CHAPTER-III

Oxidation of Aniline

Results :

3. Results :

The results of the kinetics of oxidation of Aniline by potassium bromate in sulphuric acid medium is reported here. All reacticns are carried out in pseudo first order conditions. Appropriate concentrations of potassium bromate, Aniline and sulphuric acid were used to prepare the reaction mixtures. 5 ml aliquot of the reaction mixture was titrated periodically by usual iodometric method. Experiments were designed to study the following parameters.

1. Overall order of the reaction and order with respect to each of the reactants.
2. Effect of sulphuric acid concentration on the velocity of the reaction.
3. Effect of temperature and evaluation of thermodynamic parameters.
4. Effect of salt.
5. End product analysis and free radical test.
6. Stoichiometry.

3.1 Determination of the order of Reaction :

Order of the reaction with respect to potassium bromate was determined by isolation method. The concentration of potassium bromate was varied from 2.5×10^{-3} M to 12.5×10^{-3} M at constant concentration of Aniline (0.1 M). The reaction was studied at $30^0 \pm 0.1^0$ C. However orders with respect to Aniline could not be determined by isolation method, because concentration of Aniline is higher than bromate. Hence comparable concentrations of potassium bromate and Aniline were selected to determine the overall order of the reaction. For this purpose potassium bromate concentration was kept constant (1×10^{-2} M) while concentration of Aniline was varied from 2.5×10^{-2} M to 12.5×10^{-2} M.

3.1.1 Effect of potassium bromate variation :

The results of the variation of potassium bromate concentration at constant substrate concentration (0.1 M) at 30^oC are given in the table No.3.1.1. The plot of $\log_{10}(a-x)$ versus time (t) in mixture is straight line shown in Fig No.3.1.1. It is seen that the values of k are fairly constant. This shows that there is no effect of variation of bromate concentration on the value of k. Therefore order with respect to bromate is one.

It is confirmed by ploting the graph of a-x versus time (t). The nature of the graph is hyperbola. Therefore it obeys the first order rate low.

3.1.2 Effect of variation of Aniline concentration :

The concentration of Aniline was varied from 2.5 x 10^{-2} to 12.5 x 10^{-2} M, keeping the concentration of bromate (1x10^{-2} M) constant. The results are included in the table No. 3.1.2. A plot of $\log_{10}(a-x)$ versus time (t) is straight line (fig.No. 3.1.2.). The value of k increase with the concentration of Aniline. However, the ratio of k/[Aniline] is fairly constant which shows that first order with Aniline. It is also seen from calculations of order by differential method[22] Table No.3.1.3. The graphical value of order is one(fig. No.3.1.3.).

It is also confirmed by the graph of $\log_{10}K$ versus $\log_{10}Co$. The results are given in the table No. 3.1.4. The graph is straight line having slope equal to one (Fig.No.3.1.4). This clearly indicates that order with respect to aniline is one.

3.2 Effect of sulphuric acid on Reaction rate :

The reaction was studied in strong acidic medium. The concentration of sulphuric acid was varied from 4N to 8N. It is seen that, as the concentration of acid was increased, the values of rate constant increases while Aniline, Bromate concentrations was kept constant. The results are given in the Table No.3.1.5. and the values of k are given by the graph of $\log_{10}(a-x)$ versus time (t) Fig No.3.1.5). It is found that the order with respect to Acid is one (table No.3.1.9 fig. No. 3.1.9) plot of $\log_{10}K$ versus $\log_{10}Co$. Slope equal to one.

3.3. Effect of temperature on reaction rate and calculation of thermodynamic parameters.

The reactions was studied at four different temperature (303^0K, 308^0K, 313^0K, and 318^0K). The results are given in the table No.3.1.6. Graphical representation of $\log_{10}(a-x)$ versus time (t) is shown in (Fig. No.3.1.6.) From the values of specific reaction rate K_r at different temperature it is seen that the temperature co-efficient of reaction is 1.916.

Arrhenius equation,[23]

$$Kr = Ae^{-Ea/RT} \quad ..(3.1)$$

$$\text{Or } \log_{10}Kr = \log A - \frac{E_a}{2.303\,RT} \quad ..(3.2)$$

was used to calculate the energy of activation Ea, and frequency factor A. For this, $\log_{10}K$ was ploted against $\frac{1}{T}$. Fig. No.3.17. Table No.3.1.7 which is straight line E_a was obtained from the slope. This graphical value was found to be 12.948 K cal $mole^{-1}$.

The value of Ea was, however, used to calculate the frequency factor A.

A graph of $\log_{10}K/T$ versus $\frac{1}{T}$ was straight line (Fig. No.3.1.8) Table No.3.1.7) which was used to calculate $\Delta H^{\ddagger}$ $\Delta S^{\ddagger}$ and $\Delta G^{\ddagger}$ from the usual relations.

$$\text{Slope} = -\frac{\Delta H^{\ddagger}}{2.303\,R} \quad ..(3.3)$$

$$\Delta S^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger} \quad ..(3.5.)$$

The values of energy of activation, frequency factor, enthalpy of activation, entropy of activation and free energy of activation are given in the table No.3.1.8.

3.4 Free radical detection and end-product analysis :

The absence of free radical was shown by acrylonitrile[39] test, which gives no precipitate to the reaction mixture. In a reaction mixture one ml of acrylonitrile was added, but there is no formation of precipitate takes place, which indicates the absence of free radical. End product was identified to be 0 quinone[40,10] .

3.5 It is found that there is no effect of salt on the reaction rate. The salts used were sodium sulphate, potassium sulphate, and magnessium sulphate.

3.6 Stoichiometry :

To determine the stoichiometry of bromate and Aniline the reaction mixtures was of 2.5×10^{-2} M bromate and 1×10^{-2} M Aniline. The blank and back readings were taken and the difference of these two were used to find out the stoichiometry. It is found to be 1:1 for Bromate and Aniline.

Table No.3.1.1

Effect of cocentration of Oxidant ($KBrO_3$)

[Aniline] = 1×10^{-1} M

[Sulphuric Acid] = 5N

[Sodium Thiosulphate] = 2×10^{-3}M

Temperature = 30^{o}C.

