CHM 1220-Dang

Chapter 17 - Applications of Aqueous Equilibria

17.1 Neutralization Reactions

Four Types of Neutralization Reactions:

1. Strong Acid – Strong base
2. Weak acid – Strong base
3. Strong acid – Weak base
4. Weak acid – Weak base

<u>Strong Acid - Strong Base</u>

Let consider the reaction between HCl and NaOH. If we mixed equal moles of HCl and NaOH then the concentrations of H_3O^+ and ^-OH remaining in the NaCl solution after neutralization will be the same as those in pure water, $[H_3O^+] = [^-OH] = 1.0 \times 10^{-7}$M.

$$HCl(aq) + NaOH(aq) \rightleftharpoons H_2O(l) + NaCl(aq)$$

Assume complete dissociation:

$$H_3O^+(aq) + OH^-(aq) \rightleftharpoons 2\,H_2O(l)$$

(net ionic equation)

After neutralization: **pH = 7**

The equilibrium $\mathbf{K_n}$ ("n" neutralization)

$$K_n = \frac{1}{[H_3O^+][^-OH]} = \frac{1}{K_w} = \frac{1}{1.0 \times 10^{-14}} = 1.0 \times 10^{14}$$

The value of K_n for a strong acid–strong base reaction is a very large number, which means that the neutralization reaction proceeds essentially 100% to completion.

Weak Acid – Strong Base

- Weak acid partially ionized and the net ionic equation for the neutralization reaction of a weak acid with a strong base involves proton transfer can be shown in the reaction between acetic acid, CH_3CO_2H and NaOH:

$$CH_3CO_2H(aq) + NaOH(aq) \rightleftharpoons H_2O(l) + NaCH_3CO_2(aq)$$

Assume complete dissociation:

$$CH_3CO_2H(aq) + OH^-(aq) \rightleftharpoons H_2O(l) + CH_3CO_2^-(aq)$$

(net ionic equation)

After neutralization: **pH > 7**

$$
\begin{array}{lll}
 & CH_3CO_2H(aq) + \cancel{H_2O(l)} \rightleftharpoons \cancel{H_3O^+(aq)} + CH_3CO_2^-(aq) & K_a = 1.8 \times 10^{-5} \\
 & \cancel{H_3O^+(aq)} + OH^-(aq) \rightleftharpoons \cancel{H_2O(l)} + H_2O(l) & 1/K_w = 1.0 \times 10^{14} \\
\hline
\text{Net:} & CH_3CO_2H(aq) + OH^-(aq) \rightleftharpoons H_2O(l) + CH_3CO_2^-(aq) & K_n = (K_a)(1/K_w) = (1.8 \times 10^{-5})(1.0 \times 10^{14}) \\
 & & = 1.8 \times 10^{9}
\end{array}
$$

The resulting large value of $K_n = 1.8 \times 10^9$ means that the neutralization reaction proceeds nearly 100% to completion. As a general rule, the neutralization of any weak acid with a strong base will go 100% to completion because ^-OH has a great affinity for protons. After neutralization of equal molar amounts of CH_3CO_2H and NaOH, the solution contains Na^+, which has no acidic or basic properties, and $CH_3CO_2^-$, which is a weak base. Therefore, the pH is greater than 7.

Strong Acid – Weak Base

A strong acid HCl is completely dissociated into H_3O^+ and A^- ions, and its neutralization reaction with a weak base therefore involves proton transfer from H_3O^+ to the weak base NH_3:

$$HCl(aq) + NH_3(aq) \rightleftharpoons NH_4Cl(aq)$$

Assume complete dissociation:

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

(net ionic equation)

After neutralization: **pH < 7**

$$
\begin{array}{lll}
 & NH_3(aq) + \cancel{H_2O(l)} \rightleftharpoons NH_4^+(aq) + \cancel{OH^-(aq)} & K_b = 1.8 \times 10^{-5} \\
 & \cancel{H_3O^+(aq)} + OH^-(aq) \rightleftharpoons \cancel{H_2O(l)} + H_2O(l) & 1/K_w = 1.0 \times 10^{14} \\
\hline
\text{Net:} & H_3O^+(aq) + NH_3(aq) \rightleftharpoons H_2O(l) + NH_4^+(aq) & K_n = (K_b)(1/K_w) \\
 & & = (1.8 \times 10^{-5})(1.0 \times 10^{14}) \\
 & & = 1.8 \times 10^{9}
\end{array}
$$

Again, because the equilibrium constant $K_n = 1.8 \times 10^9$ is a very large number, we know the neutralization reaction proceeds nearly 100% to the right. The neutralization of any weak base with a strong acid generally goes 100% to completion because $H_3O^+$is a powerful proton donor. After the neutralization of equal molar amounts of NH_3 and HCl, the solution contains NH_4^+, which is a weak acid, and Cl^- , which has no acidic or basic properties. Therefore, the pH is less than 7.

Weak Acid–Weak Base

Both a weak acid CH_3CO_2H and a weak base NH_3 are largely undissociated, and the neutralization reaction between them therefore involves proton transfer from the weak acid to the weak base.

$$CH_3CO_2H(aq) + NH_3(aq) \rightleftharpoons NH_4CH_3CO_2(aq)$$

Assume complete dissociation:

$$CH_3CO_2H(aq) + NH_3(aq) \rightleftharpoons NH_4^+(aq) + CH_3CO_2^-(aq)$$

(net ionic equation)

After neutralization: **pH = ?**

$$
\begin{array}{lrcll}
 & CH_3CO_2H(aq) + \cancel{H_2O(l)} & \rightleftharpoons & \cancel{H_3O^+(aq)} + CH_3CO_2^-(aq) & K_a = 1.8 \times 10^{-5} \\
 & NH_3(aq) + \cancel{H_2O(l)} & \rightleftharpoons & NH_4^+(aq) + \cancel{OH^-(aq)} & K_b = 1.8 \times 10^{-5} \\
 & \cancel{H_3O^+(aq)} + \cancel{OH^-(aq)} & \rightleftharpoons & \cancel{2\,H_2O(l)} & 1/K_w = 1.0 \times 10^{14} \\
\hline
\text{Net:} & CH_3CO_2H(aq) + NH_3(aq) & \rightleftharpoons & NH_4^+(aq) + CH_3CO_2^-(aq) & K_n = (K_a)(K_b)(1/K_w)
\end{array}
$$

$$K_n = (K_a)(K_b)\left(\frac{1}{K_w}\right) = (1.8 \times 10^{-5})(1.8 \times 10^{-5})(1.0 \times 10^{14}) = 3.2 \times 10^4$$

The value of K_n in this case is smaller than it is for the preceding three cases, indicating that the neutralization does not proceed as far toward completion. In general, weak acid–weak base neutralizations have less tendency to proceed to completion than neutralizations involving strong acids or strong bases.

17.2 The Common-Ion Effect

- The shift in the position of an equilibrium on addition of a substance that provides an ion in common with one of the ions already involved in the equilibrium.

A solution of a weak acid HA and its conjugate base A- is an important acid–base mixture because such mixtures regulate the pH in biological systems. If a conjugate base A- is added to a solution of a weak acid (HA), then A^- is considered to be a common ion because it is already present in the mixture as a product of the acid-dissociation reaction.

$$HA_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + A^-_{(aq)}$$

common ion

The solution of acetic acid (CH_3CO_2H) with $[H_3O^+] = 1.8 \times 10^{-5}$ M and a pH of 2.89. The yellow solution on the left-hand side of the figure contains a solution that is 0.10 M in both the weak acid (CH_3CO_2H) and its conjugate base ($CH_3CO_2^-$) with $[H_3O^+] = 1.3 \times 10^{-3}$ and a pH of 4.74.

$$CH_3CO_2H_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + CH_3CO_2^-{}_{(aq)}$$

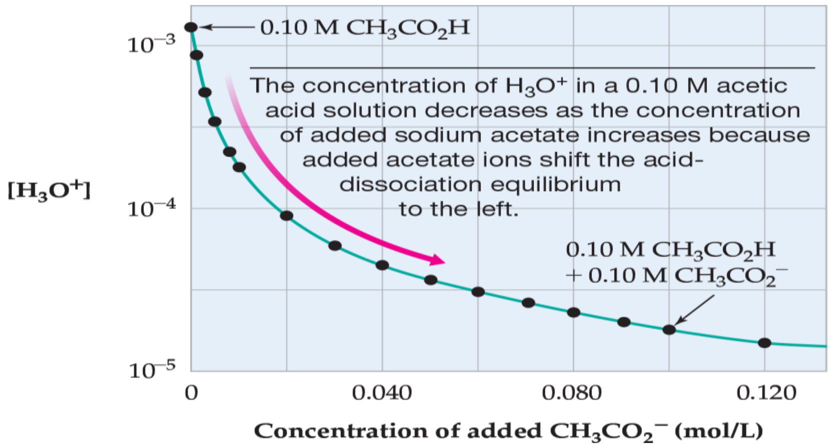
The pink solution on the right-hand side of the figure 17.1 is a 0.10 M

$CH_3CO_2H(aq)$–$CH_3CO_2Na(aq)$
$[H_3O^+] = 1.8 \times 10^{-5}$ M
pH = 4.74

$CH_3CO_2H(aq)$
$[H_3O^+] = 1.3 \times 10^{-3}$ M
pH = 2.89

The difference in pH is revealed by the color of the indicator methyl orange, which changes from yellow to red in the pH range 3.2–4.4

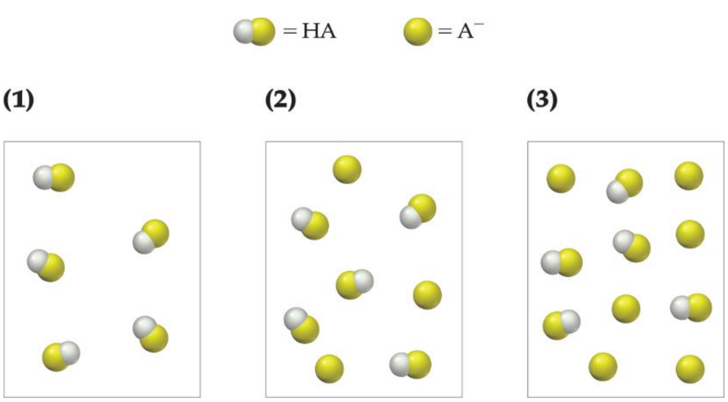
The decrease in $[H_3O^+]$ that occurs when acetate ions have been added to the acetic acid solution is an example of the **common-ion effect**, the shift in equilibrium that occurs when adding a substance that increases the concentration of an ion already involved in the equilibrium (Le Chatelier's Principle).



Example: Calculate the pH, and the percent dissociation of acetic acid in a solution that is 0.10 M in CH_3CO_2H and 0.10 M in $NaCH_3CO_2$. (For comparison, the pH of a 0.10 M CH_3CO_2H solution that contains no $NaCH_3CO_2$ is 2.89 and the percent dissociation is 1.3%.)

Example: Determining the Effect of a Common Ion on pH and Percent Dissociation

The following pictures represent initial concentrations in solutions of a weak acid HA that may also contain the sodium salt NaA. Which solution has the highest pH? Which has the largest percent dissociation of HA? (Na^+ and H_3O^+ ions and solvent water molecules have been omitted for clarity.)



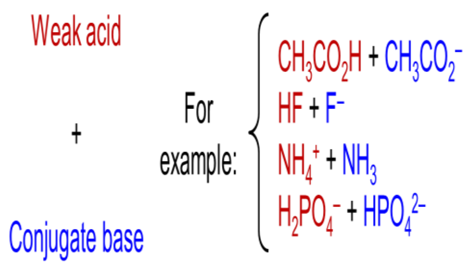
17.3 – Buffer Solutions

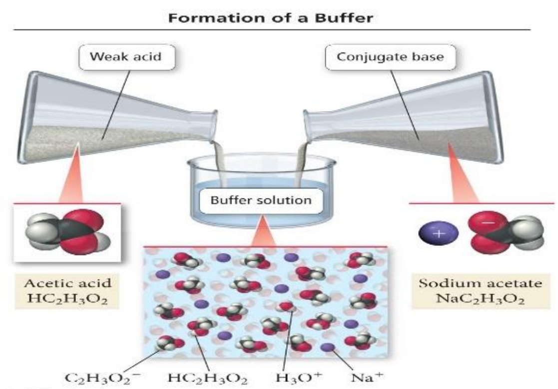
A solution of a weak acid and its conjugate base in an important acid-base mixture because such mixture regulate the pH in biological systems.

- A solution that resists changes in pH when a small amount of acid or base is added. The best buffer systems consist of either:

a) a weak acid and a salt containing its conjugate base (e.g. $HC_2H_3O_2$ and $NaC_2H_3O_2$)

b) a weak base and a salt containing its conjugate acid (e.g. NH_3 and NH_4Cl).





Buffers are important in Biochemistry because many of the enzymes that make your body run are designed to work at one particular pH, if the solution doesn't have the right pH things go wrong. Organisms (and humans) have built-in buffers to protect them against changes in pH.

Cardiac arrest is one condition that can add acid to blood due to the buildup of carbon dioxide that occurs when the heart stops circulating blood. In contrast, hyperventilation increases the amount of CO_2 removed from the body and can raise blood pH. Human blood is maintained by a combination of CO_3^{-2}, PO_4^{-3} and protein buffers.

Blood: (pH 7.4)   Death = 7.0 <pH > 7.8 = Death

How does the buffer resist the drastic change in pH?

Buffers work by applying Le Châtelier's principle to weak acid equilibrium.
Buffer solutions contain significant amounts of the weak acid molecules, HA .

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

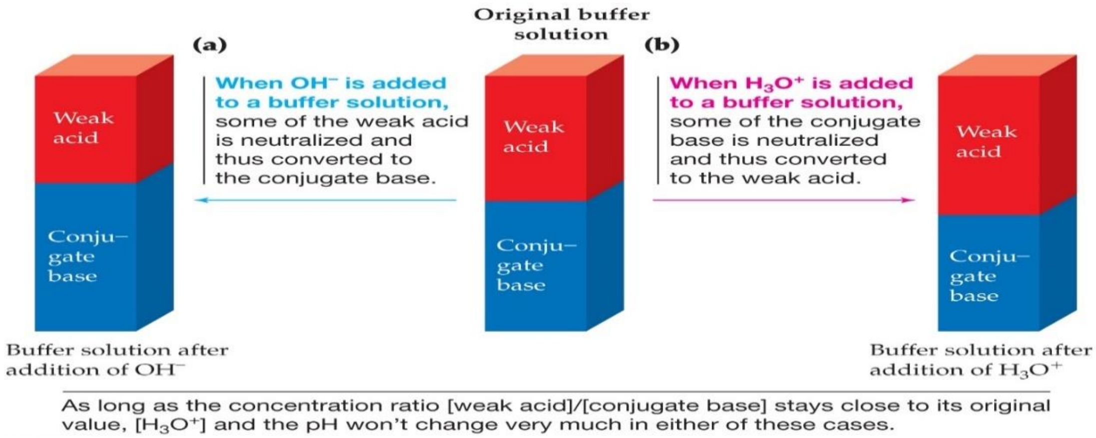
When a **strong acid (H_3O^+)** is added to a buffer solution the conjugate base present in the buffer consumes the hydronium ion converting it into water and the weak acid of the conjugate base.

The net-ionic neutralization reaction is $A^-(aq) + \mathbf{H_3O^+}(aq) \rightarrow H_2O(l) + HA(aq)$

This results in a decrease in the amount of conjugate base present and an increase in the amount of the weak acid. The pH of the buffer solution decreases by a very small amount.

When a **strong base (OH^-)** is added to a buffer solution, the hydroxide ions are consumed by the weak acid forming water and the weaker conjugate base of the acid. The amount of the weak acid decreases while the amount of the conjugate base increases. This prevents the pH of the solution from significantly rising, which it would if the buffer system was not present.

The net-ionic neutralization reaction is $\mathbf{OH^-(aq)} + HA(aq) \rightarrow H_2O(l) + A^-(aq)$



Example: pH of human blood (pH = 7.4) controlled by conjugated acid-base pairs (H_2CO_3/HCO_3^-). Write an equation for this buffer mixture then neutralization equation for the following effects.

- With addition of HCl

- With addition of NaOH

Example: Calculate the pH of the buffer that results from mixing 60.0 mL of 0.250 M $HCHO_2$ and 15.0 mL of 0.500 M $NaCHO_2$ $K_a = 1.7 \times 10^{-4}$

Calculate the pH after adding 5.00 mmoles of HNO_3 added to the solution. Assume no change in volume.

Example: Calculate the pH of 0.100 L of a buffer solution that is 0.25 M in HF and 0.50 M in NaF with an initial pH of 3.76 after the addition of 10.0 mL of 0.100M KOH.

