COMMON ION EFFECT Section - 3

The addition of an ionic salt having a common ion (anion or cation) to weak acids or weak bases, suppresses their degree of dissociation (following *LeChatelier's principle*).

Weak Acids :

Let HA be a weak acid (like CH_3COOH, HCN etc) and B^+A^- be the ionic salt (100% dissociation in solution) containing common anion (A^-) that is added to the acid.

$$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$$

$$BA(aq) \longrightarrow B^+(aq) + A^-(aq)$$

Now, the solution has excess of A^- ions. This means increasing concentration of products, in an equilibrium state, (following *LeChatelier's principle*) the reaction ($HA \rightleftharpoons H^+ + A^-$) must go in backward direction, in order to nullify the effect of added A^- ions. As a consequence, amount of H^+ in new equilibrium state will be less than before, *or* one can see that the degree of dissociation of acid (HA) is decreased.

Quantitative Aspect :

Consider a weak acid HA which dissociates as : $HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$

Its degree of dissociation $= \alpha = \sqrt{\dfrac{K_a}{c}}$ [Assuming K_a to be small]

Let M molar BA be added to it and α' be its new degree of dissociation

$$\underset{}{BA(aq)} \longrightarrow \underset{M}{B^+(aq)} + \underset{M}{A^-(aq)} \qquad \text{(Assuming BA to be 100\% ionised)}$$

$$\underset{c-c\alpha'}{HA(aq)} \rightleftharpoons \underset{c\alpha'}{H^+(aq)} + \underset{c\alpha'}{A^-(aq)}$$

Now in solution : $[HA] = c - c\alpha'$; $[H^+] = c\alpha'$

$$[A^-]_{total} = [A^-]_{From\ HA} + [A^-]_{From\ BA} = c\alpha' + M$$

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{(c\alpha')(c\alpha'+M)}{(c-c\alpha')} = \frac{\alpha'(c\alpha'+M)}{1-\alpha'}$$

$\Rightarrow \quad K_a = c\alpha'^2 + M\alpha' \qquad$ (Assuming $1-\alpha' \approx 1$)

$\Rightarrow \quad K_a = M\alpha' \qquad$ (Neglecting $c\alpha'^2$ in comparison to $M\alpha'$ as $\alpha' << 1 \Rightarrow \alpha'^2 <<< 1$]

$\Rightarrow \quad \alpha' = \dfrac{K_a}{M}$

By looking at the expressions of α and α', we can clearly figure out that $\alpha' << \alpha$]

Note : On similar lines, you can find α' for a weak base, BOH and adding B^+ ions to it.

Also, expression for K_a now becomes : $K_a = \dfrac{[H^+][A^-]_{ext.}}{[HA]}$ where $[A^-]_{ext.}$ is the externally added salt

Buffer Solutions

A solution whose pH does not change very much when H^+ (H_3O^+) or OH^- are added to it, is referred to as a *buffer solution*.

A *buffer solution* is prepared by mixing a weak acid and its salt having common anion (i.e. HA + BA forms an acidic Buffer) *or* a weak base and its salt having common cation (i.e. BOH + BA forms a Basic Buffer).

It can be prepared to have a desired value of pH by controling the amounts of acids and their salts in case of acidic buffer and of bases and their salts in basic buffer.

Acidic buffer : $CH_3COOH + CH_3COONa$, $HCN + NaCN$ **Basic buffer :** $NH_4OH + NH_4Cl$

Note : See yourself that buffer solutions are actually conjugate acid-base pairs.

Consider an *acidic buffer* containing an acid HA and say common ions A^-. Now, any H^+ (or H_3O^+) added externally to this solution with in certain limits are neutralized by A^- ions as :

$$\underset{\text{external}}{H^+} + \underset{\text{from salt}}{A^-} \rightleftharpoons \underset{\text{undissociated acid}}{HA}$$

While, addition of OH^- ions externally (with in certain limits) are neutralised by acid HA as: $HA + OH^- \rightleftharpoons H_2O + A^-$

Hence in both the cases, effect of addition of H^+ or OH^- is almost compensated for (i.e. pH almost remains constant).

