CHAPTER - III

SEC-II KINETICS OF OXIDATION OF m-TOLUIDINE

CHAPTER - III

SECTION - II

3.2   KINETICS OF OXIDATION OF m-TOLUIDINE :

Preliminary experiments were performed in order to
decide the suitable temperature and concentrations range of
the reactants. It was observed that the reaction proceeds
with measurable velocity at $35^{\circ}C$ and at concentration of
m-Toluidine of $2.5 \times 10^{-2}M$ and that of potassium bromate of
2.5×10^{-3} M and that of sulphuric acid 1.25 M. The kinetic
data are recorded in Table 3.2.1 given below :

TABLE 3.2.1

$[m-Toluidine] = 2.5 \times 10^{-2}M$ $[H_2SO_4] = 1.25$ M

$[KBrO_3] = 2.5 \times 10^{-3}M$ Temp $= 35^{\circ}C$ $[Na_2S_2O_3 \; 5H_2O]=2 \times 10^{-3}M$

Time (min)	Vol. of $Na_2S_2O_3$ (ml)	$k \times 10^2 min^{-1}$
0	38.60	-
5	35.80	1.5063
10	33.10	1.5374
15	30.80	1.5051
20	28.10	1.5876
25	25.85	1.6040
30	24.00	1.5842
35	21.80	1.6327
40	20.65	1.5641
45	19.30	1.5406
50	17.20	1.6197
55	16.00	1.6014
60	14.95	1.5811
mean $k \times 10^2 min^{-1}$		1.5720

An examination of the above data closely shows that pseudofirst order specific rate is almost constant. In this experiment the m-Toluidine concentration is in excess over that of potassium bromate concentration.

3.2.1 EFFECT OF VARIATION OF POTASSIUM BROMATE CONCENTRATION

In order to investigate the effect of concentration of potassium bromate on the reaction, kinetic runs were performed in which concentration of the bromate was varied where as that of m-Toluidine and that of sulphuric acid was kept constant. Using these experimental data the value of k was determined. Table 3.2.2 embodies the results of these kinetic runs and for the sake of comparison, the data of the Table 3.2.1 has also been incorporated in it. The data have been represented in Fig 3.2.1. The values of first order rate constant (viz k) have been evaluated from the initial slope of the curves, shown in Fig 3.2.1 as well as calculated at different times by integration method, which are in good agreement with each other.

A perusal of the data (Table 3.2.2) shows that when the m-Toluidine concentration is in excess, the pseudofirst order rate constant (k) calculated in each case is almost constant. Hence the rate of disappearance of bromate obeys the first order kinetics.

TABLE 3.2.2

Variation of Potassium Bromate Concentration

$[\text{m-Toluidine}] = 2.5 \times 10^{-2} \text{M}$ Temp $= 35^{\circ}\text{C}$

$[\text{H}_2\text{SO}_4] = 1.25 \text{ M}$ $(\text{Na}_2\text{S}_2\text{O}_3 \, 5\text{H}_2\text{O}) = 2 \times 10^{-3}\text{M}$

$[\text{KBrO}_3] \times 10^3 \text{M}$	0.625	1.250	1.875	2.50	3.125
Time(min)	Vol.(in ml) of $\text{Na}_2\text{S}_2\text{O}_3 \, 5\text{H}_2\text{O}$				
0	10.50	19.80	30.40	36.60	49.80
5	9.70	18.40	28.00	35.80	45.90
10	8.90	17.20	25.80	33.10	42.30
15	8.30	15.60	23.80	30.80	39.10
20	7.70	14.70	22.00	28.10	36.10
25	7.10	13.30	20.60	25.85	33.40
30	6.50	12.20	18.70	24.00	30.80
35	6.00	11.50	17.60	21.80	28.70
40	5.60	10.80	16.10	20.65	26.40
45	5.30	10.30	15.20	19.30	23.90
50	4.80	9.80	14.10	17.20	22.80
55	4.40	8.60	12.80	16.00	20.40
60	4.10	8.00	11.80	14.95	20.10
Graphically $k \times 10^2 \text{min}^{-1}$	1.5772	1.5228	1.6031	1.6187	1.5845
Mean $k \times 10^2 \text{min}^{-1}$	1.5772	1.5095	1.5902	1.5720	1.6002

To confirm the order of reaction with respect to bromate, the values of $(-\frac{dc_o}{dt})$ were determined by plotting the volume of $Na_2S_2O_3$ [equivalent to bromote] against time for different initial concentration of oxidant. These values are tabulated in the Table 3.2.3. The order of reaction with respect to bromate has been determined from the plot of log $(-dc_o/dt)$ Vs log C_o (Fig 3.2.2.) which comes out to be 1.05. i.e. one. The values of $(-dc_o/dt)$ and concentration (potassium bromate) i.e. C_o are substituted in the Van't Hoff[60] equation, and then the order of reaction was calculated, thereby have been recorded in Table 3.2.4. This confirms the first order behaviour of the reaction with respect to bromate.

TABLE 3.2.3.

$[KBrO_3]_o \times 10^3$ M	$(-dc_o/dt) \times 10^4$	$\log[KBrO_3]_o$	$\log(-dc_o/dt)$
0.625	0.560	- 3.2041	- 4.2518
1.250	1.114	- 2.9030	- 3.9531
1.875	1.80	- 2.7269	- 3.7447
2.50	2.411	- 2.6020	- 3.6178
3.125	3.052	- 2.5051	- 3.5154

TABLE 3.2.4

Order with respect to Potassium Bromate

$[KBrO_3]_o \times 10^3 M$	$(-dc_o/dt) \times 10^4$	Order of reaction 'n'
0.625	0.560	
1.250	1.114	0.992
1.250	1.114	
1.875	1.80	1.18
1.875	1.80	
2.500	2.411	1.01
2.500	2.411	
3.125	3.052	1.05

3.2.2 EFFECT OF VARIATION OF m-TOLUIDINE CONCENTRATION :

In order to investigate the effect of m-Toluidine concentration on the rate of oxidation of m-Toluidine, the Toluidine concentration was varied from 0.625×10^{-2} to 3.125×10^{-2} M, keeping the concentration of $KBrO_3$ and that of sulphuric acid constant. The results of these kinetic runs are recorded in Table 3.2.5 and depicted graphically in Fig 3.2.3.

The results contained in Table 3.2.5 show that the first order rate constant increases with increase in Toluidine concentration. The plots of log C against time (Fig 3.2.3) were found to be linear. The second order rate constant,

$$k_2 = \frac{k_1}{[\text{Toluidine}]_o}$$

where k_2 = secondorder rate constant.& k_1= first order
rate oonstant.

was found to be nearly constant. (Table 3.2.6), indicating
the first order dependence of the rate on Toluidine
concentration.

