).

4. $pOH_i = pK_b + \log_{10} \dfrac{\left[NH_4^+\right]_i}{[NH_4OH]_i} = 4.7.$ Therefore, $pH_i = 9.3.$

and $pOH_f = pK_b + \log_{10}\left(\dfrac{90 \times 0.1 + 10 \times 0.1}{90 \times 0.1 - 10 \times 0.1}\right) = 4.7 + \log\dfrac{5}{4} = 4.8.$ Therefore, $pH_f = 9.2$

% decrease $= \dfrac{9.3 - 9.2}{9.3} \times 100 = \dfrac{10}{9.3}\,\%.$

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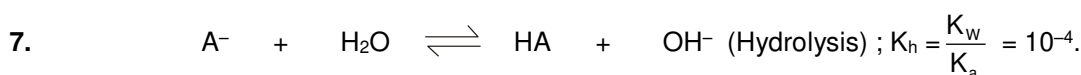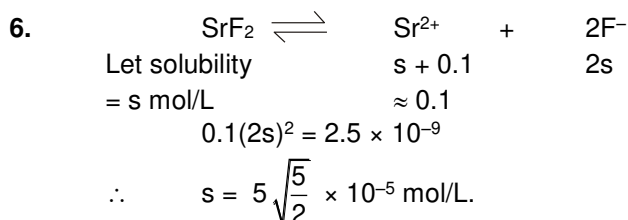
ADVIEQ(A)- 90

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) $pK_{In} + 1 = pK_{In} + \log_{10} \dfrac{\left[In^-\right]}{\left[HIn\right]}$

$\dfrac{\left[In^-\right]}{\left[HIn\right]} = 10$. So, % ionisation $\dfrac{10}{10+1} = \times 100 = \dfrac{1000}{11}$ %.

(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, pH = $\dfrac{1}{2}$ $[pK_{a_1} + pK_{a_2}]$.

6. $SrF_2 \rightleftharpoons$ Sr^{2+} + $2F^-$

Let solubility $s + 0.1$ $2s$

= s mol/L ≈ 0.1

$0.1(2s)^2 = 2.5 \times 10^{-9}$

∴ $s = 5\sqrt{\dfrac{5}{2}} \times 10^{-5}$ mol/L.

7. A^- + $H_2O \rightleftharpoons HA$ + OH^- (Hydrolysis) ; $K_h = \dfrac{K_w}{K_a} = 10^{-4}$.

$t = 0$ c   0   0

$t = eq$ $c(1 - h)$ ch   ch

$\dfrac{ch^2}{1-h} = 10^{-4}$. But $[OH^-] = ch = 10^{-5}$ M. (∵ pH = 9)

So, $\dfrac{10^{-5}}{1} \dfrac{h}{-} \dfrac{}{h} = 10^{-4}$. Therefore, h = $\dfrac{10}{11}$.

So, c = 1.1×10^{-5} M.

$K_{sp} = [Ag^+] [A^-] = c \times c(1 - h)$

$= 1.1 \times 10^{-5} \times 10^{-6}$

$= 1.1 \times 10^{-11}$.

8. In an alkaline aqueous solution, $[H^+] < [OH^-]$.

∴   pH > pOH.

Also, pH + pOH = pK_w and for pure water, pH = pOH = $\dfrac{pK_w}{2}$.

In an alkaline solution, $[H^+] < [H^+]_{H2O}$ and $[OH^-] > [OH^-]_{H2O}$.

∴   pH > $\dfrac{pK_w}{2}$ and pOH < $\dfrac{pK_w}{2}$.

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 pK_{InOH} = pOH at half ionisation point = 6.8.

$pOH_1 = pK_{InOH} + \log_{10} \dfrac{5}{1} = 7.5$.   ∴ $pH_1 = 6.5$

and $pOH_1 = pK_{In^*OH} + \log_{10} \dfrac{4}{1}$ ∴ $pK_{In^*OH} = 6.9 = pOH_2$

                                                                        ∴ $pH_2 = 7.1$.

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ADVIEQ(A)- 91

11. At 20% neutralisation, $pOH = pK_b + \log_{10} \dfrac{20}{80} = 5$.

∴ $pK_b = 5 - \log \dfrac{1}{4}$ ∴ $K_b = 2.5 \times 10^{-6}$.

At equivalence point, $pH = \dfrac{1}{2} (pK_w - pK_b - \log C)$

∴ $4.5 = \dfrac{1}{2} (14 - 5.6 - \log C)$ ∴ $C = 0.25$ M

Now, $C = \dfrac{n_{HCl}}{V_f (L)}$ ∴ $0.25 = \dfrac{0.5 \times V_L}{V_L + 0.1}$ ∴ $V_L = 0.1$ L = 100 mL.

