CHAPTER IV

CHAPTER - IV

OXIDATION OF AZELAIC AMIDE.

In order to decide the suitable temperature, concentration of the ractants and concentration of the silver catalyst some preliminary experiments were carried out. At room temp., 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 concentrations 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 B - 1.

TABLE B - 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*	$k_1 \times 10^3 min^{-1}$
0	9.44	-
20	8.95	2.606
40	8.50	2.595
60	8.08	2.579
80	7.68	2.566
100	7.31	2.554
130	6.78	2.538
160	6.30	2.525
200	5.71	2.508
240	5.18	2.496
300	4.48	2.481
360	3.87	2.470
Mean $k_1 \times 10^3$ min^{-1}	-	2.538

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

From the results contained in Table B - 1, it indicates that there is a fair constancy in the first order rate constant values, suggesting that the overall order of reaction at these concentrations of the reactants is unity. The concentration of substrate was taken in excess and so the order is with respect to $S_2O_8^{2-}$.

To decide conclusively the order with respect to $S_2O_8^{2-}$ and substrate,another kinetic run having equimoler concentrations (0.02M each) of the two reactants was studied. The results of these measurements are recorded in Table B-2.

TABLE B - 2

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

Time (min.)	C	$k_1 \times 10^3 min^{-1}$
0	9.46	-
20	8.85	3.312
40	8.28	3.299
60	7.76	3.285
80	7.28	3.272
100	6.83	3.255
130	6.20	3.243
160	5.64	3.225
200	4.97	3.212
240	4.39	3.194
300	3.64	3.180
360	3.02	3.163
Mean $k_1 \times 10^3$ min^{-1}.	-	3.240

Here again, it is seen that the first order rate constant slightly decrease with time, which most probable may be due to some inihibition as the reaction progresses. The nearly constant values of the rate constant suggest that the order with respect to substrate may be zero.

EFFECT OF $K_2S_2O_8$ CONCENTRATION

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

TABLE 8 – 3

Substrate – 5.0 $\times 10^{-2}$M, $AgNO_3$ = 1.0×10^{-3}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	4.94	–	9.44	–	14.75	–	19.55	–
20	4.65	2.931	8.95	2.606	14.09	2.267	18.81	1.900
40	4.39	2.920	8.50	2.595	13.47	2.249	18.13	1.883
60	4.15	2.897	8.08	2.579	12.89	2.237	17.46	1.874
80	3.92	2.883	7.68	2.566	12.34	2.226	16.84	1.862
100	3.70	2.871	7.31	2.554	11.82	2.208	16.24	1.851
130	3.40	2.860	6.78	2.538	11.08	2.200	15.39	1.836
160	3.13	2.844	6.30	2.525	10.39	2.187	14.60	1.823
200	2.80	2.831	5.71	2.508	9.54	2.173	13.60	1.814
240	2.51	2.820	5.18	2.496	8.77	2.162	12.68	1.802
300	2.13	2.802	4.48	2.481	7.73	2.151	11.42	1.790
360	1.80	2.790	3.87	2.470	6.83	2.140	10.33	1.772
$k_1 \times 10^3$ min^{-1}		2.859	–	2.538	–	2.200	–	1.837
$k_2 \times 10^3$ min^{-1}		1.325	–	1.215	–	1.135	–	1.012
$k \times 10^3$ min^{-1}		1.534	–	1.323	–	1.065	–	0.825

From the above results (Table B − 3), it is seen that when the concentration of $K_2S_2O_8$ was increased, there is a decrease in the first order rate constant. It must be mentioned here that in any particular run, (especially that containing high concentration of $K_2S_2O_8$) the rate constant slightly decreases with time.

Now in order to study this effect under the condition of constant ionic strength as well as at constant K^+ ion concentration four kinetic runs having different concentrations of peroxydisulphate and potassium sulphate were studied. The results of these kinetic runs are recorded in Table B − 4 and shown graphically in Fig. B − 2.

It must be mentioned here that, in all the subsequent kinetic studies, though the self decomposition of peroxydisulphate has always been investigated under the corresponding experimental conditions, the kinetic data for these runs have been omitted due to pressure on space and hence only the corresponding values of the rate constant (viz. k_2) have been directly recorded at the end of each table.

TABLE B - 4

$AgNO_3 = 1.0 \times 10^{-3}$M, Substrate = 5.0×10^{-2}M, Temp.=35°C.
μ = 0.301.

$[K_2S_2O_8]$M + $[K_2SO_4]$M	0.01 0.09	0.02 0.08	0.03 0.07	0.04 0.06
Time (min)	Vol. (in ml) of 0.02 M - $Na_2S_2O_3$ used (viz. c).			
0	4.96	9.46	14.36	19.32
20	4.74	9.09	13.88	18.79
40	4.54	8.75	13.44	18.30
60	4.35	8.42	13.01	17.82
80	4.17	8.11	12.60	17.37
100	4.00	7.82	12.21	16.93
130	3.76	7.40	11.65	16.29
160	3.53	7.01	11.13	15.68
200	3.26	6.52	10.46	14.93
240	3.00	6.07	9.87	14.22
300	2.66	5.46	9.01	13.22
360	2.36	4.91	8.24	12.29
$k_1 \times 10^3$ min^{-1}	2.120	1.881	1.602	1.309
$k_2 \times 10^3$ min^{-1}	0.690	0.670	0.670	0.660
$k \times 10^3$ min^{-1}	1.430	1.211	0.932	0.649

From the results as shown in Table B - 4 it indicates that, here again the first order rate constant is decreased when the concentration of $K_2S_2O_8$ was increased.

Table B-5 shows the comparision between k values with the increasing concentrations of peroxydisulphate without K_2SO_4 and with K_2SO_4 to maintain constant ionic strength and constent K^+ concentration in the later case.

TABLE B - 5

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

$[K_2S_2O_8]$M without $[K_2SO_4]$ M	$k\times10^3$ min^{-1}	$[K_2S_2O_8]$M without constant K^+ ionic strength	$k\times10^3$ min^{-1}
0.01	1.534	0.01	1.430
0.02	1.323	0.02	1.211
0.03	1.065	0.03	0.932
0.04	0.825	0.04	0.649

An examination of the above data ,it indicates that at constant K^+ ionic strength , the decrease in the rate constant , with increase in $K_2S_2O_8$ concentration has been minimised .

This suggest that the effect is largely due to the increase in the ionic strength as well as due to the increase in K^+ ions concenttration ,both causing inhibition. There exist a persistent rate decreasing tendancy even though the reaction is carried out at constant ionic strength as well as constant K^+ ion concentration.

A plot of −log K versus concentration of peroxydisulphate is found to be linear (Fig.B-3). The following relationship between −log k and concentration of peroxydisulphate is followed :

$$-\log k = 2.480 + 6.5\,[S_2O_8^{2-}]_o \quad \text{provided } [S_2O_8^{2-}]_o \neq \text{Zero.}$$

ORDER WITH RESPECT TO PEROXYDISULPHATE

The order with respect to peroxydisulphate was determined by Van't Hoff's[2] differential method. The volume of $Na_2S_2O_3$ (equivalent to $K_2S_2O_8$ was plotted against time for different initial concentration 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 B − 6.

TABLE B - 6

$[K_2S_2O_8]$M.	$-dc/dt \times 10^{-4}$	$Log[S_2O_8^{2-}]$	$Log(-dc/dt)$
0.01	1.880	-2.0000	-3.7447
0.02	3.715	-1.6990	-3.4300
0.03	5.643	-1.5229	-3.2484
0.04	7.591	-1.3979	-3.1197

The values of -dc/dt and concentration of [$S_2O_8^{2-}$ are substituted in the Van't Hoff's equation.

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

and the order of the reaction is calculated thereby.

The values of (-dc/dt) for different initial concentration of $S_2O_8^{2-}$ and the value of n calculated there by are recorded in Table B - 7.

TABLE B - 7

$[K_2S_2O_8]$M	$(-dc/dt) \times 10^{-4}$	Order of Reaction(n)
0.01	1.880	0.9827
0.02	3.715	
0.01	1.880	1.0005
0.03	5.643	
0.01	1.880	1.0066
0.04	7.591	
0.02	3.715	1.0306
0.03	5.643	
0.03	5.643	1.0364
0.04	7.591	

A plot of log (-dc/dt) versus log $S_2O_8^{2-}$ is shown in Fig. B - 4. The slope of the curve is 1.0000 as such the order with respect to $S_2O_8^{2-}$ is one, which is confirmed by the values of n as shown under Table B - 7.

EFFECT OF SUBSTRATE CONCENTRATION

The effect of amide concentration on the rate of reaction was studied by taking different concentrations of amide. The concentrations of $S_2O_8^{2-}$ and $AgNO_3$ are kept unchanged. Table B - 8 indicates the results of these kinetic runs,which have also been represented graphically in Fig.B-5.

TABLE B - 8

$K_2S_2O_8$ = 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	9.45	9.44	9.46	9.45	9.45
20	8.99	8.95	8.97	8.97	8.96
40	8.56	8.50	8.51	8.53	8.50
60	8.15	8.08	8.09	8.11	8.07
80	7.77	7.68	7.68	7.71	7.66
100	7.41	7.31	7.30	7.35	7.28
130	6.90	6.78	6.77	6.82	6.75
160	6.43	6.30	6.28	6.34	6.25
200	5.85	5.71	5.68	5.75	5.65
240	5.34	5.18	5.15	5.22	5.12
300	4.64	4.48	4.44	4.51	4.41
360	4.05	3.87	3.83	3.91	3.80
k_1 x 10^3 min^{-1}	2.415	2.538	2.566	2.505	2.588
k_2x 10^3 min^{-1}	1.215	1.215	1.215	1.215	1.215
k x 10^3 min^{-1}	1.200	1.323	1.351	1.290	1.373

From the results of the above table (Table B - 8), it indicates that when the concentration of amide was increased the rate constant remains constant indicating the zero order behaviour of the reaction.

The specific rate is seen to be a function of $S_2O_8^{2-}$ and $H_2N.OC.CH_2.[CH_2]_5CH_2.CONH_2$ governed by the expression.

$$k = k_{max} \cdot \frac{H_2N.OC.CH_2[CH_2]_5CH_2CONH_2}{b + (H_2N.OC.CH_2[CH_2]_5CH_2CONH_2)}$$

In support of the above equation a graph of [Amide]o/k versus concentration of amide is plotted. (Fig. B - 6) and was fcund to be linear from which k_{max} and b were evaluated as C.0030 and 0.03105 respectively. From these values k is calculated and was found to be equal to $k = 2.485 \times 10^{-3} min^{-1}$ was almost identical with $k = 2.538 \times 10^{-3}$ the experimental value.

ORDER WITH RESPECT TO SUBSTRATE

To ccnfirm the order with respect to substrate the data of Table B - 8 was subjected to Van't Hoff's differential method. From the initial slope of the concentration versus time curves,the value of -dc/dt corresponding to various initial concentration of substrate were evaluated which are given in Table B - 9.

TABLE B - 9

[Amide]M.	(-dc/dt) x 10^{-4}	Log Co	Log(-dc/dt)
0.025	2.719	-1.6020	-3.5655
0.05	2.800	-1.3010	-3.5528
0.075	2.863	-1.1249	-3.5431
0.10	2.748	-1.0000	-3.5609
0.125	2.766	-0.9030	-3.5581

A plot of Log (-dc/dt) versus Log Co is shown in Fig. B - 7, It gives the value of the slope as zero, which 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 method and are given in Table B-10.

TABLE B - 10

[Substrate]M.	$(-dc/dt) \times 10^{-4}$	Order of Reaction (n)
0.025	2.719	0.04232
0.05	2.800	
0.025	2.719	0.04697
0.075	2.863	
0.05	2.719	0.00765
0.10	2.748	
0.025	2.719	0.01064
0.125	2.766	
0.05	2.800	0.05490
0.075	2.863	
0.05	2.800	0.0133
0.125	2.766	

This confirms that the order with respect to substrate is zero.

