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Catalog No. AP7663
Publication No. 7663

Properties of Buffer Solutions

AP* Chemistry Big Idea 6, Investigation 16
An Advanced Inquiry Lab

Introduction

A buffer protects against rapid changes in pH when acids or bases are added. Every living cell is buffered to maintain constant pH and proper cell function. Consumer products are often buffered to safeguard their activity. The purpose of this lab activity is to investigate how buffers are made, the pH range in which they are effective, and their buffer capacity.

Concepts

- pH
- Dissociation constant
- Buffer
- Neutralization
- Weak acids and bases
- Conjugate acid–base pairs

Background

The ability of buffers to resist changes in pH upon addition of acid or base can be traced to their chemical composition. All buffers contain a mixture of both a weak acid (HA) and its conjugate base (A^-), which are related to each other by the dissociation reaction shown in Equation 1. The double arrow ($\rightleftarrows$) indicates that the reaction is reversible and that both the weak acid and the conjugate base are present at equilibrium.

$$\underset{\text{weak acid}}{HA} + H_2O \rightleftarrows \underset{\text{conjugate base}}{A^-} + H_3O^+ \qquad \textit{Equation 1}$$

Buffers control pH because the buffer components HA and A^- are able to neutralize either acid or base added to the solution. The weak acid component HA reacts with base to give its conjugate base A^-. The conjugate base component A^- reacts with acid to regenerate its acid partner HA. These reactions can be visualized as a cyclic process (see Figure 1). Buffer activity will continue as long as neither component A^- or HA is completely consumed by the amount of added acid or base.

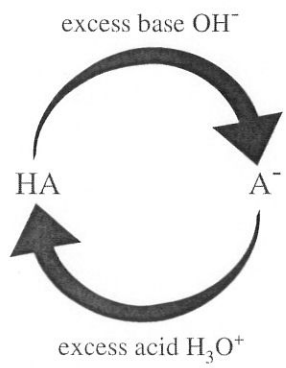

Figure 1.

Properties of Weak Acids and Bases

The properties of weak acids and their conjugate bases determine why buffers behave as they do. Dissociation of a weak acid is reversible and occurs to only a very limited degree in water. Consider *acetic acid* (CH_3COOH), the main ingredient in vinegar. A 0.1 M solution of acetic acid has a hydronium ion concentration $[H_3O^+]$ equal to 0.0013 M, giving an observed pH of 2.8–2.9. (Recall the definition and mathematical relationship between $[H_3O^+]$ and pH: pH = $-\log[H_3O^+]$.) The observed pH value suggests that only about 1% of the acetic acid molecules are dissociated to the conjugate base form, acetate ion, under these conditions. In contrast, a strong acid such as hydrochloric acid (HCl) undergoes complete and irreversible 100% dissociation in water.

The degree to which a weak acid is ionized in aqueous solution is governed by the equilibrium constant K_a for its reversible dissociation reaction (Equations 2 and 3). The K_a value for acetic acid is 1.76×10^{-5}.

$$\underset{\text{acetic acid}}{CH_3COOH} + H_2O \rightleftarrows \underset{\text{acetate ion}}{CH_3COO^-} + H_3O^+ \qquad \textit{Equation 2}$$

$$K_a = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]} = \frac{[0.0013][0.0013]}{[0.0987]} = 1.7 \times 10^{-5} \qquad \textit{Equation 3}$$

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The Buffer Equation

Generalization of Equation 3 for any weak acid HA and its conjugate base A^- gives Equation 4, which can be rearranged to solve for the $[H_3O^+]$ concentration (Equation 5). Equation 5 is sometimes known as the buffer equation; it provides the key to calculating the properties of buffer solutions.

$$K_a = \frac{[A^-][H_3O^+]}{[HA]} \qquad \textit{Equation 4}$$

$$[H_3O^+] = K_a \times \frac{[HA]}{[A^-]} \qquad \textit{Equation 5}$$

When the concentrations of the weak acid and its conjugate base are equal, the ratio in Equation 5 will be equal to one and the $[H_3O^+]$ concentration will be equal to the dissociation constant K_a for the weak acid. Careful selection of the identity of the weak acid component makes it possible to prepare a buffer solution with almost any initial pH value. In the case of acetic acid, for example, a buffer solution consisting of a 1:1 molar mixture of acetic acid and its conjugate base sodium acetate will have a hydronium ion concentration equal to 1.76×10^{-5} M, and the pH of the solution will be 4.75. Carbonic acid (H_2CO_3) has a K_a value equal to 4.4×10^{-7}. A buffer prepared from equal moles of carbonic acid and its conjugate base bicarbonate ion (HCO_3^-) will have an $[H_3O^+]$ concentration equal to 4.4×10^{-7} M and a pH value equal to 6.4.

