ACID-BASE PROPERTIES OF SALT SOLUTIONS

- A salt is an ionic substance resulting from a neutralization reaction:

$$\text{Acid} + \text{Base} \longrightarrow \text{Salt} + \text{Water}$$

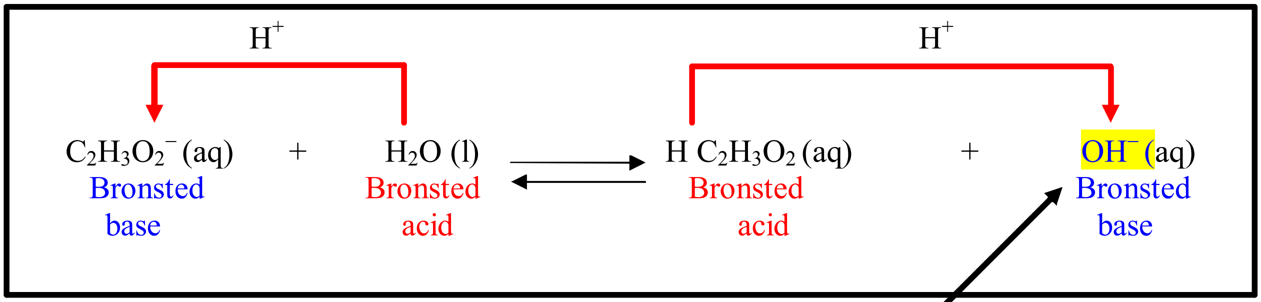
- The aqueous solution of a salt may be: basic, acidic, or neutral

- Reason: Soluble salts derived from weak acids or weak bases undergo hydrolysis (reaction with H_2O) in aqueous solution.

I. Salt of a strong base (NaOH) and a weak acid ($HC_2H_3O_2$)

$$NaC_2H_3O_2\,(aq) \xrightarrow[\text{dissociated}]{\text{completely}} Na^+\,(aq) + C_2H_3O_2^-\,(aq)$$

$$Na^+\,(aq) + H_2O\,(l) \longrightarrow \text{No Reaction}$$



$$C_2H_3O_2^-\,(aq) + H_2O\,(l) \rightleftarrows H\,C_2H_3O_2\,(aq) + OH^-\,(aq)$$

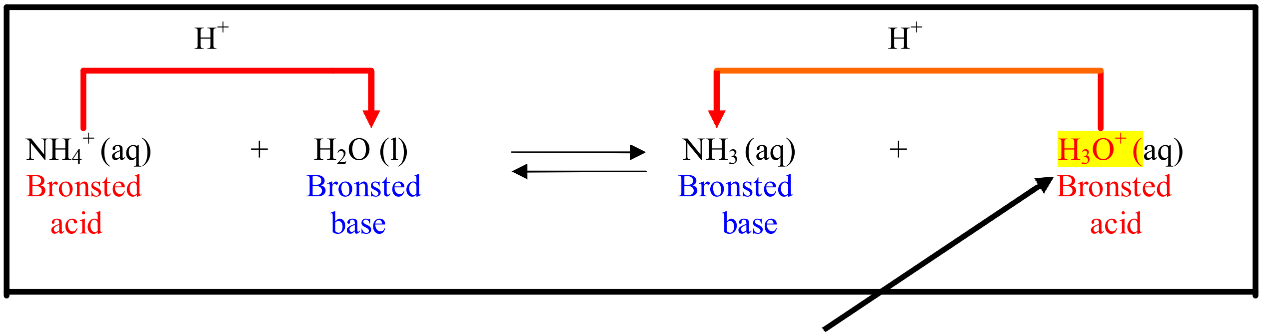
NOTE: The resulting solution is basic

- This reaction is referred to as the Hydrolysis of the acetate ($C_2H_3O_2^-$) ion

II. Salt of a weak base (NH_4OH) and a strong acid (HCl)

$$NH_4Cl\,(aq) \xrightarrow[\text{dissociated}]{\text{completely}} NH_4^+\,(aq) + Cl^-\,(aq)$$

$$Cl^-\,(aq) + H_2O\,(l) \longrightarrow \text{No Reaction}$$



$$NH_4^+\,(aq) + H_2O\,(l) \rightleftharpoons NH_3\,(aq) + H_3O^+\,(aq)$$

NOTE: The resulting solution is acidic

- The reaction is referred to as the Hydrolysis of the ammonium(NH_4^+)ion

III. Salt of a strong base (NaOH) and a strong acid (HCl)

$$NaCl\,(aq) \xrightarrow[\text{dissociated}]{\text{completely}} Na^+\,(aq) + Cl^-\,(aq)$$

$$Na^+\,(aq) + H_2O\,(l) \longrightarrow \text{No Reaction}$$

$$Cl^-\,(aq) + H_2O\,(l) \longrightarrow \text{No Reaction}$$

- The resulting solution is neutral

IV. Salt of a weak base (NH_4OH) and a weak acid ($HC_2H_3O_2$)

$$NH_4C_2H_3O_2(aq) \xrightarrow[\text{dissociated}]{\text{completely}} NH_4^+(aq) + C_2H_3O_2^-(aq)$$

