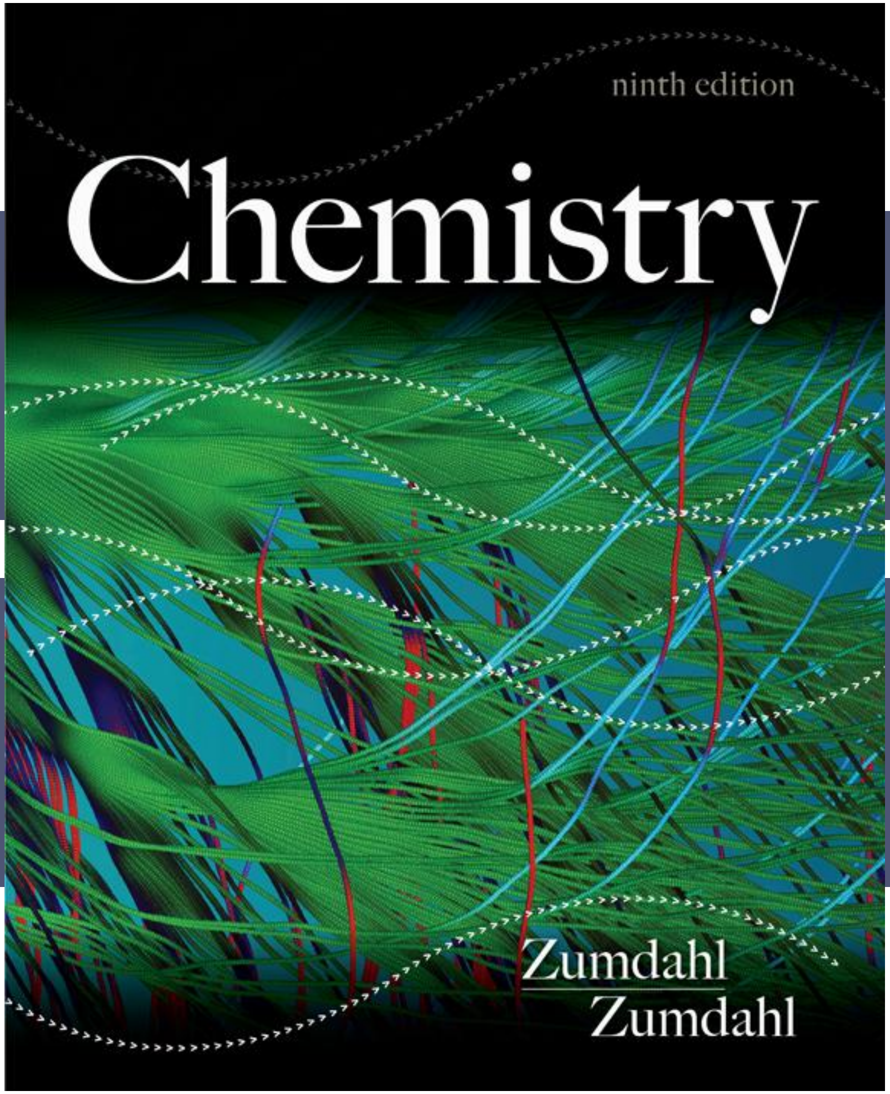


Chapter 15

Acid-Base Equilibria

Common Ion and Common Ion Effect

- Presence of an ion which is part of the equilibrium, but coming from another source. This ion is called common ion.
- Shift in equilibrium position that occurs because of the addition of the common ion is called common ion effect.
- An application of Le Châtelier's principle.

Example:

$$\underset{\text{(Weak acid)}}{HCN_{(aq)}} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + \underset{\text{(conjugate base)}}{CN^-_{(aq)}}$$

- Addition of NaCN will shift the equilibrium to the left because of the addition of CN^-, which is already involved in the equilibrium reaction.
- A solution of HCN and NaCN is less acidic than a solution of HCN alone.
- For example: addition of NaCl does not affect the equilibrium position because none of the ions (Na^++ or Cl^-) is part of the equilibrium.

