CHAPTER III

RESULTS

The malonic acid dihydrazide (MAD) and succinic acid dihydrazide (SAD) were oxidised by chloramine-T in buffered medium (pH = 9.0) at temperature 30°C. The reaction rates were measured as a function of time to the extent to which a rectants are consumed or products are formed.

As we know that so as to represent the probable mechanism of any reaction it is necessary to collect the information in the form of different reaction parameters. So we have carried out following sets of kinetic runs and results are summarised.

I. EFFECT OF CHANGE IN THE SUBSTRATE CONCENTRATION ON THE OXIDATION OF DIHYDRAZIDES BY CHLORAMINE-T

In order to investigate the effect of concentration of dihydrazides on the oxidation of dihydrazides by chloramine-T, a kinetic runs were carried out by changing the concentration of dihydrazides in the reaction mixture, where all other reaction conditions were kept unaltered. The concentrations of malonic acid dihydrazide were changed in following range 7.0×10^{-4} to 1.3×10^{-3} M. Similarly change in the concentrations of succinic acid dihydrazide were made from 2.0×10^{-4} to 8.0×10^{-4} M. The various experimental results are summarised in Table 3.1 to 3.4.

The first order rate constants were obtained from the slopes of the plots of log (a-x) versus time (t). Where, 'a' is the initial concentration of chloramine-T in terms of sodium thiosulphate 'x' is the concentration of chloramine-T at time 't' in terms of sodium thiosulphate. Rate constants are obtained using following equations,

$k_{(obs)}$ = - slope x 2.303

$$k = \frac{2.303}{t} \log \left(\frac{a}{a-x} \right) \qquad \ldots (3.1)$$

The second order rate constants (k_2') were obtained from equation (3.2) as has been done by many workers in this field so as to show that this reaction is first order.

$$k_2' = \frac{k}{[\text{concentration of hydrazide}]} \qquad \ldots (3.2)$$

Where k is a rate constant calculated by eqn. 3.1 and k_2' is not a k_2 obtained by Swan's time ratio method.

An increase in the dihydrazide concentration without change in the concentration of chloramine-T increases the rate of reaction (Fig.3.7 and 3.8) . The linearity of a plots of log (a-x) versus time 't' (Fig.No. 3.1 and 3.2) and fairly concordant values of k_2' (Table No.3.1 and 3.3) for all concentrations of dihydrazides show that reaction with respect to dihydrazides is first order. This first order dependance of this reaction on the concentrations of dihydrazides has been supported by differential methods and Van't Hoff differential method.

The values of initial rates ($-\frac{dco}{dt}$) are calculated from the plots of (a-x) versus time 't' (Fig.3.3 and 3.5), and logarithms of these initial rates were plotted against corresponding logarithm of initial concentrations of dihydrazides (Fig.3.4 and 3.6). The slopes represent the order which is found to be unity in both the cases.

Finally by J.H. Van't Hoff differential method the order of reaction is confirmed.

$$\text{Order } (n) = \frac{\log \left[-\frac{dco}{dt}\right]_2 - \log \left[-\frac{dco}{dt}\right]_1}{\log [Co]_2 - \log [Co]_1} \qquad \ldots (3.3)$$

Values obtained by this method were also found to be nearly one (Table 3.2 and 3.4).

By observing the results of above different methods it is confirmed that this reaction is first order with respect to dihydrazides.

II. EFFECT OF CHANGE IN THE REAGENT CONCENTRATIONS ON THE OXIDATION OF DIHYDRAZIDES BY CHLORAMINE-T

The effect of change in the concentrations of chloramine-T on the oxidation of malonic acid dihydrazide (MAD) and succinic acid dihydrazide (SAD) by chloramine-T (CAT) were studied by changing the concentration ofchloramine-T in the reaction mixture in which all other reaction conditions were kept unaltered. The change in the concentration of chloramine-T was made from 2.0 to 8.0 x 10^{-4}M in case of both the dihydrazides. Results obtained are summarised in Tables 3.5 to 3.8.

The first order rate constant (k) were obtained from rate equation (3.1). An increase in CAT concentration without change in [Dihydrazide] does not affect the rate of reaction Fig.3.15 and 3.16 . The order of the reaction with respect to chloramine-T was found to unity from a linear plots of log (a-x) versus time (in each case at least 70% completion of the reaction is done ~~in each case~~) (Fig.3.9 and 3.10). The constancy of k for different initial concentrations of CAT calculated from first order rate equation (Table 3.5 and 3.7) gave further evidence for first order dependance of CAT in this reaction.

This first order dependence of this reaction on the concentrations of chloramine-T has been supported by Vant Hoff differential method (Fig. 3.12 and 3.14).

TABLE - 3.1

EFFECT OF CHANGE IN THE SUBSTRATE CONCENTRATION ON THE OXIDATION OF MALONIC ACID DIHYDRAZIDES BY CHLORAMINE-T

[MAD] x 10^4 = 7.0 to 13.0 M   [CAT] x 10^3 = 1.0 M

Temp = 30^oC pH = 9.0

Sr. No.	[MAD] x10^4 M	k x$10^4 S^{-1}$	$k_{(graph)}$ x$10^4 S^{-1}$	$k'_2 M^{-1} S^{-1}$	k_1 x$10^4 S^{-1}$	k_2 x$10^4 S^{-1}$
1	7	* 0.846	0.829	0.1184	1.653	0.826
2	8	* 0.953	0.944	0.1180	1.882	0.941
3	9	1.094	1.075	0.1194	2.143	1.071
4	10	1.274	1.266	0.1266	2.524	1.262
5	11	1.452	1.458	0.1325	2.907	1.453
6	12	1.659	1.627	0.1355	3.243	1.619
7	13	1.863	1.857	0.1425	3.702	1.851

TABLE - 3.2

DATA FOR VAN'T HOFF DIFFERENTIAL AND GRAPHICAL METHOD

Sr. No.	[MA D] x10^4 M	$-\frac{dco}{dt}$	Order (n)	$1+\log\left[-\frac{dco}{dt}\right]$	4+log[Co]	$Order_{(graph)}$ Fig.3.4
1	7	0.116	-	0.0644	0.8451	
2	8	0.134	1.080	0.1271	0.9031	
3	9	0.152	1.070	0.1818	0.9542	1.064
4	10	0.170	1.062	0.2304	1.0000	
5	11	0.180	1.056	0.2742	1.0414	
6	12	0.206	1.051	0.3138	1.0792	
7	13	0.224	1.046	0.3502	1.1139	

TABLE - 3.3

EFFECT OF CHANGE IN THE SUBSTRATE CONCENTRATIONS ON THE OXIDATION OF SUCCINIC ACID DIHYDRAZIDE BY CHLORAMINE-T

[SAD] x 10^4 = 2.0 to 8.0 M   [CAT] x 10^3 = 1.0 M

Temp = 30^oC pH = 9.0

Sr. No.	[SAD] x10^4 M	k x$10^4 S^{-1}$	$k_{(graph)}$x$10^4 S^{-1}$	$k_2' M^{-1} S^{-1}$	k_1x$10^4 S^{-1}$	k_2x$10^4 S^{-1}$
1	2	0.974	0.934	0.4669	1.862	0.931
2	3	1.360	1.356	0.4520	2.703	1.351
3	4	1.735	1.752	0.4380	3.493	1.746
4	5	2.297	2.301	0.4602	4.587	2.293
5	6	2.601	2.635	0.4301	5.253	2.626
6	7	* 3.021	3.006	0.4291	5.993	2.996
7	8	* 3.541	3.506	0.4382	6.990	3.495

TABLE - 3.4

DATA FOR VAN'T HOFF DIFFERENTIAL AND GRAPHICAL METHOD

Sr. No.	[SAD] x10^4 M	$-\left[\frac{dco}{dt}\right]$	Order (n)	$1+\log\left[-\frac{dco}{dt}\right]$	4+loc [Co]	Order graph Fig. 3.6
1	2	0.1266	-	0.1024	0.3010	
2	3	0.1900	1.001	0.2788	0.4771	
3	4	0.2533	0.999	0.4036	0.6021	1.000
4	5	0.3166	0.996	0.5005	0.6990	
5	6	0.3800	1.001	0.5798	0.7782	
6	7	0.4433	0.999	0.6467	0.8451	
7	8	0.5066	0.999	0.7047	0.9031	

TABLE - 3.5

EFFECT OF CHANGE IN THE REAGENT CONCENTRATION ON THE OXIDATION OF MALONIC ACID DIHYDRAZIDE BY CHLORAMINE-T

[MAD] x 10^3 = 1.0 M [CAT] x 10^4 = 2.0 to 18.0 M

Temp = $30^{\circ}C$ pH = 9.0

Sr. No.	[CAT] x10^4 M	$k x10^4 S^{-1}$	$k_{(graph)} x10^4 S^{-1}$	$k_1 x10^4 S^{-1}$	$k_2 x10^4 S^{-1}$
1	2	1.455	1.397	2.901	1.450
2	4	1.351	1.282	2.693	1.346
3	6	1.326	1.266	2.643	1.321
4	8	1.281	1.266	2.554	1.277
5	10	1.274	1.266	2.540	1.270
6	12	1.251	1.228	2.494	1.247
7	14	1.217	1.190	2.426	1.213
8	16	1.199	1.151	2.390	1.195
9	18	1.176	1.151	2.344	1.172

TABLE - 3.6

DATA FOR VAN'T HOFF DIFFERENTIAL AND GRAPHICAL METHOD

Sr. No.	[CAT] x10^4 M	$\left[-\frac{dco}{dt}\right]$	Order (n)	$2+\log\left[-\frac{dco}{dt}\right]$	$4+\log[Co]$	Order graph Fig. 3.12
1	2	0.0350	-	0.5441	0.3101	
2	4	0.0675	0.9475	0.8292	0.6021	
3	6	0.1025	1.0302	1.010	0.7781	0.977
4	8	0.1350	0.9573	1.1303	0.9031	$\simeq$ 1.0
5	10	0.1700	1.0330	1.2304	1.0000	
6	12	0.2050	1.0268	1.3118	1.0792	
7	14	0.2400	1.0255	1.3802	1.1461	
8	16	0.2715	0.9166	1.4392	1.2041	
9	18	0.3050	0.9956	1.4843	1.2553	

TABLE - 3.7

EFFECT OF CHANGE IN THE REAGENT CONCENTRATION ON THE OXIDATION OF SUCCINIC ACID DIHYDRAZIDE BY CHLORAMINE-T

[SAD] x 10^4 = 5.0 M   [CAT] x 10^4 = 2.0 to 18.0 M

Temp = 30^oC pH = 9.0

Sr. No.	[CAT] x10^4 M	kx10^4S^{-1}	$k_{(graph)}x10^4S^{-1}$	$k_1x10^4S^{-1}$	$k_2x10^4S^{-1}$
1	2	2.420	2.341	4.825	2.412
2	4	2.382	2.301	4.749	2.374
3	6	2.340	2.301	4.665	2.332
4	8	2.303	2.301	4.591	2.295
5	10	2.297	2.301	4.579	2.289
6	12	2.272	2.301	4.530	2.265
7	14	2.283	2.301	4.551	2.275
8	16	2.248	2.175	4.482	2.241
9	18	2.236	2.175	4.458	2.229

TABLE - 3.8

DATA FOR VAN'T HOFF DIFFERENTIAL AND GRAPHICAL METHOD

Sr. No.	[CAT] x10^4 M	$\left[-\frac{dco}{dt}\right]$	Order (n)	2+log$\left[-\frac{dco}{dt}\right]$	4+log[Co]	Order graph Fig. 3.14
1	2	0.0633	-	0.8014	0.3010	
2	4	0.1266	0.9993	1.1024	0.6021	
3	6	0.1900	1.0013	1.2787	0.7781	
4	8	0.2533	0.9995	1.4036	0.9031	1.00
5	10	0.3166	0.9996	1.5005	1.0000	
6	12	0.3800	1.0011	1.5780	1.0792	
7	14	0.4493	0.9995	1.6470	1.1461	
8	16	0.5066	0.9995	1.7047	1.2041	
9	18	0.5700	1.0010	1.7560	1.2553	

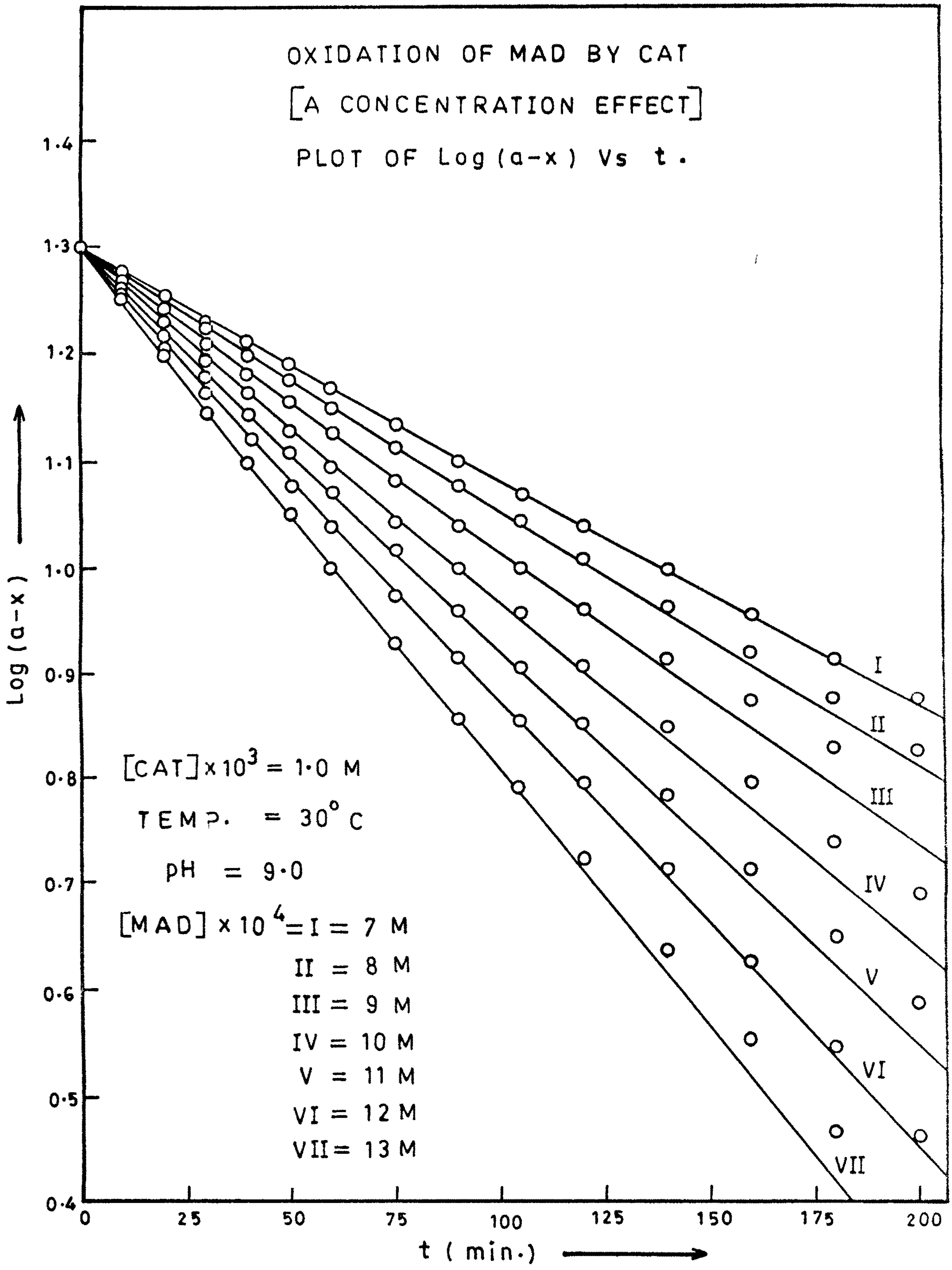

OXIDATION OF MAD BY CAT
[A CONCENTRATION EFFECT]
PLOT OF Log (a-x) Vs t.
[CAT] x 10^3 = 1·0 M
TEMP. = 30° C
pH = 9·0
[MAD] x 10^4 = I = 7 M
II = 8 M
III = 9 M
IV = 10 M
V = 11 M
VI = 12 M
VII = 13 M
I
II
III
IV
V
VI
VII
Log (a-x)
t (min.)
1·4
1·3
1·2
1·1
1·0
0·9
0·8
0·7
0·6
0·5
0·4
0
25
50
75
100
125
150
175
200

