CHAPTER - III

OXIDATION OF FORMALDEHYDE

RESULTS AND DISCUSSION :

The results on the kinetics of oxidation of formaldehyde by Mn(III) sulphate in sulphuric acid medium are reported here. Experiments were designed to include the following studies.

(1) Determination of overall order of the reaction and order with respect to the reactants.

(2) Effect of concentration of sulphuric acid.

(3) Effect of addition of Mn(II) on the rate constant of the reaction.

(4) Effect of temperature on reaction rate and evaluation of thermodynamic parameters.

(5) End product analysis and free radical detection.

3.1 DETERMINATION OF ORDER OF THE REACTION :

Order of the reaction with respect to Mn(III) was determined by isolation method. The concentration of Mn(III) was varied from 3×10^{-3}M to 8×10^{-3}M at constant concentration of formaldehyde (8×10^{-2}M). The reaction was carried out at 40°C. The order with respect to formaldehyde could not be determined by isolation method because Mn(III)

CHAPTER - III

OXIDATION OF FORMALDEHYDE

3.1 Determination of order of the reaction

3.2 Effect of temperature and calculation of thermodynamic parameters

3.3 Free radical detection and end product analysis

3.4 Mechanism

which is absorbing species could not be used in large excess as compared to formaldehyde. Hence, to determine order of the reaction with respect to formaldehyde, concentration of Mn(III) was kept constant (7 x 10^{-3}M), while the concentration of formaldehyde was varied from 4 x 10^{-2}M to 1 x 10^{-1}M.

3.1 a EFFECT OF VARIATION OF [Mn(III)] :

The results on the effect of variation of Mn(III) at constant substrate concentration (8 x 10^{-2}M) and constant ionic strength at 40°C are reported here. The observations are recorded in table 3.1. The plots of absorbence A Vs t are shown in figure 3.1. These plots are hyperbolic in nature. The plots of log A Vs t are linear as shown in figure 3.2. Pseudo-first order rate constants obtained are included in table 3.1. It is seen that these values of k_1 are nearly constant. Hence, order of the reaction with respect to Mn(III) seems to be one. The order with respect to Mn(III) was further confirmed by Van't Hoff differential method. From the plots (figure 3.1) initial rates $(-dc/dt)_0$ were evaluated and were used to calculate order of the reaction as given in table 3.2. The mean order of reaction was found to be 0.897 i.e. one.

3.1 b EFFECT OF VARIATION OF [FORMALDEHYDE] :

The concentration of formaldehyde was varied from 0.04 M to 0.1 M keeping the concentration of Mn(III) constant (7x10^{-3}M). The observations are recorded in table 3.3. The

TABLE 3.1

OXIDATION OF FERMALDEHYDE EFFECT OF VARIATION OF Mn(III) CONCENTRATION

[Formaldehyde] = 8 x 10^{-2}M, [Sulphuric acid]=5M,

Temperature = 313°K

[Mn(III)] Time in Minute	3×10^{-3}M O.D	4×10^{-3}M O.D	5×10^{-3}M O.D	6×10^{-3}M O.D	7×10^{-3}M O.D	8×10^{-3}M O.D
0	0.385	0.505	0.59	0.71	0.80	0.90
10	0.33	0.395	0.50	0.59	0.67	0.78
20	0.29	0.355	0.43	0.52	0.59	0.67
30	0.255	0.32	0.38	0.46	0.54	0.61
40	0.23	0.29	0.35	0.41	0.48	0.55
50	0.215	0.26	0.31	0.375	0.44	0.49
60	0.195	0.24	0.285	0.34	0.41	0.47
70	0.18	0.22	0.26	0.31	0.37	0.42
80	0.165	0.20	0.24	0.285	0.34	0.385
90	0.15	0.19	0.22	0.265	0.32	0.36
100	0.145	0.175	0.202	0.245	0.29	0.34
110	0.135	0.165	0.19	0.23	0.28	0.32
120	0.13	0.155	0.185	0.22	0.26	0.30
130			0.175	0.21	0.255	0.285
k_1 min^{-1} Graphical	0.0115	0.0115	0.0109	0.0109	0.0107	0.0109

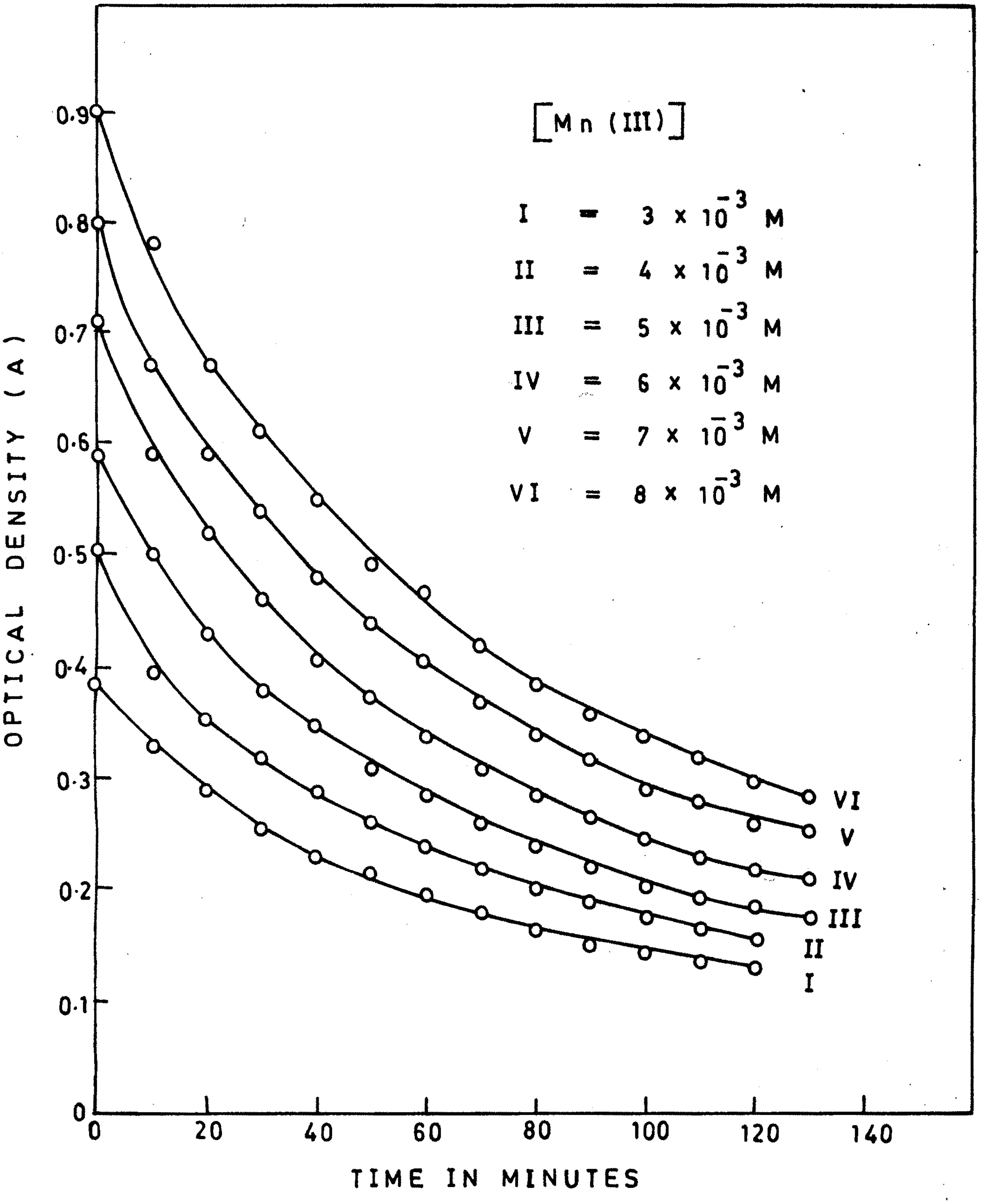


FIG. 3·1 — OXIDATION OF FORMALDEHYDE .

VARIATION OF Mn (III) .

