CHAPTER III

CHAPTER-III

RESULTS

SECTION-A

KINETICS OF OXIDATION OF ISO-NICOTINIC ACID HYDRAZIDE

In this chapter a detailed kinetic study of oxidation of iso-NICOTINIC and NICOTINIC ACID HYDRAZIDES is presented. The hexacyanoferrate(III), iso-Nicotinic acid hydrazide, sodium hydroxide and potassium chloride were used in requisite concentrations to prepare the reaction mixture and optical density was measured at 420 nm wavelength as a function of time. Experiments were set to include the following studies.

1. Overall order of the reaction and order w.r.t. reactants.

2. Effect of Hexacyanoferrate (III) concentration on the rate of the reaction.

3. Effect of Hydrazide concentration on the rate of reaction.

4. Effect of sodium hydroxide concentration.

5. Effect of temperature and evaluation of thermodynamic parameters.

6. Effect of potassium chloride concentration.

7. Effect of dielectric constant of the medium.

8. End product analysis and free radical tests.

Preliminary experiments were performed so as to decide the suitable temperature and concentrations of the reactants. It was observed that in the presence of 0.0005 M. $K_3Fe(CN)_6$, 0.0075 M

hydrazide, 0.0003 M NaOH, 0.004 M KCl and 35°C temperature. The reaction proceeds with measurable velocity. The Table 3:A:1 embodies the results of kinetic run for same.

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TABLE 3:A:1

[iso-NAH] = 7.5×10^{-3} M $\qquad$ [HCF(IIII)] = 5.0×10^{-4} M

[$\overline{OH}$] $\quad = 3.0 \times 10^{-4}$ M $\qquad$ [$\overline{Cl}$] $\quad = 4.0 \times 10^{-3}$ M

Temp $\quad = 35°C$ $\qquad$ λ max $\quad = 420$ nm

Time in min.	Optical Density O.D.	$k \times 10^2$ min^{-1}
0	0.460	
5	0.430	1.34
10	0.400	1.39
15	0.380	1.27
20	0.360	1.22
30	0.325	1.15
40	0.290	1.15
50	0.260	1.14
60	0.230	1.15
70	0.205	1.15
80	0.190	1.10
90	0.175	1.07

Mean $k \times 10^2$ min^{-1} : 1.19

An examination of the above data closely shows that the first order rate constant goes on slightly decreasing with the time. This small decrease in the rate constant with time shows that either the reaction follows an order greater than one or the reaction is attended with inhibition during the course of reaction.

DETERMINATION OF ORDER OF THE REACTION :

The determination of the order of reaction w.r.t. hexacyanoferrate (III) was done by isolation method. The concentration of hexacyanoferrate (III) was varied from 3.0×10^{-4} M to 7.0×10^{-4} M, keeping the concentration of iso-Nicotinic acid hydrazide and sodium hydroxide constant. The reaction was studied at 35°C.

However, the determination of the order of reaction w.r.t. iso Nicotinic acid hydrazide could not be done by isolation method as hexacyanoferrate (III), which is the abosrbing species could not be used in large excess as compared to iso-Nicotinic acid hydrazide. Hence, comparable concentrations of hexacyanoferrate (III) and iso-Nicotinic acid hydrazide were selected to determinee overall order of the reaction. For this, hexacyanoferrate (III) concentration was kept constant (5.0×10^{-4} M), while iso-Nicotinic acid hydrazide concentration was varied from 5.5×10^{-3} M to 9.5×10^{-3} M.

EFFECT OF HEXACYANOFERRATE(III) CONCENTRATION :

In order to investigate the effect of hexacyanoferrate (III) concentration on the specific rate, and to determine the order

of the reaction with respect to hexacyanoferrate (III), the reaction was carried out at five different initial concentrations of hexacyanoferrate (III) keeping the concentrations of hydrazide, NaOH and KCl constant.

The kinetic data for the same is recorded in the Table 3:A:2. The value of first order rate constant has been evaluated at different time intervals by integration method using the formula :

$$k = (2.303/t) \log (a/a-x)$$

TABLE 3:A:2

[iso-NAH] = 7.5×10^{-3} M   [$\overline{Cl}$] = 4.0×10^{-3} M

[$\overline{OH}$] = 3.0×10^{-4} M   Temp = 35°C.

λ max = 420 nm

[HCF(III)] M x 10^4 M	3.0	4.0	5.0	6.0	7.0
Time in min	O.D.	O.D.	O.D.	O.D.	O.D.
0	0.280	0.375	0.460	0.565	0.645
5	0.265	0.350	0.430	0.520	0.590
10	0.250	0.330	0.400	0.485	0.545
15	0.240	0.315	0.380	0.455	0.510
20	0.230	0.295	0.360	0.425	0.470
30	0.210	0.275	0.325	0.375	0.425
40	0.195	0.245	0.290	0.335	0.380
50	0.165	0.225	0.260	0.300	0.335
60	0.155	0.205	0.230	0.270	0.305
70	0.140	0.185	0.205	0.240	0.275
80	0.130	0.170	0.190	0.215	0.245
90	0.120	0.155	0.175	0.195	0.220
Mean $k \times 10^2$ min^{-1}	1.00	1.09	1.19	1.33	1.40

A perusal of the above data shows that when hydrazide concentration is in excess and by increasing the initial concentration of hexacyanoferrate (III) the pseudo first order specific rate increases with increase in oxidant concentration, showing that the rate of disappearance of hexacyanoferrate (III) obeys the first order kinetics.

The most important step in the elucidation of the mechanism of the reaction is the determination of the order of reaction. The determination of the order of the reaction can be done by one of the several methods available, provided that the reaction is not complicated by consecutive reaction, reverse reaction side reaction or other factors which influence the rate.

The order w.r.t. hexacyanoferrate (III) was determined by van't Hoff differential method. The optical density of the hexacyanoferrate (III) was plotted against time for initial concentrations of hexacyanoferrate (III), from these curves the value of initial rate (-dA/dt) in each case was determined from initial slope, from which the value of (-dc/dt) was calculated by multiplying $1/\epsilon$, which was obtained by plotting optical density Vs concentration of hexacyanoferrate (III) and value was found to be ϵ = 961 litres mole^{-1} cm.$^{-1}$

The values of -dc/dt and concentration of hexacyanoferrate (III) ie 'c' are substituted in the van't Hoff's differential equation ·

$$n = \frac{\log \left(\frac{-dC_{01}}{dt}\right) - \log \left(\frac{-dC_{02}}{dt}\right)}{\log C_1 - \log C_2}$$

and the order of the reaction 'n' was calculated. The values of initial rates -dc/dt for different initial concentrations of hexacyanoferrate (III) and the values of 'n' calculated thereby are recorded in Table 3:A:3

HCF(III) $M \times 10^4$	3.0	4.0	5.0	6.0	7.0
$\left(\frac{-dc}{dt}\right) \times 10^6$	3.12	4.14	5.20	6.24	7.31

TABLE 3:A:3

[HCF(III)] $M \times 10^4$	$(-dc/dt) \times 10^6$	Order of reaction 'n'
3.0	3.12	
4.0	4.14	0.98
4.0	4.14	
5.0	5.20	1.02
5.0	5.20	
6.0	6.24	1.00
6.0	6.24	
7.0	7.31	1.03

To confirm the order of reaction w.r.t. hexacyanoferrate (III) from the plot of log (-dc/dt) Vs log Co represented in Fig. 3:A:2. The value of the order with respect to hexacyanoferrate (III) has been evaluated, which comes out to be one. This confirms the first order behaviour with respect to hexacyanoferrate (III).

EFFECT OF HYDRAZIDE CONCENTRATION :

The effect of iso-Nicotinic acid hydrazide concentration on the rate of the reaction was studied at five different initial concentrations ie 5.5×10^{-3} to 9.5×10^{-3} M. keeping the concentrations of hexacyanoferrate (III) and sodium hydroxide constant. The results of these kinetic study are recorded in Table 3:A:4 and depicted graphically in Fig. 3:A:3.

TABLE 3:A:4

$[HCF(III)] = 5.0 \times 10^{-4} M$ $[Cl^-] = 4.0 \times 10^{-3}$ M
$[OH^-] = 3.0 \times 10^{-4}$ M   Temp $= 35°C$

λ max $= 420$ nm

$[iso-NAH]M \times 10^3$	5.5	6.5	7.5	8.5	9.5
Time in min	O.D.	O.D.	O.D.	O.D.	O.D.
0	0.460	0.460	0.460	0.460	0.460
5	0.430	0.430	0.430	0.425	0.420
10	0.410	0.405	0.400	0.395	0.390
15	0.395	0.385	0.380	0.375	0.360
20	0.380	0.365	0.360	0.350	0.330
30	0.345	0.330	0.325	0.305	0.295
40	0.315	0.295	0.290	0.265	0.260
50	0.290	0.265	0.260	0.235	0.225
60	0.275	0.245	0.230	0.205	0.200
70	0.235	0.220	0.205	0.180	0.175
80	0.215	0.200	0.190	0.165	0.160
90	0.195	0.180	0.175	0.145	0.150
Mean $K \times 10^2$ min	1.00	1.13	1.19	1.38	1.49

An examination of results given in Table 3:A:4 shows that first order rate constant increases with increase in initial concentration of hydrazide. The plots of log O.D. against time are linear. The second order rate constant.

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

Where, k_2 = second order rate constant.

k_1 = first order rate constant.

was found to be constant, indicating (Table 3:A:5), the first order dependence of the rate on hydrazide concentration.

TABLE 3:A:5

[iso-NAH] $M \times 10^3$	$k_1 \times 10^2$ min^{-1}	k_2 min^{-1} $mole^{-1}$
5.5	1.00	1.81
6.5	1.13	1.74
7.5	1.19	1.59
8.5	1.38	1.62
9.5	1.49	1.57

ORDER WITH RESPECT TO HYDRAZIDE :

The investigation of the order of the reaction w.r.t. hydrazide is done by subjecting the kinetic data of Table 3:A:3 to van't Hoff's differential method. From the initial slopes of

plots of optical density Vs time curves, the values of $(-dc/dt)_o$ corresponding to various initial concentrations of hydrazide were evaluated which are given in Table 3:A:6.

[iso–NAH] $M \times 10^3$	5.5	6.5	7.5	8.5	9.5
$(\dfrac{-dC}{dt})x$ 10^6	3.92	4.61	5.34	6.06	6.76

TABLE 3:A:6

[iso–NAH] $M \times 10^3$	$(-dc/dt) \times 10^6$	order of reaction, 'n'
5.5	3.92	
6.5	4.61	----------- 0.97
6.5	4.61	
7.5	5.34	----------- 1.03
7.5	5.34	
8.5	6.06	----------- 1.02
8.5	6.06	
9.5	6.76	----------- 0.98

A plot of log $(-dc/dt)_o$ Vs log C_o, where C_o is the initial concentration of iso-Nicotinic acid hydrazide was shown in Fig. 3:A:4. The value of the order with respect to

iso-Nicotinic acid hydrazide has been evaluated which nearly comes out to be one. This confirms first order behaviour of the reaction with respect to iso-Nicotinic acid hydrazide.

EFFECT OF SODIUM HYDROXIDE CONCENTRATION :

In order to study the effect of alkali concentration on the oxidation of iso-Nicotinic acid hydrazide, the concentration of sodium hydroxide was varied from 2.2×10^{-4} M to 3.8×10^{-4} M by keeping the concentrations of other reactants constant. The results of these runs are recorded in Table 3:A:7.

