
CHAPTER — III

RESULTS

CHAPTER - III

SECTION-I

3.1 KINETICS OF OXIDATION OF n-CAPROIC ACID HYDRAZIDE :

Preliminary experiments were performed in order to decide the suitable temperature and concentration of the reactants. It was observed that the reaction proceeds with measurable velocity at 40°C, when the concentration of n-Caproic acid hydrazide (n-CAH) was $1.0 \times 10^{-2}M$, Chloramine-T (CAT) was $1.0 \times 10^{-3}M$ and that of NaOH was $1.0 \times 10^{-2}M$. The kinetic data has been recorded in Table - 3.1.1 given below :

TABLE 3.1.1

[n-CAH] = $1.0 \times 10^{-2}M$ [NaOH] = $1.0 \times 10^{-2}M$
 [CAT] = $1.0 \times 10^{-3}M$ [Na₂S₂O₃.5H₂O] = $5.0 \times 10^{-4}M$. Temp=40°C

Time (min)	Vol.(in ml) of Na ₂ S ₂ O ₃	$k \times 10^3 \text{ min}^{-1}$
0	19.80	-
10	18.45	7.06
20	17.25	6.89
30	16.10	6.90
40	14.95	7.02
50	14.05	6.86
60	13.00	7.01
70	12.15	6.98
80	11.25	7.07
90	10.60	6.94
100	9.85	6.98
120	8.60	6.95
Mean $k \times 10^3 \text{ min}^{-1}$		6.97

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A perusal of the above data closely shows that pseudo first order specific rate is almost constant. In this experiment the hydrazide concentration is in excess (10 times) over the CAT concentration.

1) EFFECT OF CHLORAMINE-T CONCENTRATION

It was necessary to determine the order of reaction w.r.t. CAT, keeping the concentration of n-Caproic acid hydrazide and that of NaOH unchanged in order to investigate the effect of CAT concentration on the rate of the reaction. For this purpose, the reaction was carried out at 5 different concentrations of CAT by keeping the concentration of other reagents constant. Table 3.1.2 embodies the results of these kinetic runs. The values of first order rate constants (viz k) have been evaluated from the initial slope of the curves, shown in Fig 3.1.1 as well as calculated at different times by integration method, which are in good agreement with each other.

An examination of the data (Table 3.1.2) shows that when the hydrazide concentration is in excess, the pseudo first order rate constant (k) calculated in each case is almost constant. Hence, the rate of disappearance of CAT obeys the first order kinetics.

TABLE 3.1.2

$$[n\text{-CAH}]_0 = 1.0 \times 10^{-2} \text{M} \quad [\text{Na}_2\text{S}_2\text{O}_3; 5\text{H}_2\text{O}]_0 = 5.0 \times 10^{-4} \text{M}$$

$$[\text{NaOH}]_0 = 1.0 \times 10^{-2} \text{M} \quad \text{Temp} = 40^\circ\text{C}$$

Conc. of CAT = M x 10 ⁻³	0.5	1.0	1.5	2.0	2.5
Time in (min)	Vol. (in ml) of Na ₂ S ₂ O ₃				
0	9.40	19.80	30.00	39.70	48.00
10	8.70	18.45	27.95	37.00	44.70
20	8.10	17.25	26.00	34.55	41.75
30	7.60	16.10	24.20	32.15	38.90
40	7.10	14.95	22.55	30.00	36.35
50	6.60	14.05	21.05	28.00	33.80
60	6.10	13.00	19.60	26.25	31.40
70	5.70	12.15	18.30	24.40	29.50
80	5.30	11.25	17.05	22.75	27.55
90	4.90	10.60	15.80	21.20	25.65
100	4.50	9.85	14.85	19.80	23.90
110	-	-	13.80	-	-
120	-	8.60	-	-	-
Mean : kx10 ³ min ⁻¹	7.25	6.97	7.09	6.97	6.95

In order to confirm the order of reaction w.r.t. CAT, the values of $-dc/dt$ were determined by plotting the volume of $\text{Na}_2\text{S}_2\text{O}_3$ (equivalent to CAT) against time for different initial concentrations of CAT and recorded in the table 3.1.3.

TABLE 3.1.3

Initial Conc. of CAT $C_0 = M \times 10^{-3}$	$-dc/dt$ (by graph)	$\log C_0$	$\log(-dc/dt)$
0.50	0.69×10^{-5}	- 3.30	- 5.1611
1.00	1.345×10^{-5}	- 3.00	- 4.8712
1.50	2.00×10^{-5}	- 2.823	- 4.6989
2.00	2.67×10^{-5}	- 2.698	- 4.5734
2.50	3.375×10^{-5}	- 2.6020	- 4.4717

The above values of $-dc/dt$ and $[\text{CAT}]_0$ i.e. C_0 are substituted in the Van't Hoff equation i.e.

$$n = \frac{\log[-dc/dt]_1 - \log[-dc/dt]_2}{\log[C_0]_1 - \log[C_0]_2}$$

where n = order of reaction.

The results have been recorded in Table 3.1.4

TABLE 3.1.4

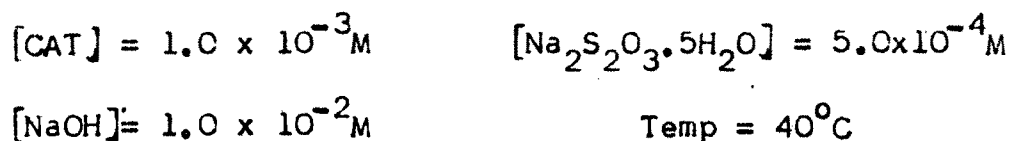
$[\text{CAT}]_0 \times 10^3$	$(-dc/dt) \times 10^5$	Order of reaction(n)
0.5	0.69	0.96
1.0	1.345	
1.0	1.345	0.97
1.5	2.00	
1.5	2.00	1.00
2.0	2.67	
2.0	2.67	1.05
2.5	3.375	

The order of reaction w.r.t. $[\text{CAT}]$ has been evaluated from the plot of $\log -dc/dt$ Vs $\log C_0$ fig 3.1.2, where C_0 is the initial concentration of CAT, which comes out to be 0.95. This confirms the first order behaviour of the reaction w.r.t. CAT.

2) EFFECT OF HYDRAZIDE (n-CAH) CONCENTRATION

In order to investigate the effect of hydrazide concentration on the rate of oxidation of n-CAH, the hydrazide concentration was varied from $0.5 \times 10^{-2} \text{ M}$ to $2.5 \times 10^{-2} \text{ M}$, keeping the concentration of CAT and that of NaOH constant. The results of these kinetic runs are recorded in Table 3.1.5 and depicted graphically in Fig 3.1.3

TABLE 3.1.5



Initial concn. of n-CAH = M x 10 ²	0.5	1.00	1.50	2.00	2.50
Time in (min)	Vol. (in ml) of Na ₂ S ₂ O ₃				
0	19.80	19.80	19.80	19.70	19.70
10	18.95	18.45	17.65	16.75	15.70
20	18.15	17.25	15.70	14.05	12.75
30	17.40	16.10	13.80	12.20	10.25
40	16.80	14.95	12.70	10.40	9.00
50	16.00	14.05	11.65	8.90	6.65
60	15.10	13.00	10.35	7.35	5.25
70	14.85	12.15	9.40	6.30	4.10
80	14.20	11.25	8.15	5.35	3.40
90	13.80	10.60	7.20	4.30	2.80
100	12.95	9.85	6.20	4.05	-
120	11.90	8.60	5.30	-	-
Mean k x 10 ³ min ⁻¹	4.25	6.97	11.20	16.41	21.73

The result contained in Table 3.1.5 shows that the first order rate constant increases with increase in the initial concentration of hydrazides.

The plots of log 'C' against time 't' (fig 3.1.3) are linear. The second order rate constant k_2 ,

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

where k_2 = Second order rate constant

k_1 = First order rate constant
was found to be constant.

TABLE 3.1.6

$[\text{n-CAH}] = M \times 10^2$	$k_1 \times 10^3 \text{ min}^{-1}$	$k_2 \times 10^1 \text{ min}^{-1}$
0.5	4.24	8.48
1.00	6.96	6.96
1.50	11.20	7.46
2.0	16.41	8.20
2.50	21.73	8.69

Table 3.1.6 indicates first order dependence of the rate on hydrazide concentration.

The order with respect to n-caproic acid hydrazide was determined by Van't Hoff differential method. The volume of $\text{Na}_2\text{S}_2\text{O}_3$ (equivalent to CAT) was plotted against time for different initial concentrations of hydrazide. From these curves, the values of $-dc/dt$ in each case was determined from the initial slope which gives the value of initial rate.

These values are recorded in Table 3.1.7. The values of $-dc/dt$ and $[\text{Hydrazide}]_0$ i.e. C_0 are substituted in the Van't Hoff equation i.e.

$$n = \frac{\log[-dc/dt]_1 - \log[-dc/dt]_0}{\log[C_0]_1 - \log[C_0]_2}$$

where n = order of reaction.

The results have been recorded in Table 3.1.8

TABLE 3.1.7

Initial conc. of n-CAH $[C_0] = M \times 10^2$	$-\frac{dc}{dt} \times 10^5$	$\log C_0$	$\log -dc/dt$
0.5	0.85	- 2.30	- 5.0705
1.0	1.60	- 2.00	- 4.7958
1.5	2.35	- 1.823	- 4.6289
2.0	3.13	- 1.698	- 4.5040
2.5	3.95	- 1.6020	- 4.4030

TABLE 3.1.8

Initial conc of n-CAH = $M \times 10^2$	$-dc/dt \times 10^5$	Order of reaction (n)
0.5	0.85	0.91
1.0	1.60	
1.0	1.60	0.94
1.5	2.35	
1.5	2.35	0.99
2.0	3.13	
2.0	3.13	1.03
2.5	3.95	

The 'n' values are fairly nearer to unity. The order of reaction w.r.t. [n-CAH] is also determined from the plot of $\log -dc/dt$ Vs $\log C_0$ (Fig 3.1.4) where C_0 is the initial concentration of n-CAH, which comes out to be 0.99. This confirms the first order behaviour of the reaction w.r.t. n-Caproic acid hydrazide.

3) EFFECT OF SODIUM HYDROXIDE CONCENTRATION

In order to study the effect of alkali concentration on the rate of oxidation of n-CAH, the concentration of NaOH was varied from $0.5 \times 10^{-2}M$ to $2.5 \times 10^{-2}M$ by keeping the concentration of other reactants constant. The results of these kinetic runs are recorded in Table 3.1.9

TABLE 3.1.9

[n-CAH] = $1.0 \times 10^{-2}M$		[Na ₂ S ₂ O ₃] = $5.0 \times 10^{-4}M$			
[CAT] = $1.0 \times 10^{-3}M$		Temp = 40°C			
[NaOH] Mx10 ²	0.5	1.0	1.5	2.0	2.5
Time in (min)	Vol. (in ml) of Na ₂ S ₂ O ₃				
0	19.80	19.80	19.80	19.80	19.80
10	18.40	18.45	18.45	18.45	18.50
20	17.10	17.25	17.25	17.25	17.30
30	15.95	16.10	16.10	16.10	16.15
40	14.80	14.95	15.00	14.95	14.95
50	13.80	14.05	13.90	14.10	14.05
60	12.90	13.00	13.00	13.05	13.05
70	11.85	12.15	12.15	12.90	12.30
80	11.10	11.25	11.35	11.25	11.40
90	10.35	10.60	10.60	10.70	10.65
100	9.70	9.85	9.85	9.70	9.90
120	8.30	8.60	8.55	8.30	8.60
Mean $k \times 10^3 \text{ min}^{-1}$	7.24	6.97	6.97	6.91	6.87

It is observed from the above results (Table 3.1.9) that the rate of oxidation of n-Caproic acid hydrazide is independent of sodium hydroxide concentration.