EFFECT OF SILVER CATALYST CONCENTRATION

The effect of five different concentrations of silver nitrate on the reaction rate was studied at 35°C. The kinetic data of these runs are recorded in Table B - 11 and shown graphically in Fig. B - 8.

TABLE B - 11

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

$[AgNO_3]$ x 10^{-3}M.	1.0	1.5	2.0	3.0	4.0
Time (min)	Vol. (in ml) of 0.02 M - $Na_2S_2O_3$ used (viz. C).				
0	9.44	9.45	9.48	9.46	9.44
20	8.95	8.93	8.92	8.82	8.73
40	8.50	8.44	8.41	8.24	8.09
60	8.08	7.99	7.93	7.70	7.50
80	7.68	7.56	7.48	7.20	6.95
100	7.31	7.16	7.05	6.73	6.45
130	6.78	6.61	6.46	6.09	5.76
160	6.30	6.10	5.93	5.51	5.15
200	5.71	5.48	5.28	4.82	4.44
240	5.18	4.93	4.72	4.23	3.83
300	4.48	4.21	3.98	3.47	3.07
360	3.87	3.59	3.36	2.85	2.46
k_1 x 10^3min^{-1}	2.583	2.747	2.938	3.386	3.792
k_2 x 10^3min^{-1}	1.215	1.305	1.378	1.514	1.682
k x 10^3min^{-1}	1.323	1.442	1.560	1.872	2.110

The data(Table B-11) indicates that the specific rate increases with increasing concentration of silver nitrate. The plot of k versus$[Ag^+]$ concentration is found to linear as shown in fig. B-9 and the following relationship is obeyed.

$$k = 2.1 \times 10^{-3} + 0.4861\ [Ag^+].$$

EFFECT OF TEMPERATURE

The reaction was studied at five different tempratures ranging from 25°C to 45°C. The concentrations of all the reactants were kept constant. These kinetic runs are recorded in table B-12 and shown graphically in fig. B -10.

TABLE B - 12

$K_2S_2O_8$=2.0 x10^{-2}M, Substrate = 5.0x10^{-2}M, $AgNO_3$=1.0 x10^{-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	9.44	9.42	9.44
20	9.19	9.10	8.95	8.74	8.52
40	8.94	8.76	8.50	8.11	7.70
60	8.71	8.44	8.08	7.53	6.96
80	8.48	8.14	7.68	7.00	6.30
100	8.26	7.85	7.31	6.51	5.70
130	7.95	7.44	6.78	5.84	4.91
160	7.65	7.05	6.30	5.23	4.23
200	7.28	6.56	5.71	4.54	3.47
240	6.93	6.13	5.18	3.93	2.85
300	6.44	5.52	4.48	3.17	2.12
360	5.99	4.98	3.87	2.57	1.58
k_1 x10^3 min^{-1}	1.331	1.846	2.538	3.674	5.019
k_2 x10^3 min^{-1}	0.670	0.820	1.215	1.618	2.505
k x10^3	0.661	1.026	1.323	2.056	2.514

The calculated values of (1/T)x10^3 and log[kr/(kT/h)] are recorded in Table B-13.

TABLE B -13

Temp. A°	(1/T)x10^3	krx10^3 min^{-1}	log kr	Log[kr/(kT/h)]
298	3.356	0.661	-4.8202	-15.9727
303	3.301	1.026	-3.0111	-15.7890
308	3.246	1.323	-3.1216	-15.6857
313	3.196	2.056	-3.3131	-15.5011
318	3.145	2.514	-3.4004	-15.4207

A plot of log kr versus $(1/T) \times 10^3$ is found to be linear (Fig. B-11) showing that the reaction obeys Arrhenius relationship.

The energy of activation from the slope of the curve is 12.666 K.cals.mole^{-1} which is in good agreement with the calculated value 12.743 K.cals.mole^{-1}. Similarly, from the slope of curve obtained by plotting $\log\{kr/(kT/h)\}$ versus $(1/T) \times 10^3$ (Fig. B-12) The value of the enthalpy change for the formation of an activated complex ($\Delta H^{\neq}$) is calculated. The values of E and $\Delta H^{\neq}$ along with other thermodynamic parameters are recorded in Table B - 14.

TABLE B - 14

Temp. A^{o}	$k_r \times 10^{3}$ min^{-1}	Temp. coeff.	E K.cal. $mole^{-1}$	$A \times 10^{4}$ litre $mole^{-1} sec^{-1}$	$\Delta G^{\neq}$ K.cal. $mole^{-1}$	$\Delta S^{\neq}$ e. u.	$\Delta H^{\neq}$ K.cal $mole^{-1}$
298	0.661	-	-	2.487	21.973	-32.78	
303	1.026	2.0015	12.650	2.0109	22.033	-32.654	
308	1.323	2.0038	13.090	1.602	22.249	-32!862	
313	2.056	1.9002	12.743	1.525	22.345	-32.672	11.842
318	2.514	-	-	1.3203	22.582	-32.942	(Graphically)
Mean	-	1.9685	12.743	1.7890	22.2364	-32.782	

A large negative value of entropy of activation is indicative 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.

$k = 1.7890 \cdot e^{-12.743/RT} \quad sec^{-1}$

EFFECT OF IONIC STRENGTH :

The effect of varying ionic strength on the reaction rate was studied by adding different amounts of K_2SO_4 to the reaction mixture. The results of these kinetic runs are recorded in Table B – 15 and shown graphically in Fig. B-13.

TABLE B - 15

$K_2S_2O_8$ =2.0 x10^{-2}M, substrate=5.0 x10^{-2}M, $AgNO_3$ =1.0 x10^{-3}M, Temp = 35°C.

K_2SO_4M	NIL	0.01	0.015	0.02	0.03	0.04
u	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	9.44	9.45	9.48	9.45	9.48	9.45
20	8.95	9.02	9.11	9.10	9.16	9.12
40	8.50	8.62	8.76	8.77	8.86	8.80
60	8.08	8.25	8.43	8.46	8.57	8.51
80	7.68	7.89	8.11	8.16	8.29	8.22
100	7.31	7.55	7.81	7.88	8.03	7.95
130	6.78	7.08	7.39	7.48	7.65	7.56
160	6.30	6.63	6.99	7.10	7.30	7.20
200	5.71	6.08	6.49	6.63	6.86	6.74
240	5.18	5.58	6.03	6.19	6.44	6.32
300	4.48	4.91	5.41	5.59	5.88	5.74
360	3.87	4.33	4.86	5.06	5.36	5.22
k_1x10^3 min^{-1}	2.538	2.225	1.915	1.794	1.640	1.708
k_2x10^3 min^{-1}	1.215	1.120	0.980	0.930	0.800	0.780
k x10^3 min^{-1}	1.323	1.105	0.935	0.864	0.840	0.928

From the results given in Table B - 15 it indicates that the salt effect is negative.

On plotting log k against $u^{1/2}$ as well as k against u as shown in Fig. 14 (A) and 14(B) respectively, it is found that log k versus $u^{1/2}$ curve is linear in the region of low ionic strength (< 0.2), while there exists no linearity in the plot k versus u . This suggests that the salt effect is at primary exponential type in the region of low ionic strength indicating that the rate determining process involves a reaction between two oppositely charged ions.

TABLE B - 16

$[K_2SO_4]$M	μ	$k \times 10^3 min^{-1}$	$\sqrt{\mu}$	Log k
Nil	0.061	1.323	0.247	-2.8784
0.01	0.091	1.105	0.302	-2.9566
0.015	0.106	0.935	0.326	-3.0292
0.02	0.121	0.864	0.348	-3.0635
0.03	0.151	0.840	0.389	-3.0757
0.04	0.181	0.928	0.425	-3.0325

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

SPECIFIC IONIC EFFECT

The following table (Table B-17) includes the result of the kinetic runs investigating the effect of vrious cations on the rate of this reaction. These data have also been shown graphically in Fig. B-15. This study has been carried out at constant ionic strength.

TABLE B - 17

$K_2S_2O_8 = 2.0 \times 10^{-2}$ M, Substrate = 5.0×10^{-2}M,
$AgNO_3 = 1.0 \times 10^{-3}$M, Temp. = 35°C, u = 0.212

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	9.44	9.48	9.46	9.45	9.48	9.45
20	8.95	9.20	9.11	9.07	9.07	9.01
40	8.50	8.94	8.79	8.71	8.69	8.61
60	8.08	8.69	8.48	8.37	8.32	8.22
80	7.68	8.45	8.18	8.04	7.98	7.86
100	7.31	8.22	7.90	7.73	7.65	7.52
130	6.78	7.89	7.50	7.30	7.19	7.03
160	6.30	7.58	7.13	6.88	6.76	6.58
200	5.71	7.19	6.66	6.38	6.23	6.02
240	5.18	6.82	6.23	5.91	5.74	5.52
300	4.48	6.30	5.64	5.28	5.09	4.84
360	3.87	5.83	5.10	4.72	4.51	4.26
$k_1 \times 10^3$ min^{-1}	2.538	1.405	1.776	1.987	2.122	2.270
$k_2 \times 10^3$ min^{-1}	1.215	0.770	0.943	0.860	0.880	0.980
$k \times 10^3$ min^{-1}	1.323	0.635	0.733	1.127	1.242	1.290

It is seen that the specific inhibitory effect of the various ions is in the order.

$K^+ > Na^+ > Li^+ > Mg^{2+} > Zn^{2+}$

EFFECT OF HYDROGEN ION CONCENTRATION

The solution of substrate was prepared in 10% acetic acid, and hence it is not possible to study the effect of acid, such as sulphuric acid on the reaction rate.

EFFECT OF ALLYL ACETATE

The reaction was carried out in the absence of and at three different initial conentrations of allyl acetate. The results of these kinetic runs are summarised in Table B-18 and shown graphically in Fig. B-16.

TABLE B - 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.

Allyl Acetate	Nil	0.001	0.005	0.01
Time (min)	Vol. (in ml.) of 0.02M - $Na_2S_2O_3$ used(viz. C)			
0	9.44	9.45	9.48	9.46
20	8.95	9.00	9.08	9.10
40	8.50	8.58	8.71	8.76
60	8.08	8.19	8.36	8.45
80	7.68	7.82	8.02	8.14
100	7.31	7.46	7.70	7.85
130	6.78	6.96	7.52	7.44
160	6.30	6.50	6.82	7.05
200	5.71	5.93	6.30	6.57
240	5.18	5.42	5.81	6.12
300	4.48	4.74	5.17	5.51
360	3.87	4.14	4.59	4.96
$k \times 10^3 min^{-1}$	2.538	2.345	2.062	1.843

From the data contained in Table B-18, indicates that allyl acetate inhibits the rate of reaction. So the reaction involving $S_2O_8^{2-}$ are greatly inhibited by allyl acetate which acts as a sulphate radical trapping reagent. The radical trapping may be due to the polymerisation of allyl acetate by sulphate ions formed from the catalysed decomposition of peroxydisulphate ion .

MOLE RATIO

For determining mole ratio between $K_2S_2O_8$ and amide, two kinetic runs were carried out simultaneously, one in the presence of amide and the other in the absence of amide. In both the kinetic runs the concentration of $K_2S_2O_8$ was the same and was five times than the concentration of amide. The concentration of the catalyst was the same in both the runs. At suitable intervals of time 5 ml. of the reaction mixture was pipetted out and estimated for unreacted $S_2O_8^{2-}$. These results are recorded in Table B - 19 and shown graphically in Fig. B - 17.

TABLE B - 19

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

Substrate	0.01	Nil
Time (min)	Vol.(in ml) of 0.02 M -$Na_2S_2O_3$ used (vizC)	
0	24.34	24.95
30	21.07	23.38
60	21.21	23.33
90	19.78	21.41
120	18.50	20.82
150	17.41	20.37
180	16.28	19.46
210	15.03	19.01
240	13.76	18.16
270	13.08	17.33
300	12.17	16.92
330	11.61	15.84
360	10.86	15.81
390	10.78	15.02
420	10.48	14.42
450	9.94	13.96
480	9.52	13.47

The curve (Fig. B-17) consists of two portions, the first for the oxidation of amide and second for self decomposition of peroxydisulphate ion.