At equivalence point, $n_{WB} = n_{HCl}$

$$\dfrac{m}{45} = 0.5 \times 0.1 \quad ∴ \quad m = 2.25 \text{ g.}$$

∴ Weight % of base in sample $= \dfrac{2.25}{2.5} \times 100 = 90\%$.

12. For getting selectively precipitated, $IP > K_{sp}$.

$[M^{2+}] [S^{2-}] > K_{sp}$

$[M^{2+}] \dfrac{K_{a_1} K_{a_2} [H_2S]}{[H^+]^2} > K_{sp}$

$\dfrac{[M^{2+}][H_2S]}{[H^+]^2} > K_{eq}$ ∴ $\dfrac{0.01 \times 0.1}{1^2} > K_{eq}$

∴ $K_{eq} < 10^{-3}$.

For PbS, above condition is satisfied.

13. $K_a(NH_4^+) = \dfrac{1}{K_{eq}} = 5 \times 10^{-10}$.

Now, $K_b(NH_3) \times K_a(NH_4^+) = K_w = 10^{-14}$.

So, $pK_b(NH_4OH) = -\log_{10} (K_b(NH_3)) = -\log_{10} (2 \times 10^{-5}) = 4.7$.

14. $p_{H_2} = 10$ atm (as 1 mole H_2 in 2.24 L at 0ºC) & $[I^-] = 0.5$ M

$K = \dfrac{[OH^-]^2 p_{H_2}}{[I^-]^2} \Rightarrow [OH^-]^2 = \dfrac{4 \times (0.5)^2 \times 10^{-9}}{10} \Rightarrow [OH^-] = 10^{-5}$ M   ∴ pOH = 5

15.

         $H_2A \rightleftharpoons H^+ + HA^-$

t = 0   0.1   0   0

t = eq $0.1(1-\alpha)$ 0.1α 0.1α
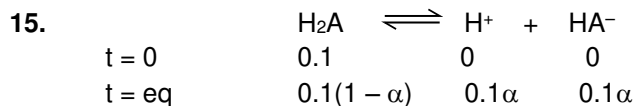
$K_{a1} = 0.05 = \dfrac{0.1 \ \alpha^2}{1-\alpha} \quad ∴ \quad \alpha = 0.5$

Now, $[A^{2-}]/[H^+] = K_{a_2}/[H^+] = \dfrac{2 \times 10^{-6}}{0.05} = 4 \times 10^{-5}$.

16.

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

t = 0   20   9.2   0   0

t = t   10.8   0   9.2   0

t = 50% neutralization (∵ $pOH = pK_b = 5$)   10   0   10

∴ 0.8 millimole more of BOH are to be neutralized by H_2SO_4.

∴ $0.8 = (0.1 \times 2) \times V_{mL} \quad ∴ \quad V_{mL} = 4$.

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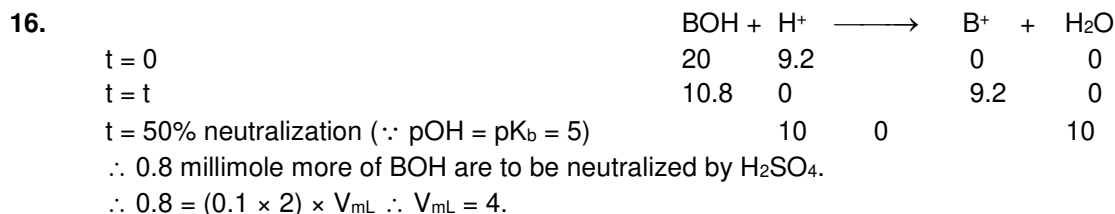
17. $s = \sqrt{K_{sp}} = 7 \times 10^{-7}$ mol/L $= \dfrac{7 \times 10^{-7} \times 188 \times 10^3}{4}$ mg / 250 mL.

$= 3.29 \times 10^{-2}$ mg / 250 mL.

$\therefore$ Percentage saturation $= \dfrac{3.29 \times 10^{-3}}{3.29 \times 10^{-2}} \times 100 = 10\%$.

18. pK_a (CH_3COOH) = 4.74

$[CH_3COOH]$ = 0.25 M, $\qquad$ $[CH_3COONa]$ = 0.15 M

$[H^+] = \dfrac{K_a \; [CH_3COOH]}{[CH_3COO^-]} = \dfrac{1.8 \times 10^{-5} \times 0.25}{0.15} = 3 \times 10^{-5}$ M

$H_2S \rightleftharpoons 2H^+ + S^{-2}$ $\qquad \Rightarrow \qquad$ $K_a = \dfrac{[H^+]^2 \; [S^{-2}]}{[H_2S]}$

$[S^{2-}] = \dfrac{9 \times 10^{-21} \times 0.1}{9 \times 10^{-10}} = 10^{-12}$ M

IP (MnS) = $[Mn^{+2}] \, [S^{-2}]$ = $1.5 \times 10^{-2} \times 10^{-12} = 1.5 \times 10^{-14}$

IP < K_{sp} $\qquad \Rightarrow$ No ppt is formed.