TABLE 3.2.5

Variation of m-Toluidine Corcentration

$[\text{KBrO}_3] = 2.5 \times 10^{-3}\text{M}$ Temp = 35°C

$[\text{H}_2\text{SO}_4] = 1.25$ M $(\text{Na}_2\text{S}_2\text{O}_3 \quad 5\text{H}_2\text{O}) = 2.0 \times 10^{-3}$ M

$[\text{m-Toluidine}] \times 10^2$M	0.625	1.250	1.875	2.5	3.125
Time (min)	Vol (in ml) of $\text{Na}_2\text{S}_2\text{O}_3$				
0	38.60	38.80	38.40	38.60	38.50
5	38.00	37.20	36.15	35.80	34.50
10	37.40	35.90	33.80	33.10	30.90
15	36.80	34.50	31.85	30.80	27.40
20	35.90	33.00	29.95	28.10	24.35
25	35.40	30.00	28.10	25.85	21.75
30	34.80	29.10	25.95	24.00	20.35
35	33.90	27.70	24.70	21.80	18.75
40	33.30	26.70	23.60	20.65	17.00
45	32.50	25.60	22.00	19.30	15.20
50	31.20	24.70	20.75	17.20	14.00
55	30.50	23.50	19.80	16.00	12.85
60	29.70	22.60	18.10	14.95	11.70
Graphically $k \times 10^2$ min^{-1}	0.3798	0.9167	1.2592	1.6041	2.0327
Mean $k \times 10^2$min^{-1}	0.3668	0.8915	1.2443	1.5720	2.1273

TABLE 3.2.6

$[m\text{-Toluidine}] \times 10^2 M$	$k_1 \times 10^2 min^{-1}$	$k_2 min^{-1}.mole^{-1}$
0.625	0.3668	0.5868
1.250	0.8915	0.7132
1.875	1.2443	0.6636
2.50	1.5720	0.6288
3.125	2.1273	0.6807

The order with respect to Toluidine was determined by Van't Hoff[60] differential method. The volume of $Na_2S_2O_3$ [equivalent to KBr O_3] was plotted against time for different initial concentration of Toluidine. From the curves, the value of $(-\frac{dc_o}{dt})$, the initial rate in each case was determined from the initial slope as given in Table 3.2.7. The value of $(-\frac{dc_o}{dt})$ and conc.(Toluidine) i.e. C_o are substituted in the Van't Hoff equation i.e.

$$n = \frac{\log\left(-\frac{dc_o}{dt_1}\right) - \log\left(-\frac{dc_o}{dt_2}\right)}{\log(Co)_1 - \log(Co)_2}$$

and the order of reaction was calculated. The values of $(-\frac{dc_o}{dt})$ for different initial concentration of Toluidine and the values of 'n' calculated, there by have been recorded in Table 3.2.8.

TABLE 3.2.7

$[\text{m-Toluidine}] \times 10^2 M$	$(-\frac{dc_o}{dt}) \times 10^4$	$\log C_o$	$\log(-\frac{dc_o}{dt})$
0.625	0.660	− 2.2041	− 4.1804
1.250	1.300	− 1.9030	− 3.8860
1.875	2.000	− 1.7269	− 3.6989
2.50	2.660	− 1.6020	− 3.5751
3.125	3.390	− 1.5051	− 3.4698

TABLE 3.2.8

Order with Respect to m-Toluidine

$[\text{m-Toluidine}]_o \times 10^2 M$	$(-\frac{dc_o}{dt}) \times 10^4$	order of reaction 'n'
0.625	0.66	0.97
1.250	1.30	
1.250	1.30	1.06
1.875	2.00	
1.875	2.00	0.99
2.50	2.66	
2.50	2.66	1.08
3.125	3.39	

In order to confirm the order of reaction with respect to m-Toluidine, from the plot of $\log(-dc_0/dt)$ Vs $\log C_0$ [represented in Fig 3.2.4], the value of the order w.r.t. m-Toluidine has been evaluated which comes out to be one. This confirms the first order behaviour of the reaction w.r.t. m-Toluidine.

3.2.3 EFFECT OF VARIATION OF SULPHURIC ACID CONCENTRATION:

The reaction was studied in strong acidic medium. In order to study the effect of acid concentration on the rate of oxidation of m-Toluidine, the concentration of sulphuric acid was varied from 1.0 M to 2.0 M, keeping the concentration of other reactant constant. The results of these kinetic runs are recorded in Table 3.2.9. A plot of log C Vs time was a straight line [Fig. 3.2.5]. First order rate constants obtained by calculation and graphically are included in Table 3.2.9. It is seen that these values of k are not constant but increase with concentration of sulphuric acid.

The order with respect to sulphuric acid was determined by Van't Hoff[60] differential method. The volume of $Na_2S_2O_3$ [equivalent to bromate] was plotted

against time for different initial concentration of acid.
From these curves, the value of $(-dc_o/dt)$ in each case
was determined from the initial slope, which indicates
value of initial rate have been given in the Table 3.2.10.
The values of $(-dc_o/dt)$ and concentration (H_2SO_4) i.e. C_o
are substituted in the Van't Hoff equation and then the
order of reaction was calculated. The values of 'n'
calculated there by have been recorded in Table 3.2.11.

In order to confirm the order of reaction w.r.t.
acid , from the plot of log $(-dc_o/dt)$ Vs log C_o, where
C_o is the initial concentration of acid [represented in
Fig 3.2.6], the value of the order has been evaluated which
comes out to be 1.25. This confirms the first order
behaviour of the reaction with respect to sulphuric acid.

TABLE 3.2.9

Variation of Sulphuric Acid Concentration

$[KBrO_3] = 2.5 \times 10^{-3}M$ Temp $= 35^{\circ}C$

$[m\text{-Toluidine}] = 2.5 \times 10^{-2}M$ $[Na_2S_2O_3 . 5H_2O] = 2.0 \times 10^{-3}M$

$[H_2SO_4]$ M	1.00	1.25	1.50	1.75	2.00
Time (min)	Vol. (in ml) of $Na_2S_2O_3.5H_2O$				
0	38.50	38.60	38.50	38.70	38.40
5	36.20	35.80	34.60	34.00	33.00
10	34.30	33.10	31.30	29.60	28.10
15	31.80	30.80	28.20	26.30	23.90
20	30.20	28.10	24.90	23.10	20.90
25	28.10	25.85	23.30	20.00	17.80
30	26.40	24.00	20.90	18.20	14.90
35	24.50	21.80	18.70	15.60	12.80
40	23.50	20.65	17.40	13.80	11.50
45	22.20	19.30	15.70	12.90	10.70
50	20.90	17.20	14.50	11.70	9.20
55	19.60	16.00	12.80	9.90	8.10
60	18.70	14.95	12.10	9.30	7.00
Mean $k \times 10^2 min^{-1}$	1.2330	1.5720	2.0363	2.5373	3.0033
Graphically $k \times 10^{+2} min^{-1}$	1.2229	1.5798	1.9574	2.4495	2.9914

TABLE 3.2.10

$[H_2SO_4]_o$ M	$(-dc_o/dt) \times 10^4$	log C_o	$\log(-dc_o/dt)$
1.0	1.792	0.0000	− 3.7466
1.25	2.368	0.0969	− 3.6256
1.50	2.992	0.1761	− 3.5240
1.75	3.6228	0.2430	− 3.4409
2.00	4.1600	0.3010	− 3.3809

TABLE : 3.2.11

Order with respect to sulphuric acid.

