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

$$H_2A \rightleftharpoons HA^- + H^+$$

at eq. $c(1-\alpha_1)$ $c\alpha_1(1-\alpha_2)$ $(c\alpha_1 + c\alpha_1\alpha_2)$

II step

$$HA^- \rightleftharpoons A^{2-} + H^+$$

$c\alpha_1(1-\alpha_2)$ $c\alpha_1\alpha_2$ $(c\alpha_1 + c\alpha_1\alpha_2)$

(on applying concept of siultaneous equilibrium)

$$K_{a_1} = \frac{[H^+]\ [HA^-]}{[H_2A]} \qquad K_{a_2} = \frac{[H^+]\ [A^{2-}]}{[HA^-]}$$

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

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

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 $\alpha_1 \le 0.1$ 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–α) 0.1α 0.1α

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

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

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

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

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

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

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: $H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-}$

$$\begin{array}{ccc} H_2PO_4^- & H^+ & HPO_4^{2-} \\ 0.024 & 0.024 & 0 \\ (0.024 - y) & (0.024 + y) & y \end{array}$$

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

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

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

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

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

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

For III step: $HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-}$

$$\begin{array}{ccc} HPO_4^{2-} & H^+ & PO_4^{3-} \\ (6.2 \times 10^{-8} - x) & (0.024 + x) & x \end{array}$$

$\therefore$ $K_3 = \dfrac{[H^+][PO_4^{3-}]}{[HPO_4^{2-}]} = \dfrac{(0.024+x)x}{(6.2\times10^{-8} - x)}$

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

$\therefore$ $3.6 \times 10^{-13} = \dfrac{0.024x}{6.2\times10^{-8}}$

$\therefore$ $x = \dfrac{3.6\times10^{-13}\times6.2\times10^{-8}}{0.024} = 9.3 \times 10^{-19}$ M

or $[PO_4^{3-}] = 9.3 \times 10^{-19}$ 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 :

$$\begin{array}{lccc} & HA & \rightleftharpoons H^+ & + \ A^- \\ t = 0 & C_2 & C_1 & 0 \\ t = eq. & C_2(1-\alpha) & C_2\alpha + C_1 & C_2\alpha \end{array} \qquad K_a = \frac{(C_2\alpha + C_1)\,C_2\alpha}{C_2(1-\alpha)} \quad ...(1)$$

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

$K_a = C_1\alpha$ ...(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.
$$\begin{array}{llll} & CH_3COOH & \rightleftharpoons CH_3COO^- & + \; H^+ \\ t = eq & C(1-\alpha) & C\alpha & 10^{-1} + C\alpha \end{array}$$

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 $\quad \therefore$ 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 :

$$\begin{array}{llll} & HA_1 \rightleftharpoons & H^+ \; + & A_1^- \\ t=0 & C_1 & 0 & 0 \\ t = eq & C_1(1-\alpha_1) & C_1\alpha_1 + C_2\alpha_2 & C_1\alpha_1 \end{array} \qquad \begin{array}{lll} HA_2 \rightleftharpoons & H^+ \; + & A_2^- \\ C_2 & 0 & 0 \\ C_2(1-\alpha_2) & C_2\alpha_2 + C_1\alpha_1 & C_2\alpha_2 \end{array}$$

(On applying concept of simultaneous equilibrium)

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

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

- Both acids will dissociate less than in their individual aqueous solutions of same concentration because of common ion effect exerted by H^+ ions of one on other.
- If the dissociation constant of one of the acid is very much greater than that of the second acid then contribution from the second acid can be neglected.
  So, $[H^+] = C_1\alpha_1 + C_2\alpha_2 \approx C_1\alpha_1$ (where C_2 is the concentration of weaker acid)