FIG.3·1

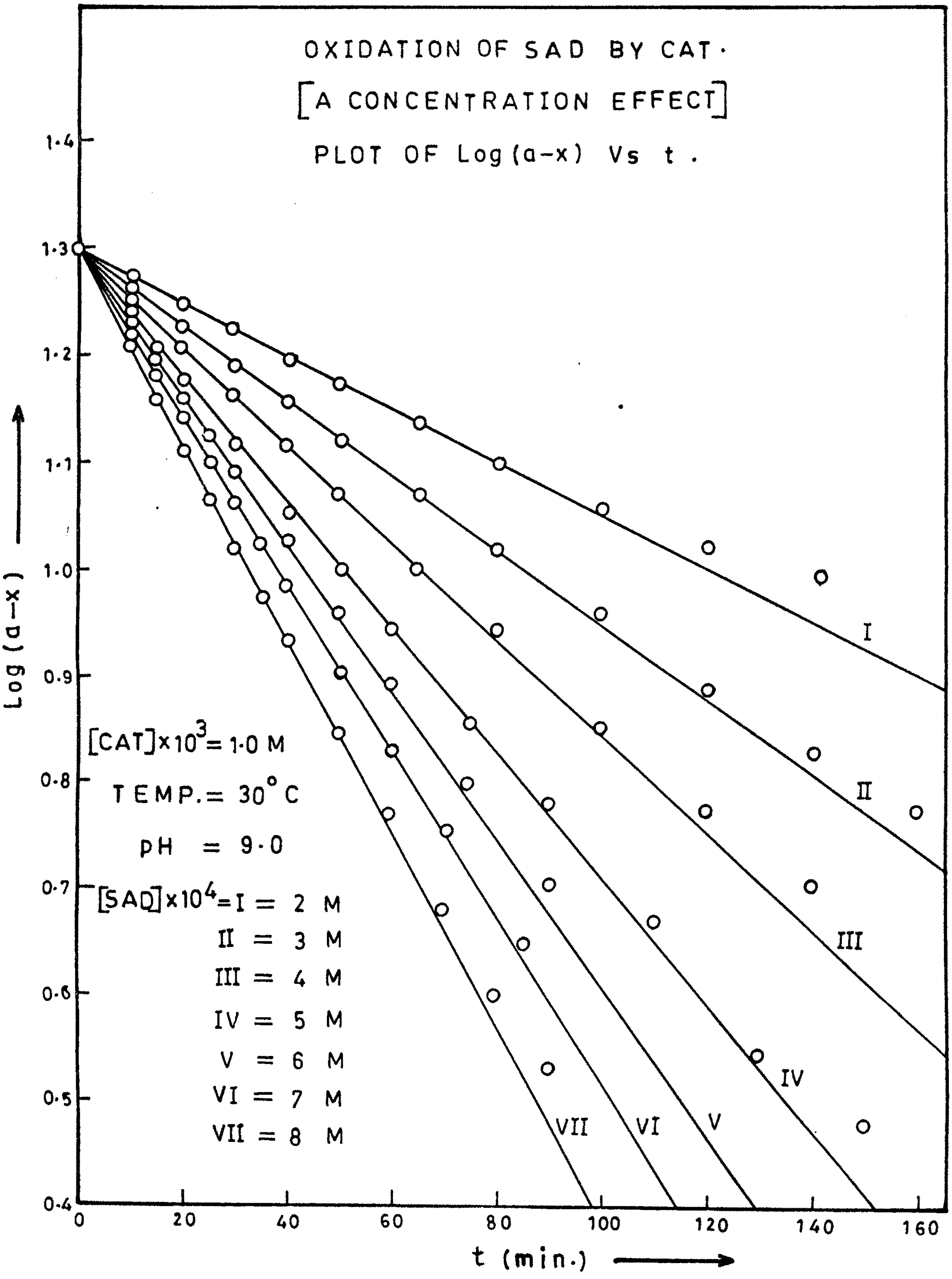

OXIDATION OF SAD BY CAT.
[A CONCENTRATION EFFECT]
PLOT OF Log(a-x) Vs t.
[CAT]x10³ = 1.0 M
TEMP. = 30° C
pH = 9.0
[SAD]x10⁴ = I = 2 M
II = 3 M
III = 4 M
IV = 5 M
V = 6 M
VI = 7 M
VII = 8 M
Log (a-x)
t (min.)
I
II
III
IV
V
VI
VII
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0
20
40
60
80
100
120
140
160

FIG. 3.2

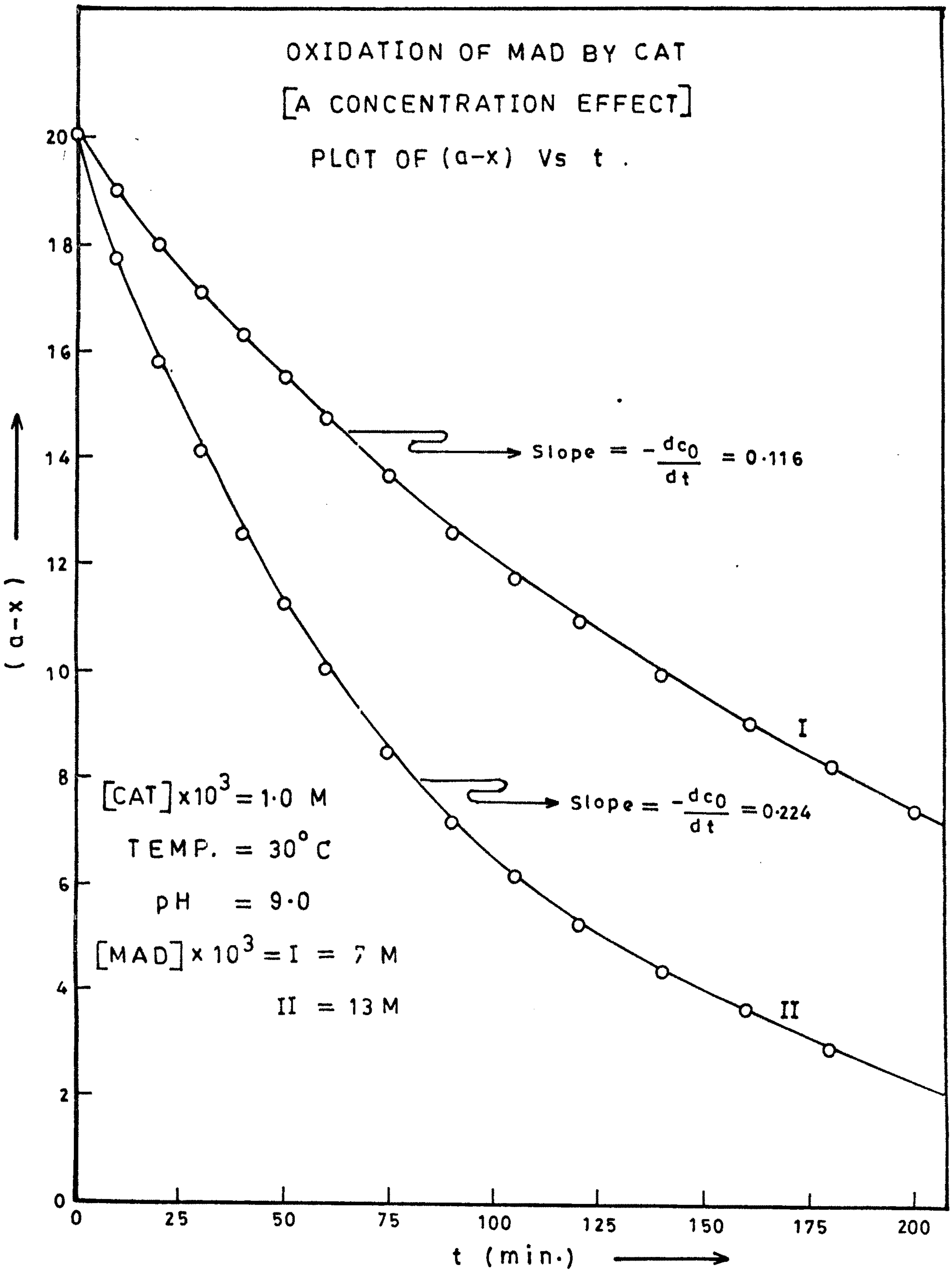

OXIDATION OF MAD BY CAT
[A CONCENTRATION EFFECT]
PLOT OF (a-x) Vs t .
Slope = $-\frac{dc_0}{dt}$ = 0·116
Slope = $-\frac{dc_0}{dt}$ = 0·224
I
II
[CAT] x 10^3 = 1·0 M
TEMP. = 30°C
pH = 9·0
[MAD] x 10^3 = I = 7 M
II = 13 M
(a-x)
t (min.)
0
2
4
6
8
10
12
14
16
18
20
0
25
50
75
100
125
150
175
200

FIG. 3·3

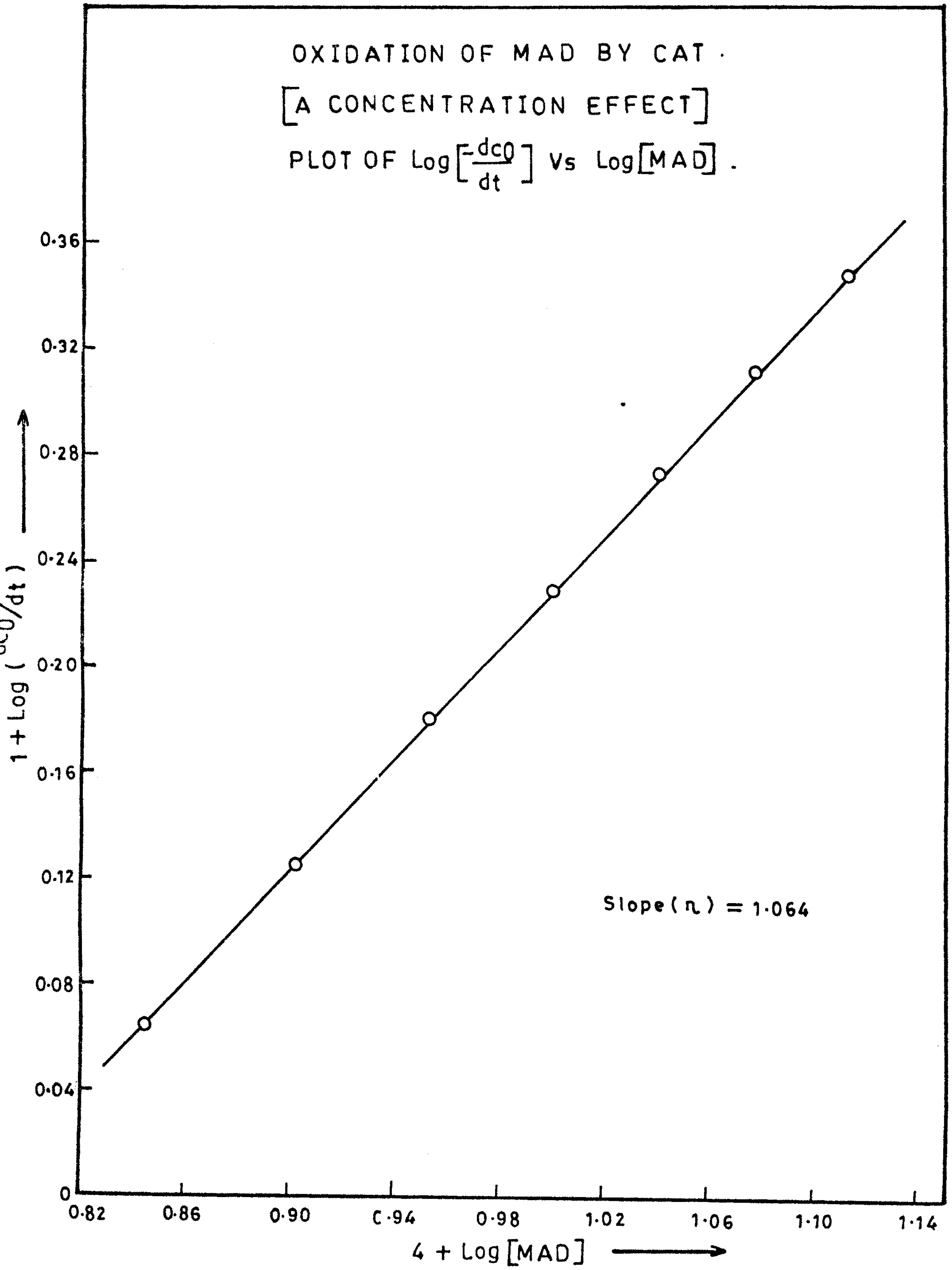
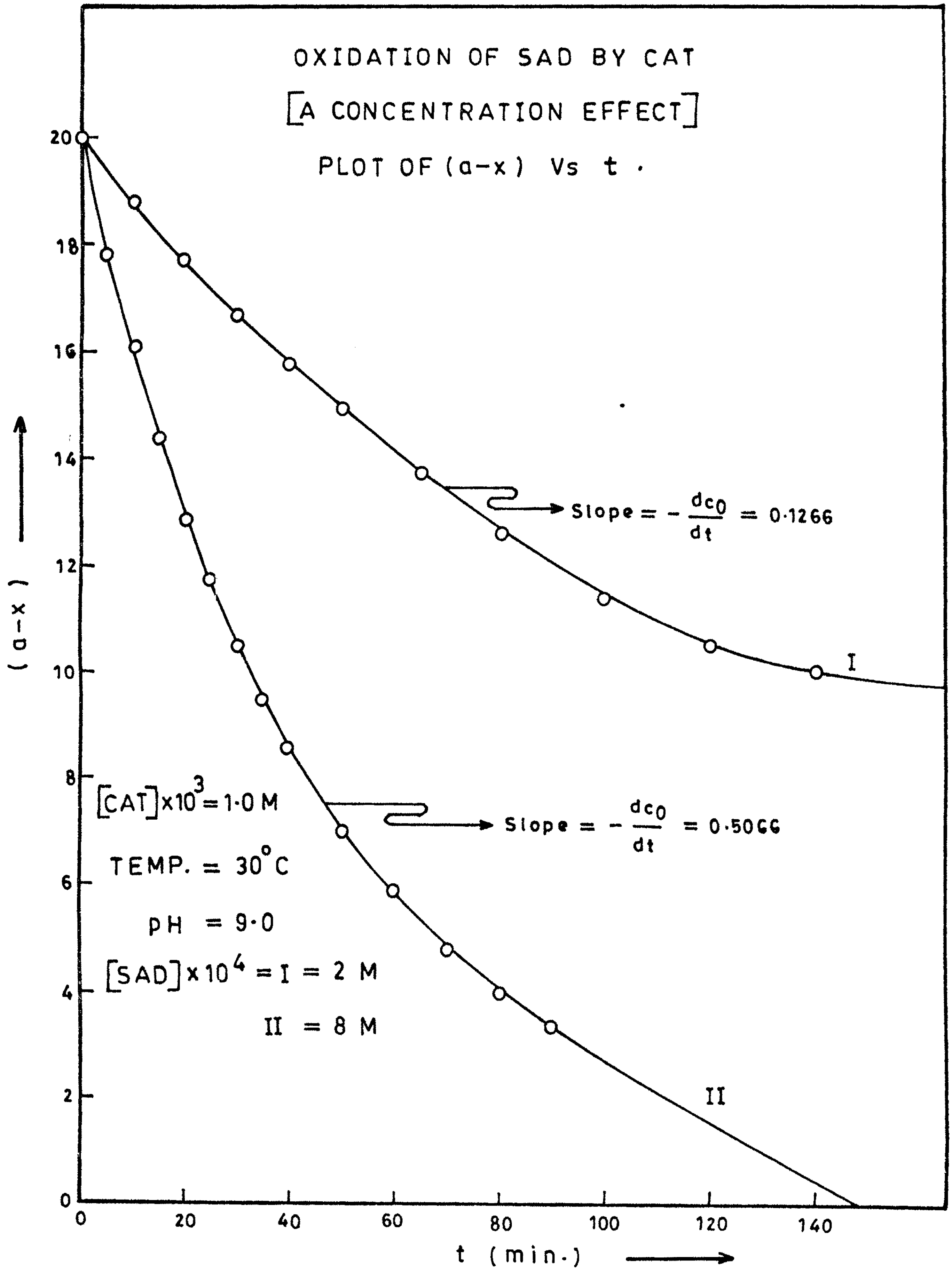
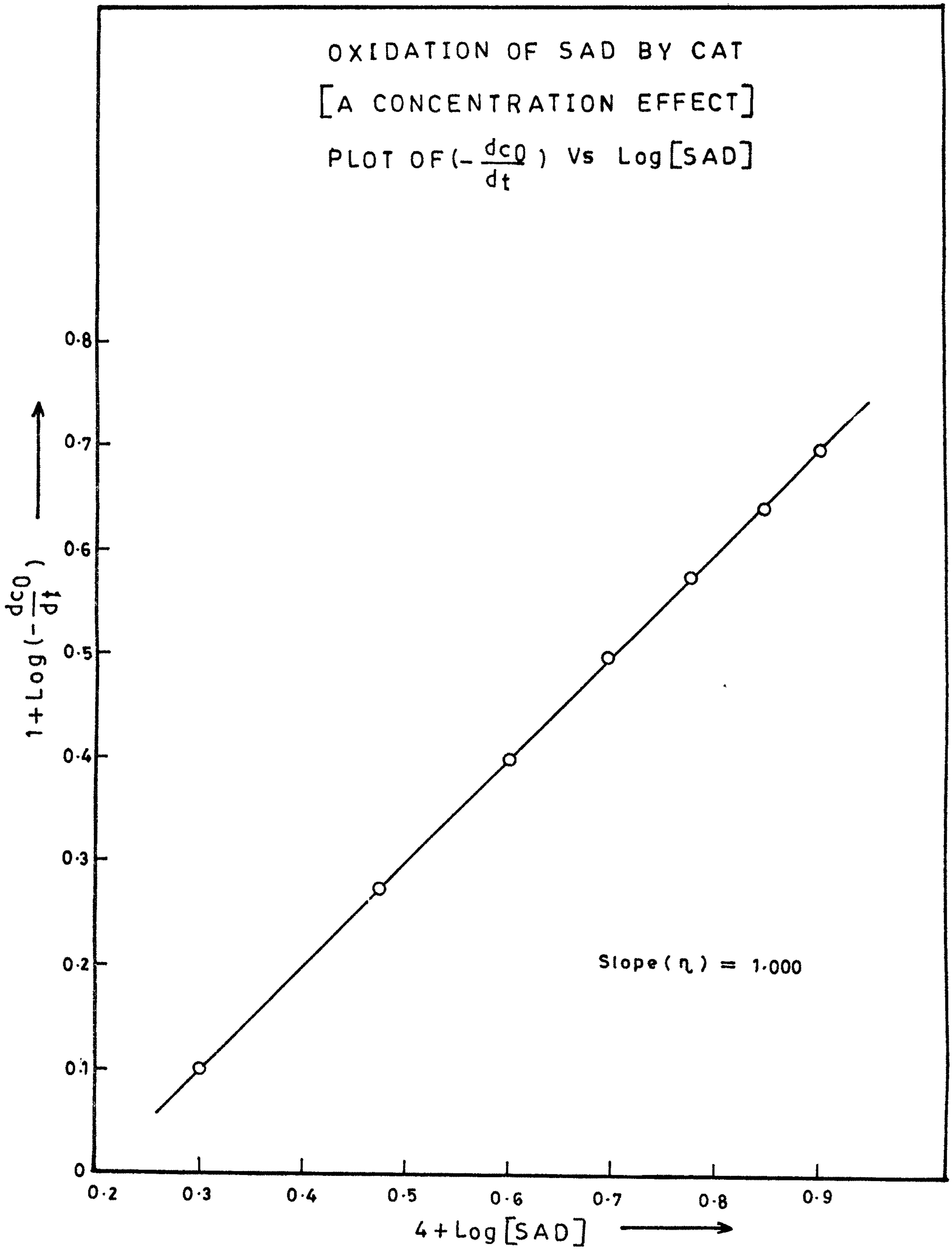

OXIDATION OF MAD BY CAT.
[A CONCENTRATION EFFECT]
PLOT OF Log[-dc0/dt] Vs Log[MAD].
1 + Log (dc0/dt)
0·36
0·32
0·28
0·24
0·20
0·16
0·12
0·08
0·04
0
Slope(n) = 1·064
0·82
0·86
0·90
0·94
0·98
1·02
1·06
1·10
1·14
4 + Log[MAD]

