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CHAPTER - III  
SEC-III KINETICS OF OXIDATION OF  
P-TOLUIDINE

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## CHAPTER - III

## SECTION - III

3.3 KINETICS OF OXIDATION OF p-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 30°C and at concentrations of  $\text{KBrO}_3$  of  $2.5 \times 10^{-3} \text{ M}$  p-Toluidine of  $1.75 \times 10^{-2} \text{ M}$  and that of sulphuric acid of 1.25 M. The kinetic data are recorded in Table 3.3.1 given below :

TABLE 3.3.1

$[\text{p-Toluidine}] = 1.75 \times 10^{-2} \text{ M}$        $[\text{H}_2\text{SO}_4] = 1.25 \text{ M}$   
 $[\text{KBrO}_3] = 2.5 \times 10^{-3} \text{ M}$ ,    Temp = 30°C.     $[\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}] = 2.0 \times 10^{-3} \text{ M}$

Time (min)	Vol. (in ml) of $\text{Na}_2\text{S}_2\text{O}_3$	$k \times 10^2 \text{ min}^{-1}$
0	38.60	-
5	37.05	0.8196
10	35.70	0.7810
15	34.05	0.8361
20	32.90	0.7988
25	31.50	0.8130
30	29.75	0.8680
35	28.60	0.8567
40	27.25	0.8704
45	26.15	0.8653
50	25.20	0.8528
60	23.45	0.8306
70	21.50	0.8359
80	19.95	0.8313
Mean $k \times 10^2 \text{ min}^{-1}$		0.8353

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

### 3.3.1 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 p-Toluidine and sulphuric acid was kept constant. Using these experimental data the value of  $k$  was determined. Table 3.3.2 embodies the results of these kinetic runs and for the sake of comparison, the data of the Table 3.2.1 have also been incorporated in it. The data has 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 3.3.2) shows that when the p-Toluidine concentration is in excess, the pseudo first order rate constant ( $k$ ) calculated in each case is almost constant. Hence the rate of disappearance of bromate obeys the first order kinetics.

TABLE 3.3.2

Variation of Potassium Bromate Concentration.

[p-Toluidine] =  $1.75 \times 10^{-2} M$       Temp =  $30^{\circ}C$ [ $H_2SO_4$ ] = 1.25 M      [ $Na_2S_2O_3 \cdot 5H_2O$ ] =  $2.0 \times 10^{-3} M$ 

[ $KBrO_3$ ] $\times 10^3 M$	1.00	1.375	1.750	2.125	2.500
Time (min)	Vol (in ml) of $Na_2S_2O_3 \cdot 5H_2O$				
0	16.30	21.50	26.80	32.70	38.60
5	15.60	20.50	25.60	31.20	37.05
10	14.80	19.60	24.70	30.10	35.70
15	14.20	18.80	23.70	28.60	34.05
20	13.80	18.20	22.70	27.70	32.90
25	12.90	17.10	21.70	26.40	31.50
30	12.20	16.50	20.90	25.50	29.75
35	11.80	16.10	20.00	24.60	28.60
40	11.50	15.50	19.10	23.50	27.25
45	11.20	15.20	18.40	22.60	26.15
50	10.80	14.30	17.80	21.70	25.20
60	10.00	13.20	16.30	20.00	23.45
70	9.15	12.10	15.00	18.80	21.50
80	8.40	11.20	13.80	16.95	19.95
Graphically $k \times 10^2 \text{min}^{-1}$	0.8290	0.8060	0.8410	0.8290	0.8290
Mean $k \times 10^{-2} \text{min}^{-1}$	0.8783	0.8386	0.8369	0.8375	0.8353

To confirm the order of reaction w.r.t. bromate, the values of  $(-dc_0/dt)$  were determined by plotting the volume of  $\text{Na}_2\text{S}_2\text{O}_3$  [equivalent to bromate] against time for different initial concentration of oxidant. These values are tabulated in Table 3.3.3. The order of reaction with respect to bromate has been determined from the plot of  $\log(-dc_0/dt)$  Vs  $\text{Log } C_0$  (Fig 3.3.2), which comes out to be 0.90, i.e. one. The values of  $(-dc_0/dt)$  and initial concentration  $[\text{KBrO}_3]$  i.e.  $C_0$  are substituted in the Van't Hoff<sup>60</sup> equation, and then the order of reaction was calculated, thereby have been recorded in Table 3.3.4. This confirms the first order behaviour of the reaction with respect to bromate.

TABLE 3.3.3

$[\text{KBrO}_3]_0 \times 10^3 \text{M}$	$(-dc_0/dt) \times 10^4$	$\log C_0$	$\log (-dc_0/dt)$
1.00	0.5840	- 3.000	- 4.2335
1.375	0.8000	- 2.8616	- 4.0969
1.750	1.0056	- 2.7569	- 3.9975
2.125	1.1600	- 2.6726	- 3.9355
2.500	1.328	- 2.6020	- 3.8768

TABLE 3.3.4

$[\text{KBrO}_3]_0 \times 10^3 \text{M}$	$(-dc_0/dt) \times 10^4$	Order of reaction 'n'
1.000	0.5840	0.9882
1.375	0.8000	
1.375	0.800	0.9484
1.75	1.0056	
1.75	1.0056	0.7356
2.125	1.1600	
2.125	1.1600	0.8322
2.500	1.328	

### 3.3.2 EFFECT OF VARIATION OF p-TOLUIDINE CONCENTRATION :

In order to investigate the effect of p-Toluidine concentration on the rate of oxidation of p-Toluidine, the Toluidine concentration was varied from  $1.00 \times 10^{-2} M$  to  $2.500 \times 10^{-2} M$ , keeping the concentration of  $KBrO_3$  and that of sulphuric acid constant. The results of these kinetic runs are recorded in Table 3.3.5 and depicted graphically in Fig 3.3.3.

The results contained in Table 3.3.5 show that the first order rate constant increases with increase in Toluidine concentration. The plots of  $\log C$  against time (Fig. 3.3.3) were linear. The second order rate constant,

$$k_2 = \frac{k_1}{[\text{Toluidine}]_0}$$

where,  $k_2$  = second order rate constant.

$k_1$  = first order rate constant.

was found to be nearly constant, [Table 3.3.6], indicating the first order dependence of the rate on Toluidine concentration.