Such a system (may be acidic or basic) finds enormous use not only in industrial processes but also (most importantly) in biological reactions. Like the pH of normal blood is 7.4 and for good health and even for the survival, it should not change below 7.1 or greater than 7.7, the body maintains it through a buffer system made of carbonate and bicarbonate ions and $H_2PO_4^-$ and HPO_4^{2-}. Similarly, the pH of gastric juice is kept constant in order to operate good digestive functions.

pH of an Acidic Buffer

If [acid] = concentration of a weak acid and [salt] = concentration of the salt that is mixed with acid to make the buffer

We have : $$[H^+] = \frac{K_a\,[HA]}{[A^-]_{ext.}} = \frac{K_a\,[acid]}{[salt]}$$ [See the derivation in the Common Ion effect section]

$$\Rightarrow \quad pH = pK_a + \log_{10}\frac{[salt]}{[acid]} \qquad (pK_a = -\log_{10} K_a)$$

pH of a Basic Buffer

We have : $pH = 14 - pOH$

If [base] = concentration of weak base and [salt] = concentration of salt that is mixed to make the buffer

$$\Rightarrow \quad [OH^-] = \frac{K_b\,[BOH]}{[B^+]_{ext.}} = \frac{K_b\,[base]}{[salt]} \quad \Rightarrow \quad pOH = pK_b + \log_{10}\frac{[salt]}{[base]} \qquad (pK_b = -\log_{10} K_b)$$

$$\Rightarrow \quad pH = 14 - pK_b - \log_{10}\frac{[salt]}{[base]}$$

Note : The above equations representing the pH of a buffer are known as *Henderson-Hasselbalch equation*.

pH of a Buffer (*When an acid or a base is added*)

We have just discussed that addition of H^+ ions or OH^- ions to an acidic buffer (HA/A^-) does not appreciably changes the pH of buffer. Similarly, we can analyse the same for a basic buffer (BOH/B^+).

In actual, pH of a buffer solution changes by a small quantity. Let us calculate this change in pH quantitatively.

- Consider an acidic buffer HA/A^- where [salt] = $[A^-]$ and [acid] = [HA]

An acidic buffer is rich in A^- ions. Let us add x mole per litre of HCl to it. This added HCl (H^+) reacts with A^- (salt) to give undissociated acid as : $\underset{}{H^+} + \underset{[\text{salt}]}{A^-} \longrightarrow \underset{[\text{acid}]}{HA}$

After adding x M H^+ ions : $[\text{salt} - x]$ $\quad [\text{acid} + x]$

Now using *Henderson's Equation* : $\text{pH (original buffer)} = pK_a + \log_{10}\dfrac{[\text{salt}]}{[\text{acid}]}$ and $\text{pH (new)} = pK_a + \log_{10}\dfrac{[\text{salt}-x]}{[\text{acid}+x]}$

$\Rightarrow$ pH of buffer *decreases*.

Change or difference in pH = pH (new) – pH (original)

Let us add x M NaOH to the buffer. This added NaOH (OH^- ions) react with acid (HA) to produce salt and H_2O.

$$OH^- + \underset{[\text{acid}]}{HA} \longrightarrow \underset{[\text{salt}]}{A^-} + H_2O$$

After adding x M OH^- ions : $[\text{acid} - x]$ $\quad [\text{salt} + x]$

$\Rightarrow$ $\text{pH (new)} = pK_a + \log_{10}\dfrac{[\text{salt}+x]}{[\text{acid}-x]}$ $\Rightarrow$ pH of buffer *increases*.

Change in pH = pH (new) – pH (original)

Note : (i) In exactly similar manner, we can calculate the change in pH of a basic buffer (BOH/B^+). Try to get a relation like this for basic buffer. Remember, it is not to be used as standard result.

(ii) A buffer solution is assumed to be destroyed if on addition of strong acid or base, its pH changes by ± 1 unit i.e., pH (new) = $pK_a \pm 1$ [if the initial pH of the buffer solution was pK_a]. This means the ratio $\dfrac{[\text{salt}]}{[\text{acid}]}$ OR $\dfrac{[\text{salt}]}{[\text{base}]}$ = 10 or 1/10.

Illustration - 5 *To 1.0 L of a decimolar solution of acetic acid, how much dry sodium acetate be added (in moles) so as to decrease the concentration of H^+ ion to 1/10th of its previous value ? $K_a = 2.0 \times 10^{-5}$.*

SOLUTION :

$$CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$$

$\Rightarrow$ $[H^+] = c\,\alpha = \sqrt{K_a c} = \sqrt{2.0\times10^{-5}\times0.1} = 1.41\times10^{-3}$ M $\quad$ [Check yourself that approximations are valid]

Note that when salt, CH_3COONa is added, the solution will behave just like an acidic Buffer solution.