Now tangents are drawn at portion 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 amide is calculated. The point Q on the curve at the same time gives the value corresponding to self decomposition of $K_2S_2O_8$.

From the graph (Fig. B - 17) it indicates that the two plots become parallel at P. At this point log C = 1.1 which corresponds to 12.58 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 = 1.23 which corresponds to 16.98 ml.

The difference between the two values is 4.4 ccs.

Therefore, 4.4 ccs of

0.02 N $Na_2S_2O_3$ = 4.4 ccs of 0.02 N $K_2S_2O_8$

= 4.4 ccs of 0.01N $K_2S_2O_8$

Hence 10 ml of 0.01 M amide = 4.4 ml. of 0.01 $K_2S_2O_8$ Thus one mole of amide consumes one mole of peroxydisulphate for completion of the reaction.

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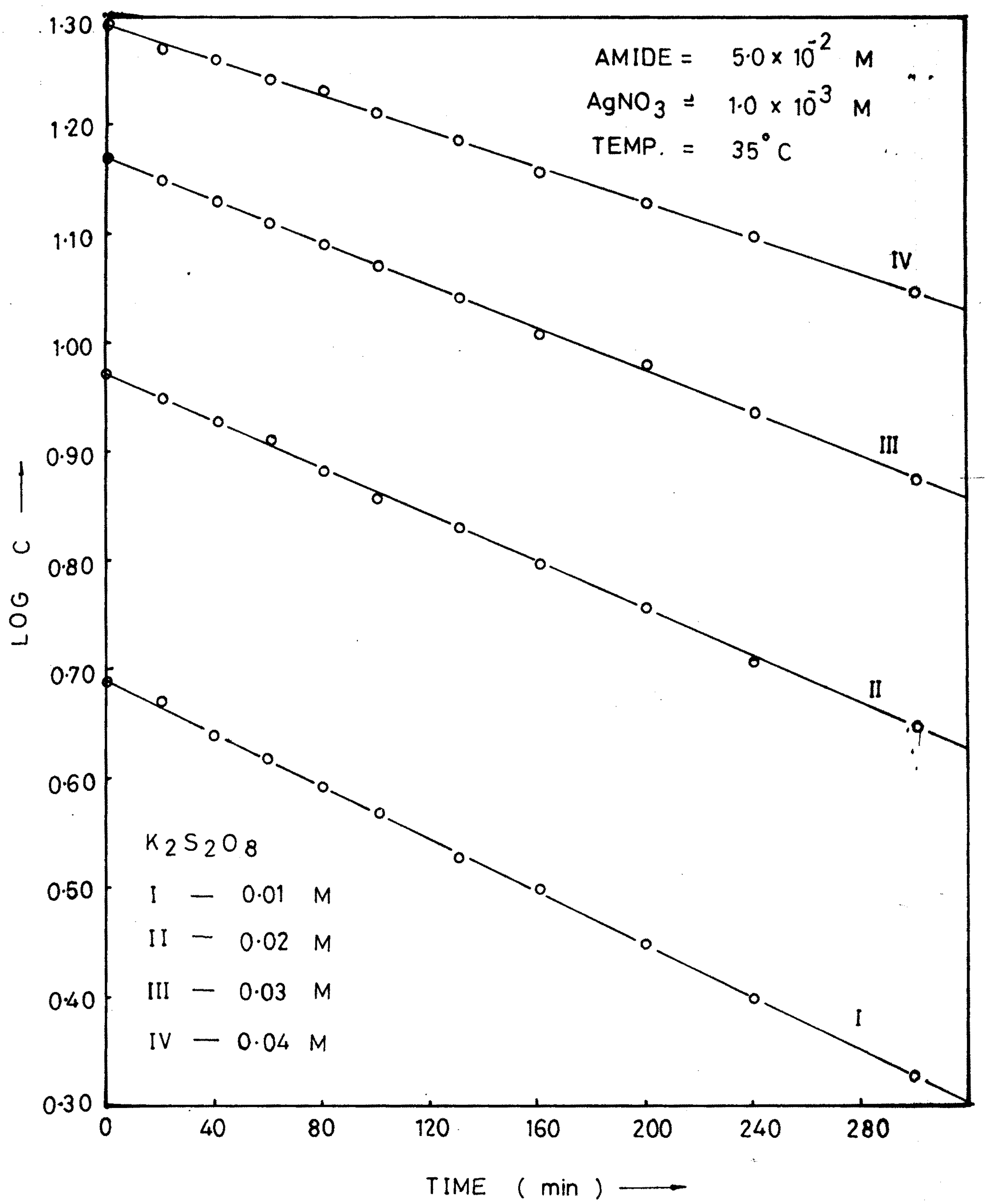