[Potassium Bromate] 10^{-3}M	2.5	5	7.5	10.0	12.5
Time (min)	(a-x)	(a-x)	(a-x)	(a-x)	(a-x)
0	10.1	19.7	30.0	40.1	48.5
5	9.5	18.3	28.0	37.5	45.5
10	8.9	16.9	25.9	34.9	42.5
15	8.1	15.8	24.3	32.4	40.0
20	7.5	14.8	22.6	30.2	37.5
25	6.9	13.8	21.0	28.0	34.8
30	6.2	12.8	19.5	26.0	32.2
35	5.6	11.9	18.3	24.0	29.8
40	5.2	11.0	17.1	22.2	27.8
45	4.9	10.4	16.1	20.7	25.9
50	4.6	9.8	15.1	19.3	24.1
55	4.3	9.3	14.1	18.0	22.3
60	4.0	8.7	13.1	17.1	21.9
K-grphically (per min.)	1.355×10^{-2}	1.382×10^{-2}	1.422×10^{-2}	1.483×10^{-2}	1.433×10^{-2}
K-Sec^{-1}	2.256×10^{-4}	2.303×10^{-4}	2.37×10^{-4}	2.471×10^{-4}	2.388×10^{-4}.

Table No.3.1.2

Effect of concentration of Substrate (Aniline)

[Potassium Bromate] = 1×10^{-2} M

[Sulphuric Acid] = 5N

[Sodium Thiosulphate] = 2×10^{-3} M

Temperature = 30^{o}C

[Aniline] 10^{-2}M	2.5	5	7.5	10	12.5
Time(min)	(a-x)	(a-x)	a-x)	(a-x)	(a-x)
0	44.0	42.8	43.1	43.1	43.1
5	43.2	41.3	41.1	40.5	39.3
10	42.7	39.9	38.7	37.5	35.8
15	41.8	38.9	36.9	34.9	32.4
20	41.0	37.8	35.1	32.5	29.5
25	--	36.0	33.2	30.1	27.2
30	39.5	35.0	31.5	27.5	24.6
35	0-0	33.5	29.5	25.5	22.2
40	38.3	32.0	28.0	24.0	20.4
45	--	31.2	26.5	22.5	18.5
50	37.0	30.0	25.2	21.0	16.9
55	--	29.0	23.9	19.5	15.5
60	35.5	28.0	22.4	18.0	14.4
K_1 graphically (per.min.)	3.913×10^{-3}	7.678×10^{-3}	1.150×10^{-2}	1.418×10^{-2}	1.809×10^{-2}
K Sec^{-1}	6.52×10^{-5}	1.279×10^{-4}	1.916×10^{-4}	2.363×10^{-4}	3.015×10^{-4}

Table No.3.1.3

order with respect to Aniline

[Aniline] $\times 10^{-2}$ M	$-\frac{dc}{dt}$	$\log_{10}Co$	$\log_{10}(-\frac{dc}{dt})$
2.5	0.1021	-1.602	-0.9010
5.0	0.2494	-1.3010	-0.6030
7.5	0.3577	-1.1249	-0.4464
10.0	0.50	-0.9999	-0.3010
12.5	0.6338	-0.9030	-0.1980

Table No.3.1.4

[Aniline] 10^{-2}	K	$\log_{10}$ K	$\log_{10}Co$
2.5	3.919×10^{-3}	-2.4068	-1.602
5.0	7.678×10^{-3}	-2.1147	-1.3010
7.5	1.150×10^{-2}	-1.9393	-1.249
10.0	1.418×10^{-2}	-1.8483	-0.9999
15.0	1.809×10^{-2}	-1.7425	-0.9030

Table No.3.1.5

Effect of Sulphuric Acid Concentration

[Potassium Bromate] = 1×10^{-2} M

[Aniline] = 1×10^{-1} M

[Sodium Thiosulphate] = 2×10^{-3} M

Temperature = $30^{o}C$

[Sulphuric Acid] (N)	4	5	6	7	8
Time (min)	(a-x)	(a-x)	(a-x)	(a-x)	(a-x)
0	38.3	38.4	38.4	38.4	38.2
5	36.4	36.4	36.0	34.3	33.3
10	34.3	33.8	32.7	31.0	29.0
15	32.2	31.1	29.5	27.5	25.5
20	30.2	28.9	27.0	24.5	21.8
25	28.3	27.0	24.7	21.8	19.2
30	26.8	25.1	22.5	19.5	17.0
35	25.2	23.2	20.4	17.6	14.9
40	23.6	21.5	18.6	15.6	13.2
45	22.2	20.1	17.0	14.5	11.8
50	20.8	18.7	15.5	13.3	10.4
55	19.6	17.4	14.5	11.9	9.5
60	18.5	16.3	13.5	10.8	9.0
K graphically (per.min)	1.213×10^{-2}	1.440×10^{-2}	1.772×10^{-2}	2.194×10^{-2}	$2.658 \times 10^{-}$
K Sec^{-1}	2.021×10^{-4}	2.4×10^{-4}	2.953×10^{-4}	3.65×10^{-4}	4.43×10^{-4}

Table No.3.1.6

Effect of Temperature

[Potassium Bromate] = 1×10^{-2} M

[Aniline] = 1×10^{-1} M

[Sodium Thiosulphate] = 2×10^{-3} M

[Sulphuric Acid] = 5N

Temperature 0C	30	35	40	45
Time (min)	(a-x)	(a-x)	(a-x)	(a-x)
0	38.5	36.5	36.5	36.5
5	36.0	32.7	31.5	29.0
10	33.5	29.2	26.9	23.5
15	31.0	25.8	22.5	19.0
20	29.0	23.0	19.5	15.5
25	27.0	20.5	16.5	12.5
30	25.0	18.3	14.3	10.5
35	23.9	16.4	12.7	8.8
40	21.4	14.6	11.1	7.3
45	20.0	13.3	9.7	6.5
50	18.6	12.1	8.8	5.8
55	17.3	11.2	7.9	5.0
60	16.1	10.3	7.1	4.1
K graphically per min.	1.535×10^{2}	2.215×10^{-2}	2.879×10^{-2}	4.335×10^{-2}
K Sec.^{1}	2.558×10^{-4}	3.691×10^{-4}	4.798×10^{-4}	7.225×10^{-4}