Using, Henderson equation : $\text{pH} = pK_a + \log_{10}\dfrac{[\text{salt}]}{[\text{acid}]}$ $\Rightarrow$ $[H^+] = K_a\dfrac{[\text{acid}]}{[\text{salt}]}$ or $[\text{salt}] = K_a\dfrac{[\text{acid}]}{[H^+]}$

Now, $[H^+]_{new} = \dfrac{1}{10}\times1.41\times10^{-3}\text{M} = 1.41\times10^{-4}$ M $\Rightarrow$ $[\text{salt}] = \dfrac{(2.0\times10^{-5})(0.1)}{1.41\times10^{-4}} = 0.0142$ M

$\Rightarrow$ moles of salt, sodium acetate = 0.0142 (≡ 14.2 mmoles) per 1.0 L is required. (V = 1.0 L)

Illustration - 6 **(a)** *A buffer solution of pH value = 4 is to be prepared, using CH_3COOH and CH_3COONa. How much amount of sodium acetate is to be added to 1.0 L of M/10 acetic acid ? $K_a = 2.0 \times 10^{-5}$.*

(b) *What will be the pH if 0.005 mol of HCl is dissolved in the above Buffer solution ? Find the change in pH value.*

(c) *How will the pH be affected if 1.5 L of H_2O is added to above buffer ?*

SOLUTION :

(a) For an acidic buffer containing acetic acid, CH_3COOH and sodium acetate, CH_3COONa, we have :

$$[H^+] = \frac{K_a\,[\text{acid}]}{[\text{salt}]}$$

Use this rather than : $pH = pK_a + \log_{10}\frac{[\text{salt}]}{[\text{acid}]}$

$[CH_3COOH] = 0.1\ M$;

$[H^+] = 10^{-4}$ M and let $[CH_3COONa] = x$ M

$\Rightarrow \quad [H^+] = 10^{-4} = \frac{2\times10^{-5}\times0.1}{x}$

$\Rightarrow \quad x = 0.02$ moles i.e. 0.02 moles of CH_3COONa is required.

(b) Now 0.01 mol of HCl ($[H^+] = 0.01$ M) is added to 1 L of buffer, this will react with acetate ion (CH_3COO^-) as :

$$CH_3COO^- + H^+ \longrightarrow CH_3COOH$$

0.02	0.005	0.1
0.015		0.105

$\Rightarrow \quad [\text{acid}] = 0.11$ M and $[\text{salt}] = 0.01$ M $[V = 1.0\ L]$

$\Rightarrow \quad pH_{new} = pK_a + \log_{10}\frac{0.015}{0.105}$

$= 4.7 + (-0.84) = 3.86$ [Use $\log_{10} 7 = 0.84$]

$\Rightarrow \quad$ Change in pH $= 3.86 - 4.0 = -0.14$

(c) Now, if 1.5 L of H_2O is added, it just increases the volume, thereby decreasing concentrations of both acid and salt. The ratio $\log_{10}\frac{[\text{salt}]}{[\text{acid}]}$ remains constant. Hence pH remains same.

Illustration - 7 *How many of the following combination can act as buffer.*

(i)	*$HCl + NaOH$*	**(ii)**	*$HCl + CH_3COO^-Na^+$*	**(iii)**	*$H_2SO_4 + NaHSO_4$*
(iv)	*$H_2CO_3 + NaOH$*	**(v)**	*$NaOH + PhCOOH$*	**(vi)**	*$HBr + NH_4OH$*
(vii)	*$CH_3COOH + NH_4OH$*	**(viii)**	*$NaOH + NH_4OH$*	**(ix)**	*$HCl + CH_3COOH$*
(x)	*Borax ($Na_2B_4O_7$) + Boric acid (H_3BO_3)*	**(xi)**	*$NaH_2PO_4 + Na_2HPO_4$*	**(xii)**	*$Na_2CO_3 + NaHCO_3$*

SOLUTION :

As we know that buffer is a mixture having weak acid and its salt with strong base or weak base and its salt with strong acid. Further a mixture of acid and base may also acts as buffer depending on the nature of acid and base (strong or weak) and their moles taken for preparation of mixture, because acid and base reacts to form salt. The combination (i) and (iii) can't acts as buffer because it does not contain weak electrolyte (weak acid or base)but combination (ii) can act as buffer if excess of CH_3COONa is mixed with limited amount of HCl.

	CH_3COONa	$+\ HCl \longrightarrow$	CH_3COOH	$+\ NaCl$	
Initially	a	b	0	0	(a > b)
After mixing	(a – b)	0	b	b	

Resulting mixture contains weak acid (CH_3COOH) and its salt with strong base (CH_3COONa). Similarly combinations $(H_2CO_3 + NaOH)$, $(PhCOOH + NaOH)$, $(NH_4OH + HBr)$ can also act as buffer.