For precipitation of MnS, the minimum concentration of $[S^{2-}]$ can be obtained as follows :

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

$1.5 \times 10^{-2} \times [S^{2-}] = 2.4 \times 10^{-13}$ $\Rightarrow$ $[S^{2-}] = 1.6 \times 10^{-11}$ M

For this $[S^{2-}]$,

$[H^+]^2 = \dfrac{K_a \; [H_2S]}{[S^{2-}]} = \dfrac{9 \times 10^{-21} \times 0.10}{1.6 \times 10^{-11}} = 7.5 \times 10^{-6}$ M

$[H^+] = \dfrac{K_a \; [CH_3COOH]}{[CH_3COO^-]}$ $\Rightarrow$ $7.5 \times 10^{-6} = \dfrac{1.8 \times 10^{-5} \times 0.25}{[CH_3COO^-]}$

$[CH_3COONa]$ = **0.6 M**

19. In all the other cases, pH = 1.

When all taps are opened,

Millimoles of H^+ = 100

Volume of solution = 2000 mL

$\therefore \qquad [H^+] = \dfrac{100}{2000} = 0.05$ M.

pH = $-\log[H^+]$ = $-\log (5 \times 10^{-2})$ = 2 $-$ log 5 $\neq$ 1.

20. pH_i = 7.

After opening S_1, solution in bucket would contain $[CH_3COOH]$ = 0.1 M. So, pH after opening

$S_1 = \dfrac{1}{2} (pK_a - \log C) = 2.8775$.

After opening S_2, solution in bucket would contain $[CH_3COONa]$ = $\dfrac{1}{15}$ M. So, pH after opening

$S_2 = \dfrac{1}{2} (pK_w + pK_a + \log C) = 8.7875$.

After opening S_3, solution in bucket would contain $[CH_3COONa]$ = $\dfrac{1}{40}$ M & $[CH_3COOH]$ = $\dfrac{1}{40}$ M. So, pH

after opening $S_3 = pK_a + \log\left(\dfrac{1/40}{1/40}\right)$ = pK_a = 4.755. (Buffer properties)

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After opening S$_4$, solution in bucket would contain [CH$_3$COOH] $\dfrac{1}{25}$ = M & [HNO$_3$] = $\dfrac{1}{50}$ M. So, pH after

opening S$_4$ = – log $\dfrac{1}{50}$ = 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 Ag$^+$ = 0.01 ;   Initial moles of IO$_3^-$ = 0.005
Initial moles of CrO$_4^{2–}$ = 0.1

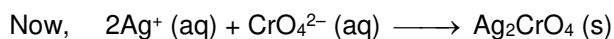[Ag$^+$] required for AgIO$_3$ precipitation = $\dfrac{K_{sp}(AgIO_3)}{[IO_3^-]}$ = $\dfrac{10^{-13}}{0.005}$ = 2 × 10^{-11} M

and [Ag$^+$] required for Ag$_2$CrO$_4$ precipitation = $\sqrt{\dfrac{K_{sp}(Ag_2CrO_4)}{[CrO_4^{2-}]}}$ = $\sqrt{\dfrac{10^{-8}}{0.1}}$ = 3.162 × 10^{-4} M

So, Ag$^+$ first combines with IO$_3^-$, almost whole of Ag$^+$ gets precipitated out, then precipitation of Ag$_2$CrO$_4$ starts.
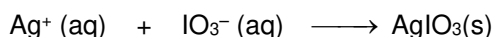
$\quad\quad$ Ag$^+$ (aq) + IO$_3^-$ (aq) $\longrightarrow$ AgIO$_3$(s)
Moles of Ag$^+$ left after the above reaction = 0.01 – 0.005 = 0.005.
Now,   2Ag$^+$ (aq) + CrO$_4^{2–}$ (aq) $\longrightarrow$ Ag$_2$CrO$_4$ (s)
Moles   0.005   0.1
Moles of CrO$_4^{2–}$ left after the above reaction = 0.1 – 0.0025 = 0.0975.
At equilibrium,
[CrO$_4^{2–}$] = **0.0975 M**

[Ag$^+$] = $\sqrt{\dfrac{K_{sp}(Ag_2CrO_4)}{[CrO_4^{2-}]}}$ = $\sqrt{\dfrac{10^{-8}}{0.0975}}$ = **3.2 × 10^{-4} M.**

[IO$_3^-$] = $\dfrac{K_{sp}(AgIO_3)}{[Ag^+]}$ = $\dfrac{10^{-13}}{3.2\times10^{-4}}$ = **3.125 × 10^{-10} M.**

Total moles of precipitate formed = 0.005 + 0.0025 = **0.0075.**