FE 211 ANALYTICAL CHEMISTRY

Experiment No. 3

OXIDATION-REDUCTION (REDOX) TITRATIONS

Chemical reactions in which a transfer of electron (s) occurs are known as oxidation-reduction or redox reactions. The most volumetric analytical methods are based upon the redox reactions.

Similar to the other titrimetric methods, three types of reagents are employed in volumetric methods based on the oxidation reduction reactions. These include substances for the preparation of standard solutions, primary standards and auxiliary reagents for the pretreatment of solutions before titration.

VOLUMETRIC DETERMINATION OF IRON

Iron may be determined in a redox titration by oxidation of Fe (II) to Fe(III) with an oxidant such as $KMnO_4$ or $K_2Cr_2O_7$. However, iron in typical iron ores occurs as Fe (III) and therefore, must be reduced to Fe (II) with $SnCl_2$ prior to titration with $KMnO_4$.

A volumetric iron determination generally consists of the following major steps:

1. Dissolution of the sample. (**or Take exactly 5.0 mL iron sample**).
2. Reduction of all ferric ion Fe (III) to ferrous ion Fe (II) and removal of the excess of whatever reducing agent, $SnCl_2$, is employed for that purpose.
3. Addition of special reagents to insure that the one proper reaction will occur during subsequent titration.
4. Titration of ferrous solution with a standard permanganate solution.

Experimental:

A) Reagents:

1. Hydrochloric acid, HCl, stock solution.

2. Mercuric chloride, $HgCl_2$, solution containing 12.5 g $HgCl_2$ per 250 mL water.

3. Potassium permanganate, $KMnO_4$, approximately 0.02 M solution, prepared by dissolving 3.3 g $KMnO_4$ in warm water, diluting to 1 liter, shaking thoroughly, letting stand overnight or longer and filtering through a fine-porosity sintered-glass funnel. Store in the dark when not in use.

4. Sodium oxalate, $Na_2C_2O_4$, analytical grade.

5. Sulfuric acid, H_2SO_4, 1 volume stock solution diluted with 17 volumes water (always add acid to water, never vice versa).

6. Stannous chloride, $SnCl_2$, solution containing 15 g of iron-free $SnCl_2.2H_2O$ per 100 mL of 6 M HCl. After the solid has dissolved store in a well-stoppered bottle. (Prepare this solution fresh within a day or two of the time used).

7. Zimmermann-Reinhardt reagent, solution prepared by dissolving 17.5 g $MnSO_4$.$4H_2O$ in 125 mL water. Carefully add with stirring 30 mL sulfuric acid, H_2SO_4 (stock solution) and 30 mL phosphoric acid, H_3PO_4. Dilute to 250 mL.

B) Procedure:

Standardization of Potassium Permanganate, $KMnO_4$, Solution with Sodium Oxalate, $Na_2C_2O_4$.

1. Conduct the standardization in duplicate.
2. Dry the sodium oxalate at 100°C for two hours.
3. Accurately weigh individual portions of 0.2 g, $Na_2C_2O_4$, each into 300 mL erlenmeyer flasks.
4. Dissolve in 100 mL sulfuric acid. (**or Take 10.0 mL of prepared $Na_2C_2O_4$ solution and add 90.0 mL of 1:17 H_2SO_4 solution**).
5. Heat the solution nearly to boiling
6. Titrate with the permanganate solution until a pink coloration appears and lasts for thirty seconds. Keeping the solution above 70°C throughout the titration.
7. Obtain a blank by heating 90 mL 1:17 H_2SO_4 solution to 80°C and titrating with permanganate.
8. From the corrected volume of permanganate, calculate the molarity of the permanganate solution.

Iron determination:

1. Conduct the determination in duplicate.
2. Dry the sample at 110°C for one hour
3. Accurately weigh individual portions of 0.7 g each into 600 mL beakers. **(or Take exactly 5.0 mL of prepared sample solution)**.
4. Dilute the sample solution to 25.0 mL with water.
5. Gently heat over a bunsen burner. (Do not boil least iron be lost as volatile $FeCl_3$)
6. Add 7 or 8 drops of stannous chloride, $SnCl_2$, solution dropwise, with stirring, to the hot sample solution until the yellow color changes to light green.
7. Dilute to 100 mL and cool to room temperature.
8. Add 10 mL of mercuric chloride, $HgCl_2$ solution rapidly with stirring. A white precipitate should form (If it is gray or black or if no precipitate forms, an incorrect amount of stannous chloride was used and sample must be discarded)
9. Dilute to 300 mL with water
10. Add 25 mL of the Zimmermann-Reinhardt reagent.
11. Titrate with permanganate solution.
12. Calculate the percentage Fe in the sample.

Chemical reactions : Reduction of ferric ion with stannous chloride in the presence of hydrochloric acid.

$$2Fe^{3+} + Sn^{2+} \rightarrow 2\ Fe^{2+} + Sn^{4+}$$

Removal of excess reducing agent:

$$2Hg^{2+} + Sn^{2+} \rightarrow Hg_2Cl_2 + Sn^{4+}$$

white ppt

The amount of stannous chloride used is quite critical. If not enough, some iron will not be reduced to the ferrous from. If too much, the following reaction at least partially takes place.

$$Hg^{2+} + Sn^{2+} \xrightarrow{HCl} Hg + Sn^{4+}$$

gray or black

Titration of ferrous ion with permanganate solution:

$$5\ Fe^{2+} + MnO_4^- + 8\ H^+ \rightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}$$

Sodium oxalate, Na2C2O4, is readily soluble in acid in which it exists in the form of undissociated oxalic acid molecules.

$$2MnO_4^- + 5H_2C_2O_4 + 6H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

FE 211 ANALYTICAL CHEMISTRY DATA SHEET

Experiment No: 3

OXIDATION-REDUCTION (REDOX) REACTIONS
VOLUMETRIC DETERMINATION OF IRON

1) Standardization of Permanganate Solution with Sodium Oxalate

Volume of $KMnO_4$ used (mL) :……..

Volume of $KMnO_4$ used for blank (mL) :…….

2) Iron Determination

Volume of Standardized $KMnO_4$ used (mL) :……..

Submitted by: Submitted to:

Date: