ALMUSTAQBAL UNIVERSITY COLLEGE

College of Medical and Health Techniques

Medical Laboratories Techniques Department

Stage : First year students

Subject : Chemistry 1 - Lecture 8

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Buffer solutions

A buffer solution is a combination of either a weak acid and its conjugate base (supplied by a salt) or a weak base and its conjugate acid (supplied by a salt). Buffer systems resist changes in the pH of a solution due to dilution or the addition of small amounts of strong acid or base. Buffers are used to maintain the pH of solutions at a relatively constant and predetermined level. Usually, buffers have a useful pH range = pK ± 1,
Buffers play a vital role in maintaining the pH of body fluids.

Calculation of the pH of different types of Buffer solutions

1. **Acidic buffers**

Consists of weak acid (HA) and its salt (A^-) .Typical example is (acetic acid – acetate salt (CH_3COOH – CH_3COO^-)

$HA + H_2O \rightleftharpoons H_3O^+ + A^-$ ———— 1

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

$A^- + H_2O \rightleftharpoons OH^- + HA$ ———— 2

$K_b = \frac{[OH][HA]}{[A-]} = \frac{Kw}{Ka}$

equilibrium① will decrease C_{HA} by the amount $[H_3O^+]$ and equilibrium ② will increase it by the amount $[OH^-]$.

$[HA]_{equil.} = C_{HA} - [H_3O^+] + [OH^-]$

Similarly, equilibrium ① will increase $[A^-]$ by the amount $[H_3O^+]$

while equilibrium ② will decrease $[A^-]$ by the amount $[OH^-]$ then

$[A^-]_{equil.} = C_{A-} + [H_3O^+] - [OH^-]$

As we have acid then

$[HA] = C_{HA} - [H_3O^+]$

$[A^-] = C_{A^-} + [H_3O^+]$

And because we have weak acids then

$[HA] \cong C_{HA}$

$[A^-] \cong C_{A-}$

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

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

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

$- \log [H_3O] = -\log K_a - \log \frac{C_{HA}}{C_{A-}}$

$$pH = pKa + \log \frac{C_A}{C_{HA}}$$

** $pH = pKa + \log \frac{C_{salt}}{C_{acid}}$ **(Henderson equation)**

Example: what is the pH of a solution that is (0.40 M) in formic acid (Ka= 1.77×10^{-4}) and (1.0 M) in sodium formate? compare it with the pH of 0.4 M formic acid solution.

Solution :

The pH of the solution will be affected by Ka of formic acid (HCOOH) and K_b of formate ion ($HCOO^-$)

$$HCOONa \rightarrow HCOO^- + Na^+$$

$$HCOOH + H_2O \rightleftharpoons HCOO^- + H_3O^+ \quad Ka = 1.77 \times 10^{-4}$$

$$HCOO^- + H_2O \rightleftharpoons HCOOH + OH^- \quad K_b = \frac{Kw}{Ka} = 5.65 \times 10^{-11}$$

Since Ka of formic acid >> K_b for formate the solution will be acidic and Ka will determine the H_3O^+ concentration.

$$pH = pKa + \log \frac{C_{salt}}{C_{acid}}$$

$$pKa = -\log Ka = -\log (1.77 \times 10^{-4}) = 3.75$$

$$pH = 3.75 + \log \frac{1.0}{0.4} = 4.14$$

Check if $\frac{[H3O^+]}{[HCOOH]} x\ 100\ \% < 10\ \%$ Then approximation is valid

$$[H_3O^+] = 10^{-pH} = 10^{-4.14} = 7.2 \times 10^{-5}$$

$\frac{7.2 \text{ x}10^{-5}}{0.4}\ x\ 100\% = 0.018\ \%$ (The approximation is valid)

B) The pH of the acid-only solution

$[H_3O^+] = \sqrt{K_a\ .C}$

$[H_3O^+] = \sqrt{1.77x10^{-4}\ x\ 0.4}$ $=8.41x10^{-3}$

pH = -log($8.41x10^{-3}$) = 2.07

Practice Exercise :

1.What is the pH of a solution containing 0.3 M HCOOH and 0.52 M HCOOK? Compare your result with the pH of a 0.3 M HCOOH solution(Ka = $1.77 \text{ x } 10^{-4}$).