TABLE 3:A:7

$[HCF(III)] = 5.0 \times 10^{-4}$ M $\qquad [Cl^-] = 4.0 \times 10^{-3}$ M

$[iso-NAH] = 7.5 \times 10^{-3}$ M $\qquad$ Temp $= 35°C$

λ max $= 420$ nm

$[NaOH]M \times 10^4$	2.2	2.6	3.0	3.4	3.8
Time in min	O.D.	O.D.	O.D.	O.D.	O.D.
0	0.460	0.460	0.460	0.460	0.455
5	0.435	0.430	0.430	0.425	0.420
10	0.415	0.405	0.400	0.400	0.390
15	0.400	0.380	0.380	0.370	0.360
20	0.380	0.360	0.360	0.350	0.340
30	0.345	0.325	0.325	0.310	0.290
40	0.325	0.290	0.290	0.270	0.255
50	0.300	0.260	0.260	0.240	0.225
60	0.275	0.230	0.230	0.210	0.200
70	0.250	0.205	0.205	0.190	0.175
80	0.235	0.190	0.190	0.170	0.160
90	0.225	0.180	0.175	0.155	0.140
Mean $k \times 10^2 min^{-1}$	0.92	1.18	1.19	1.34	1.44

An examination of the above results, it is clear that an increase in the concentration of NaOH increases the rate of reaction. The kinetic study of oxidation of iso-Nicotinic acid hydrazide by hexacyanoferrate(III) was found to be directly proportional to the concentration of sodium hydroxide.

EFFECT OF TEMPERATURE :

To determine 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°C to 45°C. The results of these kinetic study have been embodied in Table 3:A:8 and graphically represented in Fig. 3:A:5.

TABLE 3:A:8

[HCF(III)] = $5.0. \times 10^{-4}$ M   [OH$^-$] = 3.0×10^{-4} M

[iso-NAH] = 7.5×10^{-3} M   [Cl$^-$] = 4.0×10^{-3} M

λ max = 420 nm

Temperature	25°C	30°C	35°C	40°C	45°C
Time in min	O.D.	O.D.	O.D.	O.D.	O.D.
0	0.460	0.460	0.460	0.455	0.455
5	0.440	0.435	0.430	0.415	0.395
10	0.425	0.420	0.400	0.385	0.350
15	0.415	0.405	0.380	0.355	0.310
20	0.405	0.395	0.360	0.330	0.275
30	0.390	0.365	0.325	0.285	0.215

contd.

Temperature	25°C	30°C	35°C	40°C	45°C
Time in min	O.D.	O.D.	O.D.	O.D.	O.D.
40	0.370	0.345	0.290	0.240	0.180
50	0.350	0.320	0.260	0.210	0.160
60	0.340	0.300	0.230	0.185	0.140
70	0.325	0.280	0.205	0.160	0.125
80	0.310	0.270	0.190	0.155	--
90	0.300	0.260	0.175	0.140	--
Mean $kx10^2min^{-1}$	0.601	0.780	1.19	1.56	2.36

It is seen from the above results that the mean value of temperature coefficients for 10°C rise comes out to be 1.97 ie approximately doubled.

A plot of log k Vs 1/T is found to be linear as shown in Fig.3:A:6 indicating that the reaction obeys Arrhenius relationship. The value of energy of activation (Ea) evaluated from the slope of this linear plot comes out to be 12.20 Kcal/mole^{-1}. On the basis of this calculated value the frequency factor (A), free energy of activation ($\Delta G^{\neq}$) and entropy of activation ($\Delta S^{\neq}$) have been calculated by the application of the following equations.

i) $\quad k_r \ = \ A.e^{-E/RT}$

ii) $\quad k_r \ = \ (kT/h).e^{\,\Delta G^{\neq}/RT}$

iii) $\quad A \ = \ e.(kT/h).e^{\,\Delta S^{\neq}/R}$

Where, equation (iii) is applicable to the reactions taking place in the solutions. In the above equations $'k_r'$ is the specific rate 'k' is the Boltzmann constant, 'h' is the Planck's constant and 'e' is a constant (2.178) to be introduced in the equation. When the reaction takes place in solution, other symbols carry their usual meanings.

The free energy of the reaction $\triangle G^{\neq}$ was calculated by the equation :

iv) $\qquad k_r = \dfrac{kT}{h} \cdot e^{-\triangle G^{\neq}/RT}$

The values of log $[k_r/(kT/h)]$ have been plotted against $1/T$ which is shown in Fig.3:A:7. The plot is linear and from the slope of the straight line, the enthalpy change for the formation of activated complex ($\triangle H^{\neq}$) has been calculated. The value $\triangle H^{\neq}$ (13.27 kcal/mol^{-1}) was obtained. The various energy parameters obtained have been recorded in Table 3:A:9.

A large negative value of entropy of activation is indicative of the formation of an activated complex involving two oppositely charged ions.

Temp $T(k°)$	$1/T \times 10^3$	$k_r \times 10^2$ min^{-1}	log k_r	log $k_r/kT/h$
298	3.35	0.601	-2.2211	-15.0134
303	3.30	0.780	-2.1079	-14.9074
308	3.25	1.19	-1.9244	-14.7310
313	3.20	1.56	-1.8069	-14.6205
318	3.15	2.36	-1.6270	-14.4475

TABLE 3:A:9

THERMODYNAMIC PARAMETERS

Temp $T(k°)$	$k_r \times 10^{-2}$	Temp.coefficient per10°C	Ea KCal/mole^{-1} Graph	Ea KCal/mole^{-1} Calculated	$\Delta H^{\ddagger}$ KCal/mole^{-1}	$A \times 10^5$ sec^{-1}	$\Delta S^{\ddagger}$ e.u.	$\Delta G^{\ddagger}$ KCal/mole^{-1}
298	0.601	--	--	--	Graph	2.51	-24.17	20.47
303	0.780	1.98	--	12.46	--	2.28	-24.42	20.67
308	1.19	1.96	12.20	12.70	13.27	2.46	-24.33	20.76
313	1.56	1.98	--	13.30	--	2.27	-24.55	20.95
318	2.36	--	--	--	--	2.53	-24.38	21.02
Mean	--	1.97	12.20	12.82	13.27	2.41	-24.37	20.77

(56)

EFFECT OF CHLORIDE ION CONCENTRATION :

To investigate the effect of addition of chloride ion on the rate of oxidation of hydrazide, the concentration of potassium chloride was varied from 2.0×10^{-3} M to 8.0×10^{-3} M keeping all other reactants concentration constant. The perusal of the above result tabulated in the Table 3:A:10 shows that the effect of variation of chloride ion concentration on the rate of oxidation of hydrazide was found to be concentration dependent.

TABLE 3:A:10

[HCF(III)] = 5.0×10^{-4} M   [iso-NAH] = 7.5×10^{-3} M

[OH⁻] = 3.0×10^{-4} M   Temp = 35°C

λ max = 420 nm

[kCl] $M \times 10^{-3}$	2.0	4.0	6.0	8.0
Time in min	O.D.	O.D.	O.D.	O.D.
0	0.460	0.460	0.460	0.460
5	0.430	0.430	0.425	0.425
10	0.405	0.400	0.395	0.395
15	0.385	0.380	0.375	0.375
20	0.365	0.360	0.355	0.350
30	0.330	0.325	0.320	0.310
40	0.295	0.290	0.285	0.270
50	0.270	0.260	0.255	0.240
60	0.245	0.230	0.225	0.220
70	0.225	0.205	0.205	0.200
80	0.210	0.190	0.185	0.180
90	0.195	0.175	0.175	0.165
Mean $k \times 10^{2} min^{-1}$	1.11	1.19	1.26	1.32

EFFECT OF THE DIELECTRIC CONSTANT OF THE MEDIUM :

The effect of dielectric constant (D) of the medium on the rate of oxidation of is-Nicotinic acid hydrazide was studied by the addition of methanol (0.0 to 15%) to the reaction mixture, keeping the other concentrations constant. The results are tabulated in Table 3:A:11.

TABLE 3:A:11

$[HCF(III)] = 5.0 \times 10^{-4} M$ $\qquad$ $[Cl^-] = 4.0 \times 10^{-3} M$

$[iso-NAH] = 7.5 \times 10^{-3} M$ $\qquad$ $Temp = 35°C$

$[OH^-] = 3.0 \times 10^{-4}$ $\qquad$ $\lambda max = 420$ nm

Methanol % (v/v)	0.0	5.0	10.0	15.0
Time in min	O.D.	O.D.	O.D.	O.D.
0	0.460	0.460	0.460	0.460
5	0.430	0.425	0.425	0.420
10	0.400	0.395	0.395	0.390
15	0.380	0.375	0.375	0.365
20	0.360	0.350	0.345	0.340
30	0.325	0.310	0.305^c	0.295
40	0.290	0.270	0.265	0.255
50	0.260	0.240	0.230	0.220
60	0.230	0.220	0.205	0.200
70	0.205	0.200	0.180	0.175
80	0.190	0.180	0.160	0.155
90	0.175	0.165	0.140	0.135
Mean $k \times 10^2 min^{-1}$	1.19	1.32	1.40	1.50

It is observed from the Table 3:A:12 that the rate of oxidation of iso-Nicotinic acid hydrazide was found to be increased with decrease in dielectric constant of the medium. The values of dielectric constant (D) were reported by Gosta-Akerlof.

The results are depicted in the following Table

TABLE 3:A:12

Methanol (v/v)	D	$K \times 10^2 \ min^{-1}$	$10^2/D$	$2 + log \ k$
0.0	78.55	1.19	1.273	2.076
5.0	76.72	1.32	1.304	2.121
10.0	74.81	1.40	1.337	2.146
15.0	72.93	1.50	1.371	2.176

The results recorded in the above table clearly show that the decrease in dielectric constant increases the specific rate of the reaction, which may be due to the fact that the rate determining step may have involved between the ions of similar charges.

REFERENCE :

