Experiment 13

POTENTIOMETRIC TITRATION OF ACID-BASE

Objective

The purpose of this experiment is to prepare and standardize a secondary standard solution; to determine the equivalence point of titration and the acid dissociation constant (K_a) of acetic acid by using an electric potential method.

Technique

You will learn the skills of weighing chemicals, preparation of solutions, manipulating graduated pipet, buret, and pH-meter, as well as graphic method.

Introduction

I.   Standardization of a secondary 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 a known concentration with high precision. 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 higher molar mass is used. For example, sodium carbonate (Na_2CO_3) and potassium hydrogen phthalate (abbreviated as KHP) are commonly used primary standards. After standardization, we use this secondary standard as a titrant to titrate the unknown samples.

In this experiment, we will prepare a 0.1 M NaOH(aq) to be standardized with KHP. For KHP is a monoprotic weak acid, the neutralization reaction takes place in a 1:1 stoichiometic ratio (13-1). The precise concentration of sodium hydroxide solution is determined by equation 13-2.

$$HOOCC_6H_4COOK(aq) + NaOH(aq) \rightarrow$$
$$C_6H_4(COO^-)_2(aq) + K^+(aq) + Na^+(aq) + H_2O(l) \qquad (13\text{-}1)$$
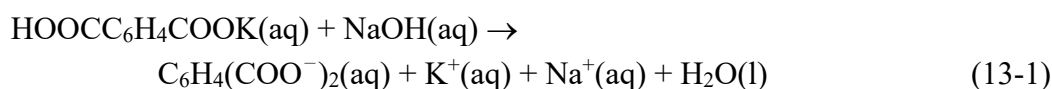
$$C_{NaOH} \cdot V_{NaOH} = n_{KHP} = \frac{mass_{KHP}}{204.22} \qquad (13\text{-}2)$$

II.   Determining the equivalence point

In an acid-base titration, the equivalence point is the point at which stoichiometrically equivalent quantities of acid and base have been brought together. 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.
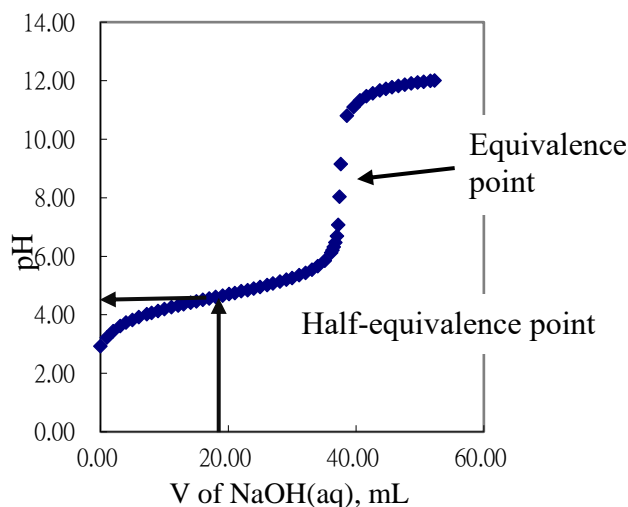

Figure 13-1 Weak acid-strong base titration curve and half-equivalence point

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

An acid-base indicator is a weak acid (HIn) having its acid form (HIn) and basic form (In⁻) with different colors (13-3). It shows acid color when pH of solution is lower than pK_{HIn} - 1 (13-4); appears basic color while pH is greater than pK_{HIn} + 1. Owing to a significant change in pH value near the equivalence point of acid-base titration, we observe the color change of added indicator that signals the end point of titration. Therefore, it is important to select a suitable indicator. It should have a sharp color change to signal the end point of titration, that coincides with the equivalence point closely. Phenolphthalein which changes color within pH 8~9 is commonly used in a weak/strong acid and strong base titration.

$$\underline{HIn} + H_2O \rightleftharpoons H_3O^+ + \underline{In^-} \qquad (13\text{-}3)$$

Acid form   Basic form
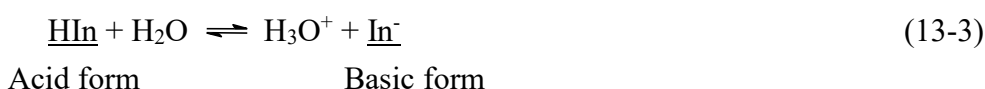
$$K_{HIn} = \frac{[In^-][H_3O^+]}{[HIn]} \qquad (13\text{-}4)$$

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 titrant. We can deduce the equivalence point by plotting the titration curves. The acid-base titration curve is a graph of the pH as a function of the volume of titrant added (Fig. 13-1). The equivalence point is the point that having the greatest slope.

V. Acid dissociation constant of a weak acid

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

$$HA + H_2O \rightleftharpoons H_3O^+ + A^- \tag{13-5}$$

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} \tag{13-6}$$

The neutralization reaction of a monoprotic weak acid and strong base (e.g. NaOH), the balanced equation is expressed as equation 13-7:

$$HA(aq) + OH^-(aq) \rightarrow A^-(aq) + H_2O(l) \tag{13-7}$$
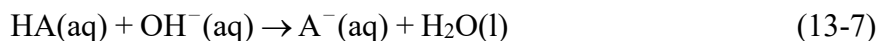
At the half-equivalence point, i.e. one-half of the acid has been neutralized and produce same amount of its conjugated base (13-8). According to equation 13-6, the [H$^+$] of the solution is equal to the K_a value at the half-equivalence point (13-9). Then, the K_a value can be determined by titration curve (Fig. 13-1) accordingly.

$$[HA] = [A^-] \tag{13-8}$$

$$[H_3O^+] = K_a \tag{13-9}$$

Equipment

pH-meter, hot plate/magnetic stirrer, magnetic stirring bar, buret (50 mL), volumetric flask (100 mL), Erlenmeyer flask (125 mL, 2), tissues.