4) EFFECT OF CHLORIDE ION CONC. ON THE RATE OF OXIDATION OF n-CAH

To investigate the effect of addition of Chloride ion on the rate of oxidation of hydrazide (n-CAH), the concentration of sodium chloride was varied from 0.0M to $4.0 \times 10^{-2}M$, keeping all the other concentrations of reactants constant. The results of which are recorded in Table 3.1.10 .

TABLE 3.1.10

[NaCl]=Mx10 ²	0.0	1.0	2.0	3.0	4.0
Time in (min)	Vol. (in ml) of Na ₂ S ₂ O ₃				
0	19.80	19.70	19.80	19.80	19.70
10	18.45	18.30	18.40	18.30	18.25
20	17.25	17.05	17.00	17.00	16.85
30	16.10	15.75	15.65	15.70	15.60
40	14.95	14.80	14.60	14.45	14.40
50	14.05	13.60	13.70	13.40	13.30
60	13.00	12.75	12.55	12.40	12.25
70	12.15	11.90	11.65	11.55	11.30
80	11.25	11.00	10.80	10.65	10.45
90	10.60	10.20	10.00	9.90	9.70
100	9.85	9.95	9.25	9.10	8.95
120	8.60	8.05	8.10	9.85	7.50
Mean kx10 ³ min ⁻¹	6.97	7.28	7.56	7.75	7.67

An examination of the above data shows (Table 3.1.10) that the effect of varying chloride ion concentration is negligible.

5) EFFECT OF CHANGE IN IONIC STRENGTH OF THE MEDIUM

To study the effect of change in ionic strength of the medium on the rate of the reaction, the concentration of Potassium Chloride is varied from $0.5 \times 10^{-1} \text{M}$ to $2.5 \times 10^{-1} \text{M}$, keeping all the other concentrations constant. An examination of the results contained in the Table 3.1.11 shows that the change in ionic strength (μ) of the medium has marginal effect on the rate of oxidation of hydrazide.

TABLE 3.1.11

$$[\text{CAT}] = 1.0 \times 10^{-3} \text{M}$$

$$[\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}] = 5.0 \times 10^{-4} \text{M}$$

$$[\text{n-CAH}] = 1.0 \times 10^{-2} \text{M}$$

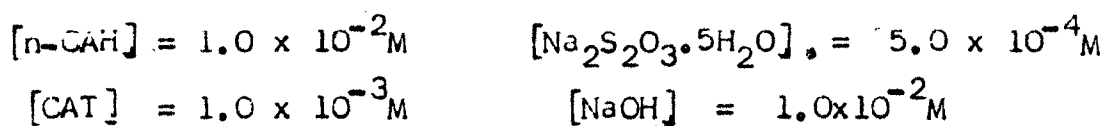
$$\text{Temp} = 40^\circ\text{C} \quad [\text{NaOH}] = 1.0 \times 10^{-2} \text{M}$$

$[\text{KCl}] = \text{M} \times 10^1$	0.5	1.0	1.5	2.0	2.5
μ	0.061	0.111	0.161	0.211	0.261
Time in (min)	Vol. (in ml) of $\text{Na}_2\text{S}_2\text{O}_3$				
0	19.80	19.80	19.80	19.70	19.80
10	18.45	18.40	18.30	18.20	18.25
20	17.25	17.00	17.00	16.80	16.85
30	16.10	15.65	15.70	15.55	15.50
40	14.95	14.60	14.45	14.40	14.30
50	14.05	13.70	13.40	13.30	13.20
60	13.00	12.55	12.40	12.30	12.25
70	12.15	11.65	11.50	11.35	11.30
80	11.25	10.80	10.60	10.50	10.45
90	10.60	10.00	9.95	9.70	9.70
100	9.85	9.25	9.10	9.05	8.85
120	8.60	8.10	7.80	7.80	7.60
Mean $k \times 10^3 \text{min}^{-1}$	6.97	7.56	7.75	7.85	8.05

6) EFFECT OF TEMPERATURE

In order to determine the various energy parameters like Energy of Activation (E_a), Enthalpy of activation (ΔH^\ddagger), Frequency factor (A), Free energy of activation (ΔG^\ddagger) and Entropy of activation (ΔS^\ddagger), the reaction was studied at five different temperatures ranging from 35°C to 55°C . The results of these kinetic runs have been tabulated in Table 3.1.12 and depicted graphically in Fig 3.1.5.

TABLE 3.1.12



Temp	35°C	40°C	45°C	50°	55°C
Time (min)	Vol. (in ml) of $\text{Na}_2\text{S}_2\text{O}_3$				
0	19.80	19.80	19.80	19.80	19.80
5	-	-	18.75	18.40	17.85
10	18.75	18.45	17.70	17.25	16.20
15	-	-	16.60	16.20	14.80
20	17.90	17.25	15.95	15.50	12.80
25	-	-	15.45	14.20	11.75
30	17.00	16.10	14.40	13.30	10.85
35	-	-	14.05	12.40	9.60
40	16.10	14.95	13.00	11.35	8.55
45	-	-	12.50	10.10	8.00
50	15.60	14.05	11.75	9.45	7.40
60	14.60	13.00	10.80	8.40	6.10
70	13.95	12.15	9.50	7.65	5.10
80	13.20	11.25	8.40	7.00	3.95
90	12.55	10.60	7.40	5.25	-
100	11.90	9.85	-	-	-
120	10.65	8.60	-	-	-
Mean $k \times 10^3 \text{ min}^{-1}$	5.089	6.97	10.60	13.80	20.09

It is seen from the results that the specific rate has approximately doubled for 10°C rise in temperature.

A plot of $\log k$ Vs $1/T$ as shown in Fig 3.1.6 is found to be linear indicating that, the reaction obeys Arrhenius relationship. The value of energy of activation (E_a) evaluated from the slope of this curve comes out to be $13.89 \text{ K. cal. mole}^{-1}$. The Arrhenius equation has been used directly to calculate energy of activation, the mean of which comes out to be $13.87 \text{ K. cal. mole}^{-1}$.

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

The value of energy of activation was used to calculate the frequency factor (A), and entropy of activation ΔS^\ddagger by the following equation

$$k_r = A \times e^{-E_a/RT} \quad \dots(2)$$

and

$$A = e. (kT/h) \times e^{\Delta S^\ddagger/R} \quad \dots(3)$$

Where (3) is valid for reactions in solution and k_r is specific rate constant, k is the Boltzman constant, 'h' is the Plank's constant and 'e' is the constant having a value of 2.718, other symbols carry their usual meanings.

Entropy of activation ΔS^\ddagger was calculated by the equation

$$\Delta S^\ddagger = 2.303 \times R \times \log \frac{A \times h}{kT} \quad \dots(4)$$

Enthalpy of activation, ΔH^\ddagger , was calculated from the equation

$$kr = \frac{kT}{h} \times e^{\Delta H^\ddagger/RT} \times e^{\Delta S^\ddagger/R} \quad (5)$$

The plot of $\log \left[\frac{kr}{kT/h} \right]$ Vs $1/T$ shown in Fig 3.1.7, is linear and from the slope of the straight line the enthalpy change (ΔH^\ddagger) for the formation of the activated complex has been calculated, which was found to be $13.23 \text{ K.cals mole}^{-1}$

The free energy for the reaction ΔG^\ddagger was calculated by equation.

$$\Delta G^\ddagger = \Delta H^\ddagger - T \Delta S^\ddagger \quad (6)$$

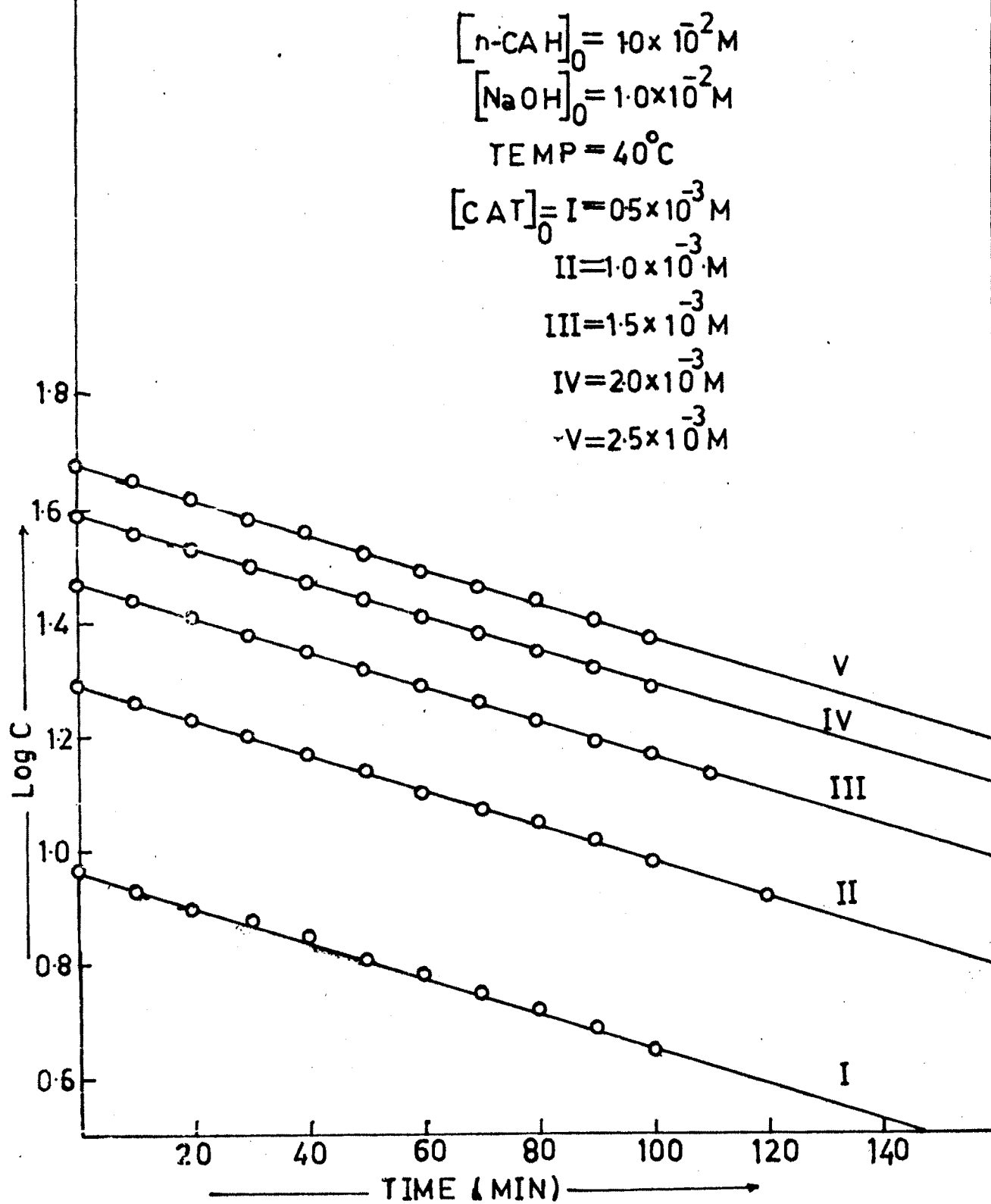
The various energy parameters obtained, have been recorded in Table 3.1.13.