FIG. 3·4



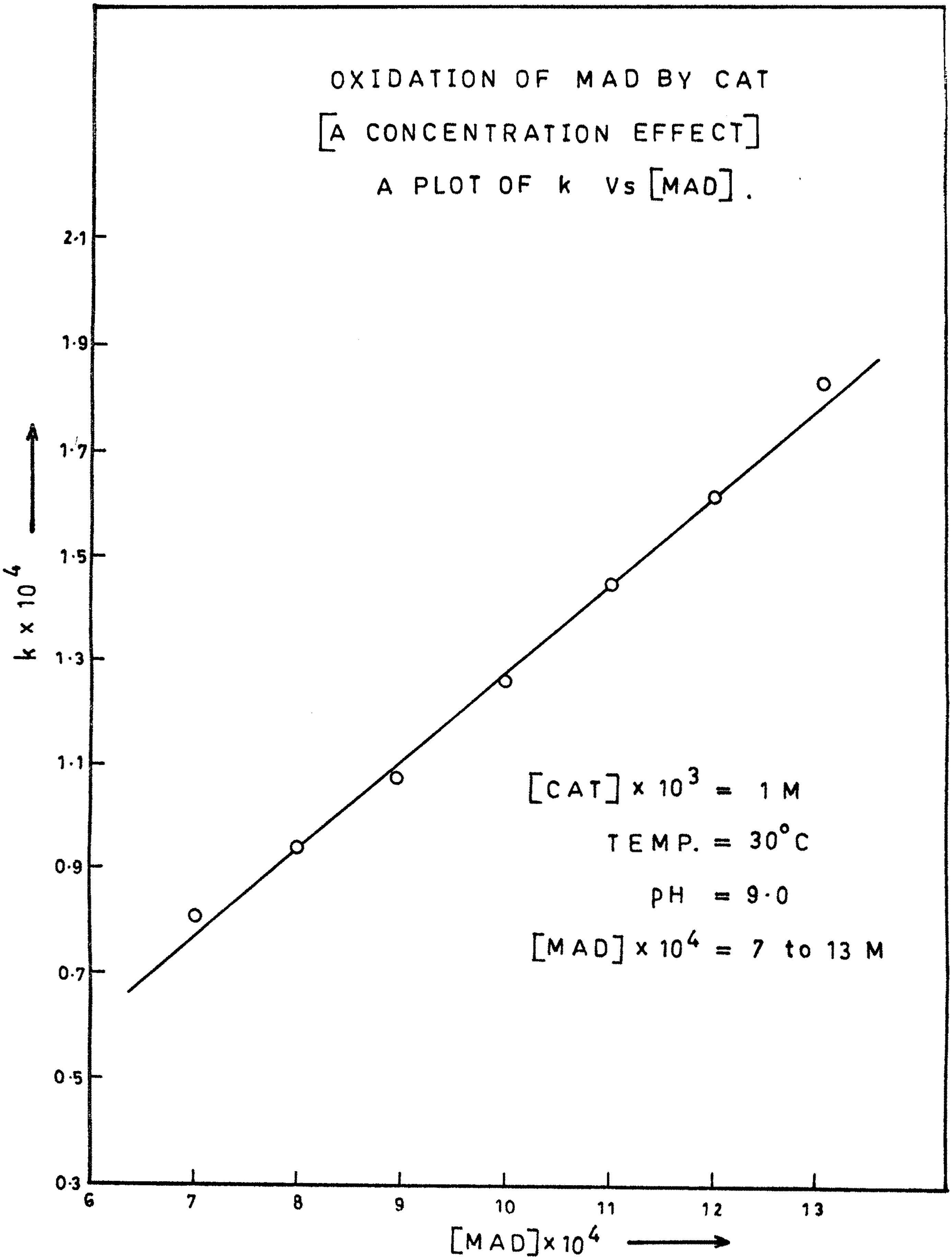
OXIDATION OF SAD BY CAT
[A CONCENTRATION EFFECT]
PLOT OF (a−x) Vs t.
Slope = − dc0/dt = 0·1266
Slope = − dc0/dt = 0·50GG
[CAT]x10^3 = 1·0 M
TEMP. = 30°C
pH = 9·0
[SAD] x 10^4 = I = 2 M
II = 8 M
I
II
(a−x)
t (min.)
0
20
40
60
80
100
120
140
2
4
6
8
10
12
14
16
18
20

FIG. 3·5



OXIDATION OF SAD BY CAT
[A CONCENTRATION EFFECT]
PLOT OF $(-\frac{dc0}{dt})$ Vs Log[SAD]
$1+Log(-\frac{dc0}{dt})$
0·8
0·7
0·6
0·5
0·4
0·3
0·2
0·1
0
0·2
0·3
0·4
0·5
0·6
0·7
0·8
0·9
4 + Log[SAD]
Slope (η) = 1·000

FIG. 3·6



OXIDATION OF MAD BY CAT
[A CONCENTRATION EFFECT]
A PLOT OF k Vs [MAD].
[CAT] x 10^3 = 1 M
TEMP. = 30°C
pH = 9·0
[MAD] x 10^4 = 7 to 13 M
k x 10^4
[MAD] x 10^4
2·1
1·9
1·7
1·5
1·3
1·1
0·9
0·7
0·5
0·3
6
7
8
9
10
11
12
13

FIG. 3·7

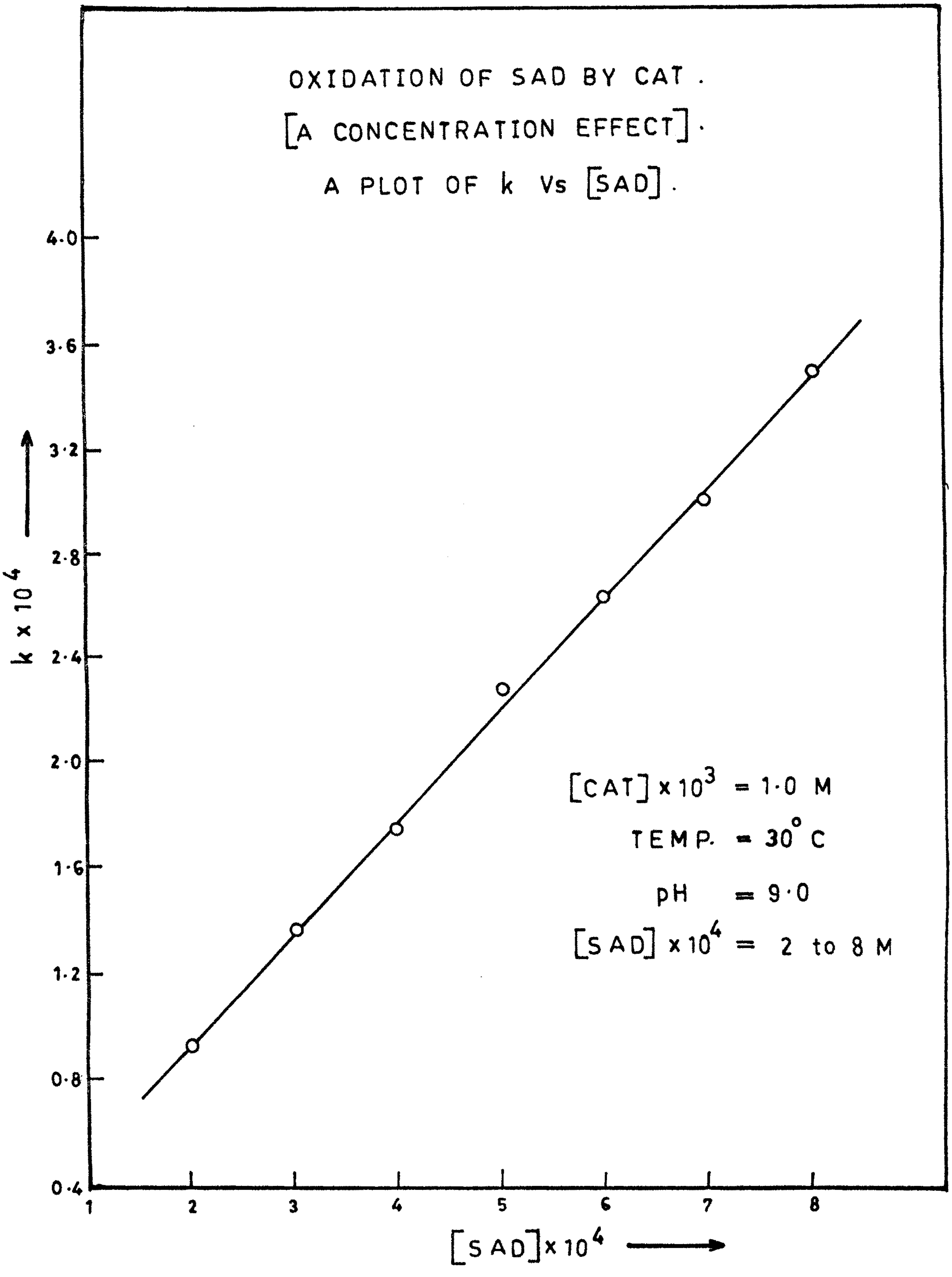

OXIDATION OF SAD BY CAT.
[A CONCENTRATION EFFECT].
A PLOT OF k Vs [SAD].
[CAT] x 10^3 = 1·0 M
TEMP. = 30° C
pH = 9·0
[SAD] x 10^4 = 2 to 8 M
k x 10^4
[SAD] x 10^4
4·0
3·6
3·2
2·8
2·4
2·0
1·6
1·2
0·8
0·4
1
2
3
4
5
6
7
8

FIG. 3·8

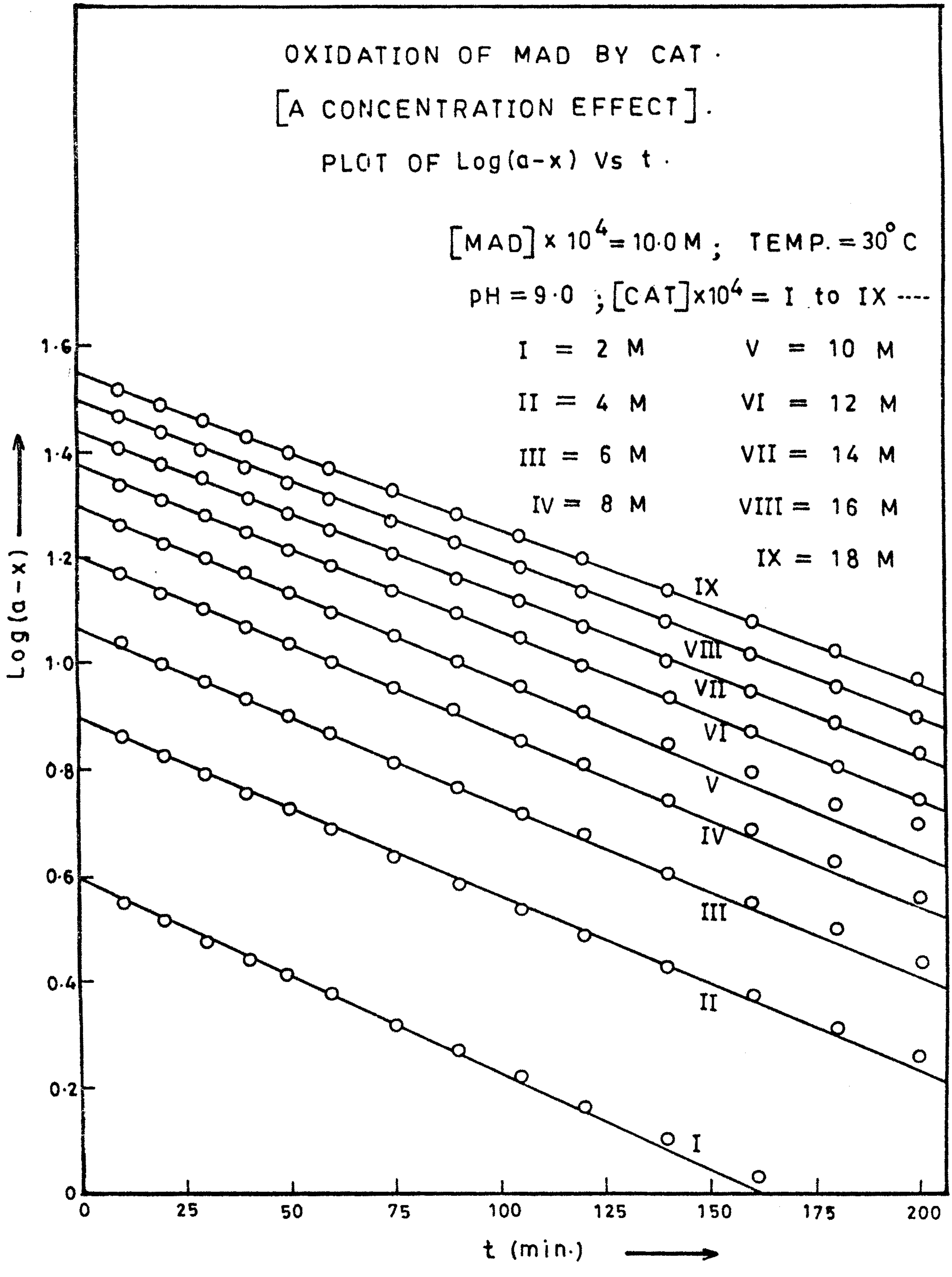

OXIDATION OF MAD BY CAT.
[A CONCENTRATION EFFECT].
PLOT OF Log(a-x) Vs t.
[MAD] x 10^4 = 10.0 M ; TEMP. = 30°C
pH = 9.0 ; [CAT] x 10^4 = I to IX ----
I = 2 M
II = 4 M
III = 6 M
IV = 8 M
V = 10 M
VI = 12 M
VII = 14 M
VIII = 16 M
IX = 18 M
Log(a-x)
t (min.)
0
0·2
0·4
0·6
0·8
1·0
1·2
1·4
1·6
0
25
50
75
100
125
150
175
200
I
II
III
IV
V
VI
VII
VIII
IX

FIG. 3·9

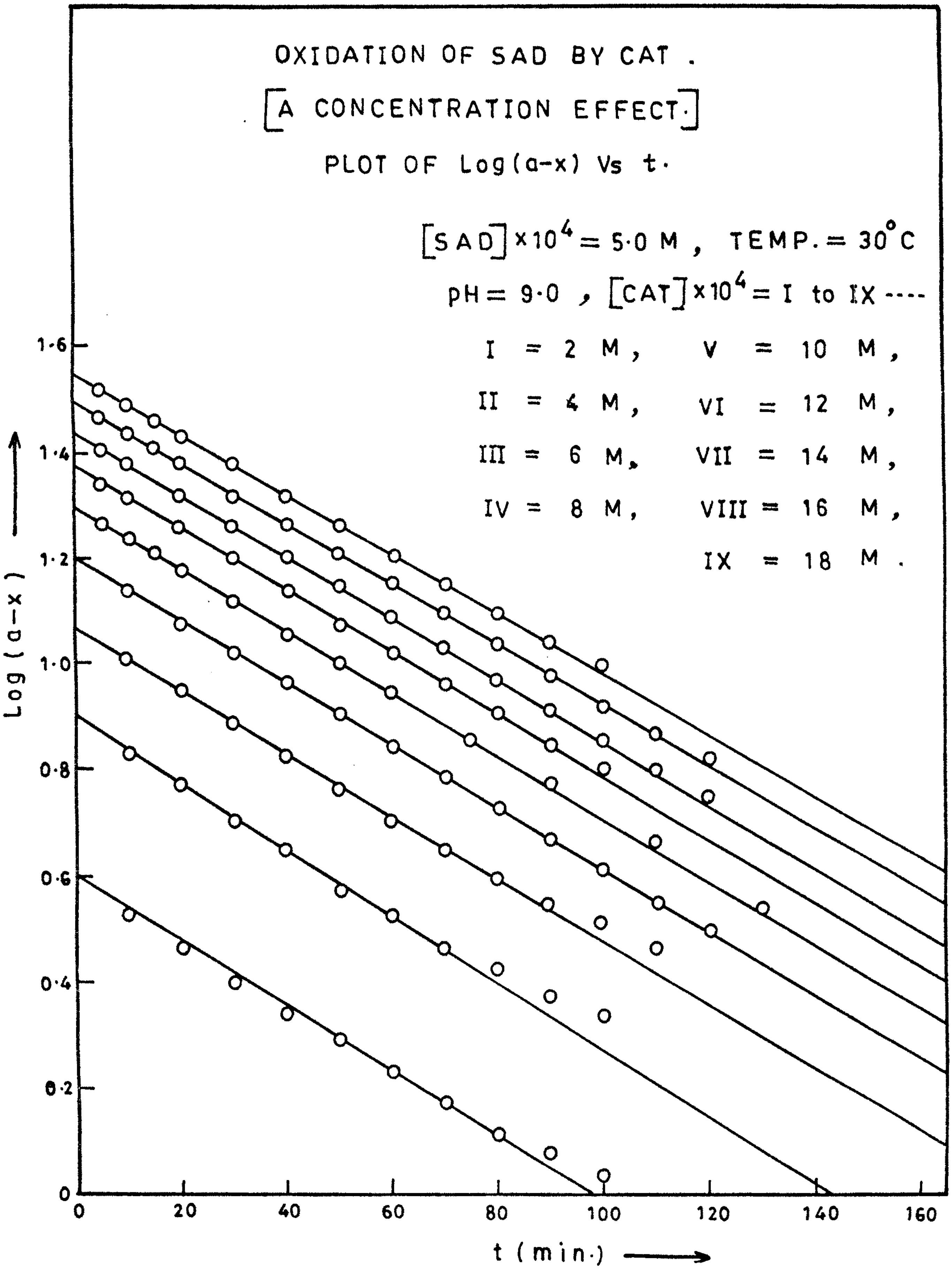

OXIDATION OF SAD BY CAT .
[A CONCENTRATION EFFECT.]
PLOT OF Log(a-x) Vs t.
[SAD]×10^4 = 5.0 M , TEMP. = 30°C
pH = 9.0 , [CAT]×10^4 = I to IX ----
I = 2 M , V = 10 M ,
II = 4 M , VI = 12 M ,
III = 6 M , VII = 14 M ,
IV = 8 M , VIII = 16 M ,
IX = 18 M .
Log (a-x)
t (min.)
0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
20
40
60
80
100
120
140
160