FIG. B-1 EFFECT OF $K_2S_2O_8$

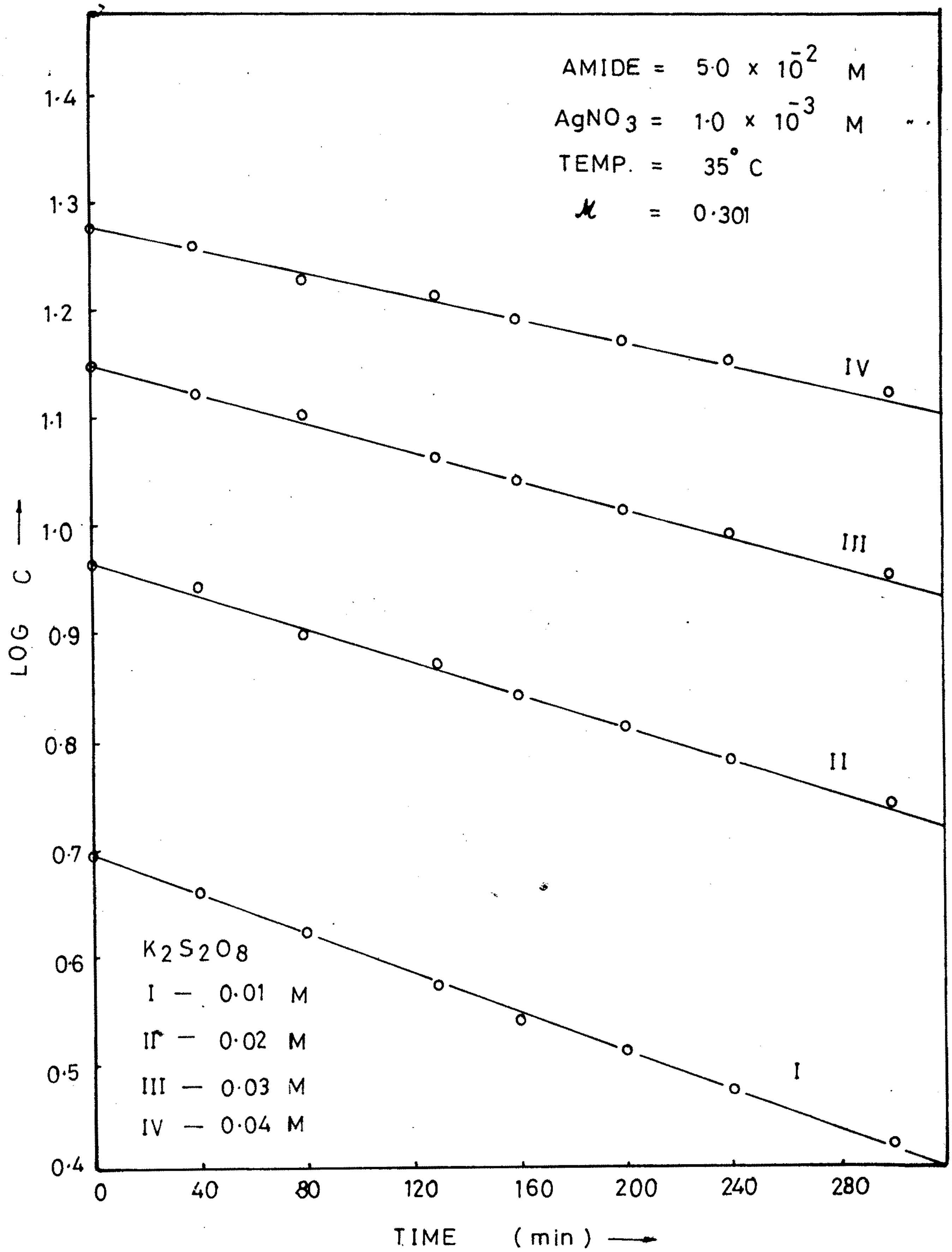


FIG- B-2 EFFECT OF $K_2S_2O_8$ AT CONSTANT μ

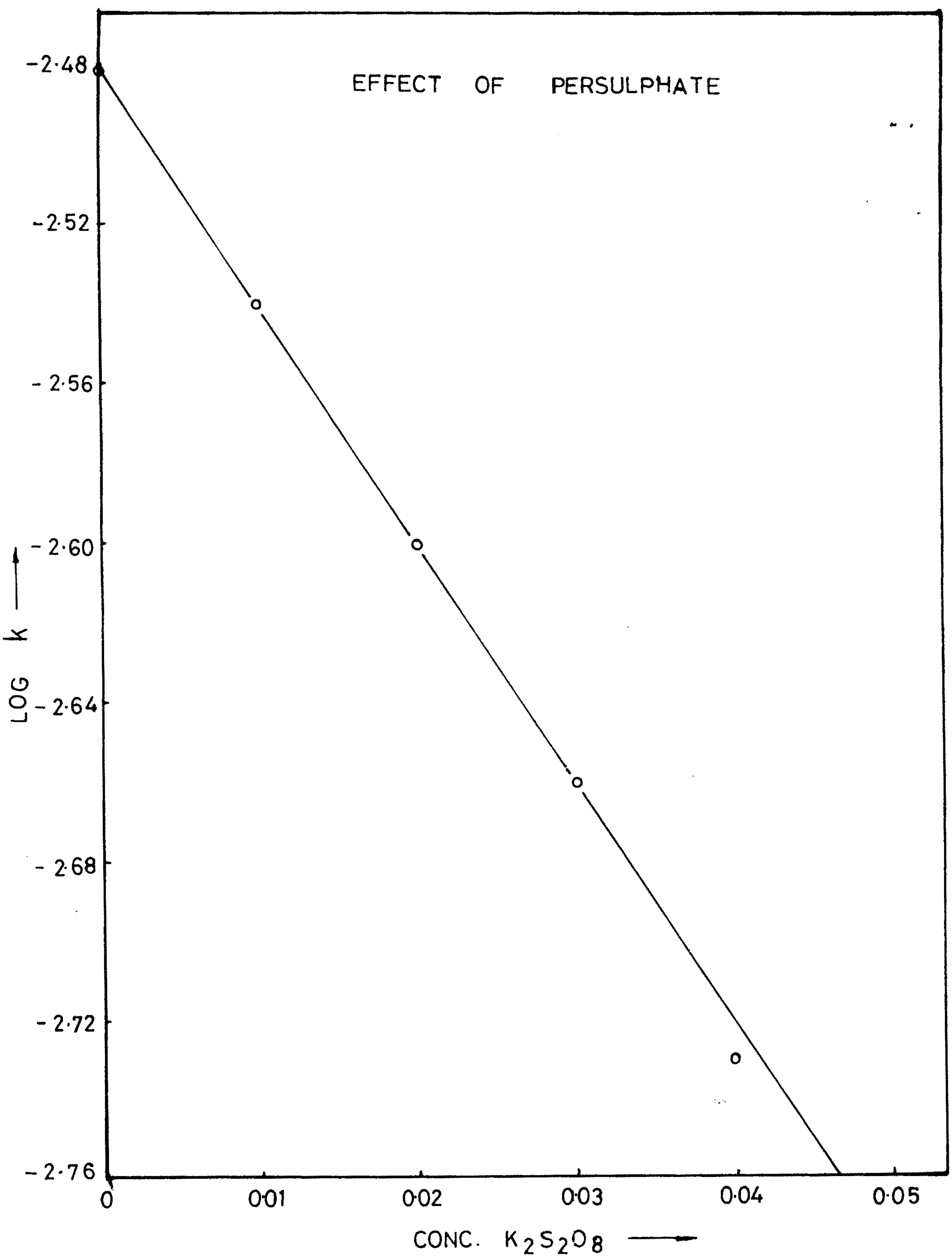


FIG. B-3 PLOT OF LOG k VS CONC. OF $K_2S_2O_8$

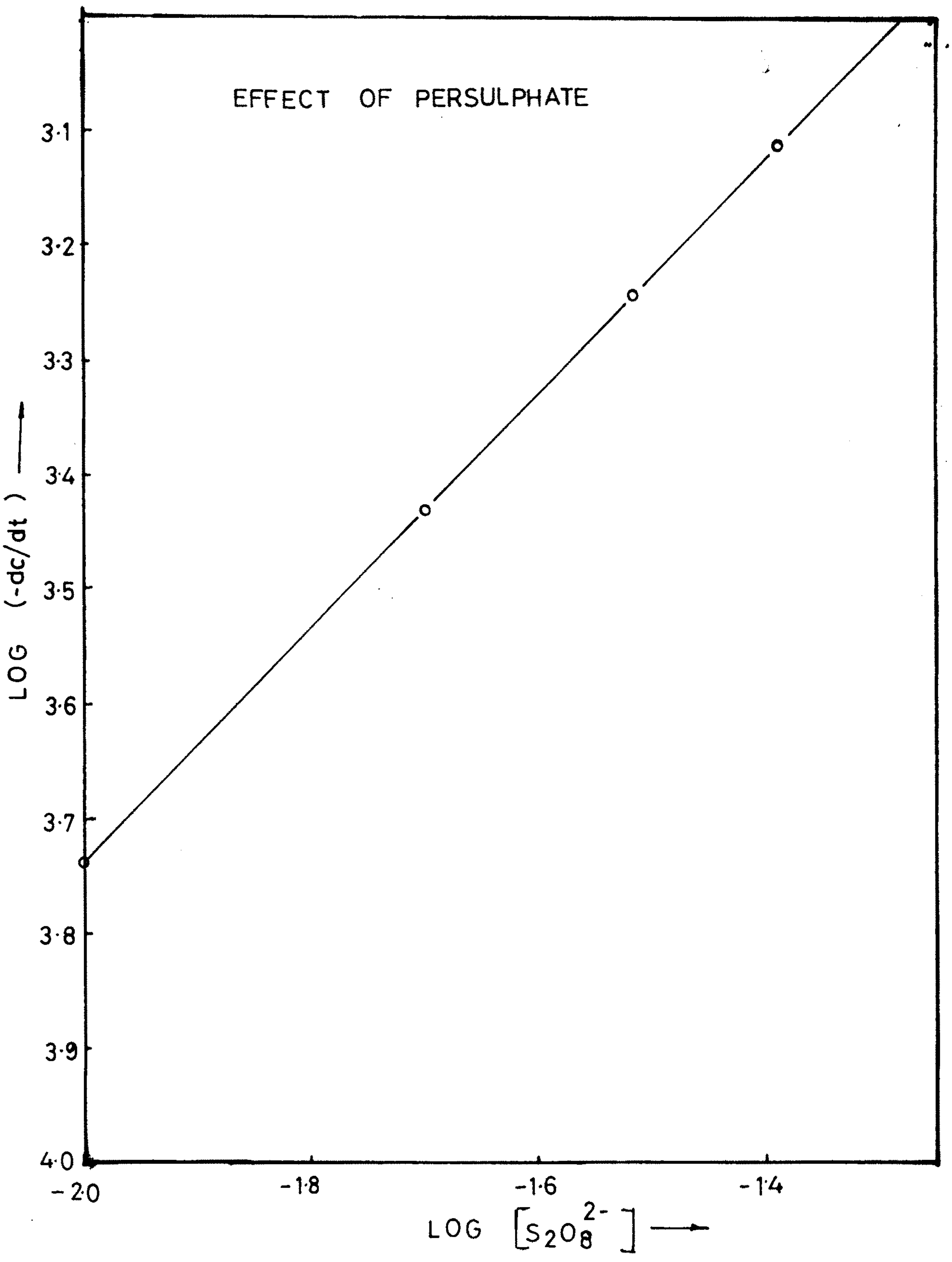


FIG. B-4 PLOT OF LOG [-dc/dt] VS LOG $[S_2O_8^{2-}]$

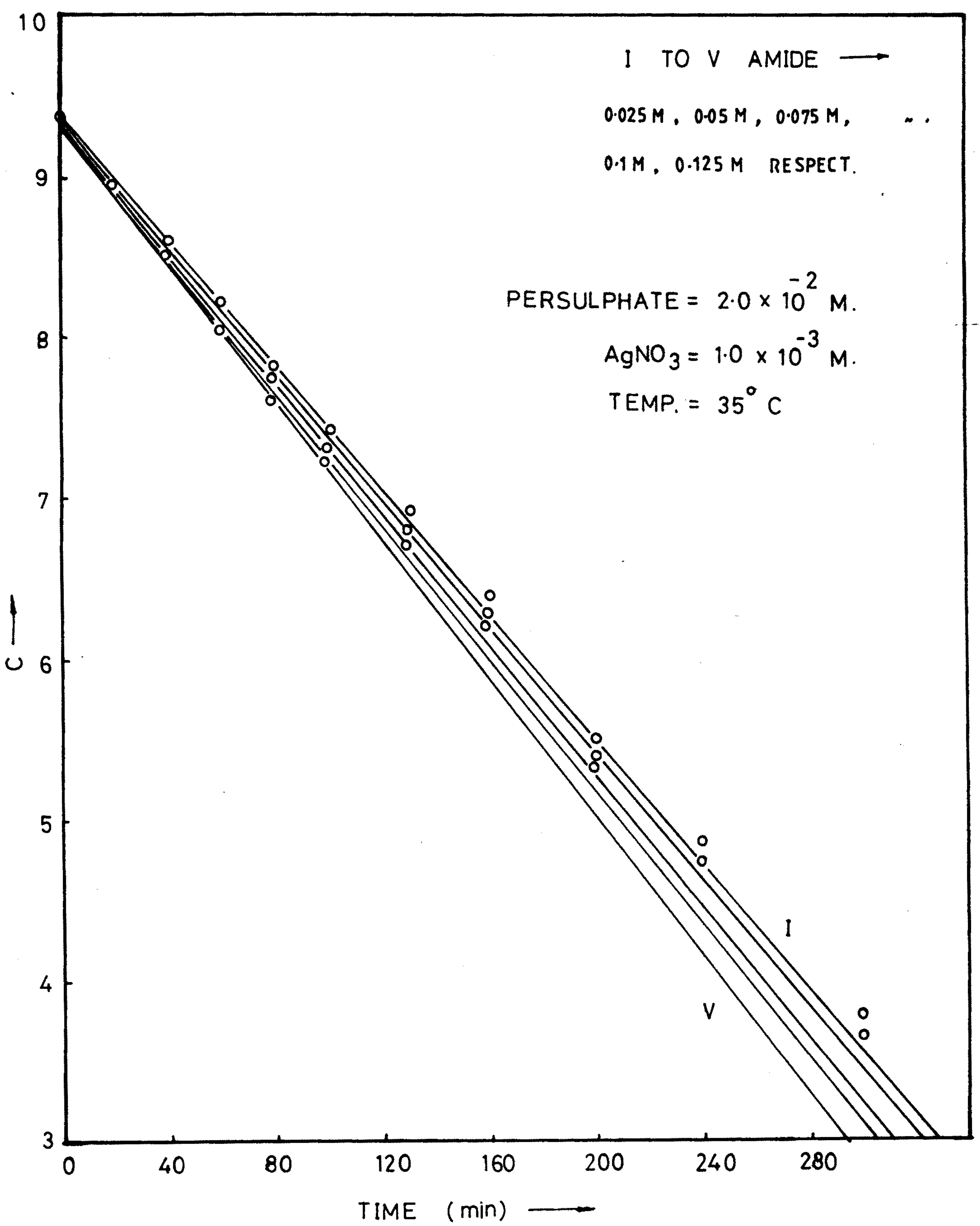


FIG. B-5 EFFECT OF AMIDE ('C' VS TIME)

