

Experiment 13

POTENTIOMETRIC TITRATION OF ACID-BASE

Objective

The purpose of this experiment is to prepare and standardize a secondary standard NaOH solution, and then determine the acid dissociation constant, K_a , and the concentration of acetic acid in vinegar by using potentiometric titration.

Lab techniques

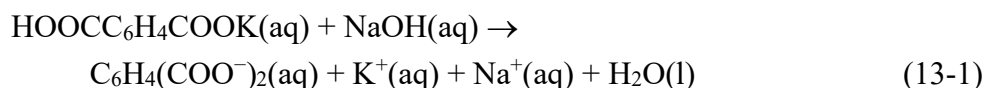
- Operating graduated pipet, buret, stirrer/hot plate, and pH meter
- Weighing chemicals
- Preparing solutions

Introduction

I. Standardization of a secondary standard base

In acid-base titrations, we need to prepare a standard acid or base solution, *i.e.* an acid or base solution having an accurately known concentration. The as-prepared standard solution is used to titrate an unknown solution and determine its acid or base concentration. To accurately determine the concentration of the standard solution, a primary standard with high purity, high stability, good solubility, high molar mass, and nonhygroscopic is used.⁽¹⁾ For example, sodium carbonate (Na_2CO_3) and potassium hydrogen phthalate (abbreviated as KHP) are common primary standards. The standardized acid or base, which is called the secondary standard solution, is used as a titrant in subsequent titrations of unknown samples.

In this experiment, we will prepare a sodium hydroxide standard solution that is standardized by KHP. Because KHP is a monoprotic weak acid, the neutralization takes place in a 1:1 ratio (13-1), and the concentration of sodium hydroxide solution is determined by stoichiometric calculations.



II. Determining the equivalence point of acid-base titration

In an acid-base titration, the equivalence point occurs when the number of moles of OH^- equals the number of moles of H^+ . The unknown acid or base concentration can then be calculated. Because the pH value of the reacting solution changes significantly near the equivalence point (Fig. 13-1), we could use an acid-base indicator or the potentiometric titration method to determine the equivalence point.

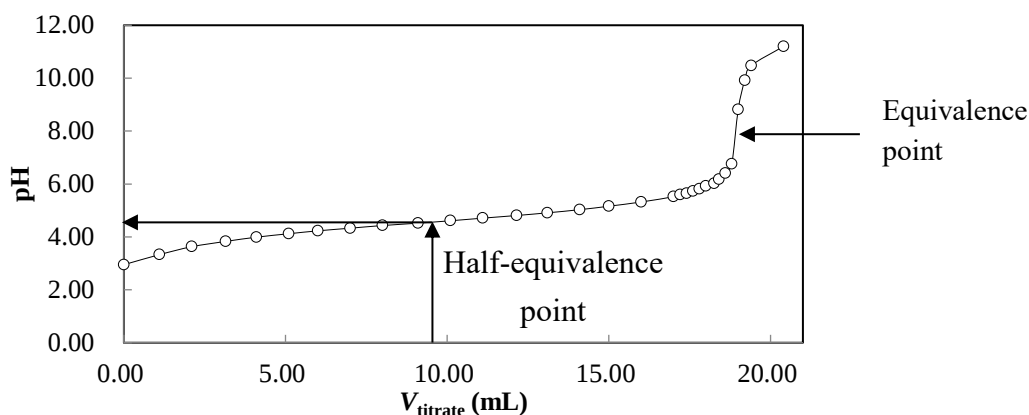


Figure 13-1 Acid-base titration curve and half-equivalence point

III. Choosing a suitable acid-base indicator in a titration

An acid-base indicator is typically a weak organic acid (denoted as HIn) whose color differs from the color of its conjugate base (In^-). Because the indicator is a weak acid with acid dissociation constant K_{In} , the $[\text{HIn}]/[\text{In}^-]$ ratio is governed by $[\text{H}_3\text{O}^+]$ of the solution (13-2~13-4):



$$K_{\text{In}} = \frac{[\text{H}_3\text{O}^+][\text{In}^-]}{[\text{HIn}]} \quad (13-3)$$

$$\text{pH} = \text{p}K_{\text{In}} + \log\left(\frac{[\text{In}^-]}{[\text{HIn}]}\right) \quad (13-4)$$

When the pH value of the solution is greater than $\text{p}K_{\text{a}} + 1$, we see the color of In^- . On the contrary, if the pH value is less than $\text{p}K_{\text{a}} - 1$, we see the color of HIn . Owing to a significant change in pH value near the equivalence point, we choose an indicator with a color change close to the pH of the equivalence point that signals the titration end point. For example, phenolphthalein changes from colorless at pH 8 to pink at pH 10 and thus is commonly used in weak acid and strong base titration.

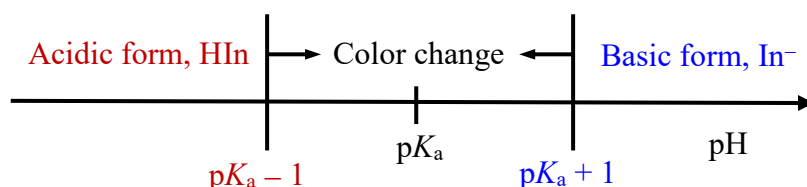


Figure 13-2 Color change of acid-base indicator

IV. Potentiometric titration

Potentiometric titrations are often applied in acid-base, oxidation-reduction, and precipitation titration experiments. For acid-base titration, a pH meter (refer to

Experiment 12) is used to monitor the pH values of the solution after delivering various volumes of a titrant. We can then deduce the equivalence point by plotting the titration curve. Three common methods (curves) are used to determine the equivalence point of titration:

1. Titration curve: The pH values (or the electric potentials) versus the volume of titrant added are plotted (Fig. 13-1). The point on the curve with the largest slope is the equivalence point. Although this is the simplest method, it is usually less accurate than the other two.
2. The first derivative of the titration curve: The changes in the pH value per unit volume of titrant added ($\Delta\text{pH}/\Delta V$) vs the volume of titrant added are plotted (Fig. 13-3). The point with the maximum $\Delta\text{pH}/\Delta V$ value is the equivalence point.

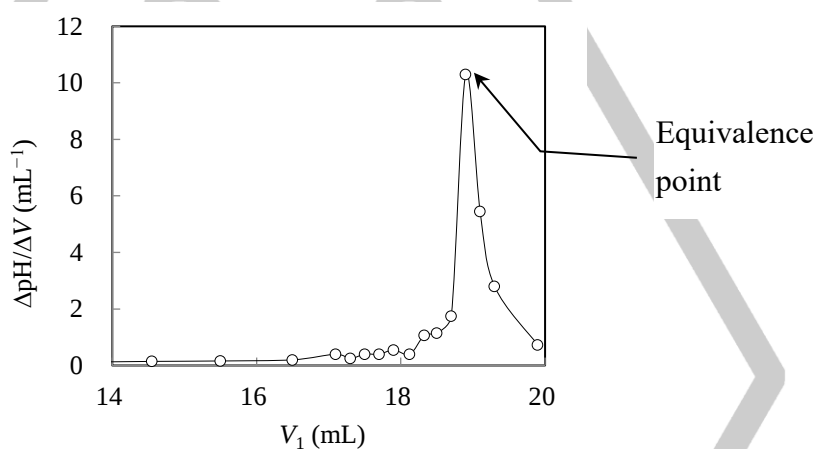


Figure 13-3 First derivative of titration curve

3. The second derivative of the titration curve: The changes in the $\Delta\text{pH}/\Delta V$ value per unit volume of titrant added vs the volume of titrant added are plotted (Fig. 13-4). The point at which its $\Delta^2\text{pH}/\Delta V^2$ equals 0 (in the graph, the x-intercept of the straight line between points A and B) is the equivalence point. This is the most accurate of the three methods.

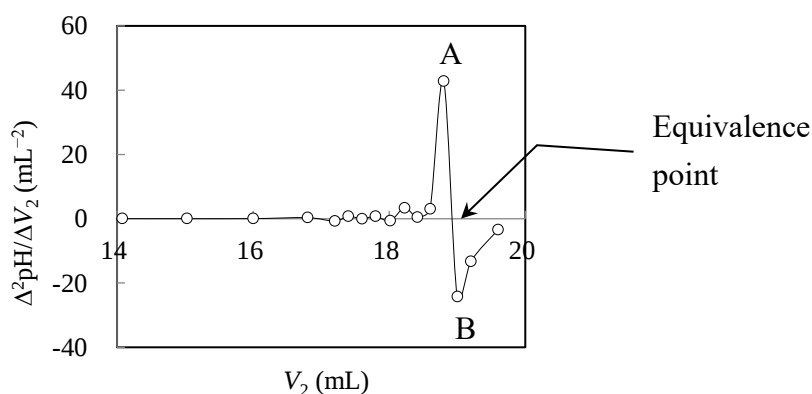


Figure 13-4 Second derivative of titration curve

Software, e.g. MS-Excel, can be used to calculate and plot the first and second

derivatives of titration curves as demonstrated in Table 13-1.

