CHAPTER - IV

OXIDATION OF ACETYLAMINOACETAMIDE

Preliminary experiments showed that the reaction of $S_2O_8^{2-}$ ion with the amide is practically zero at room temperature and without any catalyst. The reactions prodeed with a measurable velocity at 35°C and above, provided that a small amount of catalyst such as $AgNO_3$ (1.0×10^{-3}M) is added to the reaction mixture. Thus the reaction was first studied at 35°C taking the overall concentrations of amide as 0.1M, $K_2S_2O_8$ as 2.0×10^{-2}M and $AgNO_3$ as 1.0×10^{-3}M. The kinetic data of this run is recorded in the following table (Table B-1).

The data of the table (Table B-1) shows 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 amide 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 amide, another kinetic run having equimolar concentrations (0.02M) of the two reactants was carried out. The results of this kinetic data are recorded in Table B-2.

TABLE B-1

$K_2S_2O_8$= 2.0 $\times 10^{-2}$M, Amide 0.1M ,

$AgNO_3$ = 1.0$\times 10^{-3}$ M, Temperature = 35°C

Time (min)	C	$k_1 \times 10^3 min^{-1}$
0	9.46	-
20	7.86	9.270
40	6.54	9.228
60	5.45	9.191
80	4.54	9.177
100	3.78	9.175
130	2.88	9.149
160	2.20	9.118
200	1.54	9.078
240	1.08	9.044
300	0.64	8.976
360	0.38	8.932
Mean $k_1 \times 10^3 min^{-1}$		9.121

TABLE B-2

Amide = $K_2S_2O_8$ = 2.0 X 10^{-2}M, $AgNO_3$ = 1.0X 10^{-3} M

Temperature = 35° C

Time (min)	C	k x 10^3min^{-1}
0	9.44	-
20	7.38	12.310
40	5.78	12.270
60	4.54	12.200
80	3.56	12.190
100	2.80	12.150
130	1.95	12.130
160	1.37	12.070
200	0.85	12.030
240	0.53	11.990
300	0.26	11.980
360	0.13	11.910
Mean k X 10^3min^{-1}		12.110

Here again, fairly constant values of the first order specific rate are obtained, suggesting that the order with respect to $S_2O_8^{2-}$ is one.

EFFECT OF PEROXYDISULPHATE CONCENTRATION :

In order to investigate the effect of different concentrations of $S_2O_8^{2-}$ ion on the reaction rate, three more kinetic runs having different concentrations of $S_2O_8^{2-}$ were carried out. Table B-3 contains the results of these kinetic runs and the kinetic data of Table B-1 has been included in this table for the sake of comparison. These data also find a graphic representation in Fig. B-1.

The values of the first order rate constant (Viz.k_1) have been evaluated from the initial slope of the curves as shown in Fig. B-1, as well as calculated at different times by integration method.

The corresponding values of the first order rate constants for the self-decomposition of $S_2O_8^{2-}$ have been tabulated directly, as already mentioned in the experimental section of Chapter-III.

On examination of the data (Table B-3), it indicates that by increasing the concentrations of $K_2S_2O_8$ bring about a decrease in the first order rate constant. It may also be seen that in any particular run, especially that containing high concentration of $K_2S_2O_8$, the rate constant slightly decreases with time.

Now to study this effect under the conditions of constant ionic strength as well as at constant K^+ ion

TABLE B-3

Amide = 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	$k_1 x10^3$ min^{-1}	C	$k_1 x10^3$ min^{-1}	C	$k_1 x10^3$ min^{-1}	C	$k_1 x10^3$ min^{-1}
0	4.94	-	9.46	-	14.35	-	19.34	-
20	3.89	11.95	7.86	9.270	12.67	6.219	17.96	3.697
40	3.08	11.81	6.54	9.228	11.21	6.172	16.71	3.656
60	2.45	11.69	5.45	9.191	9.95	6.102	15.55	3.639
80	1.96	11.55	4.54	9.177	8.83	6.067	14.47	3.627
100	1.58	11.40	3.78	9.175	7.84	6.045	13.48	3.611
130	1.14	11.28	2.88	9.149	6.57	6.010	12.12	3.596
160	0.83	11.15	2.20	9.118	5.52	5.971	10.90	3.586
200	0.56	10.91	1.54	9.078	4.38	5.934	9.49	3.567
240	0.38	10.69	1.08	9.044	3.50	5.880	8.27	3.541
300	0.22	10.37	0.64	8.976	2.51	5.813	6.76	3.505
360	0.13	10.10	0.38	8.932	1.82	5.736	5.58	3.453
$k_1 x10^3 min^{-1}$		11.170		9.121		5.995		3.589
$k_2 x10^3 min^{-1}$		1.338		1.259		1.164		1.040
k $x10^3 min^{-1}$		9.832		7.862		4.831		2.549

TABLE B-4

Amide = 0.1M, $AgNO_3$ = 1.0 X 10^{-3}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 0.02 M-$Na_2S_2O_3$ used (Viz. C)			
0	4.95	9.48	14.36	19.35
20	4.10	8.53	13.31	18.51
40	3.40	7.69	12.36	17.71
60	2.83	6.93	11.48	16.96
80	2.25	6.25	10.66	16.24
100	1.98	5.64	9.91	15.56
130	1.52	4.84	8.90	14.60
160	1.17	4.16	7.99	13.71
200	0.84	3.40	6.94	12.63
240	0.61	2.79	6.05	11.64
300	0.38	2.07	4.94	10.33
360	0.24	1.55	4.05	9.17
$k_1 X 10^3 min^{-1}$	9.019	5.155	3.670	2.159
$k_2 X 10^3 min^{-1}$	0.690	0.680	0.660	0.660
$k\ X 10^3 min^{-1}$	8.329	4.475	3.010	1.499

concentration, four kinetic runs having different concentrations of $S_2O_8^{2-}$ were studied. The kinetic data of these 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 on account of pressure on space and only the corresponding values of the rate constants (Viz.k_2) have been directly given at the end of each table.

From the results (Table B-4) it is clear that, when the concentration of $S_2O_8^{2-}$ was increased, the first order rate constant decreased.

Table B-5 shows the comparison between k values with increasing concentration of $S_2O_8^{2-}$ without and with K_2SO_4 to maintain constant ionic strength and constant K^+ ion concentration.

TABLE B-5

Amide = 0.1M, $AgNO_3$ = 1.0 X 10^{-3}M, Temperature = 35°C

Conc. $[K_2S_2O_8]$M without $[K_2SO_4]$	k X 10^{-3} min^{-1}	Conc. $[K_2S_2O_8]$M with constant K^+ ionic strength	k X 10^{3} min^{-1}
0.01	9.832	0.01	8.329
0.02	7.862	0.02	4.475
0.03	4.831	0.03	3.010
0.04	2.549	0.04	1.499

From the results recorded in Table B-5, it shows that at constant K^+ ionic strength the decrease in the rate constant with increasing $K_2S_2O_8$ concentration has been minimised.

A plot of -log k versus concentration of peroxydisulphate is found to be linear as shown in Fig. B-3. The following relationship between -log k and concentration of peroxydisulphate is being followed

$$-\log k = 1.85 + 1.55 \left[S_2O_8^{2-}\right]_o$$

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

ORDER WITH RESPECT TO PEROXYDISULPHATE :

In order to confirm the unimolecular behaviour of the reaction with respect to $K_2S_2O_8$, the data of Table B-3 was subjected to Van't Hoff's differential method on the same lines as described in connection with the similar study of amino-acetamide.

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 initial slope as given in Table B-6.

The values of dc/dt and concentrations of $S_2O_8^{2-}$ i.e. 'C' are substituted in the Vant' Hoff's equation

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

(Where n is the order)

and the order of reaction is calculated. The values of -dc/dt for different initial concentrations of $S_2O_8^{2-}$ and the values of 'n' calculated thereby are recorded in Table B-7.

TABLE B-6

Conc. $[K_2S_2O_8]$ M	-dc/dt X 10^{-4}	log $S_2O_8^{2-}$	Log(-dc/dt)
0.01	2.000	-2.0000	-3.6990
0.02	3.935	-1.6990	-3.4051
0.03	5.887	-1.5229	-3.2301
0.04	7.946	-1.3979	-3.0990

TABLE B-7

$[K_2S_2O_8]$ M	-dc/dt X 10^{-4}	Order of reaction (n)
0.01 0.02	2.00 3.935	1.016
0.01 0.03	2.000 5.887	1.019
0.01 0.04	2.000 7.946	1.007
0.03 0.04	5.887 7.946	0.9881
0.02 0.03	3.935 5.887	1.002

A plot of $-dc/dt$ versus log $S_2O_8^{2-}$ is shown in Fig. B-4. The slope of the graph is 0.97 as such the order with respect to $S_2O_8^{2-}$ is one, which is confirmed by the values of 'n' as shown in Table B-7.

EFFECT OF AMIDE CONCENTRATION :

The effect of amide concentration on the reaction rate was studied by taking different concentrations of amide. Table B-8 embodies the results of these kinetic runs and are shown graphically in Fig. B-5.

From the results (Table B-8) it is seen that by increasing the concentrations of amide the rate of reaction does not change. Practically the rate remains constant showing the zero order behaviour of the reaction.

The specific rate is seen to be a function of the initial concentration of $S_2O_8^{2-}$ and $CH_3.CO.NHCH_2CONH_2$ governed by the expression.

$$k = k_{max} \cdot \frac{[CH_3.CO.NHCH_2CONH_2]_o}{b + [CH_3.CONH.CH_2.CONH_2]_o}$$

In support of the equation a plot of

$$\frac{[CH_3.CO.NH.CH_2.CONH_2]_o}{k}$$

versus concentration of

$$[CH_3.CO.NH.CH_2.CONH_2]$$

TABLE B-8

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

[Amide] M	0.05	0.10	0.15	0.20	0.25
Time (min)	Vol. (in ml) of 0.02 M- $Na_2S_2O_3$ used (Viz. C)				
0	9.46	9.46	9.45	9.44	9.45
20	7.86	7.86	7.79	7.73	7.67
40	6.56	6.54	6.43	6.34	6.23
60	5.48	5.45	5.31	5.20	5.06
80	4.60	4.54	4.39	4.27	5.12
100	3.87	3.78	3.62	3.51	3.35
130	3.00	2.88	2.72	2.61	2.46
160	2.60	2.20	2.05	1.95	1.81
200	1.69	1.54	1.40	1.32	1.20
240	1.24	1.08	0.96	0.90	0.80
300	0.80	0.64	0.55	0.50	0.44
360	0.52	0.38	0.32	0.28	0.24
$k_1 \times 10^3 min^{-1}$	8.785	9.121	9.559	9.877	10.318
$k_2 \times 10^3 min^{-1}$	1.259	1.259	1.259	1.259	1.259
$k \times 10^3 min^{-1}$	7.526	7.862	8.300	8.618	9.059

was plotted in Fig.B-6, and found to be linear, from which k_{max} and b were evaluated as 0.009817 and 0.0109. From these values k was calculated and found to be equal to 8.198 x $10^3 min^{-1}$ which is identical with 7.862 x$10^3 min^{-1}$, the experimental calculated value.

ORDER WITH RESPECT TO AMIDE :

To confirm the order with respect to amide, the kinetic data of Table B-8 was subjected to Van't Hoff's differential method.

From the initial slope of the concentrations versus time curves, the values of-dc/ dt corresponding to various initial concentrations of amide were evaluated. These values are recorded in Table B-9.

TABLE B-9

Conc. [Amide] M	-dc/dt x 10^{-4}	Log [Co]	Log (-dc/dt)
0.05	3.011	-1.3010	-3.5213
0.10	3.050	-1.0000	-3.5157
0.15	3.150	-0.8239	-3.5017
0.20	2.900	-0.6990	-3.5376
0.25	3.050	-0.6021	-3.5157

A plot of log-dc/dt versus log (amide) is shown in Fig. B-7. The value of the slope of this graph is zero,which suggests that the reaction is zero order with respect to amide. Calculations were made to determine the order of reaction by Van't Hoff's differential method. These values are recorded in Table B-10.

TABLE B-10

Amide M	$(-dc/dt) \times 10^{-4}$	Order of reaction (n)
0.05 0.10	3.011 3.050	0.01858
0.10 0.15	3.050 3.150	0.07945
0.05 0.20	3.011 2.900	0.02708
0.05 0.15	3.011 3.150	0.04109
0.05 0.25	3.011 3.050	0.08011
0.15 0.25	3.150 3.050	0.06317

From the above results (Table B-10) it is confirmed that the order with respect to amide is zero.

EFFECT OF CATALYST CONCENTRATION :

In order to study the effect of catalyst concentration on the reaction rate, the reaction was studied at different concentrations of $AgNO_3$ by keeping the amide and $K_2S_2O_8$ concentrations unchanged. The results of these kinetic runs are recorded in Table B-11 and shown graphically in Fig. B-8.

TABLE B-11

Amide = 0.1 M, $K_2S_2O_8$ = 2.0 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	9.46	9.45	9.44	9.42	9.40
20	7.86	7.68	7.30	6.95	6.49
40	6.54	6.25	5.73	5.15	4.41
60	5.45	5.09	4.49	3.83	3.03
80	4.54	4.15	3.53	2.86	2.08
100	3.78	3.39	2.79	2.15	1.43
130	2.88	2.50	1.98	1.41	0.82
160	2.20	1.85	1.42	0.93	0.47
200	1.54	1.24	0.92	0.55	0.23
240	1.08	0.84	0.61	0.33	0.11
300	0.64	0.46	0.33	0.15	-
360	0.38	0.26	0.19	-	-
$k_1 x10^3 min^{-1}$	9.121	10.207	11.909	14.604	18.565
$k_2 x10^3 min^{-1}$	1.259	1.326	1.326	1.540	1.693
$k x10^3 min^{-1}$	7.862	8.881	10.465	13.064	16.872

The data of the above table (Table B-11) shows that the rate of the reaction was increased linearly when the concentrations of the catalyst were increased showing the first order behaviour of the reaction.