Solved Examples

Ex-3. Calculate the pH of a solution obtained by mixing equal volume of 0.02 M HOCl & 0.2 M CH_3COOH solutions.
Given that K_a (HOCl) = 2×10^{-4} ; K_a (CH_3COOH) = 2×10^{-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

$$[H^+] = \sqrt{C_1K_{a_1} + C_2K_{a_2}} = \sqrt{2\times10^{-4}\times0.01 + 2\times10^{-5}\times0.1} = \sqrt{2\times10^{-6} + 2\times10^{-6}} = 2 \times 10^{-3} \text{ M}$$

$\therefore$ pH = 3 – log2 = 2.7

$$[OCl^-] = \frac{0.01\times2\times10^{-4}}{2\times10^{-3}} = 1 \times 10^{-3} \text{ M} \quad ; \quad [CH_3COO^-] = \frac{0.1\times2\times10^{-4}}{2\times10^{-3}} = 1 \times 10^{-3} \text{ M} ;$$

$$[OH^-] = \frac{K_w}{[H^+]} = \frac{10^{-14}}{2\times10^{-3}} = 5 \times 10^{-12} \text{ M.}$$

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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, $[H_2S] = 0.1M$, $[CH_3COOH] = 0.01$ 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.

(2^{nd} 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).

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

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

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

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.	$C_1 - C_1\alpha_1$		$0.1 + C_1\alpha_1$ (≈ 0.1)		$C_1\alpha_1$

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

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

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

⇒ 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,

$H_3\,PO_4 \rightleftharpoons H^+ + H_2PO_4^-$ $K_{a_1} = \dfrac{[H^+]\ [H_2PO_4^-]}{[H_3PO_4]}$ ...(1)

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

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

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

pH of the solution can be caculated from Ist step only because $[H^+]$ from IInd & IIIrd step can be neglected as

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

(b) $[H^+]$ from Ist dissociation will suppress the dissociation of IInd & IIIrd step.

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

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

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

t = 0 C 0 0

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

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

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

$H_2O \rightleftharpoons H^+ + OH^-$, $K_w = [H^+]\ [OH^-]$ ...(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, $K_{h_1} >> K_{h_2} >> K_{h_3}$.

Genarally, pH is calculated only using the first step hydrolysis

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

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

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

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

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

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

Solved Examples

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

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

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

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

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

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

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

$\therefore$ pH = 13.15.

Solutions containing amphiprotic anion (or cation) :

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

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

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

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

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

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

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

(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.

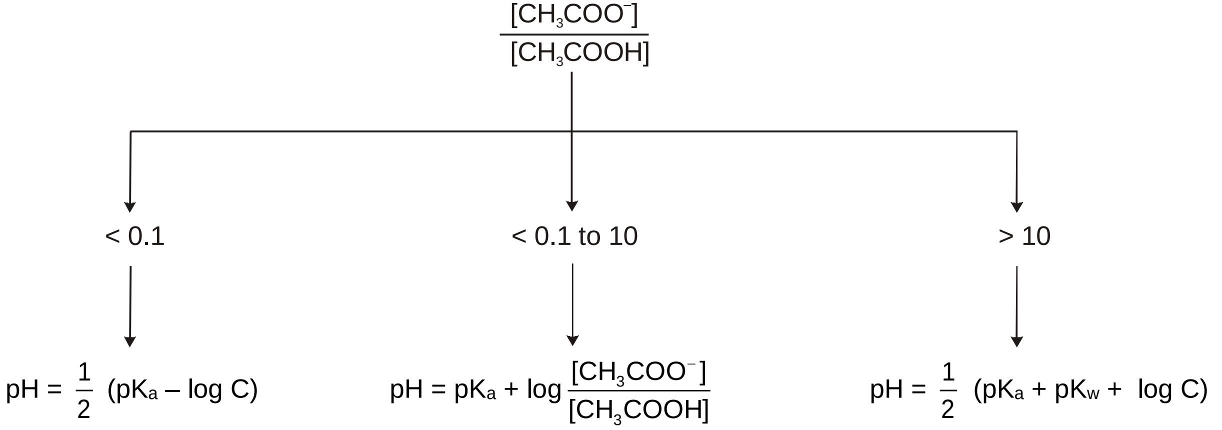
Ionic Equilibrium-II

(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 : $\frac{1}{2}$ ($pK_w + pK_a$ + log C) and for (iii), the relation used is pH = $pK_a + \log\frac{[\text{Anion of Salt}]}{[\text{Acid}]}$.