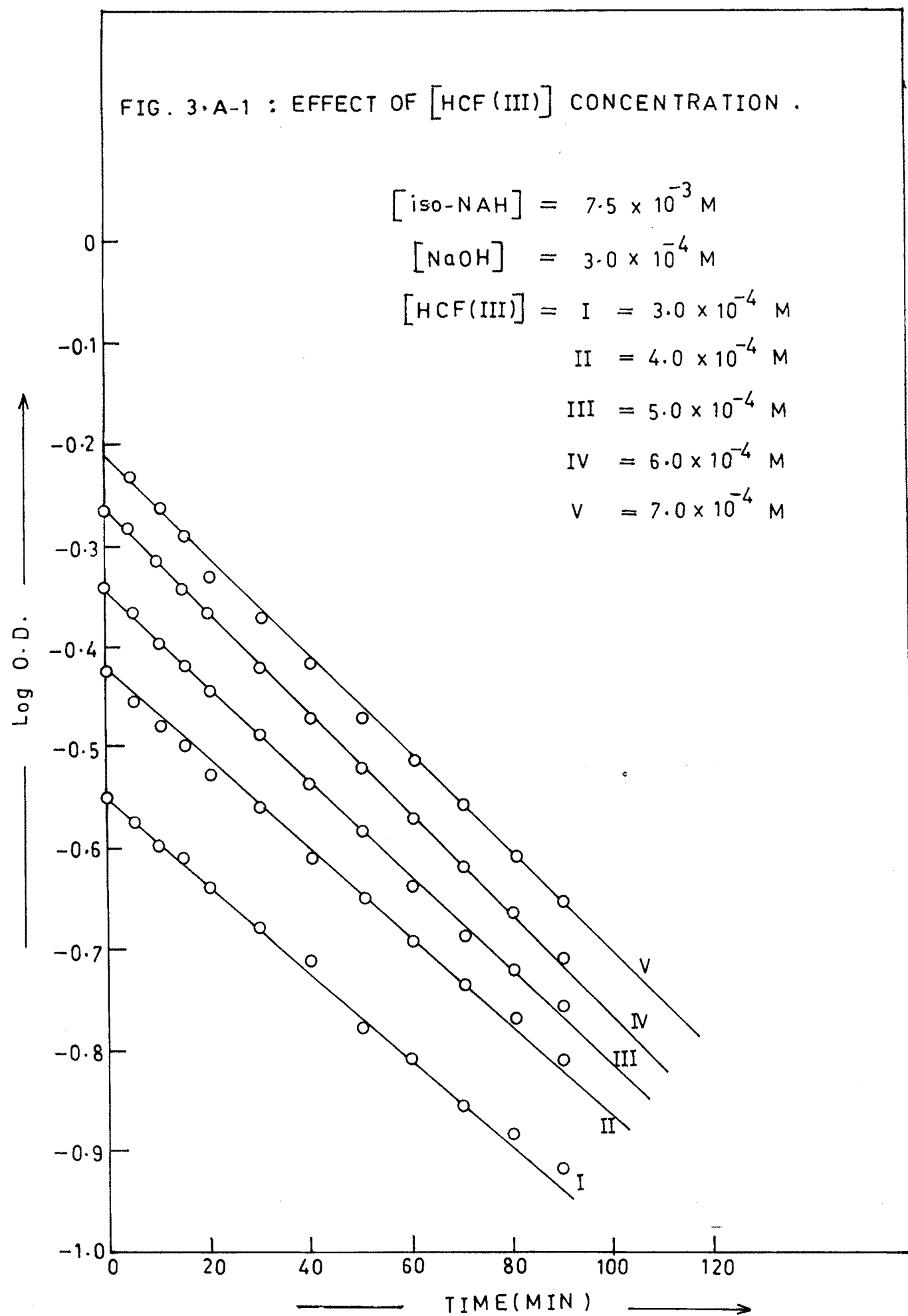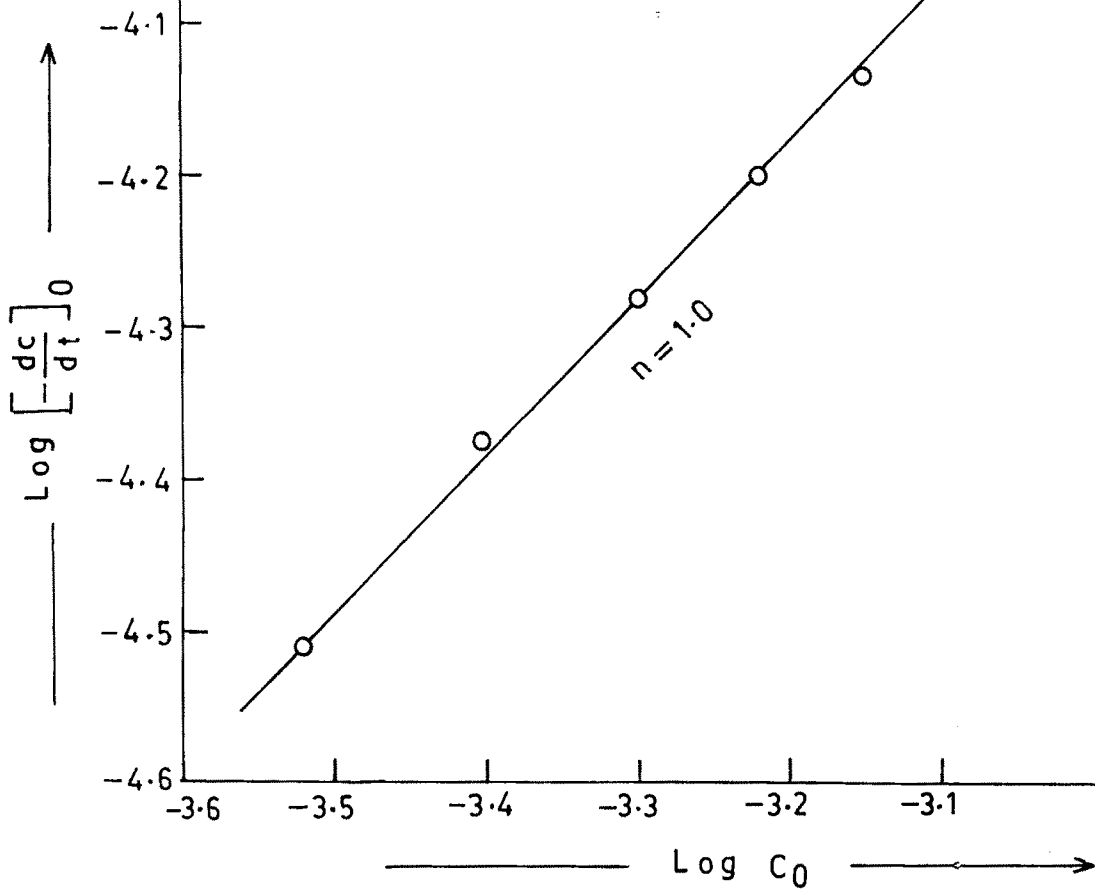1.   Gosta Akerlof, J.Am.chem.soc. (54), 4130(1932).

FIG. 3·A-1 : EFFECT OF [HCF(III)] CONCENTRATION.

$[iso\text{-}NAH] = 7.5 \times 10^{-3}$ M

$[NaOH] = 3.0 \times 10^{-4}$ M

$[HCF(III)] = $ I $= 3.0 \times 10^{-4}$ M

II $= 4.0 \times 10^{-4}$ M

III $= 5.0 \times 10^{-4}$ M

IV $= 6.0 \times 10^{-4}$ M

V $= 7.0 \times 10^{-4}$ M

FIG. 3·A·2 — PLOT OF $\text{Log}\left[-\dfrac{dc}{dt}\right]_0$ Vs $\text{Log } C_0$.

FIG. 3·A·3 — EFFECT OF [iso-NAH] CONCENTRATION.

$[HCF(III)]$ = 5.0×10^{-4} M

$[NaOH]$ = 3.0×10^{-4} M

TEMP. = $35°$ C

$[iso-NAH]$ = I = 5.5×10^{-3} M

II = 6.5×10^{-3} M

III = 7.5×10^{-3} M

IV = 8.5×10^{-3} M

V = 9.5×10^{-3} M

FIG. 3·A·4 — PLOT OF $\log\left(-\dfrac{dc}{dt}\right)_0$ Vs $\log C_0$.

$n = 1·0$

FIG. 3·A·5 — EFFECT OF TEMPERATURE.

