BUFFER SOLUTION

- Solution whose pH does not change significantly on addition of small amount of acid /alkali
- pH of this solⁿ is not affected by dilution
- Based on common ion effect.

BUFFER SOLUTION
- SIMPLE
- MIXED
  - ACIDIC
  - BASIC

SIMPLE BUFFERS:

Salt of WA & WB in Water

Eg: CH_3COONH_4 ; NH_4CN.

$$pH = \frac{1}{2}(pK_w + pK_a - pK_b)$$

$$pH = 7 + \frac{1}{2}(pK_a - pK_b)$$

MIXED BUFFERS:

- Aqueous (solution of mixture of weak acid and salt of same weak acid with any kind of strong base.

Acidic (Weak Acid with its strong or conjugate base)

WA + Salt (WASB)

WA + Conjugated ion salt

Eg: $CH_3COOH + CH_3COONa$; $HCOOH + HCOOK$; $HCN + NaCN$

$C_6H_5COOH + C_6H_5COONa$; $H_2CO_3 + Na_2CO_3$; $H_2S + NaHS$

→ pH (By Henderson's equation)

$$pH = pK_a + \log \frac{(Salt)}{(WA)}$$

$$pH = pK_a + \log \frac{[Con.\ base]}{[WA]}$$

$$pH = -\log K_a + \log \frac{[Salt]}{[WA]}$$

BASIC (Weak Base with its strong or conjugate acid)

Aqueous solution of mixture of weak base and salt of same WB with any kind of strong acid.

WB + Salt (SAWB)

WB + Conjugated ion salt.

Eg: $NH_4OH + NH_4Cl$; $NH_4OH + NH_4NO_3$

→ pOH (By Handerson's eqn)

$$pOH = pK_b + \log \frac{(Salt)}{(WB)}$$

$$pOH = -\log K_b + \log \frac{[Salt]}{[WB]}$$

NOTE: pH of Blood = 7.4
↳ Acidic Buffer Solution.
Weak Acid → Carbonic Acid (H_2CO_3)

Que 08 DPP 06: pH of sol^n by mixing 150 cm^3 (mL), 0.1 M CH_3COONa and 250 cm^3, 0.1 M CH_3COOH
[Ka of CH_3COOH = 1.8×10^{-5}]

$$pH = pKa + \log \frac{[Salt]}{[WA]}$$

$$pH = [-\log(1.8 \times 10^{-5})] + \log \frac{(15/400)}{(25/400)}$$

$= 4.7450 + (\log 3 - \log 5)$
$= 4.7450 + (-0.2200)$
$= 4.52$

$pKa = -\log Ka$
$= -\log 1.8 \times 10^{-5}$
$= -\log 1.8 + \log 10^{-6}$
$= -\log(9 \times 2) + 6$
$= -\log 9 + \log 2 + 6$
$= 0.954 + 0.3010 - 6$
$\Rightarrow 4.7450$ (4.74)

Que 10 DPP 06: pH 9 is prepared by mixing NH_4Cl & NH_4OH. Calc. the no. of moles of NH_4Cl that should be added to 1 l of 1.0 M NH_4OH [$K_b = 1.8 \times 10^{-5}$]

Solved in DPP itself.

Buffer Range / Buffer Index / Buffer Capacity

- Defined as number of moles of SA / Base required for changing its pH value by 1 unit of a one litre solution.

- No. of H^+ / OH^- added = Change in number of moles of acid / Base = change in no. of moles of salt.

Buffer range for Buffer Solⁿ of pKa ± 1

- Buffer range for buffer solⁿ = $\frac{[Salt]}{[WA]} = \frac{1}{10}$ to 10

CASE: 01

If concentration ratio of $\frac{[Salt]}{[WA]} = \frac{1}{10}$ to 10 (diffe. of ± pH)

then solution act as B.S.

$$\therefore \boxed{pH = pKa + \log \frac{[Salt]}{[WA]}}$$

CASE: 02

If concentration ratio of $\frac{[Salt]}{[WA]} > 10$ [Salt ↑, WA ↓]
∴ SBWA

then, $\boxed{pH = \frac{1}{2}(pKw + pKa + \log C)}$

CASE 03

If conc. ratio $< \frac{1}{10}$ (Salt ↓, WA ↑)

then, $pH = \frac{1}{2}(pKa - \log C)$

Que 05 DPP 06 In which of the following respective volume ratios should be of 0.1 M NH_4OH sol^n & 0.1 M HCl sol^n be mixed, so that the resulting sol^n behaves like a buffer sol^n?

$NH_4OH + HCl \rightarrow NH_4Cl + H_2O$
0.1M 0.1M 0.1M

For preparation of WBSA B.S. required NH_4Cl and NH_4OH so WB (NH_4OH),

(2:1)

Que 13 DPP 06 The ionization constant of a certain WA is 10^{-4}. What should be the [Salt] to [Acid] ratio if we have to prepare a buffer with pH = 5 using this acid and one of the salts?