What happens when strong acid or base is added to a buffer? Reaction of the weak acid component HA with additional base, such as sodium hydroxide, converts the weak acid to its conjugate base form A^- (Equation 6). Similarly, reaction of the basic component A^- with added acid results in its neutralization to the conjugate acid form HA (Equation 7).

$$HA + OH^- \rightleftarrows A^- + H_2O \qquad \textit{Equation 6}$$

$$A^- + H_3O^+ \rightleftarrows HA + H_2O \qquad \textit{Equation 7}$$

The effect of adding a strong acid or base on the pH of a buffer solution can be predicted using LeChâtelier's principle. Consider the equimolar acetic acid–acetate buffer (Equation 2). Adding HCl to the buffer solution, with its equilibrium pH = 4.75, increases the concentration of H_3O^+ ions, one of the products of the reversible reaction. This shifts the equilibrium to the left, increasing the concentration of acetic acid and decreasing the concentration of acetate ions. The ratio of [HA] to $[A^-]$ in Equation 5 increases as well, and $[H_3O^+]$ is larger—the pH decreases. The opposite effect is observed when NaOH is added to the buffer solution. OH^- ions neutralize some of H_3O^+ ions, which shifts the equilibrium to the right, increasing the concentration of acetate ions relative to acetic acid molecules. The ratio of [HA] to $[A^-]$ decreases, and $[H_3O^+]$ is smaller—the pH increases. In either case, however, as long as the $[HA]/[A^-]$ ratio stays within certain limits, the pH remain relatively constant.

Buffer Range and Buffer Capacity

A buffer composed of an equal number of moles of a weak acid and its conjugate base is sometimes called an *ideal buffer* because it is equally effective in resisting pH changes upon addition of either acid or base. As shown in the example above, in an ideal buffer solution the $[H_3O^+]$ concentration is equal to the dissociation constant (K_a) for the weak acid.

The pH range in which a buffer solution will be effective is called the *buffer range*. Since a buffer solution must always contain noticeable amounts of both a weak acid and its conjugate base, the buffer range is usually limited to concentration ratios of HA:A^- between 1:10 and 10:1. Substituting these concentration ratios into Equation 5 reveals that the effective pH range for a given buffer is plus or minus one unit on either side of the pH value of the ideal buffer. An ideal acetic acid–sodium acetate buffer has a pH of 4.75 and its buffer range is 3.75–5.75. Equation 8 shows the calculation for the lower pH limit of an acetic acid–sodium acetate buffer where the concentration ratio of the weak acid component to the conjugate base component is 10:1.

$$[H_3O^+] = 1.76 \times 10^{-5} \times \frac{[10]}{[1]} = 1.76 \times 10^{-4} \qquad \textit{Equation 8}$$

$$pH = -\log(1.76 \times 10^{-4}) = 3.75$$

The effectiveness of a buffer in resisting pH changes is called the *buffer capacity*. Consideration of Equation 5 reveals that the pH of a buffer prepared from a weak acid HA and its conjugate base A^- should be independent of their total concentration as long as the ratio [HA] to [A^-] is the same. Thus, an acetic acid–acetate buffer prepared from 0.1 mole HA and 0.1 mole A^- should have the same theoretical pH as a buffer containing 1 mole HA and 1 mole A^-. The buffer capacity of the two buffers, however, will be very different. The capacity of the 0.1 moles HA/0.1 moles A^- buffer will be overwhelmed when approximately 0.09 moles of HCl or NaOH have been added. The 1 M buffer will withstand almost 10× as much strong acid or strong base before either HA or A^- is consumed.