Both ions undergo hydrolysis:

$$C_2H_3O_2^-(aq) + H_2O(l) \rightleftharpoons HC_2H_3O_2(aq) + OH^-(aq)$$

Is the solution basic?

$$NH_4(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$$

Is the solution acidic?

- Acidity or Basicity of solution depends on the relative acid-base strength of the two ions.

K_a of NH_4^+ must be compared with **K_b of $C_2H_3O_2^-$**

- If: **K_a** $> K_b$ —> **Solution is acidic**
- If: $K_a <$ **K_b** —>**Solution is basic**

CONCLUSIONS:

- Solution of a salt of a **strong base** and weak acid is **basic**
- Solution of a salt of a weak base and a **strong acid** is **acidic**

- Solution of a salt of a strong acid and a strong base is neutral.
- Solution of a salt of a weak base and a weak acid is:
  - neutral, if: $K_a(\text{cation}) \approx K_b(\text{anion})$
  - acidic, if: $K_a(\text{cation}) > K_b(\text{anion})$
  - basic, if: $K_a(\text{cation}) < K_b(\text{anion})$

Examples:

1. For each of the following salts, indicate whether the aqueous solution will be acidic, basic or neutral.

Salt	**Parent Base**	**Parent Acid**	**Solution of salt is:**
$Fe(NO_3)_3$	$Fe(OH)_3$ insoluble	**HNO_3** **strong acid**	**acidic**
$Ca(CN)_2$	**$Ca(OH)_2$** **strong base**	HCN weak acid	**Basic**
Na_2CO_3			
Na_2S			
$KClO_4$			
$Al(NO_3)_3$			

2. Write hydrolysis equation(s) for each of the following salts:

a) Na_2CO_3

$$Na_2CO_3 \longrightarrow 2\ Na^+ + CO_3^{2-}$$

$Na^+ + H_2O \longrightarrow$ no reaction (cation of a strong base, NaOH)

$CO_3^{2-} + H_2O \rightleftarrows HCO_3^- + OH^-$ (conjugate base of a weak acid HCO_3^-)

b) Na_2S

c) $KClO_4$

THE pH OF A SALT SOLUTION

What is the pH of a 0.10 M NaCN (sodium cyanide) solution?

NOTE: NaCN is the salt of a strong base (NaOH) with a weak acid (HCN). Therefore:

- we expect the solution to be basic
- we know beforehand that the pH > 7

Consider the hydrolysis of NaCN:

$$NaCN\ (aq) \longrightarrow Na^+(aq) + CN^-(aq)$$

$$Na^+(aq) + H_2O\ (l) \longrightarrow \text{No Reaction}$$

$$CN^-(aq) + H_2O\ (l) \rightleftarrows HCN\ (aq) + OH^-(aq) \qquad K_b(CN^-) = \text{? (not readily available)}$$

- Solution: Consider the ionization equilibrium of HCN:

$$HCN\ (aq) + H_2O\ (l) \rightleftarrows H_3O^+(aq) + CN^-(aq) \qquad K_a = 4.9 \times 10^{-10}$$

$$K_a(HCN) \times K_b(CN^-) = K_w \qquad K_b(CN^-) = \frac{K_w}{K_a\ (HCN)} = \frac{1.0 \times 10^{-14}}{4.9 \times 10^{-10}} = 2.0 \times 10^{-5}$$

- Now we can calculate the pH of the solution from equilibrium data:

	$CN^-(aq)$ +	$H_2O\ (l)$ $\rightleftarrows$	$HCN(aq)$ +	$OH^-(aq)$
Initial	0.10	----	0	0
Δ	–x	----	+x	+x
Equilibrium	0.10–x	-----	x	x

$$K_b = \frac{[HCN][OH^-]}{[CN^-]} = \frac{x^2}{0.10-x} = 2.0 \times 10^{-5}$$

Consider the usual assumption: $0.10 - x \approx 0.10$

$$2.0 \times 10^{-5} = \frac{x^2}{0.10} \qquad x = [OH^-] = 1.4 \times 10^{-3}$$

$$pOH = -\log(1.4 \times 10^{-3}) = 2.85 \qquad pH = 14.00 - 2.85 = 11.15$$

Examples:

1. Household bleach is a 5% solution of sodium hypochlorite (NaClO). This corresponds to a molar concentration of about 0.70 M NaClO. K_a for HClO (hypochlorous acid) is 3.5 x 10^{-8}. What is the pH of household bleach?

$$NaClO(aq) \longrightarrow Na^+(aq) + ClO^-(aq)$$

- NaClO is the salt of a _____________base with a ____________ acid.
- Therefore the solution of this salt is expected to be _____________

$$ClO^-(aq) + H_2O(l) \rightleftharpoons HClO(aq) + OH^-(aq) \qquad K_b = ?$$

$K_b(ClO^-)$ =

	$ClO^-(aq)$ +	$H_2O(l)$ $\rightleftharpoons$	$HClO(aq)$ +	$OH^-(aq)$
Initial	0.70	----	0	0
Δ	–x	----	+x	+x
Equilibrium	0.70–x	-----	x	x

$$K_b = \frac{[HClO][OH^-]}{[ClO^-]} = \frac{x^2}{0.70-x} =$$

Consider the usual assumption: $0.70 - x \approx 0.70$

$$K_b = \frac{x^2}{0.70} = \qquad\qquad x = [OH^-] =$$

$pOH = -\log[OH^-] =$

$pH = 14.00 -$

COMMON ION EFFECT

- Common ion effect is the shift in equilibrium caused by the addition of an ion that takes part in the equilibrium.

- What is effect of adding HCl (hydrochloric acid) to a solution of $HC_2H_3O_2$ (acetic acid)?

$$\underset{\text{strong acid}}{HCl\,(aq)} + H_2O\,(l) \xrightarrow[\text{ionization}]{\text{complete}} H_3O^+\,(aq) + Cl^-\,(aq)$$

$$\underset{\text{weak acid}}{HC_2H_3O_2\,(aq)} + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + C_2H_3O_2^-\,(aq)$$

Stress: H_3O^+ (aq) added (from HCl)

Response: Equilibrium shifts ⬅

New Equil: $HC_2H_3O_2\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + C_2H_3O_2^-\,(aq)$

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$[HC_2H_3O_2(aq)]$ increases

$[C_2H_3O_2^-(aq)]$ decreases

- Net Result: Degree of ionization of acetic acid ($HC_2H_3O_2$) decreases

Examples:

1. Calculate the degree of ionization of benzoic acid, $HC_7H_5O_2$ in a 0.15 M solution to which sufficient HCl is added to make it 0.010 M. Compare the degree of ionization to that of 0.15 M benzoic acid with no HCl added (K_a of benzoic acid = 6.3×10^{-5})

Calculate the degree of ionization of benzoic acid ($HC_7H_5O_2$) with no HCl added.

	$HC_7H_5O_2$ (aq) +	H_2O (l) $\rightleftharpoons$	H_3O^+(aq) +	$C_7H_5O_2^-$ (aq)
Initial	0.15	----	0	0
Δ	–x	----	+x	+x
Equilibrium	0.15–x	-----	x	x

$$K_a = \frac{[H_3O^+][C_7H_5O_2^-]}{[HC_7H_5O_2]} = \frac{x^2}{0.15-x} \approx \frac{x^2}{0.15} = 6.3 \times 10^{-5}$$

$$x = [C_7H_5O_2^-] = 3.\underline{0}7 \times 10^{-3}$$

$$\text{Degree of Ionization \%} = \frac{[C_7H_5O_2^-]}{[HC_7H_5O_2]} \times 100 = \frac{3.\underline{0}7 \times 10^{-3}}{0.15} \times 100 = \mathbf{2.0\%}$$

Calculate the degree of ionization of benzoic acid ($HC_7H_5O_2$) with HCl added (0.010 M)

	HCl (aq) +	H_2O (l) $\longrightarrow$	H_3O^+(aq) +	Cl^- (aq)
Initial	0.010	----	0	0
End	0	----	0.010	0.010

	$HC_7H_5O_2$ (aq) +	H_2O (l) $\rightleftharpoons$	H_3O^+(aq) +	$C_7H_5O_2^-$ (aq)
Initial	0.15	----	0	0
Δ	–x	----	+x	+x
Equilibrium	0.15–x	-----	x	x

NOTE: $[H_3O^+]$ = $[H_3O^+]$ from HCl + $[H_3O^+]$ from $HC_7H_5O_2$
= **0.010** **+** **x**

$$K_a = \frac{[H_3O^+][C_7H_5O_2^-]}{[HC_7H_5O_2]} = \frac{(0.010+x)\,x}{0.15—x}$$