	H_2CO_3	$+\ 2NaOH \longrightarrow$	Na_2CO_3	$+\ H_2O$
Initially	a	2b	0	–
After mixing	(a – b)	0	b	–

$$H_2CO_3 + NaOH \longrightarrow NaHCO_3 + H_2O$$

Initially	a	b	0	–
After mixing	(a – b)	0	b	–

$$PhCOOH + NaOH \longrightarrow PhCOONa + H_2O$$

Initially	a	b	0	–
After mixing	(a – b)	0	b	–

$$NH_4OH + HBr \longrightarrow NH_4Br + H_2O$$

Initially	a	b	0	–
After mixing	(a – b)	0	b	–

The combinations (viii) and (ix) can't acts as buffer because salt component is missing.

Mixture of two salts of weak polyprotic acid can also acts as buffer because in such cases we will visualize a mixture of acid and its conjugate base as salt.

$NaHCO_3$ [having weak acid HCO_3^-] and Na_2CO_3 [having conjugate base CO_3^{2-}] acts as buffer.

Hence the combination (ii), (iv), (v), (vi), (vii), (x), (xi) and (xii) can acts as buffer.

Illustration - 8 *The pH of blood stream is maintained by a proper balance of H_2CO_3 and $NaHCO_3$ concentrations. What volume of 5M $NaHCO_3$ solution, should be mixed with 10 mL sample of blood which is 2M in H_2CO_3 in order to maintain a pH of 7.4. K_a for H_2CO_3 in blood is 4.0×10^{-7} ?*

SOLUTION :

$[H_2CO_3]$ in blood = 2M

Volume of blood = 10 mL

$[NaHCO_3] = 5M$

Let volume of $NaHCO_3$ used = V mL

$$[H_2CO_3] \text{ in mixture} = \frac{2 \times 10}{(V + 10)}$$

$$[NaHCO_3] \text{ in mixture} = \frac{(5 \times V)}{(V + 10)}$$

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

$$7.4 = -\log 4.0 \times 10^{-7} + \log \frac{(5 \times V)/(V+10)}{(2 \times 10)/(V+10)}$$

V = 40 mL

Illustration - 9 *Consider a buffer solution containing 0.1 mole each of acetic acid and sodium acetate in 1.0 L of solution. 0.01 mole of NaOH is gradually added to this buffer solution. Calculate the new $[H^+]$ is the resulting solution. $[K_a = 2 \times 10^{-5}]$*

SOLUTION :

pH of the solution is given by :

$$pH = pK_a + \log_{10} \frac{[\text{salt}]}{[\text{acid}]}$$

Initial pH of solution :

$$pH = pK_a + \log_{10} \frac{0.1}{0.1} = 4.7$$

When 0.01 M NaOH is added,

[salt] = 0.11 M and [acid] = 0.09 M

$\Rightarrow$ Final pH of solution :

$$pH = pK_a + \log_{10} \frac{0.11}{0.09} = 4.787$$

$$\Rightarrow \quad [H^+] = K_a \frac{[\text{acid}]}{[\text{salt}]}$$

$$= 2 \times 10^{-5} \times \frac{0.09}{0.11} = 1.64 \times 10^{-5} M$$

Illustration - 10 *500 ml of 0.2 M aqueous solution of acetic acid is mixed with 500 ml of 0.2 M HCl at 25°C.*

(i) *Calculate the degree of dissociation of acetic acid in the resulting solution and pH of the solution.*

(ii) *If 6g of NaOH is added to the above solution, determine the final pH.* $[K_{a\ acetic\ acid} = 2 \times 10^{-5}]$

SOLUTION :

(i) $[CH_3COOH]_{\text{Just after mixing}} = \dfrac{0.2}{2} = 0.1M$

$[HCl]_{\text{Just after mixing}} = \dfrac{0.2}{2} = 0.1M = [H^+]_{\text{From HCl}}$

Note : Equal volumes added.

$$\begin{array}{lccc} & CH_3COOH & \rightleftharpoons & CH_3COO^- + H^+ \\ t=0 \text{ (conc.)} & c & & 0 \qquad 0 \\ t = t_{eq} & c - c\alpha & & c\alpha \qquad c\alpha \end{array}$$

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = \frac{c\alpha.(c\alpha + 0.1)}{c - c\alpha}$$

$\left[\because\ [H^+]_{\text{Total}} = [H^+]_{\text{From } CH_3COOH} + [H^+]_{\text{From HCl}}\right]$

$\Rightarrow \quad c\alpha + 0.1 \sim 0.1\ ;\ c - c\alpha \sim c]$

$[\because\ \alpha$ will be small due to common ion effect]