A plot of k versus (Ag^+) concentration is found to be linear as shown in Fig. B-9 and the following relationship is obeyed.

$$k = 3.9 \times 10^{-3} + 3.3\ (Ag^+)$$

EFFECT OF TEMPERATURE :

The reaction was studied at five different temperature ranging from 25°C to 45°C. It must be mentioned here that the concentrations of amide, $K_2S_2O_8$ and $AgNO_3$ were kept unchanged. From these temperature values all the activation parameters were calculated. The results of these kinetic runs are recorded in the following table (Table B-12) and shown graphically in Fig. B-10.

TABLE B-12

Amide = 0.1M, $K_2S_2O_8 = 2.0 \times 10^{-2}$, $AgNO_3 = 1.0 \times 10^{-3}$M

Temperature	25°C	30°C	35°C	40°C	45°C
Time (min)	Vol. (in ml) of 0.02 M $-Na_2S_2O_3$ used (Viz. C)				
0	9.45	9.45	9.46	9.43	9.42
20	8.62	8.29	7.86	7.19	6.66
40	7.88	7.29	6.54	5.50	4.71
60	7.21	6.41	5.45	4.20	3.33
80	6.59	5.64	4.54	3.21	2.36
100	6.03	4.96	3.78	2.46	1.67
130	5.28	4.10	2.88	1.65	1.00
160	4.62	3.39	2.20	1.11	0.60
200	3.88	2.63	1.54	0.65	0.30
240	3.26	2.05	1.08	0.38	0.15
300	2.52	1.42	0.64	0.17	-
360	1.95	0.98	0.38	-	-
$k_1 \times 10^3 min^{-1}$	4.479	6.419	9.121	13.439	17.303
$k_2 \times 10^3 min^{-1}$	0.750	0.830	1.259	1.512	2.403
$k \times 10^3 min^{-1}$	3.729	5.589	7.862	11.927	14.900

From the results (Table B-12), it is seen that the specific rate is nearly doubled for 10°C rise in temperature.

The calculated values of $\frac{1}{T}$ and $\log\left[\frac{kr}{kT/h}\right]$ are given in Table B-13.

TABLE B-13

Temperature °A	$\frac{1}{T} \times 10^3$	$kr \times 10^3$ min^{-1}	log kr	$\log\left[\frac{kr}{kT/h}\right]$
298	3.356	3.729	-2.4285	-15.2461
303	3.301	5.589	-2.2527	-15.0775
308	3.246	7.862	-2.1045	-14.9360
313	3.196	11.927	-1.9237	-14.7621
318	3.145	14.900	-1.8265	-14.6721

A plot of log k versus $\frac{1}{T}$ is found to be linear (Fig.B-11) showing that the reaction obeys Arrhenius relationship.

The energy of activation was calculated from the slope of this plot (Fig. B-11). The energy of activation was 12.900 K.Cals.mole^{-1}, which is in good agreement with the calculated value, 13.403 K.Cal.mole^{-1}.

Similarly from the slope of the plot of $\log\left[\frac{kr}{kT/h}\right]$ versus $\frac{1}{T}$ (Fig. B-12), the enthalpy change for the formation of activated complex ($\Delta H^{\neq}$) is calculated. These values and all other energy parameters are recorded in Table B-14.

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.

TABLE B-14

Temperature °A	k X 10^3 min^{-1}	Temperature Coefficient	E K.Cals. $mole^{-1}$	A x 10^5 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	3.729	-	-	3.621	20.90	-30.80	
303	5.589	2.109	13.610	3.729	21.03	-30.66	
308	7.862	2.133	14.280	3.676	21.17	-23.24	
313	11.927	1.895	12.280	3.927	21.28	-23.16	11.745 (Graphically)
318	14.900	-	-	3.499	21.19	-23.21	
Mean	[illegible]	2.068	13.390	3.6904	21.11	-26.21	

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

$$k = 3.6904 \times 10^{5} . e^{-13.390/RT} \; sec^{-1}$$

EFFECT OF IONIC STRENGTH

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

TABLE B-15

Amide = 0.1M, $K_2S_2O_8$ =2.0×10^{-2}M, $AgNO_3$= 1.0×10^{-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 0.02M-$Na_2S_2O_3$ used (Viz. -C)					
0	9.46	9.52	9.53	9.52	9.54	9.54
20	7.86	8.11	8.16	8.52	8.78	8.88
40	6.54	6.93	7.00	7.64	8.08	8.28
60	5.45	5.91	6.01	6.86	7.45	7.73
80	4.54	5.05	5.15	6.16	6.88	7.22
100	3.78	4.31	4.43	5.54	6.36	6.76
130	2.88	3.41	3.53	4.72	5.65	6.12
160	2.20	2.70	2.81	4.04	5.04	5.57
200	1.54	1.98	2.09	3.29	4.34	4.92
240	1.08	1.45	1.55	2.68	3.75	4.36
300	0.64	0,92	1.00	1.99	3.04	3.67
360	0.38	0.58	0.64	1.49	2.48	3.12
$k_1 \times 10^3 min^{-1}$	9.121	7.860	7.633	5.372	3.996	3.381
$k_2 \times 10^3 min^{-1}$	1.259	1.190	1.168	1.124	0.820	0.770
$k \times 10^3 min^{-1}$	7.862	6.670	6.465	4.248	3.176	2.611

From these results (Table B-15), it is clear that the salt effect is negative and the reaction still retains it's unimolecular behaviour.

On plotting log k versus $(\mu)^{\frac{1}{2}}$, Fig.B-14(A) as well as k versus μ Fig. B-14(B), it has been observed that log k versus $(\mu)^{\frac{1}{2}}$ curve is linear in the region of low ionic strength (<0.20) while there exists on linearity in the plot of k versus μ . This suggests that the salt effect is of 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 X 10^3 min^{-1}	$\sqrt{\mu}$	log k
Nil	0.061	7.862	0.247	-2.1045
0.01	0.091	6.670	0.302	-2.1759
0.015	0.106	6.465	0.326	-2.1895
0.02	0.121	4.248	0.348	-2.3718
0.03	0.151	3.176	0.389	-2.4981
0.04	0.181	2.611	0.425	-2.5832

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 EFFECT :

In order to study the effect of varying concentrations of different salts on the reaction rate, the reaction was studied by the addition of different salts in the reaction mixture. This study has been carried out at constant ionic strength. The kinetic data of these runs is recorded in the following table (Table B-17) and shown graphically in Fig. B-15.

TABLE B-17

Amide = 0.1M, $K_2S_2O_8$= $2.0x10^{-2}$M, $AgNO_3$=$1.0x10^{-3}$M, Temp: 35°C

μ = 0.211

Salt added	No. salt	K_2SO_4	Na_2SO_4	Li_2SO_4	$MgSO_4$	$MnSO_4$
[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	9.46	9.65	9.64	9.62	9.60	9.60
20	7.86	9.09	9.04	8.74	8.62	8.30
40	6.54	8.57	8.48	7.95	7.75	7.18
60	5.45	8.09	7.96	7.23	6.97	6.22
80	4.54	7.64	7.47	6.58	6.28	5.39
100	3.78	7.21	7.02	5.99	5.65	4.67
130	2.88	6.61	6.39	5.20	4.84	3.78
160	2.20	6.11	5.82	4.53	4.15	3.05
200	1.54	5.48	5.14	3.77	3.39	2.31
240	1.08	4.93	4.55	3.14	2.77	1.74
300	0.64	4.23	3.79	2.39	2.06	1.15
360	0.38	3.65	3.16	1.83	1.55	0.76
$k_1 x 10^3$ min^{-1}	9.121	2.869	3.162	4.717	5.254	7.173
$k_2 x 10^3$ min^{-1}	1.259	0.750	0.810	0.840	0.880	0.970
$k x 10^3$ min^{-1}	7.862	2.119	2.352	3.877	4.374	6.203

From the data contained in the table (Table B-17), it is seen that the specific inhibitory effect of various ions is in the order

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

EFFECT OF HYDROGEN ION CONCENTRATION :

The reaction was studied at different H^+ ion concentrations by the addition of sulphuric acid. The concentrations of amide, $K_2S_2O_8$ and the catalyst were kept constant. These results are recorded in Table B-18 and shown graphically in Fig. B-16.

From these results (Table B-18), it indicates that the rate of reaction is affected by a change in pH of the reaction mixture. Lowering of pH results in the decrease of the rate constant. This decrease in the rate of the reaction may be due to an increase in ionic strength resulting by the addition of H_2SO_4.

To veryfy which of the possibility holds good, the effect was re-investigated at constant ionic strength by the addition of a mixture of H_2SO_4 and K_2SO_4 so as to maintain the ionic strength of the reaction mixture constant. These results are recorded in Table B-19 and shown graphically in Fig.B-17.

TABLE B-18

Amide = 0.1M, $K_2S_2O_8$ = 2.0×10^{-2}M, $AgNO_3$= 1.0×10^{-3}M, Temp=35°C

$[H_2SO_4]$M	Nil	0.025	0.05	0.075	0.1
Time (min)	Vol (in ml) of 0.02 M $Na_2S_2O_3$ used (Viz.C)				
0	9.46	9.52	9.54	9.52	9.53
20	7.86	8.22	8.54	8.70	8.87
40	6.54	7.10	7.66	8.00	8.25
60	5.45	6.14	6.87	7.31	7.69
80	4.54	5.31	6.16	6.70	7.16
100	3.78	4.60	5.54	6.14	6.69
130	2.88	3.71	4.71	5.40	6.03
160	2.20	3.00	4.03	4.76	5.44
200	1.54	2.27	3.27	4.02	4.74
240	1.08	1.71	2.66	3.41	4.16
300	0.64	1.13	1.97	2.67	3.42
360	0.38	0.75	1.46	2.11	2.82
$k_1\times10^3 min^{-1}$	9.121	7.226	5.394	4.334	3.509
$k_2\times10^3 min^{-1}$	1.259	0.970	0.850	0.760	0.670
$k\times10^3 min^{-1}$	7.862	6.256	4.544	3.574	2.839

TABLE B-19

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

Temperature = 35°C , μ = 0.361

$[H_2SO_4]$M	Nil	0.025	0.05	0.075	0.1
+					
$[K_2SO_4]$M	0.1	0.075	0.05	0.025	Nil
Time (min)	Vol. (in ml) of 0.02M-$Na_2S_2O_3$ used (Viz.C)				
0	9.52	9.54	9.54	9.55	9.53
20	9.12	9.12	9.00	8.92	8.87
40	8.75	8.74	8.51	8.35	8.25
60	8.40	8.37	8.04	7.81	7.69
80	8.07	8.02	7.61	7.31	7.16
100	7.75	7.68	7.19	6.85	6.69
130	7.31	7.22	6.63	6.22	6.03
160	6.90	6.79	6.12	5.65	5.44
200	6.41	6.26	5.51	4.99	4.74
240	5.96	5.79	4.98	4.42	4.16
300	5.35	5.17	4.29	3.69	3.42
360	4.83	4.63	3.72	3.10	2.82
k_1x$10^3$$min^{-1}$	2.022	2.133	2.750	3.283	3.509
k_2x$10^3$$min^{-1}$	0.600	0.620	0.640	0.640	0.670
k x$10^3$$min^{-1}$	1.422	1.513	2.110	2.643	2.839

From the results as shown in Table B-19, it is seen that as in the case of amido-acetamide here also the rate of the reaction is increased by increasing the H^+ ion concentration (and decreasing K_2SO_4 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 the H^+ ion concentration rules out (Table B-18) the possibility that the increase in the rate constant values at constant ionic strength (Table B-19) is brought about due to catalytic effect of H^+ ions. Hence it is concluded that K^+ ion causes inhibition of greater magnitude in comparison to that brought about hy H^+ ions and that the observed increase in the rate constant at constant ionic strength (Table B-19), is due to the increase in proportion of H_2SO_4 at the expense of equimolar concentration of K_2SO_4.

EFFECT OF ALLYL ALCOHOL :

The reaction was studied in the absence of allyl alcohol and in the presence of three different concentrations of allyl alcohol. The results of these kinetic runs are recorded in the following table (Table B-20) and shown graphically in Fig. B-18.

TABLE B-20

Amide =0.1M, $K_2S_2O_8$= 2.0x10^{-2}M, $AgNO_3$=1.0x10^{-3}M, Temp.=35°C

[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	9.46	9.45	9.48	9.46
20	7.86	8.17	8.53	8.91
40	6.54	7.07	7.68	8.41
60	5.45	6.13	6.91	7.93
80	4.54	5.31	6.23	7.48
100	3.78	4.60	5.62	7.06
130	2.88	3.71	4.81	6.49
160	2.20	3.00	4.13	5.96
200	1.54	2.26	3.37	5.34
240	1.08	1.71	2.75	4.79
300	0.64	1.12	2.04	4.09
360	0.38	0.73	1.52	3.50
k x$10^3$$min^{-1}$	9.121	7.183	5.177	2.889

From the above results (Table B-20), it is seen that allyl alcohol inhibits the rate of reaction.

EFFECT OF ALLYL ACETATE :

In order to study the effect of allyl acetate on the reaction rate, the reaction was studied in the absence of allyl acetate as well as at three different concentrations of allyl acetate. These results are recorded in Table B-21 and shown graphically in Fig. B-19.

TABLE B-21

Amide = 0.1M, $K_2S_2O_8$ = 2.0x10^{-2}M, $AgNO_3$=1.0x10^{-3}M, Temp.=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	9.46	9.45	9.44	9.42
20	7.86	8.17	8.49	8.66
40	6.54	7.07	7.65	7.96
60	5.45	6.14	6.89	7.32
80	4.54	5.30	6.21	6.74
100	3.78	4.59	5.60	6.21
130	2.88	3.71	4.78	5.49
160	2.20	3.00	4.11	4.87
200	1.54	2.27	3.36	4.13
240	1.08	1.70	2.74	3.52
300	0.64	1.12	2.03	2.78
360	0.38	0.74	1.51	2.20
k x10^3min^{-1}	9.121	7.183	5.205	4.147

From the above results (Table B-21) it has been observed that allyl acetate is an effective radical scavenger which inhibits the reaction rate.

