Experiment 8 – Redox Titrations

Potassium permanganate, $KMnO_4$, is a strong *oxidizing agent*. Permanganate, MnO_4^-, is an intense dark purple color. Reduction of purple permanganate ion to the colorless Mn^{+2} ion, the solution will turn from dark purple to a faint pink color at the equivalence point. No additional indicator is needed for this titration. The reduction of permanganate requires strong acidic conditions.

In this experiment, permanganate will be reduced by oxalate, $C_2O_4^{2-}$ in acidic conditions. Oxalate reacts very slowly at room temperature so the solutions are titrated hot to make the procedure practical. The unbalance redox reaction is shown below.

$$MnO_4^- + C_2O_4^{2-} \rightarrow Mn^{2+} + CO_2 \quad \text{(acidic solution)}$$

In part I of this experiment, a potassium permanganate solution will be standardized against a sample of potassium oxalate. Once the exact normality (eq/L) of the permanganate solution is determined, it can be used as a standard oxidizing solution. In part II of this experiment, the standard permanganate solution will be used to find the concentration of iron(II) in a ferrous solution (g/L). The unbalanced redox reaction is shown below.

$$MnO_4^- + Fe^{2+} \rightarrow Mn^{2+} + Fe^{3+} \quad \text{(acidic solution)}$$

Phosphoric acid will be used to ensure that the ferric product, Fe^{3+} remains in its colorless form.

Equipment and Reagents (Day 1)

$KMnO_4$ solid	weighing paper	buret
500 mL Florence Flask	$K_2C_2O_4\,H_2O$	Ring Stand
Rubber Stopper	Analytical Balance	Buret Clamp
Hot plate or Bunsen burner	250 mL Erlenmeyer Flask	6 N H_2SO_4

Procedure (Day 1)

Part (I) - <u>Preparation of a 0.1 N $KMnO_4$ Solution.</u>

1. On a centigram balance, weigh about 1.0 g $KMnO_4$ crystals on a piece of weighing paper. Add the crystals to a 500 mL Florence Flask.

2. Add about 350 mL of distilled water to the flask.

3. Heat the solution with occasional swirling to dissolve the $KMnO_4$ crystals. Do not boil the solution. This may take about 30 minutes.

4. Allow the solution to cool and stopper. You will need this solution for both day 1 and day 2.

Part (II) - <u>Standardization of a $KMnO_4$ solution</u>.

1. On weighing paper, weigh about 0.2 – 0.3 g of $K_2C_2O_2H_2O$ on the analytical balance. Record the exact mass. Transfer the sample to a 250 mL Erlenmeyer flask.

2. Rinse and fill the buret with the $KMnO_4$ solution.

3. Add 50 mL of distilled water and 20 mL of 6 N H_2SO_4 to the oxalate sample in the Erlenmeyer flask. Swirl to dissolve the solids.

4. Heat the acidified oxalate solution to about 85 °C. Do not boil the solution.

5. Record the initial buret reading. Because the $KMnO_4$ solution is strongly colored, the top of the meniscus may be read instead of the bottom.

6. Titrate the hot oxalate solution with the $KMnO_4$ solution until the appearance of a faint pink color.

7. Record the final buret reading and calculate the volume of $KMnO_4$ used in the titration.

8. Discard the titration mixture down the drain and repeat the titration with a new sample of oxalate for a total of 2 trials.

9. An oxalic acid solution may be used to wash the buret and the titration flask if a brown stain remains in the glassware.

Calculations

1. Using the half-reaction method, write a balanced redox equation for the reaction of permanganate with oxalate in an acidic solution.

2. Calculate the equivalent weight of the oxalate reducing agent from the molar mass of the oxalate sample and the equivalence of electrons lost by the reducing agent in the oxidation half-reaction.

$$equivalent\ weight = \frac{184\ g/mol}{\#\ of\ electrons\ eq/mol}$$

3. Use the sample mass and the equivalent weight to calculate the number of equivalents of oxalate in each sample.

$$equivalence\ of\ reducing\ agent = \ sample\ mass\ g \times \frac{eq}{\_\ g}$$

At the equivalence point, the equivalence of the reducing agent is equal to the equivalence of the oxidizing agent.

$$eq_{red} = eq_{ox}$$

4. Calculate the normality of the $KMnO_4$ solution from the equivalence of the oxidizing agent and the volume used in the titration.

5. Calculate the average normality of the permanganate solution.

Equipment and Reagents (Day 2)

Unknown Fe^{2+} solution	$KMnO_4$ solution	Buret Clamp
250 mL Erlenmeyer Flask	25 mL pipet	Ring Stand
6 N H_3PO_4	pipet bulb	

Procedure (Day 2)

Part (III) – <u>Determination of the Mass of Iron in a Ferrous Solution</u>.

1. Pipet a 25 mL sample of the unknown Fe^{2+} solution into a 250 mL Erlenmeyer flask.

2. Add 50 mL of distilled water and 12 mL of 6 N H_3PO_4 into the flask.

3. Fill a buret with the standard $KMnO_4$ solution and record the initial buret reading.

4. Titrate the sample with the standard $KMnO_4$ to a faint pink end-point and record the final buret reading. Calculate the volume of $KMnO_4$ used.

5. Discard the ferric solution down the drain and repeat the titration with a new sample of the ferric solution for a total of 2 trials.

6. When finished with all trials, discard the purple permanganate solution in the appropriate waste container in the fume hood.

7. Oxalic acid may be used to remove any brown stains left on the glassware.

Calculations

1. Using the half-reaction method, balance the redox reaction of permanganate with iron(II) in acidic media.

2. Calculate the equivalence of $KMnO_4$ titrated.

$$Equivalence\ of\ oxidizing\ agent = N_{ox} \times V_{ox} = (\frac{eq}{L}) \times L$$

At the equivalence point, the equivalence of the oxidizing agent is equal to the equivalence of the reducing agent.

$$eq_{ox} = eq_{red}$$

Determine the normality of the ferric reducing agent.

$$N_{red} = \frac{eq_{red}}{0.025\ L}$$

3. Calculate the molarity (mol/L) of the ferrous solution.

$$M_{Fe} = \frac{N_{Fe}}{n}$$

(n = moles of electrons lost in the oxidation half-reaction.)

4. Calculate the mass concentration (g/L) of iron in the unknown solution by multiplying the molar mass of iron by the molarity of the ferrous solution.

$$mass\ concentration = \frac{mol}{L} \times \frac{56g}{mol} = \frac{g}{L}$$

5. Calculate the average mass concentrations for the ferrous unknown solution.