TABLE 3.3.5

## Variation of p-Toluidine Concentration

$$[\text{KBrO}_3] = 2.5 \times 10^{-3} \text{ M} \quad \text{Temp} = 30^\circ \text{C}$$

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

[p-Toluidine] x 10 <sup>2</sup> M	1.00	1.375	1.750	2.125	2.500
Time (min)	Vol. (in ml) of Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>				
0	38.50	38.50	38.60	38.60	38.50
5	37.90	37.35	37.05	36.75	36.50
10	37.30	35.95	35.70	35.25	34.30
15	36.35	34.65	34.05	33.30	32.80
20	35.60	33.85	32.90	31.80	30.60
25	34.45	32.75	31.50	30.20	29.30
30	33.70	32.00	29.75	28.55	27.70
35	32.90	30.90	28.60	27.05	26.55
40	31.80	29.20	27.25	25.75	25.10
45	30.95	28.80	26.15	24.40	23.50
50	30.10	27.30	25.20	23.10	22.60
60	28.55	24.85	23.45	20.85	20.40
70	27.40	23.45	21.50	18.75	17.10
80	25.85	22.00	19.95	17.00	15.60
Graphically k x 10 <sup>2</sup> min <sup>-1</sup>	0.5014	0.7100	0.8204	1.0218	1.1083
Mean k x 10 <sup>2</sup> min <sup>-1</sup>	0.4369	0.6684	0.8353	0.9990	1.0975



TABLE 3.3.6

[p-Toluidine] x 10 <sup>2</sup> M	k <sub>1</sub> x 10 <sup>2</sup> min <sup>-1</sup>	k <sub>2</sub> mole <sup>-1</sup> min <sup>-1</sup>
1.000	0.4369	0.4369
1.375	0.6684	0.4861
1.750	0.8353	0.4773
2.125	0.9990	0.4701
2.500	1.0975	0.4390

The order with respect to Toluidine was determined by Van't Hoff<sup>60</sup> differential method. The volume of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (equivalent to KBrO<sub>3</sub>) was plotted against time for different initial concentration of Toluidine. From the curves, the values of  $(-dc_0/dt)$ , the initial rate in each case was determined from the initial slope as given in Table 3.3.7. The values of  $(-dc_0/dt)$  and conc. (Toluidine) i.e. C<sub>0</sub> are substituted in the Van't Hoff equation and order of reaction was calculated. The values of  $(-dc_0/dt)$  for different initial concentration of Toluidine and the values of 'n' calculated, thereby have been recorded in Table 3.3.8.

In order to confirm the order of reaction with respect to p-Toluidine, from the plot of  $\log(-dc_0/dt)$  Vs  $\log C_0$  [represented in Fig 3.3.4], the value of the order w.r.t. p-Toluidine has been evaluated which comes out to be 1.01 i.e. one. This confirms the first order behaviour of the reaction with respect to p-Toluidine.

TABLE 3.3.7

$[p\text{-Toluidine}]_0 \times 10^2 \text{M}$	$(-dc_0/dt) \times 10^4$	$\log C_0$	$\log(-dc_0/dt)$
1.000	0.68	- 2.000	- 4.1674
1.375	0.992	- 1.8616	- 4.0034
1.750	1.2072	- 1.7569	- 3.9182
2.125	1.4600	- 1.6726	- 3.8356
2.50	1.748	- 1.6020	- 3.7574

TABLE 3.3.8

Order with respect to p-Toluidine

$[p\text{-Toluidine}]_0 \times 10^2 \text{M}$	$(-dc_0/dt) \times 10^4$	Order of reaction 'n'
1.0000	0.68	1.1858
1.375	0.992	
1.375	0.992	0.8141
1.75	1.2072	
1.75	1.2072	0.9792
2.125	1.4600	
2.125	1.4600	1.1077
2.50	1.7480	

### 3.3.3 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 p-Toluidine, the concentration of sulphuric acid was varied from 1.0 to 2.0 M, keeping the concentration of other reactant constant. The results of these kinetic runs are recorded in Table 3.3.9. A plot of  $\log C$  Vs time was a straight line (Fig 3.3.5). First order rate constant obtained by calculation and graphically are included in Table 3.3.9. 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<sup>60</sup> differential method. The volume of  $\text{Na}_2\text{S}_2\text{O}_3$  (equivalent to bromate) was plotted against time for different initial concentration of acid, from these curves, the value of  $(-dc_0/dt)$  in each case was determined from the initial slope, which indicates value of initial rate have been given in the table 3.3.10. The values of  $(-dc_0/dt)$  and conc. i.e.  $C_0$  are substituted in the Van't Hoff equation and then the order of reaction was calculated. The values of 'n' calculated thereby have been recorded in Table 3.3.11.

In order to confirm the order of reaction with respect to acid, from the plot of  $\log (-dc_0/dt)$  Vs  $\log C_0$ , where  $C_0$  is the initial concentration of acid [represented in Fig. 3.3.6], the value of the order has been evaluated which comes out to be 1.05. This confirms the first order behaviour of the reaction w.r.t. sulphuric acid.

TABLE 3.3.9

Variation of Sulphuric Acid Concentration

 $[\text{KBrO}_3] = 2.5 \times 10^{-3} \text{M}$        $[\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}] = 2 \times 10^{-3} \text{M}$ 
 $[\text{p-Toluidine}] = 1.75 \times 10^{-2} \text{M}$       Temp =  $30^\circ\text{C}$ 

$[\text{H}_2\text{SO}_4] \text{M}$	1.00	1.25	1.50	1.75	2.00
Time (min)	Vol. (in ml) of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$				
0	38.40	38.60	38.50	38.40	38.60
5	37.25	37.05	36.65	36.30	35.85
10	36.20	35.70	35.10	34.40	33.15
15	35.15	34.05	33.25	32.00	30.70
20	33.85	32.90	31.50	30.45	28.40
25	33.00	31.50	30.10	28.75	26.25
30	32.20	29.75	28.55	27.30	24.60
35	31.20	28.60	27.10	25.45	22.75
40	30.00	27.25	26.00	24.00	21.65
45	29.40	26.15	24.55	22.80	20.45
50	28.70	25.20	22.75	21.25	18.60
60	26.75	23.45	21.40	19.20	16.55
70	25.30	21.50	19.00	17.30	14.40
80	23.75	19.95	17.10	15.20	12.35
Graphically $k \times 10^2 \text{min}^{-1}$	0.6086	0.8326	1.0286	1.1666	1.4311
Mean $k \times 10^2 \text{min}^{-1}$	0.5996	0.8353	0.9930	1.1584	1.4751

TABLE 3.3.10

$[H_2SO_4]_0 M$	$(-dc_0/dt) \times 10^4$	$\log C_0$	$\log(-dc_0/dt)$
1.00	1.0616	0.0000	- 3.9749
1.25	1.3380	0.0969	- 3.8735
1.50	1.6360	0.1761	- 3.7862
1.75	1.9636	0.2430	- 3.7069
2.00	2.2252	0.3010	- 3.6526

TABLE 3.3.11

Order with respect to sulphuric acid

$[H_2SO_4]_0 M$	$(-dc_0/dt) \times 10^4$	Order of reaction 'n'
1.00	1.0616	1.0369
1.25	1.3380	
1.25	1.3380	1.1028
1.50	1.6360	
1.50	1.6360	1.1840
1.75	1.9636	
1.75	1.9636	0.9366
2.00	2.2252	

### 3.3.4 EFFECT OF ADDED SALTS ON REACTION RATE

In order to study the effect of added salts on the rate of oxidation of p-Toluidine, the concentration of salts was varied from  $2.5 \times 10^{-3}$  to  $12.50 \times 10^{-3}$  M by keeping the concentration of other reactants constant. The results of these kinetic runs are recorded in Table 3.3.12. 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 3.3.12