MOLE RATIO :

For determining mole ratio between $K_2S_2O_8$ and amide, two different kinetic runs were made simultaneously, one run was studied in the presence of amide while the other run was carried out in the absence of amide. The procedure is as follows :

In both the runs the concentration of $K_2S_2O_8$ was five times more than that of amide. The concentration of catalyst was the same in both the runs. At suitable intervals of time, 5 ml of the reaction mixture was withdrawn and estimated for unreacted $K_2S_2O_8$. The kinetic results of these runs are recorded in Table B-22 and shown graphically in Fig. B-20.

The curve shown in the Fig. B-20 consists of two portions. The first portion is for the oxidation of amide and second portion is for the self-decomposition of peroxydisulphate. Now tangents are drawn on 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 5 ml of 0.01M amide is calculated. The point Q on the curve shows the value corresponding to self decomposed $K_2S_2O_8$.

In the Fig. B-20 , it can be observed 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

TABLE B-22

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

[Amide] M	0.01	Nil
Time (min)	Vol. (in ml)of 0.02M-$Na_2S_2O_3$ used (Viz.C)	
0	24.35	24.10
30	22.10	23.41
60	21.24	22.36
90	19.81	21.44
120	18.53	20.85
150	17.45	20.41
180	16.32	19.50
210	15.07	19.05
240	13.80	18.21
270	13.12	17.37
300	12.21	16.96
330	11.65	15.88
360	10.90	15.85
390	10.81	15.05
420	10.52	14.45
450	9.97	14.01
480	9.55	13.50

log C at the same point on the self decomposition curve is shown by point Q. At this point log C = 1.205 which corresponds to 16.03 ml. The difference between these two values (indicating the volume of $Na_2S_2O_3$) is 4.81 ml.

Therefore 4.81 ml of 0.02N $Na_2S_2O_3$ $\equiv$ 4.81 ml of 0.02N $K_2S_2O_8$

$\equiv$ 4.81 ml of 0.01M $K_2S_2O_8$

Hence ,

5 ml of 0.01 M amide = 4.81 ml of 0.01 M $K_2S_2O_8$

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

* * * *

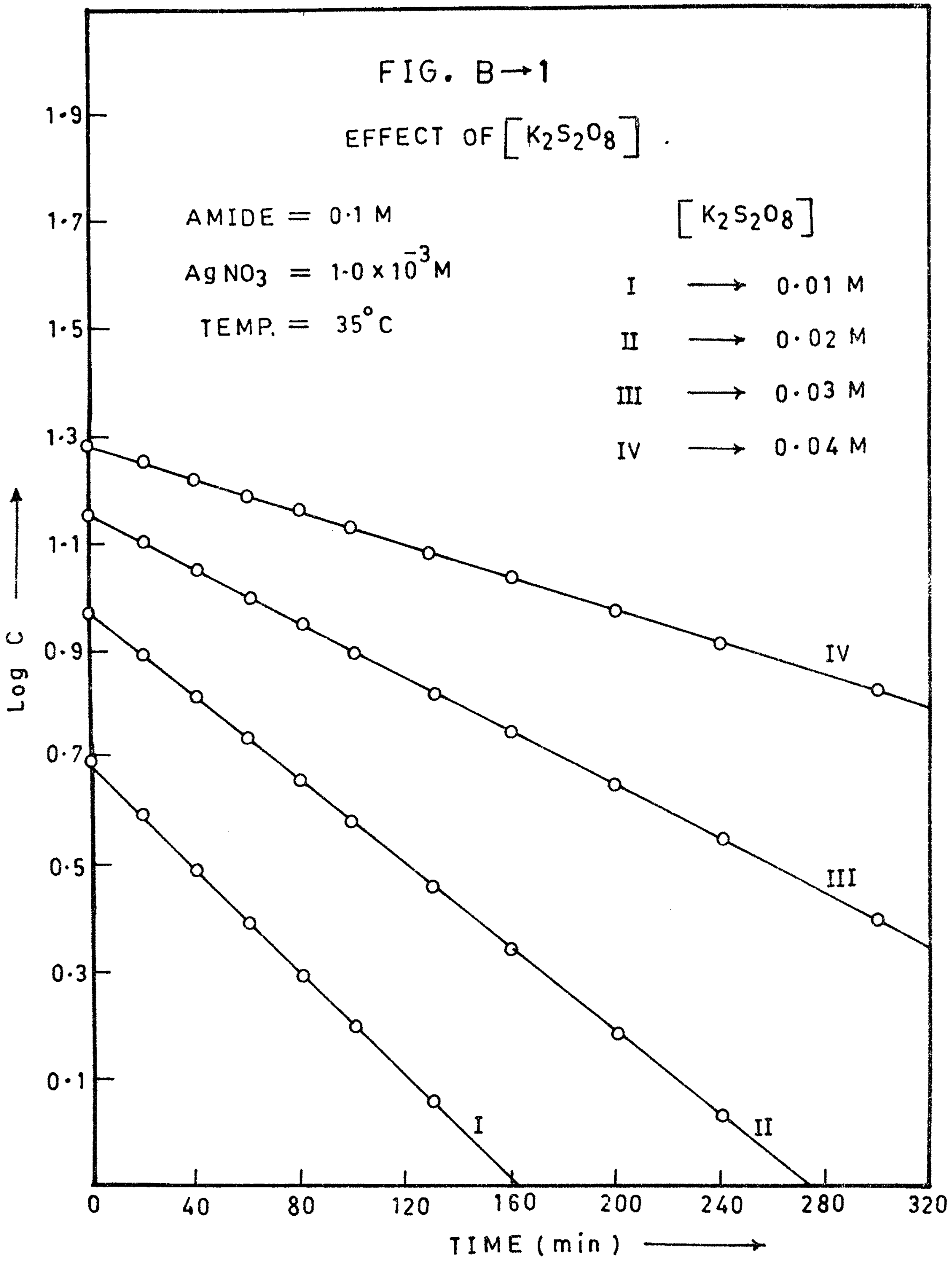
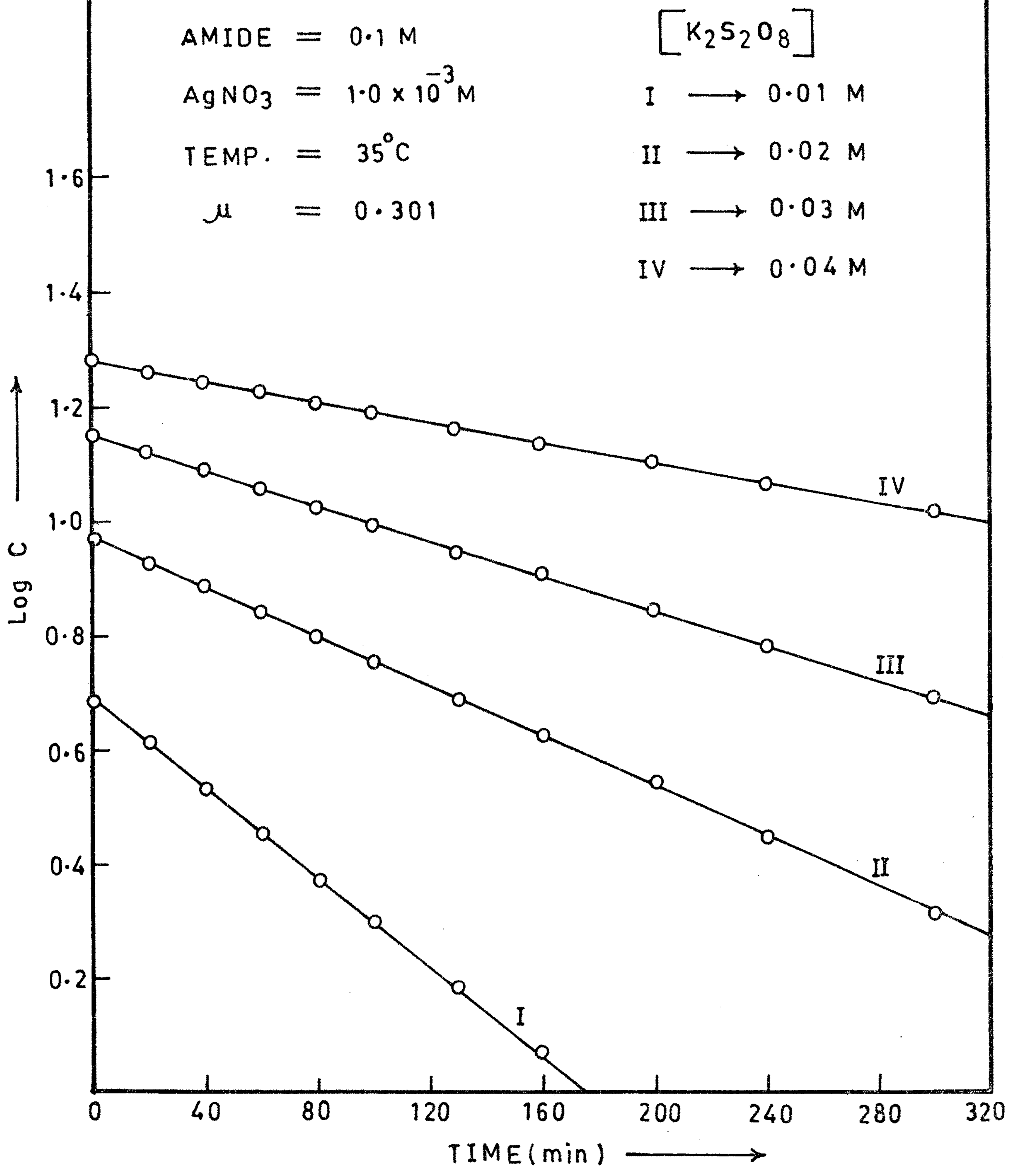


FIG. B→1

EFFECT OF $[K_2S_2O_8]$.

FIG. B→2

EFFECT OF $K_2S_2O_8$ AT CONSTANT μ.



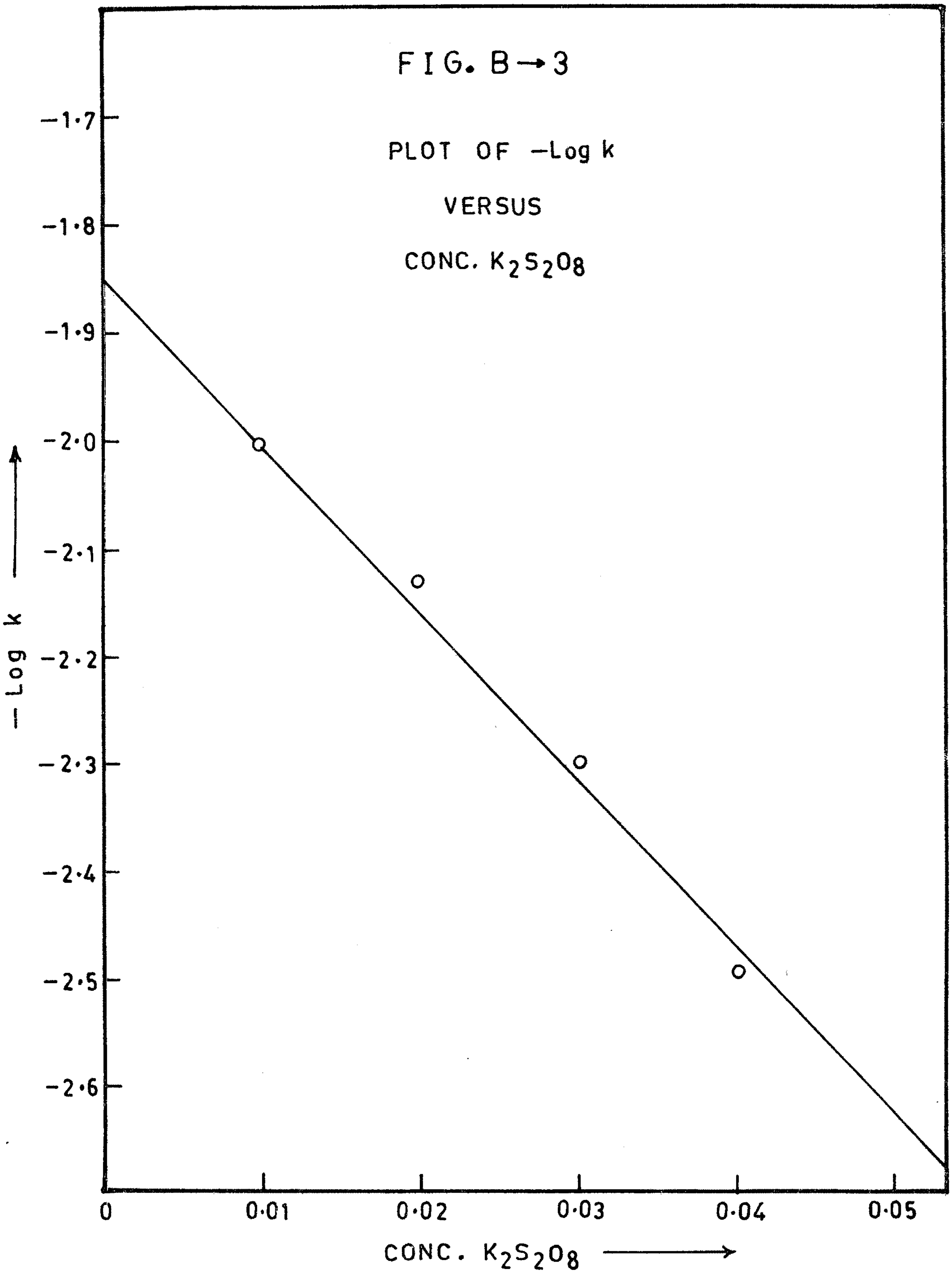


FIG. B→3

PLOT OF −Log k VERSUS CONC. $K_2S_2O_8$

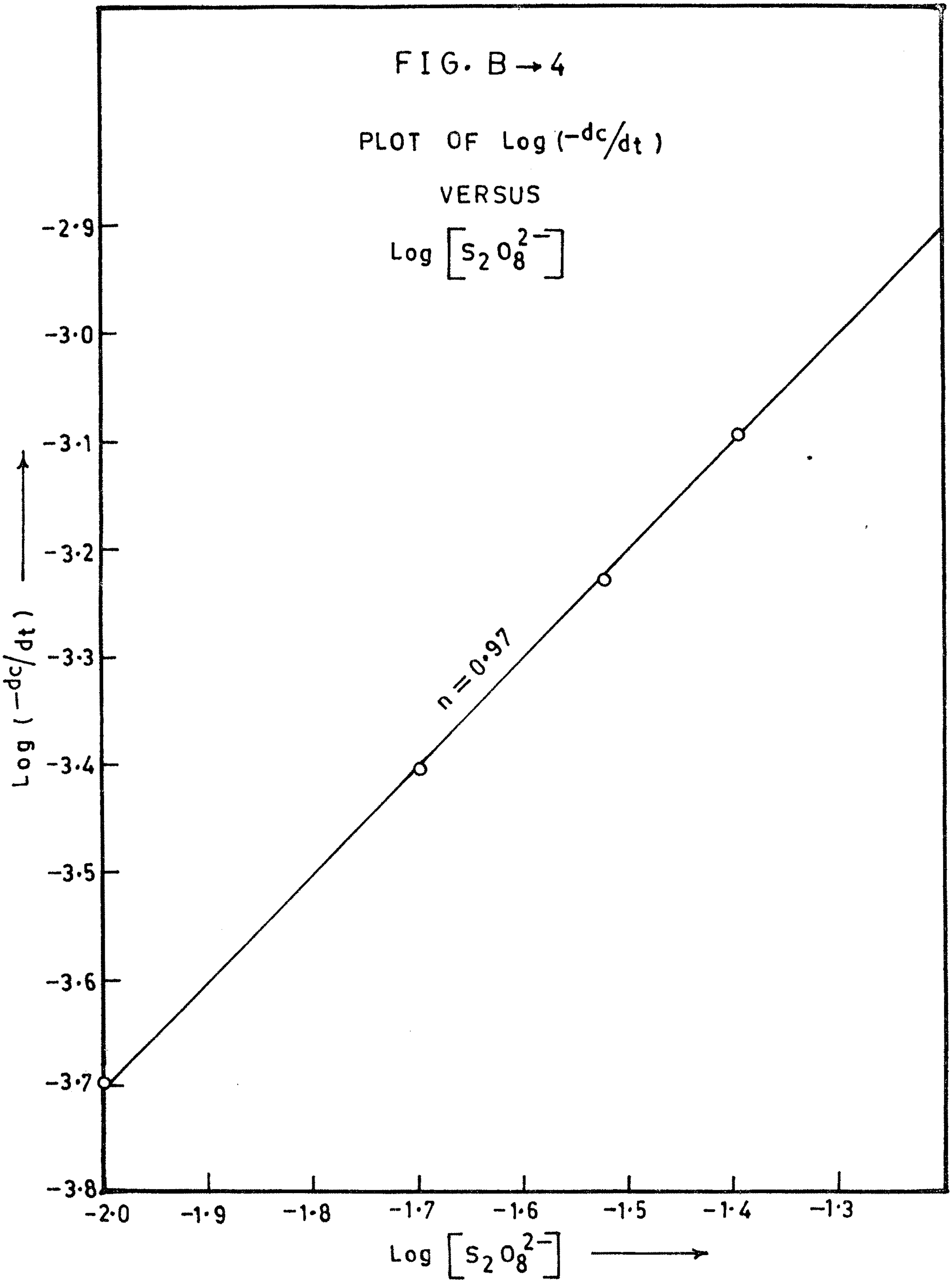


FIG. B→4

PLOT OF Log $(-dc/dt)$ VERSUS Log $[S_2O_8^{2-}]$

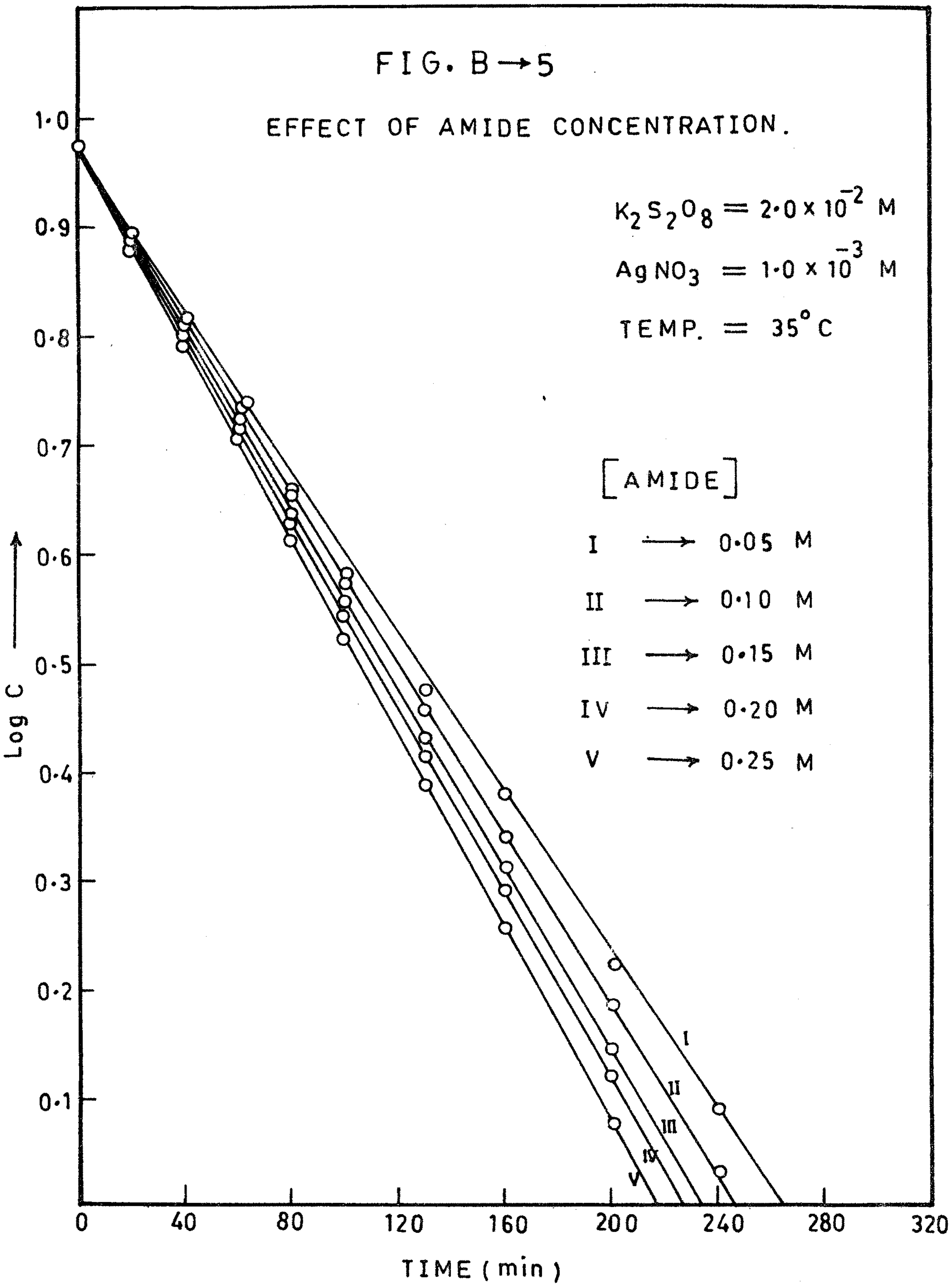


FIG. B→5

EFFECT OF AMIDE CONCENTRATION.

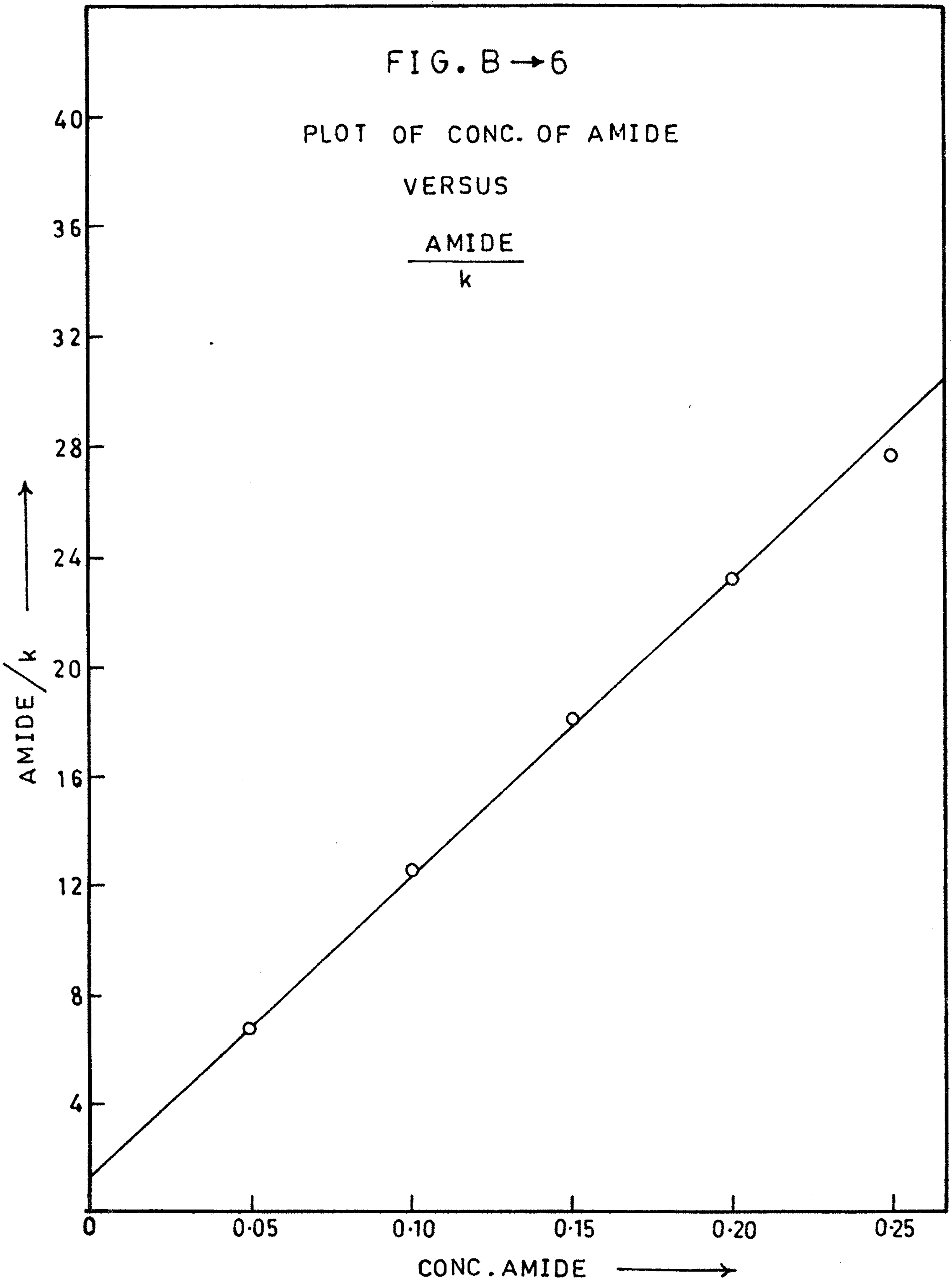
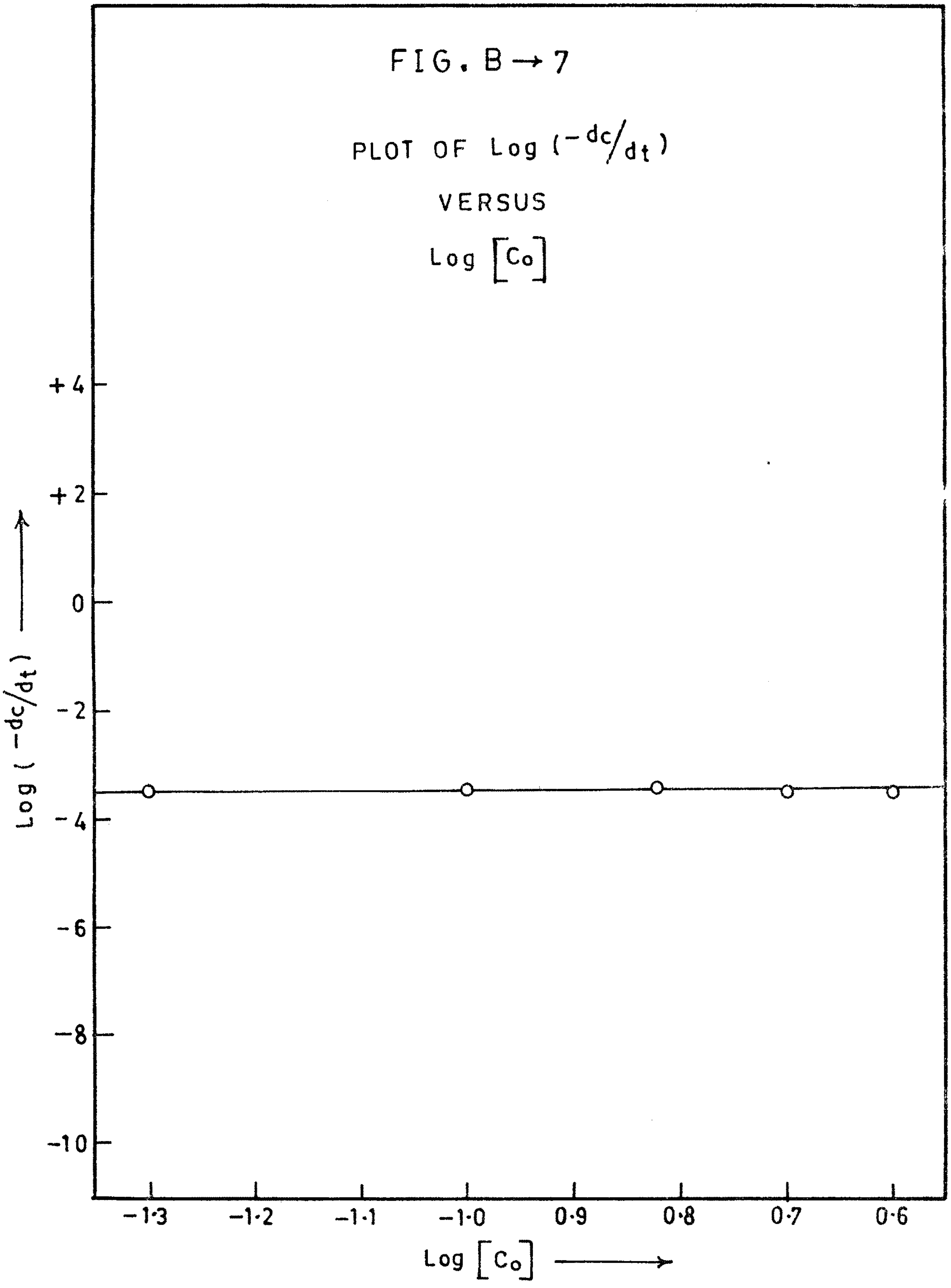