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



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

< 0.1 → $\text{pH} = \frac{1}{2}(pK_a - \log C)$

< 0.1 to 10 → $\text{pH} = pK_a + \log\frac{[CH_3COO^-]}{[CH_3COOH]}$

> 10 → $\text{pH} = \frac{1}{2}(pK_a + pK_w + \log C)$

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°C) and sodium acetate mixture can be used for preparing buffer solutions whose pH values are roughly in the range of 3.75 to 5.75. Outside this range, the buffer capacity of acetic acid–sodium acetate solution is too small to be used for any practical purpose.

Solved Examples

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

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

⇒ $7.4 = 6.7 + \log\frac{[HCO_3^-]}{[H_2CO_3]}$ ⇒ $\frac{[HCO_3^-]}{[H_2CO_3]} = 5$

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

⇒ $5 \times 2.5 \times 10 \times 10^{-3} = 5 \times V$ ⇒ 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 = $pK_a + \log \frac{b-x}{(a+x)}$.

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

Differentiating with respect to x we get

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

Taking the inverse

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

Maximum buffer capacity :

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

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

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

a – b = 0

F9 : ∴ b = a ⇒ [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 (ii) 0.2M CH_3COOH and 0.2M CH_3COONa

Given : pK_a (CH_3COOH) = 4.74

Which will be a better buffer ?

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

(i) Buffer capacity = $\frac{0.1\times0.1\times2.303}{0.1+0.1}$ = 0.11515

(ii) Buffer capacity = $\frac{0.2\times0.2\times2.303}{0.2+0.2}$ = 0.2303

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

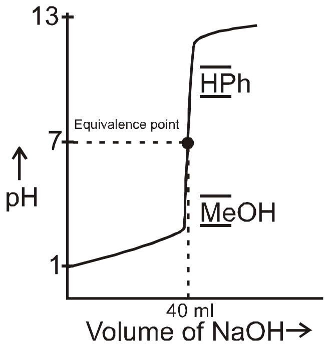
(B) pH Calculation : Monobasic acid-monoacidic base titrations

(A) Titration of SA with SB :

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

Volume of NaOH added	**pH of solution**
0 mL	1
10 mL	1.22 ($\therefore$ $[H^+] = \dfrac{40\times0.1-10\times0.1}{50} = 6 \times 10^{-2}$)
20 mL	1.48
30 mL	1.84
39 mL	2.90
39.9 mL	3.90
40.0 mL (Equivalence point : complete neutralization)	7
40.1 mL	10.1
41 mL	11.1
50 mL	12.05
60 mL	12.30 (□ $[OH^-] = \dfrac{60\times0.1-40\times0.1}{100} = 2 \times 10^{-2}$)

Figure-1



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

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

According to our data, it is 4 – 10.

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

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

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

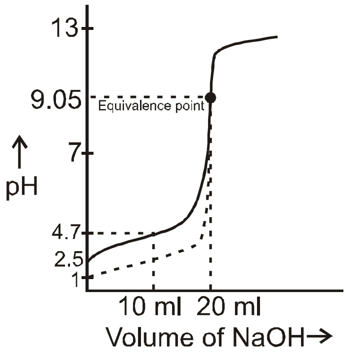
(B) Titration of SB with WA :

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 $\quad$ [$pH = \frac{1}{2}(pK_a - \log C)$]
5 mL	4.23
10 mL Half equivalence point	4.7 $\quad$ [$pH = pK_a$] (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 (Equivalence point : complete neutralization)	7 + 1/2 (4.7) + 1/2 log (1/4) = 9.05 Salt of WA & SB (CH_3COONa = 0.25 M)

