CHAPTER III

CHAPTER - III

OXIDATION OF FUMARAMIDE

In order to decide the suitable temperature, concentration of the reactants and concentration of the silver catalyst, some preliminary experiments were carried out. At room temperature, it was observed that the uncatalysed reaction is very slow . The reaction proceeds with a measurable velocity at 35°C.

Thus the reaction was first studied at 35°C using the concentration of $K_2S_2O_8$ as 2.0×10^{-2} M. Substrate as 5.0×10^{-2} M and 1.0×10^{-3} M as Silver catalyst. The results of this kinetic run is recorded in Table A - 1.

TABLE A – 1

$K_2S_2O_8$ = 2.0 x 10^{-2} M, Amide = 5.0 x 10^{-2} M,
$AgNO_3$ = 1.0 x 10^{-3}M, Temp.= 35°C

Time(min.)	C*	k_1 x 10^3 min^{-1}
0	9.45	–
20	8.95	2.704
40	8.48	2.687
60	8.05	2.660
80	7.65	2.643
100	7.28	2.602
130	6.74	2.589
160	6.26	2.566
200	5.68	2.541
240	5.15	2.528
300	4.45	2.510
360	3.84	2.500
Mean K_1 x 10^3 min^{-1}	–	2.593

[C* denotes the volume of 0.02 M $Na_2S_2O_3$in ml equivalent to unreacted $S_2O_8^{2-}$]

From the above results (Table A-1) it is seen that the first order rate constant slightly decreases with time. This suggests that either the reaction follows an order greater than one or the reaction is attained with inhibition during the course of the reaction leading to a decrease in the first order rate constant with time. In the above experiment, the quantity of substrate has been taken in excess, its concentration is greater than $S_2O_8^{2-}$ and hence the order is with respect to $S_2O_8^{2-}$ ion.

In order to decide conclusively the order with respect to $K_2S_2O_8$ as well as with respect to substrate, the reaction was studied at equimolar concentrations of $K_2S_2O_8$ and substrate (viz. 0.02 M - each) keeping the concentration of the silver catalyst unchanged. The temperature of the reaction was also adjusted to 35°C. The results of this kinetic run are recorded in Table A - 2.

TABLE A - 2

$K_2S_2O_8$ = Substrate = 2.0×10^{-2}M,
$AgNO_3$ = 1.0×10^{-3} M, Temp. = 35°C.

Time(min)	C	$K_1 \times 10^3$ min^{-1}
0	9.44	-
20	8.62	4.498
40	7.88	4.486
60	7.21	4.469
80	6.60	4.456
100	6.05	4.443
130	5.30	4.435
160	4.65	4.420
200	3.90	4.408
240	3.29	4.386
300	2.54	4.372
360	1.96	4.355
Mean $k_1 \times 10^3$ min.$^{-1}$	-	4.429

From the above results, as shown in Table A-2, it has been observed that, here also the first order rate constant slightly decreases, with time. This decrease in the rate constant may be due to some inhibition as the reaction progresses. The nearly constant values of the rate constant suggest that the order with respect to substrate is zero.

EFFECT OF $K_2S_2O_8$ CONCENTRATION :

Before studying the effect of $K_2S_2O_8$ on the reaction rate, it is necessary to study the self decomposition of peroxydisulphate without the substrate and in presence of silver catalyst. The temperature was also kept unchanged. The results of these kinetic runs are recorded in Table A - 3.

TABLE A - 3

$AgNO_3$ = 1.0 x 10^{-3}M, Temp. = 35°C

$[K_2S_2O_8]$M	0.01		0.02		0.03		0.04	
Time (min)	C	$k_2 \times 10^3$ min^{-1}	C	$k_2 \times 10^3$ min^{-1}	C	$k_2 \times 10^3$ min^{-1}	C	$k_2 \times 10^3$ min^{-1}
0	4.93	–	9.65	–	14.72	–	19.54	–
20	4.79	1.452	9.39	1.366	14.38	1.168	19.10	1.112
40	4.65	1.435	9.14	1.349	14.05	1.162	18.69	1.103
60	4.54	1.352	8.94	1.273	13.73	1.158	18.30	1.086
80	4.42	1.349	8.73	1.243	13.43	1.143	17.92	1.078
100	4.31	1.340	8.52	1.236	13.13	1.138	17.56	1.064
130	4.14	1.334	8.23	1.217	12.70	1.133	17.05	1.048
160	3.98	1.326	7.97	1.194	12.28	1.128	16.58	1.024
200	3.80	1.300	7.65	1.158	11.75	1.125	16.14	0.954
240	3.63	1.275	7.35	1.135	11.25	1.119	15.60	0.936
300	3.39	1.241	6.91	1.109	10.54	1.113	14.84	0.916
360	3.23	1.171	6.52	1.085	9.91	1.098	14.59	0.811
Mean $k_2 \times 10^3$ min^{-1}	–	1.325	–	1.215	–	1.135	–	1.012

Now in order to study the effect of $K_2S_2O_8$ concentration on the reaction rate, the reaction was studied at three different concentrations of $K_2S_2O_8$. The concentration of substrate and the catalyst was kept unchanged. The results of these kinetic runs are recorded in Table A - 4, and for the sake of comparison, the data of Table A - 1 has been incorporated in it.

TABLE A - 4

$AgNO_3$ = 1.0 x 10^{-3}M, Substrate = 5.0 x 10^{-2}M, Temp. =35°C.

$[K_2S_2O_8]$M.	0.01		0.02		0.03		0.04	
Time (min.)	C	$k_1 \times 10^3$ min^{-1}	C	$k_1 \times 10^3$ min^{-1}	C	$k_1 \times 10^3$ min^{-1}	C	$k_1 \times 10^3$ min^{-1}
0	4.95	-	9.45	-	14.35	-	19.38	-
20	4.65	3.161	8.95	2.704	13.67	2.401	18.57	2.125
40	4.36	3.149	8.48	2.687	13.03	2.393	17.81	2.108
60	4.10	3.137	8.05	2.660	12.43	2.381	17.08	2.099
80	3.85	3.128	7.65	2.643	11.86	2.373	16.40	2.085
100	3.62	3.119	7.28	2.602	11.33	2.360	15.74	2.017
130	3.30	3.107	6.74	2.589	10.57	2.349	14.81	2.069
260	3.02	3.086	6.26	2.566	9.87	2.338	13.94	2.058
200	2.68	3.064	5.68	2.541	9.01	2.322	12.87	2.047
240	2.37	3.053	5.15	2.528	8.24	2.310	11.90	2.032
300	1.98	3.039	4.45	2.510	7.19	2.301	10.57	2.021
360	1.66	3.028	3.84	2.500	6.29	2.289	9.37	2.016
Mean								
k_1 x10^3 min^{-1}	-	3.097	-	2.593	-	2.347	-	2.067
k_2 x10^3 min^{-1}	-	1.325	-	1.215	-	1.135	-	1.013
k x10^3 min^{-1}	-	1.772	-	1.378	-	1.212	-	1.058

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From the above results as shown in Table A-4, it is seen that,when the concentration of $K_2S_2O_8$ was increased,the first order rate constant was decreased. This decrease in the rate constant with an increase in the concentration of $K_2S_2O_8$ may be either due to an increase in ionic strength or due to the specific inhibitory effect of K^+ ion or due to both.

In any particular run, it has been observed that the first order rate constant decreases with time, because the reaction involving $S_2O_8^{2-}$-ions are highly susceptible to trace impurities. Hence all the precautions were taken to purify substrate and all the reagents employed for the kinetic study. These results are recorded in the above table (Table A-4) and also shown graphically in Fig. A-1. From the initial slope of the curves, the first order rate constant of the reaction (viz. k_1) is evaluated. The rate constant k_1 at different times has also been calculated by integration method. The net rate constant (viz. k) for the oxidation of the substrate is obtained after deducing the value of the rate constant (viz. k_2) for the self decomposition of $S_2O_8^{2-}$ studied similtaneously (as shown in the above table A - 3).

Here, it must be mentioned that in all subsequent kinetic studies, though the self decomposition of $S_2O_8^{2-}$ has always been investigated under the corresponding experimental conditions, the kinetic data of these runs have been omitted on account of pressure on space and only the corresponding values of the rate constant (viz.k_1) have been directly recorded at the end of each table.

It has been observed that the first order specific rate decreases by increasing the concentration of $S_2O_8^{2-}$ constant ionic strength as well as constant K^+ ion concentration. Hence it was considered reinvestigate this effect at constant ionic strength as well as at constant K^+ ion concentration, so that the effect of both these parameters may be eliminated. Hence the below table shows the data of these kinetic runs (Table A-5) carried out at constant ionic strength and constant K^+ ion concentration which have also been shown graphically in Fig. A - 2.

TABLE A - 5

$AgNO_3$=1.0 x10^{-3} M, Subastrate = 5.0 x 10^{-2} M,
Temp. = 35°C , μ = 0.301

$[K_2S_2O_8]$M	0.01	0.02	0.03	0.04
+ $[K_2SO_4]$M.	0.09	0.08	0.07	0.06
Time(min.)	Vol.(in ml.)of 0.02M - $Na_2S_2O_3$used(viz.C)			
0	4.96	9.48	14.28	19.55
20	4.72	9.11	13.79	18.93
40	4.51	8.76	13.32	18.35
60	4.30	8.42	12.88	17.79
80	4.10	8.11	12.45	17.26
100	3.92	7.80	12.04	16.75
130	3.66	7.38	11.46	16.02
160	3.42	6.98	10.92	15.33
200	3.13	6.48	10.42	14.48
240	2.86	6.38	9.62	13.35
300	2.50	5.41	8.74	12.55
360	2.19	4.88	7.96	11.55
k_1x10^3min^{-1}	2.321	1.921	1.682	1.528
k_2x10^3min^{-1}	0.690	0.670	0.670	0.660
k x10^3min^{-1}	1.631	1.251	1.012	0.868

From the above results as shown in Table A-5 it indicates that here also the first order rate constant decreases.

Table A-6 shows the comparison between k values with increasing concentration of $S_2O_8^{2-}$ with K_2SO_4 to maintain constant ionic strength and constant K^+ ion concentration in later case.

TABLE A - 6

$AgNO_3=1.0 \times 10^{-3}M$, Substrate $=5.0 \times 10^{-2}M$, Temp $=35^{\circ}C$

$[K_2S_2O_8]M$ without K_2SO_4	$k \times 10^3$ min^{-1}	$[K_2SO_2O_8]M$ with constant K^+ ionic strength	$k \times 10^3$ min^{-1}
0.01	1.772	0.01	1.631
0.02	1.378	0.02	1.251
0.03	1.212	0.03	1.012
0.04	1.055	0.04	0.868

From the above results (Table A - 6), it is seen that at constant K^+ ionic strength, there is a decrease in the rate constant. This suggests that the effect is due to the increase in ionic strength as well as due to the increase in K^+ ion concentration both causing inhibition. There exists a persistent rate decreasing tendancy even though the reaction is carried out at constant ionic strength as well as at constant K^+ ion concentration which leads to conclude that it is probably due to some trace impurity remaining in the peroxydisulphate sample itself even after repeated crystallisation which however, couldnot be characterized.

A plot of - log k versus the concentration of peroxydisulphate is found to be linear (Fig. A - 3). The following relationship between - log k and concentration of $K_2S_2O_8$ is being followed:

$$- \log k = 2.443 + 8.90 [S_2O_8^{2-}]_0$$

provided that $[S_2O_8^{2-}]_0$ is not equal to zero.

ORDER WITH RESPECT TO PEROXYDISULPHATE

The order with respect to peroxydisulphate was calculated by Van't Hoff's differential method. The volume of

$Na_2S_2O_3$ (equivalent to $K_2S_2O_8$) was plotted against time for different initial concentrations of $K_2S_2O_8$. From these curves the value of -dc/dt in each case was determined from the initial slope as given in Table A - 7.

TABLE A - 7

$[K_2S_2O_8]$	- dc/dt x 10^{-4}	Log $[S_2O_8^{2-}]$	Log (-dc/dt)
0.01	1.854	-2.0000	-3.7318
0.02	3.581	-1.6990	-3.4459
0.03	5.514	-1.5229	-3.2585
0.04	7.345	-1.3979	-3.1350

The value of -dc/dt and concentrations of $K_2S_2O_8$ i.e. 'C' are substituted in the Van't Hoff's equation and the order of the reaction is calculated thereby.

$$n = \frac{\text{Log}\ (-dc_1/dt) - \text{Log}\ (-dc_2/dt)}{\text{Log}\ C_1 - \text{Log}\ C_2}$$

The values of (-dc/dt) for different initial concentration of $S_2O_8^{2-}$ and the values of 'n' calculated thereby are recorded in Table A - 8.