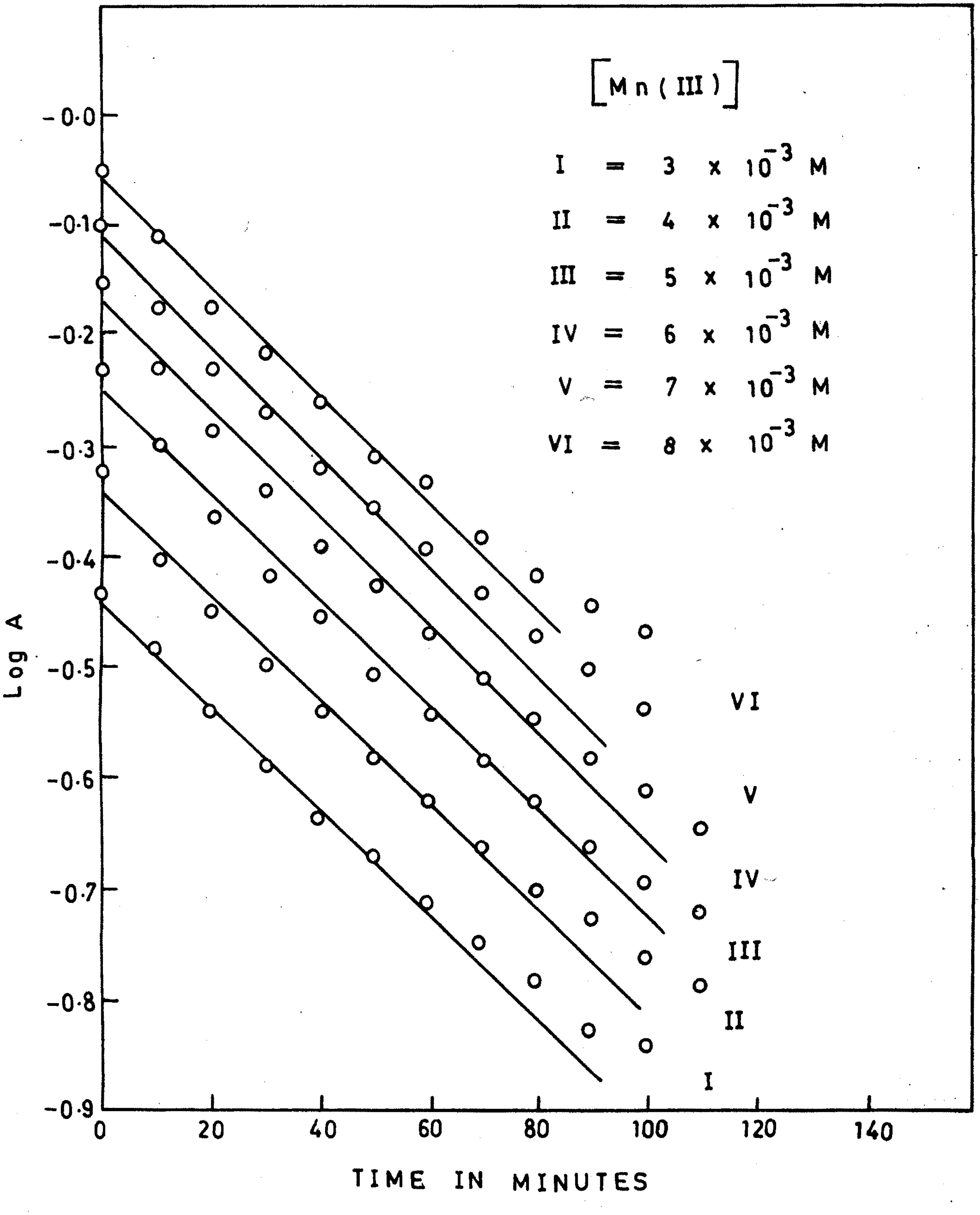


FIG. 3·2 — OXIDATION OF FORMALDEHYDE. VARIATION OF [Mn (III)].

TABLE 3.2

OXIDATION OF FERMALDEHYDE ORDER WITH RESPECT TO Mn(III) SULPHATE

[Mn(III)Sulphate]	$(-dc/dt)_o$	Order (n)
3×10^{-3}M	5.333×10^{-3}	0.900
4×10^{-3}M	6.5×10^{-3}	0.89
5×10^{-3}M	7.5×10^{-3}	0.92
6×10^{-3}M	1.055×10^{-2}	0.89
7×10^{-3}M	1.25×10^{-2}	0.88
8×10^{-3}M	1.3×10^{-2}	0.900
	Mean Order	0.9

plots of log A Vs t are linear as shown in figure 3.4. Pseudo first order rate constants obtained graphically are also included in table 3.3. It is seen that these values of k_1 are not constant but increase with concentration of formaldehyde. The ratio k_1/[HCHO] is fairly constant which shows that the reaction is first order with respect to formaldehyde. This is also seen from the calculations of the order by differential method. The values of $(-dc/dt)_0$ at different initial concentrations of formaldehyde (Co) are given in table 3.4 and the plot of log $(-dc/dt)_0$ Vs log Co is given in figure 3.5. It is seen from the figure that the plot is linear with slope equal to 0.96 which shows that order with respect to formaldehyde must be one. Similarly, a plot of log k_1 Vs log Co is a straight line with slope equal to one which further confirms that the order with respect to [HCHO] must be one.

3.2 EFFECT OF VARIATION OF [SULPHURIC ACID] :

Sulphuric acid was used as a medium for the reaction. The reaction was studied in presence of different concentrations of sulphuric acid (table 3.6). The rate constant was determined from the plots of log A Vs time (figure 3.7). These plots are all parallel straight lines indicating that $[H_2SO_4]$ does not affect the rate of the reaction. The values of first order rate constant k_1 are nearly constant which also shows that $[H_2SO_4]$ does not affect the rate of the reaction.

TABLE 3.3

OXIDATION OF FORMALDEHYDE VARIATION OF FORMALDEHYDE

[Mn(III) sulphate] = 7×10^{-3}M, [Sulphuric acid] = 5M

Temperature = 313^{o}K

[Formaldehyde] Time in Minute	0.04M O.D	0.06M O.D	0.08M O.D	0.1M O.D
0	0.80	0.80	0.80	0.80
10	0.68	0.67	0.62	0.60
20	0.65	0.60	0.58	0.55
30	0.60	0.57	0.52	0.49
40	0.57	0.53	0.48	0.44
50	0.55	0.50	0.43	0.39
60	0.54	0.46	0.39	0.34
70	0.51	0.45	0.35	0.31
80	0.49	0.40	0.32	0.28
90	0.47	0.38	0.30	0.26
100	0.45	0.34	0.27	0.23
110	0.42	0.32	0.25	0.21
k_1 min^{-1} Grpphical	0.00415	0.00628	0.00864	0.0104
$k_r = k_1$/HCHO] Lit Moles^{-1} min^{-1}	0.104	0.105	0.108	0.104

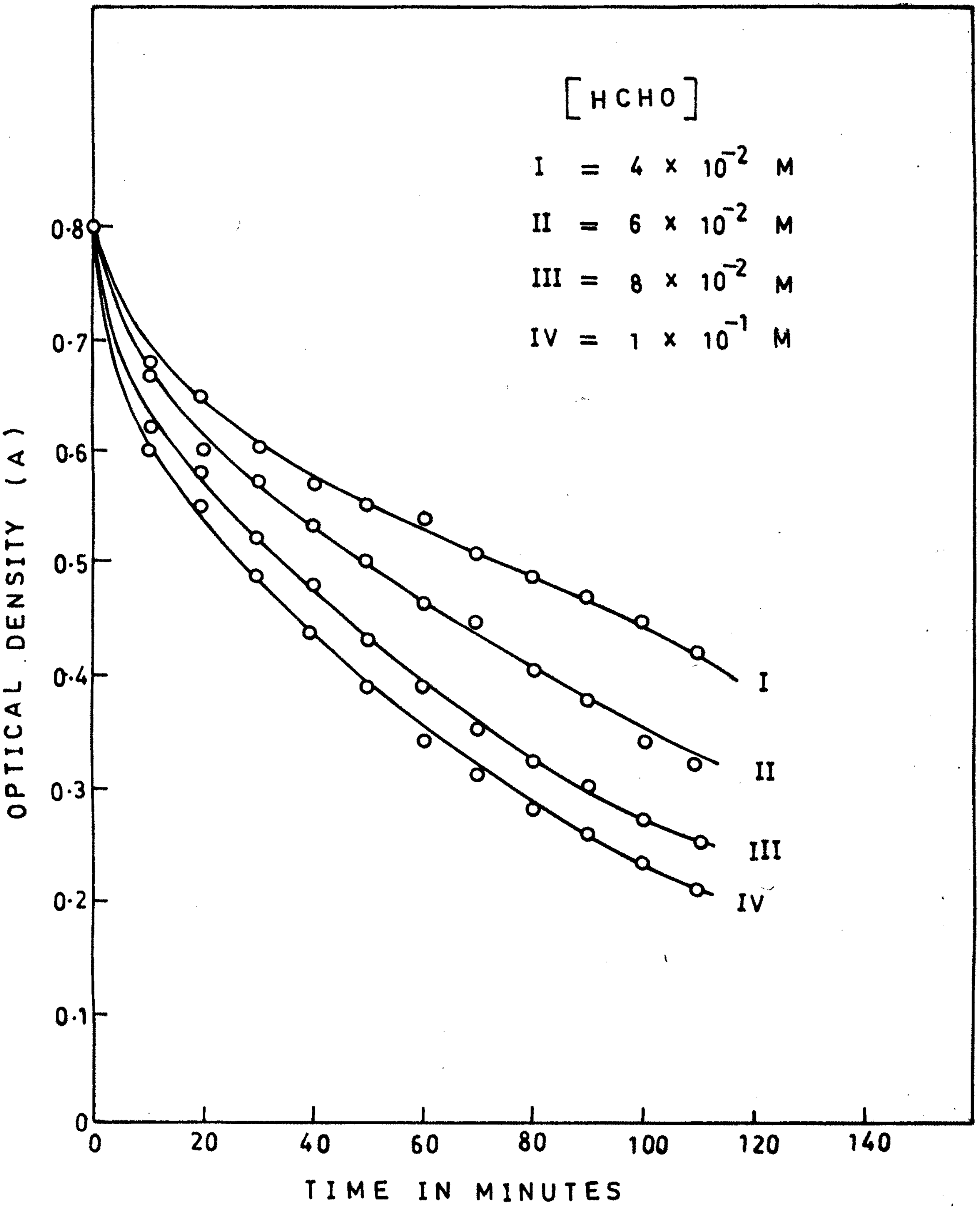


FIG. 3·3 – OXIDATION OF FORMALDEHYDE . VARIATION OF [FORMALDEHYDE] .

