

Experiment 12

BUFFER SOLUTIONS

Objective

The purpose of this experiment is to learn the properties of buffer solutions and factors affecting buffer capacity.

Lab techniques

- Weighing chemicals.
- Preparing buffer solutions.
- Operating of graduated pipet, stirrer/hot plate, and pH-meter.

Introduction

I. Buffer solution

A buffer solution consists of a conjugate acid/base pair, so it maintains a fairly constant pH value upon addition of a small amount of acid or base. A buffer solution can be prepared from a weak acid (HA) and its conjugate base (A^-) or a weak base (B) and its conjugate acid (BH^+). The equilibrium and equilibrium-constant expression for the dissociation of a weak acid are as equations 12-1 and 12-2.



$$K_a = \frac{[H^+][A^-]}{[HA]} \quad (12-2)$$

where K_a is the acid dissociation constant. Once an acid is added, it is neutralized by A^- in the buffer (12-3).



On the other hand, when a base is added, it is neutralized by HA in the buffer (12-4).



The pH value of a buffer solution depends on the K_a of HA and concentration ratios of the conjugate acid-base pair ($[A^-]/[HA]$), as shown in the Henderson-Hasselbalch equation (12-7).

$$[H^+] = \frac{K_a [HA]}{[A^-]} \quad (12-5)$$

$$pH = -\log[H^+] = -\log K_a - \log\left(\frac{[HA]}{[A^-]}\right) \quad (12-6)$$

$$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right) \quad (12-7)$$

When adding a small amount of acid or base to the solution, the change in $\log\left(\frac{[A^-]}{[HA]}\right)$ is negligible, and thus the buffer solution maintains a relatively stable pH value.

The buffer capacity is defined as the number of moles of OH^- or H^+ that causes 1 L of the buffer solution to undergo one unit change in pH. The buffer capacity depends not only on total concentrations of the two components but also on their concentration ratio. A buffer solution has the greatest capacity when the concentration ratio of the two components is 1, and better within one pH unit of pK_a .

In this experiment, you will learn to prepare different buffer solutions from acetic acid (CH_3COOH , abbreviated as HOAc) and sodium acetate (CH_3COONa , abbreviated as NaOAc). After adding certain amounts of strong acid or strong base to the buffer, pH values will be measured using a pH-meter to determine how their concentration ratios affect the buffer capacity.

II. pH-meter⁽²⁾⁻⁽⁴⁾

A pH-meter is an instrument used to measure the pH value of a solution. The instrument consists of three parts. The first part is a reference electrode (usually made of silver/silver chloride), whose potential is a fixed value. The second part is the indicator electrode (usually made of glass), whose potential changes when the concentration of H^+ varies. In a modern pH-meter, the two electrodes are combined into a pH electrode. The third part is a voltmeter, which is used to measure the potential difference between the two electrodes. When the electrodes are immersed into the analyte solution, the pH-meter automatically converts the measured cell potential to a reading of the pH value.

Equation 12-8 describes the relationship between the measured cell potential and the pH value of the solution:

$$E_m = K - 2.3 RT \text{ pH}/nF \quad (12-8)$$

where E_m : measured cell potential

K: constant, depends on the type of electrode used

R: gas constant

T: absolute temperature of the solution

pH: pH value of solution

n: number of moles of electrons transferred

F: Faraday constant

Since R, n, and F are constant during measurements, equation 12-8 can be simplified to equation 12-9.

$$E_m = mT(\text{pH}) + K \quad (12-9)$$

If temperature is kept constant while obtaining a set of measurements, E_m and pH

have a linear relationship according to equation 12-9, and the slope of the straight line is mT . We usually calibrate a pH-meter before measurements by using two standard-pH buffer solutions at constant temperature. The first standard solution (usually pH 7.00) is used to set the absolute value of the pH-meter reading, while the second standard solution (usually pH 4.00) is used to calibrate the slope, as shown in Fig. 12-1.

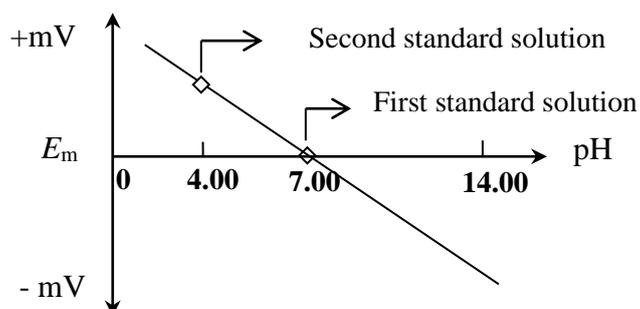


Figure 12-1 The relationship between measured cell potential and pH value

Apparatus

Volumetric flask (250 mL), graduated pipet (10 mL, 2), beaker (50 mL, 4), graduated cylinders (10 and 50 mL), dropper (2), pH-meter, magnetic stirrer and magnetic stirring bar, wash bottle, pipet filler (2), and graduated pipet (2 mL, shared).
Standard pH 7.00 and 4.00 buffer solution (shared).

