Buffer Solutions

Definition: A solution that resists change in pH on addition of limited amount of acid & base to it.

Why a buffer solution is needed?

→ In chemical, industrial & biological systems for certain rxns it is important to maintain the pH of the system.

For example: ① blood in human body is a buffer solution [pH ≈ 7.4] req. for body functioning

② In pharmaceutical practice pH may affect the solubilities of drugs that are weak acids or bases. Also it may affect the stabilities of many drugs.

∴ during the drug design & it's studies many reactions are required to be maintained at constant ~~buffer~~ pH. Therefore buffers are required.

How is a buffer made?

It is made by combining a weak acid or a weak base with it's conjugate.

Eg CH_3COOH (weak acid) + $CH_3COO^-Na^+$ (it's conjugate)

→ How is a buffer solution of a particular pH made? (2)

Using Henderson-Hasselbalch equation

$$pH_{(\text{of buffer})} = pK_a + \log \frac{[\text{conjugate base}]}{[\text{acid}]}$$ [conjugate base or salt]

Now, what is this equation? & how is it derived?

Details of the equation are as follows:-

Let us assume HA is a monoprotic acid required for the synthesis of acidic buffer & BA is the salt of HA with a strong Base

[Eg $CH_3COOH \sim HA$

$CH_3COOH + NaOH \longrightarrow \underbrace{CH_3COO^-Na^+}_{BA} + H_2O$]

Then the equations may be written as:-

$HA \rightleftharpoons H^+ + A^-$ (acid being weak dissociates incompletely)

$BA \longrightarrow B^+ + A^-$

On applying law of chemical equilibrium on dissociation of weak acid;

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

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

2 facts to be noted :-

(1) Due to common ion effect most of the ions $[A^-]$ are from BA only [Pls revise common ion effect]

(2) Since acid is mainly undissociated ∴ even at equilibrium the concentration of acid hardly changes

$\therefore$ If C_1 is the initial concentration of acid → HA

i.e. $[HA] = C_1$ [at $t = 0$]

which remains almost ~~so~~ same at equilibrium due to ~~suppose~~ supressed dissociation [common ion effect] → fact (2)

Hence $[HA]$ at Equilibrium $= C_1$

& $[A^-] = C_2$ = concentration of salt taken

= concentration of salt at equilibrium

[∵ most of the ions are coming from BA → fact (1)]

Hence

~~$K_a \Rightarrow$ β $K_a = t$~~

$[H^+] = K_a C_1/C_2$ (from equation (1) & 2 facts from above)

$\Rightarrow$ $[H^+] = K_a \dfrac{[\text{acid}]}{[\text{salt}]}$ { [acid] = initial concentration of acid, [salt] = initial concentration of salt }

taking $-\log$ on both sides

$\Rightarrow$ $-\log[H^+] = -\log K_a - \log[\text{acid}] + \log[\text{salt}]$

$$\boxed{pH = pK_a + \log \frac{[\text{salt}]}{[\text{acid}]}}$$

Hence derived equⁿ to synthesise buffer of a particular pH.

Similarly if a basic buffer has to be synthesised

then $pOH = pK_b + \log \frac{[salt]}{[acid]}$

K_b = dissociation of base constant

(* try to derive as above)

Buffer capacity & Buffer index

→ the capacity of a solution to resist alteration in its pH; is known as buffer capacity.

→ β (buffer index) $= \frac{dB}{d(pH)}$

dB is the increment of strong base added to a buffer solution

d(pH) is the resulting increment in pH

Physical meaning

→ If concentration of acid of which buffer is made is higher the buffer capacity is high if it is low then ~~bp~~ buffer capacity is low.

For eg Let us consider a buffer of

$CH_3COOH \rightarrow 0.4M$
$CH_3COO^-Na^+ \rightarrow 0.8M$
$pH = 5.0457$ given

⇒ Now if base of (NaOH) 0.03M is added :-

$$CH_3COOH + NaOH \longrightarrow CH_3COO^-Na^+ + H_2O$$
$$0.4 \quad 0.03 \quad 0.03 \ (CH_3COO^- \text{ generated})$$

$\therefore [CH_3COOH] = 0.4 - 0.03 = 0.370$
$[CH_3COO^-] = 0.003 + 0.8 = 0.803$
New concentration of acid & salt

then New pH

$$pH = pKa + \log \frac{[salt]}{[acid]} = \boxed{5.0956}$$

initial $pH = 5.0457$ & now it is $\boxed{5.0956}$

very less change in buffer ∵ if [acid] reduced then [salt] ↑ed ~~by same am~~ Hence the ratio [salt]/[acid] didn't change to a very large extend & hence pH change is ↓

~~this is~~ since change is low ∴ buffer is said to have large buffer capacity.

$$\text{Buffer index} = \frac{0.03 \ (\text{base added})}{5.0956 - 5.045} = \boxed{0.6}$$

High buffer index means ↓ ΔpH means a good buffer