FIG. 3.10

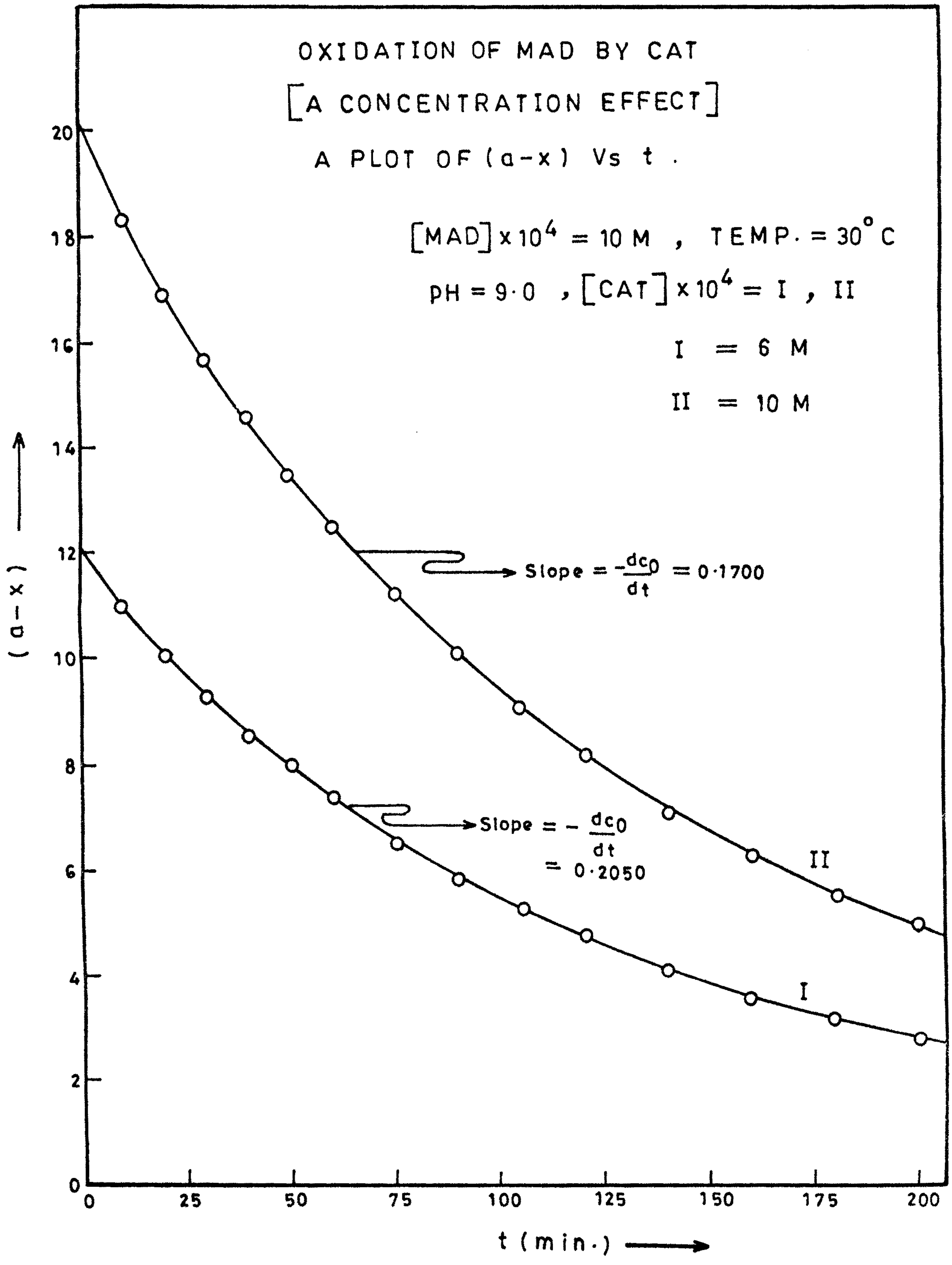
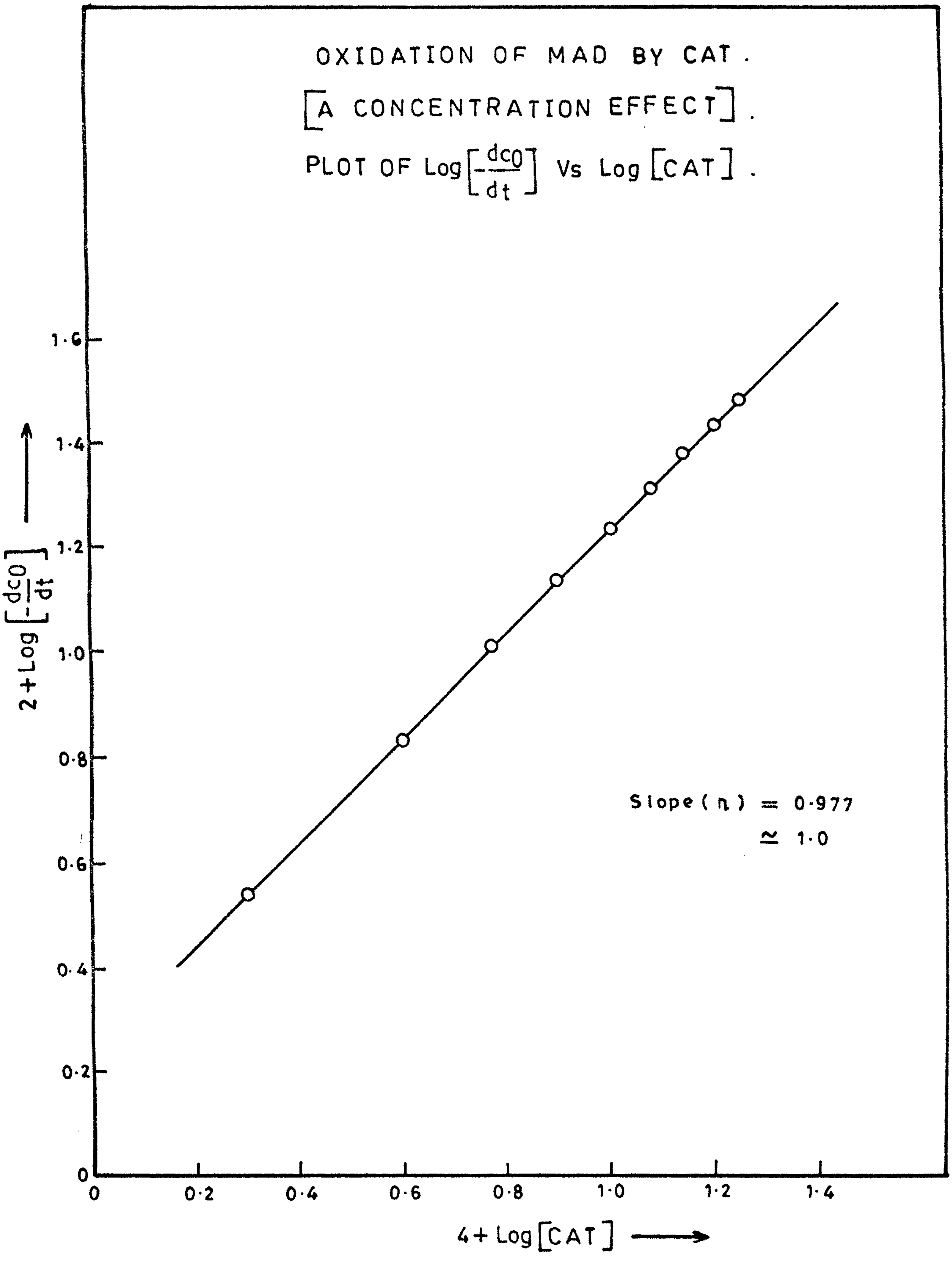

OXIDATION OF MAD BY CAT
[A CONCENTRATION EFFECT]
A PLOT OF (a-x) Vs t.
[MAD] x 10^4 = 10 M , TEMP. = 30°C
pH = 9.0 , [CAT] x 10^4 = I , II
I = 6 M
II = 10 M
Slope = -dc0/dt = 0.1700
Slope = -dc0/dt = 0.2050
II
I
(a-x)
t (min.)
0
2
4
6
8
10
12
14
16
18
20
0
25
50
75
100
125
150
175
200

FIG. 3.11



OXIDATION OF MAD BY CAT.
[A CONCENTRATION EFFECT].
PLOT OF Log[-dc0/dt] Vs Log[CAT].
2+Log[-dc0/dt]
4+Log[CAT]
Slope (n) = 0·977
≃ 1·0
0
0·2
0·4
0·6
0·8
1·0
1·2
1·4
1·6

FIG. 3·12

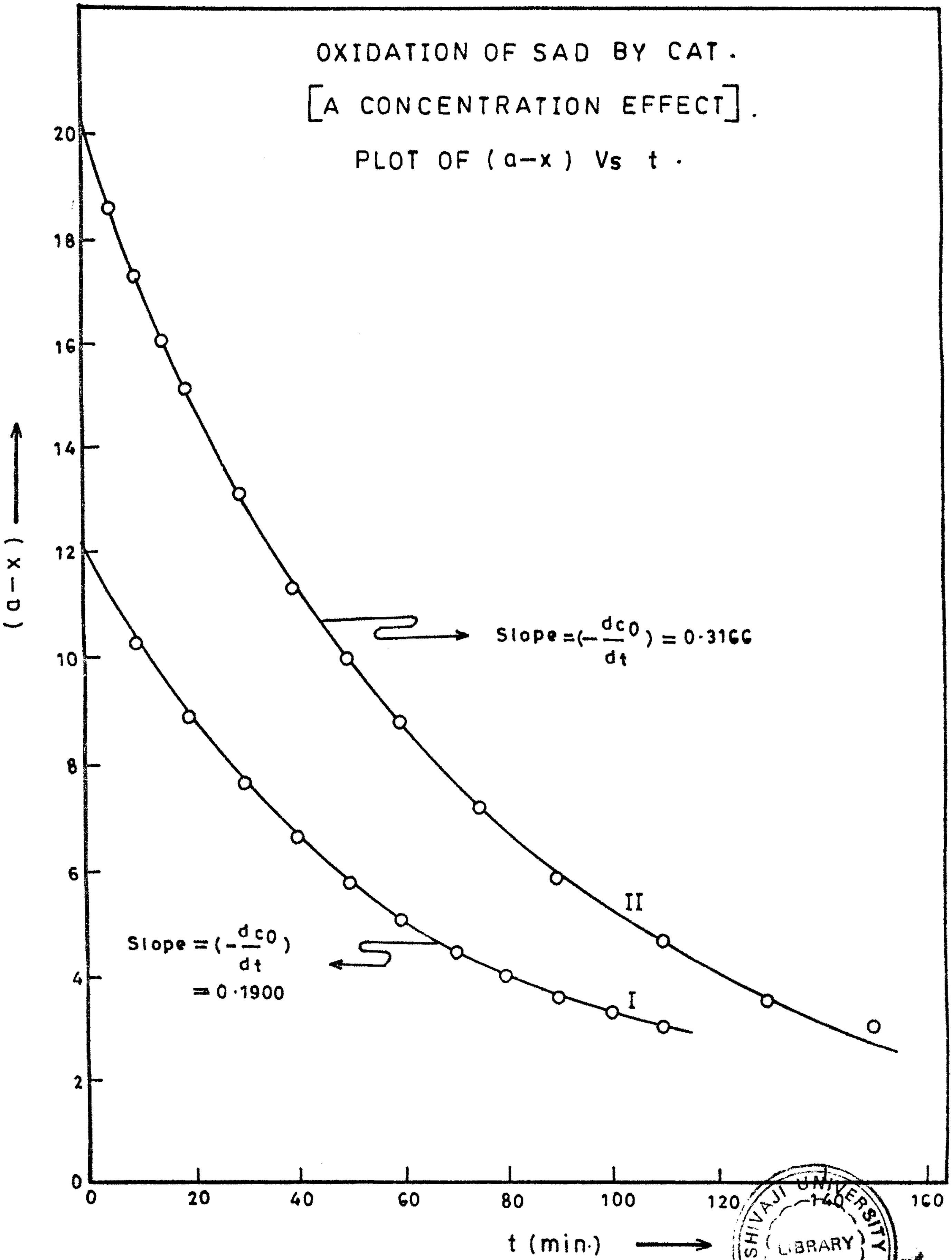

OXIDATION OF SAD BY CAT.
[A CONCENTRATION EFFECT].
PLOT OF (a−x) Vs t.
Slope = (−dc0/dt) = 0·3166
Slope = (−dc0/dt) = 0·1900
II
I
(a − x)
t (min.)
0
2
4
6
8
10
12
14
16
18
20
0
20
40
60
80
100
120
140
160

FIG. 3·13

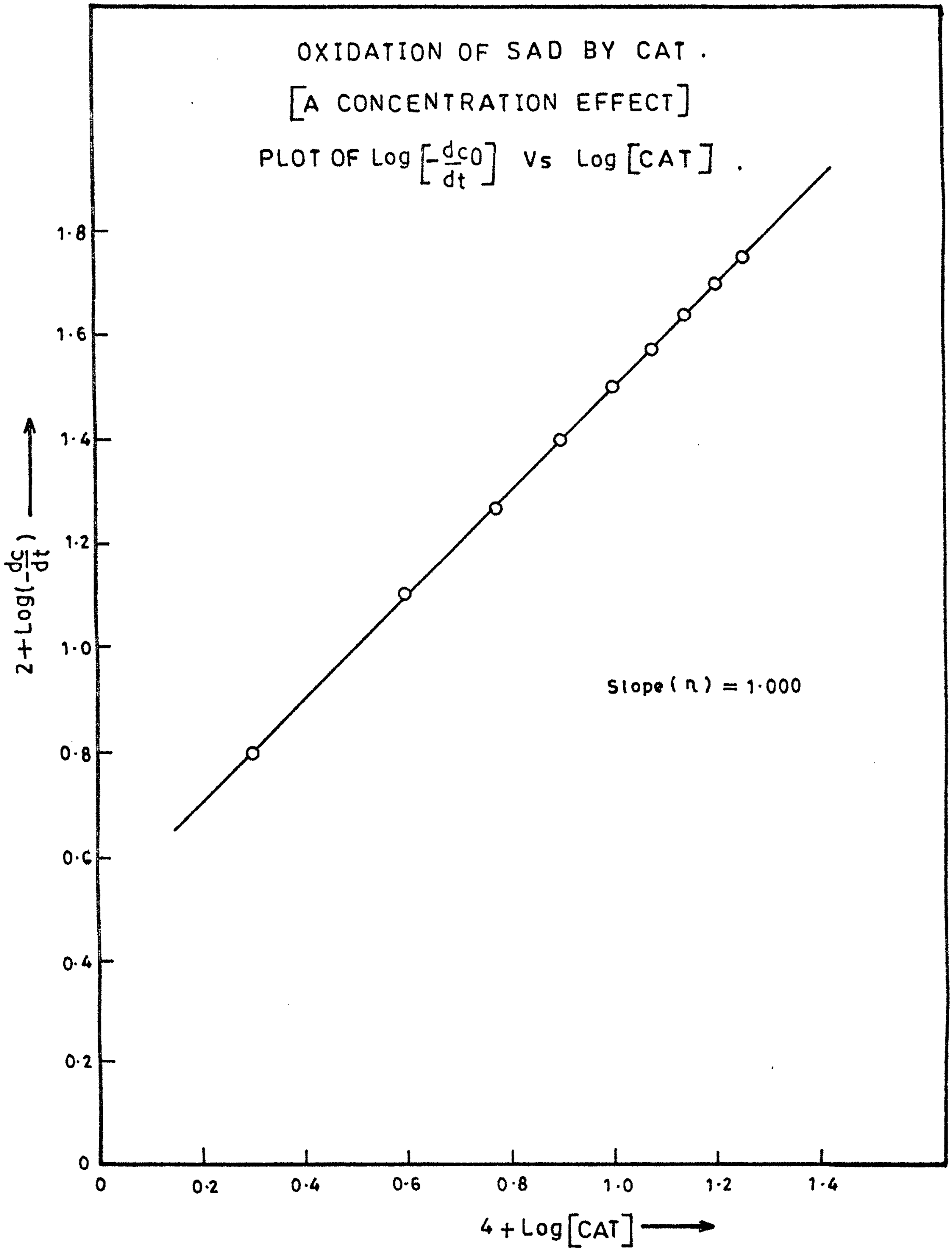

OXIDATION OF SAD BY CAT.
[A CONCENTRATION EFFECT]
PLOT OF Log [-dc0/dt] Vs Log [CAT].
Slope (n) = 1·000
2 + Log(-dc/dt)
4 + Log [CAT]
0
0·2
0·4
0·6
0·8
1·0
1·2
1·4
1·6
1·8