$[H_2SO_4]_o$ M	$(-dc_o/dt) \times 10^4$	Order of reaction 'n'
1.00	1.792	1.24
1.25	2.368	
1.25	2.368	1.28
1.50	2.992	
1.50	2.992	1.23
1.75	3.6228	
1.75	3.6228	1.03
2.00	4.1600	

3.2.4   EFFECT OF ADDED SALTS ON REACTION RATE :

In order to study the effect of added salts on the rate of oxidation of m-Toluidine, the concentration of salts was varied from 2.5×10^{-3}M to 12.50×10^{-3}M by keeping the concentration of other reactants constant. The results of these kinetic runs are recorded in Table 3.2.12. It is observed from this table that the effect of salt is negligible. The salts used were potassium sulphate, zinc sulphate and cadmium sulphate.

TABLE 3.2.12

$[KBrO_3] = 2.5 \times 10^{-3}$M $\qquad [H_2SO_4] = 1.25$ M

$[m\text{-Toluidine}] = 2.5 \times 10^{-2}$M $\qquad$ Temp $= 35^{\circ}$C

$[Na_2S_2O_3.5H\ O] = 2.00 \times 10^{-3}$M

$[K_2SO_4] \times 10^3$M	2.50	5.00	7.50	10.00	12.50
$k \times 10^2 min^{-1}$	1.5760	1.5411	1.5371	1.5339	1.5383
$[ZnSO_4] \times 10^3$M	2.50	5.00	7.50	10.00	12.50
$k \times 10^2 min^{-1}$	1.6502	1.6486	1.6449	1.6524	1.6640
$[CdSO_4] \times 10^3$M	2.50	5.00	7.50	10.00	12.50
$k \times 10^2 min^{-1}$	1.5761	1.5698	1.4425	1.5591	1.5421

3.2.5 EFFECT OF TEMPERATURE ON REACTION RATE AND CALCULATION OF THERMODYNAMIC PARAMETERS :

In order to determine the temperature coefficient, Energy of activation (Ea), Enthalpy of activation ($\Delta H^{\neq}$), frequency factor (A), Free energy of activation ($\Delta G^{\neq}$) and Entropy of activation ($\Delta S^{\neq}$), the reaction was studied at five different temperatures ranging from $25^{\circ}C$ to $45^{\circ}C$. The results of these kinetic runs have been tabulated in Table 3.2.13 and represented graphically in Fig 3.2.7.

It is seen from the Table 3.2.13 that the specific rate has approximately doubled (1.919) for $10^{\circ}C$ rise in temperature. A plot of log k Vs 1/T as shown in Fig. 3.2.8 (Table 3.2.14) is found to be linear indicating that the reaction obeys, Arrhenius relationship. The value of energy of activation (Ea) evaluated from slope of this curve comes out to be 12.202 K. cal mole^{-1}. The Arrhenius equation has been used directly to calculate energy of activation, which comes out to be 12.529 K.cal. mole^{-1} On the basis of this graphical value, the frequency factor(A) free energy of activation($\Delta G^{\neq}$) and entropy of activation ($\Delta S^{\neq}$) have been calculated using following equations.

Arrhenius[61] equation,

$$ kr = A. \ e^{-Ea/RT} \qquad ...(i) $$

$$ \text{or log } kr = \log A - \frac{Ea}{2.303 x RT} \qquad ..(ii) $$

$$ \log k_1 - \log k_2 = - \frac{Ea}{2.303 \times R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right] \qquad .(iii) $$

The values of log kr/T have been plotted against 1/T, which is shown in Fig. 3.2.9. The plot was linear and from the slope of the straight line the enthalpy change for the formation of activated complex ($\Delta H^{\neq}$) has been calculated. The value of the $\Delta H^{\neq}$ evaluated from the slope of this straight line comes out to be 11.440 K.cal mole^{-1}

The following equations were used to calculate $\Delta G^{\neq}$ and $\Delta S^{\neq}$

$$\log \frac{kr}{kT/h} = \frac{-\Delta H^{\neq}}{2.303 \ RT} + \frac{\Delta S^{\neq}}{2.303 \ R} \qquad \ldots(iv)$$

$$\Delta S^{\neq} = 2.303 \ R \ \log \frac{Ah}{kT} \qquad \ldots(v)$$

$$\text{and} \ \Delta G^{\neq} = \Delta H^{\neq} - T \ \Delta S^{\neq} \qquad \ldots(vi)$$

In above equations 'kr' is the specific rate constant. 'k' is the Boltzmann constant and h is the planck's constant. Other symbols carry their usual meanings.

The various energy parameters, obtained, have been recorded in Table 3.2.15.

From these values of Ea and A the rate constant kr is related to temperature T by the relation

$$kr = 1.2474 \times 10^{5} \ e^{-12202/RT}$$

TABLE 3.2.13

Effect of Temperature

$[KBrO_3]$ = 2.5 x 10^{-3}M $\qquad$ $[H_2SO_4]$ = 1.25 M

$[m-Toluidine]$ = 2.5 x 10^{-2}M $\quad$ $[Na_2S_2O_3.5H_2O]$ = 2.0 x 10^{-3}M

Temp (T)	25°C	30°C	35°C	40°C	45°C
Time (min)	Vol. (in ml) of $Na_2S_2O_3.5H_2O$				
0	38.40	38.20	38.60	38.30	38.50
5	36.80	36.10	35.80	34.20	33.00
10	35.15	34.00	33.10	30.40	27.90
15	33.55	32.15	30.80	26.85	24.15
20	32.30	30.30	28.10	23.90	20.50
25	30.80	28.60	25.85	21.05	17.70
30	29.75	26.85	24.00	18.75	15.30
35	28.50	25.25	21.80	16.65	13.45
40	27.70	24.15	20.65	15.50	10.75
45	26.25	22.65	19.30	13.45	9.40
50	25.40	21.85	17.20	12.75	8.60
55	24.45	20.05	16.00	12.00	7.65
60	23.30	19.65	14.95	9.70	7.20
Mean $k \times 10^2 min^{-1}$	0.8522	1.1519	1.5720	2.3031	3.0670
Graphically $k \times 10^2 min^{-1}$	0.8490	1.1810	1.6172	2.3358	3.0358

TABLE 3.2.14

$T^{o}K$	$1/T \times 10^3$	$kr \times 10^2 min^{-1}$	$\log kr$	$\log kr/T$
298	3.3557	0.8490	− 2.0710	− 4.5453
303	3.3003	1.1810	− 1.9277	− 4.4091
308	3.2467	1.6172	− 1.7912	− 4.2797
313	3.1948	2.3358	− 1.6315	− 4.1271
318	3.1446	3.058	− 1.5177	− 4.0201

FIG: 3.2.1 — EFFECT OF $KBrO_3$ CONCENTRATION

$$[m-T]_0 = 2.5 \times 10^{-2} M$$

$$[H_2SO_4]_0 = 1.25 M$$

$$TEMP = 35^{\circ}C$$

$[KBrO_3]_0$ — I = 0.625 $\times 10^{-3}$ M

II = 1.25 $\times 10^{-3}$ M

III = 1.875 $\times 10^{-3}$ M

IV = 2.50 $\times 10^{-3}$ M

V = 3.125 $\times 10^{-3}$ M

Log C

TIME (MIN)