Experiment Overview

The purpose of this advanced inquiry lab is to design an effective buffer with a specific pH value for a consumer or experimental biochemistry application. The investigation begins with an introductory activity to compare the properties of three acetate buffers containing varying ratios of HA and A^-. The results provide a model for guided-inquiry design of an experiment to prepare a desired buffer and verify its properties and performance. Five different buffer "challenges" are presented—each student group chooses one. The specifications for each buffer challenge are that (a) the pH should be within ± 0.5 pH units of the desired pH, and (b) 25 mL of the buffer should maintain the desired pH ± 1 after 10 mL of 0.02 M HCl *or* 10 mL of 0.2 M NaOH have been added. Preparation of a buffer by partial neutralization of a weak acid or a weak base offers additional opportunities for inquiry.

Pre-Lab Questions

1. Calculate the pH value in each of the following solutions, given their [H_3O^+] concentrations.

Solution	[H_3O^+] (M)
gastric juice	1.6×10^{-2}
cow's milk	2.5×10^{-7}
tomato juice	5.0×10^{-5}

2. Write balanced chemical equations for dissociation of the following weak acids and identify their conjugate bases: phosphoric acid (H_3PO_4), formic acid (HCO_2H), and boric acid (H_3BO_3).
3. What would be the composition and pH of an ideal buffer prepared from lactic acid ($CH_3CHOHCO_2\mathbf{H}$), where the hydrogen atom highlighted in boldface is the acidic hydrogen atom? The K_a value for lactic acid is 1.38×10^{-4}.
4. Use the buffer equation to calculate the pH of buffer solutions prepared by dissolving the following amounts of acetic acid and sodium acetate, respectively, in enough water to make 1 L of solution:

   a. 0.67 moles acetic acid and 0.33 moles of sodium acetate, and

   b. 0.33 moles acetic acid and 0.67 moles of sodium acetate.

Materials

Introductory Activity

Acetic acid, CH_3CO_2H, 0.1 M, 30 mL

Buffer solution, pH 7, 20 mL

Hydrochloric acid solution, HCl, 0.1 M, 25 mL

Sodium acetate solution, CH_3CO_2Na, 0.1 M, 30 mL

Sodium hydroxide solution, NaOH, 0.1 M, 25 mL

Water, distilled or deionized

Disposable pipets

Graduated cylinder, 10- or 25-mL

pH meter or paper (indicators, optional)

Pipets, graduated, Beral-type (or burets)

Stirring rod

Test tubes, medium, 5

Test tube rack

Wash bottle

Materials continued on the next page.

Guided-Inquiry Activity

Weak acid or base solutions, 0.1 M (choose one)

- Acetic acid, CH_3CO_2H
- Ammonia, NH_3
- Carbonic acid (seltzer water, assume CO_2 concentration = 0.07 M)
- Citric acid, $C_6H_8O_7$
- Sodium dihydrogen phosphate, NaH_2PO_4

Hydrochloric acid solution, HCl, 0.2 M, 40 mL

Sodium hydroxide solution, NaOH, 0.2 M, 40 mL

Conjugate bases or conjugate acids (choose one)

- Ammonium chloride, NH_4Cl
- Sodium acetate trihydrate, $CH_3CO_2Na \cdot 3H_2O$
- Sodium bicarbonate, $NaHCO_3$
- Sodium dihydrogen citrate, $NaC_6H_7O_7$
- Sodium hydrogen phosphate heptahydrate, $Na_2HPO_4 \cdot 7H_2O$

Water, distilled or deionized

Balance, electronic, 0.01-g precision

Beakers, 150-mL, 2

Burets, 25- or 50-mL, 2

Clamps, buret, 2

Graduated cylinders, 100-mL, 2

pH meter or paper (indicators, optional)

Pipets, disposable (optional)

Spatula

Support stand

Wash bottle

Weighing dishes

Safety Precautions

Dilute acid and base solutions, including acetic acid, ammonia, citric acid, hydrochloric acid, and sodium hydroxide, are skin and eye irritants. Acetic acid and ammonia solutions may be irritating to the respiratory tract. Wear chemical splash goggles, chemical-resistant gloves, and a chemical-resistant apron. Avoid exposure of all chemicals to eyes and skin and notify the teacher of any spills. Wash hands thoroughly with soap and water before leaving the laboratory. Please follow all laboratory safety guidelines.

Introductory Activity

Acetate Buffers

1. Using a clean graduated cylinder for each solution, measure and add the indicated volumes of the following solutions to five test tubes labeled A–E. Mix the contents of test tubes B, C, and D by gentle stirring, swirling or shaking.

Table 1.