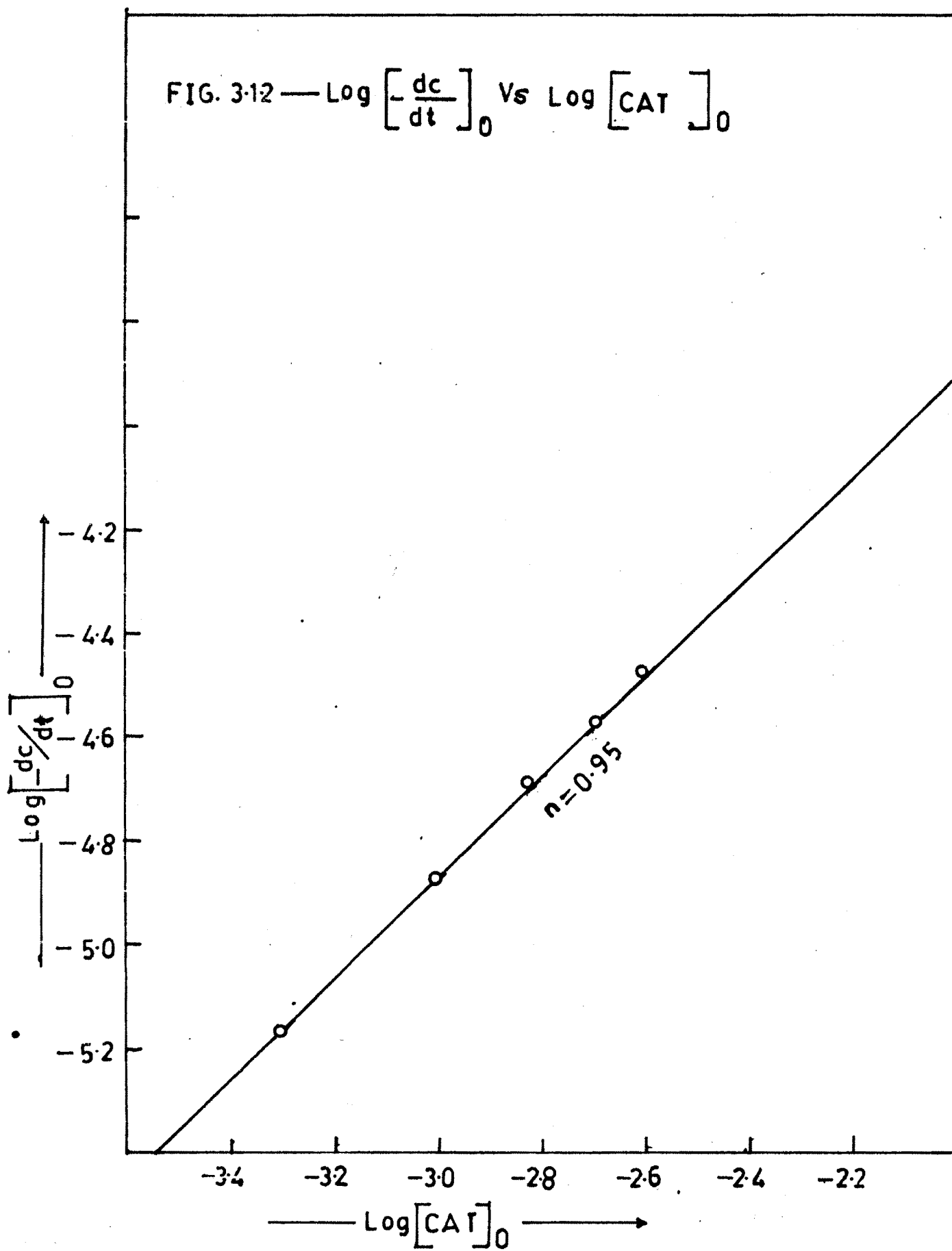
TABLE 3.1.13

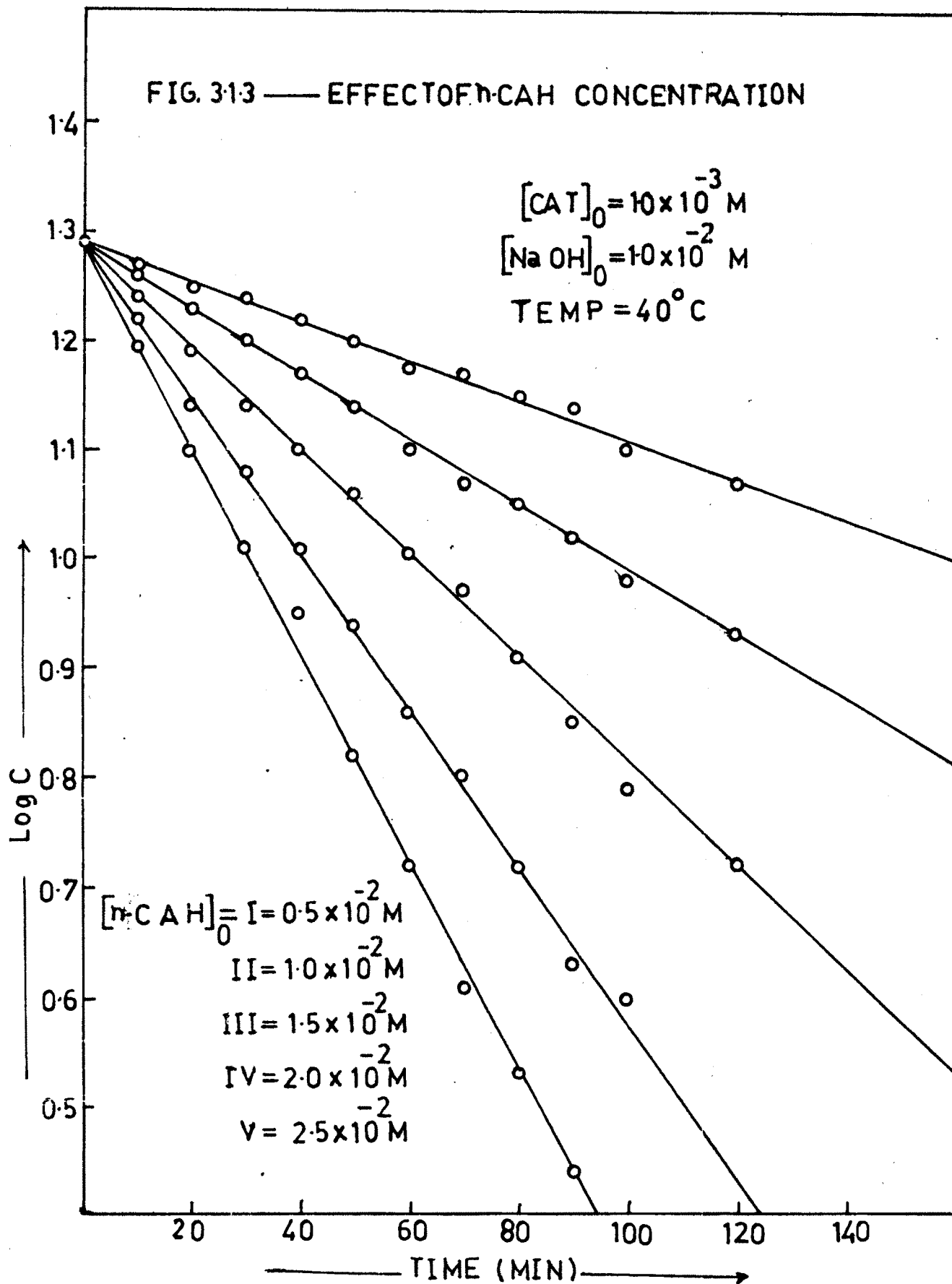
Temp K ^o	Temp coeffi- cient	Energy of activation (Ea) K.Cals mole ⁻¹	Frequency Factor (A) Ax10 ⁻⁵ sec ⁻¹	Free energy of activa- tion (ΔG^\ddagger) K.Cal mole ⁻¹	Entropy of acti- vation (ΔS^\ddagger) e.u.
318	2.04 1.96 1.98	13.89 13.55 14.19	6.00	23.14	- 32.16
313			5.75	23.34	- 32.28
318			6.01	23.48	- 32.23
323			5.65	23.69	- 32.38
328			6.10	23.82	- 32.26
	1.99	13.88	5.90	23.48	- 32.26

Enthalpy change (ΔH^\ddagger) by graph = $13.24 \text{ K. cal mole}^{-1}$
 Energ of activation(Ea)by graph = $13.89 \text{ K. cal mole}^{-1}$

FIG. 3.1.1 — EFFECT OF CAT CONCENTRATION.