$[\text{KBrO}_3] = 2.5 \times 10^{-3} \text{ M}$ $[\text{H}_2\text{SO}_4] = 1.25 \text{ M}$ $[\text{p-Toluidine}] = 1.75 \times 10^{-2} \text{ M}$ Temp = $30^\circ\text{C}$ $[\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}] = 2.0 \times 10^{-3} \text{ M}$					
$[\text{K}_2\text{SO}_4] \times 10^3 \text{ M}$	2.50	5.00	7.50	10.00	12.50
$k \times 10^2 \text{ min}^{-1}$	0.7975	0.8004	0.7719	0.7768	0.7646
$[\text{ZnSO}_4] \times 10^3 \text{ M}$	2.50	5.00	7.50	10.00	12.50
$k \times 10^2 \text{ min}^{-1}$	0.7366	0.7492	0.7132	0.7309	0.7038
$[\text{CdSO}_4] \times 10^3 \text{ M}$	2.50	5.00	7.50	10.00	12.50
$k \times 10^2 \text{ min}^{-1}$	0.7309	0.7196	0.7598	0.7479	0.7262

### 3.3.5 EFFECT OF TEMPERATURE ON REACTION RATE AND CALCULATION OF THERMODYNAMIC PARAMETERS :

In order to determine the temperature coefficient, Energy of activation, Enthalpy of activation ( $\Delta H^\ddagger$ ), and Entropy of activation ( $\Delta S^\ddagger$ ), the reaction was studied at five different temperatures ranging from 25°C to 45°C. The results of these kinetic runs have been tabulated in Table 3.3.13 and represented graphically in Fig 3.3.7.

It is seen from the Table 3.3.13 that the specific rate has approximately doubled (1.877) for 10°C rise in temperature. A plot of  $\log k_r$  Vs  $1/T$  as shown in Fig 3.3.8 (Table 3.3.14) is found to be linear indicating that the reaction obeys Arrhenius relationship. The value of energy of activation ( $E_a$ ) evaluated from slope of this curve comes out to be 11.668 K.cal mole<sup>-1</sup>. The Arrhenius equation has been used directly to calculate energy of activation, which comes out to be 11.486 K.cal.mole<sup>-1</sup>. On the basis of this graphical value, the frequency factor (A), free energy of activation ( $\Delta G^\ddagger$ ) have been calculated by the following equations :

Arrhenius<sup>61</sup> equation :

$$k_r = A \cdot e^{-E_a/RT} \quad \dots(1)$$

or

$$\log k_r = \log A - \frac{E_a}{2.303 RT} \quad \dots(2)$$

$$\log k_1 - \log k_2 = \frac{-E_a}{2.303 R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right] \quad \dots(3)$$

The values of  $\log kr/T$  have been plotted against  $1/T$ , which is shown in Fig 3.3.9. The plot was linear and from the slope of the straight line the enthalpy change for the formation of activated complex ( $\Delta H^\ddagger$ ) has been evaluated. The value of the  $\Delta H^\ddagger$  evaluated from the slope comes out to be  $11.767 \text{ K.cal mole}^{-1}$ .

The following equations were used to calculate  $\Delta G^\ddagger$ ,  $\Delta S^\ddagger$

$$\log \frac{kr}{kT/h} = \frac{-\Delta H^\ddagger}{2.303 RT} + \frac{\Delta S^\ddagger}{2.303 R} \quad \dots(4)$$

$$\Delta S^\ddagger = 2.303 R \log \frac{Ah}{kT} \quad \dots(5)$$

$$\text{And } \Delta G^\ddagger = \Delta H^\ddagger - T \Delta S^\ddagger \quad \dots(6)$$

In above equations  $kr$  is the specific rate constant,  $k$  is the Boltzmann constant ( $1.381 \times 10^{-16} \text{ erg/deg.}$ ) and  $h$  is the planck's constant ( $6.626 \times 10^{-27} \text{ erg.sec.}$ ) Other symbols carry their usual meanings.

The various energy parameters, obtained, have been recorded in Table 3.3.15.

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

$$kr = 3.4925 \times 10^4 e^{-11668/RT}$$



TABLE 3.3.13

Effect of Temperature

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

$$[\text{H}_2\text{SO}_4] = 1.25 \text{ M}$$

$$[\text{p-Toluidine}] = 1.75 \times 10^{-2} \text{ M}$$

$$[\text{Na}_2\text{S}_2\text{O}_3] = 2 \times 10^{-3} \text{ M}$$

Temp ( T )	25°C	30°C	35°C	40°C	45°C
Time (min)	Vol (in ml) of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$				
0	38.60	38.60	38.50	38.60	38.50
5	37.65	37.05	36.60	35.80	34.70
10	36.65	35.70	34.80	33.50	30.95
15	35.80	34.05	33.10	31.00	27.50
20	34.85	32.90	31.35	28.25	24.60
25	33.65	31.50	29.45	26.15	22.00
30	32.95	29.75	27.85	23.95	20.10
35	31.60	28.60	26.80	22.40	18.40
40	30.45	27.25	25.25	20.90	16.00
45	29.60	26.15	23.65	19.90	15.05
50	28.10	25.20	22.60	18.35	13.80
60	26.80	23.45	20.20	16.00	11.50
70	25.70	21.50	17.95	14.20	9.10
80	24.55	19.95	16.65	12.00	7.70
Graphically $k \times 10^2 \text{ min}^{-1}$	0.5680	0.8326	1.0501	1.4941	2.0906
Mean $k \times 10^2 \text{ min}^{-1}$	0.5576	0.8353	1.0626	1.4998	2.1267

TABLE 3.3.14

$T^{\circ}\text{K}$	$\frac{1}{T} \times 10^3$	$k_r \times 10^2 \text{min}^{-1}$	$\log k_r$	$\log k_r/T$
298	3.3557	0.5680	- 2.2456	- 4.7198
303	3.3003	0.8326	- 2.0795	- 4.5610
308	3.2467	1.0501	- 1.9787	- 4.4673
313	3.1948	1.4941	- 1.8256	- 4.3259
318	3.1446	2.0906	- 1.6797	- 4.1821

FIG: 331 ———EFFECT OF  $\text{KBrO}_3$  CONCENTRATION

$[\text{p-T}]_0 = 1.75 \times 10^{-2} \text{ M}$   
 $[\text{H}_2\text{SO}_4]_0 = 125 \text{ M}$   
TEMP =  $30^\circ\text{C}$

