

CHAPTER - II

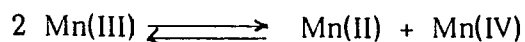
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Experimental Technique

The oxidation of triethylamine and diethylamine by Mn(III) sulphate in 5M sulphuric acid medium was studied. In solution Mn(III) disproportionates to Mn(II) and Mn(IV) by the reaction ;



The equilibrium can be shifted towards left by using highly acidic medium. This can be done by the use of 5 M sulphuric acid.^{14,15} Hence we have used 5M H₂SO₄ medium throughout this investigation.

During the course of the reaction Mn(III) is reduced to Mn(II). However Mn(III) is strongly absorbing species ($\lambda_{\text{max}} = 500 \text{ nm}$, $\epsilon_{\text{max}} = 134.79 \text{ M}^{-1} \text{ cm}^{-2}$)⁵² as compared to Mn(II) which is practically non absorbing at 500nm. So the observed absorbance (O.D.) at 500 nm may be safely taken as a measure of concentration of Mn(III) during the course of the reaction. Hence in the present investigation, reaction was followed photometrically at 500 nm wavelength. λ_{max} value viz. 500 nm was confirmed by observing O.D. values of solutions of Mn(III) sulphate of concentration $4.8 \times 10^{-3} \text{ M}$ $2.4 \times 10^{-3} \text{ M}$ (Fig.O-1 and Table O-1).

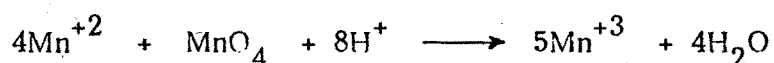
2.1 Purity of the chemicals

All the chemicals used during investigation were of AR/GR or equivalent quality. Triethylamine, diethylamine were supplied by Loba-Chemie Indoaustranal Co. Their purity was checked by determining the boiling points and densities. Triethylamine (89.3°C and $0.7275 \text{ gm\%}/\text{ml}$),^{58a} B.P.and densities of Diethylamine (56.3°C , $0.7056 \text{ gm\%}/\text{ml}$)^{58b}. The other chemicals used viz. FeSO₄(NH₄)₂SO₄, Na₂S₂O₃, KI and Acrylonitrile etc. were supplied by B.D.H., SISCO Research laboratories.

2.2 Preparation of Mn(III) sulphate

All the chemicals used for the preparation were of AR/GR quality. There are two methods generally used for the preparation of Mn(III) sulphate. By the first method⁵ we can prepare Mn(III) sulphate in the Crystalline form and by the second method⁴³, we can prepare the solution of Mn(III) sulphate of 0.07M. For the present kinetic measurements Mn⁺³ sulphate solution in presence of sulphuric acid was to be used. (Further) there is a danger of hydrolysis of crystalline Mn(III) sulphate, therefore solution of Mn(III) sulphate of molarity 0.07 was prepared by the second method and used it as a stock solution for kinetic measurements.

This method is based upon the oxidation of Manganous sulphate ($\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$) with KMnO_4 .



To 50 ml of a solution of A.R. manganous sulphate (15.1 gms in 1 litre of 6N sulphuric acid), 3 mls of conc. sulphuric acid ('Excelar' Glaxo) were added with water cooling. Then 12 ml of 0.5N Potassium permanganate solution were added, 2 ml at a time intervals of about 3 minutes. After 8 ml and again after 12 ml of KMnO_4 solution had been added continuously, a further 2ml of Conc. Sulphuric acid was introduced. The solution was stored for four hours before use, so that reduction process proceeds smoothly to Manganic sulphate and higher valancy stages never accumulate in sufficient concentration to give rise to trouble some precipitates of higher oxides. During the addition of sulphuric acid the solution was cooled in ice cold water bath. Solution of Mn(III) sulphate obtained by above procedure is deep-red coloured. It was stored in blue bottle and kept in a refrigerator when not in use. On exposure of light

in a clear bottle there is possibility of formation of black ppt. owing to the formation of quadrivalent Mn salts as $2\text{Mn}^{+3} \rightarrow \text{Mn}^{+2} + \text{Mn}^{+4}$.

2.3 Standardization of Mn(III) sulphate solution

There are again two methods for standardization. Mn(III) sulphate solution was standardized by using both the methods, so that the exact molarity of Mn(III) sulphate solution was confirmed.

Method No.1

This was effected by running the manganic sulphate solution in to standard $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4$ solution, 0.05N $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4$ solution was used as a standard solution. One drop in excess of the former gave a pink end point with yellowish tinge. A better pink colouration was obtained on addition of 2 drops of syrupy phosphoric acid. After that normality of Mn(III) sulphate was determined.

