CHAPTER - II

EXPERIMENTAL TECHNIQUE

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The oxidation of formaldehyde and benzaldehyde by Mn(III) sulphate in sulphuric acid medium was studied. In aqueous solution, Mn(III) disproportionates to Mn(II) and Mn(IV) by the equation;

$$2Mn(III) \rightleftharpoons Mn(II) + Mn(IV).$$

This disproportionation can be suppressed completely by using high acidic medium. Thus, Mn(III) is stable in 5M sulphuric acid,[14,15] acetic acid, pyrophosphoric acid etc. Hence, we have used 5M sulphuric acid medium for formaldehyde and a mixture of 3 M sulphuric acid and 4M acetic acid for benzaldehyde.

During the course of the reaction, Mn(III) is reduced to Mn(II). Mn(III) is strongly absorbing species (λmax=500 nm, ϵmax.= 113.00 Moles^{-1} cm ^{2})[46] as compared to Mn(II) which is practically non-absorbing at 500 nm. So the observed absorbence (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 spectrophotometrically at 500 nm wavelength.

2.1 PURITY OF THE CHEMICALS :

All the chemicals used during investigation, were of AR/GR or equivalent quality. Formaldehyde supplied by B.D.H. as 40 % solution in water was used. Its normality was checked by iodometric method. The purity of benzaldehyde was checked by determining its boiling point and density. The other chemicals viz. ferrous ammonium sulphate, $Na_2S_2O_3$, KI, Acrylonitrile, H_2SO_4, CH_3COOH, $MnSO_4$, $KMnO_4$ etc. were supplied by B.D.H. and SISCO research laboratories. Triply distilled water was used throughout the investigation.

2.2 PREPERATION OF Mn(III) SULPHATE :

There are two methods used for the preparation of Mn(III) sulphate. By the first method[4], Mn(III) sulphate can be prepared in crystalline form. By the second method[13], a solution of Mn(III) sulphate having strength 0.07 M can be prepared. There is a danger of hydrolysis of crystalline Mn(III) sulphate. So the solution of Mn(III) sulphate of molarity 0.07 was prepared by second method and used as a stock solution for kinetic measurements.

In this method, manganous sulphate is oxidised by $KMnO_4$.

$$4Mn^{++} + MnO_4^- + 8H^+ \longrightarrow 5Mn^{+++} + 4H_2O$$

To 50 ml of a solution of A.R. Manganous sulphate (15.1 gms in 1 litre of 5M H_2SO_4), 3 ml of conc. sulphuric acid (Excelar Glaxo) were added with water cooling. Then 12 ml of 0.5 N $KMnO_4$ 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 2 ml of concentrated sulphuric acid was added. The solution was stored for four hours before use, so that reduction process proceeds smoothly to Manganic sulphate and higher valency stages never accumulate in sufficient concentration to give rise to troublesome precipitates of higher oxides. During the addition of sulphuric acid, the solution was cooled in ice-cold water bath. The solution of Mn(III) sulphate obtained by above procedure is deep red coloured. It was stored in blue bottle and kept in refrigerator when not in use. On exposure to light in a clear bottle, there is possibility of formation of black ppt. owing to the formation of quadrivalent Mn salts as

$$2Mn(III) \longrightarrow Mn(II) + Mn(IV)$$

2.3 STANDERDIZATION OF Mn(III) SULPHATE SOLUTION :

There are 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 I :

In this method, a manganic sulphate solution was run into standard ferrous ammonium sulphate solution. 0.05 N solution of ferrous ammonium sulphate solution was used as standard solution. One drop in excess of Mn(III) sulphate solution gave a pink end point with yellowish tinge. A better pink colour was obtained by addition of 2 drops of syrupy phosphoric acid. Then normality of Mn(III) sulphate was calculated.

Method II :

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

2.4 PREPERATION OF STOCK SOLUTIONS :

Formaldehyde is supplied as 40 % aqueous solution. It was estimated by following iodometric method.

One ml formaldehyde solution was diluted to 250 ml. 25 ml of this are taken in conical flask. 50 ml of 0.1 N I_2 solution were added to it. Immediately 2 N NaOH solution was added till the liquid became pale yellow. After 10 minutes, it was acidified with 2 M HCl and the excess iodine was titrated with standard sodium thiosulphate solution using starch as an indicator. Blank determination was carried out to check the normality of iodine solution.