FIG: 32.2 ——— $Log\left[-\dfrac{dc}{dt}\right]_0$ Vs $Log\, Co$

$n = 1.05$

x-axis: $Log\, Co$ (values: -3.2, -3.0, -2.8, -2.6, -2.4)

y-axis: $Log\left[-\dfrac{dc}{dt}\right]_0$ (values: -3.4, -3.6, -3.8, -4.0, -4.2)
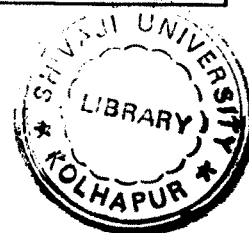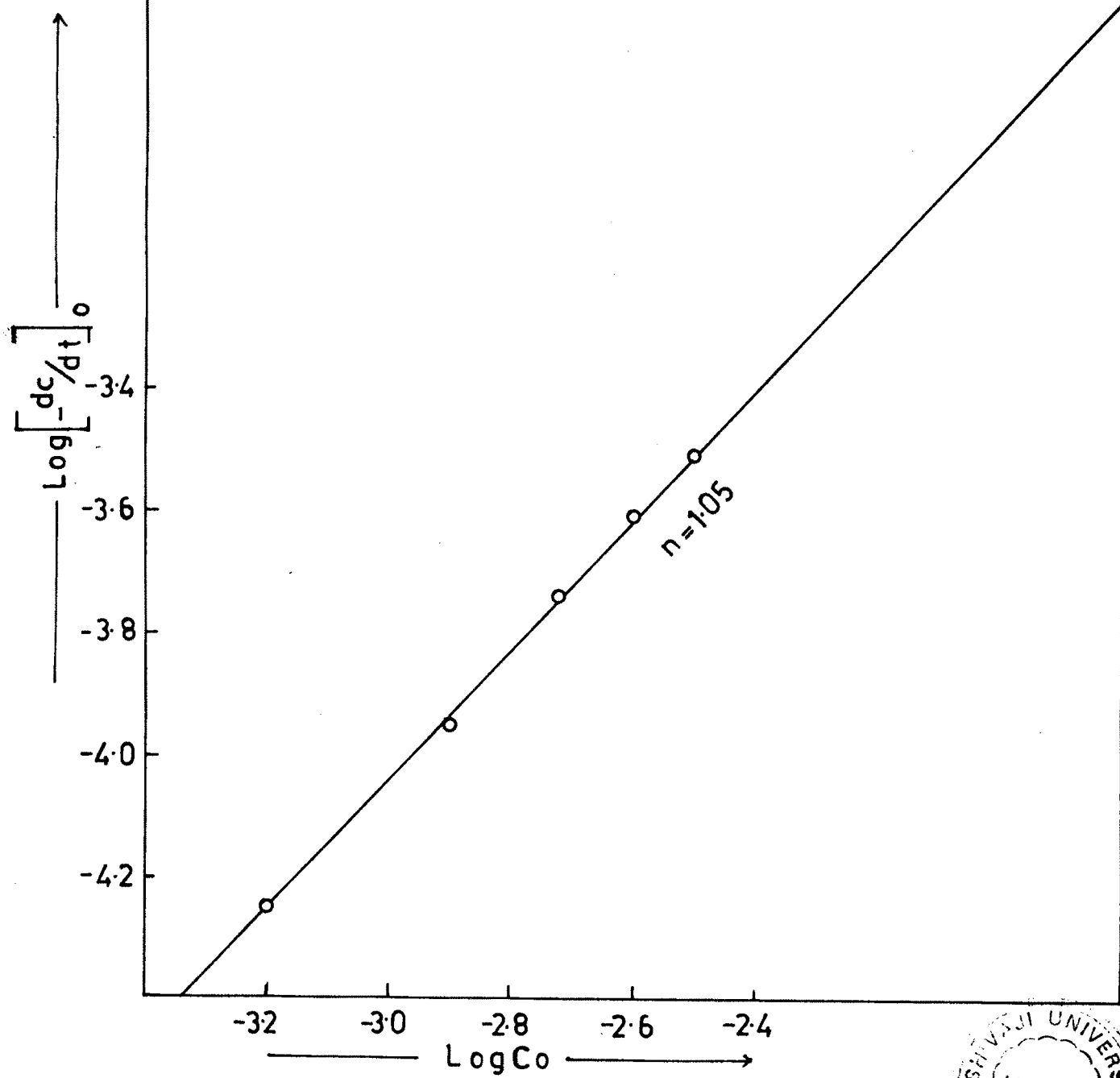
FIG: 3·2·3 ←——— EFFECT OF m-T CONCENTRATION