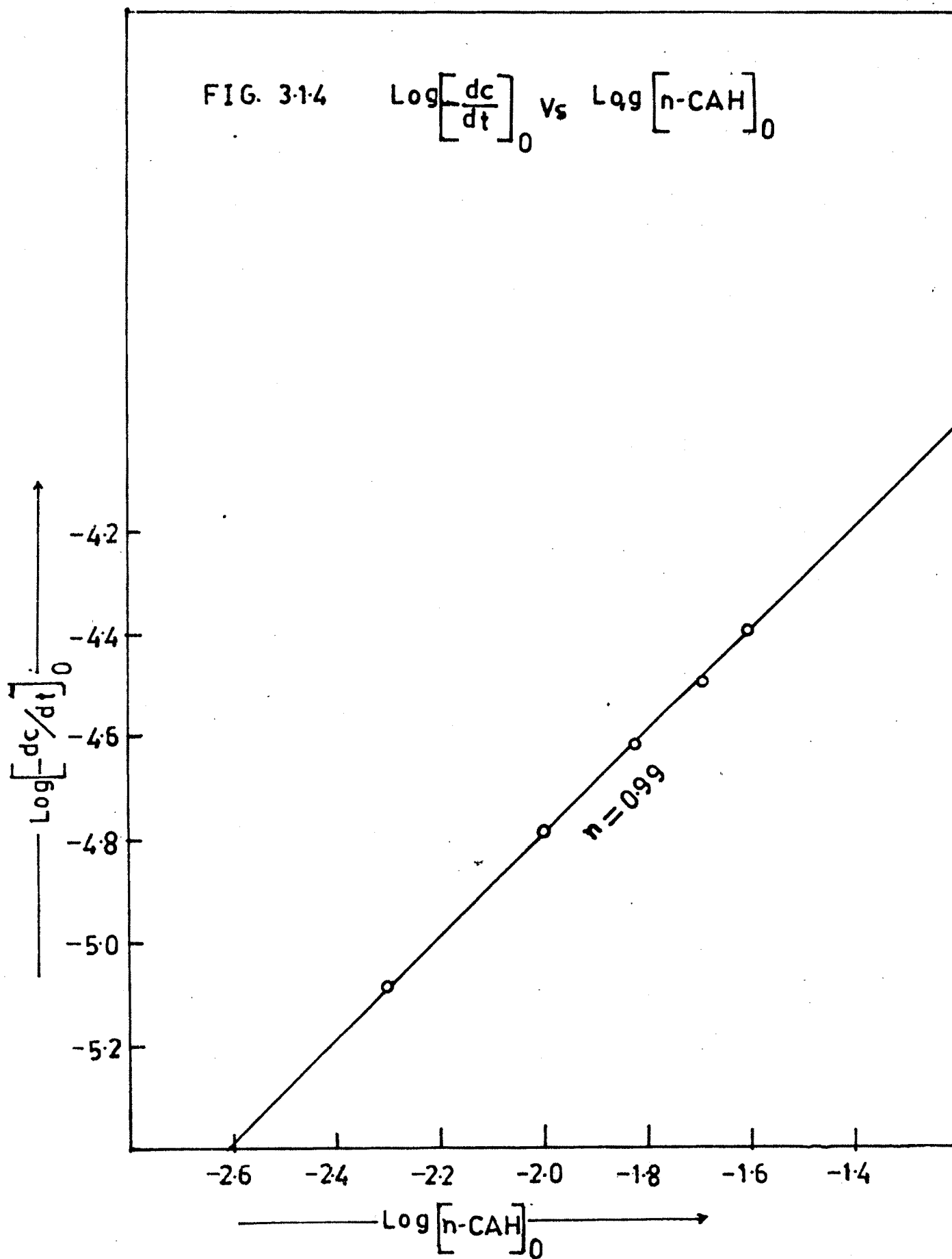


FIG. 31-5—EFFECT OF TEMPERATURE

$$[\text{CAT}]_0 = 1.0 \times 10^{-3} \text{ M}$$

$$[\text{m-CAH}]_0 = 1.0 \times 10^{-2} \text{ M}$$

$$[\text{NaOH}]_0 = 1.0 \times 10^{-2} \text{ M}$$

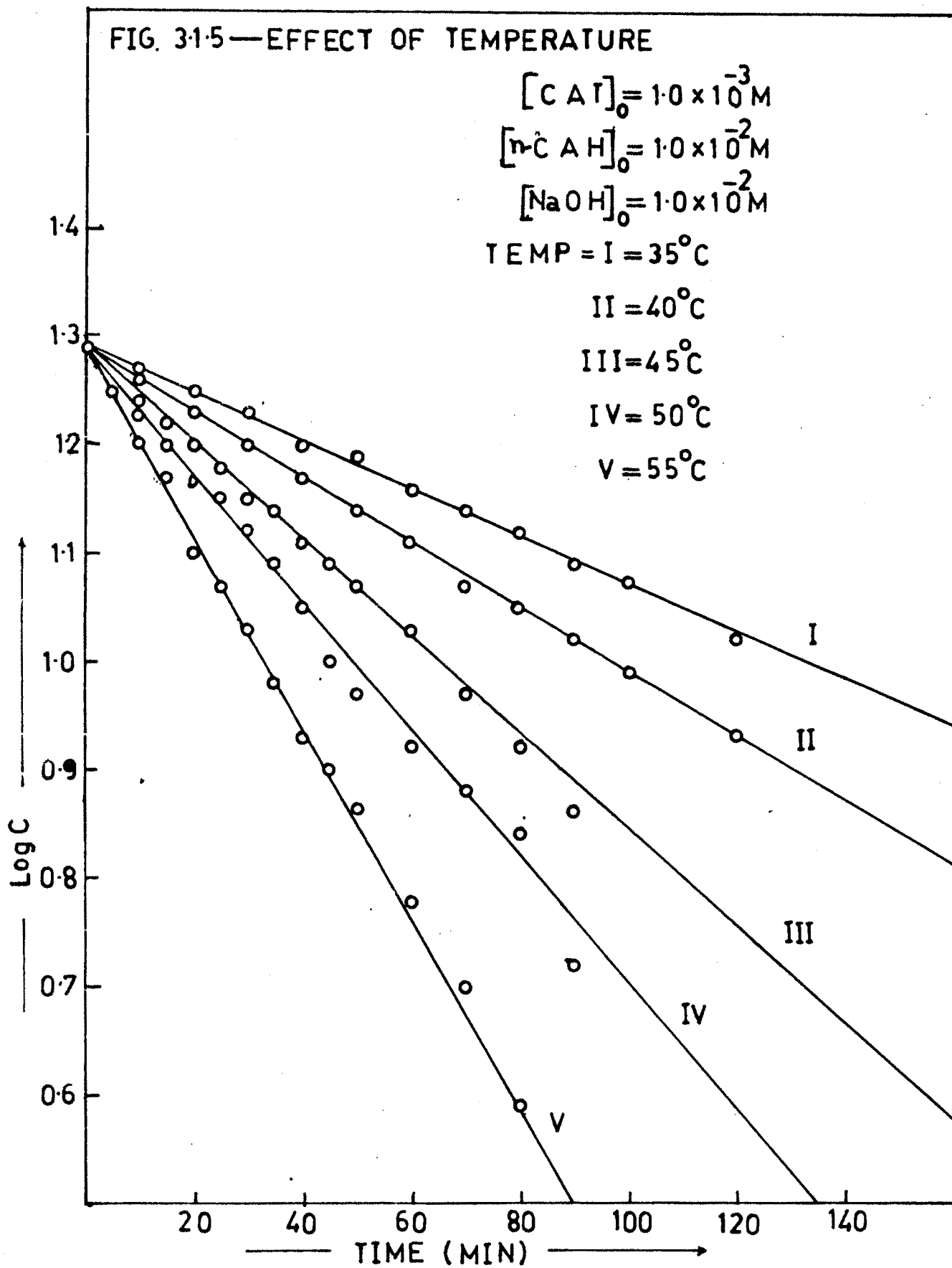
TEMP = I = 35°C

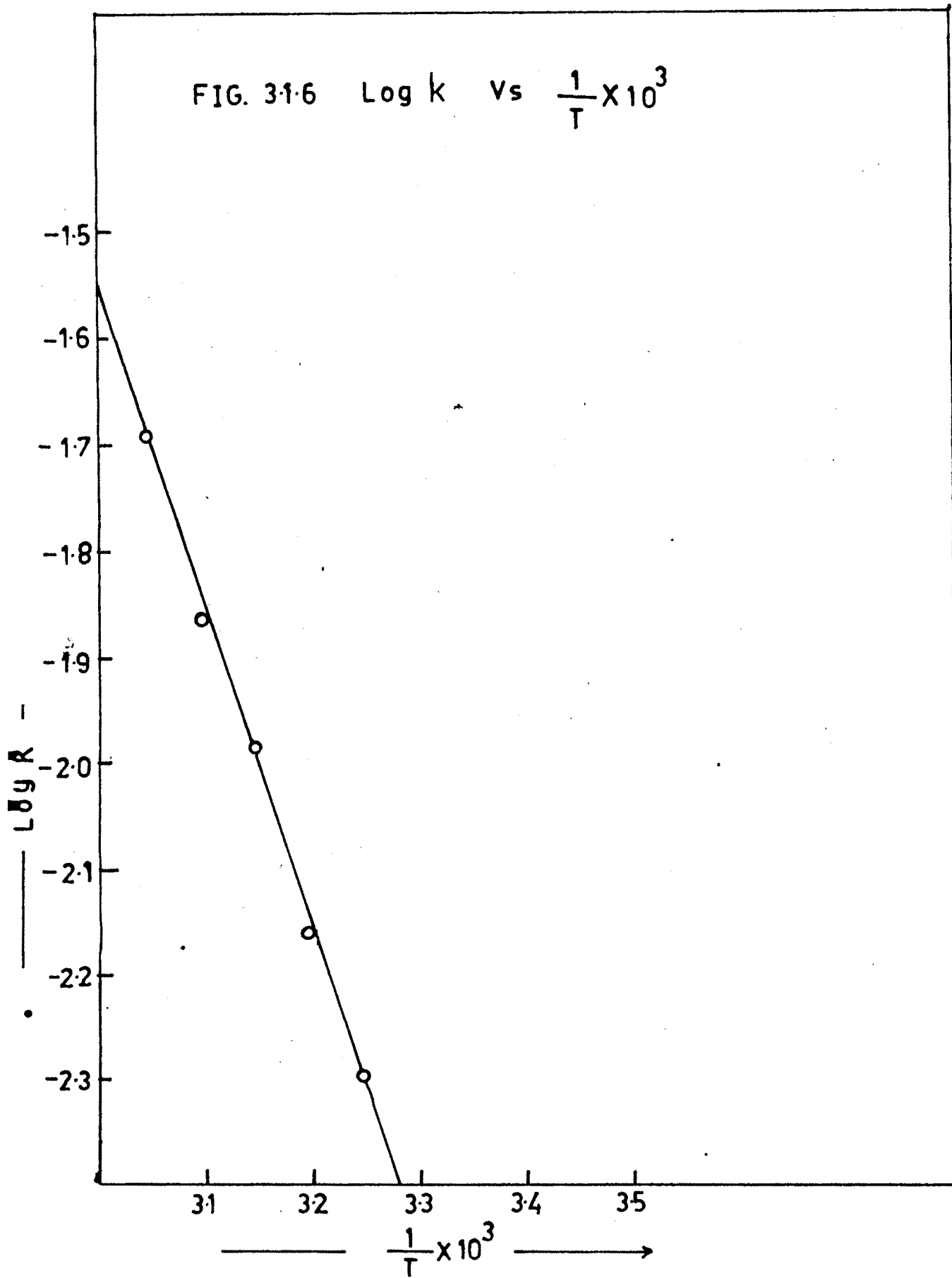
II = 40°C

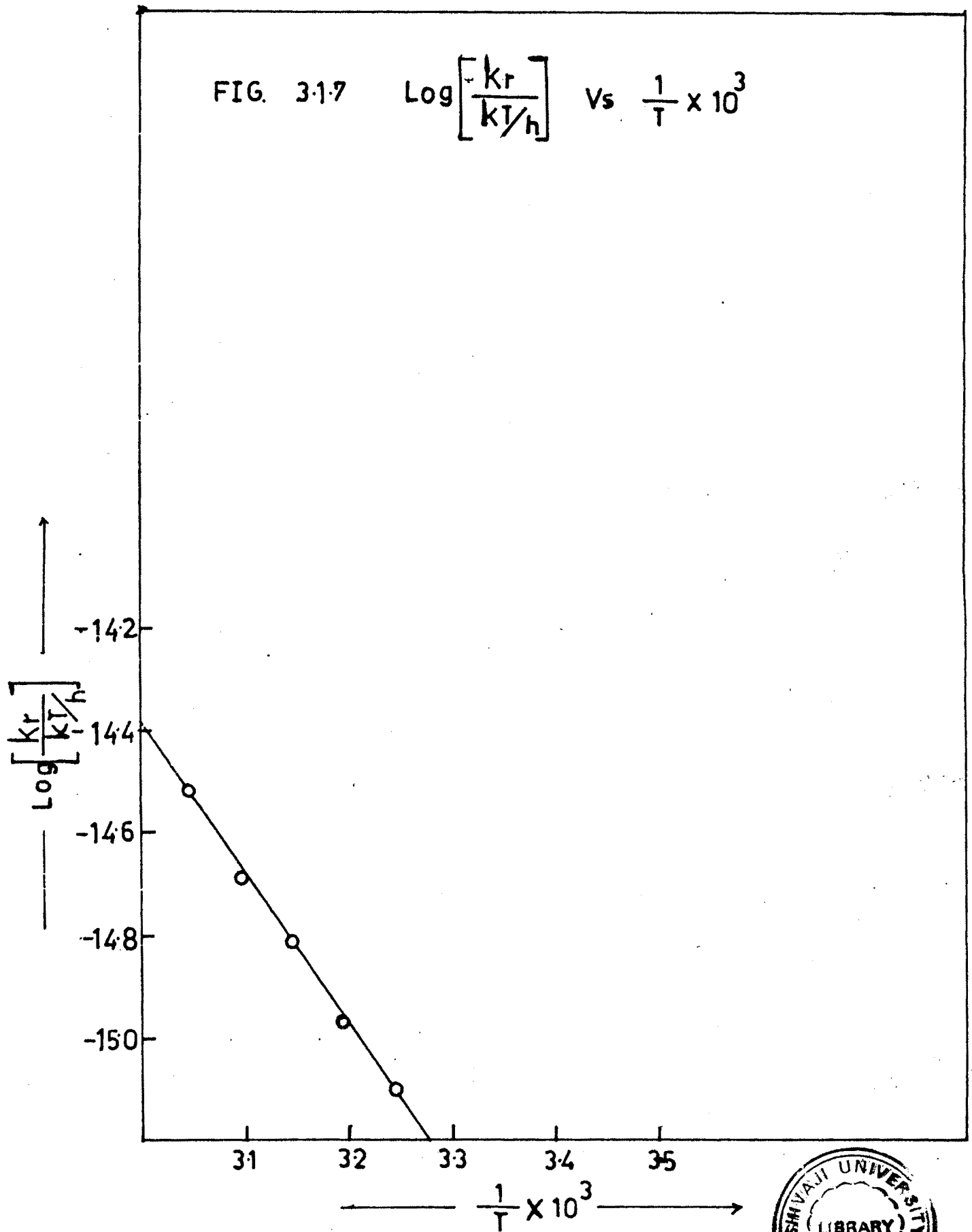
III = 45°C

IV = 50°C

V = 55°C







KINETICS OF OXIDATION OF n-HEPTANOIC ACID HYDRAZIDE (n-HAH)

Preliminary experiments were performed in order to decide the suitable temperature and concentration ranges of the reactants. It was observed that the reaction proceeds with measurable velocity at 40°C and at concentrations of n-HAH of $1.0 \times 10^{-2} M$, that of CAT = $1.0 \times 10^{-3} M$ and NaOH = $1.0 \times 10^{-2} M$. The kinetic data is recorded in the Table 3.2.1 given below:

TABLE 3.2.1

[n-HAH] = $1.0 \times 10^{-2} M$ [Na₂S₂O₃·5H₂O] = $5.0 \times 10^{-4} M$
 [CAT] = $1.0 \times 10^{-3} M$ [NaOH] = $1.0 \times 10^{-2} M$, Temp = 40°C

Time (min)	Vol.(ml) of Na ₂ S ₂ O ₃	k x 10 ³ min ⁻¹
00	19.70	-
10	18.45	6.40
20	17.35	6.33
30	16.30	6.29
40	15.30	6.31
50	14.35	6.24
60	13.50	6.29
70	12.65	6.32
80	11.90	6.30
90	11.20	6.27
100	10.50	6.29
120	9.25	6.29
140	8.20	6.25
160	7.20	6.29
Mean k x 10 ³ min ⁻¹		6.29

An examination of the above data closely shows that pseudo first order specific rate is almost constant. In this experiment the hydrazide concentration is in excess (10 times) over that of CAT concentration.

