C H A P T E R - I I I

OXIDATION OF AMINO-ACETAMIDE

Preliminary experiments were performed in order to decide the suitable temperature and concentration of the reactants and catalyst. It was observed that the uncatalysed reaction was extremely slow. In presence of 1.0×10^{-3}M, Ag^+ as catalyst the reaction proceeds with a measurable velocity at 35°C. The reaction was first carried out at 35°C, taking the overall concentration of $K_2S_2O_8$ as 0.02M and amino-acetamide as 0.1M together with 1.0×10^{-3}M $AgNO_3$ as catalyst. The kinetic data of this run is recorded in the following table (Table A-1).

From the results (Table A-1), it indicates that , the first order rate constant goes on slightly decreasing 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 experiment, the quantity of amino-acetamide has been taken in excess, its concentration is higher than that of $S_2O_8^{2-}$ and hence the order is w.r.t. $S_2O_8^{2-}$ ion.

To decide conclusively the order with respect to $S_2O_8^{2-}$ as well as with respect to substrate, the reaction was carried out at equimolar concentrations of peroxydisulphate and amino-acetamide (Viz. 0.02M each), keeping the

temperature and concentration of the catalyst unchanged.
The following table A-1 contains the results of this run
(Table A-2).

TABLE A-1

$K_2S_2O_8$ = 2.0 X 10^{-2}M   Amino-acetamide = 0.1 M

$AgNO_3$ = 1.0 X 10^{-3}M   Temperature = 35°C

Time (min)	c^*	k_1 X 10^3 min^{-1}
0	9.45	-
20	8.15	7.392
40	7.05	7.323
60	6.10	7.297
80	5.27	7.288
100	4.57	7.254
130	3.70	7.213
160	2.97	7.224
200	2.25	7.176
240	1.80	6.910
300	1.25	6.744
360	0.85	6.691
Mean k_1 X 10^3 min^{-1}	-	7.137

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

TABLE A-2

Amino-acetamide = $K_2S_2O_8$ = 2.0×10^{-2} M

$AgNO_3$ = 1.0×10^{-3} M   Temperature = 35°C

Time (min)	C	$k_1 \times 10^3$ min^{-1}
0	9.45	–
20	7.41	12.16
40	5.83	12.07
60	4.61	11.96
80	3.66	11.85
100	2.93	11.71
130	2.11	11.53
160	1.53	11.39
200	1.02	11.14
240	0.68	10.96
300	0.39	10.63
360	0.24	10.21
Mean $k_1 \times 10^3$ min^{-1}	–	11.419

Here again, it is seen that the first order rate constant slightly decreases with time, which most probably 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 amino-acetamide may be zero.

EFFECT OF PREOXYDISULPHATE CONCENTRATION :

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

TABLE A-3

$AgNO_3 = 1.0 \times 10^{-3}M$, 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	4.92	–	9.82	–	14.75	–	19.52	–
20	4.77	1.497	9.55	1.417	14.35	1.382	19.05	1.209
40	4.65	1.410	9.30	1.381	14.00	1.307	18.60	1.203
60	4.52	1.397	9.07	1.331	13.67	1.267	18.25	1.117
80	4.40	1.396	8.85	1.314	13.37	1.227	17.85	1.117
100	4.30	1.348	8.65	1.278	13.10	1.186	17.55	1.064
130	4.15	1.311	8.35	1.254	12.77	1.109	17.05	1.042
160	4.00	1.294	8.10	1.209	12.37	1.101	16.62	1.005
200	3.80	1.292	7.75	1.888	11.90	1.074	16.15	0.950
240	3.62	1.275	7.40	1.183	11.40	1.074	15.57	0.941
300	3.375	1.257	6.95	1.155	10.75	1.054	14.75	0.933
360	3.15	1.240	6.50	1.449	10.20	1.024	14.30	0.864
Mean $k_2 \times 10^3$ min^{-1}	1.338		1.259		1.164		1.040	

<u>TABLE A-4</u>

Amino-acetamide = 0.1M, $AgNO_3$ = 1.0 x 10^{-3}, Temperature = 35°C

$[K_2S_2O_8]$ M	0.01		0.02		0.03		0.04	
Time(min)	C	$k \times 10^3$ min^{-1}	C	$k \times 10^3$ min^{-1}	C	$k \times 10^3$ min^{-1}	C	$k \times 10^3$ min^{-1}
0	4.95	–	9.45	–	14.34	–	19.30	–
20	4.04	10.16	8.15	7.392	13.10	4.542	17.87	3.858
40	3.31	10.06	7.05	7.323	12.00	4.468	16.55	3.846
60	2.73	9.917	6.10	7.297	10.95	4.502	15.35	3.819
80	2.26	9.802	5.27	7.288	10.00	4.513	14.22	3.819
100	1.88	9.780	4.57	7.254	9.15	4.500	13.20	3.800
130	1.43	9.554	3.70	7.213	8.05	4.447	11.80	3.786
160	1.10	9.399	2.97	7.224	7.05	4.443	10.57	3.763
200	0.79	9.189	2.25	7.176	5.95	4.402	9.15	3.734
240	0.58	8.935	1.80	6.910	5.00	4.393	7.95	3.697
300	0.37	8.644	1.25	6.744	3.85	4.385	6.45	3.655
360	0.25	8.482	0.85	6.691	3.00	4.349	5.25	3.616
$k_1 \times 10^3 min^{-1}$	9.444		7.137		4.449		3.763	
$k_2 \times 10^3 min^{-1}$	1.338		1.259		1.164		1.040	
$k \times 10^3 min^{-1}$	8.106		5.878		3.285		2.723	

Now in order to study the effect of $S_2O_8^{2-}$ ion concentration on the reaction rate, the reaction was studied at three different concentrations of $S_2O_8^{2-}$ keeping the concentration of the substrate and catalyst unchanged. Table A-4 shows the results of these kinetic runs and for comparison's sake, the data of Table A-1 has been incorporated in it.

From the above results (table A-4), it indicates that when the concentration of $K_2S_2O_8$ was increased, the first order rate constant decreases. This decrease in the rate constant with an increase in the concentration of $S_2O_8^{2-}$ may be either due to an increase in ionic strength or due to the specific inhibitory effect of K^+ ion or due to both.

It has been observed that in any particular run , the first order rate constant decreases with time, because the reactions involving $S_2O_8^{2-}$ ions are highly susceptible to trace impurities. Hence all precautions were taken to purify the substrate and all the reagents used for 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 deducting the value of the rate constant (Viz. k_2) for the self decomposition of $S_2O_8^{2-}$ studied simultaneously (as shown in the above table A-4).

It must be mentioned here 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 for these runs have been omitted

on account of pressure on space and only the corresponding values of the rate constant (Viz. k_2) have been directly recorded at the end of each table.

TABLE A-5

Amino-acetamide = 0.1M, AgNO$_3$ = 1.0x 10^{-3}M , Temperature = 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 0.02 M Na$_2$S$_2$O$_3$ used (Viz. C)

Time (min)				
0	4.96	9.48	14.35	19.30
20	4.30	8.42	13.37	18.35
40	3.74	7.49	12.50	17.45
60	3.25	6.66	11.65	16.60
80	2.83	5.93	10.90	15.80
100	2.48	5.27	10.17	15.05
130	2.04	4.44	9.20	14.00
160	1.69	3.74	8.33	13.02
200	1.32	2.98	7.31	11.85
240	1.04	2.37	6.43	10.75
300	0.75	1.70	5.33	9.38
360	0.55	1.22	4.43	8.18

k_1X 10^{3}min^{-1}	6.762	5.825	3.401	2.467
k_2X 10^{3}min^{-1}	0.710	0.710	0.690	0.680
K X 10^{3}min^{-1}	6.052	5.115	2.711	1.787

It has been observed that the first order specific rate decreases by increasing the concentration of $S_2O_8^{2-}$. However, the kinetic runs carried out above do not have

constant ionic strength as well as constant K^+ ion concentration. Hence it was considered to re-investigate this effect at constant ionic strength as well as at constant K^+ ion concentration, so the effect of both these parameters may be eliminated. Hence the above table shows the data of these kinetic runs (Table A-5) carried out at constant ionic strength and constant K^+ ion concentration which have been shown graphically in Fig. A-2.

From the results contained in the above table (Table A-5) it is seen that here again the first order rate constant decreases.

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

TABLE A-6

Amino-acetamide = 0.01 M, $AgNO_3$ = 1.0 $X10^{-3}$M, Temp. = 35°C

Conc. $[K_2S_2O_8]$ M without $[K_2SO_4]$	$k \times 10^3$ min^{-1}	Conc. $[K_2S_2O_8]$ M with Constant K^+ ionic strength	$k \times 10^3 min^{-1}$
0.01	8.106	0.01	6.052
0.02	5.878	0.02	5.115
0.03	3.285	0.03	2.711
0.04	2.723	0.04	1.787

From the above data (Table A-6), it indicates 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 tendency even though the reaction is carried out at constant ionic steength as well as at constant K^+ ion concentration which leads to conelude that it is probably due to some trace impurity remaining in the peroxydisulphate sample it-self even after repeated crystallization which however, could not 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 peroxydisulphate is being followed :

$$-\log k = 2.83 + 1.80 \left[S_2O_8^{2-}\right]_o$$

provided that $\left[S_2O_8^{2-}\right]_o \neq$ zero

ORDER WITH RESPECT TO PEROXYDISULPHATE :

The order with respect to peroxydisulphate was calculated by Van't Hoff's differential[184] 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 $-\frac{dc}{dt}$ in each case was determined from the initial slope as given in Table A-7.

TABLE A-7

$[K_2S_2O_8]$ M	$-\frac{dc}{dt} \times 10^{-4}$	Log $[S_2O_8^{2-}]$	Log $(-\frac{dc}{dt})$
0.01	1.850	- 2.0000	- 3.7328
0.02	3.800	- 1.6990	- 3.4202
0.03	5.510	- 1.5229	- 3.2586
0.04	7.310	- 1.3979	- 3.1358

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

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

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 1.00 as such the order with respect to $S_2O_8^{2-}$ is one, which is confirmed by the values of n as shown in the following table (Table A-8).

TABLE A-8

$\left[K_2S_2O_8\right]M$	$- dc/dt \times 10^{-4}$	Order of reaction (n)
0.01	1.850	
0.02	3.800	0.9736
0.01	1.850	
0.03	5.510	1.007
0.01	1.850	
0.04	7.310	1.012
0.02	3.800	
0.03	5.510	1.034
0.03	5.510	
0.04	7.310	1.005

EFFECT OF AMINO ACETAMIDE CONCENTRATION :

To study the effect of amide concentration on the reaction rate, the reaction was studied at five different initial concentrations of amide ranging from 0.05 M to 0.25 M. The concentrations of $K_2S_2O_8$ and $AgNO_3$ were kept unchanged. These results are recorded in Table A-9 and shown graphically in Fig. A-5.

TABLE A-9

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

[Amide] M	0.05	0.1	0.15	0.20	0.25
Time (min)	Vol. (in ml) of 0.02 M $Na_2S_2O_3$ used (Viz. C)				
0	9.48	9.45	9.46	9.44	9.42
20	8.21	8.15	8.04	7.94	8.01
40	7.13	7.05	6.84	6.68	6.83
60	6.22	6.10	5.82	5.62	5.85
80	5.43	5.27	4.96	4.75	5.00
100	4.76	4.57	4.23	4.01	4.28
130	3,92	3.70	3.32	3.10	3.38
160	3.26	2.97	2.62	2.40	2.68
200	2.56	2.25	1.91	1.71	1.97
240	2.03	1.80	1.39	1.22	1.45
300	1.47	1.25	0.87	0.74	0.92
360	1.10	0.85	0.54	0.45	0.58
$k_1 \times 10^3 min^{-1}$	6.697	7.137	8.038	8.560	7.878
$k_2 \times 10^3 min^{-1}$	1.259	1.259	1.259	1.259	1.259
$k \times 10^3 min^{-1}$	5.438	5.878	6.779	7.301	6.619

From the results contained in the above table (Table A-9) it is seen that rate constant only slightly increases when the concentration of amide was increased, but the rate practically remain 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 $H_2N.CH_2.CONH_2$ governed by the expression

$$k = k_{max} \cdot \frac{(H_2N.CH_2.CONH_2)_o}{b + (H_2N.CH_2.CINH_2)_o}$$

In support of the above equation, a graph of $\dfrac{(H_2N.CH_2.CONH_2)_o}{k}$ versus $(H_2N.CH_2.CONH_2)_o$ is plotted (Fig. A-6)

The plot was found to be linear from which k_{max} and b were evaluated as 0.00833 and 0.004375. From these values k was calculated and found to be equal to $k = 5.799 \times 10^3 min^{-1}$ was almost indentical with $k = 5.878 \times 10^3 min^{-1}$, the calculated experimental value.

ORDER WITH RESPECT TO AMINO-ACETAMIDE :

A general behaviour of Ag^+ catalyst redox reactions involving peroxydisulphate ion is that the order with respect to the reductant is zero. To confirm the order of reaction with amino-acetamide, the kinetic data of Table A-9 was subjected to Van't[184] Hoff's differential method. From the initial slope of concentration versus time curves, the values of $-dc/dt$ corresponding to various initial concentrations of amino-acetamide were evaluated.

These values are given in the following table (Table A-10)

TABLE A-10

[Conc.Amino-acetamide] M	-dc/dtX10^{-4}	Log(Co)	Log(-dc/dt)
0.05	2.407	-1.3010	-3.6186
0.10	2.300	-1.0000	-3.6383
0.15	2.407	-0.8239	-3.6186
0.20	2.350	-0.6990	-3.6289
0.25	2.365	-0.6021	-3.6262

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 amino-acetamide. Calculations were made for the order of reaction by Van't Hoff's differential method as given in Table A-11.

TABLE A-11

[Amino-acetamide] M	(-dc/dt)X 10^{-4}	Order of reaction (n)
0.05	2.407	0.0654
0.1	2.300	
0.05	2.407	0.0000
0.15	2.407	
0.05	2.407	0.01711
0.20	2.350	
0.05	2.407	0.0230
0.25	2.365	
0.1	2.300	0.0312
0.20	2.350	
0.1	2.300	0.03034
0.25	2.365	

From the results (Table A-11) it is confirmed that the order with respect to amino-acetamide is zero.

EFFECT OF THE CATALYST CONCENTRATION :

In order to study the effect of catalyst concentration on the reaction rate, the reaction was studied at five different concentrations of silver nitrate, keeping peroxydisulphate and amide concentration unchanged. The kinetic results of these runs are recorded in Table A-12 and shown graphically in Fig.A-8.