Key Points about Buffered Solutions

- Buffer solutions resist the change in pH.
- They are weak acids or weak bases containing their counter conjugate as a common ion.
- *OR* Buffers are mixtures of:

A weak acid <u>and</u> its conjugate base

OR A weak base <u>and</u> its conjugate acid

- High pH-change resisting buffer has high concentrations of both of these buffer components.

Henderson–Hasselbalch Equation:

Consider the general weak acid equilibrium below:

$$HA_{(aq)} \rightleftharpoons H^{+}{}_{(aq)} + A^{-}{}_{(aq)}$$

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

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

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

- For a particular buffering system (conjugate acid–base pair), all solutions that have the same ratio $[A^{-}] / [HA]$ will have the same pH.

For the general weak base/conjugate acid buffer, B/HB^+:

$$B_{(aq)} + H_2O_{(aq)} \rightleftharpoons HB^+_{(aq)} + OH^-_{(aq)}$$

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

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

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

For a particular weak base/conjugate acid buffer, the pOH is a function of the ratio of the concentrations of HB^+/B.

Calculating the pH of buffer solutions:

What is the pH of a buffer solution that is 0.45 *M* acetic acid ($HC_2H_3O_2$) and 0.85 M sodium acetate ($NaC_2H_3O_2$)? The K_a for acetic acid is 1.8×10^{-5}.

$$CH_3COONa_{(aq)} \rightarrow \underset{0.85\ M}{CH_3COO^-_{(aq)}} + Na^+_{(aq)}$$

$$\underset{0.45\ -\ x}{CH_3COOH_{(aq)}} \rightleftharpoons \underset{x}{H^+_{(aq)}} + \underset{x}{CH_3COO^-_{(aq)}}$$

$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} \quad ; \quad [H^+] = K_a \frac{[CH_3COOH]}{[CH_3COO^-]}$$

The equilibrium concentrations are:

$[H^+] = x$; $[CH_3COO^-] = (x + 0.85\ M) \approx 0.85\ M$

From which:

$[H^+] = (1.8 \times 10^{-5})(0.45/0.85) = 9.53 \times 10^{-6}$

$pH = -\log(9.53 \times 10^{-6}) = 5.02$ <u>acidic</u>

Calculating the pH of buffer solutions:

Consider a buffer composed of base and its conjugate acid.

Weak base/conjugate acid buffer:

Example: (NH_3/NH_4^+), pH = ?

Here we calculate pOH, from which pH is calculated.

OR calculate the $[H^+]$ from $[OH^-]$ and calculate the pH.

$pOH = pK_b + \log(\text{acid/base})$ *Then* , $pH = 14.0 - pOH$

Example: NH_3/NH_4^+ Buffer ; $K_b = 1.8\text{x}10^{-5}$

Calculate the pH of a buffer of 0.25 M NH_3 and 0.40 M NH_4Cl?

$NH_4Cl_{(aq)} \rightarrow NH_4^+{}_{(aq)} + Cl^-{}_{(aq)}$ *(strong electrolyte)*

0.40 M

$NH_{3(aq)} + H_2O_{(aq)} \rightleftharpoons NH_4^+ + OH^-{}_{(aq)}$ *(weak base)*

At eq.: (0.25M – x) x x

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

At equilibrium: since x is very small, then:

$[NH_4^+] = (x + 0.40) \cong 0.4$ and $[NH_3] = (0.25M - x) \cong 0.25$

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

$$= (1.8\text{x}10^{-5})\frac{(0.25)}{(0.40)} = 1.125\text{x}10^{-5}\text{ M}$$

pOH = - log($1.125\text{x}10^{-5}$) = 4.95

pH = 14.00 – 4.95 = 9.06 *(basic)*

Or Calculate $[H^+] = 1\text{x}10^{-14}/1.125\text{x}10^{-5}$

$= 8.89\text{x}10^{-5}$

pH = 9.06

Example:

Calculate the pH of a solution produced when 0.012 mol. of HCl is added to 1.0 L of water. Assume no volume change of solution.