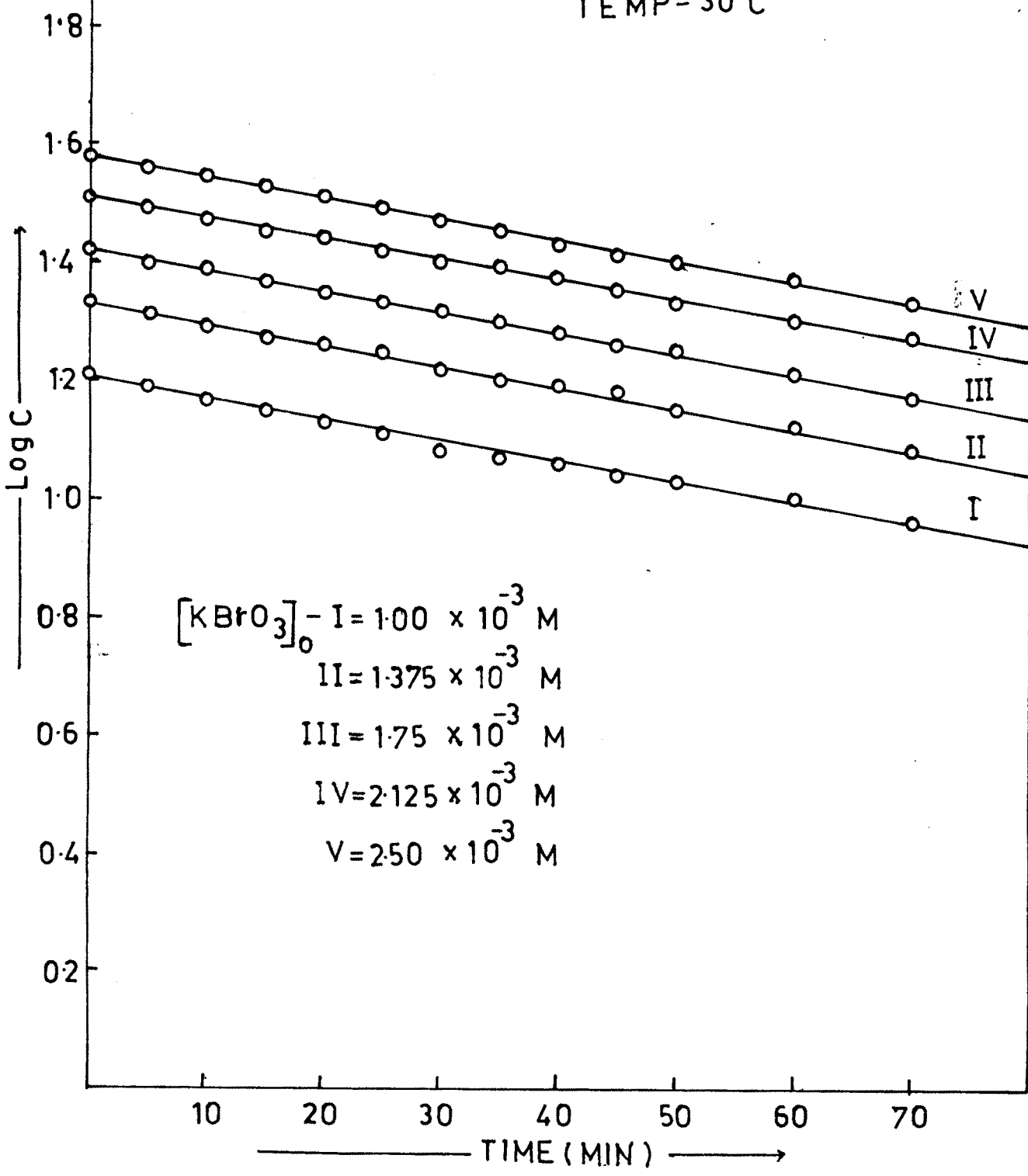


FIG:3.3.2 —  $\text{Log} \left[ \frac{dc}{dt} \right]_0$  Vs  $\text{Log } C_0$

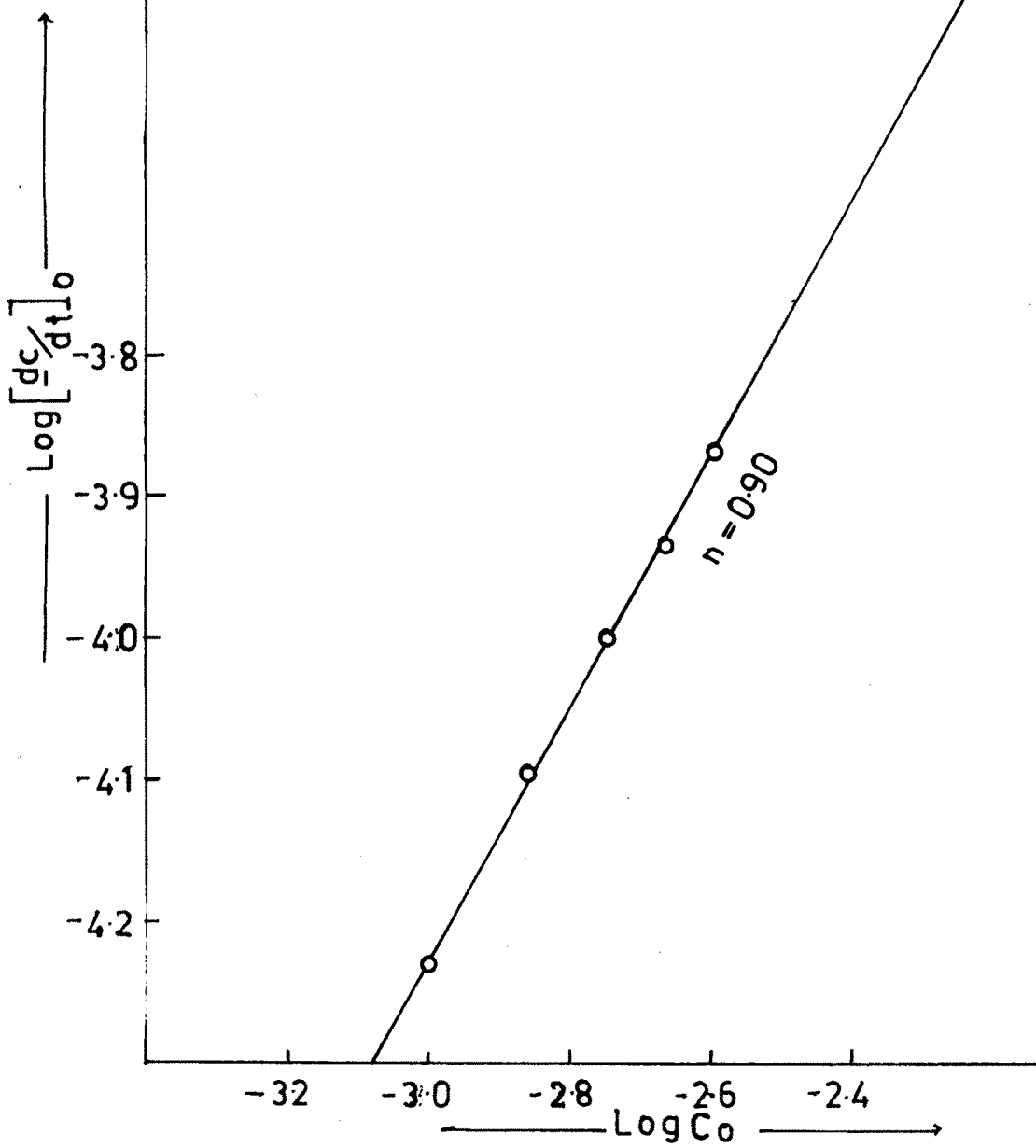


FIG: 333 — EFFECT OF p-T CONCENTRATION

$$[\text{KBrO}_3]_0 = 2.5 \times 10^{-3} \text{ M}$$