$[KBrO_3]_0 = 2.5 \times 10^{-3} M$

$[H_2SO_4]_0 = 1.25 M$

TEMP = 35°C

$[m\text{-}T]_0 \rightarrow$ I = 0.625 × 10^{-2} M

II = 1.250 × 10^{-2} M

III = 1.875 × 10^{-2} M

IV = 2.50 × 10^{-2} M

V = 3.125 × 10^{-2} M
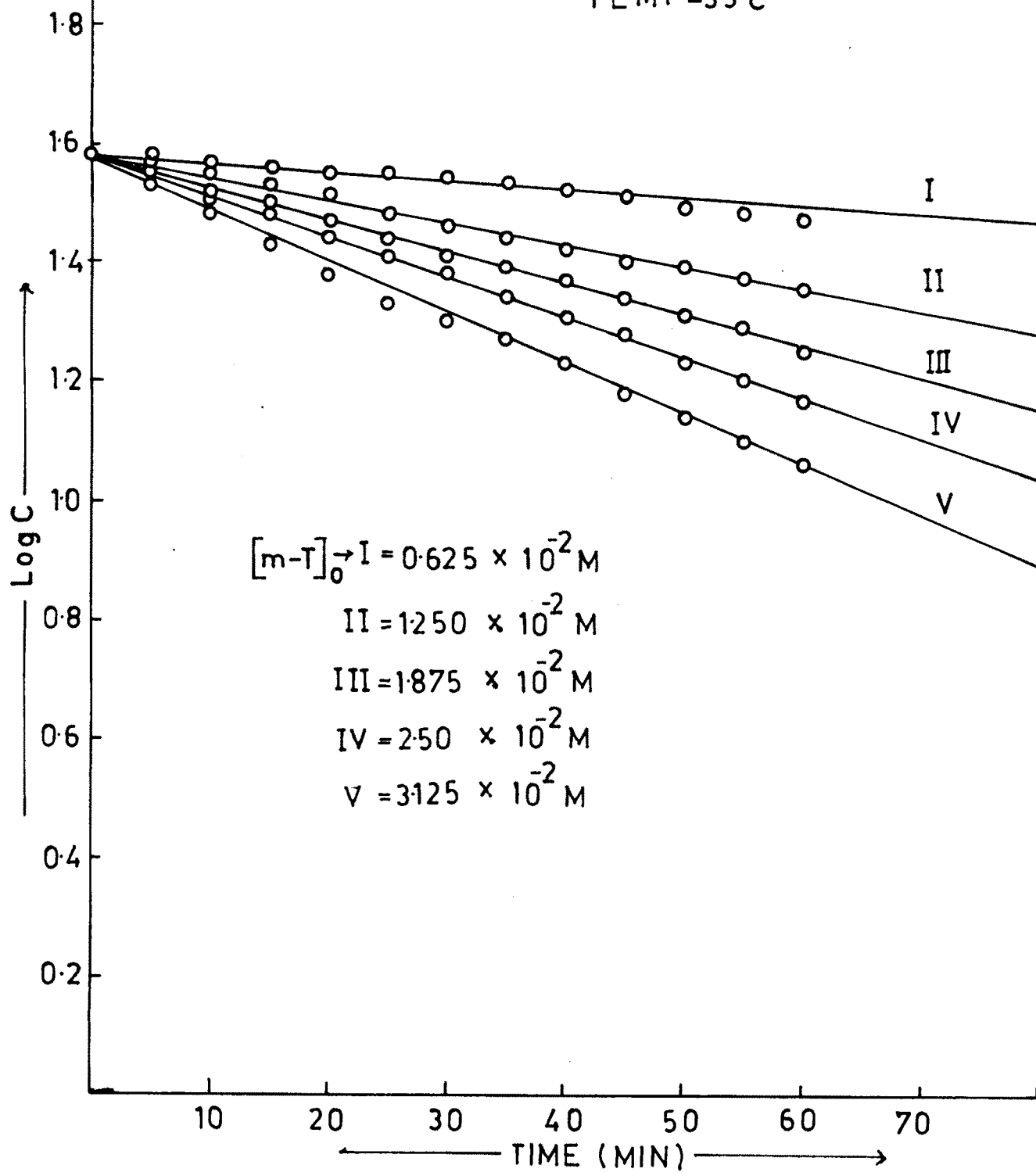
FIG: 3.2.4 —— $Log\left[-\dfrac{dc}{dt}\right]_0$ Vs $LogC_0$
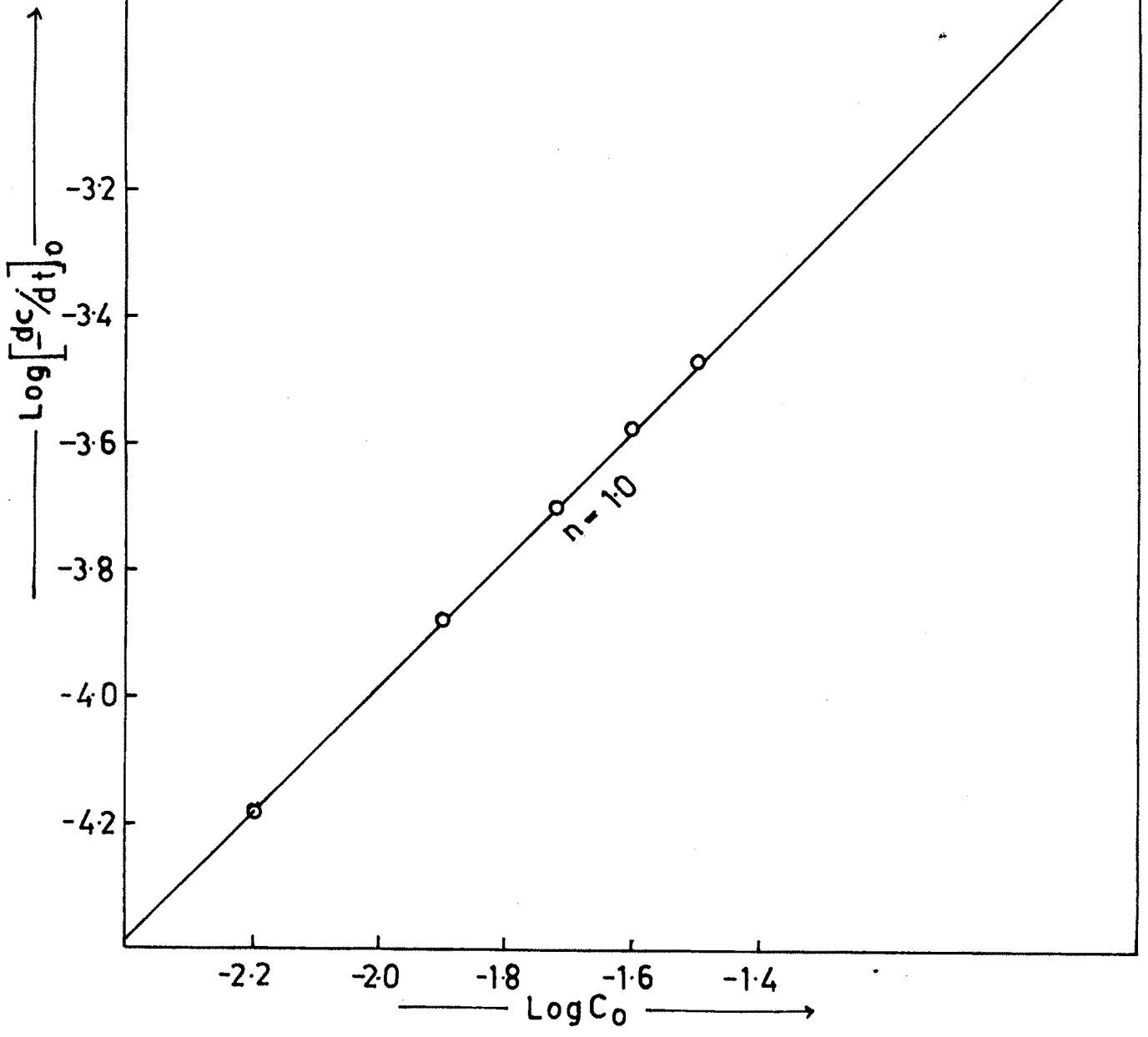
FIG: 3.2.5 — EFFECT OF H_2SO_4 CONCENTRATION