Table No.3.1.7

Temp. $T(^{o}K)$	$\frac{1}{T} \times 10^3$	K	$\log_{10}K$	$\log_{10}K/T$
303	3.301	1.535×10^{-2}	-1.8138	-4.2953
308	3.246	2.215×10^{-2}	-1.6546	-4.1431
313	3.195	2.879×10^{-2}	-1.5407	-4.0363
318	3.145	4.335×10^{-2}	-1.3630	-3.8654

Table No. 3.1.8

Temperature T (^oK)	K per.min.	Temperature coefficient	Energy of activation E_a K.cal.mole^{-1}	Enthalpy of activation $\Delta H^{\neq}$	Frequency factor (A) Sec^{-1}	Entropy of Activation $\Delta S^{\neq}$ e.u.	Free energy of Activation $\Delta G^{\neq}$ K.cal.mole^{-1}
303	1.535×10^{-2}						
308	2.215×10^{-2}	1.8755	12.948	12.4184	3.184×10^{7}	−28.2540	21.1759
313	2.879×10^{-2}	1.9571					
318	4.335×10^{-2}						

Table No.3.1.9

order with respect to Acid

[Sulphuric Acid]	K	$\log_{10}K$	$\log_{10}Co$
4	1.213×10^{-2}	-1.9161	0.6020
5	1.44×10^{-2}	-1.8416	0.6990
6	1.772×10^{-2}	-1.7515	0.7781
7	2.194×10^{-2}	-1.6627	0.8450
8	2.648×10^{-2}	-1.5770	0.9030

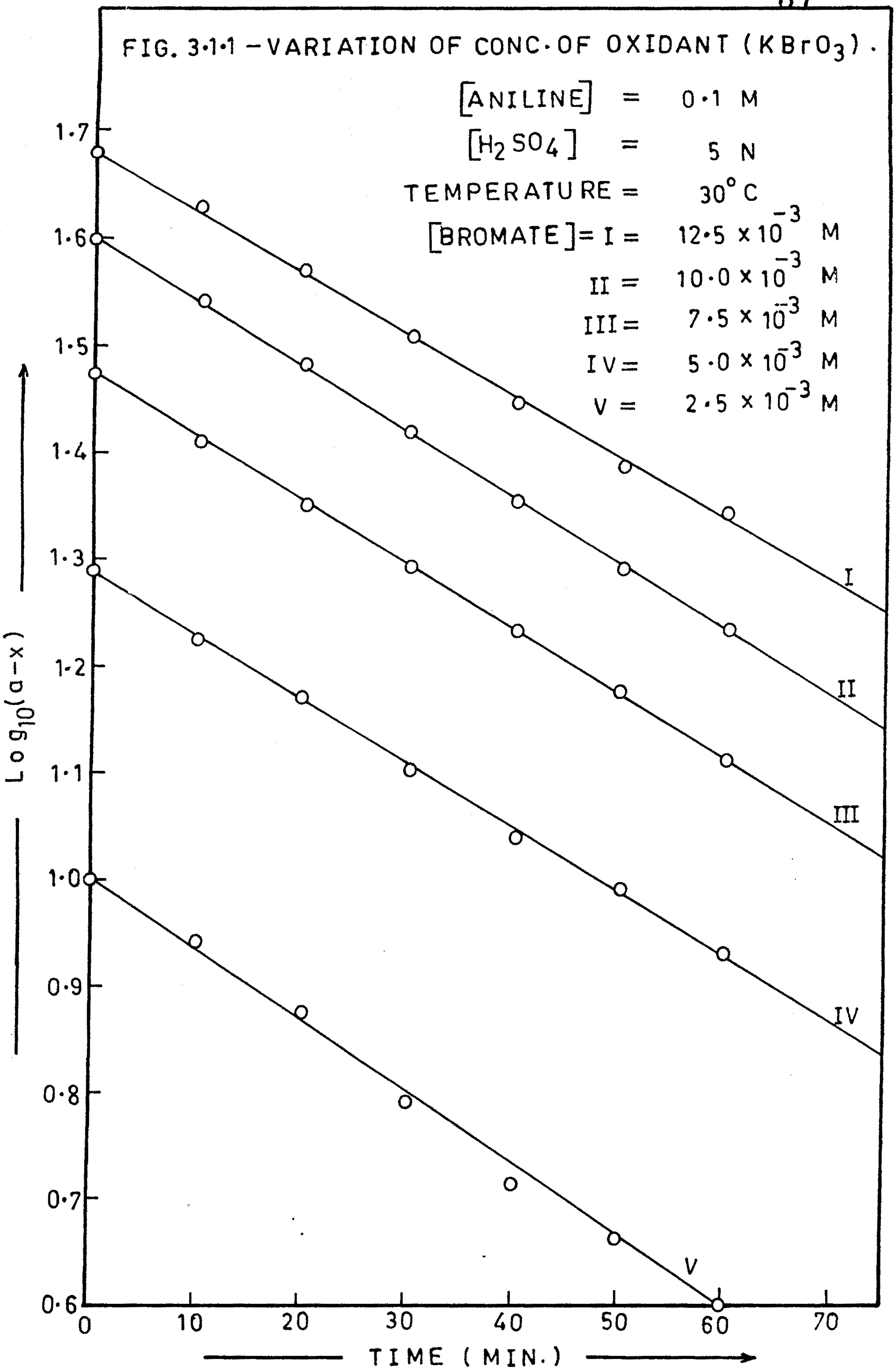


FIG. 3·1·1 – VARIATION OF CONC· OF OXIDANT (KBrO3).
[ANILINE] = 0·1 M
[H2SO4] = 5 N
TEMPERATURE = 30° C
[BROMATE] = I = 12·5 x 10-3 M
II = 10·0 x 10-3 M
III = 7·5 x 10-3 M
IV = 5·0 x 10-3 M
V = 2·5 x 10-3 M
I
II
III
IV
V
Log10(a–x)
1·7
1·6
1·5
1·4
1·3
1·2
1·1
1·0
0·9
0·8
0·7
0·6
0
10
20
30
40
50
60
70
TIME (MIN.)