Answer: HCl is strong monoprotic acid.

$$[H^+] = \frac{0.012mol}{1.0L} = 0.012\ M$$

$$pH = -\log(0.012) = 1.92$$

Example:

Calculate the pH of a buffer solution that is 0.50 M in acetic acid and 0.55M in sodium acetate?

Solution:

$$pH = pK_a + \log\frac{[CH_3COO^-]}{[CH_3COOH]}$$

$$= -log 1.8x10^{-5} + \log\frac{0.50}{0.55}$$

$$= 4.74 - 0.041 = 4.70$$

Example:

Calculate the change in pH of the buffer upon addition of 0.012 mol. of HCl to 1.0 liter of the buffer solution.

(assume no change in volume of the solution) *Homework*

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

The new concentrations of the acid and its conjugate base are:

$[CH_3COO^-]= 0.55 – 0.012 = 0.538$

$[CH_3COOH]= 0.50 + 0.012 = 0.512$

$$pH = pK_a + \log \frac{[CH_3COO^-]}{[CH_3COOH]}$$

$$= -\log 1.8 \times 10{-}5 + \log \frac{0.538}{0.512}$$

$$= 4.74 + 0.0215$$

$$= 4.76$$

NOTE about buffer solutions:

(i) Addition of HCl to Water:

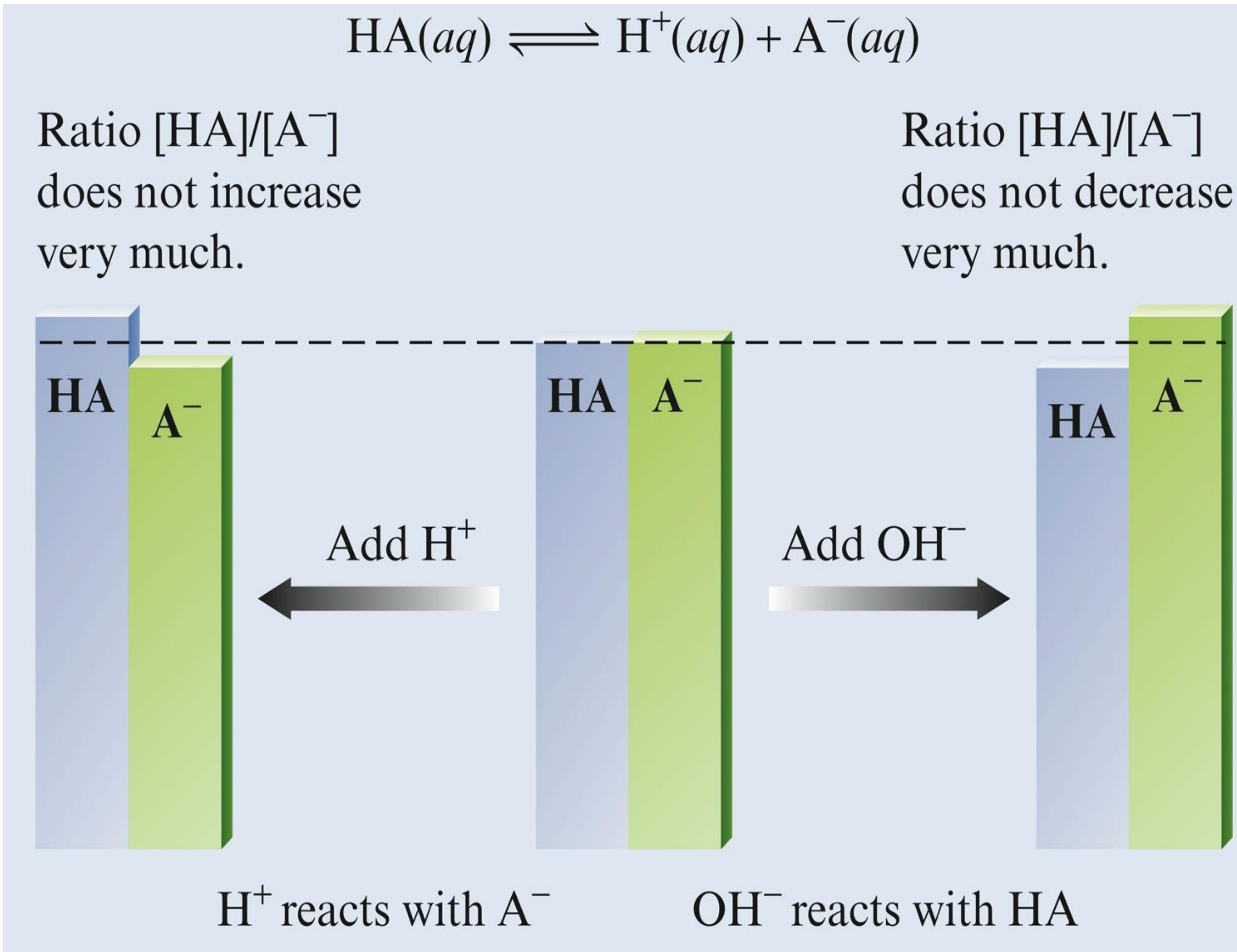
$$\Delta pH = 7.00 - 1.92 = 5.08$$

(ii) Addition of HCl to a buffer:

$$\Delta pH = 4.76 - 4.70 = 0.06$$

Draw your conclusion

How Buffers Work?



Effect of added H^+ or OH^- on a buffered system.

Buffer Solution Characteristics

- Good buffers contain relatively large concentrations of a weak acid and its conjugate base.
- An added H^+ reacts to completion with the weak base.
- An added OH^- reacts to completion with the weak acid.

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

Buffered Solution Characteristics

- The pH in the buffered solution is determined by the ratio of the concentrations of the weak acid and its conjugate base. As long as this ratio remains constant, the pH will remain the same. This will be the case as long as the concentrations of the buffering materials (HA and A^- or B and BH^+) are large compared with amounts of H^+ or OH^- added.
- Buffer Capacity.
- Resist dilution.

- Buffer Capacity is defined as the amount (moles) of protons or hydroxide ions that the buffer can consume without a significant change in pH.
- Determined by the magnitudes of [HA] and [A^-].
- A buffer with large capacity contains large concentrations of the buffering components.

- Optimal buffering occurs when [HA] is equal to [A^-].
- It is for this condition that the ratio [A^-]/[HA] is most resistant to change in pH when H^+ or OH^- is added to the buffered solution.

Choosing a Buffer

- pK_a of the weak acid to be used in the buffer should be as close as possible to the desired pH.
- Buffers are best used for solutions of pH in the range of

$$pH = pK_a \pm 1$$

pH values of Some Body Fluids	
Blood	7.35-7.45
Saliva	5.4-7.5
Gastric juice	1.5-3.5
Urine	4.5-8.5
Bile	6.0-8.5

The three main Buffer systems in body fluids:

1. Carbonic acid/carbonate buffer system.

H_2CO_3 / HCO_3^- / $CO_3^=$ K_{a1} K_{a2}

H_2CO_3 / HCO_3^- buffer system is important for blood buffering

2. Phosphate buffer system.

H_3PO_4 / $H_2PO_4^-$/ $HPO_4^=$/ PO_4^{3-} K_{a1} K_{a2} K_{a3}

$H_2PO_4^-$/ $HPO_4^=$ buffer system is important for saliva buffering

3. Protein buffer system.

Proteins are amino acids, they contain both positively charged amino groups and negatively charged carboxylic acid groups, they have ability to bind H^+ and OH^- ions, so, they have the ability to act as buffers.

End of Chapter 15