The normality of formaldehyde was found to be 14.7.N.1.47 normal solution was prepared as a stock solution. The normality of it was checked periodically by the above method. 5M sulphuric acid was used as solvent for this solution.

Benzaldehyde is insoluble in 5M sulphuric acid. A mixture of 3M sulphuric acid and 4M acetic acid was used to prepare the stock sulution of benzaldehyde 0.2 N solution of benzaldehyde was prepared as stock solution. Purity of benzaldehyde was checked by its boiling point and density. The glassware of pyrex glass was used for preparing and storing the stock solutions.

2.5 DETERMINATION OF λMAX. FOR Mn(III) SULPHATE AND VERIFICATION OF BEER-LAMBERTS LAW :

5×10^{-3} and 2.5×10^{-3}M solutions of Mn(III) sulphate in 5M sulphuric acid were prepared. Also 5×10^{-3} and 3×10^{-3} M solutions of Mn(III) sulphate in mixture of 3M H_2SO_4 and 4M CH_3COOH were prepared. Absorbence 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 done on spectronic 20 (Bausch and Lomb). The graphs of absorbence (O.D.) versus wavelength (nm) are shown in figure 2.1. It is seen that Mn(III) has a strong absorbence at 500 nm. The absorption spectra (Fig. No.2.1) of different concentrations of Mn(III) sulphate were recorded in order to see whether there is any spectral shift with change in the concentration of Mn(III) solution. The spectral pattern as well as maxima do not change with the changes in the concentration of Mn(III).

TABLE 2.1

DETERMINATION OF λmax.

Temp. = $30^{o}C$

Wavelength(nm)	$Mn^{+3} = 5x10^{-3}M$	$Mn^{+3} = 3x10^{-3}M$
	O.D(A)	O.D(A)
410	0.26	0.14
420	0.27	0.15
430	0.30	0.17
440	0.34	0.20
450	0.39	0.23
460	0.43	0.26
470	0.47	0.28
480	0.50	0.29
490	0.51	0.30
500	0.525	0.31
510	0.51	0.30
520	0.49	0.29
530	0.46	0.27
540	0.42	0.25
550	0.38	0.23