FIG. 3·14

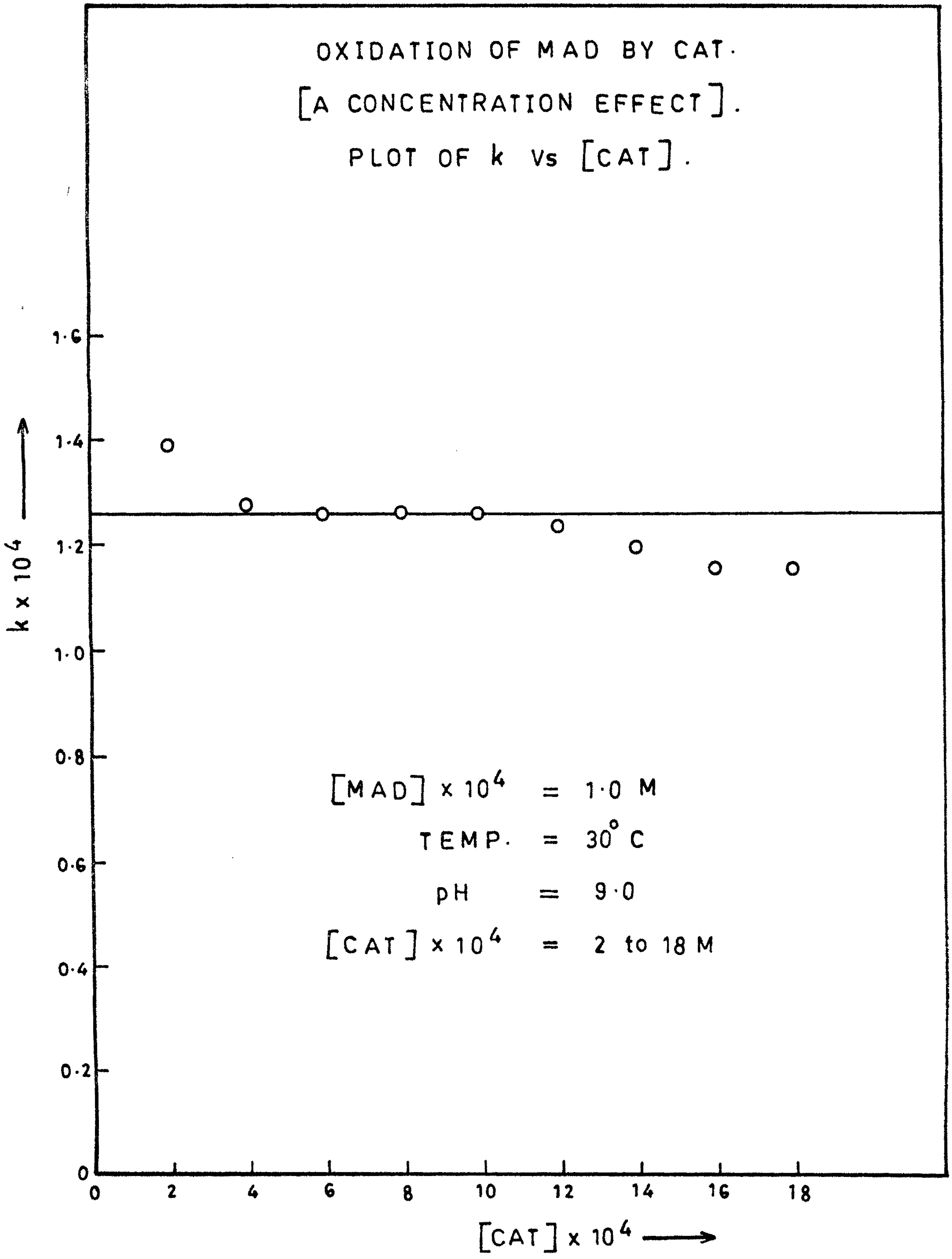

OXIDATION OF MAD BY CAT.
[A CONCENTRATION EFFECT].
PLOT OF k Vs [CAT].
k x 10^4
1·6
1·4
1·2
1·0
0·8
0·6
0·4
0·2
0
0
2
4
6
8
10
12
14
16
18
[MAD] x 10^4 = 1·0 M
TEMP. = 30° C
pH = 9·0
[CAT] x 10^4 = 2 to 18 M
[CAT] x 10^4

FIG. 3·15

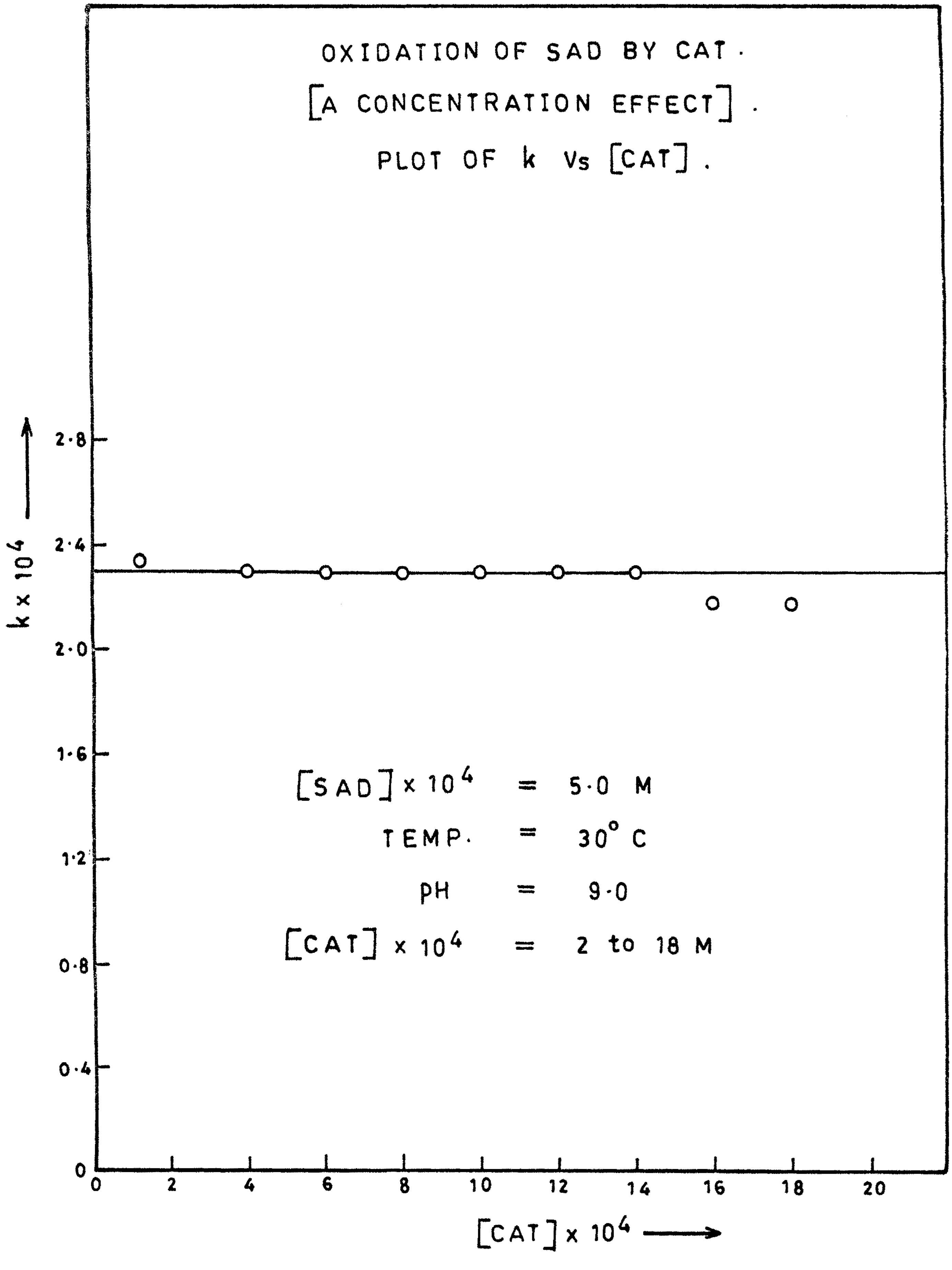

OXIDATION OF SAD BY CAT.
[A CONCENTRATION EFFECT].
PLOT OF k Vs [CAT].
k x 10^4
2·8
2·4
2·0
1·6
1·2
0·8
0·4
0
[SAD] x 10^4 = 5·0 M
TEMP. = 30° C
pH = 9·0
[CAT] x 10^4 = 2 to 18 M
0
2
4
6
8
10
12
14
16
18
20
[CAT] x 10^4

FIG. 3·16

III. EFFECT OF TEMPERATURE ON THE OXIDATION OF DIHYDRAZIDES BY CHLORAMINE-T

The effect of change in temperature on the oxidation of dihydrazides by chloramine-T was studied between the temperature range of $20^{o}C$ i.e. from 25^{o} to $45^{o}C$. The results obtained are summarised in Table 3.9 to 3.11. It is observed that the first order rate constant increases with increase in temperature in case of both the dihydrazides.

From the observed values of first order rate constants with respect to these various temperatures different theremodynamic parameters were calculated. So as to evaluate the values of parameters the equations used were as follows.

1) Frequency factor (A) :

The variations in the reaction rates with temperatures were usually expressed by the known Arrhenius equation,

$$k = Ae^{-Ea/RT} \qquad \ldots (3.4)$$

where, k = rate constant, A = frequency factor,

Ea = energy of actionation, R = gas constant and T = absolute temperature

Taking logarithms

$$\ln k = \ln A - Ea/RT \qquad \ldots (3.5)$$

or

$$\log A = \log k + Ea/2.303\ RT \qquad \ldots (3.6)$$

Using this equation the values of frequency factors in case of both dihydrazides are recorded in Table 3.11.

(2) Energy of Activation, (Ea) :

A plot of log k versus 1/T is plotted (Fig.3.19 and 3.20) from the slopes of the straight lines we can calculate the values of energy of activation as follows.

$$\text{Slope} = -\frac{Ea}{2.303\ R}$$

$$Ea = \log \frac{k_2}{k_1} \times \left[\frac{T_2 \times T_1}{T_2 - T_1}\right] \times 4.576 \qquad \ldots (3.7)$$

The values of rate constants k_2 and k_1 are at temperatures T_2 and T_1 (absolute) respectively. From the slopes of the straight line graphs (3.19 and 3.20) the values of energy of activation are calculated and using equation (3.7). Values of these energy of activation are given in Table 3.11.

(3) Entropy of Activation (ΔS^{++}) :

$$\Delta S^{++} = 4.576 \left(\log k - 10.753 - \log T + \frac{Ea}{4.576 \times T}\right) \ldots (3.8)$$

(4) Enthalpy (ΔH^{++}) :

A plot of log k/T vs. 1/T if comes out to be straight line. Then from the slope of this graph we can calculate the value of enthalpy by following equation.

$$\text{Enthalpy } (\Delta H^{++}) = \text{slope} \times 2.303\ R$$

$$\Delta H^{++} = Ea - RT \qquad \ldots (3.9)$$

We have plotted these graphs (fig.3.21 and 3.22) and value of enthalpy ΔH^{++} have been calculated. These values can also be calculated by using the equation (3.9).

5) Free energy of activation (ΔG^{++}) :

$$\Delta G^{++} = \Delta H^{++} - T\Delta S^{++} \qquad \text{... (3.10)}$$

In case of both these hydrazides we have calculated the values of entropy of activation (ΔS^{++}) enthalpy (ΔH^{++}) and free energy of activation (ΔG^{++}) by using the equations 3.8, 3.9 and 3.10 respectively. All the values of different parameters in case of both the dihydrazides are summarised in Table 3.11.

TABLE - 3.9

EFFECT OF CHANGE IN THE TEMPERATURE ON THE OXIDATION OF MALONIC ACID DIHYDRAZIDE BY CHLORAMINE-T

[MAD] x 10^3 = 1.0 M   [CAT] x 10^3 = 1.0

Temp = 298 to 318 K   pH = 9.0

Sr. No.	Temp. K	$k \times 10^4 S^{-1}$	$k_{(graph)} \times 10^4 S^{-1}$	$k_1 \times 10^4 S^{-1}$	$k_2 \times 10^4 S^{-1}$
1	298	0.8916	0,8674	1.729	0.649
2	303	1.274	1.266	2.525	1.263
3	308	1.864	1.881	3.754	1.877
4	313	2.720	2.656	5.303	2.651
5	318	3.982	3.838	7.659	3.829

DATA FOR GRAPHICAL REPRESENTATION

Sr. No.	Temp. K	$10^3/T$	5 + log k	k/T x 10^7	7 + log k/T
1	298	3.3557	0.9382	2.9107	0.4640
2	303	3.3003	1.1024	4.1780	0.6210
3	308	3.2467	1.2742	6.1071	0.7858
4	313	3.1949	1.4242	8.485	0.9287
5	318	3.1446	1.5841	12.069	1.0816

TABLE - 3.10

EFFECT OF CHANGE IN THE TEMPERATURE ON THE OXIDATION OF SUCCINIC ACID DIHYDRAZIDE BY CHLORAMINE-T

[SAD] x 10^4 = 5.0 M   [CAT] x 10^3 = 1.0 M

Temp = 298 to 318 K   pH = 9.0

Sr. No.	Temp. K	$k \times 10^4 S^{-1}$	$k_{(graph)} \times 10^4 S^{-1}$	$k_1 \times 10^4 S^{-1}$	$k_2 \times 10^4 S^{-1}$
1	298	1.554	1.561	3.112	1.556
2	303	2.297	2.301	4.589	2.294
3	308	3.382	3.352	6.680	3.340
4	313	3.978	4.875	9.729	4.864
5	318	7.233	7.043	14.08	7.043

DATA FOR GRAPHICAL REPRESENTATION

Sr. No.	Temp. K	$10^3/T$	4 + log k	k/T x 10^7	7 + log k/T
1	298	3.3557	0.1934	5.238	0.7192
2	303	3.3003	0.3619	7.6007	0.8808
3	308	3.2467	0.5253	10.883	1.0367
4	313	3.1949	0.6879	15.575	1.1924
5	318	3.1446	0.8477	22.148	1.3453

TABLE - 3.11

EFFECT OF CHANGE IN THE TEMPERATURE ON THE OXIDATION OF DIHYDRAZIDES BY CHLORAMINE-T

THERMODYNAMIC PARAMETERS

I. Malonic Acid Dihydrazide :

Sr. No.	Temp. T	Ea K cal/mole	ΔH^{++} K cal/mole	$Ax10^{-5}S^{-1}$	ΔS^{++} e.u.	ΔG^{++} K cal/mole
1	298	-	-	17.555	-	-
2	303	13.570	12.967	17.320	-78.35	36.707
3	308	14.686	14.074	17.618	-77.59	37.971
4	313	13.220	12.598	17.238	-76.94	36.680
5	318	14.563	13.931	17.462	-76.242	38.185

Fig. 3.19 Energy of Activation (Ea) = 14.054 K cal/mole
= 58.810 K joule/mole

Fig. 3.22 Enthalpy (ΔH^{++}) = 13.473 K cal/mole
= 57.378 K joule/mole

II. Succinic Acid Dihydrazide

Sr. No.	Temp. T	Ea K cal/mole	ΔH^{++} K cal/mole	$Ax10^{-5}S^{-1}$	ΔS^{++} e.u.	ΔG^{++} K cal/mole
1	298	-	-	36.283	-	-
2	303	13.925	13.323	36.0717	-77.16	36.702
3	308	13.954	13.342	35.896	-76.44	36.885
4	313	14.352	13.730	36.099	-75.73	37.433
5	318	14.555	13.923	36.483	-75.03	37.782

Fig. 3.20 Energy of activation (Ea) = 14.136 K cal/mole
= 59.132 K joule/mole

Fig. 323 Enthalpy (ΔH^{++}) = 13.619 K cal/mole
= 56.988 K joule/mole

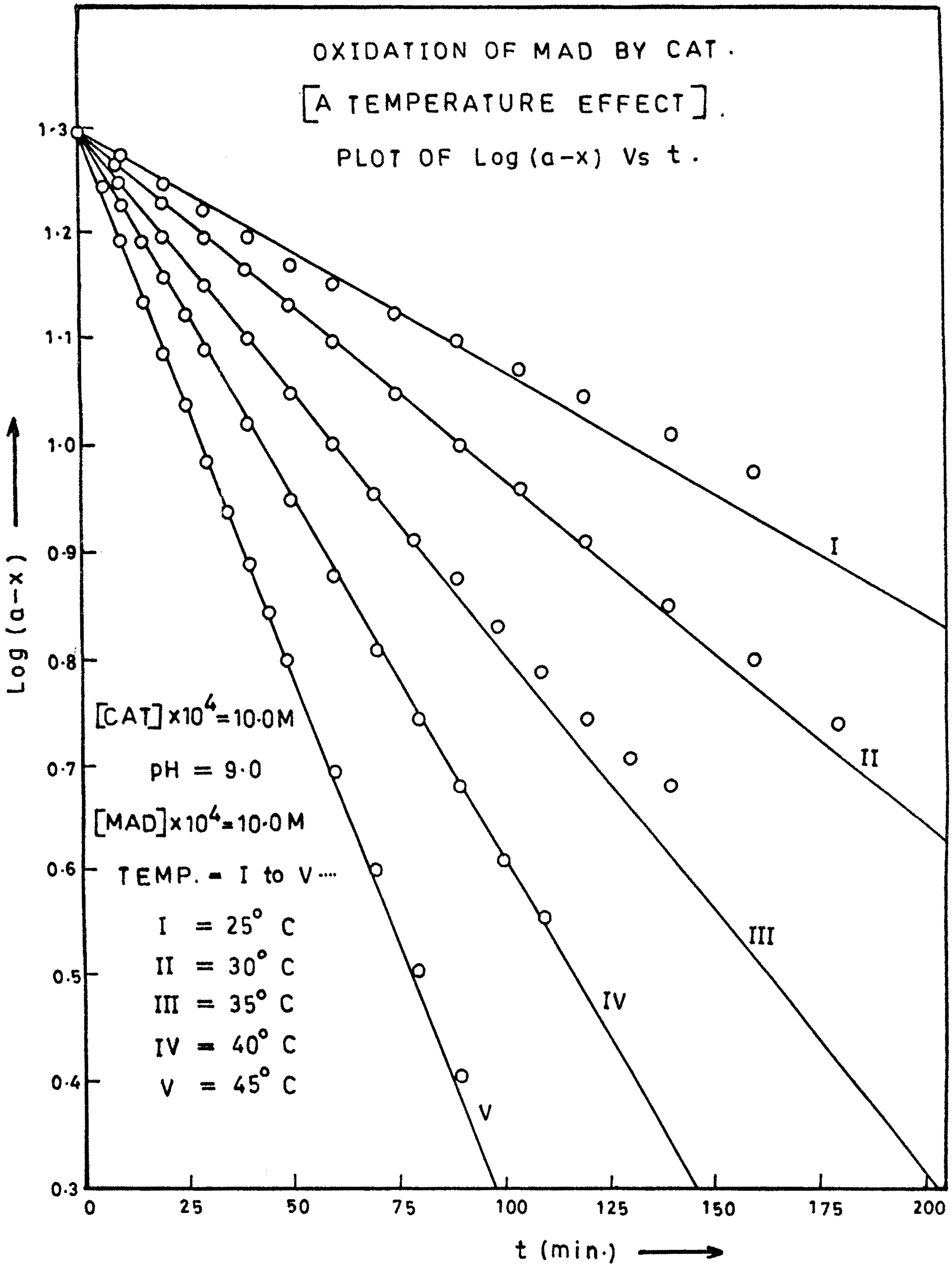
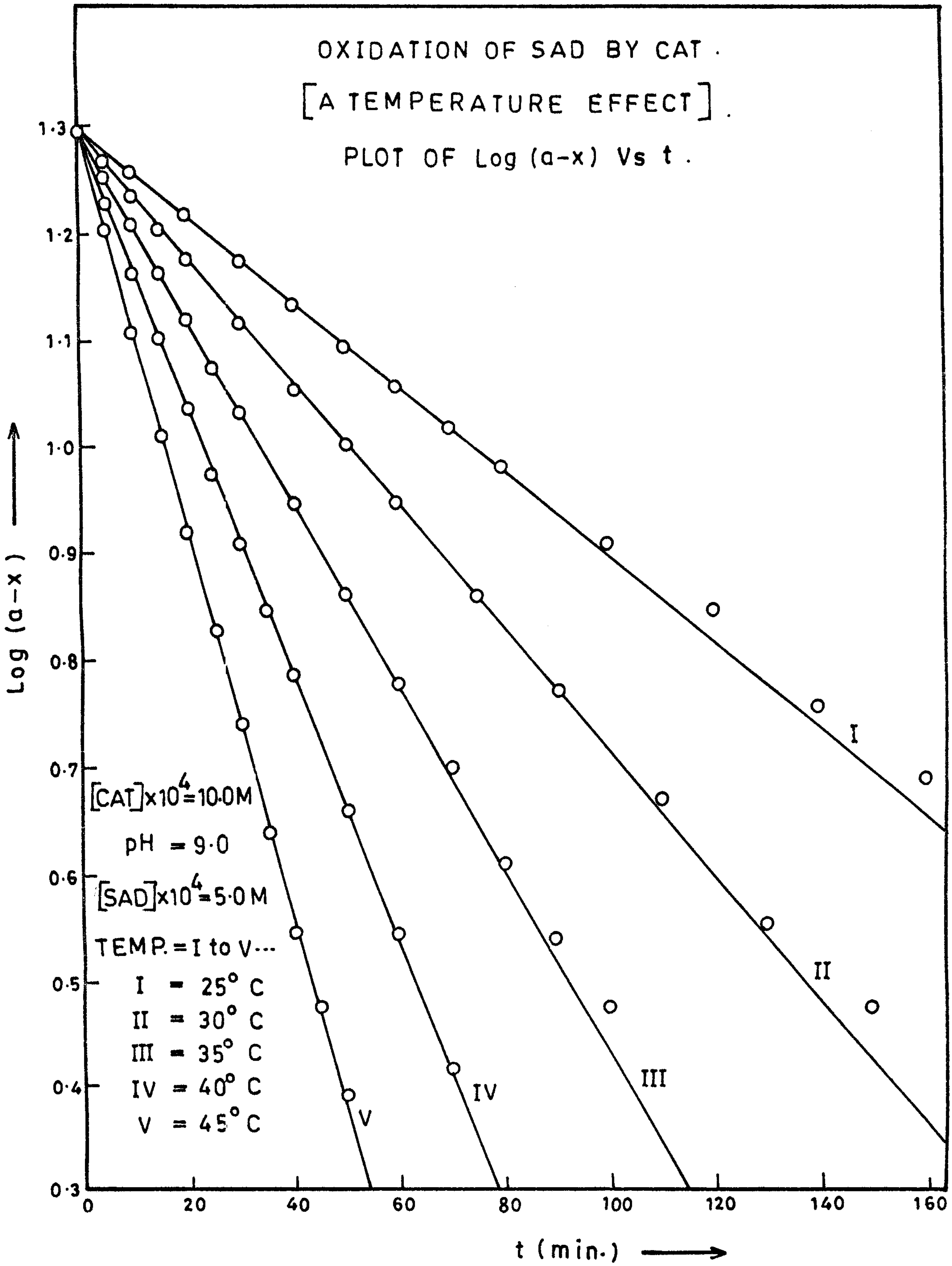
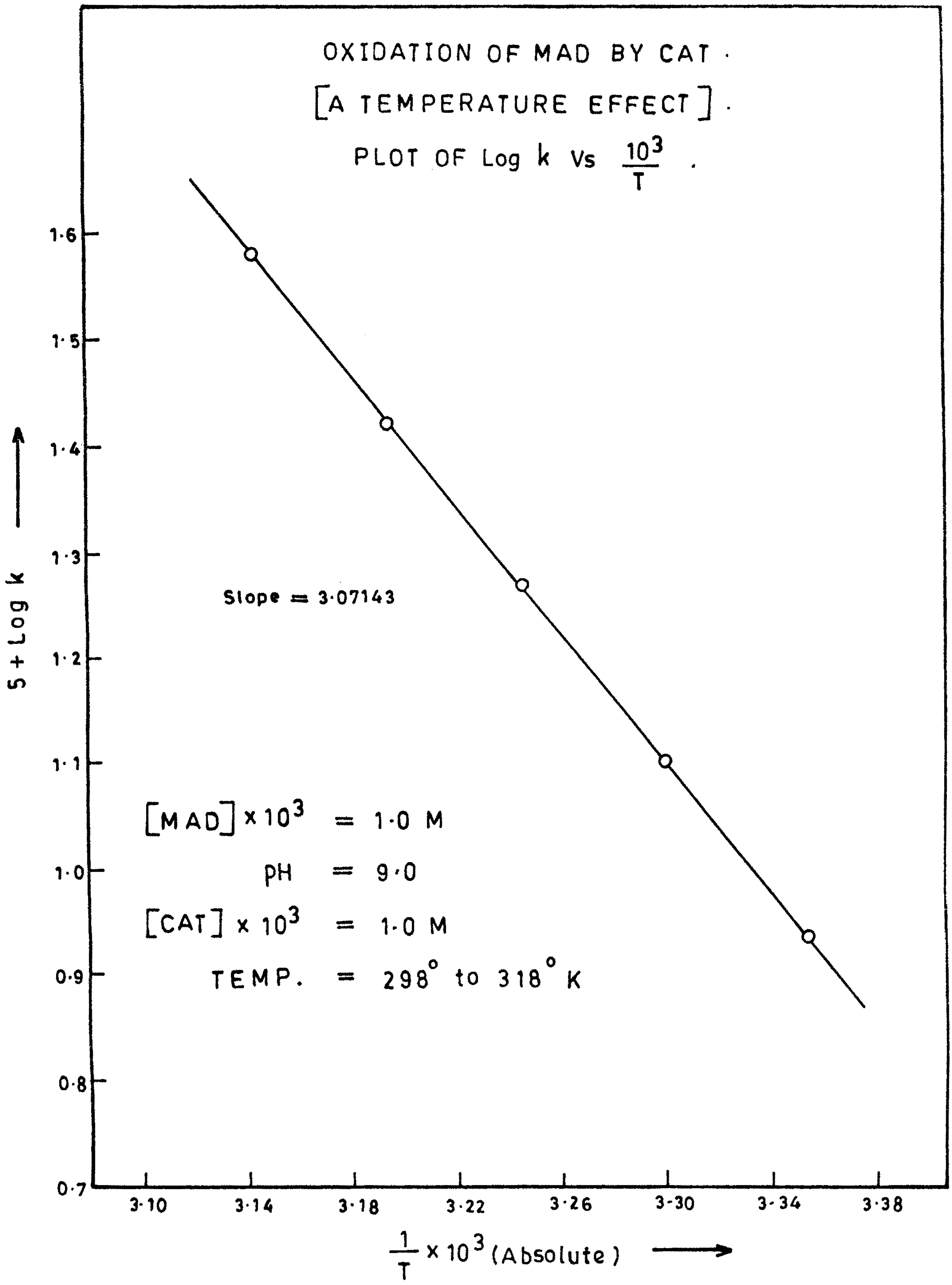

OXIDATION OF MAD BY CAT.
[A TEMPERATURE EFFECT].
PLOT OF Log(a−x) Vs t.
Log (a−x) →
t (min.) →
[CAT]x10^4=10.0M
pH = 9.0
[MAD]x10^4=10.0M
TEMP. = I to V....
I = 25° C
II = 30° C
III = 35° C
IV = 40° C
V = 45° C
I
II
III
IV
V
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0
25
50
75
100
125
150
175
200

FIG. 3.17



OXIDATION OF SAD BY CAT.
[A TEMPERATURE EFFECT].
PLOT OF Log (a-x) Vs t.
Log (a-x)
t (min.)
1·3
1·2
1·1
1·0
0·9
0·8
0·7
0·6
0·5
0·4
0·3
0
20
40
60
80
100
120
140
160
[CAT]x10^4=10.0M
pH = 9·0
[SAD]x10^4=5·0 M
TEMP.=I to V---
I = 25° C
II = 30° C
III = 35° C
IV = 40° C
V = 45° C
I
II
III
IV
V

FIG. 3.18



OXIDATION OF MAD BY CAT.
[A TEMPERATURE EFFECT].
PLOT OF Log k Vs $\frac{10^3}{T}$.
Slope = 3·07143
[MAD] x 10^3 = 1·0 M
pH = 9·0
[CAT] x 10^3 = 1·0 M
TEMP. = 298° to 318° K
5 + Log k
1·6
1·5
1·4
1·3
1·2
1·1
1·0
0·9
0·8
0·7
3·10
3·14
3·18
3·22
3·26
3·30
3·34
3·38
$\frac{1}{T}$ x 10^3 (Absolute)

FIG. 3.19

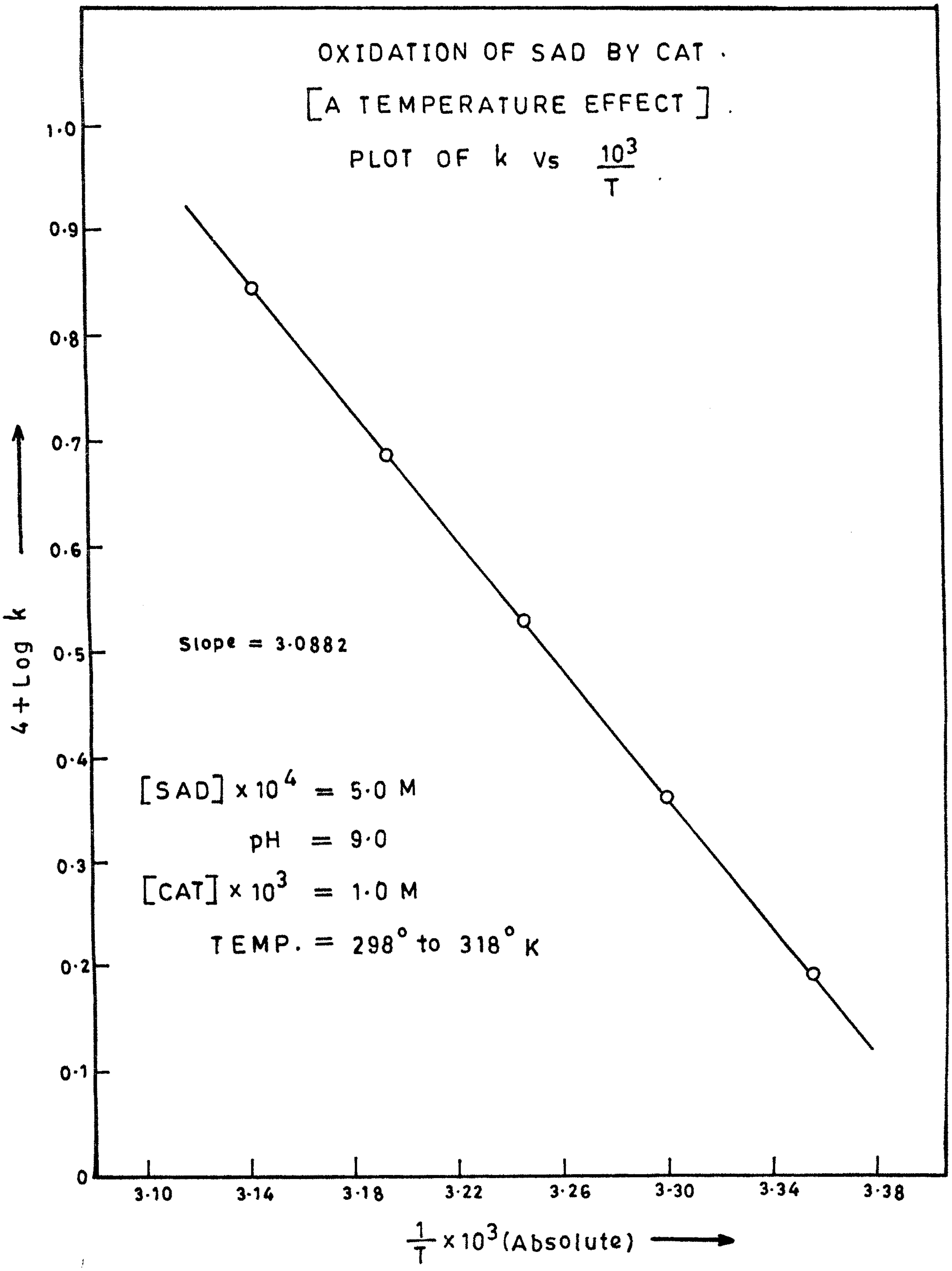

OXIDATION OF SAD BY CAT.
[A TEMPERATURE EFFECT].
PLOT OF k Vs $\frac{10^3}{T}$.
Slope = 3·0882
[SAD] × 10^4 = 5·0 M
pH = 9·0
[CAT] × 10^3 = 1·0 M
TEMP. = 298° to 318° K
4 + Log k
$\frac{1}{T}$ × 10^3 (Absolute)
1·0
0·9
0·8
0·7
0·6
0·5
0·4
0·3
0·2
0·1
0
3·10
3·14
3·18
3·22
3·26
3·30
3·34
3·38

FIG. 3·20

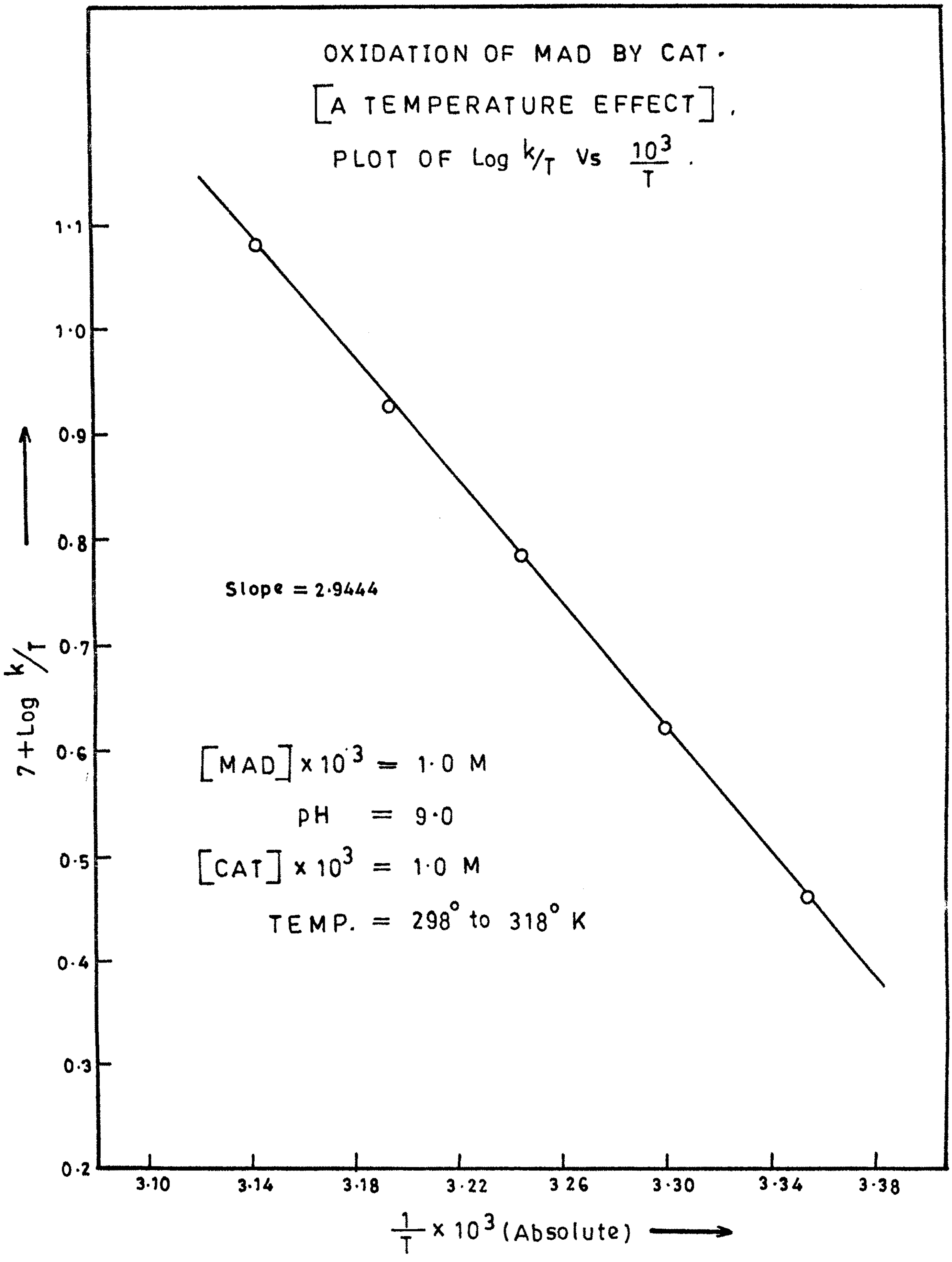

OXIDATION OF MAD BY CAT.
[A TEMPERATURE EFFECT].
PLOT OF Log k/T Vs 10³/T.
Slope = 2·9444
[MAD] x 10³ = 1·0 M
pH = 9·0
[CAT] x 10³ = 1·0 M
TEMP. = 298° to 318° K
7 + Log k/T
1·1
1·0
0·9
0·8
0·7
0·6
0·5
0·4
0·3
0·2
3·10
3·14
3·18
3·22
3·26
3·30
3·34
3·38
1/T x 10³ (Absolute)

FIG. 3·21

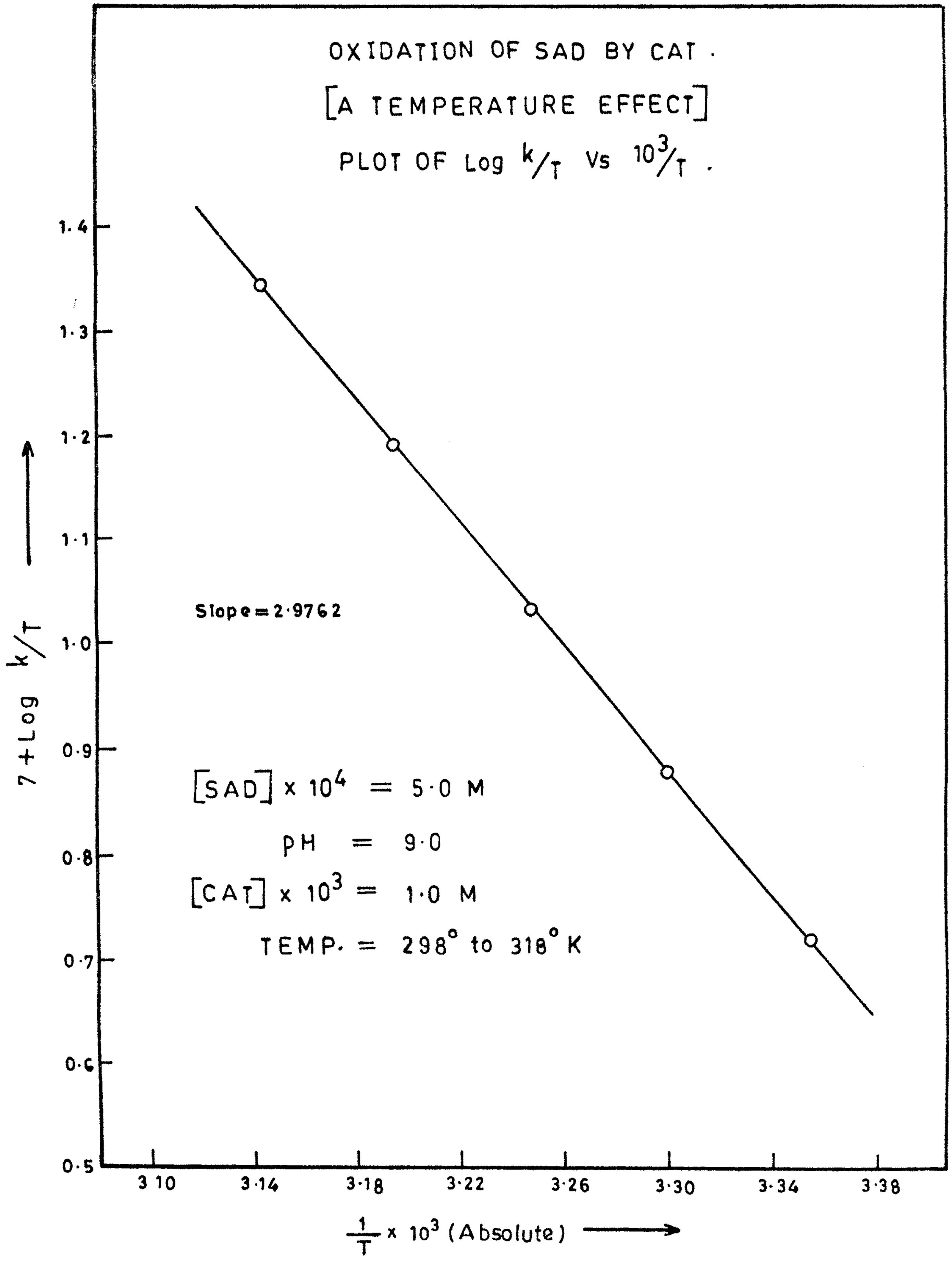

OXIDATION OF SAD BY CAT.
[A TEMPERATURE EFFECT]
PLOT OF Log k/T Vs 10³/T.
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
7 + Log k/T
Slope = 2.9762
[SAD] x 10⁴ = 5.0 M
pH = 9.0
[CAT] x 10³ = 1.0 M
TEMP. = 298° to 318° K
3.10
3.14
3.18
3.22
3.26
3.30
3.34
3.38
1/T x 10³ (Absolute)

FIG. 3.22

IV EFFECT OF CHANGE IN SOLVENT COMPOSITION ON THE OXIDATION OF DIHYDRAZIDES BY CHLORAMINE-T

To investigate the effect of solvent on the reaction rate the reaction was carried out in different percentage compositions of methanol water mixture (v/v). The kinetic runs were carried out in five different compositions of water methanol mixtures from 95/5 (v/v). The blank experiments were carried out at identical reaction conditions in absence of dihydrazides in these different composition of water methanol mixtures. Though there is negligible oxidation of methanol at these reaction conditions we have substracted the values of k observed by blank experiments. This precaution has been taken so as to increase the accuracy of our results.

The results obstained are given in Table 3.12 and 3.13. It is found that rate constant (k) decreases with increase in the percentage of methanol or in other words we can say that rate of reaction decreases with decrease in dielectric constant.

A plots of dielectric constant 1/D against log k were found to be straight lines (Fig. 3.23 and 3.24) in case of both the dihydrazides.

TABLE - 3.12

EFFECT OF CHANGE IN SOLVENT COMPOSITION ON THE OXIDATION OF MALONIC ACID DIHYDRAZIDE BY CHLORAMINE-T

[MAD] x 10^3 = 1.0 M   [CAT] x 10^3 = 1.0 M

pH = 9.0   TEMP = 30^oc

SOLVENT : WATER/METHANOL (V/V) = 95/5 to 75/25 (V/V)

Sr. No.	Solvent (v/v) Water	Methanol	k x $10^4 S^{-1}$	k_1 x $10^4 S^{-1}$	k_2 x $10^4 S^{-1}$
1	100	0	1.274	2.540	1.270
2	95	5	1.030	2.053	1.026
3	90	10	0.890	1.774	0.887
4	85	15	0.714	1.423	0.711
5	80	20	0.581	1.158	0.579
6	75	25	0.451	0.899	0.449

DATA FOR GRAPHICAL REPRESENTATION

Sr. No.	Solvent (v/v) Water	Methanol	Dielectric constant(D)*	$10^2/D$	5 + log k
1	100	0	76.73	1.3033	1.1052
2	95	5	74.50	1.3423	1.0128
3	90	10	72.37	1.3818	0.9493
4	85	15	69.75	1.4337	0.8539
5	80	20	67.48	1.4819	0.7638
6	75	25	65.06	1.5370	0.6538

* Values of dielectric constant are taken from G.Akerlot, J.Am.Chem.Soc., 1932, 54, 1125.

TABLE - 3.13

EFFECT OF CHANGE IN SOLVENT COMPOSITION ON THE OXIDATION OF SUCCINIC ACID DIHYDRAZIDE BY CHLORAMINE-T

$[SAD] \times 10^4 = 5.0$ M $[CAT] \times 10^3 = 1.0$ M

pH = 9.0 TEMP = 30^oc

SOLVENT : WATER/METHANOL (V/V) = 95/5 to 75/25 (V/V)

Sr. No.	Solvent (v/v) Water	Methanol	$k \times 10^4 S^{-1}$	$k_1 \times 10^4 S^{-1}$	$k_2 \times 10^4 S^{-1}$
1	100	0	2.297	4.579	2.289
2	95	5	1.846	3.680	1.840
3	90	10	1.468	2.927	1.463
4	85	15	1.146	2.284	1.142
5	80	20	0.893	1.780	0.890
6	75	25	0.748	1.491	0.745

DATA FOR GRAPHICAL REPRESENTATION

Sr. No.	Solvent (v/v) Water	Methanol	Dielectric constant(D)	$10^2/D$	5 + log k
1	100	0	76.73	1.3033	1.3612
2	95	5	74.50	1.3423	1.2663
3	90	10	72.37	1.3818	1.1668
4	85	15	69.75	1.4337	1.0592
5	80	20	67.48	1.4819	1.9514
6	75	25	65.06	1.5370	0.8744

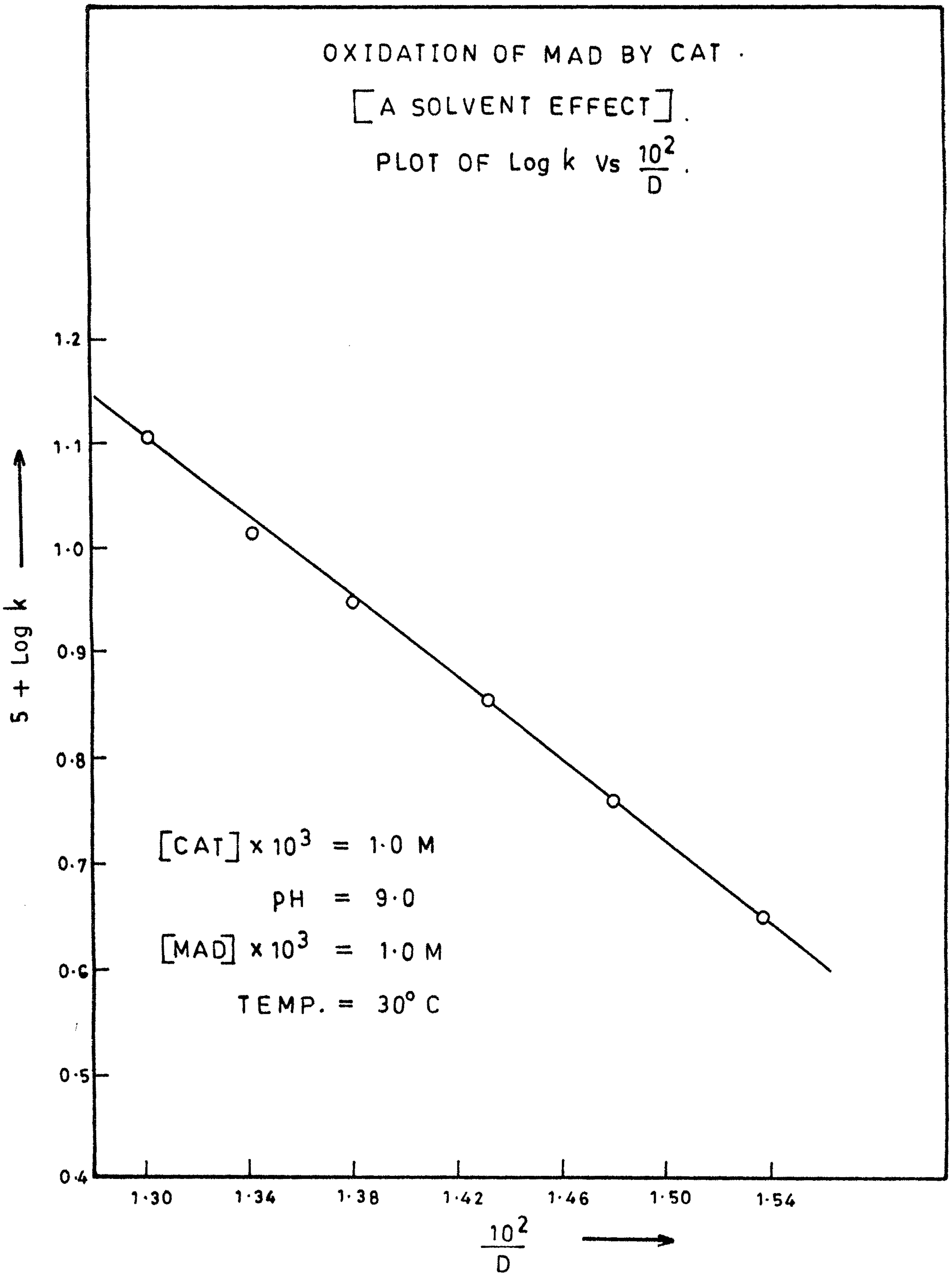

OXIDATION OF MAD BY CAT.
[A SOLVENT EFFECT].
PLOT OF Log k Vs $\frac{10^2}{D}$.
5 + Log k
$\frac{10^2}{D}$
[CAT] x 10^3 = 1·0 M
pH = 9·0
[MAD] x 10^3 = 1·0 M
TEMP. = 30° C
1·2
1·1
1·0
0·9
0·8
0·7
0·6
0·5
0·4
1·30
1·34
1·38
1·42
1·46
1·50
1·54

FIG. 3·23

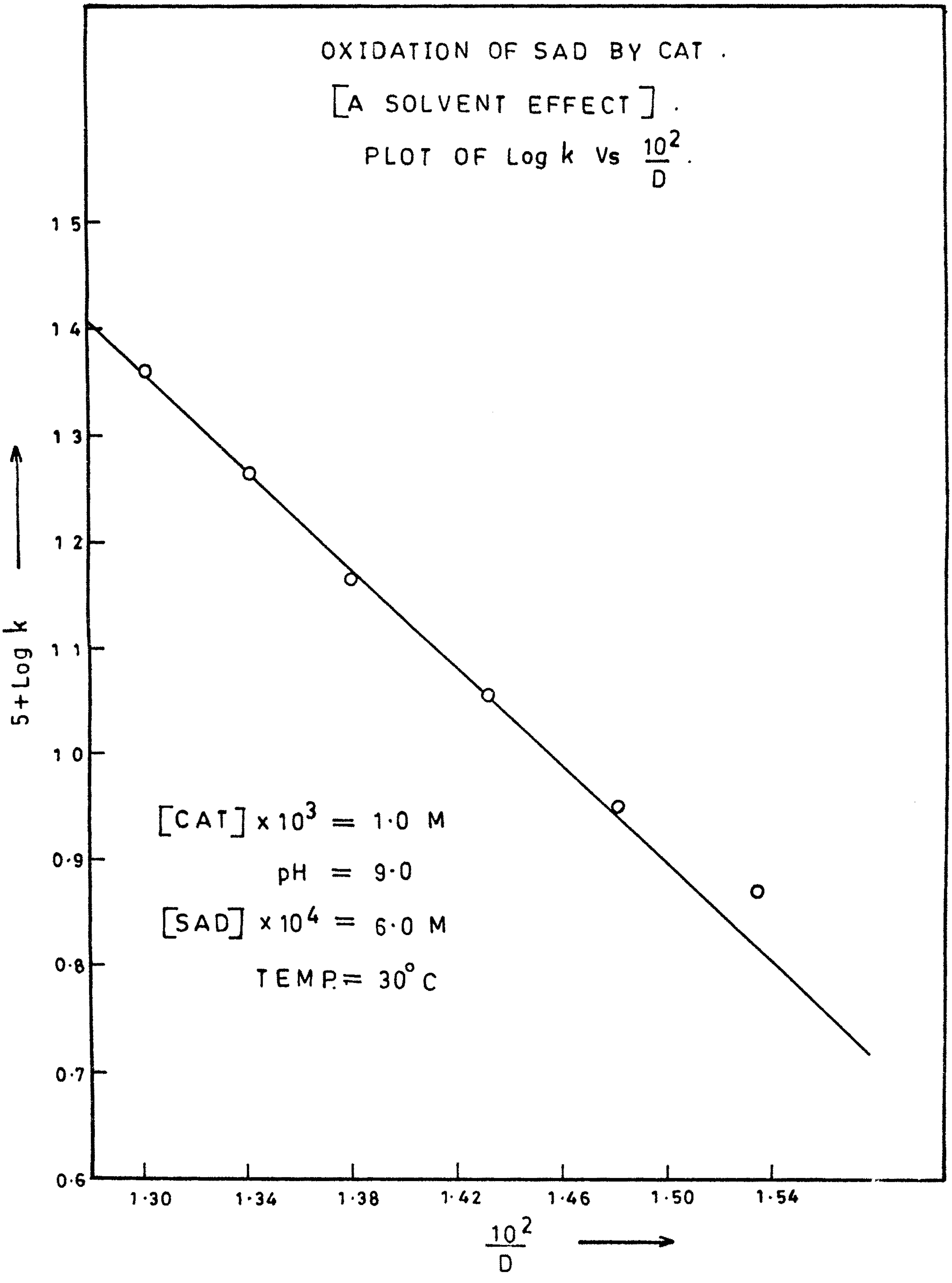

OXIDATION OF SAD BY CAT.
[A SOLVENT EFFECT].
PLOT OF Log k Vs $\frac{10^2}{D}$.
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
5+Log k
[CAT] x 10^3 = 1.0 M
pH = 9.0
[SAD] x 10^4 = 6.0 M
TEMP. = 30° C
1.30
1.34
1.38
1.42
1.46
1.50
1.54
$\frac{10^2}{D}$

FIG. 3.24

V) EFFECT OF CHANGE IN pH ON THE OXIDATION OF DIHYDRAZIDES BY CHLORAMINE-T

The effect of pH on the oxidation of dihydrazides by chloramine-T was studied by carrying out the same reaction in different buffer solutions in the pH range from 7.55 to 10.54. In all the kinetic runs, except these runs buffer solutions were prepared by mixing 10 mls of sodium carbonate (0.025 M) and 10 mls of sodium bicarbonate (0.025 M). For these kinetic runs so as to change the pH of reaction mixtures we have used different volumes of sodium carbonate (0.025) and sodium bicarbonate (0.025 M) solutions. The exact pH of these reaction mixtures were obtained by using digital pH meter.

The results obtained are summarised in Table 3.14 and 3.15. From these results it is observed that rate constant goes on decreasing with increase in the pH of reaction mixture. A plots of pH vs log k were plotted in both the cases and are shown in Fig. 3.25 and 3.26 straight line graphs are obtained in case of both the dihydrazides.

TABLE - 3.14

EFFECT OF CHANGE IN THE pH ON THE OXIDATION OF MALONIC ACID DIHYDRAZIDE BY CHLORAMINE-T

[MAD] x 10^3 = 1.0 M   [CAT] x 10^3 = 1.0 M

pH = 7.55 - 10.54   TEMP = 30^oC

Sr. No.	0.025 M $NaHCO_3$ (ml)	0.025 M Na_2CO_3 (ml)	pH	$kx10^4S^{-1}$	$k_1x10^4S^{-1}$	$K_2x10^4S^{-1}$	5+log K
0	20.0	00.0	7.55	3.389	6.757	3.378	1.5301
2	15.0	05.0	8.25	2.053	4.093	2.046	1.3124
3	10.0	10.0	9.0	1.274	2.540	1.270	1.1052
4	05.0	15.0	9.75	0.8311	1.657	0.828	0.9192
5	00.0	20.0	10.54	0.4940	0.984	0.492	0.6937

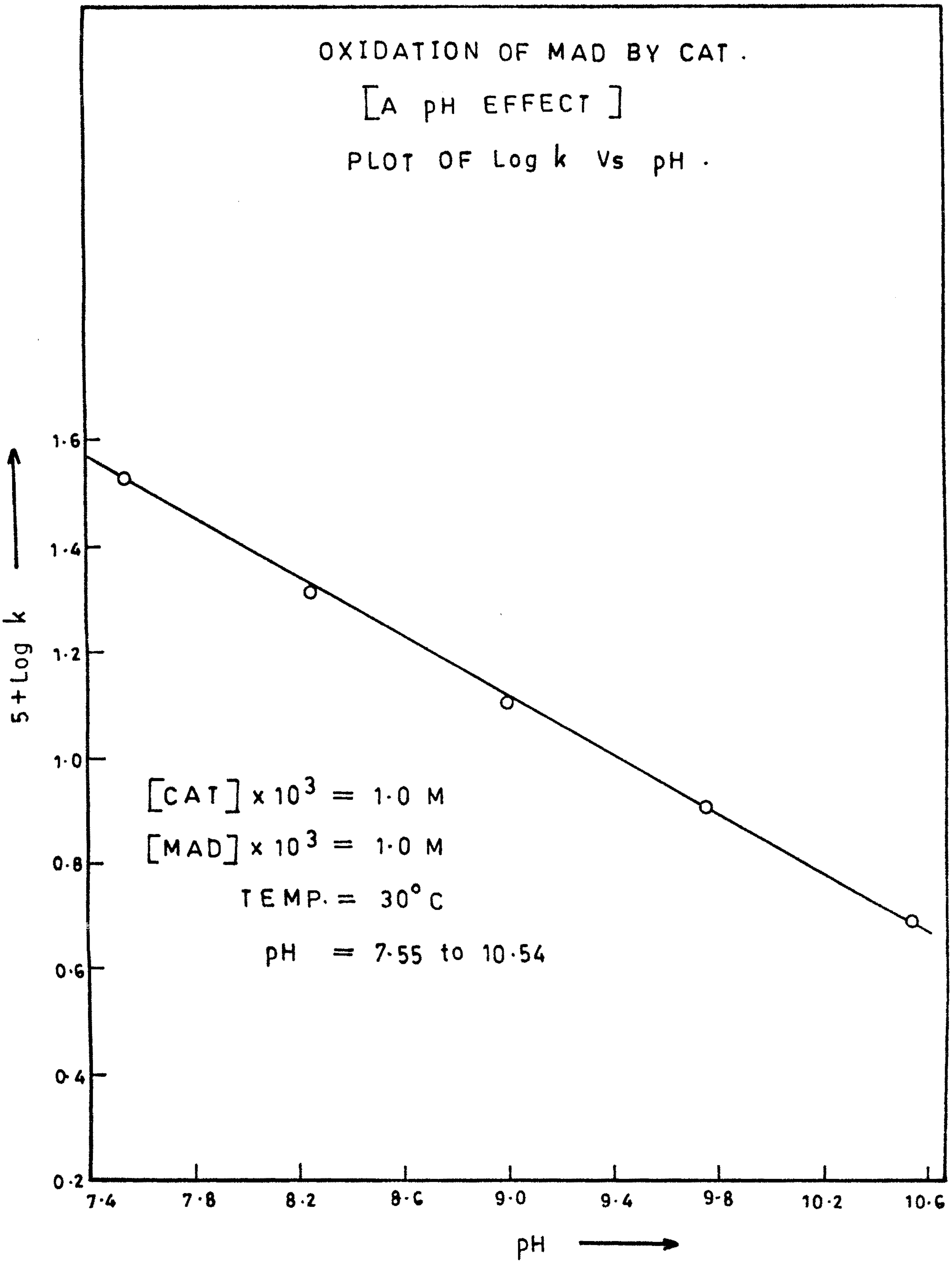
TABLE - 3.15

EFFECT OF CHANGE IN THE pH ON THE OXIDATION OF SUCCINIC ACID DIHYDRAZIDE BY CHLORAMINE-T

[SAD] x 10^4 = 5.0 M   [CAT] x 10^3 = 1.0 M

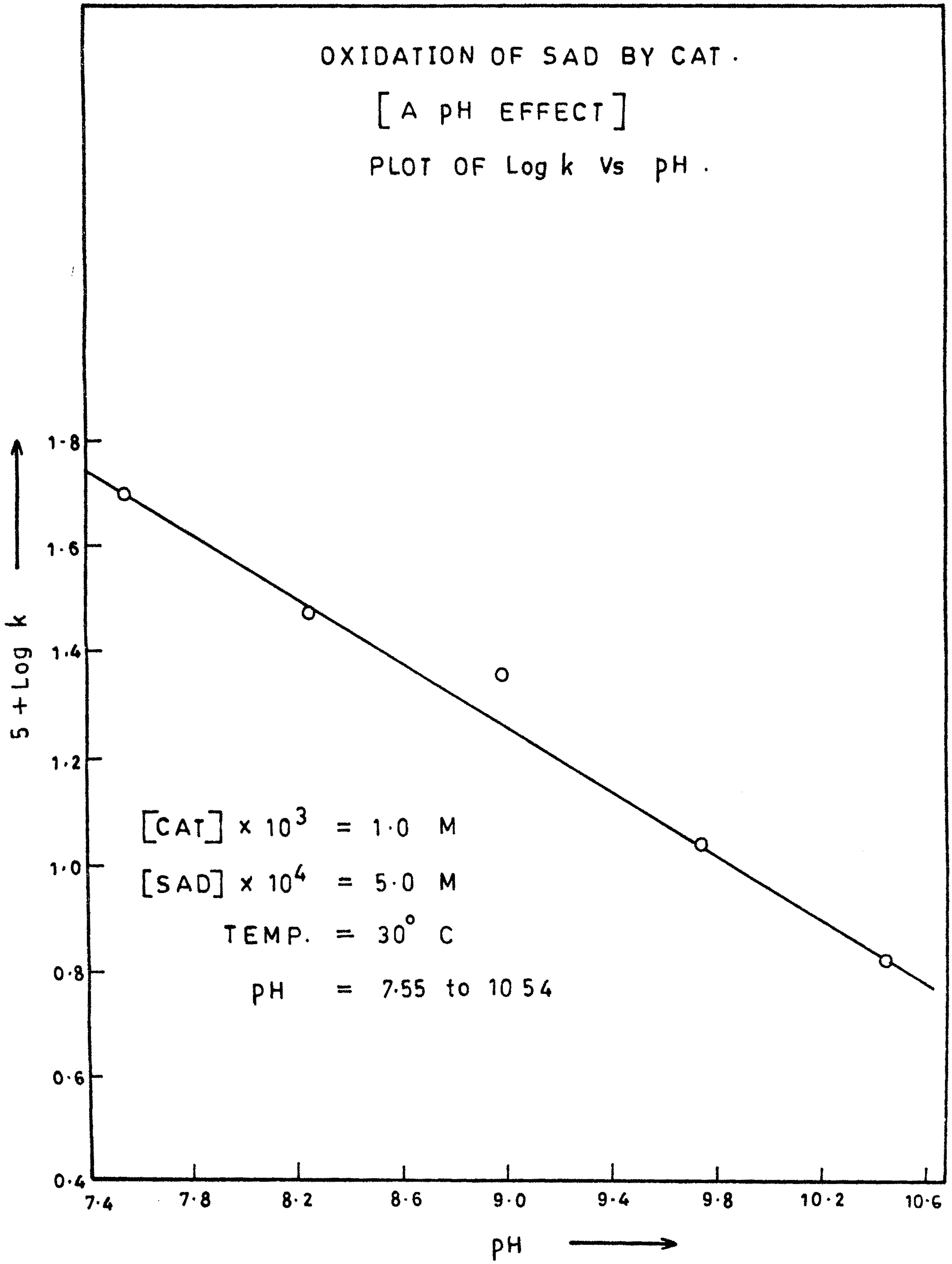
pH = 7.55 - 10.54   TEMP = 30^oC

Sr. No.	0.025 M $NaHCO_3$ (ml)	0.025 M Na_2CO_3 (ml)	pH	$kx10^4S^{-1}$	$k_1x10^4S^{-1}$	$K_2x10^4S^{-1}$	5+log K
0	20.0	00.0	7.55	5.062	10.09	5.046	1.7044
2	15.0	05.0	8.25	2.989	5 5.959	2.979	1.4754
3	10.0	10.0	9.0	2.297	4.579	2.289	1.3414
4	05.0	15.0	9.75	1.121	2.235	1.117	1.0496
5	00.0	20.0	10.54	0.6621	1.320	0.660	0.8210



OXIDATION OF MAD BY CAT.
[A pH EFFECT]
PLOT OF Log k Vs pH.
5 + Log k
[CAT] x 10^3 = 1.0 M
[MAD] x 10^3 = 1.0 M
TEMP. = 30°C
pH = 7.55 to 10.54
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
7.4
7.8
8.2
8.6
9.0
9.4
9.8
10.2
10.6
pH

FIG. 3.25



OXIDATION OF SAD BY CAT.
[A pH EFFECT]
PLOT OF Log k Vs pH.
[CAT] x 10^3 = 1.0 M
[SAD] x 10^4 = 5.0 M
TEMP. = 30° C
pH = 7.55 to 10.54
5 + Log k
pH
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
7.4
7.8
8.2
8.6
9.0
9.4
9.8
10.2
10.6

FIG. 3.26

VI. EFFECT OF ADDITION OF COMMON SALT ON THE OXIDATION OF DIHYDRAZIDES BY CHLORAMINE-T

In order to investigate the effect of added common salt on the oxidation of dihydrazides by chloramine-T, different kinetic runs were carried out in presence of different concentrations of potassium chloride in the reaction mixture without altering the other reaction conditions.

The various results obtained are given in Table 3.16 and 3.17. It is observed from these results that added potassium chloride 0.001 to 0.01 M has no effect on the rate of the reaction.

VII. EFFECT OF ADDITION OF p-TOLUENE SULPHONAMIDE ON THE OXIDATION OF DIHYDRAZIDES BY CHLORAMINE-T

The effect of addition of p-toluene sulphonamide (PTS) on the oxidation of dihydrazides were studied so as to get the information whether p-toluene sulphonamide is a oxidising species or not. For this one particular kinetic run is selected and different runs were carried out in presence of different concentrations of p-toluene sulphonamide at the same reaction conditions. The results that are obtained are given in table 3.18 and 3.19. It is observed from these results that p-toluene sulphonamide is not particularly as a oxidising species in these reactions.

TABLE - 3.16

EFFECT OF ADDITION OF COMMON SALT ON THE OXIDATION OF MALONIC ACID DIHYDRAZIDE BY CHLORAMINE-T

[MAD] x 10^3 = 1.0 M   [CAT] x 10^3 = 1.0 M

pH = 9.0   TEMP = 30^{o}C

[KCl] x 10^3 = 1 to 10 M

Sr. No.	[KCl] M	$k \times 10^4 S^{-1}$	$k_1 \times 10^4 S^{-1}$	$k_2 \times 10^4 S^{-1}$
1	0.000	1.274	2.540	1.270
2	0.001	1.276	2.544	1.272
3	0.005	1.265	2.522	1.261
4	0.010	1.253	2.498	1.249

TABLE - 3.17

EFFECT OF ADDITION OF COMMON SALT ON THE OXIDATION OF SUCCINIC ACID DIHYDRAZIDE BY CHLORAMINE-T

[SAD] x 10^4 = 5.0 M   [CAT] x 10^3 = 1.0 M

pH = 9.0   TEMP = 30^{o}C

[KCl] x 10^3 = 1 to 10 M

Sr. No.	[KCl] M	$k \times 10^4 S^{-1}$	$k_1 \times 10^4 S^{-1}$	$k_2 \times 10^4 S^{-1}$
0	0.000	2.297	4.579	2.289
2	0.001	2,286	4,457	2,278
3	0.005	2.276	4.537	2,268
4	0.010	2.253	4.492	2.246

TABLE - 3.18

EFFECT OF ADDITION OF p-TOLUENE SULPHONAMIDE ON THE OXIDATION OF MALONIC ACID DIHYDRAZIDE BY CHLORAMINE-T

[MAD] x 10^3 = 1.0 M   [CAT] x 10^3 = 1.0 M

pH = 9.0   TEMP = 30^oC

[PTS] x 10^2 = 1 to 5 M

Sr. No.	[PTS] M	$k x 10^4 S^{-1}$	$k_1 x 10^4 S^{-1}$	$k_2 x 10^4 S^{-1}$
1	0.00	1.277	2.540	1.270
2	0.01	1.230	2.452	1.226
3	0.03	1.211	2.414	1.207
4	0.05	1.175	2.342	1.171

TABLE - 3.19

EFFECT OF ADDITION OF p-TOLUENE SULPHONAMIDE ON THE OXIDATION OF SUCCINIC ACID DIHYDRAZIDE BY CHLORAMINE-T

[SAD] x 10^4 = 5.0 M   [CAT] x 10^3 = 5.0 M

pH = 9.0   TEMP = 30^oC

[PTS] x 10^2 = 1 to 5 M

Sr. No.	[PTS] M	$k x 10^4 S^{-1}$	$k_1 x 10^4 S^{-1}$	$k_2 x 10^4 S^{-1}$
1	0.00	2.297	4.579	2.289
2	0.01	2.294	4.573	2.286
3	0.03	2.256	4.498	2.249
4	0.05	2.243	4.468	2.234

VIII. EFFECT OF ADDITION OF ALLYL ACETATE ON THE OXIDATION OF DIHYDRAZIDES BY CHLORAMINE-T

As we know that compounds like allyl acetate or acryl amide are able to give free radical test easily if added in the reaction mixture. Therefore so as to get the information whether in this reaction free radicals are participating or not, we have carried out different kinetic runs. In these kinetic runs the concentrations of reactants and reaction conditions are kept constant but the concentration of allyl acetate is changed. It is observed that change in the concentration of allyl acetate or even its presence or absence in this reaction has no any effect on the reaction clearly indicating that there are absence of free radicals during the course of these reactions (Table 3.20 and 3.21).

TABLE - 3.20

EFFECT OF ADDITION OF ALLYL ACETATE ON THE OXIDATION OF MALONIC ACID DIHYDRAZIDE BY CHLORAMINE-T

[MAD] x 10^3 = 1.0 M   [CAT] x 10^3 = 1.0 M

pH = 9.0   TEMP = 30^oC

[ALLYL ACETATE] x 10^2 = 1 to 5 M

Sr. No.	Allyl acetate M	$kx10^4S^{-1}$	$k_1x10^4S^{-1}$	$k_2x10^4S^{-1}$
1	0.00	1.277	2.540	1.270
2	0.01	1.313	2.618	1.308
3	0.03	1.346	2.683	1.341
4	0.05	1.366	2.723	1.362

TABLE - 3.21

EFFECT OF ADDITION OF ALLYL ACETATE ON THE OXIDATION OF SUCCINIC ACID DIHYDRAZIDE BY CHLORAMINE-T

[SAD] x 10^4 = 5.0 M   [CAT] x 10^3 = 1.0 M

pH = 9.0   TEMP = 30^oC

[ALLYL ACETATE] x 10^2 = 1 to 5 M

Sr. No.	Allyl acetate M	$kx10^4S^{-1}$	$k_1x10^4S^{-1}$	$k_2x10^4S^{-1}$
1	0.00	2.297	4.579	2.289
2	0.01	2.310	4.605	2.303
3	0.03	2.381	4.747	2.373
4	0.05	2.350	4.685	2.342

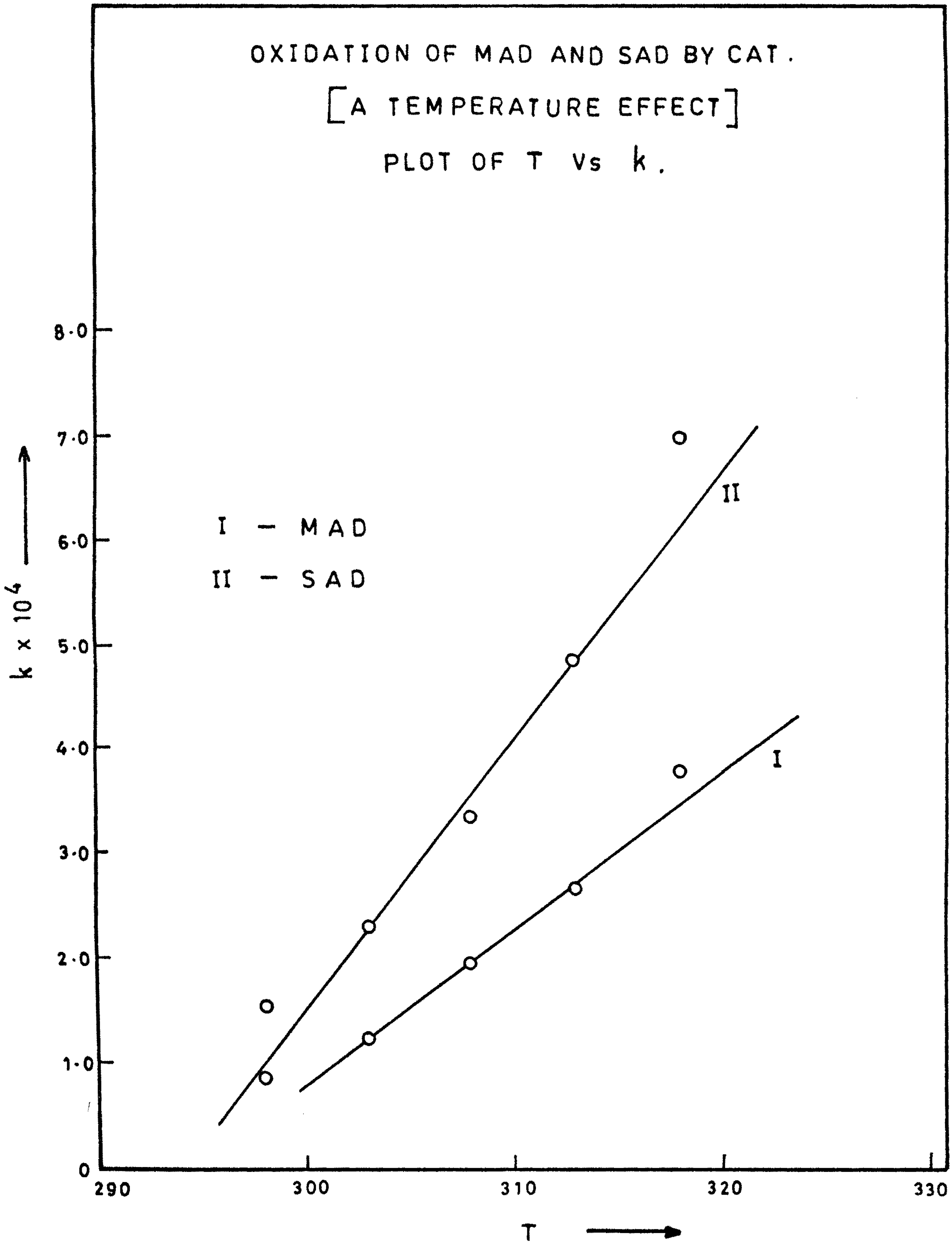

OXIDATION OF MAD AND SAD BY CAT.
[A TEMPERATURE EFFECT]
PLOT OF T Vs k.
I – MAD
II – SAD
I
II
$k \times 10^4$
0
1·0
2·0
3·0
4·0
5·0
6·0
7·0
8·0
290
300
310
320
330
T

FIG. 3·27