DETERMINATION OF THE OXALIC ACID CONCENTRATION BY PERMANGANOMETRIC TITRATION (6)

Objective

To become familiar with the techniques of titration, to learn how to use the buret and the pipet.

Theoretical background

Titration is a quantitative analytical method based on volume measurement, in which the concentration of a substance (a solution to be titrated, analyte or titrand) is determined from a known concentration of a reagent (titrant) using a rapid chemical reaction with a stoichiometry of

$$\nu_A A + \nu_B B = \ldots \quad ,$$

from which the unknown amount of B can be calculated by measuring the volume and the amount of A.

During titration, the equivalence point or end point is the state when the titrand is in stoichiometric ratio with the titrant, i.e.,

$$\frac{n_A}{\nu_A} = \frac{n_B}{\nu_B} \quad .$$

The end point is typically indicated by a sharp color change of an added compound, so-called indicator. The precise concentration of the titrant usually is determined by independent titration of known amount of high purity material, known as standardization.

During the practice, oxalic acid is titrated with potassium permanganate in acidic solution

$$2\,MnO_4^- + 5\,(COOH)_2 + 6\,H^+ \rightarrow 2\,Mn^{2+} + 10\,CO_2 + 8\,H_2O$$

so permanganate can be reduced to Mn^{2+} ion, while carbon dioxide is generated from the oxalic acid. The reaction is slow at room temperature but heating the solution up sufficiently accelerates it. The reaction rate further increases as the produced Mn^{2+} ions catalyze the reaction.

No extra compound is added, since potassium permanganate acts as a self-indicator. The color of potassium permanganate disappears upon its reduction by oxalic acid. After the complete consumption of oxalate ions, the end point is indicated by the appearance of a light pink color produced by the addition of a slight excess of the unreacted potassium permanganate.

Potassium permanganate solution with accurate concentration cannot be prepared from solid potassium permanganate. Therefore, first it has to be standardized. Finally, the molarity of the oxalic acid with unknown concentration has to be determined.

Materials

beaker of 100 cm^3 volume (2 pieces)
volumetric flask of 100 cm^3 volume
buret of 25 cm^3 volume
pipet of 10 cm^3 volume
pipet bulb
wide-neck Erlenmeyer flask of 200 cm^3 (3 pieces)
graduated cylinder of 10 cm^3 volume
wash bottle
Bunsen stand
buret clamp
Bunsen burner
metal tripod stand
wire gauze

Experimental overview

A pre-prepared solution of potassium permanganate will be used. You'll receive 10.00 ml of oxalic acid solution of 0.500 mol/dm^3 solution in a volumetric flask of 100 cm^3 which should be diluted to 100 cm^3. With the known concentration of oxalic acid you standardize the potassium permanganate solution. Then you'll receive 10.00 ml of oxalic acid solution of unknown concentration, the concentration of which will be determined by permanganometric titration.

Procedure

Assembly of the apparatus

- Place the Bunsen burner on the desk, far from the buret. Place the metal tripod stand with the wire gauze on it. If needed, ask the instructor to show how to use it.
- Place the buret in a stand with a buret clamp.
- Close the buret stopcock and fill the buret with distilled water. Check that the buret is closing tightly. If needed, ask for the help of the instructor.
- Pour some potassium permanganate solution into a clean and dry beaker of 100 cm^3 volume. This will be used to pour the titrant into the buret. You can use the beaker provided next to the potassium permanganate bottle for this purpose.
- Place a beaker below the buret which will be used to store the waste solution. Rinse the buret with a small amount of potassium permanganate solution. Fill the buret. Make sure there is no air bubble in the tip. *Tips: NEVER pour the titrant back to the storage bottle as you can contaminate it. The waste should be poured into the waste containers.*
- Place a white tile or sheet of paper on the desk, below the buret for better visualization.