1) EFFECT OF CHLORAMINE-T CONCENTRATION

In order to investigate the effect of concentration of CAT on the reaction, kinetic runs were performed in which the concentration of CAT was varied, whereas that of $(n\text{-HAE})$ and $[\text{NaOH}]$ were 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 values of first order rate constant (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.

TABLE 3.2.2

$$[n\text{-HAH}] = 1.0 \times 10^{-2} \text{M} \quad [\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}] = 5.0 \times 10^{-4} \text{M}$$

$$[\text{NaOH}] = 1.0 \times 10^{-2} \text{M} \quad \text{Temp} = 40^\circ\text{C}$$

Conc. of CAT = $\text{M} \times 10^3$	0.5	1.00	1.50	2.00	2.50
Time (min)	Vol. (in ml) of $\text{Na}_2\text{S}_2\text{O}_3$				
0	9.60	19.70	29.80	39.80	49.00
10	9.00	18.45	27.90	37.30	46.00
20	8.45	17.35	26.20	35.05	43.30
30	7.95	16.30	24.55	32.90	40.75
40	7.50	15.30	23.00	30.85	38.40
50	7.00	14.35	21.00	29.00	36.10
60	6.60	13.50	20.25	28.20	34.00
70	6.20	12.65	19.00	25.50	32.15
80	5.85	11.90	17.80	23.95	30.30
90	5.50	11.20	16.75	22.60	28.50
100	5.20	10.50	15.70	21.25	26.85
120	4.60	9.25	13.80	18.80	23.80
140	4.10	8.20	12.15	-	-
160	-	7.20	-	-	-
Mean $k \times 10^3 \text{ min}^{-1}$	6.23	6.29	6.49	6.28	6.09

To determine the order of reaction w.r.t. CAT, the values of $-dc/dt$ were evaluated by plotting the volume of $\text{Na}_2\text{S}_2\text{O}_3$ (equivalent to CAT) against time for different initial concentrations of oxidant. These values are tabulated in the Table 3.2.3.

TABLE 3.2.3

Initial conc. CAT=C ₀ X10 ³	$-\frac{dc}{dt} \times 10^5$	log C ₀	log $[-\frac{dc}{dt}]$
0.5	0.5689	- 3.3010	- 5.2464
1.0	1.145	- 3.00	- 4.9411
1.5	1.725	- 2.8239	- 4.7634
2.0	2.287	- 2.6989	- 4.6406
2.5	2.893	- 2.6020	- 4.5386

The order of reaction w.r.t., CAT has been determined from the plot of Log $[-dc/dt]$ Vs Log C₀ (Fig. 3.2.2) which comes out to be 0.98. This establishes the first order behaviour of the reaction w.r.t. CAT.

The above values of $-dc/dt$ and $[CAT]_0$ i.e. C₀ substituted in the Van't Hoff equation i.e.

$$n = \frac{\text{Log}[-dc/dt]_1 - \text{Log}[-dc/dt]_2}{\text{Log}[C_0]_1 - \text{Log}[C_0]_2}$$

where n = order of reaction.

The results have been recorded in Table 3.2.4

TABLE 3.2.4

$[CAT]_0 \times 10^3$	$(-dc/dt) \times 10^5$	Order of reaction(n)
0.5	0.5689	1.01
1.0	1.145	
1.0	1.145	1.01
1.5	1.725	
1.50	1.725	0.98
2.0	2.875	
2.0	2.2875	-1.05
2.5	2.8928	

2) EFFECT OF HYDRAZIDE [n-HAH] CONCENTRATION

In order to investigate effect of hydrazide concentration on the rate of oxidation of n-Heptanoic acid hydrazide, the hydrazide concentration was varied from $0.5 \times 10^{-2} M$ to $2.5 \times 10^{-2} M$. Keeping the concentration of CAT NaOH constant, the results of these kinetic runs are tabulated in Table 3.2.5 and depicted graphically in Fig. 3.2.3.

TABLE 3.2.5

[CAT] = $1.0 \times 10^{-3} \text{M}$. $[\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}] = 5.0 \times 10^{-4} \text{M}$
 [NaOH] = $1.0 \times 10^{-2} \text{M}$ Temp = 40°C

[n-HAH]= $\text{M} \times 10^2$	0.5	1.0	1.5	2.0	2.5
Time (min)	Vol. (in ml) of $\text{Na}_2\text{S}_2\text{O}_3$				
0	19.70	19.70	19.70	19.70	19.70
10	19.05	18.45	17.95	17.40	16.85
20	18.50	17.35	16.40	15.35	14.40
30	17.90	16.30	14.90	13.55	12.50
40	17.35	15.30	13.60	12.00	10.80
50	16.80	14.35	12.40	10.70	9.40
60	16.30	13.50	11.30	9.60	8.05
70	15.80	12.65	10.30	8.60	6.90
80	15.30	11.90	9.40	7.60	6.00
90	14.85	11.20	8.60	6.85	5.20
100	14.40	10.50	7.85	6.10	4.50
120	13.60	9.25	6.50	4.95	-
140	12.80	8.20	5.45	-	-
160	-	7.20	-	-	-
Mean $k \times 10^3 \text{min}^{-1}$	3.16	6.29	9.24	12.06	15.06

The results contained in Table 3.2.5 show that the first order rate constant increases with increase in hydrazide concentration. The plots of Log C. Vs time 't' (Fig 3.2.3) are found to be linear. The second order rate constant k_2 .

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

where k_2 = Second order rate constant and

k_1 = First order rate constant.

k_2 is found to be constant (Table 3.2.6), indicating the first order dependence of the rate on hydrazide concentration.

TABLE 3.2.6

$[\text{HAH}]_0 = M \times 10^2$	$k_1 \times 10^3 \text{ min}^{-1}$	$k_2 \times 10^1 \text{ min}^{-1}$
0.50	3.16	6.32
1.00	6.29	6.29
1.50	9.24	6.16
2.00	12.06	6.03
2.50	15.06	6.02

The order w.r.t. n-Heptanoic acid hydrazide was also determined by Van't Hoff differential method. The values of $-dc/dt$ and initial concentrations of hydrazide (C_0) are given in the Table 3.2.7 and these values are substituted in the Van't Hoff's equation i.e.

$$n = \frac{\text{Log} [-dc/dt]_1 - \text{Log} [-dc/dt]_2}{\text{Log} [C_0]_1 - \text{Log} [C_0]_2}$$

The order of reaction was calculated which is found to be almost Unity (one).

The volume of $\text{Na}_2\text{S}_2\text{O}_3$ (equivalent to CAT) was plotted against time for different initial concentrations of hydrazide. From the curves, the value of $-\text{dc}/\text{dt}$, the initial rate, in each case was determined from initial slope as given in Table 3.2.8

TABLE 3.2.7

$[\text{n-HAH}]_0 \times 10^2 \text{M}$	$-\text{dc}/\text{dt} \times 10^5$	Order of reaction (n)
0.50	0.58	0.98
1.00	1.16	
1.00	1.16	1.04
1.50	1.76	
1.50	1.76	1.00
2.00	2.35	
2.00	2.35	1.02
2.50	2.95	

TABLE 3.2.8

$[\text{n-HAH}]_0$ $C_0 = \text{M} \times 10^2$	$-\frac{\text{dc}}{\text{dt}}_0 \times 10^5$	$\text{Log } C_0$	$\text{Log } [-\text{dc}/\text{dt}]$
0.50	0.58	- 2.30	- 5.23
1.00	1.16	- 2.00	- 4.94
1.50	1.76	- 1.82	- 4.75
2.00	2.35	- 1.70	- 4.63
2.50	2.95	- 1.60	- 4.53

In order to confirm the order of reaction w.r.t. n-Heptanoic acid hydrazide, from the plot of $\log [-\text{dc}/\text{dt}]$ Vs $\text{Log } C_0$ (represented in Fig 3.2.4), the value of the order

w.r.t. n-HAH has been evaluated which comes out to be 1.01. This confirms the first order behaviour of the reaction w.r.t. (n-HAH).

3) EFFECT OF SODIUM HYDROXIDE CONCENTRATION

In order to study the effect of alkali concentration on the rate of oxidation of n-HAH, the concentration of NaOH was varied from $0.5 \times 10^{-2} \text{ M}$ to $2.5 \times 10^{-2} \text{ M}$, keeping the concentration of other reactants constant. The results of these kinetic runs are recorded in Table 3.2.9.

TABLE 3.2.9

$[\text{n-HAH}] = 1.0 \times 10^{-2} \text{ M}$		$[\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}] = 5.0 \times 10^{-4} \text{ M}$			
$[\text{CAT}] = 1.0 \times 10^{-3} \text{ M}$		Temp = 40°C			
$[\text{NaOH}] = \text{M} \times 10^2$	0.5	1.0	1.5	2.0	2.5
Time (min)	Vol. (in ml) of $\text{Na}_2\text{S}_2\text{O}_3$				
0	19.70	19.70	19.60	19.60	19.70
10	18.50	18.45	18.50	18.45	18.45
20	17.40	17.35	17.30	17.30	17.30
30	16.35	16.30	16.25	16.30	16.20
40	15.40	15.30	15.30	15.20	15.20
50	14.45	14.35	14.40	14.30	14.25
60	13.60	13.50	13.45	13.50	13.50
70	12.75	12.65	12.60	12.60	12.55
80	12.00	11.90	11.90	11.90	11.90
90	11.20	11.20	11.15	11.10	11.05
100	10.70	10.50	10.00	9.40	9.40
120	9.40	9.25	9.20	9.20	9.10
140	8.35	8.20	8.15	8.10	8.00
160	7.40	7.20	7.10	7.15	7.05
Mean $k \times 10^3 \text{ min}^{-1}$	6.18	6.29	6.25	6.33	6.51

Examination of the above results shows that, the effect of hydroxide ion concentration is negligible and hence the rate of reaction is independent of alkali concentration.