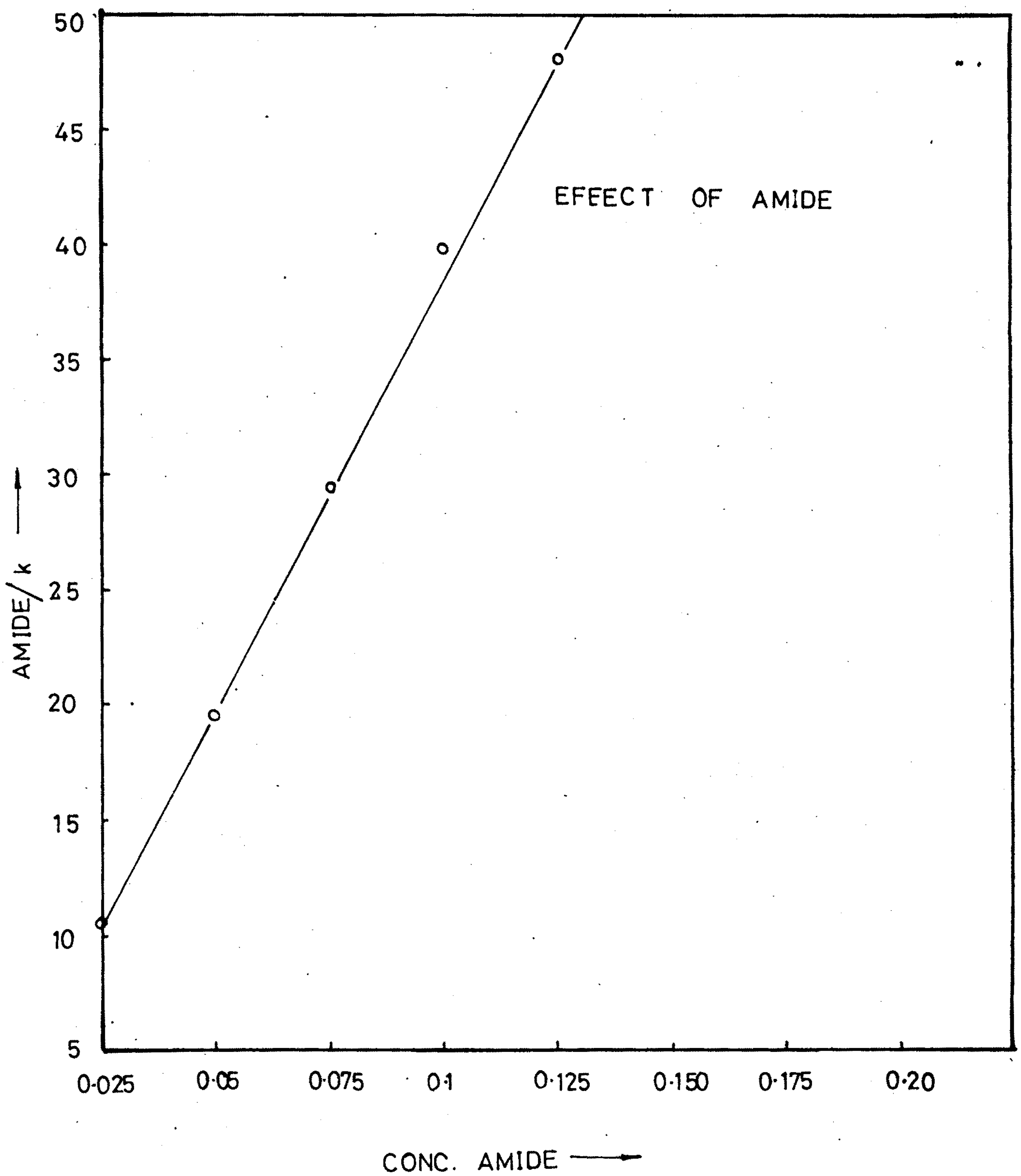


FIG. B-6 PLOT OF AMIDE/k VS k

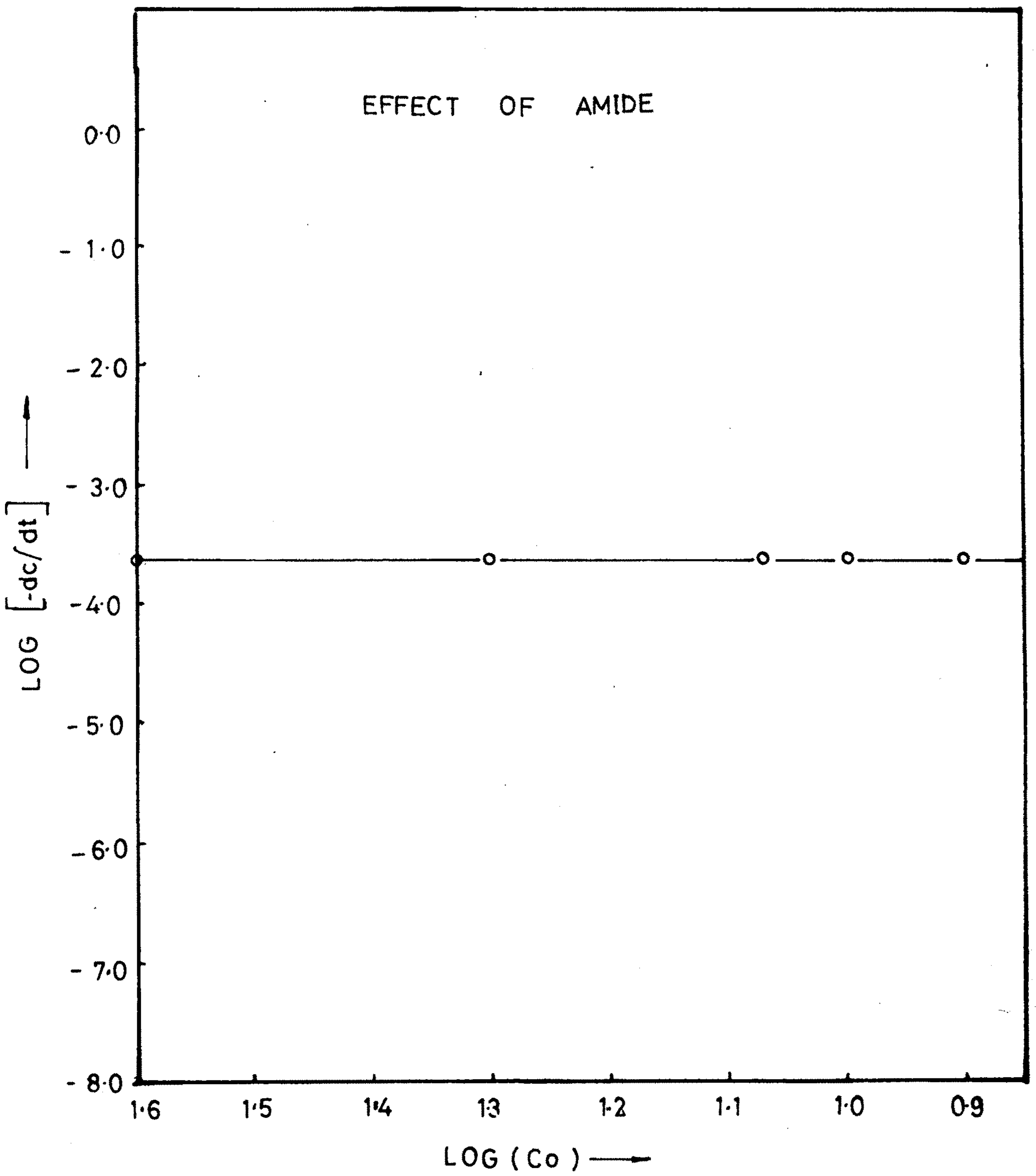


FIG. B-7 PLOT OF LOG [-dc/dt] VS LOG [Co]

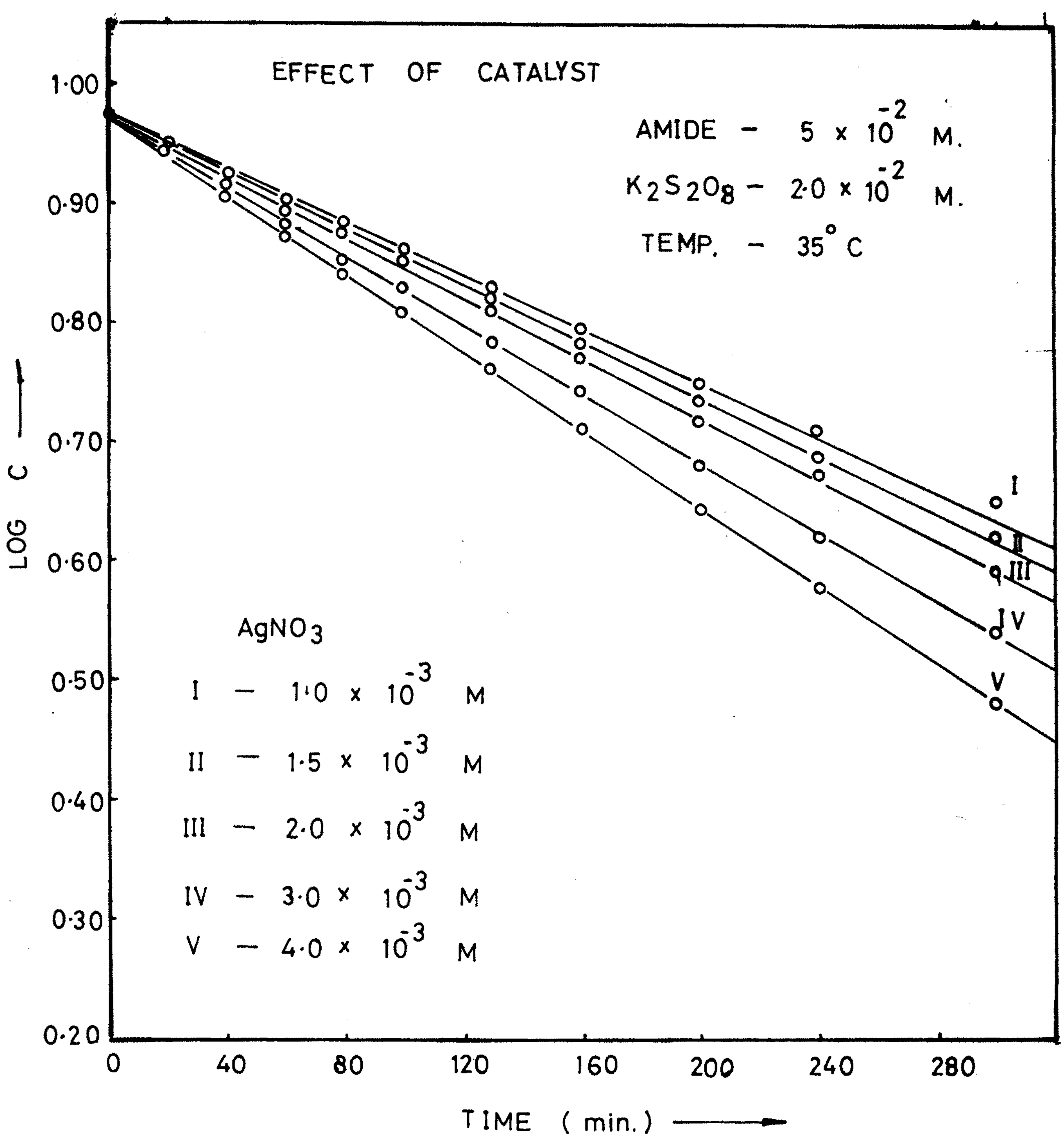


FIG. B - 8 PLOT OF LOG C VS TIME

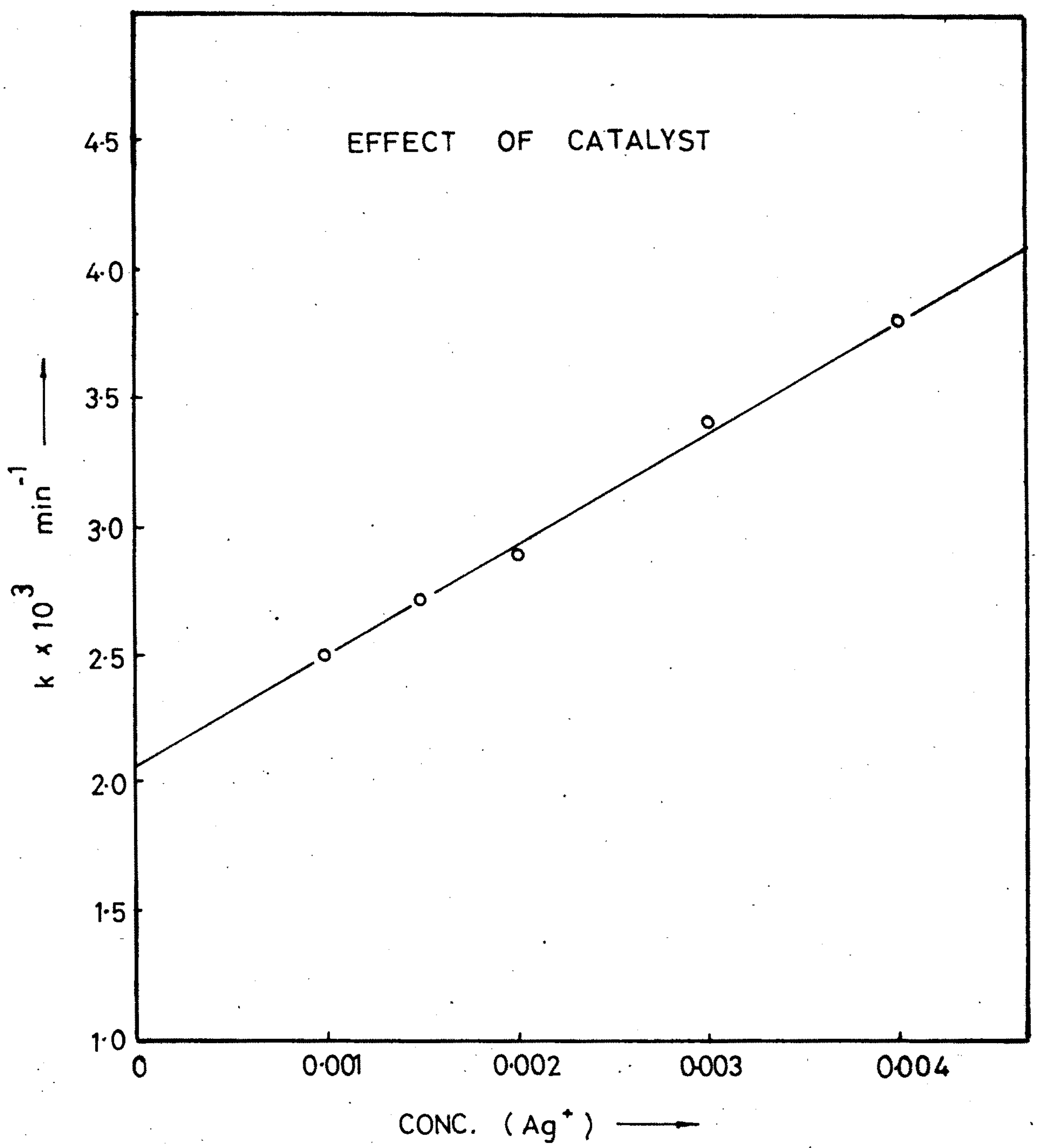


FIG. B-9 PLOT OF $k \times 10^{3}$ VS CONC.(Ag^{+})

