

EXPERIMENTAL TECHNIQUE :

Peroxydisulphuric acid and its salts have been used for the oxidation of many systems. Oxidation by peroxydisulphate ion generally takes place slowly (180), but becomes fairly rapid in the presence of a catalyst.

The reactions of $S_2O_8^{2-}$ are known to be greatly influenced by the traces of impurities (181), hence all possible precautions were taken to avoid the presence of impurities in the reaction system.

Potassium peroxydisulphate (GR E. Merck) was always used after its purification by recrystallisation. As the reaction rate is affected even by the presence of traces of impurities, the solutions were always prepared in conductivity water. Potassium peroxydisulphate slowly decomposes not only in the solution but also in solid state, hence it was tested periodically for sulphate ions. The presence of slight traces, if any, of sulphate ions in the sample were removed by recrystallisation:

All the solutions required were prepared in conductivity water. Conductivity water was prepared by distilling water twice in the presence of a few crystals of $KMnO_4$ and a few pellets of KOH , in all corning glass distilling assembly. The purity of conductivity water occasionally checked by conductivity measurement.

The catalyst used was AgNO_3 (B.D.H., AR). The standard solution of AgNO_3 was prepared by weighing required amount of salt and dissolving it in conductivity water. The solution of AgNO_3 was stored in stoppered flask of pyrex glass coated on the outside with black paint

Standard solution of $\text{K}_2\text{S}_2\text{O}_8$ was always prepared by dissolving calculated amount of recrystallised sample in conductivity water using pyrex glass vessels. The aqueous solution of $\text{K}_2\text{S}_2\text{O}_8$ decomposes slightly on standing, therefore, a fresh solution of peroxydisulphate was always used. The strength of $\text{K}_2\text{S}_2\text{O}_8$ solution was occasionally checked by arsenic method (182) or iodometric method.

The following procedure was followed for the preparation of hydrazides (183). A mixture of equimolar quantities of methyl or ethyl esters of corresponding acids and hydrazine hydrate (90 %) was refluxed on water bath till the two layers disappeared and a homogeneous solution was formed. The excess of hydrazine hydrate and other unreacted material were removed by distilling the solution under reduced pressure. The hydrazides were recrystallised from slightly warmed ethanol.

The following hydrazides were prepared :

n - Caproic acid hydrazide ... (M.P.) 78°C

n - Heptanoic acid hydrazide... (M.P.) 85°C

Above two hydrazides were soluble in water at room temperature. The standard solutions of these were prepared by dissolving the calculated quantity in conductivity water.

Freshly prepared starch solution was used as an indicator during iodimetric titrations.

All the reactions were carried out in iodine flasks coated on the outside with black paint to avoid any photochemical effect.

For kinetic study, a constant temperature water thermostat maintained at the required temperature by electronic relay was used. The variation in temperature of the bath was within $\pm 0.1^{\circ}\text{C}$.

Measured quantities of solutions of hydrazide, peroxydisulphate and silver nitrate were taken along with the calculated quantity of conductivity water in separate flasks. These flasks were placed in a thermostat maintained at the temperature of the experiment, and allowing them for a period of 10 minutes to attain the temperature of the bath. The solutions of hydrazide, peroxydisulphate and silver nitrate were mixed thoroughly and shaken properly. The progress of the reaction was followed at different time intervals by estimating the unreacted peroxydisulphate iodometrically as follows, various iodometric methods

(11, 184-189) for estimating unconsumed peroxydisulphate were suggested from time to time. But in this kinetic study the method of Szabo and Csanyi (190) as modified by Khulbe and Srivastava (191) has been employed which is described below.

Usually (unless otherwise mentioned) ten millilitre of reaction mixture was pipetted out into the iodine flask containing an ice-cold mixture of FeSO_4 , CuSO_4 and KI solutions of the following compositions.

CuSO_4	1 %	1 ml.
FeSO_4	1 %	1 ml.
KI	5 %	10 ml

Immediately, about 2 ml dilute HCl (1N) was added to precipitate out Ag^+ as AgCl and to stop the catalytic action of Ag^+ ion. The iodine flask was allowed to stand for about 10 min., after shaking vigorously, for complete liberation of iodine. Then the liberated iodine was estimated by titrating it against a standard solution of $\text{Na}_2\text{S}_2\text{O}_3$ using freshly prepared starch solution as an indicator. Solution of $\text{Na}_2\text{S}_2\text{O}_3$ was standardised against a standard solution of arsenious oxide by the usual method.

The blank titrations were performed by taking 10 ml of 5 % KI, 1 ml of 1 % CuSO_4 and 1 % FeSO_4 in order to evaluate the quantity of $\text{Na}_2\text{S}_2\text{O}_3$ corresponding to the iodine liberated by CuSO_4 alone. The volume of $\text{Na}_2\text{S}_2\text{O}_3$ equivalent to unconsumed potassium peroxydisulphate was determined by deducting the volume of $\text{Na}_2\text{S}_2\text{O}_3$ solution corresponding to the iodine liberated by CuSO_4 alone, from the main titration value.

In recording the observations for kinetic runs the following abbreviations have been used.

- 1) 'a' represents the volume in ml of standard solution of $\text{Na}_2\text{S}_2\text{O}_3$ when $t = 0$.
- 2) '(a-x)' represents the volume in ml of standard solution of $\text{Na}_2\text{S}_2\text{O}_3$ equivalent to the unreacted peroxydisulphate at any time (t);
- 3) ' k_1 ' represents the first order rate constant for the total reaction.
- 4) ' k_2 ' denotes the first order rate constant for the Ag^+ catalysed self-decomposition of $\text{S}_2\text{O}_8^{2-}$ ion under corresponding conditions. It is well known that the self-decomposition of $\text{S}_2\text{O}_8^{2-}$ ion is first order reaction.

In present study, Ag^+ catalysed self-decomposition of $\text{S}_2\text{O}_8^{2-}$ ion is not considered because of negligible value of specific reaction rate (i.e. $2.1 \times 10^4 \text{ min}^{-1}$). As the concentration of Ag^+ catalyst used ($1.5 \times 10^{-3} \text{ M}$) is very small, and at such concentration of Ag^+ catalyst, the specific rate of self-decomposition of $\text{K}_2\text{S}_2\text{O}_8$ is very small as compared to the specific rate of the overall reaction. Hence, k_2 is not deducted from k_1 . Thus 'k' the rate constant for the oxidation of organic substrate alone was taken.

- 5) 'n-Cap.A.H.' represents the n-caproic acid hydrazide and 'n-Hep.A.H.' represents the n-Heptanoic acid hydrazides.

KINETICS OF OXIDATION OF n-CAPROIC AND n-HEPTANOIC
ACID HYDRAZIDES : (n-CAP. A.H. & n-HEP. A.H.)

A detailed kinetic study of silver catalysed oxidation of n-caproic and n-heptanoic acid hydrazides has been presented in this chapter.

Preliminary experiments were performed to decide the ranges of temperature and concentration of the reactants and the catalyst. It was found that the uncatalysed reaction at 35°C was very slow. But in the presence of $1.5 \times 10^{-3} \text{ M}$ AgNO_3 catalyst, the reaction was found to proceed with a measurable velocity. The reaction was first carried out at 35°C, using $2.0 \times 10^{-3} \text{ M}$ $\text{K}_2\text{S}_2\text{O}_8$ and $1.0 \times 10^{-2} \text{ M}$ hydrazide and that of $1.5 \times 10^{-3} \text{ M}$ AgNO_3 solution. The kinetic data have been given in Table 2:1. The values of k the rate constant have been determined by using the first order rate equation.

Table - 2.1Conc. of Hydrazides = $1.0 \times 10^{-2}M$ $[AgNO_3] = 1.5 \times 10^{-3}M$ $[K_2S_2O_8] = 2.0 \times 10^{-3}M$, $[Na_2S_2O_3 \cdot 5H_2O] = 4.0 \times 10^{-3}M$.Temp. = $35^\circ C$

Time (min)	n-cap. A.H.		n-Hep. A.H.	
	(a-x) ml	$k \times 10^2 \text{ min}^{-1}$	(a-x) ml	$k \times 10^2 \text{ min}^{-1}$
0	9.7	-	9.7	-
5	9.05	1.39	-	-
10	8.50	1.32	8.15	1.68
20	7.55	1.25	7.10	1.63
30	6.70	1.24	5.95	1.63
40	5.90	1.24	5.05	1.63
50	-	-	4.35	1.59
60	4.65	1.23	-	-
70	-	-	3.50	1.46
80	3.70	1.20	-	-
90	-	-	2.70	1.42
100	2.90	1.20	-	-
110	-	-	2.10	1.39
120	2.35	1.20	-	-
130	-	-	1.60	1.39
Mean k $\times 10^2 \text{ min}^{-1}$	-	1.25	-	1.54

The results in the above table clearly show that the first order rate constant goes on slightly decreasing with time. This small decrease in the rate constant with increase in time suggests that either the reaction follows an order greater than one or the reaction is inhibited during the course of reaction. As self decomposition of peroxydisulphate is not appreciable i.e. $k_2 = 2.13 \times 10^4 \text{ min}^{-1}$ under the experimental conditions employed, the specific rate of oxidation of substrate was evaluated without subtracting the rate constant of self decomposition of $\text{S}_2\text{O}_8^{2-}$ from the observed rate constant. It may be noted that in this experiment the concentration of hydrazide was in excess as compared to that of $\text{S}_2\text{O}_8^{2-}$ and hence the order determined was that w.r.t. $\text{S}_2\text{O}_8^{2-}$ ion.

To know the overall order of the reaction w.r.t. $\text{S}_2\text{O}_8^{2-}$ and hydrazides, the reaction was carried out with equimolar concentrations of peroxydisulphate and hydrazides (viz $2.0 \times 10^{-3} \text{ M}$ each), keeping the temperature and concentration of the catalyst unchanged. The results are given in Table 2:2.

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Table 2:2

Conc. of Hydrazides = $[K_2S_2O_8] = 2.0 \times 10^{-3} M.$

$[AgNO_3] = 1.5 \times 10^{-3} M.$

$[Na_2S_2O_3 \cdot 5H_2O] = 4.0 \times 10^{-3} M.$ Temp. = $35^\circ C$

Time (min)	n-Cap. A.H.		n-Hep. A.H.	
	(a-x)ml	$k \times 10^2 \text{ min}^{-1}$	(a-x)m	$k \times 10^2 \text{ min}^{-1}$
0	9.70	-	9.80	-
10	9.30	0.42	9.35	0.47
20	-	-	9.00	0.43
25	8.75	0.41	-	-
40	-	-	8.30	0.42
50	8.00	0.39	-	-
60	-	-	7.70	0.40
75	7.25	0.39	-	-
90	-	-	6.90	0.39
110	6.45	0.37	-	-
125	-	-	6.00	0.39
140	5.85	0.36	-	-
175	-	-	5.00	0.38
180	5.10	0.36	-	-
220	4.50	0.35	-	-
250	-	-	4.00	0.36
260	4.00	0.34	-	-
300	-	-	3.30	0.36
Mean k $\times 10^2 \text{ min}^{-1}$	-	0.36	-	0.40

Careful examination of the above data shows that the reaction follows the first order behaviour with equimolar concentration of the reactants. Slight decrease in the first order rate constant with time may be due to some inhibition as reaction progresses. However, almost constant values of the specific rate suggest that the order of the reaction w.r.t. hydrazides may be zero.

EFFECT OF PEROXYDISULPHATE ION CONCENTRATION :

In order to investigate the effect of $S_2O_8^{2-}$ ion concentration on the specific rate, it was also necessary to employ the data of the kinetic runs to determine the order of the reaction w.r.t. peroxydisulphate, keeping the concentrations of hydrazides and that of the catalyst unchanged, and vary the concn of $S_2O_8^{2-}$. Thus the reaction was carried out at three different concentrations of $S_2O_8^{2-}$ ion. Tables 2:3A and 2:3B embody the results of kinetic runs, and for the purpose of comparison, the data of Table 2:1 has also been incorporated. The data had been represented in Figs. 2:1A and 2:1 B. The values of the first order rate constant (viz k) have been calculated at different time intervals by integration method using the formula

$$k = \frac{2.303}{t} \log_{10} \frac{a}{a-x}$$

An examination of the data in the Tables 2:3A and 2:3B shows that by increasing the initial concentration of $K_2S_2O_8$, the first order rate constant decreases. This decrease in the rate constant with increase in the concentration of $S_2O_8^{2-}$ ion may be either due to an increase in ionic strength or due to the specific inhibitory effect of K^+ ion or due to both.

Table 2:3A

[n-Cap.A.H.] = 1.0×10^{-2} M. [AgNO₃] = 1.5×10^{-3} M. [Na₂S₂O₃·5H₂O] = 4.0×10^{-3} M.
Temp. = 35°C

Conc. of K ₂ S ₂ O ₈ × 10 ³ Time (Min)	$\frac{1.00}{(a-x)\text{ml}} \frac{\text{K} \times 10^2}{\text{min}^{-1}}$	$\frac{2.00}{(a-x)\text{ml}} \frac{\text{K} \times 10^2}{\text{min}^{-1}}$	$\frac{3.00}{(a-x)\text{ml}} \frac{\text{K} \times 10^2}{\text{min}^{-1}}$	$\frac{4.00}{(a-x)\text{ml}} \frac{\text{K} \times 10^2}{\text{min}^{-1}}$
0	4.80	9.70	14.50	19.40
5	4.40	1.74	9.05	1.39
10	4.05	1.70	8.50	1.32
15	3.75	1.65	-	-
20	3.45	1.65	7.55	1.25
30	2.95	1.65	6.70	1.24
40	2.40	1.62	5.90	1.24
50	2.15	1.61	-	8.40
60	-	-	4.65	1.23
70	1.55	1.61	-	7.00
90	-	-	-	5.85
100	-	-	2.90	1.20
110	-	-	-	4.80
120	-	-	2.35	1.20
130	-	-	-	4.00
Mean $\text{K} \times 10^2$ min^{-1}	1.65	1.25	1.09	0.75

Table 2:3B

[n-Hep.A.H.] = 1.0×10^{-2} M. [AgNO₃] = 1.5×10^{-3} M. [Na₂S₂O₃·5H₂O] = 4.0×10^{-3} M.

Temp. = 35°C

Conc. of K ₂ S ₂ O ₈ × 10 ³ M Time (Min)	$\frac{1.00}{(a-x)\text{ml}} \text{ kx}10^2$ min ⁻¹	$\frac{2.00}{(a-x)\text{ml}} \text{ kx}10^2$ min ⁻¹	$\frac{3.00}{(a-x)\text{ml}} \text{ kx}10^2$ min ⁻¹	$\frac{4.00}{(a-x)\text{ml}} \text{ kx}10^2$ min ⁻¹
0	4.80	9.70	14.50	19.40
5	4.35	1.97	-	-
10	3.95	1.95	1.68	1.52
15	3.60	1.92	-	-
20	3.30	1.88	1.63	1.45
25	3.00	1.88	-	-
30	2.75	1.86	1.63	1.41
40	2.30	1.84	1.63	1.39
50	2.00	1.75	1.59	1.39
70	1.50	1.66	1.46	1.36
90	-	-	1.42	1.35
110	-	-	1.39	1.32
130	-	-	1.39	1.29
Mean $\frac{\text{kx}10^2}{\text{min}}$	-	1.86	1.54	1.39
				1.01

If any particular run is observed carefully, it is seen that the first order rate constant decreases with time, since the reaction involving $S_2O_8^{2-}$ ion are highly susceptible to traces of impurities (181), hence hydrazides were recrystallised and the effect of $S_2O_8^{2-}$ ion concentration was again studied using purified sample of hydrazides. The similar results were obtained. However, the kinetic study of peroxydisulphate concentration effect was carried out which did not have constant K^+ ion concentration, so it was considered necessary to investigate this effect at constant ionic strength as well as constant K^+ ion concentrations, so that the effect of both these parameters may be eliminated. Four kinetic runs were carried out to study the effect of $S_2O_8^{2-}$ ion concentration at constant ionic strength as well as at constant K^+ ion concentration. These results were recorded in the Tables 2:4 A, 2:4 B and represented graphically in Figs. 2:2 A and 2:2 B.

Table 2:4 A

[n-CapA.H.] = $1.0 \times 10^{-2}M$, [AgNO₃] = $1.5 \times 10^{-3}M$, [Na₂S₂O₃, 5H₂O] = $4.0 \times 10^{-3}M$
 μ = 0.0305, Temp. = 35°C

$K_2S_2O_8 \times 10^3 M$	1.00	2.00	3.00	4.00				
$K_2SO_4 \times 10^3 M$	9.00	8.00	7.00	6.00				
Time (min)	$(a-x)ml$: $k \times 10^2$: $(a-x)ml$: $k \times 10^2$: $(a-x)ml$: $k \times 10^2$	min^{-1}	min^{-1}	min^{-1}	min^{-1}			
0	4.80	-	9.70	-	14.50	-	19.40	-
5	-	-	-	-	13.90	0.85	18.60	0.84
10	4.40	0.87	8.90	0.86	13.35	0.83	17.85	0.83
15	-	-	-	-	12.80	0.83	17.15	0.82
20	4.10	0.79	8.20	0.84	12.30	0.82	16.45	0.82
25	-	-	-	-	11.80	0.82	15.80	0.82
30	3.8	0.78	7.55	0.84	-	-	15.20	0.81
35	-	-	-	-	10.90	0.82	14.60	0.81
40	3.55	0.75	7.0	0.82	-	-	14.05	0.81
50	3.30	0.75	6.45	0.82	10.05	0.80	-	-
60	3.05	0.75	6.00	0.80	8.95	0.80	12.10	0.79
70	2.85	0.74	5.55	0.80	-	-	-	-
80	-	-	-	-	7.65	0.80	10.25	0.79
90	2.50	0.72	4.60	0.75	-	-	-	-
110	2.20	0.71	-	-	-	-	-	-
120	-	-	3.9	0.75	-	-	-	-
Mean $k \times 10^2$ min^{-1}		0.76		0.81		0.82		0.82



Table 2:4 B

[n-Hept. A.H.] = $1.0 \times 10^{-2}M$, $[AgNO_3] = 1.5 \times 10^{-3}M$. $[Na_2S_2O_3 \cdot 5H_2O] = 4.0 \times 10^{-3}M$.

$\mu = 0.0305$, Temp. = $35^\circ C$

$K_2S_2O_8 \times 10^3 M$	1.00	2.00	3.00	4.00
$K_2SO_4 \times 10^3 M$	9.00	8.00	7.00	6.00
Time (min)	$(a-x) ml : k \times 10^2 : (a-x) ml : k \times 10^2$ min^{-1}	$(a-x) ml : k \times 10^2 : (a-x) ml : k \times 10^2$ min^{-1}	$(a-x) ml : k \times 10^2 : (a-x) ml : k \times 10^2$ min^{-1}	$(a-x) ml : k \times 10^2 : (a-x) ml : k \times 10^2$ min^{-1}
0	4.80	9.70	14.50	19.40
5	4.5	1.51	9.00	13.50
10	4.15	1.46	8.40	12.60
15	3.90	1.38	-	11.80
20	3.65	1.37	7.35	11.10
30	3.25	1.30	6.50	9.75
40	2.85	1.30	5.70	8.60
50	2.55	1.27	5.05	7.55
70	2.00	1.25	4.00	6.20
90	1.60	1.22	3.10	5.10
110	-	-	2.40	-
130	-	-	-	-
Mean $k \times 10^2$ min	1.34	1.34	1.32	1.33

Results contained in the above tables show that specific rate remains fairly constant even though the concentration of $S_2O_8^{2-}$ ion was increased. If the results contained in the tables 2:3 A, 2:3 B and 2:4 A, 2:4 B are compared, it reveals that the decrease in the specific rate by increasing the concentration of $S_2O_8^{2-}$ ion is effectively eliminated when the effect is studied at constant ionic strength and constant K^+ ion concentration.

The decrease in the rate constant by increasing the concentration of $S_2O_8^{2-}$ ion was largely due to the increase in ionic strength as well as an increase in K^+ ion concentration, both exerting inhibitory effect on the reaction rate.

The most important step in the elucidation of the mechanism of the reaction is the determination of the order of reaction. It can be determined 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 with respect to peroxydisulphate was determined by Van't Hoff differential method. The volume of $Na_2S_2O_3$ (equivalent to unconsumed $K_2S_2O_8$) was plotted against time for different initial concentrations of $K_2S_2O_8$, from these curves, the value of initial rate, $-dc/dt$ in each case was

determined from initial slope and are given in Table 2:5. The values of $-dc/dt$ and conc. of $S_2O_8^{2-}$ ion i.e. 'C' are substituted in the van't Hoff equation i.e.

$$n = \frac{\log\left(\frac{-dc_1}{dt}\right) - \log\left(\frac{-dc_2}{dt}\right)}{\log c_1 - \log c_2}$$

and the order of reaction 'n' was calculated. The values of initial rates $-dc/dt$ for different initial concentrations of $S_2O_8^{2-}$ ion and the values of 'n' calculated thereby are recorded in Table 2:6.

Table 2:5

Conc. of $K_2S_2O_8 \times 10^3 M (C_0)$		1.00	2.00	3.00	4.00
$-dc/dt \times 10^{-4}$	n-cap.A.H.	3.07	5.91	9.2	11.85
$-dc/dt \times 10^{-4}$	n-Hep.A.H.	3.16	6.25	9.2	12.59

Table 2:6

Conc. of $K_2S_2O_8 \times 10^3 M (C_0)$	n-cap.A.H.		n-Hep. A.H.	
	$\frac{-dc}{dt} \times 10^{-4}$	order of reaction 'n'	$\frac{-dc}{dt} \times 10^{-4}$	order of reaction 'n'
$\frac{1}{2}$	$\frac{3.07}{5.91}$	1.04	$\frac{3.16}{6.25}$	1.01
$\frac{1}{3}$	$\frac{3.07}{9.2}$	1.00	$\frac{3.16}{9.2}$	1.03
$\frac{1}{4}$	$\frac{3.07}{11.85}$	1.04	$\frac{3.16}{12.59}$	1.00
$\frac{2}{3}$	$\frac{5.91}{9.2}$	0.96	$\frac{6.25}{9.2}$	1.02
$\frac{2}{4}$	$\frac{5.91}{11.85}$	1.00	$\frac{6.25}{12.59}$	0.99
$\frac{3}{4}$	$\frac{9.2}{11.85}$	1.03	$\frac{9.2}{12.95}$	0.97

In order to confirm the order of reaction w.r.t. $S_2O_8^{2-}$ ion from the plot of $\log -dc/dt$ vs $\log C_0$ represented in Figs. 2:5 A and 2:5 B, the value of the order w.r.t. $S_2O_8^{2-}$ ion has been evaluated, which comes out to be 1.00. This confirms the first order behaviour of the reaction w.r.t. $S_2O_8^{2-}$ ion.

A perusal of plots in Figs. 2:1 A, 2:1 B reveals that the plots of $\log (a-x)$ against time are almost linear in the earlier part of the reaction, with a tendency to deviate from linearity in the latter stage. This suggests that the traces of impurities present in hydrazides may be one of the reasons for this behaviour or some other reaction may be taking place in the later stages. It is known that with the progress of the reaction not only the ionic strength increases due to splitting up of one $S_2O_8^{2-}$ ion into two SO_4^{2-} ions, but K^+ ions are also present in the solution. Since both, the increase in ionic strength and presence of K^+ ion concentration cause an inhibitory effect on the reaction. Hence with the progress of the reaction both these effects come into play and thus decrease the rate constant continuously with time.

EFFECT OF n-CAPROIC AND n-HEPTANOIC ACID HYDRAZIDES
CONCENTRATION :

The effect of n-caproic and n-Heptanoic acid hydrazides concentration on the rate of the reaction was studied by taking five different initial concentrations of n-caproic and

n-Heptanoic acid hydrazides, keeping the concentrations of $K_2S_2O_8$ and of $AgNO_3$ constant. The results of these kinetic runs are recorded in Table 2:7 and depicted graphically in Figs. 2:3 A and Fig. 2:3 B.

The results given in the table 2:7 show that the first order rate constant increases with increase in [substrate concentration] hydrazides concentration. Such behaviour has been reported by Srivastava and Hambir Singh (142-144), Sankpal (154), Hiran and Joshi (61).

The specific rate is seen to be a function of the initial concentration of hydrazides being governed by the equation.

$$k = k_{\max} \times \frac{[\text{Hydrazide}]_0}{b + [\text{Hydrazide}]_0}$$

Where, 'k max = slope and 'b' = Intercept/slope. are evaluated by plotting a graph of $\frac{[\text{Hydrazide}]_0}{k}$ vs $[\text{Hydrazide}]_0$

Table 2:7

$$[K_2S_2O_8] = 2.0 \times 10^{-3} M. \quad [AgNO_3] = 1.5 \times 10^{-3} M. \quad [Na_2S_2O_3, 5H_2O] = 4.0 \times 10^{-3} M.$$

$$Temp. = 35^\circ C$$

Conc. of: Hydrazine des	0.5	:	0.75	:	1.00	:	1.25	:	1.50	
$\times 10^2 M.$	n-Cap. : A.H.	:	n-Hep. : A.H.	:	n-Cap. : A.H.	:	n-Hep. : A.H.	:	n-Cap. : A.H.	
Time (Min)	Vol (in ml) of $Na_2S_2O_3, 5H_2O$									
0	9.80	9.80	9.75	9.80	9.70	9.70	9.75	9.80	9.80	9.80
5	-	-	-	-	9.05	-	9.05	9.00	9.05	8.90
10	8.75	8.55	8.60	8.45	8.50	8.15	8.45	8.15	8.40	8.10
15	-	-	-	-	-	-	7.90	7.60	7.80	7.40
20	8.00	7.50	7.70	7.35	7.55	7.10	7.40	7.00	7.25	6.80
25	-	-	-	-	-	-	-	-	6.75	-
30	7.25	6.60	6.90	6.40	6.70	5.95	6.50	5.95	-	5.70
35	-	-	-	-	-	-	-	-	5.85	-
40	6.60	5.80	6.20	5.55	5.90	5.05	5.75	5.05	-	4.80
45	-	-	-	-	-	-	-	-	5.1	-
50	6.00	5.15	5.55	4.85	-	4.35	5.10	4.30	-	4.10
55	-	-	-	-	-	-	-	-	4.50	-
60	-	-	-	-	4.65	-	-	-	-	-
70	5.00	4.00	4.50	3.70	-	3.50	4.00	3.10	3.70	3.00
80	-	-	-	-	3.70	-	-	-	-	-
90	4.15	3.15	3.65	2.85	-	2.70	3.10	2.30	-	2.15
100	-	-	-	-	2.90	-	-	-	-	-
110	3.50	2.45	3.10	2.20	-	2.10	-	1.70	-	-
120	-	-	-	-	2.35	-	-	-	-	-
130	3.00	1.95	2.60	1.75	-	1.60	-	-	-	-
Mean k $\times 10^2$ min^{-1}	0.99	1.29	1.12	1.40	1.25	1.54	1.36	1.65	1.49	1.80

The nature of the plots were given in Figs. 2:4A, 2:4B and were found to be linear. So the expression can be given as

$$k = 0.0208 \times \frac{[n\text{-Cap. A.H.}]_0}{0.007916 + [n\text{-Cap. A.H.}]_0}$$

and

$$k = 0.0277 \times \frac{[n\text{-Hep. A.H.}]_0}{0.009444 + [n\text{-Hep. A.H.}]_0}$$

k values determined by using above expression, are in good agreement with the experimental values.

ORDER WITH RESPECT TO HYDRAZIDES :

A general behaviour of Ag^+ catalysed redox reaction involving persulphate ion, is that the order with respect to the reductant is zero. To investigate the order of the reaction w.r.t. hydrazides, the kinetic data of Table 2:7 was subjected to Van't Hoff differential method. From the initial slopes of the plots of concentration Vs time curves, the values of $(-dc/dt)_0$ corresponding to various initial concentrations of hydrazides were evaluated, which are given in Table 2:8

Table 2:8

Conc. of hydrazides $\times 10^2 \text{ M}$	0.50	0.75	1.00	1.25	1.50
$-dc/dt \times 10^4$ n-Cap.A.H.	4.59	4.90	5.22	5.33	5.70
n-Hep.A.H.	4.69	5.10	5.30	5.47	5.80

A plots of $\log (-dc/dt)_0$ Vs $\log (\text{Hydrazides})_0$ shown in figs. 2:6 A and 2:6 B. which gave the values of the slopes

as 0.23 and 0.24, for n-Cap. A.H. and n-Hep. A.H. respectively. The order of the reaction may also be calculated by Van't Hoff differential equation, as contained in Table 2:9.

Table 2:9

Conc. of Hydrazides $\times 10^2 M$ (Co)	n-Cap.A.H.		n-Hep.A.H.	
	$\frac{-dc}{dt} \times 10^4$	Order of reaction(n)	$\frac{-dc}{dt} \times 10^4$	Order of reaction(n)
$\frac{0.5}{0.75}$	$\frac{4.59}{4.90}$	0.14	$\frac{4.69}{5.10}$	0.13
$\frac{0.5}{1.00}$	$\frac{4.59}{5.22}$	0.18	$\frac{4.69}{5.30}$	0.17
$\frac{0.5}{1.25}$	$\frac{4.59}{5.33}$	0.22	$\frac{4.69}{5.47}$	0.21
$\frac{0.5}{1.50}$	$\frac{4.59}{5.70}$	0.26	$\frac{4.69}{5.80}$	0.24
$\frac{0.75}{1.00}$	$\frac{4.90}{5.22}$	0.12	$\frac{5.10}{5.30}$	0.13
$\frac{0.75}{1.25}$	$\frac{4.90}{5.33}$	0.15	$\frac{5.10}{5.47}$	0.16
$\frac{0.75}{1.50}$	$\frac{4.90}{5.70}$	0.17	$\frac{5.10}{5.80}$	0.18
$\frac{1.00}{1.25}$	$\frac{5.22}{5.33}$	0.13	$\frac{5.30}{5.47}$	0.12
$\frac{1.00}{1.50}$	$\frac{5.22}{5.70}$	0.14	$\frac{5.30}{5.80}$	0.13
$\frac{1.25}{1.50}$	$\frac{5.33}{5.70}$	0.11	$\frac{5.47}{5.80}$	0.11

This confirms that the order with respect to each hydrazide is nearly zero. The functional order obtained may be due to the effect of its own concentration, which accelerates its own oxidation.

EFFECT OF SILVER NITRATE CONCENTRATION :

In order to determine the effect of varying concentration of the catalyst on the reaction rate, the reaction was studied at five different concentrations of silver nitrate, the kinetic data of which have been represented in Tables 2:10A, 2:10B and plotted in Figs. 2:10A, 2:10B respectively.

Table 2:10 A

$[n\text{-Cap.A.H.}] = 1.0 \times 10^{-2} \text{M}$. $[\text{K}_2\text{S}_2\text{O}_8] = 2.0 \times 10^{-3} \text{M}$.

$[\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}] = 4.0 \times 10^{-3} \text{M}$. Temp. = 35°C

Conc. of AgNO_3 ($\text{M} \times 10^3$)	1.00	1.50	2.00	2.50	3.00
Time (min)	Vol. (in ml) of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$				
0	9.80	9.70	9.70	9.70	9.70
5	-	9.05	8.80	8.55	8.40
10	8.90	8.50	8.00	7.55	7.30
15	-	-	7.25	6.70	6.35
20	8.10	7.55	6.66	6.00	5.60
25	-	-	-	5.35	4.90
30	7.40	6.70	5.50	4.80	4.35
40	6.75	5.90	4.55	3.85	3.35
50	6.20	-	3.85	3.05	2.60
60	-	4.65	-	-	-
70	5.25	-	2.70	2.00	1.60
80	-	3.70	-	-	-
90	4.55	-	1.90	-	-
100	-	2.90	-	-	-
110	4.00	-	-	-	-
120	-	2.35	-	-	-
130	3.45	-	-	-	-
Mean k $\times 10^2 \text{ min}^{-1}$	0.89	1.25	1.89	2.39	2.73

Table 2:10 B

$$[\text{n-Hep.A.H.}] = 1.10^{-2} \text{M.} \quad [\text{K}_2\text{S}_2\text{O}_8] = 2 \times 10^{-3} \text{M.}$$

$$[\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}] = 4.0 \times 10^{-3} \text{M} \quad \text{Temp} = 35^\circ\text{C}$$

Conc. of AgNO_3 ($\text{M} \times 10^{-3}$)	1.00	1.50	2.00	2.50	3.00
Time (Min)	Vol (in ml) of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$.				
0	9.80	9.70	9.80	9.75	9.70
3	-	-	-	-	8.80
5	-	-	8.75	8.45	-
6	-	-	-	-	8.00
10	8.70	8.15	7.85	7.40	7.05
15	-	-	7.05	6.45	6.05
20	7.75	7.10	6.40	6.65	5.20
25	-	-	-	4.95	4.50
30	6.90	5.95	5.25	4.35	3.90
40	6.20	5.05	4.30	3.35	3.00
50	5.55	4.35	3.60	2.65	2.30
70	4.50	3.50	2.60	1.70	-
90	3.75	2.70	1.90	-	-
110	3.10	2.10	-	-	-
130	2.40	1.60	-	-	-
Mean k $\times 10^2 \text{min}^{-1}$	1.104	1.54	2.08	2.70	3.09

An examination of the results in the Tables 2:10A and 2:10B reveals that an increase in the concentration of the catalyst greatly enhances the reaction rate. Further, like other Ag^+ - catalysed $\text{S}_2\text{O}_8^{2-}$ ion reactions, the rate is found to be linearly related to the Ag^+ ion concentration, which is evident from the linearity of the curves shown in Figs. 2:7 A 2:7 B respectively.

Mishra and Ghosh (192) have however, reported a non-linear behaviour, but have failed to account for this abnormal behaviour.

EFFECT OF TEMPERATURE :

In order to determine the temperature coefficient, energy of activation (E), 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 30°C to 50°C . The results of these kinetic runs have been tabulated in Tables 2:11 A, 2:11 B and graphically represented in Figs. 2:11 A, 2:11 B respectively.

Table 2:11 A

$[n\text{-Cap.A.H.}] = 1.0 \times 10^{-2} \text{ M.}$, $[\text{AgNO}_3] = 1.5 \times 10^{-3} \text{ M.}$

$[\text{K}_2\text{S}_2\text{O}_8] = 2.0 \times 10^{-3} \text{ M.}$ $[\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}] = 4.0 \times 10^{-3} \text{ M.}$

Temp.	30°C	35°C	40°C	45°C	50°C
Time (min)	Vol (in ml) of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$				
0	9.70	9.70	9.70	9.70	9.70
5	-	9.05	8.85	8.60	8.35
10	8.75	8.50	8.10	7.70	7.20
15	-	-	-	6.90	6.25
20	7.95	7.55	6.95	6.30	5.40
25	-	-	-	-	4.75
30	7.25	6.70	5.90	5.10	4.15
40	6.60	5.90	5.00	4.15	3.15
50	6.05	-	4.30	3.55	2.50
60	-	4.65	3.60	-	2.00
70	5.05	-	-	2.50	-
75	-	-	2.90	-	-
80	-	3.70	-	-	-
90	4.20	-	2.35	1.80	-
100	-	2.90	-	-	-
110	3.50	-	-	-	-
120	-	2.35	-	-	-
Mean $\text{k} \times 10^2$ min^{-1}	0.96	1.25	1.67	2.13	2.85

Table 2:11 B

[n-Hep.A.H.] = 1.0×10^{-2} M. [AgNO₃] = 1.5×10^{-3} M.

[K₂S₂O₈] = 2.0×10^{-3} M. [Na₂S₂O₃, 5H₂O] = 4.0×10^{-3} M.

Temp.	30°C	35°C	40°C	45°C	50°C
Time (min)	Vol (in ml) of Na ₂ S ₂ O ₃ , 5H ₂ O				
0	9.70	9.70	9.80	9.75	9.90
5	-	-	8.90	8.60	8.35
10	8.50	8.15	8.00	7.60	7.20
15	-	-	7.25	6.75	6.20
20	7.50	7.10	6.60	6.00	5.35
25	-	-	-	5.30	4.60
30	6.65	5.95	5.45	4.70	4.00
35	-	-	-	4.20	-
40	5.85	5.05	4.50	-	3.15
50	5.20	4.35	3.75	2.95	2.40
70	4.10	3.50	2.60	1.85	1.40
90	3.25	2.70	1.80	-	-
110	2.60	2.10	-	-	-
130	2.05	1.60	-	-	-
Mean kx10 ² min ⁻¹	1.24	1.54	1.96	2.43	2.99

It is seen from the above results that the mean values of temperature coefficient for 10°C rise come out to be 1.71 for n-caproic acid hydrazide and 1.56 for n-Heptanoic acid hydrazide respectively, such type of behaviour has been reported by Singh H., Govil J.C., Saksena, S.C. (193) in their kinetic study of silver catalysed oxidation of α -hydroxymonocarboxylic acids by $K_2S_2O_8$. A plots of $\log k$ Vs $\frac{1}{T}$ are found to be linear as shown in Figs. 2:9 A and 2:9 B. This shows that the reaction obeys Arrhenius relationship. The values of energy of activation (E) evaluated from the slope of this curves come out to be 10.4 for n-caproic acid hydrazide and 8.83 k cal $s\ mole^{-1}$ for n-Heptanoic acid hydrazide respectively.

The Arrhenius equation has been used directly to calculate energies of activation, which come out to be 10.52 K cal $s\ mole^{-1}$ for n-caproic acid hydrazide and 8.66 k cal $s\ mole^{-1}$ for n-Heptanoic acid hydrazide. On the basis of these calculated values the frequency factor A, free energy of activation (ΔG^\ddagger) and entropy of activation (ΔS^\ddagger) have been calculated by the application of the following equations :

$$\begin{aligned} \text{i) } kr &= A \cdot e^{-E/RT} & \text{ii) } kr &= \frac{kT}{h} \cdot e^{-\Delta G^\ddagger/RT} \\ \text{iii) } A &= e \cdot \frac{kT}{h} \cdot e^{\Delta S^\ddagger/R}. \end{aligned}$$

Where equation (iii) is applicable to the reactions taking place in solution. In the above equations : 'kr' is the specific rate, 'k' is the Boltzmann constant, 'h' is the Planck's constant and 'e' is 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 for the reaction, ΔG^\ddagger was calculated by using the equation

$$\text{iv) } k_r = \frac{kT}{h} \cdot e^{-\frac{\Delta G^\ddagger}{RT}}$$

equation (ii) can be expressed in terms of enthalpy change as

$$k_r = \frac{kT}{h} \cdot e^{-\frac{\Delta H^\ddagger}{RT}} \cdot e^{\frac{\Delta S^\ddagger}{R}}$$

OR

$$\log \frac{k_r}{kT/h} = -\frac{\Delta H^\ddagger}{2.303RT} + \frac{\Delta S^\ddagger}{2.303R}$$

The values of $\log \left[\frac{k_r}{kT/h} \right]$ have been plotted against $\frac{1}{T}$ in Figs. 2:9 A and 2:8 B, from the slope of which the enthalpy change for the formation of activated complex (ΔH^\ddagger) has been calculated. The values of ΔH^\ddagger , obtained from the graphs are 9.59 k cal mole⁻¹ for n-Cap. A.H. and 7.69 k cal mole⁻¹ for n-Hep. A.H. These have been used to calculate ΔS^\ddagger from the above equation. The various energy parameters obtained, have been recorded in Tables 2:12 A and 2.12:B.

A large negative value of entropy of activation is indicative of the formation of an activated complex involving two oppositely charged ions or an ion and a neutral molecule.

So the rate constant for this reaction may be expressed by the following equation.

$$k_r = 6.15 \times 10^2 \cdot e^{-\frac{10520}{RT}} \text{ sec}^{-1} \quad \text{and} \quad k_r = 3.65 \times 10^2 \cdot e^{\frac{8660}{RT}} \text{ sec}^{-1}$$

Table 2:12 A

Temp. °k	Temp. Coefficient	Energy of activation E_a (k cal mole ⁻¹)	Frequency Factor $A \times 10^2$ Sec ⁻¹	Entropy of Activation ΔS^\ddagger (e.u.)	Free energy of activation ΔG^\ddagger (k cal mole ⁻¹)
303	-	-	6.21	- 35.09	20.55
308	1.74	10.43	6.08	- 35.16	20.73
313	1.70	10.38	6.18	- 35.16	20.90
318	1.70	10.74	6.04	- 35.24	20.09
323	-	-	6.24	- 35.20	21.25
Mean	1.71	10.52	6.15	- 35.17	20.70

1) Graphically energy of activation = 10.4 k cal

2) Graphically $\Delta H^\ddagger = 9.59$ k cal mole⁻¹

Table 2:12 B

Temp °k	Temp coefficient	Energy of activation E_a (k cal mole ⁻¹)	Frequency factor $A \times 10^2$ sec ⁻¹	Entropy of activation ΔS^\ddagger (e.u.)	Free energy of activation ΔG^\ddagger k cal mole ⁻¹
303	-	-	3.68	-43.31	20.39
308	1.58	8.63	3.62	-43.34	20.61
313	1.58	8.88	3.67	-43.50	20.80
318	1.52	8.48	3.66	-43.50	21.00
323	-	-	3.64	-43.49	21.21
Mean	1.56	8.66	3.65	-43.43	20.80

1) Graphically energy of activation = 8.83 k cal mole⁻¹

2) Graphically $\Delta H^\ddagger = 7.67$ k cal mole⁻¹.

EFFECT OF IONIC STRENGTH :

To investigate the effect of ionic strength, the reaction was studied by adding different amounts of K_2SO_4 to the reaction mixture in order to get the desired ionic strength. The results of these kinetic runs have been reported in the Tables 2:13 A and 2:13 B respectively.

An examination of the results contained in the Tables 3:13 A and 3:13 B shows that the specific rate decreases with the increasing ionic strength, meaning thereby that the salt effect is negative. It is also observed that the reaction retains its first order behaviour.

As it is already observed that the salt effect is negative, it is also essential to investigate the nature of observed negative salt effect, graphs of k vs μ were drawn as shown in Figs. 2:12 A and 2:12 B respectively. It is seen that there exists no linearity between k and μ . The linearity exists only in the region of low ionic strength (< 0.2101), showing that the negative salt effect is of the primary exponential type in the region of low ionic strength. This suggests that the rate determining process may be between two oppositely charged ions.

Table 2:13 A

[n-Cap.A.H.] = 1.0×10^{-2} M. [AgNO₃] = 1.5×10^{-3} M

[K₂S₂O₈] = 2.0×10^{-3} M. [Na₂S₂O₃, 5H₂O] = 4.0×10^{-2} M.

Temp. = 35°C.

Conc. of K ₂ SO ₄ × 10 ³ M	Nil	2.00	4.00	5.00	6.00	8.00	10.00
μ	:0.0075	:0.0135	:0.0195	:0.0225	:0.0255	:0.0315	:0.0375
Time(min)	Vol (in ml) of Na ₂ S ₂ O ₃ , 5H ₂ O						
0	9.70	9.70	9.70	9.70	9.70	9.70	9.70
5	9.05	-	-	-	-	-	9.30
10	8.50	8.60	8.70	8.80	8.85	8.90	8.95
20	7.55	7.70	7.80	8.00	8.15	8.20	8.30
30	6.70	6.90	7.25	7.30	7.50	7.55	7.70
40	5.90	6.15	6.60	6.70	6.90	7.00	7.15
50	-	5.50	6.00	6.20	6.35	6.45	-
60	4.64	-	-	-	-	6.00	6.15
70	-	4.50	5.10	5.30	5.40	5.55	-
80	3.70	-	-	-	-	-	5.30
90	-	3.85	4.35	4.50	4.70	4.75	-
100	2.90	-	-	-	-	-	4.60
110	-	3.00	3.65	3.80	4.00	4.10	-
120	-	2.70	3.10	3.25	3.45	-	-
130	-	2.70	3.10	3.25	3.45	-	-
Mean × 10 ² min ⁻¹	1.25	1.10	0.96	0.90	0.84	0.82	0.77

Table 2:13 B

[n-Hep. A.H.] = 1.0×10^{-2} M. [AgNO₃] = 1.5×10^{-3} M

[K₂S₂O₈] = 2.0×10^{-3} M. [Na₂S₂O₃, 5H₂O] = 4.0×10^{-3} M.

Temp. = 35°C

Conc. of K ₂ SO ₄ x 10 ³ M	Nil	2.00	4.00	5.00	6.00	8.00	10.00
μ	:0.0075	:0.0135	:0.0195	:0.0225	:0.0255	:0.0315	:0.0375
Time(min)	Vol(in ml) of Na ₂ S ₂ O ₃ , 5H ₂ O						
0	9.70	9.80	9.80	9.70	9.80	9.80	9.80
5	-	-	-	-	-	-	-
10	8.15	8.45	8.50	8.50	8.60	8.65	8.75
20	7.10	7.30	7.40	7.45	7.60	7.70	7.80
30	5.95	6.30	6.50	6.55	6.75	6.90	7.00
40	5.05	5.55	5.70	5.75	6.00	6.20	6.25
50	4.35	4.85	5.05	5.10	5.30	5.50	5.70
70	3.50	3.70	3.90	3.95	4.15	4.40	4.60
90	2.70	2.80	3.00	3.15	3.30	3.60	3.80
110	2.10	2.20	2.30	2.50	2.65	3.00	3.50
130	1.60	1.70	1.85	2.00	2.10	2.50	2.90
Mean k x 10 ² min ⁻¹	1.54	1.42	1.34	1.28	1.23	1.14	1.06

SPECIFIC ION EFFECT :

It is intended to determine specific ionic effect of other cations, if there is any, the reaction was studied in presence of six different salts at constant ionic strength. The

results of these measurements are contained in Tables 2:14A, and 2:14B and graphically represented in Figs.2:13A, and 2:13B respectively.

Table 2:14 A

$$[\text{n-Cap. A.H.}] = 1.0 \times 10^{-2} \text{M.} \quad [\text{AgNO}_3] = 1.5 \times 10^{-3} \text{M}$$

$$[\text{K}_2\text{S}_2\text{O}_8] = 2.0 \times 10^{-3} \text{M.} \quad [\text{Na}_2\text{S}_2\text{O}_3, 5\text{H}_2\text{O}] = 4.0 \times 10^{-3} \text{M}$$

$$\text{Temp.} = 35^\circ\text{C} \quad \mu = 0.0180$$

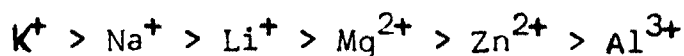
Cations	: K ⁺	: Na ⁺	: Li ⁺	: Mg ²⁺	: Zn ²⁺	: Al ³⁺
Conc. x 10 ³ M	: 5.00	: 5.00	: 5.00	: 3.75	: 3.75	: 1.00
Time (min)	Vol (in ml) of Na ₂ S ₂ O ₃ , 5H ₂ O					
0	9.70	9.75	9.80	9.80	9.80	9.70
10	8.80	8.75	8.80	8.70	8.70	8.55
20	8.00	7.90	7.90	7.80	7.75	7.55
30	7.30	7.15	7.10	7.00	6.95	6.70
40	6.70	6.45	6.40	6.25	6.20	5.90
50	6.20	5.85	5.80	5.60	5.55	5.25
70	5.30	4.80	4.70	4.50	4.45	4.10
90	4.50	3.95	3.90	3.60	3.55	3.30
110	3.80	3.30	3.25	2.85	2.90	2.60
130	3.25	2.75	2.65	2.35	2.40	2.10
Mean x 10 ² min ⁻¹	0.90	1.02	1.05	1.12	1.14	1.22

Table 2:14 B

[n-Hep. A.H.] = 1.0×10^{-2} M. [AgNO₃] = 1.5×10^{-3} M.
 [K₂S₂O₈] = 2.0×10^{-3} M. [Na₂S₂O₃, 5H₂O] = 4.0×10^{-3} M
 $\mu = 0.0108$ Temp. = 35°C

Cations	: K ⁺	: Na ⁺	: Li ⁺	: Mg ²⁺	: Zn ²⁺	: Al ³⁺
Conc. x 10 ³ M	: 5.00	: 5.00	: 5.00	: 3.75	: 3.75	: 1.00
Time(min)	Vol (in ml) of Na ₂ S ₂ O ₃ , 5H ₂ O.					
0	9.80	9.80	9.80	9.80	9.80	9.80
10	8.50	8.45	8.45	8.35	8.40	8.35
20	7.50	7.45	7.20	7.25	7.20	7.15
30	6.45	6.40	6.30	6.25	6.20	6.10
40	5.65	5.60	5.45	5.35	5.30	5.20
50	4.95	4.80	4.75	4.60	4.50	4.40
70	3.75	3.60	3.55	3.50	3.35	3.30
90	2.90	2.85	2.65	2.60	2.50	2.40
110	2.25	2.20	2.05	2.00	1.85	1.75
130	1.75	1.60	1.55	1.50	1.45	-
Mean ₂ x 10 ₁ ² min	1.35	1.40	1.45	1.49	1.51	1.57

A close scrutiny of the above data shows that all these cations have specific inhibitory effect on the reaction. This inhibitory effect is not of the same magnitude, but varying magnitude, it being in the order of



EFFECT OF HYDROGEN ION CONCENTRATION :

Investigation of the effect of hydrogen ion on the rate of the reaction was undertaken. It was found that the reaction did not take place in acidic medium indicating that protonated species did not undergo oxidation by peroxydisulphate.

EFFECT OF ALLYL ACETATE :

It is well known that the reaction involving $S_2O_8^{2-}$ ion is inhibited by allyl acetate (194,195). It has been shown by Kolthoff et. al.(196), Wiberg (195) and Ball and Co-workers(197) that the allyl acetate is an efficient scavenger for sulphate ion radical ($\dot{S}O_4$), which is known to be formed in the oxidation reactions involving $S_2O_8^{2-}$ ion. Hence, it was considered necessary to investigate the effect of allyl acetate on peroxydisulphate oxidation of organic substrates. The reaction was carried out in the absence of and at four different initial concentrations of allyl acetate. The results of these kinetic runs are tabulated in Tables 2:15 A, 2:15 B and shown graphically in Figs. 2:14 A, 2:14 B, respectively.

The results contained in Tables 2:15A and 2:15 B show that allyl acetate inhibits the rate of reaction, and therefore, the reactions involving $S_2O_8^{2-}$ ion are inhibited by allyl acetate acting as trapping agent (194, 197) for sulphate radical ion. Here, it may be pointed out that allyl acetate does not act as an efficient radical capture agent. The radical capture may be due to subsequent polymerisation of allyl

acetate by sulphate radical ions formed from the catalysed decomposition of peroxydisulphate ion. Gupta and Srivastava (198) have observed that the reaction is considerably inhibited by allyl acetate and allyl alcohol, when they studied the effect of these inhibitors on oxidation of aromatic amines. They also observed that the extent of inhibition in each case is a function of its concentration.

Table 2:15 A

$$[n\text{-Cap.A.H.}] = 1.0 \times 10^{-2} \text{M.} \quad [\text{AgNO}_3] = 1.5 \times 10^{-3} \text{M}$$

$$[\text{K}_2\text{S}_2\text{O}_8] = 2.0 \times 10^{-3} \text{M.} \quad [\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}] = 4.0 \times 10^{-3} \text{M}$$

$$\text{Temp} = 35^\circ\text{C}$$

Allyl acetate conc x 10^2 M.	: Nil : 1.00 : 2.00 : 3.00 : 4.00				
Time (Min).	Vol. (in ml) of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$				
0	9.70	9.80	9.75	9.70	9.80
5	-	-	-	9.25	-
10	8.50	8.70	8.80	8.90	9.00
20	7.55	7.80	8.00	8.10	8.30
30	6.70	7.05	7.25	7.45	7.65
40	5.90	6.35	6.55	6.80	7.10
50	-	5.70	5.95	-	6.55
60	4.65	-	-	5.70	-
70	-	4.60	5.00	-	5.60
80	3.70	-	-	4.95	-
90	-	3.70	4.15	-	4.80
100	2.90	-	-	4.10	-
110	-	3.05	3.50	-	4.10
120	2.35	-	-	3.50	-
130	-	2.50	3.00	-	3.00
Mean $k \times 10^2$ min^{-1}	1.25	1.10	0.97	0.89	0.81

Table 2:15 B

[n-Hep.A.H.] = 1.0×10^{-2} M. [AgNO₃] = 1.5×10^{-3} M.
 [K₂S₂O₈] = 2.0×10^{-3} M. [Na₂S₂O₃, 5H₂O] = 4.0×10^{-3} M
 Temp. = 35°C

Allyl ace- tate conc x 10 ² M.	Vol (in ml) of Na ₂ S ₂ O ₃ , 5H ₂ O				
: Nil	1.00	2.00	3.00	4.00	
Time (min)	Vol (in ml) of Na ₂ S ₂ O ₃ , 5H ₂ O				
0	9.70	9.80	9.75	9.80	9.70
10	8.15	8.35	8.40	8.55	8.55
20	7.10	7.15	7.25	7.50	7.60
30	5.95	6.15	6.30	6.60	6.75
40	5.05	5.45	5.55	5.80	6.00
50	4.35	4.60	4.75	5.10	5.35
70	3.50	3.55	3.60	4.00	4.30
90	2.70	2.75	2.80	3.10	3.40
110	2.10	2.20	2.30	2.40	2.70
130	1.60	1.70	1.80	1.90	2.20
Mean k x 10 ² min ⁻¹	1.54	1.51	1.44	1.30	1.19

IDENTIFICATION OF OXIDATION PRODUCT :

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

The reaction was carried out by using n-caproic acid hydrazide and peroxydisulphate solution in excess and overall

concentration of silver nitrate was maintained at $1.5 \times 10^{-3} M$ to accelerate the rate of oxidation. The flask containing reaction mixture was kept in thermostated water bath, whose temperature was maintained at $35^{\circ}C$. Few drops of dil. HCl(1N) were added to the reaction after it was kept for 24 hrs. in the thermostated water bath to precipitated Ag^{+} as AgCl. The filtered solution was heated to destroy peroxydisulphate (tested with KI and starch). The solution was further concentrated and was used for identification of the end products. The n-caproic acid was identified, as oxidation product. Similarly, the n-Heptanoic acid was identified by using the same procedure.

- i) Carboxylic acid, a functional group, was detected by $NaHCO_3$ test.
- ii) Amide (199) derivatives were prepared -
 - a) M.P. for n-caproamide = $99^{\circ}C$ ($100^{\circ}C$).
 - b) M.P. for n-Heptamide = $95^{\circ}C$ ($96^{\circ}C$).
- iii) From the reaction mixture n-caproic acid was separated by paper chromatographic technique (200) using ethanol-ammonia-water (80:4:16) solvent system.

The paper chromatogram was sprayed with bromothymol-blue (40 mg in 100 ml H_2O) and was exposed for short time to NH_3 vapour, a yellow spot indicates the presence of n-caproic acid.

Same procedure was followed to identify n-Heptanoic acid. The yellow spot on paper chromatogram indicates the presence of n-Heptanoic acid.

- i) R.F. value for n-caproic acid = 0.70
- ii) R.F. value for n-Heptanoic acid = 0.75
respectively.
- iii) Nitrogen was detected by lime test (201).

FIG. 2:1 A

EFFECT OF VARYING $[S_2O_8^{2-}]$ AT $35^\circ C$.

$$[n\text{-Cap. A. H.}] = 1.0 \times 10^{-2} \text{ M}$$

$$[AgNO_3] = 1.5 \times 10^{-3} \text{ M}$$

$$[S_2O_8^{2-}] = I = 1.0 \times 10^{-3} \text{ M}$$

$$II = 2.0 \times 10^{-3} \text{ M}$$

$$III = 3.0 \times 10^{-3} \text{ M}$$

$$IV = 4.0 \times 10^{-3} \text{ M}$$

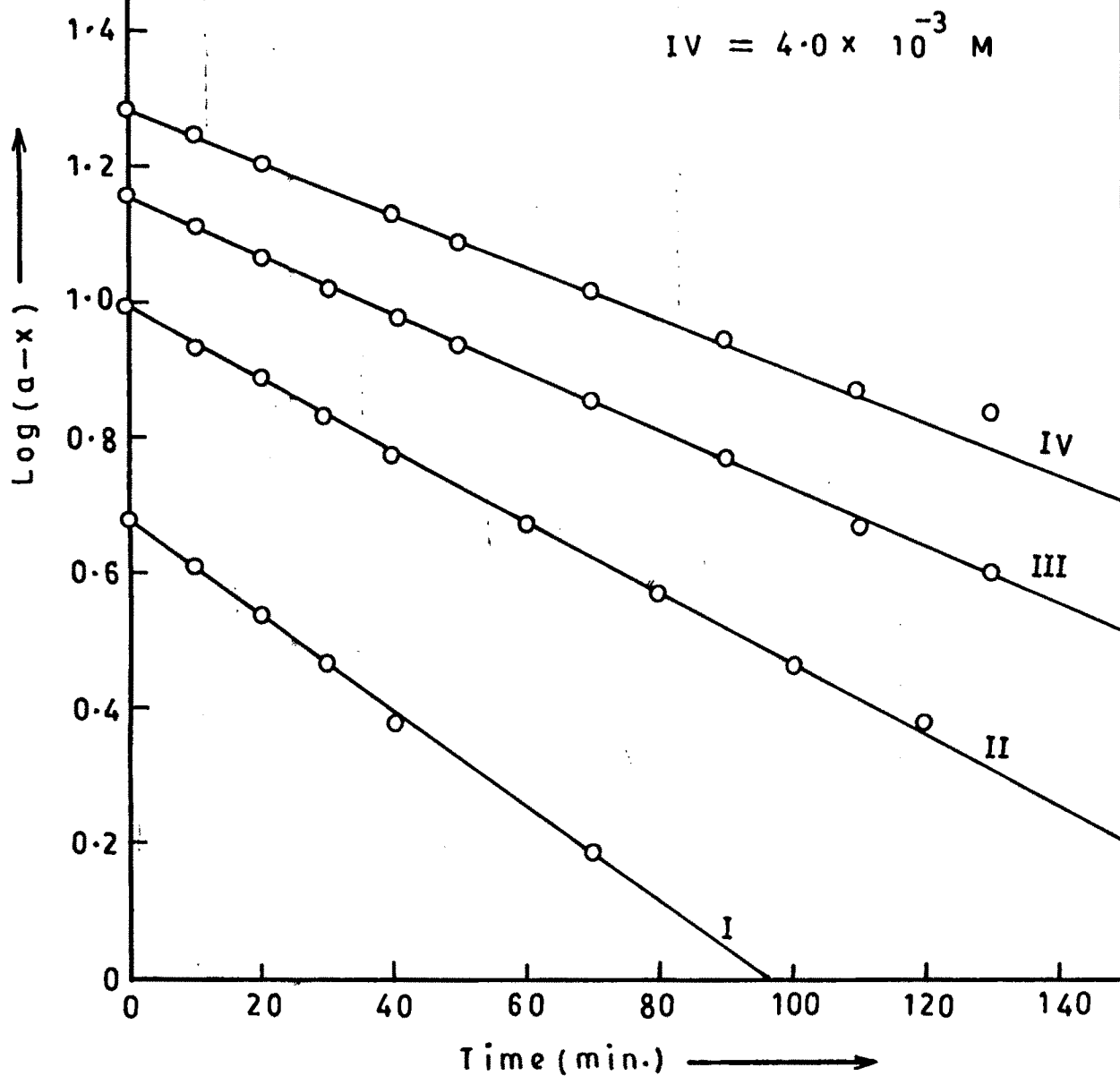


FIG. 2:1 B

EFFECT OF VARYING $[S_2O_8^{2-}]$ AT $35^\circ C.$

$$[n\text{-Hep. A.H.}] = 1.0 \times 10^{-2} \text{ M}$$

$$[AgNO_3] = 1.5 \times 10^{-2} \text{ M}$$

$$[S_2O_8^{2-}] = I = 1.0 \times 10^{-3} \text{ M}$$

$$II = 2.0 \times 10^{-3} \text{ M}$$

$$III = 3.0 \times 10^{-3} \text{ M}$$

$$IV = 4.0 \times 10^{-3} \text{ M}$$

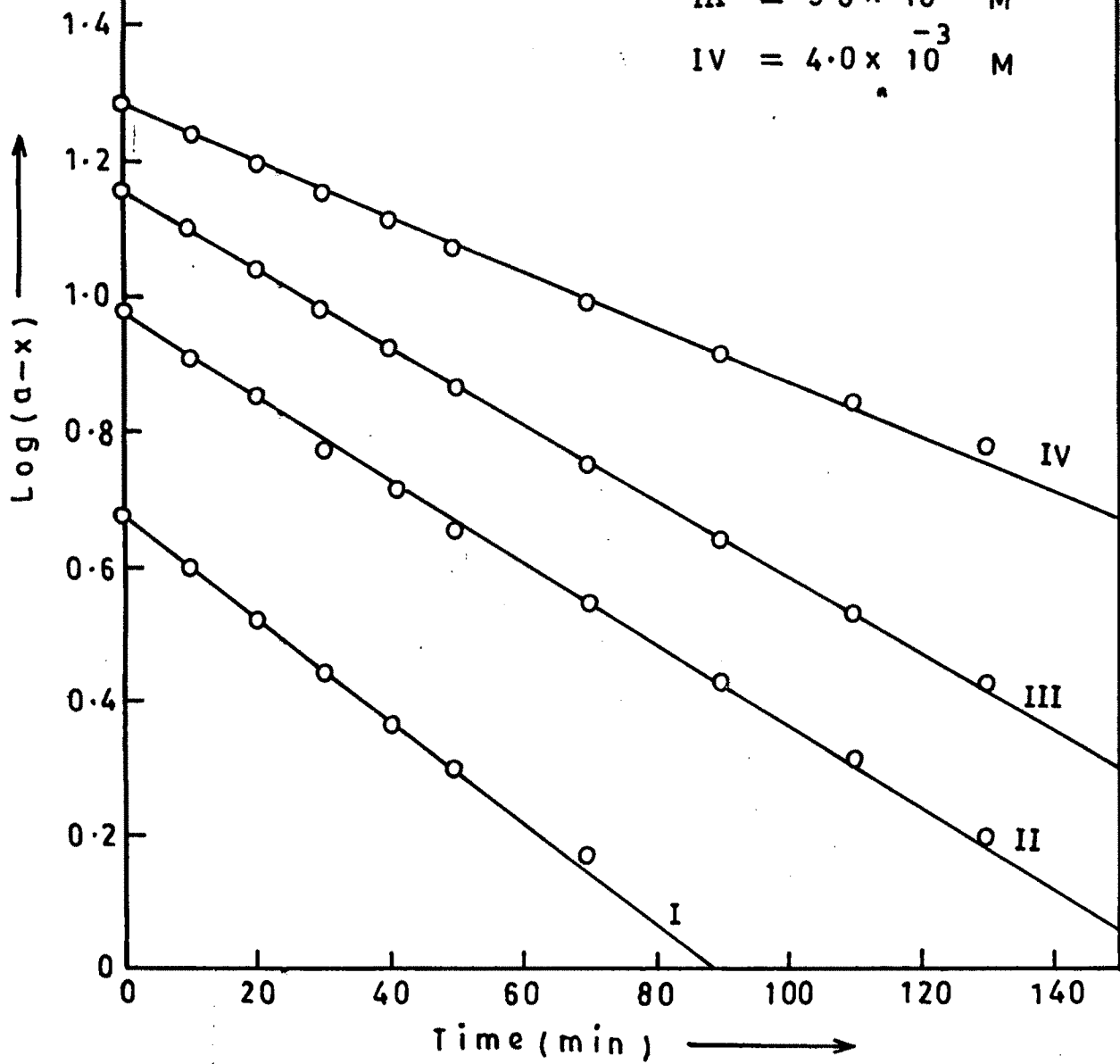


FIG. 2:2 A

EFFECT OF VARYING $[S_2O_8^{2-}]$ AT
CONSTANT IONIC STRENGTH (μ).

$$[n\text{-Cap. A. H.}] = 1.0 \times 10^{-2} \text{ M}$$

$$[AgNO_3] = 1.5 \times 10^{-3} \text{ M}$$

$$\mu = 0.0305$$

$$[K_2S_2O_8] = I = 1.0 \times 10^{-3} \text{ M}$$

$$II = 2.0 \times 10^{-3} \text{ M}$$

$$III = 3.0 \times 10^{-3} \text{ M}$$

$$IV = 4.0 \times 10^{-3} \text{ M}$$

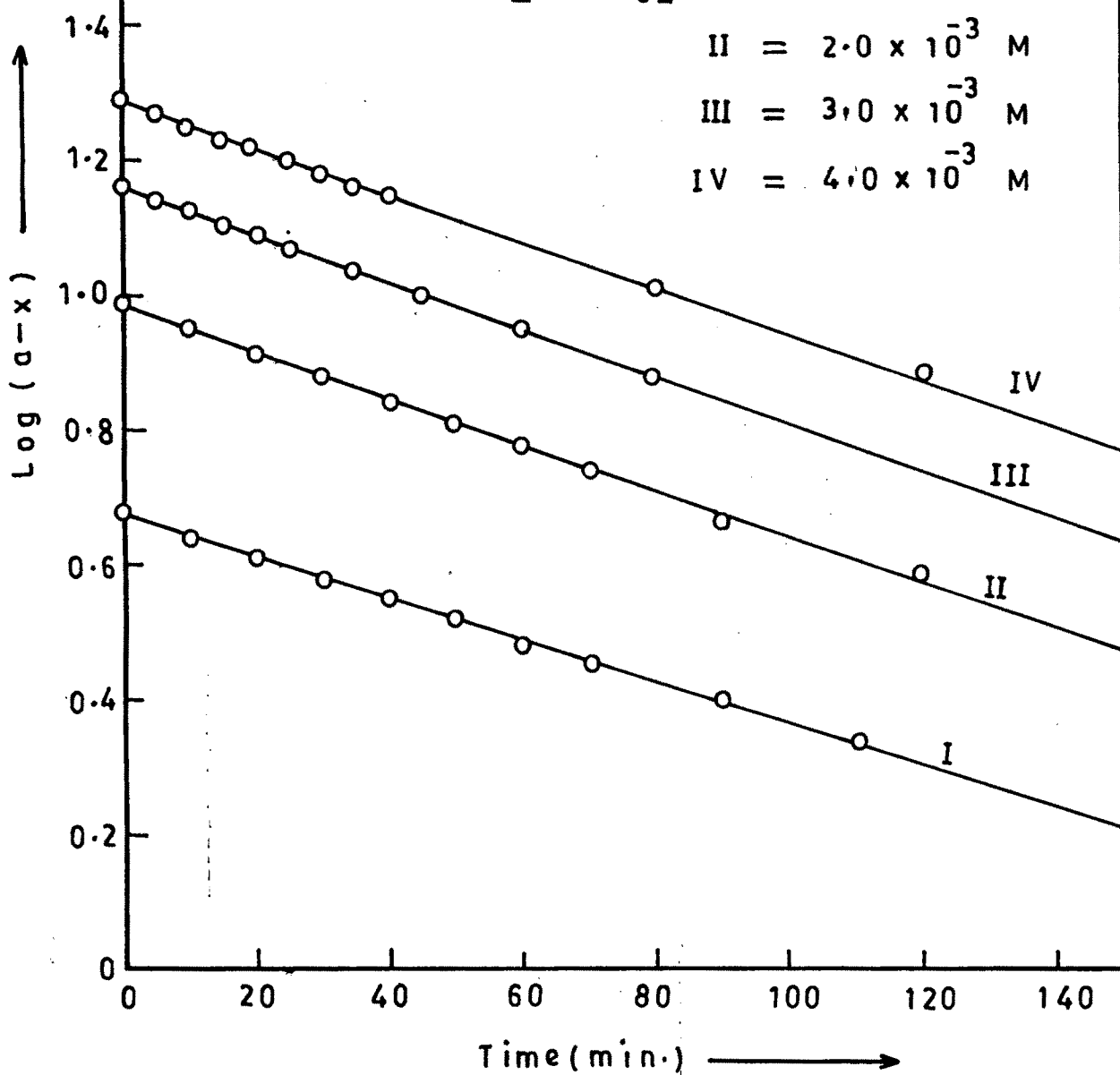


FIG. 2:2 B

EFFECT OF VARYING $[S_2O_8^{2-}]$ AT
 CONSTANT IONIC STRENGTH (μ).

$$[n\text{-Hep. A. H.}] = 1.0 \times 10^{-3} \text{ M}$$

$$[AgNO_3] = 1.5 \times 10^{-3} \text{ M}$$

$$\mu = 0.0305$$

$$[K_2S_2O_8] = I = 1.0 \times 10^{-3} \text{ M}$$

$$II = 2.0 \times 10^{-3} \text{ M}$$

$$III = 3.0 \times 10^{-3} \text{ M}$$

$$IV = 4.0 \times 10^{-3} \text{ M}$$

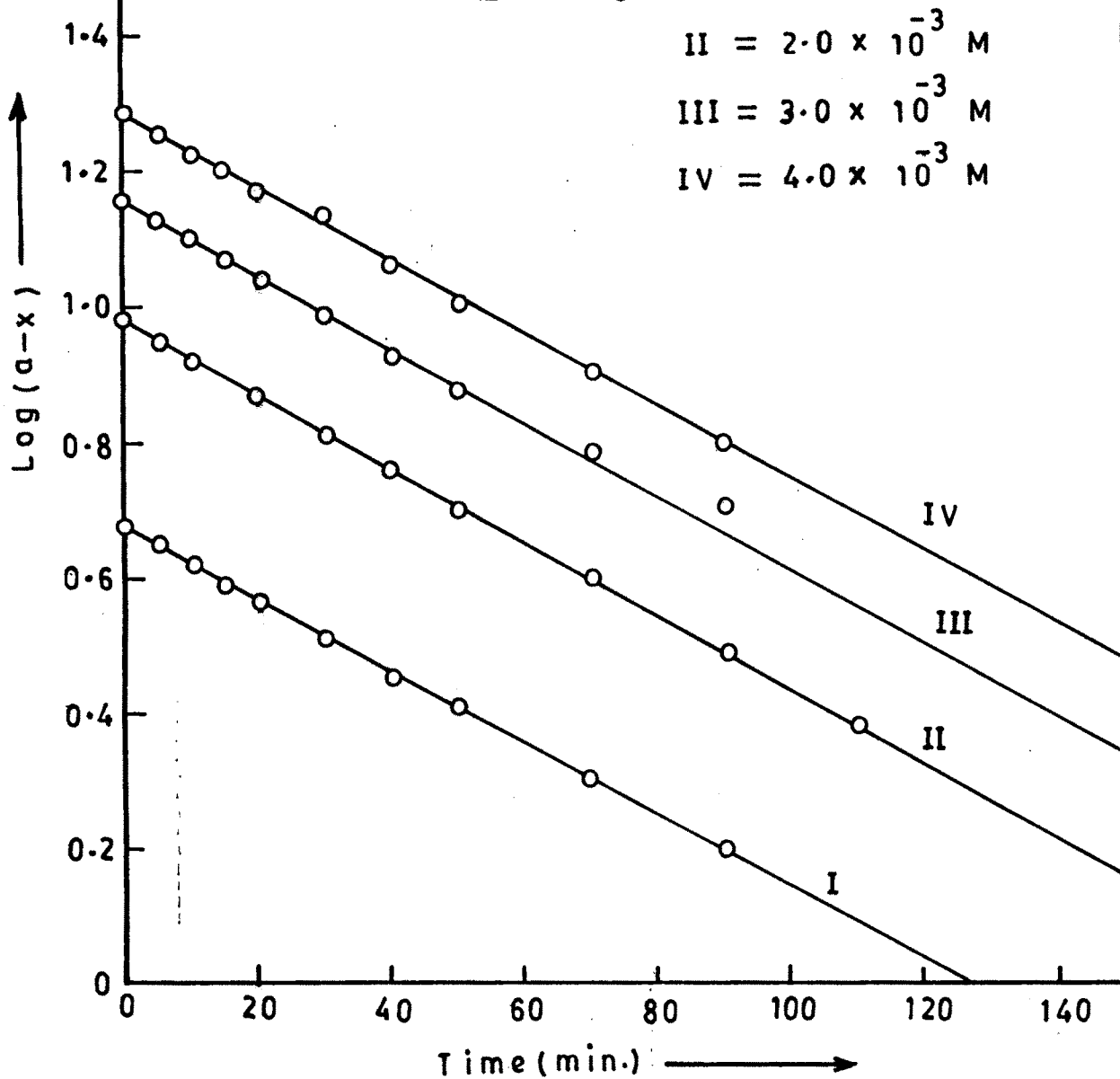


FIG. 2:3 A

EFFECT OF VARYING n-CAP. A.H. CONC. AT 35° C.

$$[K_2S_2O_8] = 2.0 \times 10^{-3} \text{ M}$$

$$[AgNO_3] = 1.5 \times 10^{-3} \text{ M}$$

$$[n\text{-Cap. A.H.}] = \text{I} = 0.5 \times 10^{-2} \text{ M}$$

$$\text{II} = 0.75 \times 10^{-2} \text{ M}$$

$$\text{III} = 1.0 \times 10^{-2} \text{ M}$$

$$\text{IV} = 1.25 \times 10^{-2} \text{ M}$$

$$\text{V} = 1.50 \times 10^{-2} \text{ M}$$

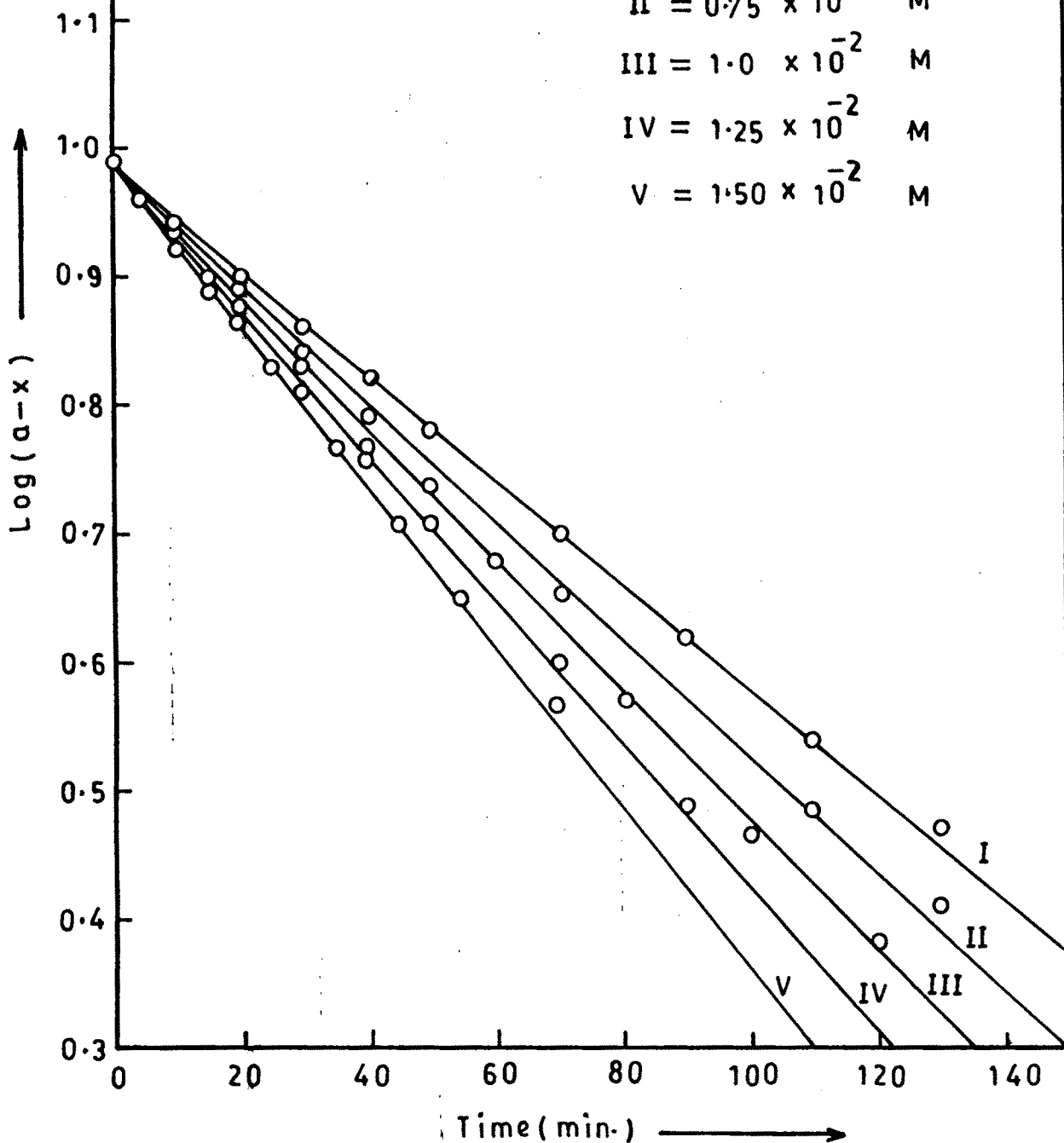


FIG. 2:3 B

EFFECT OF VARYING n-HEP. A. H. CONC. AT 35° C.

$$[K_2S_2O_8] = 2.0 \times 10^{-3} \text{ M}$$

$$[AgNO_3] = 1.5 \times 10^{-3} \text{ M}$$

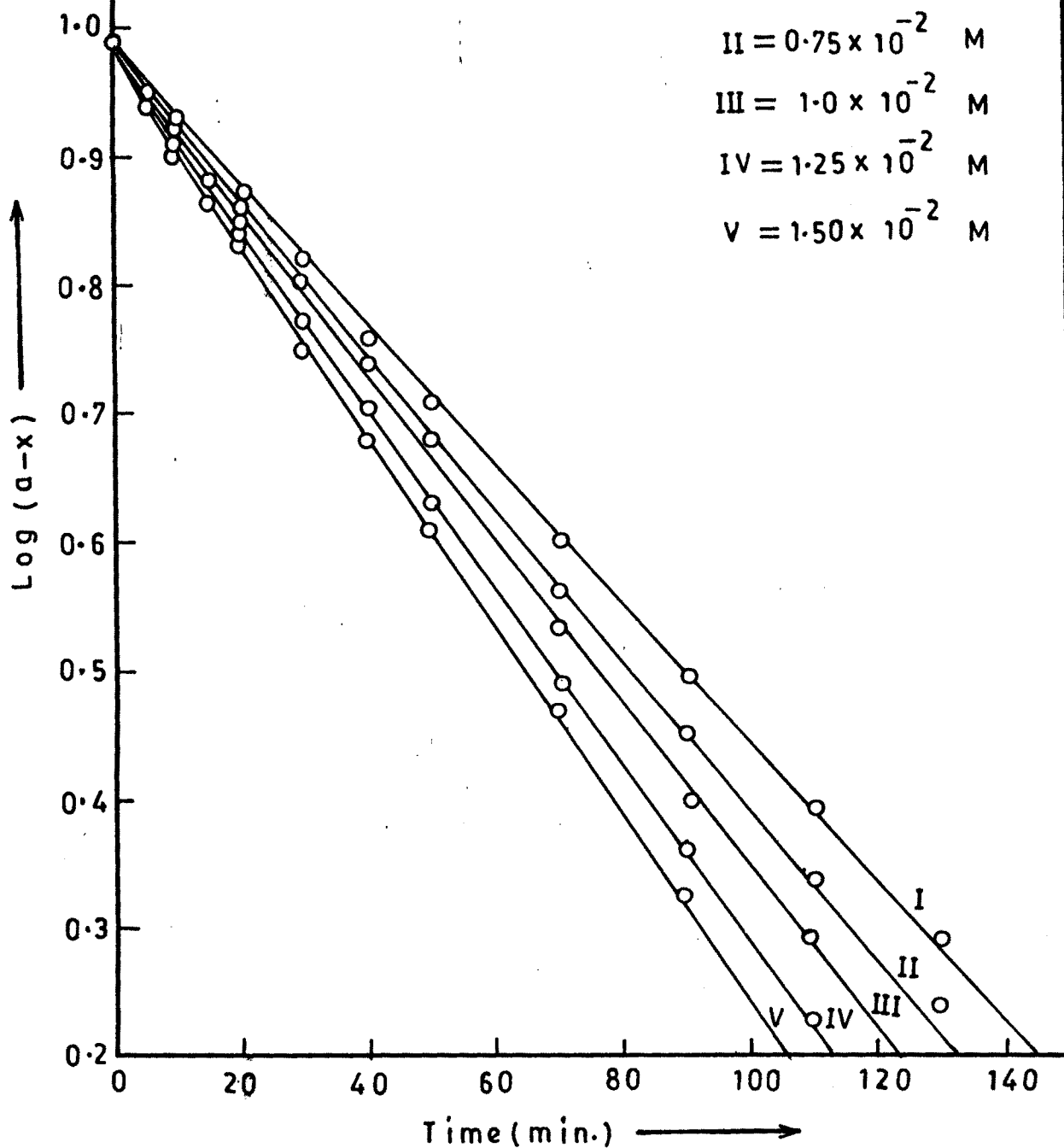
$$[n\text{-Hep, A. H.}] = I = 0.5 \times 10^{-2} \text{ M}$$

$$II = 0.75 \times 10^{-2} \text{ M}$$

$$III = 1.0 \times 10^{-2} \text{ M}$$

$$IV = 1.25 \times 10^{-2} \text{ M}$$

$$V = 1.50 \times 10^{-2} \text{ M}$$



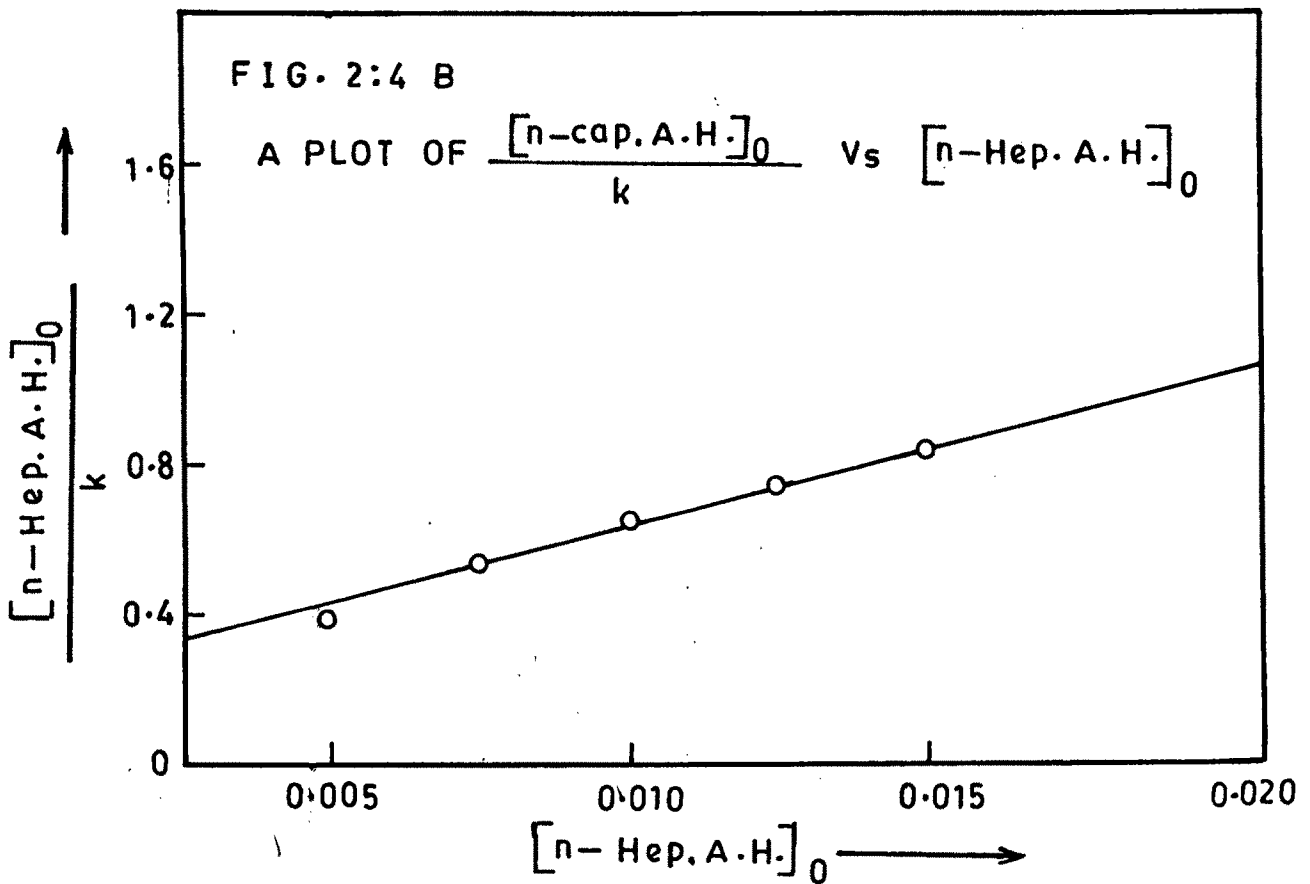
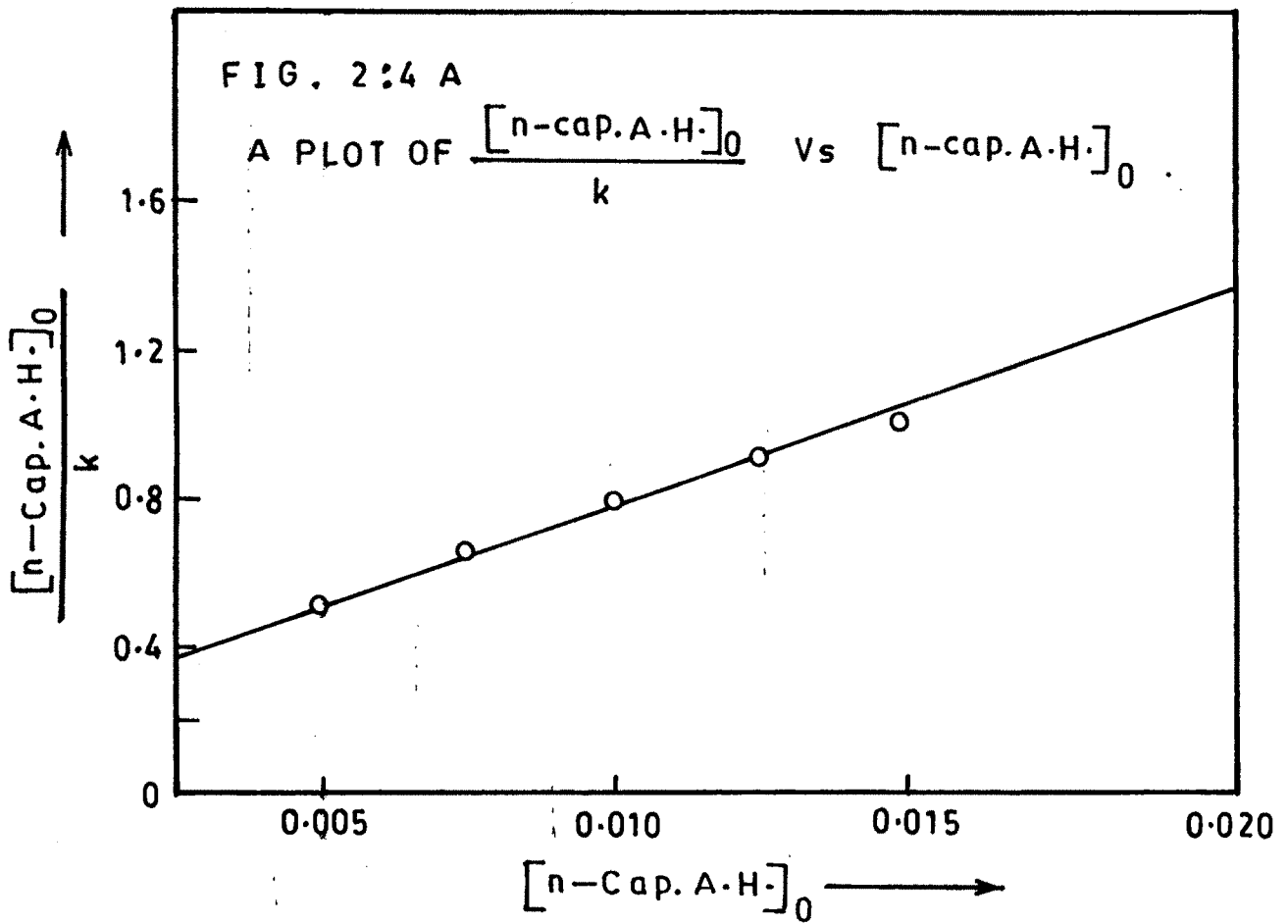


FIG. 2:5 A

A PLOT OF $\text{Log}(-\frac{dc}{dt})$ Vs $\text{Log} [S_2O_8^{2-}]_0$.

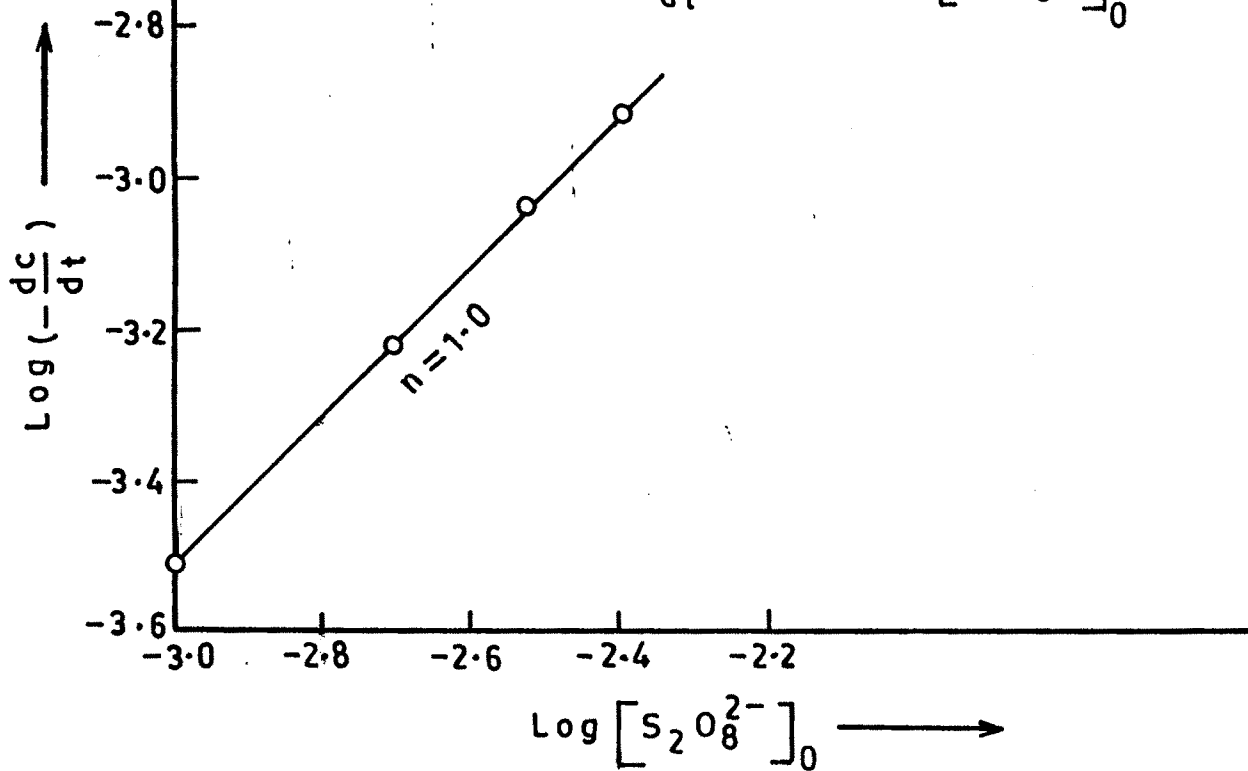
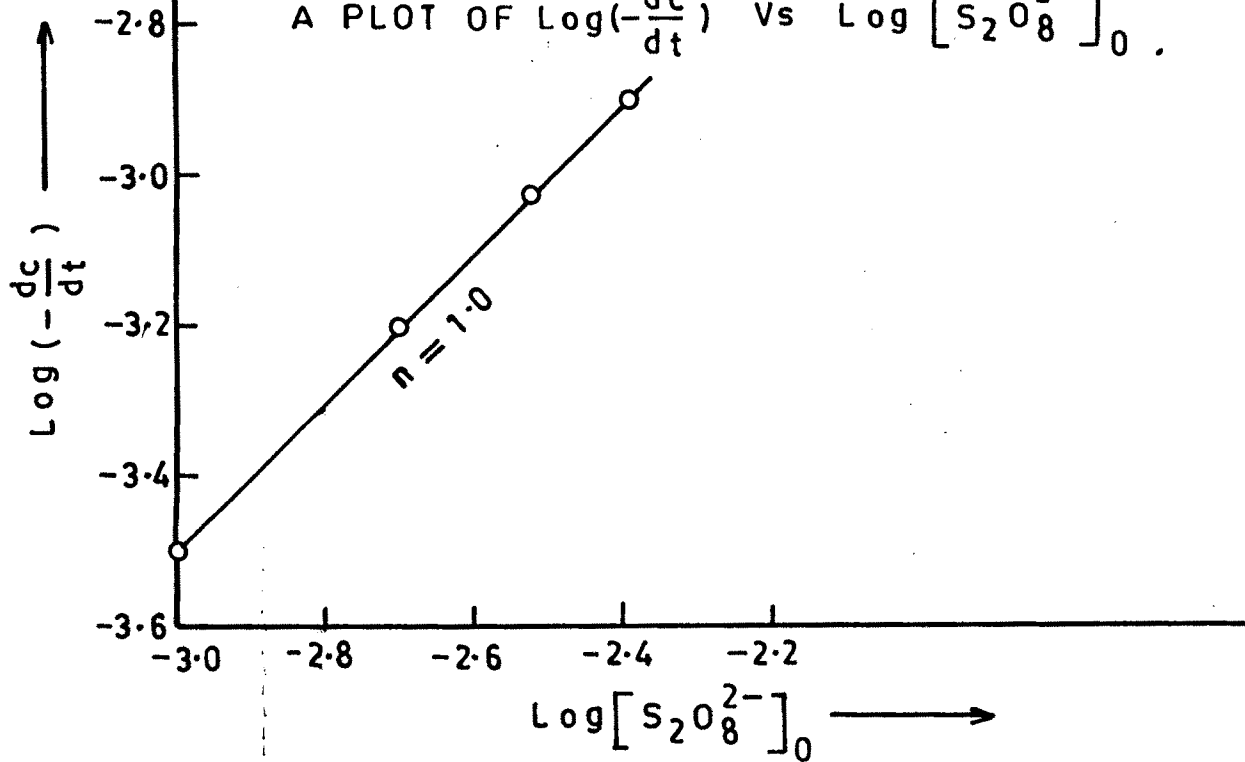


FIG. 2:5 B

A PLOT OF $\text{Log}(-\frac{dc}{dt})$ Vs $\text{Log} [S_2O_8^{2-}]_0$.



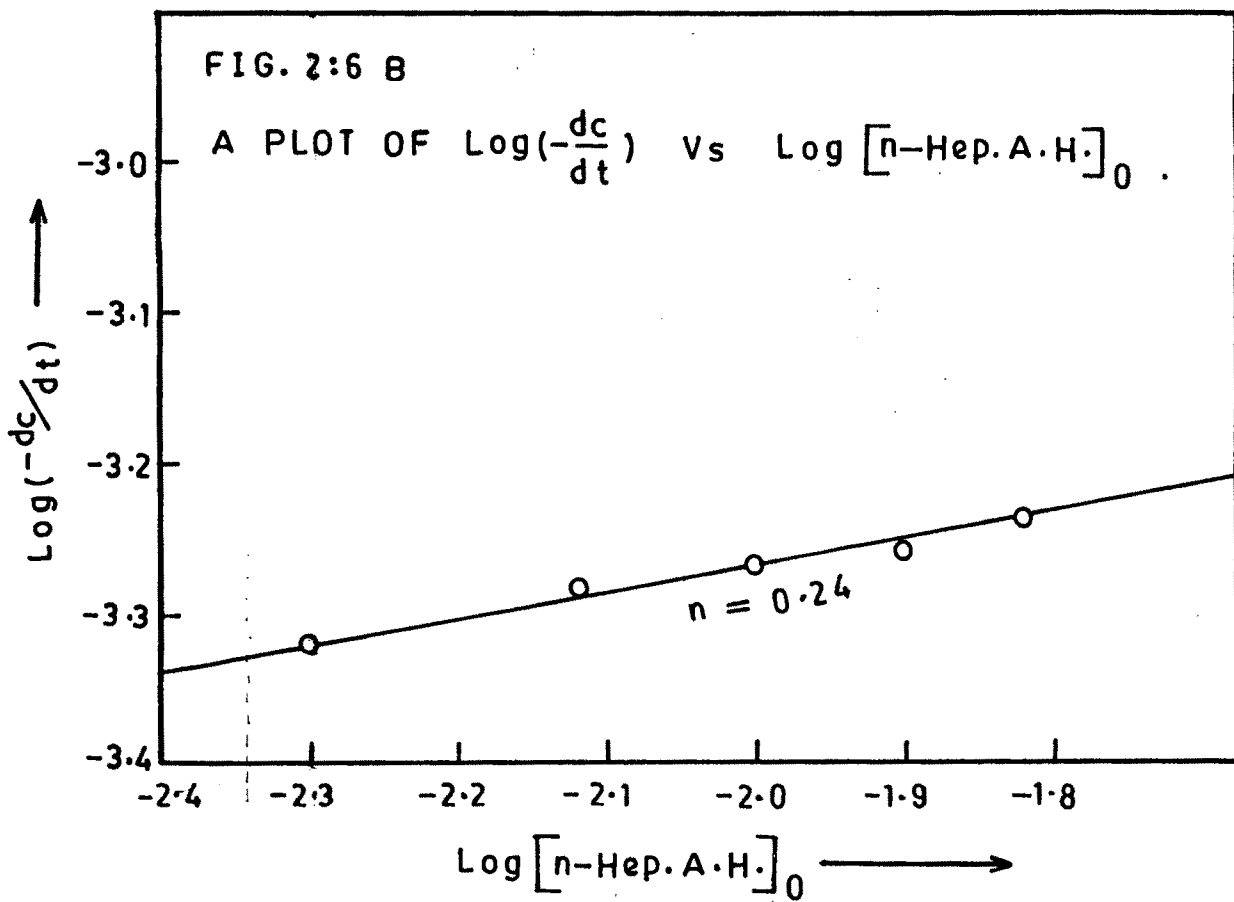
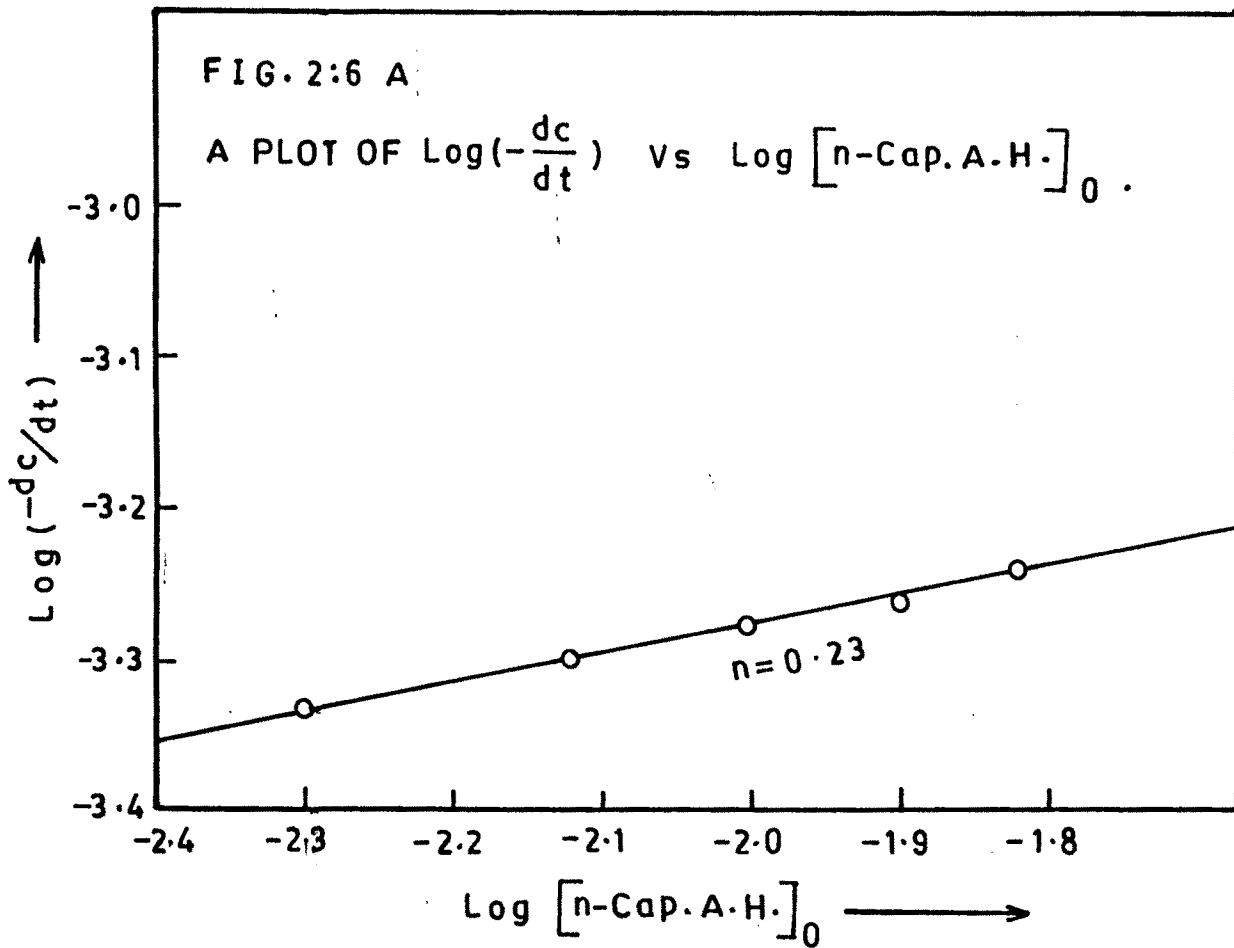


FIG. 2:7 A

A PLOT OF k VS $[Ag^+]_0$.

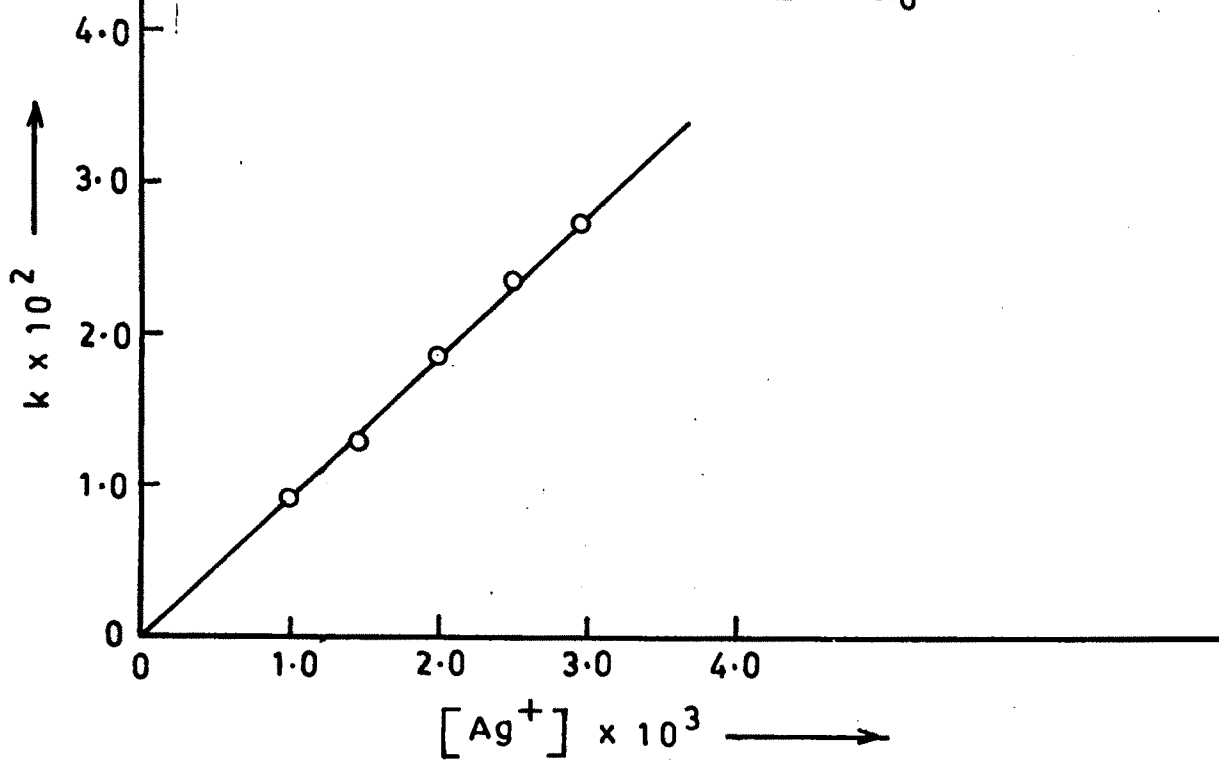
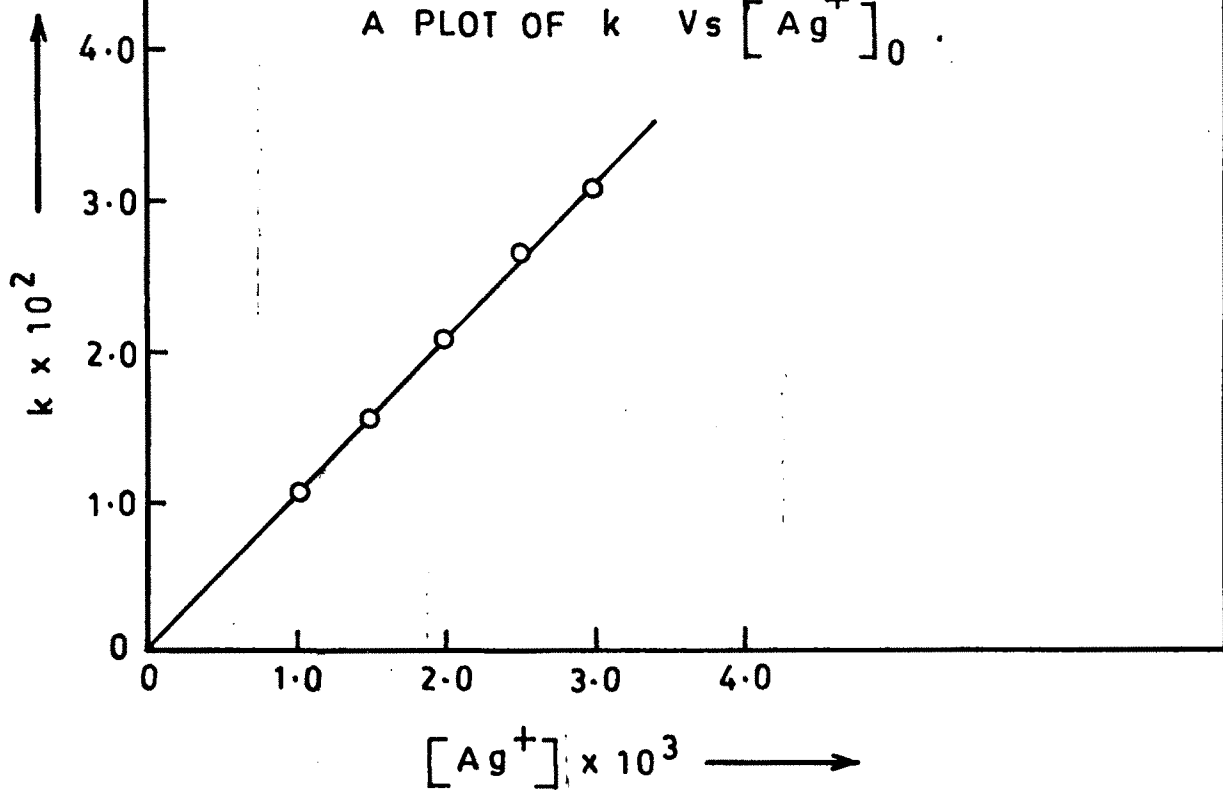
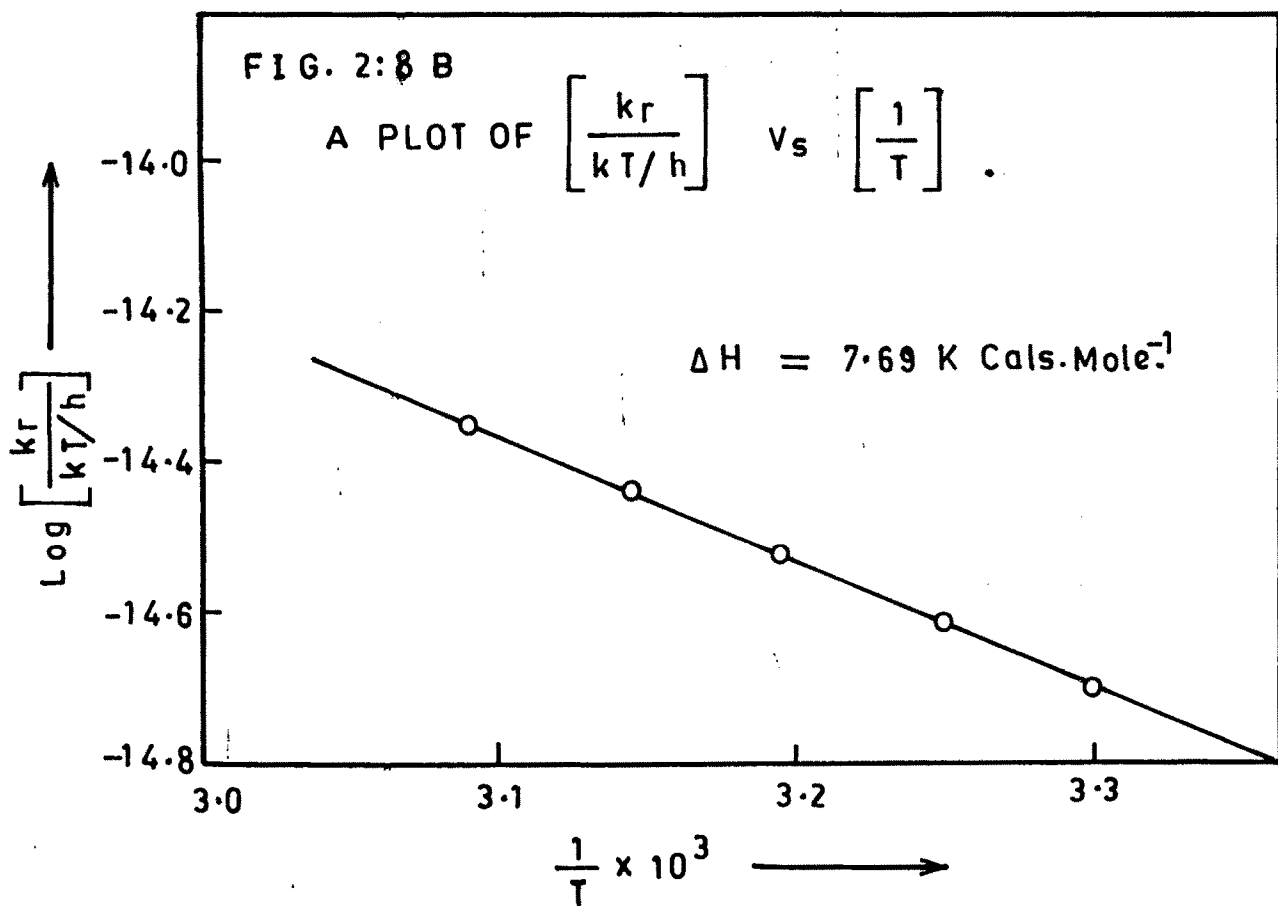
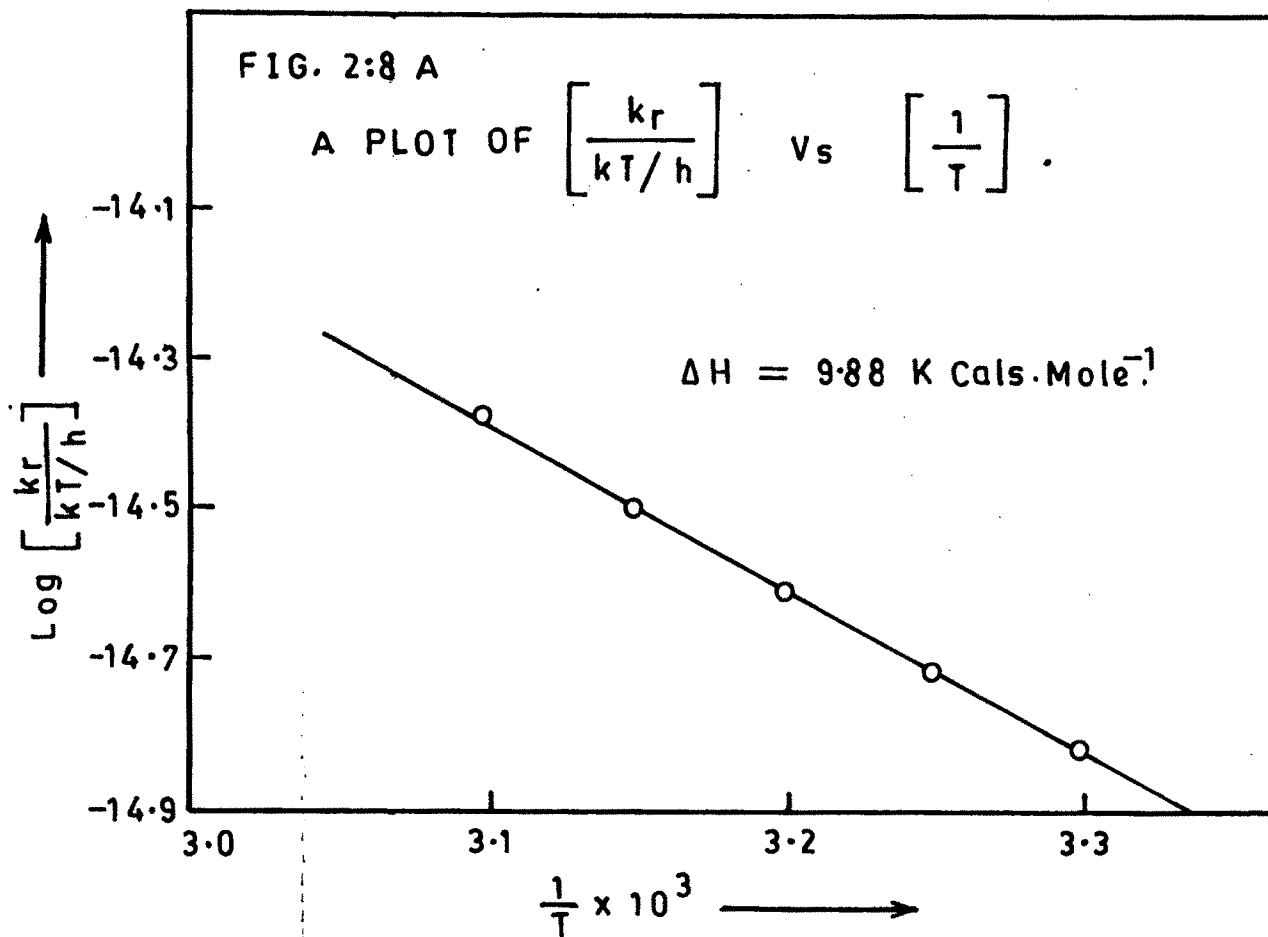


FIG. 2:7 B

A PLOT OF k VS $[Ag^+]_0$.





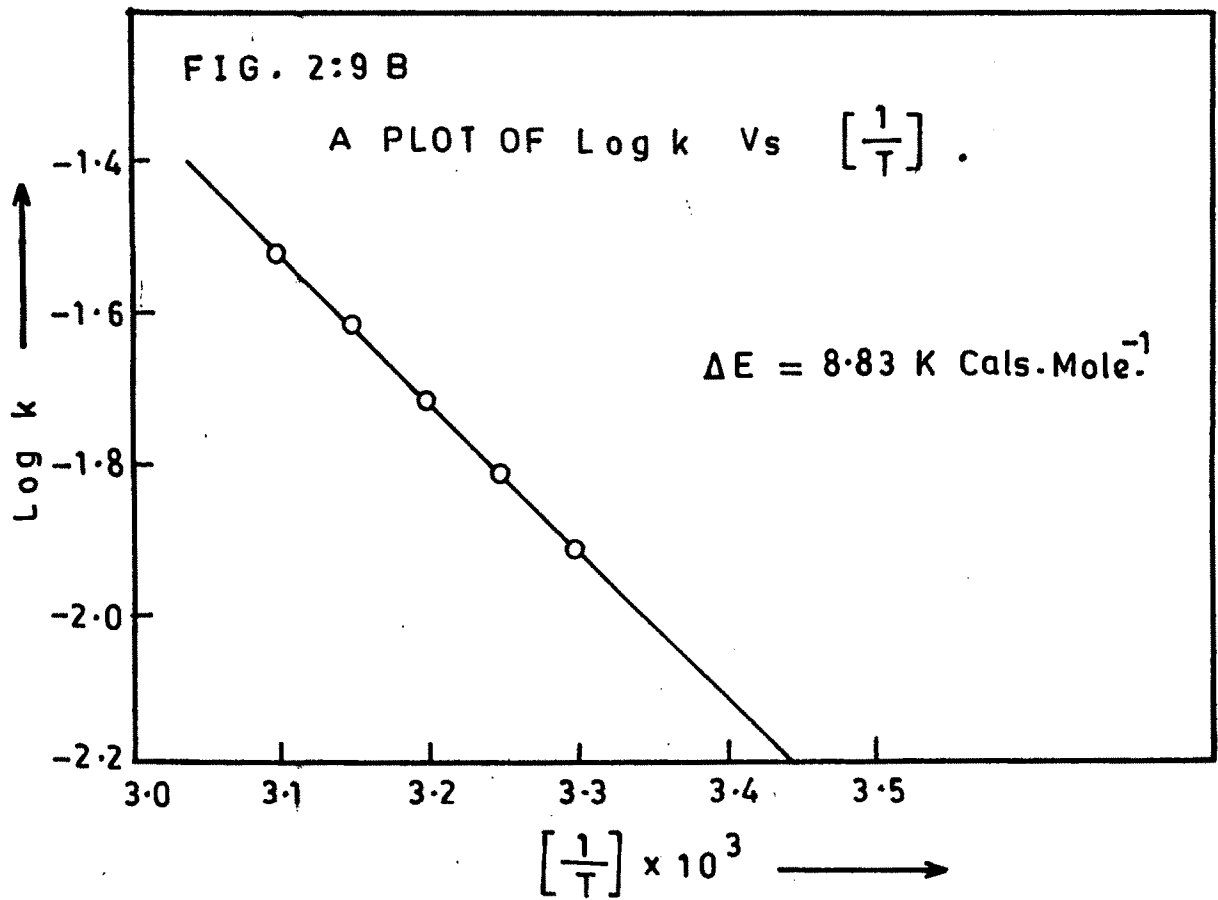
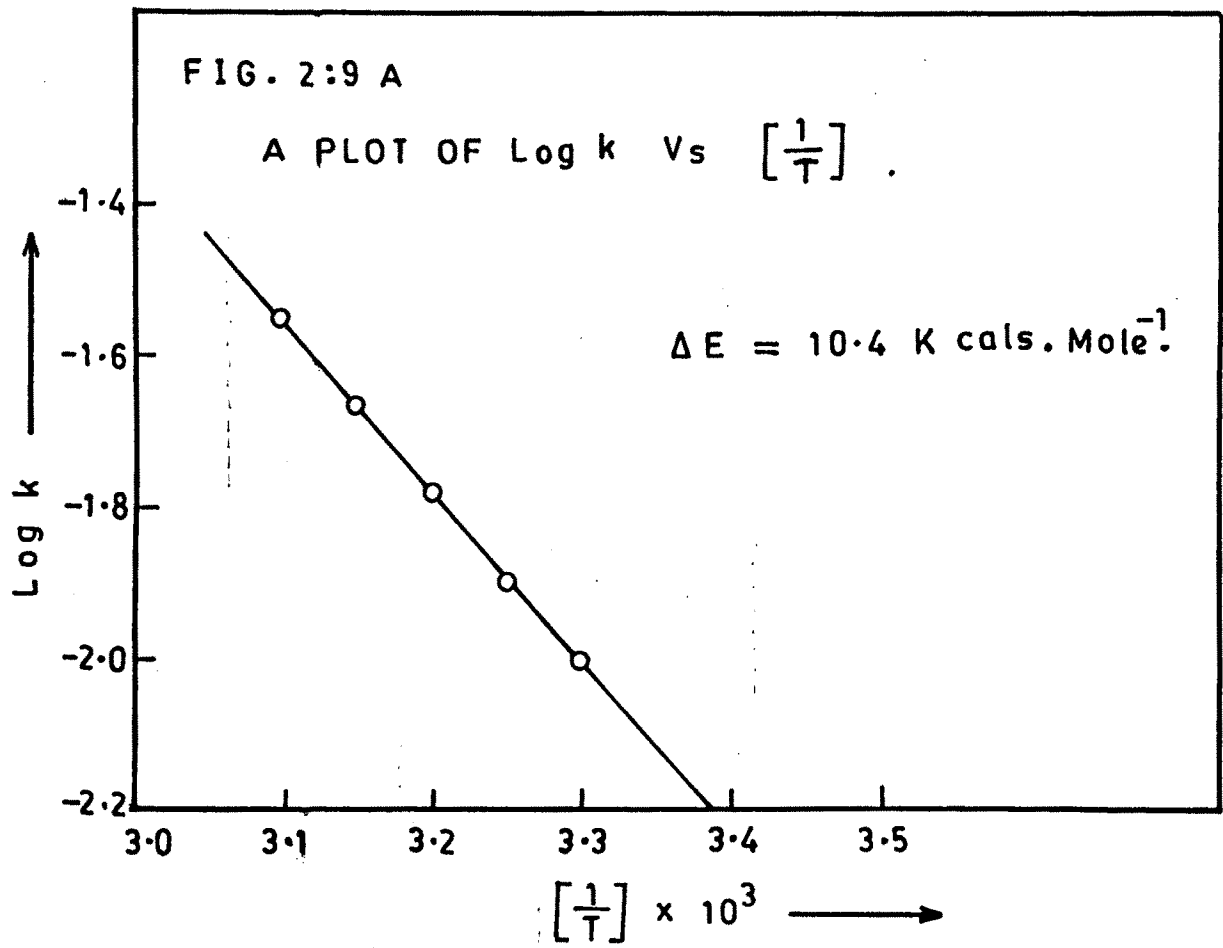


FIG. 2:10 A

EFFECT OF VARYING AgNO_3 CONC. AT 35°C .

$[\text{n-Cap. A.H.}] = 1.0 \times 10^{-2} \text{ M}$

$[\text{K}_2\text{S}_2\text{O}_8] = 2.0 \times 10^{-3} \text{ M}$

$[\text{AgNO}_3] = \text{I} = 1.0 \times 10^{-3} \text{ M}$

II = $1.5 \times 10^{-3} \text{ M}$

III = $2.0 \times 10^{-3} \text{ M}$

IV = $2.5 \times 10^{-3} \text{ M}$

V = $3.0 \times 10^{-3} \text{ M}$

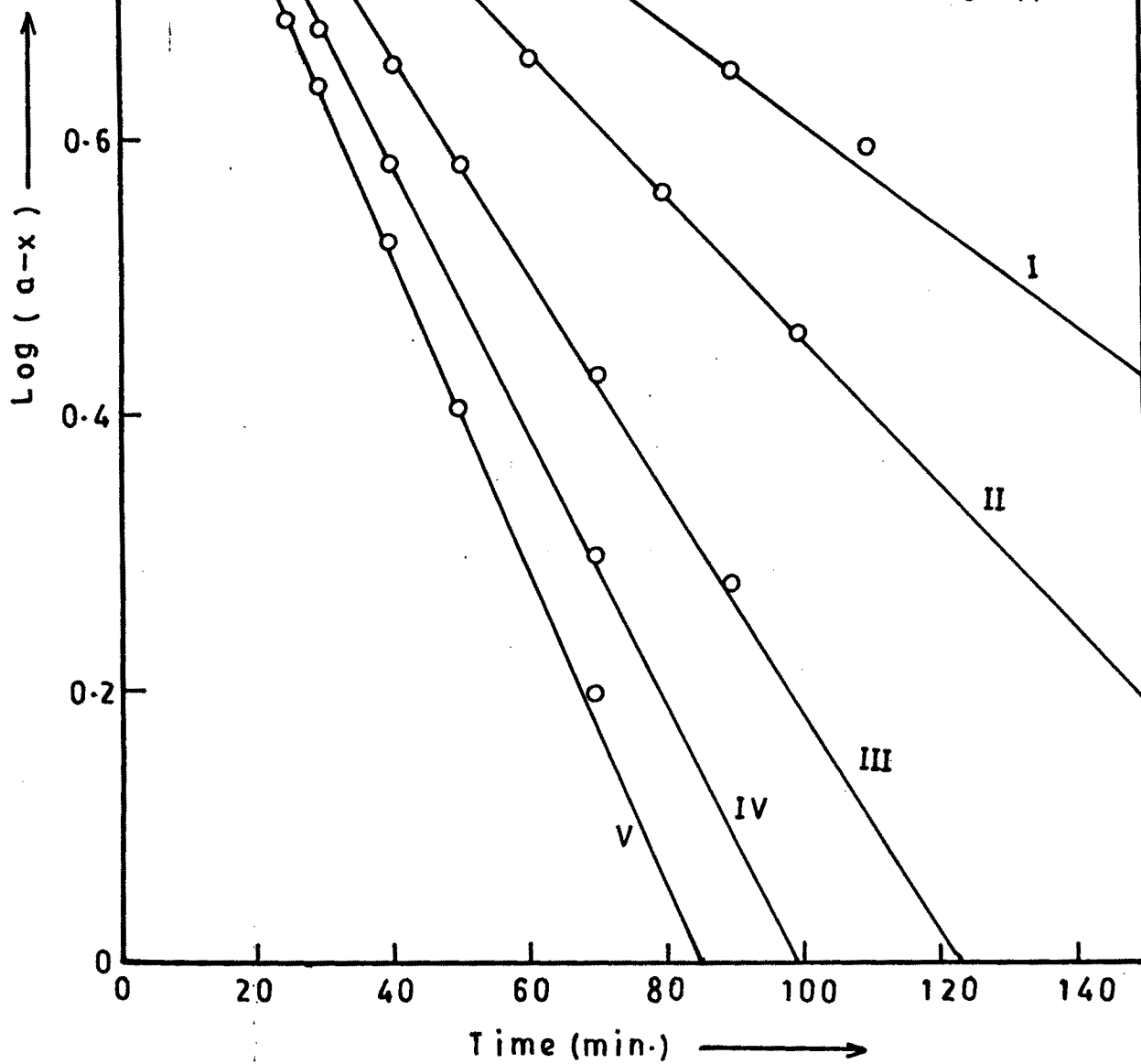


FIG. 2:10 B

EFFECT OF VARYING AgNO_3 CONC. AT 35°C .

$$[\text{n-Hep. A.H.}] = 1.0 \times 10^{-2} \text{ M}$$

$$[\text{K}_2\text{S}_2\text{O}_8] = 2.0 \times 10^{-3} \text{ M}$$

$$[\text{AgNO}_3] = \text{I} = 1.0 \times 10^{-3} \text{ M}$$

$$\text{II} = 1.5 \times 10^{-3} \text{ M}$$

$$\text{III} = 2.0 \times 10^{-3} \text{ M}$$

$$\text{IV} = 2.5 \times 10^{-3} \text{ M}$$

$$\text{V} = 3.0 \times 10^{-3} \text{ M}$$

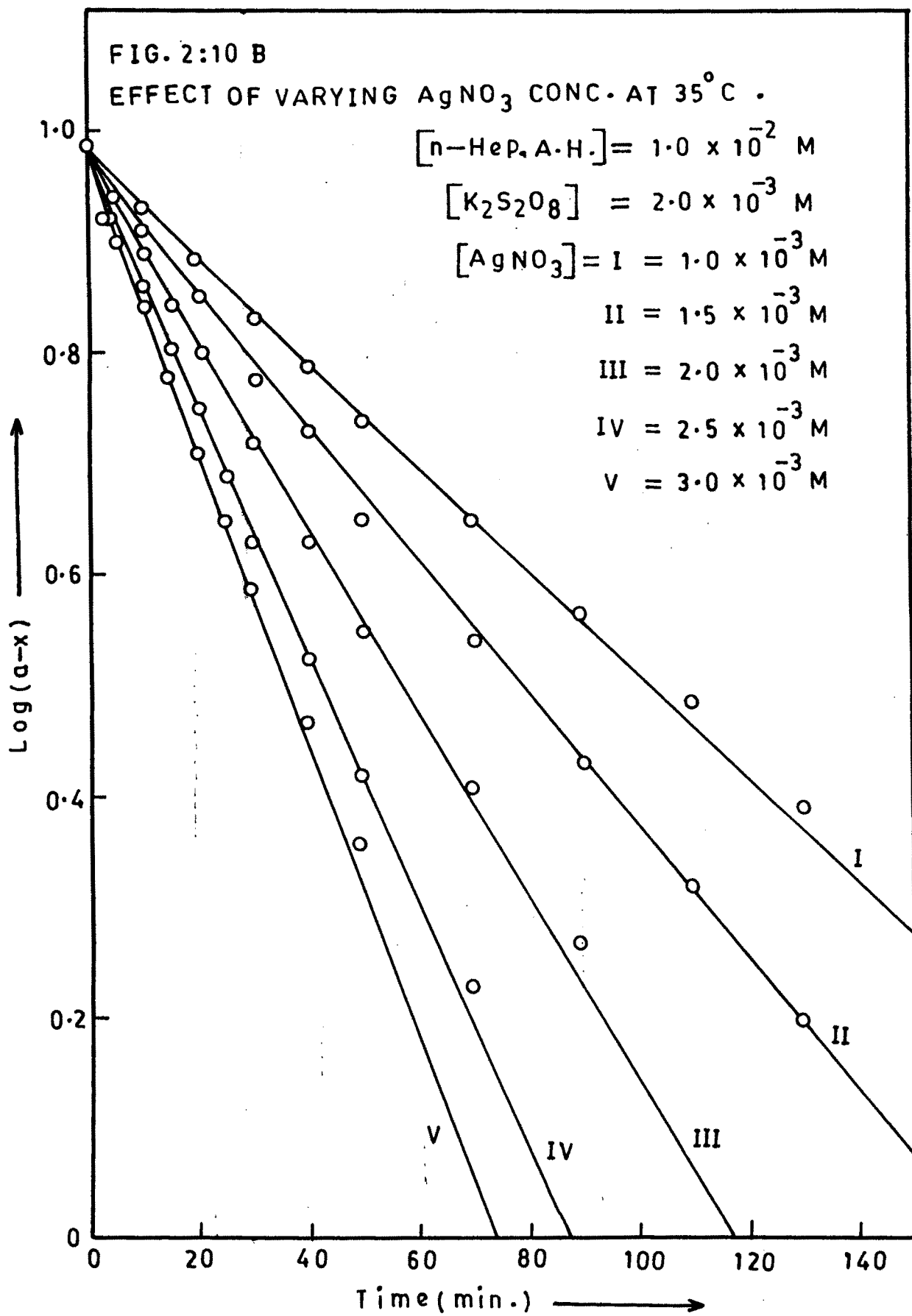


FIG. 2 ; 11 A

EFFECT OF TEMPERATURE .

$[n\text{-Cap. A. H.}] = 1.0 \times 10^{-2} \text{ M}$

$[K_2S_2O_8] = 2.0 \times 10^{-3} \text{ M}$

$[AgNO_3] = 1.5 \times 10^{-3} \text{ M}$

TEMPERATURE=I = 30°C

II = 35°C

III = 40°C

IV = 45°C

V = 50°C

↑
Log(a-x)

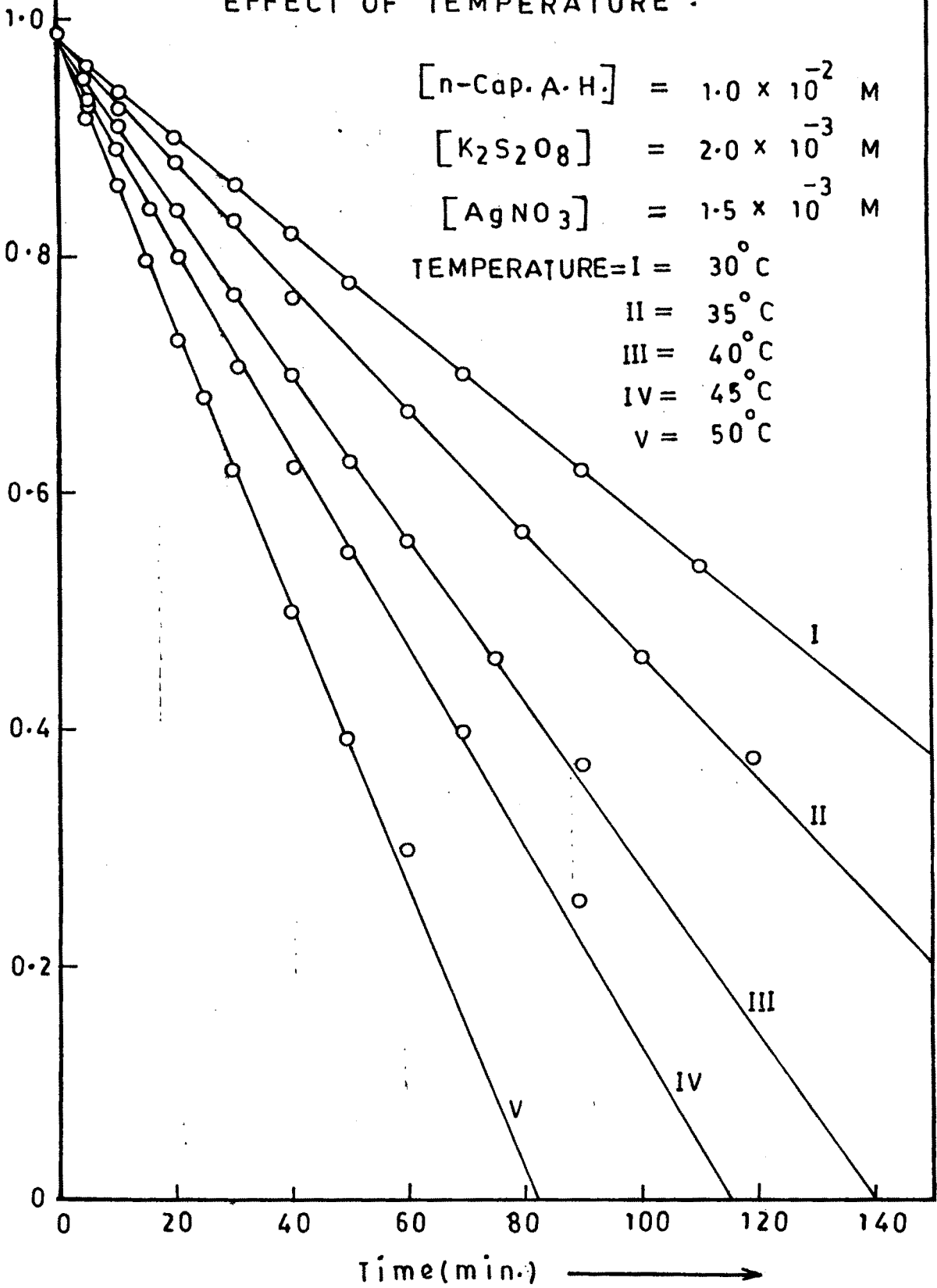


FIG. 2:11 B

EFFECT OF TEMPERATURE .