2. Determine the pH of (a) a 0.40 M CH_3COOH solution(Ka = $1.8\text{x } 10^{-5}$),

(b) a solution that is 0.40 M CH_3COOH and 0.20 M CH_3COONa.

B) Basic Buffers

It is composed of a solution of a weak base (B) and it`s conjugate acid (Salt) BH^+ e.g : NH_3-NH_4Cl .

1) $B + H_2O \rightleftharpoons BH^+ + OH^-$ $\quad K_b = \frac{[OH^-][BH^+]}{[B]}$

$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

2) $BH^+ + H_2O \rightleftharpoons H_3O^+ + B$ $\quad K_a = \frac{Kw}{Kb} = \frac{[H_3O^+][B]}{[BH^+]}$

$NH_4^+ + H_2O \rightleftharpoons H_3O^+ + NH_3$

[B] will decrease in equilibrium ① by amount $[OH^-]$ & increase in equilibrium ② by $[H_3O^+]$

Then $[B] = C_B - [OH^-] + [H_3O^+]$

Similarly $[BH^+]$ will increase in equilibrium① By $[OH^-]$ and decrease in equilibrium② by $[H_3O^+]$.

Then $[BH^+] = C_{BH+} + [OH^-] - [H_3O^+]$

$[B] \equiv C_B$ and $[BH^+] \equiv C_{BH+}$ (by approximation)

$$K_b = \frac{[OH^-][BH^+]}{[B]}$$

$$[OH^-]= K_b \frac{C_B}{C_{BH+}}$$

$$pOH= pK_b + \log\frac{[BH^+]}{[B]}$$

$$pOH = pK_b + \log\frac{C_{salt}}{C_{base}} \quad \text{(Henderson equation)}$$

In General:

$$\mathbf{pH = pK_a + \log\frac{C_{salt}}{C_{acid}}} \quad \textbf{(for acidic buffer)}$$

$$\mathbf{pOH = pK_b + \log\frac{C_{salt}}{C_{base}}} \quad \textbf{(for basic buffer)}$$

$pH = 14 - pOH$

Example:

Calculate the pH of a solution that is 0.1 M in NH_3 ($K_b = 1.75 \times 10^{-5}$) and 0.15 M in NH_4Cl.

Solution:

$\mathbf{NH_4Cl \rightarrow NH_4^+ + Cl^-}$

$\mathbf{NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+}$ $\quad Ka = \frac{K_w}{K_b} = \frac{10^{-14}}{1.75 \times 10^{-5}} = 5.7 \times 10^{-10}$

$\mathbf{NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-}$ $\quad K_b = 1.75 \times 10^{-5}$

because $K_b >> K_a$ the solution is assumed to be basic

$$pOH = pK_b + \log\frac{C_{salt}}{C_{base}}$$ **(for basic buffer)**

$pK_b = -\log K_b = -\log(1.75 \times 10^{-5}) = 4.75$

$$pOH = 4.75 + \log\frac{0.15}{0.1} = 4.93$$

To check the validity of approximation we calculate $[OH^-]$

then Check if $\frac{[OH^-]}{[Base]} x\ 100\ \% < 10\ \%$ Then approximation is valid

$[OH^-] = 10^{-pOH} = 10^{-4.93} = 1.17 \times 10^{-5}$

Then $\frac{1.17\ x\ 10^{-5}}{0.2} \times 100\ \% = 5.85 \times 10^{-3}$ **(approximation is valid)**

$pH = 14 - 4.93 = 9.07$

Exercise:

Determine the pH of (a) a 0.20 M NH_3 solution, (b) a solution that is 0.20 M in NH_3 and 0.30 M NH_4Cl.

Properties of buffer solution:

① Effect of dilution:

The pH of the buffer solution remains independent of dilution until the concentration of species it contains is decreased to the point where the approximation mentioned above becomes invalid.