Standardization of potassium permanganate solution

- Dilute the 10.00 cm^3 oxalic acid of $c_{ox,0}$ = 0.500 mol/dm^3 molarity with the wash bottle to the mark on the volumetric flask. Mix it well.
- Pour some oxalic acid solution into a clean and dry beaker of 100 cm^3.
- Take the 3 Erlenmeyer flasks on the desk and pipet out from the oxalic acid solution into each flask a known volume of 10.00 cm^3.
  - In case of manual pipets: Wipe off any solution outside and at the tip of the pipet. Pipet a small amount of oxalic acid solution with a pipet bulb and rinse the pipet with it. The solution should go to the waste. During pipeting hold the pipet in an upright position while the beaker at an angle. The tip of the pipet should be in the solution during sucking up the solution. Then the outside of the pipet should be wiped off and the pipet should be set to the upper mark on the pipet. Then let the solution out to the Erlenmeyer flask until the lower mark. *Tips: Do not lay down the pipet with the pipet bulb on it. Avoid handling pipet tips with bare hands.*
  - In case of automatic pipets: Set the desired volume by turning the plunger. Place the clean and dry tip onto the pipet. Press the plunger until the first stop. Place the tip into the solution. Keep the pipet in an upright position when slowly releasing the plunger. Remove the tip from the solution and place it into the Erlenmeyer flask. Slowly push the plunger down to the first stop, then to the second stop to be sure that all solution has been pushed out of the tip. *Tips: Do not lay the pipet down to the desk with the tip left on it.*
- Add 5 cm^3 of a 20 % w/w sulphuric acid solution with a graduated cylinder into each Erlenmeyer flask.

Titration

- Set the potassium permanganate solution in the buret to the zero line. Since the solution is of dark color, the upper meniscus should be considered for the buret readings.
- Take the first Erlenmeyer flask on the desk so the tip of the buret is inside the flask.
- Add a few drops of potassium permanganate solution to the Erlenmeyer flask.
- Heat the oxalic acid solution up to 50–60 °C on the metal tripod with the Bunsen burner.
- Add the titrant from the buret in small volumes to the warm oxalic acid solution while swirling the contents of the flask gently. The violet color of permanganate solution disappears on reaction with oxalic acid. The end point is indicated by the appearance of a permanent light pink color due to a slight excess of permanganate solution. *Tips: Add the titrant quickly at first, but close to the end point add it dropwise. From time to time, tilt the flask and wash the drops of titrant solution from the wall of the flask into the solution with your wash bottle. Remove the last (broken) drop from the tip by touching it to the wall of the flask and wash it into the solution. The waste should be placed into the waste containers.*
- Read the volume of the titrant consumed and record it in the record sheet.
- Fill the buret with the titrant and set to zero.
- Repeat the titration at least two more times.
- If needed, perform more experiments to have three readings close to one another. Calculate the average volume of the titrant from these values.

Tips: The first titration can be less accurate. During the second and third titration add the potassium permanganate solution moderately fast reaching the end point to ∼1.00 cm^3, then add dropwise the titrant to obtain the end point accurately.

Analysis of oxalic acid with unknown molarity

- Wash the volumetric flask carefully and rinse it with distilled water. Give it to the technician to obtain your unknown. The unknown is a 10.00 cm^3 oxalic acid stock solution with unknown molarity.
- Dilute the sample to the mark of 100 cm^3 with your wash bottle. Mix it well.
- Prepare 3 samples as described previously. Do not forget to use another clean and dry beaker to store your unknown oxalic acid for pipeting.
- Titrate as described previously.
- Calculate the concentration of the unknown diluted oxalic solution. Calculate the concentration of the oxalic acid stock solution.

Sample calculation

Standardization of potassium permanganate solution

Concentration of the diluted oxalic acid: $c_{ox} = \frac{c_{ox,0} \times 10\ \text{cm}^3}{100\ \text{cm}^3} = \frac{c_{ox,0}}{10} = 0.0500\ \text{mol/dm}^3$

Amount of oxalic acid in the Erlenmeyer flask: $n_{ox} = c_{ox} \times V_{pipet}$

Amount of potassium permanganate in the Erlenmeyer flask at the end point: $n_{KMnO_4} = \frac{2n_{ox}}{5}$

Precise concentration of the titrant: $c_{KMnO_4} = \frac{n_{KMnO_4}}{V_{buret}}$

Analysis of oxalic acid with unknown molarity

Amount of potassium permanganate in the Erlenmeyer flask at the end point: $n_{KMnO_4} = c_{KMnO_4} \times V_{buret}$

Amount of oxalic acid at the end point from the stoichiometry of the reaction: $n_{ox} = \frac{5n_{KMnO_4}}{2}$

Molarity of oxalic acid in the pipet (and in the volumetric flask): $c_{ox} = \frac{n_{ox}}{V_{pipet}}$.

Concentration of the oxalic acid stock solution: $c_{ox,0} = \frac{c_{ox} \times 100\ \mathrm{cm}^3}{10\ \mathrm{cm}^3} = c_{ox,0} \times 10$