$[HCF(III)] = 5.0 \times 10^{-4}$ M

$[NaOH] = 3.0 \times 10^{-4}$ M

$[iso\text{-}NAH] = 7.5 \times 10^{-3}$ M

$[TEMP] =$ I $= 25°$ C

II $= 30°$ C

III $= 35°$ C

IV $= 40°$ C

V $= 45°$ C
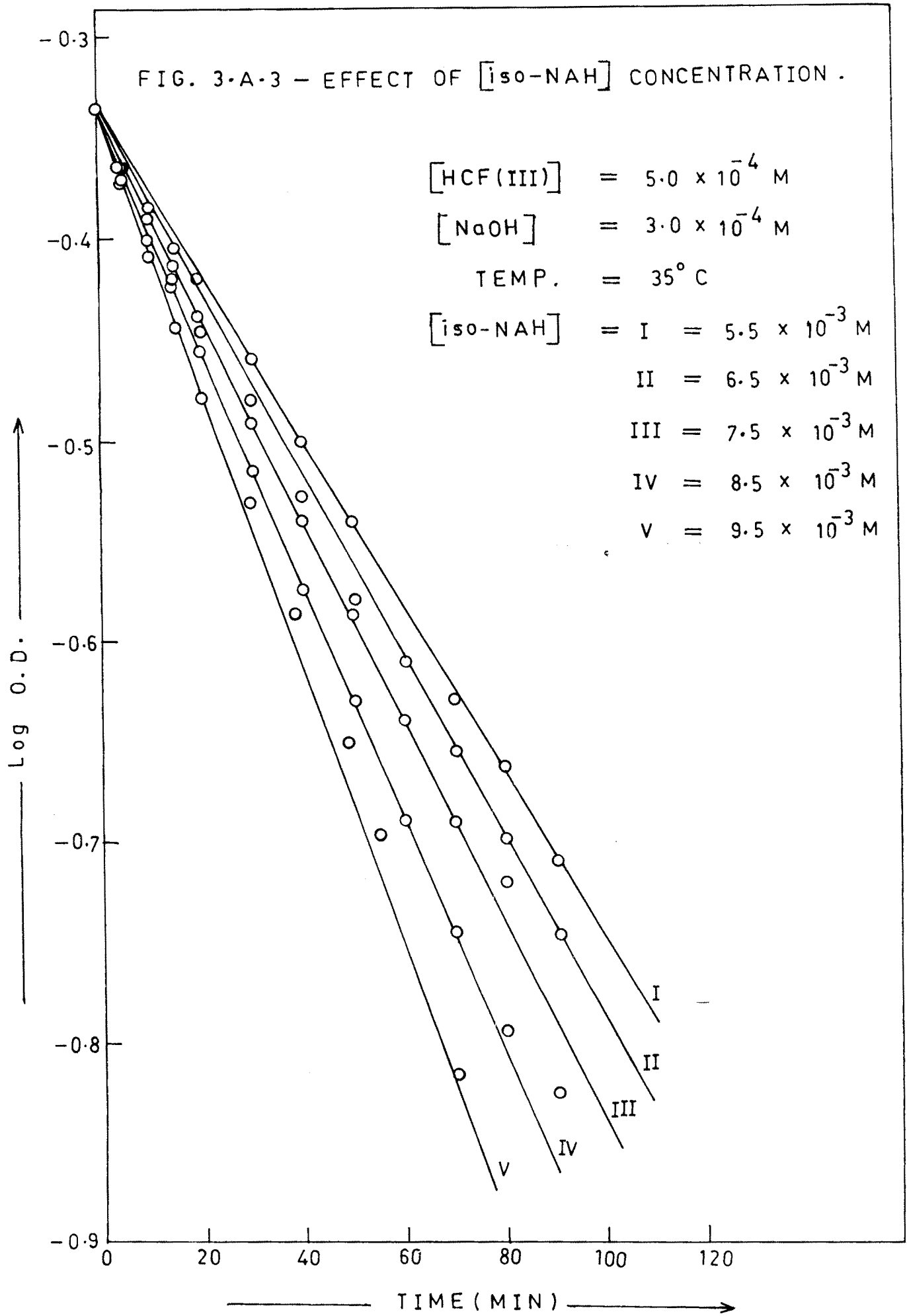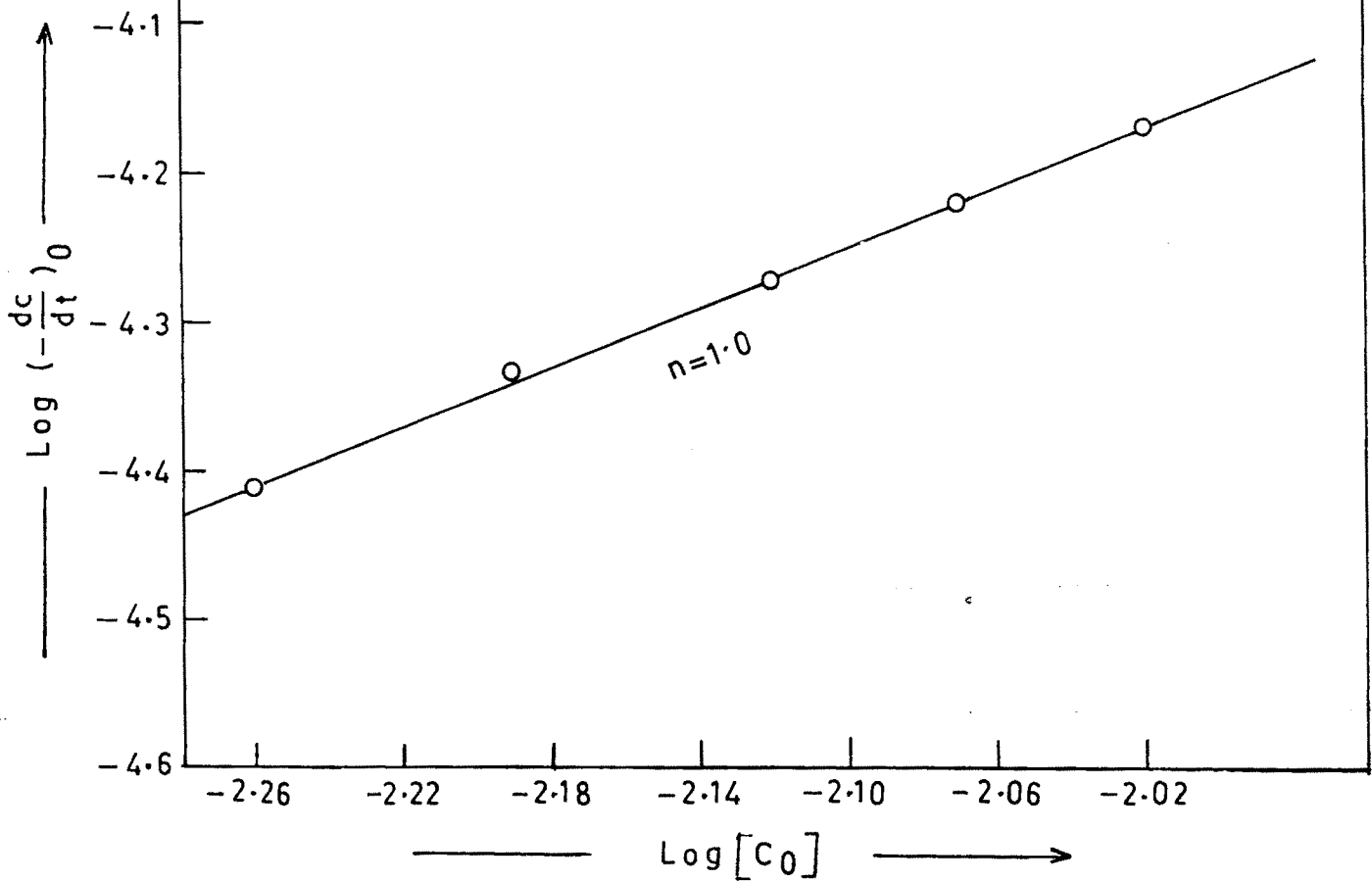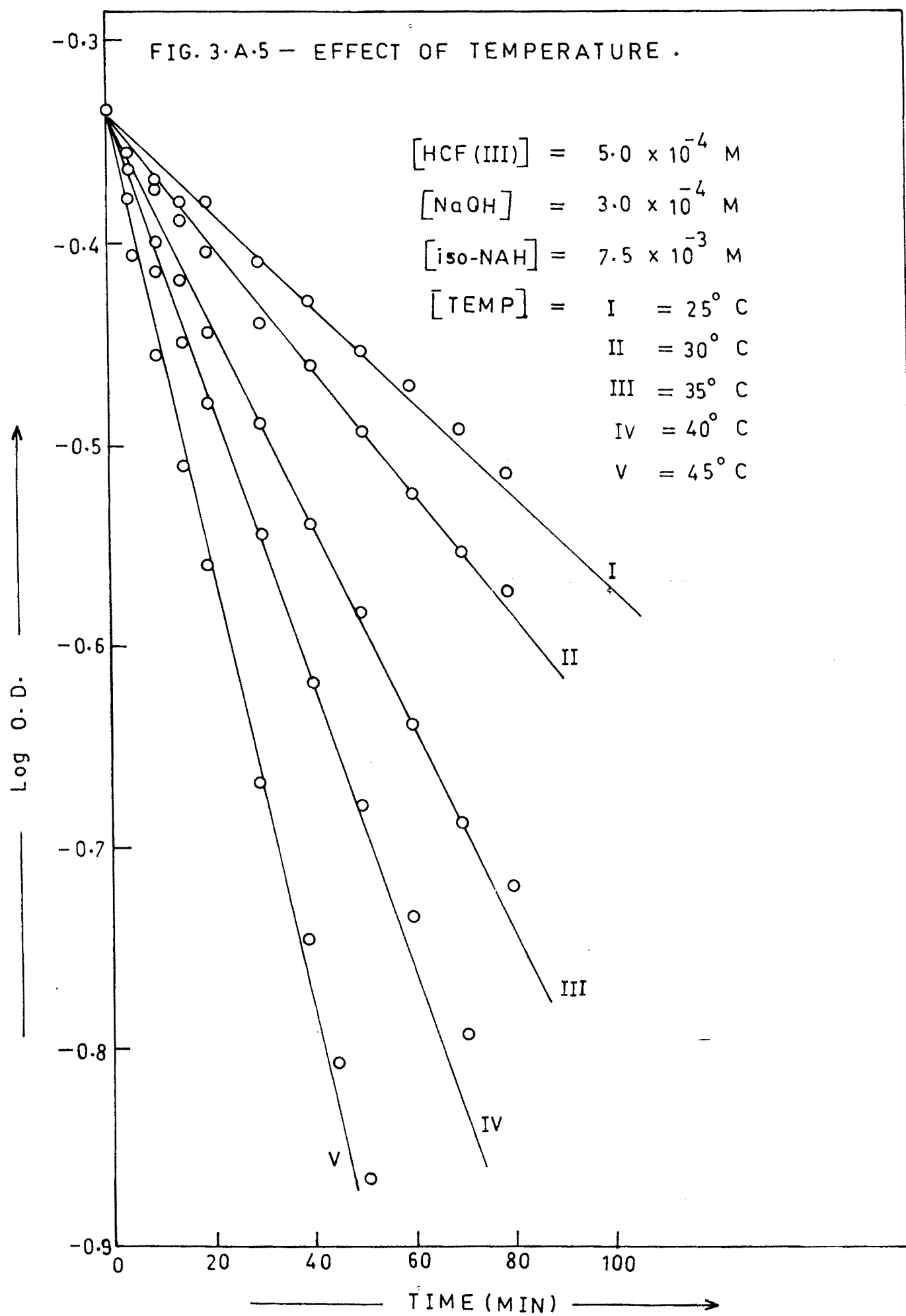
FIG. 3·A·6 — PLOT OF Log k_r Vs $\frac{1}{T}$.

Log k_r

$\frac{1}{T} \times 10^3$
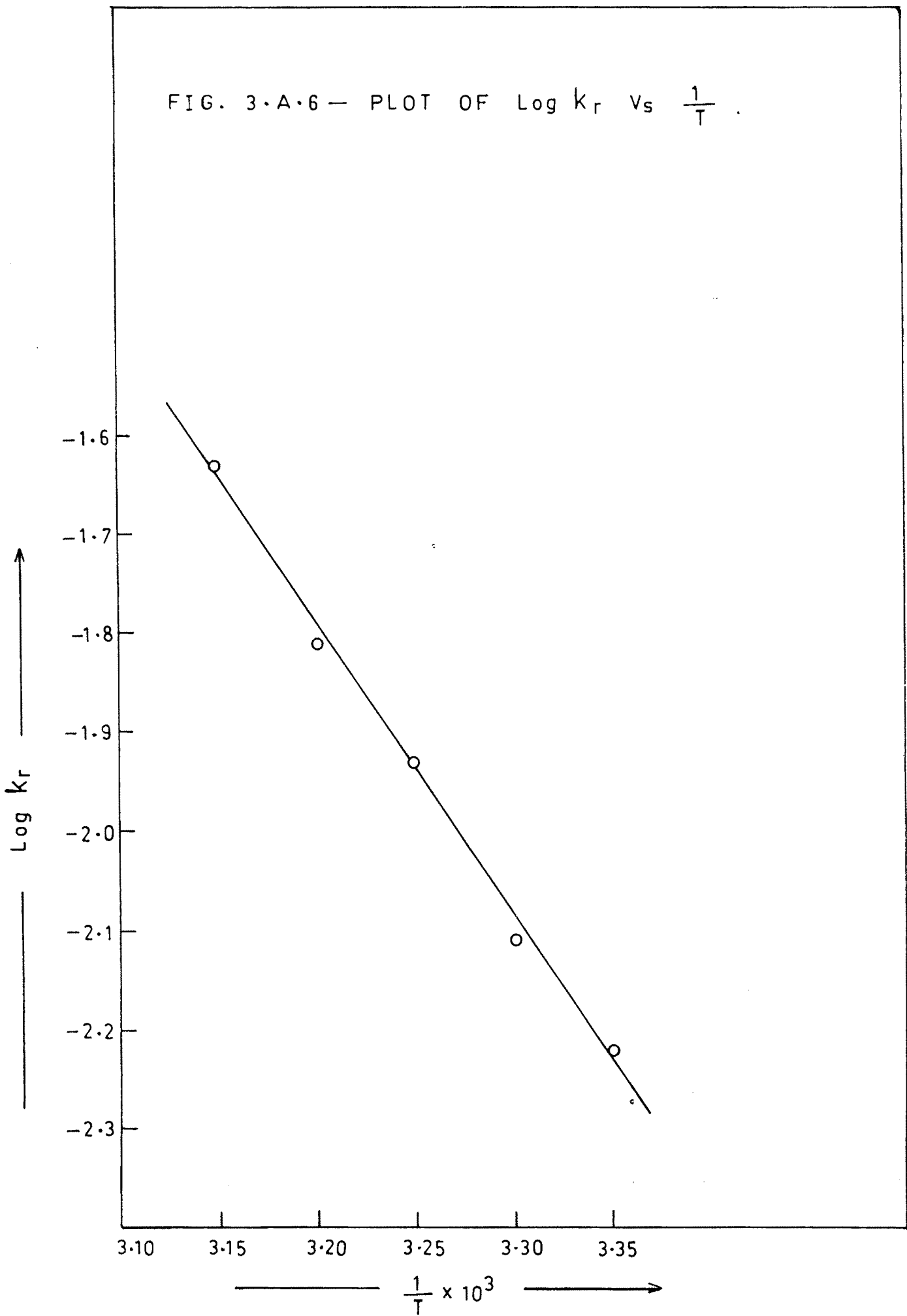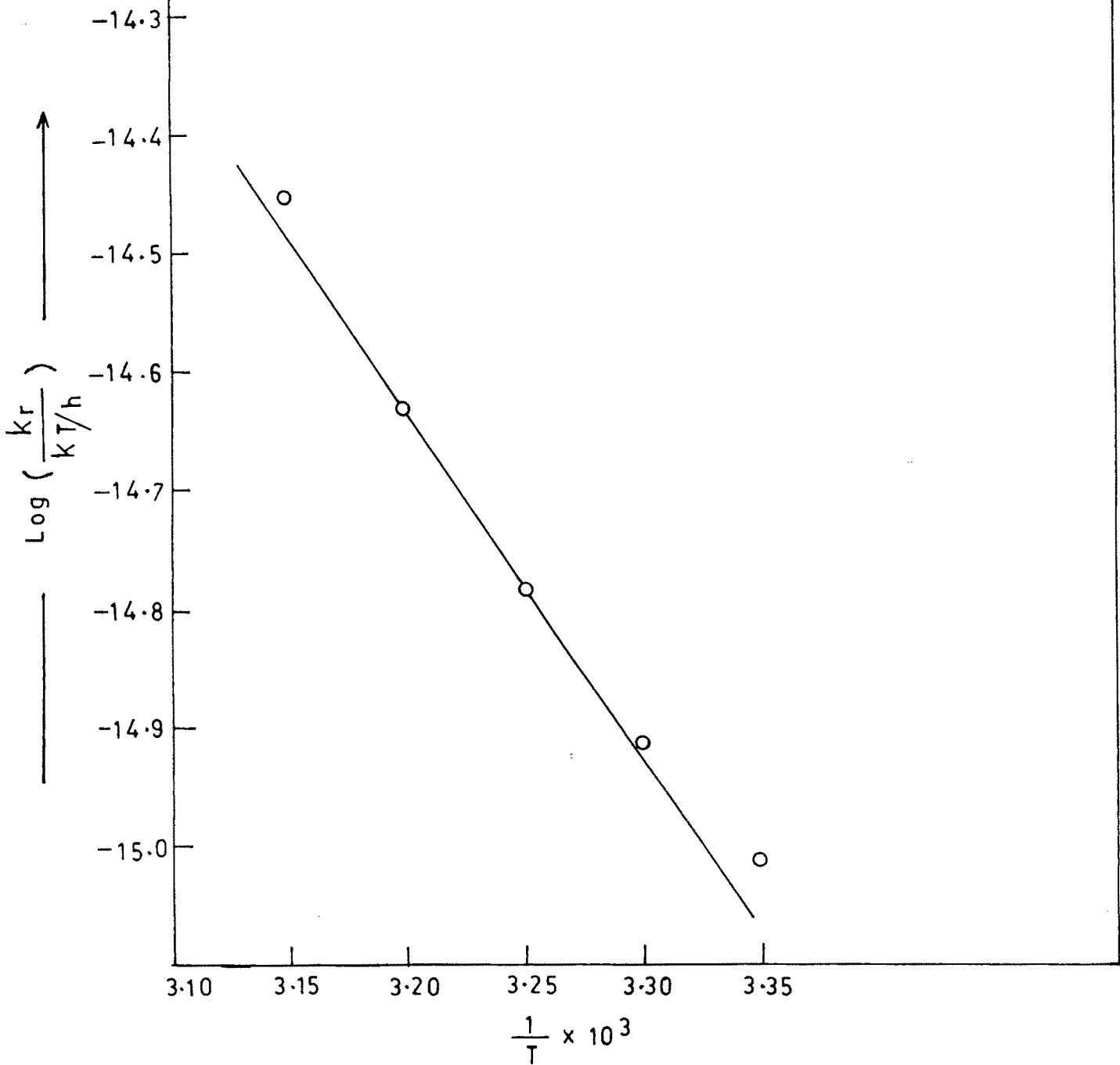
FIG. 3·A·7 — PLOT OF Log $\left(\dfrac{k_r}{kT/h}\right)$ Vs $\dfrac{1}{T}$.