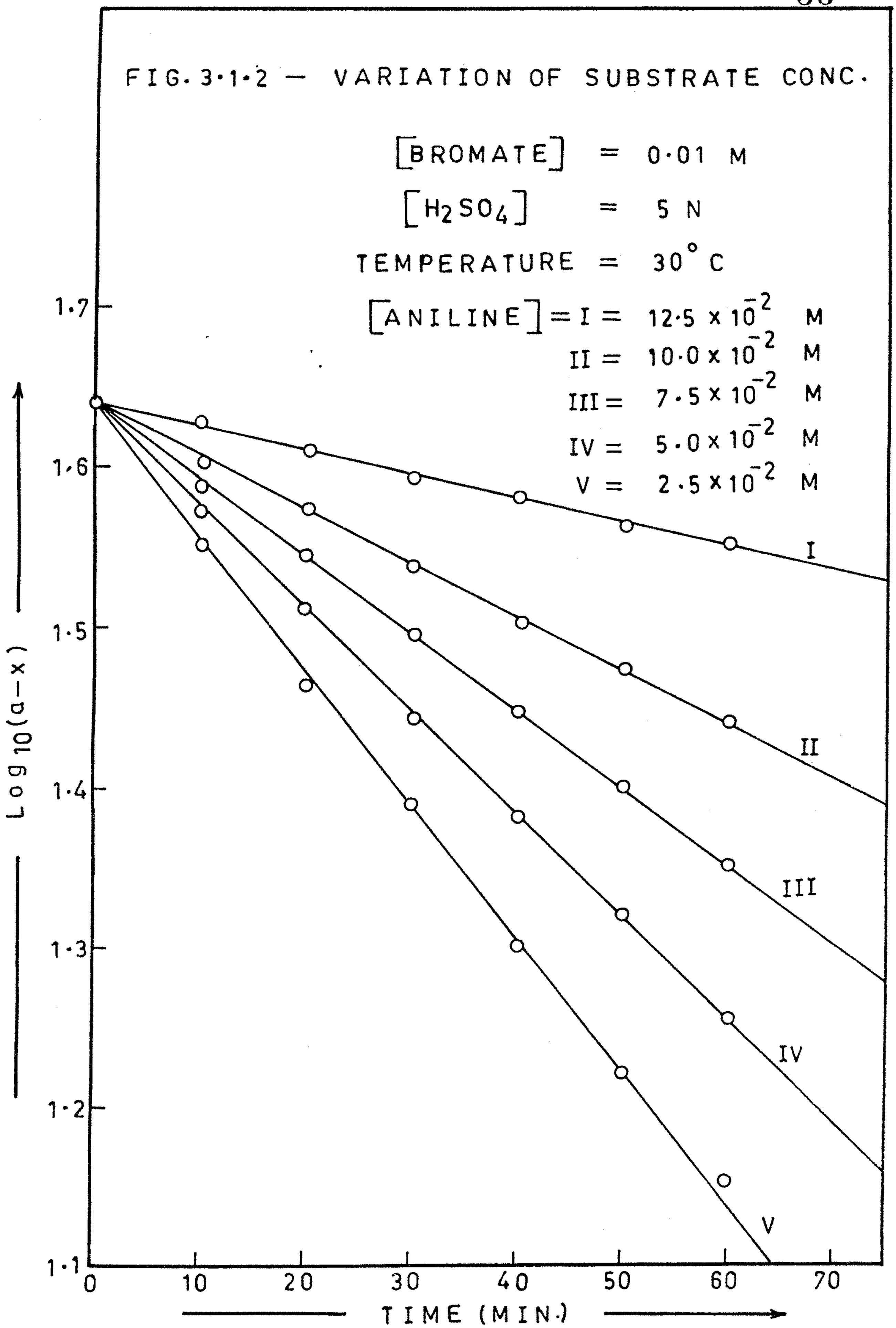


FIG. 3·1·2 — VARIATION OF SUBSTRATE CONC.
[BROMATE] = 0·01 M
[H_2SO_4] = 5 N
TEMPERATURE = 30° C
[ANILINE] = I = 12.5×10^{-2} M
II = 10.0×10^{-2} M
III = 7.5×10^{-2} M
IV = 5.0×10^{-2} M
V = 2.5×10^{-2} M
I
II
III
IV
V
1·7
1·6
1·5
1·4
1·3
1·2
1·1
$Log_{10}(a-x)$
0
10
20
30
40
50
60
70
TIME (MIN.)

FIG. 3.13 — VARIATION OF SUBSTRATE CONC.

PLOT OF $\mathrm{Log}_{10}\left(-\frac{dc}{dt}\right)_0$ VERSUS $\mathrm{Log}_{10}\, C_0$.