Again a plot of log -dc/dt versus log $[S_2O_8^{2-}]$ is shown in Fig. A - 4. The slope of the curve is 0.9375 as such the order with respect to $S_2O_8^{2-}$ is one, which is confirmed by the value of 'n' as shown in the following table(TableA-8)

TABLE A - 8

$[K_2S_2O_8]$M	$-dc/dt \times 10^{-4}$	order of Reaction (n)
0.01	1.854	0.9471
0.02	3.581	
0.01	1.854	0.9920
0.03	5.514	
0.01	1.854	0.9928
0.04	7.345	
0.02	3.581	1.0641
0.03	5.514	
0.03	5.514	0.9967
0.04	7.345	

EFFECT OF SUBSTRATE CONCENTRATION

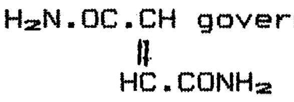
In order to study the effect of amide concentration on the reaction rate, the reaction was studied at five different concentrations of amide. The concentrations of $K_2S_2O_8$ and $AgNO_3$ were kept unchanged. The results of these kinetic runs are recorded in Table A - 9 and shown graphically in Fig. A - 5.

TABLE A - 9

$K_2S_2O_8$= 2.0 x 10^{-2}M, $AgNO_3$ = 1.0 x 10^{-3}M, Temp. = 35°C

[Amide]M	0.025	0.05	0.075	0.1	0.125
Time(min)	Vol. (in ml) of 0.02 M -$Na_2S_2O_3$ used (Viz.C)				
0	9.43	9.45	9.46	9.45	9.43
20	8.94	8.95	8.94	8.93	8.93
40	8.49	8.48	8.47	8.45	8.46
60	8.07	8.05	8.02	8.00	8.02
80	7.67	7.65	7.60	7.57	7.61
100	7.30	7.28	7.21	7.17	7.22
130	6.77	6.74	6.65	6.61	6.68
160	6.28	6.26	6.15	6.10	6.19
200	5.69	5.68	5.54	5.48	5.58
240	5.16	5.15	5.00	4.94	5.05
300	4.46	4.45	4.28	4.21	4.33
360	3.85	3.84	3.68	3.61	3.73
k_1 x 10^3min^{-1}	2.547	2.593	2.695	2.737	2.645
k_2 x 10^3min^{-1}	1.215	1.215	1.215	1.215	1.215
k x 10^3min^{-1}	1.332	1.378	1.480	1.522	1.430

From the above results (Table A - 9) it is seen that the rate constant only slightly increases when the concentration of amide was increased, but the rate practically remained constant showing the zero order behaviour of the reaction.

The specific rate is seen to be a function of the initial concentration of both $S_2O_8^{2-}$ and  $\begin{matrix}H_2N.OC.CH\\ \|\\ HC.CONH_2\end{matrix}$ governed by the expression.

$$k = k_{(max.)} \times \frac{\left[\begin{array}{c} H_2N.OC.CH \\ \parallel \\ HC.CONH_2 \end{array}\right]_0}{b + \left[\begin{array}{c} H_2N.OC.CH \\ \parallel \\ HC.CONH_2 \end{array}\right]_0}$$

In support of the above equation, a graph of Amide/k, versus concentration of amide is plotted. The plot was found to be linear from which k_{max} and b were evaluated as 0.00272 and 0.02675. From these values k was calculated and found to be equal to $2.557 \times 10^{-3} min^{-1}$ which was almost identical with $k = 2.593 \times 10^{-3} min^{-1}$, calculated experimental value.

ORDER WITH RESPECT TO SUBSTRATE :

In order to confirm the order of the reaction with respect to substrate, the kinetic data of Table A-9 was subjected to Van't Hoff's differential method. From the initial slope of concentration versus time curves, the value of -dc/dt corresponding to various initial concentrations of substrate were evaluated. These values are recorded in Table A-10.

TABLE A - 10

[Amide]M	$(-dc/dt) \times 10^{-4}$	Log Co	Log(-dc/dt)
0.025	2.910	-1.6020	-3.5361
0.05	3.016	-1.3010	-3.5205
0.075	2.940	-1.1249	-3.5316
0.10	3.025	-1.0000	-3.5192
0.125	2.960	-0.9030	-3.5287

A plot of Log (-dc/dt) versus Log Co is shown in Fig. A-7. It gives the value of the slope as zero. This suggests that the reaction is zero order with respect to substrate. Calculations were made for the order of the reaction by Van't Hoff's differential method as given in Table A - 11.

TABLE A - 11

[Substrate] M	$(-dc/dt) \times 10^{-4}$	Order of Reaction(n)
0.025	2.910	0.0518
0.05	3.016	
0.025	2.910	0.0094
0.075	2.940	
0.05	2.910	0.0280
0.10	3.025	
0.025	2.910	0.0105
0.125	2.960	
0.05	3.016	0.0629
0.075	2.940	
0.05	3.016	0.0204
0.125	2.960	

From the above results as shown in Table A - 11 it is confirmed that the order with respect to substrate is zero.

EFFECT OF SILVER CATALYST CONCENTRATION

The reaction was studied at five different concentrations of silver nitrate. The concentration of $K_2S_2O_8$ and the substrate were kept unchanged. These kinetic results are recorded in Table A-12 and shown graphically in Fig.A-8.

TABLE A - 12

$K_2S_2O_8 = 2.0 \times 10^{-2}$M, Substrate = 5.0×10^{-2}M,
Temp.= 35°C.

$[AgNO_3]$ $\times 10^{-3}$M.	1.0	1.5	2.0	3.0	4.0
Time(min.)	Vol.(in ml.) of 0.02M $Na_2S_2O_3$ used (Viz.C)				
0	9.45	9.44	9.44	9.42	9.42
20	8.95	8.85	8.77	8.62	8.45
40	8.48	8.30	8.15	7.90	7.58
60	8.05	7.80	7.59	7.24	6.81
80	7.65	7.32	7.06	6.64	6.13
100	7.28	6.88	6.57	6.09	5.51
130	6.74	6.27	5.91	5.35	4.70
160	6.26	5.71	5.32	4.71	4.01
200	5.68	5.06	4.61	3.97	3.25
240	5.15	4.60	4.00	3.35	2.63
300	4.45	3.85	3.25	2.60	1.92
360	3.84	3.23	2.63	2.03	1.42
$k_1 \times 10^3 min^{-1}$	2.593	3.111	3.599	4.336	5.345
$k_2 \times 10^3 min^{-1}$	1.215	1.305	1.378	1.514	1.682
$k \times 10^3 min^{-1}$	1.378	1.806	2.221	2.822	3.663

From the above results it has been observed that, when the concentration of silver catalyst was increased the rate was also linearly increased . This clearly indicates that the reaction is first order with respect to catalyst .

A plot of k versus $[Ag^+]$ shown in Fig. A-9 is found to be linear and the following relationship is obeyed.

$$k = 1.56 \times 10^{-3} + 0.9375\,[Ag^+].$$

EFFECT OF TEMPERATURE

For determining the temperature coefficient, energy of activation, and various other parameters, the reaction was studied at five different temperatures ranging from 25°C. to 45°C. The results of these kinetic runs are recorded in Table A - 13 and shown graphically in Fig.A-10.

TABLE A - 13

$K_2S_2O_8$ = 2.0×10^{-2}M, Substrate = 5.0×10^{-2} M,
$AgNO_3$ = 1.0×10^{-3}M.

Temp.	25°C	30°C	35°C	40°c	45°C
Time(min.)	Vol.(in ml.) of 0.02M - $Na_2S_2O_3$ used (Viz.C).				
0	9.46	9.46	9.45	9.43	9.43
20	9.18	9.01	8.95	8.76	8.47
40	8.91	8.74	8.48	8.14	7.61
60	8.66	8.42	8.05	7.57	6.85
80	8.42	8.11	7.65	7.20	6.16
100	8.19	7.81	7.28	6.56	5.55
130	7.86	7.39	6.74	5.90	4.74
160	7.54	7.00	6.26	5.31	4.05
200	7.15	6.51	5.68	4.61	3.29
240	6.77	6.07	5.15	4.01	2.67
300	6.25	5.45	4.45	3.25	1.95
360	5.77	4.91	3.84	2.64	1.43
$k_1 \times 10^3 min^{-1}$	1.423	1.890	2.593	3.601	5.290
$k_2 \times 10^3 min^{-1}$	0.670	0.820	1.215	1.618	2.505
$k \times 10^3 min^{-1}$	0.753	1.070	1.378	1.983	2.785

From the above results as shown in Table A - 13, it is seen that, the specific rate has been nearly doubled for 10°C rise in temperature . A plot of log k versus $1/T \times 10^3$ is found to be linear (Fig. A-11) showing that the reaction obeys Arrhenius relationship.

The energy of activation from the slope of this plot is 12.666 K.cals.mole^{-1} which is in good agreement with the calculated value 12.116 K.cals.mole^{-1}. The calculated values of $1/T \times 10^3$ and Log [kr/(kT/h)] are recorded in Table A - 14.

TABLE A - 14

Temp.A°	$1/T\times10^3$	$kr\times10^3 min^{-1}$	Log kr	Log [kr/{kT/h}]
298	3.356	0.753	-4.8768	-15.9161
303	3.301	1.070	-3.0293	-15.7708
308	3.246	1.378	-3.1392	-15.6681
313	3.196	1.983	-3.2974	-15.5168
318	3.145	2.785	-3.4448	-15.3763

By using Arrhenius equation at different temperatures, the value of energy of activation was calculated by the following equation.

$$\log k_1 - \log k_2 = [-E/2.303 \times R]\ [(1/T_1) -(1/T_2)] \quad \ldots (1)$$

The value of energy of activation was then used to calculate the frequency factor A and entropy of activation ΔS^* by the application of the following equations :

$$kr = A\ e^{-(\Delta E)/RT} \quad \ldots (2)$$

and

$$A = e\ (kT/h)\ e^{-(\Delta S^*)/R} \quad \ldots (3)$$

Where the equation (3) is valid for reactions in solutions. In the above expression, **kr** is the specific rate constant, **K** is the Boltzman constant, h is the Plank's constant, e is a constant having a value of 2.718 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 is calculated by the equation.

$$Kr = (kT/h).\ e^{-(\Delta G)/RT} \qquad \ldots (4)$$

Entropy of activation $\Delta S^{\neq}$ is given by the relationship,

$$kr = e.(kT/h).e^{-(\Delta S)^{\neq}/R} \times e^{-(E/RT)} \qquad \ldots (5)$$

OR

$$\ln kr = \ln e + \ln(kT/h) + (\Delta S)^{\neq}/R - (E/RT) \qquad \ldots (6)$$

from which $\Delta S^{\neq}$ can be calculated.

Enthalpy of activation $\Delta H^{\neq}$ was calculated from the relation.

$$kr = kT/h\ .\ e^{-\Delta H^{\neq}/RT}\ .\ e^{(\Delta S)^{\neq}/R} \ \ldots \qquad \ldots (7)$$

$$\text{OR} \qquad \text{Log}\ \frac{kr}{KT/h} = -\frac{\Delta H^{\neq}}{2.303 \times RT} + \frac{\Delta S^{\neq}}{2.303 \times R} \ \ldots \qquad \ldots (8)$$

The values of $\text{Log}\left[\frac{kr}{kT/h}\right]$ have been plotted against 1/T in Fig. A - 12, from the slope of which the enthalpy change for the formation of activated complex $\Delta H^{\neq}$ has been calculated.

The values of temperature coefficient, energy of activation, frequency factor and all other energy parameters are recorded in Table A - 15.

TABLE A - 15

Temp. A°	$k \times 10^3$ min^{-1}	Temp. coeff.	E Kcal mole^{-1}	$A \times 10^4$ litre mole^{-1}sec^{-1}	$\Delta G^{\neq}$ Kcals mole^{-1}	$\Delta S^{\neq}$ e. u.	$\Delta H^{\neq}$ K.cals mole^{-1}
298	0.753	–	–	9.001	21.846	-34.64	
303	1.070	1.830	11.030	8.596	22.01	-34.66	
308	1.378	1.853	11.620	8.002	22.23	-34.84	11.722
313	1.983	2.021	13.700	8.412	22.36	-34.74	(graphically)
318	2.785	–	–	8.711	22.52	-34.72	
Mean	–	1.901	12.116	8.544	22.19	-34.72	

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

The rate constant for this reaction may be expressed by the following relation.

$$k = 8.544 \times 10^{3} . e^{(-12.116/RT)} \quad Sec^{-1}$$

EFFECT OF IONIC STRENGTH :

For studying the effect of ionic strength on reaction rate, the reaction was studied in presence of different concentrations of potassium sulphate. The kinetic results of these runs are recorded in Table A-16 and shown graphically in Fig.A-13.

TABLE A - 16

$K_2S_2O_8$= 2.0 x 10^{-2} M, Subatrate = 5.0 x 10^{-2} m,
$AgNO_3$ = 1.0 x 10^{-3}M, Temp. = 35°C.

$[K_2SO_4]$M	Nil	0.01	0.015	0.02	0.03	0.04
μ	0.061	0.091	0.106	0.121	0.151	0.181
Time (min)	Vol. (in ml) of 0,02 M - $Na_2S_2O_3$ used (viz.C).					
0	9.45	9.46	9.50	9.50	9.45	9.46
20	8.95	8.99	9.09	9.13	9.13	9.18
40	8.48	8.56	8.70	8.78	8.83	8.92
60	8.05	8.15	8.34	8.45	8.55	8.67
80	7.65	7.77	7.99	8.14	8.27	8.43
100	7.28	7.41	7.66	7.85	8.01	8.20
130	6.74	6.89	7.19	7.42	7.64	7.87
160	6.26	6.42	6.76	7.03	7.29	7.56
200	5.68	5.84	6.23	6.53	6.85	7.16
240	5.15	5.32	5.74	6.08	6.44	6.79
300	4.45	4.63	5.09	5.46	5.88	6.27
360	3.84	4.04	4.53	4.91	5.37	5.79
k_1x 10^3min^{-1}	2.593	2.429	2.132	1.896	1.628	1.412
k_2x 10^3min^{-1}	1.215	1.120	0.980	0.930	0.800	0.780
k x 10^3min^{-1}	1.378	1.309	1.152	0.966	0.828	0.632

From the above results (Table A - 16) it has been observed that, on increasing ionic strength, the specific rate decreases. This indicates that the salt effect is negative.