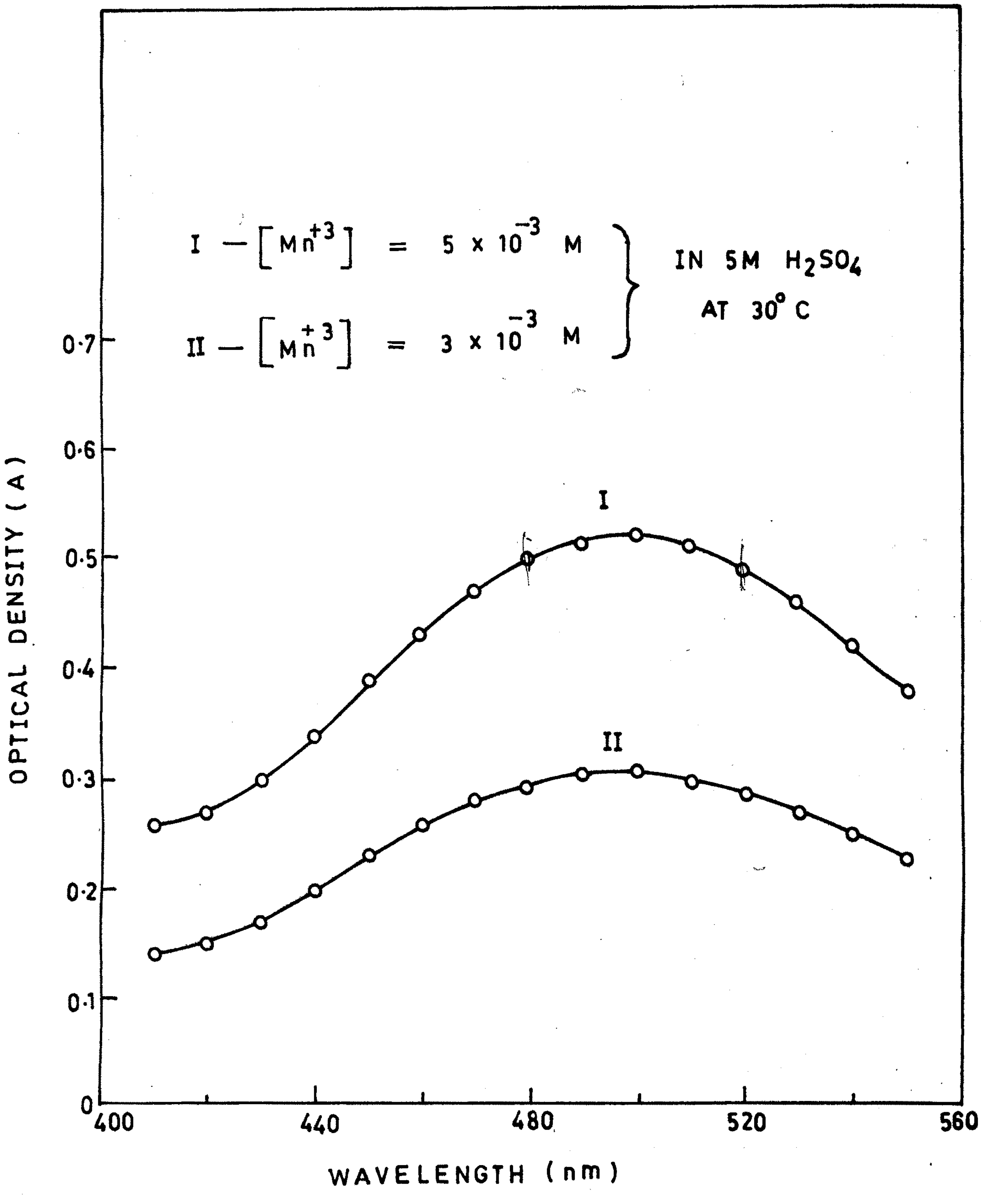

FIG. 2·1 — DETERMINATION OF λ_{max} ·

VERIFICATION OF BEER-LAMBERT'S LAW :

For the verification of Beer-Lambert's law, solutions of Mn(III) sulphate having concentrations in the range of 1×10^{-3}M to 5×10^{-3}M were prepared. The O.D. value of each solution was recorded at $\lambda = 500$ nm with spectronic 20. O.D. values were plotted against concentrations of Mn(III) sulphate (fig. No. 2.2). A straight line passing through origin was obtained indicating that Beer-Lambert's law is valid in the above concentration range. Thus, from the above observation, it is clear that Mn(III) sulphate is stable in this concentration range.

2.6 METHOD USED FOR KINETIC MEASUREMENTS :

During the course of reaction, Mn(III) is reduced to Mn(II). Mn(II) has practically no absorbence at 500 nm. During the course of reaction, the optical density is decreased due to decrease in concentration of Mn(III). All the kinetic measurements were carried out in pyrex glassware, which were coated outside with Japan black to avoid photochemical effects especially on Mn(III) sulphate. The stock solutions of Mn(III) sulphate and the organic substrates were kept well stoppered in refrigerator. The required volumes of these solutions were mixed in an iodine flask. The reaction mixture was transferred into cuvettes. These

TABLE 2.2

VERIFICATION OF BEER-LAMBERT'S LAW

At λmax.= 500 nm

[Mn(III)]	O.D(A)	ϵ M^{-1} cm^{2}
1×10^{-3}	0.11	110
2×10^{-3}	0.23	115
3×10^{-3}	0.34	111.33
4×10^{-3}	0.47	117.50
5×10^{-3}	0.59	118
6×10^{-3}	0.71	118.33
7×10^{-3}	0.82	117.14
	Mean	115.8

ϵ Graphical = 113.00 M^{-1} cm^{2}.