TABLE A-12

Amino-acetamide = 0.1M, $K_2S_2O_8$ = 2.0 $X10^{-2}$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	8.15	8.04	7.46	6.95	9.46
40	7.05	6.36	5.92	5.13	4.43
60	6.10	5.86	4.72	3.72	3.04
80	5.27	5.00	3.78	2.80	2.09
100	4.57	4.27	3.04	2.07	1.44
130	3.70	3.38	2.21	1.31	0.82
160	2.97	2.67	1.62	0.84	0.47
200	2.25	1.96	1.08	0.46	0.22
240	1.80	1.44	0.74	0.25	0.11
300	1.25	0.91	0.43	0.11	-
360	0.85	0.58	0.26	0.05	-
$k_1 X10^3$min^{-1}	7.137	7.898	11.064	15.080	18.780
$k_2 X10^3$min^{-1}	1.259	1.326	1.444	1.540	1.693
k X 10^3min^{-1}	5.878	6.572	9.620	13.540	17.087

From the above results (Table A-12) it is observed
that, when the concentrations of $AgNO_3$ were increased, the
reaction rate was also increased linearly. This indicates
that the reaction is first order with respect to catalyst.

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

$$k = 2.0 \times 10^{-3} + 3.9 \ (Ag^+)$$

EFFECT OF TEMPERATURE :

In order to determine the temperature coefficient,
energy of activation and various other energy parameters ,
the reaction was studied at five different temperatures
ranging from 25°C to 45°C. The results of these kinetic
runs have been recorded in the following table and shown
graphically in Fig. A-10.

From the results contained in table (Table A-13),
it indicates that the specific rate has been nearly doubled
for 10°C rise in temperature. A plot of Log k versus 1/T
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 12.900 K.Cals $mole^{-1}$ which is in good agreement with

TABLE A-13

Amino-acetamide = 0.1M, $K_2S_2O_8$ = 2.0x10^{-2}M, $AgNO_3$ = 1.0x10^{-3}M

Temperature	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	9.44	9.42
20	8.74	8.51	8.15	7.56	7.05
40	8.09	7.67	7.05	6.07	5.28
60	7.49	6.91	6.10	4.88	3.96
80	6.94	6.23	5.27	3.94	2.97
100	6.42	5.61	4.57	3.19	2.23
130	5.72	4.81	3.70	2.33	1.45
160	5.11	4.12	2.97	1.71	0.94
200	4.38	3.36	2.25	1.14	0.53
240	3.77	2.74	1.80	0.78	0.30
300	3.01	2.02	1.25	0.44	0.13
360	2.41	1.50	0.85	0.26	-
k_1X10^{3}min^{-1}	3.868	5.201	7.137	10.320	14.220
k_2X10^{3}min^{-1}	0.750	0.830	1.259	1.512	2.403
k X10^{3}min^{-1}	3.118	4.371	5.878	8.808	11.810

the calculated value, 12.610 K.Cals.Mole^{-1}. The calculated value of 1/T .10^3 and $Log\left[\dfrac{kr}{kT/h}\right]$ are recorded in Table A-14.

TABLE A-14

Temp. °A	$\frac{1}{T} X10^3$	$kr \times 10^3 min^{-\ddagger}$	Log kr	Log $\left[\frac{kr}{kT/h} \right]$
298	3.356	3.118	-2.5061	-15.3232
303	3.301	4.371	-2.3594	-15.1877
308	3.246	5.878	-2.2308	-15.0623
313	3.196	8.808	-2.0551	-14.8935
318	3.145	11.817	-1.9255	-14.7730

Similarly, by making the use of Arrhenius equation at different temperature, the value of energy of activation has been calculated by the following equation.

$$\log k_1 - \log k_2 = \frac{-E}{2.303 \, R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad \ldots \quad (1)$$

The value of energy of activation was then used to calculate the frequency factor A and entropy of activation $\Delta S^{\neq}$ by the application of the following equations.

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

and

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

where equation (3) is valid for reactions in solutions. In the above expression, kr is the specific rate constant, k is the Boltzmann constant, h is the planck'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

$$kr = \frac{kT}{h} \, e^{-\Delta G^{\neq}/RT} \qquad \dots \quad (4)$$

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

$$kr = e \cdot \frac{kT}{h} \cdot e^{\Delta S^{\neq}/R} \cdot e^{-E/RT} \qquad \dots \quad (5)$$

or

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

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

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

$$kr = \frac{kT}{h} \cdot e^{-\Delta H^{\neq}/RT} \cdot e^{\Delta S^{\neq}/R} \qquad \dots \quad (7)$$

or

$$\text{Log} \, \frac{kr}{kT/h} = \frac{-\Delta H^{\neq}}{2.303RT} + \frac{\Delta S^{\neq}}{2.303 \, R} \qquad \dots \quad (8)$$

The values of $\log\left[\dfrac{kr}{kT/h}\right]$ have been plotted against $\frac{1}{T}$ 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 the following table (Table A-15).

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.

TABLE A-15

Temperature °A	k x 10³ min⁻¹	Temperature coefficient	E K.Cals. mole⁻¹	A X 10⁴ litre mole⁻¹ Sec⁻¹	$\Delta G^{\neq}$ K.Cals. mole⁻¹	$\Delta S^{\neq}$ e.u.	$\Delta H^{\neq}$ K.Cals. mole⁻¹
298	3.118	-	-	8.030	21.02	-29.74	-
303	4.371	1.885	11.060	7.914	21.17	-29.76	
308	5.878	2.015	13.200	7.603	21.36	-29.86	12.170
313	8.808	2.009	13.580	8.217	21.47	-29.72	(Graphically)
318	11.817	-	-	8.019	21.34	-29.78	
Mean	-	1.969	12.613	7.956	21.27	-29.77	

TABLE A-16

Amino-acetamide = 0.1M, $K_2S_2O_8$ = 2.0X10^{-2}M, AgNO$_3$=1.0X10^{-3}M, Temp = 35°C

$[K_2SO_4]$ M	Nil	0.01	0.015	0.02	0.03	0.04
λ	0.061	0.091	0.106	0.121	0.151	0.181
Time (min)	Vol. (in ml) of 0.02 M Na$_2$S$_2$O$_3$ used (Viz. C)					
0	9.45	9.58	9.56	9.55	9.53	9.54
20	8.15	8.39	8.43	8.83	8.92	8.95
40	7.05	7.36	7.43	8.18	8.35	8.39
60	6.10	6.45	6.56	7.58	7.87	7.89
80	5.27	5.66	5.80	7.03	7.35	8.42
100	4.57	4.97	5.13	6.52	6.90	6.99
130	3.70	4.09	4.26	5.84	6.29	6.41
160	2.97	3.37	3.55	5.23	5.74	5.88
200	2.25	2.61	2.79	4.53	5.13	5.27
240	1.80	2.02	2.24	3.93	4.55	4.74
300	1.25	1.38	1.54	3.22	3.85	4.09
360	0.85	0.95	1.08	2.64	3.29	3.56
k_1x10^{3}min^{-1}	7.137	6.537	6.195	3.772	3.156	3.030
k_2x10^{3}min^{-1}	1.259	1.190	1.168	1.124	0.820	0.770
k x10^{3}min^{-1}	5.878	5.347	5.027	2.648	2.336	2.260

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

$$k = 7.956 \times 10^4 \cdot e^{-12.613/RT} \; sec^{-1}$$

EFFECT OF IONIC STRENGTH :

In order to study the effect of ionic strength on reaction rate, the reaction was studied in presence of different concentrations of potassium sulphate. The results of these kinetic runs are summarised in the above table (Table A-16) and shown graphically in Fig. A-13.

From the results contained in the above table (Table A-16) it is seen that, on increasing the ionic strength, the specific rate decreases. It indicates that the salt effect is negative. The reaction however retains its first order behaviour.

In order to decide the nature of the observed negative salt effect, graphs were plotted between log k and $(\mu)^{\frac{1}{2}}$ as well as between k and μ as shown in Fig. 14(A) and 14(B) respectively. It is observed that a linear relationship is maintained between log k and $(\mu)^{\frac{1}{2}}$ whereas there exists no linearity between K and μ. The linearity between log k and $(\mu)^{\frac{1}{2}}$ exists only in the region of low ionic strength (< 0.2). Thus it 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	$k \times 10^3$ min^{-1}	$\sqrt{\mu}$	log k
Nil	0.061	5.878	0.247	-2.2308
0.01	0.091	5.347	0.302	-2.2718
0.015	0.106	5.007	0.326	-2.2987
0.02	0.121	2.648	0.348	-2.5771
0.03	0.151	2.336	0.389	-2.6315
0.04	0.181	2.260	0.425	-2.6459

It may be stated that the ionic strength employed
is rather high for Bronsted[185] relationship to be strictly
quantitatively applicable, but still the agreement is found
to be fairly good.

SPECIFIC IONIC STRENGTH :

To determine the specific ionic effect on the
reaction rate, the reaction was studied in presence of
different salts at constant ionic strength. These results
are recorded in the following table (Table A-18).

On comparing the rate constants from the data of
Table A-18, it is observed that the specific inhibitory
effect of the various ions is in the order

$$K^+ > Na^+ > Li^+ > Mg^{++} > Zn^{++}$$
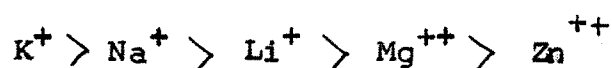
From the above results, we can conclude that the salt effect
is negative.

TABLE A-18

Ammino-acetamide = 0.1M , $K_2S_2O_8$ = 2.0 X 10^{-2} M

$AgNO_3$ = 1.0 X 10^{-3} M , Temperature = 35°C, μ = 0.211

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)

Time (min)						
0	9.45	9.65	9.64	9.62	9.64	9.60
20	8.15	9.13	9.03	8.87	8.94	8.64
40	7.05	8.65	8.45	8.18	8.30	7.78
60	6.10	8.20	7.92	7.55	7.71	7.02
80	5.27	7.77	7.43	6.98	7.16	6.33
100	4.57	7.37	6.97	6.45	6.65	5.71
130	3.70	6.82	6.33	5.74	5.97	4.89
160	2.97	6.31	5.76	5.11	5.35	4.19
200	2.25	5.71	5.09	4.39	4.64	3.43
240	1.80	5.17	4.50	3.78	4.03	2.80
300	1.25	4.48	3.75	3.03	3.27	2.06
360	0.85	3.89	3.14	2.45	2.66	0.96

k_1X10^3min^{-1}	7.137	2.660	3.227	3.591	3.680	5.184
k_2X10^3min^{-1}	1.259	1.130	1.141	0.840	0.880	0.970
k X10^3min^{-1}	5.878	1.530	2.086	2.751	2.800	4.214

EFFECT OF HYDROGEN ION CONCENTRATION :

In order to study whether the reaction is affected when the pH of the reaction system is changed, the reaction was studied at different H^+ ion concentration by addition of sulphuric acid. The results of these kinetic runs are recorded in Table A-19 and shown graphically in Fig. A-16.

From the results contained in Table A-19, it is seen that the rate of the reaction is affected by a change in pH of the reaction mixture. When the pH is lowered then there is a decrease in the rate constant also. Now it is possible that this decrease in the rate of the reaction may not be due to a change in pH but also may be due to an increase in ionic strength resulting by the addition of H_2SO_4.

To verify which of the possibilities hold good, the effect was re-investigated at constant ionic strength by adding a mixture of K_2SO_4 and H_2SO_4 , so as to maintain the ionic strength of the reaction mixture constant. the results of which have been recorded in Table A-20 and shown graphically in Fig. A-17.

TABLE A-19

Amino-acetamide = 0.1M, $K_2S_2O_8$ = 2.0X10^{-2}M, AgNO$_3$ = 1.0X10^{-3}M

Temperature = 35°C

$[H_2SO_4]$ M	Nil.	0.025	0.05	0.075	0.1
Time(min)	Vol.(in ml) of 0.02 M Na$_2$S$_2$O$_3$ used (Viz.C)				
0	9.45	9.55	9.55	9.54	9.52
20	8.15	8.42	8.68	8.78	8.97
40	7.05	7.43	7.89	8.09	8.46
60	6.10	6.57	7.18	7.45	7.98
80	5.27	5.79	6.54	6.87	7.53
100	4.57	5.13	5.95	6.34	7.11
130	3.70	4.26	5.18	5.62	6.54
160	2.97	3.55	4.54	4.99	6.01
200	2.25	2.80	3.77	4.26	5.39
240	1.80	2.19	3.16	3.65	4.84
300	1.25	1.54	2.43	2.90	4.14
360	0.85	1.08	1.88	2.31	3.56
k_1 X 10^{3}min^{-1}	7.137	6.190	4.680	4.058	2.882
k_2 X 10^{3}min^{-1}	1.259	0.970	0.850	0.760	0.670
k X 10^{3}min^{-1}	5.878	5.220	3.830	3.298	2.212

TABLE A-2D

Amino-acetamide = 0.1M, $K_2S_2O_8$ = 2.0 X 10^{-2} M

$AgNO_3$ = 1.0 x 10^{-3} M , Temperature = 35°C, μ = 0.361

$[H_2SO_4]$ M	nil.	0.025	0.05	0.075	0.100
$[K_2SO_4]$ M	0.100	0.075	0.05	0.025	Nil

Time(min)   Vol. (in ml) of 0.02 M, $Na_2S_2O_3$ used (Viz.C)

Time(min)					
0	9.53	9.53	9.52	9.52	9.52
20	9.17	9.14	9.11	9.08	8.97
40	8.83	8.78	8.72	8.67	8.46
60	8.51	8.44	8.35	8.30	7.98
80	8.21	8.11	8.00	7.94	7.53
100	7.92	7.78	7.66	7.60	7.11
130	7.50	7.35	7.20	7.13	6.54
160	7.14	6.94	6.76	6.69	6.01
200	6.66	6.45	6.24	6.16	5.39
240	6.23	6.00	5.76	5.69	4.84
300	5.66	5.40	5.13	5.07	4.14
360	5.16	4.88	4.59	4.55	3.56

$k_1 \times 10^3 min^{-1}$	1.817	1.984	2.137	2.218	2.882
$k_2 \times 10^3 min^{-1}$	0.600	0.620	0.640	0.640	0.670
$k \times 10^3 min^{-1}$	1.217	1.364	1.497	1.578	2.212

From the above results (Table A-20), it is seen
that the rate of the reaction is increased by increasing H^+
ion concentration. This suggests that either the reaction
may be catalysed by H^+ ions or both K^+ and H^+ ions have
specific inhibitory effect and that the specific inhibitory
effect of K^+ ion is greater than that of H^+ ions. A sharp
fall in the reaction rate by increasing H^+ ion concentration
rules out (Table A-19) the possibility that the increase in
the rate constant values at constant ionic strength (Table A-20)
is brought about due to catalytic effect of H^+ ions, leaving
thus only to conclude that K^+ ions cause inhibition of
greater magnitude in comparison to that brought about by H^+
ions and that the observed increase in the rate constant at
constant ionic strength (Table A-20) is due to the increasing
proportion of H_2SO_4 at the expense of equimolar
concentration of K_2SO_4.

