

Experiment 13

POTENTIOMETRIC TITRATION OF ACID-BASE

Objective

The purpose of this experiment is to prepare and to standardize secondary standard solution; to determine the concentration and the dissociation constant of acetic acid by using an electric potential method.

Lab techniques

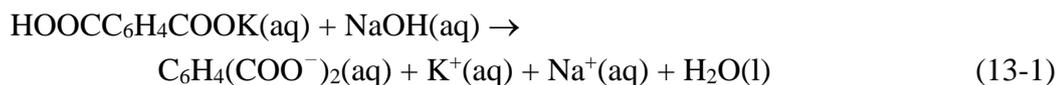
- Weighing chemicals.
- Preparing solutions.
- Operating graduated pipet, buret, stirrer/hot plate, and pH-meter.

Introduction

I. Standardization of a standard acid or 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 content. To accurately determine the concentration of the standard solution, a primary standard with high purity and high molar mass is used⁽¹⁾. For example, sodium carbonate (Na_2CO_3) and potassium hydrogen phthalate (abbreviated as KHP) are common primary standards. The standardized acid (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 sodium hydroxide standard solution that is standardized with 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 (13-2).



$$C_{\text{NaOH}} \cdot V_{\text{NaOH}} = n_{\text{KHP}} = \frac{\text{Mass}_{\text{KHP}}}{204.22} \quad (13-2)$$

II. Determining the equivalence point

In an acid-base titration, the equivalence point occurs when the number of moles of added OH^- equals the number of moles of H_3O^+ originally present.

Therefore, 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 electric potential method to determine the equivalence point.

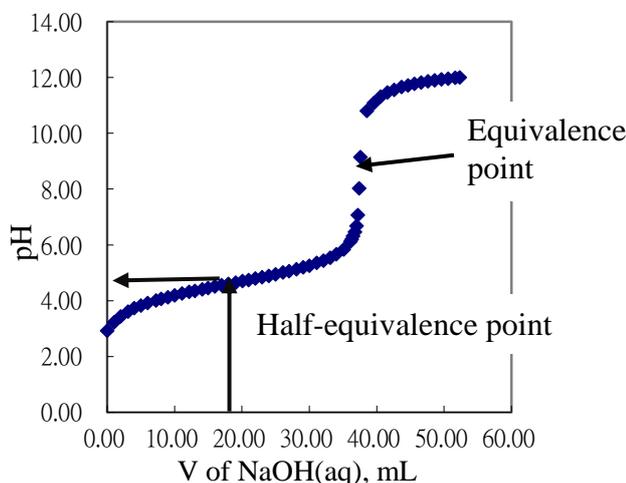
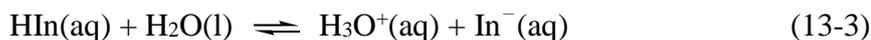


Figure 13-1 Weak acid-strong base titration curve and half-equivalence point

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

An acid-base indicator is 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 an acid dissociation constant K_a , the $[\text{HIn}]/[\text{In}^-]$ ratio is governed by the $[\text{H}_3\text{O}^+]$ of the solution (13-3~13-5).



$$K_a(\text{HIn}) = \frac{[\text{H}_3\text{O}^+][\text{In}^-]}{[\text{HIn}]} \quad (13-4)$$

$$\frac{[\text{HIn}]}{[\text{In}^-]} = \frac{[\text{H}_3\text{O}^+]}{K_a} \quad (13-5)$$

When solution is more acidic and $[\text{HIn}] \geq 10[\text{In}^-]$, that is $\text{pH} \leq \text{p}K_a - 1$, we observe the color of HIn. On the other hand, if pH of solution is greater than $\text{p}K_a + 1$, it shows the color of In^- (Fig. 13-2).

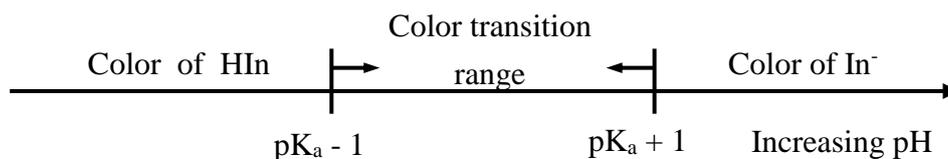


Figure 13-2 Color of acid-base indicator depends on pH of solution

Owing to a significant change of pH near the equivalence point, we choose an

indicator with a color change close to the pH of the equivalence point that signals the end point of titration. For example, phenolphthalein ($pK_a = 9$) changes from colorless at pH 8 to pink at pH 10 that is commonly used in a weak acid and strong base titration.