4) EFFECT OF CHLORIDE ION CONC. ON THE RATE OF OXIDATION OF n-HAH :

To investigate the effect of addition of chloride ion on the rate of oxidation of n-HAH, the concentration of NaCl was varied from 0.0M to 4.0×10^{-2} M, keeping all the other concentrations constant. The results are listed in the

Table 3.2.10

TABLE 3.2.10

$$[n\text{-HAH}] = 1.0 \times 10^{-2} \text{M} \quad [\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}] = 5.0 \times 10^{-4} \text{M}$$

$$[\text{CAT}] = 1.0 \times 10^{-3} \text{M} \quad [\text{NaOH}] = 1.0 \times 10^{-2} \text{M} \quad \text{Temp} = 40^\circ \text{C}$$

[NaCl]=Mx10 ²	0.00	1.0	2.0	3.0	4.0
Time (min)	Vol. (in ml) of Na ₂ S ₂ O ₃				
0	19.70	19.70	19.60	19.70	19.70
10	18.45	18.50	18.35	18.45	18.40
20	17.35	17.40	17.20	17.30	17.20
30	16.30	16.40	16.10	16.20	16.05
40	15.30	15.45	15.10	15.20	15.00
50	14.35	14.50	14.15	14.25	14.00
60	13.50	13.70	13.30	13.50	13.10
70	12.65	12.90	12.45	12.55	12.25
80	11.90	12.10	11.70	11.90	11.45
90	11.20	11.40	10.90	11.05	10.70
100	10.50	10.75	10.20	9.35	10.00
120	9.25	9.50	9.00	9.10	8.75
140	8.20	8.45	7.95	8.00	7.70
160	7.20	7.50	7.00	7.05	6.70
Mean kx10 ³ min ⁻¹	6.29	6.09	6.51	6.42	6.78

An examination of the results contained in the above table shows that the effect of chloride ion is negligible.

5) EFFECT OF CHANGE IN IONIC STRENGTH OF THE MEDIUM

To study the effect of change in ionic strength of the medium on the rate of oxidation of hydrazide, the concentration of potassium chloride is varied from $0.5 \times 10^{-1} \text{M}$ to $2.5 \times 10^{-1} \text{M}$, keeping all other concentrations constant. The results of which are recorded in the table 3.2.11

TABLE 3.2.11

$[\text{n-HAH}] = 1.0 \times 10^{-2} \text{M}$		$[\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}] = 5.0 \times 10^{-4} \text{M}$			
$[\text{CAT}] = 1.0 \times 10^{-3} \text{M}$		$[\text{NaOH}] = 1.0 \times 10^{-2} \text{M}$ Temp = 40°C			
$[\text{KCl}] = \text{M} \times 10^1$	0.5	1.0	1.5	2.0	2.5
μ	0.061	0.111	0.161	0.211	0.261
Time (min)	Vol. (in ml) of $\text{Na}_2\text{S}_2\text{O}_3$				
0	19.70	19.70	19.60	19.80	19.70
10	18.45	18.45	18.30	18.45	18.30
20	17.35	17.30	17.15	17.25	17.05
30	16.30	16.20	16.00	16.10	15.90
40	15.30	15.20	15.00	15.00	14.80
50	14.35	14.25	14.05	14.05	13.75
60	13.50	13.50	13.10	13.10	12.80
70	12.65	12.50	12.30	12.25	11.90
80	11.90	11.90	11.50	11.40	11.20
90	11.20	11.00	10.75	10.70	10.35
100	10.50	9.35	10.05	10.00	9.65
120	9.25	9.15	8.80	8.70	8.40
140	8.20	8.00	7.75	7.60	7.30
160	7.20	7.05	6.80	6.70	6.40
Mean $K \times 10^3 \text{ min}^{-1}$	6.29	6.52	6.69	6.87	7.16

A perusal of the data contained in this table shows that the change of ionic strength (μ) of the medium has marginal effect on the rate of oxidation of hydrazide.

6) EFFECT OF TEMPERATURE

In order to determine the temperature coefficient, energy of activation (E_a), enthalpy of activation (ΔH^\ddagger), frequency factor (A), free energy of activation (ΔG^\ddagger) and entropy of activation (ΔS^\ddagger), the reaction was studied at five different temperatures ranging from 35°C to 55°C . The results of these kinetic runs have been tabulated in Table 3.2.12 and depicted graphically in Fig. 3.2.5.

TABLE 3.2.12

$$[\text{n-HAH}] = 1.0 \times 10^{-2} \text{ M} \quad [\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}] = 5.0 \times 10^{-4} \text{ M}$$

$$[\text{CAT}] = 1.0 \times 10^{-3} \text{ M} \quad [\text{NaOH}] = 1.0 \times 10^{-2} \text{ M}$$

Temp $^\circ\text{C}$	35°	40°	45°	50°	55°
Time (min)	Vol. (in ml) of $\text{Na}_2\text{S}_2\text{O}_3$				
0	19.70	19.70	19.70	19.70	19.70
5	-	-	18.90	18.45	18.10
10	18.85	18.45	18.15	17.30	16.75
15	-	-	17.40	16.20	15.40
20	18.10	17.35	16.75	15.20	14.30
25	-	-	16.10	14.30	13.20
30	17.35	16.30	15.45	13.40	12.20
35	-	-	14.80	12.60	11.30
40	16.60	15.30	14.25	11.85	10.45
45	-	-	13.70	11.15	9.70
50	15.95	14.35	13.20	10.50	9.00
60	15.30	13.50	12.20	9.40	7.75
70	14.40	12.65	11.25	8.40	6.60
80	14.10	11.90	10.40	7.65	5.75
90	13.80	11.20	9.60	6.80	5.00
100	13.00	10.50	8.90	6.00	4.40
120	12.05	9.25	7.60	4.85	-
140	11.10	8.20	-	-	-
160	10.30	7.20	-	-	-
Mean $k \times 10^3 \text{ min}^{-1}$	4.20	6.29	8.08	12.51	15.83

It is seen from the above results (Table 3.2.12) that the specific rate has approximately doubled for 10°C rise in temperature.

A plot of $\text{Log } k$ Vs $1/T$ as shown in Fig 3.2.6 is found to be linear showing that the reaction obeys the Arrhenius relationship. The value of energy of activation (E_a) evaluated from the slope of this curve comes out to be 14.08 K.Cals mole⁻¹. The Arrhenius equation has been used directly to calculate energy of activation, which comes out to be 13.26 K. Cals mole⁻¹. On the basis of this value, the frequency factor (A) and entropy of activation (ΔS^\ddagger) have been calculated.

Plot of $\text{Log } \frac{k_r}{kT/h}$ Vs $\frac{1}{T}$ (Fig 3.2.7) gives a straight line and from the slope of which the enthalpy change for the formation of activated complex (ΔH^\ddagger) has been calculated. The value of ΔH^\ddagger , (13.20 K.Cal Mole⁻¹) obtained from the graph has been used to calculate free energy of activation (ΔG^\ddagger) by the equation given in Section-I of temperature effect.

The various energy parameters obtained, have been recorded in Table 3.2.13.

TABLE 3.2.13

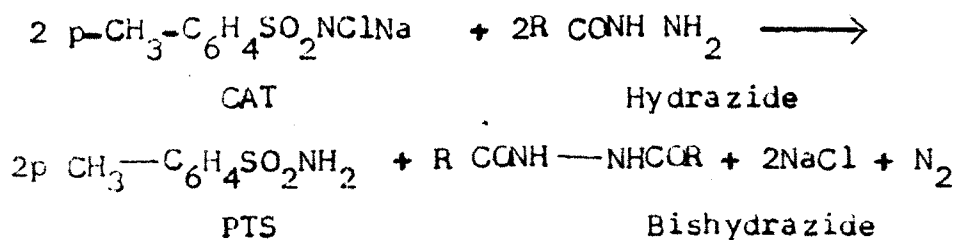
Temp k ^o	Temp co-effi- cient	Energy of activation(Ea) K.Cals mole ⁻¹	Frequency factory (A) Ax10 ⁻⁵ sec ⁻¹	Free energy (ΔG [‡]) K.cals.	Entropy of activa- tion [‡] (ΔS [‡]) e.u.
308			6.48	23.04	-32.02
313	1.96	13.18	7.05	23.16	-31.88
318	1.90	12.89	6.18	23.41	-32.17
323	1.92	13.70	6.65	23.53	-32.06
328			6.05	23.76	-32.28
Mean	1.93	13.26	6.48	23.38	-32.08

Enthalpy change (ΔH[‡]) by graph = 13.18 K.cal/mole⁻¹

Energy of activation(Ea)by graph= 14.08 K.cal/mole⁻¹

(1) STOICHIOMETRY :

The ratio of Chloramine-T to hydrazide was varied in the presence of sodium hydroxide and was equilibrated at 35^oC for 24 hours. The estimation of unreacted chloramine-T indicated that one mole of Chloramine-T was consumed for one mole of hydrazide. The Stoichiometry was found to be 1:1 which can be represented as below :