Method No.2

2 ml stock solution of Mn(III) sulphate was taken in an iodine flask; 10 ml of KI (5%) solution was added to it. The liberated iodine was titrated against 0.05N sodium thiosulphate solution by using starch as an indicator from which normality of Mn(III) sulphate was determined.

2.4 Preparation of solution

Stock solutions of triethylamine (0.5M) and diethylamine (2M) were prepared by weighing the required quantity of the reagent and dissolved in 5M sulphuric acid. The solutions were stored in dark place. The glassware used for the preparation of and storing the solution was of pyrex glass. The stock solution of Mn(III) sulphate (0.07M) was kept in blue bottle and the bottle

was always kept in refrigerator. The strength of Mn(III) sulphate was checked periodically with the use of standardization methods given in 2.3.

2.5 Determination of λ max for Mn(III) sulphate and verification of Beer-Lambert's Law

$4.8 \times 10^{-3} \text{M}$ and $2.4 \times 10^{-3} \text{M}$ solution of Mn(III) sulphate in 5M sulphuric acid were prepared. Absorbance of these solutions were measured as a function of wavelength in the range of 410-630 nm. 5M Sulphuric acid was used as a reference. Measurements were made on spectronic 20 (Bausch and Lomb). The graph of absorbance (O.D.) versus wavelength (nm) is shown in Fig.No.O-1. It is seen that Mn(III) sulphate has a strong absorbance at 500 nm. The absorption spectra (Fig.No.O-1) of different concentrations of Manganese(III) sulphate were recorded with an idea to see whether there is any spectral shift with changes in the concentration of Mn(III) solution. The spectral pattern as well as maxima do not change with the changes in the concentration of manganese(III) (Fig.O-1).

Verification of Beer-Lambert's Law

Beer-Lambert's law has been found to be valid for the Mn(III) sulphate in the range $(1 \text{ to } 5) \times 10^{-3} \text{M}$. For the verification of above Law solutions of Mn(III) sulphate having concentrations in the range of 1.6 to $5.4 \times 10^{-3} \text{M}$ were prepared in 5M sulphuric acid. The O.D. value of each solution was recorded at $\lambda = 500 \text{ nm}$ with Spectronic 20. O.D. values are plotted against concentrations of Mn(III) sulphate. (Fig.No.O-2, Table No.O-2). A straight line passing through origin was obtained, indicating that Beer-Lambert's Law is valid in the above concentration range $(1 \text{ to } 5 \times 10^{-3} \text{M})$. Therefore from above observation it is clear that Mn(III) sulphate is stable in this concentration range.

TABLE NO. O-1 *Showing absorbance*Determination of λ_{\max}

Wavelength <i>nm</i>	$\text{Mn}^{+3} = 4.8 \times 10^{-3} \text{M}$ <i>Absorbance</i>	$\text{Mn}^{+3} = 2.4 \times 10^{-3} \text{M}$ <i>Absorbance</i>
410	0.60	0.270
420	0.60	0.270
430	0.610	0.260
440	0.680	0.285
450	0.700	0.320
460	0.750	0.350
470	0.800	0.370
480	0.800	0.390
490	0.820	0.390
500	0.825	0.410
510	0.820	0.400
520	0.750	0.380
530	0.700	0.350
540	0.640	0.310
550	0.600	0.300
560	0.520	0.260
570	0.440	0.230
580	0.400	0.180
590	0.325	0.170
600	0.280	-
610	0.260	-
620	0.210	-

