CHAPTER IV : RESULTS

A) EFFECT OF CONCENTRATION OF ALKALINE POTASSIUM PERMANGANATE

The rate of reaction between amides (nicotinamide, iso-nicotinamide) and alkaline potassium permanganate were studied at different concentrations of permanganate, keeping concentration of amides constant. From the slope of the plots of absorption vs time, the rates of oxidation of nicotinamide and iso-nicotinamide have been determined as shown in Fig 1 & 2 and tabulated in Table 1 & 2. It is observed from Table 1 and 2 that the values of rate coefficient at different concentrations of permanganate and constant concentration of amide are found to be constant which indicates that the reaction is zero order with respect to potassium permanganate, which is in agreement with the Duke's work.[1]

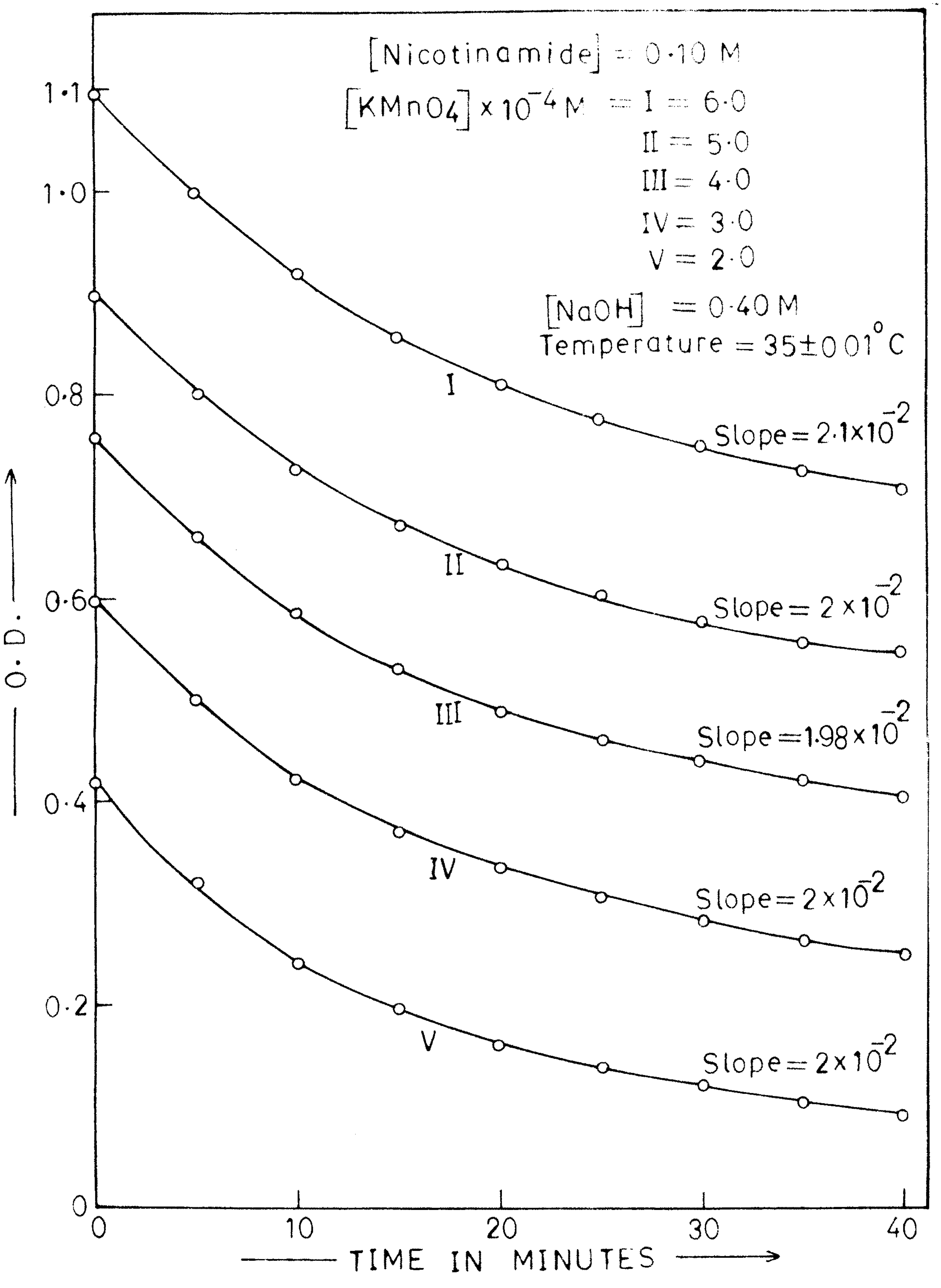

Fig. 1 : EFFECT OF VARYING [KMnO4].

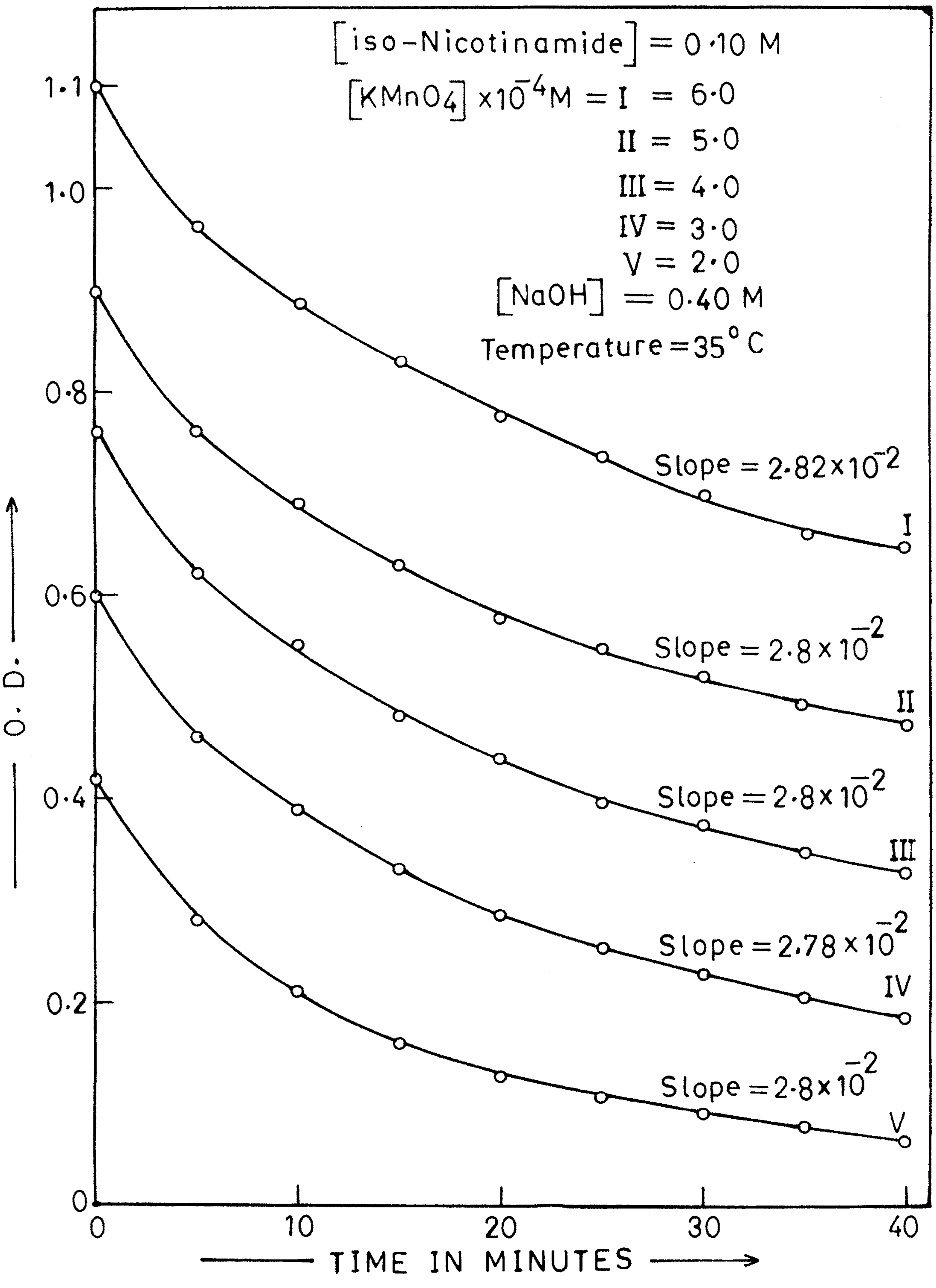

Fig. 2 : EFFECT OF VARYING [KMnO4] .

TABLE 1. EFFECT OF VARYING $[KMnO_4]$ ON THE RATE OF OXIDATION OF NICOTINAMIDE

NaOH = 0.40 M, NICOTINAMIDE = 1×10^{-1} M,

TEMP. = 35 ± 0.01°C

$[KMnO_4] \times 10^4$ M	2	3	4	5	6
$\left(-\frac{dc}{dt}\right) \times 10^2$ min^{-1}	2	2	1.98	2	2.1

TABLE 2. EFFECT OF VARYING $[KMnO_4]$ ON THE RATE OF OXIDATION OF ISO-NICOTINAMIDE

NaOH = 0.40 M, iso-NICOTINAMIDE = 1×10^{-1} M,

TEMP. = 35 ± 0.01°C

$[KMnO_4] \times 10^4$ M	2	3	4	5	6
$\left(-\frac{dc}{dt}\right) \times 10^2$ min^{-1}	2.8	2.78	2.8	2.8	2.82

B) EFFECT OF CONCENTRATION OF ALKALI

The rate coefficients are determined at constant concentrations of potassium permanganate and amides varying concentration of alkali. From the slope of the plot of absorption vs time (Fig 3 & 4), it has been observed that the rate coefficient increases with rise in concentration of alkali as shown in Table 3 & 4. A plot of the [hydroxyl ion] against $\frac{dc}{dt} / [\text{Amide}]$ gives a straight line passing through the origin indicating first order dependence on hydroxyl ion concentration (Fig 5 & 6).

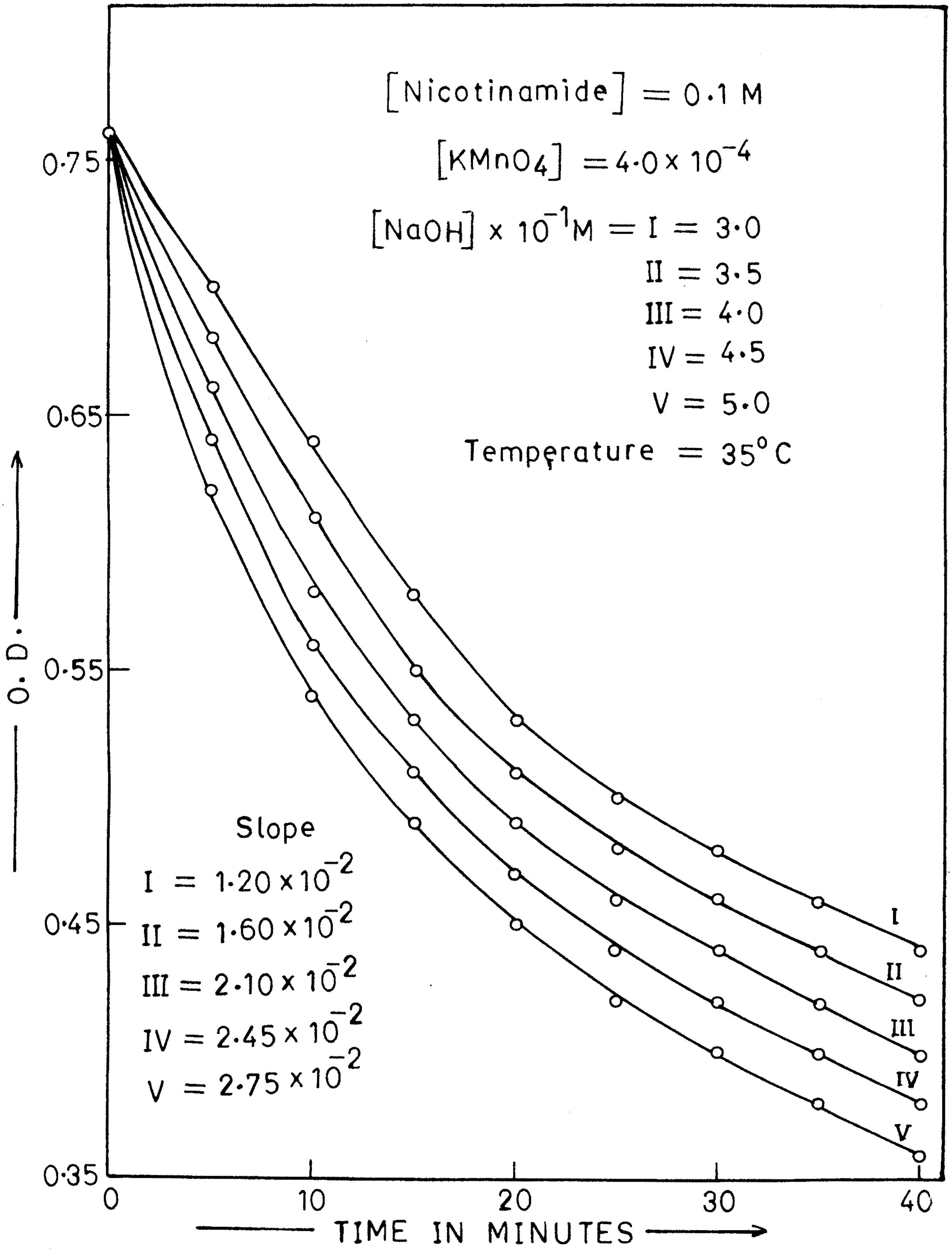

Fig. 3 : EFFECT OF VARYING [NaOH].

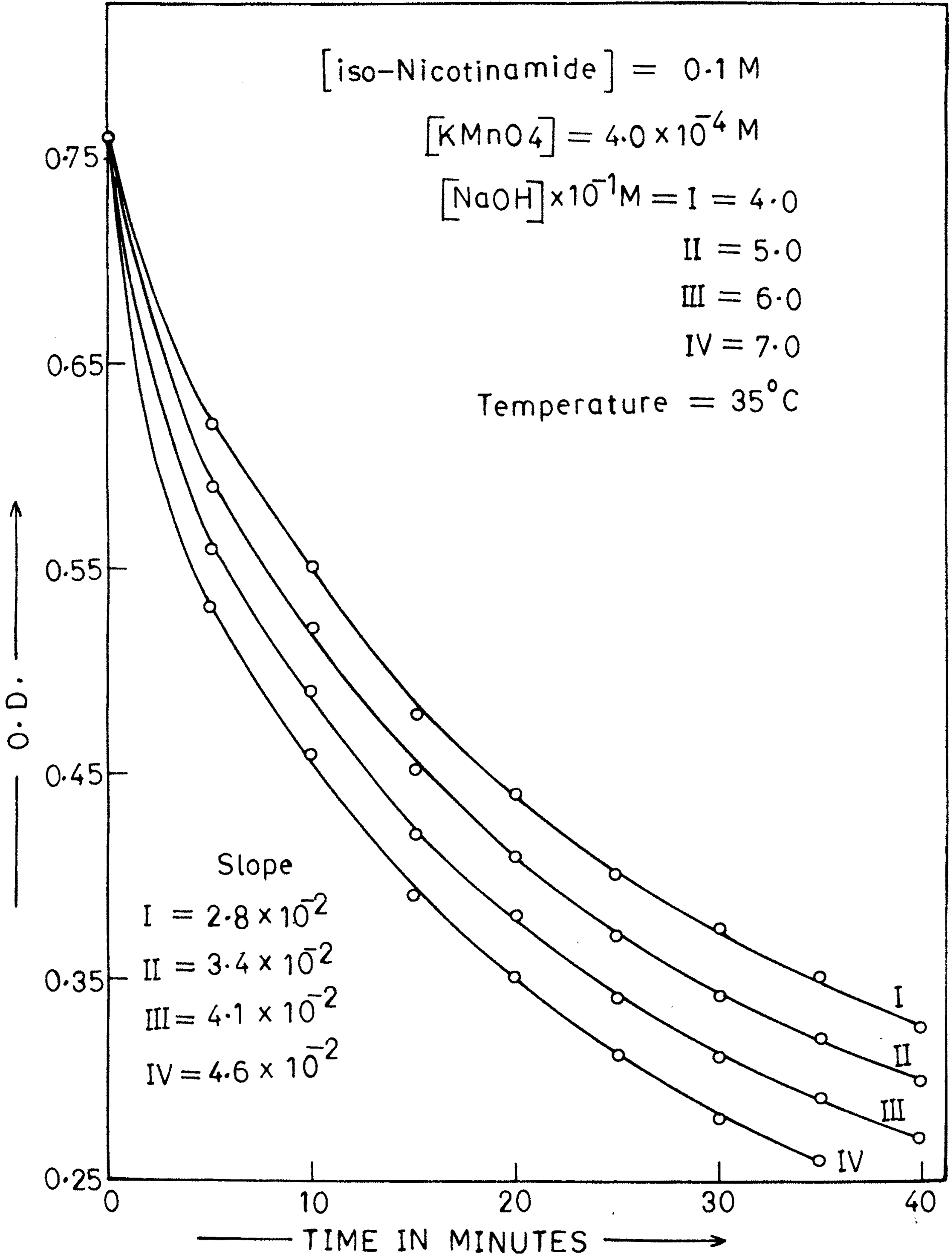

Fig. 4 : EFFECT OF VARYING [NaOH]

TABLE 3. EFFECT OF VARYING [NaOH] ON THE RATE OF OXIDATION OF NICOTINAMIDE

Nicotinamide = 1.0×10^{-1} M, $KMnO_4$ = 4.0×10^{-4} M,

Temp. = 35 ± 0.01°C

[NaOH] M	0.30	0.35	0.40	0.45	0.50
$\left(-\frac{dc}{dt}\right) \times 10^{2}$ min^{-1}	1.2	1.6	2.1	2.45	2.75
$\frac{\left(-\frac{dc}{dt}\right) \times 10^{1}}{[\text{Nicotinamide}]}$	1.2	1.6	2.1	2.45	2.75

TABLE 4. EFFECT OF VARYING [NaOH] ON THE RATE OF OXIDATION OF iso-NICOTINAMIDE

iso-Nicotinamide = 1.0×10^{-1} M, $KMnO_4$ = 4.0×10^{-4} M,

Temp. = 35 ± 0.01°C

[NaOH] M	0.40	0.50	0.60	0.70
$\left(-\frac{dc}{dt}\right) \times 10^{2}$ min^{-1}	2.8	3.4	4.1	4.6
$\frac{\left(-\frac{dc}{dt}\right) \times 10^{1}}{[\text{iso-Nicotinamide}]}$	2.8	3.4	4.1	4.6

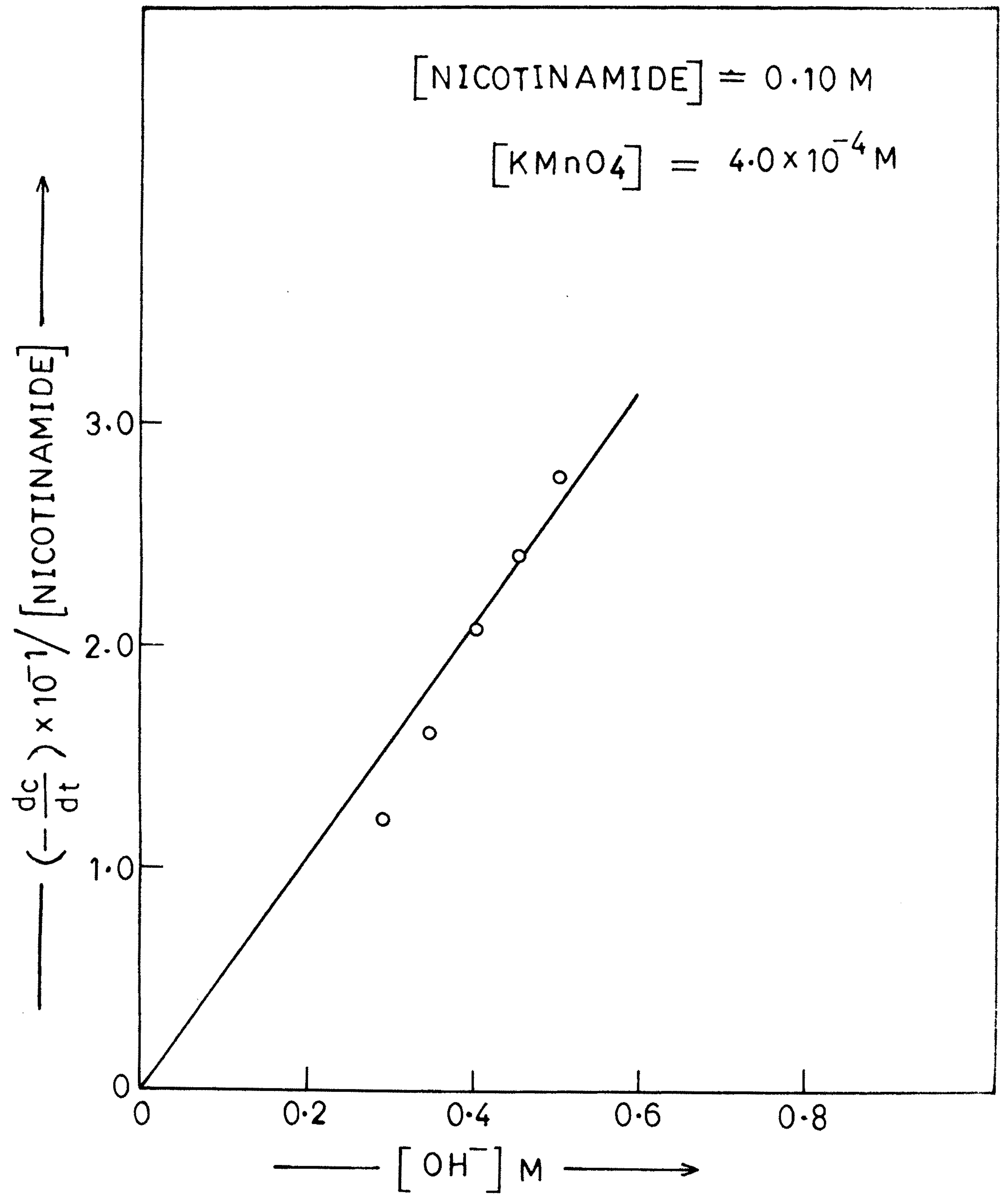

Fig. 5 : EFFECT OF $[OH^-]$ ON THE RATE OF PERMANGANATE OXIDATION OF NICOTINAMIDE.

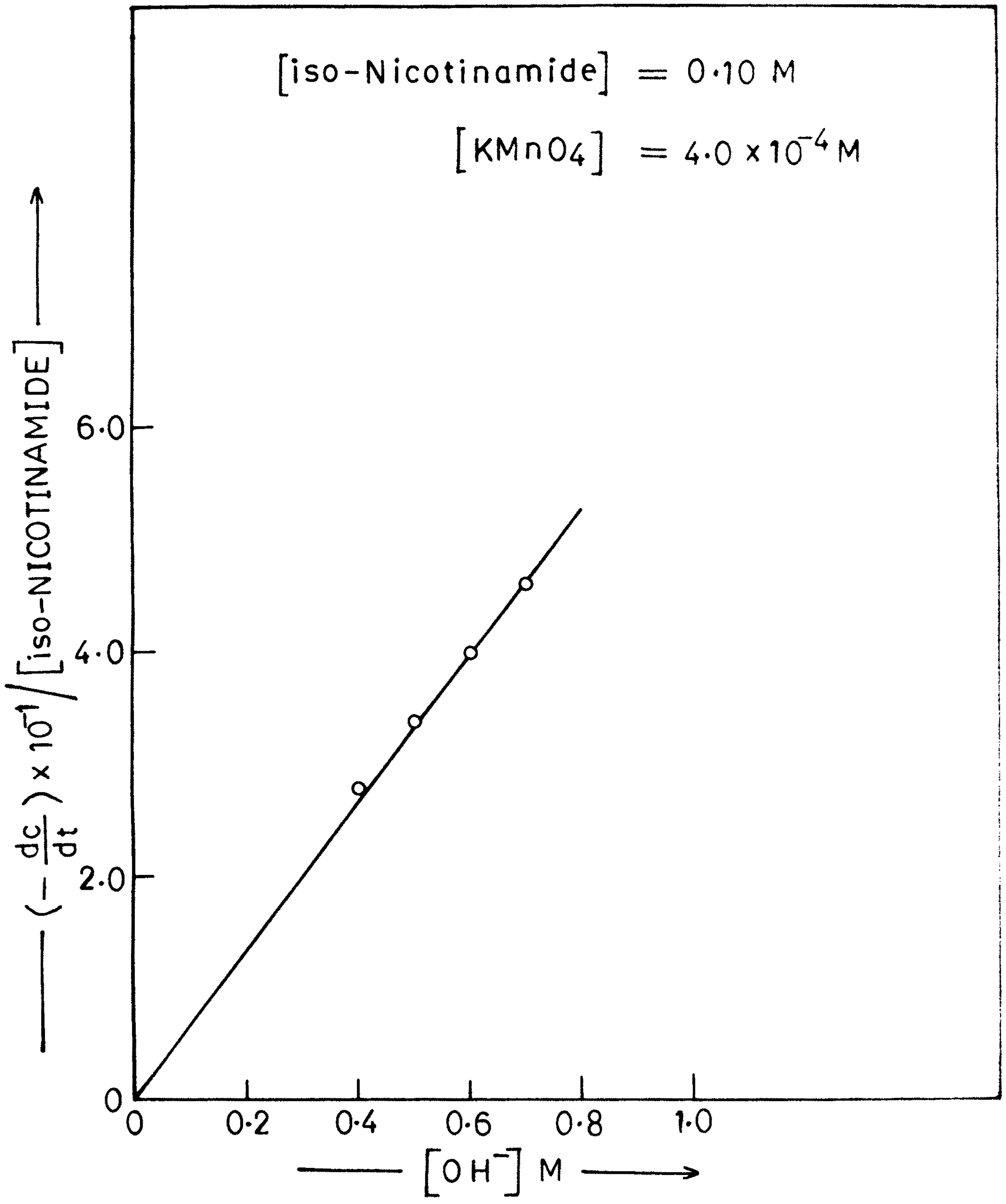

Fig. 6 : EFFECT OF $[OH^-]$ ON THE RATE OF PERMANGANATE OXIDATION OF [iso-NICOTINAMIDE].

C) EFFECT OF CONCENTRATION OF AMIDES

The rate coefficients are determined at different concentrations of amide keeping constant concentration of alkaline potassium permanganate. From the slope of the plot of absorption vs time (Fig 7 & 8) tabulated in Table 5 & 6, it is observed that the rate follows first order kinetics which increases linearly with increase in concentration of amide. The first order rate constant has been determined by using the first order rate equation and graphically, from the slope of the plot of log of optical density vs time (Fig 9 & 10). The order of reaction with respect to amide is determined by using van't Hoff's differential equation. The values of order of reaction are found to be nearly equal to one suggesting that the rate follows first order kinetics with respect to amide. This is further confirmed from the constancy of values of $\frac{dc}{dt} \Big/ [\text{Amide}]$ at constant hydroxyl ion and permanganate concentrations (Table 5 & 6). The second order rate constants k_2 are calculated by using the equation $k_2 = k_1 \Big/ [\text{Amide}]$. Where k_1 is first order rate constant (Table 5 & 6).

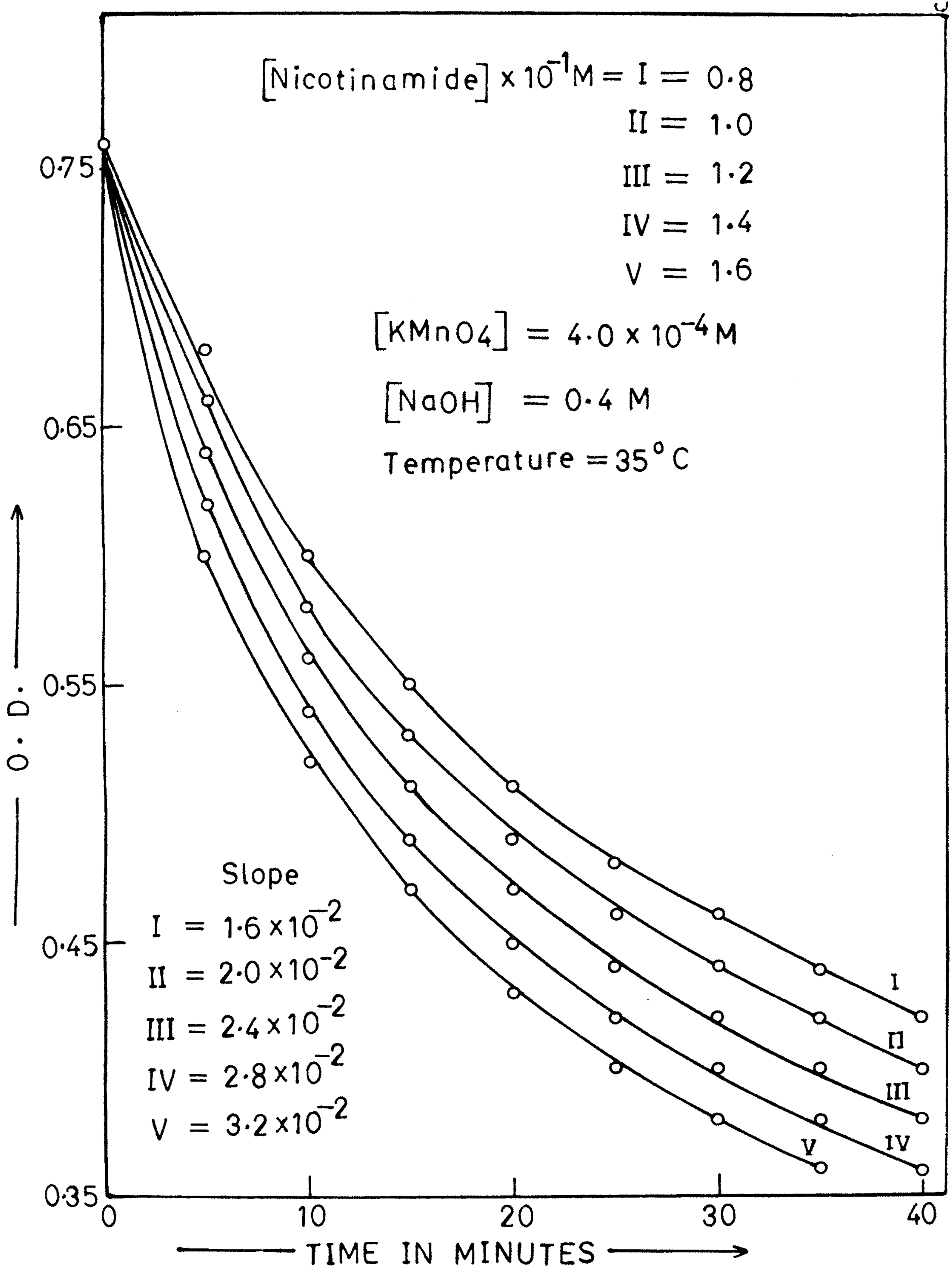

Fig. 7 : EFFECT OF VARYING [NICOTINAMIDE]

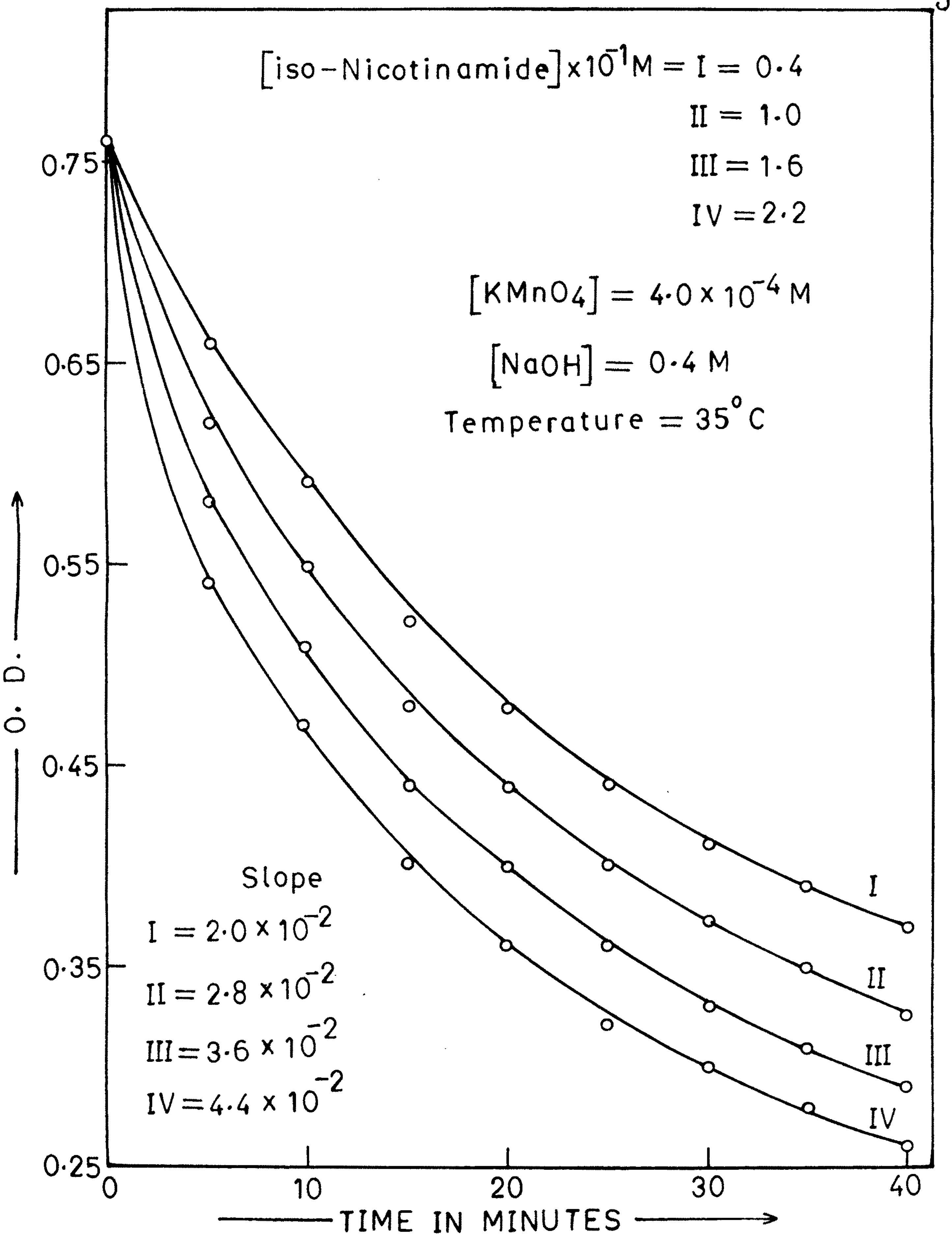

Fig. 8 : EFFECT OF VARYING [iso-NICOTINAMIDE].

TABLE 5. EFFECT OF VARYING [NICOTINAMIDE] ON THE RATE OF OXIDATION

$KMnO_4 = 4.0 \times 10^{-4}$ M, NaOH = 0.40 M, Temp. 35 ± 0.01°C

[Nicotinamide] x 10^{-1} M	0.80	1.00	1.20	1.40	1.60
$\left(-\frac{dc}{dt}\right) \times 10^{2}$ min^{-1}	1.60	2.00	2.40	2.80	3.20
$\dfrac{\left(-\frac{dc}{dt}\right) \times 10^{1} \text{ min}^{-1}}{[\text{Nicotinamide}]}$	2.00	2.00	2.00	2.00	2.00
$k_1 \times 10^{2}$ min^{-1} (graphical)	2.21	2.92	3.43	4.06	4.71
$k_1 \times 10^{2}$ min^{-1} (calculated mean value)	2.15	2.87	3.60	4.20	4.83
$k_2 \times 10^{1}$ lit mole^{-1} min^{-1}	2.46	2.92	2.86	2.90	2.94

$$\text{where } k_2 = \frac{k_1}{[\text{Nicotinamide}]}$$

TABLE 6. EFFECT OF VARYING [iso-NICOTINAMIDE] ON THE RATE OF OXIDATION

$KMnO_4 = 4.0 \times 10^{-4}$ M NaOH = 0.40 M Temp.= 35 ± 0.01°C

[iso-Nicotinamide] 10^{1} M	0.4	1.0	1.6	2.2
$\left(-\frac{dc}{dt}\right) \times 10^{2}$ min^{-1}	2.0	2.8	3.6	4.4
$\dfrac{\left(-\frac{dc}{dt}\right) \times 10^{1} \text{ min}^{-1}}{[\text{iso-Nicotinamide}]}$	5.0	2.8	2.25	2.0
$k_1 \times 10^{2}$ min^{-1} (graphical)	2.81	4.05	5.40	6.83
$k_1 \times 10^{2}$ min^{-1} (Calculated mean value)	2.75	4.12	5.60	6.91
$k_2 \times 10^{1}$ lit mole^{-1} min^{-1}	7.03	4.05	3.37	3.10

$$\text{where } k_2 = \frac{k_1}{[\text{iso-nicotinamide}]}$$

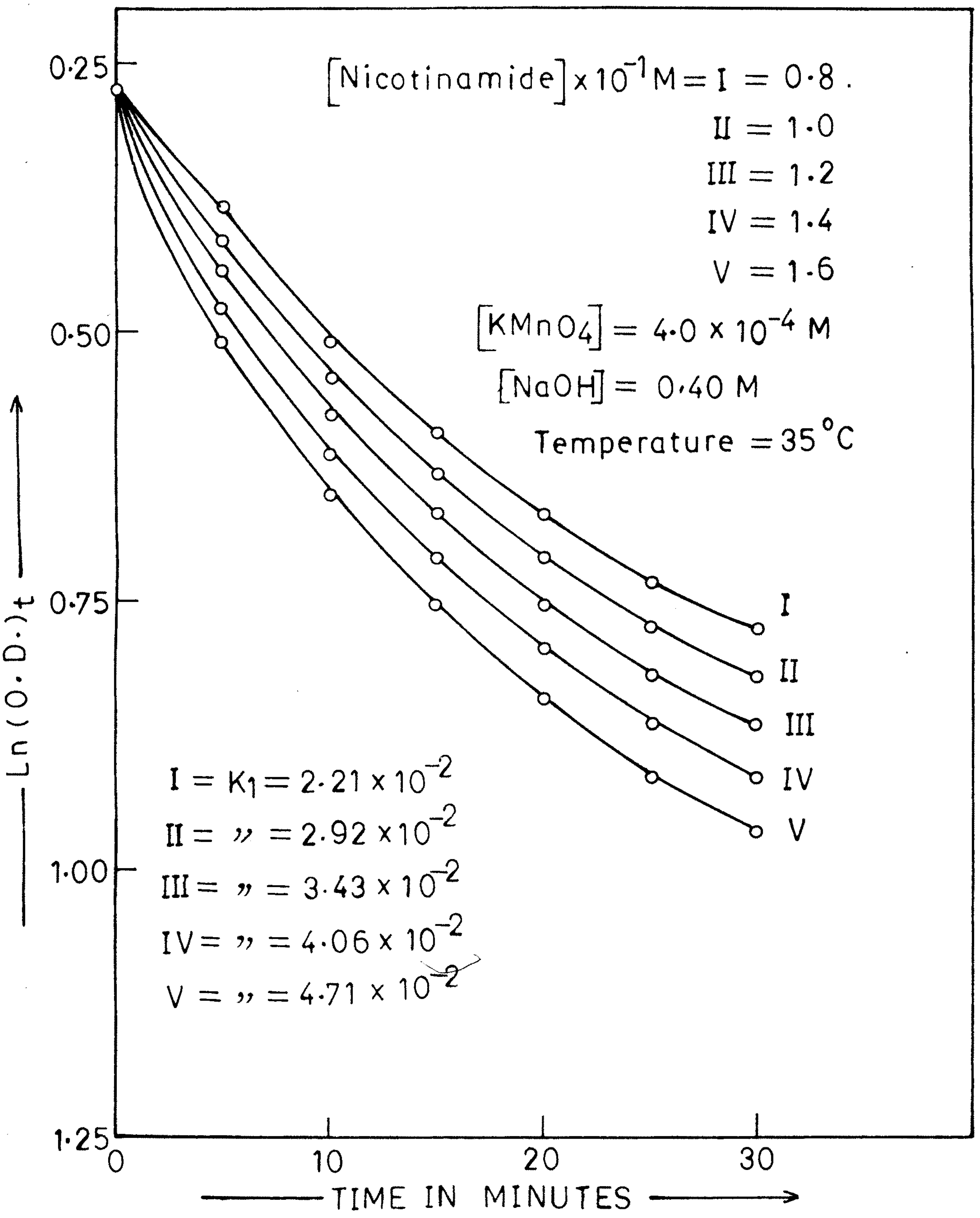

Fig. 9 : EFFECT OF VARYING [NICOTINAMIDE] ON THE RATE CONSTANT.

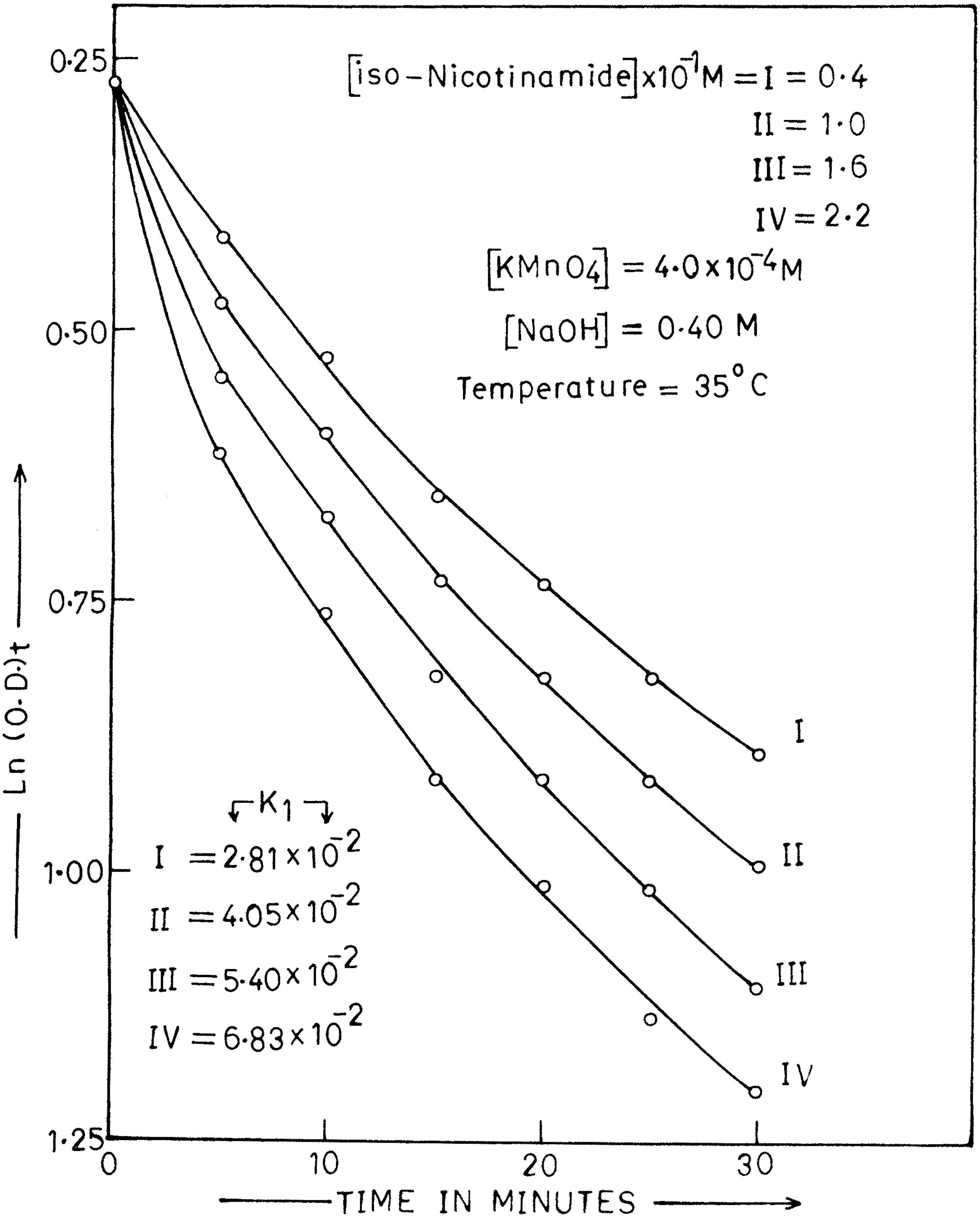

Fig. 10 : EFFECT OF VARYING [iso-NICOTINAMIDE] ON THE RATE CONSTANT.

D) SALT EFFECT

The rate coefficients are determined at different concentrations of sodium sulfate and at constant concentration of permanganate, amide and alkali. From the slope of the plot of optical density vs time (Fig 11 & 12), it is observed that the second order rate constant for the oxidation of amides increase with increase in concentration of salt (Table 7 & 8). The increase in [Salt] increases slight, rate constant indicating that the reaction is subjected to slight positive salt effect.

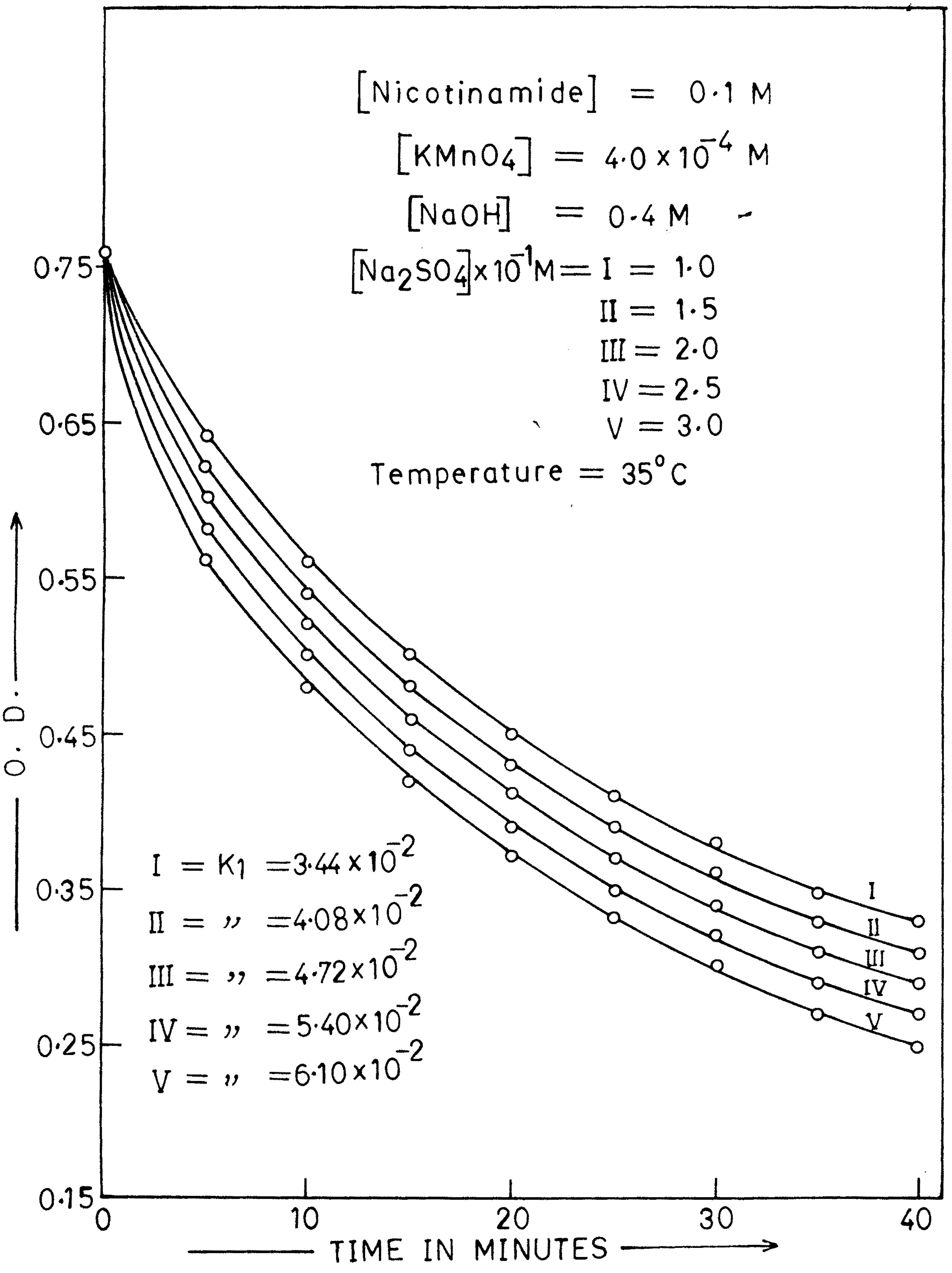

Fig. 11 : EFFECT OF VARYING $[Na_2SO_4]$ ON THE OXIDATION OF NICOTINAMIDE.

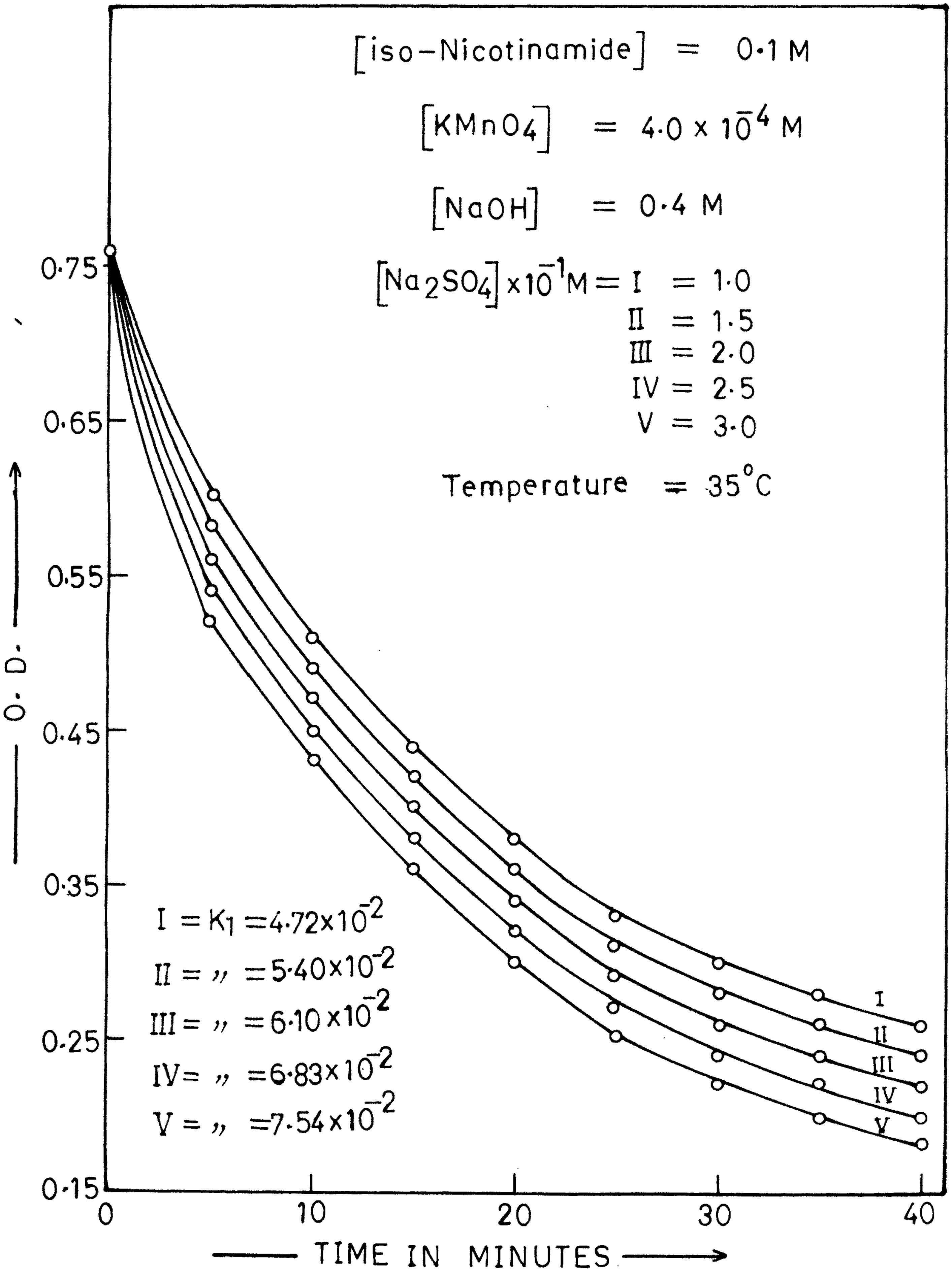

Fig. 12 : EFFECT OF VARYING $[Na_2SO_4]$ ON THE OXIDATION OF iso – NICOTINAMIDE.

TABLE 7. EFFECT OF VARYING $[Na_2SO_4]$ ON THE RATE CONSTANT

Nicotinamide = 0.10 M, $KMnO_4$ = 4.0 x 10^{-4} M, NaOH = 0.40 M,

Temp. = 35 ± 0.01°C

$[Na_2SO_4] \times 10^1$ M	0.00	1.00	1.50	2.00	2.50	3.00
$\left(-\frac{dc}{dt}\right) \times 10^2$ min^{-1}	2.00	2.42	2.30	3.24	3.60	4.00
$\dfrac{\left(-\frac{dc}{dt}\right) \times 10^1 \text{ min}^{-1}}{[\text{Nicotinamide}]}$	2.00	2.42	1.867	1.62	1.44	1.33
$k_1 \times 10^2$ min^{-1}	2.81	3.44	4.08	4.72	5.40	6.10
$k_2 \times 10^1$ lit mole^{-1} min^{-1}	2.81	3.44	4.08	4.72	5.40	6.10

TABLE 8. EFFECT OF VARYING $[Na_2SO_4]$ ON THE RATE CONSTANT

iso-Nicotinamide = 0.10 M, $KMnO_4$ = 4.0 x 10^{-4} M, NaOH = 0.40 M,

Temp. = 35 ± 0.01°C

$[Na_2SO_4] \times 10^1$ M	0.00	1.00	1.50	2.00	2.50	3.00
$\left(-\frac{dc}{dt}\right) \times 10^2$ min^{-1}	2.80	3.24	3.60	4.10	4.40	4.80
$\dfrac{\left(-\frac{dc}{dt}\right) \times 10^1 \text{ min}^{-1}}{[\text{iso-Nicotinamide}]}$	2.80	3.24	3.60	4.05	4.40	4.80
$k_1 \times 10^2$ min^{-1}	4.08	4.72	5.40	6.10	6.83	7.59
$k_2 \times 10^1$ lit mole^{-1} min^{-1}	4.08	4.77	5.40	6.10	6.83	7.59

E) EFFECT OF TEMPERATURE

The course of the reaction is studied at the various temperatures between the range 30°-45°C. The second order rate constant is calculated. The values of energy of activation are determined by integration method and also graphically (Fig 13 & 14). The thermodynamic constants such as ΔH, ΔG, ΔS and frequency factor have been calculated (Table 9 & 10). The values of activation parameters for the studied reactions are in agreement with the other oxidation[2,3] reactions.

1) Energy of activation

$$\log \frac{k_2}{k_1} = \frac{Ea}{4.576} \left[\frac{T_2 - T_1}{T_1 T_2} \right] \text{-----} (1)$$

where k_1 and k_2 are rate constants at temperature T_1 & T_2.

2) Frequency factor

$$\log A = \log k^1 + \frac{E_a}{4.576\ T} \text{-----} (2)$$

where k^1 is the rate constant.

3) Entropy of activation

$$\Delta S^{\ddagger} = 4.576 \left[(\log k^1 - 10.576 - \text{lot } T) + \frac{E_a}{4.576\ T} \right] \text{---} (3)$$

4) Enthalpy of activation

$$\Delta H^{\ddagger} = E_a - RT \text{-----} (4)$$

5) Free energy for the reaction

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger} \text{-----} (5)$$

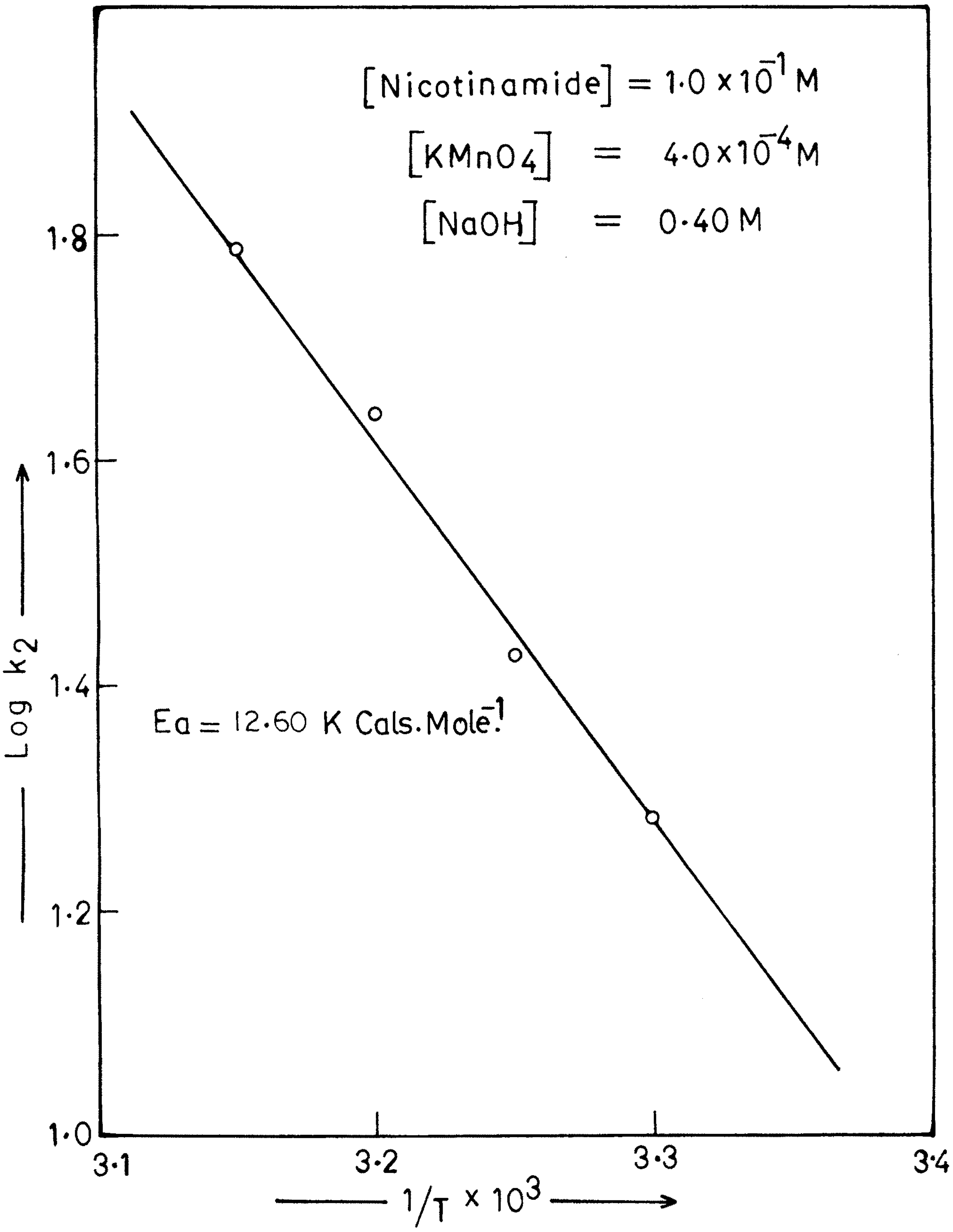

Fig. 13 : EFFECT OF TEMPERATURE ON THE RATE CONSTANT ON OXIDATION OF NICOTINAMIDE.

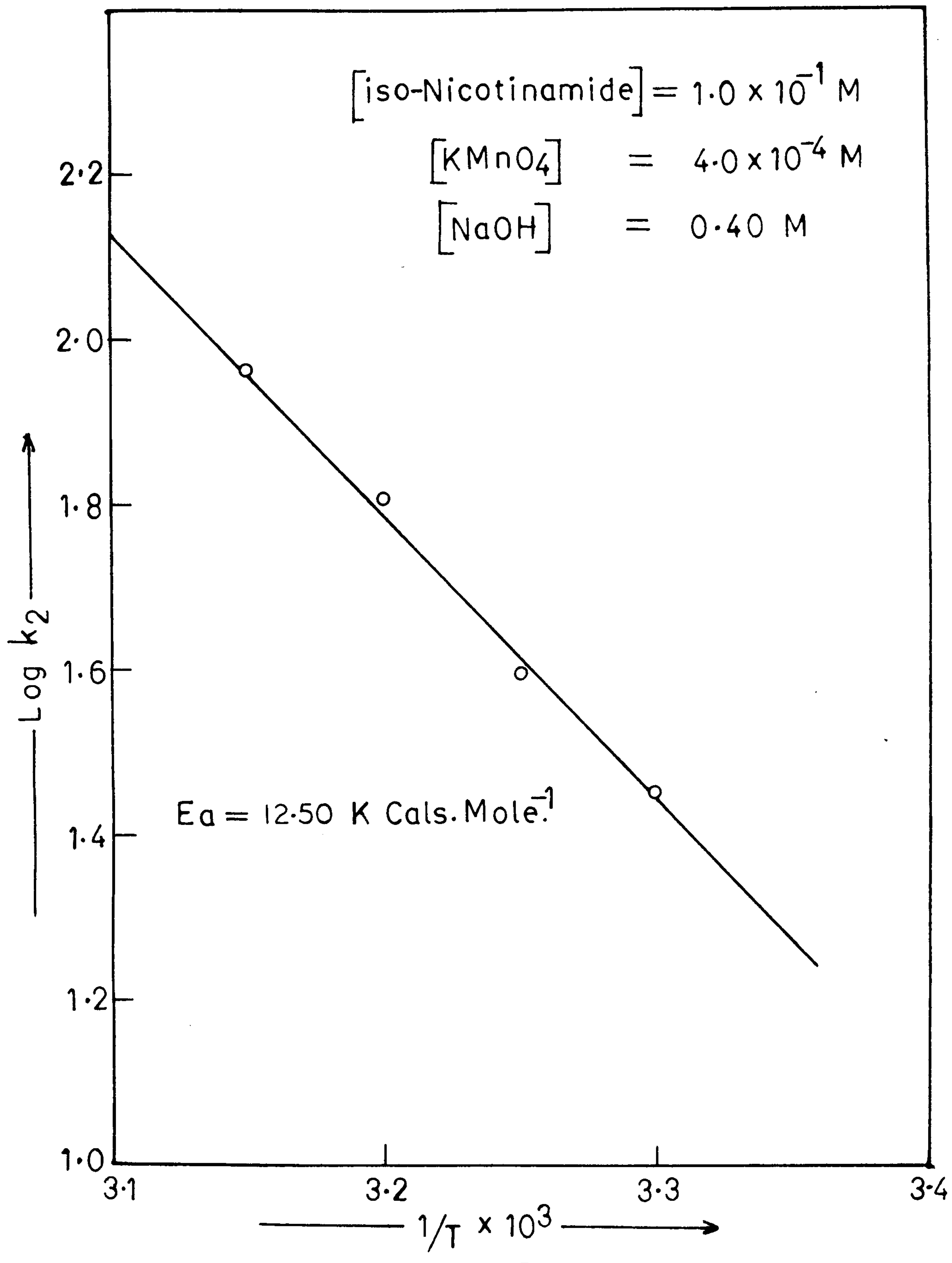

Fig.14: EFFECT OF TEMPERATURE ON THE RATE CONSTANT ON OXIDATION OF iso-NICOTINAMIDE.

TABLE 9. EFFECT OF TEMPERATURE ON THE RATE OF OXIDATION OF NICOTINAMIDE

(Kinetics Parameters)

Nicotinamide = 0.10 M,

$KMnO_4$ = 4.0×10^{-4} M,

NaOH = 0.40 M

Ea	12.6 ± 0.3	K cals/mole^{-1}
$\Delta H^{\ddagger}$	12.00	K cals/mole^{-1}
$\Delta S^{\ddagger}$	- 21.4	e.u.
$\Delta G^{\ddagger}$	18.6	K cals/mole^{-1}
A	2.1×10^{8}	min^{-1}

TABLE 10. EFFECT OF TEMPERATURE ON THE RATE OF OXIDATION OF iso-NICOTINAMIDE

(Kinetics Parameters)

iso-Nicotinamide = 0.10 M,
$KMnO_4 = 4.0 \times 10^{-4}$ M,
NaOH = 0.40 M

Ea	12.5 ± 0.3	K cals/mole^{-1}
$\Delta H^{\ddagger}$	11.9	K cals/mole^{-1}
$\Delta S^{\ddagger}$	-21.0	e.u.
$\Delta G^{\ddagger}$	18.2	K cals/mole^{-1}
A	2.9×10^{8}	min^{-1}

F) DETERMINATION OF RELATIVE RATES OF OXIDATION OF AMIDES

The kinetic experiments were carried out under identical conditions of concentration of substrate; oxidant and alkali at constant temperature. The graphs are plotted for all the amides between optical density vs time (Fig 15 - 18). From the plots, the rate of oxidation of each amide is determined as shown in Table 11.

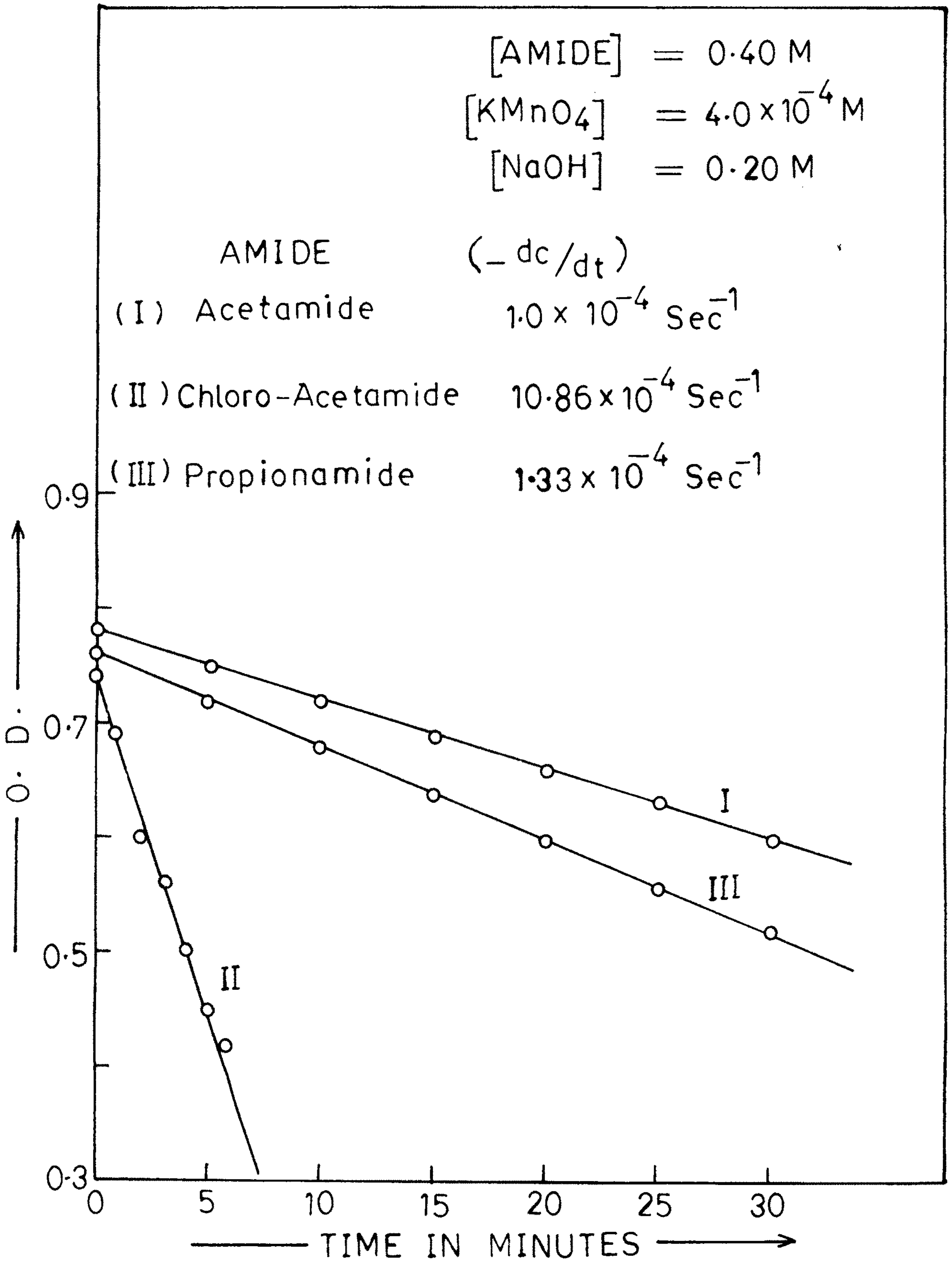

Fig. 15 : EFFECT OF SUBSTITUENT ON THE RATE OF OXIDATION OF AMIDES .

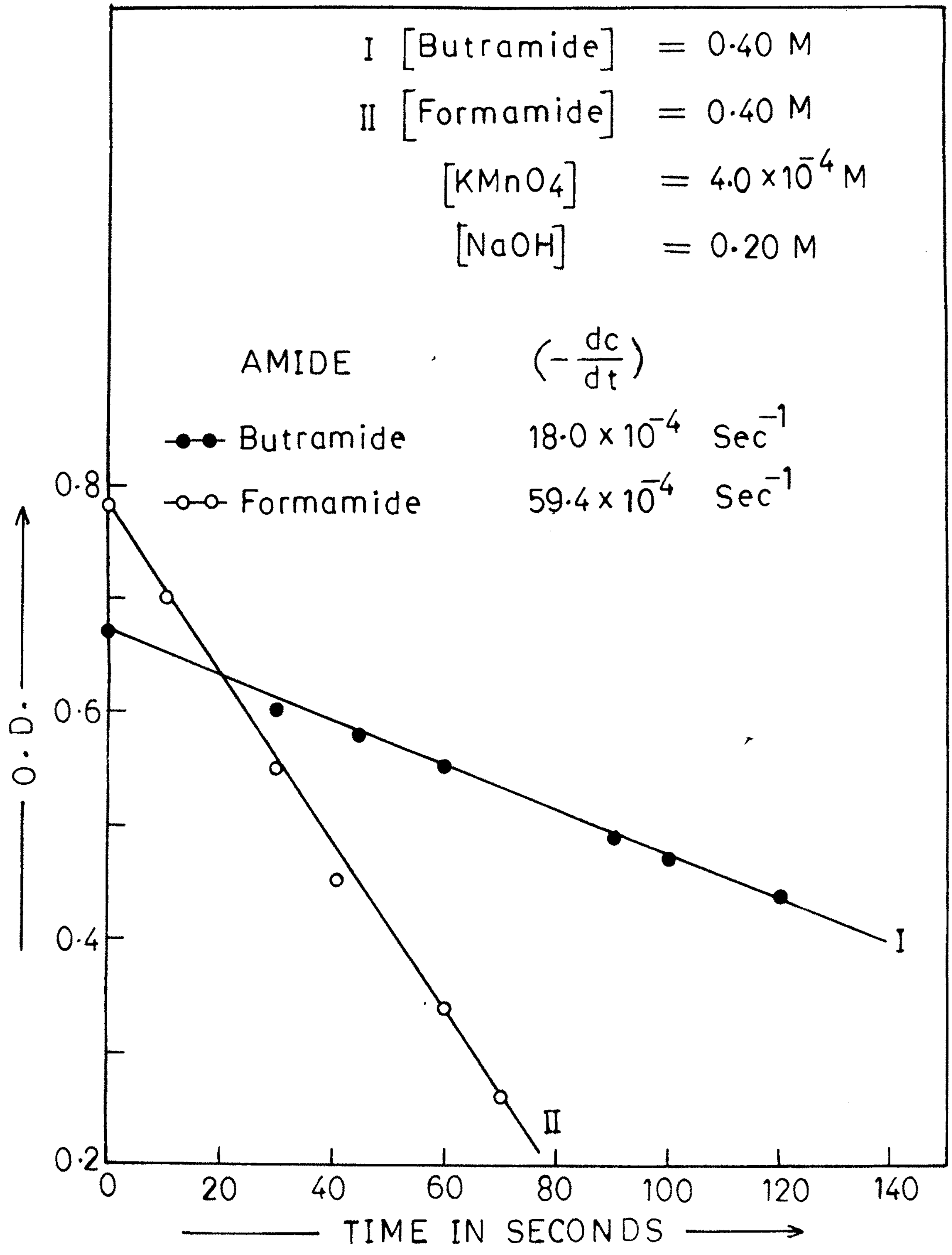

Fig. 16 : EFFECT OF SUBSTITUENT ON THE RATE OF OXIDATION OF AMIDES.

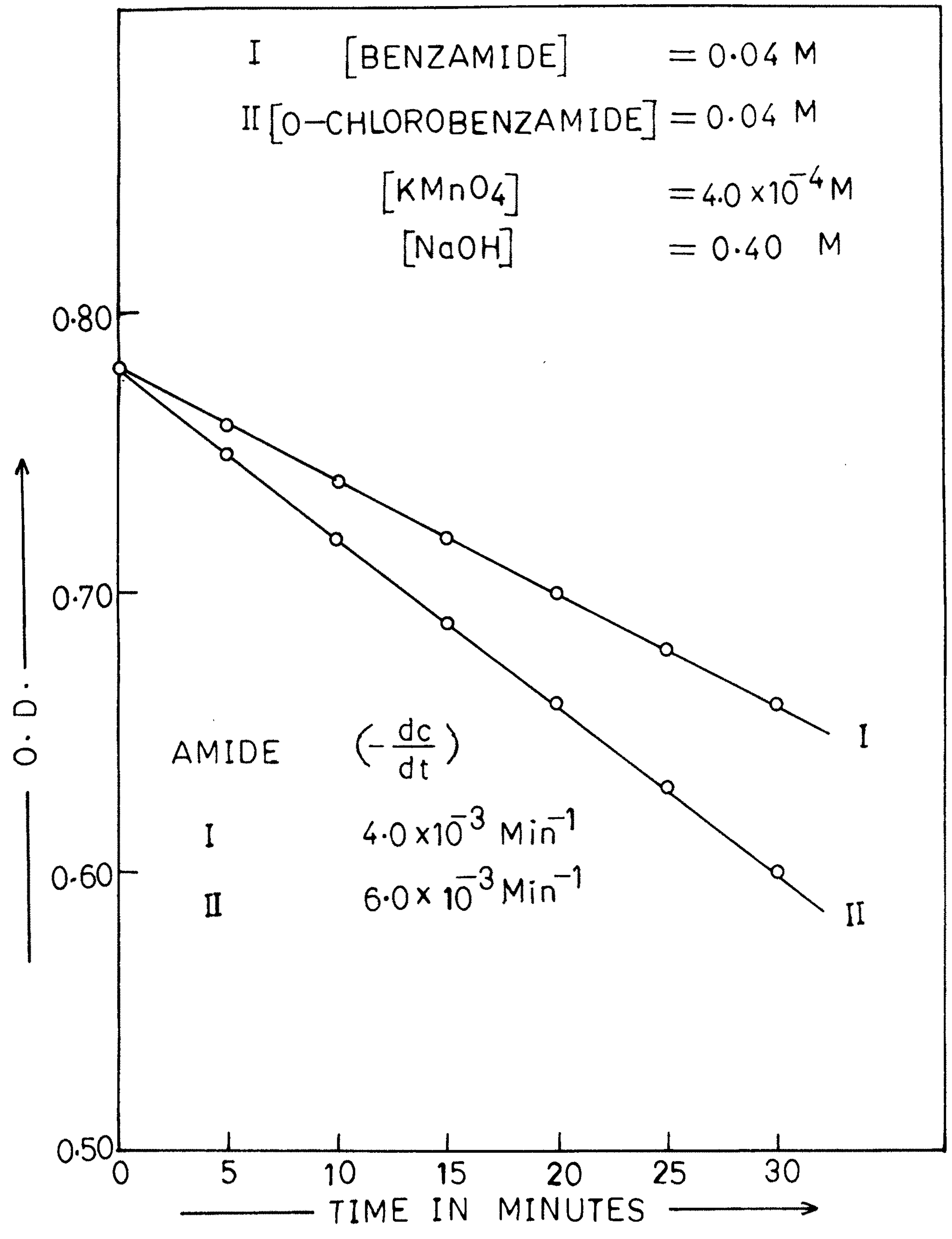

Fig. 17 : EFFECT OF SUBSTITUENT ON THE RATE OF OXIDATION.

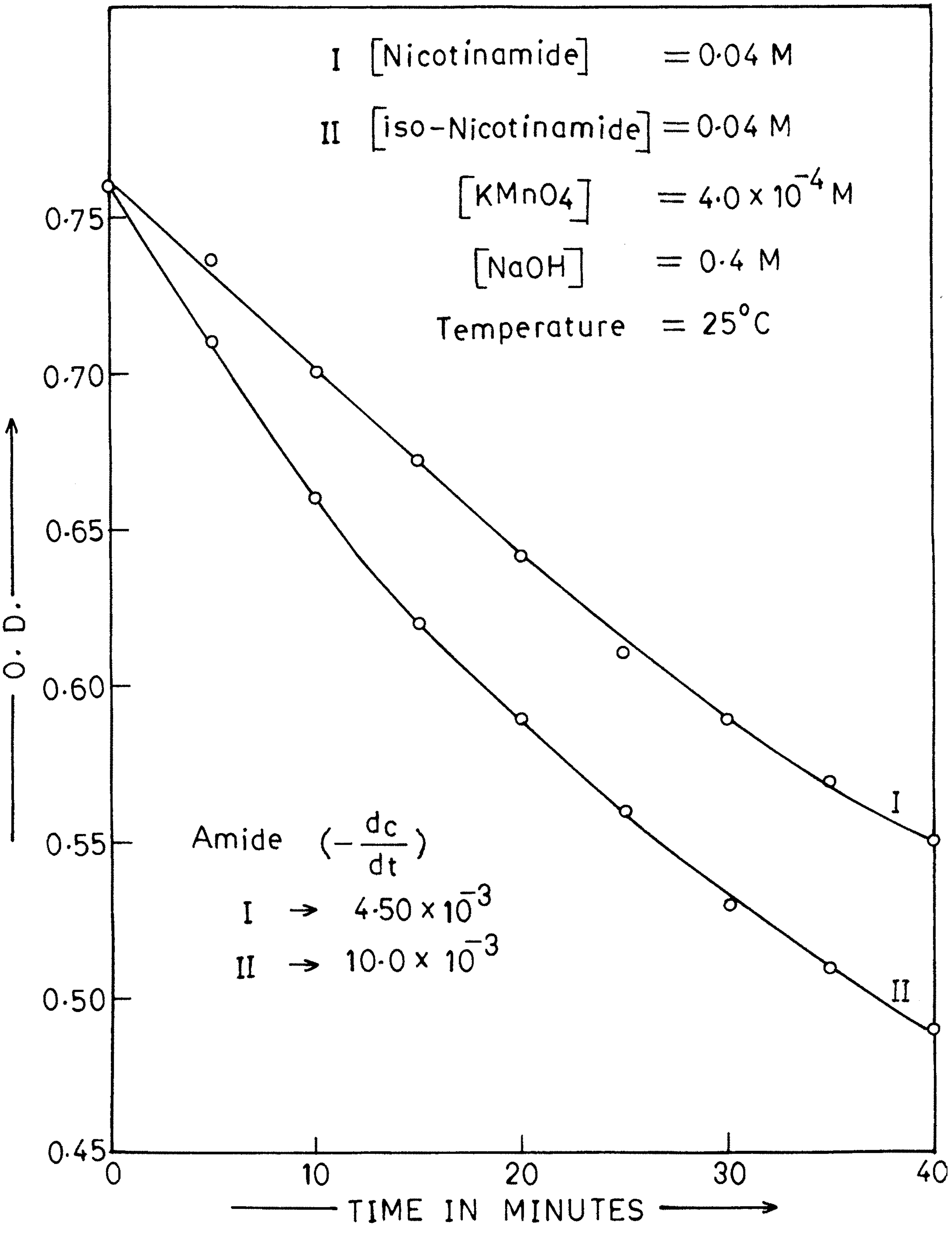

Fig. 18 : THE RATE OF OXIDATION OF (I) NICOTINAMIDE AND (II) iso-NICOTINAMIDE.

TABLE 11. EFFECT OF SUBSTITUENT ON THE RATE OF OXIDATION OF AMIDES

$KMnO_4$ = 4.0 x 10^{-4} M, NaOH = 0.4 M, Aliphatic amide = 0.4 M, Aromatic amide = 0.04 M, Temp. = 25 ± 0.01°C

Aliphatic amide	$-\frac{dc}{dt} \times 10^4$ sec^{-1}	$k_2 \times 10^3$ lit $mole^{-1}$ sec^{-1}
$HCONH_2$	59.40	15.00
CH_3CONH_2	1.00	0.11
$ClCH_2CONH_2$	10.86	1.60
$CH_3CH_2CONH_2$	1.33	0.21
$CH_3(CH_2)_2CONH_2$	18.00	3.50
Aromatic amide	$-\frac{dc}{dt} \times 10^3$ min^{-1}	$k_2 \times 10^2$ lit $mole^{-1}$ min^{-1}
$C_6H_5CONH_2$	4.00	13.01
o-$ClC_6H_4CONH_2$	6.00	19.60
Nicotinamide	4.50	18.08
iso-Nicotinamide	10.00	33.97

G) IDENTIFICATION OF OXIDATION PRODUCTS

A knowledge of the products formed in a reaction, subjected to kinetic study, is an important step in elucidation of the mechanism of the reaction. Therefore, it was considered necessary to identify the various products formed in these reactions.

The reaction mixture was prepared by mixing equal quantities of alkaline permanganate with nicotinamide or iso-nicotinamide and the reaction mixture was kept for 24 hours to complete the oxidation. The solution was, further, concentrated and used for identification of the end products.

TESTS FOR NICOTINIC AND ISONICOTINIC ACID

I) In a micro test tube, one drop of the concentrated hydrochloric acid solution of the test sample (which is prepared by adding HCl in test solution) and some grains of zinc are taken. This mixture is then warmed for about 5 minutes on water bath till the metal is completely dissolved. After cooling one drop of 5% copper sulfate and then ammonium hydroxide solution is added until the blue colour appears. The blue coloured solution is shaken with two drops of mixture of 1 volume of carbon disulphide and 3 volume of benzene. The appearance of yellow brown colour in benzene layer shows the presence of nicotinic and iso-nicotinic acid.

The above tests are carried out according to F.Feigl.[3]

II) To the test solution, a mixture of HBr, KCN and benzidine is added. Red colour obtained indicates the presence of nicotinic acid.

III) To the test solution $Na_3Fe(CN)_5NH_2$ is added which gives red colouration. This shows the presence of iso-nicotinic acid.

IV) Nicotinic acid and iso-Nicotinic acid was precipitated from the reaction mixture as its insoluble copper salt[4].

V) Nicotinic acid and iso-Nicotinic acid is detected by TLC.[5]

The nitrogen evolved in the reaction is collected over water similar to Dumas method[6] and identified.

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