Assumptions: $0.010 + x \approx 0.010$ $0.15 - x \approx 0.15$

$$K_a = \frac{0.010\,x}{0.15} = 6.3 \times 10^{-5} \qquad x = [C_7H_5O_2^-] = 9.\underline{4}5 \times 10^{-4}$$

$$\text{Degree of Ionization} = \frac{[C_7H_5O_2^-]}{[HC_7H_5O_2]} \times 100 = \frac{9.\underline{4}5 \times 10^{-4}\text{ M}}{0.15\text{ M}} \times 100 = \mathbf{0.63\ \%}$$

NOTE: **0.63 %** <<<<<<< **2.0%**
(with HCl) (without HCl)

2. Calculate the pH of a 0.10 M solution of hydrofluoric acid (HF) to which sufficient NaF is added to make the concentration of NaF 0.20 M. (K_a of HF = 6.8×10^{-4})

	$HF(aq)$ +	$H_2O(l)$ $\rightleftharpoons$	$H_3O^+(aq)$ +	$F^-(aq)$
Initial		----		
Δ		----		
Equilibrium		-----		

Assume x is small. Therefore,

$[F^-]$ =

$[HF]$ =

$$K_a = \frac{[H_3O^+][F^-]}{[HF]} =$$

$x = [H_3O^+] =$

$pH = -\log(H_3O^+] =$

BUFFERS

- Buffers are solutions that have the ability to resist changes in pH when limited amounts of acid or bases are added to it.

- What does a buffer do?

Consider:

Solution	**1 L pure water** pH = 7.00	**1L buffered solution** pH = 9.43
Addition	0.01 mol HCl pH changes to 2.00	0.01 mol HCl pH changes to 9.33
Change in pH	7.00–2.00 = **5.00**	9.43–9.33 = **0.10**

- Types of buffer solutions

There are two types of buffer solutions:

1. Solution of a weak acid and its conjugate base

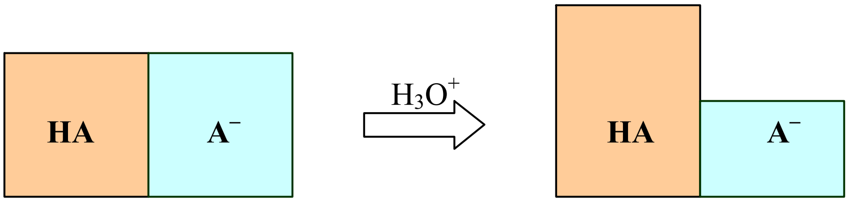
$HC_2H_3O_2$ and $NaC_2H_3O_2$

2. Solution of a weak base and its conjugate acid

NH_3 and NH_4Cl

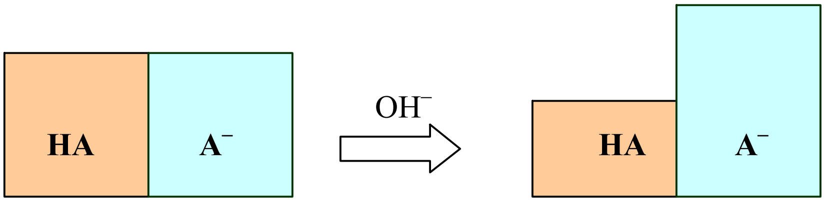
- How do buffers function?

I. A mixture of a weak acid (HA) and its conjugate base (A^-)



$$H_3O^+(aq) + A^-(aq) \longrightarrow HA(aq) + H_2O(l)$$

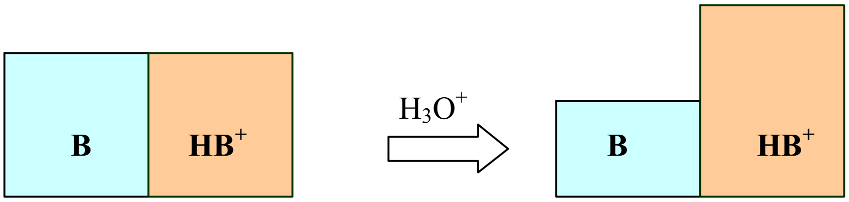
Results: ➢ H_3O^+ is used up ➢ little change in pH



$$OH^-(aq) + HA(aq) \longrightarrow A^-(aq) + H_2O(l)$$

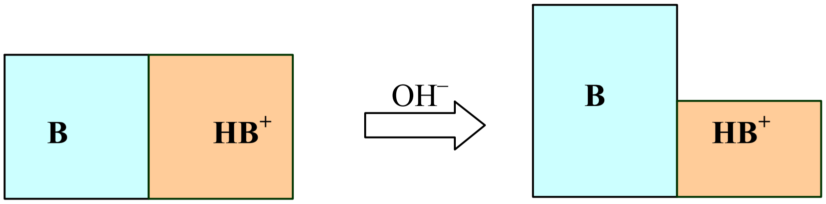
Results: ➢ OH^- is used up ➢ little change in pH