SECTION-B

KINETICS OF OXIDATION OF NICOTINIC ACID HYDRAZIDE

Preliminary experiments were performed so as to decide the suitable temperature and concentrations of the reactants. It was observed that in the presence of 0.0005 M $k_3Fe(CN)_6$, 0.0075 M hydrazide, 0.0003 M NaOH, 0.004 M KCl & at 35°C temperature; the reaction proceeds with measurable velocity. The Table 3:B:1 embodies the results of kinetic data for the same.

TABLE 3:B:1

[NAH] = 7.5×10^{-3} M	[HCF(III)] = 5.0×10^{-4} M
[OH$^-$] = 3.0×10^{-4} M	[Cl$^-$] = 4.0×10^{-3} M
Temp = 35°C	λmax = 420 nm

Time in min	Optical density	$k \times 10^2$ min^{-1}
0	0.460	--
5	0.430	1.34
10	0.400	1.40
15	0.375	1.36
20	0.350	1.37
30	0.315	1.26
40	0.280	1.24
50	0.250	1.22
60	0.220	1.23
70	0.200	1.19
80	0.180	1.17
90	0.165	1.13

Mean $k \times 10^2$ min^{-1} : 1.26

An examination of the above data closely shows that the first order rate constant goes on slightly decreasing with the time. This small decrease in the rate constant with time shows that either the reaction follows an order greater than one or the reaction is attended with inhibition during the course of reaction.

DETERMINATION OF ORDER OF THE REACTION :

The determination of the order of reaction w.r.t. hexacyanoferrate (III) was done by isolation method. The concentration of hexacyanoferrate (III) was varied from 3.0×10^{-4} M to 7.0×10^{-4} M, Keeping the concentration of Nicotinic acid hydrazide and sodium hydroxide constant. The reaction was studied at 35°C.

However, the determination of the order of reaction w.r.t. Nicotic acid hydrazide could not be done by isolation method as hexacyanoferrate (III), which is the absorbing species could not be used in large excess as compared to Nicotinic acid hydrazide. Hence comparable concentrations of hexacyanoferrate (III) and nicotinic acid hydrazide were selected to determine overall order of the reaction. For this, hexacyanoferrate (III) concentration was kept constant $(5.0 \times 10^{-4}$ M), while Nicotinic acid hydrazide concentration was varied from 5.5×10^{-3} M to 9.5×10^{-3} M.

EFFECT OF HEXACYANOFERRATE (III) CONCENTRATION :

In order to investigate the effect of hexacyanoferrate (III) concentration on the specific reaction rate, and to determine the order of the reaction with respect to hexacyanoferrate (III)

the kinetic runs were performed in which the concentration of the hexacyanoferrate (III) was varied, where as that of hydrazide and NaOH concentrations were kept constant. Using these experimental data, the value of k was determined. The Table 3:B:2 embodies the results of these kinetic runs, and the data have been represented in Fig. 3:B:1. The values of the first order rate constant have been evaluated at different time intervals by integration method.

TABLE 3:B:2

$[NAH] = 7.5 \times 10^{-3} M$ $\qquad$ $[Cl^-] = 4.0 \times 10^{-3} M$

$[OH^-] = 3.0 \times 10^{-4} M$ $\qquad$ Temp = 35°C

$\lambda max = 420$ nm

$[HCF(III)]$ $M \times 10^4$	3.0	4.0	5.0	6.0	7.0
Time in min	O.D.	O.D.	O.D.	O.D.	O.D.
0	0.280	0.375	0.460	0.565	0.645
5	0.260	0.350	0.430	0.520-	0.590
10	0.245	0.330	0.400	0.480	0.540
15	0.235	0.315	0.375	0.450	0.500
20	0.225	0.295	0.350	0.420	0.460
30	0.205	0.265	0.315	0.370	0.410
40	0.190	0.235	0.280	0.325	0.360
50	0.165	0.210	0.250	0.285	0.315
60	0.155	0.185	0.220	0.255	0.280
70	0.145	0.170	0.200	0.225	0.245
80	0.135	0.155	0.180	0.200	0.225
90	0.120	0.140	0.165	0.185	0.200
Mean $k \times 10^2 min^{-1}$	1.08	1.18	1.26	1.41	1.51

An examination of the above data shows that when the hydrazide concentration is in excess, pseudo first order specific rate increases ∧ in hyxacyanoferrate (III) concentration indicating
with increase
that the rate of disappearence of hexacyanoferrate (III), obey's the first order kinetics. To confirm the order of the reaction w.r.t. hexacyanoferrate (III), the values of (-dc/dt) were determined by plotting the optical density against time for different initial concentrations of oxidant. The order with respect to hexacyanoferrate (III) has been determined from the plot of log (-dc/dt) Vs log Co tabulated in the table 3:B:3 and graphically represented in Fig. 3:B:2. The order comes out to be nearly one.

This establishes the first order behaviour of the reaction with respect to hexacyanoferrate (III).

$[HCF(III)]$ $M \times 10^4$	3.0	4.0	5.0	6.0	7.0
$(\frac{-dc}{dt}) \times 10^6$	2.94	3.90	4.90	5.88	6.89

TABLE 3:B:3

$[HCF(III)]$ $M \times 10^4$	$(-dc/dt) \times 10^6$	Order of reaction 'n'
3.0	2.94	
4.0	3.90	0.98
4.0	3.90	
5.0	4.90	1.02
5.0	4.90	
6.0	5.88	1.00
6.0	5.88	
7.0	6.89	1.03

EFFECT OF HYDRAZIDE CONCENTRATION :

In order to determine the effect of hydrazide concentration on the rate of oxidation, the reaction was carried out at varied concentrations of hydrazide, keeping the concentration of hexacyanoferrate (III) and alkali constant. The results of these kinetic runs are recorded in Table 3:B:4 and depicted graphically in Fig. 3:B:3.

TABLE 3:B:4

$[HCF(III)]$ = 5.0 x 10^{-4}M $\qquad$ $[Cl^-]$ = 4.0 x 10^{-3}M

$[OH^-]$ = 3.0 x 10^{-4}M $\qquad$ Temp = 35°C

λmax = 420 nm

[NAH]Mx10^3	5.5.	6.5	7.5	8.5	9.5
Time in min	O.D.	O.D.	O.D.	O.D.	O.D.
0	0.460	0.460	0.460	0.460	0.460
5	0.435	0.430	0.430	0.420	0.415
10	0.410	0.405	0.400	0.385	0.380
15	0.395	0.385	0.375	0.365	0.355
20	0.375	0.365	0.350	0.345	0.335
30	0.345	0.325	0.315	0.310	0.300
40	0.310	0.290	0.280	0.280	0.270
50	0.280	0.260	0.250	0.245	0.235
60	0.260	0.240	0.220	0.220	0.215
70	0.235	0.220	0.200	0.200	0.190
80	0.215	0.200	0.180	0.180	0.170
90	0.195	0.180	0.165	0.160	0.150
Mean kx10^2min^{-1}	1.00	1.14	1.26	1.37	1.48

From the results of above Table 3:B:4 it is concluded that first order rate constant increases with increase in initial concentration of hydrazide. The plots of log O.D. Vs time are linear. The second order rate constant was $k_2 = k_1/[hydrazide]_0$

where, k_2 = second order rate constant.

k_1 = first order rate constant.

found to be constant, indicating (Table 3:A:5) the first order dependence of the rate on hydrazide concentration.

TABLE 3:B:5

[NAH] $Mx10^3$	k_1 x $10^2 min^{-1}$	k_2 min^{-1} $mole^{-1}$
5.5	1.00	1.81
6.5	1.14	1.75
7.5	1.26	1.68
8.5	1.37	1.61
9.5	1.48	1.56

ORDER WITH RESPECT OF HYDRAZIDE :

The investigation of the order of the reaction w.r.t. hydrazide is done by subjecting the kinetic data of Table 3:B:3 to van't Hoff differential method. From the initial slopes of plots of optical density Vs time curves, the values of $(-dc/dt)_0$ corresponding to various initial concentrations of hydrazide were evaluated which are given in Table 3:B:6.

[NAH] $M \times 10^3$	5.5	6.5	7.5	8.5	9.5
$(\frac{-dc}{dt}) \times 10^6$	3.78	4.50	5.18	5.85	6.53

A plot of log $(-dc/dt)_0$ Vs log Co, where Co is the initial concentration of Nicotinic acid hydrazide was shown in Fig. 3:B:4. The value of the order w.r.t. Nicotinic acid hydrazide has been evaluated which comes out to be nearly one. This confirms first order behaviour of the reaction w.r.t. Nicotinic acid hydrazide.

TABLE 3:B:6

[NAH] $M \times 10^3$	$(-dc/dt) \times 10^6$	order of reaction
5.5	3.78	
6.5	4.50	1.04
6.5	4.50	
7.5	5.18	0.98
7.5	5.18	
8.5	5.85	0.97
8.5	5.85	
9.5	6.53	0.99

EFFECT OF SODIUM HYDROXIDE CONCENTRATION :

To investigate the effect of sodium hydroxide concentration on the rate of oxidation of Nicotinic acid hydrazide, the concentration of NaOH was varied from 2.2×10^{-4} M to 3.8×10^{-4} M by keeping the concentrations of other reactants constant. The Table 3:B:7 embodies the results of the same.