$[m-T]_0 = 2.5 \times 10^{-2}$ M

$[KBrO_3]_0 = 2.5 \times 10^{-3}$ M

TEMP = 35°C

$[H_2SO_4]_0 = $ I $= 1.00$ M

II $= 1.25$ M

III $= 1.50$ M

IV $= 1.75$ M

V $= 2.00$ M

Log C

TIME (MIN)
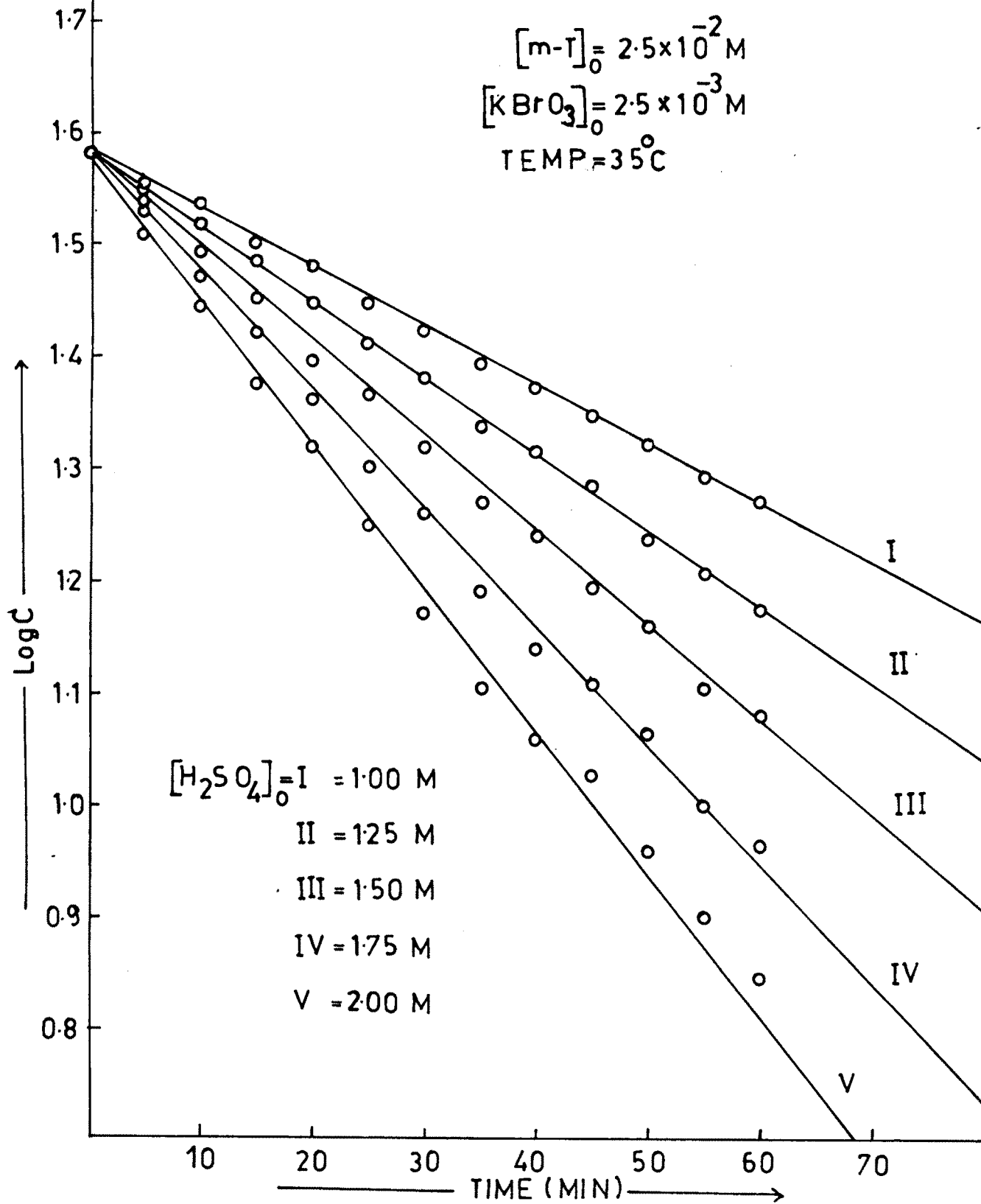
FIG:3·2·6 ——— $Log\left[-\dfrac{dc}{dt}\right]_0$ Vs $Log\,C_0$

$Log\left[-\dfrac{dc}{dt}\right]_0$

$n = 1·26$

$Log\,C_0$
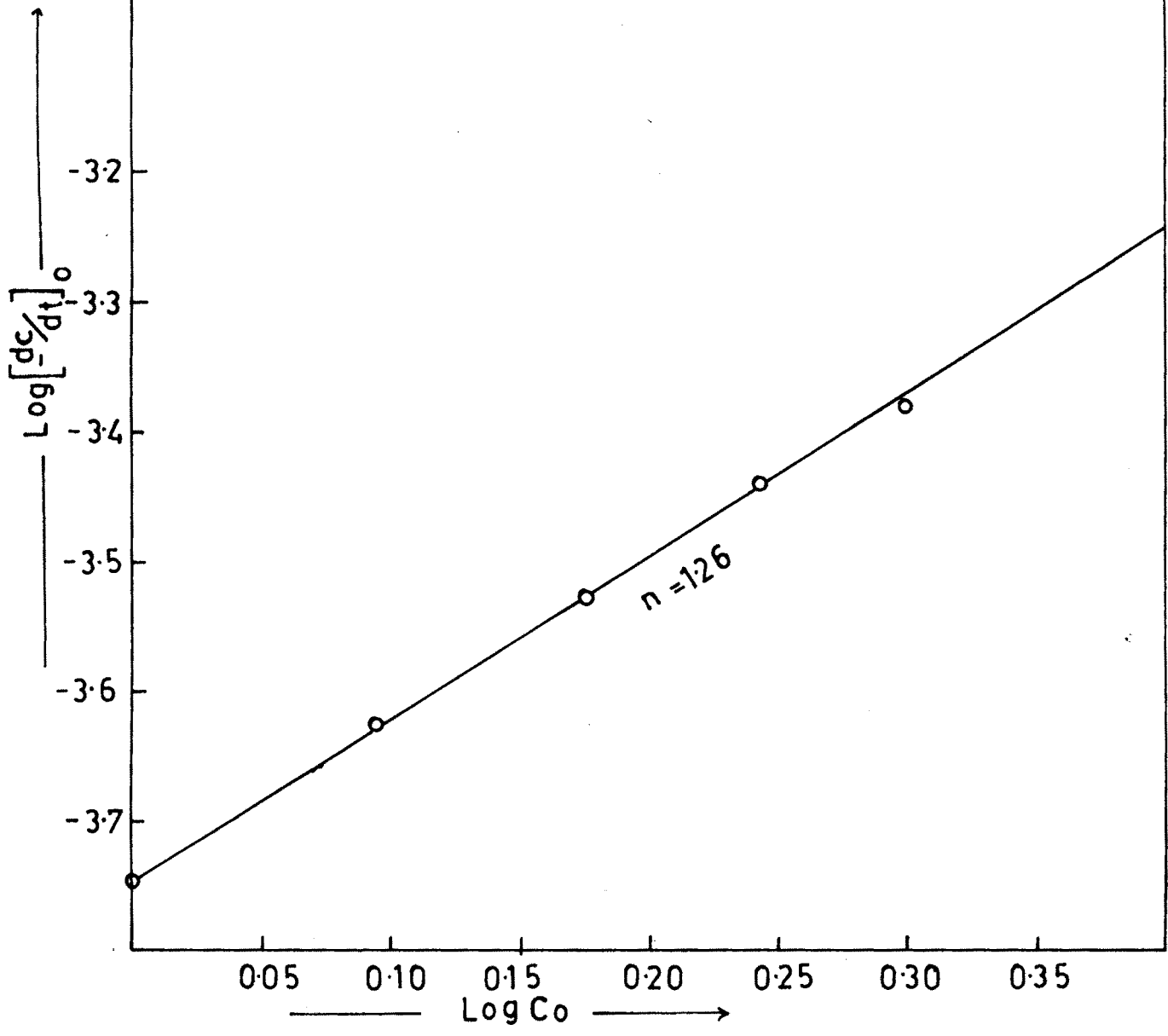
FIG: 32.7 —— EFFECT OF TEMPERATURE