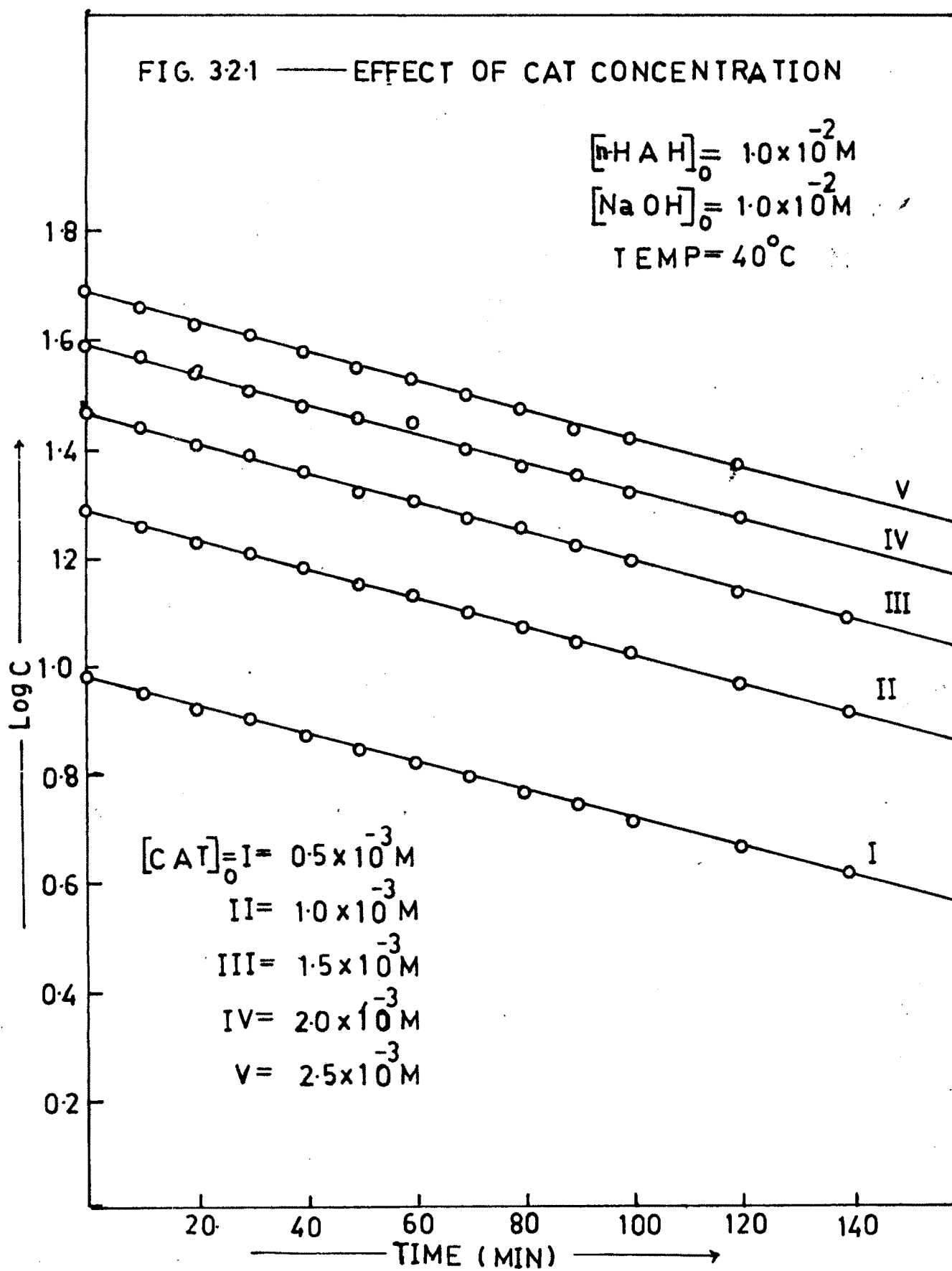


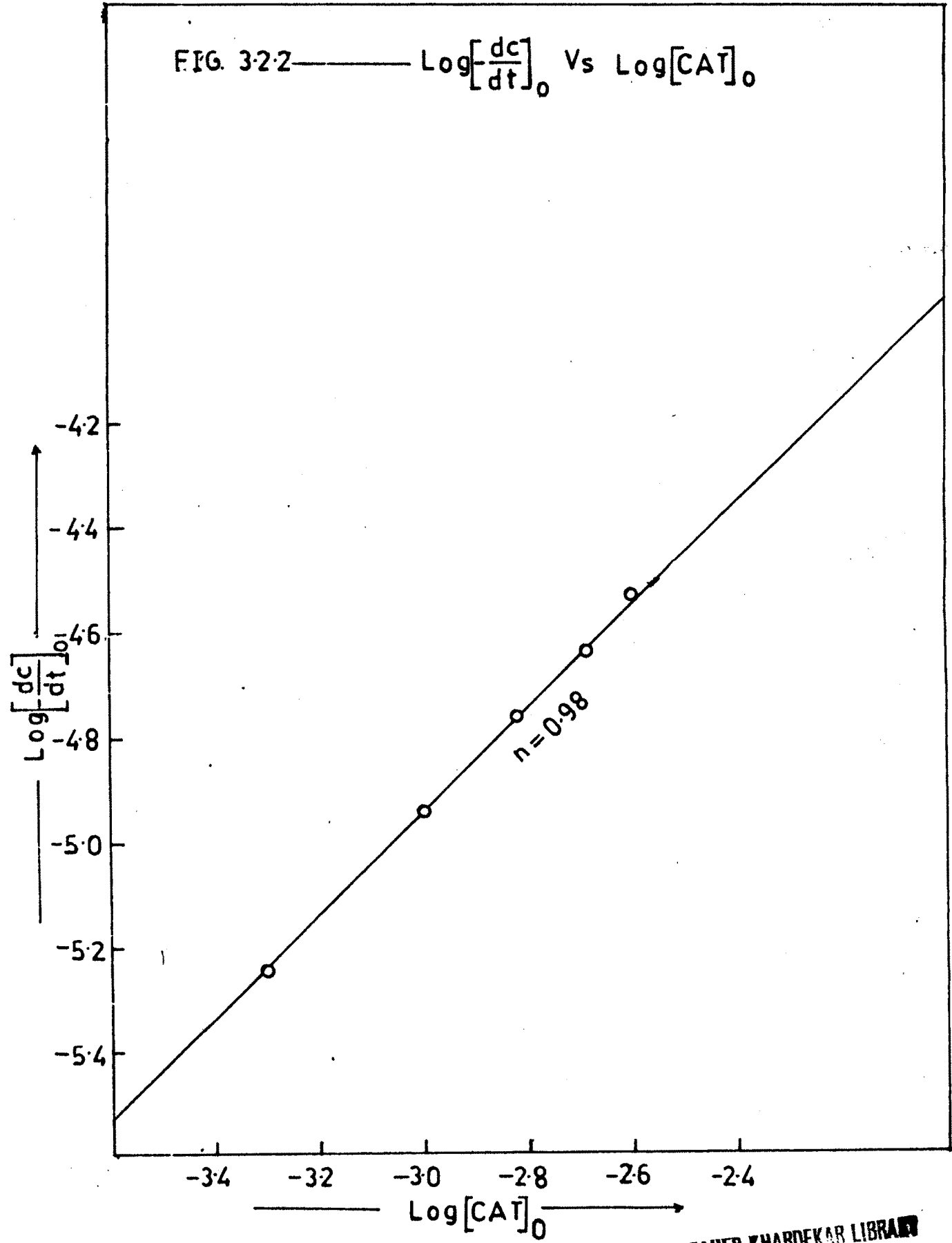
(2) PRODUCT ANALYSIS :

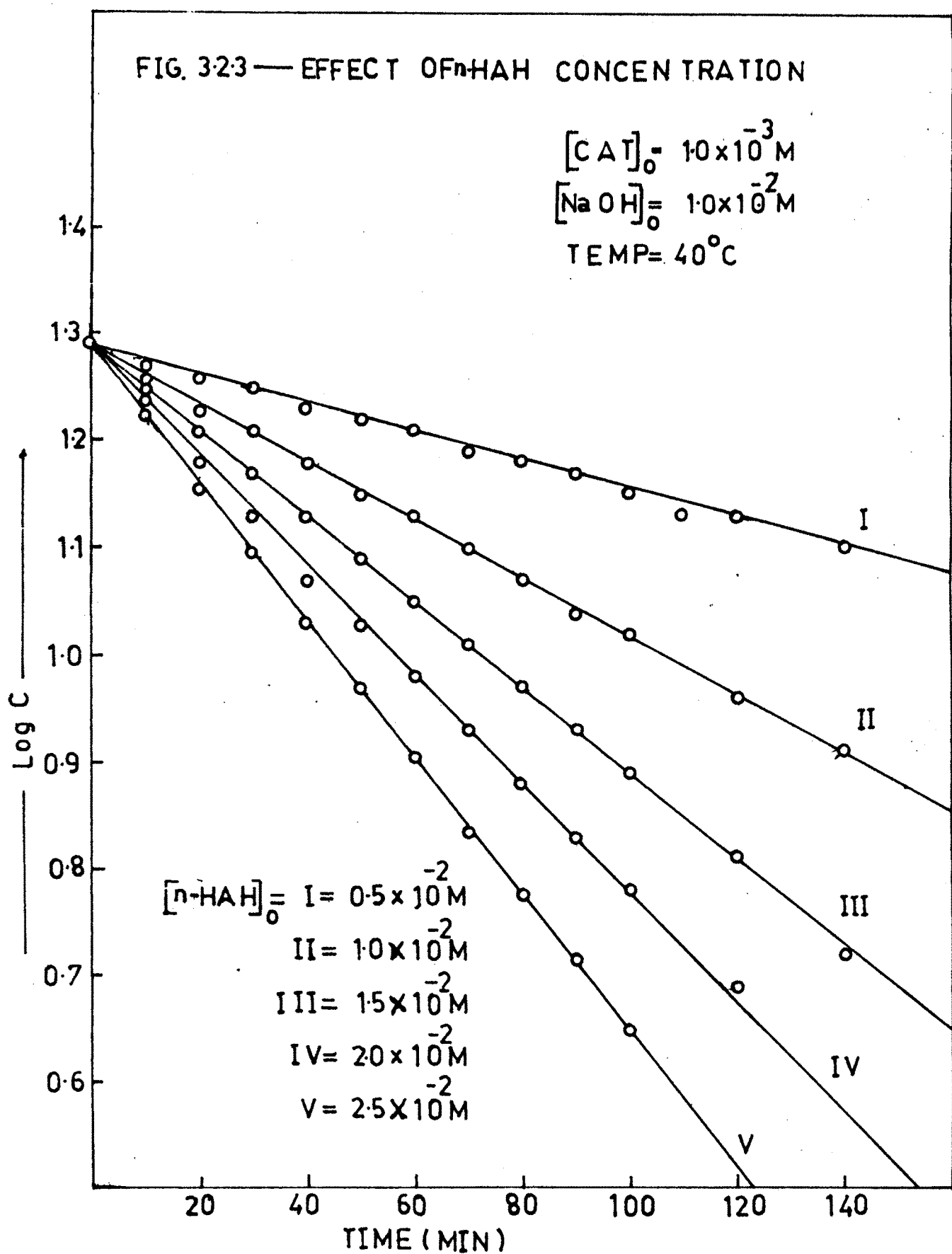
The knowledge of the products formed in a reaction, subjected to the kinetic study, is an important step in elucidation of the mechanism of a reaction. Therefore, it was necessary to identify the products formed in the reaction.

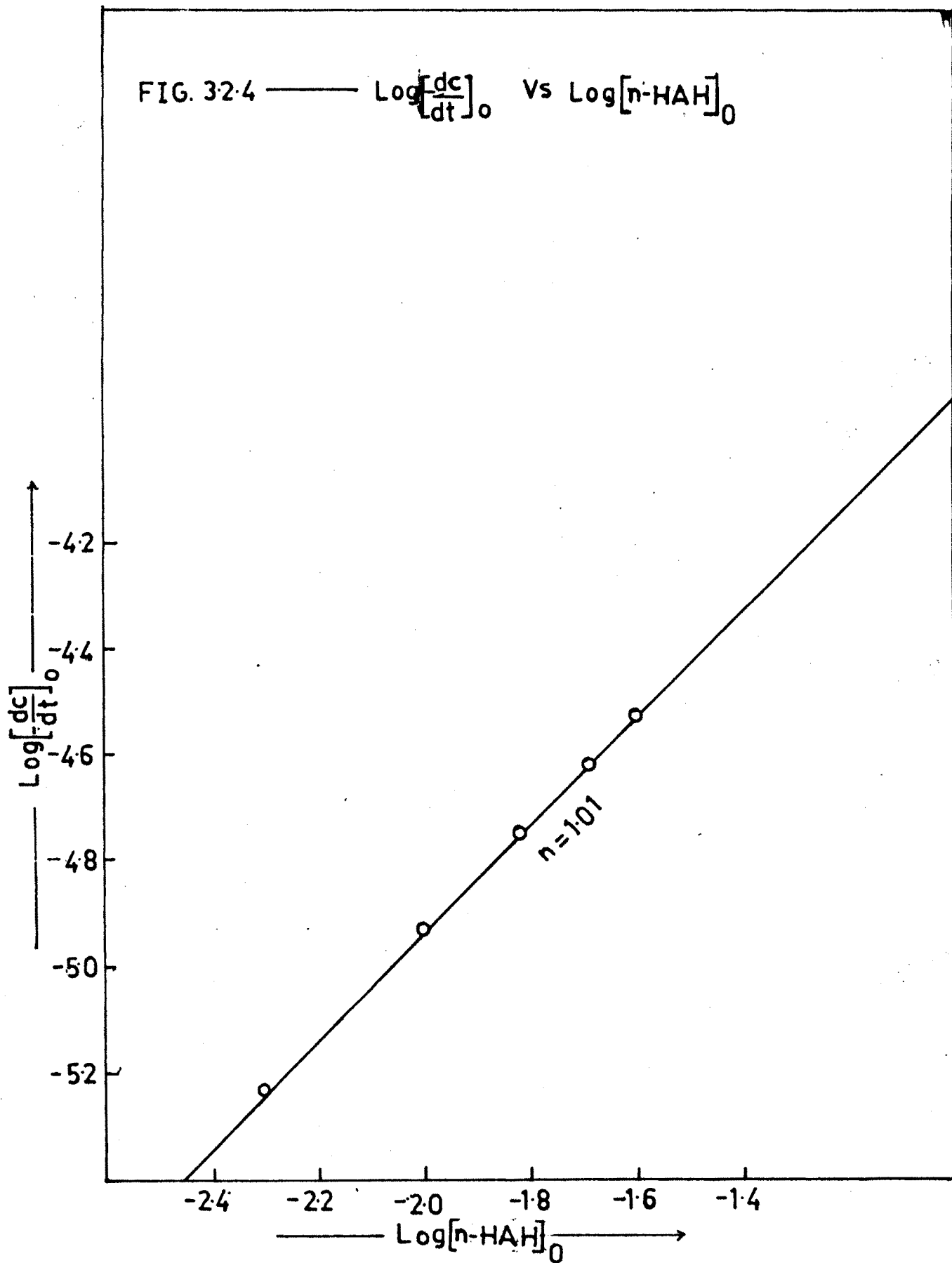
Detection of p-toluene sulphonamide has been done by paper chromatographic method. Benzyl alcohol saturated with water was used as the solvent. 0.5 % Vaniline in 1 % HCl solution in ethanol was used as the spraying reagent.