II. A mixture of a weak base (B) and its conjugate acid (HB^+)



$$H_3O^+(aq) + B(aq) \longrightarrow HB^+(aq) + H_2O(l)$$

Results: ➢ H_3O^+ is used up ➢ little change in pH



$$OH^-(aq) + HB^+(aq) \longrightarrow B(aq) + H_2O(l)$$

Results: ➢ OH^- is used up ➢ little change in pH

CONCLUSION:

- A buffer system (solution) resists changes in pH through its ability to combine with both H_3O^+ ions and OH^- ions.

PROPERTIES OF BUFFERS

Uses & Importance of Buffers:

1. In biological fluids
   - Blood is a buffer solution (containing H_2CO_3, weak acid and HCO_3^- as its conjugate base and several other buffer systems) with a pH = 7.4.
   - A change in more than 0.1 in the pH of blood would cause blood to lose its capacity to carry oxygen to the cells.

2. Commercial applications
   - Fruit juice mixes contain citric acid (a weak acid) and sodium citrate (the citrate anion is the conjugate base of citric acid) which ensure that the pH is maintained ("the tartness is regulated)

Characteristics of Buffers

1. pH

2. Buffer Capacity
   - ➢ The amount of acid or base the buffer can react with before giving a significant pH change

depends on:

- ➢ amount of weak acid (HA) and its conjugate base (A^-) in solution

OR

- ➢ amount of weak base (B) and its conjugate acid (HB^+) in solution
- ➢ This dependence is usually expressed as a ratio:

$$\frac{HA}{A^-} \quad \text{or} \quad \frac{HB^+}{B} \qquad \text{(should be close to 1)}$$

$$\mathbf{\frac{1}{10} < \frac{HA}{A^-} \quad or \quad \frac{HB^+}{B} < \frac{10}{1}}$$

Or simply: $$\boxed{\mathbf{0.1 < (HA/\ A^- \ or\ \ HB^+/B) < 10}}$$

Examples:

1. A buffer solution is prepared to be 0.10 M acetic acid ($HC_2H_3O_2$) and 0.20 M sodium acetate ($NaC_2H_3O_2$). What is the pH of this buffer system at 25°C (K_a of acetic acid = 1.7×10^{-5})

	$HC_2H_3O_2\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+(aq) + C_2H_3O_2^-\,(aq)$			
Initial	0.10	----	0	0.20
Δ	–x	----	+x	+x
Equilibrium	0.10–x	-----	x	0.20 + x

$$K_a = \frac{[H_3O^+][C_2H_3O_2^-]}{[HC_2H_3O_2]} = \frac{x\,(0.20 + x)}{(0.10 - x)} \approx \frac{0.20\,x}{0.10} = 1.7 \times 10^{-5}$$

$x = [H_3O^+] = 8.5 \times 10^{-6}$

pH = - log (8.5×10^{-6}) = **5.07**

2. Calculate the pH of a buffer that is 1.00 M in NH_3 and 0.80 M in NH_4Cl. (K_b for NH_3 = 1.8×10^{-5})

Initial				
Δ				
Equilibrium				

PREPARATION OF BUFFER SOLUTIONS

- Many buffer problems can be solved by using the following stepwise procedure:

    1. Calculate the initial molarities of solutions
    2. Calculate the equilibrium concentrations of common species
    3. Calculate $[H_3O^+]$ and pH of solution from K_a

Examples:

1. What is the pH of a buffer made by mixing 1.00 L of 0.020 M benzoic acid ($HC_7H_5O_2$) with 3.00 L of 0.060 M sodium benzoate ($NaC_7H_5O_2$) ? K_a of benzoic acid = 6.3×10^{-5}

Step 1: Calculate the initial molarities of solutions:

$$\text{Initial molarity } HC_7H_5O_2 = 1.00 \text{ L x } \frac{0.020 \text{ mol}}{1.00 \text{ L}} \text{ x } \frac{1}{4.00 \text{ L}} = 0.0050 \text{ M}$$

$$\text{Initial molarity of } NaC_7H_5O_2 = 3.00 \text{ L x } \frac{0.060 \text{ mol}}{1.00 \text{ L}} \text{ x } \frac{1}{4.00 \text{ L}} = 0.045 \text{ M}$$