EFFECT OF ALLYL ALCOHOL AND ALLYL ACETATE

It is well known that the reaction involving $S_2O_8^{2-}$
ion is inhibited by allyl acetate and allyl alcohol. It has
been shown by Kolthoff[186] et al., Wiberg[187], Ball[188] and
Co-workers that allyl acetate is an efficient capture for
sulphate ion radical (SO_4^-), which is known to be formed in
oxidation reactions involving $S_2O_8^{2-}$ ion. Hence it was
considered to investigate the effect of allyl alcohol and
allyl acetate on peroxydisulphate oxidation of organic
substrates studied in this thesis.

EFFECT OF ALLYL ALCOHOL :

The reaction was studied in absence of and in presence
of three different initial concentrations of allyl alcohol.
The results of these kinetic runs are recorded in the following
table (Table A-21) and shown graphically in Fig. A.18.

TABLE A-21

Amino-acetamide = 0.1M, $K_2S_2O_8$ = 2.0×10^{-2}M, $AgNO_3$ = 1.0×10^{-3}M

[Allyl alcohol] M	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	9.45	9.45
20	8.15	8.28	8.51	8.84
40	7.05	7.25	7.66	8.28
60	6.10	6.35	6.91	7.76
80	5.27	5.57	6.23	7.27
100	4.57	4.89	5.62	6.82
130	3.70	4.02	4.83	6.21
160	2.97	3.32	4.14	5.65
200	2.25	2.57	3.39	5.00
240	1.80	2.00	2.78	4.43
300	1.25	1.38	2.06	3.72
360	0.85	0.95	1.54	3.14
$k \times 10^3 min^{-1}$	7.137	6.556	5.165	3.219

On examination of the above data (Table A-21), it indicates that the reaction is suppressed by the addition of allyl alcohol.

EFFECT OF ALLYL ACETATE :

The reaction was studied at varying concentrations of allyl acetate ranging from 0.001M to 0.01M. The concentrations of amide, $K_2S_2O_8$, and the catalyst were kept unchanged. The results of these kinetic runs are recorded in the following table (Table A-22) and shown graphically in Fig. A-19.

TABLE A-22

Amino-acetamide = 0.1M, $AgNO_3=1.0x10^{-3}M$, $K_2S_2O_8=2.0x10^{-2}M$
Temperature = 35°C

Allyl Acetate M	Nil	0.001	0.005	0.01
Time (min)	Vol. (in ml) of $0.02M-Na_2S_2O_3$ used (Viz. C)			
0	9.45	9.48	9.48	9.46
20	8.15	8.30	8.71	8.92
40	7.05	7.28	8.01	8.42
60	6.10	6.38	7.37	7.95
80	5.87	5.60	6.78	7.51
100	4.57	4.92	6.24	7.10
130	3.70	4.05	5.52	6.52
160	2.97	3.33	4.88	6.00
200	2.25	2.58	4.15	5.37
240	1.80	2.01	3.54	4.82
300	1.25	1.35	2.79	4.10
360	0.85	0.94	2.21	3.51
$k \times 10^3 min^{-1}$	7.137	6.545	4.154	2.853

Here again it indicates that allyl acetate suppresses the reaction appreciably. The effect of allyl acetate is more than that of allyl alcohol.

MOLE RATIO :

In order to determine the number of moles of peroxydisulphate with one mole of amide   the graphical method was employed. This method is described as follows :

Potassium peroxydisulphate was taken in excess as compared to amide. Simultaneously, a blank run was also performed. At suitable intervals of time 5 ml of the reaction mixture was pipetted out and unreacted $K_2S_2O_8$ was estimated. These results are recorded in Table A-23 and shown graphically in Fig. A-20.

As shown in the figure A-20, it is seen that the curve consists of two portions. The first portion is for oxidation of amide and the second portion for the self decomposition of peroxydisulphate. Now tangents are drawn on portions of the curves 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 0.01M amide is calculated. The point Q on the curve B at the same time gives the value corresponding to self decomposed $K_2S_2O_8$.

<u>TABLE A-23</u>

$K_2S_2O_8$ = 0.05M, $AgNO_3$ = 1.0 x 10^{-3}M, Temp. = 35°C

[Amide] M	0.01	Nil
Time (min)	Vol. (in ml) of 0.02 M-$Na_2S_2O_3$ used(Viz.C)	
0	24.40	24.10
30	22.05	23.41
60	21.36	22.36
90	19.93	21.44
120	18.62	20.85
150	17.36	20.41
180	16.20	19.50
210	15.12	19.05
240	13.95	18.21
270	13.26	17.37
300	12.55	16.96
330	11.74	15.88
360	11.15	15.85
390	10.71	15.05
420	10.49	14.45
450	9.94	14.01
480	9.32	13.50

From the graph shown in the Fig. A-20, it is seen that the two plots become parallel at P. At this point log C = 1.02 which corresponds to 10.47 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 = 1.20 which corresponds to 15.85 ml. The difference between these two values (indicating the volume of $Na_2S_2O_3$) is 5.38 ml.

Therefore 5.38 ml of $\equiv$ 0.02N $K_2S_2O_8$
0.02N $Na_2S_2O_3$

$\equiv$ 5.38 ml of 0.01M $K_2S_2O_8$
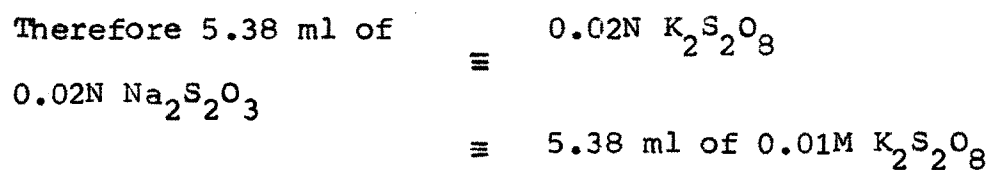
Hence 5 ml of 0.01 M amide $\equiv$ 5.38 ml of 0.01M $K_2S_2O_8$

So one mole of amide approximately consumes one mole of $K_2S_2O_8$ for complete reaction.

* * * * *

FIG. A→1

EFFECT OF $K_2S_2O_8$

AMIDE $= 0.1$ M

$AgNO_3 = 1.0 \times 10^{-3}$ M

TEMP. $= 35°C$

$[K_2S_2O_8]$

I $\rightarrow$ 0.01 M

II $\rightarrow$ 0.02 M

III $\rightarrow$ 0.03 M

IV $\rightarrow$ 0.04 M

Log C

TIME (min)
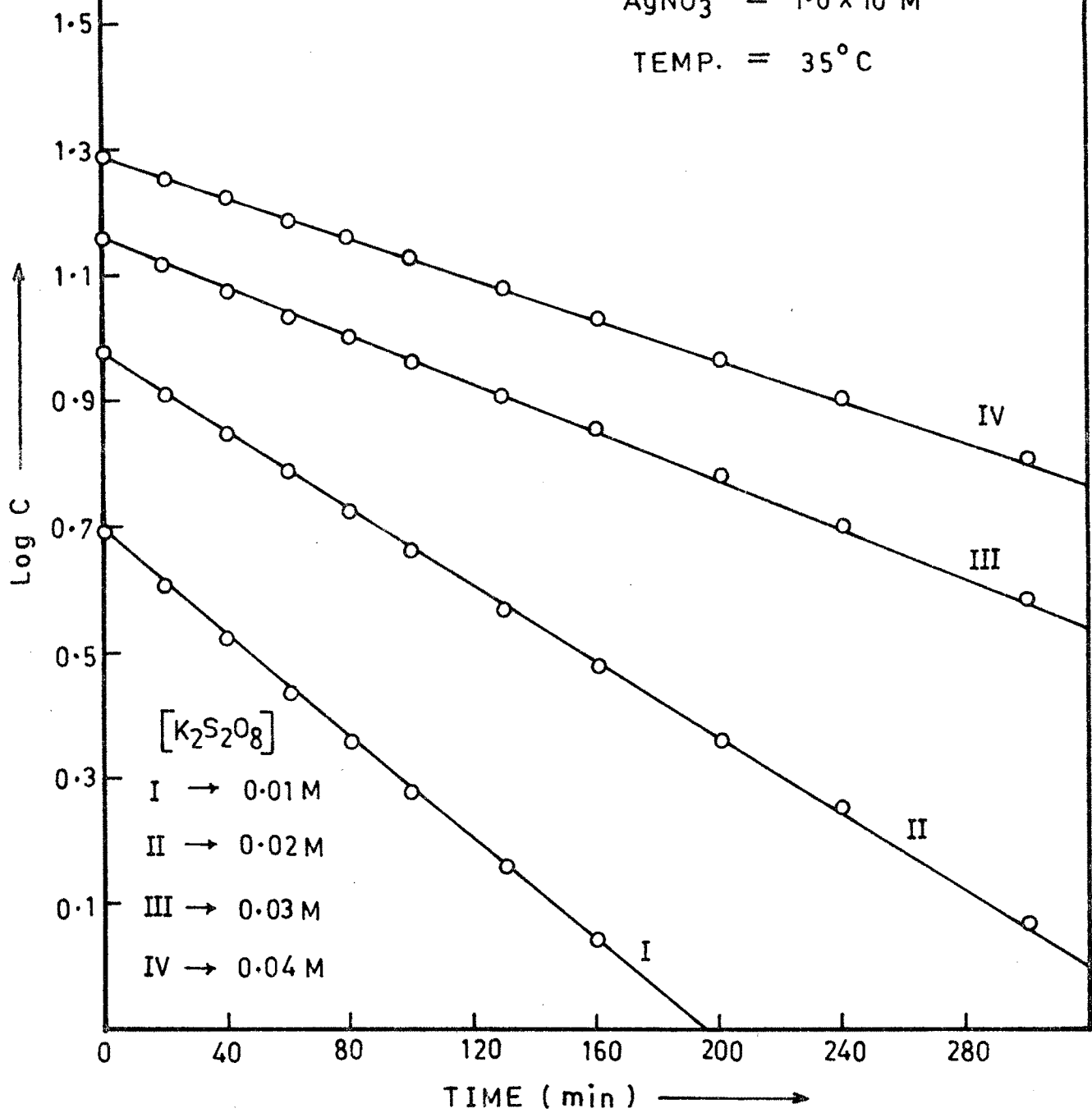
FIG. A → 2

EFFECT OF $K_2S_2O_8$ AT CONSTANT μ.

AMIDE = 0·1 M

$AgNO_3$ = 1·0 × 10^{-3} M

TEMP. = 35°C

μ = 0·301

$[K_2S_2O_8]$

I → 0·01 M
II → 0·02 M
III → 0·03 M
IV → 0·04 M
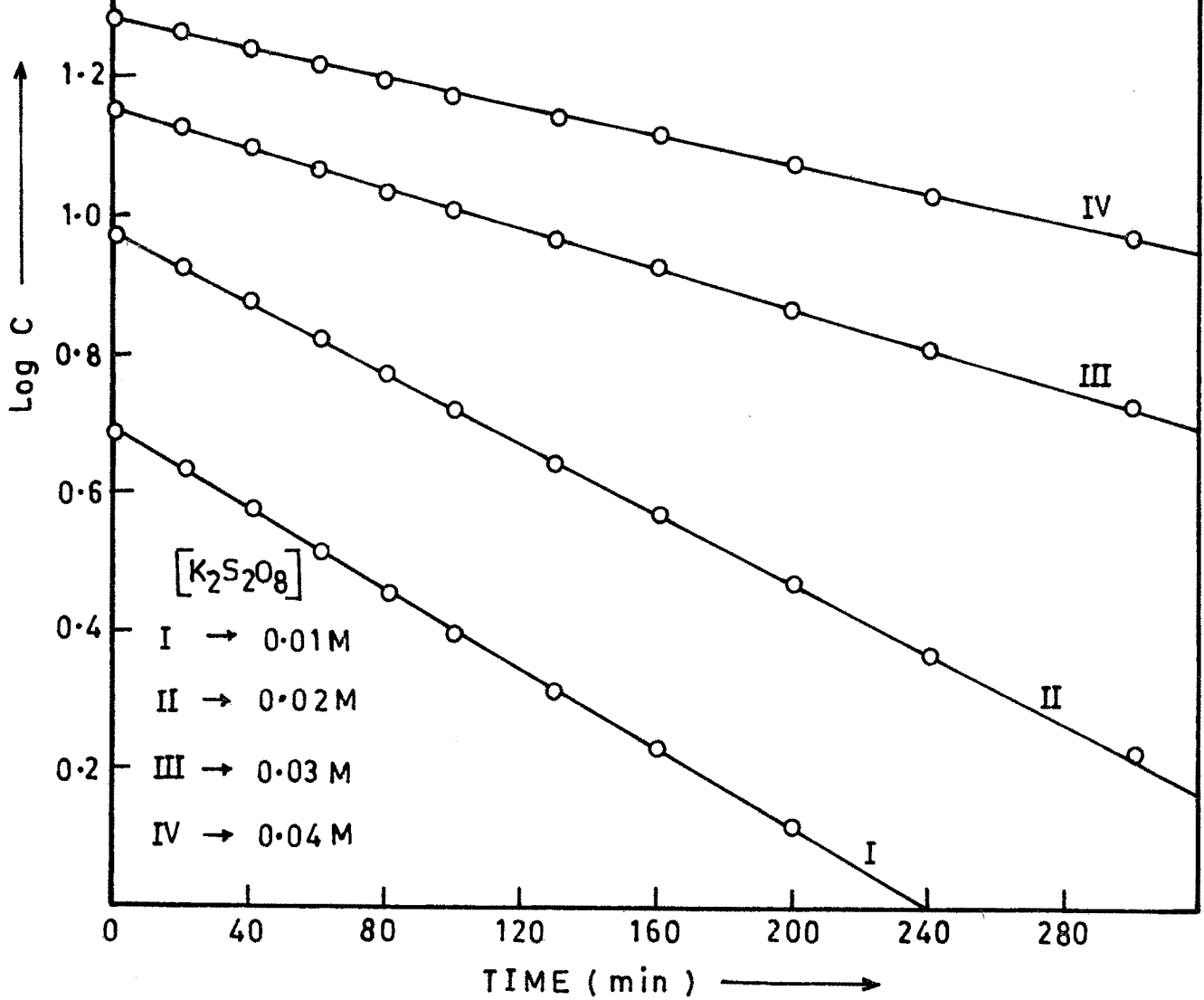
FIG. A→3