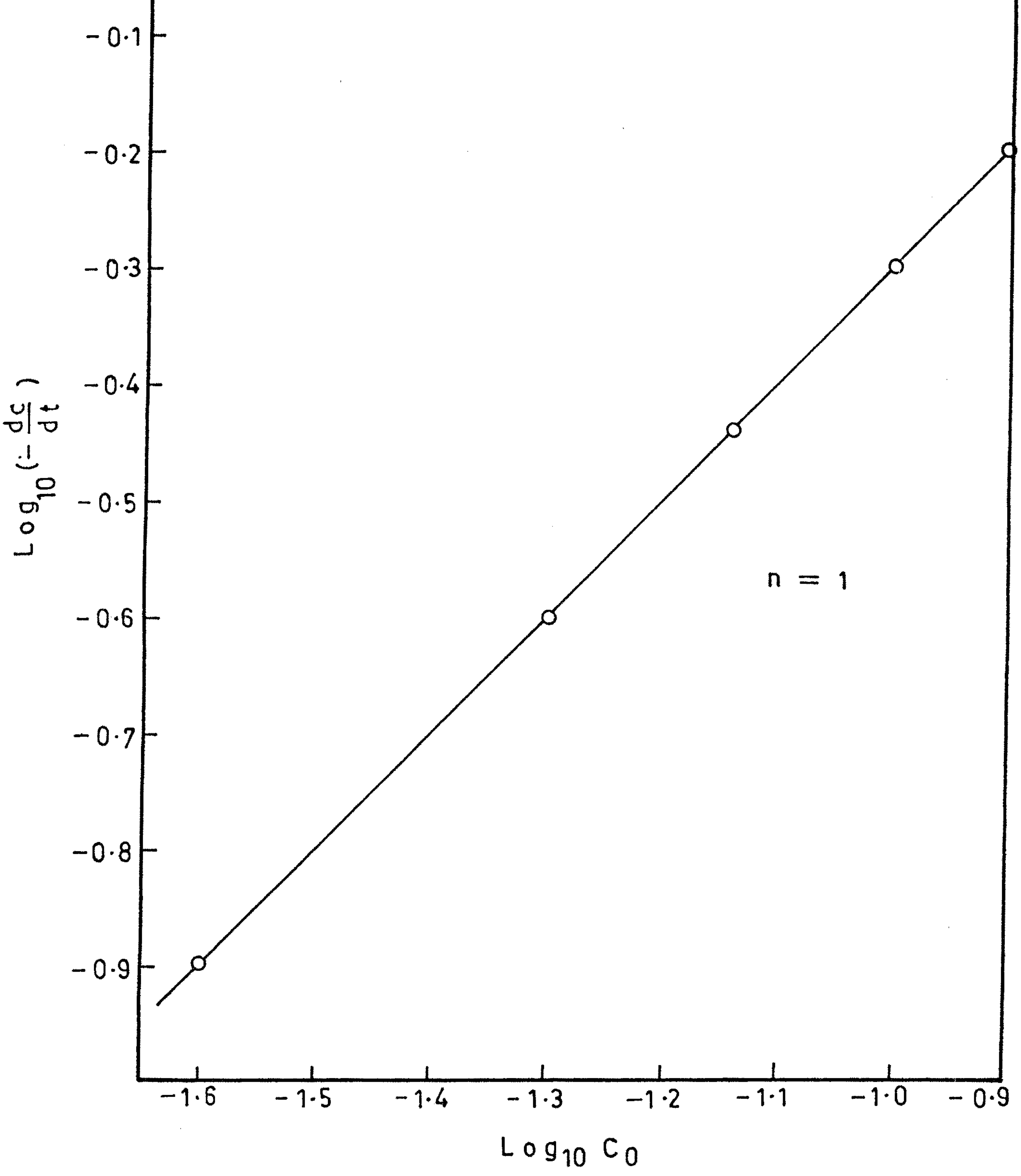
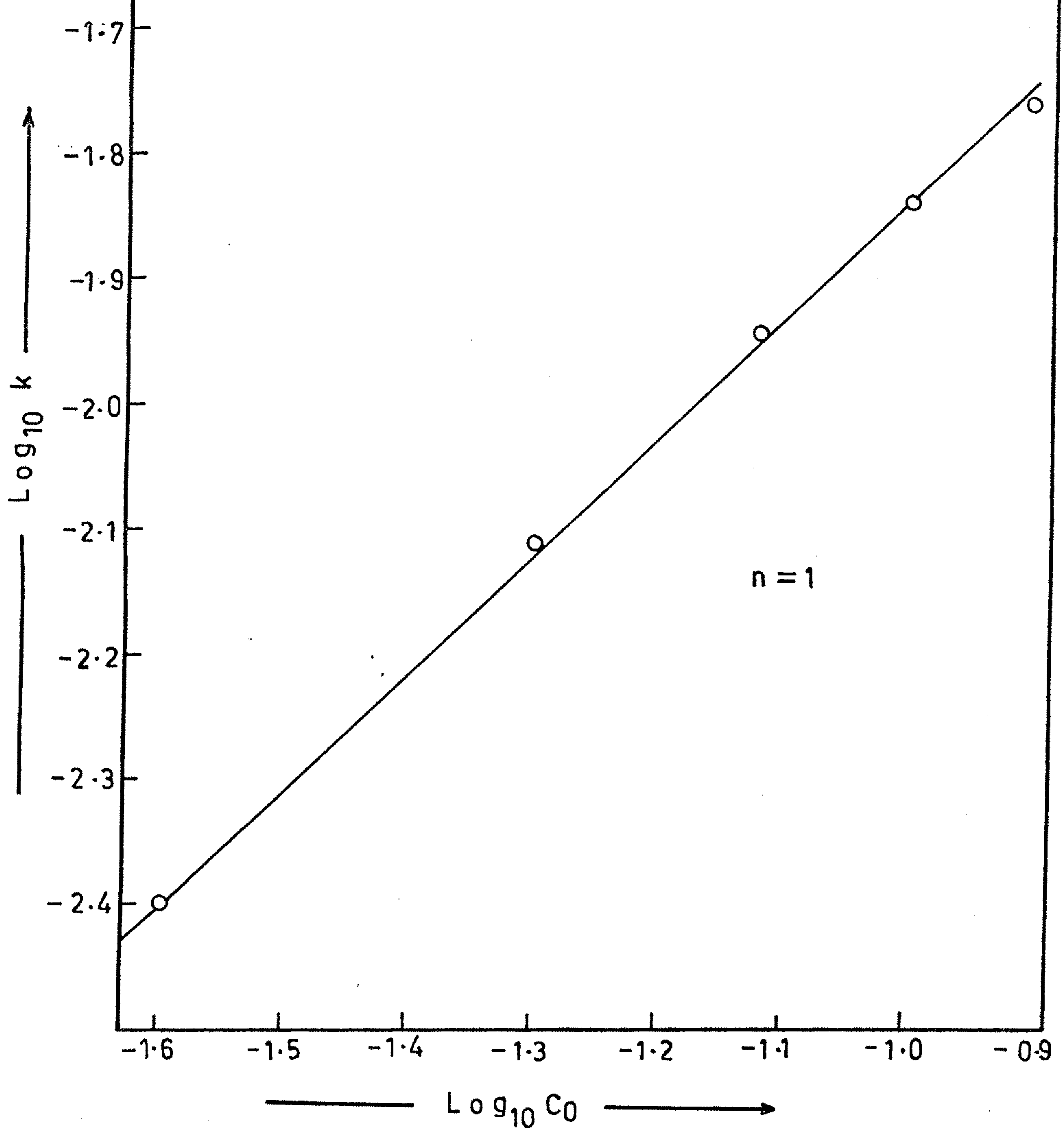


FIG. 3·1·4 — VARIATION OF SUBSTRATE CONC.