Solution	**Test Tube**				
	A	**B**	**C**	**D**	**E**
Acetic acid, 0.1 M	0	6.7 mL	5 mL	3.3 mL	0
Sodium acetate, 0.1 M	0	3.3 mL	5 mL	6.7 mL	0
Distilled water	10 mL	0	0	0	0
pH 7 Buffer	0	0	0	0	10 mL

2. Measure and record the initial pH of the water in test tube A using either a pH meter or a combination of wide-range and narrow-range pH paper or indicators.
3. Add 1 drop of 0.1 M HCl to the water in test tube A and measure the pH.
4. If using a pH meter, rinse the electrode with distilled water and blot dry.
5. Measure and record the initial pH of the buffer in test tube B.
6. Using a graduated pipet or buret, add 1 mL of 0.1 M HCl to the buffer in test tube B. Measure and record the pH.
7. Add an additional 2 mL of 0.1 M HCl to test tube B, and again measure the pH.

8. Add an additional 3 mL of 0.1 M HCl to test tube B, and again measure the pH.
9. Rinse the pH meter with distilled water (if applicable).
10. Repeat steps 5–9 three more times to test the buffer solutions in test tubes C, D and E.
11. Dispose of the solutions in test tubes A–E. Rinse the test tubes with distilled water and blot dry with a paper towel.
12. Refill all test tubes A–E with the designated solutions shown in Table 1.
13. Measure the initial pH of the water in test tube A. Add 1 drop of 0.1 M NaOH, and again measure the pH.
14. If using a pH meter, rinse the electrode with distilled water and blot dry.
15. Measure and record the initial pH of buffer B.
16. Using a graduated pipet or buret, add 1 mL of 0.1 M NaOH to buffer B. Measure and record the pH.
17. Add an additional 2 mL of 0.1 M NaOH to buffer B, and again measure the pH.
18. Add an additional 3 mL of 0.1 M NaOH to buffer B, and again measure the pH.
19. If using a pH meter, rinse the electrode with distilled water and blot dry.
20. Repeat steps 15–19 three more times to test the buffer solutions in test tubes C, D and E.
21. Dispose of the solutions in test tubes A–E.

Analyze the Results

- Compare the observed pH changes for distilled water versus the buffers in test tubes B–E when either HCl or NaOH was added.
- Which acetate buffer (B, C or D) was most effective with respect to added HCl? Explain.
- Which acetate buffer (B, C or D) was most effective with respect to added NaOH? Explain.
- Which acetate buffer (B, C or D) has the composition of an "ideal buffer?" Do the results support this description? Explain.

Guided-Inquiry Design and Procedure

Form a working group with other students and discuss the following questions.

1. Recalling that pH = $-\log[H_3O^+]$ and pK_a = $-\log K_a$, transform Equation 5 in the *Background* section to the Henderson-Hasselbach equation relating the pH of a buffer solution to the pK_a value of a weak acid and the concentrations of the weak acid and its conjugate base.
2. Citric acid is a *triprotic* weak acid with three ionizable hydrogen atoms. See its structure and formula below. Write equations for the three stepwise deprotonation reactions of citric acid and its conjugate base anions. *Hint:* Salts of the conjugate bases are called sodium dihydrogen citrate, sodium hydrogen citrate, and sodium citrate.

Citric acid molecular formula = $C_6H_8O_7$ Citric acid structure = $HO_2C{-}CH_2{-}\underset{\displaystyle CO_2H}{\overset{\displaystyle OH}{C}}{-}CH_2{-}CO_2H$

3. The pK_a values for the three stepwise dissociations of citric acid are 3.1, 4.8 and 6.4.
   a. What is the expected composition of a citrate buffer having a pH value = 3.1?
   b. What is the expected composition of a citrate buffer having a pH value = 6.4?
4. Basic buffers, that is, those with pH values > 7, are derived from weak acids and their conjugate bases having pK_a values greater than 7. Consider bicarbonate ion and its conjugate base carbonate ion (Equation 9). The value of the dissociation constant for this reaction is 4.7×10^{-11}. Describe the pH and composition of an ideal bicarbonate/carbonate buffer.

$$HCO_3^- + H_2O \rightleftarrows CO_3^{2-} + H_3O^+ \qquad \textit{Equation 9}$$

5. Ammonia is a weak base.

   a. Write an equation for the reaction of ammonia with water and identify its conjugate acid.

   b. The pK_b value for this reaction is 4.7. Recalling that the relationship between pK_a and pK_b for a conjugate acid–base pair is $pK_a + pK_b = 14$, predict the pH of an equimolar solution containing ammonia and its conjugate acid.