Buffer Capacity

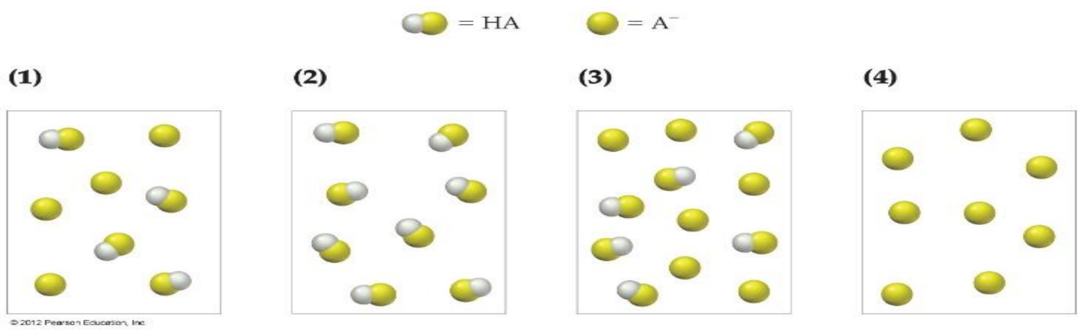
The buffer capacity is the amount of acid or base the buffer can neutralize before there is a significant change in pH. The buffer capacity is a measure of the effectiveness of a buffer.

- A measure of amount of acid or base that the solution can absorb without a significant change in pH.
- Depends on how many moles of weak acid and conjugated base are present.
- Buffer capacity is greater when larger amounts of HA and A- are present.

The buffering range is the pH range the buffer can be effective. The pH will stay relatively constant as long as [HA] and [A-] are greater than the amount of acid or base added.

- Buffers work best when [HA] and [A-] are approximately equal.
- For buffers to be effective, 0.1 < [base] : [acid] < 10.
- For an equal volume of solution: the more concentrated the solution, the greater buffer capacity
- For an equal concentration: the greater the volume, the greater the buffer capacity

Example: The following pictures represent solutions that contain a weak acid HA and/ or its sodium salt NaA. (Na+ ions and solvent water molecules have been omitted for clarity



a. Which of the solutions are buffer solution?

b. Which solution has the greatest buffer capacity?

The Henderson-Hasselbalch Equation

An equation derived from the Ka expression that allows us to calculate the pH of a buffer solution.

The equation calculates the pH of a buffer from the pK_a and initial concentrations of the weak acid and salt of the conjugate base, as long as the "x is small" approximation is valid.

Weak acid Conjugate base

$$\text{Acid}(aq) + H_2O(l) \rightleftharpoons H_3O^{1+}(aq) + \text{Base}(aq)$$

$$K_a = \frac{[H_3O^{1+}][\text{Base}]}{[\text{Acid}]} \qquad [H_3O^{1+}] = K_a \frac{[\text{Acid}]}{[\text{Base}]}$$

$$\boxed{pH = pK_a + \log\left(\frac{[\text{Base}]}{[\text{Acid}]}\right)}$$

The real importance of the Henderson–Hasselbalch equation, particularly in biochemistry, is that it tells us how the pH affects the percent dissociation of a weak acid.

$$\text{At pH} = \text{p}K_a + 2.00 \quad \frac{[\text{Base}]}{[\text{Acid}]} = 1.0 \times 10^{2} = \frac{100}{1} \quad 99\% \text{ dissociation}$$

$$\text{At pH} = \text{p}K_a + 1.00 \quad \frac{[\text{Base}]}{[\text{Acid}]} = 1.0 \times 10^{1} = \frac{10}{1} \quad 91\% \text{ dissociation}$$

$$\text{At pH} = \text{p}K_a + 0.00 \quad \frac{[\text{Base}]}{[\text{Acid}]} = 1.0 \times 10^{0} = \frac{1}{1} \quad 50\% \text{ dissociation}$$

$$\text{At pH} = \text{p}K_a - 1.00 \quad \frac{[\text{Base}]}{[\text{Acid}]} = 1.0 \times 10^{-1} = \frac{1}{10} \quad 9\% \text{ dissociation}$$

$$\text{At pH} = \text{p}K_a - 2.00 \quad \frac{[\text{Base}]}{[\text{Acid}]} = 1.0 \times 10^{-2} = \frac{1}{100} \quad 1\% \text{ dissociation}$$

Example: Calculate the pH of a buffer solution that is 0.0500 M in benzoic acid ($HC_7H_5O_2$) and 0.150 M in sodium benzoate ($NaC_7H_5O_2$). $K_a = 6.5 \times 10^{-5}$

Example: What $[NH_3]/[NH_4^+]$ ratio is required for a buffer solution that has pH = 7.00. Is a mixture of NH_3 and NH_4Cl a good choice for a buffer having pH= 7.00?