21 mL	12.09
30 mL	13

Figure-2

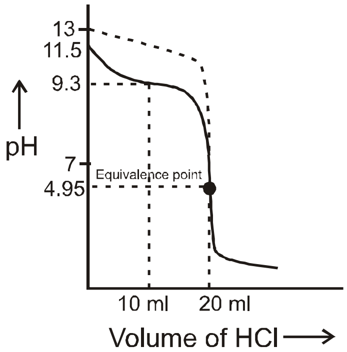


- pH calculation at all volumes of NaOH in between 0 mL & 20 mL can be done by concept of buffer of WA & its salt with SB & further data by excess NaOH.
- Initially, fast change in pH is due to free ions available from weak acid.
- Slow down of pH change thereafter is due to buffer formation. Least pH 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) $CH_3COONa + HCl \longrightarrow NaCl + CH_3COOH$

	CH_3COONa	HCl	NaCl	CH_3COOH
t = 0	5 millimole	1 millimole	0	0
finally	4 millimole	0	–	1 millimole ⇒ 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)

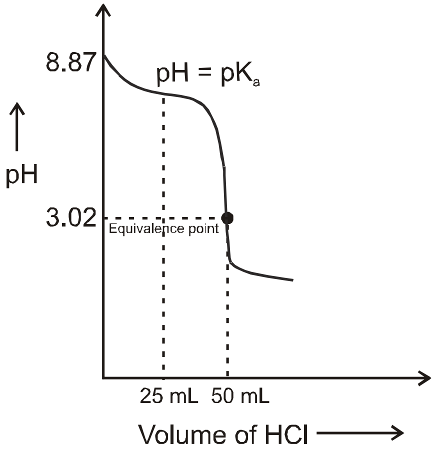
(f) [HCl] = 1/100 M ; pH = 2.1

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

(g) [HCl] = $\frac{2.5}{125}$ 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

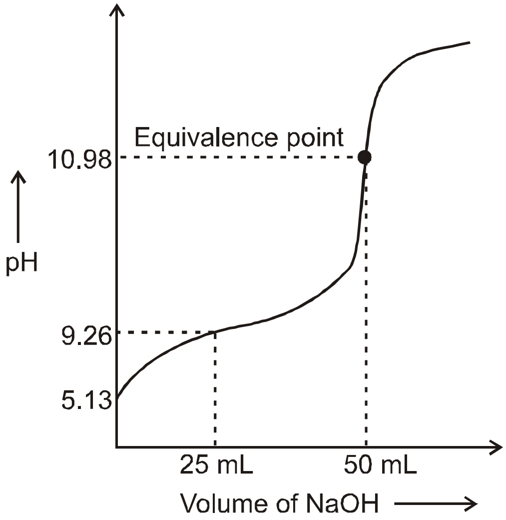
50 mL of 0.1 M NH_4Cl is titrated with 0.1 M NaOH. Calculate pH when volume of NaOH added is :

(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 sliver 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 :

$$AgSCN \rightleftharpoons \underset{x+y}{Ag^+} + \underset{x}{SCN^-} \qquad AgBr \rightleftharpoons \underset{x+y}{Ag^+} + \underset{y}{Br^-}$$

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

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

On solving, we get $x = 2y$

So, $y = 4.08 \times 10^{-7}$ M and $x = 8.16 \times 10^{-7}$ 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 $Ag_2SO_4 \rightleftharpoons \underset{2s}{2Ag^+} + \underset{s}{SO_4^{2-}}$

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

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

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

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

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

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

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

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

It is thus evident that,

$$[Ag^+]^2\,[CrO_4^{2-}] = (0.869 \times 10^{-2})^2 \times (3.78 \times 10^{-7}) = 2.85 \times 10^{-11}\ (> K_{sp}\ Ag_2CrO_4)$$

Thus Ag_2CrO_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_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 $CaCO_3$, $K_{sp} = x = [Ca^{2+}]\,[CO_3^{2-}] = [Ca^{2+}] \times 2$ (□ CO_3^{2-} mainly coming from Na_2CO_3)

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

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

Check List

Definitions (D)