$$[\text{H}_2\text{SO}_4]_0 = 1.25 \text{ M}$$

$$\text{TEMP} = 30^\circ \text{C}$$

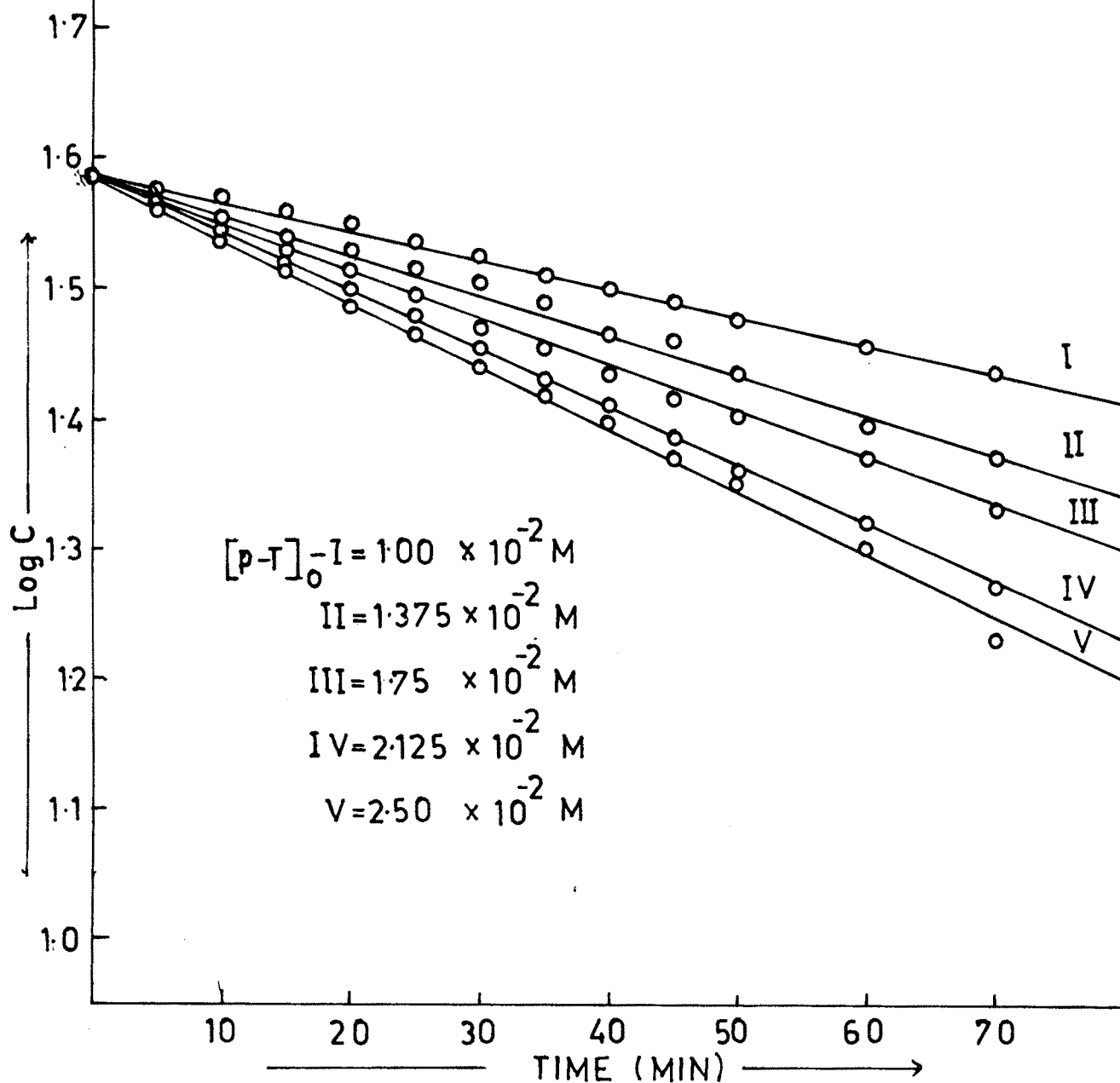


FIG: 33.4 ———  $\text{Log} \left[ \frac{dc}{dt} \right]_0$  Vs  $\text{Log } C_0$