6. The purpose of this activity is to design a buffer for a specific consumer or biochemical application. The weak acids that are available to prepare the target buffers include acetic acid, ammonium chloride, carbonic acid, citric acid and sodium dihydrogen phosphate (0.1 M solutions of each are provided). Carbonic acid is present in seltzer water, which contains approximately 0.07 moles of carbon dioxide per liter. Write equations for the reactions of these weak acids with water, identify their conjugate bases, and determine the pK_a value for each.

7. Each group should choose one of the buffer challenges from the following table and select an appropriate weak acid–conjugate base pair to prepare the buffer.

   Table 2.

Buffer	Purpose	Target pH
1	Exfoliant or face "peel" formulation for a cosmetic product	3.1
2	Antifungal agent in a food additive to prevent mold in foods	4.7
3	Model blood buffer to study the effect of CO_2 buildup in emphysema patients	6.8
4	Contact lens disinfectant solution	7.2
5	Culture medium for alkaline bacteria	9.2

8. The specifications for each buffer are that the initial pH should be within ± 0.5 pH units of the target pH, and 25 mL of the buffer should be able to maintain the desired pH within ± 1 pH unit after the addition of either 10 mL of 0.2 M HCl or 10 mL 0.2 M NaOH. Predict the ratio of weak acid/conjugate base to meet the buffer challenge, and determine the amounts of HA and A^- to provide the desired buffer capacity.

9. Write a detailed step-by-step procedure for preparing the selected buffer and testing its buffer capacity. Include all the materials, glassware and equipment that will be needed, safety precautions that must be followed, amounts of each reactant, etc.

10. Review additional variables that may affect the reproducibility or accuracy of the investigation, and how these variables will be controlled.

11. Carry out the investigation and record results in appropriate data tables and graphs.

12. Each group should present evidence in the form of titration curves to show that the respective buffer specifications have been achieved.

Analyze the Results

Organize a collaborative class research meeting to discuss the results.

Opportunities for Inquiry

Buffers can be prepared by partial neutralization of a weak acid with sodium hydroxide. Carbonate buffers covering the pH range from 9.4 to 10.8 can be prepared by combining the appropriate volumes of 0.2 M sodium bicarbonate and 0.2 M NaOH. Predict the appropriate volumes of $NaHCO_3$ and NaOH to combine to make buffers with pH values equal to 9.7, 10.3 and 10.8.

AP Chemistry Review Questions

Integrating Content, Inquiry and Reasoning

1. The major buffer in blood is composed of the weak acid carbonic acid (H_2CO_3) and its conjugate base, bicarbonate ion (HCO_3^-). The normal pH of blood is 7.2–7.4, which is very far removed from the pK_a value. The pH is kept in check by the lungs, which remove CO_2 via exhalation, and by the kidneys, which excrete acid (H_3O^+) in the urine. People with impaired lung function are not able to exchange carbon dioxide efficiently between the lungs and air. The result is an increase in the amount of CO_2 dissolved in the blood.

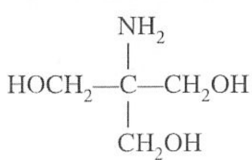
   a. How does this affect the buffer balance in the blood?

   b. Which term, respiratory acidosis or respiratory alkalosis, would better describe the resulting condition?

2. Explain why a mixture of the strong acid HCl and its conjugate base NaCl does not provide buffering action.

3. Forensic analysis of DNA by electrophoresis requires the use of a pH 8.3 buffer to ensure that the DNA phosphate groups remain negatively charged. The major constituent of electrophoresis buffers is called TRIS, which stands for tris(hydroxymethyl)aminomethane. Its structure is shown below. What weak acid/weak base combination used in this activity is TRIS most analogous to? Identify the basic functional group in TRIS that is protonated to give a weak acid.

   TRIS



4. Many soft drinks contain phosphate buffers. Calculate the pH of an 8 oz. soft drink containing 4.4 g of sodium dihydrogen phosphate (formula weight = 120 g/mole) and 5.4 g of sodium hydrogen phosphate (formula weight = 142 g/mole).