$[m\text{-}T]_0 = 2.5 \times 10^{-2} M$

$[KBrO_3]_0 = 2.5 \times 10^{-3} M$

$[H_2SO_4]_0 = 1.25 M$

TEMP — I = $25^{\circ}C$

II = $30^{\circ}C$

III = $35^{\circ}C$

IV = $40^{\circ}C$

V = $45^{\circ}C$

Log C

TIME (MIN)
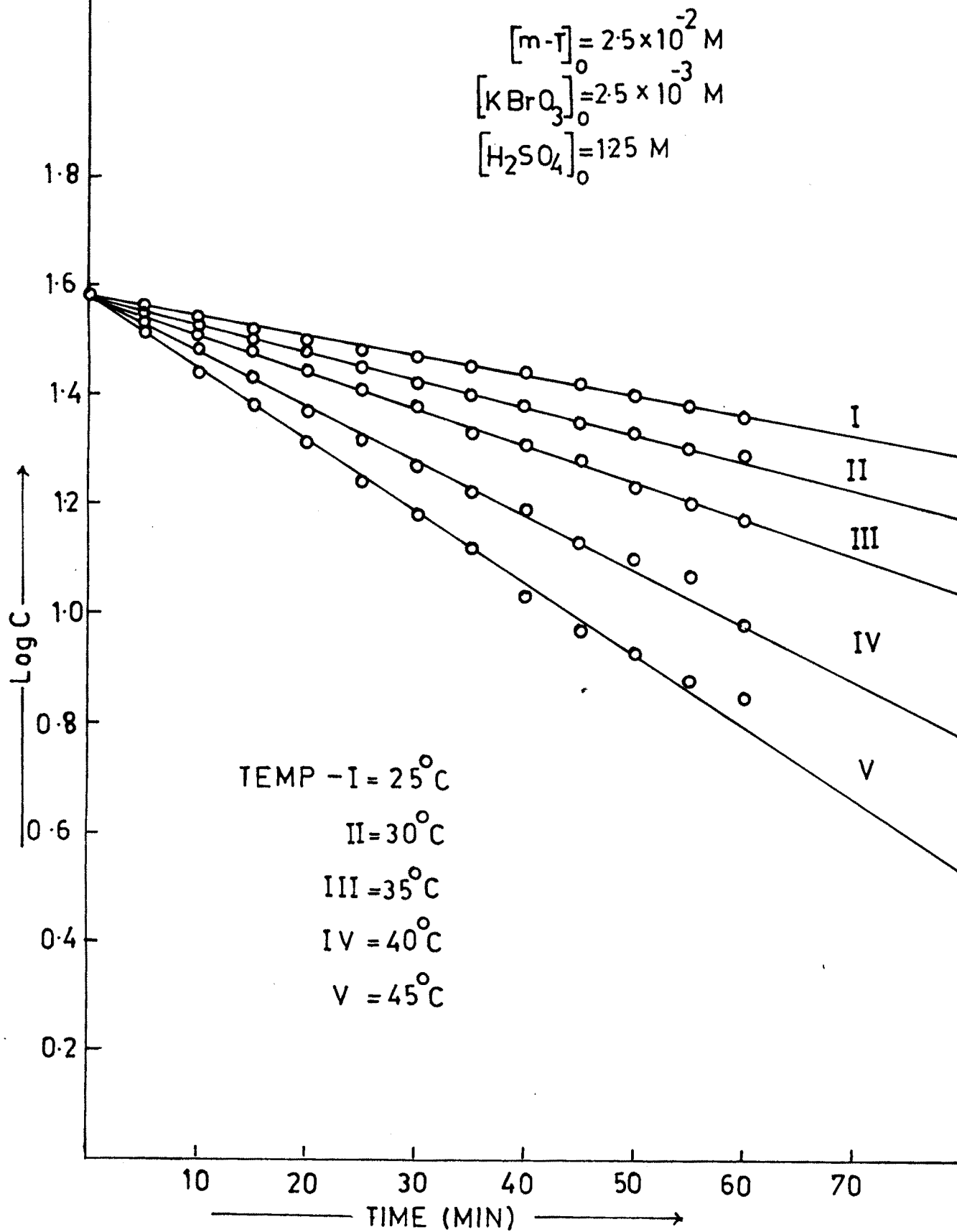
FIG: 3·2·8 ——— Log kr Vs $\dfrac{1}{T}$
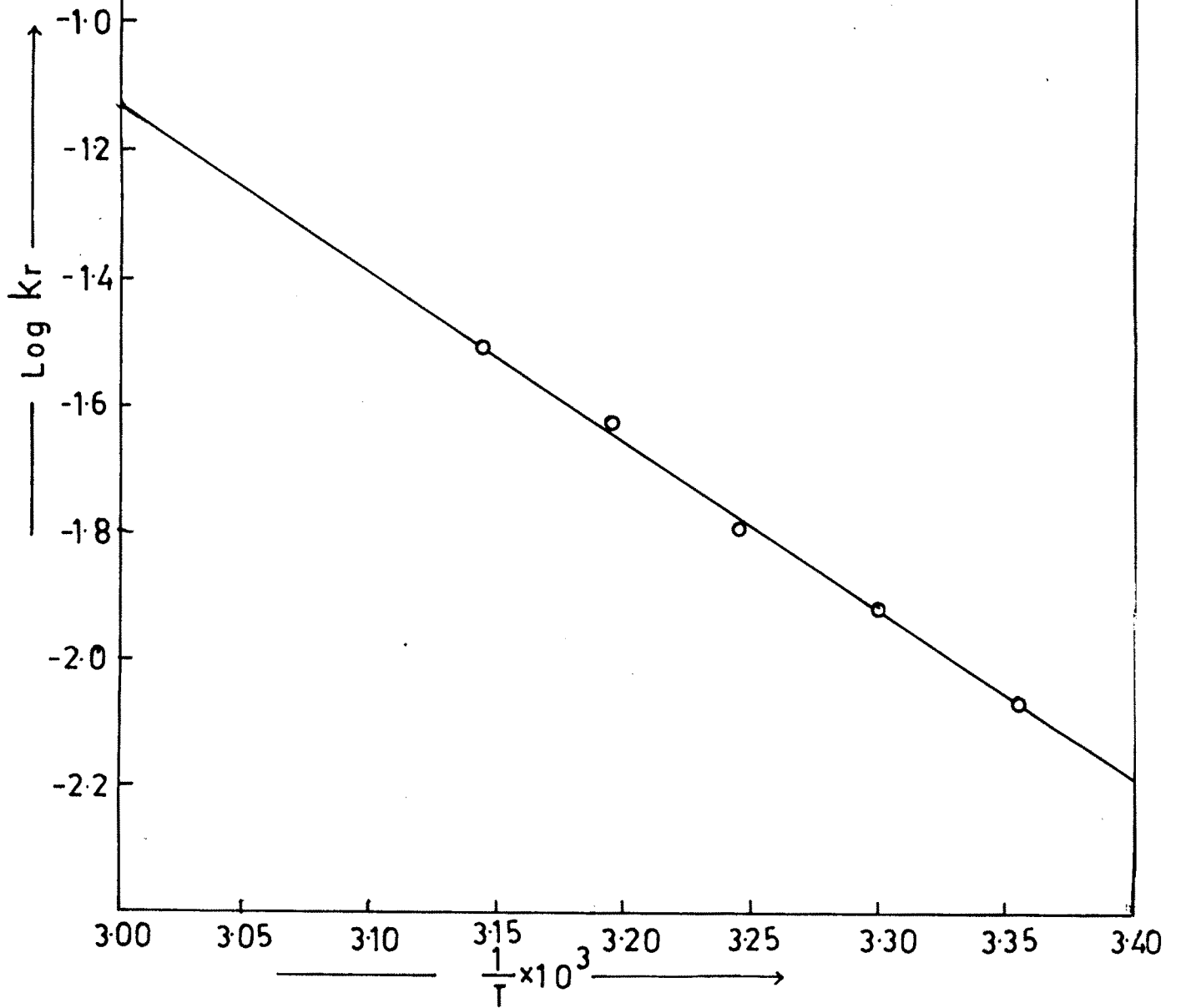
FIG: 3·2·9 —— Log $\frac{k_r}{T}$ Vs $\frac{1}{T}$
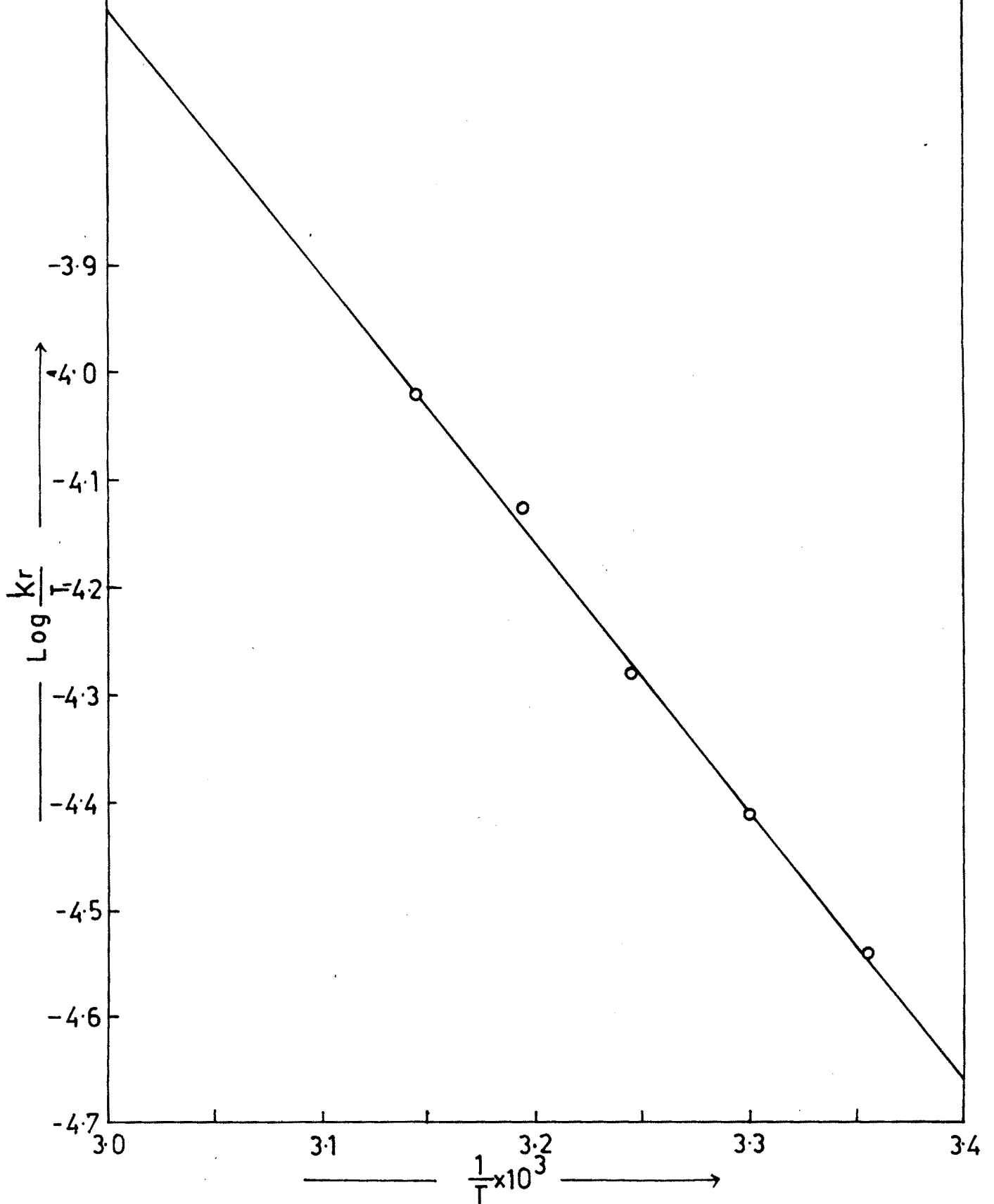
TABLE 3.2.15

