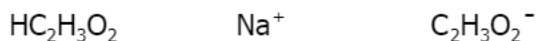# EXPERIMENT 16   BUFFER SOLUTIONS
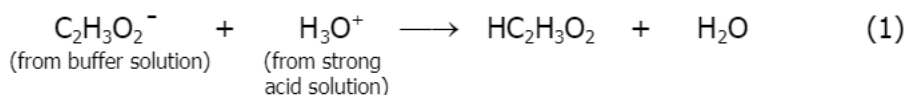
INTRODUCTION

A buffer is a solution that resists change in its pH upon addition of limited amounts of strong acid or strong base or upon dilution.

Consider a buffer solution that is a mixture on the weak acid, acetic acid, and its salt, sodium acetate. In the buffer solution, the solute particles are:
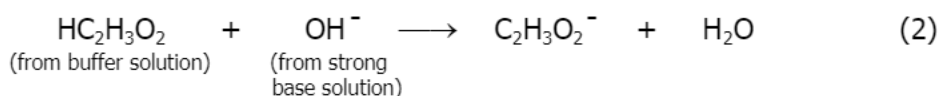
$$HC_2H_3O_2 \qquad\qquad Na^+ \qquad\qquad C_2H_3O_2^-$$

Notice: the buffer solute particles include the weak acid $HC_2H_3O_2$ and its conjugate base $C_2H_3O_2^-$. These are the particles that will do the buffering. The sodium ion is a spectator ion.

If a strong acid solution were added to the buffer solution, the $C_2H_3O_2^-$ ions in the buffer solution would react with (neutralize) the H_3O^+ ions from the strong acid as shown in the net ionic equation for the neutralization reaction:

$$\underset{\text{(from buffer solution)}}{C_2H_3O_2^-} \quad + \quad \underset{\substack{\text{(from strong} \\ \text{acid solution)}}}{H_3O^+} \quad\longrightarrow\quad HC_2H_3O_2 \quad + \quad H_2O \qquad\qquad (1)$$

Or, if a strong base were added to the buffer solution, the $HC_2H_3O_2$ molecules in the buffer solution would react with (neutralize) the OH^- ions from the strong base as shown in the net ionic equation for the neutralization reaction:

$$\underset{\text{(from buffer solution)}}{HC_2H_3O_2} \quad + \quad \underset{\substack{\text{(from strong} \\ \text{base solution)}}}{OH^-} \quad\longrightarrow\quad C_2H_3O_2^- \quad + \quad H_2O \qquad\qquad (2)$$

The equations above show that a buffer solution (often called "buffer system") will maintain its pH even when considerable amounts of strong acid or base are added. Up until enough strong acid solution is added to use up most of the $C_2H_3O_2^-$ ions present in the buffer (see equation 1), or up until enough strong base solution is added to use up most of the $HC_2H_3O_2$ in the buffer solution (see equation 2), the buffer pH will remain constant to ± 1.

The ability of a buffer solution to maintain its pH is called its ***buffering capacity***. Greatest buffering capacity is obtained if the buffer solution contains equimolar concentrations (equal molar concentrations) of the weak acid and its conjugate base. In the case of our buffer system, that means

$$[HC_2H_3O_2] = [C_2H_3O_2^-]$$

In the buffer solution, $HC_2H_3O_2$ ionizes very little because of the presence of its conjugate base, $C_2H_3O_2^-$, which is its common ion.

$$HC_2H_3O_2 \ + \ H_2O \ \rightleftharpoons \ H_3O^+ + C_2H_3O_2^-$$
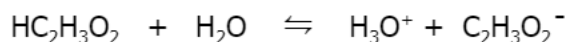
therefore, at equilibrium, in the buffer solution, we can assume that

$$[HC_2H_3O_2] \ = \ \underline{M}\ HC_2H_3O_2 \qquad \text{and} \qquad [C_2H_3O_2^-] \ = \ \underline{M}\ C_2H_3O_2^-$$

Consequently,

$$\left[\frac{[C_2H_3O_2^-]}{[HC_2H_3O_2]}\right] \quad = \quad \left[\frac{\underline{M}\ C_2H_3O_2^-}{\underline{M}\ HC_2H_3O_2}\right] \quad = \quad 1$$

As a result, in a buffer solution containing equimolar concentrations of $HC_2H_3O_2$ and $C_2H_3O_2^-$, the hydronium ion concentration, $[H_3O^+]$, is equal to the K_a:

$$K_a \ = \ [H_3O^+] \left[\frac{[C_2H_3O_2^-]}{[HC_2H_3O_2]}\right] \overset{\displaystyle 1}{\longleftarrow}$$

1

therefore: $$K_a = [H_3O^+]$$

and

$$\frac{K_a}{[H_3O^+]} = \frac{[C_2H_3O_2^-]}{[HC_2H_3O_2]}$$

HOW TO MAKE A BUFFER SOLUTION:

One way to make a buffer solution is to first select a weak acid that has a K_a that is close to the

	ACID	K	CONJUGATE BASE
Hydrogen sulfate ion	HSO_4^-	$K_a = 1.1 \times 10^{-2}$	SO_4^{2-}
Sulfurous acid	H_2SO_3	$K_a = 1.3 \times 10^{-2}$	HSO_3^-
Phosphoric acid	H_3PO_4	$K_a = 6.9 \times 10^{-3}$	$H_2PO_4^-$
Formic acid	$HCHO_2$	$K_a = 1.7 \times 10^{-4}$	CHO_2^-
Acetic acid	$HC_2H_3O_2$	$K_a = 1.7 \times 10^{-5}$	$C_2H_3O_2^-$
Carbonic Acid	H_2CO_3	$K_a = 4.3 \times 10^{-7}$	HCO_3^-
Hypochlorous acid	$HClO$	$K_a = 3.5 \times 10^{-8}$	ClO^-
Dihydrogen phosphate ion	$H_2PO_4^-$	$K_a = 6.2 \times 10^{-8}$	HPO_4^{2-}
Bicarbonate ion	HCO_3^-	$K_a = 4.8 \times 10^{-11}$	CO_3^{2-}
Ammonium ion	NH_4^+	$Ka = 5.6 \times 10^{-10}$	NH_3
	BASE		CONJUGATE ACID
Ammonia	NH_3	$K_b = 1.8 \times 10^{-5}$	NH_4^+

$[H_3O^+]$ that you desire for your solution, or select a weak base whose K_b is close to the desired $[OH^-]$.

For example, if you wished to prepare a buffer solution of pH 4.20 —that is, $[H_3O^+] = 6.3 \times 10^{-5}$, you would look for the acid whose K_a is closest to 6.3×10^{-5}.

In this case, the best choice is $HC_2H_3O_2$ with $K_a = 1.7 \times 10^{-5}$, because it will give you the greatest buffering capacity.

$$HC_2H_3O_2 + H_2O \rightleftharpoons H_3O^+ + C_2H_3O_2^-$$
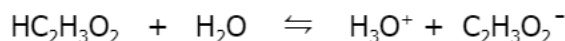
You will then calculate the ratio of Ka to desired $[H_3O^+]$ which is equal to the ratio of conjugate base to acid that you want to have in your buffer solution:

$$\frac{K_a}{[H_3O^+]} = \frac{[C_2H_3O_2^-]}{[HC_2H_3O_2]} \quad \begin{array}{l} \longleftarrow \quad conjugate\ base \\ \longleftarrow \quad acid \end{array}$$

$$\frac{1.7 \times 10^{-5}}{6.3 \times 10^{-5}} = \frac{0.27}{1} = \frac{[C_2H_3O_2^-]}{[HC_2H_3O_2]}$$

Therefore the ratio of M $C_2H_3O_2^-$ to M $HC_2H_3O_2$ in the buffer solution is 0.27 to 1. And since we will be using equimolar concentrations of conjugate base and acid, the ratio of the volume of conjugate base solution to volume of acid solution in the buffer will be 0.27 to 1

$$\frac{M\ C_2H_3O_2^-}{M\ HC_2H_3O_2} = \frac{0.27}{1} = \frac{V\ conjugate\ base\ soluton}{V\ acid\ solution}$$

To prepare a particular volume of this buffer, in which there are .27 parts conjugate base to 1 p art acid, first add the parts to get the total parts (in this case 1 + .27 = 1.27), and then divide the buffer solution volume by the total parts to get the volume per part. For example, if we wanted 30 mL of this buffer,

$$\frac{30\ mL}{1.27\ parts} = 23.6\ mL/part$$

Therefore the volume of acid solution is: 1 part acid x 23.6 mL/part = 23.6 mL acid solution
And the volume of conjugate base solution is: 30.0 mL – 23.6 mL = 6.4 mL conjugate base solution

The buffer solution is then prepared by adding 23.6 mL of the acid solution to 6.4 mL of the conjugate base solution.

EXPERIMENT

Check out a pH pen from the stockroom

A.   AMMONIUM ACETATE BUFFER SOLUTION + STRONG ACID

1.   Measure the pH of 1.0 $\underline{M}$ $NH_4C_2H_3O_2$ solution. Record the pH on the report sheet.

2.   Prepare 1 $\underline{M}$ HCl solution:

Prepare about 25 mL of 1 $\underline{M}$ HCl solution by diluting 6 $\underline{M}$ HCl (bottle #2 at your bench) with deionized water. **MIX WELL.**
Calculate volume of 6 $\underline{M}$ HCl needed:

3.   Label 2 test tubes and prepa re the following mixtures.

Tube #1:   5 mL deionized water + 2 drops methyl orange indicator
Tube #2:   5 mL 1.0 $\underline{M}$ $NH_4C_2H_3O_2$ (buffer) solution + 2 drops methyl orange indicator

4.   To Tube #1 add the 1 $\underline{M}$ HCl solution prepared in step 2 above drop by drop, stirring, and counting the number of drops needed to change the color of methyl orange (at about pH 3).

5.   Measure 10 mL of the 1 $\underline{M}$ HCl solution into your 10 mL graduated cylinder. Add the 1 $\underline{M}$ HCl solution to Tube #2 until the color of methyl orange has changed (about pH 3). You do not need to count drops, instead, read the final volume of HCl solution in your graduated cylinder and calculate the volume HCl add ed by taking the difference between 10 mL and the final volume. Record the volume on your report sheet.

SAVE THE REMAINNG 1 $\underline{M}$ HCl SOLUTION FOR USE IN PART C

B. AMMONIUM ACETATE BUFFER SOLUTION + STRONG BASE

   1.   Prepare 1 $\underline{M}$ NaOH solution:

        Prepare about 25 mL of 1 $\underline{M}$ NaOH solution by diluting 6 $\underline{M}$ NaOH (bottle #7 at your bench) with deionized water. **MIX WELL.**
        Calculate volume of 6 $\underline{M}$ NaOH needed:

   2.   Label 2 test tubes and prepare the following mixtures.

            Tube #1:   5 mL deionized water + 2 drops Alizarin Yellow R indicator
            Tube #2:   5 mL 1.0 $\underline{M}$ $NH_4C_2H_3O_2$ (buffer) solution + 2 drops Alizarin Yellow R indicator

   3.   To Tube #1 add the 1 $\underline{M}$ NaOH solution prepared in step 2 above drop by drop, stirring, and counting the number of drops needed to change the color of Alizarin Yellow R (at about pH 11).