Example: calculate the change in pH of a buffer containing (0.4M) Benzoic acid C_6H_5COOH (Ka =6.3×10^{-5}) and (1M) sodium benzoate C_6H_5COONa after dilution by a factor of 10 times .

Solution:

$$C_6H_5COONa \rightarrow C_6H_5COO^- + Na^+$$

$C_6H_5COOH + H_2O \rightleftharpoons C_6H_5COO^- + H_3O^+$ Ka = 6.3×10^{-5}

$C_6H_5COO^- + H_2O \rightleftharpoons C_6H_5COOH + OH^-$ $K_b = \frac{Kw}{Ka} = 1.58 \times 10^{-10}$

Since Ka of benzoic acid >> K_b for benzoate the solution will be acidic.

$$pH = pKa + \log\frac{[C6H5COONa]}{[C6H5COOH]}$$

$pKa = -\log(6.3 \times 10^{-5}) = 4.2$

a. Before Dilution

$$pH = 4.2 + \log\frac{1}{0.4} = 4.59$$

Check if $\frac{[H3O^+]}{[C6H5COOH]}\,x\,100\% < 10\,\%$ Then approximation is valid

$[H_3O^+] = 10^{-pH} = 10^{-4.59} = 2.57 \times 10^{-5}$

$\frac{2.57 \times 10^{-5}}{0.4}\,x\,100\% = 0.0064\%$ (**The approximation is valid**)

b. After dilution with 10 times.

$M_1V_1 = M_2V_2$

for $[C_6H_5COOH]$

$0.4 \times 1 = M_2 \times 10$

$[C_6H_5COOH] = \frac{0.4}{10} = 0.04M$

For $[C_6H_5COO^-]$

$1 \times 1 = M_2 \times 10$

$[C_6H_5COO^-] = \frac{1}{10} = 0.1M$

$$pH = pKa + \log\frac{[C6H5COONa]}{[C6H5COOH]} = 4.2 + \log\frac{0.1}{0.04} = 4.59$$

Check if $\frac{[H3O^{+}]}{[C6H5COOH]}\ x\ 100\ \% < 10\ \%$ Then approximation is valid

$[H_3O^+] = 10^{-pH} = 10^{-4.59} = 2.57 \times 10^{-5}$

$\frac{2.57\ x10^{-5}}{0.04}\ x\ 100\% = 0.0064\ \%$ (**The approximation is valid**)

∴ NO change in pH occurs after 10 times dilution($\Delta PH = 0$)

② Effect of adding strong acid or base:

Buffer solution resists the pH change after the addition of a small amount of strong acid or base.

Example:

Calculate the pH change that takes place when 100 mL of:

a) 0.05 M NaOH **b)** 0.05 M HCl

is added separately to 400 mL of buffer solution of (0.3M) NH_4Cl and (0.2M) NH_3 ($K_b = 1.75x10^{-5}$).

Solution:

A.The original buffer before addition

$\mathbf{NH_4Cl \rightarrow NH_4^+ + Cl^-}$

$\mathbf{NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+}$ $Ka = \frac{K_w}{K_b} = \frac{10^{-14}}{1.75\ x\ 10^{-5}} = 5.7\ x\ 10^{-10}$

$\mathbf{NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-}$ $K_b = 1.75x10^{-5}$

because $K_b >> K_a$ the solution is assumed to be basic

$\mathbf{pOH = pK_b + \log\frac{C_{salt}}{C_{base}}}$ **(for basic buffer)**

$pK_b = -\log K_b = -\log (1.75 \times 10^{-5}) = 4.76$

$pOH = pK_b + \log\frac{C_{NH_4Cl}}{C_{NH_3}} = 4.76 + \log\frac{0.3}{0.2} = 4.93$