PLOT OF $Log_{10}\,k$ VERSUS $Log_{10}\,C_0$.



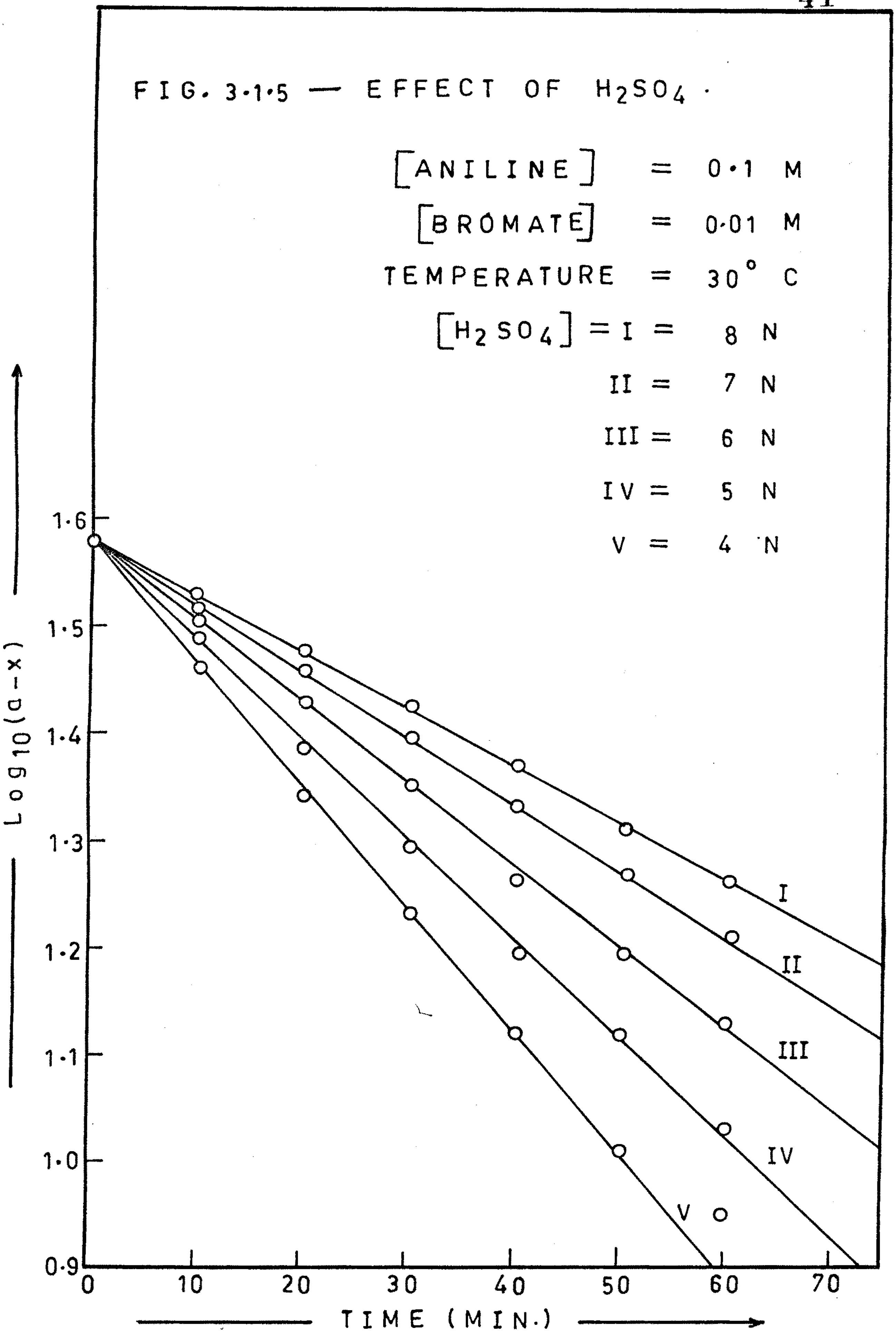


FIG. 3·1·5 — EFFECT OF H2SO4.
[ANILINE] = 0·1 M
[BROMATE] = 0·01 M
TEMPERATURE = 30° C
[H2SO4] = I = 8 N
II = 7 N
III = 6 N
IV = 5 N
V = 4 N
Log10(a−x)
1·6
1·5
1·4
1·3
1·2
1·1
1·0
0·9
0
10
20
30
40
50
60
70
TIME (MIN.)
I
II
III
IV
V