PLOT OF −Log k

VERSUS

CONC. $K_2S_2O_8$
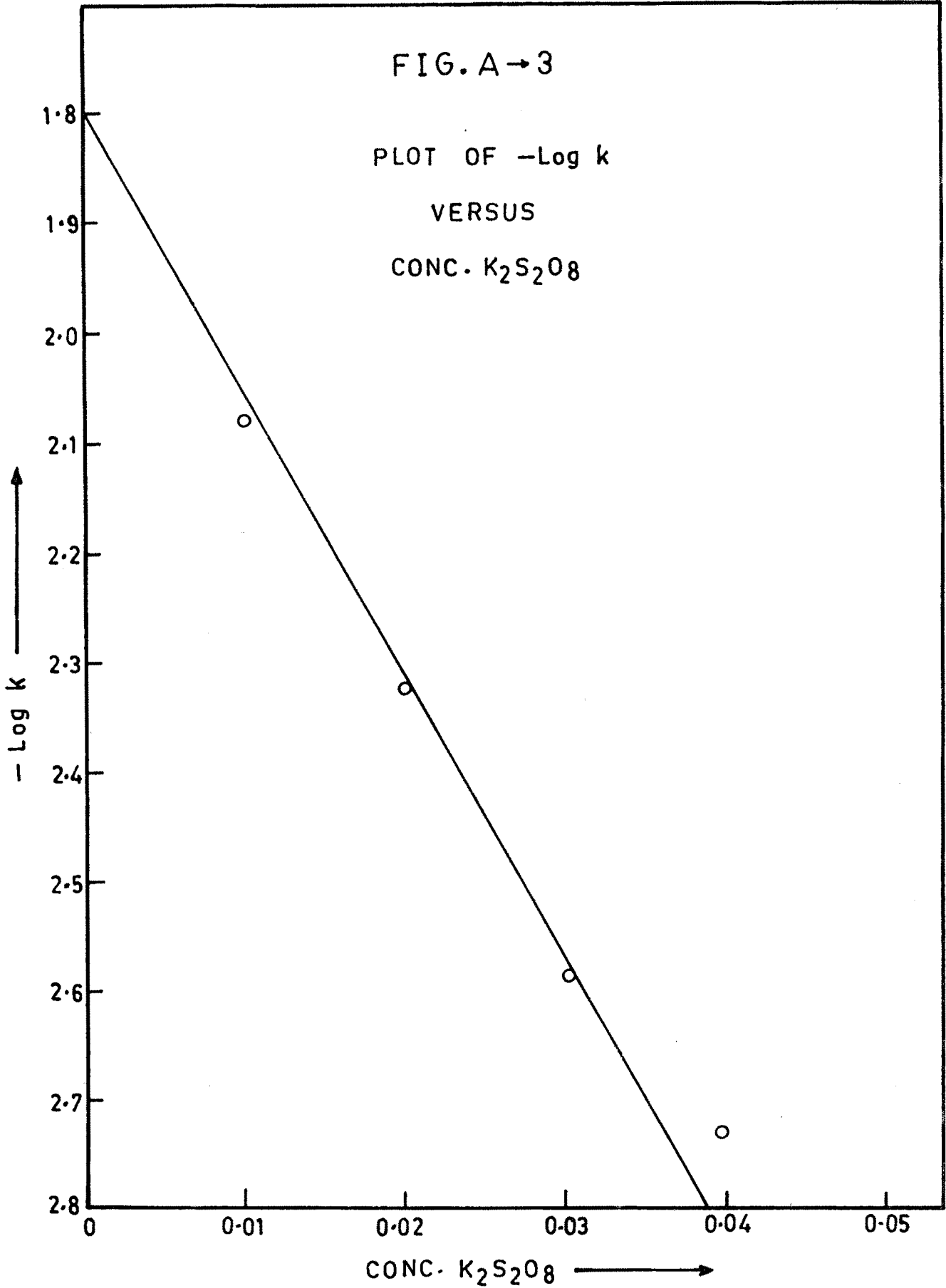
FIG. A → 4

PLOT OF $Log\left(^{-dc}/_{dt}\right)$

VERSUS

$Log\left[S_2 O_8^{2-}\right]$

$n = 1.0$

$Log\left(^{-dc}/_{dt}\right)$

$Log\left[S_2 O_8^{2-}\right]$
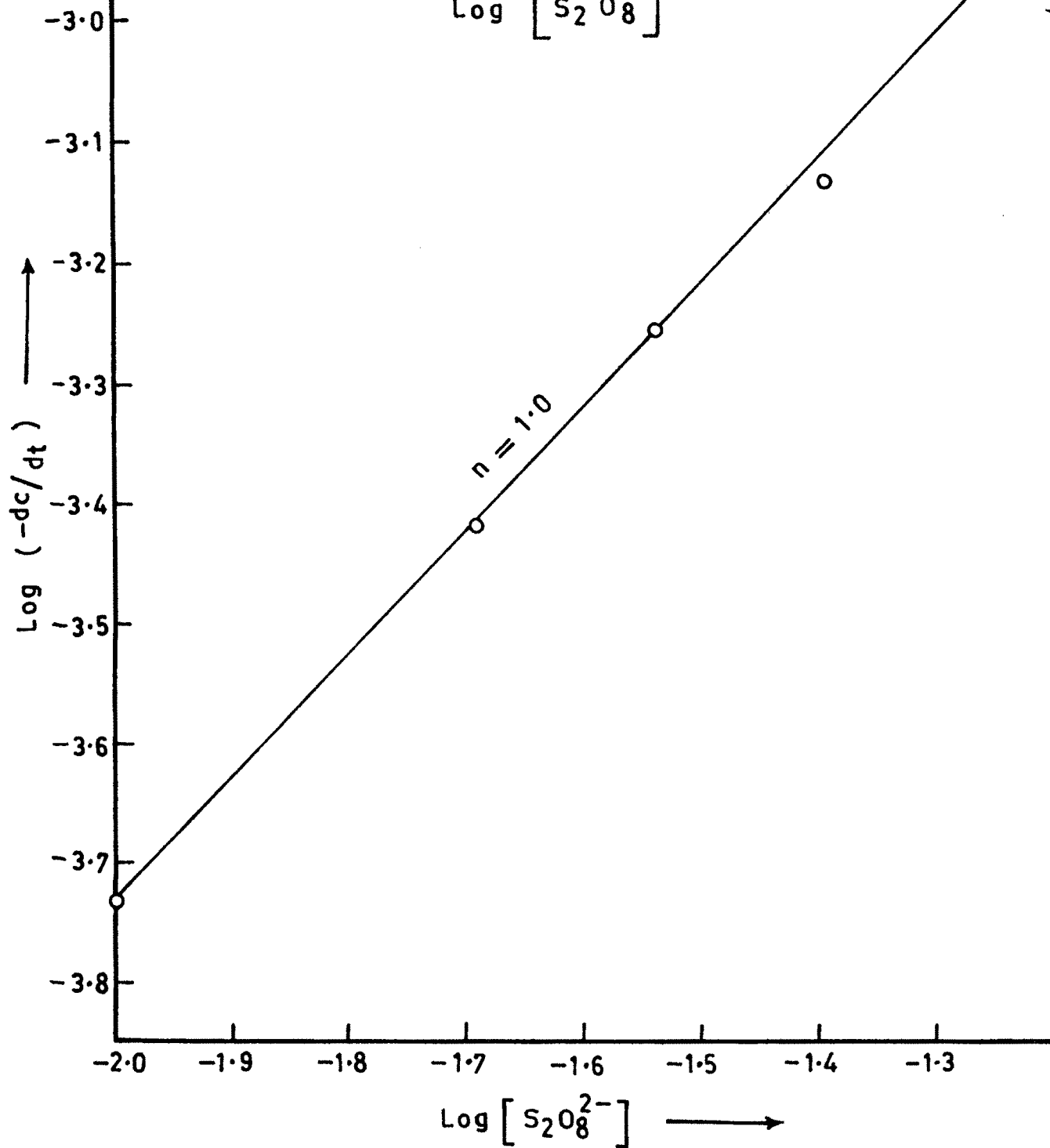
FIG. A → 5

EFFECT OF AMIDE CONCENTRATION

$K_2S_2O_8 = 2.0 \times 10^{-2}$ M

$AgNO_3 = 1.0 \times 10^{-3}$ M

TEMP. = 35°C

[AMIDE]

