Experiment 14

REDOX TITRATION OF POTASSIUM PERMANGANATE

Objective

The purpose of this experiment is to determine the iron content of an unknown sample by redox titration with standardized potassium permanganate solution.

Lab techniques

➢ Weighing chemicals
➢ Preparing solutions
➢ Operation of buret (titration) and stirrer/hot plate

Introduction

I. The oxidative property of the permanganate ion

Permanganate ion (MnO$_4^-$) is a strong oxidizing agent. In acidic solution, it undergoes reduction to give manganese(II) ions (Mn$^{2+}$). The reduction half-reaction is shown as equation 14-1.

$$\text{MnO}_4^- (aq) + 8H^+(aq) + 5e^- \rightarrow \text{Mn}^{2+}(aq) + 4H_2O(l) \quad E^0 = 1.51 \text{ V} \quad (14-1)$$

Since MnO$_4^-$ shows intense purple color and after being reduced to colorless (lightly pink) Mn$^{2+}$(aq) in acidic solution, so an indicator is not ordinary required for titration. Aqueous solutions of permanganate are not completely stable because of the tendency to react with water as equation 14-2.

$$4\text{MnO}_4^- (aq) + 2H_2O(l) \rightarrow 4\text{MnO}_2(s) + 3O_2(g) + 4OH^- (aq) \quad (14-2)$$

The decomposition has been shown to be catalyzed by light, heat, acid, base, Mn$^{2+}$, and MnO$_2$. In order to obtain a stable reagent for analysis, it is necessary to minimize the influence of these effects. The decomposition of permanganate solution is greatly accelerated in the presence of MnO$_2$. Since it is also a product of the decomposition, this solid has an autocatalytic effect upon the process. Thus solid MnO$_2$ needs to be filtered out during preparation of a permanganate solution to enhance the stability.

II. Standardization of permanganate solution

Solid potassium permanganate, which is ordinarily used for the preparation of permanganate solutions, is inevitably contaminated with manganese dioxide to some extent; as a result, preparation of standard permanganate solutions directly by weight is not possible. Instead, a permanganate solution is usually further standardized with sodium oxalate (Na$_2$C$_2$O$_4$), arsenic(III) oxide, potassium iodide, or metallic iron. In
this experiment, sodium oxalate is used to standardize a potassium permanganate in acidic solution as equation 14-3.

\[
2\text{MnO}_4^-(aq) + 5\text{C}_2\text{O}_4^{2-}(aq) + 16\text{H}^+(aq) \rightarrow 2\text{Mn}^{2+}(aq) + 10\text{CO}_2(g) + 8\text{H}_2\text{O}(l) \quad (14-3)
\]

This reaction is complex and proceeds slowly at room temperature; even at elevated temperature it is not rapid unless catalyzed by Mn\(^{2+}\) ion. Thus, several seconds are required to decolorize a hot oxalic acid solution at the outset of a permanganate titration. Later, when the concentration of Mn\(^{2+}\) ion has become appreciable, decolorization becomes rapid as a consequence of the autocatalysis.

The standardization of permanganate solution with oxalic acid has been investigated in great detail by McBride\(^1\) (1912), and more recently by Fowler and Bright\(^2\) (1935). In the McBride method, the temperature of the solution is kept at 60-90°C, while titration is carried out until the faint pink color of MnO\(_4^-\) persists for 30 seconds as an indication of the end point. However, Fowler and Bright have demonstrated, however, that this titration consumes 0.1 to 0.4% too little permanganate, due perhaps to air oxidation of a small part of the oxalic acid (14-4). In the hot solution, the peroxide is postulated to decompose spontaneously to oxygen and water (14-5).

\[
\begin{align*}
\text{H}_2\text{C}_2\text{O}_4(aq) + \text{O}_2(g) &\rightarrow \text{H}_2\text{O}_2(aq) + 2\text{CO}_2(g) \quad (14-4) \\
2\text{H}_2\text{O}_2(aq) &\rightarrow 2\text{H}_2\text{O}(l) + \text{O}_2(g) \quad (14-5)
\end{align*}
\]

To reduce the titration error, Fowler and Bright devised a scheme for standardization in which 90-95% of the required permanganate is added rapidly to sodium oxalate solution at room temperature. After all of this reagent has reacted, the solution is heated to 55-60°C and titrated to the end point.

