

KINETICS OF THE DISSOLUTION OF COPPER IN
AQUEOUS ALIPHATIC AMINES

And

CATALYTIC REDUCTION OF NICKEL ION
BY MOLECULAR HYDROGEN

by

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standard required from candidates for the
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Members of the Department of
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ABSTRACT

Kinetics of the Dissolution of Copper in Aqueous Aliphatic Amines.

An investigation was made of the dissolution of copper metal in aqueous solutions of methyl, ethyl and n-butyl amine and ammonia, as well as in solutions of their aminium and ammonium ions, under oxygen pressure. Study of the kinetics of the dissolution was carried out over a wide range of concentrations. It was observed that there are two regions of oxygen pressure dependency of the rate. The range of oxygen pressure, where rate is independent of oxygen pressure, was investigated in detail.

The rate process has been established to obey the relation

$$R = \frac{k_1[A]}{k_1[A] + 1} \left[k_2[A] + k_3[AH^+] \right]$$

for all the systems studied.

A mechanism for the dissolution reaction has been proposed.

ABSTRACT

Catalytic Reduction of Nickel Ion by Molecular Hydrogen.

The rate of precipitation of nickel from salt solution by molecular hydrogen in the presence of catalyst has been investigated over a wide range of concentrations. The variables studied are concentration of nickel, hydrogen pressure, amount of catalyst, concentration of hydrogen ion and temperature. The rate of reduction is found to obey an equation of the form:

$$\frac{d C_{Ni^{++}}}{dt} = -k_1[S][P_{H_2}]^{1/2} [Ni^{++}] + k_2[S][H^+]$$

The activation energy is found to be 25 ± 2 kcal/mol.

The equilibrium constant k for the reaction $Ni^{++} + H_2 \rightleftharpoons Ni^0 + 2 H^+$ is found to be $4.65 \times 10^{-6} \text{ atm}^{-1}$ at 140°C .

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Date May 22, 1959.

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KINETICS OF THE DISSOLUTION OF COPPER IN AQUEOUS ALIPHATIC AMINES.

INTRODUCTION

The corrosion of metals has attracted the attention of scientific investigators for over a hundred years. The main effort and interest in this problem, however, have been directed towards prevention of corrosion. In the past few decades, the attention of investigators has been focussed¹ more on the nature and causes of corrosion processes. Up to the present time, however, detailed understanding of the kinetic process involved in corrosion has been gained in only a very few instances.^{2,3,4,5}

Among the systems which have been studied with a view to determining the kinetic aspects of the corrosion process, the dissolution of copper has been the most thoroughly investigated.

Yamasaki⁶ was one of the first to study the problem of dissolution of copper in ammonia solution in the presence of purified air. He observed the dissolution rate to be independent of the concentration of ammonia. He concluded, moreover, that the dissolution process is autocatalytic, the cupric ammonia complex acting as catalyst.

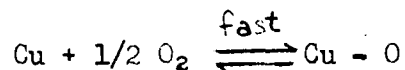
From studies of the dissolution of copper in ammonium compounds, Zaretskii and Akimov⁷ concluded that three important steps are involved in the dissolution process. The steps are (i) electrochemical dissolution of copper with formation of cuprous ammonia, (ii) oxidation of this species to the cupric ammonia complex and (iii) electrochemical reduction of the cupric ammonia complex at the metal surface.

More recent work of Lane and McDonald⁸ on dissolution of copper in ammonia solution led them to believe that no autocatalytic effect is present and that the dissolution rate is in fact dependent on the concentration of ammonia.

All of these investigators have observed that the rate of dissolution is strongly dependent on the stirring rate.

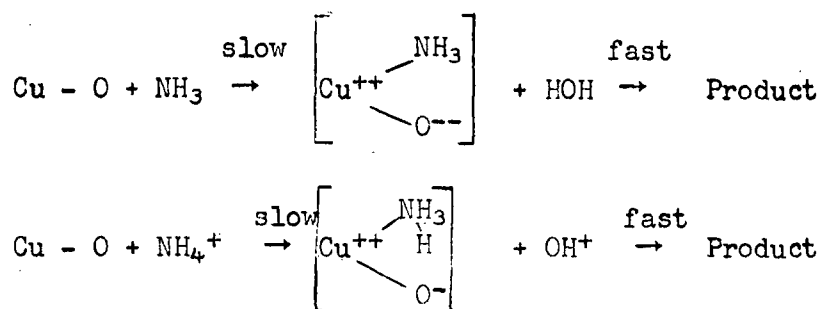
A detailed study of dissolution of copper in ammonia and in mixtures of ammonia and ammonium ion has been made by Halpern.⁹ He found two regions in the dependence of rate of dissolution of copper on the oxygen pressure. In the range of low oxygen pressure, he observed that the rate of dissolution of copper is dependent on the oxygen pressure and that the rate of dissolution is independent of oxygen pressure at higher pressure. The activation energies found by him for the oxygen pressure dependent rate and oxygen pressure independent rate are 1.33 and 5.54 kcal/mol respectively. From the low activation energy for rates at low oxygen pressure, he concluded that the rate controlling step is a physical process, such as diffusion of oxygen from the bulk of solution to the metal surface. The higher activation energy for the oxygen pressure independent rate has been taken as indicating that some chemical step is involved in the rate controlling process. From his work in the region of chemically-controlled rate, he has proposed the following mechanism:

1. Adsorption of dissolved oxygen on the surface.



2. Reaction of ammonia or ammonium ion with the copper-oxygen complex

on the surface, followed by desorption of the complex



Studies on the kinetics of the dissolution of copper by chelating agents were carried out by Milants,¹⁰ in the range of chemically-controlled rate, to elucidate the kinetic process further. His studies indicated that the stability constants of chelate complexes and dissolution rate are related to one another. Due to the small number of systems studied, the exact correlation of complexity constants and dissolution rates has not been established. The mechanism of the kinetic process was found to be analogous to that of ammonia.

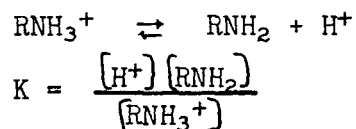
Scope of Present Work

In the light of the results obtained for dissolution of copper by chelating agents, it was considered worthwhile to study the kinetics of the attack of the copper surface by non-chelating agents, such as the aliphatic amines, to elucidate the mechanism. It was also a purpose of this work to look for possible differences in the kinetic processes involved in case of ammonia and aliphatic amines.

The rate of a heterogeneous reaction may be controlled by one or more of several physical or chemical processes (adsorption of gaseous reactant in solution, transport of dissolved reactants from bulk of solution to the surface, reaction on the surface, and desorption of reaction product). The present work was planned primarily to find out the chemical processes

involved in the dissolution of copper by aliphatic amines. The complexing agents used in this work were methyl, ethyl, and n-butyl amines, and ammonia.

Present knowledge of the nature of the complexes formed in aqueous solution between alkyl amines and copper ion is not well advanced. Ammonia is known to form several different amine complexes with copper,¹¹ and indications for complex formation with alkyl amines have been noted.¹² The constants for the dissociation



where R = H, or an alkyl group,
are given in Table I.

Table I

Acid dissociation constants for aminium ions.

	K (M)
Ammonia	5.68 x 10 ⁻⁹ (13)
Methyl amine	2.30 x 10 ⁻⁹ (14)
Ethyl amine	1.80 x 10 ⁻⁹ (14)
n-Butyl amine	2.46 x 10 ⁻⁹ (14)

The order of stability of copper complexes may be closely related to the stability of the RNH_3^+ species.

Since the main aim of the present work was the study of the chemical aspects of the reaction, the variables studied were concentration of reactants (amine and aminium ion concentration) and hydrogen ion concentration. Some observations were made of the effect of variation of oxygen

pressure in order to ensure that the experiments were not carried out in the range of oxygen pressure where diffusion of oxygen is rate controlling.

EXPERIMENTAL

Preparation of the Copper Sample.

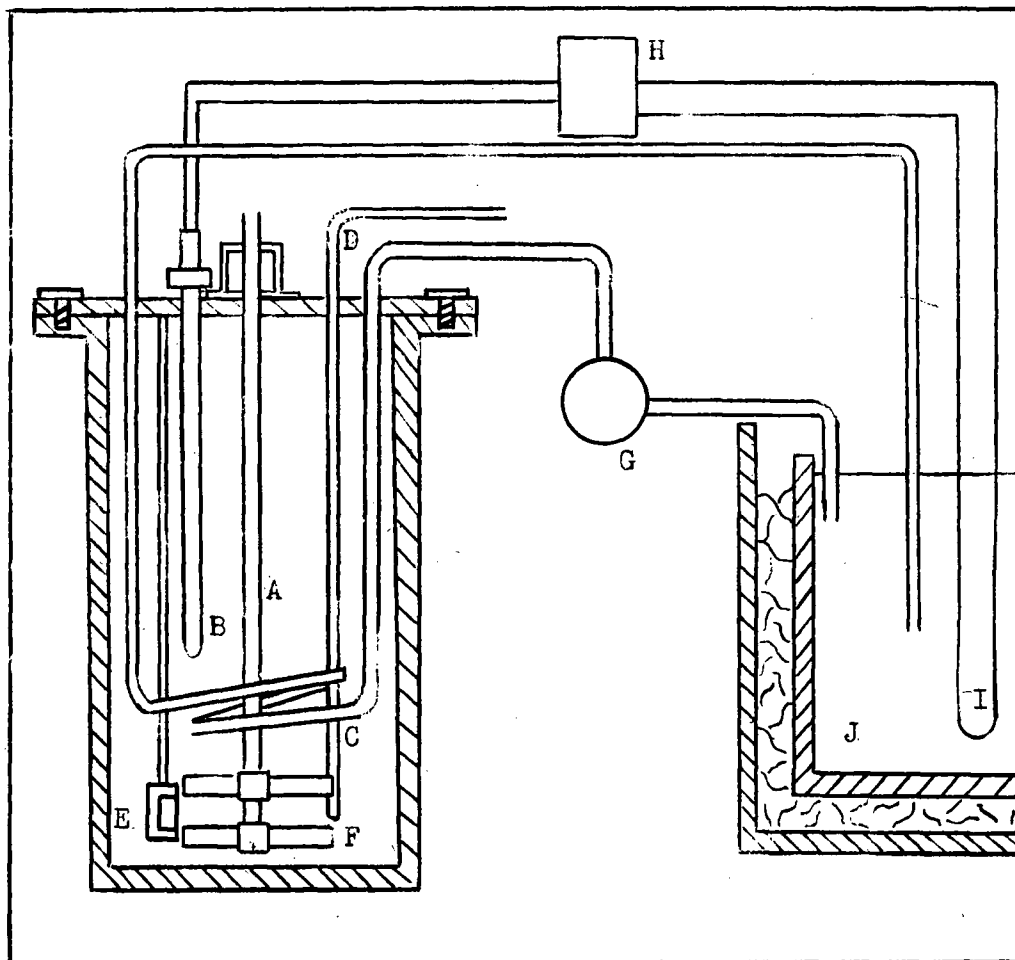
In this work were used the same copper specimens as were used by Milants.¹⁰ These specimens were prepared from conductivity copper, by melting and casting in a spectroscopic graphite crucible and grain refined by cold working and annealing. Finally they were mounted in bakelite leaving one exposed face whose surface area was about 2 cm.².

The purity (in this case 99.99%) and the grain size were found by Milants not to influence the rate. The average grain size of the specimen used in this work was 0.12 mm. (A.S.T.M. nonferrous grain size standard).

Before each experiment, the specimen was polished with 4/0 emery paper, and was lightly etched with a sodium persulphate ammonia mixture. The geometric area of the exposed surface was measured by means of a microscope with a calibrated eye piece (calibrated to 0.01 mm.). The area was computed from the mean of several measurements. In practice, the specimens were always etched just before the experiment, and when not in use, were stored in a desiccator.

Apparatus.

The experiments were carried out in an autoclave, shown in Figure 1, designed for working at pressures up to 8 atmospheres. The autoclave was made from 316 stainless steel. A titanium liner was used to contain the solution to avoid corrosion of the steel by the reagents used. The bakelite-mounted copper specimen was held in place by means of a stainless steel rod, this being screwed into the lid of the autoclave.



A = shaft
 B = thermoregulator well
 C = cooling coil
 D = sampling tube
 E = copper sample

F = impeller
 G = pump
 H = relay
 I = heater
 J = thermostat

Fig. 1. Schematic diagram of the autoclave and temperature control system.

Agitation was provided by a double turbine-type impeller which swept a cylindrical volume 8 cm. in diameter. It was driven at 750 RPM for all the experiments. It was found¹⁰ that under the experimental conditions used, the stirring rate had no effect on the rate of dissolution of copper.

Oxygen, obtained from Canadian Liquid Air Company, was supplied to the autoclave from a cylinder through a pressure-regulating gauge. An additional pressure gauge was mounted on the oxygen supply line to check the pressure.

Temperature Control.

The temperature of the reaction solution was held at $25 \pm 0.1^\circ\text{C}$ by forcing controlled-temperature water through a stainless steel coil fitted into the autoclave. The temperature of the circulating water was controlled by a mercury-contact thermoregulator. The water circulation was maintained with the help of a centrifugal pump.

Chemical Reagents.

The methyl, ethyl and n-butyl amines as well as the carbamate were Eastman Kodak white label grade. Ammonia and sodium hydroxides were chemically pure quality supplied by Nichols Chemical Company. Anhydrous reagent grade sodium perchlorate was supplied by the G. Frederick Smith Chemical Company.

The experimental solutions were prepared by diluting solutions of known strength to the required concentration. All the solutions were checked by titration against standard sulphuric acid to the methyl-red end point. In order to avoid changes in the salt effect at low concentrations,⁹ 0.1 or 0.2 mol/l. of sodium perchlorate was added to autoclave solution. The volume of

the solution was shown¹⁰ to have no effect on the rate of dissolution.

Analytical Procedure.

Determination of copper was done colorimetrically by means of the yellow chelate compound formed by sodium diethyl thiocarbamate. This method has been described by several authors.^{15,16,17} It has been reported by these authors that the stability of the colloidal copper carbamate complex is affected by daylight. To avoid this effect, gum arabic was added to stabilise the colour.¹⁷ The carbamate-gum arabic solution was prepared in the following way: 0.2 gms. of carbamate was dissolved in 200 ml of distilled water and this solution was subsequently added to 500 ml of 1% gum arabic solution. The resultant solution was diluted to 1000 ml and 1 ml of toluene was added. It was finally filtered in the dark and stored in a cold, dark place. All the analytical work was done in an artificially lighted room. The stability of the chelate complex is reported¹⁷ to be independent of pH only within the range of 7.5 to 9.2. For this reason, all analyses were carried out at pH 9.0.

Samples for analysis were prepared in the following way: To an aliquot of the sample taken from the autoclave, 5 ml of 20% ammonium citrate was added to complex accidental traces of iron and the pH was adjusted to 9.0 by addition of 1:1 ammonia or 1:1 perchloric acid. Then 10 ml of carbamate solution was added, and the mixture was diluted in a volumetric flask to 50 ml. It was mixed carefully and its optical density was determined with a Beckman model-Dk2 ratio-recording spectrophotometer, at a wave length of 437 millimicrons. The solutions were found to obey Beer's law over a sufficient range of concentration for convenient analysis. The calibration curve is given in Figure 2. The results from this method were found to be reproducible to within $\pm 0.5\%$. It was also observed that the presence of the amines used

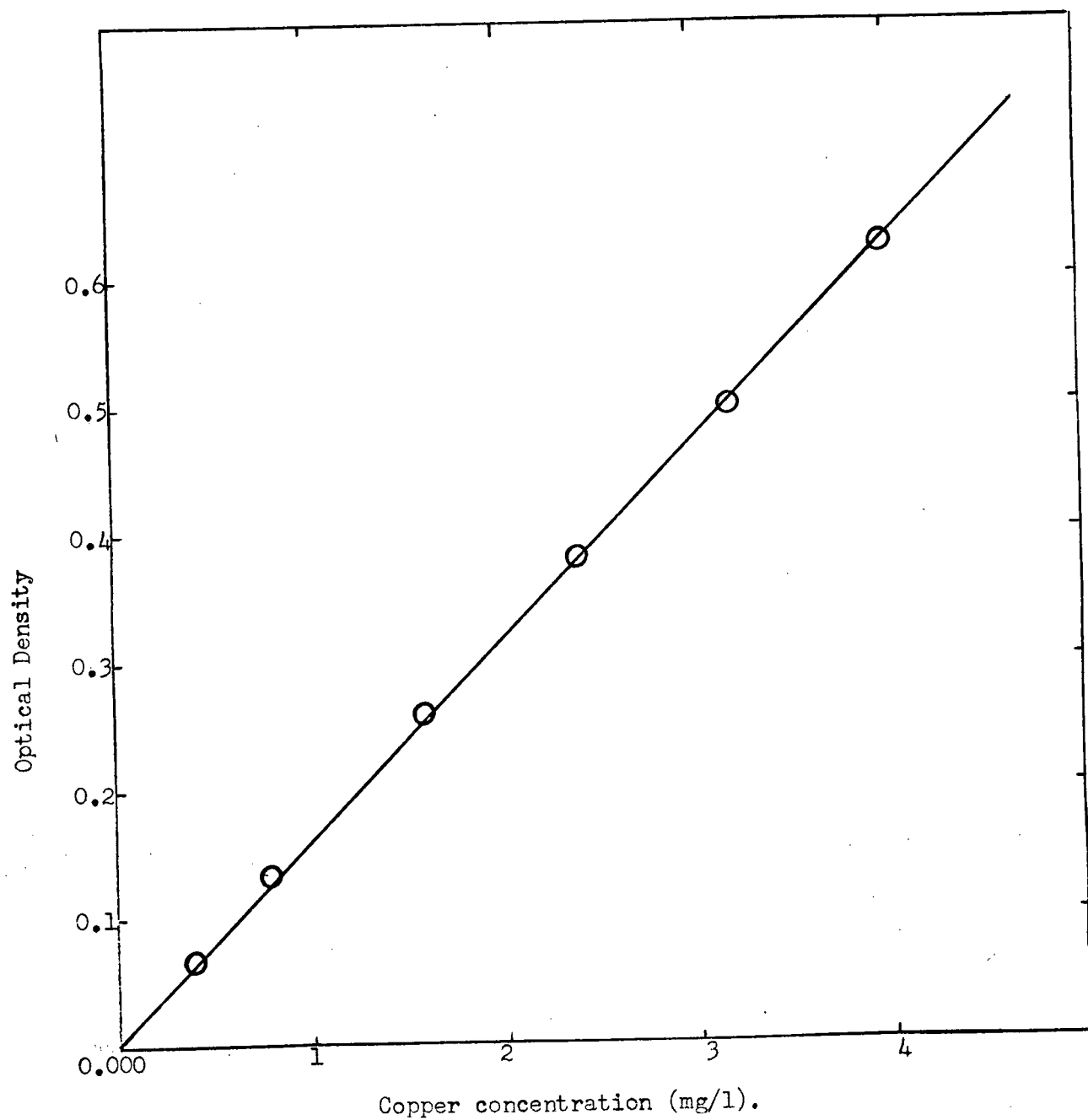


Fig. 2. Calibration curve for analysis of copper.

in this work does not have any effect on the optical density.

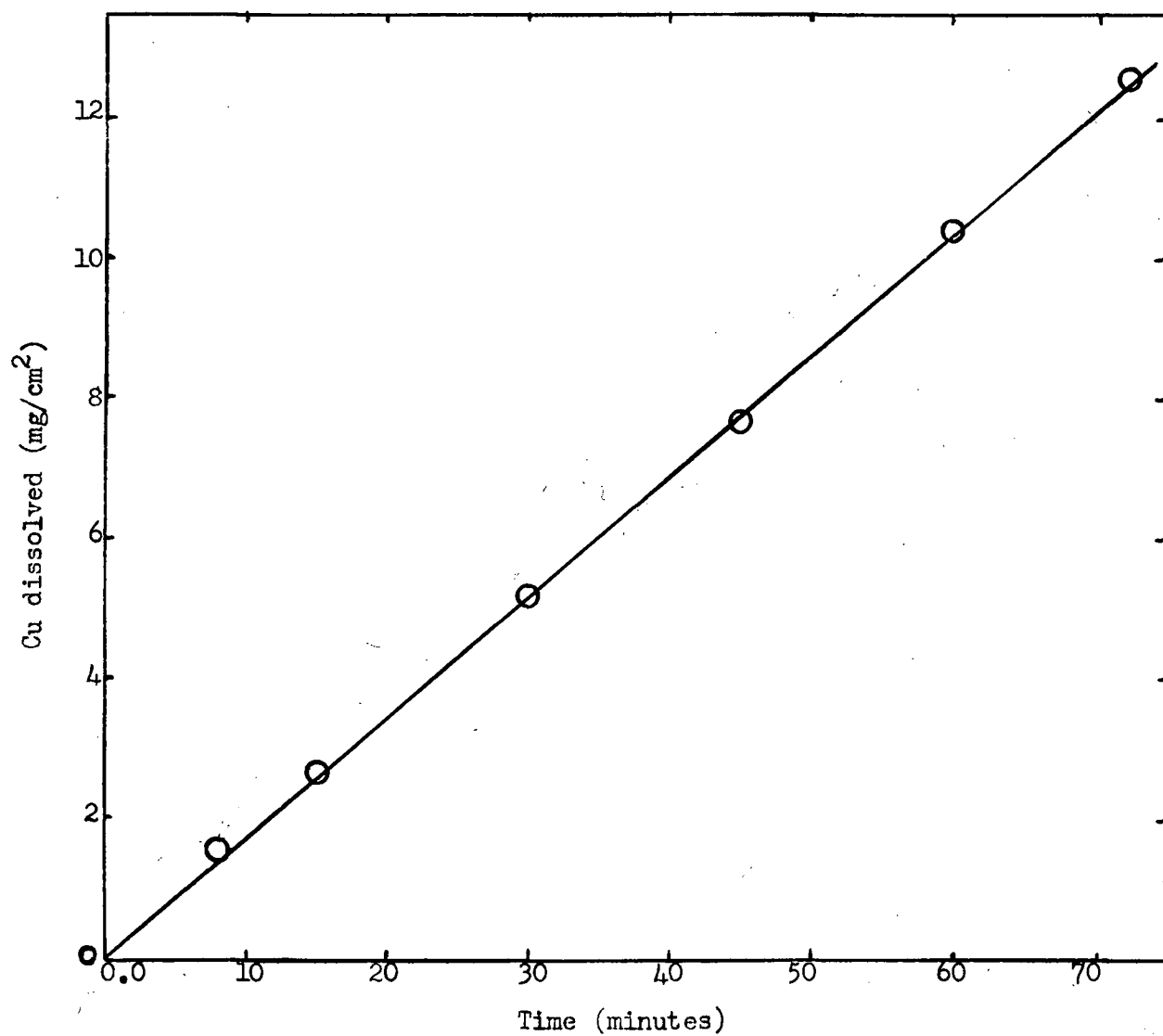
Experimental Procedure.

The procedure used for measuring the rate of dissolution of copper in different solutions was as follows: The autoclave was first charged with the desired solution and, with the copper sample in place, the solution was allowed to stand under a nitrogen atmosphere until the required temperature was reached. Then the autoclave was flushed several times very quickly with oxygen and the oxygen pressure raised to the final desired value. This last was taken as zero time. To follow the course of the reaction, measured volumes of solution were removed from the autoclave by means of a sampling tube, at various time intervals. These samples were analysed for copper. Using these results, the known surface area of the copper and the volume of the solution at the time of sampling, the total amount of copper dissolved per unit area for each sampling time was computed. The experiments usually lasted about 75 minutes. In a typical experiment, the amount of copper dissolved was usually between 0.5 and 2.0×10^{-3} mol/l. This is too small a quantity to cause any significant decrease in the concentration of the complexing agents.

Preliminary Results.

In a series of preliminary experiments, it was hoped to determine (i) the nature of the rate plots, and (ii) the nature of the dependence of the rate on the oxygen pressure.

A typical rate plot is shown in Figure 3. The linear form of this plot is in agreement with the findings of Halpern⁹ and Milants¹⁰ and indicates that the reaction is of zero order in dissolved copper. It was



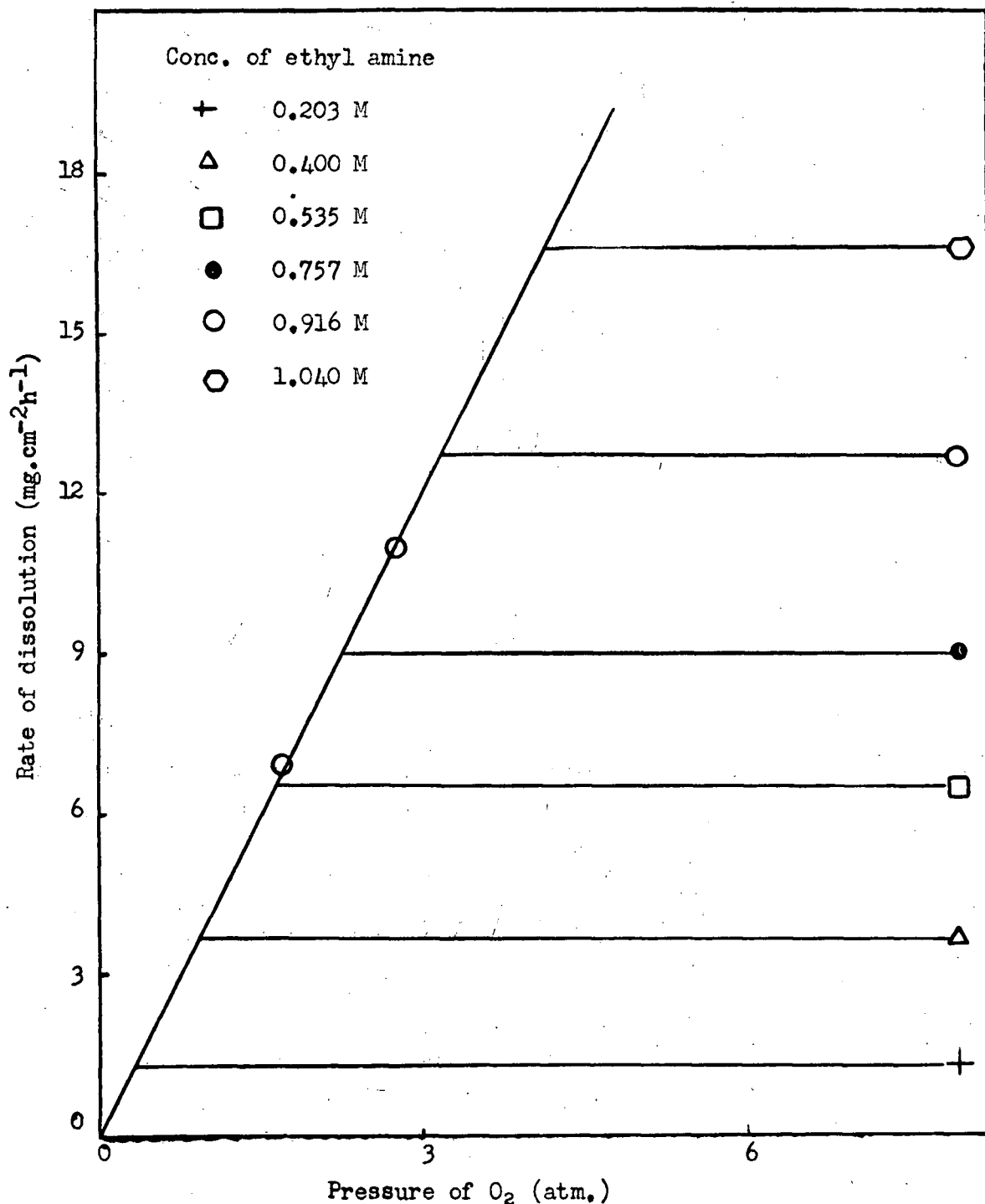
Conditions: 0.801 (M) methyl amine; stirring rate 750 RPM;
Temperature 25°C; NaClO₄ 0.1 M; oxygen pressure 7.9 atm.

Fig. 3. Typical curve for the dissolution of copper.

found that the rates, as determined from the slope of the rate plots, were reproducible to better than $\pm 2\%$.

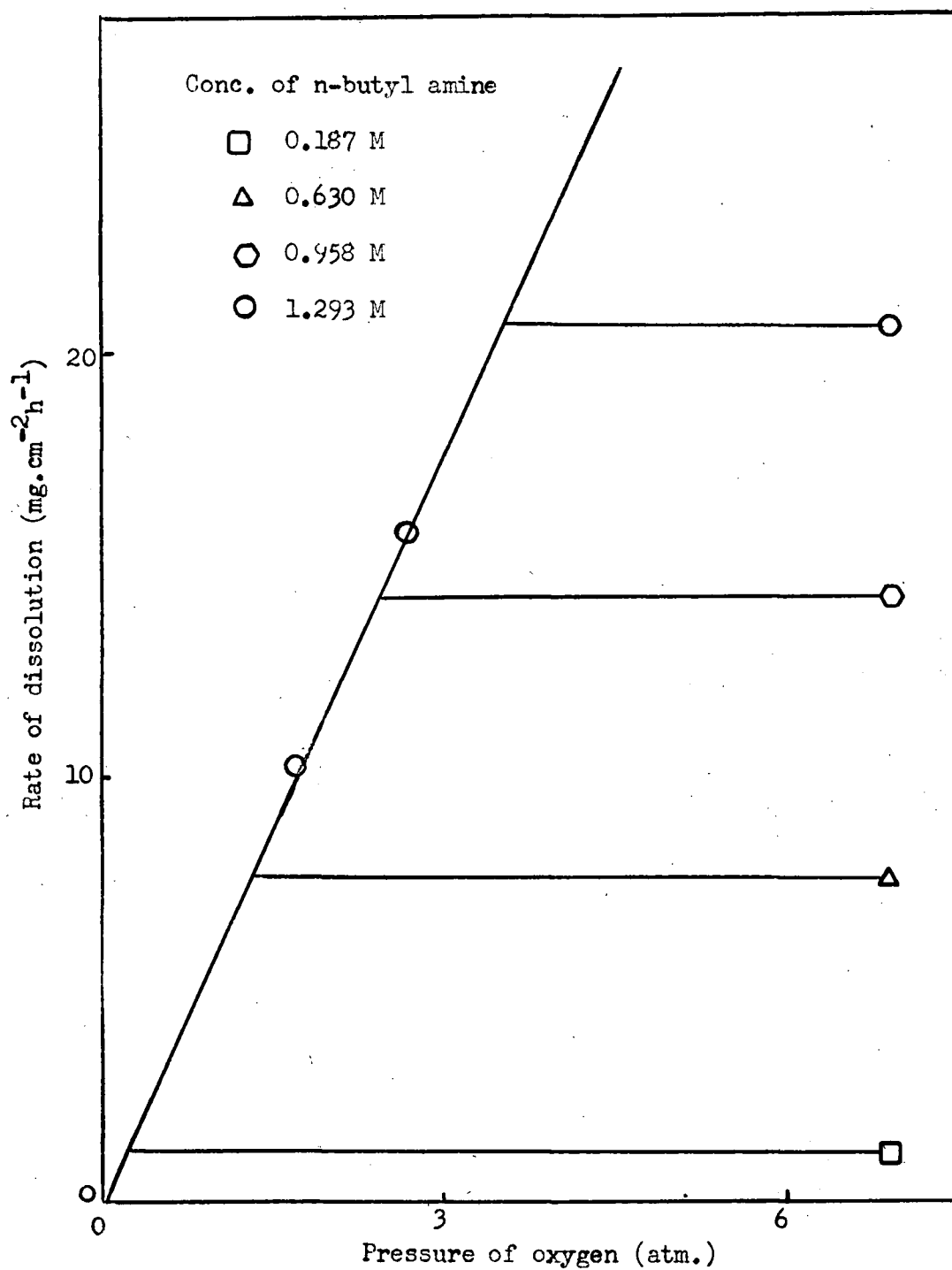
Earlier work^{9,10} showed that for the rate of dissolution, there exists two separate regions of pressure dependence. In the low pressure region, the rate is proportional to the pressure of oxygen, while at high pressure, the rate is independent of oxygen pressure. Results of experiments performed in this work and shown in Figures 4 and 5 show conformity with those of previous observations. This type of behaviour has been shown⁹ to be the result of a transition from diffusion control to control by the reaction on the surface.

Since in the present work, the main aim was to study the chemical attack on the copper surface, all experiments were carried out at sufficiently high pressures of oxygen to eliminate diffusion control.



Conditions: Temperature 25°C ; stirring rate 750 RPM;
 NaClO_4 0.1M

Fig. 4. Pressure dependence curve for ethyl amine.



Conditions: Temp. 25°C; stirring rate 750 RPM; NaClO_4 0.1M.

Fig. 5. Pressure dependence curve for butyl amine.

RESULTS AND DISCUSSION

Free Amines

The values of the rates measured for methyl, ethyl and n-butyl amines are given in Table IA, IIA and IIIA in the Appendix. A typical family of rate curves is given for methyl amine in Figure 6.

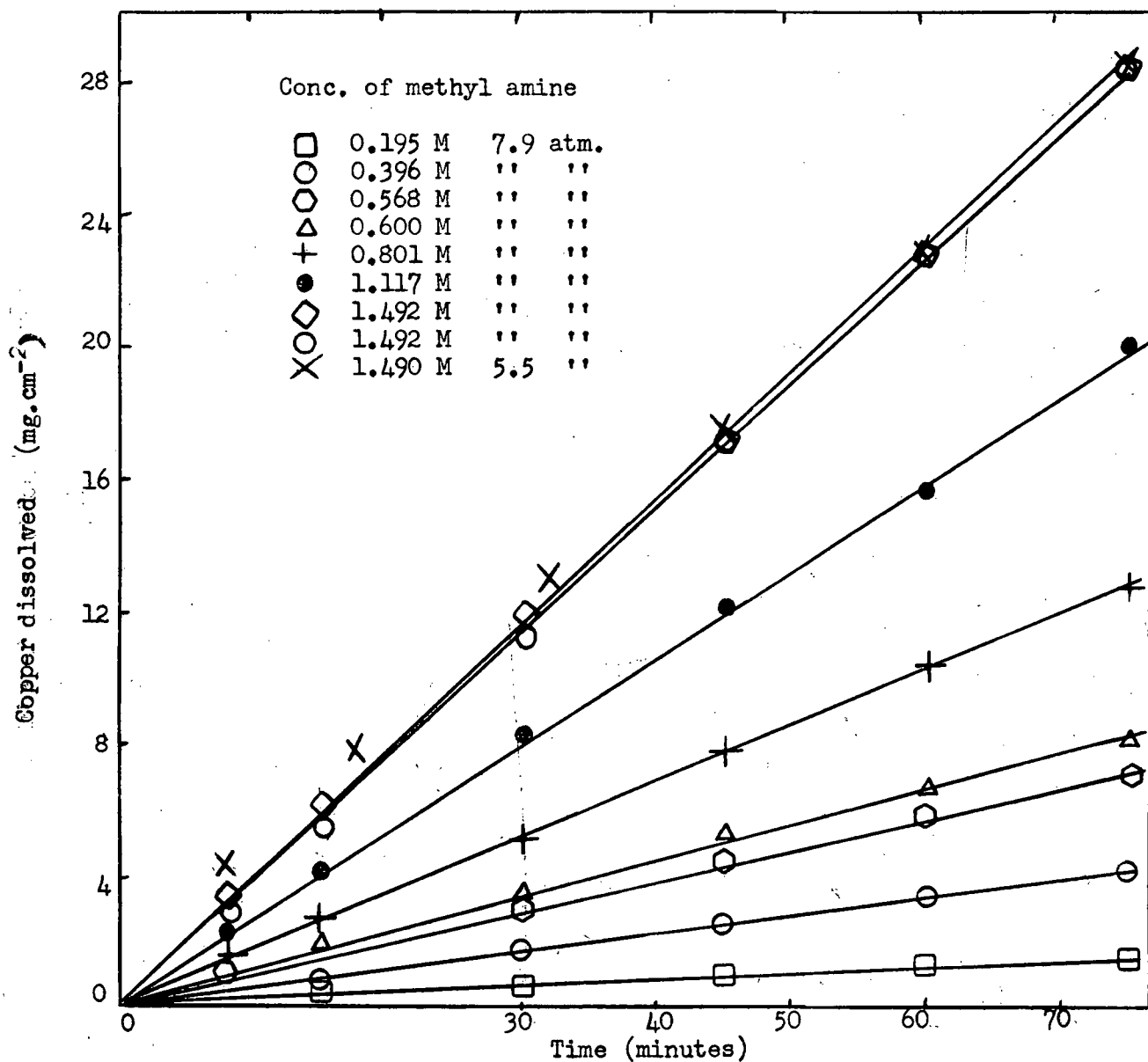
The relation between the rate and the amine concentration is given in Figures 7, 8, and 9, for methyl, ethyl and n-butyl amines respectively. The similarity among these curves is quite evident. The form of these curves indicates a rate dependence approximately second-order at low amine concentration and approaching first order at higher concentration. This behaviour suggests that some adsorption pre-equilibrium may be important in controlling the reaction rate. It was found that the data can be best fitted by an expression of the form

$$\frac{d [Cu^{++}]}{dt} = R = \frac{k_1 [A]}{k_1 [A] + 1} (k_2 [A]) \quad (1)$$

where R stands for rate of dissolution, [A] stands for concentration of amines and k_1 and k_2 are constants, the significance of which will be discussed later. Equation (1) can also be expressed in the form

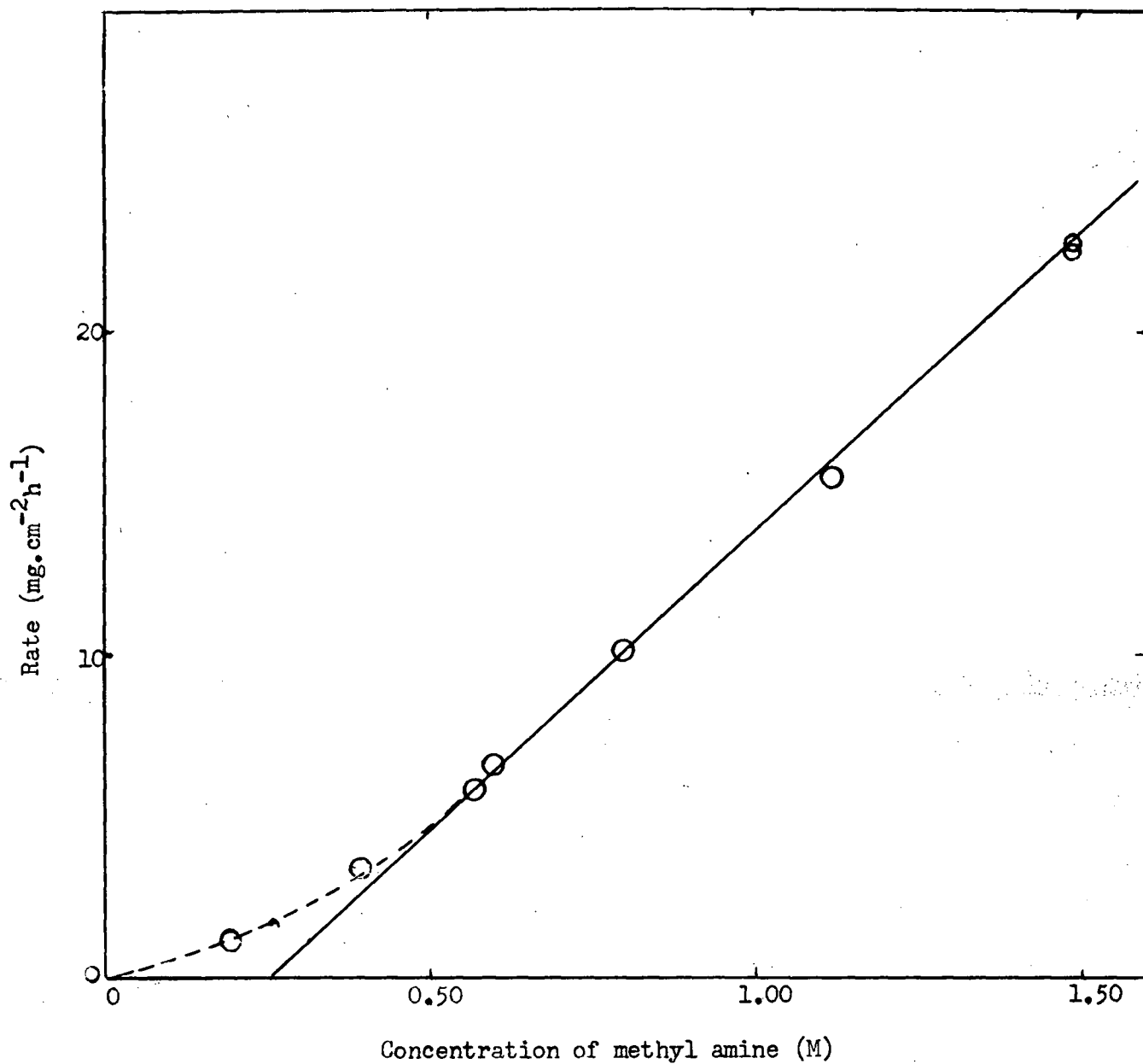
$$\frac{[A]^2}{R} = \frac{[A]}{k_2} + \frac{1}{k_1 k_2} \quad (2)$$

from which it is possible to evaluate the constants k_1 and k_2 . It is seen in Figures 10, 11, and 12 that Equation (2) fits the data quite well. The values of k_2 for the three amines were evaluated from the slopes of linear portion of the curves 7, 8 and 9, and from the slopes of the linear plots of Equation (2). The constant k_1 was evaluated in each case from the intercept



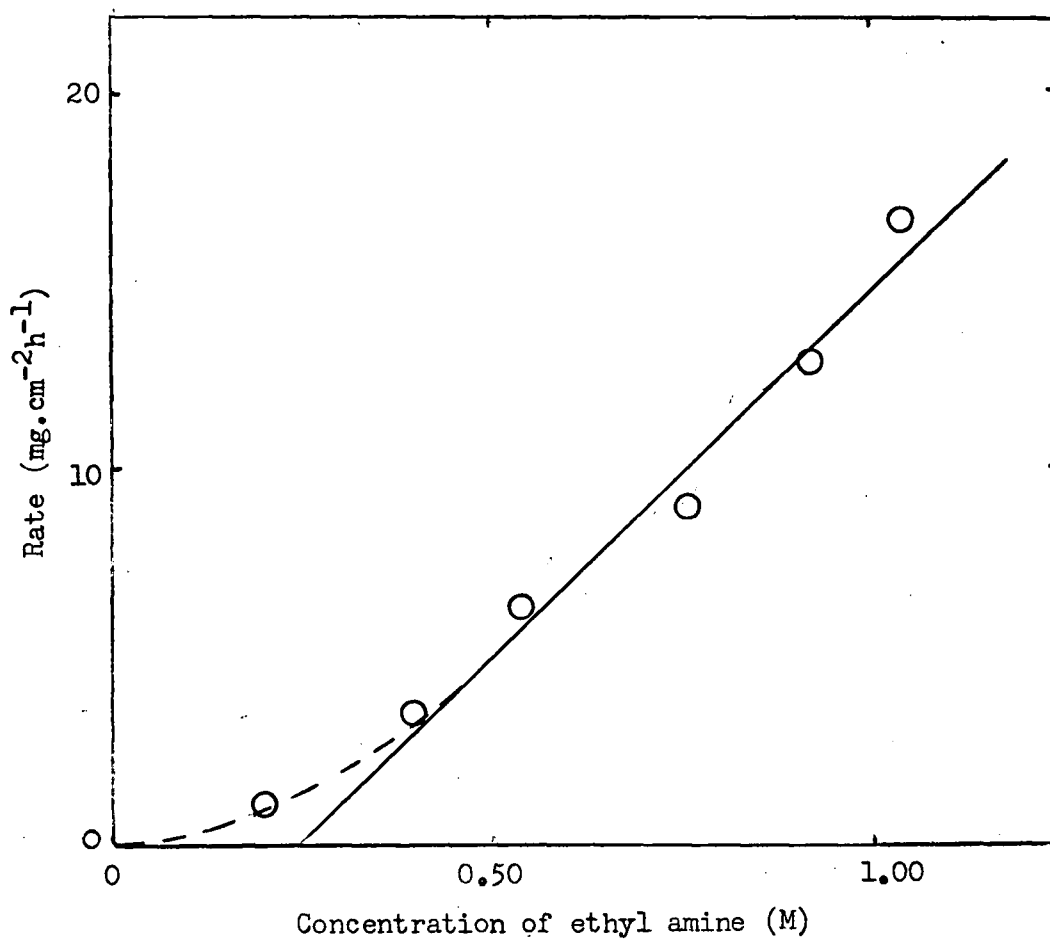
Conditions: Temperature 25°C; stirring rate 750 RPM;
NaClO₄ 0.1 M.