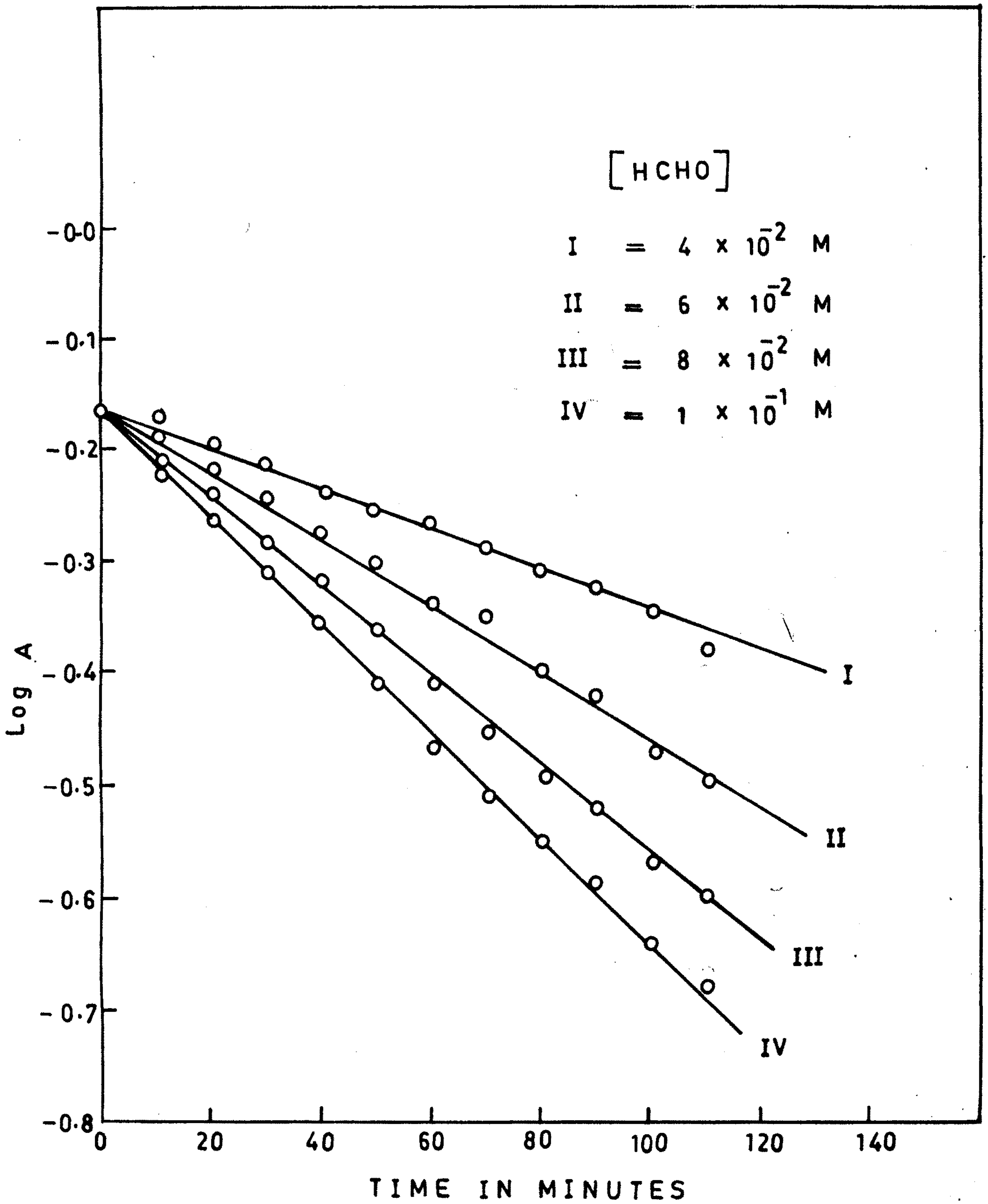


FIG. 3·4 – OXIDATION OF FORMALDEHYDE. VARIATION OF [FORMALDEHYDE].

TABLE 3.4

OXIDATION OF FORMALDEHYDE.
DETERMINATION OF ORDER WITH RESPECT TO FORMALDEHYDE

[HCHO]	$(-dc/dt)_o$	$\log(-dc/dt)_o$	log Co
0.04 M	0.00956	- 2.995	- 1.3979
0.06 M	0.0146	- 1.8356	- 1.2218
0.08 M	0.0172	- 1.7645	- 1.0969
0.1 M	0.0225	- 1.6478	- 1.00

Order with respect to formaldehyde from graph = 0.96

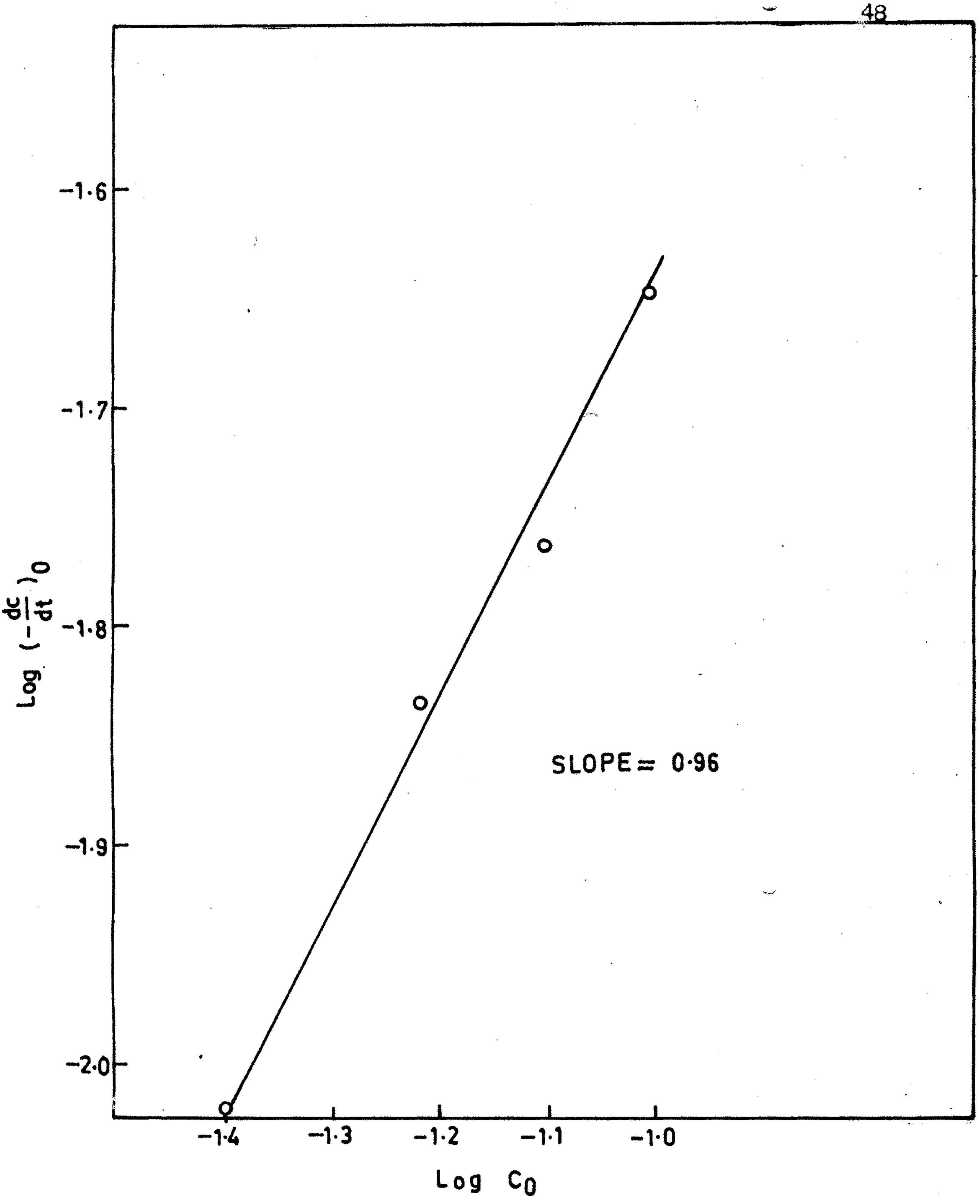


FIG. 3·5 — OXIDATION OF FORMALDEHYDE.
DETERMINATION OF ORDER w.r.t. HCHO.