FIG. B→6

PLOT OF CONC. OF AMIDE
VERSUS
$\frac{\text{AMIDE}}{k}$

FIG. B → 7

PLOT OF Log $(-dc/dt)$
VERSUS
Log $[C_o]$



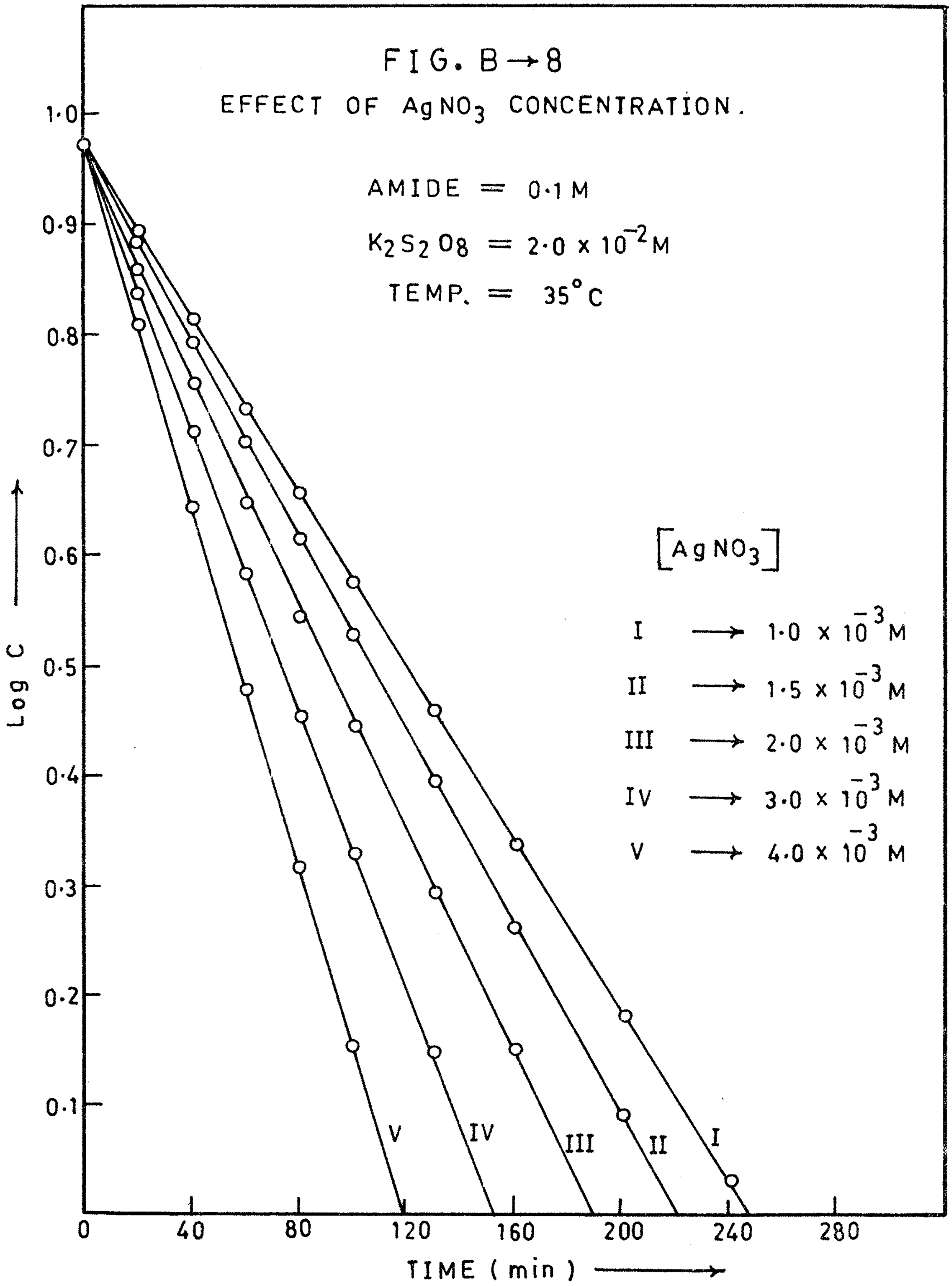
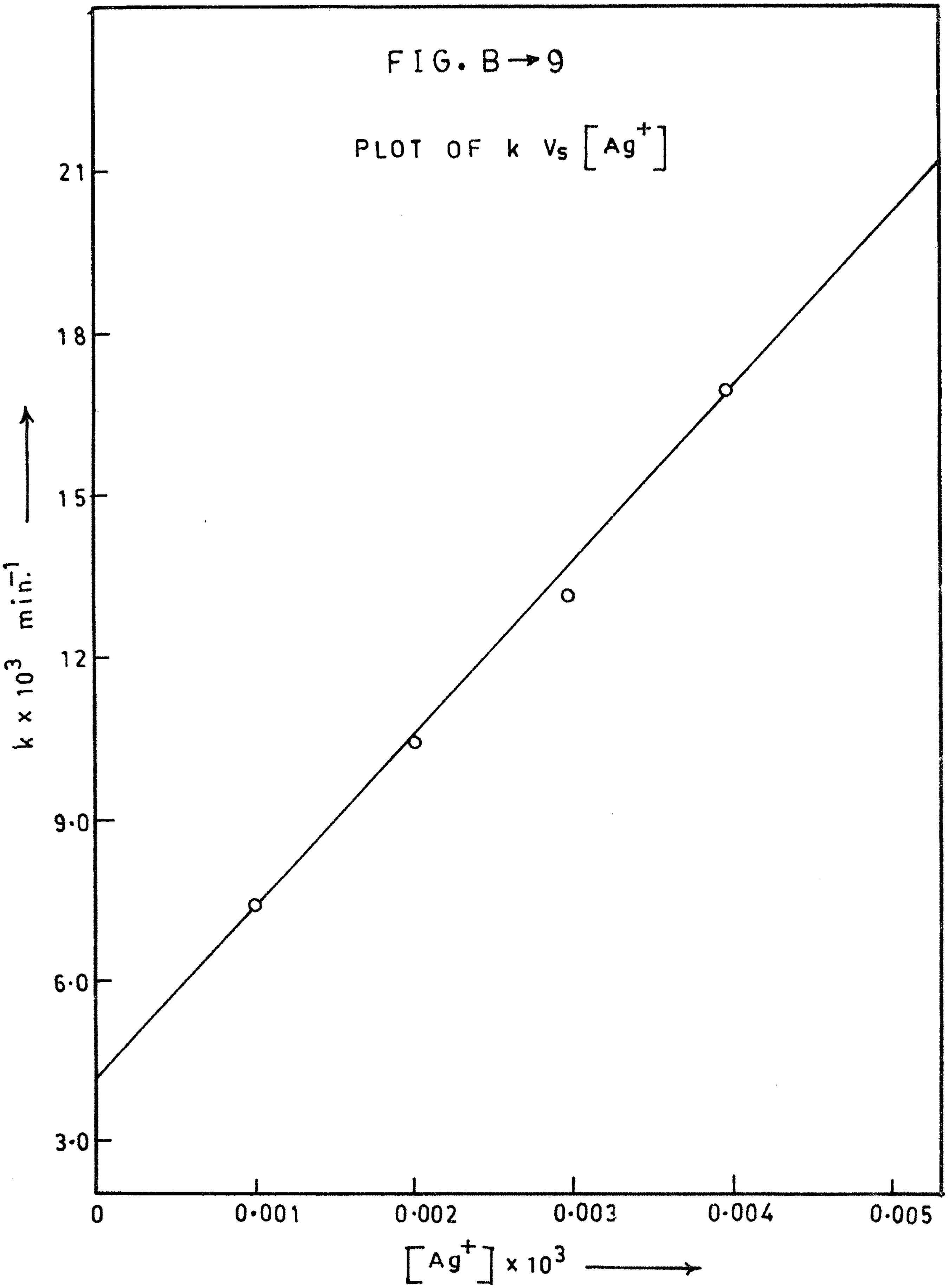


FIG. B→8

EFFECT OF $AgNO_3$ CONCENTRATION.

FIG. B→9

PLOT OF k Vs $[Ag^+]$



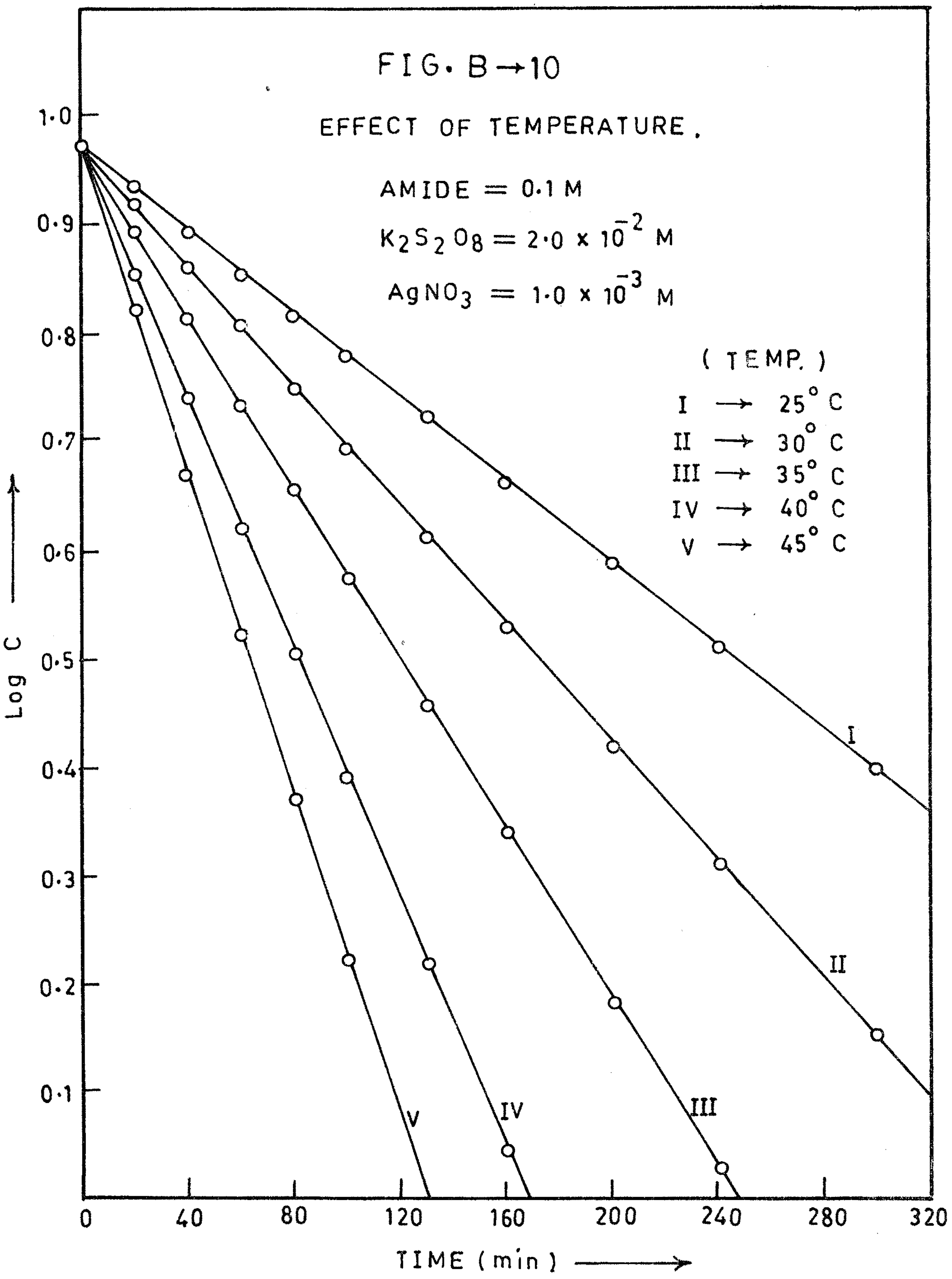


FIG. B→10

EFFECT OF TEMPERATURE.