$pKa = \log 10^{-4} = 4$

$$pH = pka + \log \frac{(Salt)}{[Acid]}$$

$$5 = 4 + \log \frac{[Salt]}{[Acid]} \Rightarrow 5 = 4 + \log \frac{(100)}{(10)}$$

$5 = 4 + 1 \Rightarrow 5 = 5$

Que14 PP:06 In a mixing of acetic acid and sodium acetate, the ratio of conc. of the salts to the acid is ↑esed by ten times. Then the pH of the solution:

~~Solved in DPP itself~~

☀ HOW BUFFER SOLUTION WORK [COMMON ION EFFECT]

$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$ —— (1)

$CH_3COONa \longrightarrow CH_3COO^- + Na^+$ ⟶ (2)

COMMON ION EFFECT

$CH_3COOH + CH_3COONa \longrightarrow CH_3COO^- + H^+ + Na^+$ (Net rxn)

CASE 01: If Acid (H^+) ion add then eqn (1) move backward direction according to Le-Chatlier Principle, so pH of Buffer solution not decrease after adding acid in marginal quantity.

> If H^+ add then eq 1 suppressed (←)

CASE 02: If Base (OH^-) ion is added then eqn: 01 move forward direction according to Le-Chatlier Principle, so PH of Buffer solution not increase after adding base in marginal quantity.

If OH^- add then eq. 1 moves forward.

TYPES OF SOLUTION BASED ON SOLUBILITY OF SOLUTE

① **Highly Soluble Salt:**
Those salt which have solubility more than 0.1 Molar (0.1M)
Eg: NaCl, KCl, Na_2SO_4 etc.

② **Partial Soluble Salt:**
Those salt which have solubility is between 0.01 to 0.1 M
Eg: Weak electrolytes.

3) **Sparingly Soluble Salt:**
Those salt which have solubility is less than 0.01M. Very low quantity is soluble in salt.
Eg: AgCl, HgCl, ~~CO~~ $CoCl_2$, $HgCl_2$, $AuCl_3$ etc.

RELATION BETWEEN SOLUBILITY PRODUCT CONSTANT (Ksp) AND SOLUBILITY (S):

$$AgCl(s) + H_2O(l) \rightleftharpoons \underset{S}{Ag^+}(aq.) + \underset{S}{Cl^-}(aq.)$$

$$K = \frac{[Ag^+][Cl^-]}{[AgCl]}$$

$$\boxed{K_{sp} = [Ag^+][Cl^-]} \quad \boxed{K_{sp} = S^2} \Rightarrow \boxed{S = \sqrt{K_{sp}}}$$

$$\boxed{S = (K_{sp})^{1/2}} \quad \text{— Eq: 01}$$

Case 01 5. Ksp for AB_2 type salt :- ($HgCl_2$)

$$AB_2(s) \rightleftharpoons A^{2+}(aq) + 2B^-(aq)$$
$$\quad\quad\quad\quad s \quad\quad\quad 2s$$

$$K_{sp} = [A^{+2}][B^-]^2$$
$$K_{sp} = (s)(2s)^2$$

$$\boxed{K_{sp} = 4s^3} \quad \boxed{s = \left(\frac{K_{sp}}{4}\right)^{1/3}} \text{ — (2)}$$

Case : 02 Ksp for AB_3 type salt

$$AB_3(s) \rightleftharpoons A^{3+}(aq) + 3B^-(aq)$$
$$\quad\quad\quad s \quad\quad\quad 3s$$

$$K_{sp} = s(3s)^3$$

$$\boxed{K_{sp} = 27s^4} \text{ — (3)}$$

Case 03 A_2B_3 type salt :

$$A_2B_3(s) \xrightleftharpoons{H_2O} 2A^{+3}(aq) + 3B^{-2}(aq)$$
$$\quad\quad\quad 2s \quad\quad\quad 3s$$

$$K_{sp} = (2s)^2(3s)^3$$

$$\boxed{K_{sp} = 108s^5}$$

Que:05 Ksp of $Ag_2CrO_4 \rightarrow 32\times10^{-12}$
DPP:07 concentration of CrO_4^{2-} ions in that solution.

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

$$Ksp = 4S^3$$

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

$$S = (8\times10^{-12})^{1/3}$$

$$S = [2^3 \times 10^{-4\times3}]^{1/3}$$

$$S = 2\times10^{-4}$$

Que06 Solubility $(BaSO_4)$ in $H_2O \rightarrow 2.33\times10^{-3}$ g/litre
DPP:07 Its solubility product will be (M.M of $BaSO_4 = 233$)

It is given that,

Solubility$(BaSO_4) = 2.33\times10^{-3}$ g/Litre → Convert into mol/Litre.

$$S = \frac{2.33\times10^{-3}}{233\times100} = 10^{-5}$$

$$BaSO_4 \rightleftharpoons \underset{S}{Ba^+} + \underset{S}{SO_4^-}$$

$$Ksp = [S]^2 = [10^{-5}]^2 = [10^{-10}]$$

Que 07 Ksp of $AgCl = 1.8\times10^{-11}$
DPP 07 Max. vol. of water required to dissolve 1.9 mg of AgCl is approximately: