

ALMUSTAQBAL UNIVERSITY COLLEGE

College of Engineering and Engineering Techniques

Biomedical Engineering Department

Stage : Second year students

Subject : Chemistry 1 - Lecture 9

Lecturer: Assistant professor Dr. SADIQ . J. BAQIR



Buffer solutions

The buffer is a mixture of a weak acid and its conjugate base (Salt) or a weak base and its conjugate acid (Salt) , that resists change in pH of a solution due to dilution or addition of a small amounts of strong acid or base . Buffers are used to Maintain the pH of solutions at relatively constant and predetermined level.

Usually, buffers have a useful pH range = $pK \pm 1$,

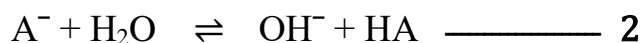
Calculation of the pH of different types of Buffer solutions

1. Acidic buffers

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



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



$$K_b = \frac{[OH][HA]}{[A^-]} = \frac{K_w}{K_a}$$

equilibrium ① will decrease C_{HA} by amount $[H_3O^+]$ and equilibrium ② will increase it by amount $[OH^-]$.

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

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

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

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

As we have acid then

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

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

And because we have weak acid then

$$[HA] \cong C_{HA}$$

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

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

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

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

$$-\log [\text{H}_3\text{O}^+] = -\log K_a - \log \frac{C_{\text{HA}}}{C_{\text{A}^-}}$$

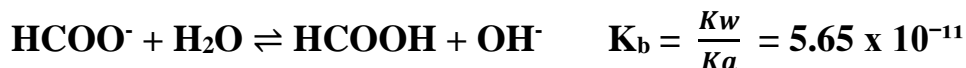
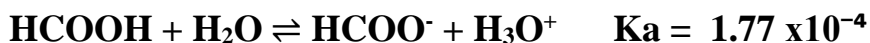
$$\text{pH} = \text{pK}_a + \log \frac{C_{\text{A}^-}}{C_{\text{HA}}}$$

$$** \quad \text{pH} = \text{pK}_a + \log \frac{C_{\text{salt}}}{C_{\text{acid}}} \quad (\text{Henderson equation})$$

Example: what is the pH of a solution that is (0.40 M) in formic acid ($K_a = 1.77 \times 10^{-4}$) and (1.0 M) in sodium formate ?

Solution :

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



Since K_a of formic acid $\gg K_b$ for formate the solution will be acidic and K_a will determine the H_3O^+ concentration.

$$\text{pH} = \text{pK}_a + \log \frac{C_{\text{salt}}}{C_{\text{acid}}}$$

$$\text{pK}_a = -\log K_a = -\log (1.77 \times 10^{-4}) = 3.75$$

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

$$[\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-4.14} = 7.2 \times 10^{-5}$$

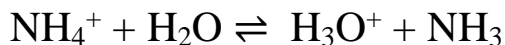
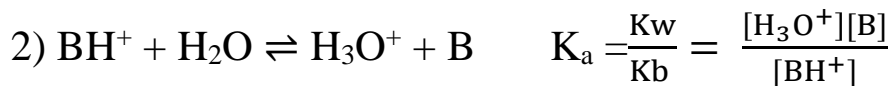
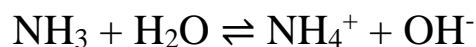
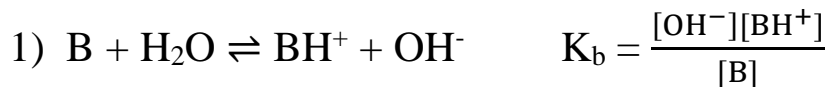
Check if $\frac{[H_3O^+]}{[HCOOH]} \times 100 < 10\%$ Then approximation is valid

$$\frac{7.2 \times 10^{-5}}{0.4} \times 100 = 0.018\%$$

The approximation is valid:

B) Basic Buffers

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



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

$$\text{Then } [B] = C_B - [OH^-] + [H_3O^+]$$

Similarly $[BH^+]$ will increase in equilibrium ① by $[OH^-]$ and decrease in equilibrium ② by $[H_3O^+]$.

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

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

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

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

$$\text{pOH} = \text{p}K_b + \log \frac{[\text{BH}^+]}{[\text{B}]}$$

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

In General:

$$\text{pH} = \text{p}K_a + \log \frac{C_{\text{salt}}}{C_{\text{acid}}} \quad (\text{for acidic buffer})$$

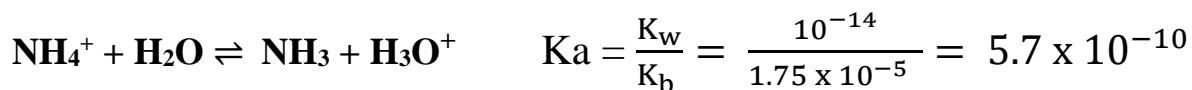
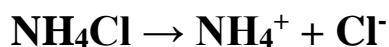
$$\text{pOH} = \text{p}K_b + \log \frac{C_{\text{salt}}}{C_{\text{base}}} \quad (\text{for basic buffer})$$

$$\text{pH} = 14 - \text{pOH}$$

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:



because $K_b \gg K_a$ the solution is assumed to be basic

$$\text{pOH} = \text{p}K_b + \log \frac{C_{\text{salt}}}{C_{\text{base}}} \quad (\text{for basic buffer})$$

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

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

To check the validity of approximation we calculate $[\text{OH}^-]$

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

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

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

$$\text{pH} = 14 - 4.93 = 9.07$$

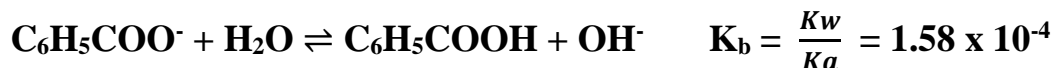
Properties of buffer solution:

① Effect of dilution:

The pH of the buffer solution remains independent of dilution until the concentration of species it's contain are decreased to the point where the approximation mentioned above become invalid .

Example: calculate the change in pH of a buffer containing (0.4M) formic acid $\text{C}_6\text{H}_5\text{COOH}$ ($K_a = 6.3 \times 10^{-5}$) and (1M) sodium benzoate $\text{C}_6\text{H}_5\text{COONa}$ after dilution by a factor of 50 times .

Solution:



Since K_a of formic acid $\gg K_b$ for formate the solution will be acidic.

$$\text{pH} = \text{p}K_a + \log \frac{[\text{C}_6\text{H}_5\text{COONa}]}{[\text{C}_6\text{H}_5\text{COOH}]}$$

$$\text{pK}_a = -\log(3.6 \times 10^{-3}) = 2.2$$

a. Before Dilution

$$\text{pH} = 2.2 + \log \frac{1}{0.4} = 2.59$$

$$[\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-2.59} = 2.57 \times 10^{-3}$$

Check if $\frac{[\text{H}_3\text{O}^+]}{[\text{C}_6\text{H}_5\text{COOH}]} \times 100 < 10\%$ Then approximation is valid

$$\frac{2.57 \times 10^{-3}}{0.4} \times 100 = 0.64\%$$

The approximation is valid.

b. After dilution with 10 times .

$$M_1V_1 = M_2V_2$$

for $[\text{C}_6\text{H}_5\text{COOH}]$

$$0.4 \times 1 = M_2 \times 10$$

$$[\text{C}_6\text{H}_5\text{COOH}] = \frac{0.4}{10} = 0.04\text{M}$$

For $[\text{C}_6\text{H}_5\text{COO}^-]$

$$1 \times 1 = M_2 \times 10$$

$$[\text{C}_6\text{H}_5\text{COO}^-] = \frac{1}{10} = 0.1\text{M}$$

$$\text{pH} = 2.2 + \log \frac{1}{0.04} = 3.59$$

$$[\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-3.59} = 2.57 \times 10^{-4}$$

Check if $\frac{[\text{H}_3\text{O}^+]}{[\text{C}_6\text{H}_5\text{COOH}]} \times 100 < 10\%$ Then approximation is valid

$$\frac{2.57 \times 10^{-4}}{0.04} \times 100 = 0.64\%$$

The approximation is valid.