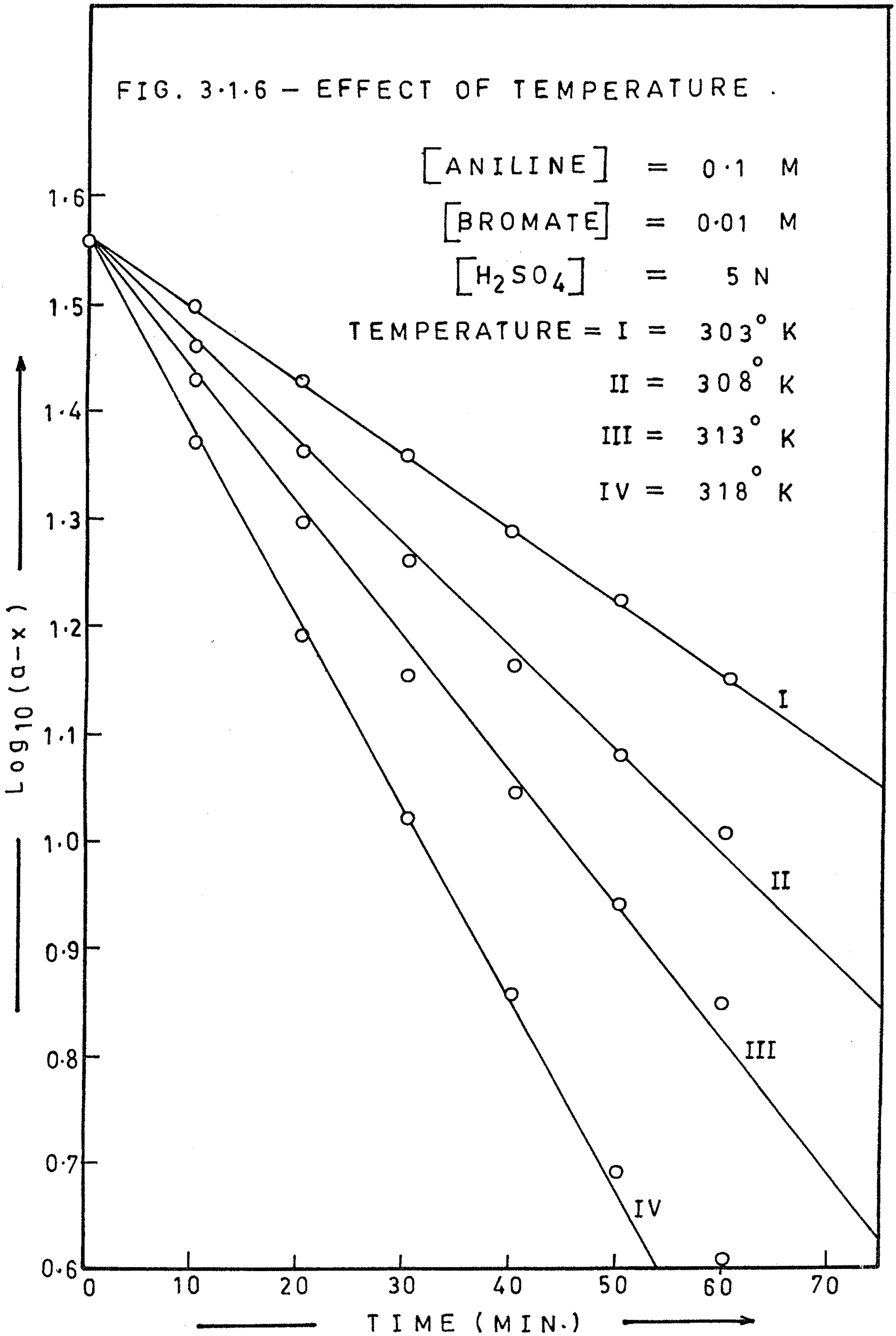


FIG. 3·1·6 – EFFECT OF TEMPERATURE.
[ANILINE] = 0·1 M
[BROMATE] = 0·01 M
[H2SO4] = 5 N
TEMPERATURE = I = 303° K
II = 308° K
III = 313° K
IV = 318° K
I
II
III
IV
Log10 (a−x)
1·6
1·5
1·4
1·3
1·2
1·1
1·0
0·9
0·8
0·7
0·6
0
10
20
30
40
50
60
70
TIME (MIN.)