Step 2: Calculate the equilibrium concentrations of common species

	$HC_7H_5O_2$ (aq) +	H_2O (l) $\rightleftharpoons$	H_3O^+(aq) +	$C_7H_5O_2^-$ (aq)
Initial	0.0050	----	0	0.045
Δ	–x	----	+x	+x
Equilibrium	0.0050–x	-----	x	0.045 + x

Step 3: Calculate $[H_3O^+]$ and pH from K_a

$$K_a = \frac{[H_3O^+][C_7H_5O_2^-]}{[HC_7H_5O_2]} = \frac{x\,(0.045 + x)}{(0.0050 - x)} \approx \frac{0.045\,x}{0.0050} = 6.3 \times 10^{-5}$$

$x = [H_3O^+] = 7.0 \times 10^{-6}$ M

pH = - log (7.0×10^{-6}) = **5.15**

2. A buffer is prepared by adding 115 mL of 0.30 M NH_3 to 145 mL of 0.15 M NH_4NO_3. What is the pH of the final solution? (K_b of ammonia = 1.8×10^{-5})

Step 1: Calculate the initial molarities of solutions:

Total Volume of Solution =

Initial molarity of NH_3 =

Initial molarity of NH_4NO_3 =

Step 2: Calculate the equilibrium concentrations of common species

	NH_3	+ H_2O (l) $\rightleftharpoons$	NH_4^+	+ OH^-
Initial		----		
Δ		----		
Equilibrium		-----		

Step 3: Calculate $[H_3O^+]$ and pH from K_b

K_b =

x =

pOH =

pH =

3. Calculate the pH of a solution prepared by mixing 400. mL of a 0.200 M acetic acid solution and 100. mL of a 0.300 M sodium hydroxide solution. (K_a acetic acid = $1.7x10^{-5}$)

$$HC_2H_3O_2 + NaOH \rightarrow NaC_2H_3O_2 + H_2O$$

NOTE:
NaOH is a strong base, and reacts with acetic acid to form sodium acetate. If an appreciable amount of excess acetic acid is still present after the NaOH has reacted, the excess acetic acid and the newly formed sodium acetate form a buffer solution.

Step 1: Calculate the amount of acetic acid neutralized:

$$\text{mmol of acetic acid} = 400.\ \text{mL} \times \frac{0.200\ \text{mol}}{1.00\ \text{L}} = 80.0\ \text{mmol}$$

$$\text{mmol of NaOH} = 100.\ \text{mL} \times \frac{0.300\ \text{mol}}{1.00\ \text{L}} = 30.0\ \text{mmol}$$

	$HC_2H_3O_2$ +	$NaOH$ ⟶	$NaC_2H_3O_2$ +	H_2O
Initial	80.0	30.0	0	----
Δ				----
End				----

Step 2: Calculate the concentration of species present after neutralization:

$$\text{Conc. of } HC_2H_3O_2 = \frac{\text{mmol } HC_2H_3O_2}{\text{mL solution}} =$$

$$\text{Conc. of } NaC_2H_3O_2 = \frac{\text{mmol } NaC_2H_3O_2}{\text{mL solution}} =$$

Step 3: Calculate the equilibrium concentrations of common species

	$HC_2H_3O_2$ +	H_2O $\rightleftharpoons$	H_3O^+ +	$C_2H_3O_2^-$
Initial		----		
Δ		----		
Equilibrium		-----		

Step 3: Calculate $[H_3O^+]$ and pH from K_a

K_a =

x = $[H_3O^+]$ =

pH =

ADDITION OF ACID OR BASE TO A BUFFER

- Addition of acid or base to a buffer will cause a slight change in pH
- This change in pH can be calculated.

A buffer is prepared by mixing 525 mL of 0.50 M formic acid, $HCHO_2$, and 475 mL of 0.50 M sodium formate, $NaCHO_2$. (K_a for formic acid = 1.7×10^{-4})

1. Calculate the pH of the buffer solution.
2. What would be the pH of 85 mL of the buffer to which 8.5 mL of 0.15 M hydrochloric has been added?