TABLE 3.5

OXIDATION OF FORMALDEHYDE
DETERMINATION OF ORDER WITH RESPECT TO FORMALDEHYDE

[HCHO]	k_1 min^{-1}	log k_1	log C_o
0.04 M	0.00414	- 2.383	- 1.3979
0.06 M	0.00628	- 2.202	- 1.2218
0.08 M	0.00864	- 2.0635	- 1.0969
0.1 M	0.0104	- 1.983	- 1.00

Order of reaction with respect to formaldehyde from graph = 1

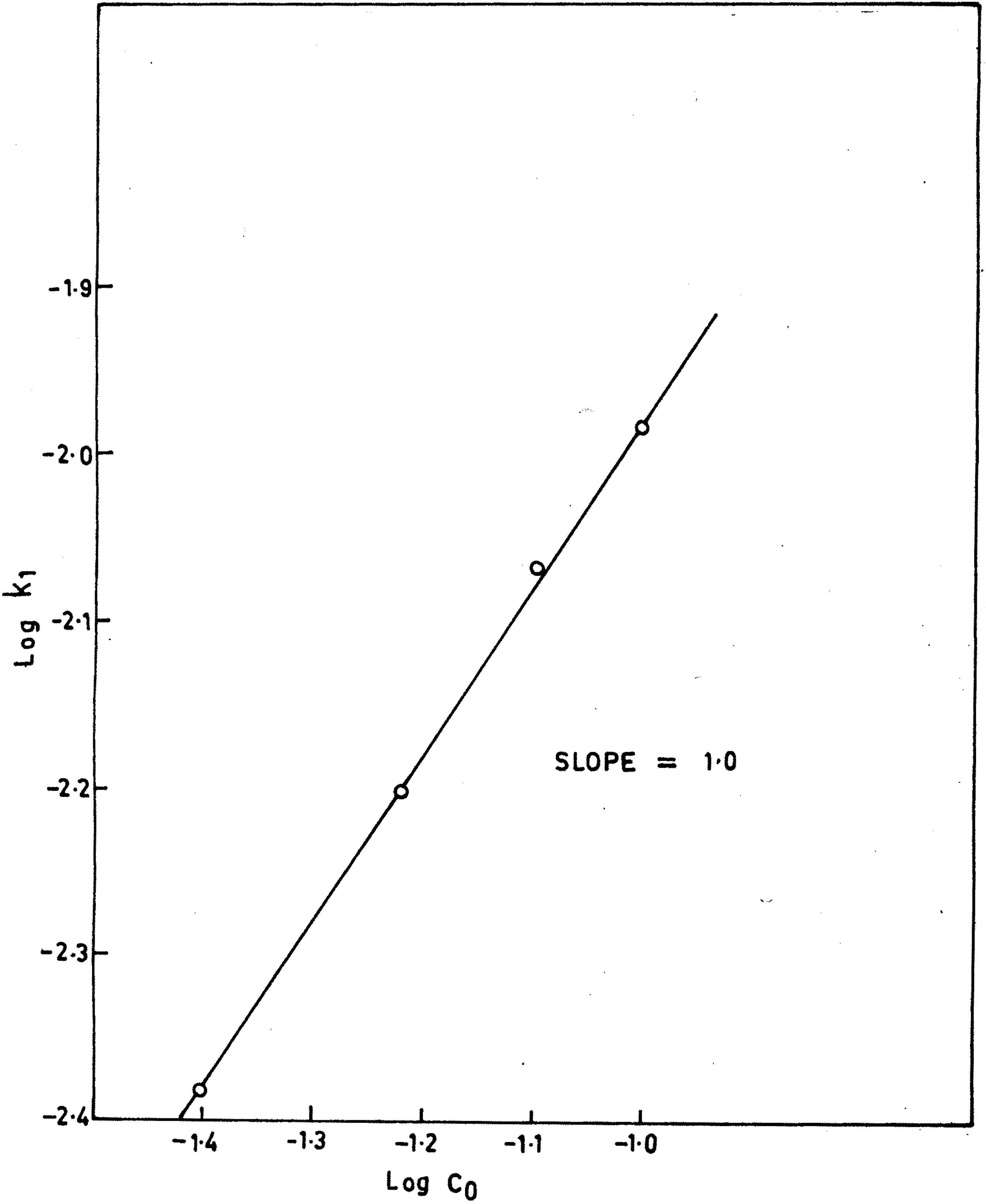


FIG. 3·6 — OXIDATION OF FORMALDEHYDE .
DETERMINATION OF ORDER w.r.t. HCHO ,

TABLE 3.6

OXIDATION OF FORMALDEHYDE
EFFECT OF SULPHURIC ACID CONCENTRATION

[Mn(III) sulphate] = 7×10^{-3}M, [Formaldehyde]=8×10^{-2}M

Temperature = 313°K

[Sulphuric acid] Time(minutes)	6 N O.D	8 N O.D	10 N O.D	12 N O.D
0	0.68	0.75	0.80	0.95
10	0.54	0.62	0.67	0.80
20	0.47	0.53	0.58	0.71
30	0.425	0.47	0.52	0.63
40	0.38	0.41	0.48	0.57
50	0.35	0.37	0.43	0.52
60	0.31	0.33	0.40	0.48
70	0.28	0.30	0.38	0.45
80	0.255	0.28	0.35	0.42
90	0.225	0.26	0.33	0.40
100	0.21	0.24	0.31	0.38
110	0.195	0.22	0.29	0.36
k_1 min^{-1} Graphical	0.00863	0.0086	0.0863	0.0084

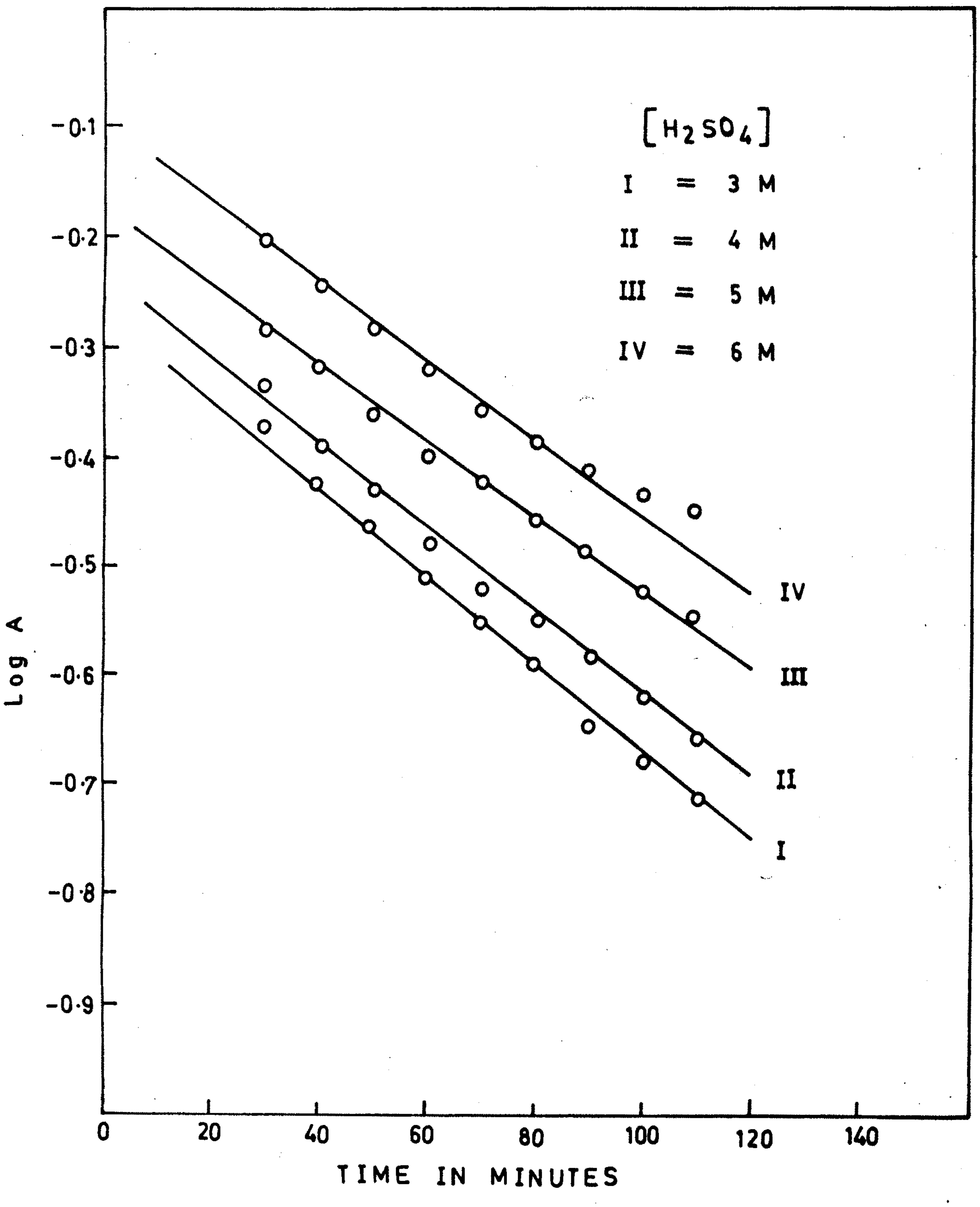


FIG. 3·7 — OXIDATION OF FORMALDEHYDE.