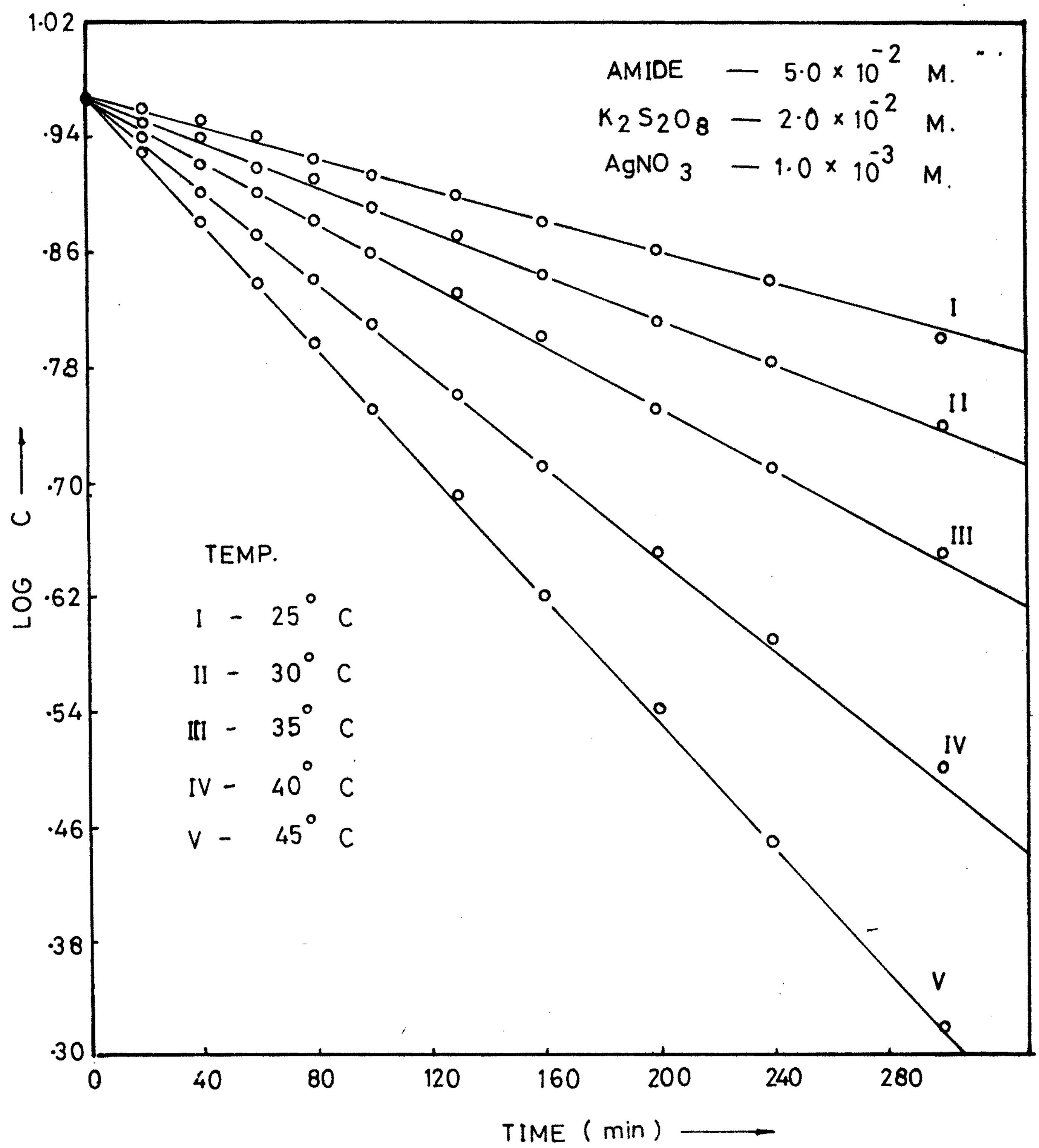


FIG. B - 10 EFFECT OF TEMPERATURE

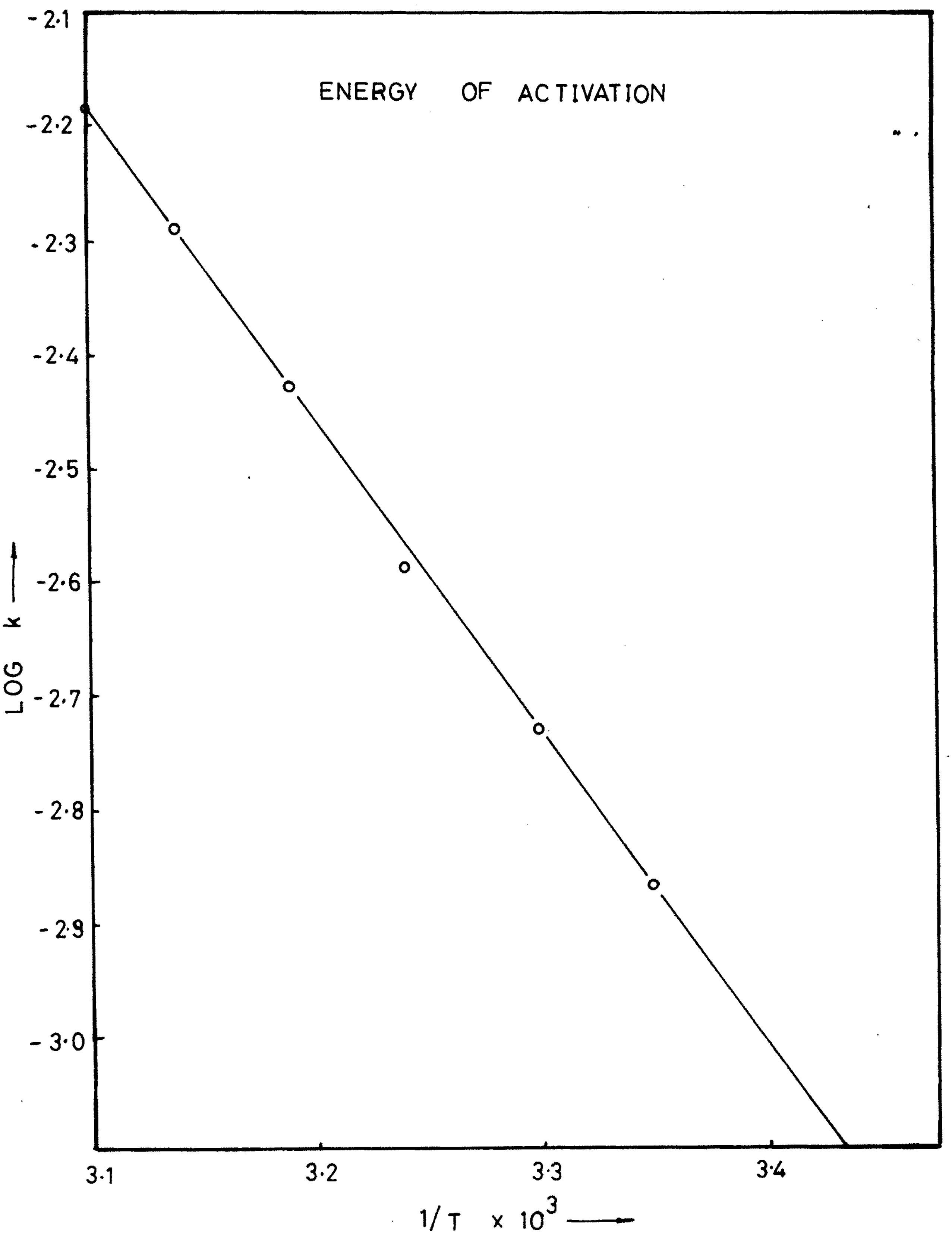


FIG. B-11 PLOT OF LOG k VS $1/T \times 10^3$

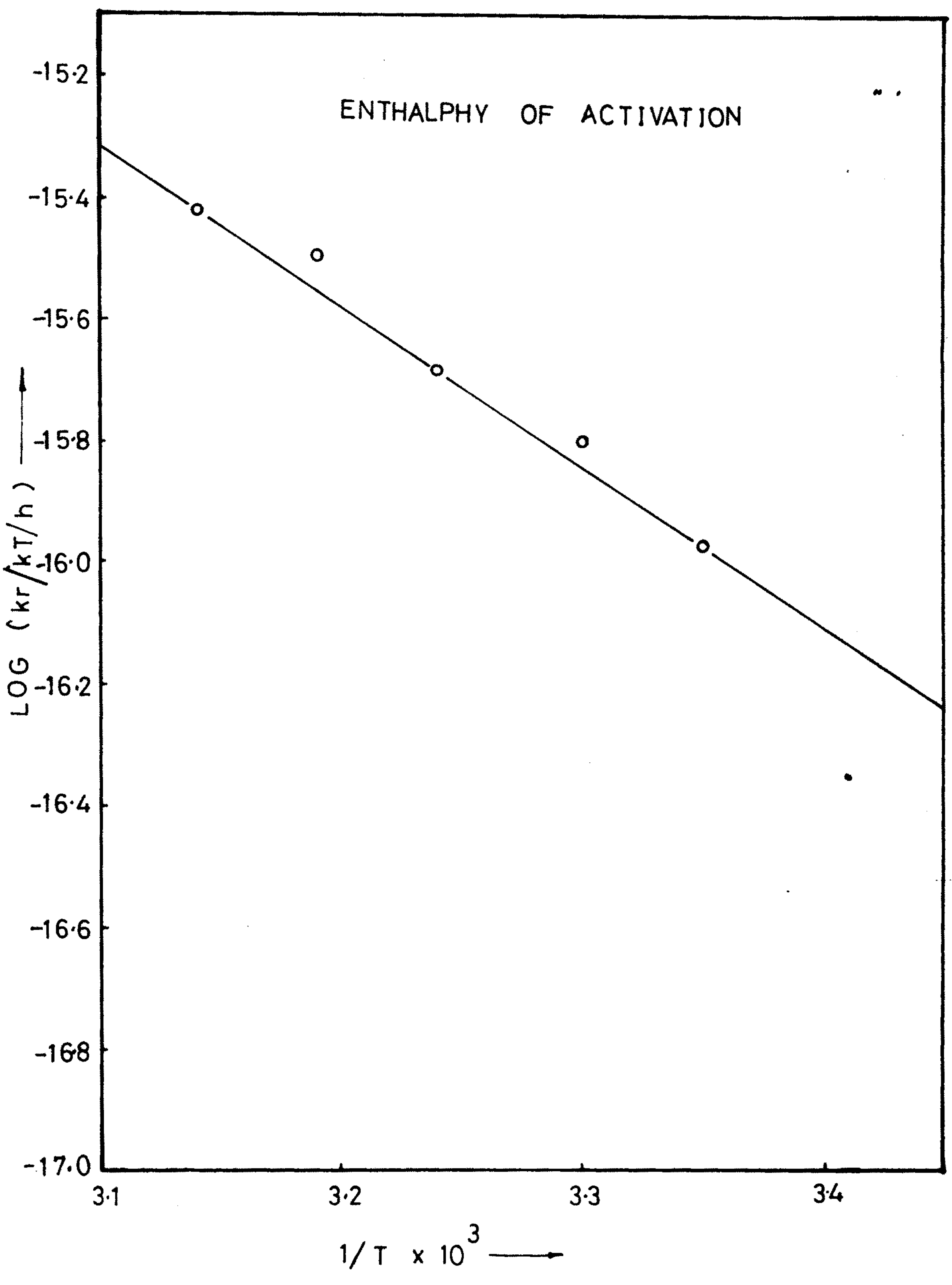
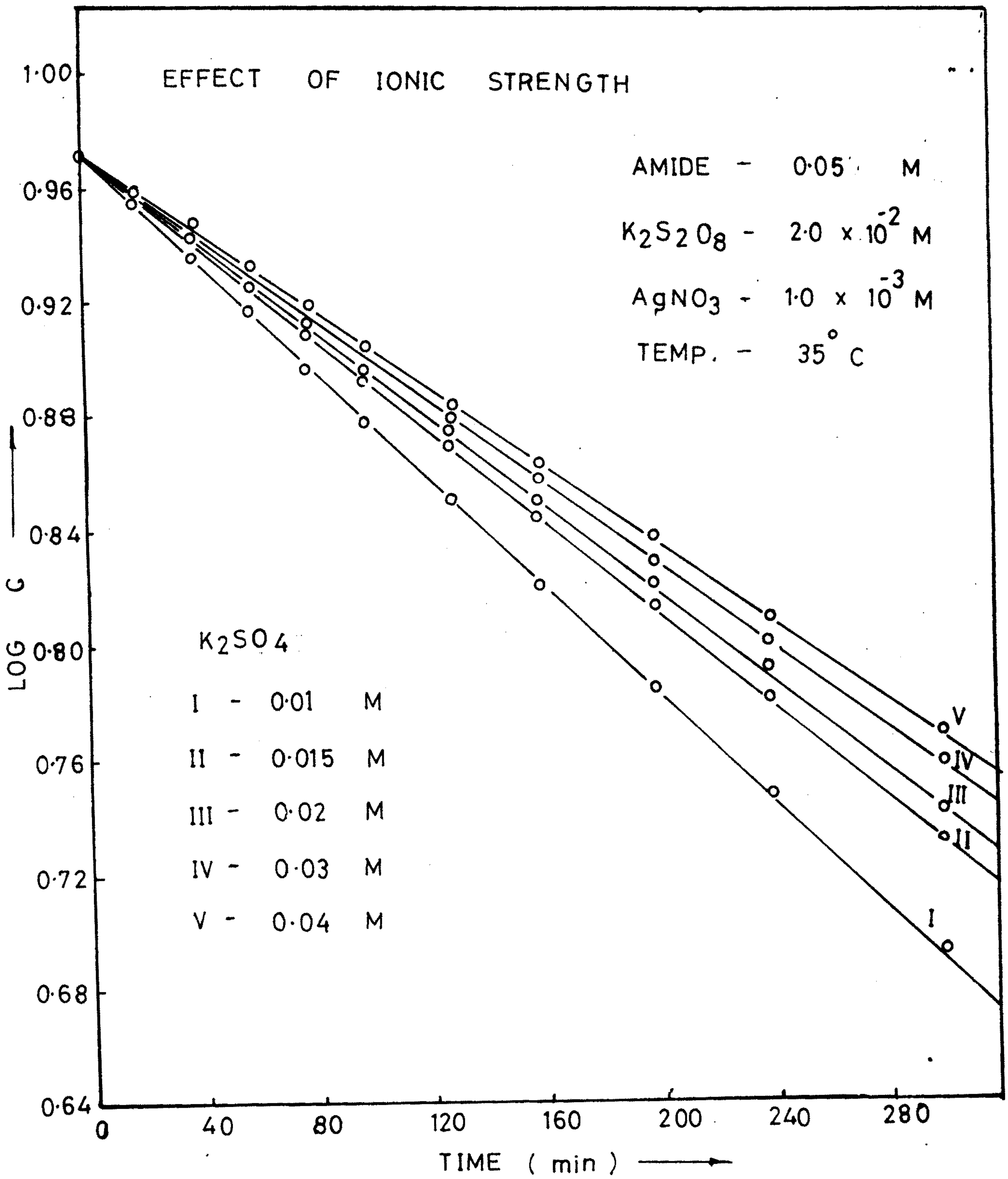