A perusal of the results from Table 3:B:7 shows that increase in the concentration of NaOH enhances the rate of the reaction. The kinetic study of Nicotinic acid hydrazide by hexacyanoferrate (III) was found to be directly proportional to the concentration of sodium hydroxide.

TABLE 3:B:7

[HCF(III)	$= 5.0 \times 10^{-4}$ M		$[Cl^-] = 4.0 \times 10^{-3}$ M
[NAH]	$= 7.5 \times 10^{-3}$ M		Temp = 35°C

λmax $= 420$ nm

[NaOH]M$\times 10^4$	2.2	2.6	3.0	3.4	3.8
Time in min	O.D.	O.D.	O.D.	O.D.	O.D.
0	0.460	0.460	0.460	0.460	0.460
5	0.430	0.425	0.430	0.420	0.420
10	0.405	0.395	0.400	0.390	0.385
15	0.390	0.380	0.375	0.370	0.365
20	0.375	0.365	0.350	0.350	0.345
30	0.345	0.335	0.315	0.315	0.310
40	0.315	0.305	0.280	0.280	0.275
50	0.290	0.280	0.250	0.250	0.245
60	0.265	0.245	0.220	0.220	0.215
70	0.245	0.230	0.200	0.200	0.195
80	0.225	0.210	0.180	0.180	0.175
90	0.205	0.200	0.165	0.160	0.150
Mean k$\times 10^2$min^{-1}	1.10	1.14	1.26	1.34	1.40
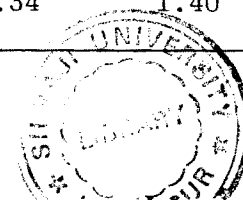
EFFECT OF TEMPERATURE :

        In order to determine the temperature coefficient, energy of activation (Ea), Enthalpy of activation ($\Delta H^{\ddagger}$), frequency factor (A), free energy of activation ($\Delta G^{\ddagger}$) 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:B:8 and graphically depicted in Fig. 3:B:5.

TABLE 3:B:8

[HCF(III)] = 5.0×10^{-4} M   [OH$^-$] = 3.0×10^{-4} M

[NAH] = 7.5×10^{-3} M   [Cl$^-$] = 4.0×10^{-3} M

λ max = 420 nm

Temperature	25°C	30°C	35°C	40°C	45°C
Time in min	O.D.	O.D.	O.D.	O.D.	O.D.
0	0.460	0.460	0.460	0.460	0.460
5	0.440	0.435	0.430	0.415	0.390
10	0.425	0.415	0.400	0.380	0.355
15	0.415	0.400	0.375	0.350	0.310
20	0.405	0.385	0.350	0.325	0.275
30	0.385	0.355	0.315	0.275	0.215
40	0.365	0.325	0.280	0.240	0.180
50	0.340	0.305	0.250	0.205	0.140
60	0.325	0.280	0.220	0.180	0.125
70	0.310	0.265	0.200	0.155	--
80	0.295	0.255	0.180	0.135	--
90	0.285	0.245	0.165	--	--
Mean $k \times 10^2$ min^{-1}	0.638	0.860	1.26	1.71	2.49

A perusal of the above results shows that the mean value of temperature coefficients for 10°C rise comes out to be 1.98 ie approximately doubled.

A plot of log k Vs 1/T is found to be linear as shown in Fig. 3:B:6 indicating that the reaction obeys Arrhenius relationship. The value of energy of activation (Ea) calculateed from the slope of this linear plot comes out to be 12.81 kCal/ mole^{-1}. On the basis of this evaluated value the frequency factor (A) free energy of activation ($\Delta G^{\neq}$) and entropy of activation ($\Delta S^{\neq}$) have been calculated by the application of the following equations :

i) $k_r = A.e^{-E/RT}$

ii) $k_r = (kT/h).e^{\Delta G^{\neq}/RT}$

iii) $A = e.(kT/h).e^{\Delta S^{\neq}/R}$

Where equation (iii) is applicable to the reactions taking place in the solutions. In the above equations "k_r" is the specific rate, 'k' is the Boltzmann constant, 'h' is the Planck's constant and 'e' is a constant (2.178) to be introduced in the equation, when the reaction takes place in solution, other symbols carry their usual meanings.

The free energy of the reaction $\Delta G^{\neq}$ was calculated by the equation.

iv) $k_r = (kT/h).e^{-\Delta G^{\neq}/RT}.$

The values of log $[k_r /(kT/h)]$ have been plotted against $1/T$ which is shown in Fig. 3:B:7. The plot is linear and from the slope of the straight line, the enthalpy changes for the formation of activated complex ($\Delta H^{\neq}$) has been calculated. The value of $\Delta H^{\neq}$ (12.58 kcal/mole^{-1}) was obtained. The various energy parameters obtained have been tabulated in Table 3:B:9.

A large negative values of entropy of activation is indicative of the formation of an activated complex involving two oppositely charged ions.

Temp T(k°)	$1/T \times 10^3$	$k_r \times 10^2 min^{-1}$	log k_r	log k_r/kT/h
298	3.35	0.638	−2.1952	−14.9875
303	3.30	0.860	−2.0655	−14.8650
308	3.25	1.26	−1.8996	−14.7062
313	3.20	1.71	−1.7670	−14.5806
318	3.15	2.49	−1.6038	−14.4243

EFFECT OF CHLORIDE ION CONCENTRATION :

To study the effect of addition of chloride ion on the rate of oxidation of Nicotinic acid hydrazide the concentration of potassium chloride was varied from 2.0×10^{-3} M to 8.0×10^{-3} M, keeping all the other concentrations constant. An examination of the results contained in the Table 3:B:10 shows that the increase in chloride ion concentration increases the specific rate slightly ie concentration dependent.

TABLE 3:B:9

THERMODYNAMIC PARAMETERS

Temp T(k°)	$k_r \times 10^{-2}$	Temp co-efficient Per 10°C	Ea kcal/mole^{-1} Graph	Ea kcal/mole^{-1} Calculated	$\triangle H^{\neq}$ kCal/mole^{-1}	$A \times 10^5$ Sec^{-1}	$\triangle S^{\neq}$ e. u.	$\triangle G^{\neq}$ kcal/mole^{-1}
298	0.64	--	--	--	--	3.109	-26.37	20.43
303	0.86	1.98	--	12.46	--	2.93	-26.50	20.61
308	1.26	1.99	12.81	12.97	12.58	3.034	-26.45	20.72
313	1.71	1.98	--	12.30	--	2.94	-26.53	20.88
318	2.49	--	--	--	--	3.10	-26.41	20.98
Mean	--	1.98	12.81	12.91	12.58	3.021	-26.45	20.72

TABLE 3:B:10

$[HCF(III)] = 5.0 \times 10^{-4}M$ $[NAH] = 7.5 \times 10^{-3}$ M

$[OH^-] = 3.0 \times 10^{-4}M$ Temp $= 35°C$

λ max $= 420$ nm

$[kCl]$ $Mx10^{-3}$	2.0	4.0	6.0	8.0
Time in min	O.D.	O.D.	O.D.	O.D.
0	0.460	0.460	0.460	0.460
5	0.430	0.430	0.425	0.425
10	0.405	0.400	0.400	0.400
15	0.385	0.375	0.375	0.375
20	0.365	0.350	0.355	0.350
30	0.330	0.315	0.320	0.310
40	0.295	0.280	0.285	0.270
50	0.270	0.250	0.260	0.245
60	0.245	0.220	0.225	0.220
70	0.225	0.200	0.205	0.200
80	0.210	0.180	0.185	0.180
90	0.195	0.165	0.175	0.165
Mean $kx10^2min^{-1}$	1.10	1.26	1.27	1.30

EFFECT OF DIELECTRIC CONSTANT OF MEDIUM :

To investigate the effect of change in dielectric constant of the medium on the rate of oxidation of Nicotinic acid hydrazide, the percentage (v/v) of methanol is varied from (0.0% to 15.0%) keeping all other concentrations unchanged. The results are depicted in Table 3:B:11.

TABLE 3:B:11

[HCF(III)]   = 5.0 x10^{-4}M   [OH$^-$] = 3.0x 10^{-4} M

[NAH]   = 7.5 z10^{-3}M   [Cl$^-$] = 4.0x 10^{-3} M

λmax   = 420 nm   Temp = 35°C

Methanol % (v/v)	0.0	5.0	10.0	15.0
Time in min	O.D.	O.D.	O.D.	O.D.
0	0.460	0.460	0.460	0.460
5	0.430	0.420	0.415	0.415
10	0.400	0.385	0.380	0.380
15	0.375	0.365	0.355	0.350
20	0.350	0.345	0.335	0.330
30	0.315	0.310	0.300	0.290
40	0.280	0.280	0.270	0.250
50	0.250	0.245	0.235	0.210
60	0.220	0.220	0.215	0.190
70	0.200	0.200	0.190	0.165
80	0.180	0.180	0.170	0.150
90	0.165	0.160	0.150	0.135
Mean kx10^2min^{-1}	1.26	1.38	1.49	1.62

A perusal of the data from the Table 3:B:12 shows
that the rate of oxidation of Nicotinic acid hydrazide was found
to be increased with decrease in dielectric constant of the medium.

The values of dielectric constant (D) were reported by Gosta-Akerlof[1]. The results are represented in the following Table 3:B:12.

TABLE 3:B:12

Methanol (v/v) %	D	$kx10^2$ min^{-1}	$\dfrac{10^2}{D}$	2 + log k
0.0	78.55	1.26	1.273	2.100
5.0	76.71	1.38	1.304	2.140
10.0	74.81	1.49	1.337	2.173
15.0	72.93	1.62	1.371	2.210

From the results mentioned in above Table 3:B:12 clearly shows that the decrease in dielectric constant increases the specific rate of the reaction, which may be due to the fact that the rate determining step may have involved between the ions of similar charges.

REFERENCE :