I. Calculate the pH of the buffer solution

Step 1: Calculate the initial molarities of solutions:

Total Volume of Solution = 525 mL + 475 mL = $10\underline{0}0.$ mL = 1.00 L

$$\text{Initial molarity } HCHO_2 = 525\text{ mL x } \frac{0.50\text{ mol}}{1000\text{ mL}} \text{ x } \frac{1}{1.00\text{ L}} = 0.2\underline{6}3\text{ M}$$

$$\text{Initial molarity of } NaCHO_2 = 475\text{ mL x } \frac{0.50\text{ mol}}{1000\text{ mL}} \text{ x } \frac{1}{1.00\text{ L}} = 0.2\underline{3}8\text{ M}$$

Step 2: Calculate the equilibrium concentrations of the common species:

	$HCHO_2$ (aq) +	H_2O (l) $\rightleftharpoons$	H_3O^+(aq) +	CHO_2^- (aq)
Initial	$0.2\underline{6}3$	----	0	$0.2\underline{3}8$
Δ	$-x$	----	$+x$	$+x$
Equilibrium	$0.2\underline{6}3 - x$	-----	x	$0.2\underline{3}8 + x$

Assume x is small:

$[HCHO_2]$(total) = $0.2\underline{6}3$ M – x ≈ $0.2\underline{6}3$ $[CHO_2^-]$(total) = $0.2\underline{3}8$ M + x ≈ $0.2\underline{3}8$

Step 4: Calculate $[H_3O^+]$ and pH from K_a

$$K_a = \frac{[H_3O^+][CHO_2^-]}{[HCHO_2]} = \frac{0.2\underline{3}8\text{ x}}{0.2\underline{6}3} = 1.7 \times 10^{-4}$$

$x = [H_3O^+] = 1.\underline{8}8 \times 10^{-4}$ M   pH = - log ($1.\underline{8}8 \times 10^{-4}$) = **3.73**

II. Calculate the pH of the solution after 8.5 mL of 0.15 M hydrochloric acid added to 85 mL of the buffer

Data: 8.5 mL HCl, 0.15 M
85 mL formic acid, $HCHO_2$, $0.2\underline{6}3$ M
85 mL formate ion, CHO_2^-, $0.2\underline{3}8$ M

Step 1: Calculate the mmol of the species involved before addition:

$$\text{mmoles HCl} = 8.5\text{ mL x }\frac{0.15\text{ mol}}{1\text{ L}} = 1.\underline{2}8\text{ mmol}$$

$$\text{mmoles HCHO}_2 = 85\text{ mL x }\frac{0.2\underline{6}3\text{ mol}}{1\text{ L}} = 2\underline{2}.4\text{ mol}$$

$$\text{mmoles CHO}_2^- = 85\text{ mL x }\frac{0.2\underline{3}8\text{ mol}}{1\text{ L}} = 2\underline{0}.2\text{ mol}$$

Step 2: Calculate the mmol of the species involved after addition:

	HCl (aq) +	H_2O (l) ⟶	H_3O^+ (aq) +	Cl^- (aq)
Initial	$1.\underline{2}8$	----	0	0
End	0	-----	$1.\underline{2}8$	$1.\underline{2}8$

All of the H_3O^+ reacts with the CHO_2^- ion:

	H_3O^+ (aq) +	CHO_2^- ⟶	$HCHO_2$ (aq) +	H_3O (l)
Initial	$1.\underline{2}8$ mmol **L.R.**	$2\underline{0}.2$ mmol **excess**	$2\underline{2}.4$ mmol	-----
Change (Δ)	−1.28	$-1.\underline{2}8$	$+1.\underline{2}8$	-----
End	**0**	**$1\underline{8}.9$**	**$2\underline{3}.7$**	

Step 3: Find the starting concentrations (molarities) of the species involved

Total Volume of Solution = 85 mL buffer + 8.5 mL HCl = 93.5 mL

$$\frac{\text{mmol HCHO}_2}{\text{mL solution}} = \frac{2\underline{3}.7\text{ mmol}}{93.5\text{ mL}} = 0.2\underline{5}3\text{ M} \qquad \frac{\text{mmol CHO}_2^-}{\text{mL solution}} = \frac{1\underline{8}.9\text{ mmol}}{93.5\text{ mL}} = 0.2\underline{0}2\text{ M}$$

Step 4 : Calculate $[H_3O^+]$ and pH from K_a and equilibrium concentrations

	$HCHO_2$ (aq) +	H_2O (l) $\rightleftharpoons$	H_3O^+(aq) +	CHO_2^- (aq)
Initial	$0.2\underline{5}3$	----	0	$0.2\underline{0}2$
Δ	$-x$	----	$+x$	$+x$
Equilibrium	$0.2\underline{5}3 - x$	-----	x	$0.2\underline{0}2 + x$

$$K_a = \frac{[H_3O^+][CHO_2^-]}{[HCHO_2]} = \frac{x\,(0.2\underline{0}2 + x)}{(0.2\underline{5}3 - x)} \approx \frac{0.2\underline{0}2\,x}{0.2\underline{5}3} = 1.7 \times 10^{-4}$$

$x = [H_3O^+] = 2.\underline{1}3 \times 10^{-4}$ M

pH = – log $(2.\underline{1}3 \times 10^{-4})$ = **3.67 (with HCl added)**

Compare: pH = **3.73 (without HCl added)**

CONCLUSION:

- pH was lowered by 0.06 upon addition of HCl (minimal change)

FOLLOW-UP:

What is the pH of the solution if 8.5 mL of 0.15 NaOH were added to 85 mL of the buffer solution?