I → 0.05 M

II → 0.10 M

III → 0.15 M

IV → 0.20 M

V → 0.25 M
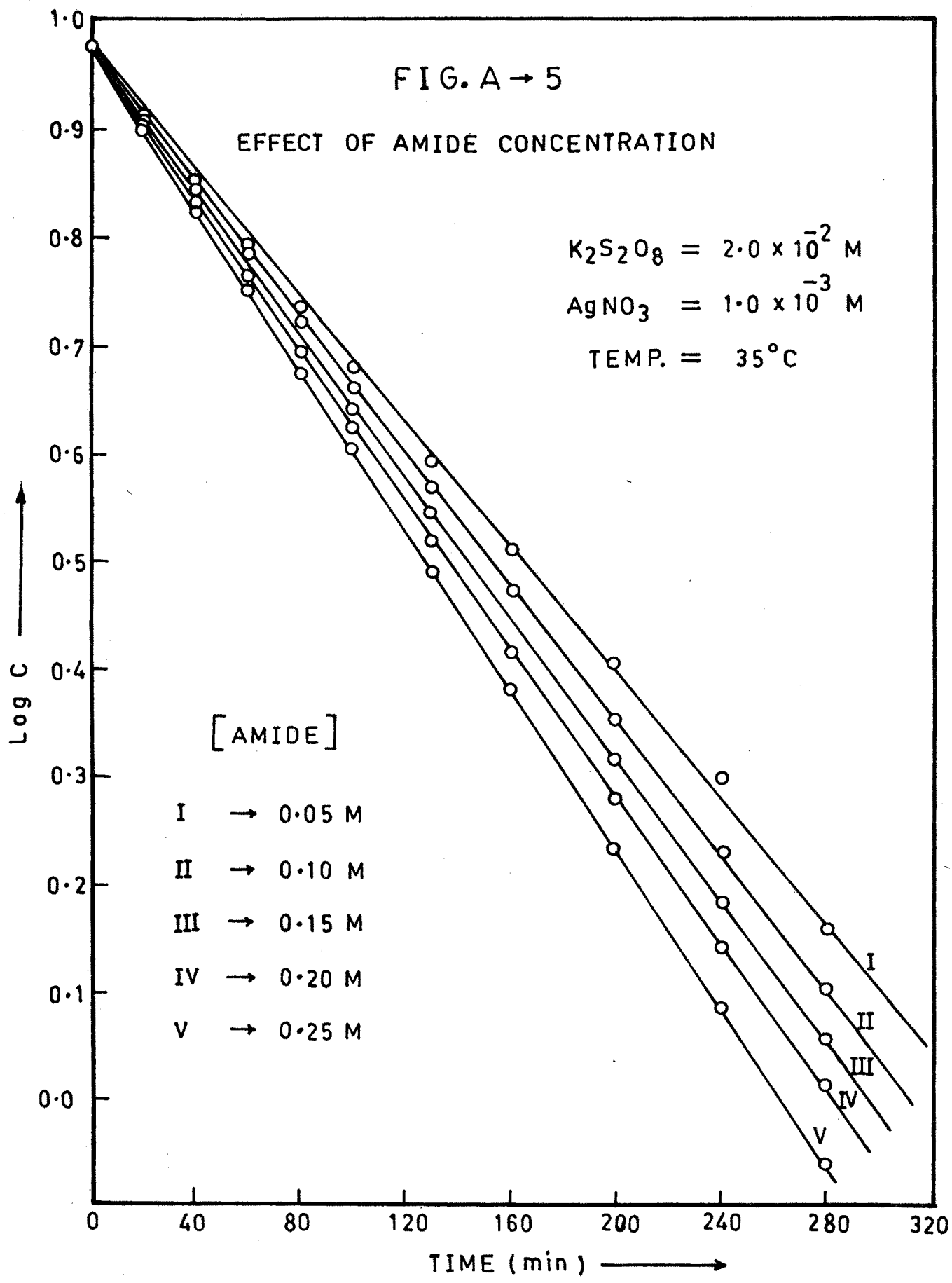
FIG. A→6

PLOT OF CONC. OF AMIDE

VERSUS

$$\frac{\text{AMIDE}}{k}$$
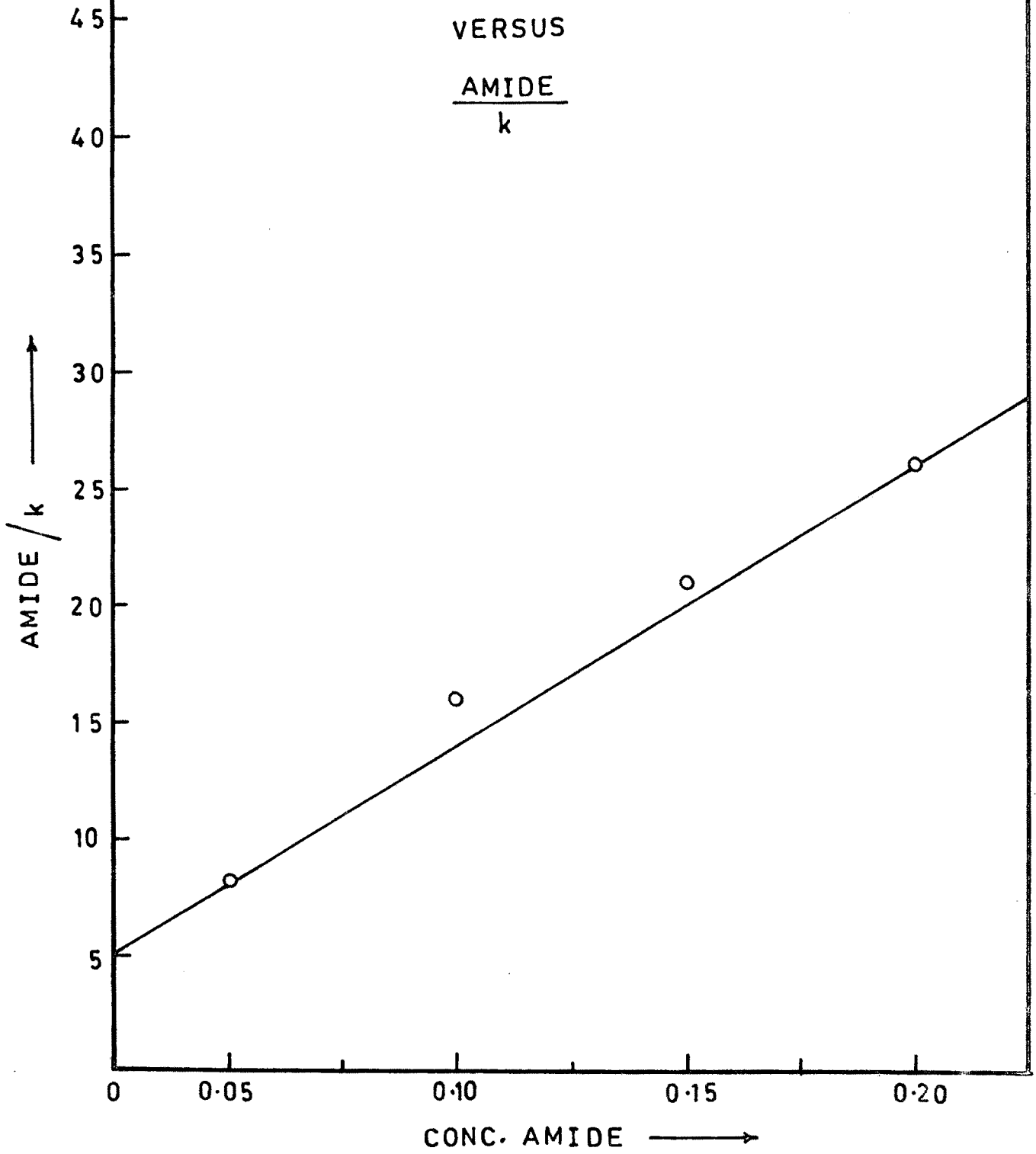
FIG. A→7

PLOT OF $Log(^{-dc}/_{dt})$

VERSUS

$Log \left[C_o \right]$
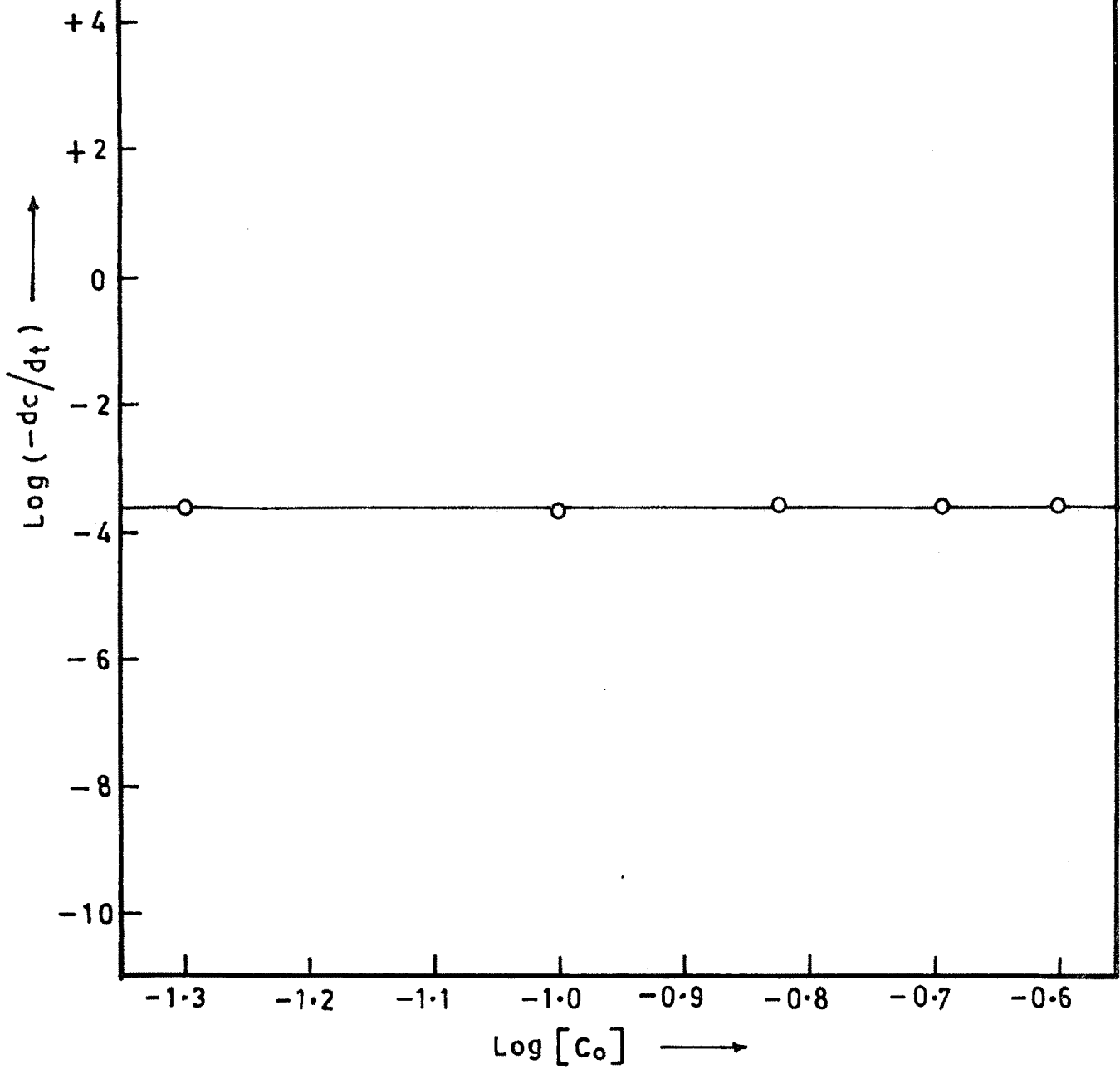
FIG. A→8

AMIDE = 0.1 M

$K_2S_2O_8$ = 2.0×10^{-2} M

TEMP. = 35°C

$[AgNO_3]$

I → 1.0×10^{-3} M

II → 1.5×10^{-3} M

III → 2.0×10^{-3} M

IV → 3.0×10^{-3} M

V → 4.0×10^{-3} M

Log C

TIME (min.) →

FIG. A→9

PLOT OF k VERSUS $\left[Ag^+\right]$.

y-axis: $k \times 10^3 \ min.^{-1}$

x-axis: $\left[Ag^+\right] \times 10^3$
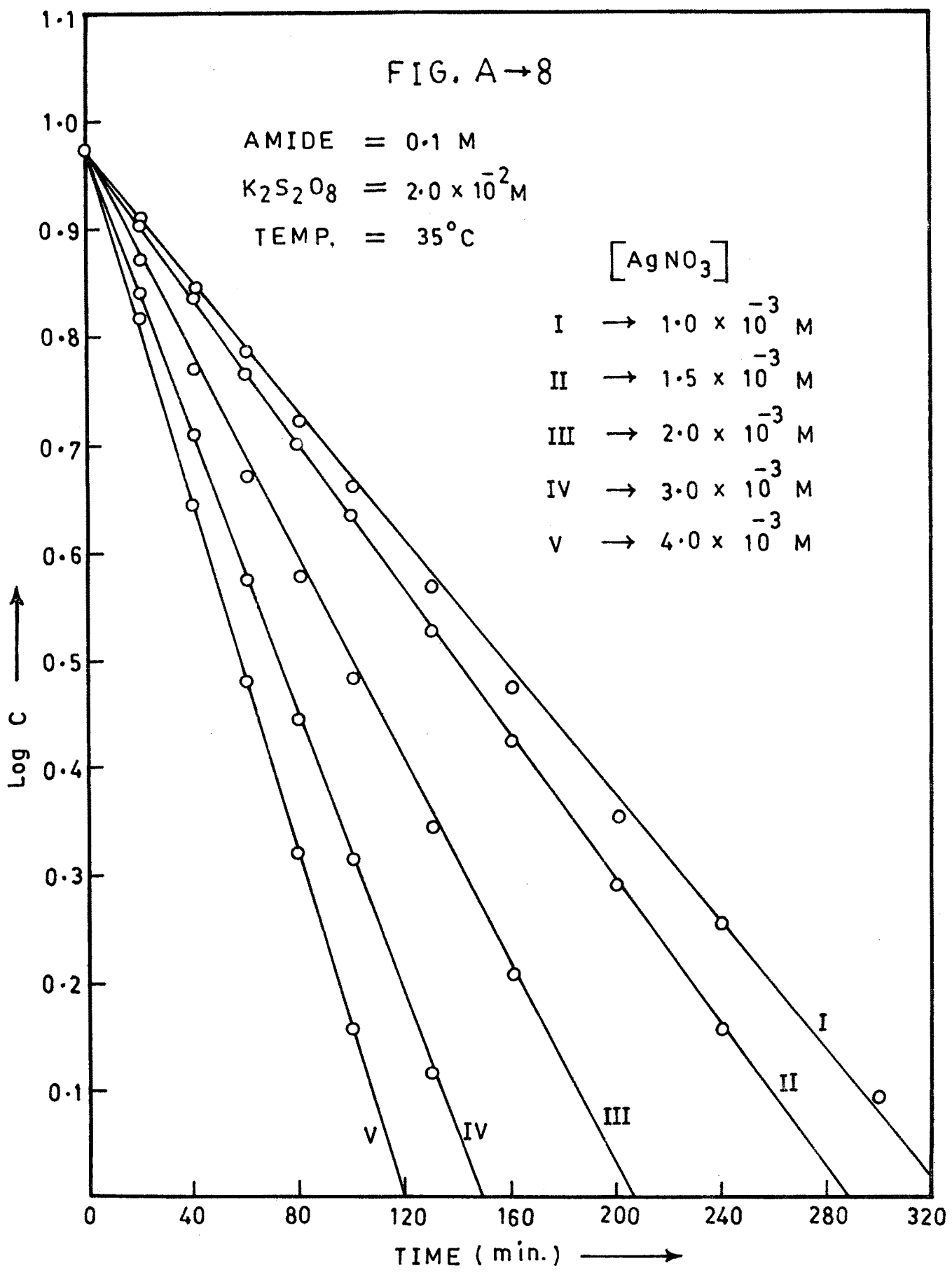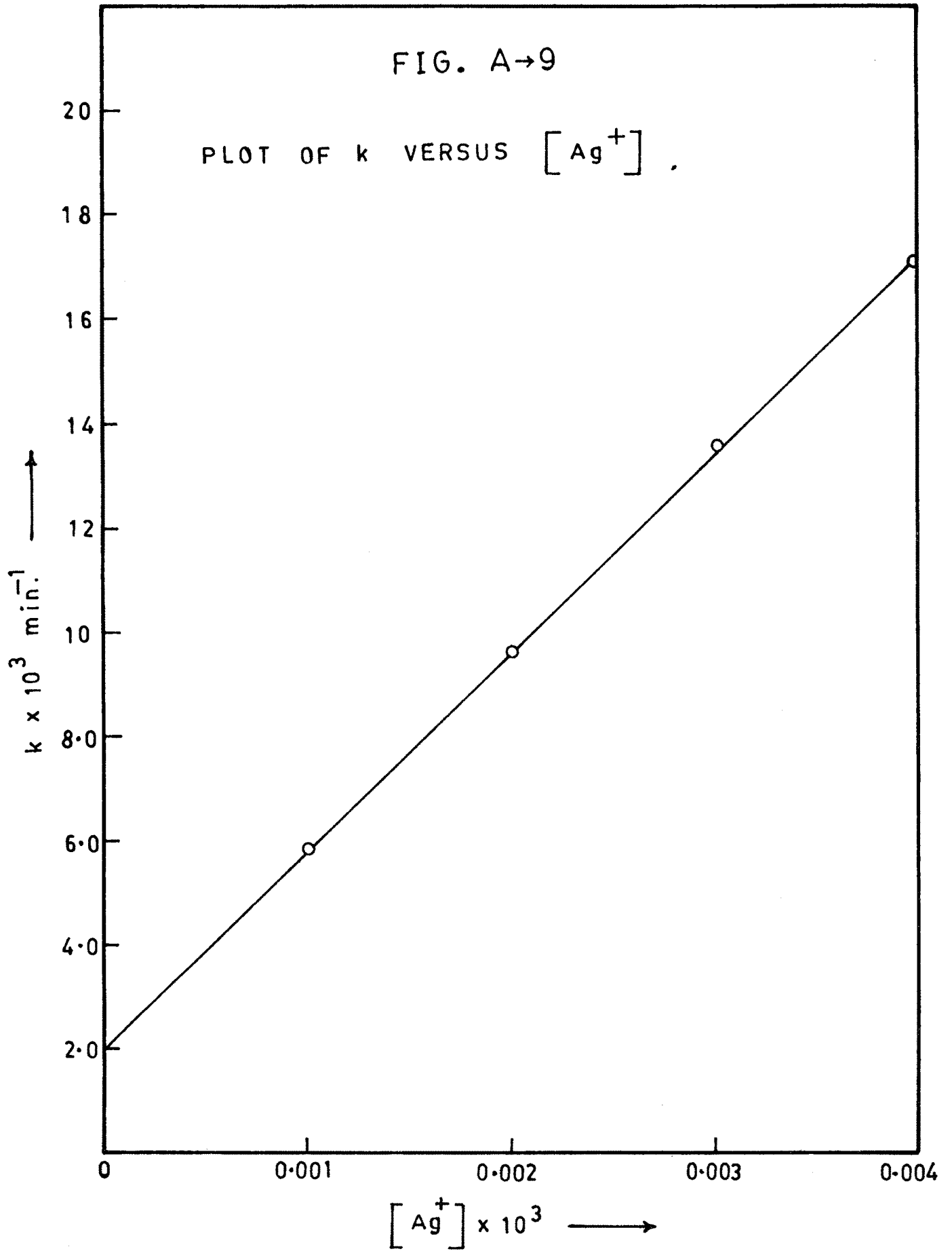
FIG. A → 10

EFFECT OF TEMPERATURE

AMIDE = 0·1 M

$K_2S_2O_8$ = 2·0 × 10^{-2} M

$AgNO_3$ = 1·0 × 10^{-3} M

(TEMP.)