$\Rightarrow \quad K_a \sim \alpha \times 0.1$

$\Rightarrow \quad \alpha = \dfrac{K_a}{0.1} = 2 \times 10^{-4}$

[Check : $1 - \alpha = 1 - 2 \times 10^{-4} \sim 1$]

and $\quad [H^+]_{\text{Total}} = c\alpha + 0.1 = 0.1 \times 2 \times 10^{-4} + 0.1 \sim 0.1\ M$

$\Rightarrow \quad pH = 1$

(ii) $6\text{ gm NaOH} \equiv \dfrac{6}{40/1} = 0.15\text{ gmeq} \equiv 150\text{ mmoles NaOH}$

Mmoles $HCl = 500 \times 0.2 = 100$ mmoles

NaOH will first react with HCl and if there is a leftover then it will react with CH_3COOH

$\Rightarrow \quad$ Mmoles NaOH left $= 150 - 100 = 50$

These will react with CH_3COOH as :

$$\begin{array}{ccccccc} NaOH & + & CH_3COOH & \rightleftharpoons & CH_3COONa & + & H_2O \\ 50 & & 100 & & - & & - \\ - & & 50 & & 50 & & \end{array}$$

$\Rightarrow \quad$ Formation of an acidic buffer

$\Rightarrow \quad pH = pK_a + \log_{10}\dfrac{[\text{Salt}]}{[\text{Acid}]}$

$= 4.7 + \log_{10}\dfrac{50/V_{\text{Total}}}{50/V_{\text{Total}}} = 4.7$

IN-CHAPTER EXERCISE - B

1. *How many moles of NH_4Cl should be added to 200 cc solution of 0.18 M NH_4OH to have a pH equal 9.60. Dissociation constant of NH_4OH is 2×10^{-5}.*

2. *A buffer solution contains 0.25 M NH_4OH and 0.3 M NH_4Cl. Calculate pH of the solution. How much NaOH should be added to 1 liter of solution to change the pH by 0.6 ? $K_b = 2 \times 10^{-5}$.*

3. *A buffer solution was obtained by adding 15.0 g of CH_3COOH and 20.5 of $CH_3.COONa$. The buffer is diluted to 1.0 L. Calculate the pH of the solution. What will be the change in pH, if 10.0 mL of 1.0 M HCl is added to it ? pK_a of acetic acid = 4.74 [Given $\log_{10}(13/12) = 0.035$]*

4. Choose the correct alternative. Only one choice is correct.

(i) *The pK_a of acetylsalicylic acid (aspirin) is 3.5. The pH of gastric juice in human stomach is about 2-3 and the pH in the small intestine is about 8. Aspirin will be :*

(A) *unionised in the small intestine and in the stomach*
(B) *completely ionized in the small intestine and in the stomach*
(C) *ionised in the stomach and almost unionised in the small intestine*
(D) *ionised in the small intestine and almost unionised in the stomach*

(ii) *A weak acid HA has $K_a = 10^{-6}$. What would be the molar ratio of this acid and its salt with strong base so that pH of the buffer solution is 5 ?*

(A) 1 **(B)** 2 **(C)** 10 **(D)** 1/10

(iii) *Which of the following can be used as a buffer solution ?*

(A) *A solution containing NaCl and NaOH* **(B)** *A solution containing NaCl and NH_4OH*
(C) *A solution containing sodium acetate and acetic acid*
(D) *A solution containing ammonium acetate*

(iv) *Which of the following solutions containing weak acid and salt of its conjugate base has maximum buffer capacity ?*

(A) [salt] = [acid] **(B)** [salt] > [acid]
(C) [salt] < [acid] **(D)** [salt] + [acid] is minimum

(v) *The addition of sodium acetate to 0.1 M acetic acid will cause :*

(A) *increase in its pH value* **(B)** *decrease in its pH value*
(C) *no change in pH value* **(D)** *change in pH which cannot be predicted*

(vi) *In an acidic buffer solution containing acetic acid and sodium acetate, if some HCl is added, its pH will :*

(A) *increase* **(B)** *decrease*
(C) *remain constant* **(D)** *change but can't be predicted*

(vii) *On diluting a buffer solution, its pH :*

(A) *increases* **(B)** *decreases*
(C) *remains same* **(D)** *can't say*

***(viii)** *Which of the following solution may behave as a buffer ?*

(A) H_2CO_3 / HCO_3^- **(B)** CH_3COOH/CH_3COONa
(C) NH_4OH/NH_4Cl **(D)** $HCl/NaCl$