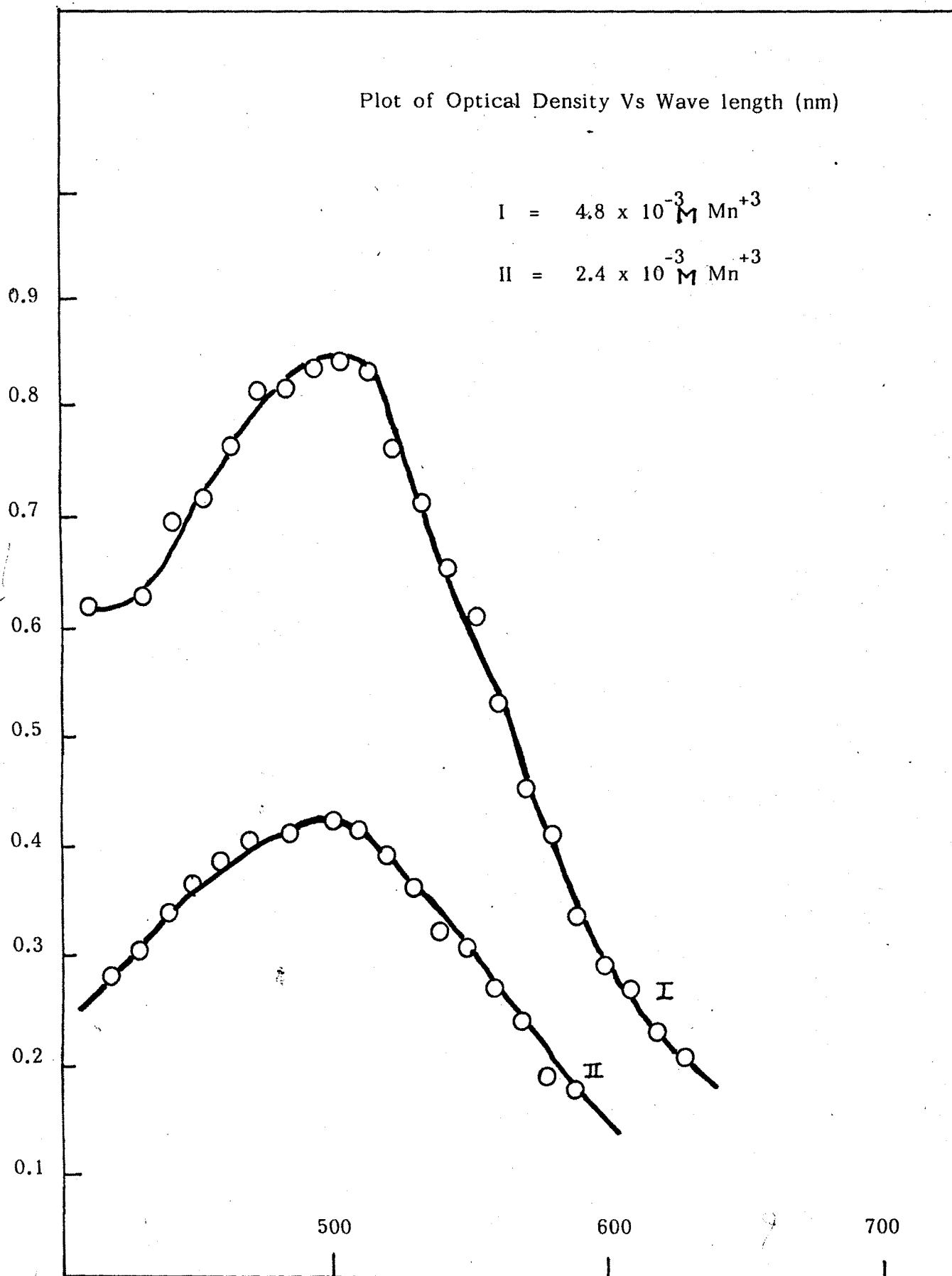


Fig.No.O-1 : DETERMINATION OF λ_{max} .

TABLE NO.O-2Verification of Beer-Lambert's LawAt $\lambda_{\text{max}} = 500 \text{ nm}$

Concentration of Mn(III) sulphate x 10^3 M	O.D.	$\epsilon \text{ m}^{-1} \text{ cm}^{-2}$
1.6	0.220	137.5
2.2	0.300	136.36
3.2	0.430	134.37
3.8	0.526	136.8
4.8	0.640	134.16
5.4	0.700	129.6
		134.79 Mean

