BUFFER SOLUTION

A buffer is a solution that resists the change in pH when limited amounts of acid or base are added to it.

One buffer system consists of a mixture of acetic acid and sodium acetate. The mixture would contain the following particles: Na^+, $C_2H_3O_2^-$, $HC_2H_3O_2$

The reactions of added H^+ or of added OH^- with particles in this buffer solution will be:

$$H^+_{added} + C_2H_3O_2^- \rightleftharpoons HC_2H_3O_2$$

$$OH^-_{added} + HC_2H_3O_2 \rightleftharpoons H_2O + C_2H_3O_2^-$$

The equations above show that a buffer system will maintain a relatively fixed pH even when considerable acid or base is added. Until enough acid has been added to almost exhaust the supply of $C_2H_3O_2^-$ ions, the pH of the solution will remain in the order of magnitude of its original value. In the same way, the pH of the mixture will remain almost constant until about all $HC_2H_3O_2$ molecules are exhausted by the added OH^- ions.

Notice, as demonstrated by the equilibrium expression below, that a mixture of equal volumes of equimolar $HC_2H_3O_2$ and $C_2H_3O_2^-$ (for example 1M solution of each) will have a $[H_3O^+]$ ion concentration nearly equal to its ionization constant.

$$HC_2H_3O_2 + H_2O \rightleftharpoons H_3O^+ + C_2H_3O_2^-$$

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

TO MAKE A BUFFER SOLUTION:

One way to make a buffer solution is to choose a weak acid (with a K_a value of approximately the H_3O^+ concentration you want.) or a weak base (with a K_b value of approximately the OH^- concentration you want). Then calculate the conjugate-base/acid or conjugate-acid/base ratio needed for your exact pH. (See the calculation immediately below.) For example, if you want to prepare a buffer solution of pH=4.2, that is, a $[H_3O^+]$ = 6.3x 10^{-5} M, you need to choose a weak acid that has a K_a in the neighborhood of 6.3x 10^{-5}. It seems that $HC_2H_3O_2$ is a good choice because it has a K_a of 1.8 x10^{-5}. You will see from the following calculation that by rearranging the equation for the equilibrium expression, you may obtain the required ratio of volumes of equimolar solutions of acid and conjugate base that you should mix.

$$HC_2H_3O_2 + H_2O \rightleftharpoons H_3O^+ + C_2H_3O_2^-$$

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

$$\frac{K_a}{[H_3O^+]} = \frac{[C_2H_3O_2^-]}{[HC_2H_3O_2]} = \frac{\text{moles of conjugate base}/V_{final}}{\text{moles of acid}/V_{final}}$$

Since both compounds will now be in the same total volume of solution, V_{final}, this same ratio will be the ratio of ***moles*** needed.

$$\frac{K_a}{[H_3O^+]} = \frac{\text{moles of conjugate base}}{\text{moles of acid}} = \frac{M_{conj.\ base} \cdot V_{conj.\ base}}{M_{acid} \cdot V_{acid\ solution}}$$

If you use ***equimolar*** solutions of the two solutes (solutions of the same molarity before mixing), then the calculated ratio will also be the ***ratio of volumes*** of the two solutions to use.

$$\frac{K_a}{[H_3O^+]} = \frac{V_{conj.\ base}}{V_{acid\ solution}}$$

See how we specifically arrange to have:

molarity ratio= mole ratio=volume ratio

This is only true for ***equimolar*** starting solution.

EXPERIMENT:

pH OF AMMONIUM ACETATE SOLUTION:

1. Measure the pH of 1.0 M $NH_4C_2H_3O_2$ solution. Record your result and answer the questions on your report sheet.

AMMONIUM ACETATE AS A BUFFER:

2. Place 5 ml of distilled water in one test tube and 5 ml of 1.0 M $NH_4C_2H_3O_2$ solution in another. Add two drops of methyl orange indicator to each.