To check the validity of approximation we calculate $[OH^-]$ then

Check if $\frac{[OH-]}{[Base]}\ x\ 100$ ‹ 10 % Then approximation is valid

$[OH^-]= 10^{-pOH} = 10^{-4.93} = 1.17 \times 10^{-5}$

Then $\frac{1.17\ x\ 10^{-5}}{0.2}$ x 100% = 5.85×10^{-3} % **(approximation is valid)**

pH =14 - 4.93 = 9.07

B. after the addition of a strong base or acid

1) addition of NaOH converts part of NH_4^+ in the buffer to NH_3

$NH_4^+ + OH^- \rightleftharpoons NH_3 + H_2O$ (OH^- from NaOH)

The analytical concentration of NH_3 and NH_4Cl become :

$$C_{NH_3} = \frac{\text{original No.of moles of NH}_3 + \text{moles of produced NH}_3}{\text{Total New volume (L)}}$$

Or $$C_{NH_3} = \frac{\text{original No.of mmoles of NH}_3 + \text{mmoles of produced NH}_3}{\text{Total New volume (mL)}}$$

No. of moles of produced NH_3 = No. of moles of reacted NaOH

$$C_{NH_3} = \frac{M_{NH_3}V_{NH_3} + M_{NaOH}V_{NaOH}}{V_{NH_3} + V_{NaOH}}$$

$$C_{NH_3} = \frac{400x0.2+100x0.05}{[400+100\}} = \frac{85}{500} = 0.17M$$

$$C_{NH4+} = \frac{\text{original No. of moles of NH}_4{}^+ - \text{moles of reacted NH}_4{}^+}{\text{Total New volume(L)}}$$

Or $$C_{NH4+} = \frac{\text{original No. of mmoles of NH}_4{}^+ - \text{mmoles of reacted NH}_4{}^+}{\text{Total New volume(mL)}}$$

No. of moles of consumed NH_4^+ = No. of moles of reacted NaOH

$$C_{NH_4Cl} = \frac{M_{NH_4Cl}V_{NH_4Cl} - M_{NaOH}V_{NaOH}}{VNH_4Cl + V_{NaOH}}$$

$$C_{NH_4Cl} = \frac{400x0.3-100x0.05}{[400+100]} = \frac{115}{500} = 0.23M$$

$pOH = 4.76 + \log \frac{0.23}{0.17} = 4.89$ (Henderson equation)

To check the validity of the approximation we calculate

if $\frac{[OH^-]}{[Base]} x\ 100 < 10$ % Then the approximation is valid

$[OH^-] = 10^{-pOH} = 10^{-4.89} = 1.29 \times 10^{-5}$

Then $\frac{1.29\ x\ 10^{-5}}{0.17}$ x 100 % = 7.59×10^{-3} (approximation is valid)

pH =14 - 4.89 = 9.11

$\Delta pH = 9.11 - 9.07 = 0.04$

2) The addition of HCl converts part of NH_3 to NH_4Cl

$NH_3 + H_3O^+ \rightleftharpoons NH_4^+ + H_2O$ (H_3O^+ from HCl)

$C_{NH3} = \frac{\text{original No.of moles of } NH_3 - \text{moles of reacted } NH_3}{\text{Total New volume (L)}}$

Or $C_{NH3} = \frac{\text{original No.of mmoles of } NH_3 - \text{mmoles of reacted } NH_3}{\text{Total New volume (mL)}}$

No.of moles of consumed NH_3 = No. of moles of reacted HCl

$$C_{NH_3} = \frac{M_{NH_3}V_{NH_3} - M_{HCl}V_{HCl}}{V_{NH_3} + V_{HCl}}$$

$$C_{NH_3} = \frac{400 \text{ x } 0.2 - 100 \text{ x } 0.05}{[400+100\}} = 0.150M$$

$$C_{NH_4^+} = \frac{\text{original No of moles of } NH_4^+ + \text{moles of produced } NH_4^+}{\text{Total New volume (L)}}$$

Or $C_{NH_4^+} = \frac{\text{original No of mmoles of } NH_4^+ + \text{mmoles of produced } NH_4^+}{\text{Total New volume (mL)}}$

No. of moles of produced NH_4 = No. of moles of reacted HCl

$$C_{NH_4Cl} = \frac{M_{NH_4Cl}V_{NH_4Cl} + M_{HCl}V_{HCl}}{V_{NH_4Cl} + V_{HCl}}$$