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

Formulae (F)

F1	pH of a solution of a weak polyprotic acid
F2	$[H^+]$ in a solution containg 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	$pH(H_2PO_4^-)$ & $pH(HPO_4^{2-})$
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

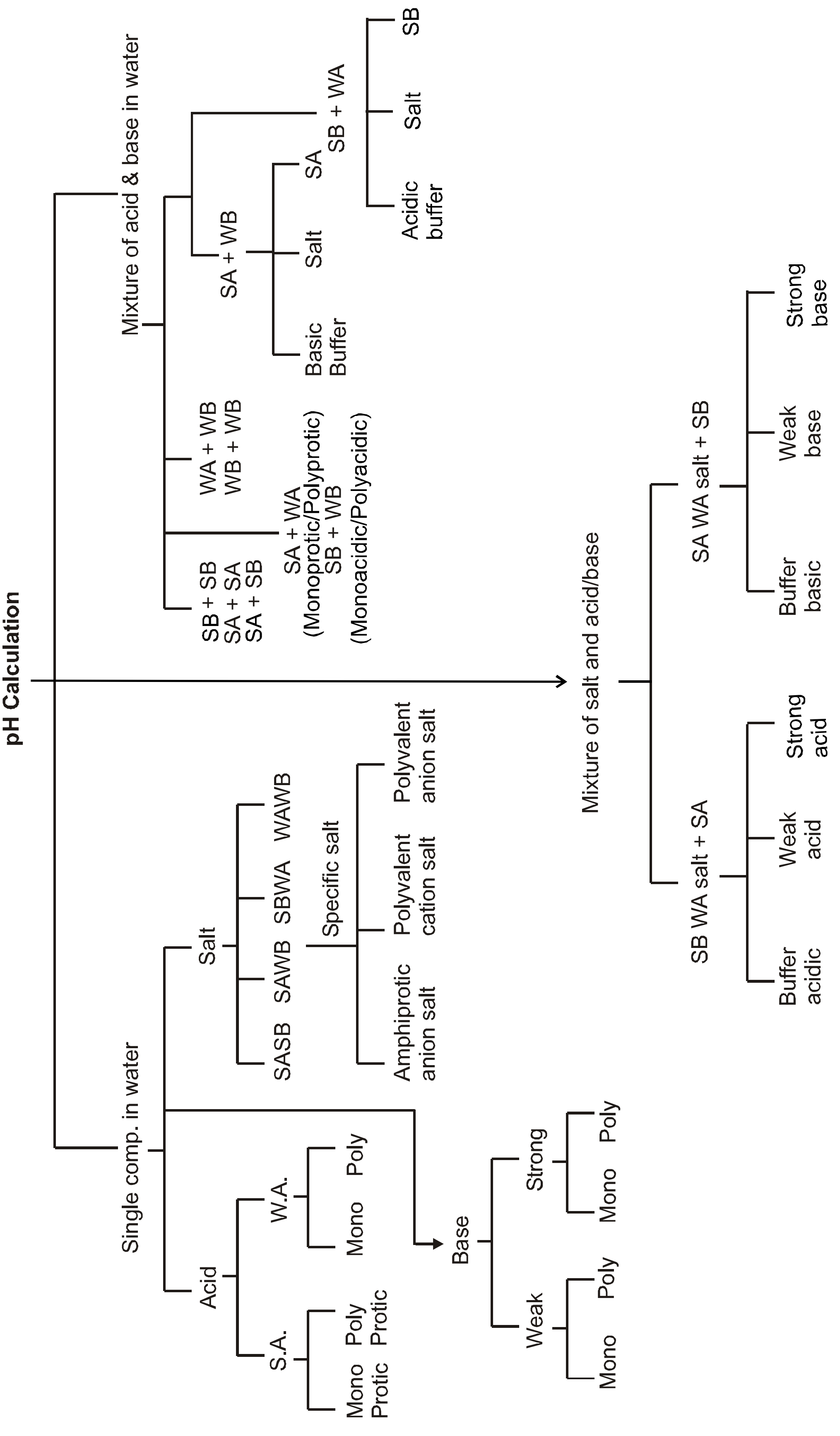
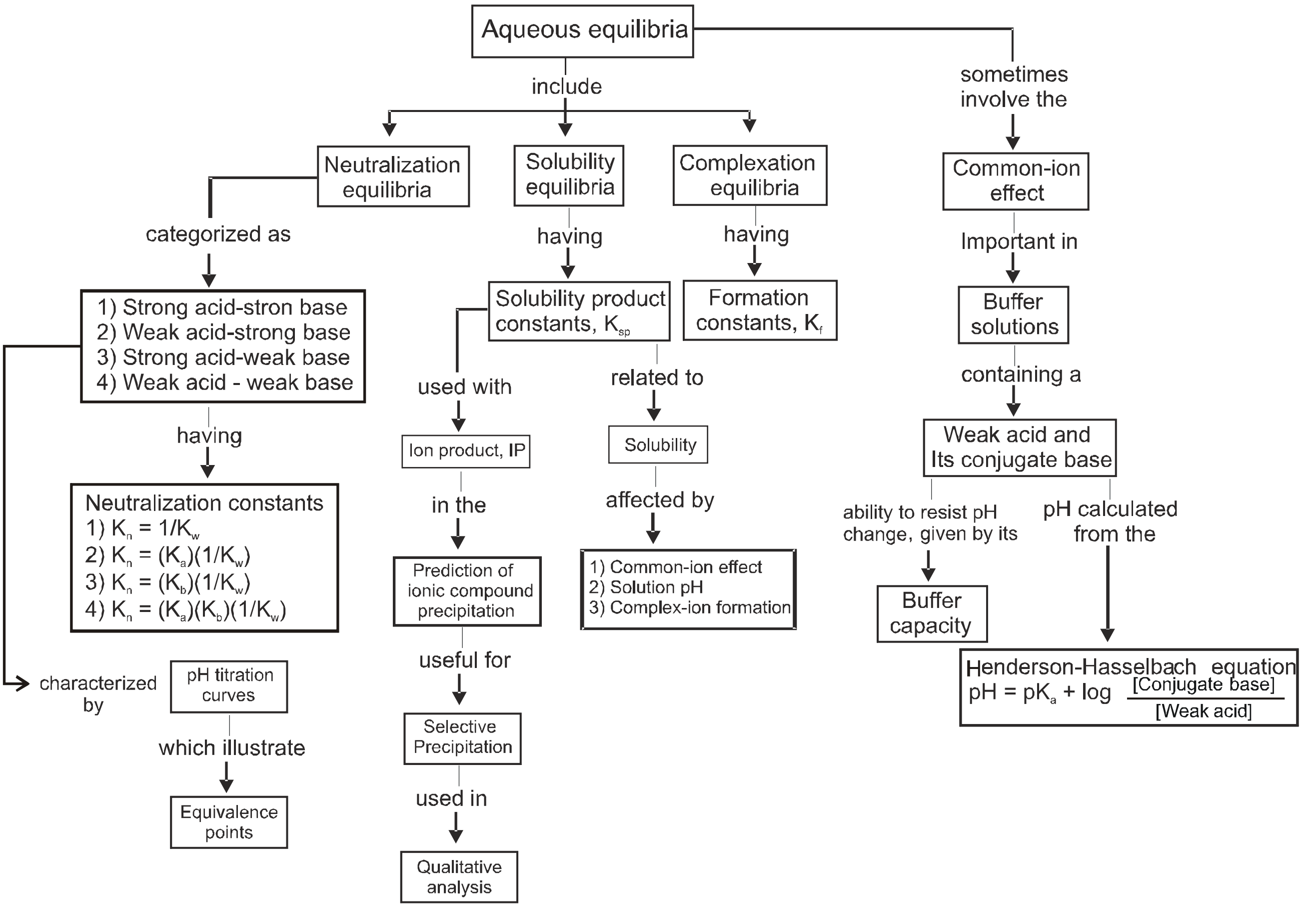