VARIATION OF $[H_2SO_4]$.

Further, it is noted that initial optical density (Ao) is seen to be increasing with $[H_2SO_4]$ showing thereby that extinction coefficient (ϵ) of Mn(III) increases with $[H_2SO_4]$.

3.3 EFFECT OF VARIATION OF [Mn(II)] :

The reaction was studied using different concentrations of Mn(II) sulphate (0, 1.5×10^{-3}M, 3.5×10^{-3}M, 5×10^{-3}M). Concentrations of Mn(III) (7×10^{-3}M) and formaldehyde (8×10^{-2}M) were kept constant. The reaction was studied in 5M H_2SO_4 medium at 40 °C (table 3.7). The first order rate constants were determined from the plots of log A Vs time (figure 3.8). These plots are all parallel straight lines indicating that Mn(II) ions does not affect the rate of the reaction. The values of first order rate constant are nearly constant which also shows that Mn(II) ions does not affect the rate of the reaction.

3.4 EFFECT OF TEMPERATURE ON REACTION AND CALCULATION OF THERMODYNAMIC PARAMETERS :

For the study of temperature effect, 8×10^{-2}M formaldehyde and 7×10^{-3}M Mn(III) sulphate solutions were used. The reaction was studied at four different temperatures viz. 35°C, 40°C, 45°C, 50°C. The observations are recorded in table 3.8. Plots of log A Vs time are shown in figure 3.9. First order rate constants are calculated at different temperatures. The temperature coefficient of the reaction is 2.7. The energy of activation Ea and the frequency factor A

TABLE 3.7

OXIDATION OF FORMALDEHYDE
EFFECT OF ADDITION OF Mn(II).

[Mn(III) sulphate]=7×10^{-3}M, [Formaldehyde] = 8×10^{-2}M

[Sulphuric acid] = 5 M Temperature = 313°K

[Mn(II)] Time (minute)	0 O.D	1.5×10^{-3}M O.D	3.5×10^{-3}M O.D	5×10^{-3}M O.D
0	0.85	0.86	0.85	0.88
10	0.67	0.74	0.77	0.80
20	0.58	0.66	0.70	0.73
30	0.52	0.60	0.64	0.67
40	0.48	0.55	0.60	0.63
50	0.45	0.51	0.56	0.60
60	0.42	0.47	0.53	
65				0.54
70	0.39	0.45	0.50	
80	0.36	0.42	0.47	0.49
90	0.34	0.39	0.45	
95				0.46
100	0.33	0.37	0.42	
110	0.30	0.35	0.40	0.43
120	0.29	0.34	0.39	
125				0.40
140				0.38
155				0.36
k_1 min^{-1} Graphical	0.0074	0.00767	0.00767	0.0072

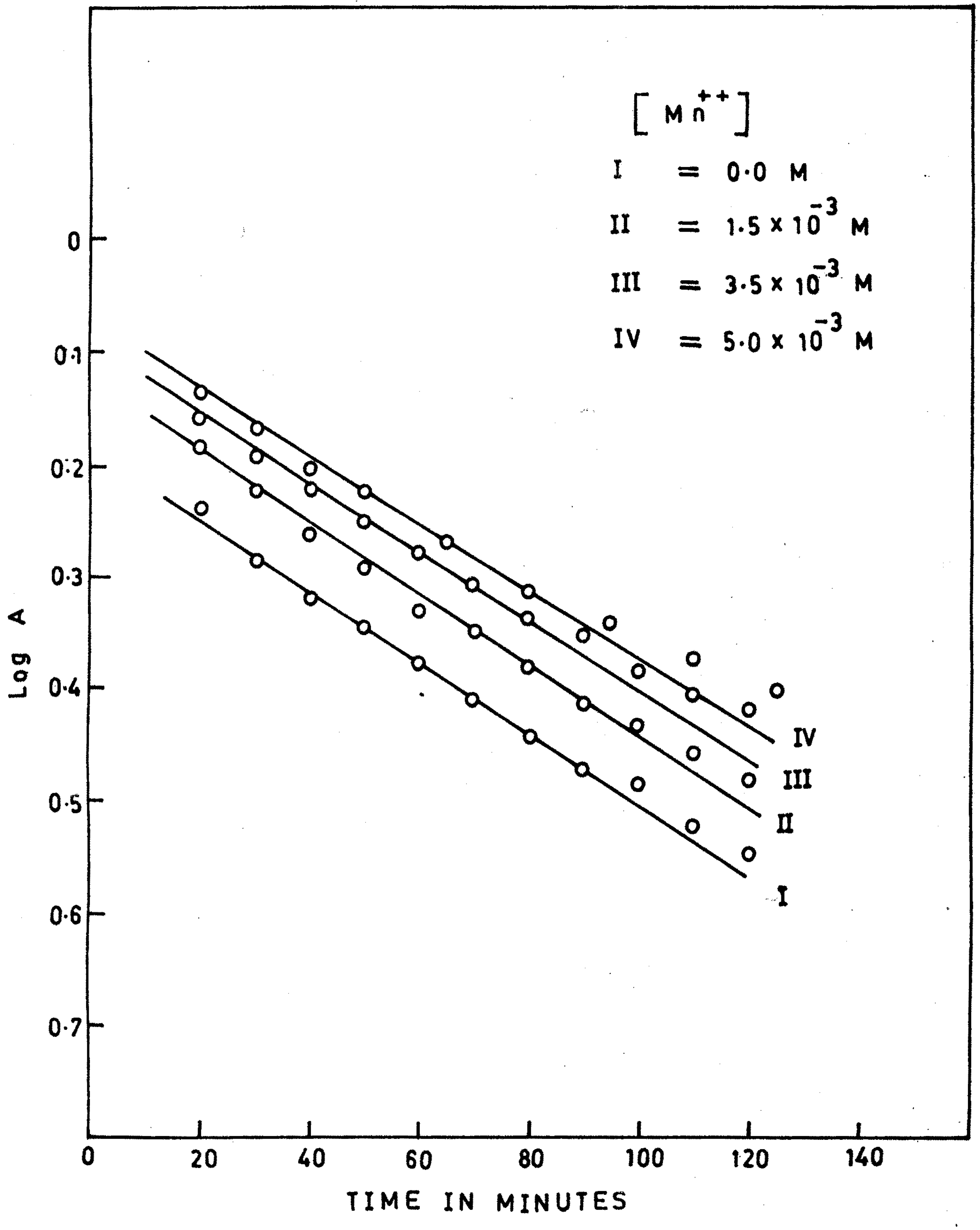


FIG. 3·8 — OXIDATION OF FORMALDEHYDE VARIATION OF $[Mn^{++}]$.

TABLE 3.8

OXIDATION OF FORMALDEHYDE
VARIATION OF TEMPERATURE

[Mn(III)Sulphate] = 7×10^{-3}M, [Formaldehyde] = 7×10^{-2}M

[Sulphuric acid] = 5 M

Temp °K	308	313	318	323
Time (minute)	O.D	O.D	O.D	O.D
0	0.80	0.81	0.80	0.81
10	0.70	0.67	0.59	0.53
20	0.63	0.58	0.48	0.41
30	0.58	0.53	0.41	0.33
40	0.53	0.48	0.35	0.28
50	0.50	0.45	0.31	0.235
60	0.48	0.42	0.28	-
70	0.46	0.39	0.25	-
80	0.43	0.36	0.23	-
90	0.42	0.34	-	-
100	0.40	0.32	-	-
110	0.38	0.31	-	-
120	0.365	-	-	-
130	0.355	-	-	-
k_1(graphical) min^{-1}	0.0046	0.00785	0.0130	0.0207
Sec^{-1}	7.66×10^{-5}	1.308×10^{-4}	2.166×10^{-4}	3.45×10^{-4}