FIG. B—12 PLOT OF LOG (kr/kT/h) VS $1/T \times 10^3$



EFFECT OF IONIC STRENGTH
AMIDE - 0·05 M
$K_2S_2O_8$ - 2·0 x 10^{-2} M
$AgNO_3$ - 1·0 x 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
LOG C
TIME (min)
1·00
0·96
0·92
0·88
0·84
0·80
0·76
0·72
0·68
0·64
0
40
80
120
160
200
240
280
I
II
III
IV
V

FIG. B-13

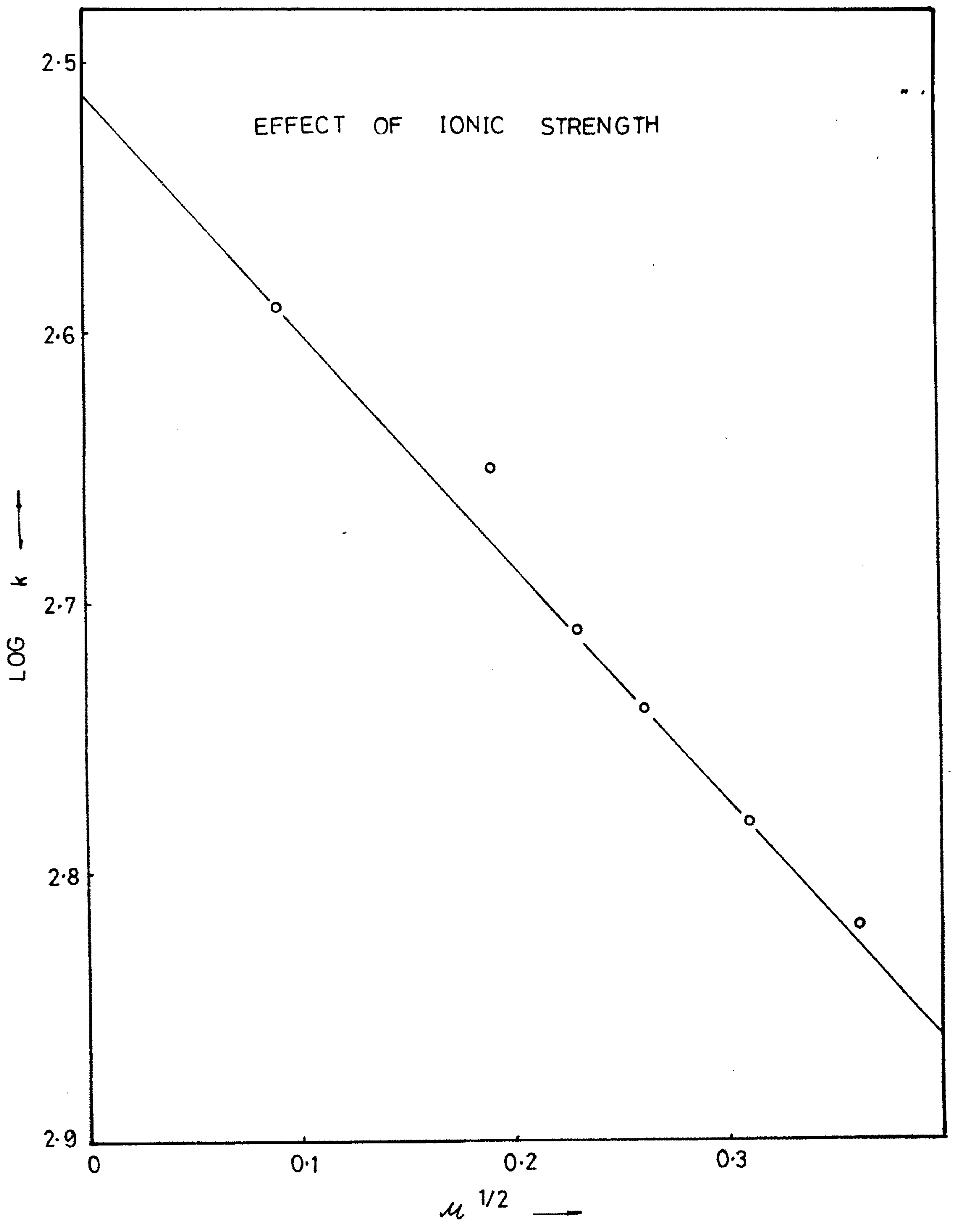


FIG. B-14 (a) PLOT OF LOG k VS $\mu^{1/2}$

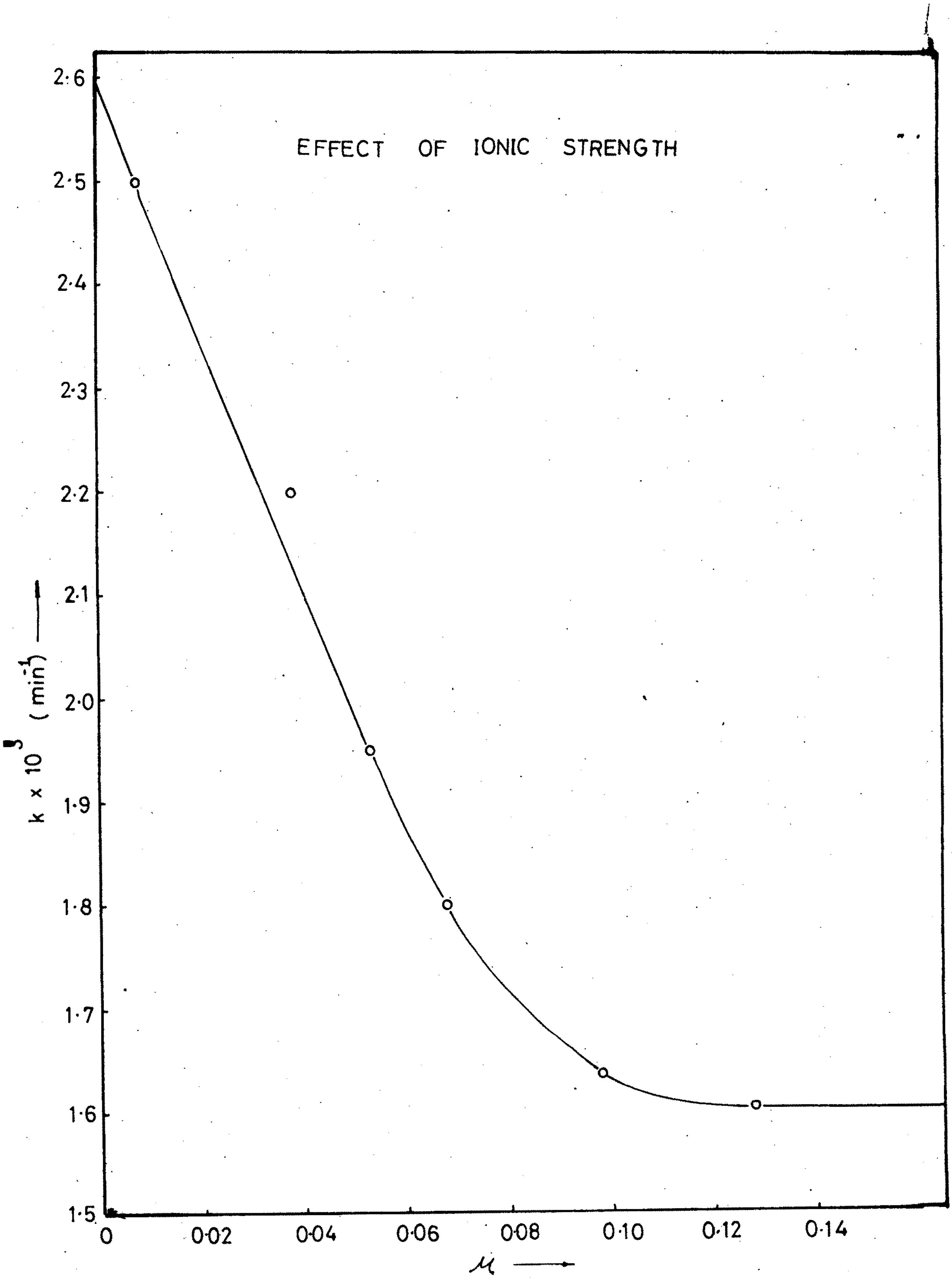


FIG. B-14 (b) PLOT OF k VS μ

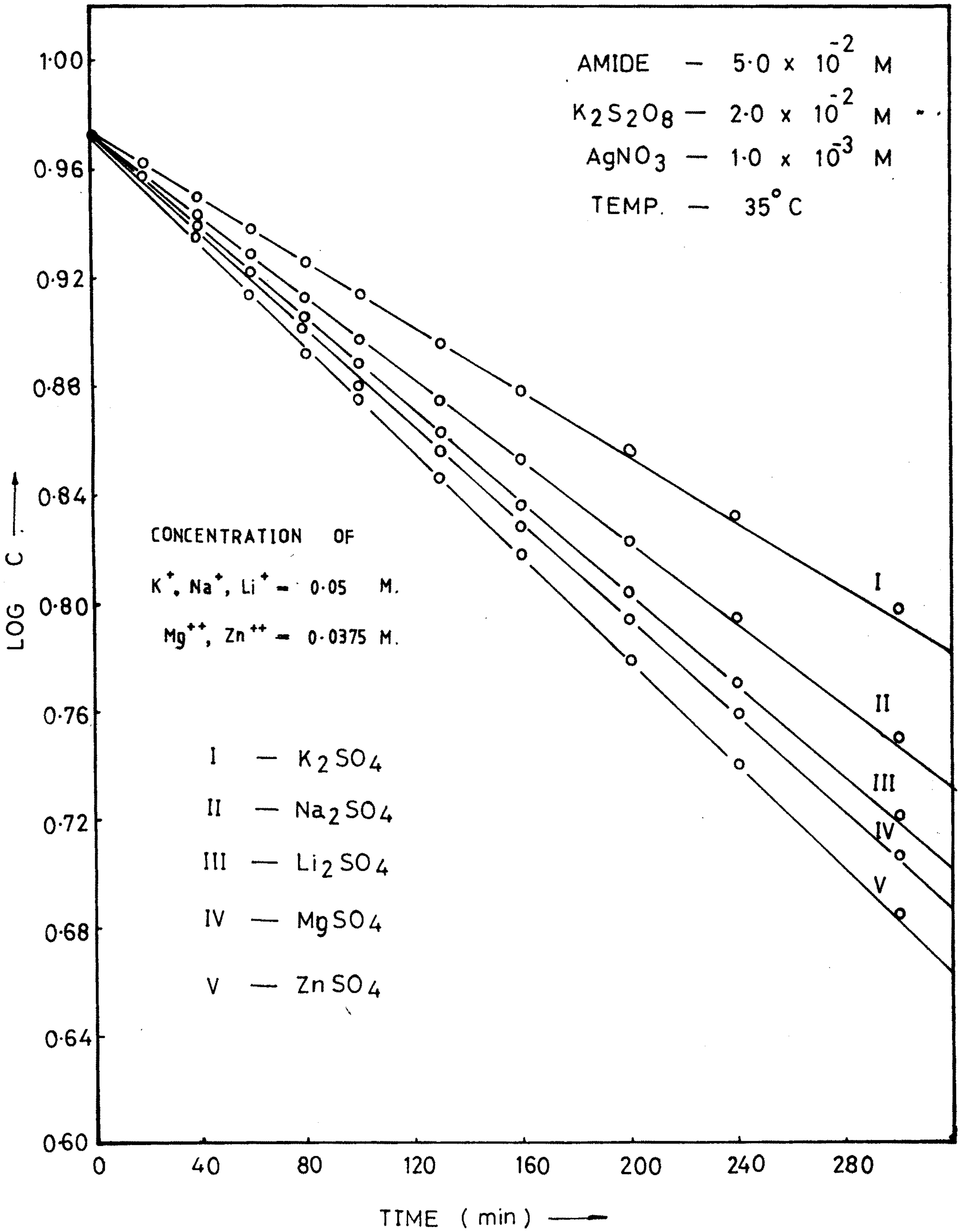

AMIDE — 5·0 x 10^-2 M
K2S2O8 — 2·0 x 10^-2 M
AgNO3 — 1·0 x 10^-3 M
TEMP. — 35° C
CONCENTRATION OF
