# CHAPTER II

CHAPTER-II

EXPERIMENTAL TECHNIQUE

The oxidation by hexacyanoferrate(III) ion takes place slowly but proceeds with a measurable rate in alkaline medium. The oxidation of iso-Nicotinic and Nicotinic acid hydrazides by hexacyanoferrate(III) in alkaline medium is under taken. In solution Fe(III), accepts electron from anion of the substrate, formed by abstraction of proton due to alkali. The reaction under equilibrium can be represented[1] as,

$$Fe(CN)_6^{3-} + e^- \longrightarrow Fe(CN)_6^{4-}$$

The equilibrium can be shifted towards right by using alkaline medium. Hence alkaline medium is used throughout investigation.

Iron(III) forms a large number of complexes, mostly octahedral. Ferrous complex is normally oxidised to ferric complex. The potential of the reaction

$$[Fe(CN)_6]^{3-} + e^- \longrightarrow [Fe(CN)_6]^{4-}; \quad E = 0.36 \text{ volt.}$$
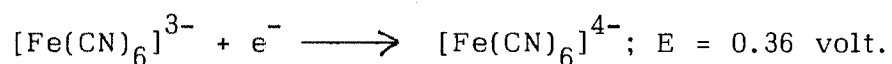
The potassium ferricyanide is poisonous and generally prepared by oxidation of the hexacyanoferrate(III) with chlorine by electrolytic method.[2]

During the course of the reaction, Fe(III) is reduced to Fe(II). However, Fe(III) is strongly absorbing species[3] as compared to Fe(II), which is practically non absorbing at 420 nm.

So the observed absorbance (A) at 420 nm may be safely taken as a measurement of concentration of Fe(III) during the course of the reaction. Hence, in present investigation, reaction was followed photo-chemically at 420 nm wavelength.

PURITY OF THE CHEMICALS :

All the chemicals used during the investigation were of AR/GR quality, iso-Nicotinic acid hydrazide and Nicotinic acid hydrazide were prepared in the laboratory.[4] The impurity present in the reagents generally influences the rate of chemical reaction, hence all possible precautions were taken to avoid the impurities present in the reaction system. Their purity was checked after recrystallisation by determining their physical constant.

Iso-Nicotinic acid hydrazide = M.P. 169°C (171-73°C)

Nicotinic acid hydrazide = M.P. 161°C (160-163)

The chemicals other than above viz. $K_3Fe(CN)_6$, NaOH, KCl, Methanol were of A.R.grade.

PREPARATION OF HYDRAZIDES :

The iso-Nicotinic and Nicotinic acid hydrazides[4] were prepared by refluxing equimolar quantities of methyl ester of correspondingg carboxylic acid with hydrazine hydrate (B.D.H.99%) on water bath till the two layers disappeared and homogeneous solution was formed. The refluxion was continued for more than three hours. The excess of hydrazine hydrate and other unreacted material were removed by distilling the solution under reduced

pressure. The hydrazides were purified by recrystallisation from slightly warmed ethanol. The purity was checked by determining their melting points. Standard solutions were prepared by exactly weighing the calculated quantities of hydrazides and dissolving them in double distilled water in standard pyrex glass flask.

STANDARDISATION OF HEXACYANOFERRATE(III) :

The exact molarity of hexacyanoferrate(III) solution was confirmed by standardisation method.[5] In this method 2 ml stock solution of hexacyanoferrate(III) was taken in Iodine flask, 10 ml of KI (5%) and 2 ml of 0.5% Potassium-iodate were added to it. The liberated iodine was titrated against 0.05 N sodium-thiosulphate solution and molarity of hexacyanoferrate(III) was determined.

PREPARATION OF SOLUTIONS :

Stock solutions of iso-Nicotinic and Nicotinic acid hydrazides were prepared by weighing the required quantities of hydrazides and dissolving in distilled water. The solutions were stored in dark place. The glass-wares used for the preparation and storing the solutions were pyrex glass. The stock solution of hexacyanoferrate(III) was kept in amber coloured bottle and the bottle was always kept in dark place. The strength of hexacyanoferrate (III) was checked periodically.[5] Stock solutions of sodium hydroxide and potassium chloride were also prepared by above procedure.

DETERMINATION OF λMAX FOR HEXACYANOFERRATE(III) :

5.0×10^{-4} M Solution of hexacyanoferrate(III) was prepared

in the double distilled water. Absorbance of this solution was measured as a function of wavelength in range of 400-700 nm, water was used as a reference. It is observed from the graph of absorbance(A) or optical density (O.D.) Vs wavelength that the hexacyanoferrate(III) has a strong absorption at 420 nm[3].

FOLLOWING THE KINETICS :

All the kinetic measurements were carried out in pyrex glass-ware which was coated outside with Japan black to avoid photochemical effects. Stock solutions of hexacyanoferrate(III), the organic substrate (is0-Nicotinic acid hydrazide and Nicotinic acid hydrazide) and sodium hydroxide, were kept in separate well stoppered bottles and equilibrated to the required temperature in a thermostat with ∓ 0.1°C accuracy for about 10 to 15 minutes. The required volume of these solutions were mixed in an iodine flask (total volume of the solution 100 ml) and optical density (O.D.) of the reaction mixture at 420 nm was measured at definite time intervals. The reaction mixture was transferred into the spectrophotometer. By using this method minimum errors were observed, reference solution used was water. The reaction was usually followed upto 80% completion. The data was used to calculate (-dc/dt), velocity constants etc. The following variations were studied :

1.   Variation of concentration of hexacyanoferrate(III).

2.   Variation of substrate concentration.

3.   Variation of alkali concentration.

4.   Variation of temperature of the experiment.

5.   Effect of salt and dielectric constant of medium.

The observations, graphs and results are given and discussed in chapter III and IV.

In recording of the observations of kinetic runs the following abbreviations have been used :

1.   HCF(III) represents, Hexacyanoferrate(III)

2.   [iso-NAH] and [NAH] denotes iso-Nicotinic acid and Nicotinic acid hydrazide concentration respectively.

3.   [$\bar{OH}$] denotes alkali concentration.

4.   'O.D.' denotes the optical density of the HCF(III) soln.

5.   'Min' denotes the time in minutes.

6.   'k' represents the first order rate constant for the total reaction.

7.   W.r.t. stands for with respect to.

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