$C_{NH_4Cl} = \frac{400 \text{ x } 0.3 + 100 \text{ x } 0.05}{[400+100]} = 0.25M$

pOH= pK_b + $\log \frac{NH_4Cl}{C_{NH_3}}$ (Henderson equation)

pOH $= 4.76 + \log \frac{0.25}{0.15} = 4.98$

To check the validity of approximation we calculate $[OH^-]$ then

Check if $\frac{[OH^-]}{[Base]} x\ 100$ ‹ 10 % Then approximation is valid

$[OH^-] = 10^{-pOH} = 10^{-4.98} = 1.05 \text{ x } 10^{-5}$

Then $\frac{1.05\ x\ 10^{-5}}{0.15}$ x 100% = 0.007% (approximation is valid)

pH =14 - 4.98 = 9.02

$\Delta pH = 9.02 - 9.07 = -0.05$

Addition	**ΔpH**
100 mL 0.05 M NaOH	0.04
100 mL 0.05 M HCl	- 0.05

Example

Calculate the pH change that take place when 100 mL of:

a) 0.05 M NaOH **b)** 0.05 M HCl

is added seperately to 400 mL of buffer solution of (0.1M) CH_3COOH and (0.2M) CH_3COONa ($K_a = 1.8 \text{ x} 10^{-5}$) .

solution:

a. The pH of the buffer before addition:

$$\mathbf{CH_3COONa \rightarrow CH_3COO^- + Na^+}$$

$$\mathbf{CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+ \quad Ka = 1.8 \text{ x} 10^{-5}}$$

$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$ **$K_b = \frac{Kw}{Ka} = 5.55 \times 10^{-10}$**

Since Ka of acetic acid >> K_b for acetate the solution will be acidic and Ka will determine the H_3O^+ concentration.

$$pH = pKa + \log \frac{C_{salt}}{C_{acid}}$$

$$pKa = -\log Ka = -\log (1.8 \times 10^{-5}) = 4.74$$

$$pH = 4.74 + \log \frac{0.2}{0.1} = 5.04$$

Check if $\frac{[H3O^+]}{[CH3COOH]} x\ 100 < 10\ \%$ Then approximation is valid

$$[H_3O^+] = 10^{-pH} = 10^{-5.06} = 8.7 \times 10^{-6}$$

$\frac{8.7\text{x}10^{-6}}{0.1}\ x\ 100 = 0.009\ \%$ (***The approximation is valid***)

B. addition of 100 mL of 0.05 M NaOH

$CH_3COOH + NaOH \rightleftharpoons CH_3COONa + H_2O$

From the above reaction [CH_3COOH] is decreased and [CH_3COONa] is increased

$$C_{CH_3COONa} = \frac{\text{original No. of mmoles of } CH_3COONa + \text{ mmoles of produced } CH_3COONa}{\text{Total New volume (mL)}}$$

No. of moles of CH_3COONa produced = No. of moles of NaOH reacted

$$C_{CH_3COONa} = \frac{\text{original No. of mmoles of } CH_3COONa + \text{ mmoles of NaOH reacted}}{\text{Total New volume (mL)}}$$

$$C_{CH_3COONa} = \frac{400 \text{ x } 0.2 + 100 \text{ x } 0.05 \text{ mmoles}}{400+100} = 0.17$$

$$C_{CH_3COOH} = \frac{\text{original No. of mmoles of } CH_3COOH - \text{ mmoles of } CH_3COOH \text{ consumed}}{\text{Total New volume (mL)}}$$

