Almustaqbal University College

Medical Laboratories Techniques Department

First year students

Subject: General chemistry - Lecture 9

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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 small amounts of strong acid or base. Buffers are used to maintain the pH of solutions at relatively constant and predetermined level.

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_3COONa)

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

HA= weak acid A^- =Cojugate base(salt of the weak acid)

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

The salt of the weak acid (e.g: NaA) is a strong electrolyte that dissociate completely to give (A^-) as shown in the following equation

$NaA \rightarrow Na^+ + A^-$

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

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

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

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

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

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

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

To simplify the solution some approximations are done :

1. As we have acid then $[OH^-]$ is omitted then:

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

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

2. And because we have Weak acid then $[H_3O^+]$ is omitted 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= 1.80 x 10^{-4}) and (1.0 M) in sodium formate?

Solution :

Method 1: (الطريقه التفصيليه)

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

$HCOOH + H_2O \rightleftharpoons HCOO^- + H_3O^+$ Ka = 1.77 x10^{-4}

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

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

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

$[HCOOH] \cong C_{HCOOH} = 0.4\ M$

$[HCOO^-] \cong C_{HCOONa} = 1.0\ M$

$$Ka = \frac{[H_3O^+][HCOO^-]}{[HCOOH]}$$

$$[H_3O^+] = K_a \frac{[HCOOH]}{[HCOO^-]}$$

$$[H_3O^+] = 1.77 \times 10^{-4} \times \frac{0.4}{1.0} = 7.08 \times 10^{-5}\ M$$

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

$$\frac{7.08 \times 10^{-5}}{0.4} x\ 100 = 0.018\ \%$$

The assumption that $[H_3O^+] << C_{HCOOH}$ and that $[H_3O^+] << C_{HCOO^-}$ and can be neglected and the approximation is valid:

$pH = -\log (7.08 \times 10^{-5}) = 4.15$

Second method:

Check if $\frac{[w.acid]}{Ka} > 10 \rightarrow$ Use Henderson equation directly

$$\frac{[w.acid]}{Ka} = \frac{0.4}{1.77\ x\ 10^{-4}} = 2259 \quad (i.e: > 10)$$

$$pH = pKa + \log \frac{C_{HCOO}}{C_{HCOOH}} \quad \text{(Henderson equation)}$$

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

$$pH = 3.75 + \log \frac{1.0}{0.4} = 4.15$$

Third method:(Apply the buffer formula directly and check)

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

pH = 3.75 + log $\frac{1.0}{0.4}$ = 4.15

$[H_3O^+] = 10^{-pH}$

$[H_3O^+] = 10^{-4.15} = 7.08 \times 10^{-5}$

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

$\frac{[H3O^+]}{[HCOOH]}\ x\ 100\ =\ \frac{7.08\ x10^{-5}}{0.4}\ x\ 100 = 0.018\ \%$ (i.e: ‹ 10)

The approximation is valid

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

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

$NH_4Cl \rightarrow NH_4^+ + Cl^-$

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

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)

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

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

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

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

In General:

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

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

$pH = 14 - pOH$

Example:

Calculate the pH of a solution that is 0.2 M in NH_3 ($K_b = 1.75 \times 10^{-5}$) and 0.3 M in NH_4Cl.

Solution:

$NH_4Cl \rightarrow NH_4^+ + Cl^-$

$\mathbf{NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+}$

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

$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = 1.75 \times 10^{-5}$

$Ka = \frac{K_w}{K_b} = \frac{10^{-14}}{1.75 \times 10^{-5}} = 5.7 \times 10^{-10}$

because $K_b >> K_a$ the solution is assumed to be basic and $[OH^-] >> [H_3O^+]$

Method 1 (الطريقه التفصيليه)

$[NH_4^+] = C_{NH_4Cl} - [H_3O^+] + [OH^-]$

$[NH_3] = C_{NH_3} + [H_3O^+] - [OH^-]$

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

$[OH^-] >> [H_3O^+]$ Then cancelling $[H_3O^+]$ gives:

$[NH_4^+] = C_{NH4Cl} + [OH^-]$

$[NH_3] = C_{NH3} - [OH^-]$

Assume $[OH^-] << C_{NH_4Cl}$ and C_{NH_3} as we have a weak base then :

$[NH_4^+] = C_{NH_4Cl} = 0.30M$

$[NH_3] = C_{NH3} = 0.2\ M$

$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$

$[OH^-] = Kb \frac{[NH_3]}{[NH_4+]}$

$[OH^-] = 1.75X10^{-5} x \frac{C_{NH3}}{C_{NH4Cl}}$

$[OH^-] = \frac{1.75x10^{-5}x\ 0.20}{0.30} = 1.17 \times 10^{-5}M$

$[OH^-] << C_{NH_4Cl}$ [0.30] , $[OH^-] << C_{NH_3}$ [0.20]

To check the validity of approximation by checking if

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

$\frac{[OH^-]}{[NH_3]}$ x100 = $\frac{1.17\ x\ 10^{-5}}{0.2}$ x 100 = 5.85 x 10^{-3} (approximation is valid)

pOH= pK_b + log $\frac{[Salt]}{[Base]}$

pOH= pK_b + log $\frac{[NH_4^+]}{[NH_3]}$

pK_b = -log[1.75 x 10^{-5}] = 4.76

pOH= 4.76 + log $\frac{[0.3]}{[0.2]}$ = 4.93

Or pOH = - log [1.17 x 10^{-5}] = 4.93

Then pH= $14 - 4.93 = 9.07$

<u>Second method</u>

0.20 M NH_3 and 0.30 M in NH_4Cl

Check if $\frac{[w.base]}{Kb} > 10 \rightarrow$ Use Henderson equation directly

$\frac{[w.base]}{Kb} = \frac{0.2}{1.75\ x\ 10^{-5}}$ = 11428.5 (i.e: > 10)

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

$$pOH = 4.76 + \log \frac{0.3}{0.2} = 4.93$$

$$pH = 14 - pOH$$

$$pH = 14 - 4.93 = 9.07$$

Third method (Apply the buffer formula & check)

$$pOH = pK_b + \log \frac{Salt}{Base}$$

$$pOH = 4.76 + \log \frac{0.3}{0.2} = 4.93$$

$$[OH^-] = 10^{-pH}$$

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

Check If $\frac{[OH^-]}{[NH3]} \times 100\% < 10\%$ then approximation is valid and the buffer equation can be applied directly

$$\frac{[OH-]}{[NH_3]} \times 100\% = \frac{1.17 \times 10^{-5}}{0.2} \times 100\% = 5.85 \times 10^{-3} \text{ (i.e:} < 10\ \%)$$

The approximation is valid