I   →   25°C

II →   30°C

III →   35°C

IV →   40°C

V   →   45°C

Log C

TIME (min) →
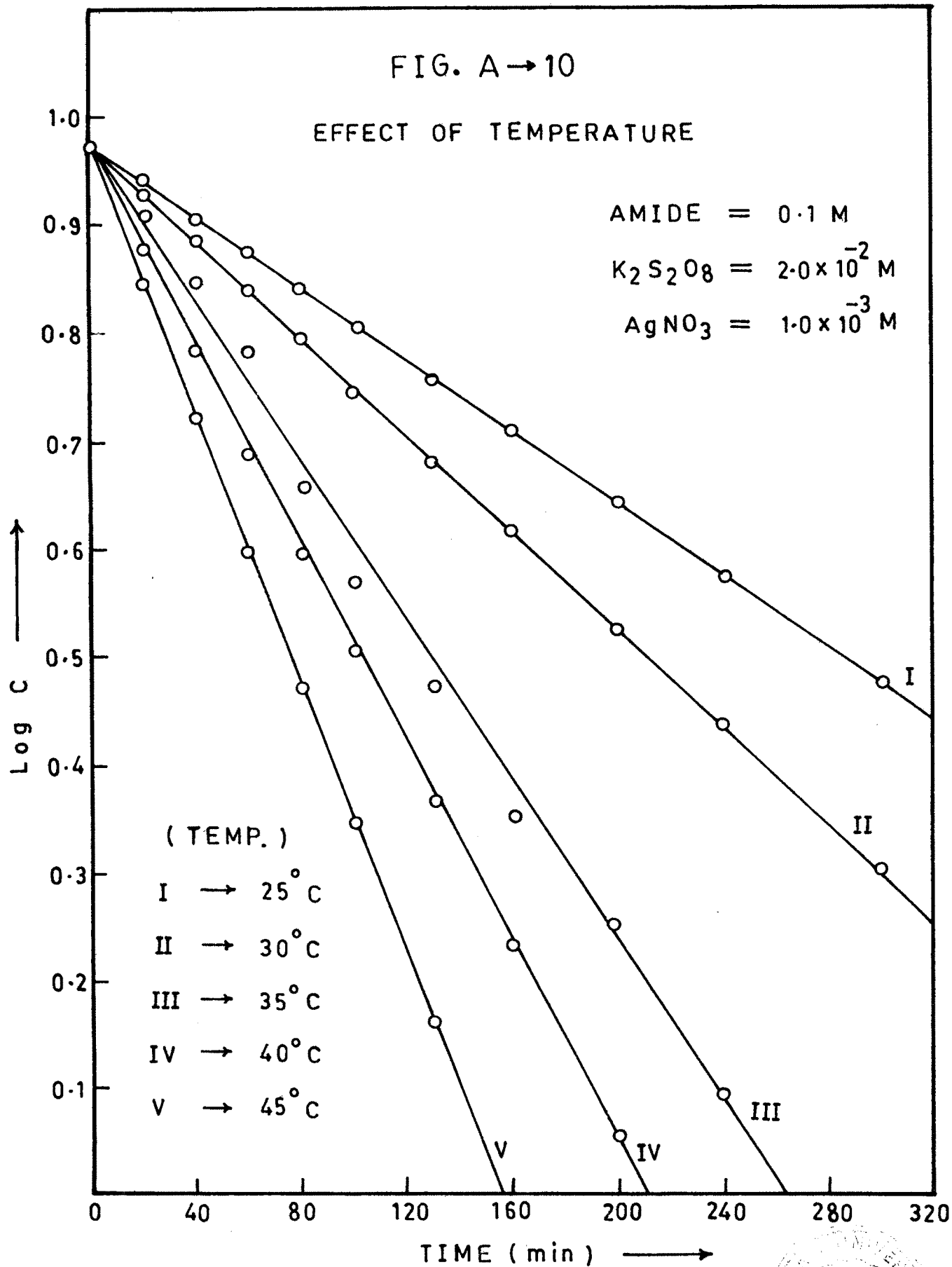
FIG. A → 11

PLOT OF — Log k

VERSUS

$\frac{1}{T} \times 10^3$
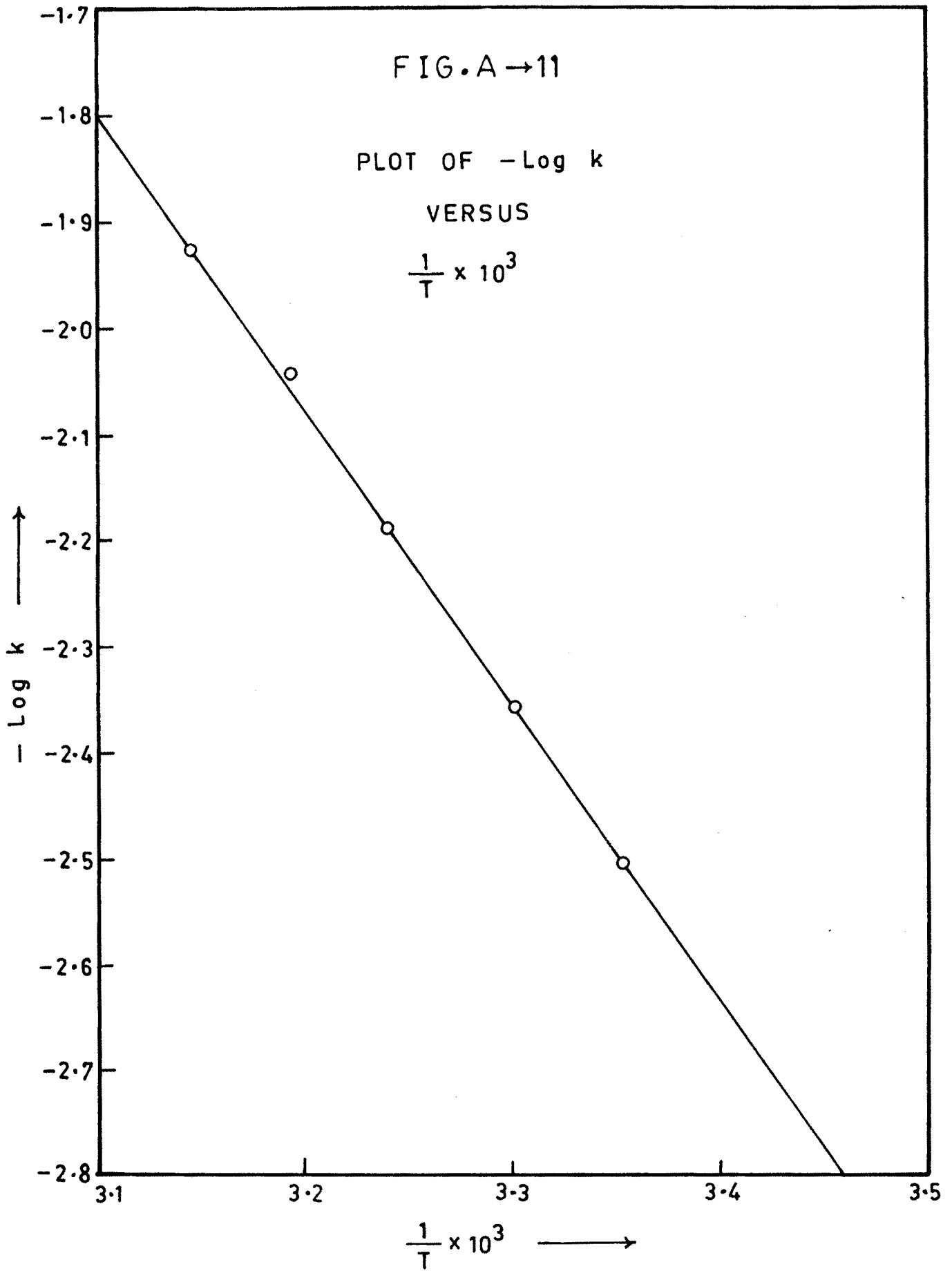
FIG. A→12

PLOT OF $\log\left[\dfrac{k_r}{kT/h}\right]$

VERSUS

$\dfrac{1}{T} \times 10^3$
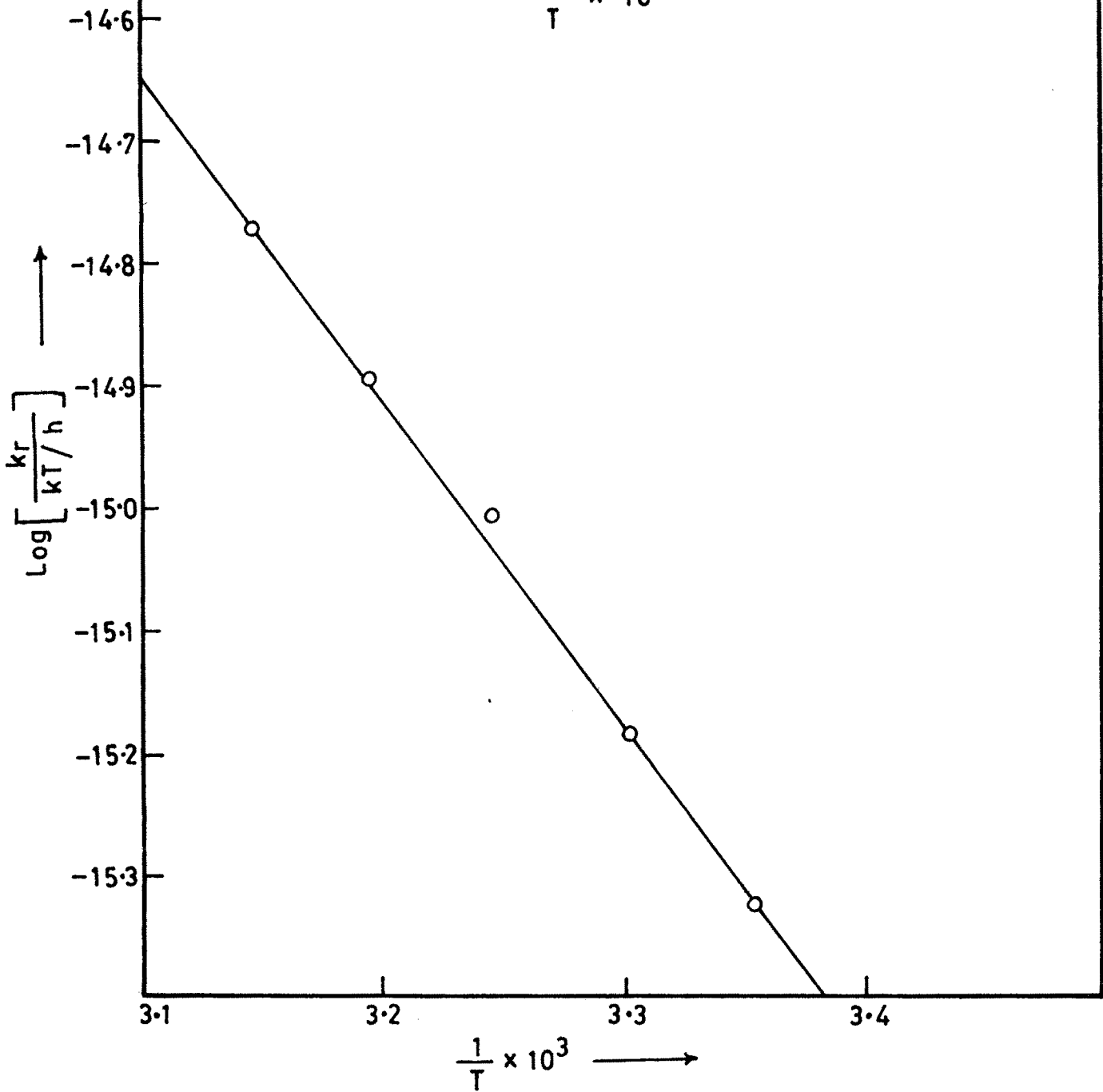
FIG. A→13

EFFECT OF IONIC STRENGTH.

AMIDE = 0.1 M

$K_2S_2O_8$ = 2.0×10^{-2} M

$AgNO_3$ = 1.0×10^{-3} M

TEMP. = 35°C

$[K_2SO_4]$

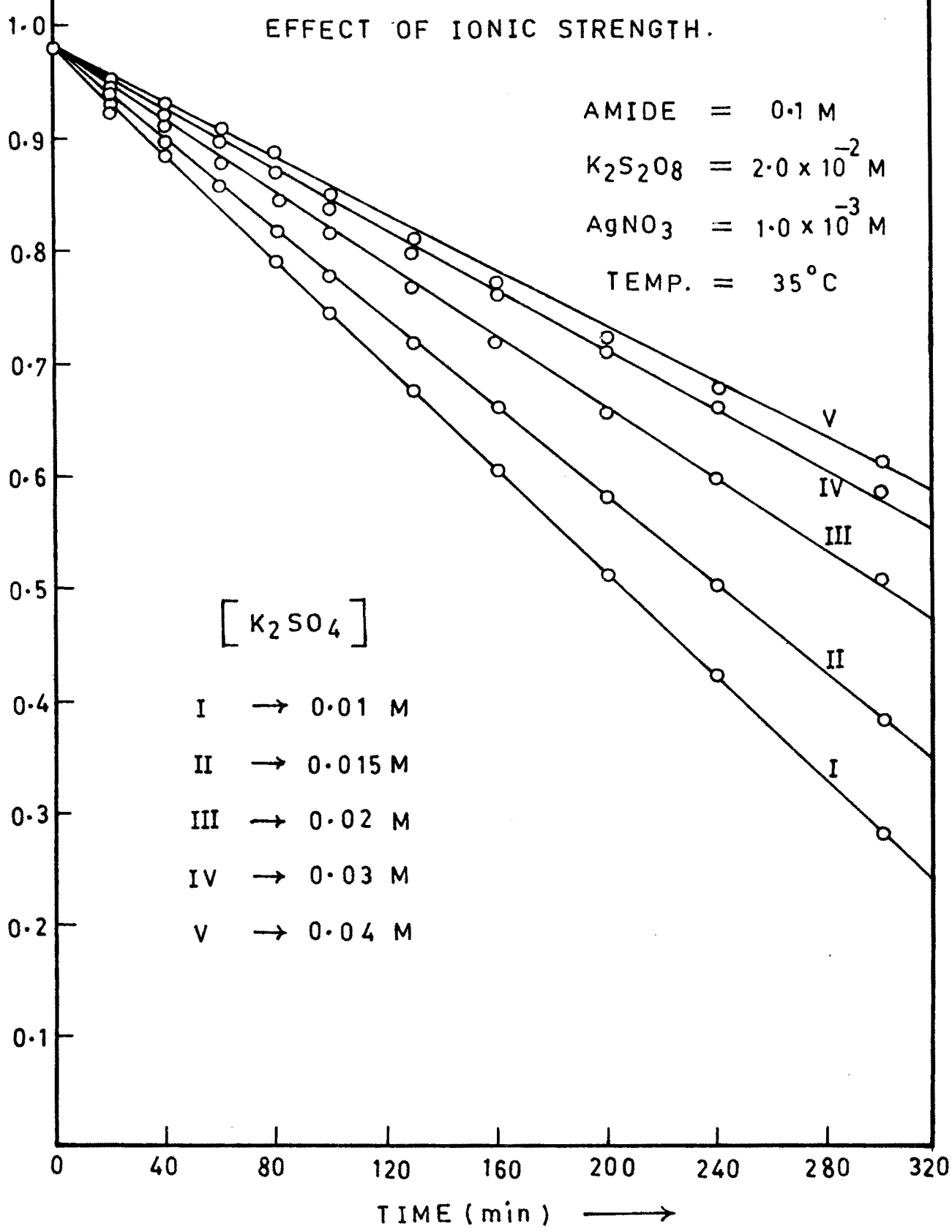I → 0.01 M

II → 0.015 M

III → 0.02 M

IV → 0.03 M

V → 0.04 M

Log C

TIME (min) →

FIG. A → 14(A)