In order to decide the nature of the observed negative salt effect, graphs were plotted between log k and $\mu^{1/2}$as well as between k and μ as shown in Fig. 14 (A) and 14 (B) respectively. It has been observed that, a linear relationship is maintained between log k and $\mu^{1/2}$ where as there exist no linearity between k and μ.

The linearity between log k and $\mu^{1/2}$ exists only in the region of low ionic strength (<0.2). Thus it is follows that the negative salt effect is of 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 A - 17

$[K_2SO_4]$M	μ	k x 10^3min^{-1}	$\sqrt{\mu}$	Log k
Nil	0.061	1.378	0.247	-2.8607
0.01	0.091	1.309	0.302	-2.8830
0.015	0.106	1.152	0.326	-2.9385
0.02	0.121	0.966	0.348	-3.0150
0.03	0.151	0.828	0.389	-3.0819
0.04	0.181	0.632	0.425	-3.1992

It may be stated that the ionic strength employed is rather high for Bronsted[191] relationship to be strictly quantitatively applicable, but still the agreement is found to be fairly good.

SPECIFIC IONIC STRENGTH :

In order to determine the specific ionic effect on the reaction rate, the reaction was studied by the addition of different salts to the reaction mixture, at constant ionic strength. The kinetic results of these runs are recorded in Table A - 18 and shown graphically in Fig. A - 15.

TABLE A - 18

$K_2S_2O_8$=2.0 x 10^{-2} M, Substrate = 5.0 x 10^{-2} M,
$AgNO_3$ = 1.0 x 10^{-3} M, Temp. = 35° C.

Salt added	No salt	K_2SO_4	Na_2SO_4	Li_2SO_4	$MgSO_4$	$ZnSO_4$
(Conc)M.	0.00	0.05	0.05	0.05	0.0375	0.0375
Time (min)	Vol.(in ml.) of 0.02 M - $Na_2S_2O_3$ used (viz.C).					
0	9.45	9.48	9.46	9.46	9.48	9.50
20	8.95	9.21	9.16	9.11	9.08	9.05
40	8.48	8.95	8.88	8.78	8.71	8.62
60	8.05	8.72	8.62	8.47	8.36	8.23
80	7.65	8.48	8.36	8.17	8.02	7.85
100	7.28	8.26	8.12	7.89	7.70	7.50
130	6.74	7.95	7.77	7.49	7.25	7.00
160	6.26	7.64	7.45	7.11	6.83	6.54
200	5.68	7.27	7.03	6.63	6.31	5.97
240	5.15	6.91	6.65	6.20	5.83	5.46
300	4.45	6.43	6.12	5.60	5.18	4.78
360	3.84	5.97	5.63	5.07	4.61	4.20
$k_1 \times 10^3 min^{-1}$	2.593	1.353	1.503	1.795	2.058	2.345
$k_2 \times 10^3 min^{-1}$	1.215	0.770	0.830	0.860	0.880	0.980
$k \times 10^3 min^{-1}$	1.378	0.583	0.673	0.935	1.178	1.365

From the above results as shown in Table A -18, it has been observed that the specific inhibitory effect of various ions is in the order.

$K^+ > Na^+ > Li^+ > Mg^{++} > Zn^{++}$

Thus, we can conclude that the salt effect is negative.

EFFECT OF HYDROGEN ION CONCENTRATION

The amide solution was prepared in 10 % acetic acid, hence no attempt was made to study the effect of acid, such as sulphuric acid on the reaction rate.

EFFECT OF ALLYL ACETATE

It is well known that the reaction involving $S_2O_8^{2-}$ ion is inhibited by allyl acetate. It was shown by Kolthoff[192] and coworkers ,Wiberg[193],Ball[194] and coworkers that allyl acetate is an efficient capture of sulphate ion radical $(\overset{\cdot -}{SO_4})$ which is known to be formed in oxidation reactions involving $S_2O_8^{2-}$ ion. Hence it was considered to investigate effect of allyl acetate on peroxydisulphate oxidation of organic compounds studied in this thesis.

To study the effect of the allyl acetate on the reaction rate, the reaction was studied in presence of three different concentrations of allyl acetate. The results of these kinetic runs are recorded in Table A-19 and shown graphically in Fig.A-16.

TABLE A - 19

Substrate = 5.0×10^{-2}M, $K_2S_2O_8$ = 2.0×10^{-2}M,
$AgNO_3$ = 1.0×10^{-3}M, Temp. = 35°C.

Allyl Acetate	Nil	0.001	0.005	0.01
Time (min.)	Vol. (in ml.) of 0.02 M $Na_2S_2O_3$ used(viz.C)			
0	9.45	9.46	9.48	9.50
20	8.95	9.00	9.03	9.12
40	8.48	8.56	8.62	8.76
60	8.05	8.15	8.23	8.42
80	7.65	7.77	7.85	8.10
100	7.28	7.41	7.50	7.80
130	6.74	6.90	7.01	7.36
160	6.26	6.43	6.55	6.95
200	5.68	5.85	5.99	6.45
240	5.15	5.33	5.47	5.98
300	4.45	4.63	4.78	5.36
360	3.84	4.02	4.20	4.80
$k \times 10^3 min^{-1}$	2.593	2.425	2.320	1.955

From the above results (Table A - 19) it has been observed that allyl acetate inhibits the rate of reaction. It may be pointed out that allyl acetate does not act as a very efficient radical capture reagent in this case. The radical capture may be due to polymerization at allyl acetate by sulphate radical ions formed from the catalysed decomposition of $S_2O_8^{2-}$ ion.

MOLE RATIO

In order to determine the number of moles of $S_2O_8^{2-}$ reaction with one mole of amide, the graphical method was employed. $K_2S_2O_8$ was taken in excess as compared to amide. Simultaneously, a blank run was also carried out. At suitable intervals of time, 5 ml. of the reaction mixture was pipetted out and estimated for unreacted $K_2S_2O_8$ The kinetic results of these runs are recorded in Table A-20 and shown graphically in Fig.A-17.

The curves consist of two portions - the first, for the oxidation of amide and second for the self decomposition of $S_2O_8^{2-}$ ion. Now the tangents are drawn on the portions of the curve which intersect at point P. From this point of intersection, the value of $K_2S_2O_8$consumed in the complete oxidation of 10 ml. of 0.01 M amide is calculated. The point Q on the curve at the same time gives the value corresponding to self decomposed $K_2S_2O_8$.

TABLE A -20

$K_2S_2O_8 = 5.0 \times 10^{-2}M$, $AgNO_3 = 1.0 \times 10^{-3}M$,
Temp. = 35°C.

Substrate	0.01	Nil
Time(min.)	Vol.(in ml.) of 0.02M.- $Na_2S_2O_3$ used (Viz.c).	
0	24.12	29.90
30	21.90	23.39
60	21.22	22.34
90	19.79	21.42
120	18.51	20.83
150	17.43	20.40
180	16.30	19.48
210	14.94	19.03
240	13.60	18.19
270	13.10	17.35
300	12.19	16.94
330	11.63	15.86
360	10.88	15.83
390	10.79	14.98
420	10.50	14.43
450	9.95	13.98
480	9.53	13.48

From the graph (Fig. A - 17) it indicates that the two plots become parallel at P. At this point log C = 1.05 which corresponds to 11.22 ml.

The corresponding value of log C at the same time on the self decomposition curve is shown by point Q. At this point log C = 1.21 which corresponds to 16.21 ml.

The difference between the two values is 4.99 ccs. Therefore, 4.99 ccs of

0.02 N $Na_2S_2O_3$ = 4.99 ccs of 0.02 N $K_2S_2O_8$

= 4.99 ccs of 0.01 N $K_2S_2O_8$

Hence 10 ml of 0.01 M amide = 4.99 ml. of 0.01 M $K_2S_2O_8$. Thus one mole of amide consumes one mole of peroxydisulphate for completion of the reaction.

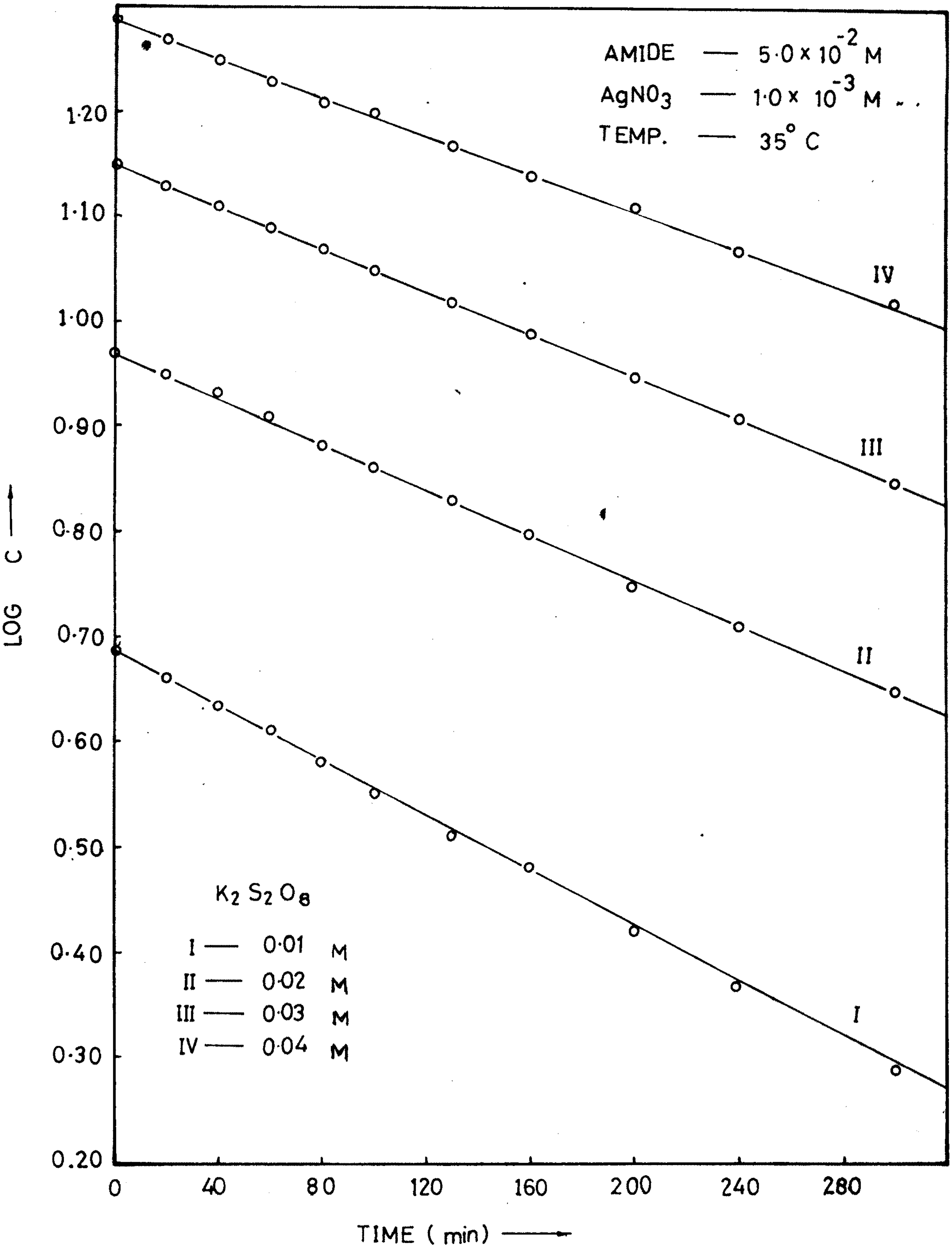


FIG. A-1 EFFECT OF $K_2S_2O_8$.

