Experiment 12

BUFFER SOLUTIONS

Objective

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

Lab techniques

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

Introduction

I. Buffer solution

A buffer solution can maintain a fairly constant pH value upon adding 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 for the dissociation of a weak acid can be described by equations 12-1 and 12-2:

$$\mathrm{HA(aq)} \rightleftharpoons \mathrm{H^+(aq)} + \mathrm{A^-(aq)} \qquad (12\text{-}1)$$

$$K_\mathrm{a} = \frac{[\mathrm{H^+}][\mathrm{A^-}]}{[\mathrm{HA}]} \qquad (12\text{-}2)$$

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

$$\mathrm{A^-(aq)} + \mathrm{H^+(aq)} \rightarrow \mathrm{HA(aq)} \qquad (12\text{-}3)$$

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

$$\mathrm{HA(aq)} + \mathrm{OH^-(aq)} \rightarrow \mathrm{H_2O(l)} + \mathrm{A^-(aq)} \qquad (12\text{-}4)$$

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):

$$[\mathrm{H^+}] = \frac{K_\mathrm{a}[\mathrm{HA}]}{[\mathrm{A^-}]} \qquad (12\text{-}5)$$

$$\mathrm{pH} = -\log[\mathrm{H^+}] = -\log K_\mathrm{a} - \log\left(\frac{[\mathrm{HA}]}{[\mathrm{A^-}]}\right) \qquad (12\text{-}6)$$

$$\mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log\left(\frac{[\mathrm{A^-}]}{[\mathrm{HA}]}\right) \qquad (12\text{-}7)$$

When adding a small amount of acid or base to the solution, the change in $\log\left(\frac{[\mathrm{A}^-]}{[\mathrm{HA}]}\right)$ 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 the 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, we will 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 concentrations affect the buffer capacity.

II. pH meter

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 thermometer probe to measure the temperature of the solution. The second part is a combination pH electrode composed of a reference electrode (an internal Ag/AgCl reference electrode with a fixed potential) and an indicator electrode (a glass electrode whose potential changes with the concentration of H+). The third part is a voltmeter, which measures the potential difference between the two electrodes. When the thermometer probe and the pH electrode are immersed in the analyte solution, the pH meter automatically performs temperature compensation calibration based on the measured solution temperature and directly converts the measured potential into a pH value.

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

$$E_m = K - 2.3\,RT\,\mathrm{pH}/nF \tag{12-8}$$

where E_m: measured cell potential

K: constant, depending on the type of electrode used

R: gas constant

T: absolute temperature of the solution

pH: pH value of the solution

n: number of electrons transferred in the electrode reaction

F: Faraday constant

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

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

If the 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 using two standard-pH buffer solutions at a 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.

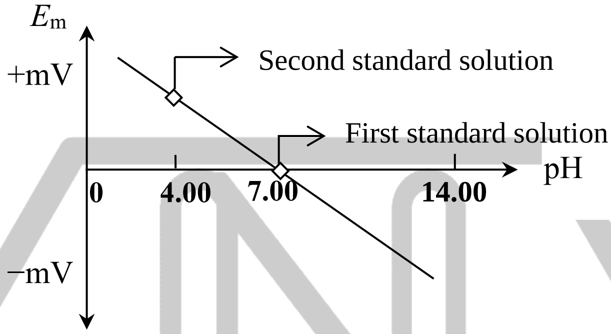


Figure 12-1 The relationship between measured cell potential and pH value

Apparatus

Volumetric flask (250 mL), graduated pipet (10 mL, 2) and pipet filler (2), beaker (50 mL, 4; 400 mL, 1), graduated cylinder (10 and 50 mL), dropper (2), pH meter, stirrer/hot plate and stir bar, funnel, facial tissue, and wash bottle.

Shared: electronic balance, pH 7.00 and 4.00 standard buffer solutions, and graduated pipet (2 mL).

Chemicals

Sodium acetate trihydrate, $CH_3COONa{\cdot}3H_2O$

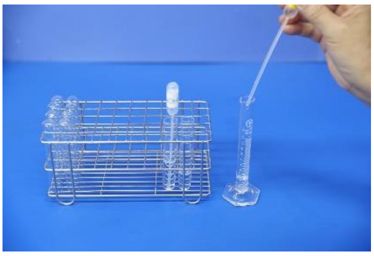
Concentrated acetic acid, 17 M CH_3COOH

1.0 M Hydrochloric acid, HCl(aq)

1.0 M Sodium hydroxide, NaOH

Procedure

Procedure		Illustration
1.	Calibrate the pH meter: (1) Press the “POWER” button to turn the pH meter on and warm up for 10 min. (2) Press the “MODE” button until “°C” is shown on the display to confirm and record the solution temperature, which should be close to room	