Prepare about 25 ml of 1 M HCl by dilution of the 6 M HCl at your desk. Mix well and fill your 10 ml graduated cylinder.
Setup for dilution calculation:

Add this 1M HCl solution drop by drop with stirring, to the test tube containing the distilled water until the reddish methyl orange end point is reached at about pH 3. How many drops were needed?

Again fill the 10 ml graduate cylinder with 1 M HCl solution. Determine the volume of the acid solution needed to obtain the same color change in the ammonium acetate solution. (Note, you do no need to count the drops, if more than ten drops or so are needed. Just read how many ml of acid solution are still in your graduated cylinder, to find by difference how many ml you used.)

SAVE THE REMAINNG 1 M HCl SOLUTION FOR USE IN PART 4

3. Again place 5 ml of distilled water in one test tube and 5 ml of 1.0 M $NH_4C_2H_3O_2$ solution in another. Add two drops of Alizarin yellow R to each.

   Prepare about 25 ml of 1 M NaOH by dilution of the 6 M NaOH at your desk. Mix well and fill the graduated cylinder just to the 10 ml mark.
   Setup for dilution calculation:

   Add this NaOH solution drop by drop, with stirring, to the test tube containing distilled water until the change in indicator color is reached, about pH 11. Record the approximate number of drops of 1 M NaOH needed to cause this color change.

Again fill the 10 ml graduate cylinder with the 1 M NaOH solution. Determine the volume of the NaOH needed to obtain the same color change in the ammonium acetate solution. Answer the questions on the report sheet.

SAVE THE REMAINNG 1 M NaOH FOR USE IN PART 4

<u>SODIUM BICARBONATE AS A BUFFER:</u>

4. Put 5.0 ml portions of 0.10 M $NaHCO_3$ into each of two clean test tubes.

To one add 2 drops of methyl orange, followed by 1 M HCl until the indicator color change is reached, about pH 3. Record the volume of acid used. Complete part 4 of the report.

To the other, add 2 drops of Alizarin yellow R, followed by 1 M NaOH solution until the indicator color change is reached, about pH 11. Record the volume of NaOH used. Complete part 4 of the report.

<u>PREPARATION OF A BUFFER MIXTURE:</u>

5. The instructor will assign you a pH for which you are to prepare about 20 to 30 ml of buffer mixture. A selection of **<u>0.10 M</u>** solutions for the possible buffer combinations listed below are available on the Chem 111 shelves. Choose a suitable pair and calculate what volume of each to use. Make the mixture, then with your instructor check it with the pH pen. Complete part 5 of the report sheet.

Possible buffer pair	**Acid ionization constant**
HSO_4^-, SO_4^{2-}	K_{a2}= 1.2 x 10^{-2}
$HCHO_2$, CHO_2^- (formic acid, formate ion)	K_a= 2.1 x 10^{-4}
$HC_2H_3O_2$, $C_2H_3O_2^-$	K_a= 1.8 x 10^{-5}
$H_2PO_4^-$, HPO_4^{2-}	K_{a2}= 6.3 x 10^{-8}
NH_4^+, NH_3	K_a= 5.6 x 10^{-10}
HCO_3^-, CO_3^{2-}	K_{a2}= 4.7x 10^{-11}

Report Sheet
Buffer Solutions

Name __________________
Last First
Instructor's approval____________

pH of ammonium acetate solution:

1. pH of 1.0 M $NH_4C_2H_3O_2$ solution pH __________

Ammonium acetate as a buffer:

2. Volume of 1 M HCl needed to decrease the pH of distilled water from pH 7 to 3 (in drops or in ml)

______________drops

Volume of 1 M HCl needed to decrease the pH of 1.0 M $NH_4C_2H_3O_2$ from pH 7 to pH 3

______________ml

Write the net-ionic equation for the reaction of HCl with $NH_4C_2H_3O_2$

____

3. Volume of 1 M NaOH needed to increase the pH of distilled water from pH 7 to 11 (in drops or in ml)

______________drops

Volume of 1 M NaOH needed to increase the pH of 1.0 M $NH_4C_2H_3O_2$ from pH 7 to pH 11.