K+, Na+, Li+ = 0·05 M.
Mg++, Zn++ = 0·0375 M.
I — K2SO4
II — Na2SO4
III — Li2SO4
IV — MgSO4
V — ZnSO4
I
II
III
IV
V
LOG C
1·00
0·96
0·92
0·88
0·84
0·80
0·76
0·72
0·68
0·64
0·60
0
40
80
120
160
200
240
280
TIME (min)

FIG. B –15

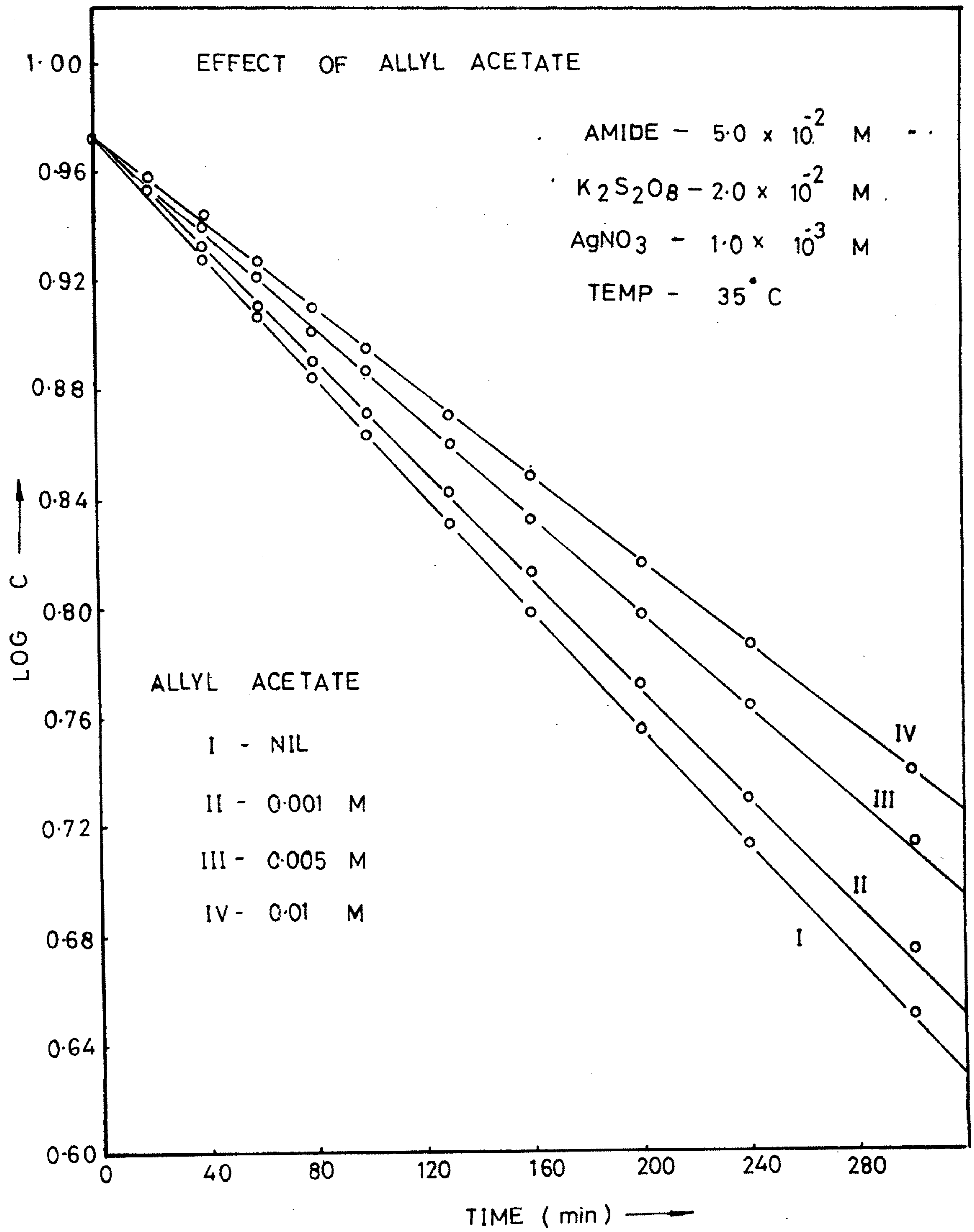

EFFECT OF ALLYL ACETATE
AMIDE – 5·0 x 10⁻² M
K2S2O8 – 2·0 x 10⁻² M
AgNO3 – 1·0 x 10⁻³ M
TEMP – 35° C
ALLYL ACETATE
I - NIL
II - 0·001 M
III - 0·005 M
IV - 0·01 M
LOG C
TIME (min)
1·00
0·96
0·92
0·88
0·84
0·80
0·76
0·72
0·68
0·64
0·60
0
40
80
120
160
200
240
280
I
II
III
IV

FIG. B - 16

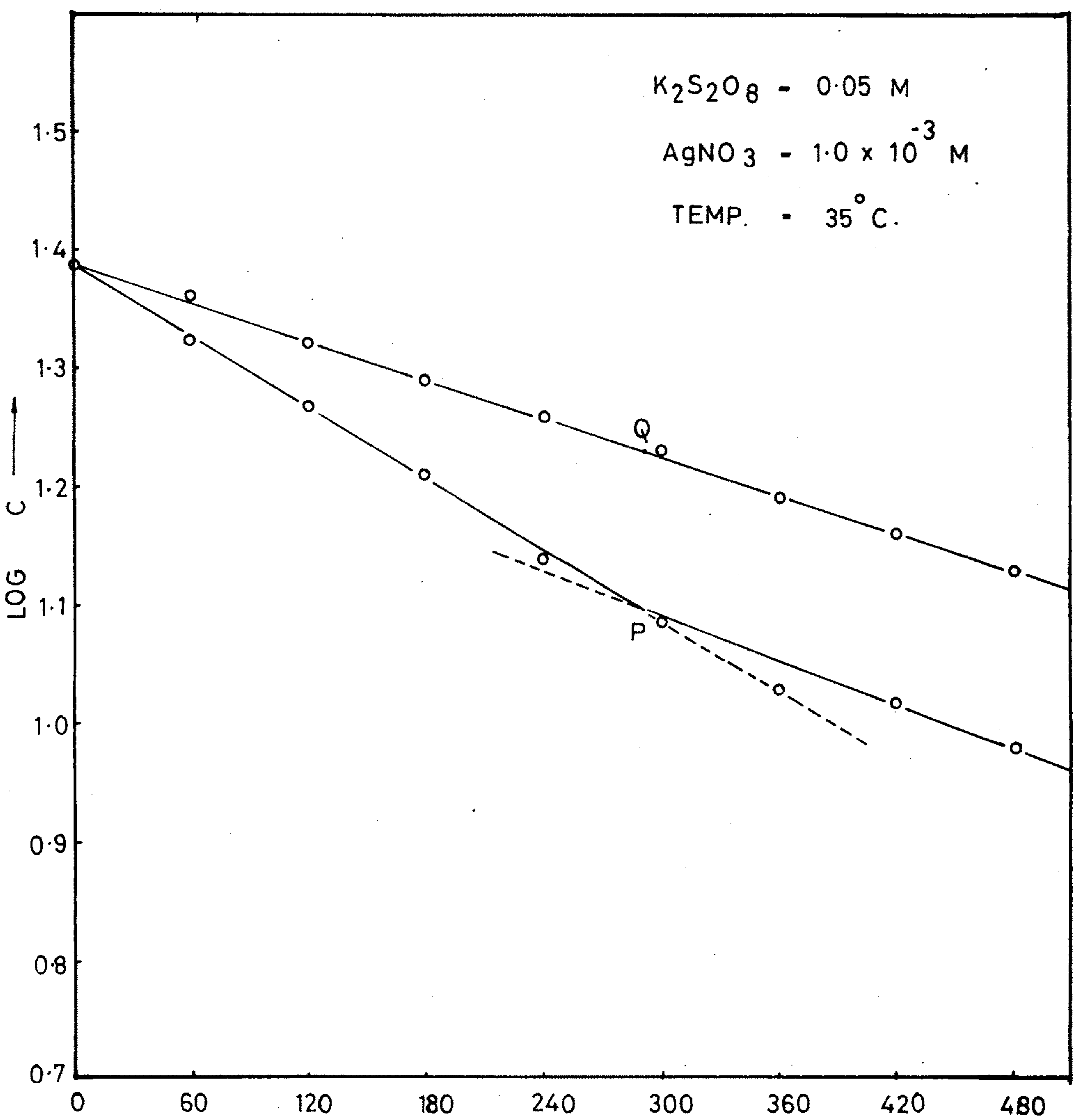


FIG. B - 17 MOLE RATIO