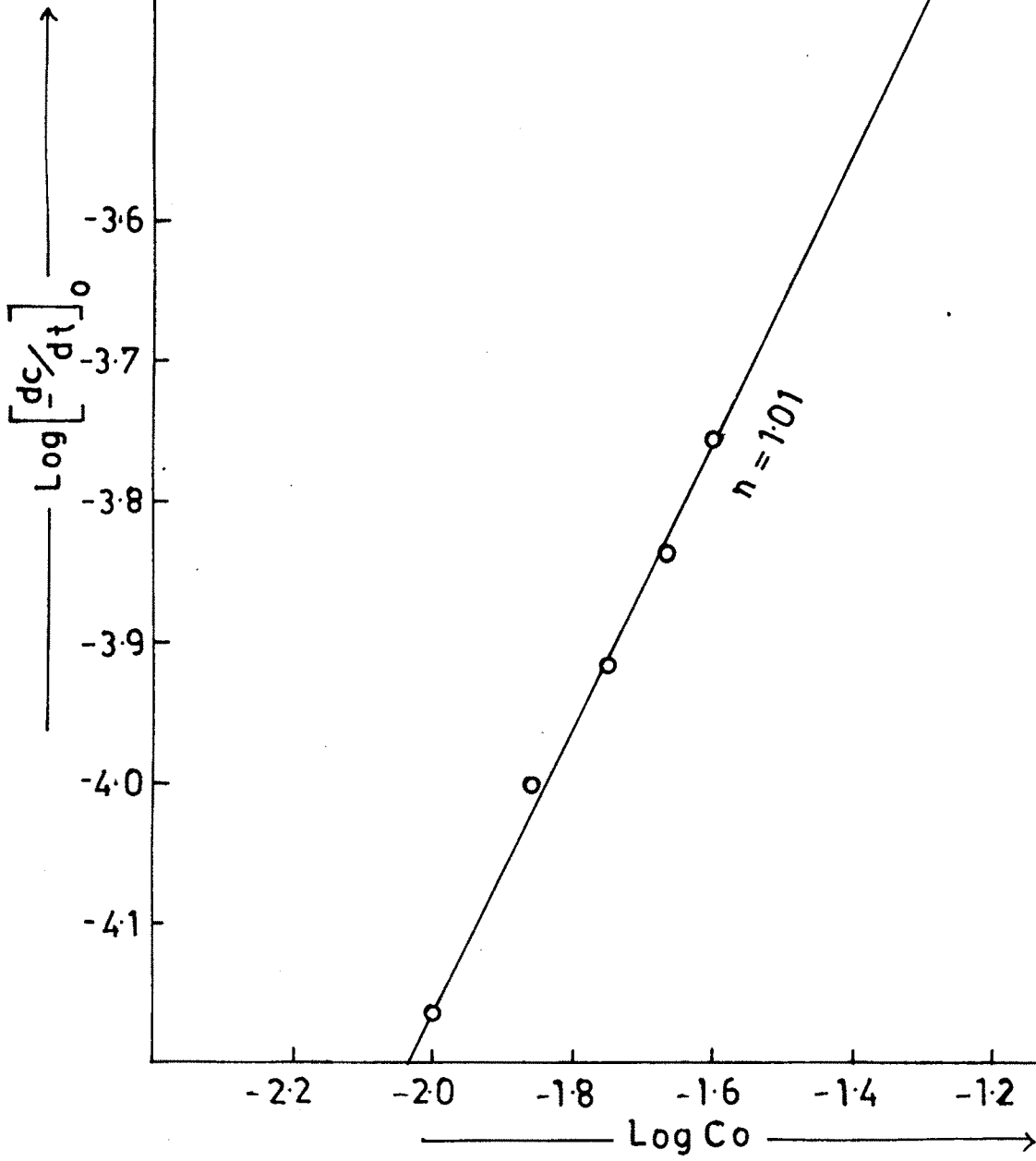
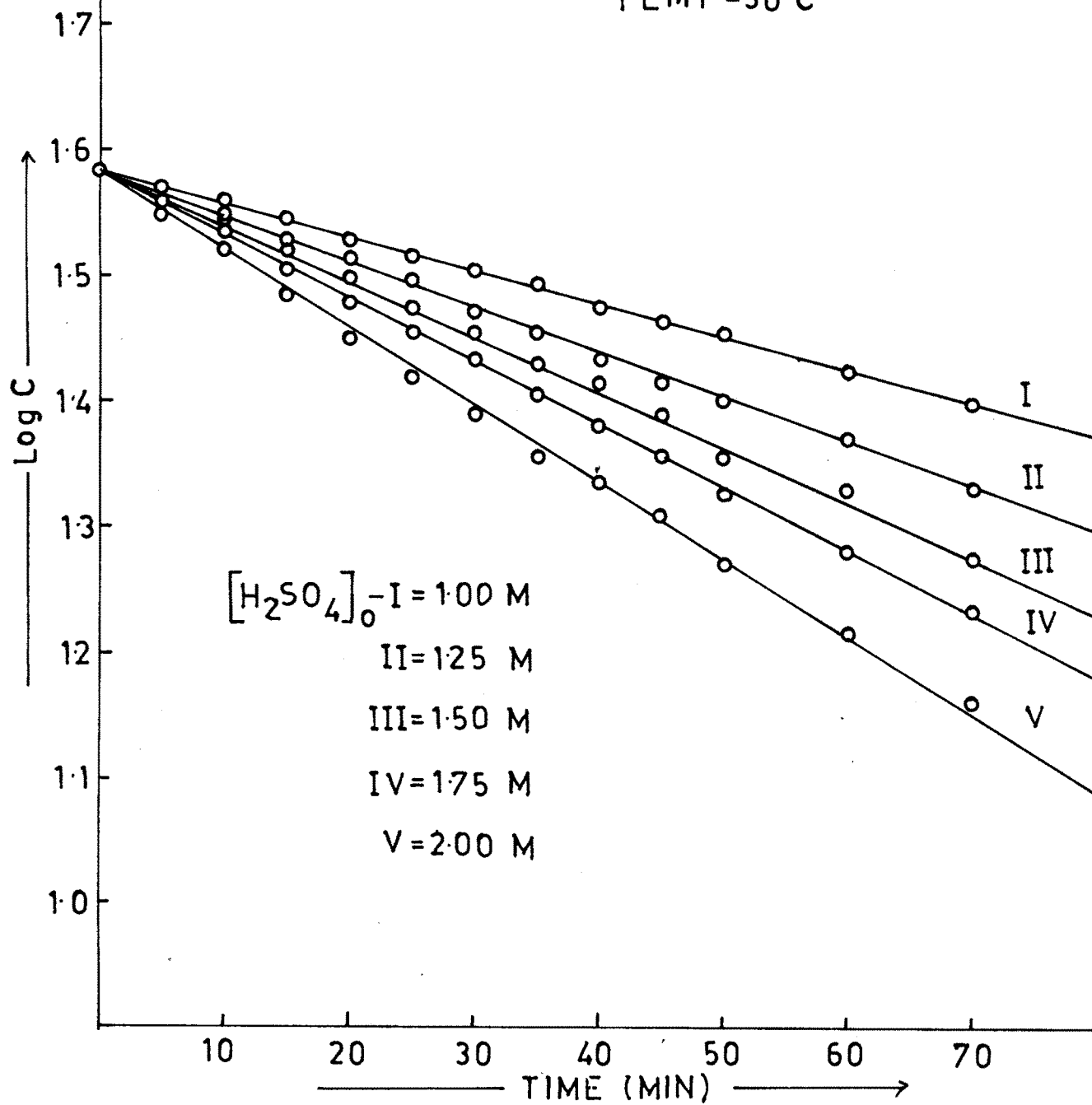


FIG:335 — EFFECT OF  $H_2SO_4$  CONCENTRATION

$$[p-T]_0 = 1.75 \times 10^{-2} \text{ M}$$

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

TEMP =  $30^\circ\text{C}$



EIG: 33.6 ———  $\text{Log} \left[ \frac{dc}{dt} \right]_0$  Vs  $\text{Log } C_0$