______________ml

Write the net-ionic equation for the reaction of NaOH with $NH_4C_2H_3O_2$

____

$NaHCO_3$ as a buffer:

Volume of 1 M HCl needed to decrease the pH of 0.10 M $NaHCO_3$ to pH=3 ________ml

4. Write the net-ionic equation for the reaction of HCl with $NaHCO_3$.

____

Volume of 1 M NaOH needed to increase the pH of 0.10 M $NaHCO_3$ to pH=11______ml

Write the net-ionic equation for the reaction of NaOH with $NaHCO_3$.

____

Preparation of a buffer mixture:

Assigned pH = ________

$[H_3O^+]$ = ____________

Buffer pair chosen ________and ___________

K_a for the acid/conjugate- base chosen = _________

Notice that each buffer pair consists of a Bronsted-Lowry acid, HX, and its conjugate base, X^-

$$\underset{\textbf{acid}}{HX\ (aq)} + H_2O\ (l) \rightleftharpoons H_3O^+\ (aq) + \underset{\textbf{conjugate base}}{X^-\ (aq)}$$

The equilibrium expression for the above reaction:

$$K_a = \frac{[H_3O^+]\ [X^-]}{[HX]}$$

Solve for the $[X^-]/[HX]$ concentration ratio for your chosen pair at the assigned pH value.

Setup:

$$\frac{K_a}{[H_3O^+]} = \frac{[X^-]}{[HX]} = \_\_\_\_\_\_\_\_\_\_\_\_ = \frac{\_\_\_\_\_\_\_\_\_}{1}$$

Summary :

To prepare my buffer solution, I will:

Mix _________ ml of ______M ___________

With _________ml of ______M ___________

Show your calculation to your instructor before you mix the solutions.

Instructor's approval of calculation__________

Now mix the suggested solutions. What reading does your buffer give on the pH pen?

pH= ________

Instructor's approval of pH reading ___________

Exercises

1. Write net-ionic equations for the reaction of the buffer mixture, Na_2HPO_4 with NaH_2PO_4
   a. with added H^+ ions : ______________________________

   b. with added OH^- ions: ______________________________

2. Write the formulas of the particles present in each of the following solutions. Then classify these particles as Bronsted-Lowry acids or bases. If more than one Bronsted-Lowry acid is present, list the strongest one first. Decide on which of the solutions below would show a buffer action. (A buffer must be able to react with both H^+ and OH^- ions.

Solute	Particles present	Bronsted base (capable in reacting with H^+ ions)	Bronsted acid (capable in reacting with OH^- ions)	Buffer (yes, or no?)
NH_4HSO_4				
NH_3, NH_4Cl				
HCl, $NaCl$				
NH_4Cl, $NaCl$				
H_2CO_3, $KHCO_3$				
$HC_2H_3O_2$, HCl				
$H_2C_2O_4$, KHC_2O_4				
KHS, Na_2S				

3. Calculate the pH of an equimolar mixture of H_2S and $NaHS$. Show the setup. Ka1 for H_2S is 1.1×10^{-7}.

Setup:

Answer__________

4. a. Define : Buffer

b. How will the pH of a buffer solution change if we add water? (increases, decreases, or remain the same)

c. Consider the table given below and write a **balanced** chemical equation for any reaction taking place between solute particles. Then write the formulas of the **major** particles present (just as you would for a net-ionic equation) in each of the following solutions below. Decide on which of the solutions below would show a buffer action.

	Particles present	**Is it a buffer? (Yes or No)**
Na_2CO_3		
$NaHSO_4$		
NaF		
Equal volumes of **0.10 M** HCN and **0.05** M NaOH Equation:		
Equal volumes of **0.05 M** H_2S and **0.10** M NaOH Equation:		
$NaHC_2O_4$		

	Particles present	**Is it a buffer? (Yes or No)**
Equal volumes of **0.10** M NH_3 (aq) and **0.10** M HCl Equation:		
Equal volumes of **0.10** M NH_3 and **0.05** M HNO_3 Equation:		
Equal volumes of **0.10** M H_2CO_3 and **0.10** M KOH Equation:		