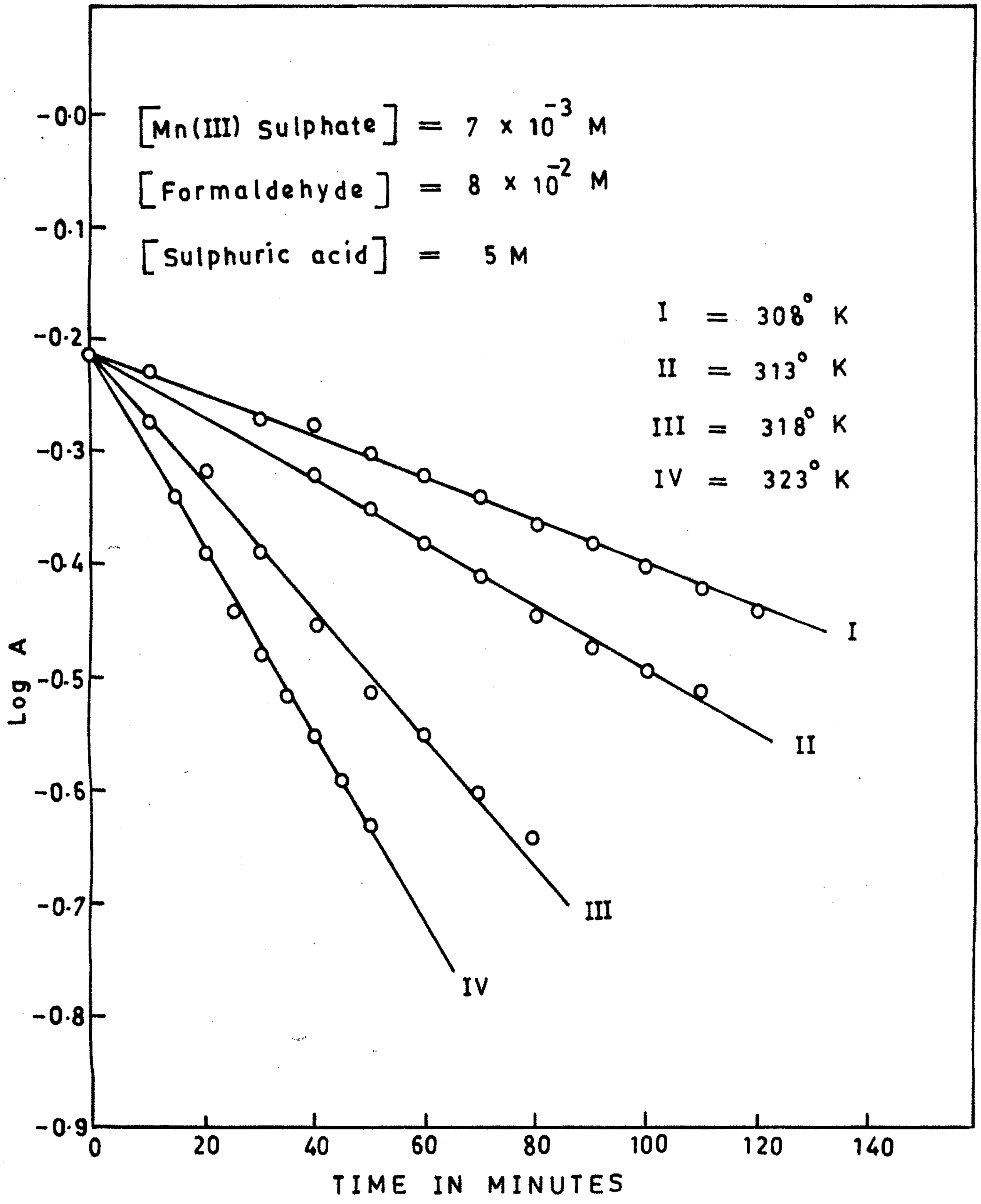


FIG. 3·9 — OXIDATION OF FORMALDEHYDE .
VARIATION OF TEMPERATURE .

were calculated using the following equations.

$$k_1 = A \cdot e^{-Ea/RT} \qquad \ldots(3.1)$$

$$\text{or } \log k_1 = \log A - \frac{Ea}{2.303\ RT} \qquad \ldots(3.2)$$

Table 3.9 was used to plot log k_1 Vs 1/T. It was a straight line. Ea was obtained from the slope. This graphical value of Ea was found to be 19.74 K cal/mole (figure 3.10). Ea was calculated also by direct substitution of k_1 and k_2 at temperatures T_1 and T_2 in the following equation.

$$Ea = \frac{2.303 \log (k_2/k_1)\ R\ T_1\ T_2}{(\ T_2 - T_1\ )} \qquad \ldots(3.3)$$

The mean value of Ea obtained was 20.00 K cal/mole which is very close to the graphical value (19.740 K cal/mole).

DETERMINATION OF ΔH^*

We have the equation

$$k_1 = \frac{kT}{h} \times e^{\Delta S^*/R} \times e^{-\Delta H^*/RT}$$

$$\therefore \log k_1 = \log \frac{kT}{h} + \frac{\Delta S^*}{2.303\ R} - \frac{\Delta H^*}{2.303\ RT}$$

$$\therefore \log (\ k_1/T\ ) = \log (\ k/h\ ) + \Delta S^*/2.303R - \Delta H^*/2.303RT$$

$$\ldots(3.4)$$

TABLE 3.9

OXIDATION OF FORMALDEHYDE

DETERMINATION OF Ea

k_1 Sec^{-1}	T°K	Log k_1	$\frac{1}{T} \times 10^{-3}$	Ea calculated K cal/mole
7.66×10^{-5}	308	- 4.1158	3.247	20.39
1.308×10^{-4}	313	- 3.8835	3.195	
2.166×10^{-4}	318	- 3.6643	3.145	19.62
3.45×10^{-4}	323	- 3.4622	3.096	

Energy of activation (Graphical) = 19.74 K cal/mole

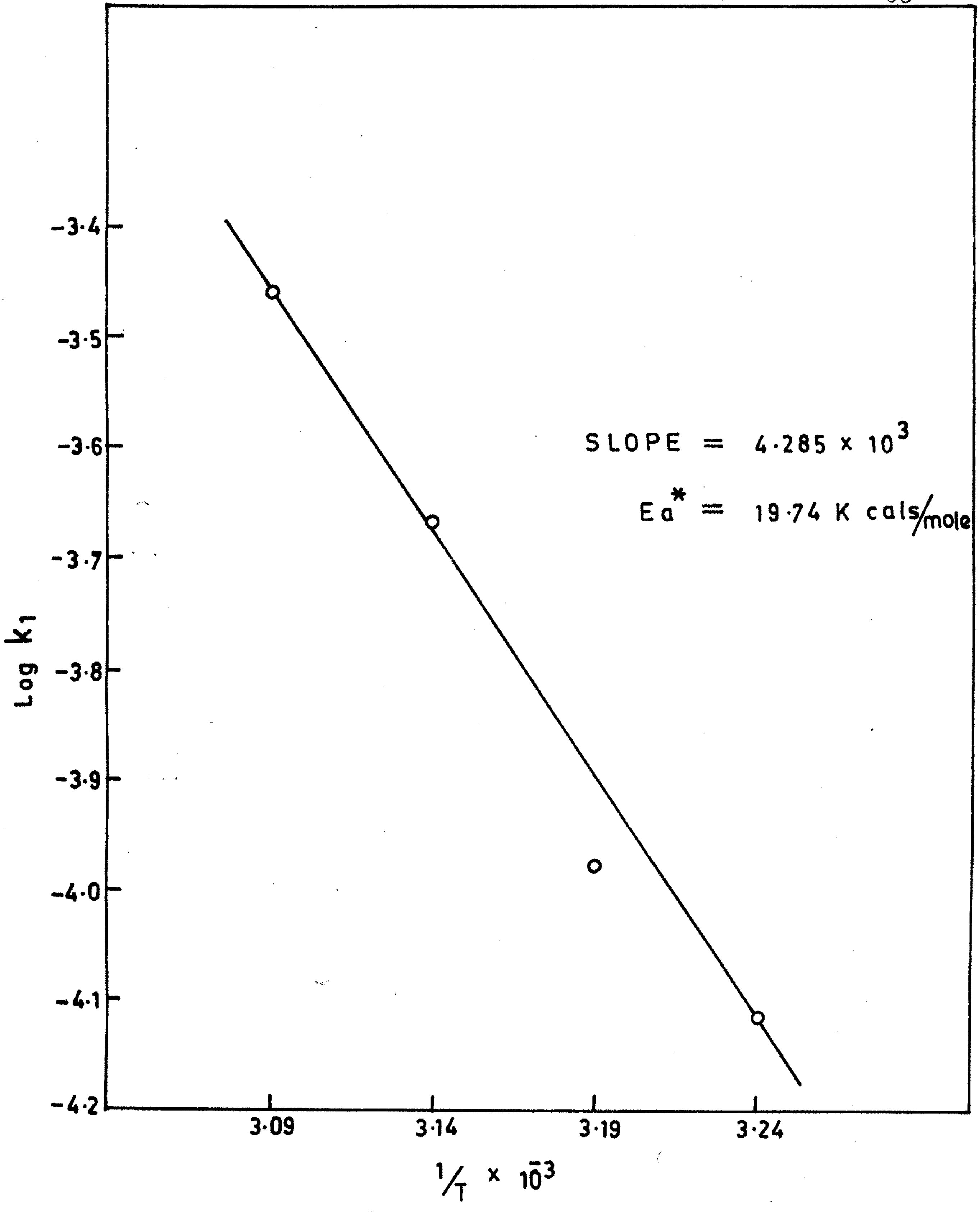


FIG. 3·10 — OXIDATION OF FORMALDEHYDE. DETERMINATION OF Ea^*.

ΔH^* can be found from the slope of the linear plot of $\log k_1/T$ Vs $1/T$.

$$\text{Slope} = -\Delta H^*/2.303\ R.$$

$$\text{i.e. } \Delta H^* = -2303\ R \times \text{slope.}$$

A graph of $\log (k_1/T)$ Vs $1/T$ was a straight line (figure 3.11). The value of ΔH^* was found to be 19.740 K cal/mole.