Fig. 6. Typical family of rate curves for methyl amine.



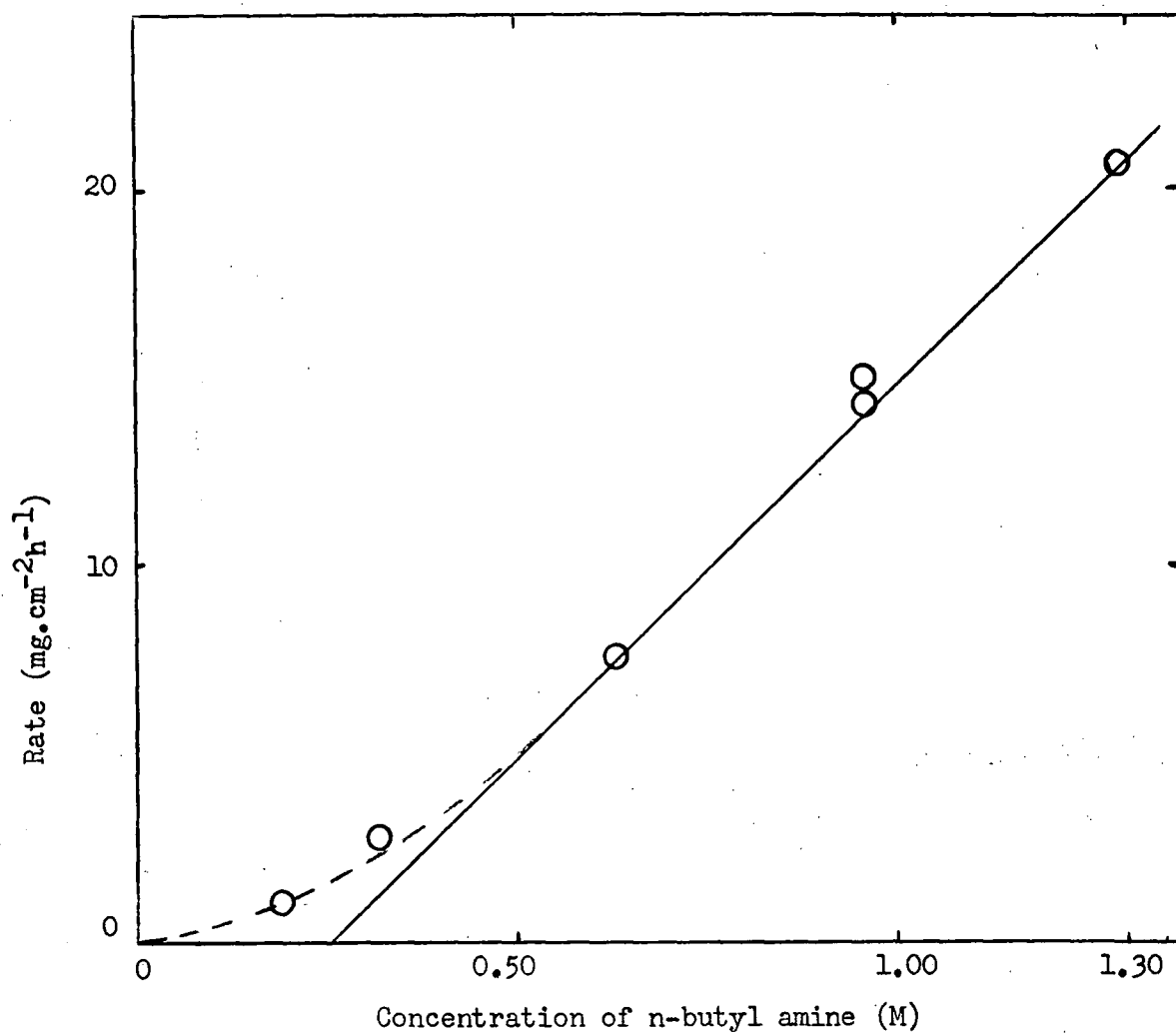
Conditions: Temperature 25°C; stirring rate 750 RPM;
NaClO₄ 0.1 M; oxygen pressure 7.9 atm.

Fig. 7. Plot of rate vs concentration for methyl amine.



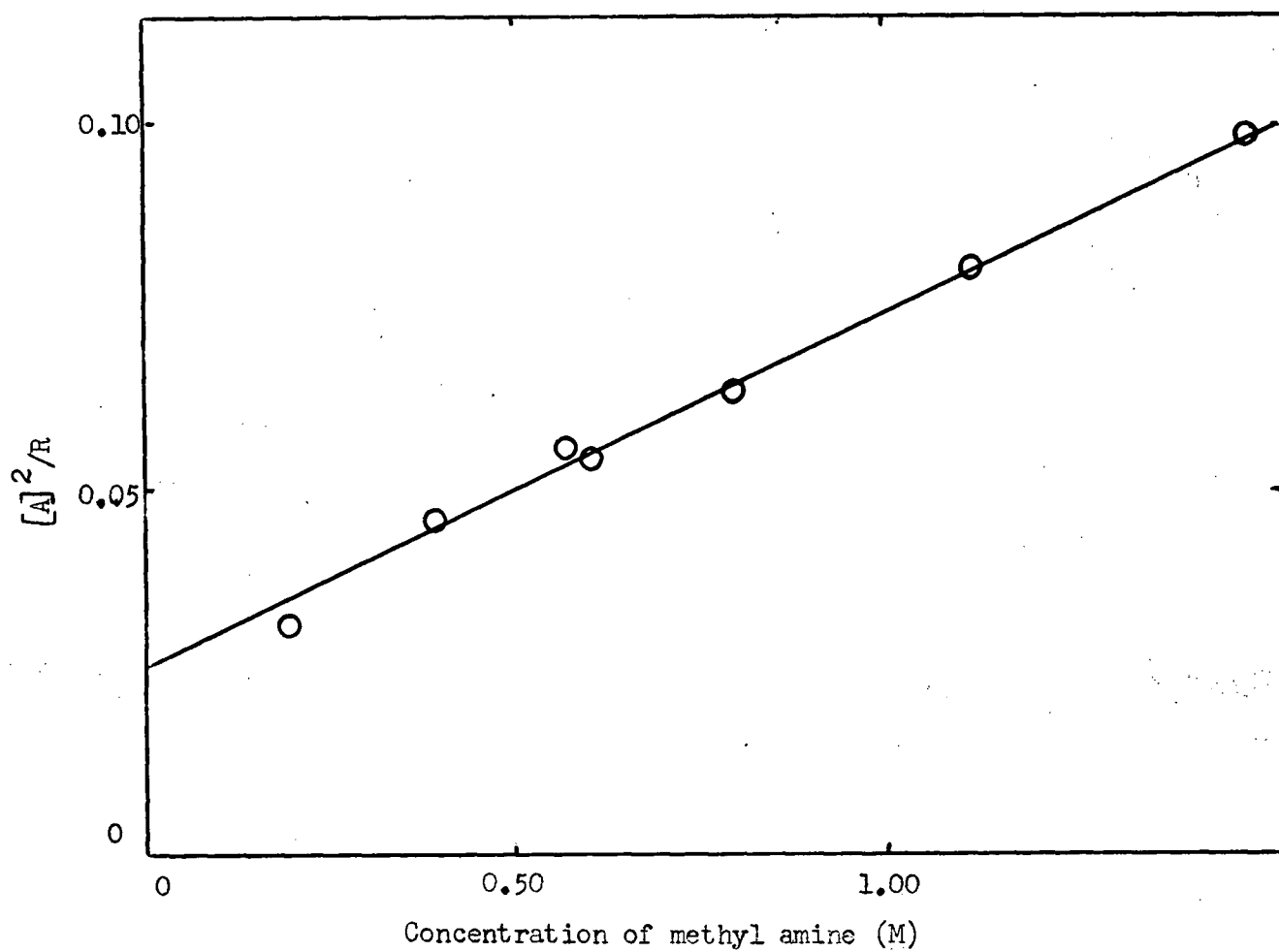
Conditions: Temperature 25°C; stirring rate 750 RPM;
NaClO₄ 0.1M; oxygen pressure 7.9 atm.

Fig. 8. Plot of rate vs concentration of ethyl amine.



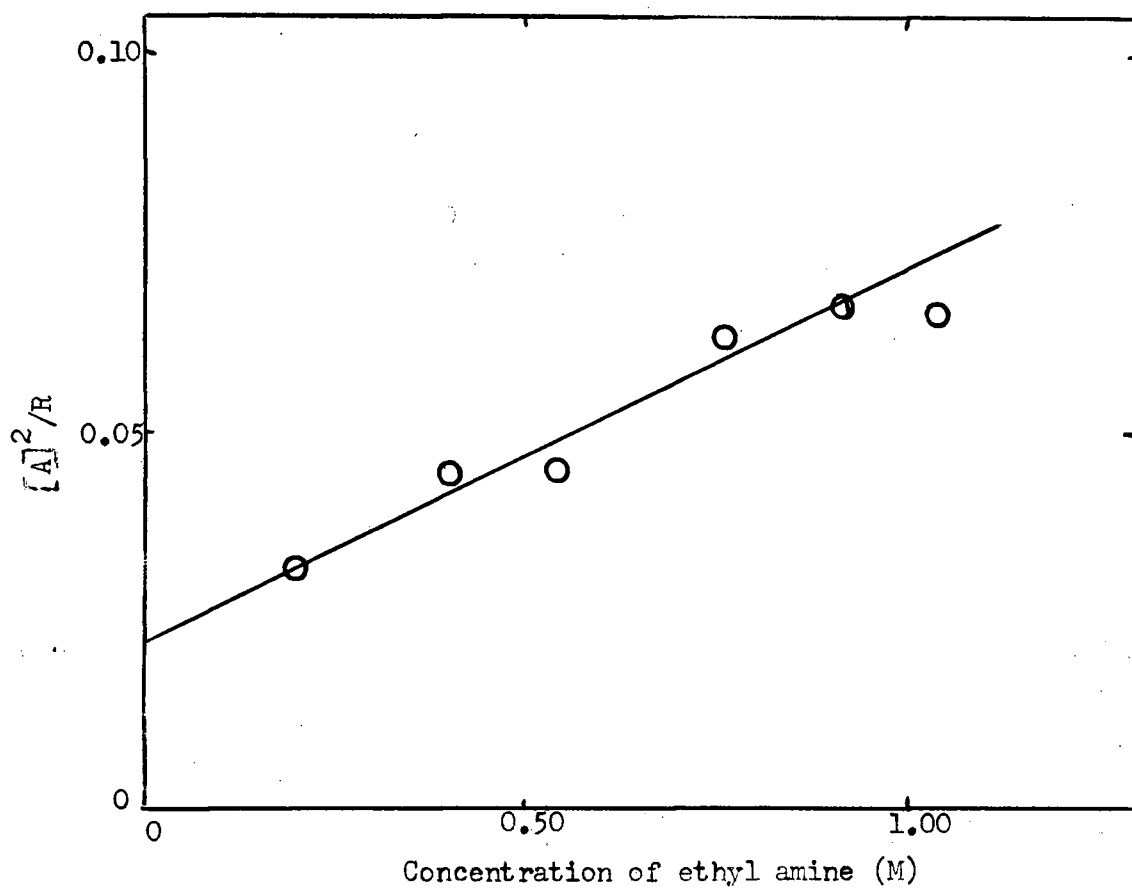
Conditions: Temperature 25°C; Stirring rate 750 RPM.
NaClO₄ 0.1M; oxygen pressure 6.9 atm.

Fig. 9. Plot of rate vs concentration of n-butyl amine.



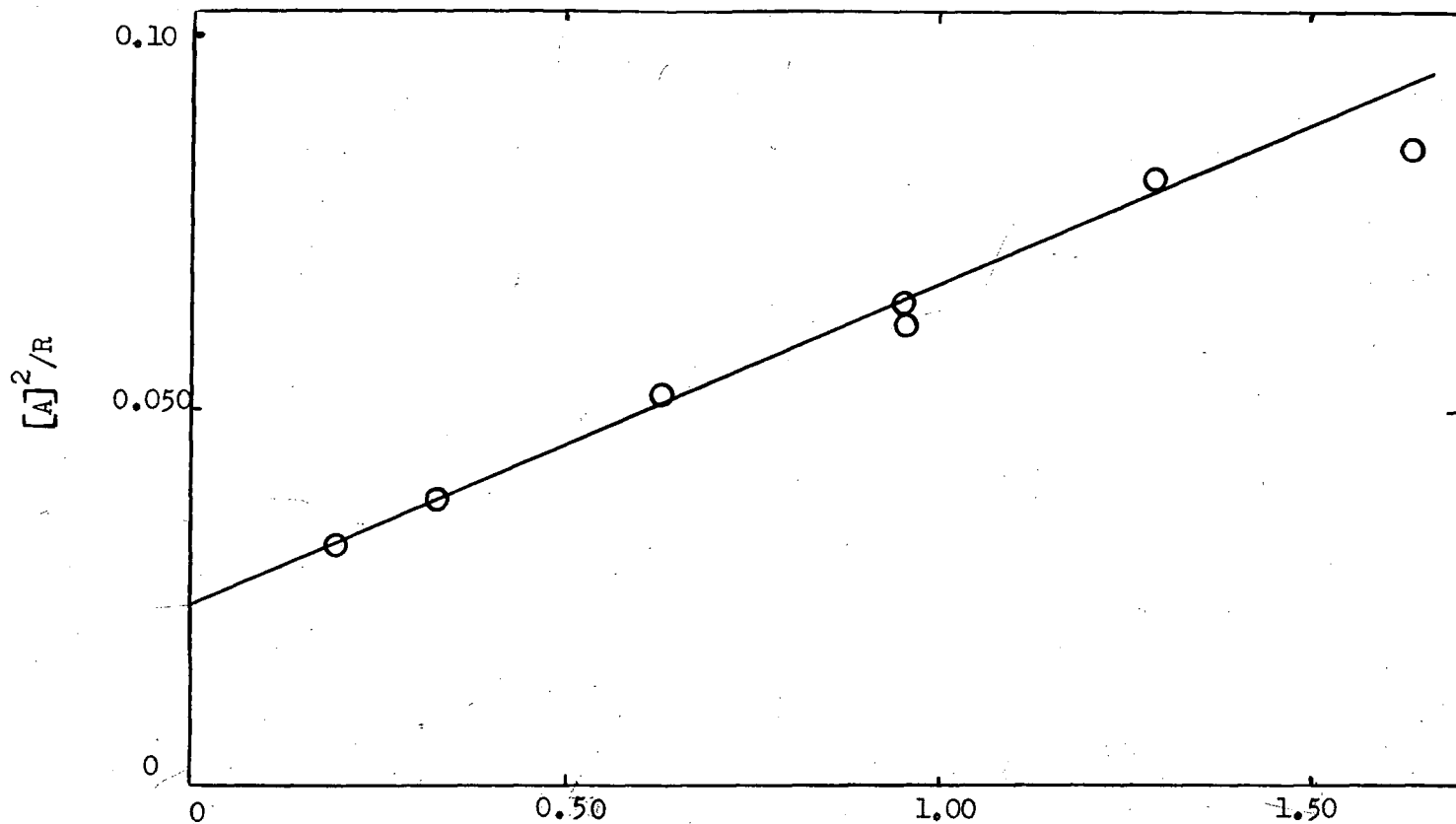
Conditions: Temperature 25°C; stirring rate 750 RPM;
 NaClO_4 0.1M; oxygen pressure 7.9 atm.

Fig. 10. Plot of $[A]^2/R$ vs $[A]$ for methyl amine.



Conditions: Temperature 25°C; stirring rate 750 RPM
NaClO₄ 0.10M; oxygen pressure 7.9 atm.

Fig. 11. Plot of $[A]^2/R$ vs $[A]$ for ethyl amine.



Concentrate of n-butyl amine (M)

Conditions: Temperature 25°C; stirring rate 750 RPM.
NaClO₄ 0.10M; oxygen pressure 6.9 atm.

Fig. 12. Plot of $[A]^2/R$ vs $[A]$ for n-butylamine

of the straight line in Figures 10, 11, and 12. The values of k_1 and k_2 are given in Table II.

Table II

Values of the constants k_1 and k_2 in Equation (1), for the amines studied.

Complexing agent	$k_1(M^{-1})$ from intercepts of Figs. 10, 11 and 12.	$k_2(mg.cm^{-2}h^{-1}M^{-1})$ from Figs. 7, 8, and 9.	$k_2(mg.cm^{-2}h^{-1}M^{-1})$ from Figures 10, 11 and 12.
Methyl amine	1.86	18.20	20.8
Ethyl amine	2.27	19.20	20.0
n-Butyl amine	1.85	20.00	23.0

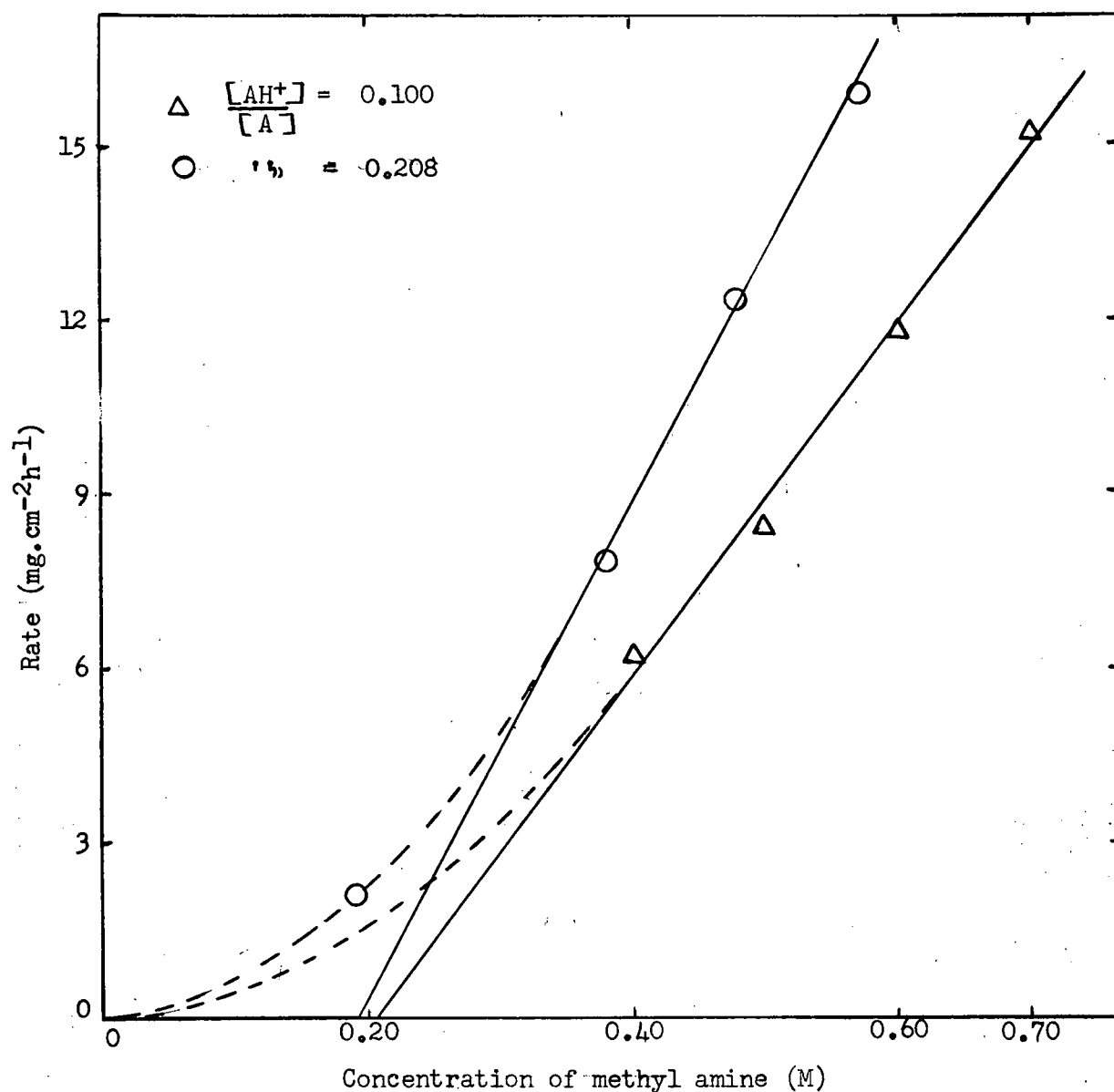
It is evident from a comparison of the two sets of values for k_2 that curves in Figures 7, 8, and 9 had not yet become quite linear, so that the values from Figures 10, 11, and 12 are likely to be the more correct.

It is apparent from the values given in Table II for the constants that the three amines are very nearly identical in their behaviour. It is doubtful whether any real significance can be attached to the small differences observed.

Effect of Acid.

The effect of acid was studied in two ways; for methyl amine only, at constant pH, constant ratio of aminium to amine and for all three amines at constant free amine concentration.

The results of experiments performed at constant pH are shown in Figure 13 (the rate values are given in the Appendix, Table IB). This indicates that the variation of the hydrogen ion concentration has no effect on the qualitative nature of the rate dependence.



Conditions: Temperature 25°C; stirring rate 750 RPM;
Oxygen pressure 7.9 atm.

Fig. 13. Plot of rate vs concentration of methyl amine at constant pH.

The results of experiments at constant amine concentration are shown in Figures 14, 15 and 16 for methyl, ethyl and n-butyl amines respectively (see Tables IC, IIB, and IIIB in the Appendix for rate values). The linear relationship between rate and aminium ion (AH^+) concentration suggests that Equation (1) be modified slightly:

$$R = \frac{k_1 [A][A]}{k_1 [A+1]} [k_2 + k_3 \alpha] \quad (3)$$

where $\alpha = \frac{[AH^+]}{[A]}$. This relation can also be expressed as

$$\frac{[A]^2}{R} = \frac{[A]}{k_2 + k_3 \alpha} + \frac{1}{k_1 (k_2 + k_3 \alpha)} \quad (4)$$

A linear plot is shown for methyl amine in Figure 17. The values of k_3 obtained for the three amines are given in Table III.