Table 13-1 Examples of the first and second derivatives of the titration curve

V_{read} (mL)	V_{titrant} ($V_{\text{read}} - V_i$) (mL)	pH	First derivative		Second derivative	
			V_1^a (mL)	$\Delta\text{pH}/\Delta V$ (mL^{-1})	V_2^b (mL)	$\frac{\Delta(\Delta\text{pH}/\Delta V)}{\Delta V_1}$ (mL^{-2})
0.50	0.00	2.95	0.55	0.35 ^c	1.08	-0.05 ^d
1.60	1.10	3.33	1.60	0.30	2.11	-0.11
2.60	2.10	3.63	2.63	0.19	3.13	-0.02
3.65	3.15	3.83	3.63	0.17	4.11	-0.04
...	...	...	...	...	...	...
18.90	18.40	6.18	18.50	1.15	18.60	3.00
19.10	18.60	6.41	18.70	1.75	18.80	42.75
19.30	18.80	6.76	18.90	10.30	19.00	-24.25
19.50	19.00	8.82	19.10	5.45	19.20	-13.25
19.70	19.20	9.91	19.30	2.80	19.60	-3.45

^a V_1 : average of two consecutive volumes of V_{titrant} , *e.g.* $(0.00 + 1.10)/2 = 0.55$

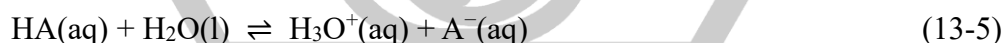
^b V_2 : average of two consecutive volumes of V_1 , *e.g.* $(0.55 + 1.60)/2 = 1.08$

^c $(3.33 - 2.95) / (1.10 - 0.00) = 0.35$

^d $(0.30 - 0.35) / (1.60 - 0.55) = -0.05$

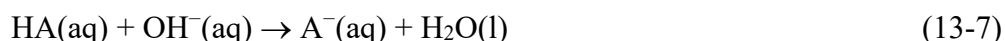
V. Acid dissociation constant of a weak acid

A weak acid (HA) only dissociates partially in an aqueous solution and reaches equilibrium with its conjugate base (A^-) as described in equation 13-5. The acid dissociation constant expression is shown in equation 13-6.



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} \quad (13-6)$$

When the weak acid is titrated with a strong base (*e.g.* NaOH), the neutralization reaction is expressed in equation 13-7:



When the half-equivalence point is reached, *i.e.* the point on a titration curve where the volume added is exactly one-half of that found at the equivalence point, there is

$$[\text{HA}] = [\text{A}^-]$$

$$[\text{H}_3\text{O}^+] = K_a$$

Therefore, the $\text{p}K_a$ value of the weak acid equals the pH value of the reacting

solution at the half-equivalence point, as marked in Fig. 13-1.

Apparatus

Stirrer/hot plate, stir bar, pH meter, buret (25 mL), funnel, volumetric flask (100 mL), Erlenmeyer flask (125 mL, 2), beaker (250 mL, 1 L), wash bottle, and facial tissue.

Shared: analytical balance, graduated pipet (5 mL), pipet filler, pH 7.00 and 4.00 standard buffer solutions.

Chemicals

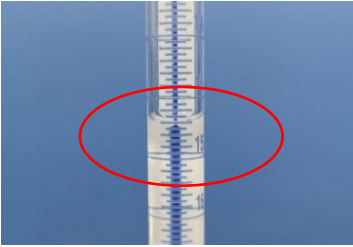
Vinegar (acetic acid, ethanoic acid, CH_3COOH)

0.1% Phenolphthalein

1.0 M Sodium hydroxide, NaOH

Potassium hydrogen phthalate (KHP), $\text{HOOC}_6\text{H}_4\text{COOK}$ (KHP has been heated and dried at 110°C for 2 hours and placed in a desiccator for cooling before use.)