Shared: graduated pipet (5 mL), pipet filler, analytical balance, and standard buffer solutions (pH 7.0 and 4.0).

Chemicals

Vinegar

1% Phenolphthalein

1.0 M Sodium hydroxide, NaOH

Potassium hydrogen phthalate, HOOCC$_6$H$_4$COOK

Note: KHP must be dried at 110°C for 2 hours (done by the staff in the preparation room) and cooled in desiccators before being weighed.

Procedure

I. Preparation of a secondary standard base solution

1. Prepare 100 mL of 0.1 M NaOH solution from 1.0 M NaOH by using 100 mL volumetric flask.

    Note: Write down the calculation and preparation methods in the prelab report.

2. Wash a 50 mL buret with water and rinse it with ca. 5 mL 0.1 M NaOH(aq) twice. Fill the buret with the base solution. Read the initial volume (V_i) to 0.01 mL.

Note: Do not waste your prepared NaOH solution to ensure that you have enough solution to conduct the whole experiment. Refer to the experimental skills video to learn how to use a buret.

II.   Standardization of sodium hydroxide solution with KHP

3.   Weigh 0.2~0.22 g KHP directly into a 125 mL Erlenmeyer flask. Record its accurate weight and dissolve it with 50 mL distilled water.
   Note: Use an analytical balance to weigh the KHP with a precision of 0.1 mg.

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 remains at least 30 s. Record the final volume (V_f) to 0.01 mL.
   Note 1:   Add only 2-3 drops of acid base indicator into the solution to avoid titration error because 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 by a stoichiometric calculation.

5.   Use the titration volume of NaOH ($V_{NaOH} = V_f - V_i$) to calculate the precise concentration of sodium hydroxide (C_{NaOH}).

6.   Repeat steps 3~5 to perform a duplicate test and calculate the average concentration of NaOH solution.

III.   Calibrate pH-Meter

7.   Push the "POWER" button of pH-meter and allow it to warm up for 10 min. Calibrate it with two standard buffer solutions (pH 7.0 and pH 4.0).

8.   Press "MODE" button and switch to "TEMP" function that shows "ºC". 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 D.I. water to rinse electrode and thermoprobe. Blot electrode and thermoprobe by tissues and put them into pH 7.0 buffer solution, press "HOLD" again to unlock the screen.

11.   Adjust "CALIB." knob until meter shows "7.00".

12.   Repeat step 10, but replace the electrode and thermoprobe into pH 4.0 buffer solution, adjust "SLOPE" knob until meter shows "4.00" and complete calibration.
   Note: Refer to the experimental skills video to learn how to operate a pH-meter.

IIII. Titration of vinegar

13.   Use a 5 mL graduated pipet to transfer exactly 2.5 mL vinegar into a 100 mL beaker. Add 40 mL D.I. water and 2 drops 1% phenolphthalein indicator to the beaker.

14.   Set up the apparatus according to Fig. 13-2. 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 video to learn how to operate a hot plate/magnetic stirrer.

15. Titrate the vinegar solution with the standardized 0.1 M NaOH. Record the pH values after adding approximately 1.0 mL portions of NaOH solution each time. Once the pH value changes more rapidly (within the range of pH 6-10 in this experiment), add NaOH solution at 0.2 mL intervals. When the pH value is over 11 you may stop titrating. Observe and record any color-changes of the solution during the titration.

16. The aqueous waste containing sodium acetate salt can be discarded into the sink.

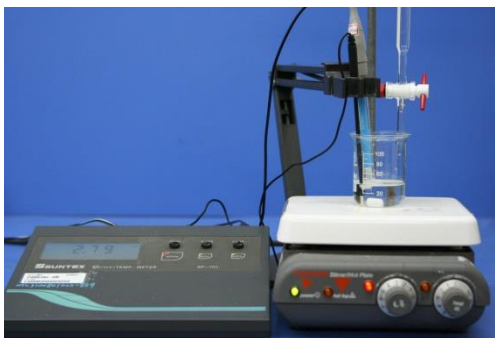Figure 13-2 Set up of pH-meter and apparatus for titration

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.

Name _____   Student ID No. _____

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I. Experimental Data and Results

1. The calculation and preparation methods of 100 mL of 0.1 M NaOH.

2. Standardizing the concentration of NaOH solution with KHP

Trial	Mass of KHP (g)	V_i (mL)	V_f (mL)	V_{NaOH} = V_f - V_i (mL)	C_{NaOH} (M)
1					
2					

Average concentration of NaOH solution: _____

Calculation:

3. Titration of vinegar

   (1) Brand name of vinegar_____

   (2) Indicated acetic acid content_____

   (3) Volume of vinegar used in the titration _____ mL

   (4) Titration of vinegar with NaOH solution

V_{read}	pH	Color	V_{read}	pH	Color

(5) Plot the acid-base titration curve with pH on the y-axis and titration volume of NaOH (V) on the x-axis.

(6) Determine the equivalence point, equivalence volume (V_{eq}), and half-equivalence point from titration curve.

(7) Assume that all of the acid in the vinegar is acetic acid (CH_3COOH) and the density of the vinegar is 1.0 g/cm^3. Use the equivalence volume to calculate the molar concentration (mol/L) of acetic acid in the vinegar, and its percentage by mass (%, w/w). Compare with that indicated on label.

(8) Determine the pK_a of acetic acid from half-equivalence point of your experimental data and compare with the theoretical value.