Table 3.10 was used to calculate ΔS^*, ΔG^* and frequency factor. The following relations were used for above calculations.

$$\Delta S^* = 2.303\ R \log\ Ah/k_1T \qquad \ldots(3.5)$$

$$\Delta G^* = \Delta H^* - T\Delta S^* \qquad \ldots(3.6)$$

$$\log\ A = \log k_1 + Ea/2.303\ RT$$

The values of energy of activation (Ea), frequency factor(A), enthalpy change (ΔH^*), entropy change (ΔS^*) and free energy change (ΔG^*) obtained are given in table 3.11.

3.5 FREE RADICAL DETECTION AND END PRODUCT ANALYSIS :

Existence of free radical during the course of the reaction was shown by acrylonitrile polymerisation test. When acrylonitrile (1 ml) was added to the reaction mixture (5 ml) containing both the Mn(III) and formaldehyde, white ppt. was

TABLE 3.10

OXIDATION OF FORMALDEHYDE

DETERMINATION OF ΔH^{*}

k_1 Sec^{-1}	T^{o} K	$k_1/T \times 10^{-7}$	Log k_1/T	$1/T \times 10^{-3}$
7.66×10^{-5}	308	2.48	- 6.6055	3.24
1.308×10^{-4}	313	4.18	- 6.3788	3.19
2.166×10^{-4}	318	6.8	- 6.1675	3.14
3.45×10^{-4}	323	10.68	- 5.9714	3.09

ΔH^{*} By graph = 19.739 K cal/mole

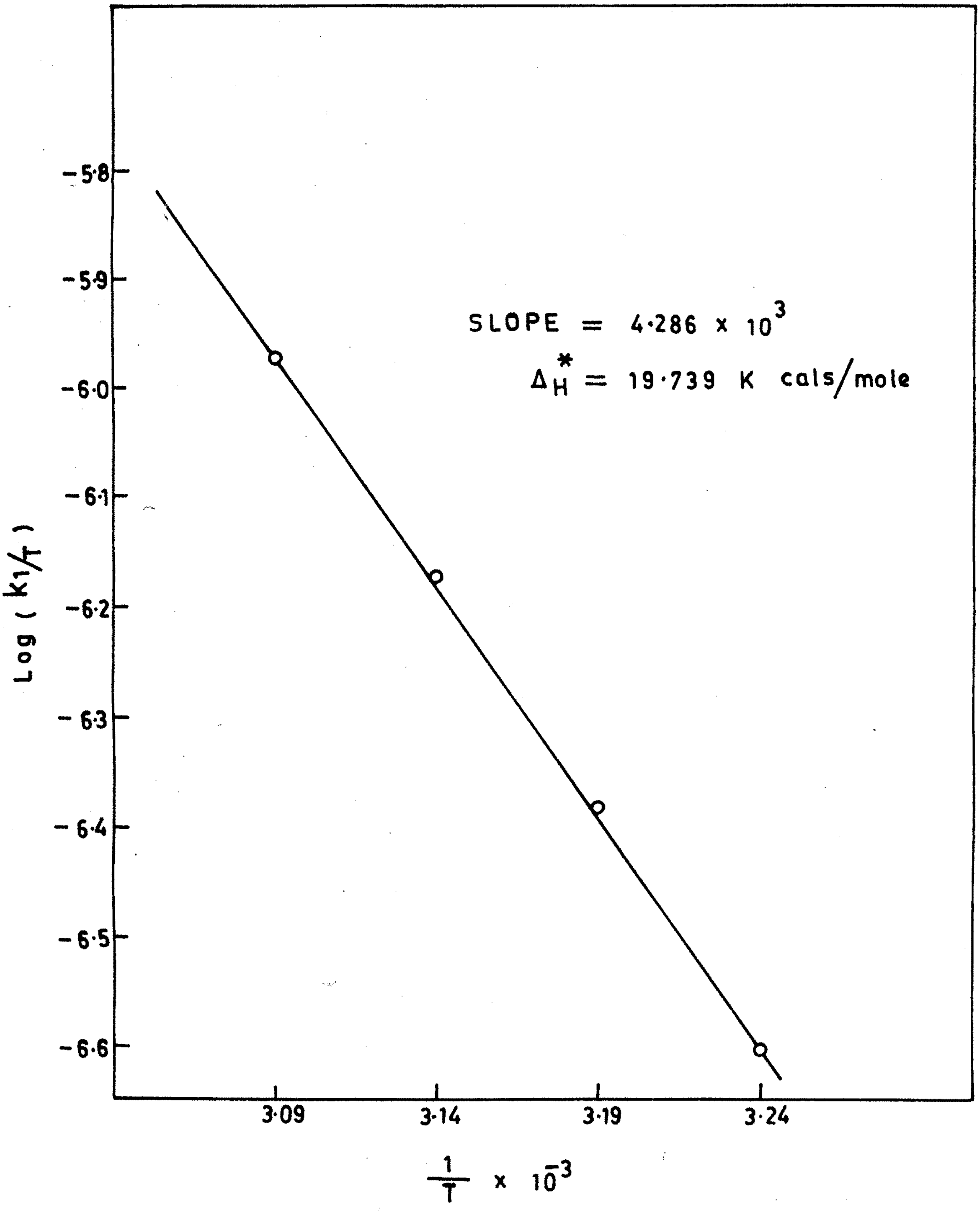


FIG. 3·11 — OXIDATION OF FORMALDEHYDE DETERMINATION OF ΔH^*.

TABLE 3.11

THERMODYNAMIC PARAMETERS FOR THE OXIDATION OF FORMALDEHYDE

Temperature ^{o}K	K‡ Sec^{-1}	Temperature Co-efficient	Ea K cal/mole		ΔH^{*} K cal/mole	Frequency factor $A \times 10^{9}$ Sec^{-1}	ΔS^{*} e.u.	ΔG^{*} K cal/mole
			By graph	By Calculation				
308	7.66×10^{-5}	2.63		20.39		6.299	-100.20	50.60
313	1.308×10^{-4}	2.64	19.74	19.62	19.74	6.440	-101.26	51.43
318	2.166×10^{-4}					6.498	-102.28	52.26
323	3.45×10^{-4}					6.401	-103.27	53.10
Mean			19.74	20.00	19.74		-101.75	51.85

formed. However, such ppt. was not obtained when Mn(III) or formaldehyde alone was present in the solution. This clearly indicates that reaction proceeds via free radical formation.

The end product was identified to be CO_2. It was confirmed by the lime water test.

3.6 MECHANISM :

From this work, the following results were obtained.

(1) The order of reaction with respect to Mn(III) is one.

(2) The order of reaction with respect to formaldehyde is one.

(3) There is no effect of sulphuric acid on the rate of reaction.

(4) There is no effect of Mn(II) on the rate of reaction.

(5) The temperature coefficient of the reaction is 2.7.

(6) The energy of activation is 20.00 K cal/mole.

(7) The values of ΔH^{*}, ΔS^{*} and ΔG^{*} are 19.74 K cal/mole, -101.75 e.u. and 51.85 K cal/mole respectively.

(8) The reaction proceeds via free radical formation and the end product is CO_2.

Before going to decide the mechanism of the reaction in the present study, it is worthwhile to summarize the various mechanisms suggested for the oxidation of formaldehyde.

Kinetics and mechanism of reaction of ammonium nitrate with formaldehyde has been reported. Under the condition $[NH_4NO_3] \gg [HCHO]$, the order of reaction with respect to formaldehyde was found to be two. The order of reaction with respect to NH_4NO_3 was found to be 0.66. From this it appears that NH_4NO_3 reacts with HCHO rapidly to form possibly a complex in a fast step.

$$NH_4NO_3 + HCHO \xrightarrow[\text{fast}]{k} \text{complex.}$$

The complex so formed might react with another HCHO molecule to give the product in slow step.

$$\text{Complex} + HCHO \xrightarrow[\text{slow}]{k} CH_3NH_3NO_3 + HCOOH.$$

The Osmium (VIII) catalysed oxidation of formaldehyde by chloramine-T in alkaline medium has been reported. It showed first order dependence to [Chloramine-T] and [Osmium(VIII)]. It showed inverse first order to [alkali] and zero order dependence to the [formaldehyde]. The energy and entropy of activation for the oxidation are 15.2 K cal/mole and - 16.9 cal/deg. mole

The mechanism suggested involves following steps.

Formaldehyde is hydrated in fast step.

$$H\,CHO + H_2O \rightleftharpoons H\,CH\,(OH)_2 \quad \text{..... fast}$$

An intermediate complex between N-chlorotoluene-p-sulphonamide and Os (VIII) is formed in slow rate determining step.

$$CH_3C_6H_4SO_2N\,HCl + Os\,(VIII) \longrightarrow \text{Intermediate (A) ... slow}$$

This intermediate abstracts hydride ion from the hydrated formaldehyde in the fast step.

$$A + HCH\,(OH)_2 \longrightarrow \text{Products .... fast.}$$

A fast hydride ion transfer from the hydrated form of the aldehyde has been suggested in the oxidation of aldehydes by Chromium (VI),[64,65] bromine[66] and acid permanganate.[67].