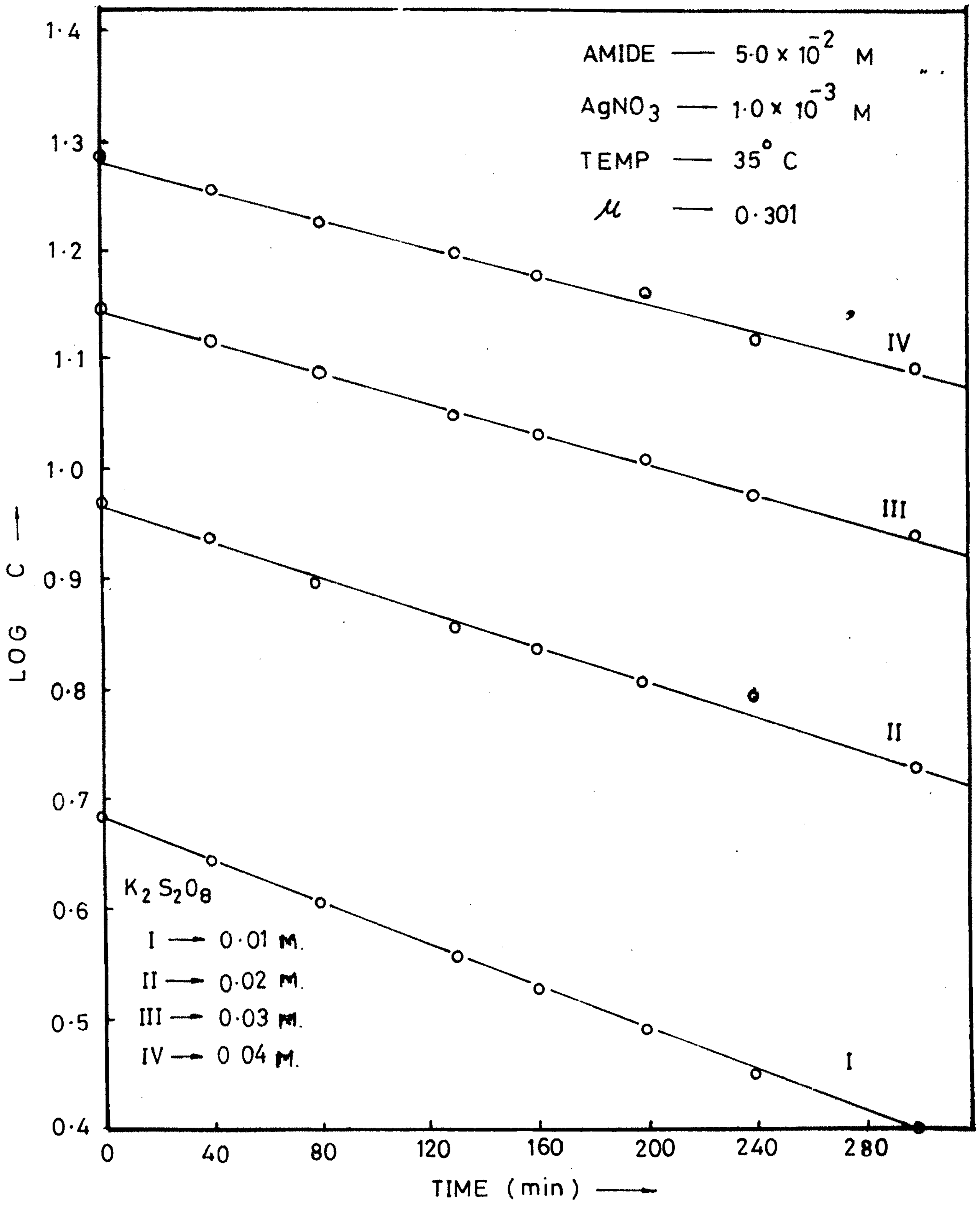


FIG. A-2 EFFECT OF $K_2S_2O_8$ AT CONSTANT μ.

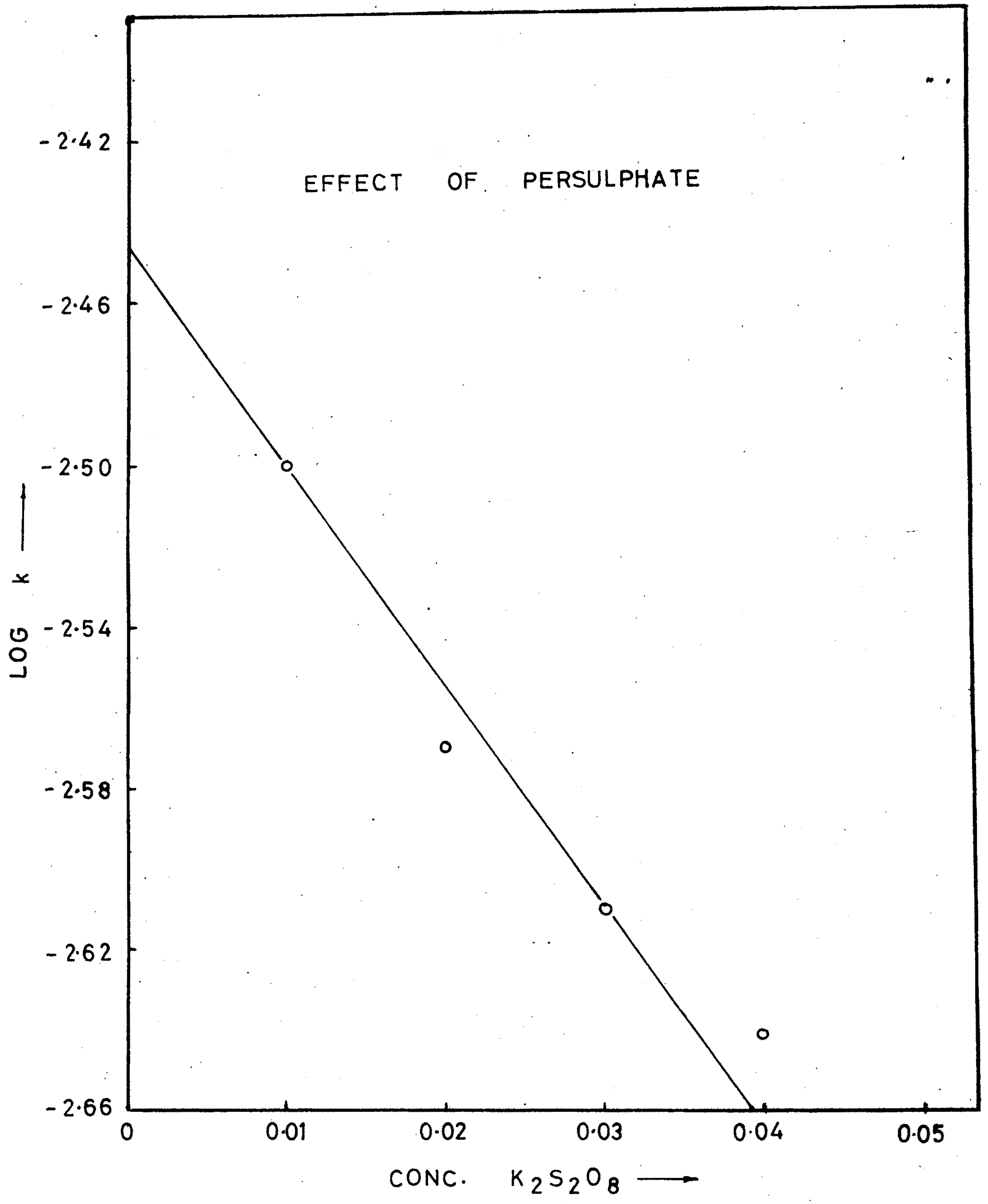


FIG. A-3 PLOT OF LOG k VS CONC. OF $K_2S_2O_8$

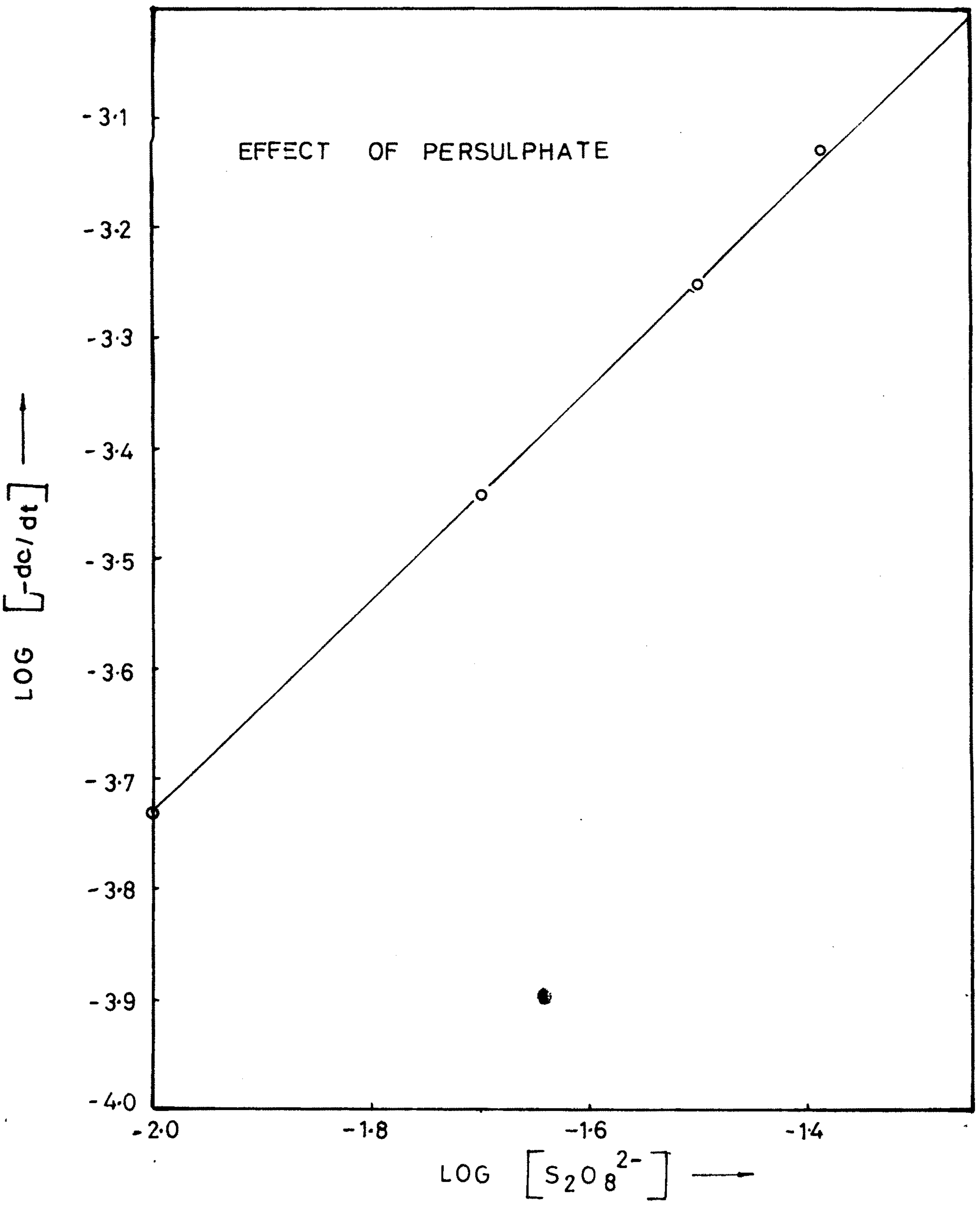


FIG A-4 PLOT OF LOG [-dc/dt] VS LOG [$S_2O_8^{2-}$]

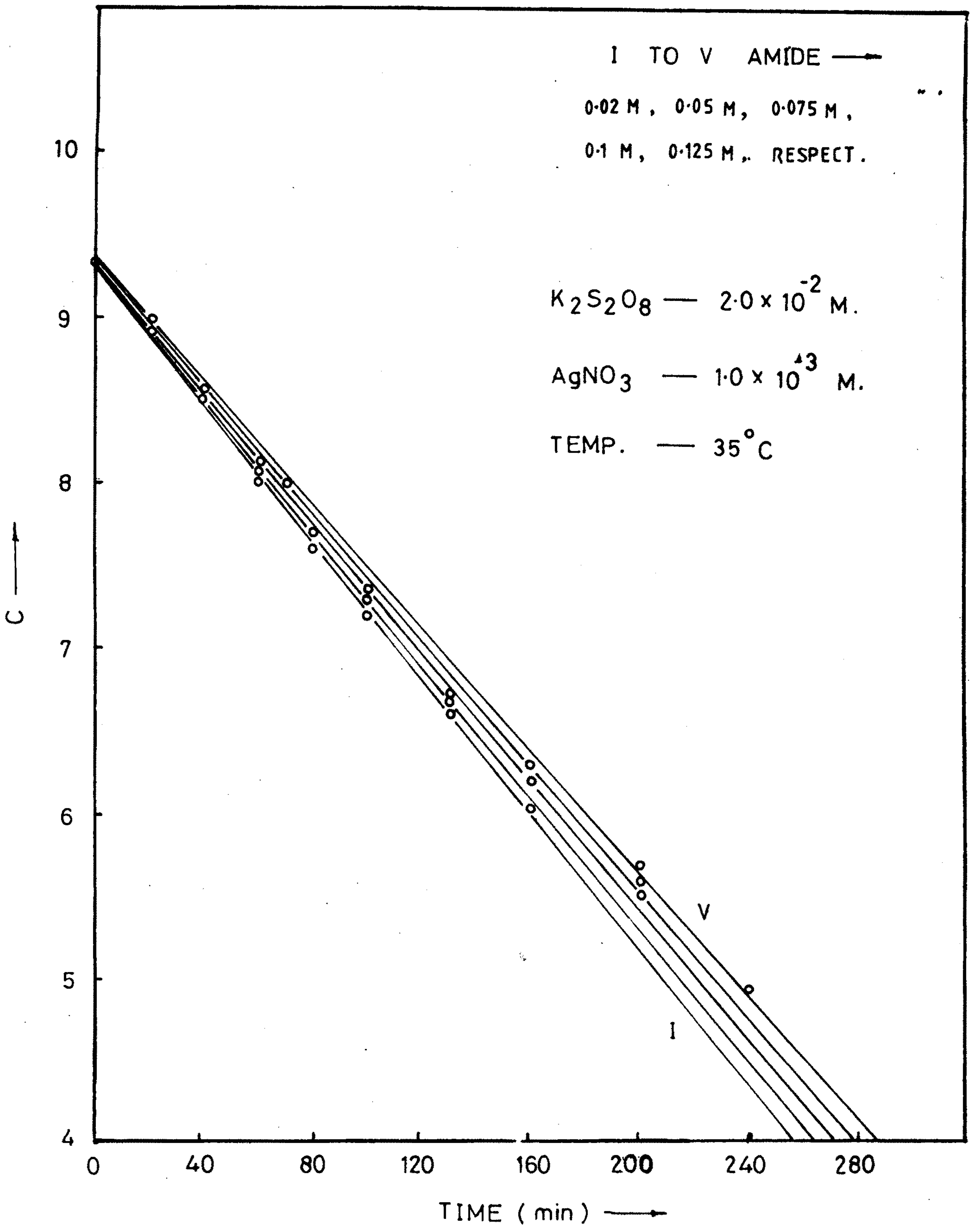


FIG A-5 EFFECT OF AMIDE ['C' VS TIME]