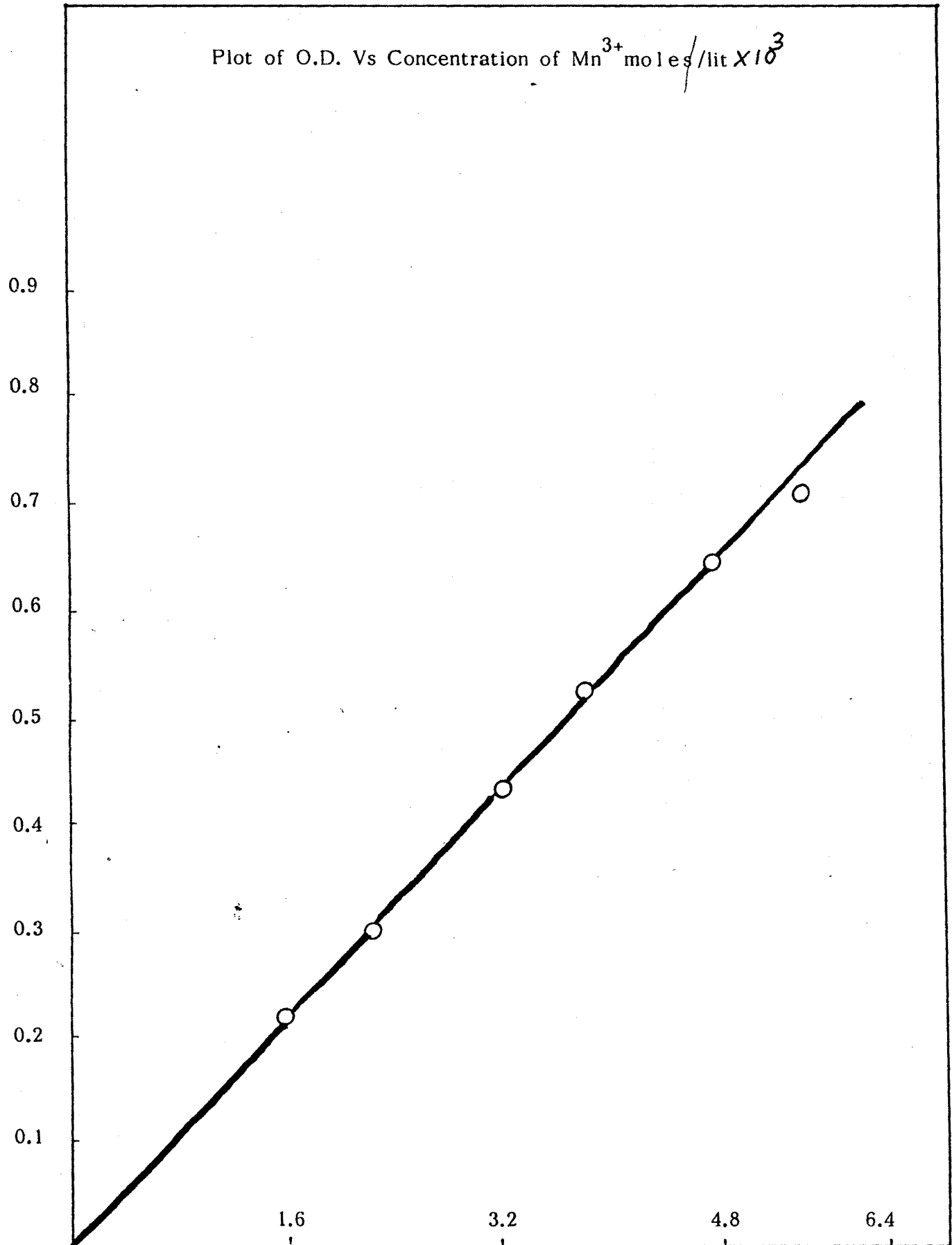


Fig.No. O-2 : DETERMINATION OF EXTENSION COEFFICIENT (ϵ)

2.6 Principle of the Method used for Kinetic measurements

During the course of oxidation of the substrate (triethyl or diethyl amine) Mn^{3+} is itself reduced to Mn^{2+} . As at 500 nm wavelength Mn^{2+} has practically no absorbance and therefore during oxidation process optical density is decreased due to decrease in concentration of Mn^{3+} .

Following the Kinetics

All the Kinetic measurements were carried out in Pyrex glassware which was coated out side with Japan black to avoid photochemical effects particularly on Mn(III) sulphate. 20-25 ml of the stock solution of Mn(III) sulphate, the organic substrate (triethylamine and diethylamine) and 5M sulphuric acid were kept in separate well stoppered bottles/iodine flask and equilibrated to the required temperature in a thermostat (VEB MOLW PRVFGERATE WERE made in Germany) with $\pm 0.1^{\circ}C$ accuracy for about 15-20 minutes. The required volume of these solutions were mixed in an iodine flask (Total volume of the solution 25 ml) and O.D. of the reaction mixture at 500 nm was measured at definite time. For this reaction mixture was transferred into the cuvettes directly. These cuvettes were kept in the thermostat and at definite time intervals, the O.D. of reaction mixture was measured. By using this method minimum error was observed. A reference solution contained all the other reactants except Mn(III) sulphate. The reaction was usually followed upto 80% completion. This data was then used to calculate Pseudo first order velocity constants, $(-dc/dt)$ etc. Following variations were studied.

- 1) Variation of concentration of Mn(III) sulphate
- 2) Variation of substrate concentration
- 3) Variation of sulphuric acid concentration

- 4) Variation of temperature of the experiment
- 5) Effect of addition of Mn^{2+} .