1.   Gosta Akerlof, J.Am. chem.soc. (54), 4130 (1932).
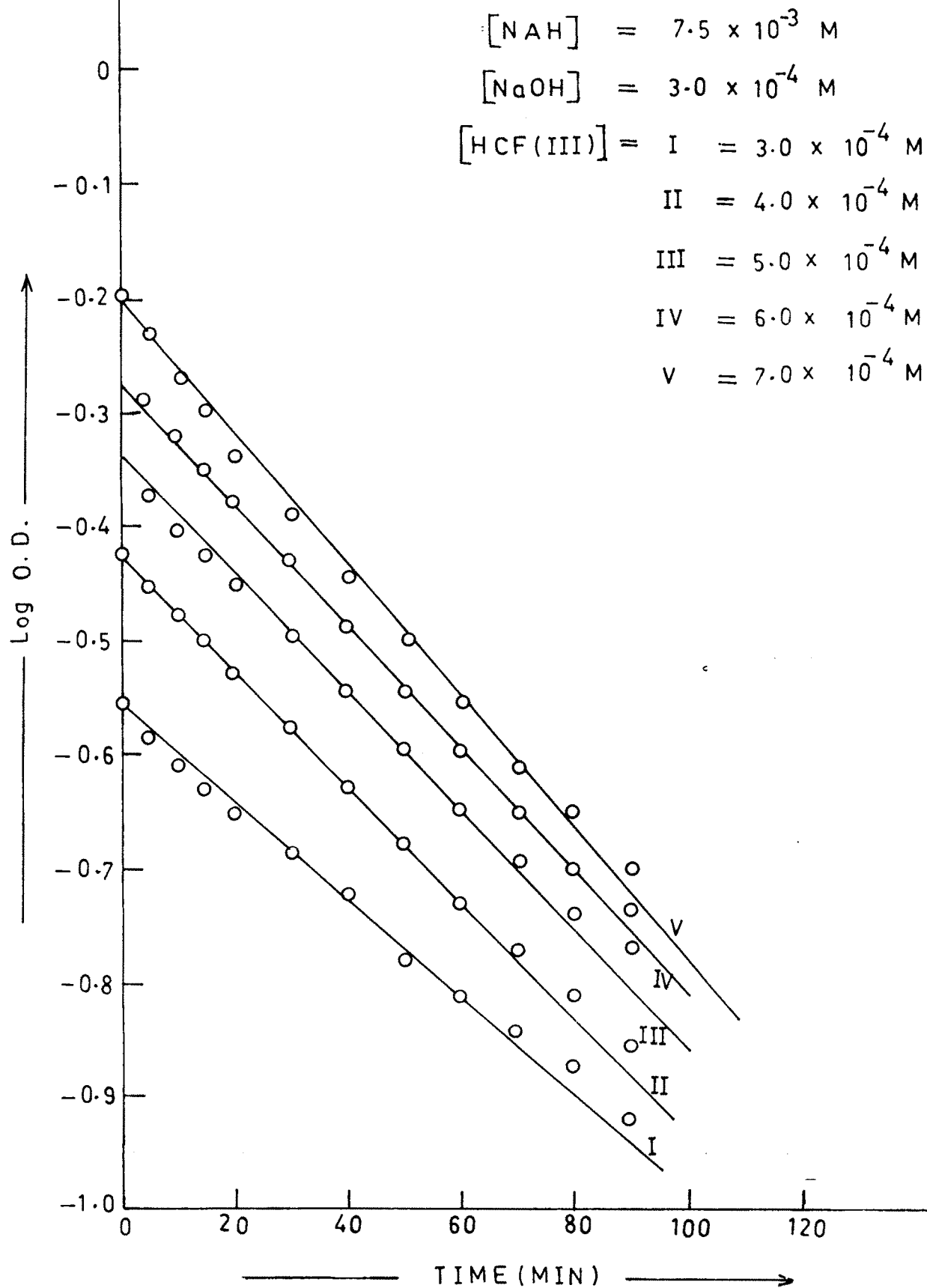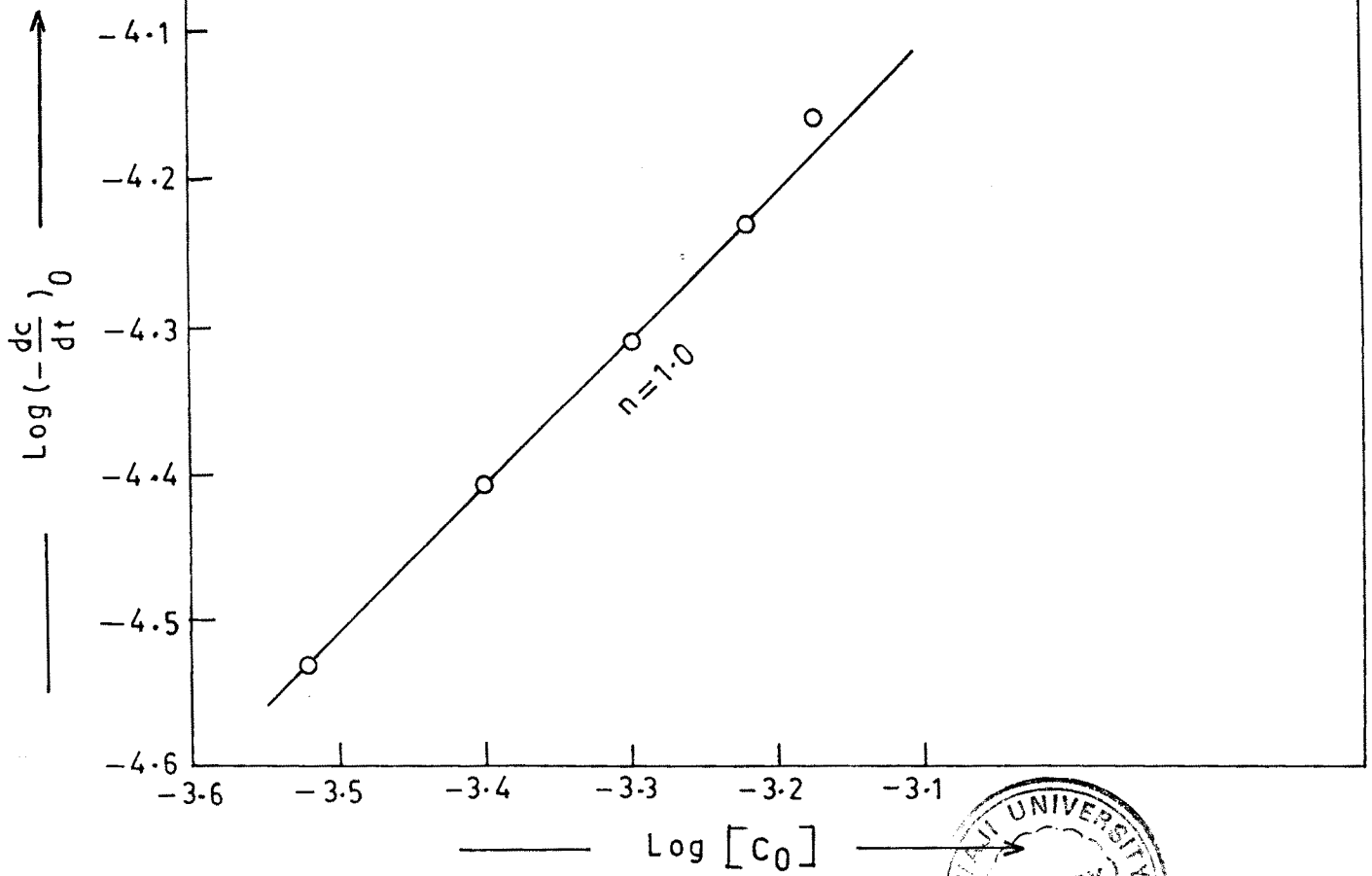
FIG. 3·B·1 — EFFECT OF $\left[HCF(III)\right]$ CONCENTRATION.

$$\left[NAH\right] = 7.5 \times 10^{-3} \text{ M}$$

$$\left[NaOH\right] = 3.0 \times 10^{-4} \text{ M}$$

$$\left[HCF(III)\right] = I = 3.0 \times 10^{-4} \text{ M}$$

$$II = 4.0 \times 10^{-4} \text{ M}$$

$$III = 5.0 \times 10^{-4} \text{ M}$$

$$IV = 6.0 \times 10^{-4} \text{ M}$$

$$V = 7.0 \times 10^{-4} \text{ M}$$

Log O.D.

TIME (MIN)

FIG. 3.B.2 — PLOT OF $\log(-\frac{dc}{dt})_0$ Vs $\log C_0$

$n = 1.0$

$\log(-\frac{dc}{dt})_0$

$\log [C_0]$

FIG. 3·B·3 — EFFECT OF [NAH] CONCENTRATION.

$[HCF (III)] = 5.0 \times 10^{-4}$ M

$[NaOH] = 3.0 \times 10^{-4}$ M

TEMP. $= 35°$ C

$[NAH] = I = 5.5 \times 10^{-3}$ M

$II = 6.5 \times 10^{-3}$ M

$III = 7.5 \times 10^{-3}$ M

$IV = 8.5 \times 10^{-3}$ M

$V = 9.5 \times 10^{-3}$ M

FIG. 3·B·4 — PLOT OF $\log\left(-\frac{dc}{dt}\right)_0$ V$_s$ Log C_0.

FIG. 3·B·5 — EFFECT OF TEMPERATURE.

$[HCF(III)] = 5.0 \times 10^{-4}$ M

$[NaOH] = 3.0 \times 10^{-4}$ M

$[NAH] = 7.5 \times 10^{-3}$ M

$[TEMP] = I = 25° C$

$II = 30° C$
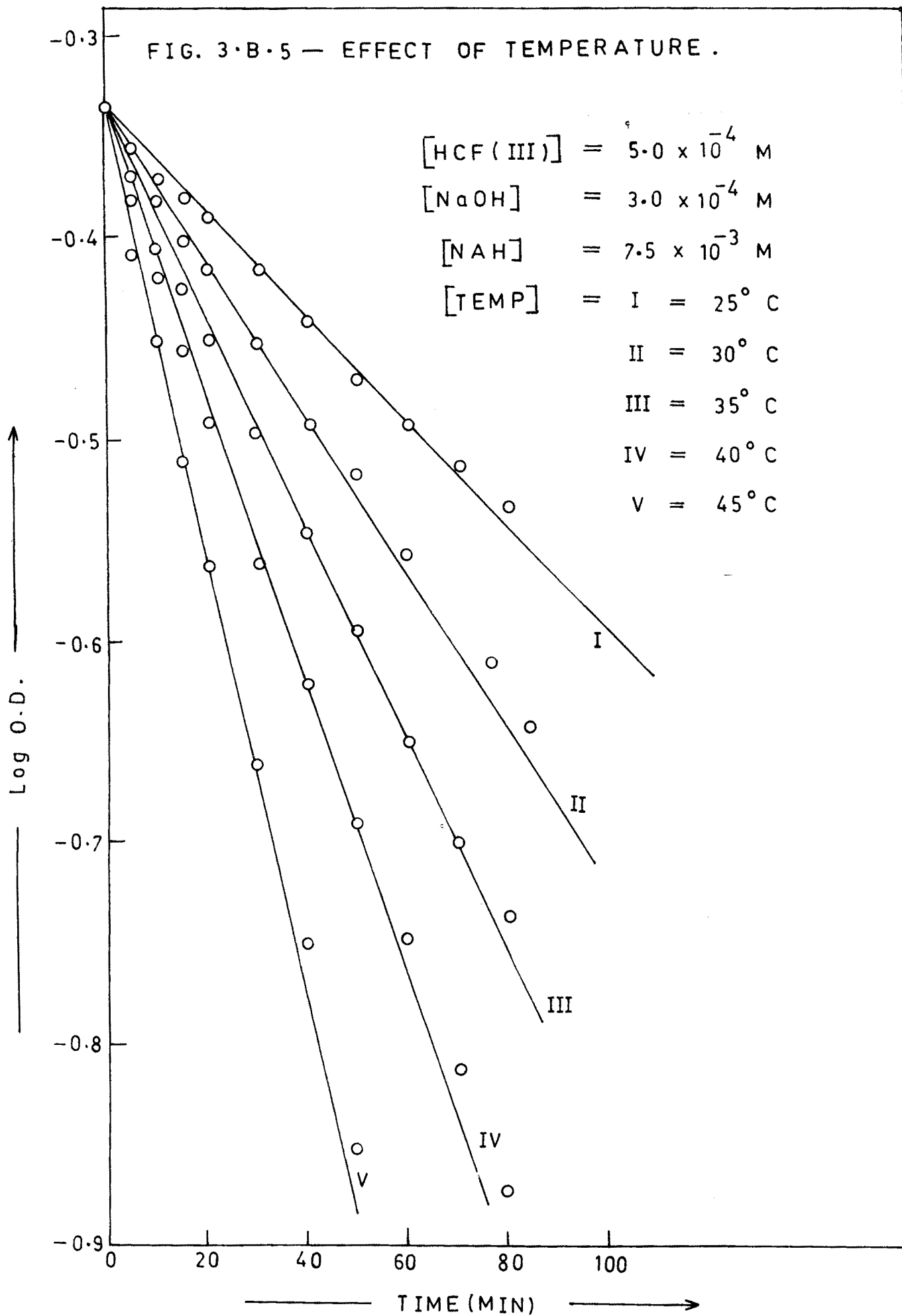
$III = 35° C$

$IV = 40° C$

$V = 45° C$

Log O·D.