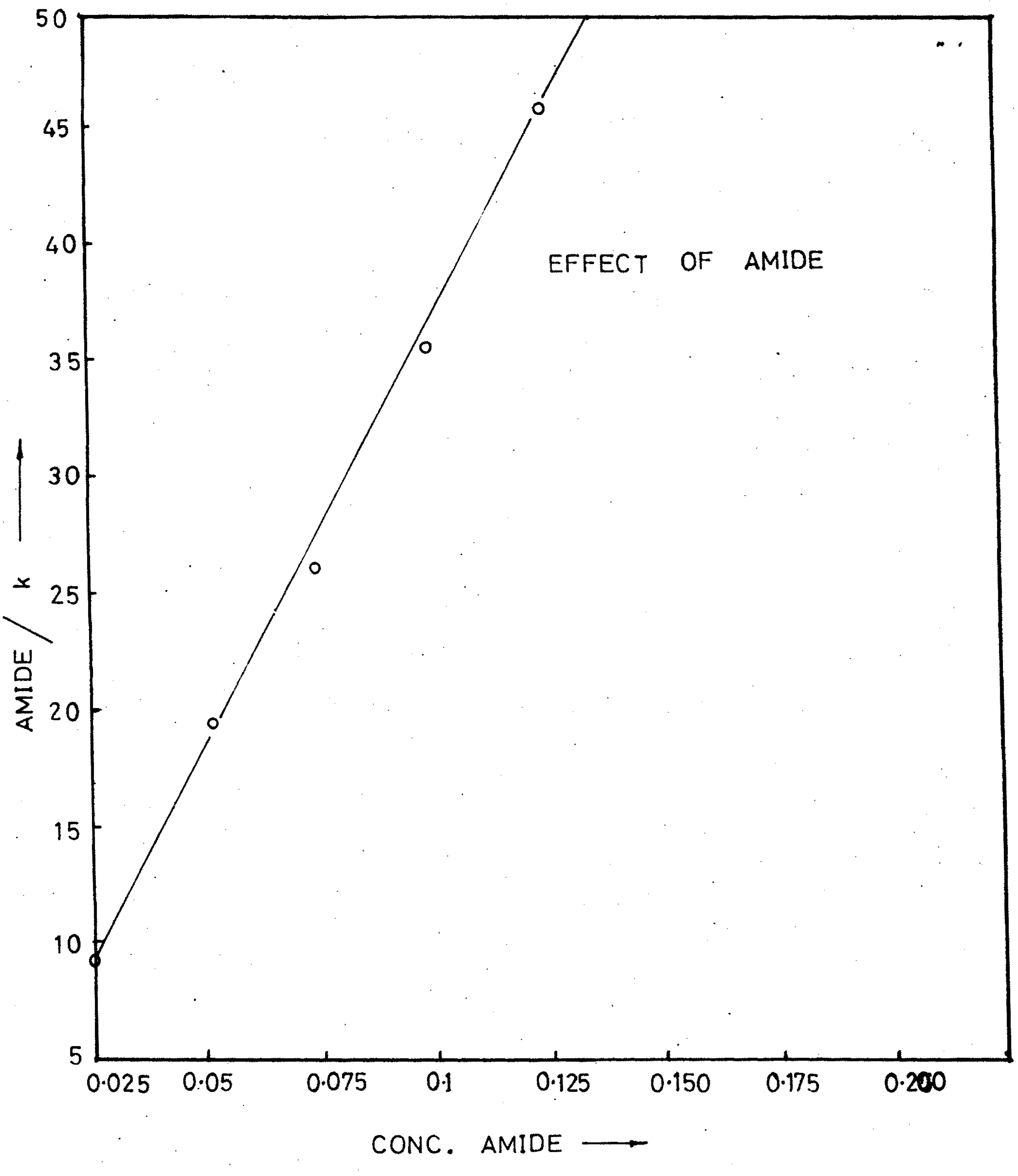


FIG A-6 PLOT OF AMIDE/ k VS k

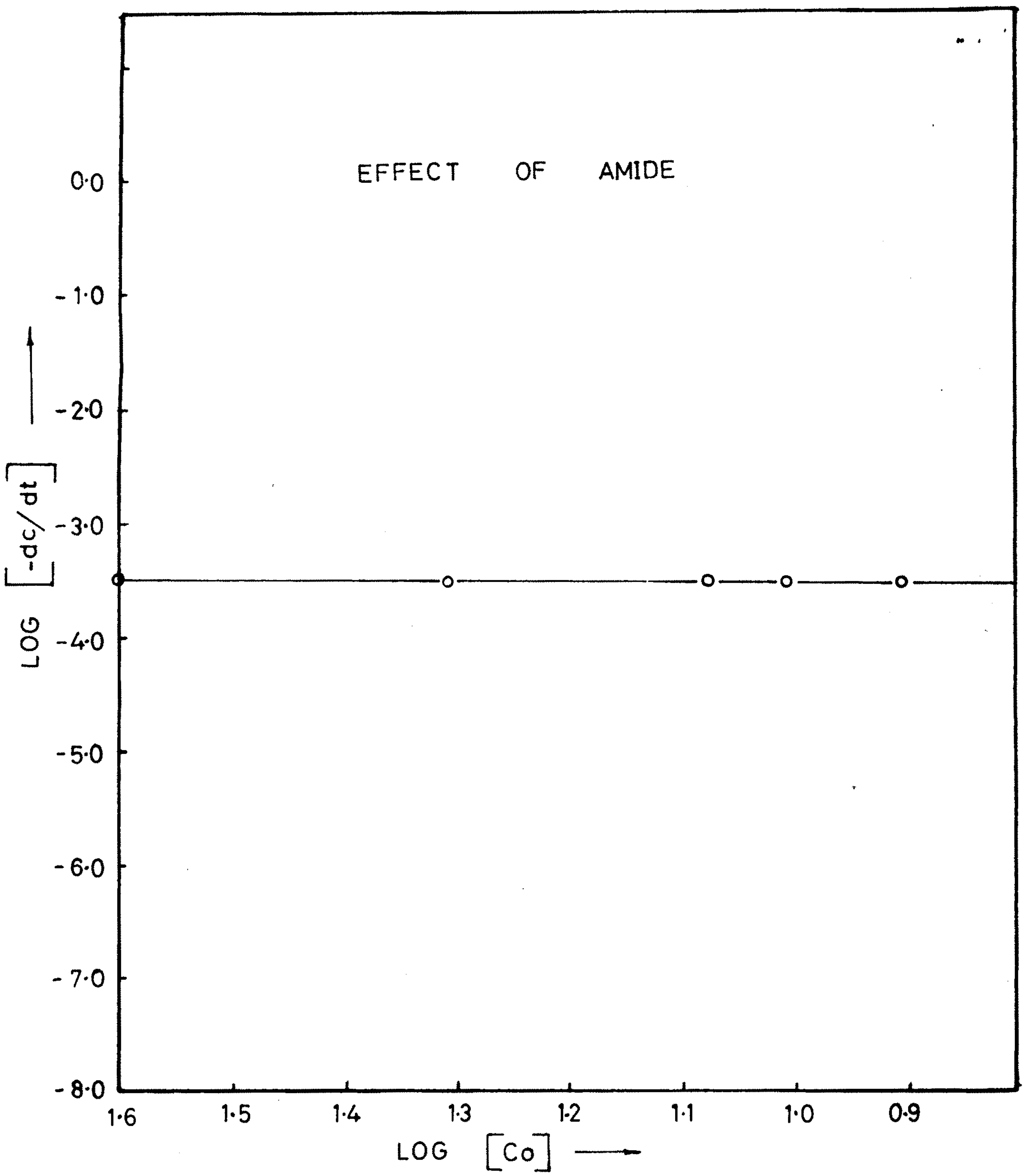


FIG A-7 PLOT OF LOG [-dc/dt] VS LOG [Co]