AMIDE = 0·1 M

$K_2S_2O_8 = 2{\cdot}0 \times 10^{-2}$ M

$AgNO_3 = 1{\cdot}0 \times 10^{-3}$ M

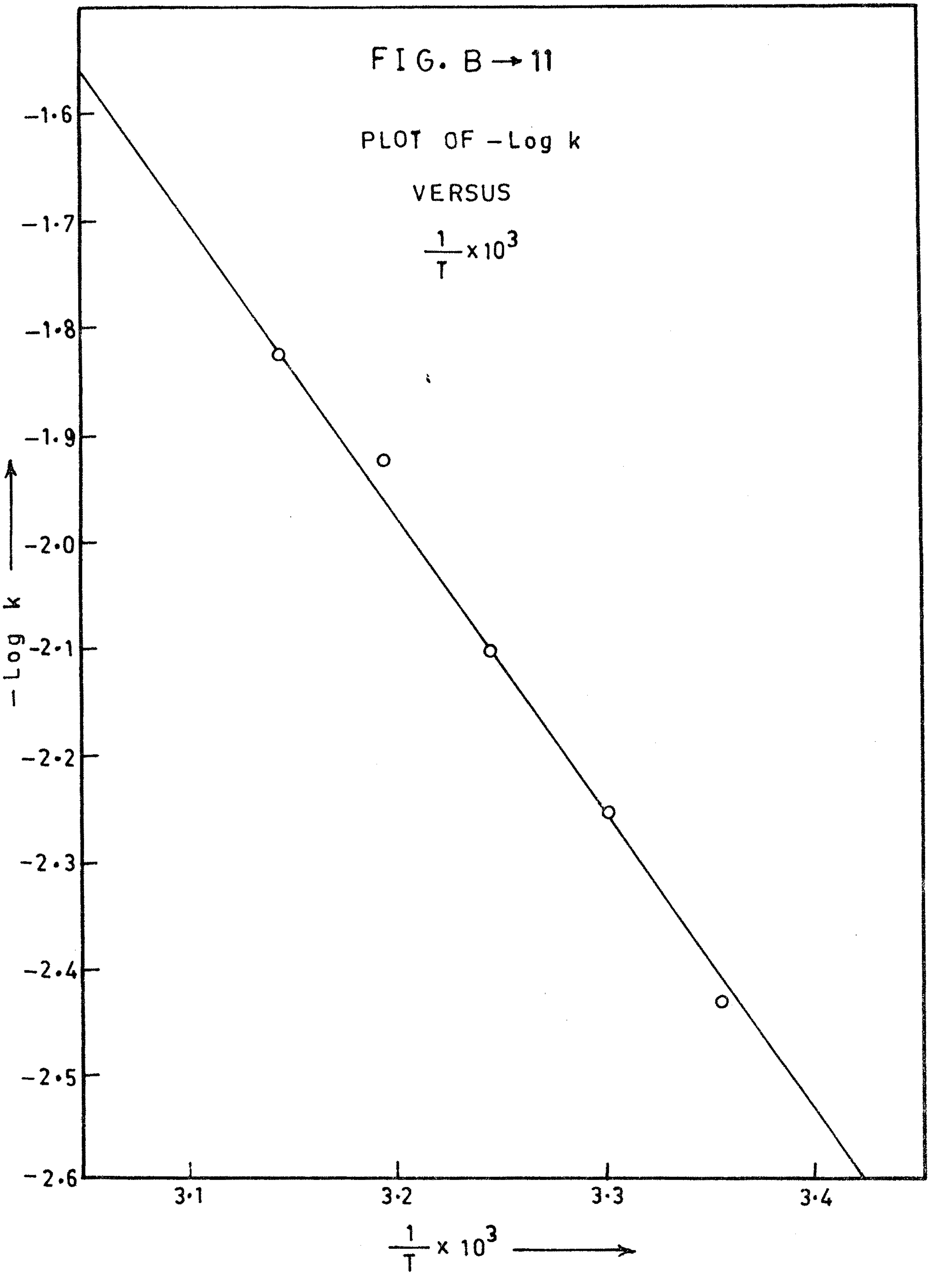


FIG. B → 11

PLOT OF −Log k VERSUS $\frac{1}{T} \times 10^3$

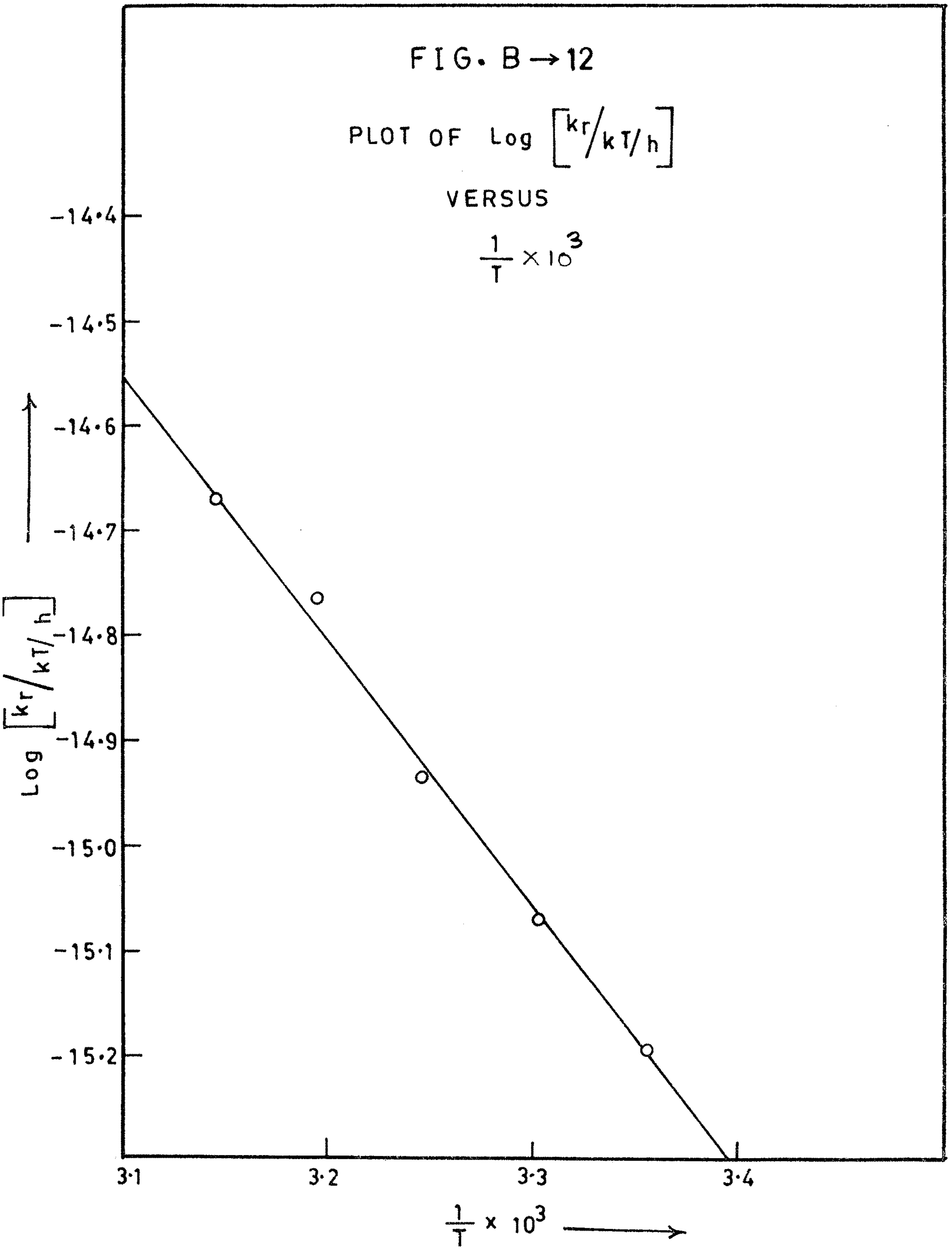


FIG. B → 12

PLOT OF Log $\left[k_r / kT/h \right]$

VERSUS

$\frac{1}{T} \times 10^3$

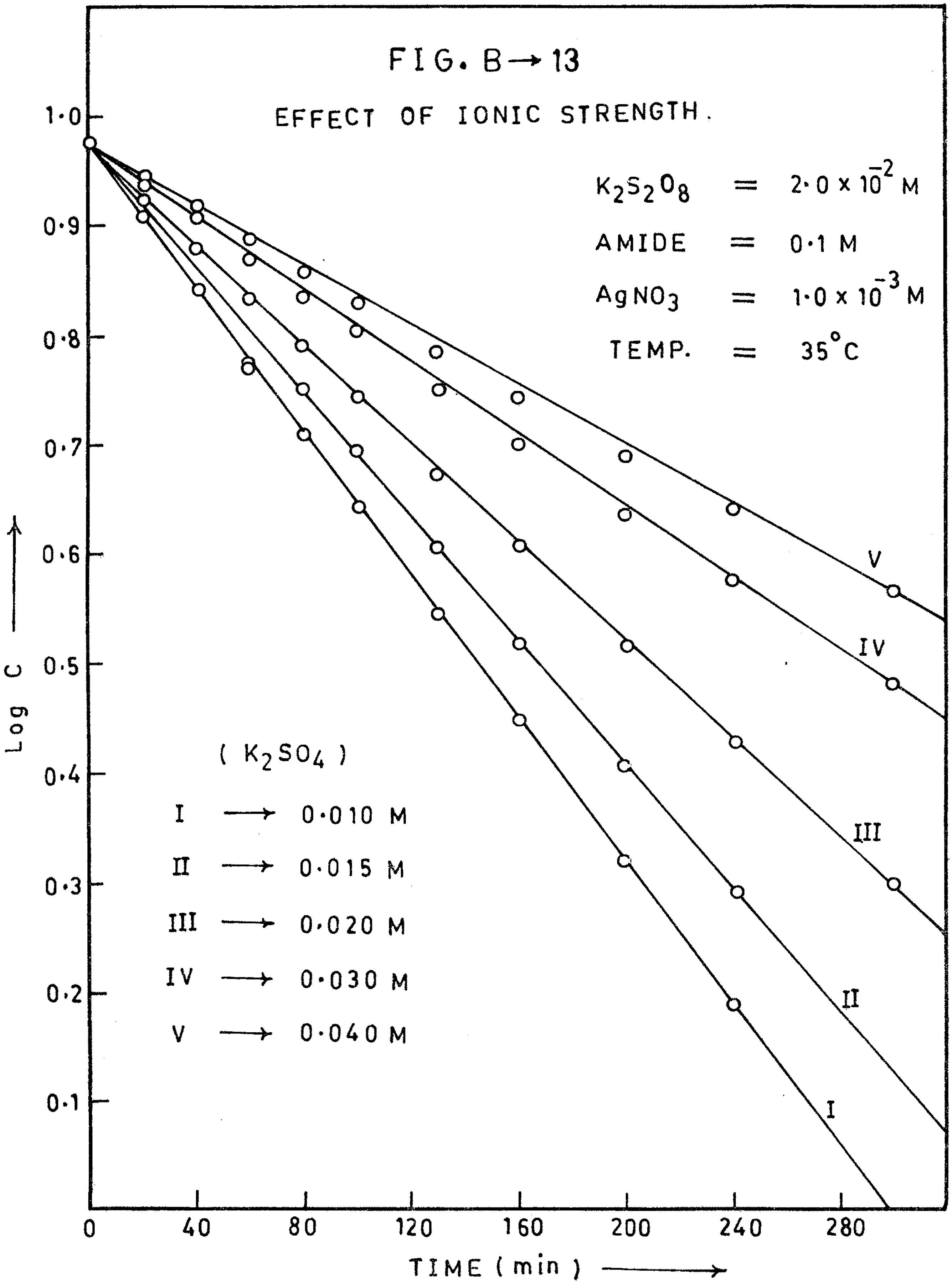
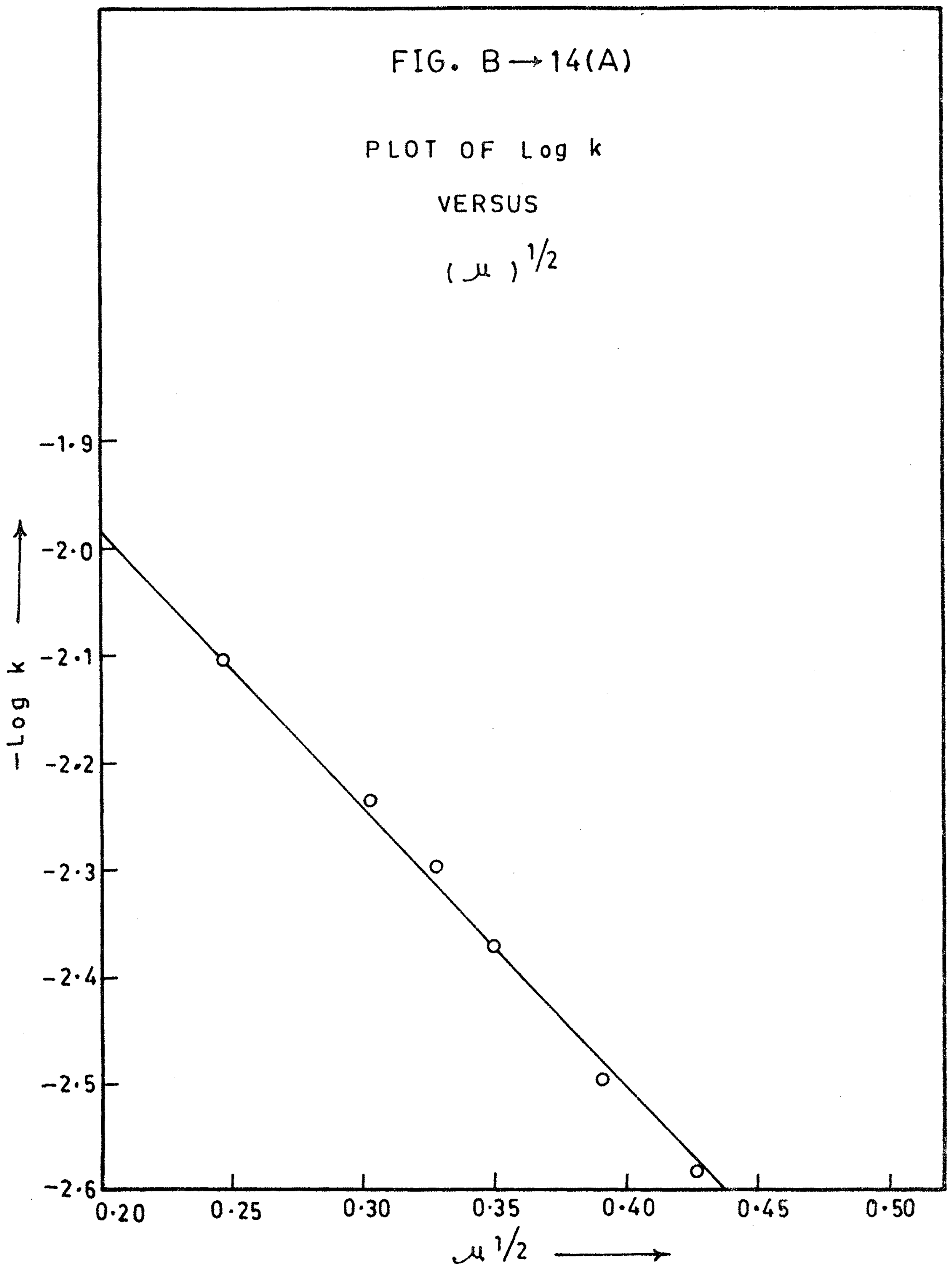


FIG. B→13

EFFECT OF IONIC STRENGTH.