∴ NO change in pH occur after 50 times dilution($\Delta PH = 0$)

② Effect of adding strong acid or base:

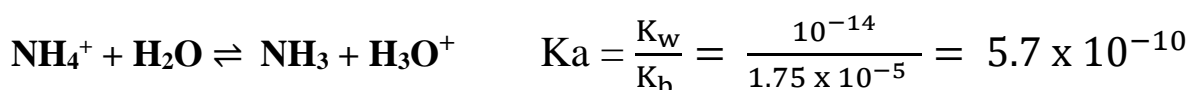
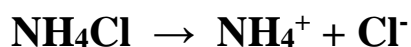
Buffer solution resist the pH change after addition of small amount of strong acid or base.

Example: Calculate the pH change that take place when 100 mL portion of:
a) 0.05 M NaOH b) 0.05 M HCl

is added seperately to 400 mL of buffer solution of (0.3M) NH_4Cl and (0.2M) NH_3 ($K_b = 1.75 \times 10^{-5}$).

Solution:

a. The original buffer before addition



because $K_b \gg K_a$ the solution is assumed to be basic

$$\text{pOH} = \text{p}K_b + \log \frac{C_{\text{salt}}}{C_{\text{base}}} \quad (\text{for basic buffer})$$

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

$$\text{pOH} = \text{p}K_b + \log \frac{C_{\text{NH}_4\text{Cl}}}{C_{\text{NH}_3}} = 4.76 + \log \frac{0.3}{0.2} = 4.93$$

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

To check the validity of approximation we calculate $[\text{OH}^-]$ then

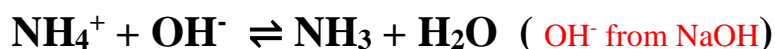
Check if $\frac{[\text{OH}^-]}{[\text{Base}]} \times 100 < 10\%$ Then approximation is valid

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

$$\text{pH} = 14 - 4.93 = 9.07$$

b. after addition of strong base or acid

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



The analytical concentration of NH_3 and NH_4Cl become :

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

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

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

$$C_{\text{NH}_3} = \frac{M_{\text{NH}_3}V_{\text{NH}_3} + M_{\text{NaOH}}V_{\text{NaOH}}}{V_{\text{NH}_3} + V_{\text{NaOH}}}$$

$$C_{\text{NH}_3} = \frac{400 \times 0.2 + 100 \times 0.05}{[400 + 100]} = \frac{85}{500} = 0.17\text{M}$$

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

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

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

$$C_{\text{NH}_4\text{Cl}} = \frac{M_{\text{NH}_4\text{Cl}}V_{\text{NH}_4\text{Cl}} - M_{\text{NaOH}}V_{\text{NaOH}}}{V_{\text{NH}_4\text{Cl}} + V_{\text{NaOH}}}$$

$$C_{NH_4Cl} = \frac{400 \times 0.3 - 100 \times 0.05}{[400 + 100]} = \frac{115}{500} = 0.23M$$

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

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

To check the validity of approximation we calculate

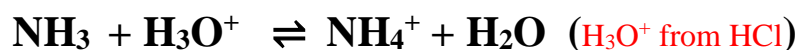
$$\text{if } \frac{[OH^-]}{[Base]} \times 100 < 10\% \text{ Then approximation is valid}$$

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

$$pH = 14 - 4.89 = 9.11$$

$$\Delta pH = 9.11 - 9.07 = 0.04$$

2) addition of HCl converts part of NH_3 to NH_4Cl



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

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

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

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

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

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

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

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

$$C_{\text{NH}_4\text{Cl}} = \frac{M_{\text{NH}_4\text{Cl}}V_{\text{NH}_4\text{Cl}} + M_{\text{HCl}}V_{\text{HCl}}}{V_{\text{NH}_4\text{Cl}} + V_{\text{HCl}}}$$

$$C_{\text{NH}_4\text{Cl}} = \frac{400 \times 0.3 + 100 \times 0.05}{[400+100]} = 0.25\text{M}$$

$$\text{pOH} = \text{pK}_b + \log \frac{[\text{NH}_4\text{Cl}]}{[\text{NH}_3]} \quad (\text{Henderson equation})$$

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

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

To check the validity of approximation we calculate $[\text{OH}^-]$ then

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

$$\text{Then } \frac{1.05 \times 10^{-5}}{0.2} \times 100 = 5.25 \times 10^{-3} \quad (\text{approximation is valid})$$

$$\text{pH} = 14 - 4.98 = 9.02$$

$$\Delta\text{pH} = 9.02 - 9.07 = -0.05$$

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

Exercise:

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

a) 0.05 M NaOH b) 0.05 M HCl is added seperately to 400 mL of buffer solution of (0.1M) CH₃COOH and (0.2M) CH₃COONa (K_a = 1.74x10⁻⁵).