IV. Electric potential titration

Electric potential methods are often applied in acid-base, oxidation-reduction, and precipitation titration experiments. For acid-base titrations, a pH electrode is used to monitor the pH values of solution after delivering various volumes of a titrant. We can then deduce the equivalence point by plotting the titration curves. Three common methods (curves) that are used to determine the equivalence point of titration are described:

1. Titration curve: Plot pH values (or electric potential) versus volume of titrant added (Fig. 13-1). The equivalence point is the point on the curve having the maximum slope. Although this method is the simplest one, it is not as accurate as the other two methods.
2. The first derivative of titration curve: The changes in pH value per unit volume of titrant added ($\Delta pH/\Delta V$) vs volume of titrant added are plotted (Fig. 13-3). The point having a maximum $\Delta pH/\Delta V$ value is the equivalence point.

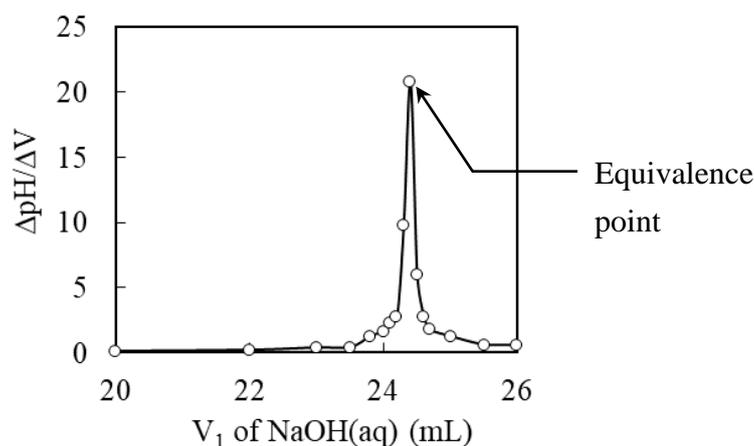


Figure 13-3 First derivative of titration curve

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

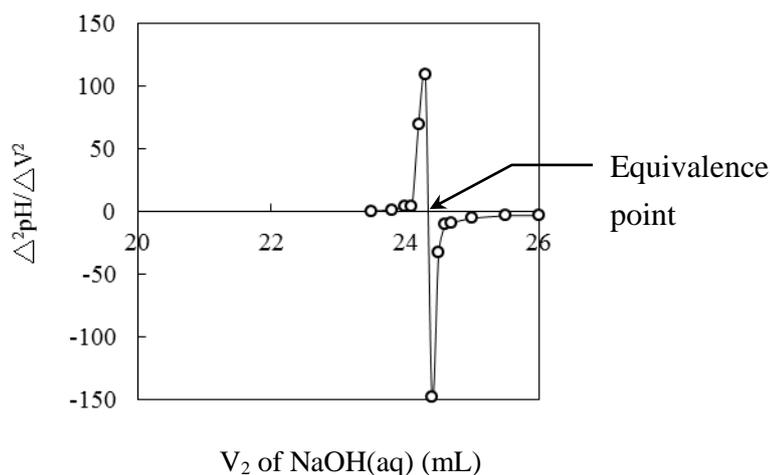


Figure 13-4 Second derivative of titration curve

4. Software, e.g. MS-Excel, can be used to calculate and plot the first and second derivatives of titration curves as tabulated in Table 13-1.

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

NaOH Volume V (mL)	pH	First derivative		Second derivative	
		V_1^a	$\Delta\text{pH}/\Delta V$	V_2^b	$\frac{\Delta(\Delta\text{pH}/\Delta V)}{\Delta V}$
34.02	5.54	34.52	0.16 ^c	35.02	0.04 ^d
35.02	5.70				
36.01	5.90	35.52	0.20	36.01	0.13
37.01	6.23	36.51	0.33	37.01	0.94
38.00	7.49	37.51	1.27	38.00	1.66
39.00	10.42	38.50	2.93	39.00	-2.47
40.00	10.88	39.50	0.46	40.00	-0.25
40.52	11.02	40.26	0.27		

a: V_1 : average of two consecutive volumes (V)