PLOT OF Log k
VERSUS
$(\mu)^{1/2}$

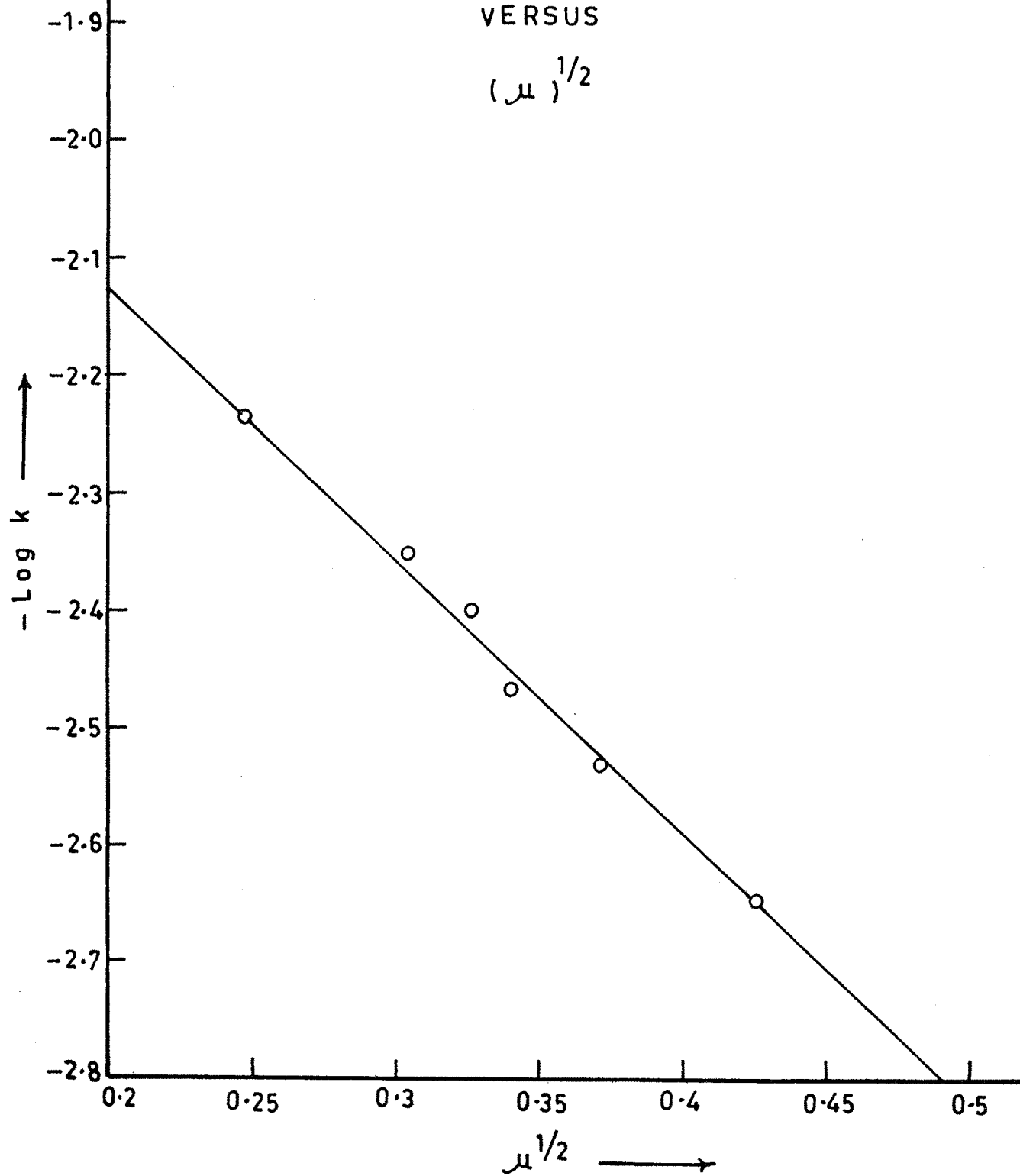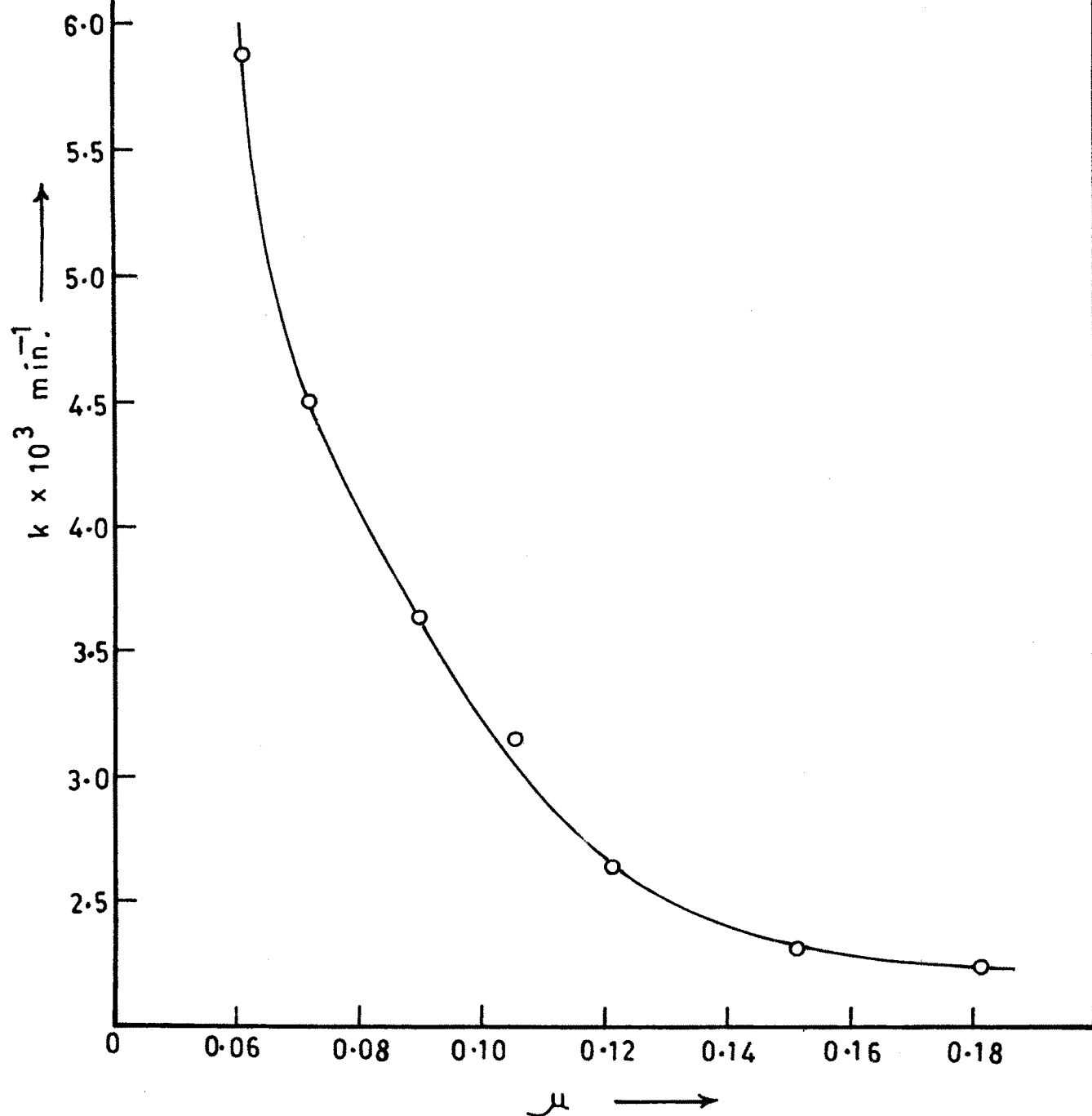$\mu^{1/2}$ →

−Log k

FIG. A → 14·(B)

PLOT OF k

VERSUS

μ

FIG. A→15

SPECIFIC ION EFFECT

AMIDE $= 0.1$ M

$K_2S_2O_8 = 2.0 \times 10^{-2}$ M
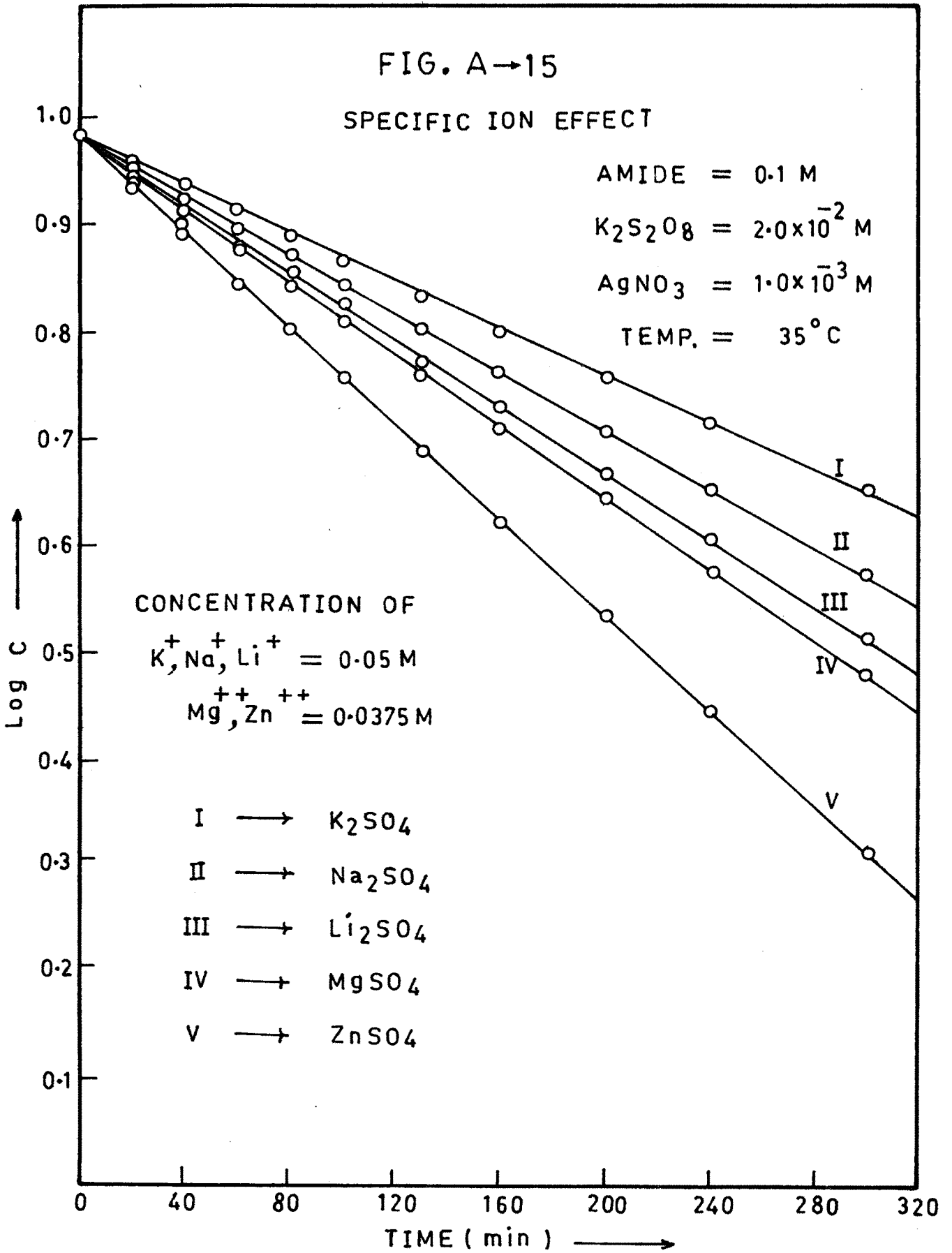
$AgNO_3 = 1.0 \times 10^{-3}$ M

TEMP. $= 35°C$

CONCENTRATION OF

$K^+, Na^+, Li^+ = 0.05$ M

$Mg^{++}, Zn^{++} = 0.0375$ M

I $\longrightarrow$ K_2SO_4

II $\longrightarrow$ Na_2SO_4

III $\longrightarrow$ Li_2SO_4

IV $\longrightarrow$ $MgSO_4$

V $\longrightarrow$ $ZnSO_4$

Log C

TIME (min)

FIG. A→16

EFFECT OF (H$^+$).

AMIDE = 0·1 M

K$_2$S$_2$O$_8$ = 2·0 x 10^{-2} M

AgNO$_3$ = 1·0 x 10^{-3} M

TEMP. = 35 °C

[H$_2$SO$_4$]

I   ⟶   0·10   M

II   ⟶   0·075 M

III ⟶   0·050 M

IV ⟶   0·025 M

V   ⟶   NIL

Log C

TIME (min.) ⟶
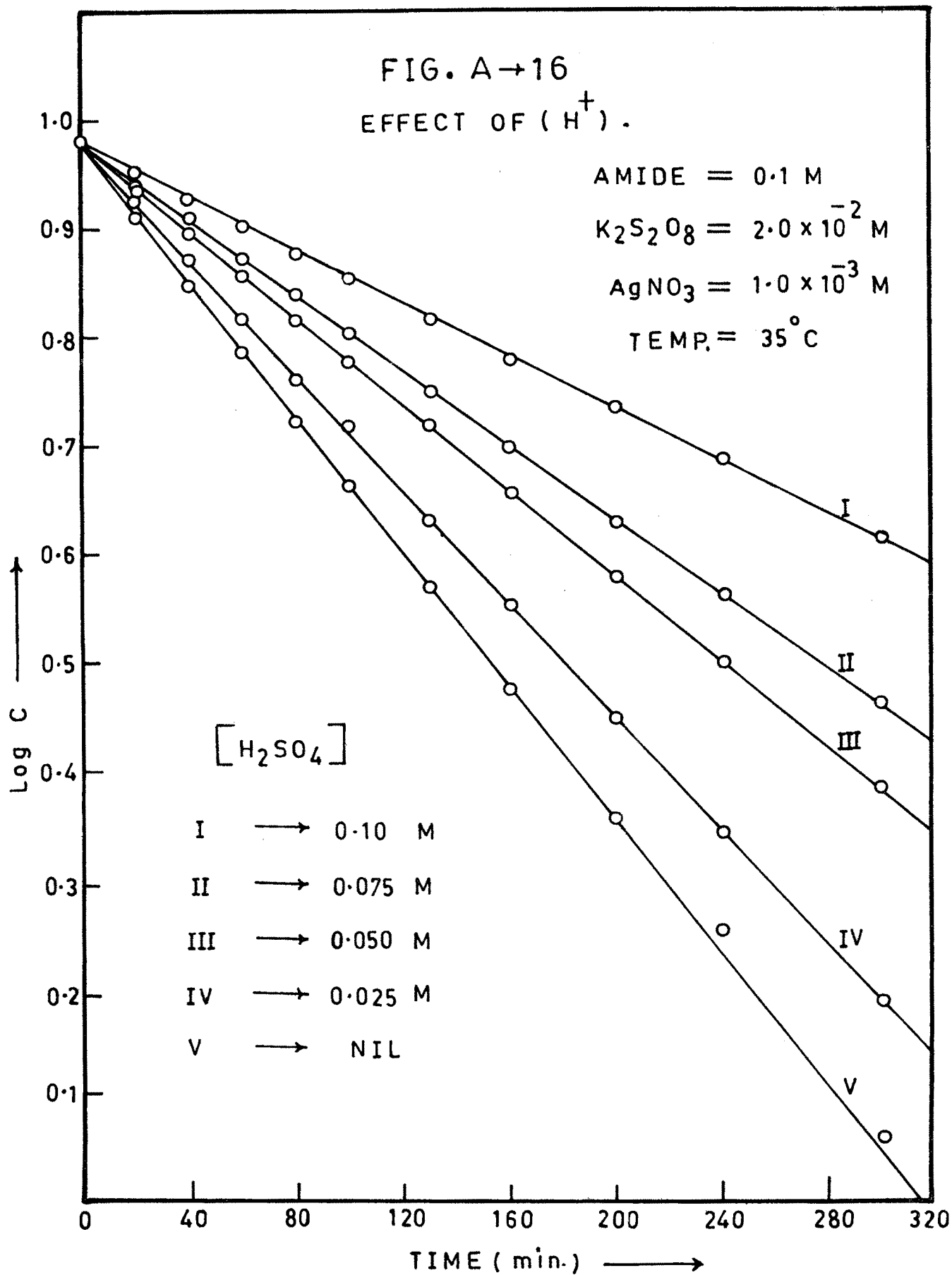
FIG. A→17

EFFECT OF (H^+) AT CONSTANT μ.