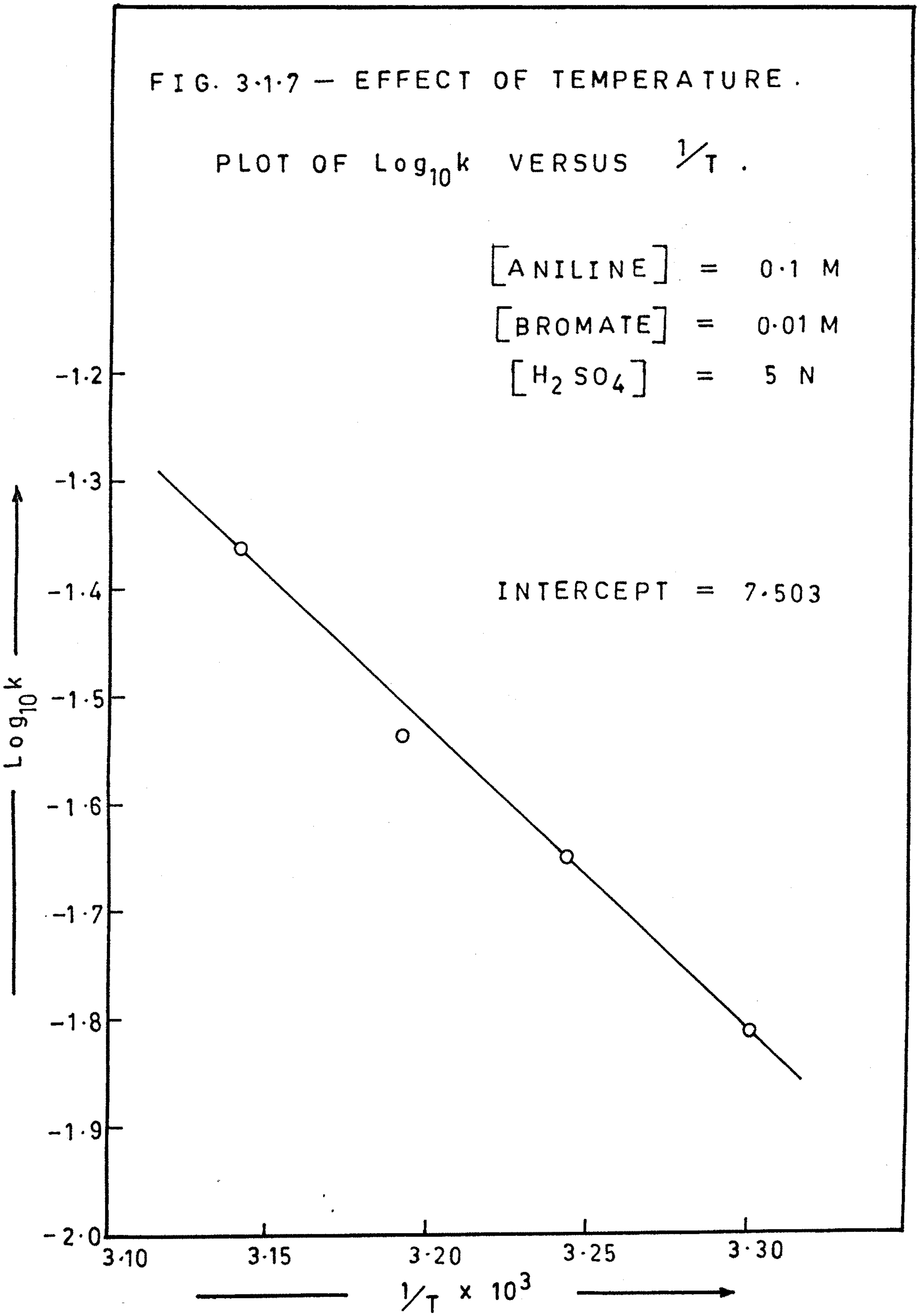


FIG. 3·1·7 — EFFECT OF TEMPERATURE.
PLOT OF Log10k VERSUS 1/T.
[ANILINE] = 0·1 M
[BROMATE] = 0·01 M
[H2 SO4] = 5 N
INTERCEPT = 7·503
Log10k
-1·2
-1·3
-1·4
-1·5
-1·6
-1·7
-1·8
-1·9
-2·0
3·10
3·15
3·20
3·25
3·30
1/T x 10^3

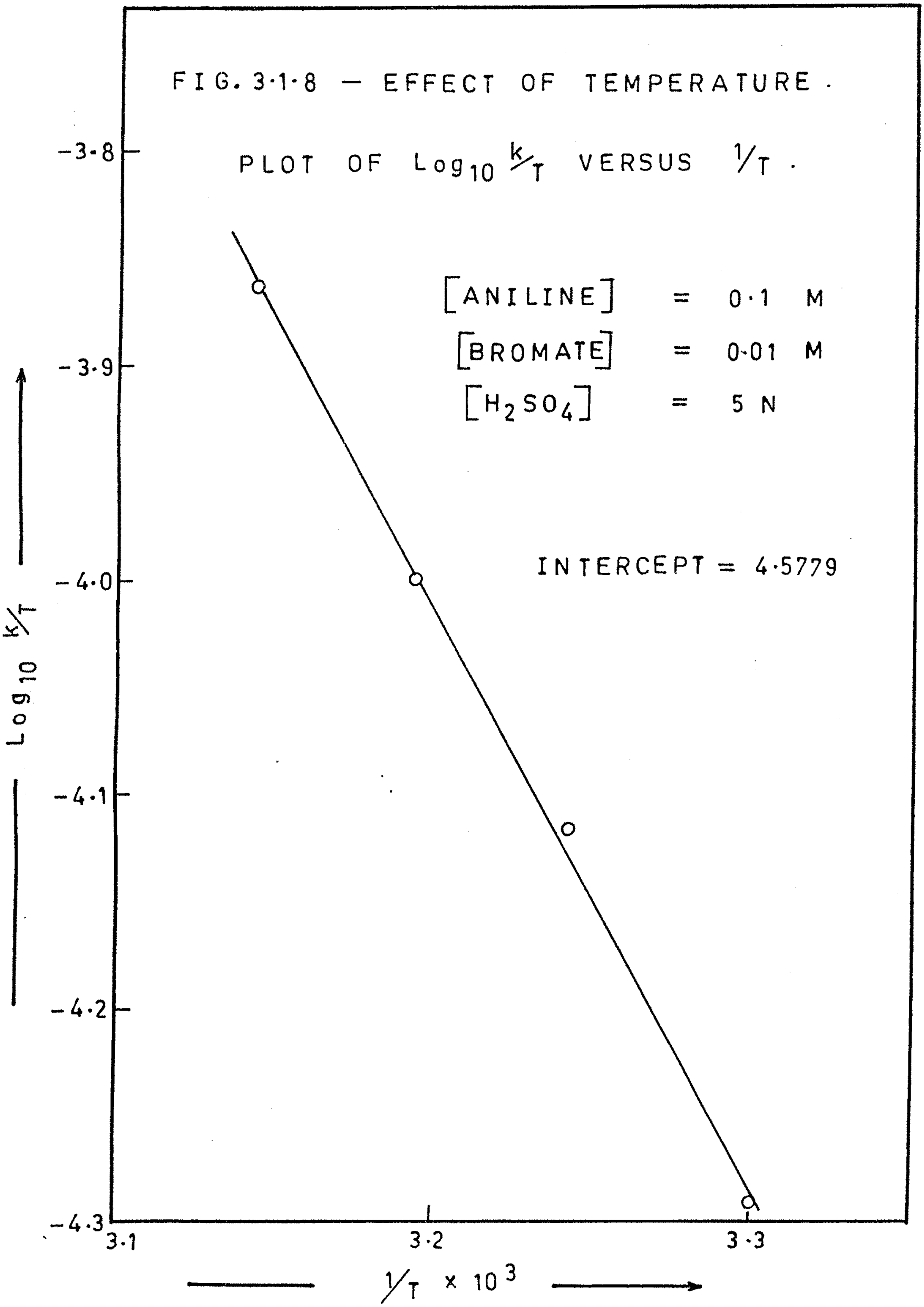


FIG. 3·1·8 — EFFECT OF TEMPERATURE. PLOT OF $\text{Log}_{10}\, k/T$ VERSUS $1/T$.

FIG. 3·1·9 – EFFECT OF H_2SO_4 CONCENTRATION.

PLOT OF $Log_{10}\,k$ VERSUS $Log_{10}\,C_0$.