Thermodynamic Parameters

Temp T°K	$kr \times 10^2$ min⁻¹	Temp coefficient	Ea K.cal mole⁻¹ Graph	Ea K.cal mole⁻¹ Calculation	$\Delta H^{\neq}$ K.cal mole⁻¹	$A \times 10^{-5}$ Sec⁻¹	ΔS^{*} e.u.	$\Delta G^{\neq}$ K.cal mole⁻¹
298	0.849					1.2551	−35.21	21.93
303	1.1810	1.904		12.506		1.2427	−35.26	22.12
308	1.6172	1.977	12.202	12.258	11.440	1.2247	−35.32	22.31
313	2.3358	1.877		12.854		1.2864	−35.25	22.47
318	3.0358					1.2282	−35.38	22.69
Mean		1.919	12.202	12.539	11.440	1.2474	−35.28	22.30

3.2.6   STOICHIOMETRY :

To determine the mole ratio of m-Toluidine to potassium bromate, the reaction mixture was taken to be 2.5×10^{-2}M m-Toluidine and 5.0×10^{-2}M potassium bromate. The reaction was followed at 35°C and sharp break in volume of $Na_2S_2O_3$ Vs time plot was taken for calculation of mole ratio.   The mole ratio was found to be 1:1 for m-Toluidine to potassium bromate.

3.2.7   FREE RADICAL DETECTION AND END PRODUCT ANALYSIS:

The reaction did not promote polymerization of acrylonitrile[62] indicating absence of free radical when acrylonitrile (1 ml) was added to the reaction mixture(5 ml) containing both $KBrO_3$ and m-Toluidine, a precipitate was not formed.   This clearly indicates that reaction proceeds in absence of free radical formation.

The oxidation product O-Benzoquinone[31,12] was identified by TLC with the authentic sample prepared by the literature method. Evolution of ammonia[19] during the course of the reaction was also detected.

Ammonia was detected by adding Nessler's reagent in alkaline solution of reaction mixture,which has given buff coloured precipitate.