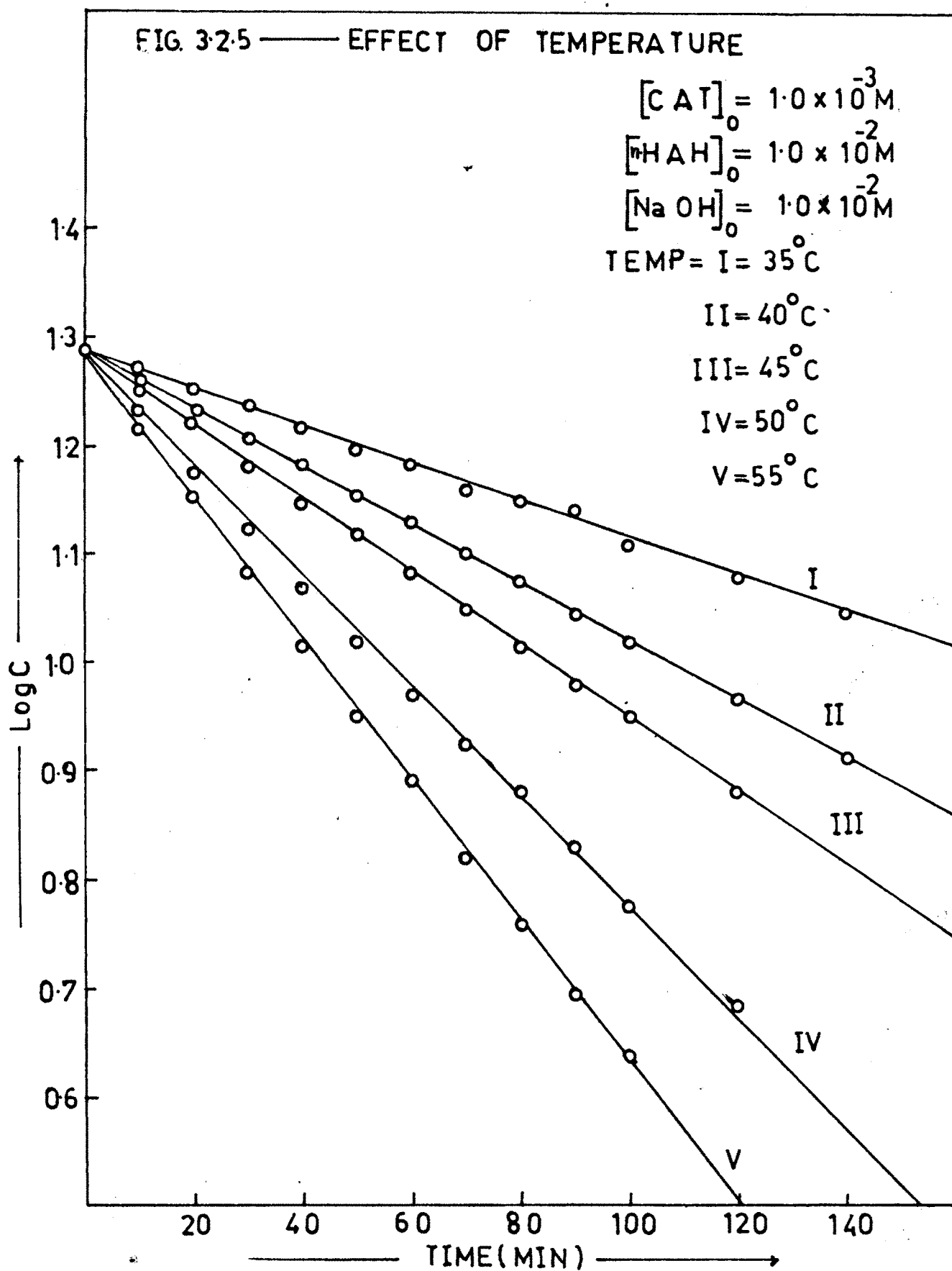
The oxidation product, bishydrazide was identified by TLC with authentic samples prepared by the literature method. Nitrogen is detected by lime test.^{1,2}

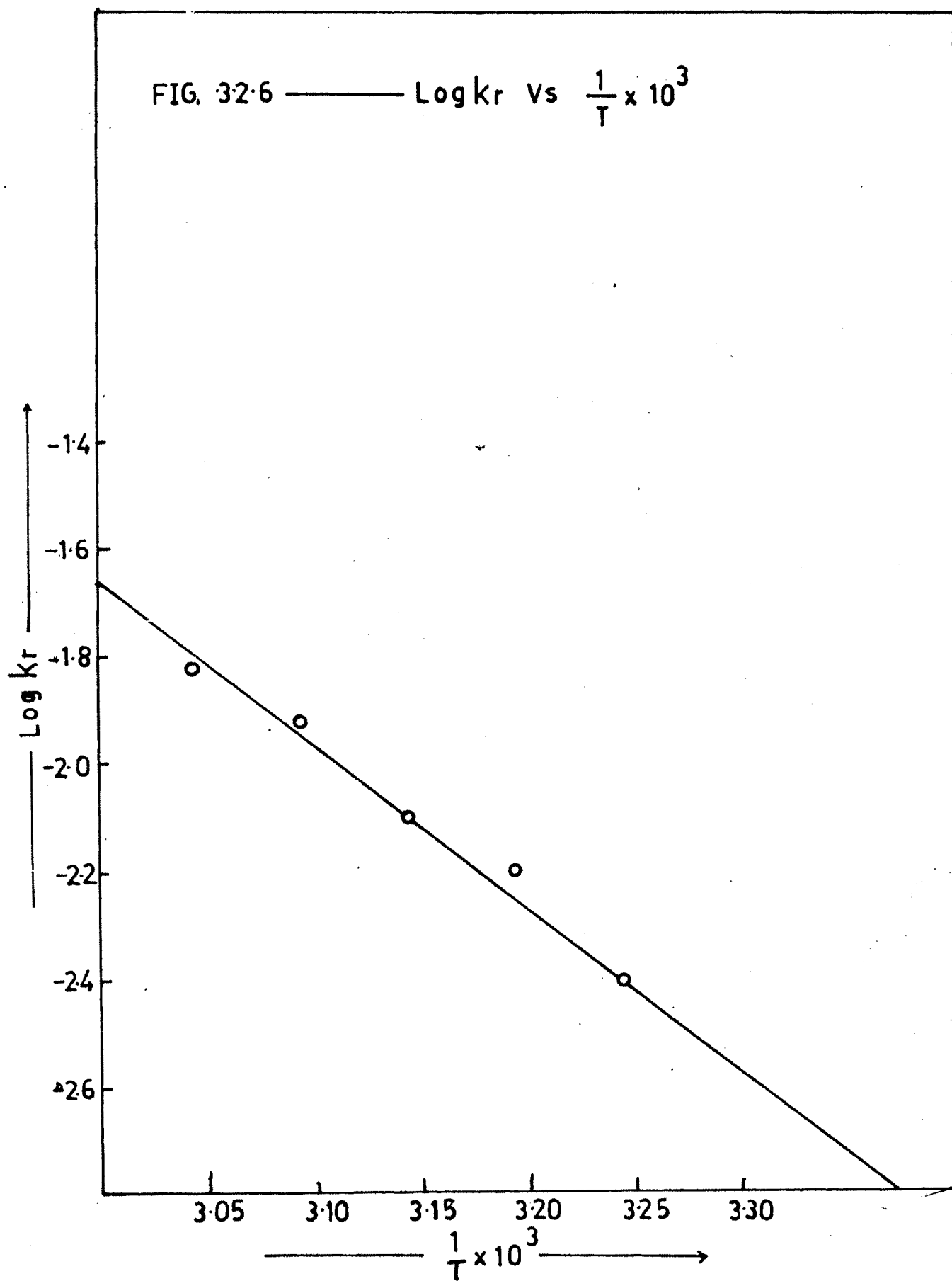


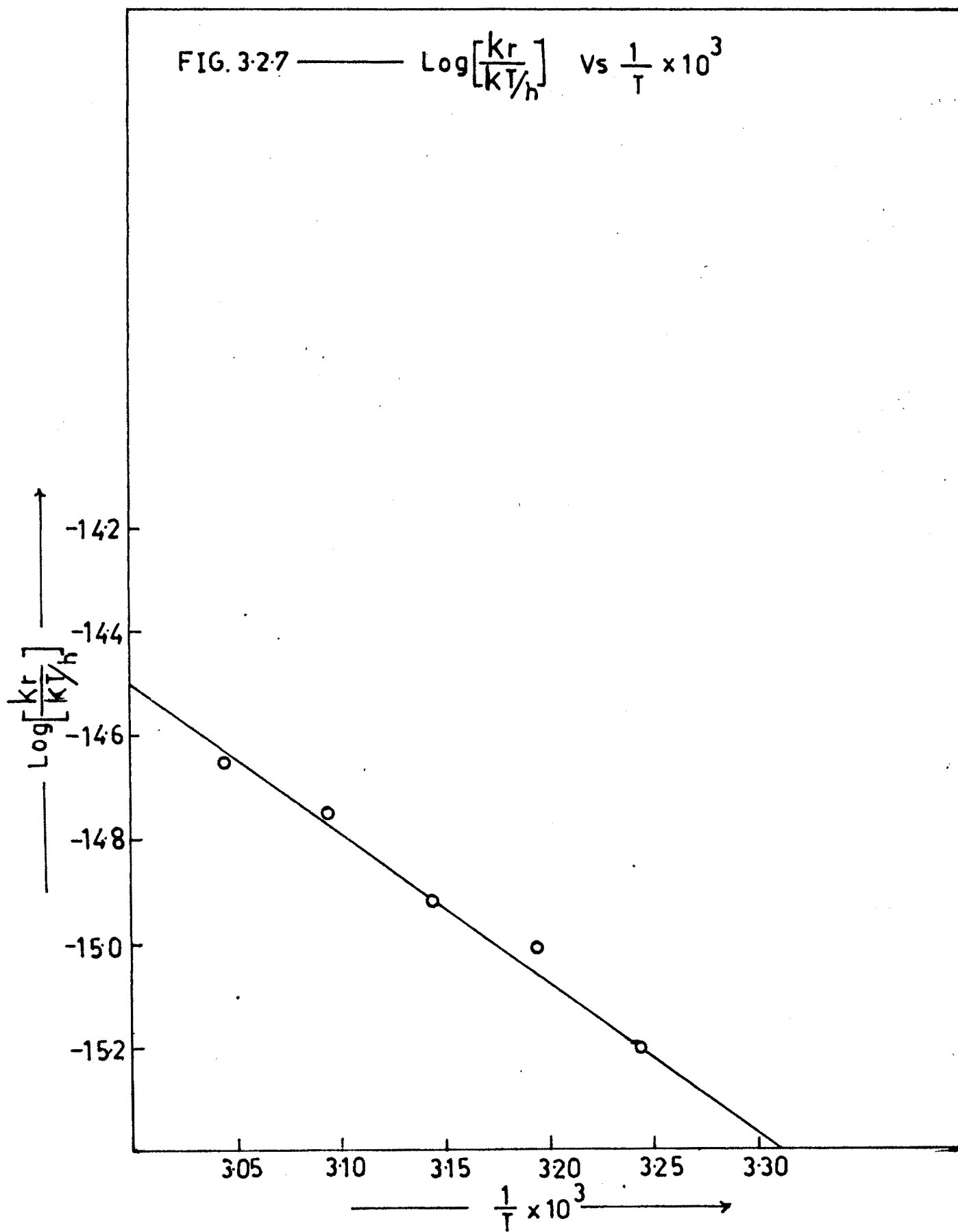












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