Procedure

Procedure		Illustration
I. Preparation of a secondary standard NaOH solution		
1.	Prepare 100 mL of 0.1 M NaOH from 1.0 M NaOH by using a 100 mL volumetric flask. Pour it into a 250 mL beaker. Note: Write down the preparation method and calculation in the prelab report.	
2.	Wash a 25 mL buret with water and then rinse it twice with <i>ca.</i> 5 mL of 0.1 M NaOH each time. Fill the buret with the NaOH solution. Read the initial volume (V_i) to 0.01 mL. Note: Do not use too much prepared NaOH solution to rinse the buret. Ensure you have enough solution to conduct the whole experiment.	
II. Standardization of NaOH solution with KHP		

3.	Use an analytical balance to weigh 0.2~0.22 g KHP and record its accurate weight to 0.1 mg. Transfer the KHP to a 125 mL Erlenmeyer flask and dissolve it with <i>ca.</i> 50 mL of DI water.	
4.	Add 2 drops of 0.1% phenolphthalein indicator to the KHP solution. Titrate it with 0.1 M NaOH. The end point is reached when the solution turns pink and the color persists for 30 s. Record the final volume (V_f) to 0.01 mL. Repeat steps 3~4 to duplicate the standardization. Note 1: Add only 2~3 drops of indicator to the solution to avoid titration error, for the indicator is also a weak acid. Note 2: Before titration, the titration volume of the NaOH solution can be estimated from the number of moles of KHP using a stoichiometric calculation.	
5.	Use the titration volume of NaOH ($V_{\text{NaOH}} = V_f - V_i$) to calculate the concentration of sodium hydroxide (C_{NaOH}); take the average value as the standardized concentration of NaOH.	$n_{\text{KHP}} = \frac{\text{Mass}_{\text{KHP}}}{204.22}$ $n_{\text{KHP}} = C_{\text{NaOH}} \times V_{\text{NaOH}}$
III. Titration of vinegar		
6.	Calibrate the pH meter: Refer to the Experiment 12 or Laboratory Techniques. Caution: The pH electrode is very expensive and easily broken. Be sure to handle it with caution.	
7.	Use a 5 mL graduated pipet to transfer exactly 2.50 mL of vinegar into a 100 mL beaker. Add <i>ca.</i> 40 mL of DI water and 2 drops of phenolphthalein indicator to the beaker.	

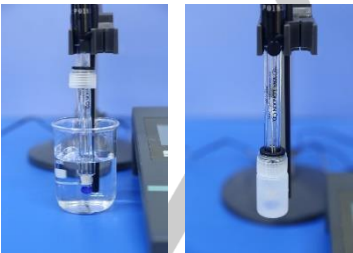
8.	Set up the apparatus according to Fig. 13-5. Immerse the pH electrode and thermometer probe into the vinegar solution. Stir the solution with a stir bar.	
9.	Titrate the vinegar solution with the standardized 0.1 M NaOH. Record the pH values after adding approximately 1 mL of NaOH(aq) each time. Once the pH value starts to change rapidly (around pH 5.5 in this experiment), add 0.2 mL of NaOH solution each time and record the pH value after each addition. When the pH value exceeds 10, 1 mL of NaOH solution is added each time until the pH value is over 11 and near pH 12. Observe and record any color changes in the solution during the titration.	
10.	(1) The aqueous waste containing sodium acetate can be discarded into the sink. Pour the unused NaOH(aq) to the recycling waste bottle. (2) The cleaned buret should be clamped upside-down on the buret clamp. (3) Rinse and then immerse the pH electrode in clean DI water (use a 100 mL beaker), or place the electrode in a plastic cap filled with 3 M KCl. (4) Switch off the pH meter. (5) Return the stir bar to the lab instructor.	



Figure 13-5 pH Meter and setup for titration

References

1. Skoog, D. A.; West, D. M.; Holler, F. J. *Fundamentals of Analytical Chemistry*, 5th ed., 1988, Saunders College Publishing: New York.
2. Harris, D. C. *Quantitative Chemical Analysis*, 5th ed., 1999, W. H. Freeman and Co.: New York.
3. Zumdahl, S. S.; *Chemical Principles*, 3rd ed., 1998, Houghton Mifflin Co.: New York, p.286.