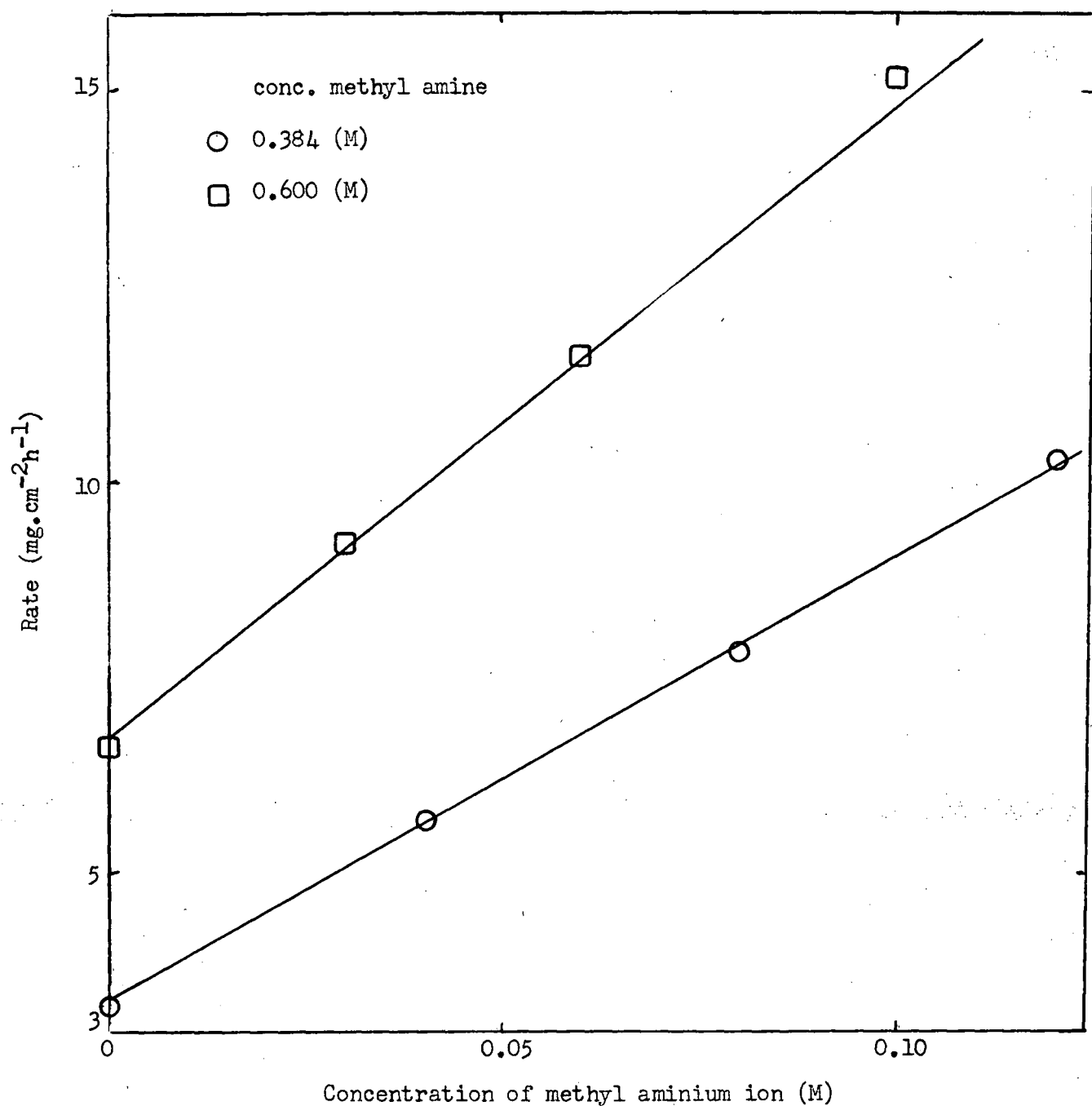
Table III

Values obtained for k_3

Complexing Agent	Values of k_3 ($\text{mg.cm}^{-2}\text{h}^{-1}\text{M}^{-1}$)		
	From Figures 13, 14, 15.	From Equation (4)	Calc. from Equation (3)*
Methyl amine	140, 153	160	146
Ethyl amine	93	x	93
n-Butyl amine	103	x	94

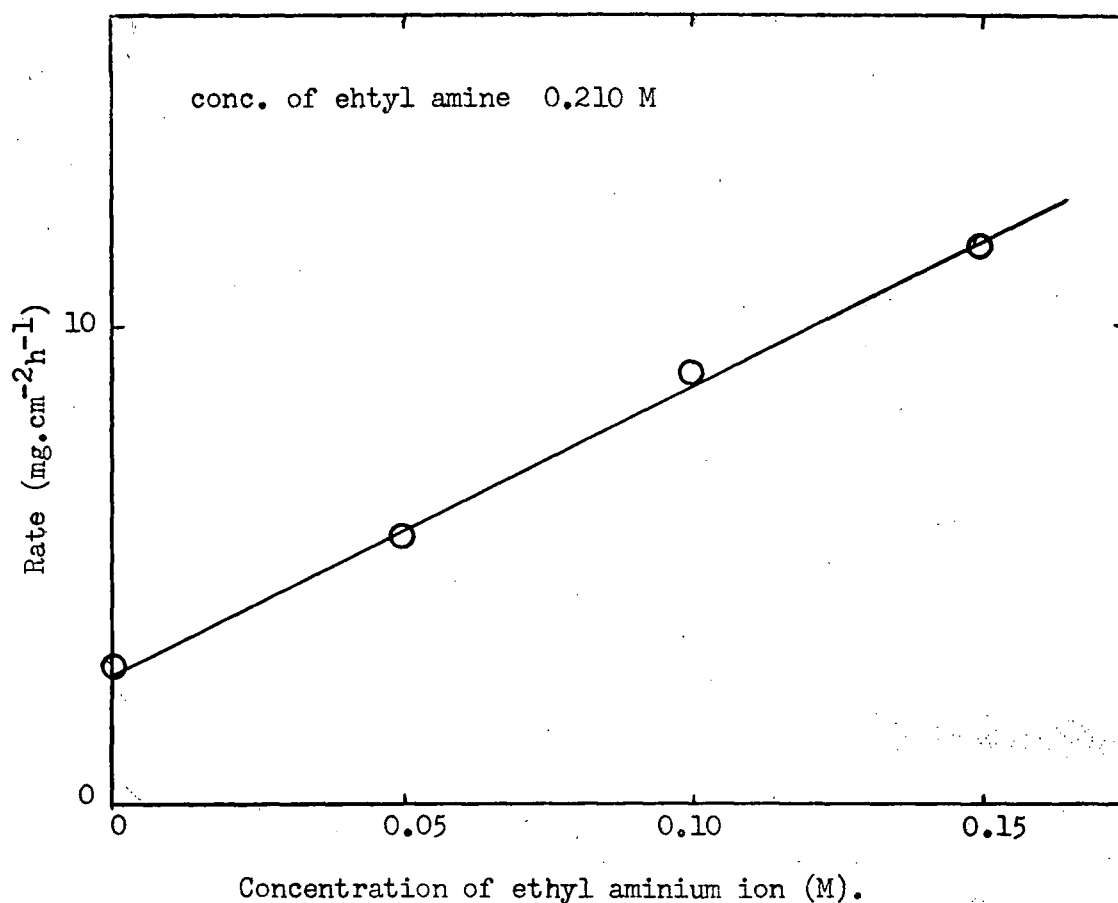
* These values of k_3 are mean values. Values of all concentrations studied are given in Tables ID, IIB, and IIIB in the Appendix.

The values for k_3 determined by different methods are in good agreement with each other. The value of k_3 for methyl amine is strikingly different from the values for the other amines.



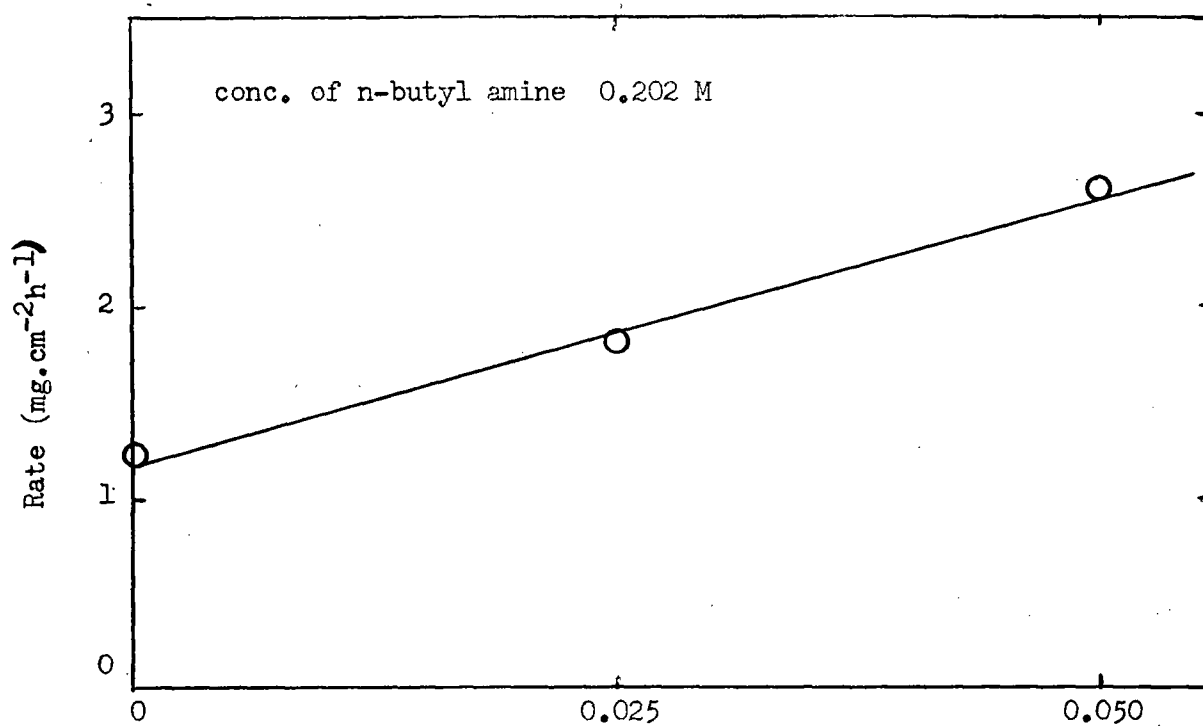
Conditions: Temperature 25°C ; stirring rate 750 RPM;
Oxygen pressure 7.9 atm.

Fig. 14. Relation between the rate and methyl aminium ion concentration.



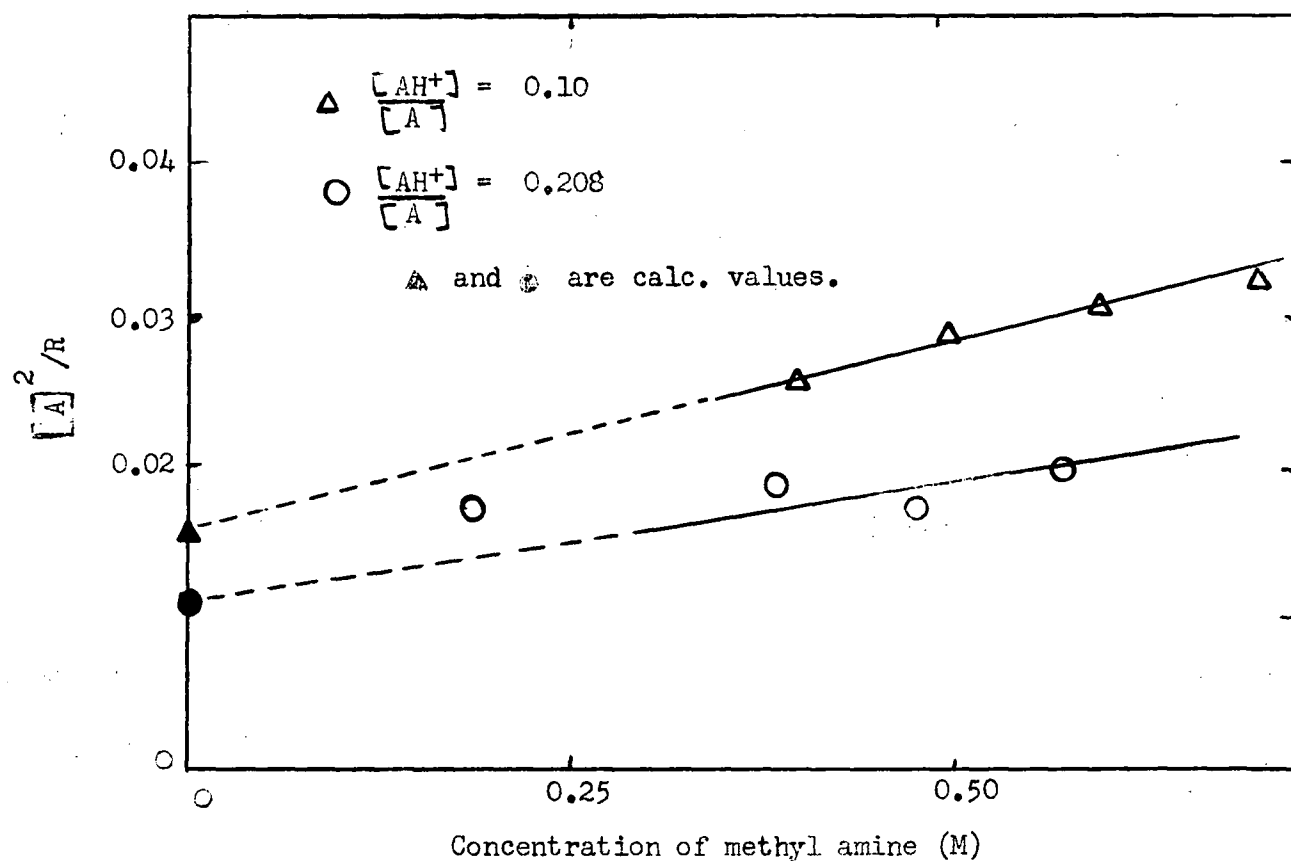
Conditions: Temperature 25°C; stirring rate 750 RPM;
Oxygen pressure 7.9 atm.

Fig. 15. Relation between the rate and ethyl aminium ion concentration.



Conditions: Temperature 25°C; stirring rate 750 RPM;
Oxygen pressure 6.9 atm.

Fig. 16. Relation between rate and n-butyl aminium ion concentration.



Conditions: Temperature 25°C; stirring rate 750 RPM;
 Oxygen pressure 7.9 atm.

Fig. 17. Plot of $[A]^2/R$ vs $[A]$ for methyl amine at constant pH.

Values of the rates obtained at constant high methyl amine concentration and at different amounts of aminium species are given in Appendix.I. These rate values observed in higher range of concentration do not appear to follow Equation (3). The reason for this is not yet clear.

Ammonia.

It was found that the ammonia system showed a pattern of a kinetic behaviour very similar to that described for the aliphatic amines. The experimental data are presented in Figures 18, 19, and 20 and Tables IVA, IVB, and IVC in the Appendix. The values of the constants for ammonia are given in Table IV.

Table IV.

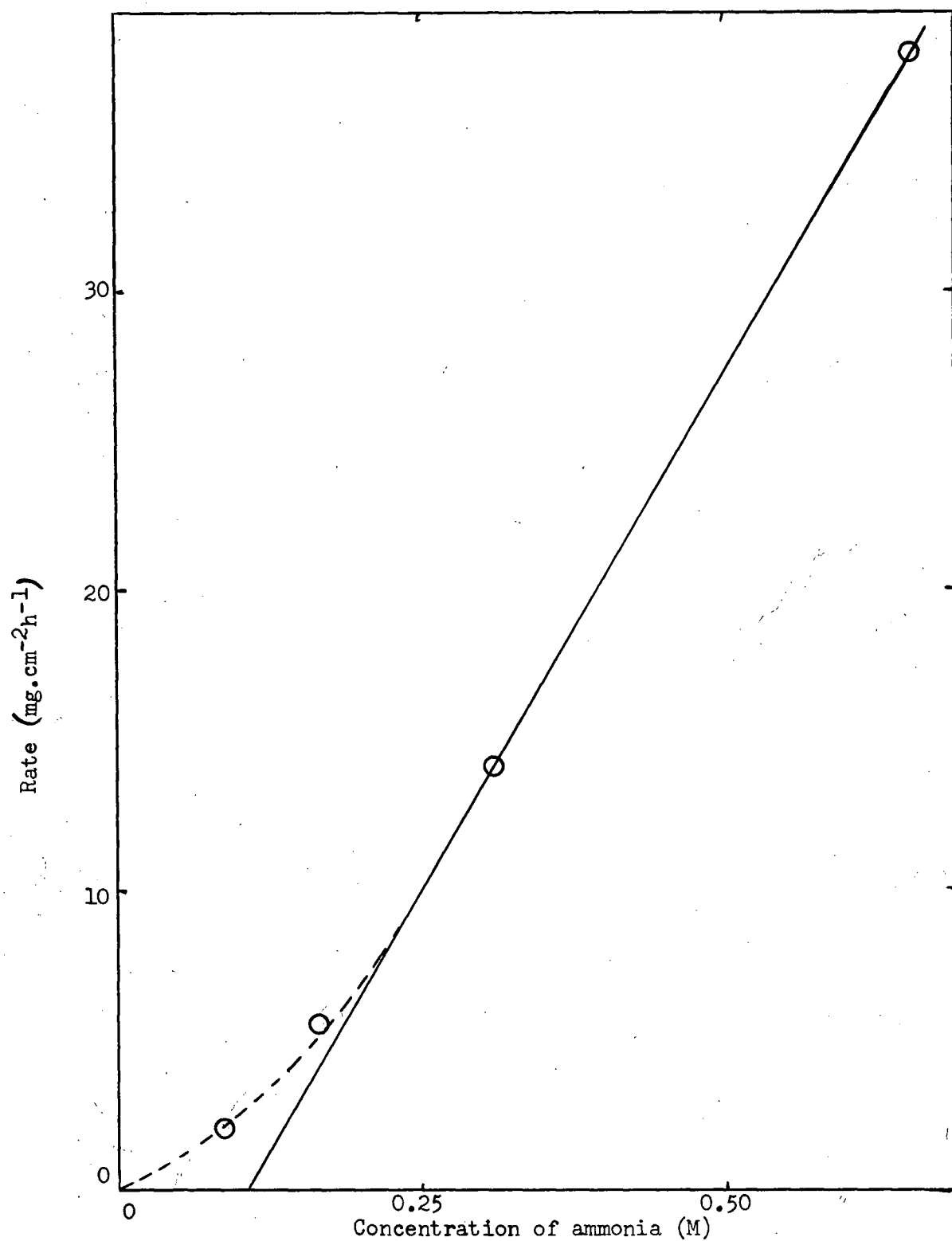
Values of constants for ammonia.

	$k_1(M^{-1})$	$k_2(mg.cm^{-2}h^{-1}M^{-1})$	$k_3(mg.cm^{-2}h^{-1}M^{-1})$
From Figure 18	x	69.5	x
From Figure 19	4.65	77.0	x
From Figure 20	x	x	2445, 2420
From Equation (3), Mean value	assumed 4.65	assumed 77.0	2450
From Ref. 9.		84	

From all the experimental results, it is found that the nature of the kinetic process for dissolution of copper is the same for ammonia and aliphatic amines. However, the values of the constants for ammonia are quite different from those of the amines.

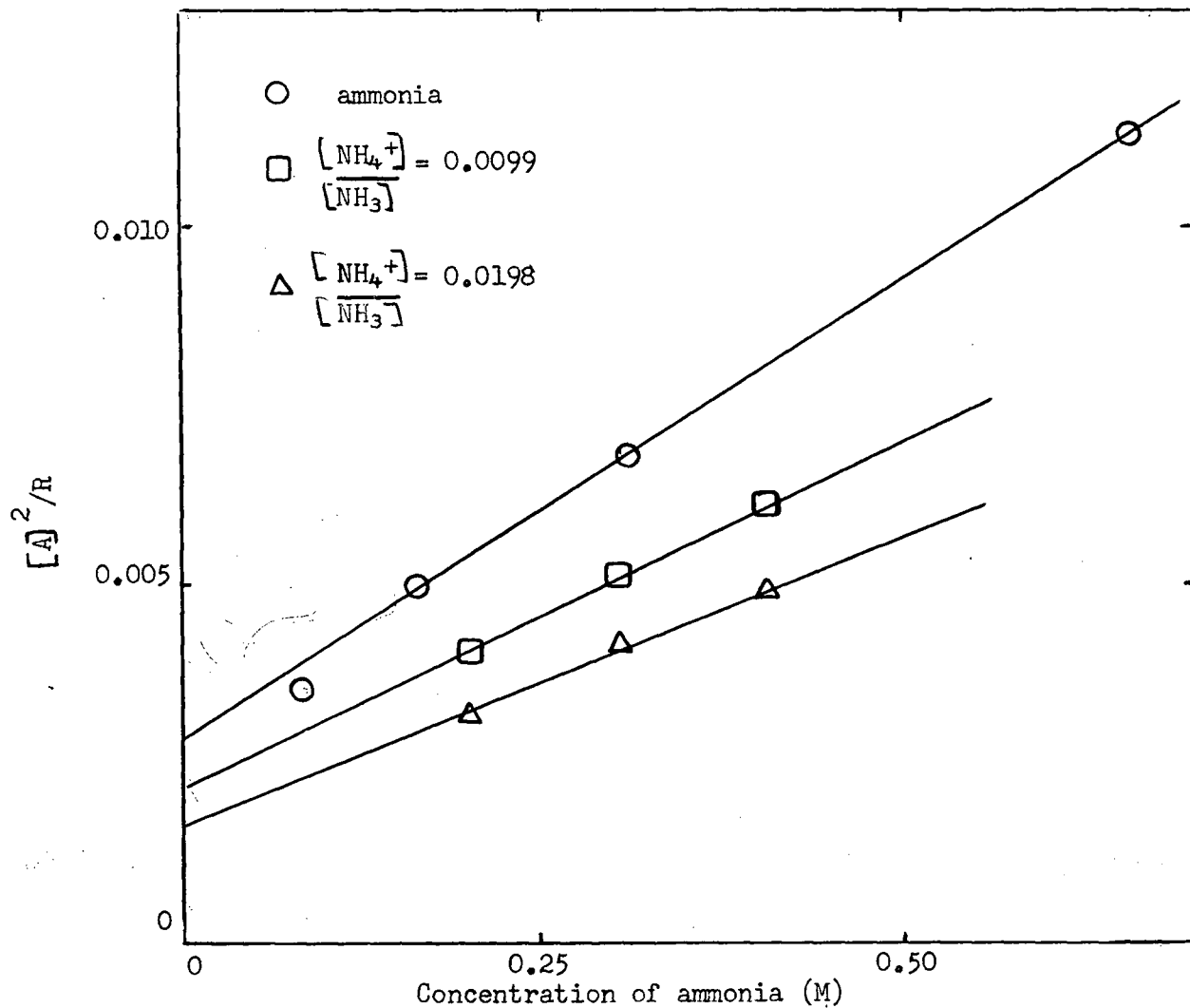
Reaction Mechanism.

The form of Equation (3) suggests that the total reaction may involve an adsorption equilibrium followed by two parallel independent first



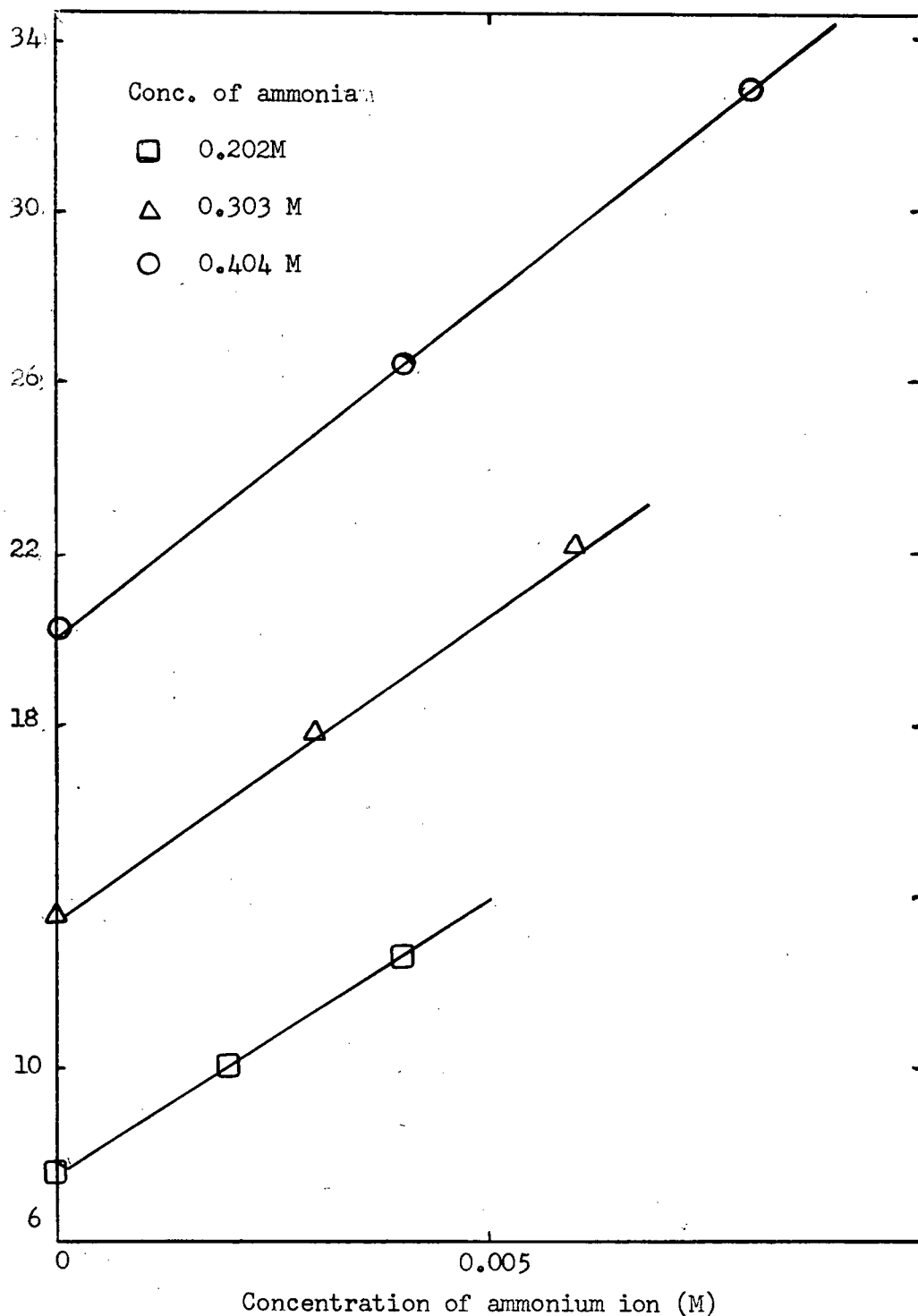
Conditions: Temperature 25°C; stirring rate 750 RPM;
NaClO₄ 0.10; oxygen pressure 7.9 atm.

Fig. 18. Plot of rate vs concentration for ammonia.



Conditions: Temperature 25°C; stirring rate 750 RPM;
 MaClO_4 0.10; oxygen pressure 7.9 atm.

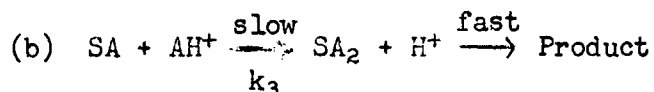
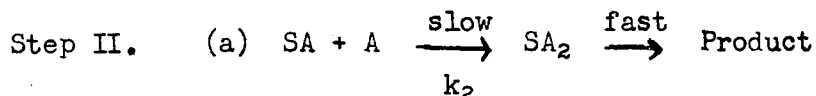
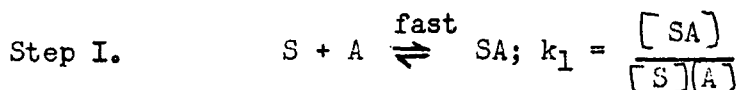
Fig. 19. Plot of $[\text{A}]^2/\text{R}$ vs $[\text{A}]$ for ammonia.



Conditions: Temp. 25°C; stirring rate 750 RPM; NaClO₄ 0.10; O₂ press. 7.9 atm.

Fig. 20. Relation between the rate and ammonium ion concentration.

order steps. These steps may be formulated as follows (S stands for copper atom on the surface).



In addition to these steps, the oxygen adsorption equilibrium must be considered. This is assumed to be fast and essentially complete. There is no way of deciding unambiguously whether oxygen adsorption step precedes or follows the amine adsorption step. However, it is thought likely this step precedes the amine adsorption step under the conditions used in the present study. The occurrence of a parallel equilibrium step involving adsorption of AH^+ species is not indicated by the observation that the dissolution of copper does not proceed in the presence of aminium or ammonium ion alone and that the plots of rate vs $[AH^+]$ are linear (Figures 14, 15, 16 and 20).

From consideration of the above mentioned steps, the rate law will be given by the expression

$$R = k_2 [SA][A] + k_3 [SA][AH^+] \quad (5)$$

Considering the surface balance $S_0 = S + SA$, and the equilibrium Step I, the final rate expression can be formulated as,

$$R = \frac{k_1[A]}{k_1[A] + 1} \left[k_2[A] + k_3[AH^+] \right] \quad (6)$$

where R is expressed in rate per unit area. This is identical with

Equation (3) derived from the kinetic data.

Selected values for the constants k_1 , k_2 and k_3 for methyl, ethyl, n-butyl amine and ammonia are given in Table V.

Table V.

Selected values of constants.

Complexing agents	$k_1(M^{-1})$	$k_2(mg.cm^{-2}h^{-1}M^{-1})$	$k_3(mg.cm^{-2}h^{-1}M^{-1})$	k_3/k_2
Ammonia	4.65	77	2450	31.80
Methyl amine	1.86	20.8	146	7.00
Ethyl amine	2.27	20.0	93	4.65
n-butyl amine	1.85	23.0	94	4.10

It is evident from the values of the constants that the length of the carbon chain exerts very little influence on the rate. It is, however, quite apparent that the effect due to addition of a proton to form the AH^+ ion is very pronounced in all the cases studied.

Significance of k_1 :

According to the proposed scheme for the reaction, k_1 is the equilibrium constant for the adsorption process. It is apparent from the k_1 values that ammonia is much more strongly adsorbed than the other amines. The adsorption characteristics of methyl, ethyl and n-butyl amines appear to be essentially the same.

Significance of k_2 :

The significance of the values of k_2 is as an indication of attack of surface adsorbed species by those in the solution. The values of k_2 for the amines are almost the same for the three amines and widely different from

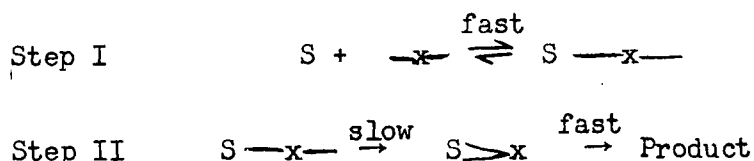
that of ammonia. It is difficult to draw any definite conclusion about the difference between the k_2 values of amines and ammonia. It may be perhaps largely due to a steric factor; the ammonia has a smaller chance of unsuccessful collision with the reaction site than have the amines.

Significance of k_3 :

The value of k_3 indicates the attack of surface adsorbed species by AH^+ or NH_4^+ species from solution. The difference of values in k_3 between the amines and ammonia is perhaps also due to a steric effect.

The difference in surface attack by A and AH^+ species are evident from the difference in value of k_2 and k_3 . Perhaps for the latter species, the electron exchange is much facilitated due to presence of charge on the AH^+ species.

In the light of the foregoing discussion, it appears likely that the difference in order of reaction observed in the case of chelating agents¹⁰ and that in the case of amines and ammonia may arise from the difference in the number of functional groups present in these two types of compound. For the chelating agents, consequently, it appears to be a unimolecular reaction, the adsorption step being the only observable step. The reaction can be represented by the following sequence of steps:



---x- - stands for bidentate chelating agent.

These steps are essentially similar to those proposed for amines except that the slow step does not involve a second molecule.

In view of the present results, it appears that further work ought to be done to extend the same work to other complexing systems. In this sense it would be interesting to investigate the following:

- (1) Rate measurements with mixtures of amine and aminium ion ($[A] + [AH^+] = \text{constant}$) over a wide range of pH.
- (2) Rate measurements with mixtures of primary amines and secondary amines.
- (3) Investigation of the rate process with 3- and 4-carbon chain diamines.

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CATALYTIC REDUCTION OF NICKEL ION

BY MOLECULAR HYDROGEN

INTRODUCTION

The possibility of reduction of metal ions from solution by molecular hydrogen has been recognized for a long time. Among early investigators, Ipatiew^{1,2,3} has perhaps made the greatest contribution. In recent years, more detailed studies of these reduction processes have been made by Shaufelberger,⁴ Mackiw, Lin and Kunda,⁵ and Knacke, Pawlek and Süssmuth.⁶ An excellent review of hydrometallurgical processes at high pressure is by Forward and Halpern.⁷

Early attempts of Ipatiew to displace metals from solutions at high pressures and temperatures met with varying degrees of success. His work was usually done at high temperature (300°C) and pressure (7000 psi) and for times as long as several days. He succeeded in precipitating by hydrogen reduction, either as the metal or as a basic salt, the following metals; platinum, iridium, copper, nickel, cobalt, lead, tin, arsenic, antimony and bismuth.

Shaufelberger⁴ has investigated the possibility of reduction of copper and nickel by molecular hydrogen. From examination of the thermodynamic data, he concluded that such reduction is possible at high temperature (~200°C) and at suitable hydrogen ion concentration. The effects of hydrogen ion concentration and complex formation were investigated by him to arrive at a suitable system for the complete removal of the metal ion from solution.

The kinetics of the reduction of nickel in ammoniacal solution was studied by Mackiw, Lin and Kunda.⁵ The conditions under which this work was done were similar to those adopted by Sherritt Gordon Mines Ltd., for recovery of nickel.

Knacke, Pawlek and Süssmuth⁶ investigated the kinetics of the homogeneous reduction of silver and copper and heterogeneous catalytic reduction of nickel, from their sulphate solutions. The results for precipitation of silver and copper are not in agreement with those found by later workers.^{8,9} The rate of reduction of copper and silver was found to be dependent on the pressure of hydrogen while according to Pawlek and co-workers, it depends on the square root of hydrogen pressure. For the reduction of nickel, the value of the activation energy was found⁶ to be 4.12 kcal/mol, which suggests that in his work, the reduction rate was diffusion controlled. The rate equation proposed by these workers

$$-\frac{dc}{dt} = 5.59 \times 10^{-2} C_{Ni^{++}}^{1/2} P_{H_2} e^{\frac{-4.12}{RT}}$$

does not suggest that hydrogen ion has effect on the rate of reduction.

Halpern and Peters⁸ have investigated the homogeneous activation of hydrogen by cupric ion, and the reduction of copper from the solution. The product can be copper or cuprous oxide depending on the pH of the solution and the temperature of the reaction. It has also been found from a study of the copper sulphate system,¹⁰ that the reaction process is reversible. This reversibility is strongly hydrogen-ion-concentration dependent.

Reduction of the metals, copper, silver and mercury has been found to be homogeneously catalysed by the metal ions and by their complex ions. But for reduction of nickel or cobalt, it has always been necessary to add a

heterogeneous catalyst. Among catalysts used are nickel powder, ferrous sulphate, colloidal graphite and hydroquinone.¹¹ In the work reported here, nickel powder is used as a catalyst.

Scope of the Work.

In the present work an attempt was made to elucidate the kinetics of reduction of nickel from salt solutions by molecular hydrogen in the presence of nickel powder catalyst. In the light of previous work, it was thought worthwhile to study the reduction of nickel from a buffered solution and a few unbuffered solutions. It is also an aim of this work to evaluate the equilibrium constant for the equilibrium $\text{Ni}^{++} + \text{H}_2 \rightleftharpoons \text{Ni}^0 + 2 \text{H}^+$, at high temperature.

EXPERIMENTAL

Apparatus.

The reaction studies were conducted in a one-gallon stainless-steel autoclave manufactured by Autoclave Engineers Inc.¹² Additional fittings included an arrangement to drop the catalyst from a sealed glass capsule and an arrangement in the sampling tube to collect the sample under pressure. These are shown in Figure 1. Since for the system studied, the stainless steel autoclave may act as a catalyst, a glass liner with a titanium baffle was used to contain the solution. The impeller, thermocouple well and sampling tubes were also made of titanium. The autoclave was heated by a gas ring burner, and the temperature was controlled to within $\pm 1.5^\circ\text{C}$ using a Leeds and Northrup micromax controller.

All pH measurements were made at room temperature, using a Beckman model GS pH meter.

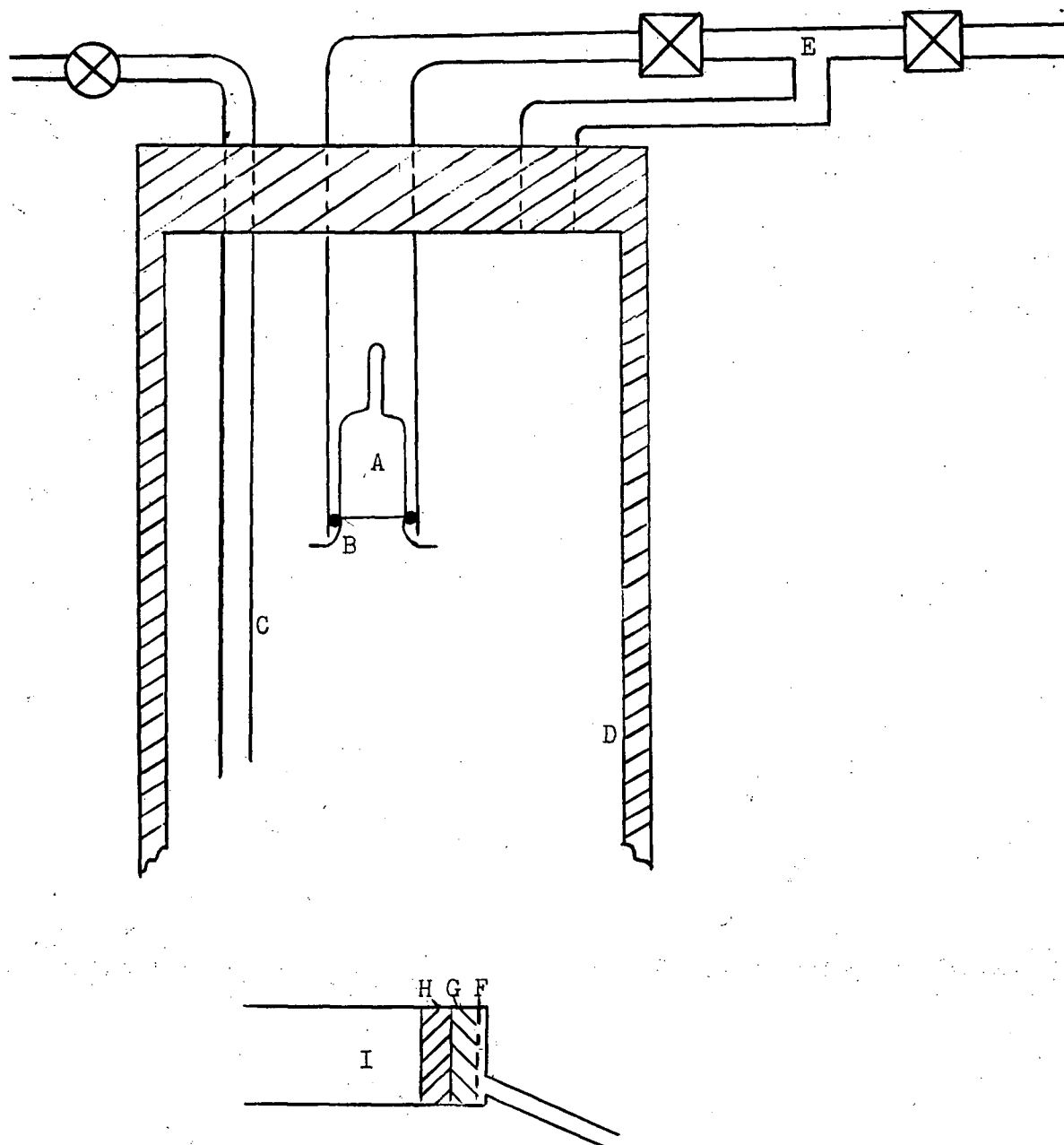
Catalyst.

The catalyst used in these experiments was standard 'A' carbonyl nickel powder, prepared by the Mond Nickel Company, Ltd. These are spherical particles, and of 100% -350 mesh. The surface area was found^{*} to be $1.85 \text{ m}^2/\text{gm}$.

Reagents.

The nickel acetate, acetic acid, and anhydrous sodium acetate used in these experiments were all reagent grade, obtained from the Allied Chemical and Dye Company and the Nichols Chemical Company. Other incidental chemicals were also reagent grade. Hydrogen gas supplied by the Canadian Liquid Air Company was used without further purification. All the solutions for

* The author is grateful to Mr. Peter Hennes for surface area determination.



- | | |
|------------------------------------|-----------------------------|
| A = glass capsule | F = wire gauge |
| B = O-ring arrangement | G = glass wool |
| C = sampling tube | H = asbestos |
| D = autoclave wall | I = total filtering device. |
| E = gas inlets to push the capsule | |

Fig. 1. Schematic diagram for holding catalyst and filtering under pressure.

experiments were prepared by diluting solutions of known strength. Measured volumes of sodium acetate, acetic acid and nickel acetate were transferred to a 2000 ml volumetric flask and diluted up to volume to get a solution of the desired concentration. Distilled water was used for preparation of all the solutions.

Analysis.

Determination of nickel was done colorimetrically using dimethyl glyoxime.^{13,14} A Beckman Model DK -2 ratio-recording spectrophotometer was used for measurement of optical density. Measurements were made at a wavelength of 450 millimicrons. The analysis was performed in the following way: To an aliquot of the sample were added 2 ml of saturated bromine water 4.5 ml of concentrated ammonia, 7 ml of 1% solution of dimethyl glyoxime in alcohol, and 5 ml of alcohol, and the whole was diluted to 25 ml. Measurements were made within 10 minutes of mixing. Beer's law is obeyed, as seen from Figure 2, over a sufficient range of concentration to permit analysis following appropriate dilution.

Experimental Procedure.

The experiments were done in the following way; the required amount of catalyst was weighed and placed in a glass capsule and the capsule was filled with distilled water and sealed. Then it was placed in the autoclave as shown in Figure 1. The autoclave was charged with the required solution. After the autoclave was sealed, it was flushed several times with hydrogen and was heated under hydrogen at a pressure of about 200 psi. It was flushed again at about 80°C, and finally heated up to the required temperature under 200 psi of hydrogen pressure. Samples were removed after attainment of the final temperature to ascertain the zero time concentration. The capsule of

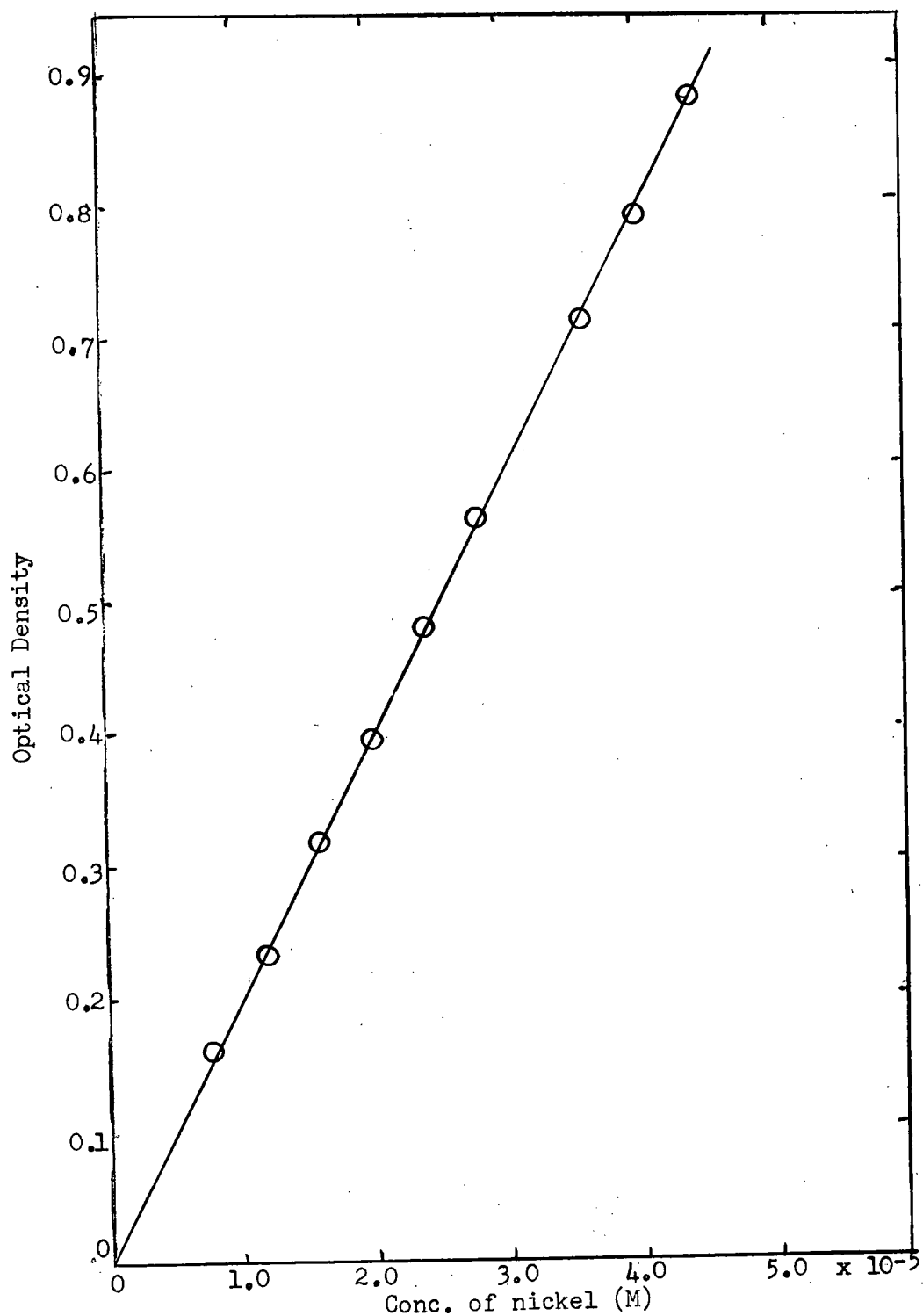


Fig. 2. Calibration curve for the determination of nickel.

catalyst was injected by hydrogen pressure into the autoclave where it was smashed by the impeller. The hydrogen pressure was then adjusted to the required value. The time when the catalyst was dropped into solution was taken as zero time. Samples were collected through the sampling device (through which samples are filtered out from solution under hydrogen pressure), at suitable time intervals for nickel analysis by the method already described.

Preliminary Experiments.

Preliminary experiments were conducted to examine (i) the nature of the reduction process in unbuffered solutions (solutions of nickel sulphate and nickel perchlorate), (ii) the variation of the pH of the solution resulting from the reduction of nickel ion, (iii) the variation of the reduction rate using different types of catalysts and (iv) the nature of the rate curve.

(i) Reduction from nickel sulphate and perchlorate solutions:

Experiments using nickel perchlorate and sulphate solutions were found to give only a very small amount of reduction (10% of a 0.1 M solution at 160°C). It was observed that during this process, the pH of the solution fell to about 2.4 and the reaction stopped. For perchlorate solutions still less reduction was found. For this reason, further work described in this thesis was done with buffered solutions.

(ii) Variation of pH:

All the pH measurements were done at room temperature. It was found that the initial and final pH of the buffered system after reduction differed only slightly (for example, from pH 4.25 to 4.15). This difference increases as the amount of nickel reduced increases. In spite of the small change it was felt desirable to use only the initial rate in studying the mechanism since only in the initial part can the conditions for reaction be known with

any certainty.

(iii) Different types of catalyst:

Three types of nickel powder were tried as catalyst.

(a) Dense nickel powder: These were dense granular nickel powders obtained from Sherritt Gordon Mines Ltd. The particles used for this test were 20-30 microns in diameter. These were annealed in a hydrogen atmosphere before use. It was found that this catalyst was not active enough to make the reduction of nickel ion from solution possible. Instead, dissolution of nickel powder continued for a few hours. It was found that starting with two different initial concentrations of nickel, the dissolution approaches a type of pseudoequilibrium. This powder was not used because of its lack of catalytic activity.

(b) 'Nucleating powder': This powder, obtained from Sherritt Gordon Mines Ltd., was less than three microns in diameter and of irregular shape. This catalyst was found to be very active, but reproducibility of rate measurements was poor.

(c) Carbonyl nickel powder: (This catalyst has already been described). It was found to be quite active and as well gave good reproducibility. The difference in the reproducibility of rate measurements for catalyst (b) and (c) is perhaps due to the nature of the catalyst surface and its shape. The carbonyl nickel catalyst was used for all the experiments described hereafter.

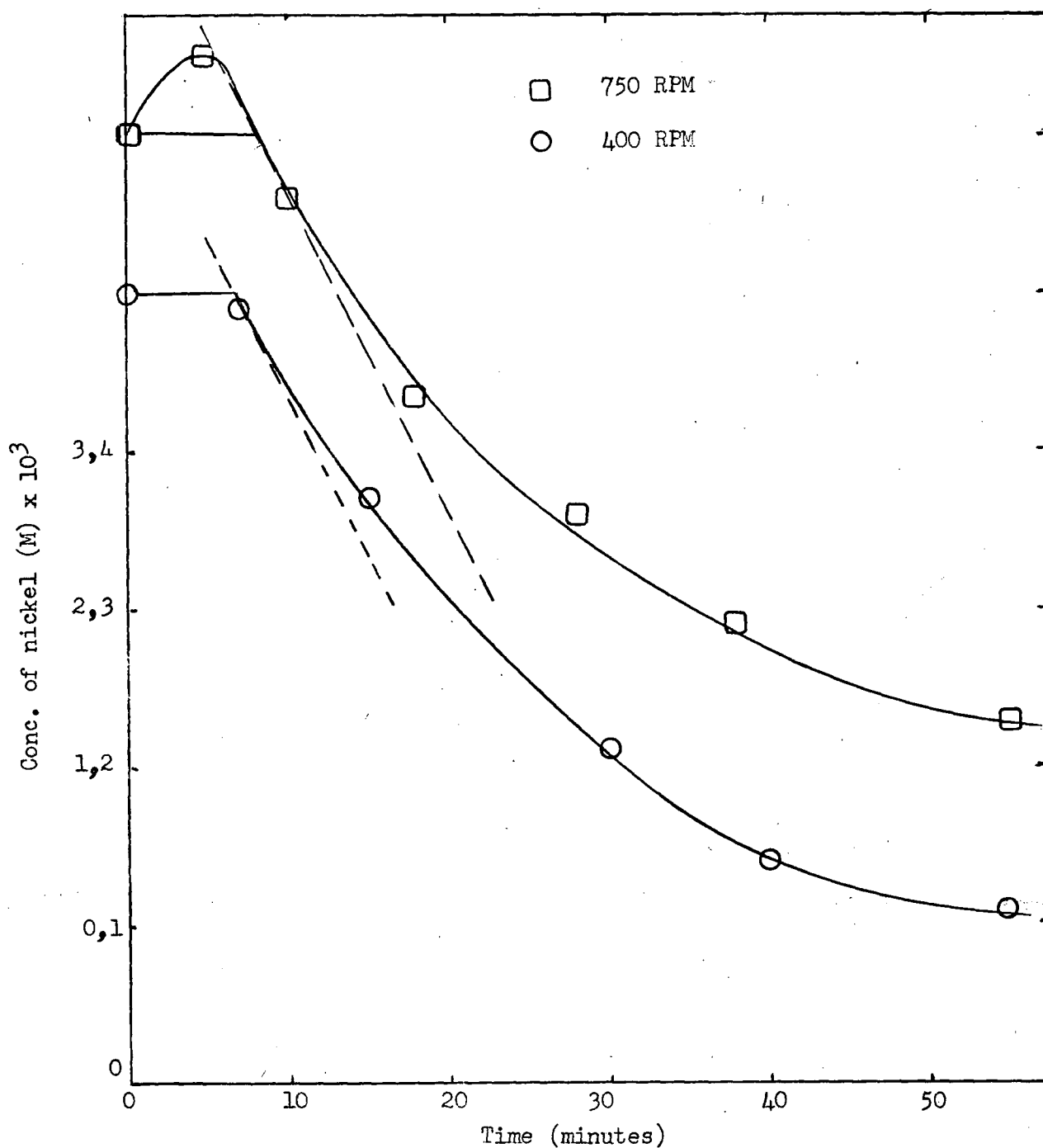
(iv) Nature of the reduction curves:

The rate curves in which nickel concentration is plotted against time, were found to show an induction period of variable length. These curves were of two types, (a) at high stirring rate (750 RPM), the nickel concentration in solution was found to increase considerably and then to

decrease, (b) at lower stirring rate (400 RPM), the nickel concentration remained constant for a few minutes and then decreased. In all cases, however, neither the measured reduction rate, nor the final equilibrium concentration was dependent on the stirring rate. The two types of rate curve are shown in Figure 3. It is also made clear in Figure 3 how the rates were evaluated from the data.

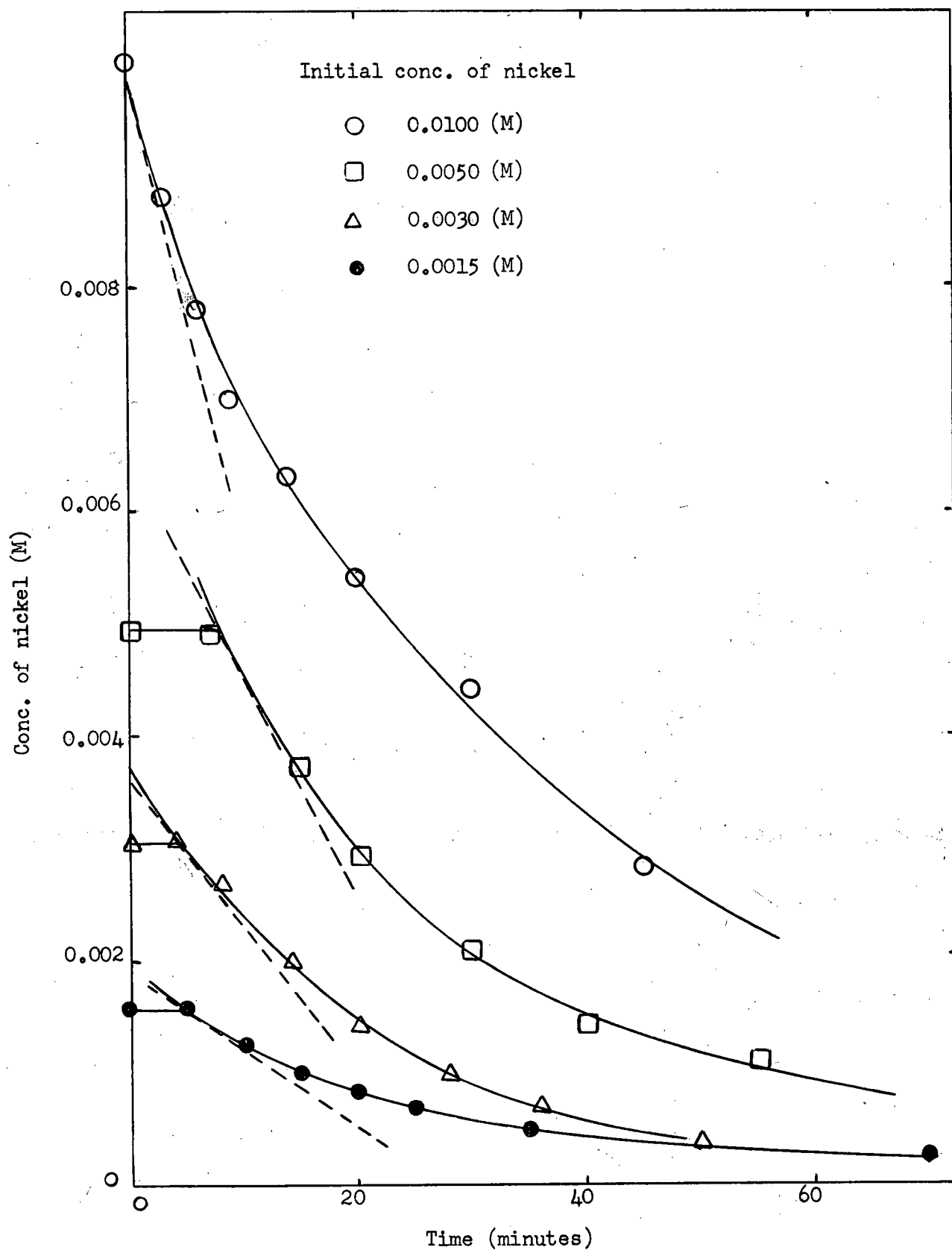
The reason for there being two types of rate curves was not ascertained. However, it may be conjectured that the cause may lie in the presence of an oxide layer on the catalyst surface, which in one case is being dissolved before being reduced and in the other case is reduced in situ. It seems inconsistent, however, that pre-treatment of the catalyst (the powder was treated with warm acetic acid, washed with alcohol, dried at 60°C) did not appear to affect the duration or the nature of the induction period. This may signify that either the oxide film resists this treatment or forms after this treatment at a very rapid rate.

It was found that although the duration of the induction period was variable, measured values of the initial rates were consistent. Table I in the Appendix gives values showing stirring effect, reproducibility and effect of chemical treatment. Figure 4 gives a typical family of rate curves (all at 400 RPM). Independent evaluation of rates from these curves gave values which, though different by as much as 20%, were consistent among themselves.



Conditions: Temperature 140°C; Catalyst 10 gms/1400 ml;
 Hydrogen 13.55 atm; Acetic acid 0.2 M; Total acetate
 0.06 M; Initial nickel 0.005 M.

Fig. 3. Typical plot showing two types of rate curves.



Conditions: Temp. 140°C; Catalyst 10 gms/1400 ml; Hydrogen 13.55 atm;
 Acetic acid 0.2 (M); Total acetate 0.06 (M);
 Stirring rate 400 RPM; initial pH 4.25.

Fig. 4. Typical family of rate curves.

RESULTS AND DISCUSSION

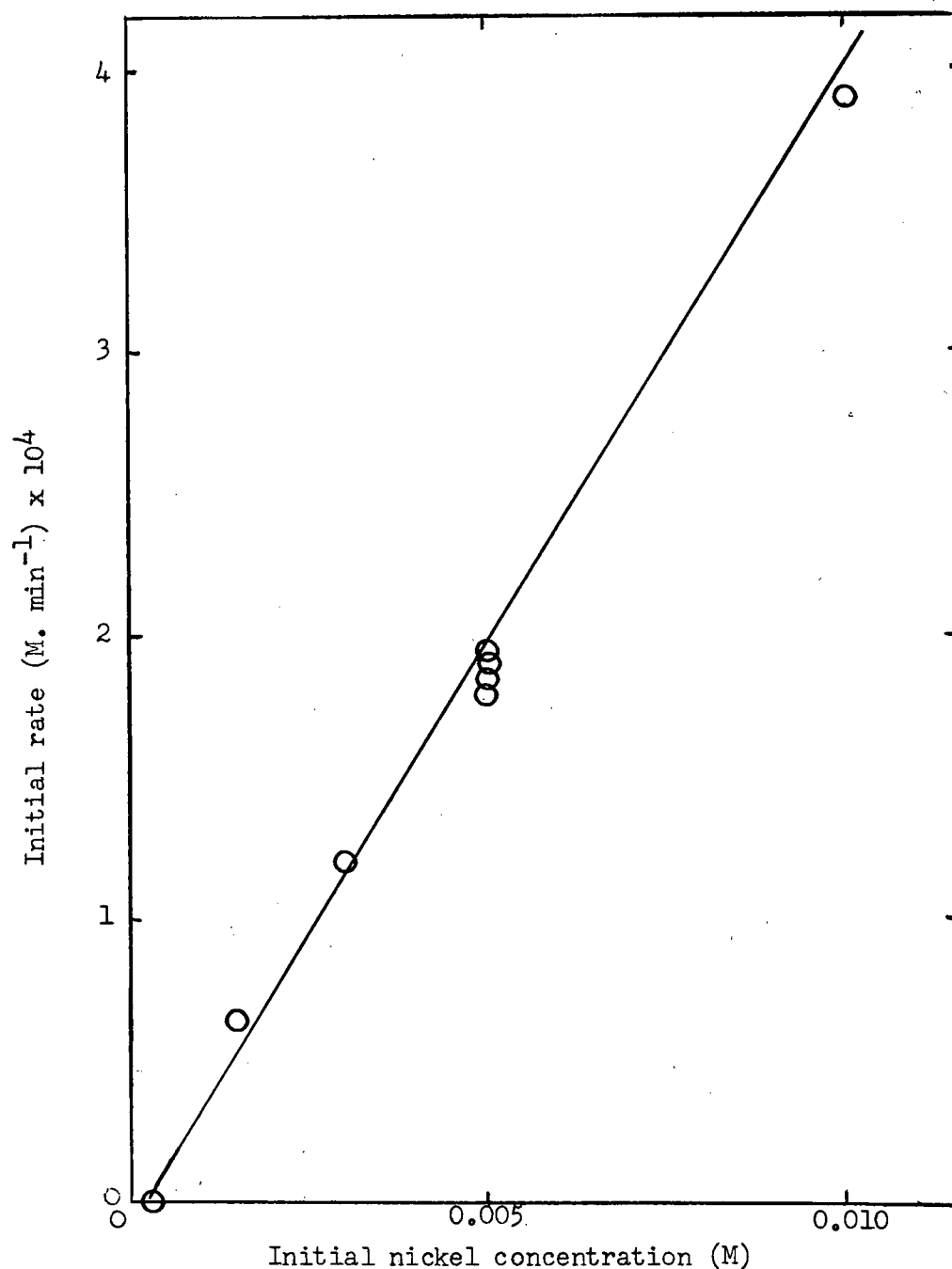
The variables studied in an attempt to elucidate the mechanism of reduction of nickel from solution by molecular hydrogen in the presence of a nickel catalyst were (a) initial nickel concentration, (b) amount of catalyst, (c) pressure of hydrogen, (d) initial hydrogen ion concentration and (e) reaction temperature. The experimental data are given in Tables I to VIII in Appendix II.

(a) Dependence of the rate on nickel concentration.

The initial rate for any concentration was obtained from the rate plots as shown in Figure 4. These runs were made at 140°C, 13.55 atm. hydrogen pressure, 10.00 gms of catalyst in 1400 ml solution and solution pH of 4.25 and varying initial concentration of nickel. The variation in initial rate with initial nickel concentration is shown in Figure 5. This plot shows a linear dependence of the rate on the nickel concentration. The plot passes through the value of the equilibrium nickel concentration for the conditions used. The first order dependence on nickel concentration is confirmed by a plot of \log (conc. of nickel) vs \log (initial rate) shown in Figure 6. The measured slope of this line, 0.93 is satisfactorily close to 1.

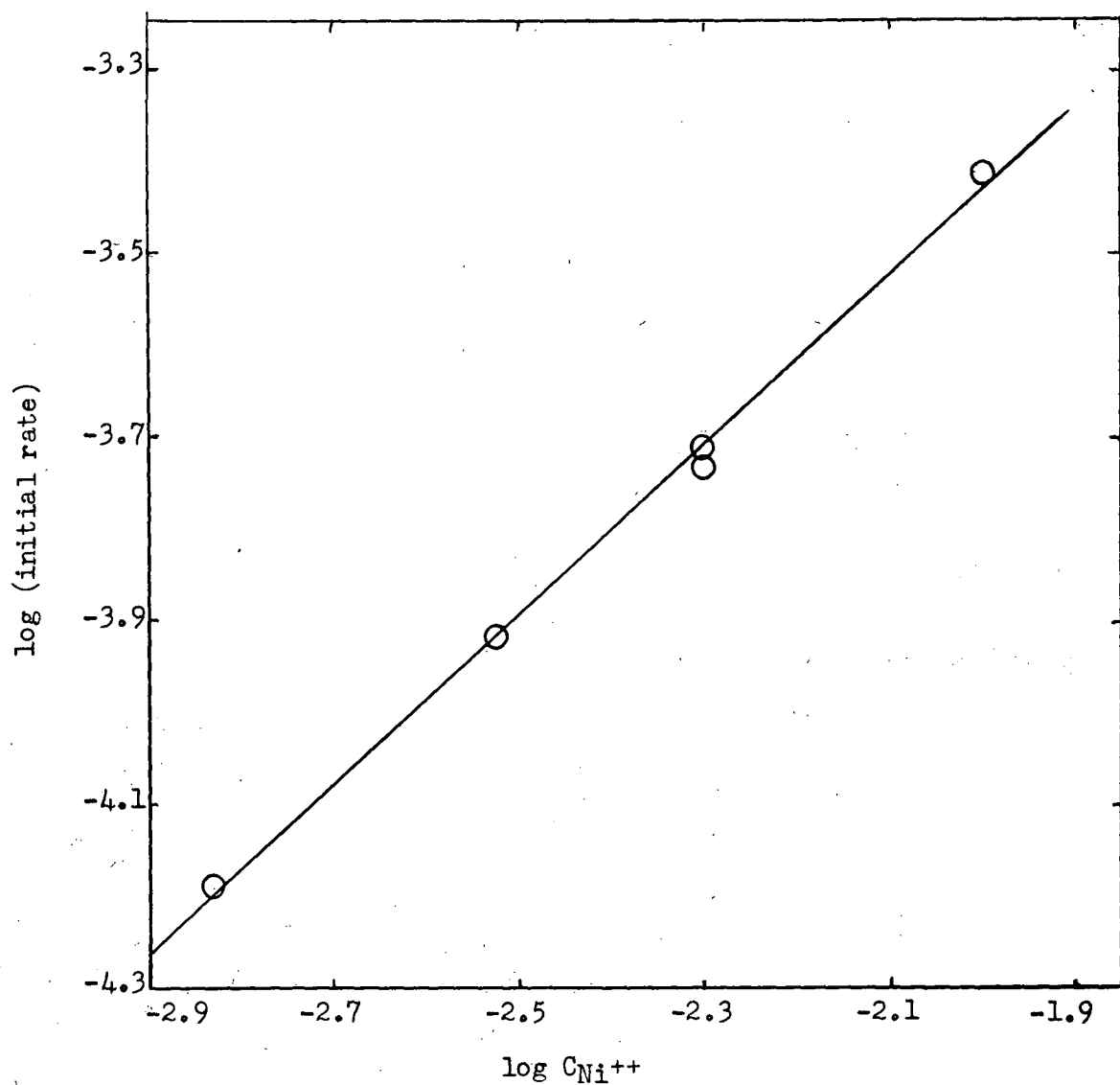
(b) Effect of the amount of catalyst.

A number of runs were done varying the amount of catalyst, at a constant initial nickel concentration of 0.005 (M) with other conditions being the same as given above. First order dependence of the rate on the catalyst area is shown by the linearity of the plot given in Figure 7. The fact that the straight line passes through the origin is consistent with the observation that no reaction occurs in the absence of a catalyst.



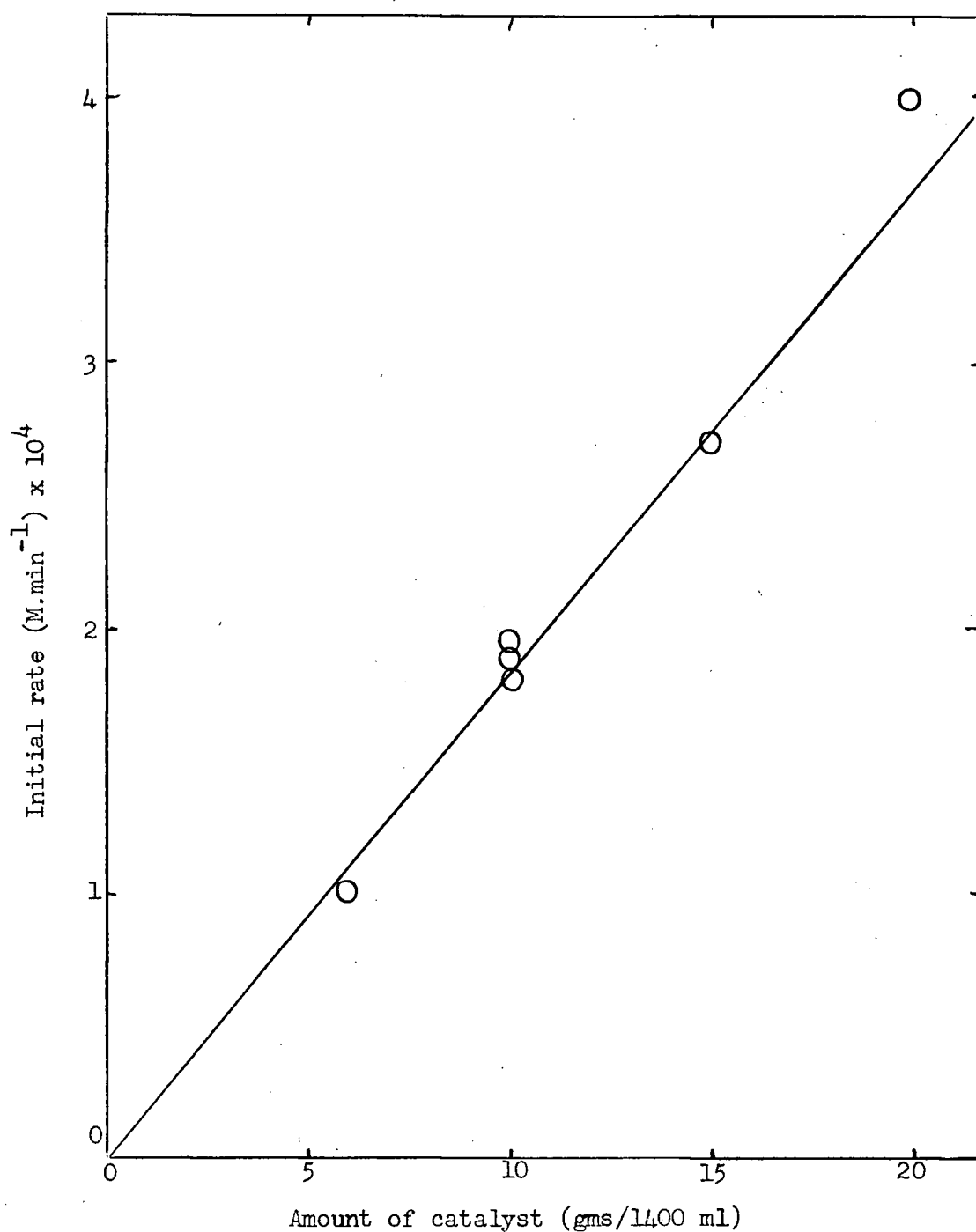
Conditions: Temperature 140°C; Catalyst 10 gms/1400 ml;
Hydrogen 13.55 atm; Acetic acid 0.2 (M);
Total acetate 0.06 (M); Initial pH 4.25.

Fig. 5. Effect of initial concentration on the initial rate.



Conditions: Temperature 140°C; Catalyst 10 gms/1400 ml;
Hydrogen 13.55 atm; Acetic acid 0.2 (M);
Total acetate 0.06 (M); Initial pH 4.25.

Fig. 6. Plot of $\log (\text{initial rate})$ vs $\log (\text{initial conc.})$.



Conditions: Temperature 140°C; Hydrogen 13.55 atm;
 Acetic acid 0.2 (M); Total acetate 0.06 (M);
 Initial nickel concentration 0.005 (M);
 Initial pH 4.25.

Fig. 7. Effect of amount of catalyst on the initial rate.

(c) Effect of hydrogen pressure.

Results of experiments conducted at different hydrogen pressures, showed that the rate is directly proportional to the square root of the hydrogen pressure. The data are presented in Figure 8. At sufficiently high pressures, the rate is seen to drop from this dependency, which may indicate saturation of catalyst surface. This type of dependence suggests that the rate-determining step may be one involving atomic hydrogen.

(d) Dependence of the rate on hydrogen ion concentration.

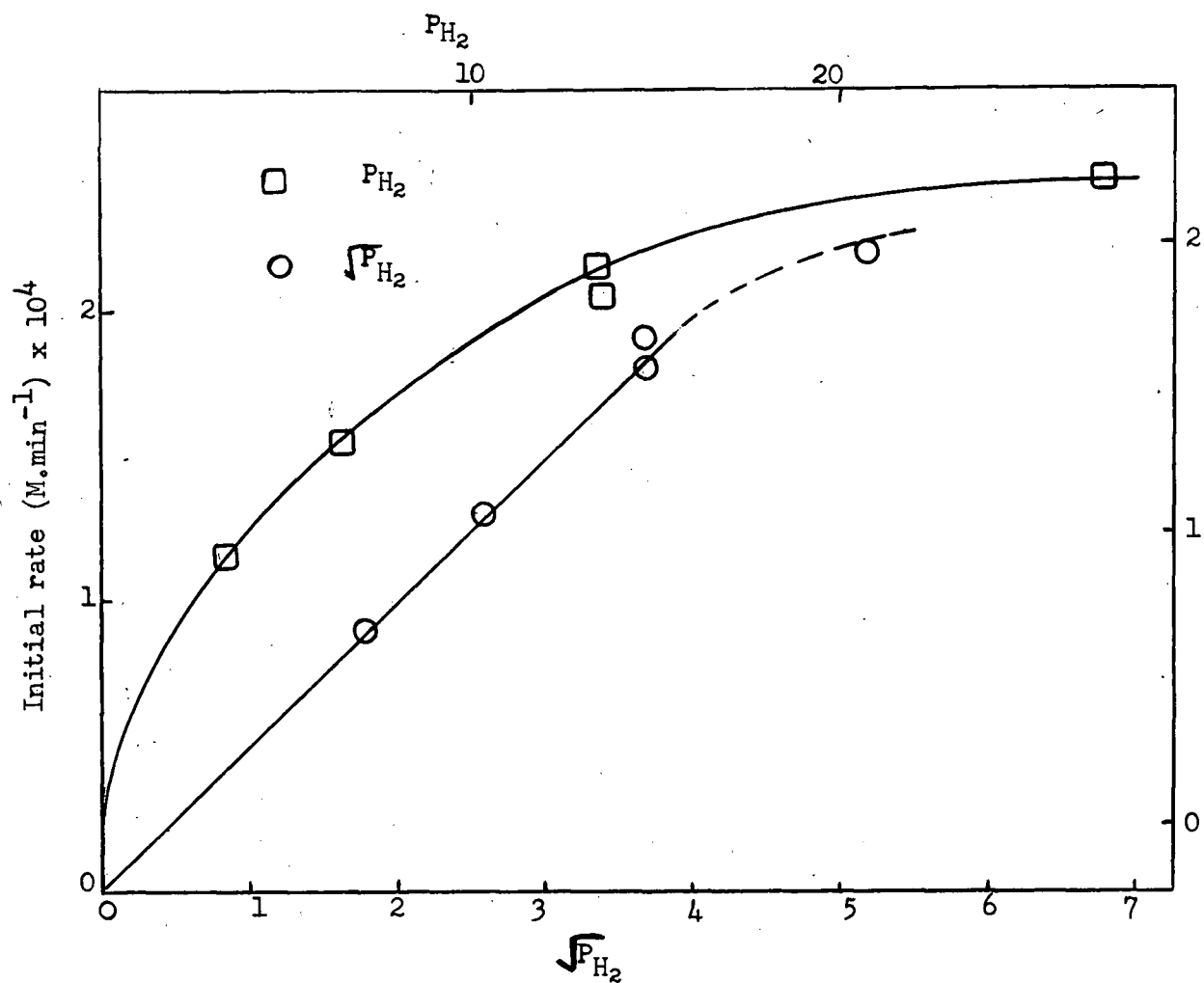
Experiments designed to test the dependence of the rate on hydrogen ion concentration were performed under the same conditions as described above, but with different initial hydrogen ion concentrations. The results shown in Figure 9 show that the rate decreases in an approximately linear fashion with increasing concentration of hydrogen ion.

(e) Temperature dependence.

Temperature variation was studied to determine the activation energy and thereby perhaps to be able to make some decision as to the nature of the rate limiting step. The measurements were made over the temperature range 130 to 160°C. The activation energy determined from Arrhenius' plot shown in Figure 10 appears to be 25 ± 2 kcal/M. This value for the activation energy strongly supports the view that the rate process measured is not one which is controlled by diffusion.

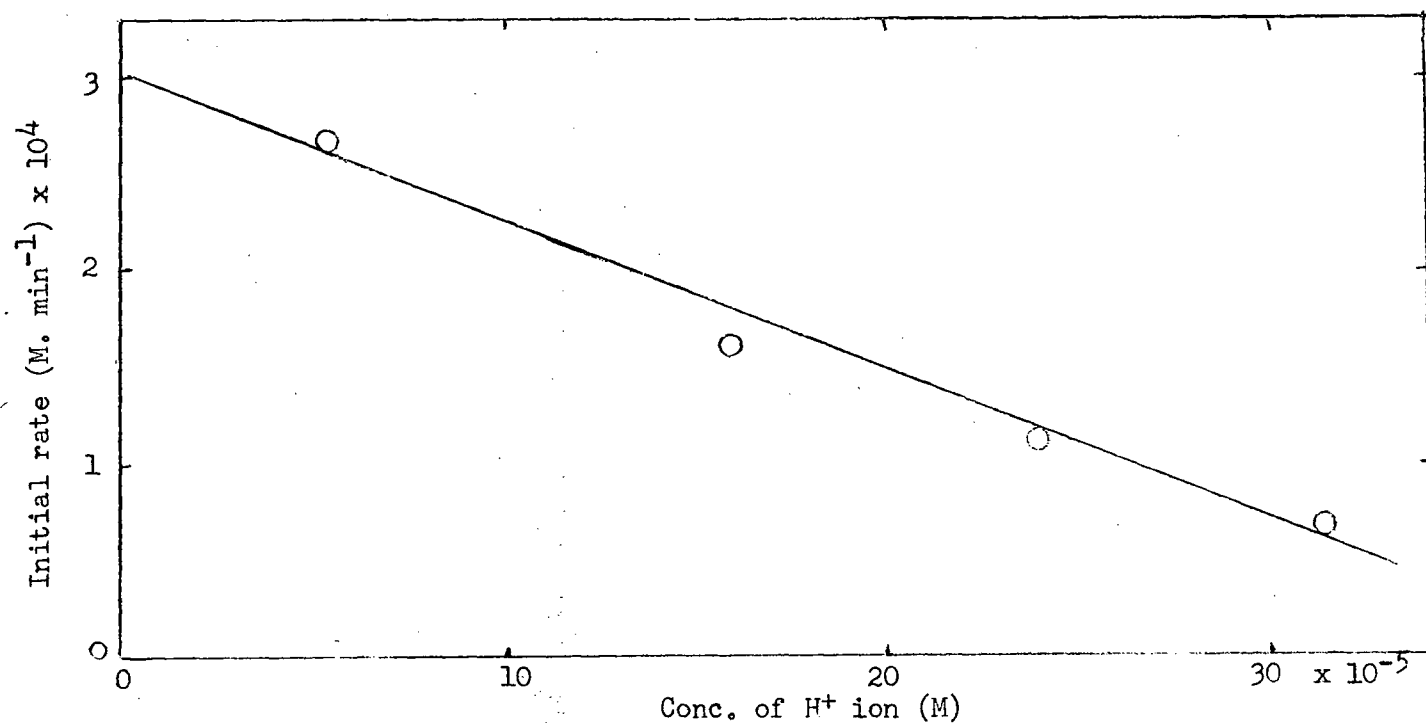
From the above experimental results, the rate equation can be expressed as

$$\frac{d[Ni^{++}]}{dt} = -k_1[S][H_2]^{1/2}[Ni^{++}] + k_2[S][H^+]$$



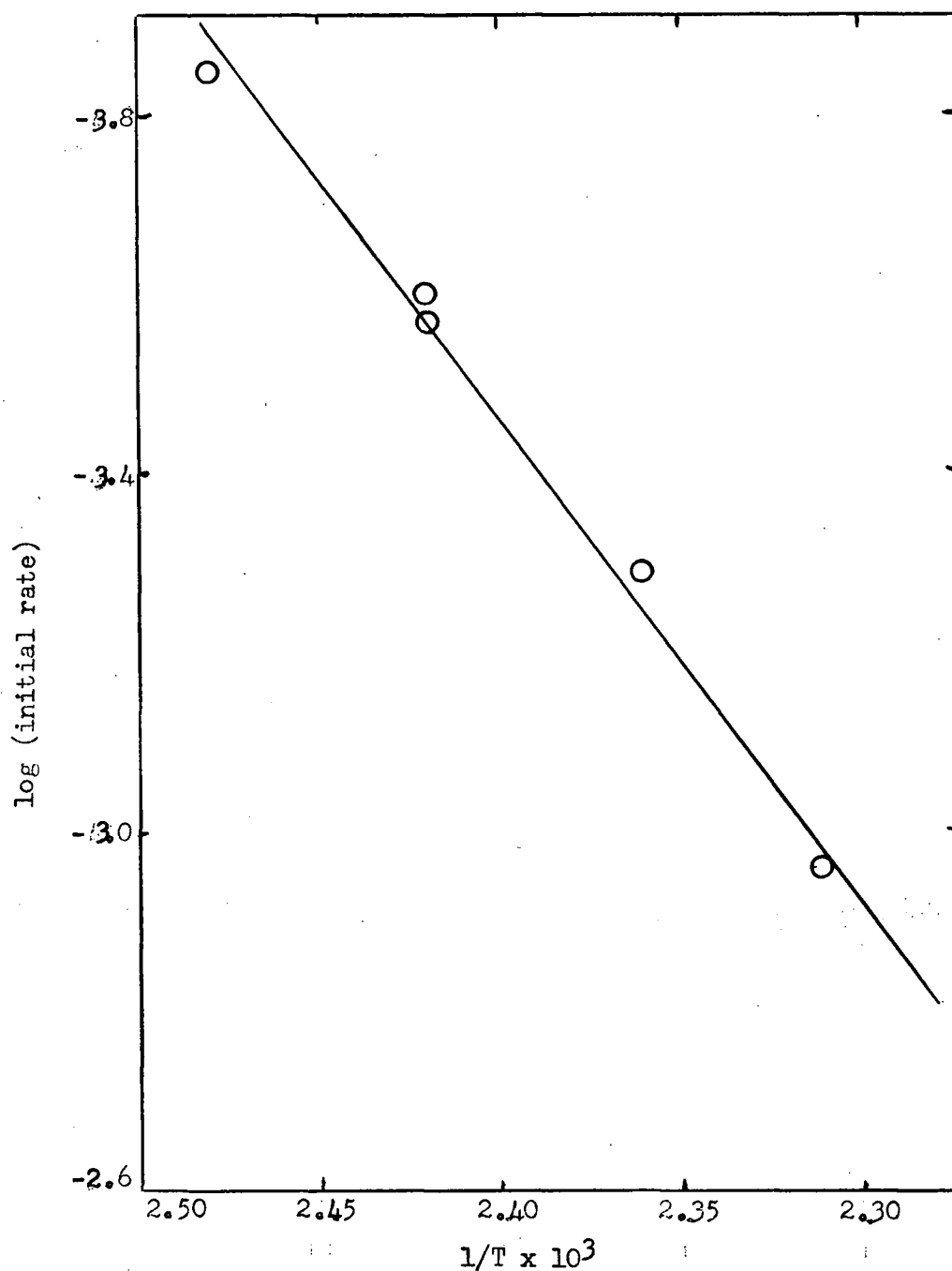
Conditions: Temperature 140°C; Catalyst 10 gms/1400 ml; Initial nickel concentration 0.005 M; Acetic acid 0.2 (M); Total acetate 0.06 M; Initial pH 4.25.

Fig. 8. Effect of hydrogen pressure on the initial rate.



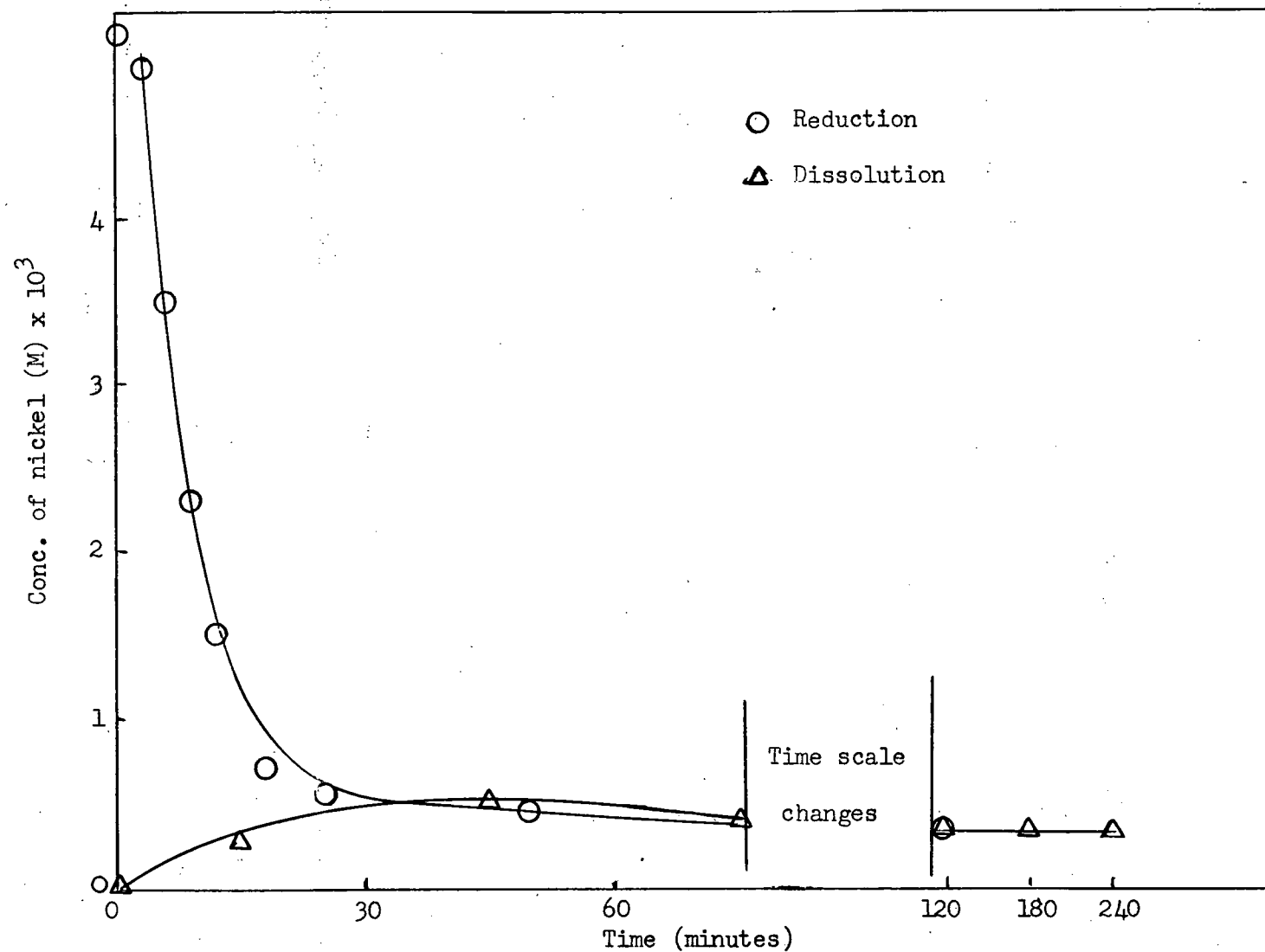
Conditions: Temperature 140°C; Catalyst 15 gms/1400 ml; Hydrogen 13.55 atm;
Initial nickel concentration 0.005 M.

Fig. 9. Effect of initial hydrogen ion concentration on the initial rate.



Conditions: Catalyst 15 gms/1400 ml; Hydrogen 13.55 atm;
 Initial concentration of nickel 0.005 M;
 Acetic acid 0.2 (M); Total acetate 0.06 (M);
 Initial pH 4.25.

Fig. 10. Plot of $\log(\text{initial rate})$ vs reciprocal of temperature.



Conditions: Temperature 140°C; Hydrogen 13.55 atm.;
Initial pH 4.25.

Fig. 11. A plot showing approach to equilibrium from dissolution of nickel and reduction of nickel.

where $[Ni^{++}]$ and $[H^+]$ are concentrations and $[S]$ is the catalyst surface area. Although the mechanism of the reduction reaction can not be deduced with any assurance from the above presented information, it is now clear that the activated complex is of the form $\text{surface} \begin{matrix} \swarrow Ni^{++} \\ H \end{matrix}$. The reverse reaction - nickel dissolution appears to go through an activated complex of the type $\text{surface} \begin{matrix} \swarrow H^+ \\ Ni \end{matrix}$. The form of the rate equation is similar to that found by Pawlek; but in this work, importance of hydrogen ion is clearly shown to be involved in the kinetics of rate of reduction.

Use of the equilibrium nickel concentrations for calculation of the thermodynamic equilibrium constant:

The experiments from which the nature of the dependence of the rate on the pressure of hydrogen and on the hydrogen ion concentration has been derived, were usually prolonged for a sufficient time to obtain the equilibrium nickel concentration. A plot showing the approach to equilibrium nickel concentration from reduction of nickel as well as dissolution of nickel is shown in Figure 11.

From the values of the equilibrium nickel concentration and corresponding hydrogen pressure and hydrogen ion concentrations, an attempt was made to evaluate the equilibrium constant for the reaction

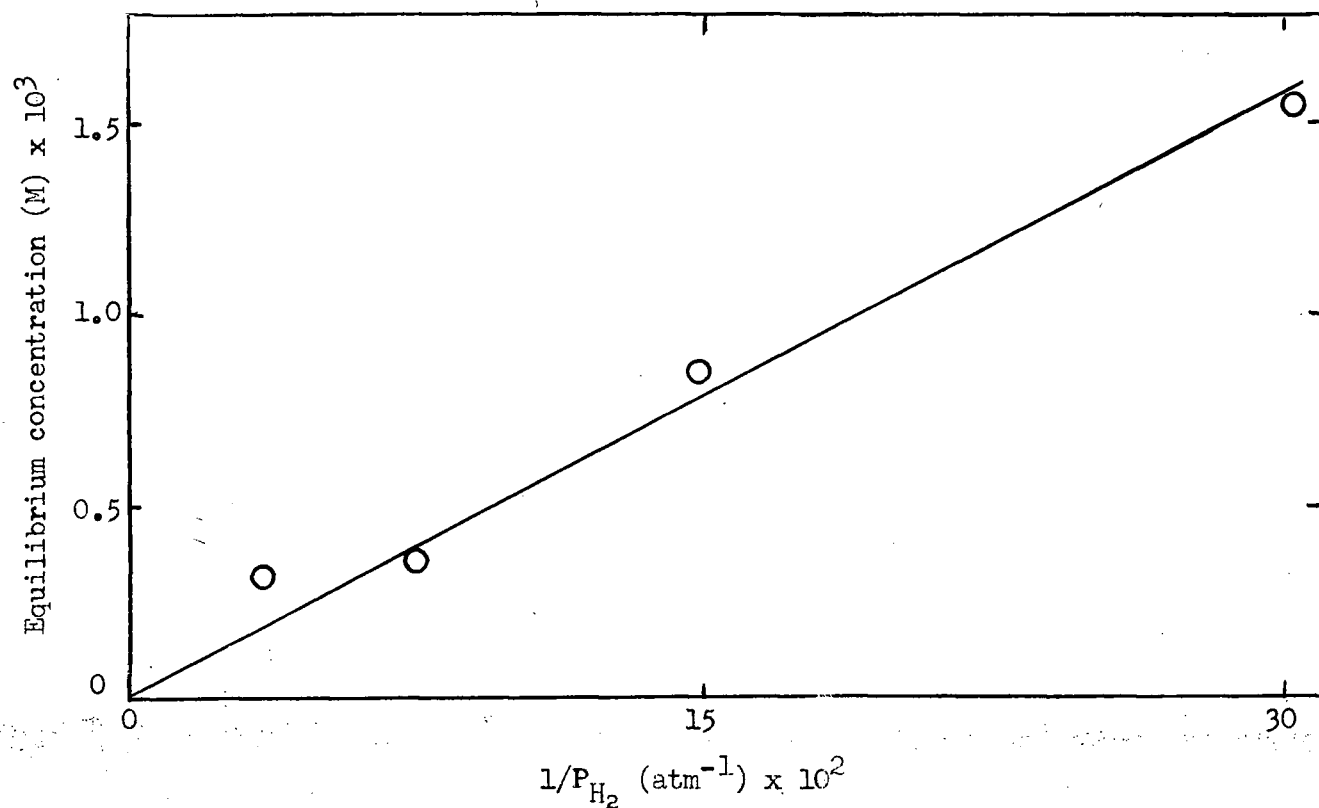


$$K = \frac{[H^+]^2}{[Ni^{++}]_{\alpha} [P_{H_2}]}$$

where $[Ni^{++}]_{\alpha}$ is the equilibrium nickel concentration

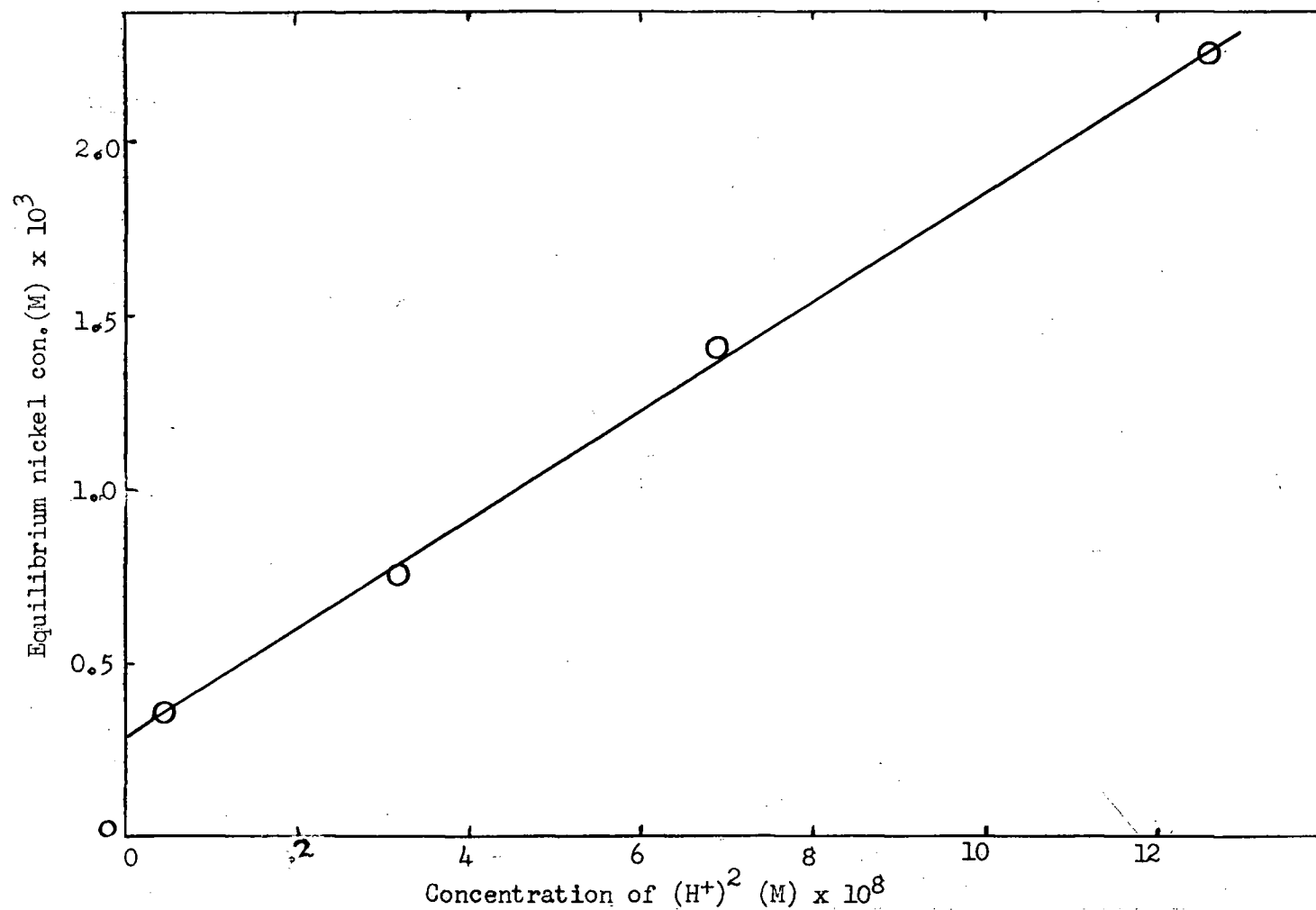
$[H^+]$ is the hydrogen ion concentration

$[P_{H_2}]$ is the pressure of hydrogen



Conditions: Initial pH 4.25; temperature 140°C; initial nickel concentration 0.005.(M)

Fig. 12. Plot of equilibrium nickel concentration vs reciprocal of hydrogen pressure.



Conditions: Temp. 140°C; catalyst 15/gms/1400 ml; Hydrogen 13.55 atm.; initial concentration of nickel 0.005 (M).

Fig. 13. Plot of equilibrium nickel concentration vs final hydrogen ion concentration.

A plot of the equilibrium concentration of nickel in solution against reciprocal of hydrogen pressure (at constant $[H^+]$) is given in Figure 12. It is seen to be a straight line passing through the origin in agreement with expectation.

The equilibrium nickel concentration was found to be a linear function of the square of hydrogen ion concentration as is seen in Figure 13. The straight line does not pass through the origin, since the values used for the hydrogen ion concentrations are those measured at room temperature. The difference will be a constant factor related to the intercept. Hydrogen ion concentration from the plot was found to be 1.6×10^{-4} at 140°C (the room temperature value being 7×10^{-5}). The values of constant k calculated with the help of corrected hydrogen ion concentration and slopes of plots 12 and 13, are 4.7×10^{-6} and 4.6×10^{-6} respectively. The value of constant k was calculated from thermodynamic data^{*} available for room temperature (extrapolated to 140°C , using relation $\Delta F_{T_2} = \Delta F_{T_1} - (T_2 - T_1) \Delta S$). The value obtained from this calculation is 7.6×10^{-6} . The agreement between experimental and calculated values is satisfactory, since validity of extending thermodynamic data to higher temperature, and of the assumption of the activity of nickel to be equal to that of total nickel present are very uncertain. The agreement indicates, however, that the assumptions used are not grossly incorrect.

* Refs. 15 and 16.

$$F_{Ni^{++}} = -11.53 \text{ kcal/m} \quad H_{Ni^{++}} = -15.3 \text{ kcal/m}$$

$$S_{Ni^{++}} = -38.1 \text{ cal/degree}$$

$$S_{H_2(\text{gas})} = +31.2 \text{ cal/degree}$$

$$S_{Ni(\text{solid})} = +7.1 \text{ cal/degree}$$

It is apparent that before further work is done on this problem, the nature of the catalyst surface must be studied in an attempt to understand and eliminate the various uncertainties and anomalies which persisted throughout the present work. After elimination of the troubles arising out of uncertainty in the nature of catalyst surface, further work may be enlightening in obtaining a more quantitative approach to the reaction mechanism.

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APPENDIX I

Experimental data pertaining to dissolution of copper

Table IA

Methyl amine

Run No.	Oxygen pressure (Atm.).	Ionic Strength (M)	Amine [A] concentration (M)	Rate (R) (Mg.cm ⁻² h ⁻¹)	$\frac{[A]^2}{R}$
1	7.9	0.10	0.568	5.80	0.05560
2	"	"	1.117	15.60	0.07998
3	"	"	0.801	10.20	0.06290
4	"	"	0.600	6.60	0.05450
5	"	"	0.396	3.40	0.04613
6	"	"	0.195	1.20	0.03169
7	"	"	1.492	22.60	0.09850
7R	"	"	"	22.70	0.09800
23	5.5	"	"	22.90	0.09700

Table IB

Methyl amine

Oxygen pressure - 7.9 atm. . . .

Run No.	Ionic strength (M)	Free amine [A] Conc'n. (M)	Aminium [AH ⁺] Conc'n. (M)	Rate (R) (Mg.cm ⁻² h ⁻¹)	$\frac{[A]^2}{R}$
16	0.10	0.192	0.040	2.10	0.0176
17	0.20	0.384	0.080	7.80	0.1880
18	"	0.576	0.120	16.70	0.1980
19	"	0.480	0.100	12.60	0.183
25	0.1	0.600	0.060	11.60	0.0310
26	"	0.400	0.040	6.20	0.0258
27	"	0.700	0.070	15.20	0.0322
29	"	0.500	0.050	8.60	0.0291

Appendix I (cont'd.)

Table IC

Methyl amine

Oxygen pressure - 7.9 atm.

Run No.	Ionic strength (M)	Free amine [A] Concentration (M)	Aminium Ion [AH ⁺] Concentration (M)	Rate (Mg.cm ⁻² h ⁻¹)
25	0.10	0.600	0.060	11.60
28	"	"	0.100	15.20
30	"	"	0.030	9.20
20	0.20	0.384	0.120	10.30
21	"	"	0.040	5.70
17	"	"	0.080	7.80

Table ID

Methyl amine

Oxygen pressure - 7.9 atm.

Run No.	Ionic strength (M)	Free amine [A] Concentration (M)	Aminium ion [AH ⁺] Concentration (M)	k ₃ (mg.cm ⁻² h ⁻¹ M ⁻¹) where k ₁ =1.86, k ₂ =20.8
25	0.100	0.600	0.060	140
28	"	"	0.030	160
30	"	"	"	137
26	"	0.400	0.040	156
27	"	0.700	0.070	124
29	"	0.500	0.050	136
20	0.200	0.384	0.120	140
21	"	"	0.040	142
17	"	"	0.080	135
16	0.100	0.192	0.040	100(excluded from mean)
18	0.200	0.576	0.120	169
19	"	0.480	0.100	167

Appendix I (cont'd.)Table IEMethyl amine.

Ionic strength = 0.20(M)

Oxygen pressure = 7.9 atm. . . .

Run No.	Free amine Concentration (M)	Aminium ion $[H^+]$ Concentration (M)	Rate $(mg.cm^{-2}h^{-1})$
8	0.800	0.195	50.0
9	"	0.050	18.0
10	"	0.125	52.0
11	"	0.025	15.0
12	"	0.040	17.0
13	"	0.100	55.6
14	"	0.075	48.8
15	"	0.05	18.0

Table IIAEthyl amine

Ionic strength = 0.10(M)

Run No.	Oxygen pressure (atm.)	Amine $[A]$ Concentration (M)	Rate (R) $(mg.cm^{-2}h^{-1})$	$\frac{[A]^2}{R}$
1	7.9	0.203	1.30	0.0316
2	"	0.400	3.60	0.0445
3	"	0.757	9.00	0.0636
4	"	0.916	12.60	0.0666
5	1.71	"	6.90	
6	2.74	"	11.00	
O.R.	7.90	0.535	6.40	0.0447
11	"	1.040	16.60	0.0650

Appendix I (cont'd.)

Table IIB

Ethyl amine

Oxygen pressure = 7.9 atm.

Run No.	Ionic Strength (M)	Free amine Conc'n. (M)	Aminium ion Conc'n. (M)	Rate $\text{mg.cm}^{-2}\text{h}^{-1}$	$k_3(\text{mg.cm}^{-2}\text{h}^{-1}\text{M}^{-1})$ where $k_1=2.27, k_2=20.0$
8	0.350	0.210	0.100	4.50	97.0
9	0.200	0.210	0.050	2.80	90.0
10	0.200	0.210	0.150	5.80	92.

Table IIIA

n-Butyl amine

Ionic strength = 0.10 (M)

Run No.	Oxygen pressure (atm.)	Amine [A] Concentration (M)	Rate (R) $(\text{mg.cm}^{-2}\text{h}^{-1})$	$\frac{[A]^2}{R}$
1	6.9	0.326	2.80	.0381
2	"	0.958	14.30	0.0641
3	"	"	15.00	0.0620
4	"	0.630	7.60	0.0523
5	"	0.187	1.10	0.0318
6	"	1.641	32.30	0.0844
7R	"	1.293	20.70	0.0809
8	1.71	"	10.20	
9	2.74	"	15.80	

Appendix I (cont'd.)Table IIIBn-Butyl amine

Ionic strength = 0.20 (M)

Oxygen pressure = 6.9 atm. . .

Run No.	Free amine Concentration (M)	Aminium ion Concentration (M)	Rate (R) (mg.cm ⁻² h ⁻¹)	k ₃ (mg.cm ⁻¹ h ⁻¹ M ⁻¹) where k ₁ =1.85; k ₂ =23.0
12	0.202	0.050	2.60	98.0
15	0.202	0.025	1.80	80.0
17	0.398	0.025	5.00	105.

Table IVA
Ammonia

Oxygen pressure = 7.9 atm. . .

Ionic strength = 0.10(M)

Run No.	Ammonia [A] Concentration (M)	Rate (R) (mg.cm ⁻² h ⁻¹)	$\frac{[A]^2}{R}$
1	0.65	5.45	0.00500
2	0.655	38.00	0.01130
3	0.310	14.10	0.00680
4	0.086	2.10	0.00352

Table IVBAmmonia

Oxygen pressure = 7.9 atm. . .

Ionic strength = 0.10 (M)

Run No.	Free ammonia [A] Concentration (M)	Ammonium ion [NH ₄ ⁺] Concentration (M)	Rate (R) (mg.cm ⁻² h ⁻¹)	$\frac{[A]^2}{R}$
5	0.404	0.0040	26.40	0.00615
6	"	0.0080	32.80	0.00495
7	0.303	0.0030	17.80	0.00515
8	"	0.0060	22.20	0.00414
9	0.202	0.0020	10.00	0.00407
10	"	0.0040	12.60	0.00322

Appendix I (cont'd.)

Table IVC.

Ammonia

Run No.	Free ammonia Concentration (M)	Ammonium ion Concentration (M)	k_3 (mg.cm ⁻² h ⁻¹ M ⁻¹) where $k_1 = 4.65$, $k_2 = 77$
5	0.404	0.0040	2350
6	"	0.0080	2410
7	0.303	0.0030	2340
8	"	0.0060	2420
9	0.202	0.0020	2600
10	"	0.0040	2540

APPENDIX II

Experimental data pertaining to catalytic
reduction of nickel ion by hydrogen.

Table I

Test on reproducibility, stirring effect,
and treatment of catalyst.

Run No.	Stirring rate RPM	Initial conc.'n. of nickel (M)	Initial rate (M.min ⁻¹) x 10 ⁴	Remarks
R	400	0.005	1.95	
R ₂	"	"	1.85	
R ₃	740	"	1.80	
R ₄	550	"	1.80	
R ₆	400	"	1.90	0.3 gms. FeAc ₃ added
R' ₁	"	"	1.95	Catalyst treated with acetic acid.

Conditions:

Concentration of acetic acid - 0.2M
 Concentration of total acetate - 0.06M
 Temperature - 14.0° ±1.5
 Catalyst - 10 gms/1400 ml.
 P_{H₂} - 13.55 atm.
 Initial pH - 4.25

Appendix II (cont'd.)Table II

Values of initial rate and initial concentration.

Run No.	Initial concentration of nickel (M)	Initial rate (M.min ⁻¹) x 10 ⁴
R ₁	0.005	1.95
R ₂	" "	1.85
R ₅	0.003	1.20
R ₇	0.0015	0.65
R ₈	0.010	3.90

Conditions:

Concentration of acetic acid	-	0.2M
Concentration of total acetate	-	0.06M
Pressure of hydrogen	-	13.55 atm. . .
Temperature	-	140°C
Initial pH	-	4.25
Catalyst	-	10 gms/1400 ml.
Stirring rate	-	400 RPM.

Table III

Initial rate and amount of catalyst

Run No.	Amount of catalyst in gms. for 1400 ml. of solution	Initial rate (M.min ⁻¹) x 10 ⁴
RR ₁	6	1.00
RR ₂	20	4.00
RR ₃	15	2.70
R ₁ and R ₂	10	1.95, 1.85

Conditions:

Concentration of acetic acid	-	0.2M
Concentration of total acetate	-	0.06M
Temperature	-	140°C
Pressure of hydrogen	-	13.55 atm. . .
Initial concentration of nickel	-	0.005M
Initial pH	-	4.25
Stirring rate	-	400 RPM

Appendix II (cont'd.)

Table IV

Initial rate and hydrogen pressure

Run No.	P_{H_2} in (atm.)	$\sqrt{P_{H_2}}$	Initial rate (M.min ⁻¹) x 10 ⁴
P ₁	27.2	5.22	2.20
P ₂	6.70	2.59	1.30
P ₃	3.30	1.82	0.90
R ₁ and R ₂	13.55	3.68	1.95, 1.85

Conditions:

Concentration of acetic acid - 0.2M
 Concentration of total acetate - 0.06M
 Temperature - 140°C
 Catalyst - 10gms/1400 ml.
 Stirring rate - 400 RPM
 Initial pH - 4.25

Table V

Initial rate and initial hydrogen ion concentration.

Run No	Conc'n. of acetic acid (M)	Initial conc'n. of hydrogen ion (M)	Initial rate (M.min ⁻¹) x 10 ⁴
H ₁	0.80	3.16 x 10 ⁻⁴	0.65
H ₂	0.40	1.60 x 10 ⁻⁴	1.60
H ₃	0.60	2.40 x 10 ⁻⁴	1.10
RR ₃	0.20	5.6 x 10 ⁻⁵	2.70

Conditions:

Catalyst - 15 gms/1400 ml.
 Temperature - 140°C
 P_{H_2} - 13.55 atm.
 Initial concentration of nickel - 0.005M
 Total concentration of acetate - 0.06M.

Appendix II (cont'd.)

Table VI

Initial rate and temperature

Run No.	Temperature °C.	$\frac{1}{T} \times 10^3$ (K)	Initial rate (M.min ⁻¹)	log (initial rate)
T ₁	160	2.31	1.1×10^{-3}	-2.96
T ₂	151	2.36	5.1×10^{-4}	-3.29
T ₃	130	2.48	1.4×10^{-4}	-3.85
RR ₃	140	2.42	2.5×10^{-4}	-3.60
R ₁	140	2.42	2.7×10^{-4}	-3.57 (rate converted to 15 gm/1400 ml)

Conditions:

Concentration of acetic acid - 0.2M
 Concentration of total acetate - 0.06M
 Catalyst - 15gms/1400 ml.
 Initial pH - 4.25
 Initial concentration of nickel - 0.005M
 Pressure of hydrogen - 13.55 atm.

Table VII

Final hydrogen ion concentration and corresponding
equilibrium nickel ion concentration.

Run No.	pH		CH ⁺² (final)	Equilibrium nickel Concentration (M) $\times 10^3$
	Initial	Final		
H ₁	3.50	3.45	12.6×10^{-8}	2.25
H ₂	3.80	3.75	3.2×10^{-8}	0.75
H ₃	3.62	3.58	6.9×10^{-8}	1.40
RR ₃	4.25	4.15	5.0×10^{-9}	0.35

Appendix II (cont'd.)

Table VIII

Hydrogen pressure and corresponding equilibrium
nickel concentration.

Run No.	Pressure of H ₂ (atm.).	$\frac{1}{P_{H_2}} \times 10^2$	Equilibrium concentration of nickel (M) $\times 10^3$
P ₁	27.2	3.67	0.30
P ₂	6.70	14.90	0.85
P ₃	3.30	30.30	1.55
RR ₂	13.55	7.40	0.35

PUBLICATIONS:

Sisir Coomar SIRCAR

1. Studies on the behaviour of bi-univalent salts in aqueous solution, Part VII, Copper Acetate, (with S. Aditya and B. Prasad), J. Indian Chem. Soc., 30, 633, 1953.
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5. Studies on the behaviour of uni-bivalent salts in aqueous solution, Part III, $\text{Na}_2\text{C}_2\text{O}_4$, (with B. Prasad), J. Indian Chem. Soc., (in press).
6. Studies on the behaviour of bi-bivalent salts in aqueous solution, Part II, ZnSO_4 , (with B. Prasad), J. Indian Chem. Soc., (communicated).
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