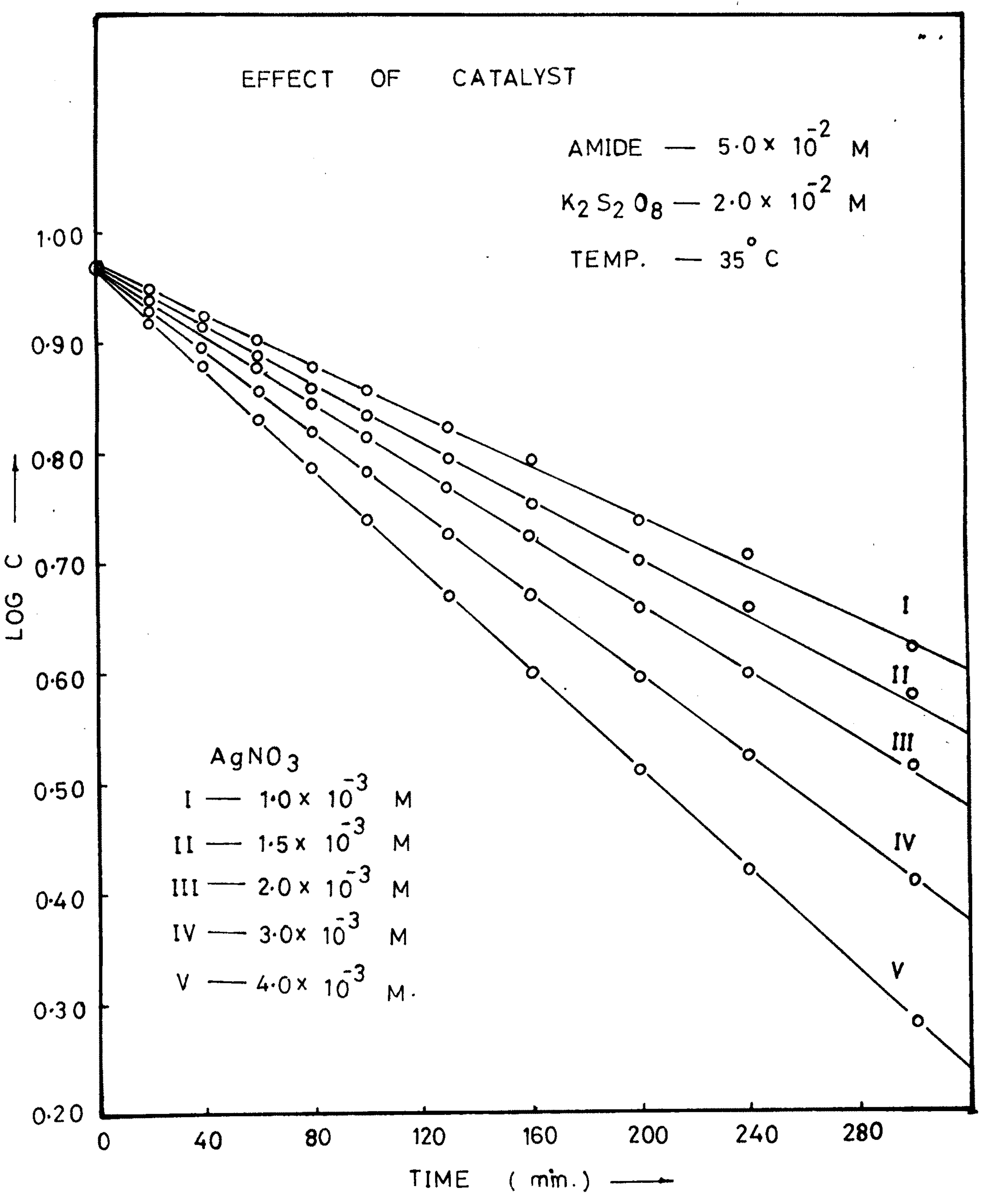


FIG A-8 PLOT OF LOG C VS TIME

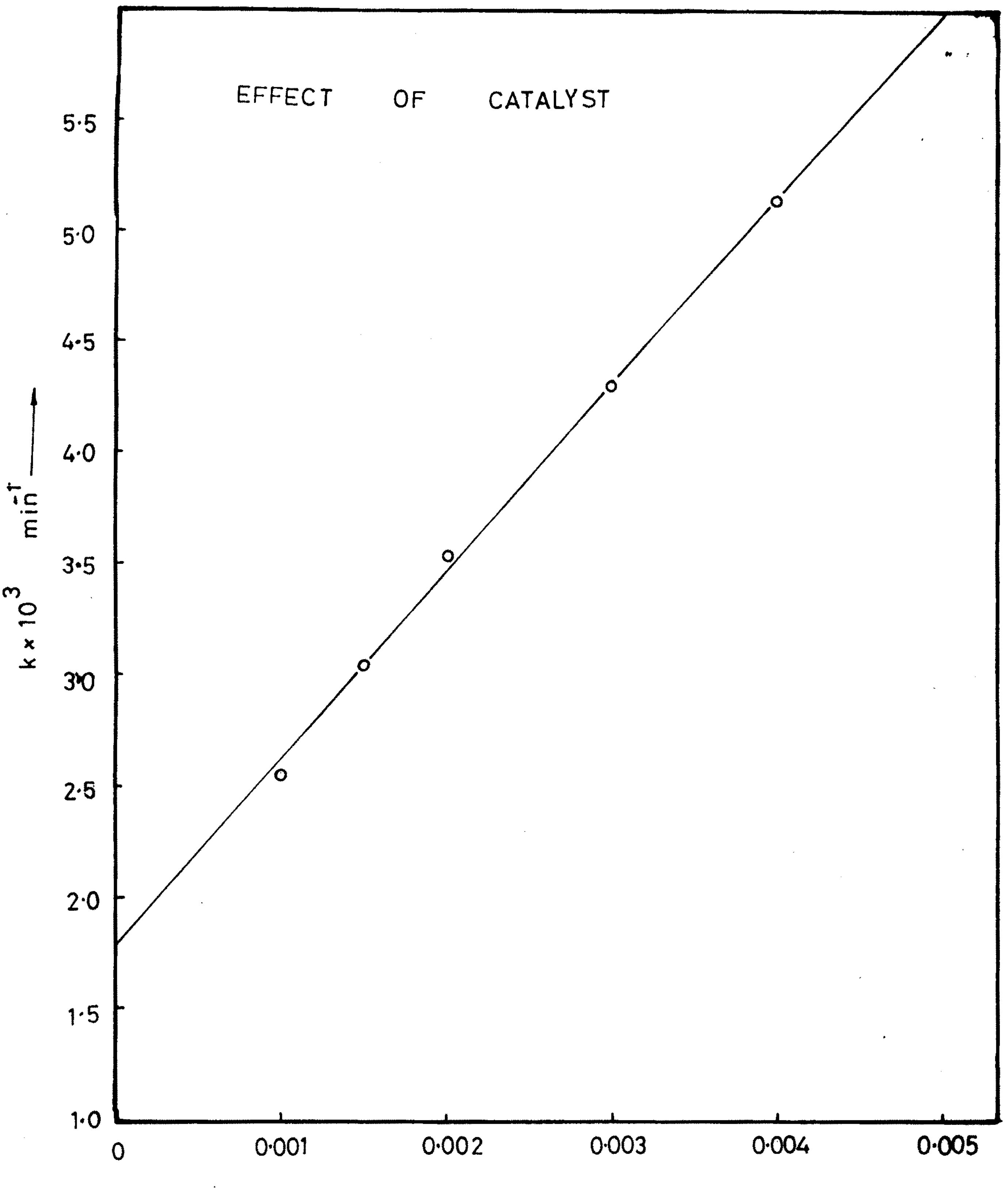


FIG — A-9 PLOT OF $k \times 10^3$ VS CONC (Ag^+)