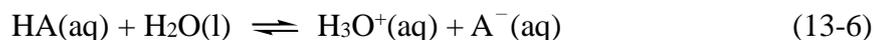
b: V_2 : average of two consecutive volumes (V_1)

c: $(5.70 - 5.54)/(35.02 - 34.02) = 0.16$

d: $(0.20 - 0.16)/(35.52 - 34.52) = 0.04$

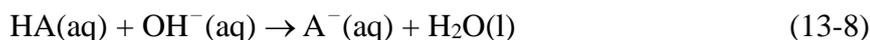
V. Acid dissociation constant of a weak acid

A weak acid (HA) only dissociates partially in aqueous solution and reaches equilibrium with its conjugate base (A^-) as equation 13-6. The acid dissociation constant expression is shown in equation 13-7.



$$K_a = \frac{[H_3O^+][A^-]}{[HA]} \quad (13-7)$$

When the weak acid is titrated with a strong base (e.g. NaOH), the neutralization reaction is expressed in equation 13-8:



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:

$$[HA] = [A^-], \text{ then } [H_3O^+] = K_a$$

Therefore, the pK_a value of the weak acid is equal to the pH value of the reacting solution at the half-equivalence point.

Apparatus

pH-Meter, stirrer/hot plate, magnetic stirring bar, buret (25 mL), volumetric flask (100 mL), Erlenmeyer flask (125 mL, 2), tissues, and funnel.

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

Chemicals

Vinegar

1% Phenolphthalein

1 M Sodium hydroxide, NaOH

Potassium hydrogen phthalate (KHP), $HOOC_6H_4COOK$

Note: KHP must be dried at 110°C for 2 hours and cooled in desiccators before being weighed.

Procedure

I. Preparation of a secondary standard NaOH solution

1. Prepare 100 mL of 0.1 M NaOH solution from 1 M NaOH solution by using 100 mL volumetric flask.

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 ca. 5 mL 0.1 M NaOH solution 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 buret to ensure you have enough solution to conduct the whole experiment. Refer to the experimental skills videos to learn how to use a buret.

II. Standardization of NaOH solution with KHP

3. Use analytical balance to weigh 0.2~0.22 g KHP and transfer to a 125 mL Erlenmeyer flask. Record its accurate weight and dissolve it with 50 mL of DI water.
4. Add 2 drops of 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.

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: Prior to titration, the titration volume of 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 standardized concentration of sodium hydroxide (C_{NaOH}).
6. Repeat steps 3~5 to duplicate the analysis, and calculate the average concentration of NaOH solution.

III. Calibration of pH-Meter

7. Push the "POWER" button of pH-meter and allow it to warm up for 10 min. Calibrate with two standard buffer solutions (pH 7.00 and pH 4.00).
8. Press "MODE" button and switch to "TEMP" function that shows "°C". Confirm the temperature of solution is close to room temperature and record it.
9. Press "MODE" button and switch to "pH" function, and start calibrating pH-meter.
10. Press "HOLD" to lock the screen and use DI water to rinse electrode and thermoprobe. Blot electrode and thermoprobe by tissues and put them into pH 7.00 buffer solution, press "HOLD" again to unlock the screen.
11. Adjust "CALIB" knob until meter shows "7.00".
12. Repeat step 10, but place the electrode and thermoprobe into pH 4.00 buffer solution, adjust "SLOPE" knob until meter shows "4.00" and complete calibration.

Notice: pH-electrode is expensive and easily broken, ought to handle with care.

Note: Refer to the experimental skills video to learn how to operate a pH-meter.

IV. Titration of vinegar

13. Use a 5 mL graduated pipet to transfer 2.5 mL of vinegar into a 100 mL beaker. Add 40 mL of DI water and 2 drops of phenolphthalein indicator to the beaker.
14. 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 magnetic stirring bar.
Note: The front end of pH electrode should be fully immersed in solution to ensure a stable measurement. Avoid stirring bar colliding with the electrode. Refer to the experimental skills videos to learn how to operate a stirrer/hot plate.
15. Fill up the buret with the standardized 0.1 M NaOH. Read the V_i of buret and pH value of vinegar solution. Start titration and record the pH values after adding approximately 1 mL of NaOH(aq) each time. Once the pH value changes more 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. Observe and record any color-changes in the solution during the titration.
16. The neutralized aqueous waste containing sodium acetate can be discarded into the sink. Store the pH electrode in a beaker with DI water or plastic-cap that containing 3 M KCl.



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.