No. of moles of CH_3COOH consumed = No. of moles of NaOH reacted

$$C_{CH_3COOH} = \frac{\text{original No. of mmoles of } CH_3COOH - \text{ mmoles of } NaOH \text{ reacted}}{\text{Total New volume (mL)}}$$

$$C_{CH_3COOH} = \frac{(400\text{x } 0.1 - 100\text{x}0.05 \text{) m moles}}{\text{Total New volume (mL)}} = \frac{(35 \text{) m moles}}{500} = 0.07$$

$$pH = 4.74 + \log\frac{0.17}{0.07} = 5.12$$

Δ pH = 5.12 – 5.06 = 0.06

c) Addition of 100 mL of 0.05 HCl to the buffer

$CH_3COONa \rightarrow CH_3COO^- + Na^+$

$CH_3COO^- + HCl \rightleftharpoons CH_3COOH$

From the above reaction [CH_3COONa] is decreased and [CH_3COOH] is increased

$$C_{CH_3COONa} = \frac{\text{original No. of mmoles of } CH_3COONa - \text{ mmoles of } CH_3COONa \text{ consumed}}{\text{Total New volume (mL)}}$$

No. of moles of CH_3COONa consumed = No. of moles of HCl reacted

$$C_{CH_3COONa} = \frac{\text{original No. of mmoles of } CH_3COONa - \text{ mmoles of HCl reacted}}{\text{Total New volume (mL)}}$$

$$C_{CH_3COONa} = \frac{400 \text{ x } 0.2 - 100 \text{ x } 0.05 \text{ mmoles}}{400+100} = 0.15$$

$$C_{CH_3COOH} = \frac{\text{original No. of mmoles of } CH_3COOH + \text{ mmoles of } CH_3COOH \text{ produced}}{\text{Total New volume (mL)}}$$

No. of moles of CH_3COOH produced = No. of moles of HCl reacted

$$C_{CH_3COOH} = \frac{\text{original No. of mmoles of } CH_3COOH + \text{mmoles of } HCl \text{ reacted}}{\text{Total New volume (mL)}}$$

$$C_{CH_3COOH} = \frac{(400x\ 0.1+100x0.05\ )m\ moles}{Total\ New\ volume\ (mL)} = \frac{(45\ )m\ moles}{500} = \mathbf{0.09}$$

$$pH = 4.74 + \log\frac{0.15}{0.09} = 4.96$$

Δ pH = 4.96 – 5.06 = - 0.1

Addition	ΔpH
100 mL 0.05 M NaOH	0.06
100 mL 0.05 M HCl	- 0.1

Exercise:

1. Calculate the pH of the buffer solution of 0.40 M HF (Ka = $3.2x10^{-4}$) and 0.48 *M* KF. What is the pH after the addition of 15 mL of 0.10 *M* HCl to 50 mL of the buffer solution?

2. Determine the pH of (a) a 0.20 M NH_3 (K_b = $1.75x10^{-5}$) solution,

(b) a solution that is 0.20 M in NH_3 and 0.30 M in NH_4Cl.

Preparation of buffer:

To prepare a buffer, it is to choose the acid with the pK_a close to the desired pH. Usually, buffers have a useful pH range = $pK_a \pm 1$, but the closer it is to the weak acid's pKa, is the better**.**

Example:

Describe how you might prepare approximately (500 mL) of pH 4.5 buffer solution from 1 M acetic acid CH_3COOH (Ka=1.74 $x10^{-5}$) and sodium acetate CH_3COONa (82.03 g /mole).

Solution:

For acidic buffer (pH= 4.5)

$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$

pH = pKa + log $\frac{C_{salt}}{C_{acid}}$ (Henderson equation for acidic buffers)

pKa = - log(1.8 x 10^{-5}) = 4.74

4.5 = 4.74 + log $\frac{[CH_3COO^-]}{[CH_3COOH]}$

4.5 = 4.74 + log $\frac{[CH_3COO^-]}{[1]}$

4.5 – 4.74 = log [CH_3COO^-] – log 1

log [CH_3COO^-]= - 0.24

[CH_3COO^-] = $10^{-0.24}$ = 0.575 M

Mass of CH_3COONa needed = Molarity(M) x V(liter) x Mwt

Mass of CH_3COONa = 0.575 (mol/L) x $\frac{500}{1000}$ L x 82.03(g/mol) = 23.58 g

The required buffer is to be made by dissolution of 23.58 g of CH_3COONa and completing the volume to 500 mL with 1M CH_3COOH