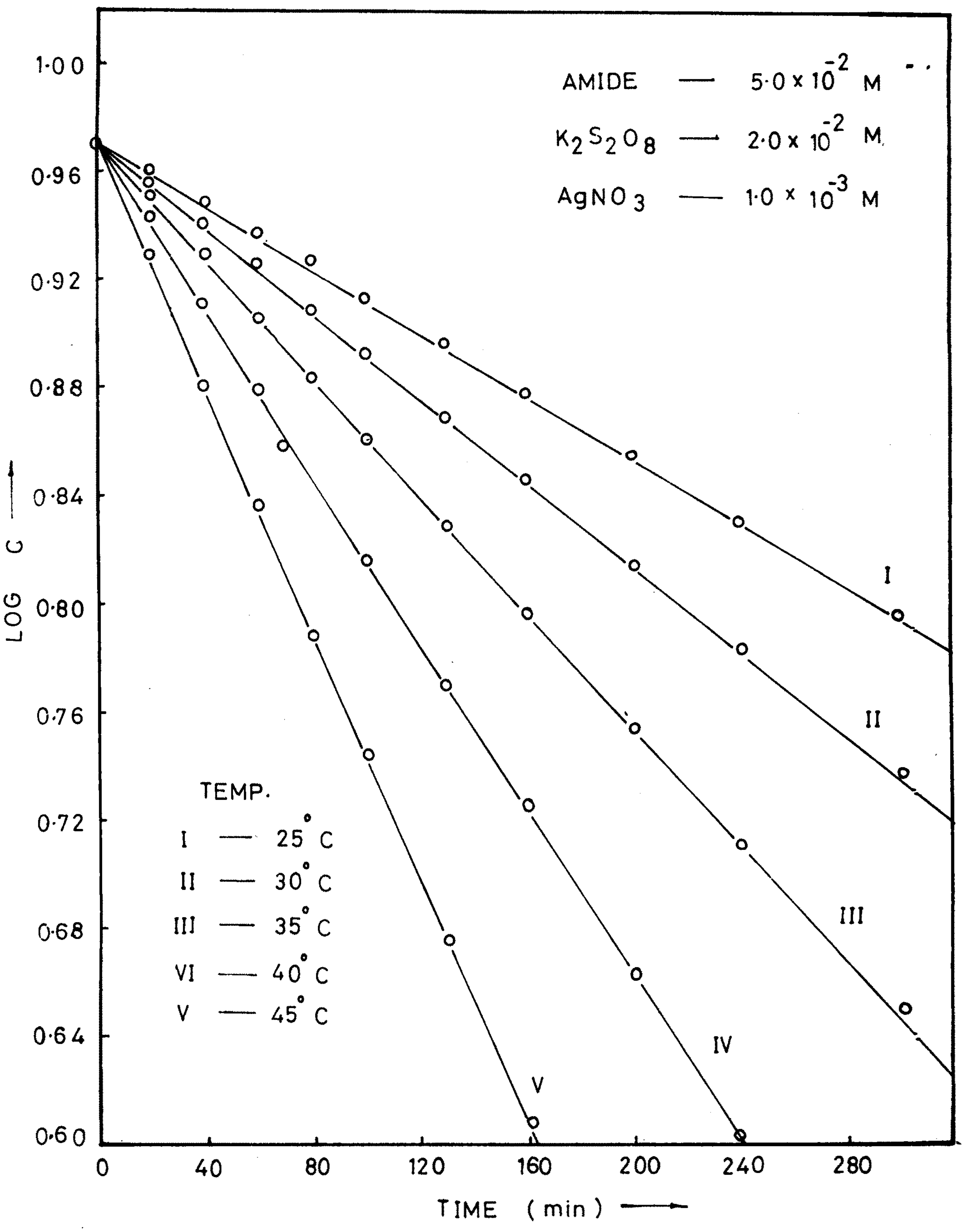


FIG A-10 EFFECT OF TEMPERATURE

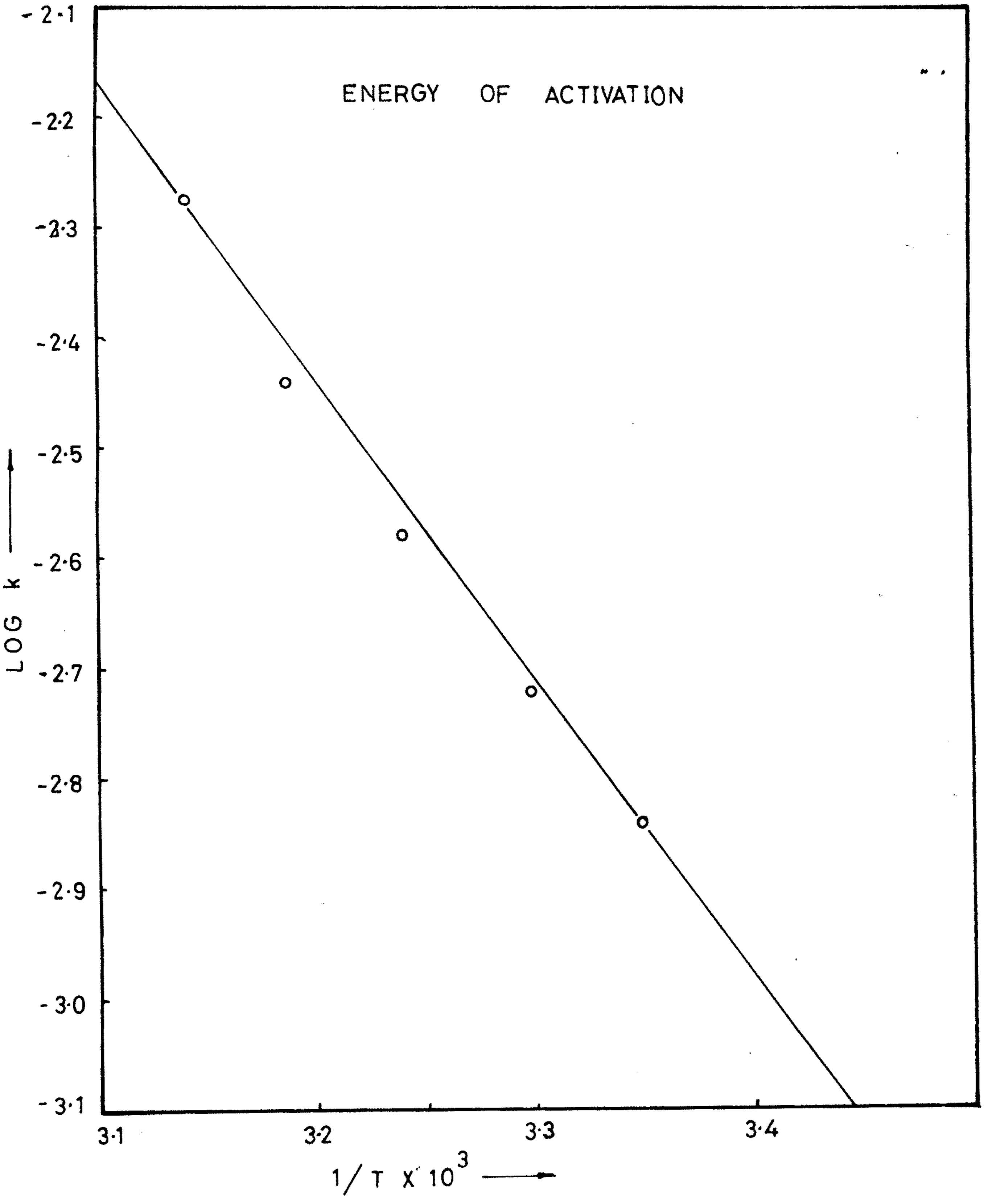


FIG A-11 PLOT OF LOG k VS $1/T \times 10^3$

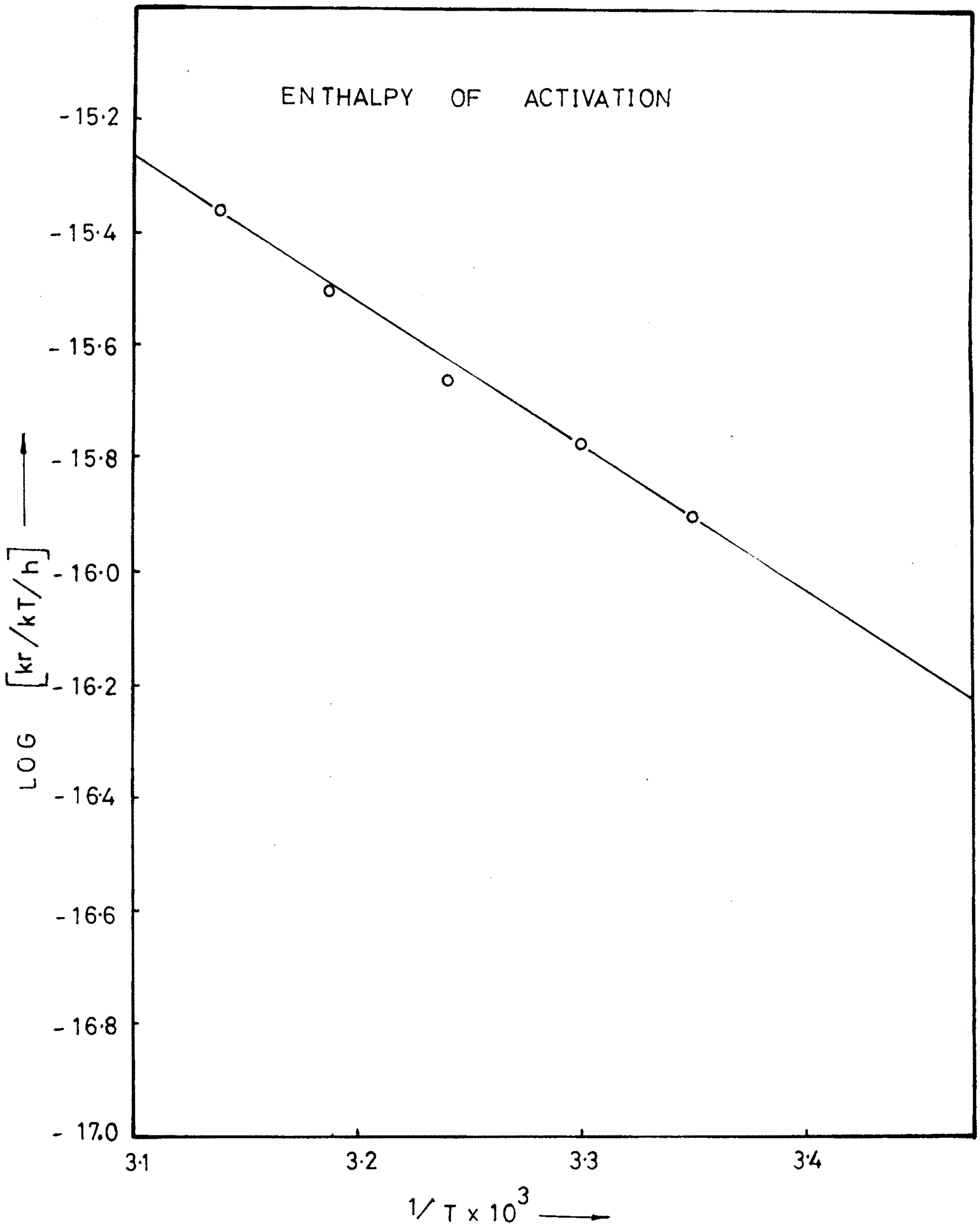


FIG A-12 PLOT OF LOG [kr/ kT/h] VS 1/T x 10^3

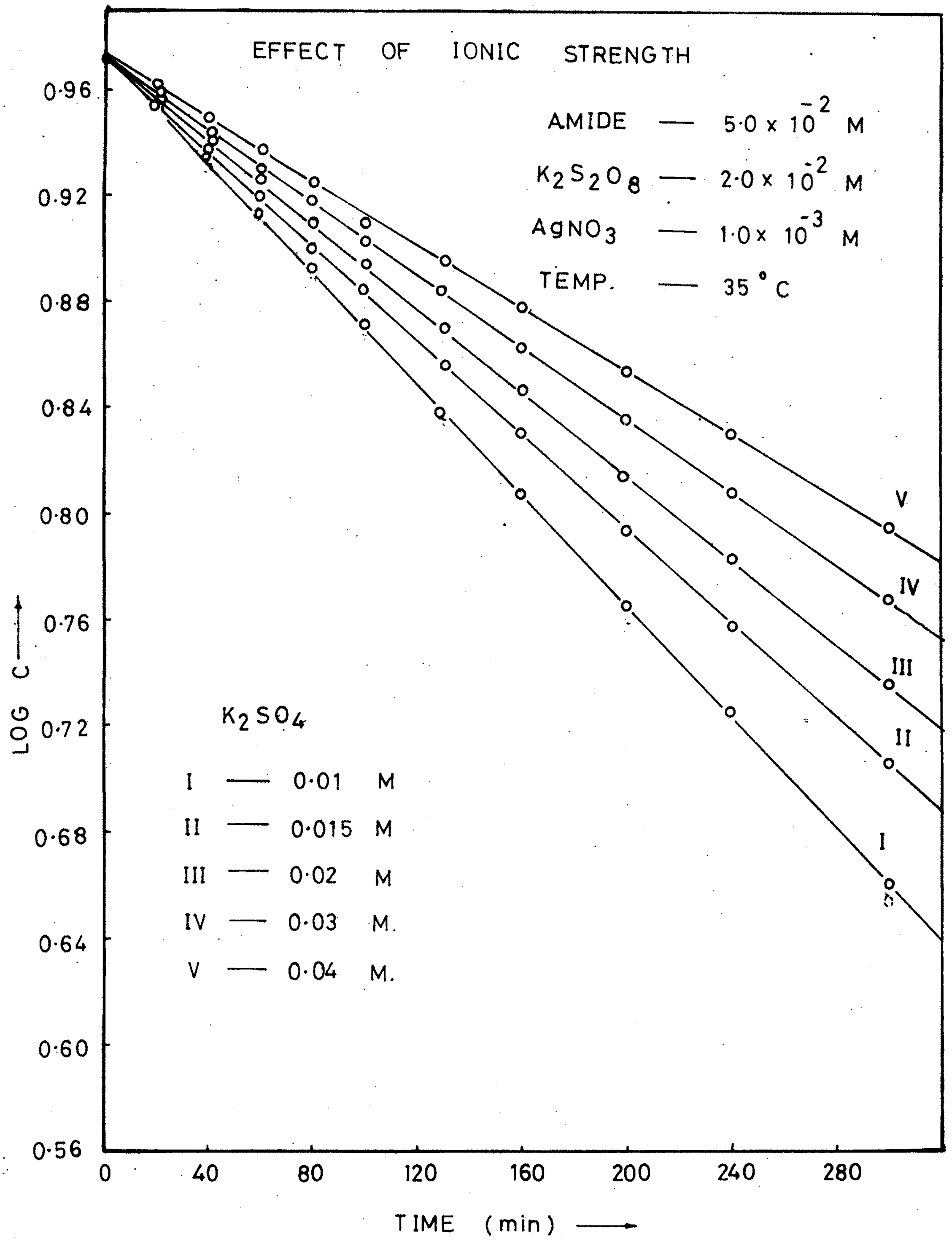

EFFECT OF IONIC STRENGTH
AMIDE — 5.0×10^{-2} M
$K_2S_2O_8$ — 2.0×10^{-2} M
$AgNO_3$ — 1.0×10^{-3} M
TEMP. — 35 °C
K_2SO_4
I — 0·01 M
II — 0·015 M
III — 0·02 M
IV — 0·03 M.
V — 0·04 M.
V
IV
III
II
I
LOG C
0·96
0·92
0·88
0·84
0·80
0·76
0·72
0·68
0·64
0·60
0·56
0
40
80
120
160
200
240
280
TIME (min)