$$[n\text{-Hep}\cdot\text{A}\cdot\text{H}\cdot] = 1.0 \times 10^{-2} \text{ M}$$

$$[\text{K}_2\text{S}_2\text{O}_8] = 2.0 \times 10^{-3} \text{ M}$$

$$[\text{AgNO}_3] = 1.5 \times 10^{-3} \text{ M}$$

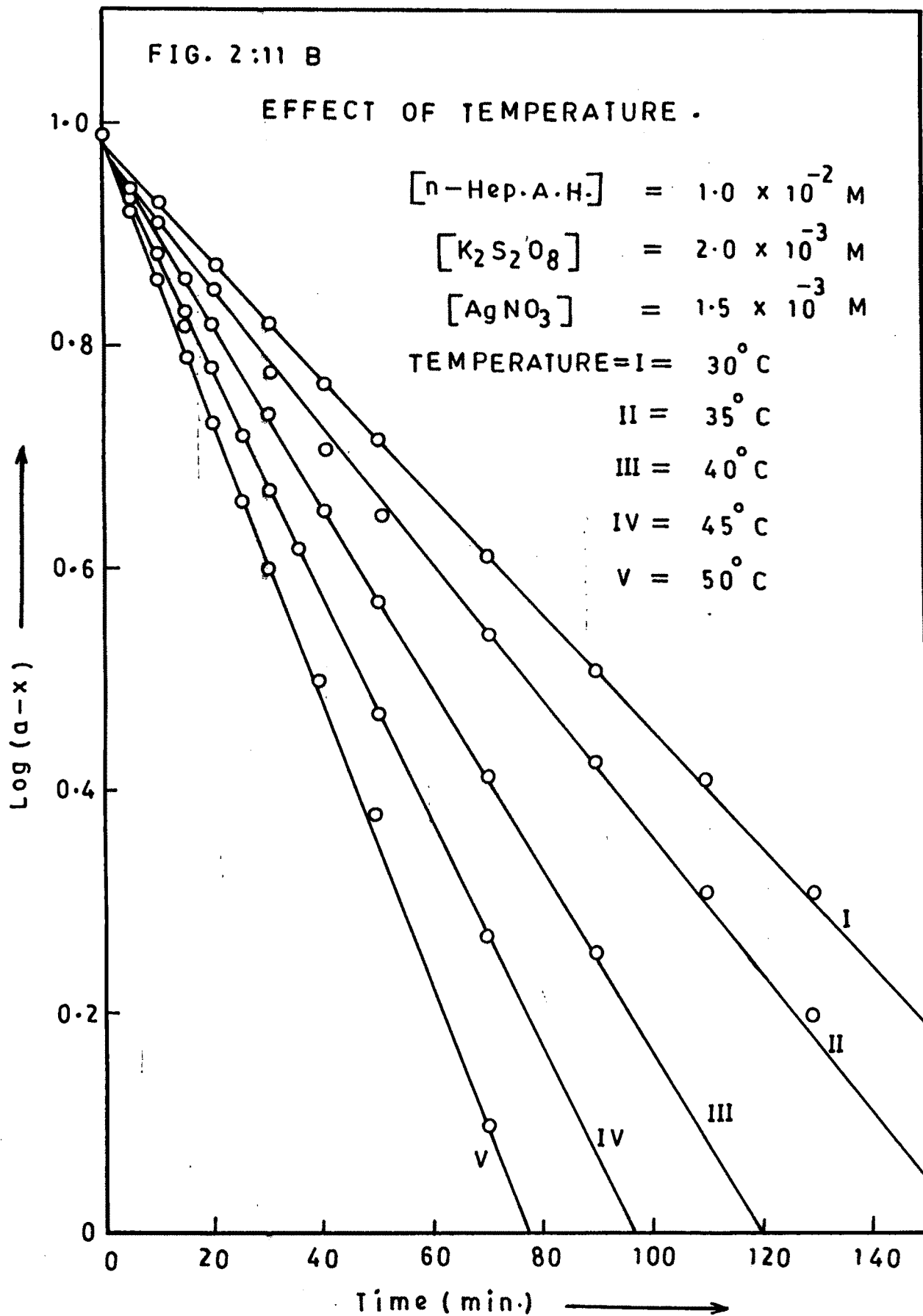
TEMPERATURE = I = 30° C

II = 35° C

III = 40° C

IV = 45° C

V = 50° C



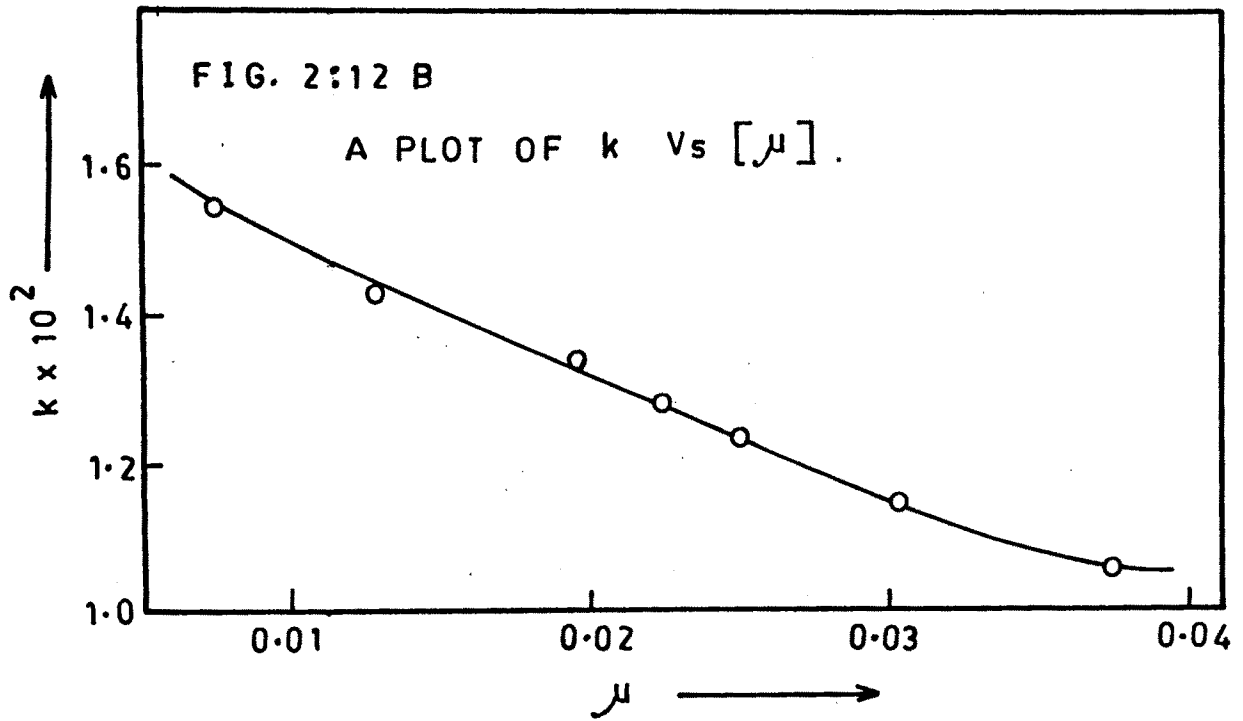
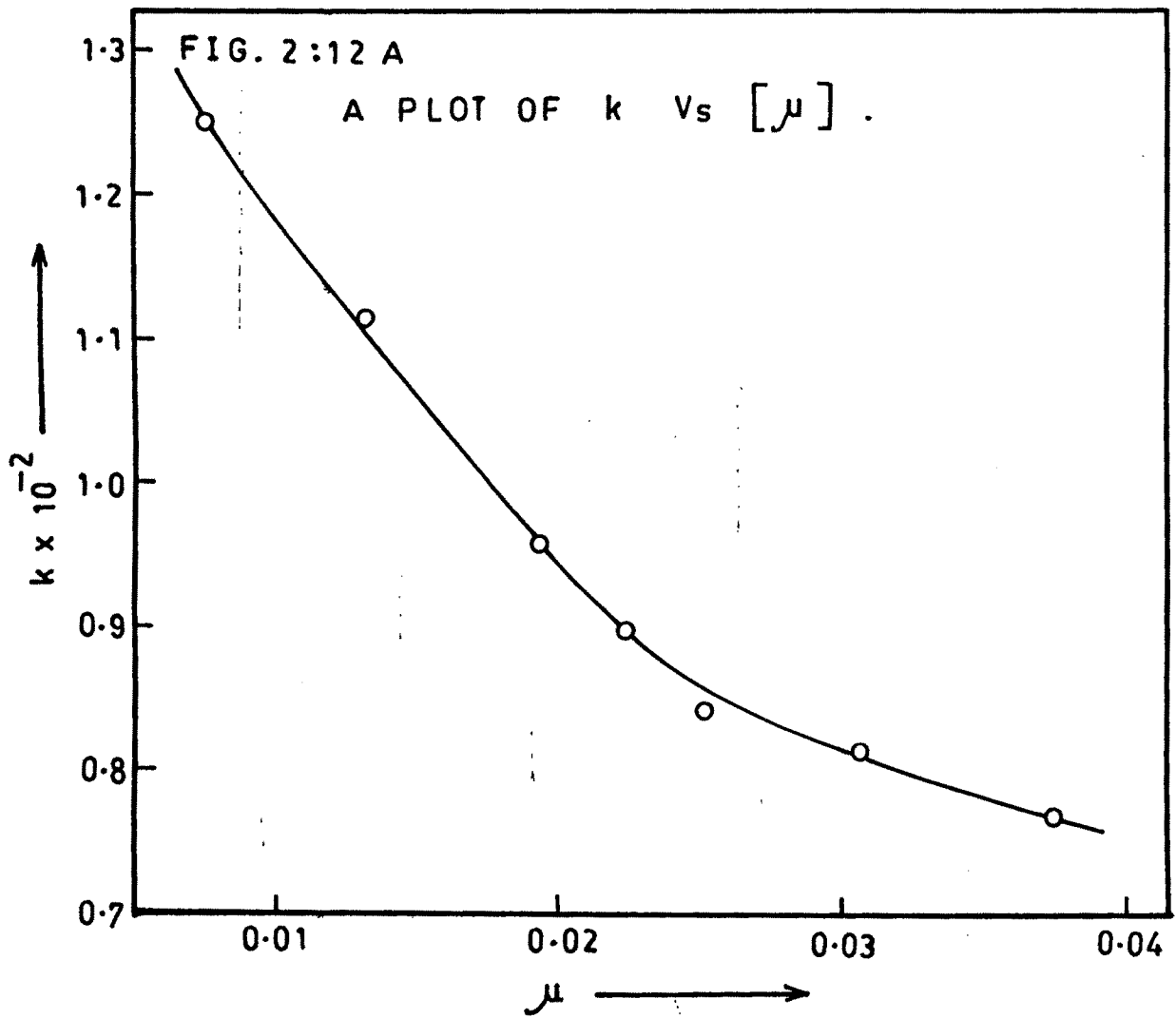


FIG. 2;13 A

EFFECT OF SPECIFIC CATION CONC. AT 35° C .

$$[\text{n-Cap. A.H.}] = 1.0 \times 10^{-2} \text{ M}$$

$$[\text{K}_2\text{S}_2\text{O}_8] = 2.0 \times 10^{-3} \text{ M}$$

$$[\text{AgNO}_3] = 1.5 \times 10^{-3} \text{ M}$$

$$\mu = 0.0180$$

↑
Log (a-x)

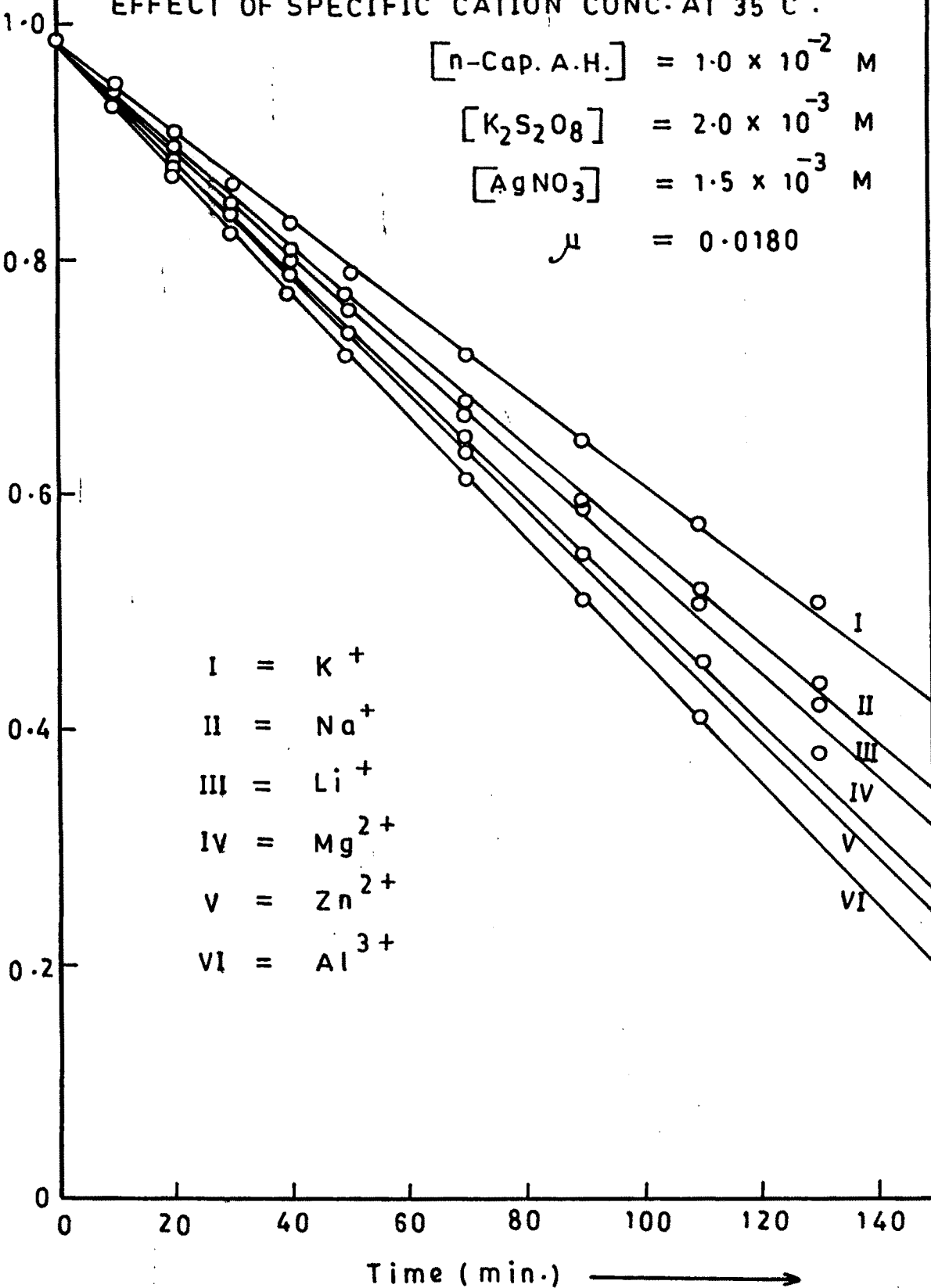


FIG. 2:13 B

EFFECT OF SPECIFIC CATION CONC. AT 35°C

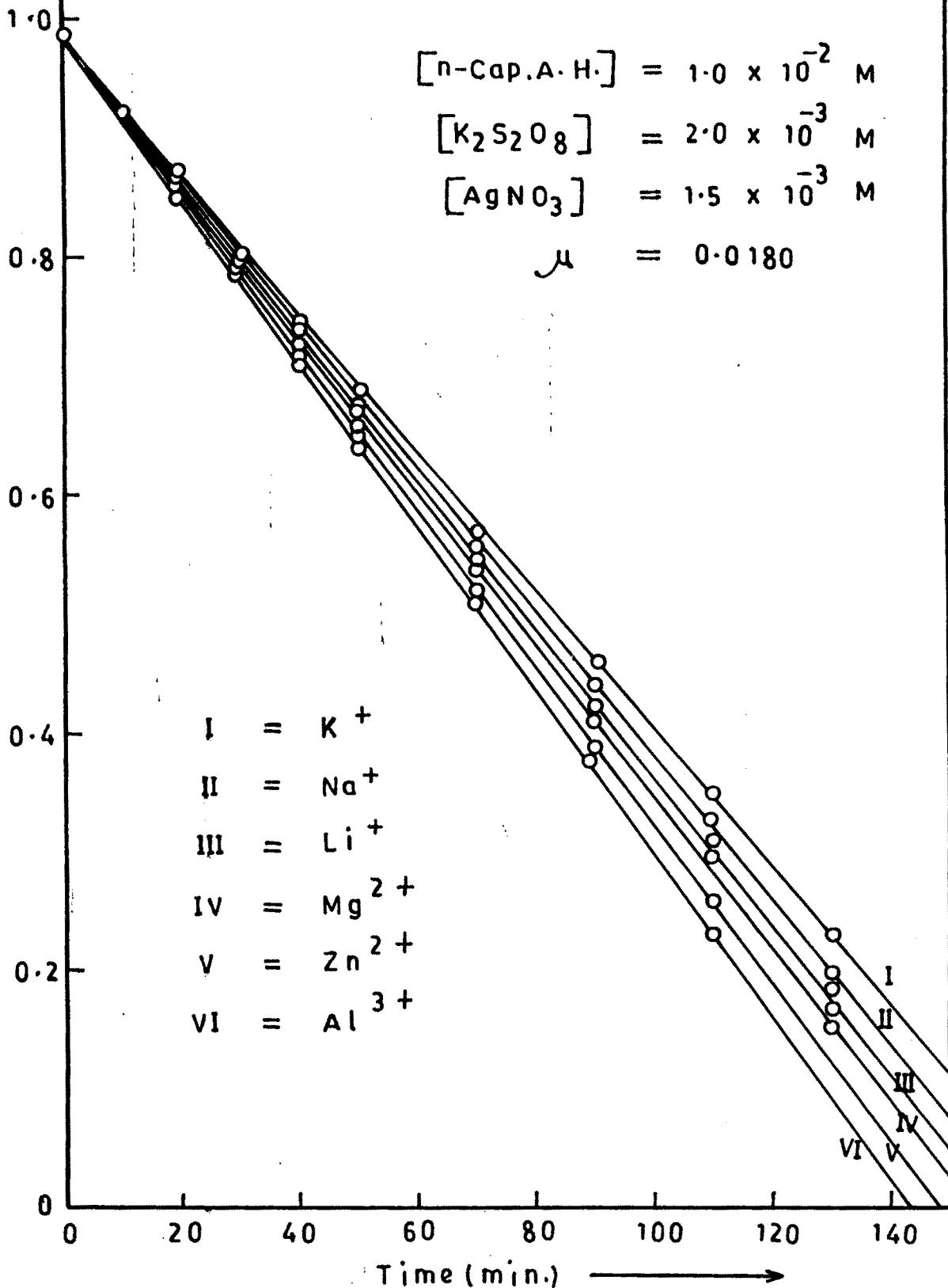
$[n\text{-Cap.A.H.}] = 1.0 \times 10^{-2} \text{ M}$

$[K_2S_2O_8] = 2.0 \times 10^{-3} \text{ M}$

$[AgNO_3] = 1.5 \times 10^{-3} \text{ M}$

$\mu = 0.0180$

↑
Log(a-x)



- I = K⁺
- II = Na⁺
- III = Li⁺
- IV = Mg²⁺
- V = Zn²⁺
- VI = Al³⁺

- I
- II
- III
- IV
- VI
- V

FIG.2:14 A

EFFECT OF VARYING ALLYL ACETATE AT 35° C .

$$[\text{n-Cap. A. H.}] = 1.0 \times 10^{-2} \text{ M}$$

$$[\text{K}_2\text{S}_2\text{O}_8] = 2.0 \times 10^{-3} \text{ M}$$

$$[\text{AgNO}_3] = 1.5 \times 10^{-3} \text{ M}$$

$$[\text{ALLYL ACETATE}] = \text{I} = 0.000 \text{ M}$$

$$\text{II} = 1.0 \times 10^{-2} \text{ M}$$

$$\text{III} = 2.0 \times 10^{-2} \text{ M}$$

$$\text{IV} = 3.0 \times 10^{-2} \text{ M}$$

$$\text{V} = 4.0 \times 10^{-2} \text{ M}$$

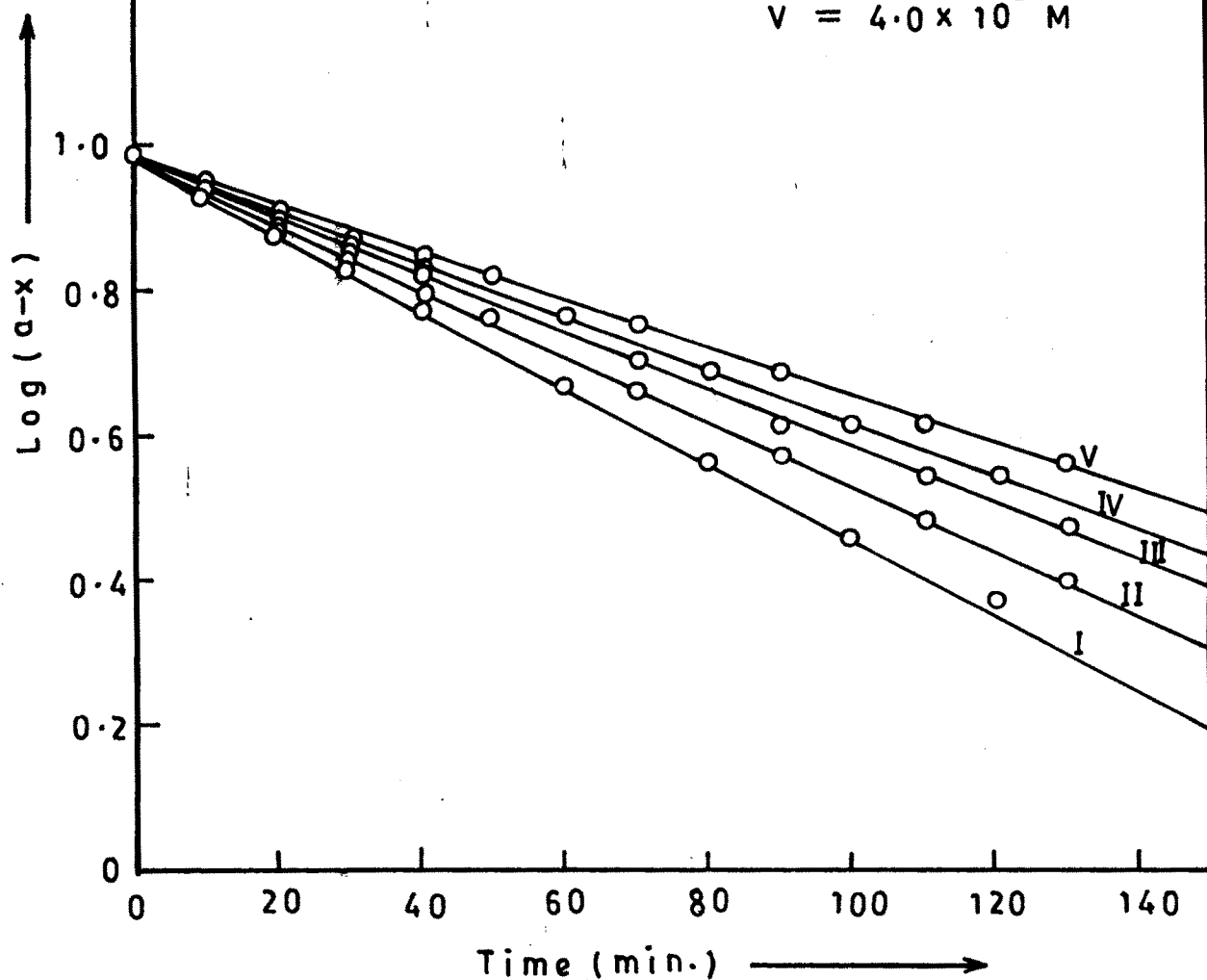


FIG. 2;14 B

EFFECT OF VARYING ALLYL ACETATE AT 35° C .

$$[n\text{-Hep. A. H.}] = 1.0 \times 10^{-2} \text{ M}$$

$$[K_2S_2O_8] = 2.0 \times 10^{-3} \text{ M}$$

$$[AgNO_3] = 1.5 \times 10^{-3} \text{ M}$$

$$[ALLYL \text{ ACETATE}] = I = 0.000 \text{ M}$$

$$II = 1.0 \times 10^{-2} \text{ M}$$

$$III = 2.0 \times 10^{-2} \text{ M}$$

$$IV = 3.0 \times 10^{-2} \text{ M}$$

$$V = 4.0 \times 10^{-2} \text{ M}$$