Thermodynamic parameters at 45°C are as follow

$$k_1 = 9.96 \times 10^{-2}\ sec^{-1}$$

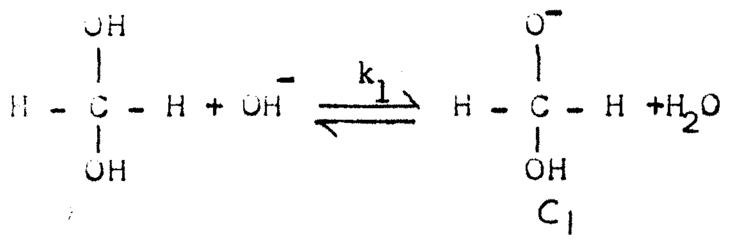
$$Ea = 15.2\ K\ cal/mole$$

$$\Delta H^* = 14.5\ K\ cal/mole$$

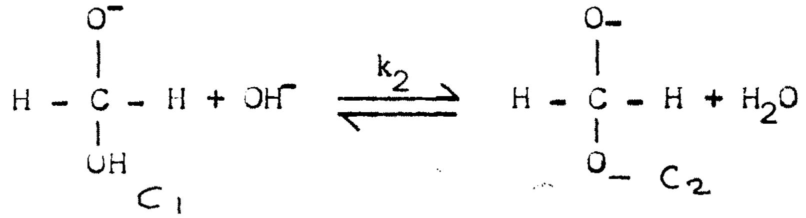
$$Log\ A = 9.33$$

$$\Delta S^* = -16.9\ e.u.$$

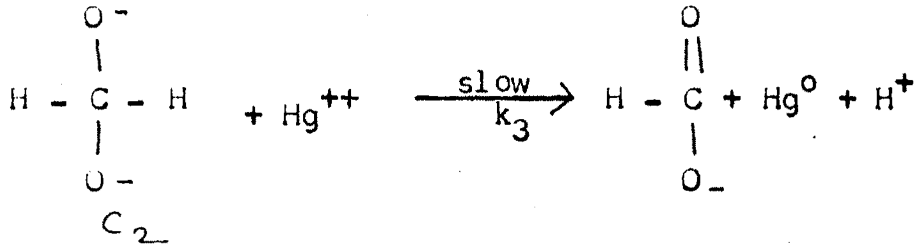
Oxidation of formaldehyde by Nessler's reagent in alkaline medium has been reported. The reaction shows first order dependence both in $[Hg(II)]$ and $[HCHO]$. The rate is inversely proportional to $[I^-]$ and directly proportional to $[OH^-]^2$. In aquous solution, formaldehyde is in hydrated form.



$$H-\overset{OH}{\underset{OH}{C}}-H + OH^- \overset{k_1}{\rightleftharpoons} \underset{C_1}{H-\overset{O^-}{\underset{OH}{C}}-H} + H_2O \qquad (I)$$



$$\underset{C_1}{H-\overset{O^-}{\underset{OH}{C}}-H} + OH^- \overset{k_2}{\rightleftharpoons} \underset{C_2}{H-\overset{O^-}{\underset{O^-}{C}}-H} + H_2O \qquad (II)$$



$$\underset{C_2}{H-\overset{O^-}{\underset{O^-}{C}}-H} + Hg^{++} \xrightarrow[k_3]{slow} H-\overset{O}{\underset{O^-}{\overset{\|}{C}}} + Hg^{o} + H^{+} \qquad (III)$$

The existence of species C_1 and C_2 have been confirmed by Cannizzaro reaction.[68] The doubly charged anion C_2 has been considered to be more reactive. This is further supported by Neorgi,[69] Barmashenko,[70] Lukes[71] and Shanker[72] for the oxidation of formaldehyde.[73] The rate determining step III involves two electron transfer. This has already been established by Helpern[74] and Littler.[75]

Kinetics of oxidation of formaldehyde by Bromamine-T in perchloric acid medium has been reported. The rate followed first order kinetics each in [HCHO] and [BAT]. The rate was zero order in $[H^+]$. It was further noticed that formic acid is the product of oxidation and it is not oxidised to CO_2. This was because the concentration of formic acid is very low (about 0.001 moles/dm^3). The mechanism involves following steps.

$$H\,CH(OH)_2 + RNHBr \xrightarrow{slow} H_2C(OH)\,O\,Br + RNH_2.$$

$$H_2C(OH)\,O\,Br \xrightarrow{fast} H\,COOH + H^+ + Br^-.$$

Kinetics of oxidation of formaldehyde by Co(III) has been reported.

The initiation step in the oxidation is the reduction of the Co(III) ion to Co(II) as follow.

$$HCHO + Co^{+++} \longrightarrow \dot{C}HO + H^+ + Co^{++}$$

It is highly probable that the Co(III) ion is co-ordinated to water and the preliminary process may be the replacement of one of the co-ordinated molecules of the cobaltic shell by formaldehyde. Although there is no direct evidence for this replacement in this perticular case, aldehydes are known to form complexes with other heavy ion salts.[76] Initial complex formation, therefore, being assumed, the following reaction mechanism is proposed which is in broad agreement with experimental findings.

$$\begin{array}{lll}
HCHO + Co^{+++} & \longrightarrow (HCHO.Co^{+++}) & \ldots 1 \\
(HCHO.Co^{+++}) & \longrightarrow Co^{++} + H^+ + H\dot{C}O & \ldots 2 \\
H\,\dot{C}O + Co^{+++} & \longrightarrow Co^{++} + H^+ + Co & \ldots 3 \\
H\dot{C}O + H_2O & \longrightarrow HCHO + \dot{O}H & \ldots 4 \\
 & \longrightarrow HCOOH + \dot{H} & \ldots 5 \\
\dot{O}H + HCHO & \longrightarrow H_2O + H\dot{C}O & \ldots 6 \\
 & \longrightarrow HCOOH + \dot{H} & \ldots 7 \\
\dot{H} + HCHO & \longrightarrow H_2 + H\dot{C}O & \ldots 8
\end{array}$$

In the present study, the reaction is found to be first order with respect to the substrate (formaldehyde) and the oxidant Mn(III). But it is independent of $[H^+]$ and $[Mn(II)]$. Similarly, ionic strength does not affect the rate constant. This shows that the rate determining step involves Mn(III) and formaldehyde. Although aldehydes have been shown to form complexes with heavy metal ions,[76] Mn(III) does not seem to form any complex with formaldehyde and hence we may suggest the rate determining step as

$$HCHO + Mn(III) \xrightarrow{k_1} \text{Products.}$$

Bawn and White[53] have assumed the formation of $H\dot{C}O$, $\dot{O}H$ and $\dot{H}$ radicals during the oxidation of formaldehyde by Co(III). Since Mn(III) and Co(III) are one electron oxidants, the mechanism suggested by them may also be applied to the present case. Hence, we can write the following steps for the reaction.

(1) $$HCHO + Mn(III) \xrightarrow[\text{slow}]{k_1} Mn(II) + H^+ + H\dot{C}O$$

(2) $$H\dot{C}O + H_2O \xrightarrow[\text{fast}]{k_2} HCOOH + \dot{H}$$

(3) $$HCOOH + Mn(III) \xrightarrow[\text{fast}]{k_3} Mn(II) + H^+ + HCO\dot{O}$$

(4) $$H\dot{C}O + H_2O \xrightarrow[\text{fast}]{k_4} HCHO + \dot{O}H$$

(5) $$HCO\dot{O} + \dot{O}H \xrightarrow[\text{fast}]{k_5} CO_2 + H_2O$$

(6) $$\dot{H} + Mn(III) \xrightarrow[\text{fast}]{k_6} Mn(II) + H^+$$

The mechanism given above suggests that the rate expression for the reaction should be of the form

$$-\left(\frac{dc}{dt}\right) = k_1 \, [HCHO] \, [Mn(III)] \qquad \ldots(3.7)$$

It has been experiment ly verified independently that the rate of oxidation of HCOOH is nearly 100 times greater than that of HCHO by Mn(III). As such we should have $k_3 > k_1$ so that formic acid is consumed as soon as it is formed by oxidation of HCHO. In the present study, formic acid was not detected during the reaction and CO_2 was the only final product of the reaction. This also shows that $k_3 > k_1$. The above mechanism suggested by us required that the mole ratio of oxidant : substrate should be 3:1. However, this could not be confirmed experimently as Mn(III) is the absorbing species and could not be used in large excess over formaldehyde. The mechanism suggested above is in accordence with our observations namely,

(1) Order with respect to [HCHO] and [Mn(III)] is one.

(2) The reaction rate is independent of $[H_2SO_4]$ i.e. $[H^+]$ and [Mn(II)].

(3) End product of the reaction is CO_2 and not formic acid as has been suggested for many other oxidation reactions of HCHO.

(4) Since the rate determining step involves an ion and a neutral molecule, it should not exhibit any ionic strength effect as is observed in the present study.

(5) The reaction proceeds via free radical formation as it is observed in the present study.

The values of Ea and ΔH^{*} obtained by us are 20.00 K cal/mole and 19.740 K cal/mole respectively. These values are slightly higher than the values of Ea and ΔH^{*} (15.2 K cal/mole and 14.5 K cal/mole) reported by Ram Sanehi, Agrawal and Mushran[55] for the oxidation of formaldehyde by Chloramine-T, in alkaline medium. This difference may be probably due to the fact that Mn(III) exists as a complex in strong sulphuric acid medium.[4]