FIG. A-13

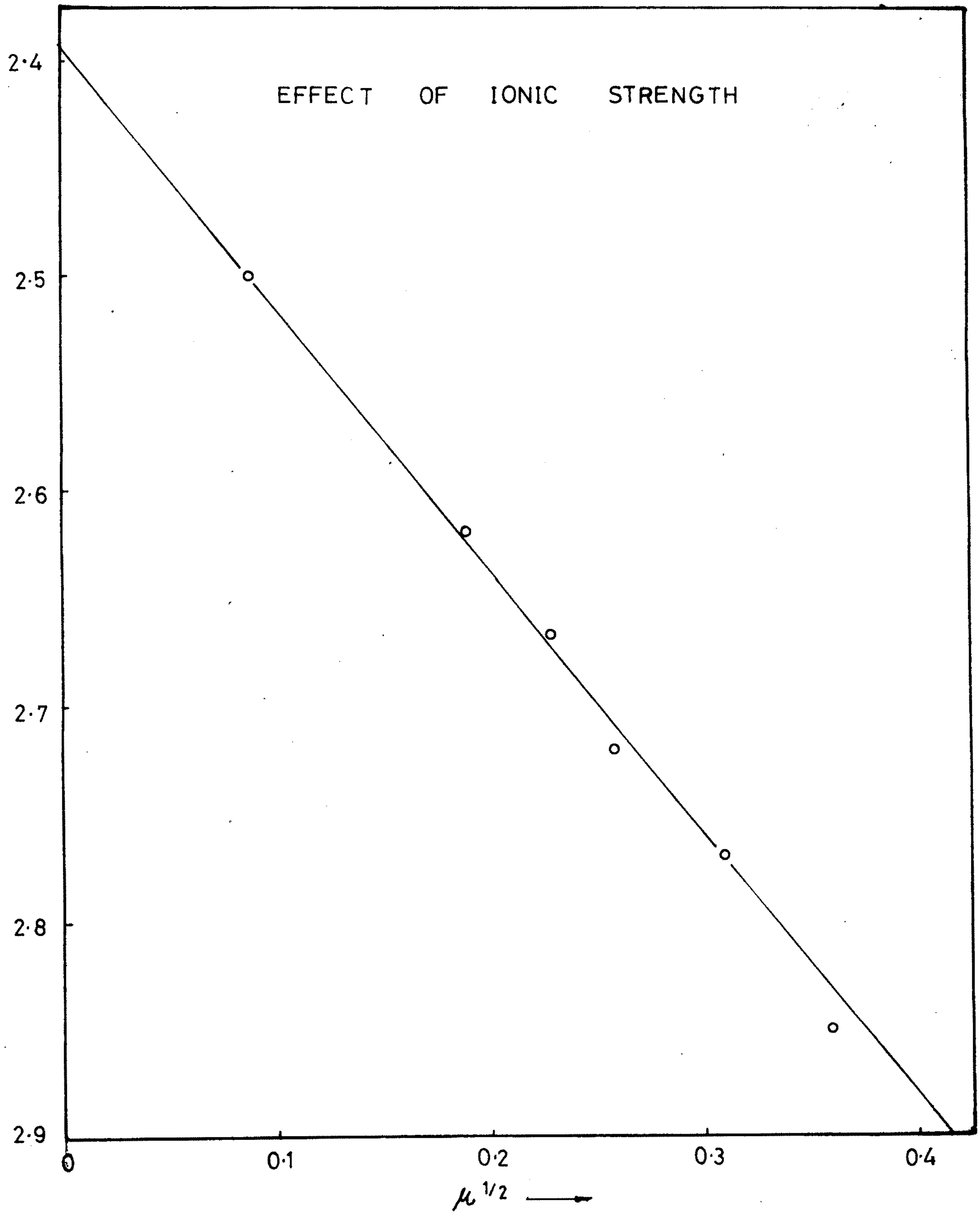


FIG. A-14 (A) PLOT OF LOG k VS $\mu^{1/2}$

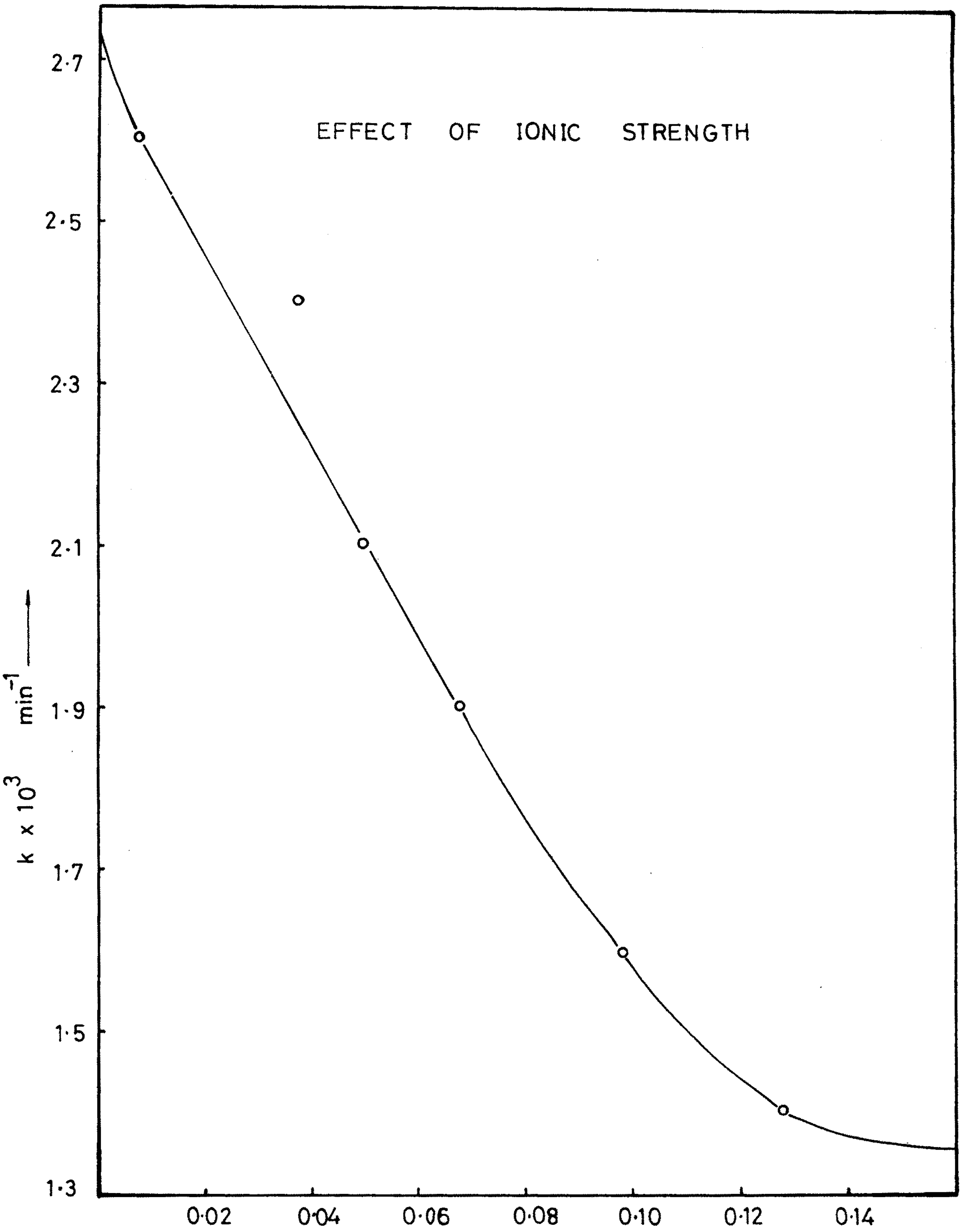
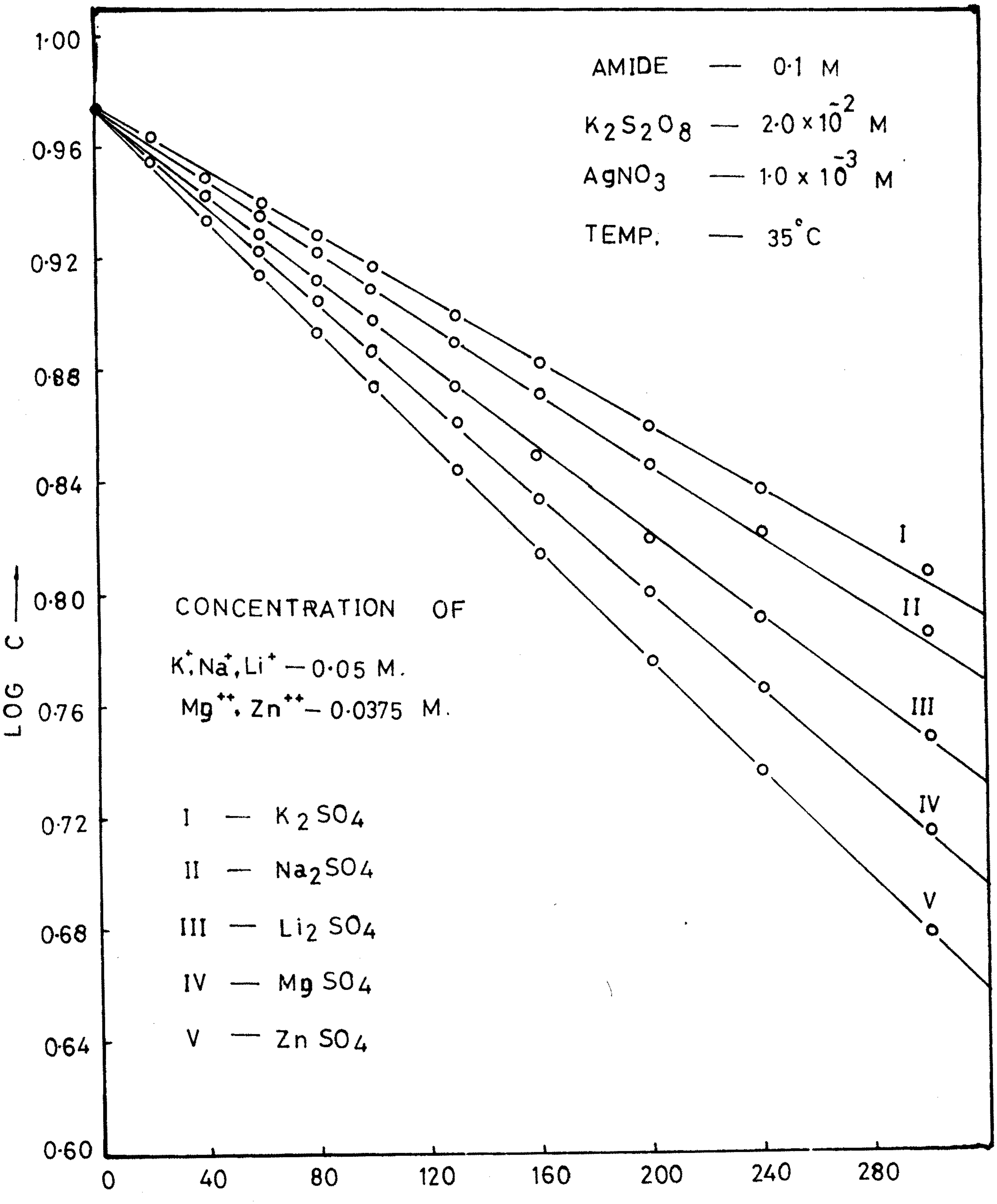


FIG A-14(B) PLOT OF $k \times 10^3$ VS μ



AMIDE — 0·1 M
$K_2S_2O_8$ — 2.0×10^{-2} M
$AgNO_3$ — 1.0×10^{-3} M
TEMP. — 35°C
CONCENTRATION OF
K^+, Na^+, Li^+ — 0·05 M.
Mg^{++}, Zn^{++} — 0·0375 M.
I — K_2SO_4
II — Na_2SO_4
III — Li_2SO_4
IV — $MgSO_4$
V — $ZnSO_4$
I
II
III
IV
V
LOG C
1·00
0·96
0·92
0·88
0·84
0·80
0·76
0·72
0·68
0·64
0·60
0
40
80
120
160
200
240
280
TIME (min)

FIG. A-15

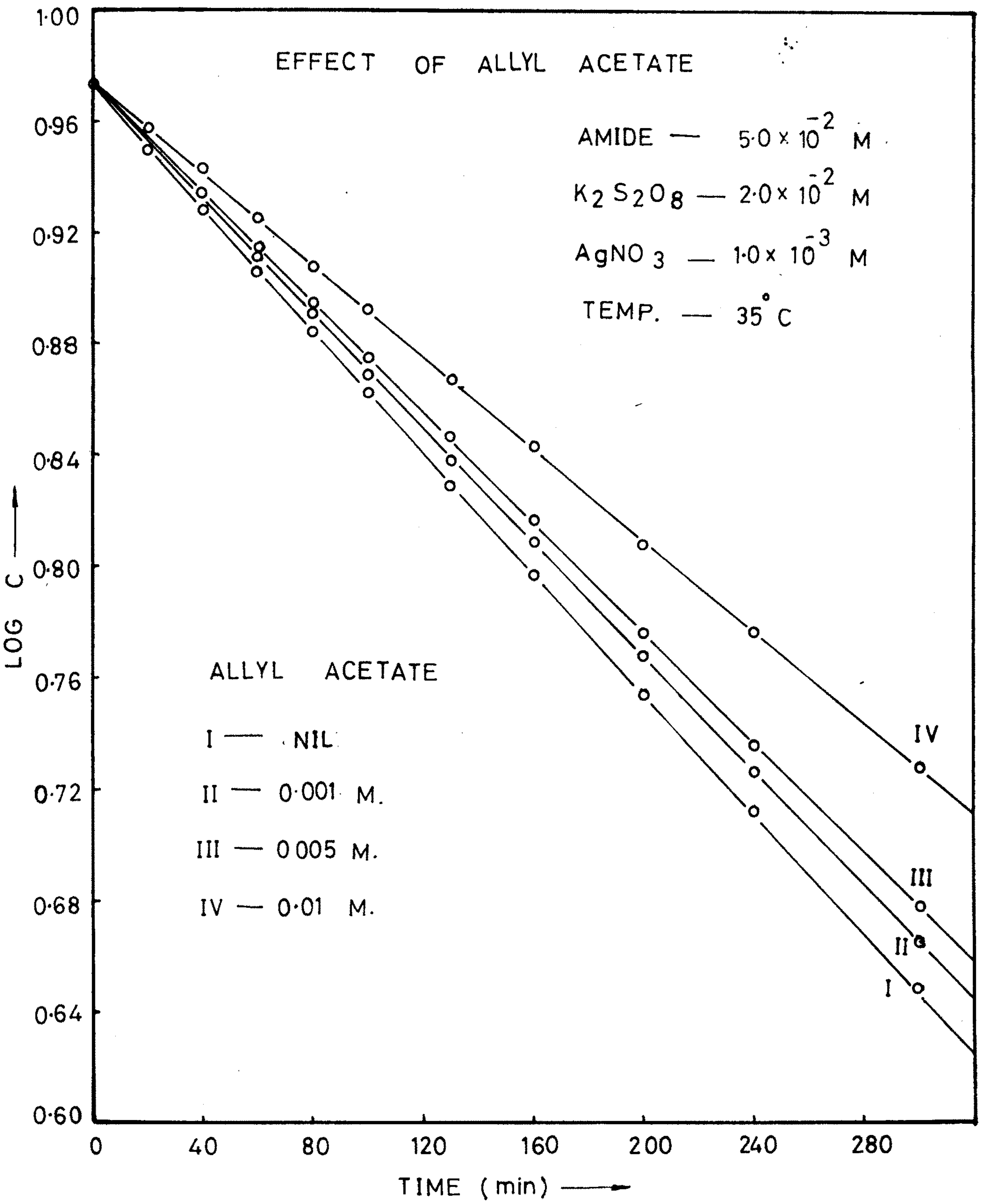

EFFECT OF ALLYL ACETATE
AMIDE — 5·0 × 10⁻² M
K₂S₂O₈ — 2·0 × 10⁻² M
AgNO₃ — 1·0 × 10⁻³ M
TEMP. — 35°C
ALLYL ACETATE
I — NIL
II — 0·001 M.
III — 0 005 M.
IV — 0·01 M.
I
II
III
IV
LOG C
1·00
0·96
0·92
0·88
0·84
0·80
0·76
0·72
0·68
0·64
0·60
0
40
80
120
160
200
240
280
TIME (min)

FIG. A-16

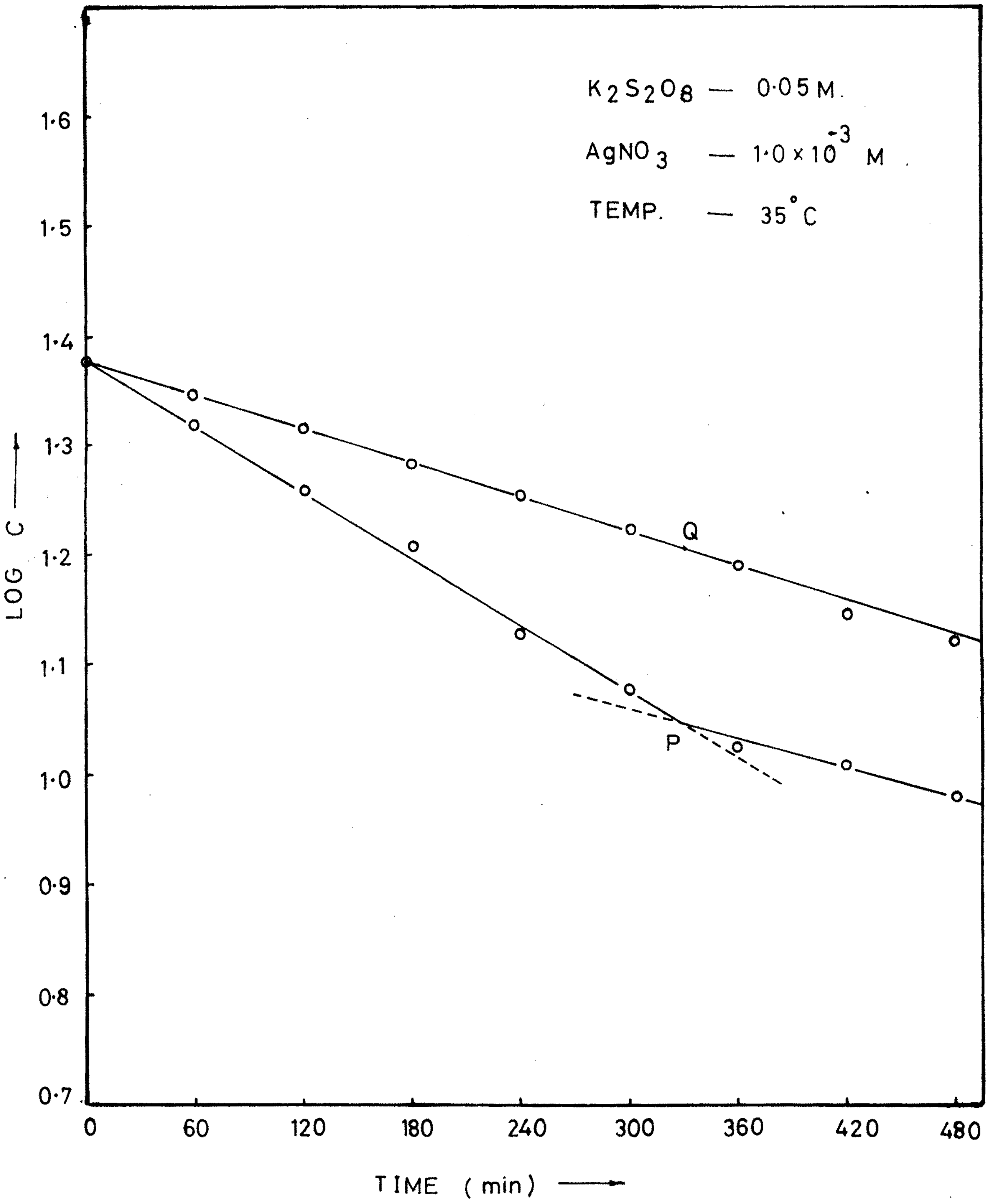


FIG A-17 MOLE RATIO