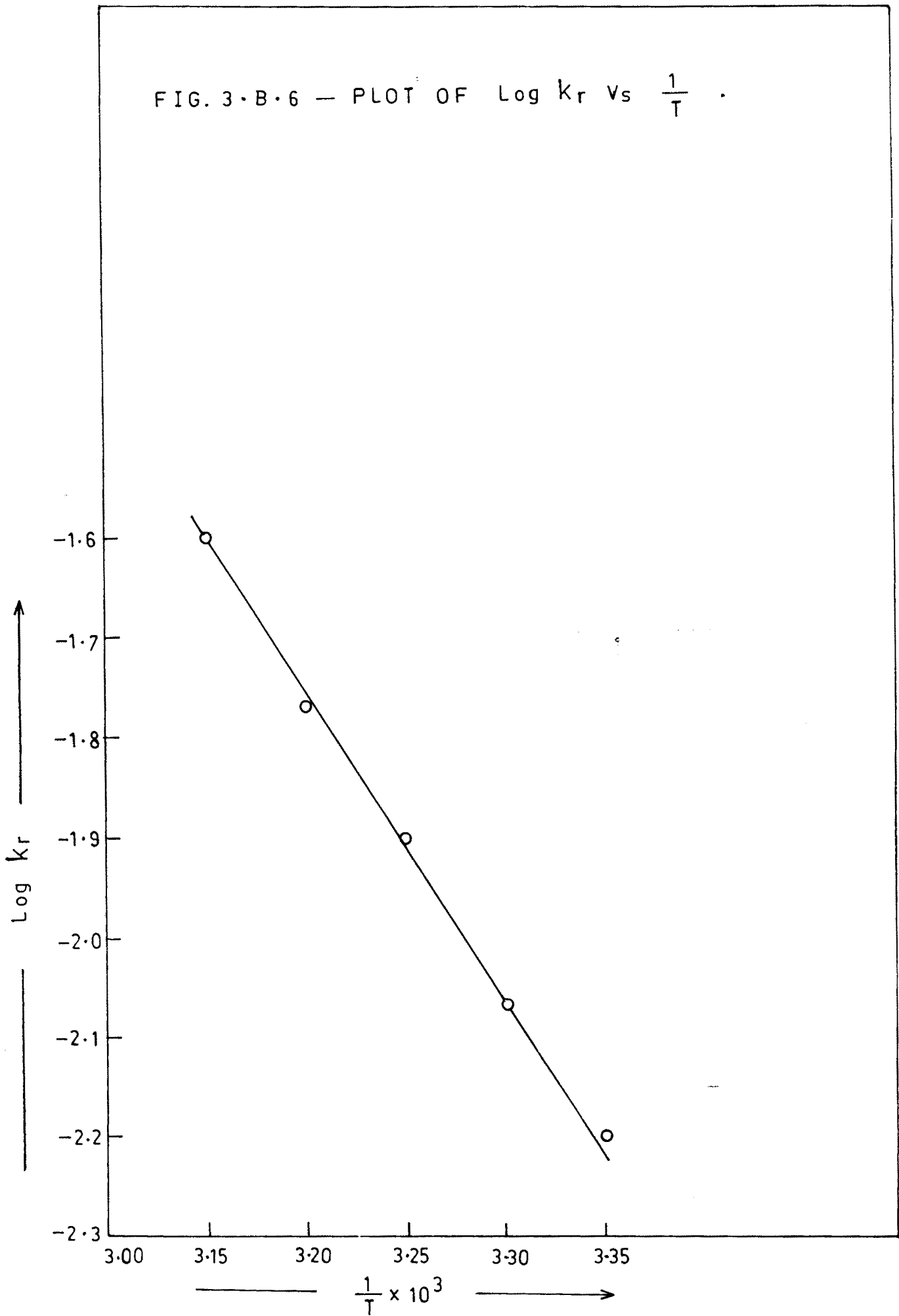TIME (MIN)
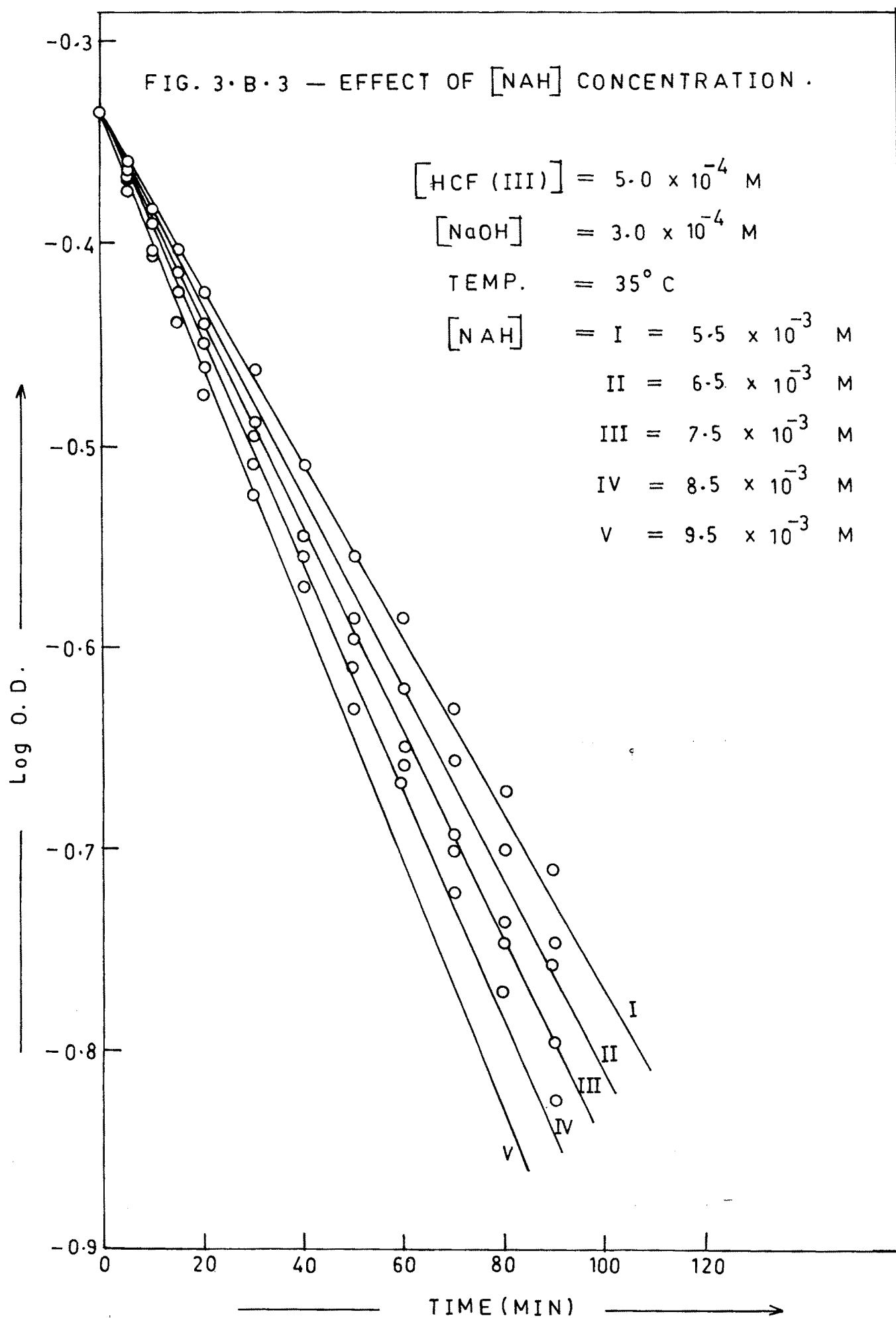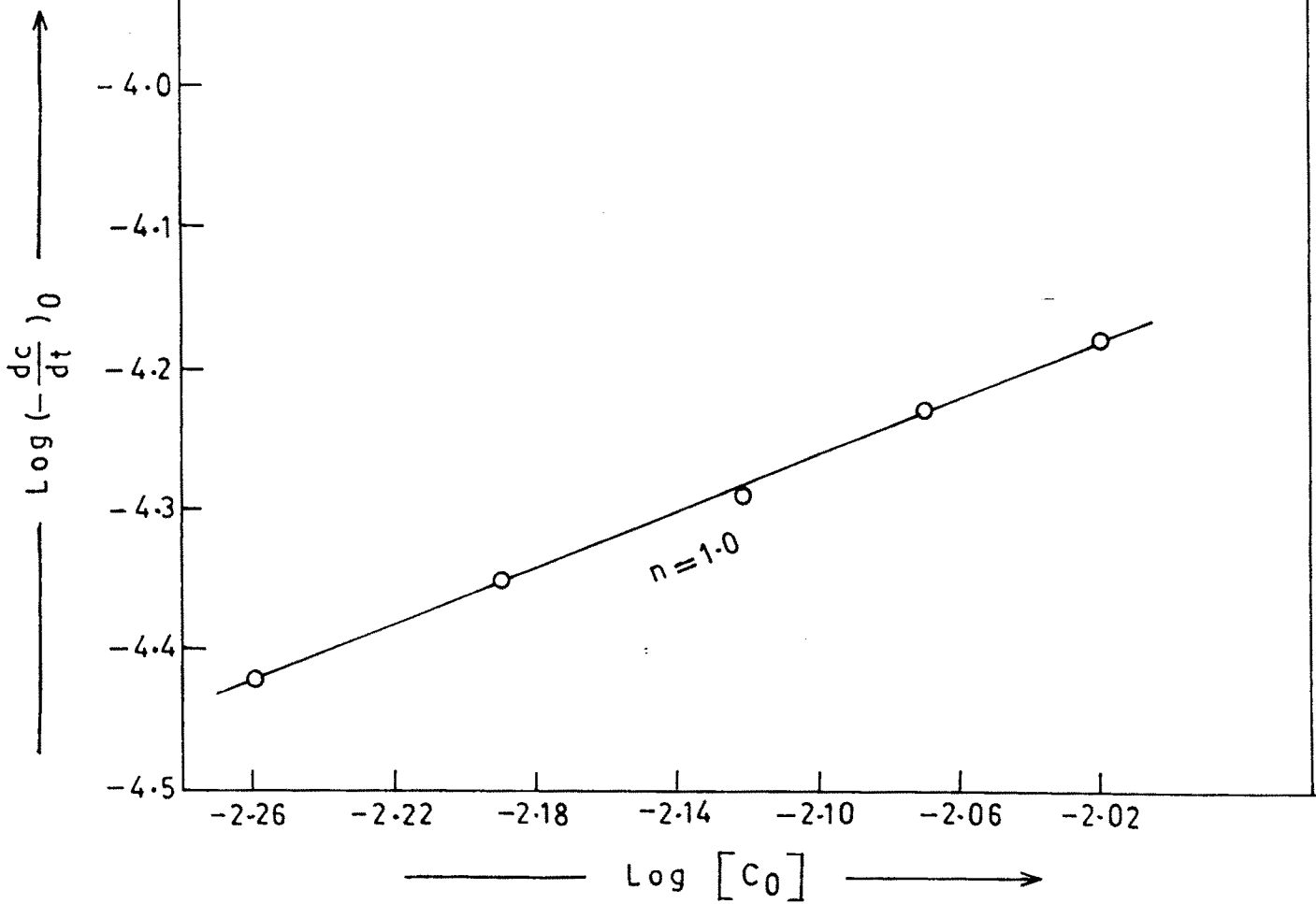
FIG. 3·B·6 — PLOT OF Log k_r Vs $\frac{1}{T}$.

FIG. 3·B·7 — PLOT OF $Log\left(\dfrac{k_r}{kT/h}\right)$ Vs $\dfrac{1}{T}$.