FIG. B → 14(A)

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



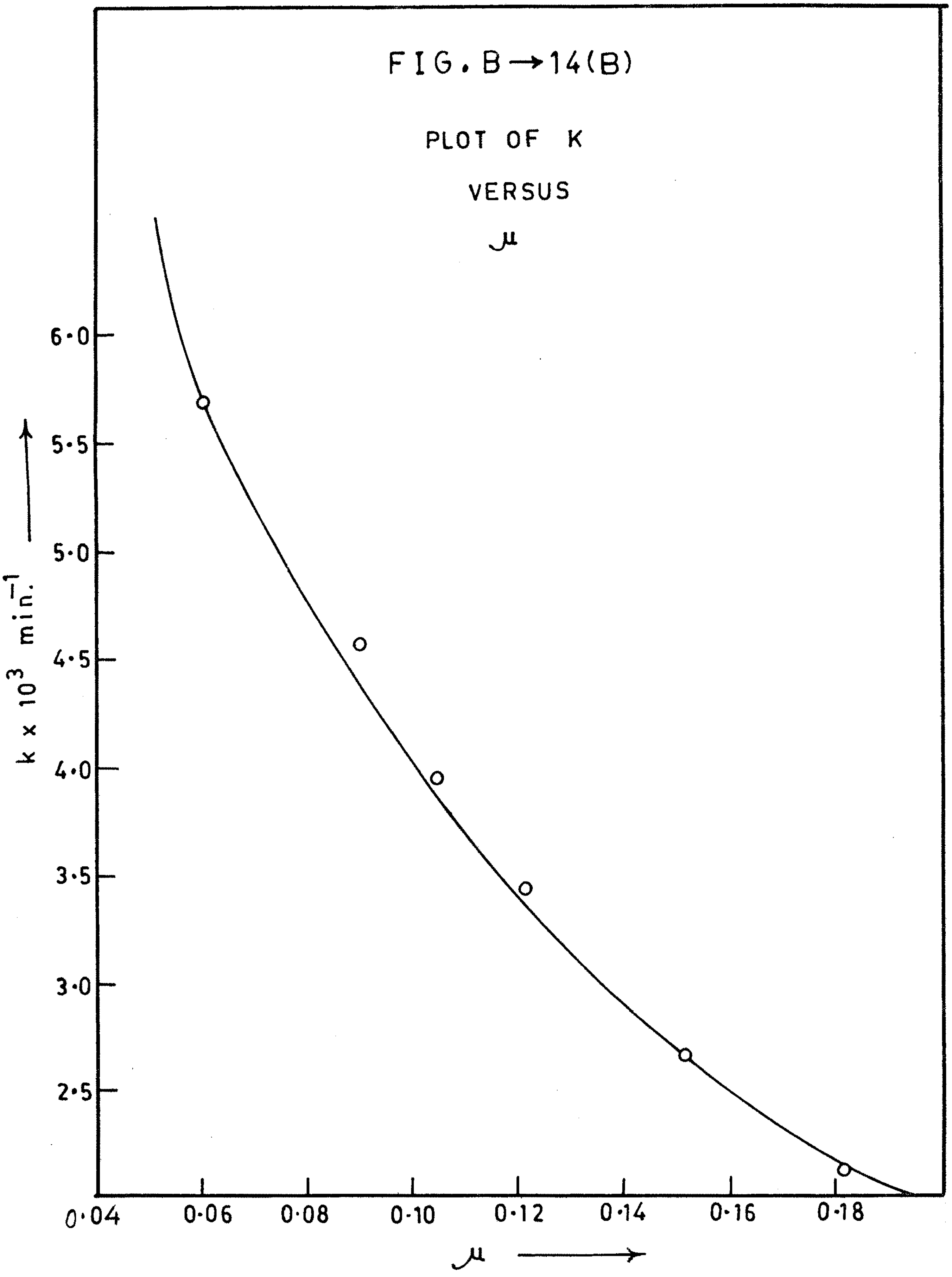
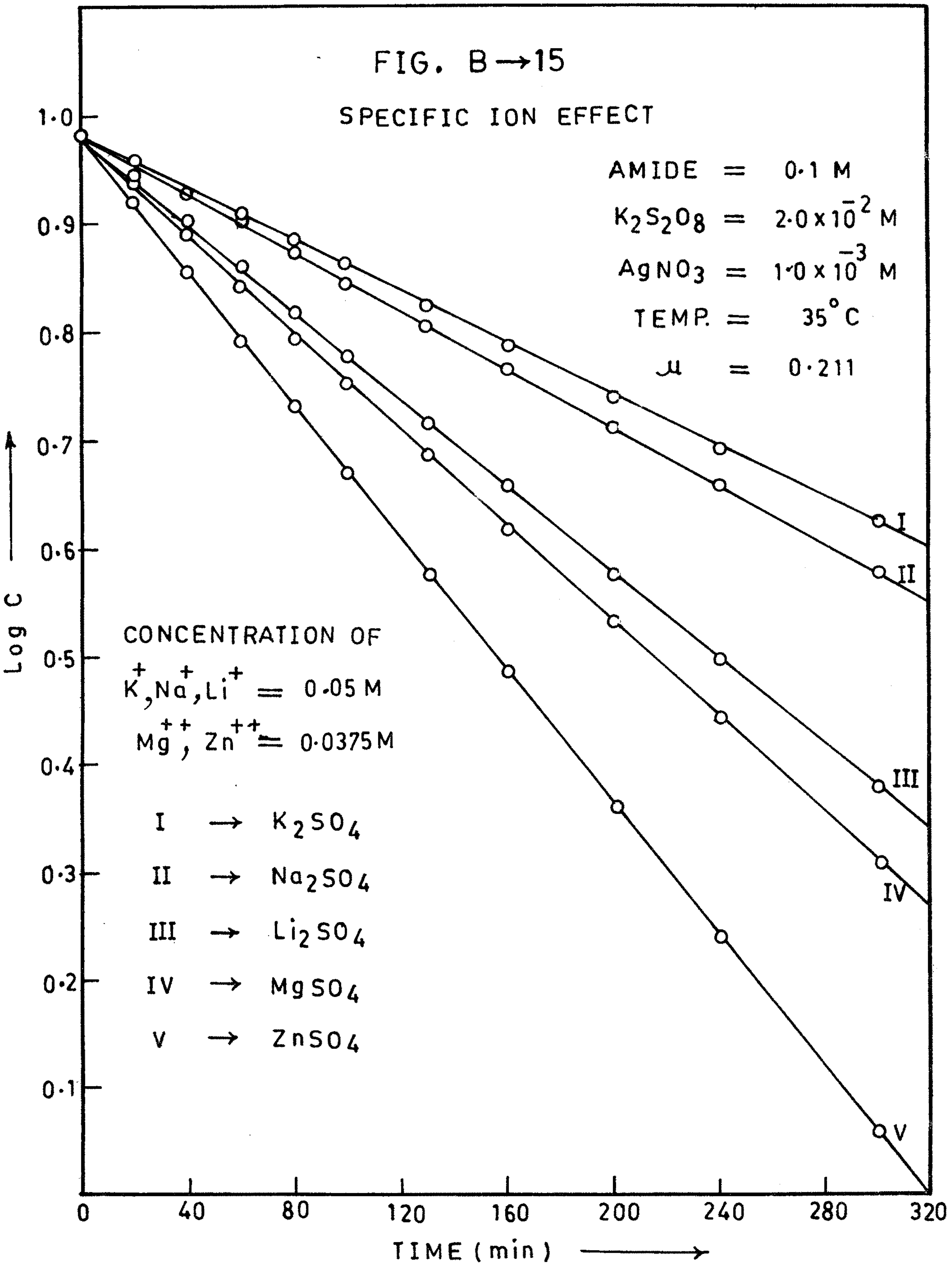


FIG. B→14(B)

PLOT OF K VERSUS μ

FIG. B→15

SPECIFIC ION EFFECT



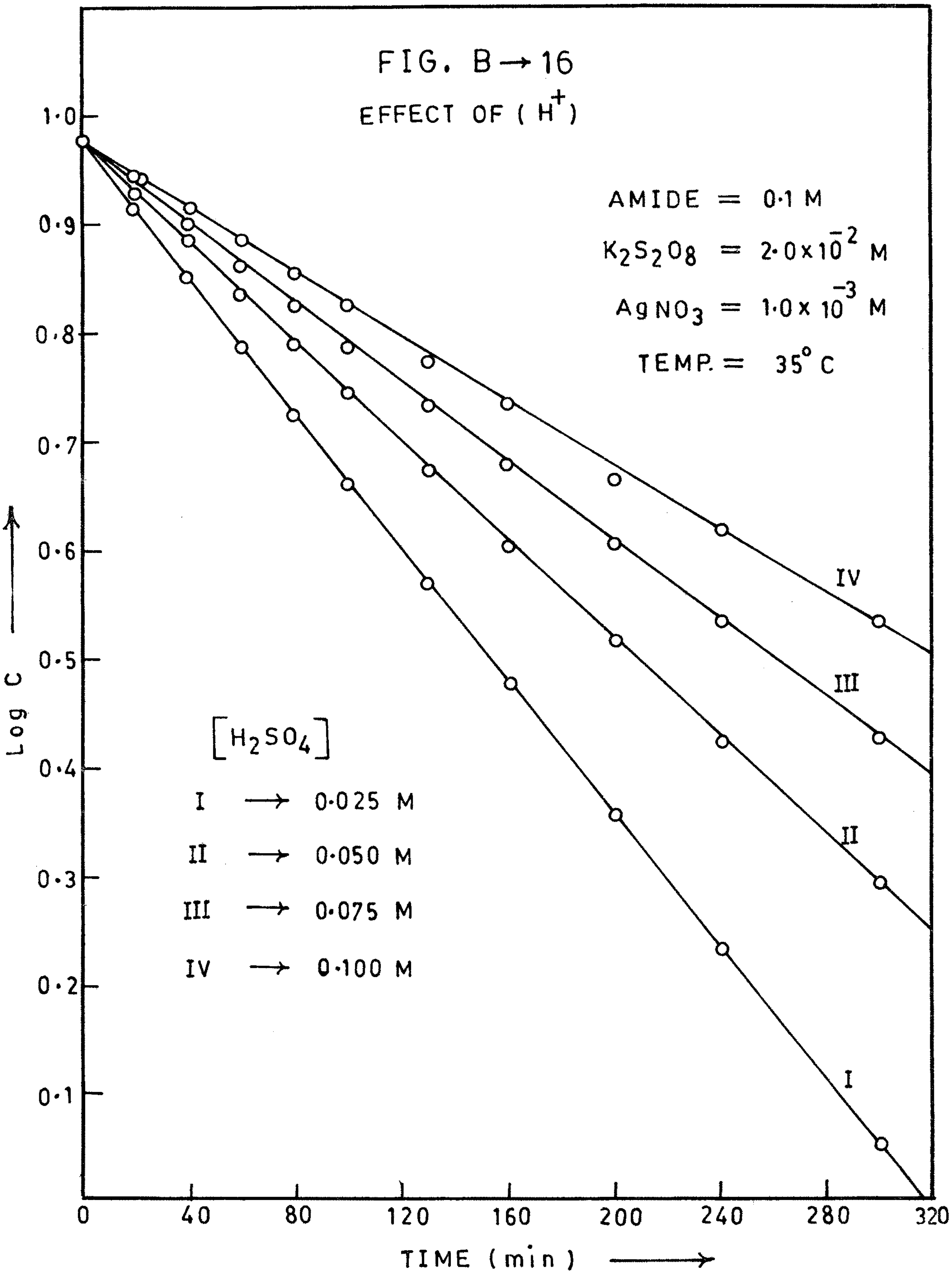


FIG. B → 16

EFFECT OF (H^+)

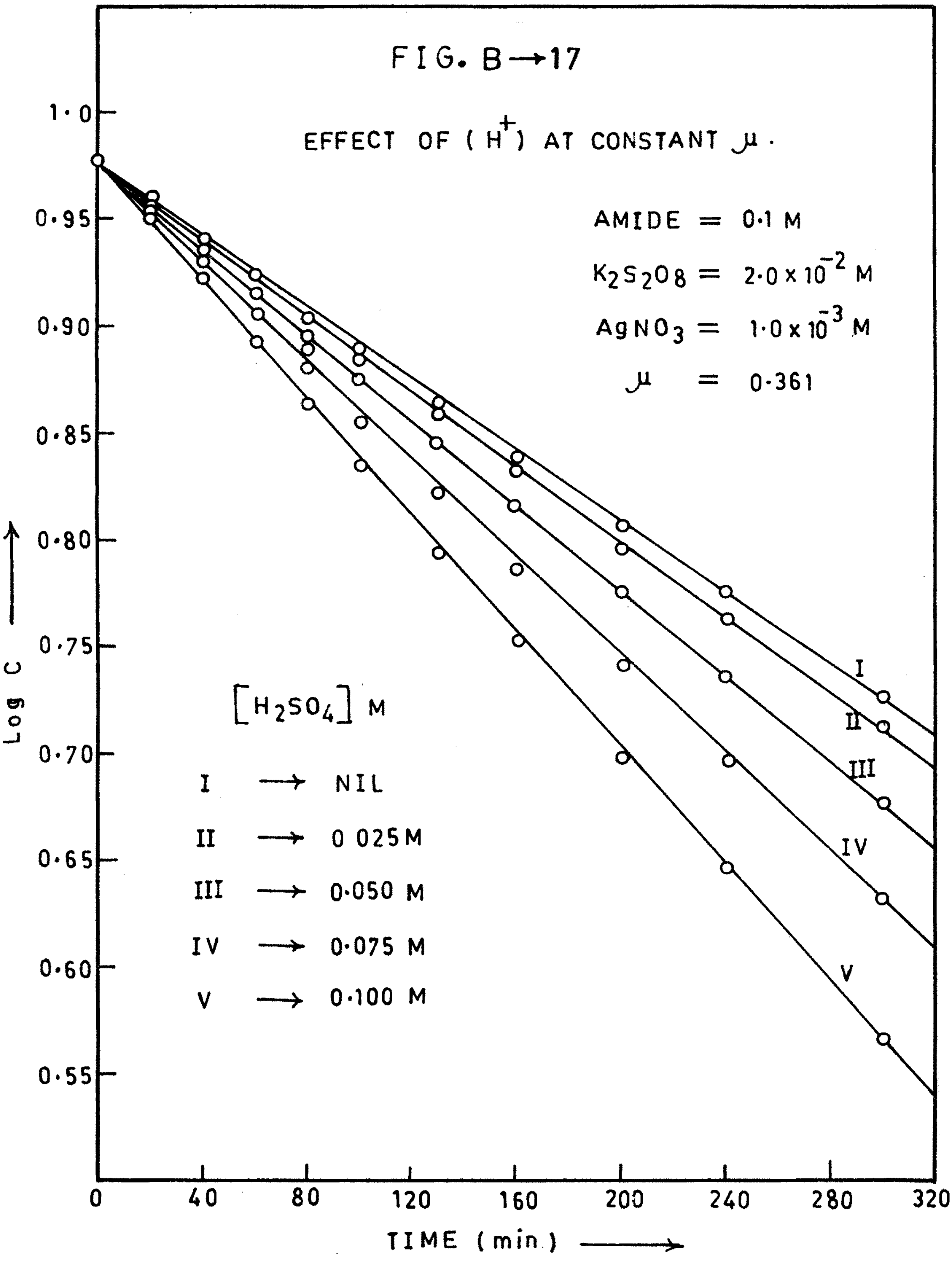


FIG. B→17

EFFECT OF (H^+) AT CONSTANT μ.