pH Calculation
Mixture of acid & base in water
SB + SB
SA + SA
SA + SB
SA + WA
(Monoprotic/Polyprotic)
SB + WB
(Monoacidic/Polyacidic)
WA + WB
WB + WB
SA + WB
Basic Buffer
Salt
SA
SB + WA
Acidic buffer
Salt
SB
Mixture of salt and acid/base
SB WA salt + SA
Buffer acidic
Weak acid
Strong acid
SA WA salt + SB
Buffer basic
Weak base
Strong base
Single comp. in water
Acid
S.A.
Mono Protic
Poly Protic
W.A.
Mono
Poly
Salt
SASB
SAWB
SBWA
WAWB
Specific salt
Amphiprotic anion salt
Polyvalent cation salt
Polyvalent anion salt
Base
Weak
Mono
Poly
Strong
Mono
Poly

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

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

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

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

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 $\frac{1}{1099} = 9.1 \times 10 \times 10^{-4}$ & 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

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

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

$$[H^+] = \sqrt{C_1K_{a_1} + C_2K_{a_2}} = \sqrt{0.1\times1.8\times10^{-4} + 0.1\times3.3\times10^{-4}} = 7.14 \times 10^{-3}\ M$$

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. $H_2S \rightleftharpoons H^+ + HS^-$; $K_{a_1} = 10^{-7}$

$HS^- \rightleftharpoons H^+ + S^{2-}$; $K_{a_2} = 1.3 \times 10^{-13}$

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

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.

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

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

$$\therefore \quad [HS^-] = \frac{10^{-7}\times0.1}{0.3} = \mathbf{3.3\times10^{-8}\ M}$$

Further $$K_{a_2} = \frac{[H^+][S^{2-}]}{[HS^-]} \quad \Rightarrow \quad 1.3\times10^{-13} = \frac{[0.3][S^{2-}]}{3.3\times10^{-8}}$$

$$\therefore \quad [S^{2-}] = \frac{1.3\times10^{-13}\times3.3\times10^{-8}}{0.03} = \mathbf{1.43\times10^{-19}\ M}$$

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 +	CH_3COOH →	CH_3COONa +	H_2O
Millimole added	20 × 0.2 = 4	50 × 0.2 = 10	0	0
Millimole after reaction	0	6	4	4

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

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

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

$$\therefore \quad pH = -\log 1.8\times10^{-5} + \log\frac{4/70}{6/70} = \mathbf{4.56}$$

(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 +	CH_3COOH →	CH_3COONa +	H_2O
Millimole added	0.2 × V = 0.2 V	50 × 0.2 = 10	0	0
Millimole after reaction	0	(10 – 0.2 V)	0.2 V	0.2V

$$\therefore \quad [\text{Acid}] = \frac{10-1.2V}{50+V}; \qquad [\text{Salt}] = \frac{0.2V}{50+V}$$

$$\therefore \quad 4.74 = -\log 1.8\times10^{-5} + \log\frac{(0.2V)/(50+V)}{(10-0.2V)/(50+V)} \qquad \therefore \quad V = \mathbf{25\ mL}$$

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

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

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

$\therefore$ $3b = 0.6$ or $b = 0.2$ 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 $Hg_2I_2 = 2.5 \times 10^{-26}$

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 $[I^-] = 5 \times 10^{-13}$ 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 $[Ag^+]_{left}\,[I^-] = \left(K_{sp}\right)_{AgI}$

$$\therefore \quad [Ag^+]_{left} = \frac{8.5\times10^{-17}}{5.0\times10^{-13}} = 1.7 \times 10^{-4}\ \text{M}$$

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

$$\therefore \quad \%\ \text{of}\ Ag^+\ \text{precipitated} = \frac{0.1-1.7\times10^{-4}}{0.1}\times100 = \mathbf{99.83\%}$$

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 $CaSO_4 = p$

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

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,

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

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

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

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

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