Buffered Solutions

In the FORCE must you trust…

From Ch 15, we have learned that the common-ion effect can shift the equilibrium of a weak electrolyte due to the presence of a common ion.

For example:

\[ \text{AgNO}_3(s) \rightleftharpoons \text{Ag}^+(aq) + \text{NO}_3^-(aq) \]

Can be shifted by the addition of HCl

\[ \text{Ag}^+(aq) + \text{Cl}^-(aq) \rightarrow \text{AgCl}(s) \]

1. Calculate the pH for a 1.0 \( M \) HF solution and for a solution containing 1.5 \( M \) HF and 1.5 \( M \) NaF.

For the reaction:

\[ \text{HF}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{F}^-(aq) \]

\[ K_a = 7.2 \times 10^{-4} \]

The most practical application for acid-base solutions containing common ions is for buffering.

A buffered solution (or buffer) is an aqueous solution that resists changes in pH.

A buffered solution may contain a weak acid and a salt of its conjugate base, or a weak base and a salt of its conjugate acid.

Consider a solution of NH\(_3\) (a weak base) and NH\(_4\)Cl (a salt of the conjugate acid)

- This is a basic solution:
  \[ \text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^- \]
  \[ K_b = 1.8 \times 10^{-5} \]

- The Species present in the solution include: NH\(_3\), H\(_2\)O, NH\(_4^+\), OH\(^-\) and Cl\(^-\).

- Notice, the chlorine does not affect the chemical system since it has no affinity for any other species present.

- If we add acid:
  \[ \text{H}^+ + \text{NH}_3 \rightarrow \text{NH}_4^+ \]

- If we add base:
  \[ \text{OH}^- + \text{NH}_4^+ \rightarrow \text{NH}_3 + \text{H}_2\text{O} \]

Notice, only the concentration of conjugate changes, not the \( \text{H}^+ \) or \( \text{OH}^- \); therefore, no appreciable change in pH
When looking at any solution, it is important to identify every species present and try to reason the interactions between all species present.

Examine the species present in problem 1 above:

What is the buffer system in this solution?

Write the reactions for the addition of an acid and a base to this solution.

If a small amount of hydroxide is added to an equimolar solution of HF in NaF, for example, the HF reacts with the OH\(^{-}\) to make F\(^{-}\) and water.

\[
\text{OH}^{-} + \text{HF} \rightarrow \text{H}_2\text{O} + \text{F}^{-}
\]

If acid is added, the F\(^{-}\) reacts to form HF and water.

\[
\text{H}^{+} + \text{F}^{-} \rightleftharpoons \text{HF}
\]

Notice, no appreciable change in pH

2. Write the reactions for the addition of acid and base to the following buffer systems:
   
   A) acetic acid in lithium acetate
   
   B) benzoic acid in sodium benzoate
   
   C) carbonic acid in sodium carbonate
   
   Make sure to think about all species present

It is important for you to identify why a buffered solution resists changes in pH. (focus on the conjugates)

Take H\(_2\)CO\(_3\) in NaHCO\(_3\)

The solution is acidic by nature:

\[
\text{H}_2\text{CO}_3 \rightleftharpoons \text{H}^{+} + \text{HCO}_3^{-} \quad K_a = 4.3 \times 10^{-7}
\]

By adding NaHCO\(_3\), what happens to the equilibrium? pH?
So, how does the Common-ion effect and Le Chatelier’s Principle describe the operation of a buffer?

By adding acid, we would expect the pH to lower, however it doesn’t:

\[ \text{H}^+ + \text{HCO}_3^- \rightleftharpoons \text{H}_2\text{CO}_3 \]

Notice, free H\(^+\) ions do not accumulate, so if the acid concentration and conjugate base concentrations are high enough, no change in pH occurs.

What would happen to the system if it were very dilute concentration of acid or salt?

Likewise, by adding base we would expect an increase in pH

\[ \text{OH}^- + \text{H}_2\text{CO}_3 \rightarrow \text{H}_2\text{O} + \text{HCO}_3^- \]

Again, notice that the OH\(^-\) concentration does not increase, only conjugate base ions decrease.

Let’s investigate the pH of a buffered solution.

3. Calculate the pH of a buffered solution containing 0.50 M acetic acid \((K_a = 1.8 \times 10^{-5})\) and 0.50 M sodium acetate.

4. a) How does the pH of the buffered solution in problem 3 compare to the pH of the unbuffered 0.50 M acetic acid solution?

b) Does this make sense?

5. Lactic acid \((\text{HC}_3\text{H}_5\text{O}_3)\) is a common constituent of biological systems. Calculate the pH of a solution containing 0.75 M lactic acid \((K_a = 1.4 \times 10^{-4})\) and 0.25 M sodium lactate.
Examine the equilibrium expression for a weak acid:

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

To investigate the pH of a buffered solution, we simply need to rearrange the equation to solve for [H+], the derivative of pH.

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

from this expression, we note that [H+], and thus pH, is determined by two factors: the value of \( K_a \) for the weak-acid component of the buffer, and the ratio of the concentrations of the conjugate acid-base pair, \([HA][A^-]\)

\[ [H^+] = K_a \left( \frac{[HA]}{[A^-]} \right) \]

Now, look at what happens to the pH if acid or base is added to the buffered solution.

As long as the change in the ratio \([HA][A^-]\) is small, the change in pH will be small.

This is what makes buffers resistant to changes in pH when strong acids or bases are added, and why they are so important in biological systems.

Observe:

\[ -\log[H^+] = -\log K_a \left( \frac{[HA]}{[A^-]} \right) \]

\[ \text{pH} = -\log K_a + \left( -\log \frac{[HA]}{[A^-]} \right) \]

\[ \text{pH} = pK_a + \log \left( \frac{[A^-]}{[HA]} \right) \]

This expression is not particularly useful in this form, however, by taking the –log of the expression, we have a formula that will provide us with the pH of any buffered solution given the initial weak acid/conjugate base concentrations.

Likewise, we can calculate the initial concentrations needed to produce a buffered solution at any particular pH.

Rewritten:

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

\( \text{Henderson-Hasselbalch equation} \)

Or for a buffered base:

\[ \text{pOH} = pK_b + \log \left( \frac{\text{Acid}}{\text{Base}} \right) \]

Try to derive this expression from a weak base equilibrium (AP Equation sheet)

How is the 5% assumption related to the Henderson-Hasselbalch equation?

7. A buffered solution contains 0.25 $M$ ammonia and 0.40 $M$ ammonium bromide. Calculate the pH of the solution.

(AP Equation sheet)

$K = \ldots$