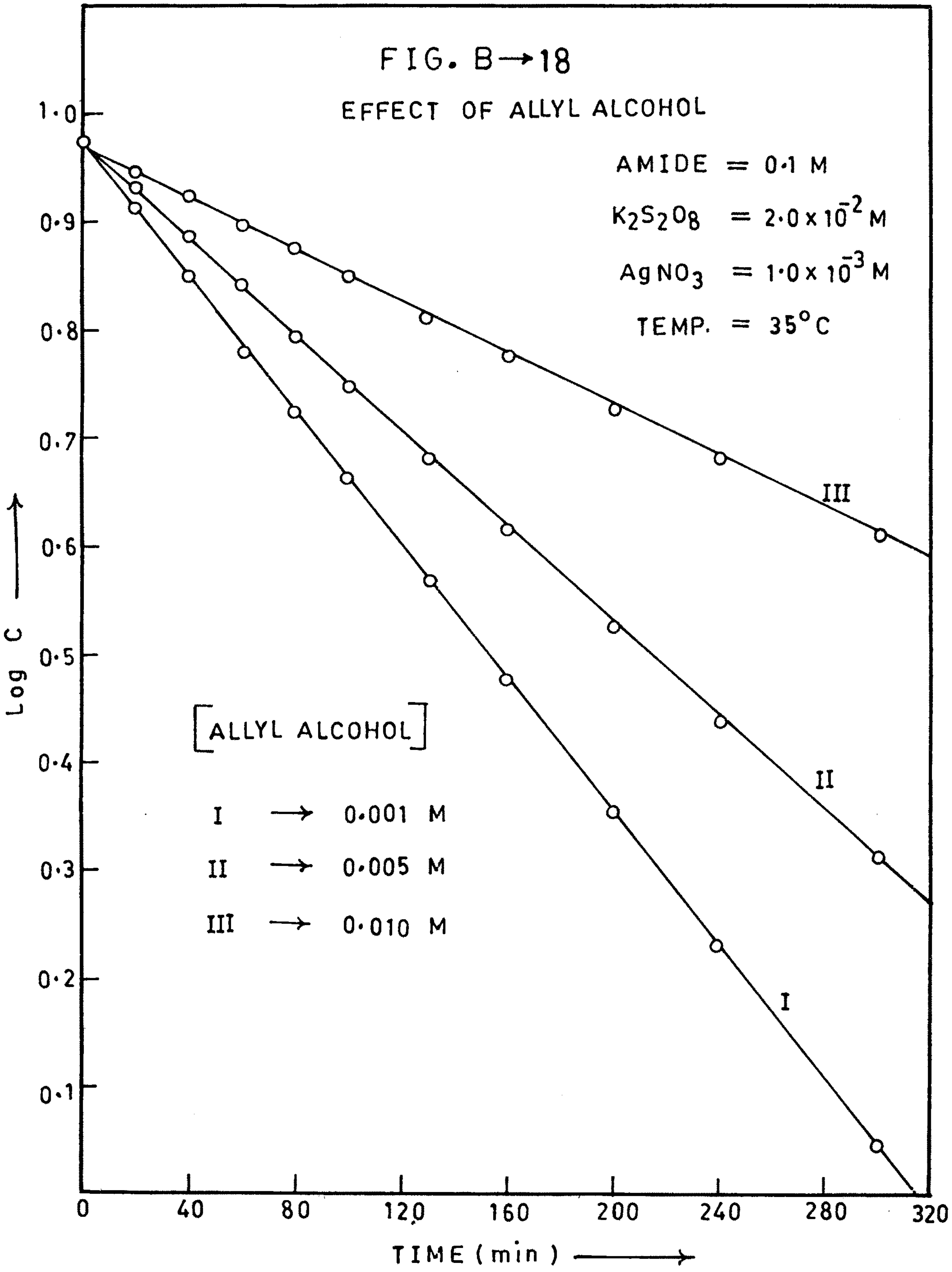


FIG. B→18

EFFECT OF ALLYL ALCOHOL

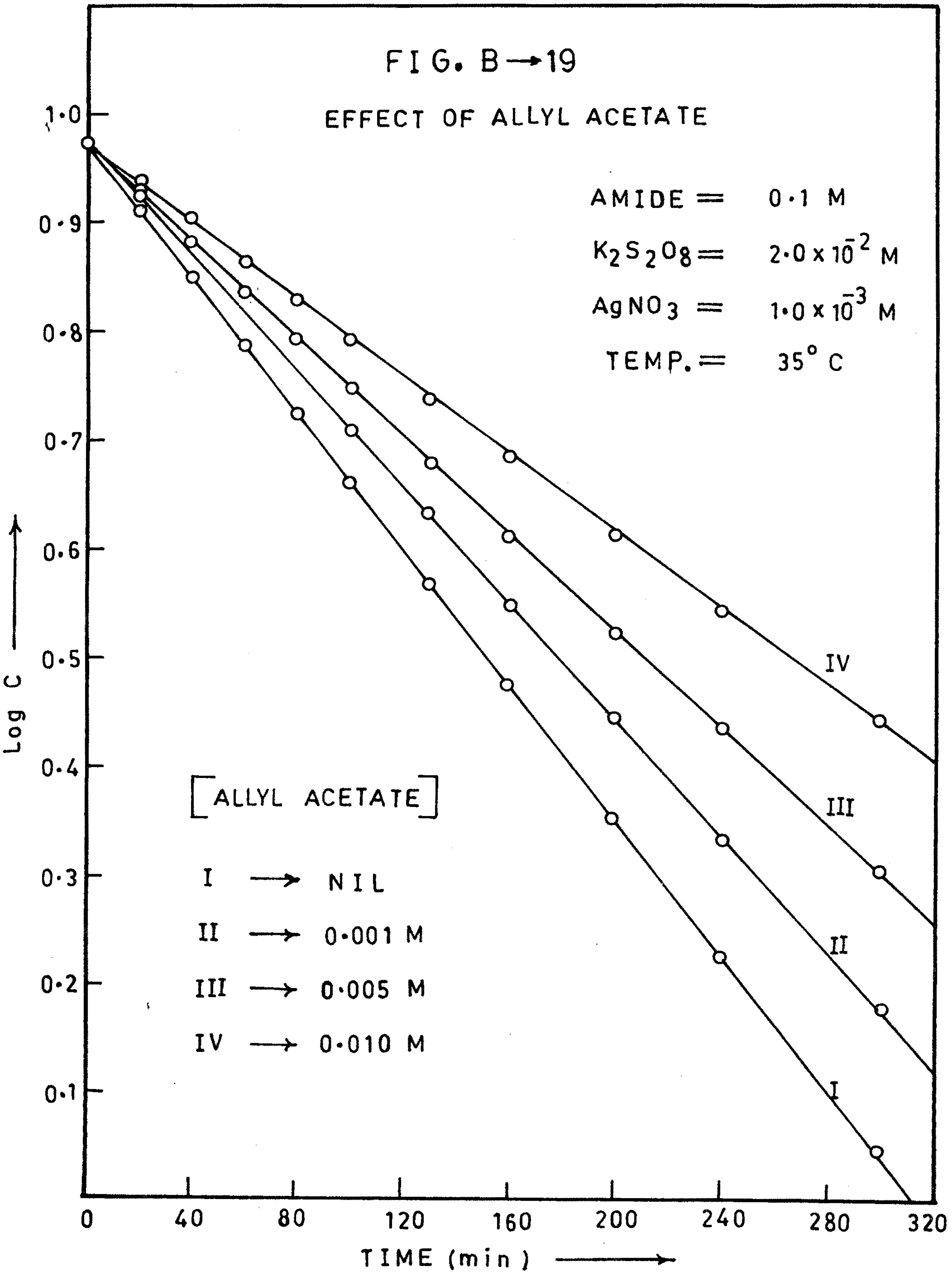


FIG. B→19

EFFECT OF ALLYL ACETATE

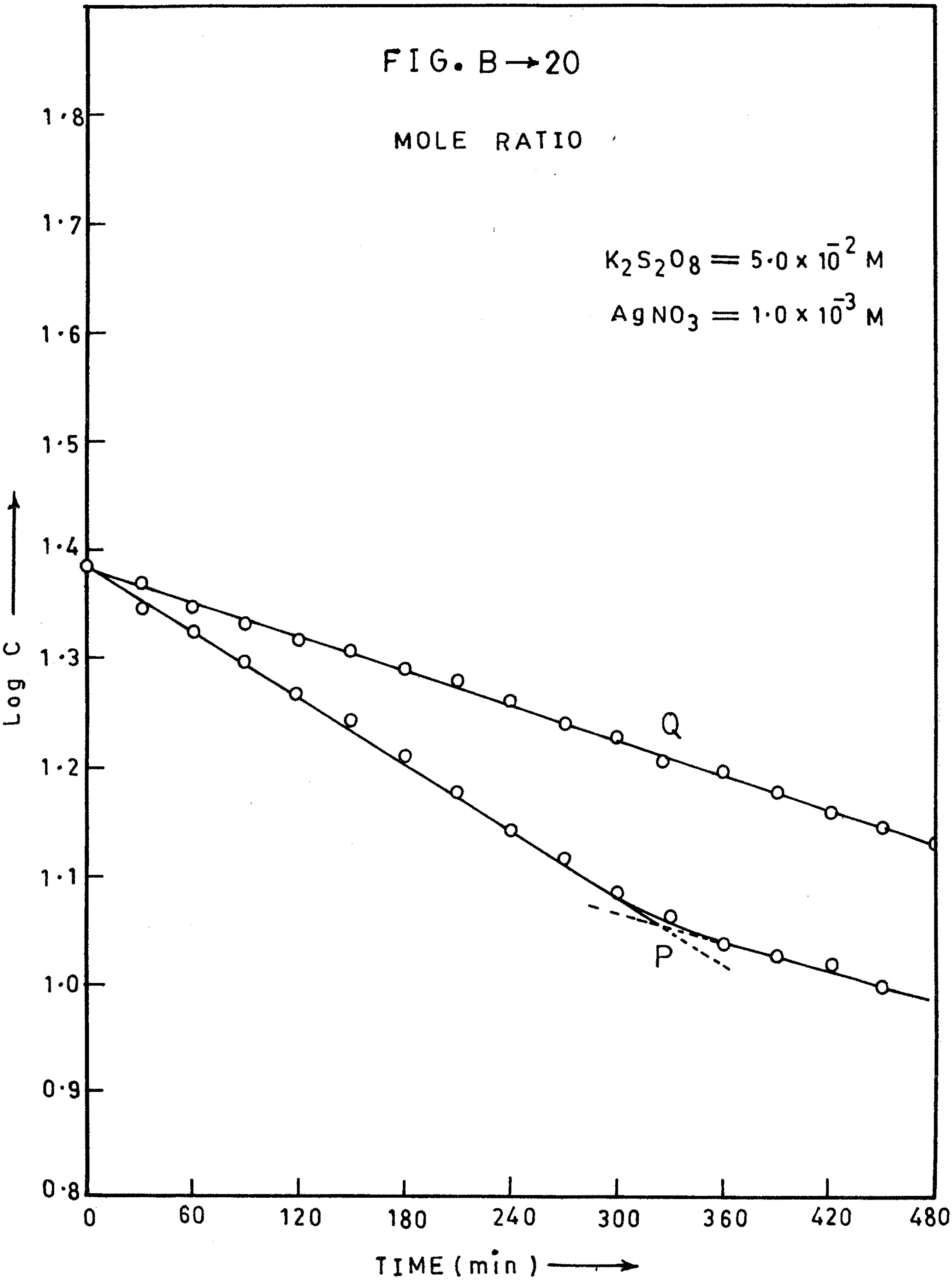


FIG. B→20

MOLE RATIO
$K_2S_2O_8 = 5.0 \times 10^{-2}$ M
$AgNO_3 = 1.0 \times 10^{-3}$ M
Q
P
Log C
1·8
1·7
1·6
1·5
1·4
1·3
1·2
1·1
1·0
0·9
0·8
0
60
120
180
240
300
360
420
480
TIME (min)