	temperature. Then press the “MODE” button again until the “pH” function is shown. (3) Press the “HOLD” button to lock the display reading. Remove the pH electrode and thermometer probe from the solution, rinse with DI water, and blot them dry with facial tissue. (4) Immerse the pH electrode and thermometer probe into the pH 7.00 standard buffer solution. Press the “HOLD” button again to unlock the display. Adjust the “CALIB.” knob until the display shows “7.00”. (5) Rinse the pH electrode and thermometer probe with DI water and blot them dry. Place them into the pH 4.00 buffer, and adjust the “SLOPE” knob until the display shows “4.00”. (6) Rinse the pH electrode and thermometer probe, then immerse into a beaker filled with DI water. Caution: The pH electrode is very expensive and easily broken. Be sure to handle it with caution.	   
2.	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 flasks, respectively. Then pour the solutions into 400 mL beakers. Note: Write down the preparation method in the prelab report.	
3.	Prepare two clean and dry test tubes and take 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 drops of each solution. Calculate the average volume of one drop of each solution. Note: Use intact glass droppers or plastic droppers to drop the acid and base solutions to avoid significant differences in the volumes of individual drops.	

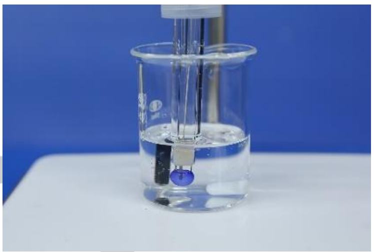
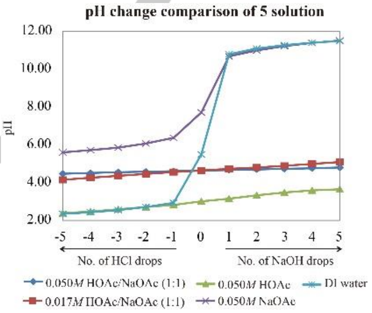
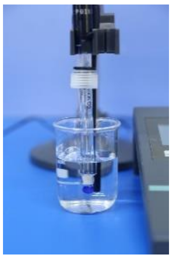
4.	Referring to Table 12-1, use 10 mL pipets to measure 15 mL of 0.050 *M* HOAc and 15 mL of 0.050 *M* NaOAc into a 50 mL beaker to prepare test solution (a).	
5.	Set up the apparatus according to Fig. 12-2. Measure the initial pH value of solution (a). Note: Stir the solution with a stirrer set on low speed. Adjust the position of the glass electrode to prevent it from being struck by the stir bar. The salt bridge of the electrode must be immersed in the solution as shown.	
6.	Add 1 drop of 1.0 *M* HCl from a dropper into solution (a). Mix the solution well and then read and record its pH value. Repeat the addition five times. Note: Keep the dropper vertical while delivering the HCl(aq) to ensure a constant volume of each drop.	
7.	Prepare solution (a) in another 50 mL beaker. Repeat the procedure described in steps 5 and 6, but use 1.0 *M* NaOH instead of 1.0 *M* HCl. Record the pH values.	
8.	Repeat steps 4~7 for test solutions (b), (c), (d), and (e) listed in Table 12-1. Use a 50 mL graduated cylinder to measure DI water. Note: The pH values of (e) DI water are greatly affected by trace amounts of acid and base. Analyze it as the last one.	
9.	(1) Waste liquids (salt solutions) can be discarded in the sink after neutralization. (2) Rinse and immerse the pH electrode in clean DI water (use a 100 mL beaker), or place it in an electrode cap filled with 3 *M* KCl. (3) Switch off the pH meter. (4) Return the stir bar to the lab instructor.	 

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)	15	15	0
(b)	5	5	20
(c)	30	0	0
(d)	0	30	0
(e)	0	0	30

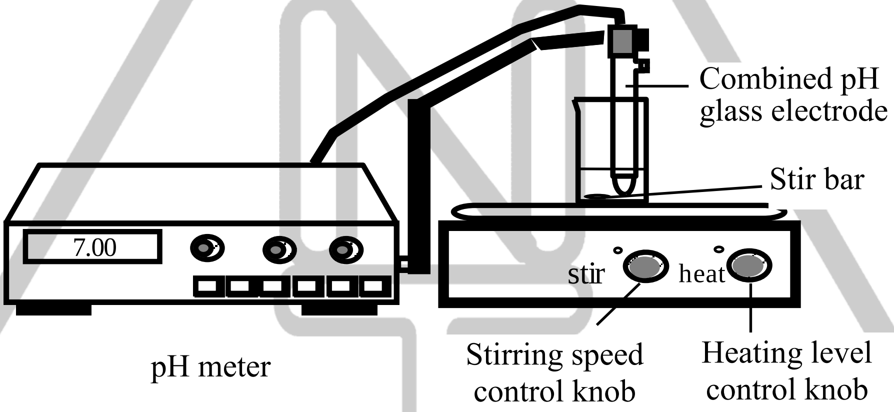


Figure 12-2 Measuring the pH value of a solution with a pH meter

References

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