**III. Determination of iron content of unknown sample**

The redox titration of permanganate ions is commonly used to determine the iron content of a sample, such as iron ores. The balanced chemical reaction equation is shown as equation 14-6:

\[
\begin{align*}
\text{MnO}_4^-(aq) + 8\text{H}^+(aq) + 5\text{Fe}^{2+}(aq) &\rightarrow \text{Mn}^{2+}(aq) + 5\text{Fe}^{3+}(aq) + 4\text{H}_2\text{O}(l) \quad (14-6)
\end{align*}
\]

Volumetric analysis of iron sample consists of three steps:

1. Dissolution of the sample
2. Reduction of the iron to Fe(II) ion
3. Titration with a standard permanganate solution

During the preparation of iron sample may involve a large amount of chloride ions (i.e. using concentrated hydrochloric acid to dissolve iron ores). The chloride ions, when catalyzed by Fe(II) ions, react readily with permanganate ions to produce chlorine. Thus Z-R reagent (Zimmermann-Reinhardt reagent) needs to be added to the solution
to lower the electric potential between Mn(II) and Mn(VII) ions, thereby inhibiting the production of chlorine molecules. Moreover, Z-R reagent contains dihydrogen phosphate (H$_2$PO$_4^-$) which reacts with Fe(III) ions to give a stable complex. This prevents Fe(III) ions from reacting with chloride ions to produce a pale yellow complex which could in turn interfere with the visual determination of the end point.

**Apparatus**
Erlenmeyer flask (250 mL, 4), volumetric flask (100 mL), burette (25 mL), funnel, beaker (100, 400 mL), graduated cylinder (10, 50 mL), dropper, thermometer, stirrer/hot plate, analytic balance.

**Chemicals**
Potassium permanganate, KMnO$_4$
Sodium oxalate, Na$_2$C$_2$O$_4$ (Oven-dry at 110-120°C for 1 h, then put in a desiccator and allow to cool.)
1 M Sulfuric acid, H$_2$SO$_4$
Ammonium iron(II) sulfate hexahydrate, (NH$_4$)$_2$Fe(SO$_4$)$_2$·6H$_2$O
Iron(II) sulfate heptahydrate, FeSO$_4$·7H$_2$O

**Procedure**

**I. Preparation of 0.02 M potassium permanganate solution**
1. Weigh about 0.3 g KMnO$_4$ and dissolve completely to 100 mL with DI water by using volumetric flask.
   
   Note 1: The color of the solution is very deep. Make sure that the solid has been dissolved and the solution is homogeneous.
   
   Note 2: If the standardization of KMnO$_4$ and sample analysis are not performed on the same day, the solution needs to be heated until boiling and maintained at high temperature for about 1 hour.
   
   Note 3: Store the solution in a covered container and allow it to cool overnight. Remove the solid MnO$_2$ with a thin aperture glass filtration funnel. Store the solution in a clean glass flask in a dark place.

**II. Standardization against sodium oxalate – method of McBride**
2. Accurately weigh about 0.1-0.15 g dry Na$_2$C$_2$O$_4$ and transfer to a 250 mL Erlenmeyer flask. Record the mass to 0.1 mg.
3. Add approximately 50 mL of 1 M sulfuric acid to dissolve the solid Na$_2$C$_2$O$_4$.
4. Heat the Na$_2$C$_2$O$_4$ solution to 80-90°C, then titrate with KMnO$_4$ solution with stirring. The reagent should be introduced slowly so that the pink color is discharged before further additions are made. Reheat if the temperature drops below 60°C. The end point is the first persistent pink color for 15-20 s. Record the initial (V$_i$) and final volumes (V$_f$) of KMnO$_4$ in the titration to 0.01 mL.
5. Correct the titration for an end-point blank determined by titrating a 50 mL of 1 M sulfuric acid with reference to step 4.

**III. Standardization against sodium oxalate – method of Fowler-Bright**

6. Accurately weigh about 0.1-0.15 g of dry Na$_2$C$_2$O$_4$ and transfer to a 250-mL Erlenmeyer flask. Record the mass to 0.1 mg.

7. Add about 50 mL of 1 M sulfuric acid to dissolve the solid Na$_2$C$_2$O$_4$.

8. Introduce from buret sufficient permanganate to consume about 80% of the oxalate.

9. Let stand at room temperature until the solution is decolorized with stirring. Then warm to 55-60°C, and complete the titration. Record the titration volume to 0.01 mL.

10. Correct the titration for an end-point blank determined by titrating a 50 mL of 1 M sulfuric acid with reference to step 8-9.

**IV. Determining the mass percent composition of iron(II) in an unknown sample**

11. Accurately weigh about 0.2 g of an unknown sample that containing Fe(II), and transfer to a 250 mL Erlenmeyer flask.

12. Add about 50 mL of 1 M sulfuric acid to dissolve the solid unknown.

13. Titrate with 0.02 M KMnO$_4$ to the first faint pink that persists for 15 to 20 s.

14. Correct the titration volume of KMnO$_4$ for the blank titration and calculate the mass percent composition of iron in the unknown sample.

15. Dispose the liquid waste to the designated waste container.

**Reference**