Hint:



Preparation of buffer:

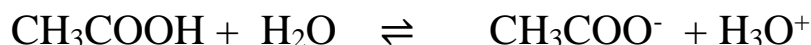
To prepare a buffer, it is to choose the acid with the pK_a close to the desired pH. Usually, buffers have a useful pH range = pK_a ± 1, but the closer it is to the weak acid's pK_a, is the better .

Example:

Describe how you might prepare approximately (500 mL) of pH 4.5 buffer solution from 1 M acetic acid CH₃COOH (K_a=1.74 x 10⁻⁵) and sodium acetate CH₃COONa (82.03 g /mole).

Solution:

For acidic buffer(pH= 4.5)



$$\text{pH} = \text{pK}_a + \log \frac{C_{\text{salt}}}{C_{\text{acid}}} \quad (\text{Henderson equation for acidic buffers})$$

$$\text{pK}_a = -\log(1.74 \times 10^{-5}) = 4.76$$

$$4.5 = 4.76 + \log \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

$$4.5 = 4.76 + \log \frac{[\text{CH}_3\text{COO}^-]}{[1]}$$

$$4.5 - 4.76 = \log [\text{CH}_3\text{COO}^-] - \log 1$$

$$\log [\text{CH}_3\text{COO}^-] = -0.26$$

$$[\text{CH}_3\text{COO}^-] = 10^{-0.26} = 0.549 \text{ M}$$

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

$$\text{Mass of } \text{CH}_3\text{COONa} = 0.549(\text{mol/L}) \times \frac{500}{1000} \text{ L} \times 82.03(\text{g/mol}) = 22.52 \text{ g}$$

The required buffer is to be made by dissolution of 22.52 g of CH_3COONa and completing the volume to 500 mL with 1M CH_3COOH

Buffer capacity

It is defined as the number of moles of an acid or base added to 1 liter of a buffer solution to cause its pH to change by 1 unit.

Buffer capacity depends on the amount of acid and base used to prepare the buffer. For example, if you have a 1-L buffer solution made of (1 M CH_3COOH and 1 M CH_3COONa) and a 1-L buffer solution that is (0.1 M CH_3COOH and 0.1 M CH_3COONa), although they will both have the same pH, the first buffer solution will have a greater buffer capacity because it has a higher amount of CH_3COOH and CH_3COO^- .

To calculate buffer capacity, we use the following formula:

$$\beta = n / \Delta\text{pH}$$

β is buffer capacity (it is unitless)

n is the number of moles of an acid or base (that were added to the buffer) per liter of the buffer

$$n = \frac{\text{No. of moles of acid or base added}}{\text{vol of buffer(L)}}$$

ΔpH is the difference between the initial pH of the buffer and the pH of the buffer after the acid or base is added

The higher the capacity (**β**), the more acid and base can be added to the buffer before its pH changes significantly.

Example:

A volume of 150 mL of 0.2 M HCl was added to 600 mL of buffer with a pH of 7.39. which gives the buffer solution a new pH of 7.03. What is the capacity of this buffer solution?

Solution:

No. of moles = Molarity (M) x V(L)

Number of moles of HCl = 0.2 M \times 0.150 L = 0.03 mol

$$n = \frac{\text{No. of moles of acid or base added}}{\text{vol of buffer(L)}} = \frac{0.03 \text{ mole}}{0.6 \text{ L}} = 0.05 \text{ mol/L}$$

$$n = 0.05 \text{ mol/L}$$

$$\Delta\text{pH} = |7.03 - 7.39| = 0.36$$

$$\beta = \frac{n}{\Delta\text{pH}} = \frac{0.05}{0.36} = 0.14$$

Thus, the buffer capacity of our buffer solution is 0.14.