

Q:19 pKa of acetic acid and pKb of ammonium hydroxide are 4.76 and 4.75 resp. calculate pH of NH_4 -acetate solⁿ.

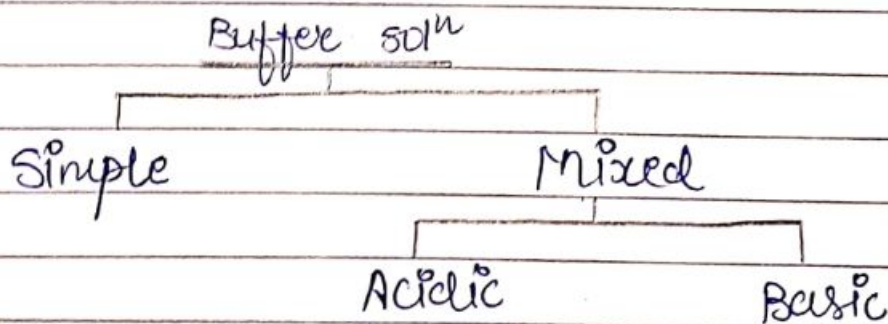
→ pKa slight high. hence, basic.

$$\text{pH} = 7 + \frac{1}{2} (4.76 - 4.75) \quad \rightarrow \quad 7 + \frac{1}{2} (0.01) \quad = \underline{7.005}$$

Buffer solution:

- solution whose pH does not change significantly on addition of small amount of acid or alkali.
- pH of Buffer solution is not affected by dilution.
- based on common ion effect.

#> Types:



* Simple Buffers:

- salt of weak acid and weak base in water.
- eg: $\text{CH}_3\text{COONH}_4$; NH_4Cl .

$$\text{pH} = \frac{1}{2} (\text{pKw} + \text{pKa} - \text{pKb}) \quad \text{or} \quad \frac{7 + 1}{2} (\text{pKa} - \text{pKb})$$

* Mixed Buffers:

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

1) Acidic: (weak acid with its strong base)

→ $W.A + \text{Salt (WASB)}$
or $W.A + \text{conjugated ion salt}$

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

M.S. $C_6H_5COOH + C_6H_5COONa$; $H_2CO_3 + Na_2CO_3$; $H_2S + NaHS$

→ pH (by Henderson's eqn):

$$pH = pK_a + \log \frac{[SALT]}{[W.ACID]} \quad \text{or} \quad pH = pK_a + \log \frac{[conj. base]}{[w. acid]}$$

$$\text{or} \quad pH = -\log K_a + \log \frac{[Salt]}{[w. acid]}$$

2) Basic: (weak base with its strong acid)

→ aqueous solution of mixture of weak base and salt of same weak base with any kind of strong acid

→ $WB + \text{Salt (SAWB)}$
or $WB + \text{conjugated ion salt}$

eg: $NH_4OH + NH_4Cl$; $NH_4OH + NH_4NO_3$;

→ pOH (by Henderson's eqn):

$$pOH = pK_b + \log \frac{[Salt]}{[w. base]} \quad \text{or} \quad pOH = -\log K_b + \log \frac{[Salt]}{[w. base]}$$

Q: 20 $B^- = HB^+$'s concentrations. for B^- is 10^{-10} . pH?

$$pOH = (-\log K_b) + \log \frac{[salt]}{[weak\ acid]}$$

$$= (-\log 10^{-10}) + \log \frac{[B^-]}{[HB^+]} (1) :$$
$$= \underline{10}.$$

$$\log 1 = 0.$$

$$pH = 14 - 10 \longrightarrow \underline{4}.$$

Q: 21 NH_3 conc. 0.30 M and NH_4^+ conc. 0.20 M

$$K_b = 1.8 \times 10^{-5} \quad pH = ?$$

$$pOH = -\log 1.8 \times 10^{-5} + \log \left[\frac{0.2}{0.3} \right]$$

$$= -\log 1.8 \times 10^{-5} + \log \left[\frac{2}{3} \right]$$

$$= 5 - \log 1.8 + \log \left[\frac{2}{3} \right]$$

$$pOH = 5 + \log \left[\frac{2}{3 \times 1.8} \right]$$

$$= 5 + \log \left[\frac{1}{2.7} \right] \longrightarrow 5 - \log(2.7).$$

$$\therefore pOH = 5 - 0.43$$
$$= \underline{4.57}.$$

$$\therefore pH = 14 - 4.57$$
$$= \underline{9.43}$$

$$\begin{array}{r} 29.10 \\ 14.50 \\ \hline 4.57 \\ 9.43 \end{array}$$

Buffer capacity / index / range:

- defined as number of moles of strong acid / base required for changing its pH value by 1 unit of a one litre solution.
- number of H^+ / OH^- added = change in number of moles of acid / base = change in no. of mole of salt

Buffer range for buffer solⁿ of $pK_a \pm 1$:

- buffer range for buffer solⁿ = $\frac{[salt]}{[w. acid]} = 1$ to 10 .

→ CASE: I

if concⁿ ratio of $\frac{[salt]}{[w. acid]} = 1$ to 10 .
(diff. of ± 1 of pH)

then, solⁿ act as buffer solⁿ

$$pH = pK_a + \log \frac{[salt]}{[w. acid]}$$

→ CASE: II

if concⁿ ratio of $\frac{[salt]}{[w. acid]} > 10$ (Salt \uparrow w_A \downarrow)
% of SBWA

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

→ CASE: III

if concⁿ ratio $< 1/10$ (Salt \downarrow w_A \uparrow).

$$pH = \frac{1}{2} (pK_a - \log C)$$