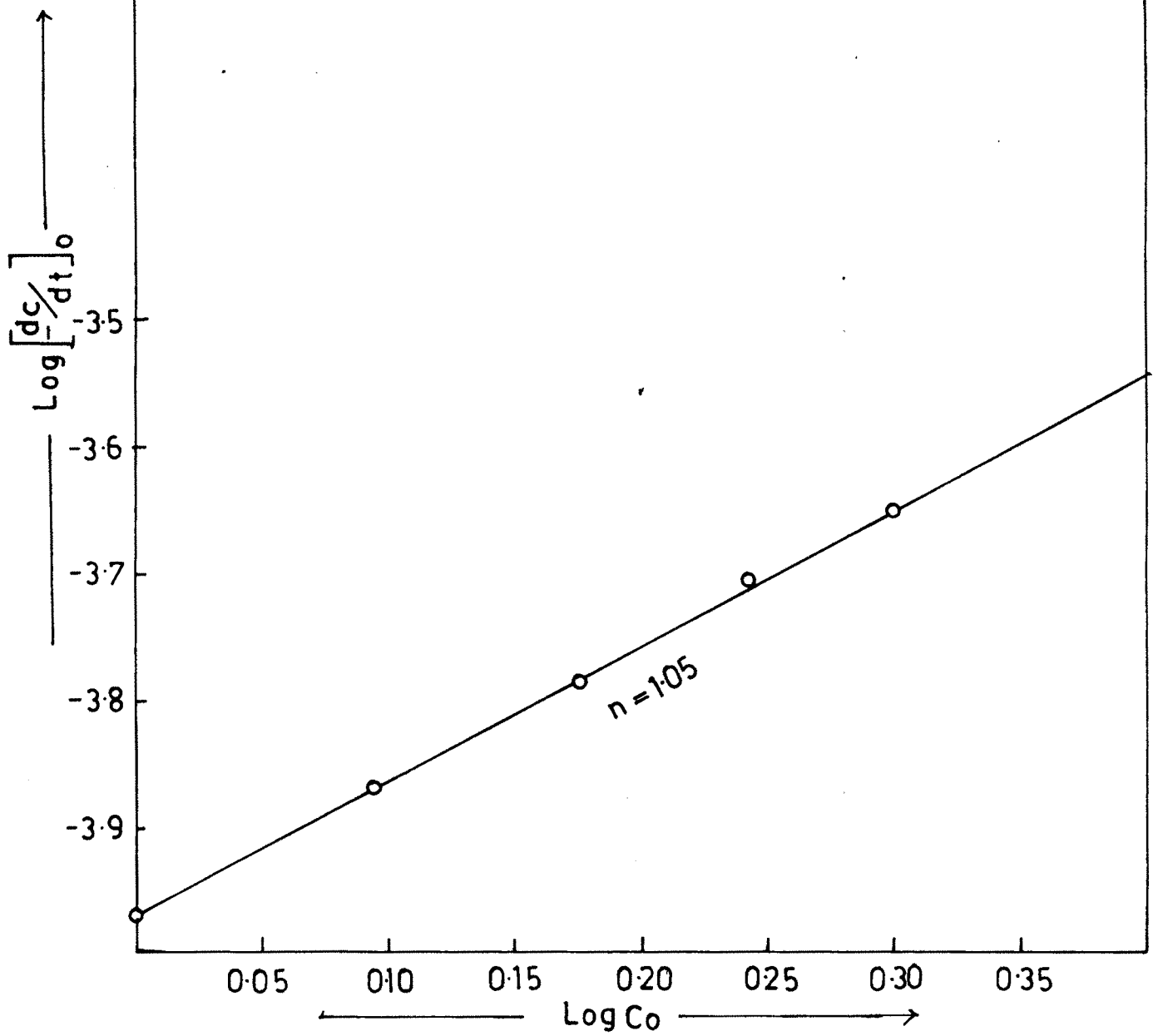




FIG: 337 — EFFECT OF TEMPERATURE

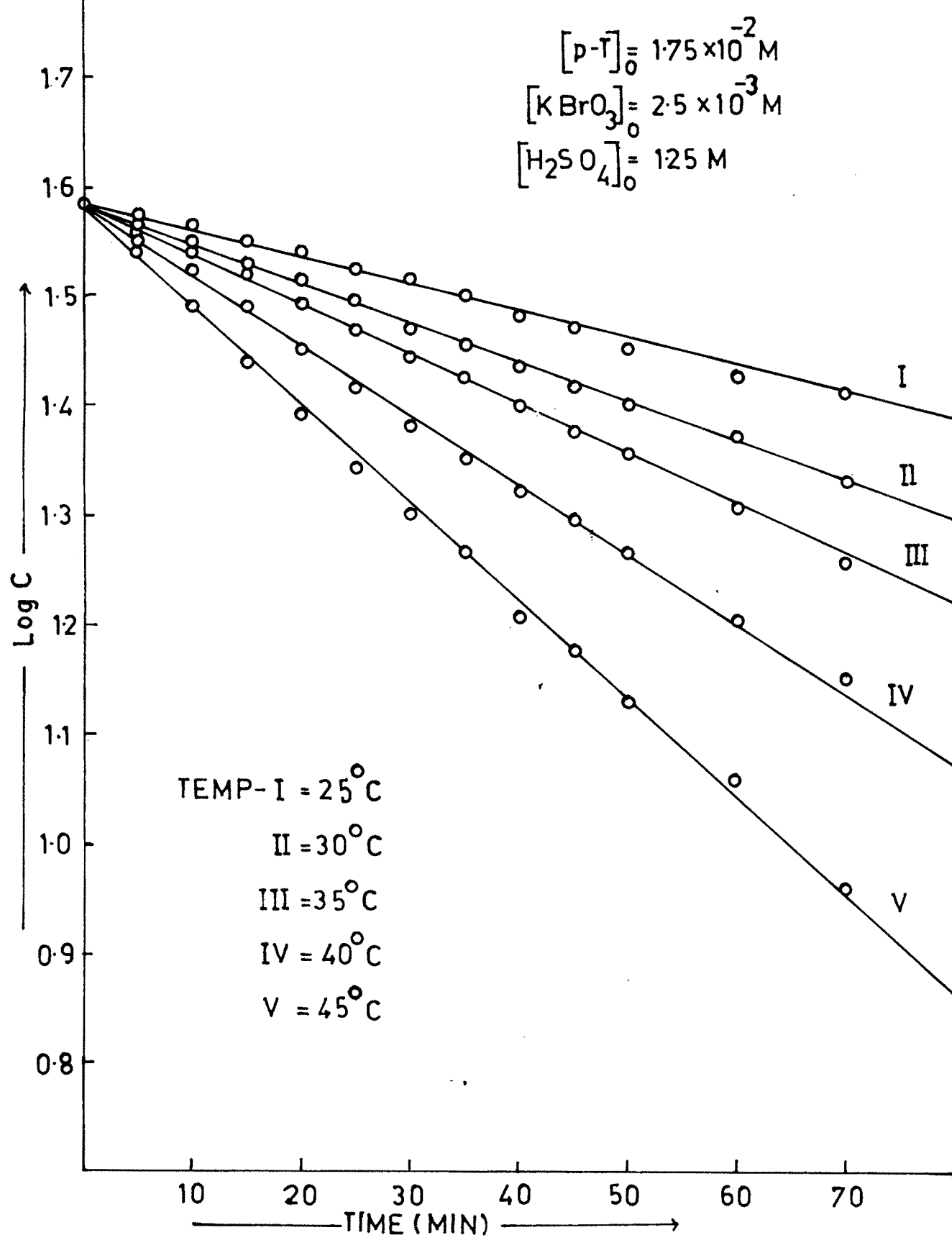


FIG: 33-8 ——— Log kr Vs  $\frac{1}{T}$

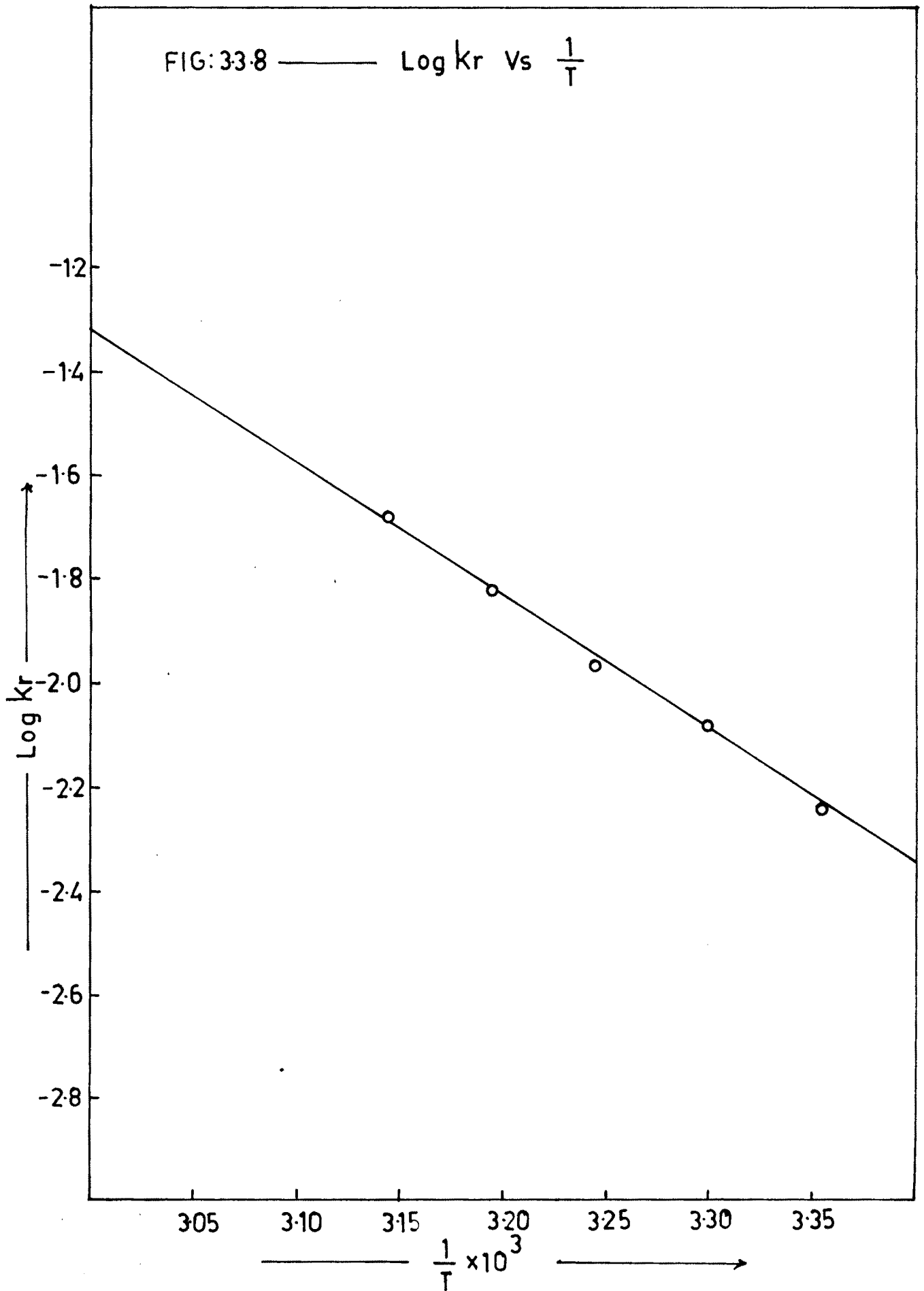


FIG: 33-9 ———  $\text{Log } \frac{k_r}{T}$  Vs  $\frac{1}{T}$

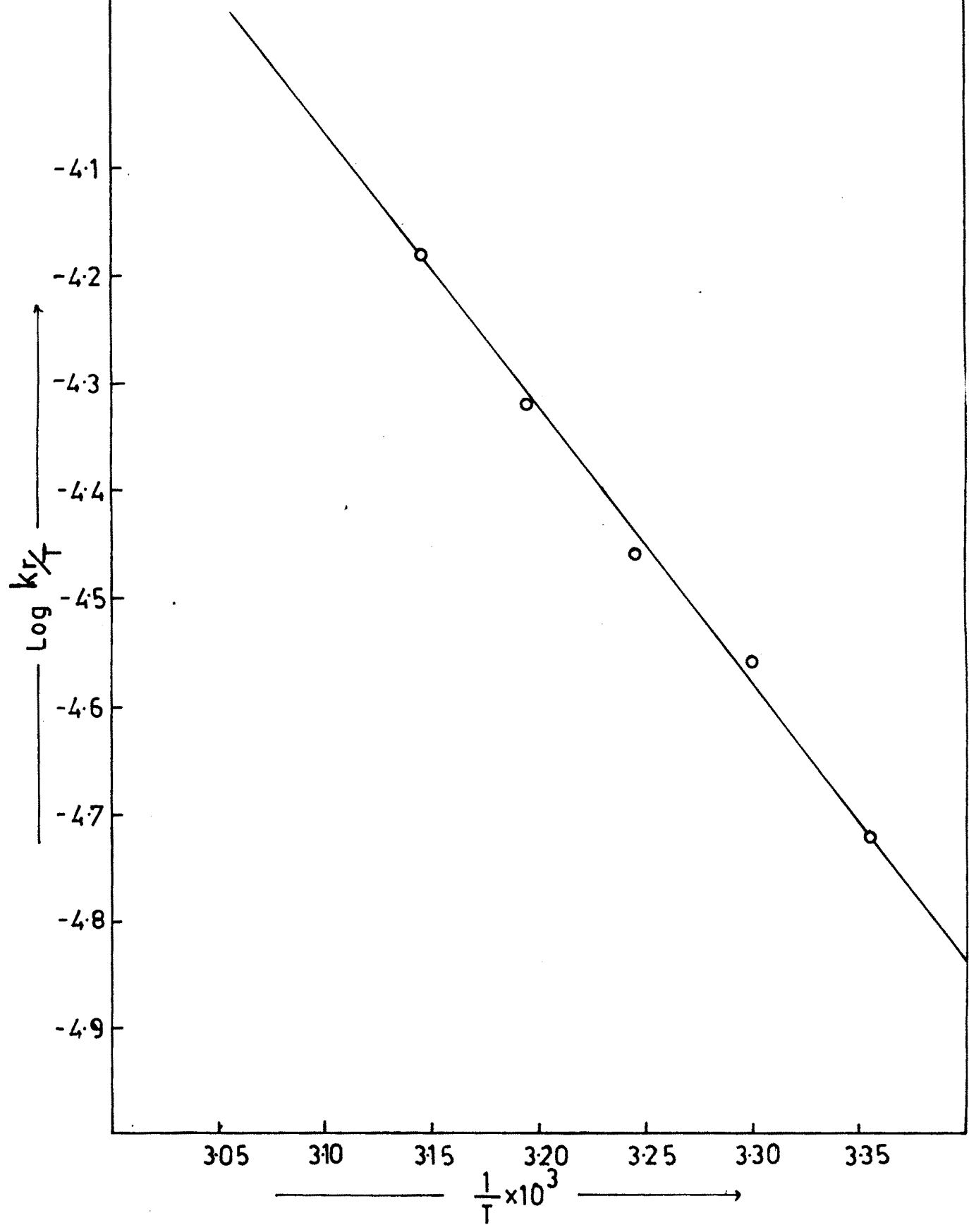


TABLE 3.3.15

## Thermodynamic Parameters

Temp T °K	kr x10 <sup>2</sup> min <sup>-1</sup>	Temp coefficient	Ea. K. cal mole <sup>-1</sup> Graph Calculation	$\Delta H^\ddagger$ K. cal mole <sup>-1</sup>	Ax10 <sup>-4</sup> Sec <sup>-1</sup>	$\Delta S^\ddagger$ e.u. K. cal mole <sup>-1</sup>	$\Delta G^\ddagger$
298	0.5680			Graph	3.4083	-37.8011	23.031
303	0.8326	1.848	11.020		3.6094	-37.7202	23.196
308	1.0501	1.794	11.668	11.767	3.3237	-37.9166	23.445
313	1.4941	1.990			3.4875	-37.8530	23.615
318	2.0906				3.6335	-37.8030	23.788
Mean		1.877	11.668	11.486	3.4925	-37.8187	23.415

### 3.3.6 STOICHIOMETRY :

To determine the mole ratio of p-Toluidine to potassium bromate, the reaction mixture was taken to be  $2.5 \times 10^{-2} \text{M}$  p-Toluidine and  $5.0 \times 10^{-2} \text{M}$  potassium bromate. The reaction was followed at  $35^{\circ}\text{C}$  and sharp break in volume of  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  Vs time plot was taken for calculation of mole ratio. The mole ratio was found to be 1:1, for p-Toluidine to potassium bromate.

### 3.3.7 FREE RADICAL DETECTION AND END PRODUCT ANALYSIS :

The reaction did not promote polymerization of acrylonitrile<sup>62</sup> indicating absence of free radical. When acrylonitrile (1 ml) was added to the reaction mixture (5 ml) containing both  $\text{KBrO}_3$  and p-Toluidine, a precipitate was not formed. This clearly indicates that reaction proceeds in absence of free radical formation.

The oxidation product o-Benzoquinone<sup>31, 12</sup> was identified by TLC with the authentic sample prepared by the literature method. Evolution of ammonia<sup>19</sup> 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.