HENDERSON – HASSELBALCH EQUATION

- How do you prepare a buffer of a desired pH?

Consider the following buffer: $HA(aq)$ + $A^-(aq)$

weak acid — its conjugate base

$$HA(aq) + H_2O \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} \qquad [H_3O^+] = K_a \times \frac{[HA]}{[A^-]}$$

$[HA]$, $[A^-]$

- ➢ should be equilibrium concentrations
- ➢ are not exactly equilibrium concentrations, since there is excess of A^- in the buffer solution
- ➢ they do not differ significantly from the equilibrium concentrations, since A^- represses the ionization of HA

$$[H_3O^+] = K_a \times \frac{[HA]}{[A^-]}$$

NOTE: If $[HA] \approx [A^-]$

then $[H_3O^+] \approx K_a$

- Take negative logs of both parts of the equation:

$$-\log [H_3O^+] = -\log\left[K_a \times \frac{[HA]}{[A^-]}\right] = -\log K_a - \log\frac{[HA]}{[A^-]}$$

$$\downarrow \qquad\qquad\qquad \downarrow$$

$$-\log [H_3O^+] = pH \qquad\qquad -\log K_a = pK_a$$

$$pH = pK_a - \log\frac{[HA]}{[A^-]} = pK_a + \log\frac{[A^-]}{[HA]}$$

$$\boxed{pH = pK_a + \log\frac{[A^-]}{[HA]}} \qquad \boxed{pH = pK_a + \log\frac{\text{base}}{\text{acid}}}$$

Henderson-Hasselbalch Equation

- The Henderson-Hasselbalch Equation can be used for both type of buffers.

- To prepare a buffer with a specific pH:

  - A weak acid and its conjugate base must be found for which the pK_a of the weak acid is close to the desired pH.

  - The pH value is fine tuned using the acid-base ratio

<u>Examples</u>:

1. A buffer with a pH of 4.90 is desired. Would $HC_2H_3O_2/ C_2H_3O_2^-$ be a suitable buffer system?

$K_a(HC_2H_3O_2) = 1.7 \text{ x } 10^{-5}$

$pK_a = - \log (1.7 \text{ x } 10^{-5}) =$ **4.77**

This is relatively close to the desired pH (**4.77** versus **4.90**)

The pH may be increased by increasing the ratio: $\dfrac{\mathbf{[C_2H_3O_2^-]}}{\mathbf{[HC_2H_3O_2]}}$

1. Calculate the pH of a buffer containing 0.10 M NH_3 and 0.2 M NH_4^+. $K_b(NH_3) = 1.8 \text{ x } 10^{-5}$

$$K_a(NH_4^{+)} = \frac{K_w}{K_b(NH_3)} = \frac{1.0 \text{ x } 10^{-14}}{1.8 \text{ x } 10^{-5}} = 5.\underline{56} \text{ x } 10^{-10}$$

$$pK_a = - \log (5.\underline{56} \text{ x } 10^{-10}) = 9.25$$

$$pH = pK_a + \log \frac{\mathbf{[NH_3]}}{\mathbf{[NH_4^+]}} = 9.25 + \log \frac{\mathbf{0.10}}{\mathbf{0.20}} = \mathbf{8.95}$$

3. 1.5 mL of 1 M HCl is added to each of the following solutions. Which one will show the least change in pH?

a) 15 mL of 0.1M NaOH	The solution is a strong base. The addition of a strong acid will lower the pH considerably.
b) 15 mL of 0.1M $HC_2H_3O_2$	The solution is a weak acid. The addition of a strong acid will lower the pH considerably
c) 30 mL of 0.1M NaOH and 30 mL of 0.1M $HC_2H_3O_2$	After mixing, the solution is 0.05 M $NaC_2H_3O_2$, a basic salt, not a buffer. The addition of a strong acid will lower the pH considerably.
d) 30 mL of 0.1M NaOH and 60 mL of 0.1M $HC_2H_3O_2$	After mixing, the solution contains: $[NaC_2H_3O_2] = 0.0030$ moles/0.090 L = 0.033 M $[HC_2H_3O_2] = 0.0030$ moles/0.090 L = 0.033 M **This solution is a buffer and as such the addition of a strong acid will show the least change in pH**