CHAPTER - II

EXPERIMENTAL TECHNIQUES

EXPERIMENTAL

Reagent grade chemicals were used and double distilled water was used throughout the work.

The vanadium (V) solution was prepared by dissolving NH_4VO_3 in distilled water. For standardisation first ferrous ammonium sulphate solution was standardised with potassium dicromate solution by using diphenylamine sulphonate (0.2%) indicator. The vanadium (V) solution was standardised against ferrous ammonium sulphate solution by using diphenyl amine.

Hydrazine solution was prepared by dissolving hydrazine sulphate in water. Similarly thiosemicarbazide solution was prepared by dissolving thiosemicarbazide (BDH) in water.

To maintain ionic strength, sodium perchlorate was used which was prepared by dissolving equivalent quantities of sodium carbonate (Loba GR) and perchloric acid (E. Merck 70%) in water.

KINETIC STUDIES

In case of vanadium (V) oxidation of hydrazine the ionic strength was maintained at 0.01 M using sodium perchlorate. In a typical run oxidant and reductant are

taken in a separate conical flasks along with required quantities of sulphuric acid and sodium perchlorate and are kept in a thermostat at 25 ± 0.1°C for half an hour. The kinetics were followed by mixing thermally equilibrated solutions of reactants and transferring the reaction mixture to 1 cm cuvettes. The absorbance at 430 nm was followed with Bausch and Lomb spectronic 20 spectrophotometer. While in case of thiosemicarbazide oxidation by vanadium (V) the reaction was followed at 390 nm by using Shimadzu UV-160 A spectrophotometer in perchloric acid medium. At the wavelength of 390 nm only the complex between vanadium (V) and thiosemicarbazide will have the absorbance. The initial rates were determined for both reactions by plotting absorbance against time and using plane mirror method. The orders were determined by plotting log. Inl. Rate against log. Concentration.

STOICHIOMETRY

The stiochiometry was studied by keeping the oxidant in excess over that of the substrate and allowed to stand for six hours. The vanadium (IV) produced was determined by measuring its absorbance at 760 nm (ε = 17). The stoichiometry in case of hydrazine was found to be 3.6 where as for thiosemicarbazide it was found to be 6. Therefore, the thiosemicarbazide will be oxidized to thiocyanate.