Chemicals

Sodium acetate trihydrate, $\text{CH}_3\text{COONa}\cdot 3\text{H}_2\text{O}$

Concentrated acetic acid, 17 M CH_3COOH

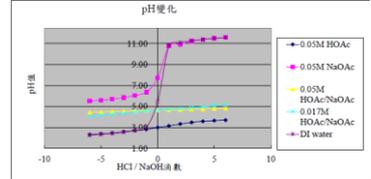
1.0 M Hydrochloric acid, $\text{HCl}(\text{aq})$

1.0 M Sodium hydroxide, NaOH

Procedure

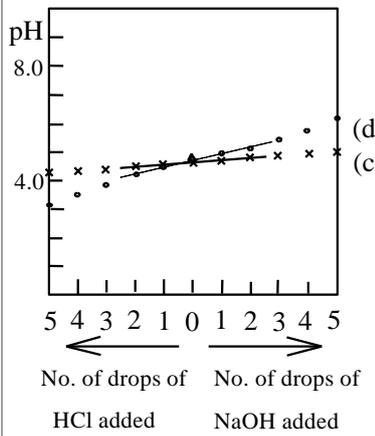
Procedure	Illustration
I. Effect of concentration on buffer capacity	
1. Calibrate the pH-meter: (1) Press the "POWER" key to turn pH-meter on and warm up for 10 min. (2) Immerse the thermometer probe (black one) and pH-electrode into standard pH 7.00 buffer	

	<p>solution, and check the temperature first.</p> <p>(3) Calibrate the pH-meter with pH 7.00 (adjust with “CALIB.” knob) and pH 4.00 (adjust with “SLOPE” knob) standard-pH buffer solutions in sequence.</p> <p>Notice: The pH-electrode is very expensive and easily broken; ought to handle with care.</p> <p>Note: Refer to the experimental skills videos to learn how to use a pH-meter.</p>	 
2.	<p>Prepare 0.050 M HOAc and 0.050 M NaOAc solutions (250 mL each) from concentrated acetic acid (17 M) and sodium acetate trihydrate salt with volumetric flask, separately. Then pour the solutions into beakers.</p> <p>Note 1: Write down the preparation method in the prelab report.</p> <p>Note 2: Refer to the experimental skills videos to learn how to use a volumetric flask.</p>	 
3.	<p>Prepare two clean and dry test tubes and measure 5 mL of 1.0 M HCl and 1.0 M NaOH to tubes, separately. Use a 10 mL graduated cylinder to measure the volume of 30~40 drops of 1.0 M HCl or NaOH solution. Calculate the average volumes of each drop of the solutions.</p> <p>Note: Use intact droppers to drop the acid or base solutions to avoid significant differences in the volumes of the individual drops.</p>	
4.	<p>Referring to Table 12-1(c), use 10 mL pipets to measure 15.0 mL of 0.050 M HOAc and 15.0 mL of 0.050 M NaOAc into a 50 mL beaker to prepare the test solutions.</p>	

5.	<p>Set up the apparatus according to Fig. 12-2. Measure the initial pH value of solution (c).</p> <p>Note: Stir the solution with a magnetic stirrer set on low speed. Adjust the position of the glass electrode to prevent it from being struck by the magnetic stirring bar. The front end of the electrode must be immersed in the solution as shown.</p>																																									
6.	<p>Add 1 drop of 1.0 M HCl from a dropper into solution (c). Mix the solution well and then read and record its pH value. Repeat addition five times.</p> <p>Note: Keep the dropper vertical while delivering the acid solution to ensure a constant volume of each drop.</p>																																									
7.	<p>Prepare solution (c) in another 50 mL beaker. Repeat the procedure described in step 5 and 6, but use 1.0 M NaOH instead of 1.0 M HCl. Record the pH values.</p>																																									
8.	<p>Repeat steps 4~7 for solutions (a), (b), (d), and (e) listed in Table 12-1.</p> <p>Note: The pH values of (e) DI water fluctuate a lot. Analyze it as the last one.</p>																																									
II. Effect of $[\text{OAc}^-]/[\text{HOAc}]$ ratio on buffer capacity (optional)																																										
9.	<p>Repeat steps 4~7. Determine the changes in pH of test solutions (f), (g), (h), and (i) listed in Table 12-1.</p>	<table border="1" data-bbox="1023 1402 1294 1615"> <thead> <tr> <th>Test solution</th> <th>0.050 M HOAc (mL)</th> <th>0.050 M NaOAc (mL)</th> <th>Distilled Water (mL)</th> </tr> </thead> <tbody> <tr> <td>(a)</td> <td>30</td> <td>0</td> <td>0</td> </tr> <tr> <td>(b)</td> <td>0</td> <td>30</td> <td>0</td> </tr> <tr> <td>(c)</td> <td>15</td> <td>15</td> <td>0</td> </tr> <tr> <td>(d)</td> <td>5</td> <td>5</td> <td>20</td> </tr> <tr> <td>(e)</td> <td>0</td> <td>0</td> <td>30</td> </tr> <tr> <td>(f)</td> <td>5</td> <td>25</td> <td>0</td> </tr> <tr> <td>(g)</td> <td>10</td> <td>20</td> <td>0</td> </tr> <tr> <td>(h)</td> <td>20</td> <td>10</td> <td>0</td> </tr> <tr> <td>(i)</td> <td>25</td> <td>5</td> <td>0</td> </tr> </tbody> </table>	Test solution	0.050 M HOAc (mL)	0.050 M NaOAc (mL)	Distilled Water (mL)	(a)	30	0	0	(b)	0	30	0	(c)	15	15	0	(d)	5	5	20	(e)	0	0	30	(f)	5	25	0	(g)	10	20	0	(h)	20	10	0	(i)	25	5	0
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III. Waste disposal and cleanup																																										
10.	<ol style="list-style-type: none"> (1) Rinse the pH electrode with DI water and immerse it into clean distilled water. (2) Turn the pH meter off. (3) Hand in magnetic stirring bar to lab instructor. (4) Waste liquids (salts) can be disposed in sink after neutralization. 																																									

10.	<p>(5) Rinse the pH electrode with DI water and immerse it into clean distilled water.</p> <p>(6) Turn the pH meter off.</p> <p>(7) Hand in magnetic stirring bar to lab instructor.</p> <p>(8) Waste liquids (salts) can be disposed in sink after neutralization.</p>	
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IV. Calculation

11	<p>Concentration and buffer capacity</p> <p>(1) Plot the pH values of solutions (a), (b), (c), (d), and (e) against number of drops of acid or base added, as shown in the diagram on the right.</p> <p>(2) Using the central five points of each data set obtained from solutions (c) and (d), plot least square regression lines with Microsoft Excel software. Calculate their slopes ($\Delta\text{pH}/\text{drop}$ of acid or base).</p> <p>(3) In this experiment, the concentration of HCl or NaOH is 1.0 M, and the volume of each buffer solution is 30 mL. Use these values as well as the slope and the volume of a drop of solution (V_{drop}) to calculate the buffer capacities of solution (c) and (d).</p>	
$\text{Buffer Capacity (meq/L} \cdot \text{pH)} = \frac{1}{\text{slope}} (\text{drop} / \text{pH}) \times V_{\text{drop}} (\text{mL} / \text{drop}) \times C_M (\text{eq} / \text{L}) \times \frac{1000 (\text{mL} / \text{L})}{30 \text{mL}}$		

References

- King, E. J. *Qualitative Analysis and Electrolytic Solutions*; Harcourt, Brace: New York, 1976.
- Advanced General Chemistry C/F 1507 Laboratory Manual*; Columbia Univ., 1991.
- Russel, A. A.; Siebert, E. D. *Experiments for General Chemistry*; 5th ed., Burgess International Group, Inc.: Minnesota, 1989; pp 18.
- Skoog, D. A.; Leary, J. J. *Principles of Instrumental Analysis*; 4th ed., Saunders College Publishing: Chicago, 1988; pp 477, 479, 495, 496.

Table 12-1 Preparation of various solutions for buffer capacity test

Test solutions	0.050 M HOAc (mL)	0.050 M NaOAc (mL)	DI water (mL)
(a)	30.0	0	0
(b)	0	30.0	0
(c)	15.0	15.0	0
(d)	5.0	5.0	20.0
(e)	0	0	30.0
(f)	5.0	25.0	0
(g)	10.0	20.0	0
(h)	20.0	10.0	0
(i)	25.0	5.0	0

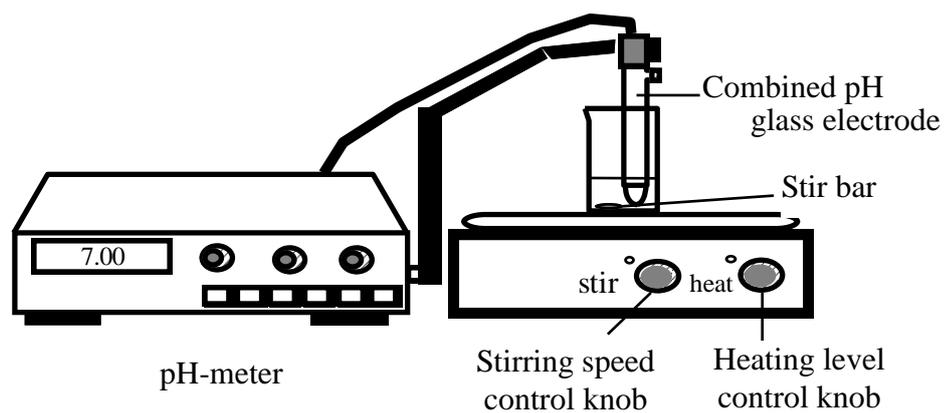


Figure 12-2 Measuring pH values of a solution with a pH-meter