AMIDE $=$ 0·1 M

$K_2S_2O_8 =$ 2·0 $\times 10^{-2}$ M

$AgNO_3 =$ 1·0 $\times 10^{-3}$ M

μ $=$ 0·361

$\left[H_2SO_4\right]$

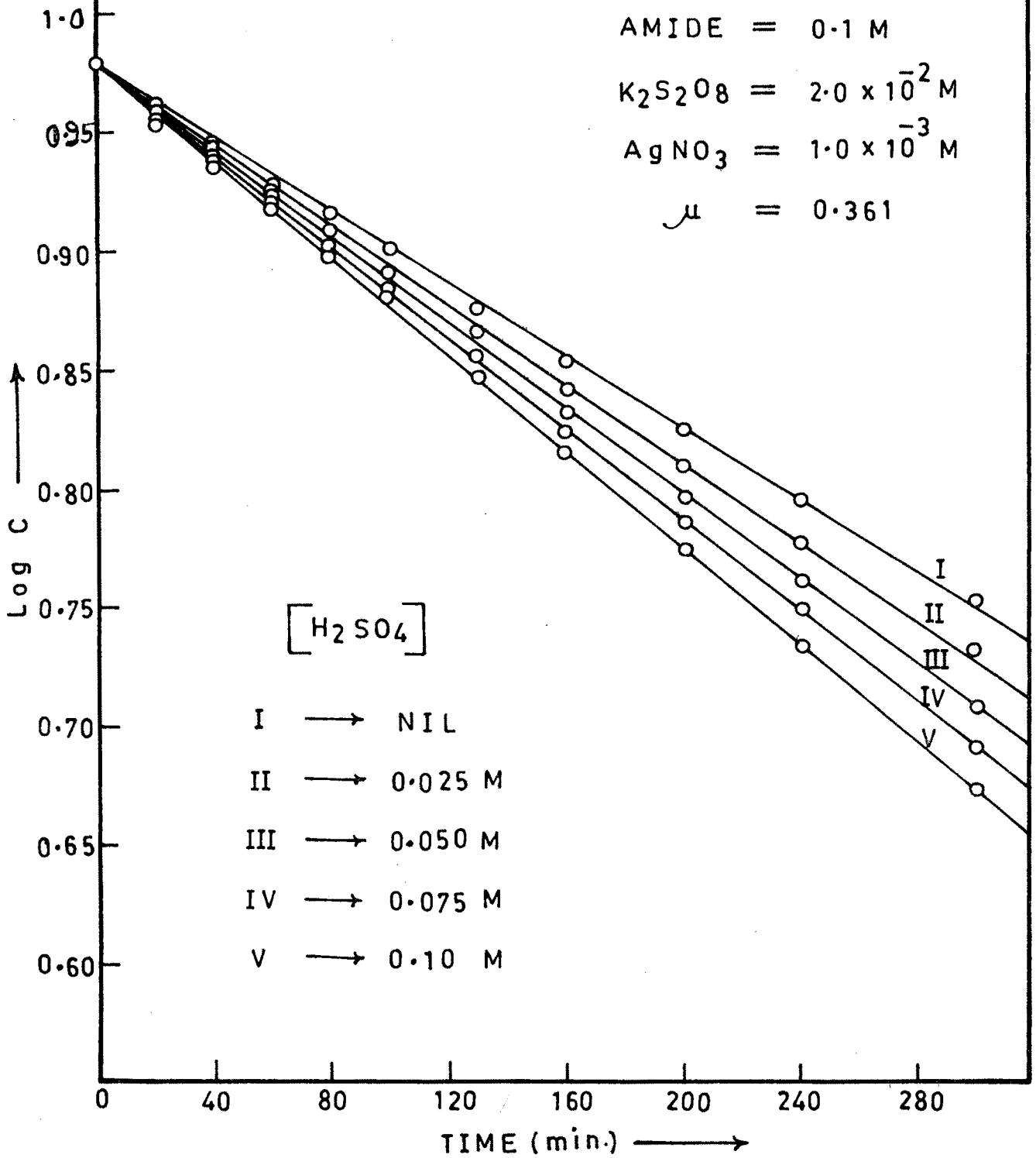|		
I	$\longrightarrow$	NIL
II	$\longrightarrow$	0·025 M
III	$\longrightarrow$	0·050 M
IV	$\longrightarrow$	0·075 M
V	$\longrightarrow$	0·10 M

Log C

TIME (min.) $\longrightarrow$

FIG. A → 18

EFFECT OF ALLYL ALCOHOL.

AMIDE = 0·1 M

$K_2S_2O_8$ = 2·0 × 10^{-2} M

$AgNO_3$ = 1·0 × 10^{-3} M

TEMP. = 35°C

[ALLYL ALCOHOL]

I ────→ 0·001 M

II ────→ 0·005 M

III ────→ 0·010 M

Log C

TIME (min.) ────→
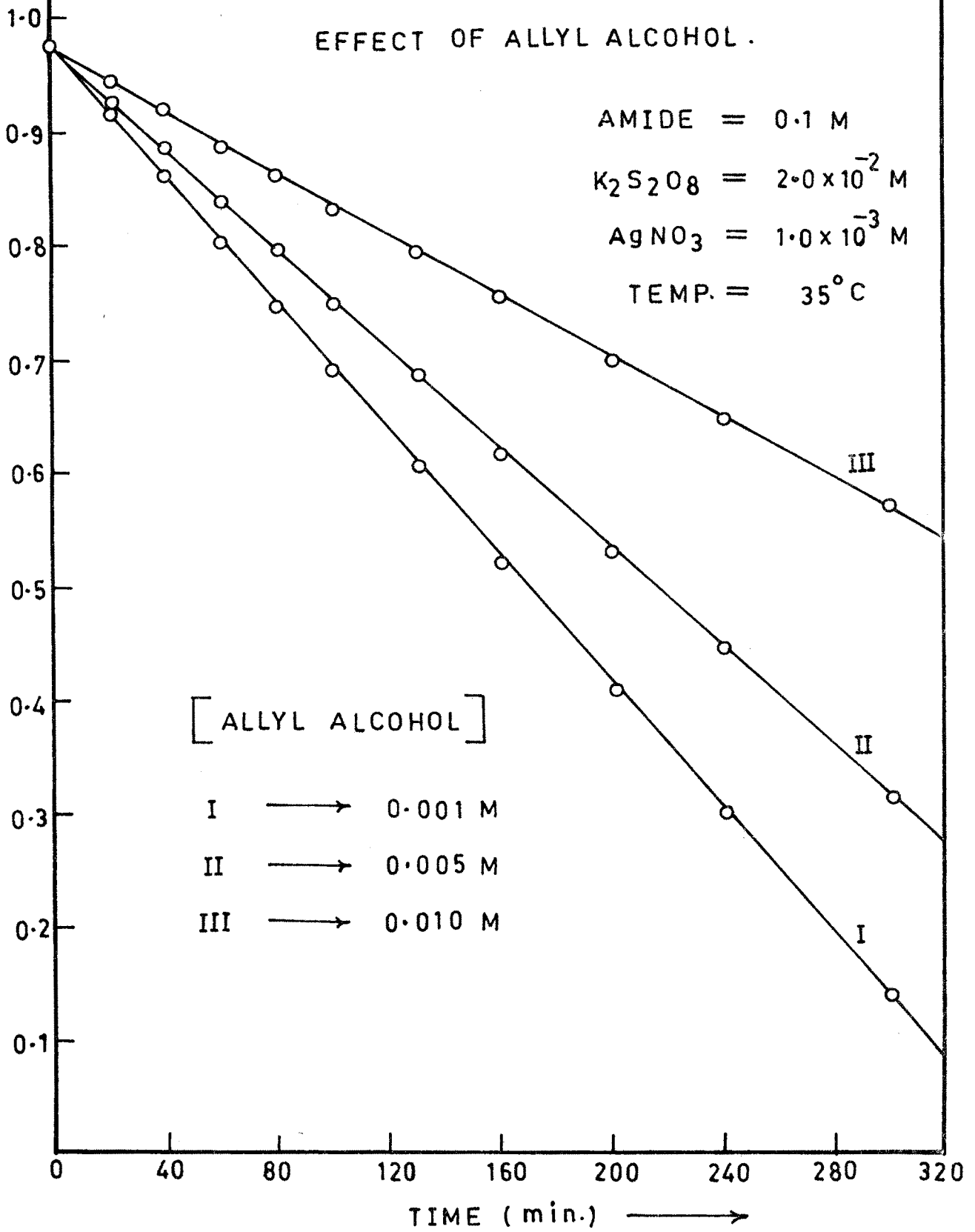
FIG. A→19
EFFECT OF ALLYL ACETATE

AMIDE $= 0.1$ M

$K_2S_2O_8 = 2.0 \times 10^{-2}$ M

$AgNO_3 = 1.0 \times 10^{-3}$ M

TEMP. $= 35°$ C

[ALLYL ACETATE]

I $\longrightarrow$ NIL

II $\longrightarrow$ 0.001 M

III $\longrightarrow$ 0.005 M

IV $\longrightarrow$ 0.010 M
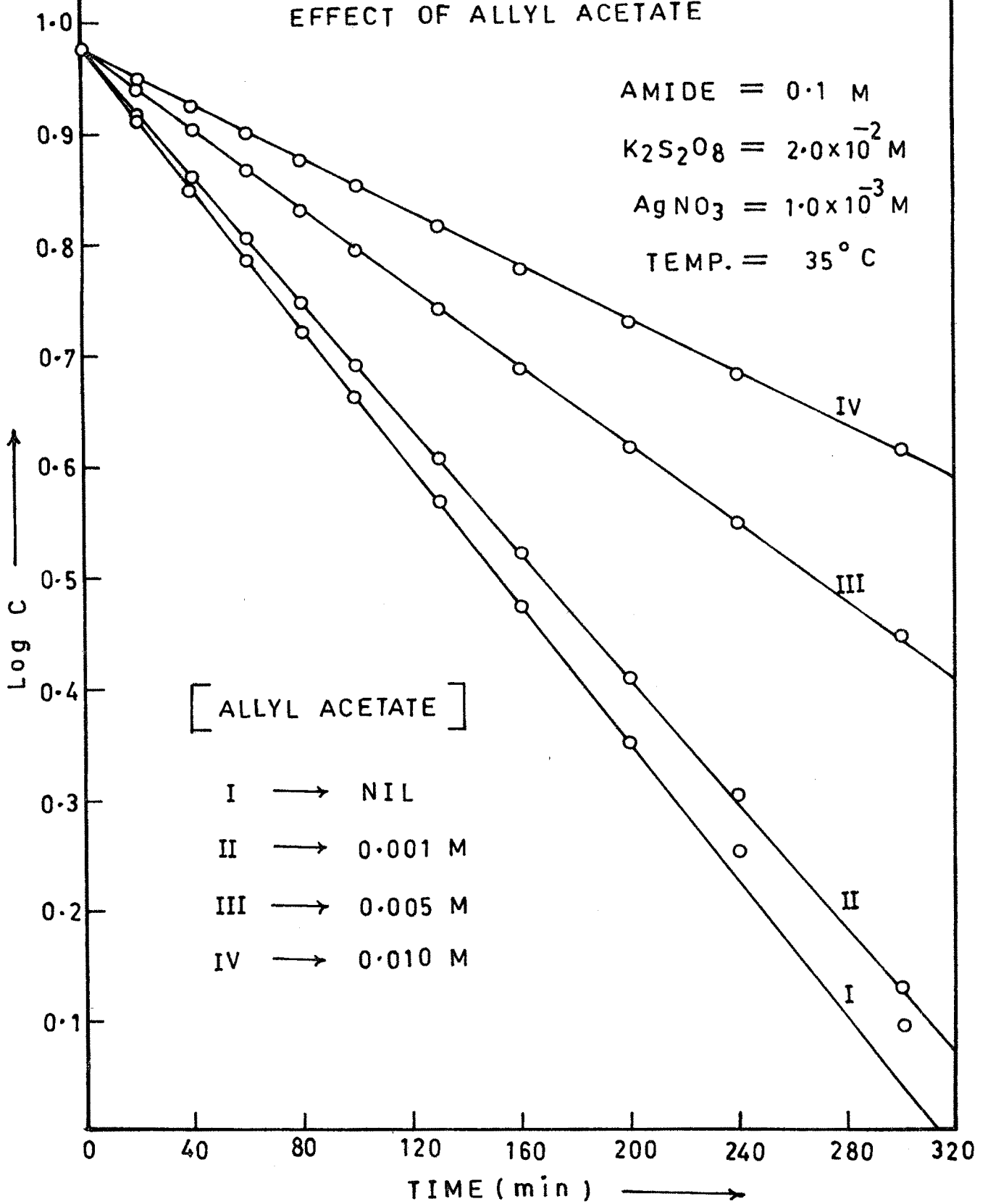
Log C

TIME (min)

FIG. A→20

MOLE RATIO

$K_2S_2O_8 = 5.0 \times 10^{-2}$ M

$AgNO_3 = 1.0 \times 10^{-3}$ M

TEMP. $= 35^{\circ}C$

Q

P

Log C

TIME (min) →