   4.   Measure 10 mL of the 1 $\underline{M}$ NaOH solution into your 10 mL graduated cylinder. Add the 1 $\underline{M}$ NaOH solution to Tube #2 until the color of Alizarin Yellow R has changed (about pH 11). You do not need to count drops, instead, read the final volume of NaOH solution in your graduated cylinder and calculate the volume NaOH added by taking the difference between 10 mL and the final volume. Record the volume on your report sheet.

SAVE THE REMAINNG 1 $\underline{M}$ NaOH SOLUTION FOR USE IN PART C

C. SODIUM BICARBONATE BUFFER

   1.   Measure the pH of 0.10 $\underline{M}$ $NaHCO_3$ solution. Record the pH on the report sheet.

   2.   Label 2 test tubes and prepare the following mixtures.

            Tube #1:   5.00 mL 0.10 $\underline{M}$ $NaHCO_3$ + 2 drops methyl orange indicator
            Tube #2:   5.00 mL 0.10 $\overline{\underline{M}}$ $NaHCO_3$ + 2 drops Alizarin Yellow R indicator

   3.   Measure 10 mL of the 1 $\underline{M}$ HCl solution into your 10 mL graduated cylinder. Add the 1 $\underline{M}$ HCl solution to Tube #1 until the color of methyl orange has changed (about pH 3). Record the volume 1 $\underline{M}$ HCl solution required on your report sheet.

   4.   Measure 10 mL of the 1 $\underline{M}$ NaOH solution into your 10 mL graduated cylinder. Add the 1 $\underline{M}$ NaOH solution to Tube #2 until the color of Alizarin Yellow R has changed (about pH 11). Record the volume of 1 $\underline{M}$ NaOH solution required on your report sheet.

D. PREPARATION OF A BUFFER SOLUTION:

Your instructor will assign you a pH for your buffer solution. You will then prepare 20 to 30 mL of the buffer solution To do this, first choose from the table below the acid whose K_a is closest to your assigned $[H_3O^+]$.

	Acid	K_a	CONJUGATE BASE	SOLUTIONS FOR BUFFER PREPARATION	
				ACID OR ACID SALT	SALT OF CONJUGATE BASE
hydrogen sulfate ion	HSO_4^-	$K_a = 1.1 \times 10^{-2}$	SO_4^{2-}	0.1 M $NaHSO_4$	0.1 M Na_2SO_4
formic acid	$HCHO_2$	$K_a = 1.7 \times 10^{-4}$	CHO_2^-	0.1 M $HCHO_2$	0.1 M $NaCHO_2$
acetic acid	$HC_2H_3O_2$	$K_a = 1.7 \times 10^{-5}$	$C_2H_3O_2^-$	0.1 M $HC_2H_3O_2$	0.1 M $NaC_2H_3O_2$
dihydrogen phosphate ion	$H_2PO_4^-$	$K_a = 6.2 \times 10^{-8}$	HPO_4^{2-}	0.1 M NaH_2PO_4	0.1 M Na_2HPO_4
bicarbonate ion	HCO_3^-	$K_a = 4.8 \times 10^{-11}$	CO_3^{2-}	0.1 M Na HCO_3	0.1 M Na_2CO_3
ammonium ion	NH_4^+	$Ka = 5.6 \times 10^{-10}$	NH_3	0.1 M NH_4Cl	0.1 M NH_3

Then calculate the ratio of volumes of conjugate base soluti on to acid solution:

$$\frac{K_a}{[H_3O^+]} = \frac{V \text{ conjugate base soluton}}{V \text{ acid solution}}$$

Decide on the exact volume of buffer solution you will make (anywhere from 20 to 30 mL) and calculate the volumes of acid solution and conjugate base solution you will use to prepare the buffer. Show your calculations in part D on the report sheet (items 8 – 11 on page 8) and ask your instructor to check them before you prepare your buffer solution.

Prepare the buffer solution and ask your instructor to verify your measured pH.