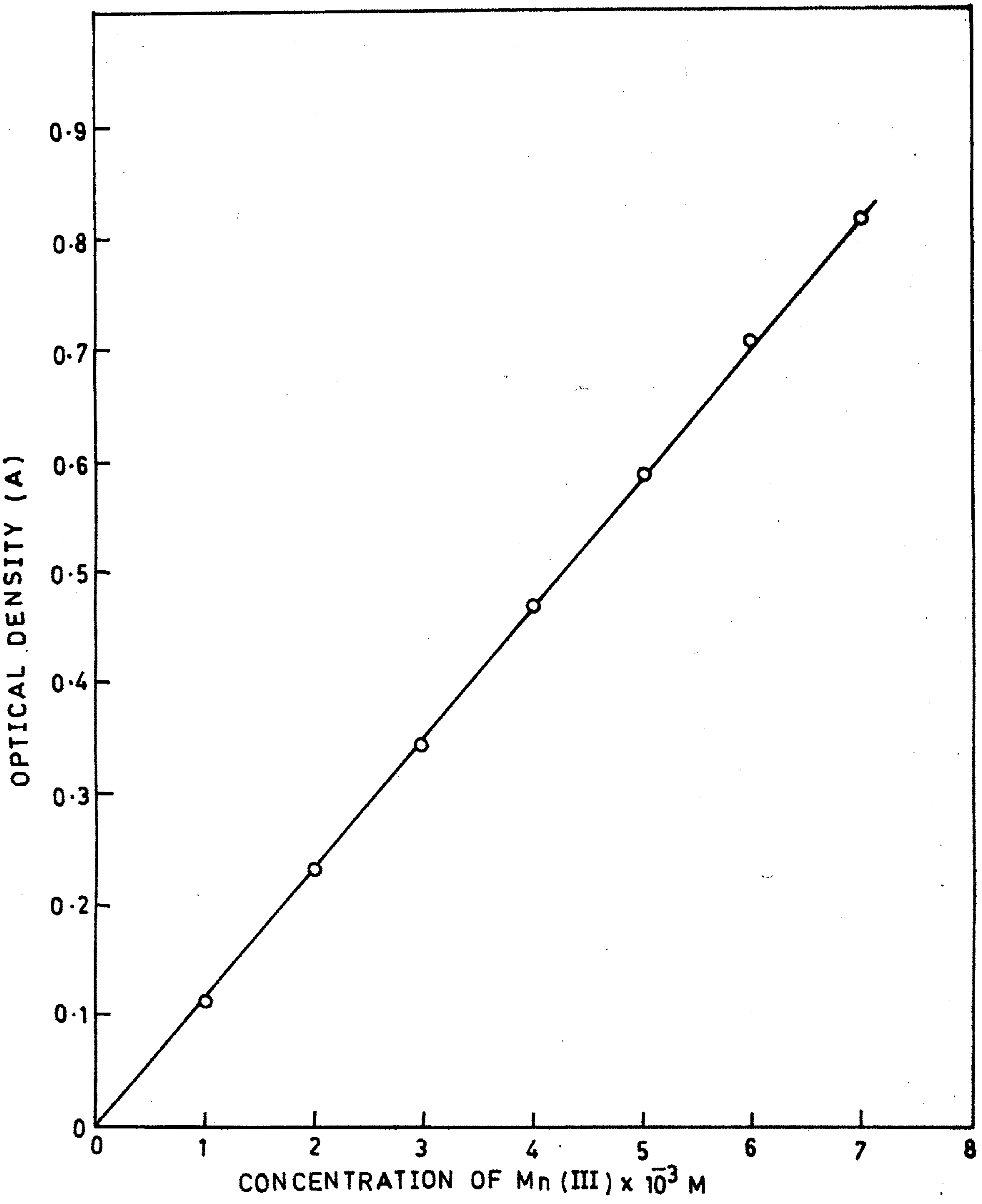

FIG. 2·2 — VERIFICATION OF BEER-LAMBERT'S LAW.

cuvettes were kept in the thermostat and at definite time intervals, the optical density of the reaction mixture was measured. By this method minimum error was observed. The reference solution contained all the reactants except Mn(III) sulphate. The reaction was usually followed upto 80 % completion. The following variations were studied

1) Variation of concentration of Mn(III) sulphate.
2) Variation of concentration of substrate.
3) Variation of concentration of sulphuric acid.
4) Variation of temperature.
5) Effect of addition of Mn(II).

2.7 DETECTION OF END PRODUCTS :

The end product of oxidation of formaldehyde is CO_2. It is detected by lime water test. The liberated gas is passed through freshly prepared lime water. It turns milky indicating the presence of CO_2 gas. The end product of oxidation of benzaldehyde is benzoic acid. It is filtered, recrystallised from hot water and confirmed by following tests :

i) Effervescence of CO_2 with saturated $NaHCO_3$.

ii) Neutral solution of it gives buff coloured precipitate with aqueous $FeCl_3$ solution.

iii) Physical constant - M.P. = 121°C