A KINETIC STUDY OF THE DISSOLUTION OF ZINC IN

AQUEOUS AMMONIA AND ETHYLENEDIAMINE

by

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ABSTRACT

The kinetics of the dissolution of zinc in aqueous solutions of ammonia and ethylenediamine under oxygen pressure were investigated at a temperature of $25^{\circ}C$. The variables investigated included free amine concentration, oxygen pressure and stirring rate.

Two regions of kinetic control were observed having different dependences on oxygen pressure. At low oxygen pressures, the rate of dissolution of zinc is first order in oxygen pressure, dependent on stirring rate and independent of the free amine concentration. At higher oxygen pressures, an adherent oxide layer is formed on the zinc surface and the rate of dissolution is first order with respect to free amine concentration and independent of oxygen pressure.

These results indicate that at low oxygen pressures the rate is controlled by the diffusion of oxygen to the zinc surface; and at high oxygen pressures, the rate of reaction is chemically controlled at the film-solution interface.

ACKNOWLEDGEMENT

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INTRODUCTION

The corrosion resistance of zinc is of great industrial importance. The greatest use of zinc is in the galvanizing industry where zinc coatings are used to protect iron and steel on exposure to the atmosphere, to natural waters and to sea water, (or wherever corrosion resistance is desired). As well, much zinc is used in rolled products where resistance to atmospheric corrosion is of prime importance. The protective effect of zinc is twofold; it affords sacrificial protection to many other metals and a film of corrosion products is formed which limits the eventual rate of the corrosion of zinc.

A great deal of work has been done to determine corrosion rates of zinc under exposure to various atmospheric conditions and much empirical data has been tabulated. [1,2,3] It is reported that on exposure to the atmosphere, a protective coating of zinc oxide is first formed. This is converted in time to basic zinc carbonate in indoor atmospheres, and to basic zinc carbonate, sulphate or both in outdoor atmospheres. Both these coatings are very adherent and have no tendency to flake off.

The corrosion rates of zinc in aqueous media have also been studied extensively. It has been found that domestic waters are less corrosive to zinc than distilled waters [4] because of the presence of anions such as carbonates and silicates which form zinc salts of low solubilities.

Corrosion rates are low in the pH range of 6 to 12.5 and domestic waters generally fall within this range. In acid and alkali solutions, the rate of corrosion is high in comparison with other metals. Very low concentrations of most of the common acids give rates which render zinc useless under these conditions. The attack of alkalis is less severe but still high. Aqueous ammonia is reported to corrode zinc rather readily with the formation of a soluble complex hydrate of zinc and ammonia.[5]

Zinc is anodic in aqueous solution to most of the common industrial metals -- iron, nickel, lead, copper, aluminum and their various alloys.[5] This galvanic behaviour of zinc has led to its use as sacrificial protection for aluminum in chemical equipment, for iron and steel in oil and gas fields, for brass on ships hulls, and for steel pilings in sea water.

Although much empirical data is available on the corrosion of zinc under a variety of conditions, little attempt has been made to examine the fundamental mechanisms. A basic difficulty is the thermodynamic instability of zinc with respect to the decomposition of water. This reaction is normally prevented by the high hydrogen overvoltage on zinc, but traces of metal impurities having a lower hydrogen overvoltage within the system can cause the addition of an electrochemical reaction to the chemical reaction under investigation. If such impurities are not excluded, corrosion studies in aqueous media cannot be readily interpreted in terms of basic mechanisms.

Recently studies have been carried out within the Department of Mining and Metallurgy on the dissolution of copper in ammoniacal and organic amine solutions.[10,11] It was felt that a comparative investigation

of zinc would be interesting in view of the rather different complexing tendencies of the two metal ions. Formation constants for their complexes with ammonia and ethylenediamine are known and are shown in Table 1.

TABLE I

Complex	Formation Constant	Reference
$Cu(NH_3)_4^{++}$	13.32	6
$Cu(en)_2^{++}$	19.60	7
$Zn(NH_3)_4^{++}$	9.46	6
$Zn(en)_3^{++}$	12.09	7,8,9

These show the greater stability of the copper amine complexes over the corresponding complexes of zinc. Moreover, since Zn:O complexes are preferred over Cu:O complexes, it would be expected that the oxidation of zinc in aqueous ammonia and amine solutions would indicate a greater tendency for formation of oxide or hydroxide films than was observed in the analogous copper study. In addition, there is considerable interest at the present time in the behaviour of zinc electrodes in the $Zn-Ag_2O$ wet-storage battery. This useful battery is greatly handicapped by the short life of the battery due to corrosion of the zinc electrodes in the alkali battery electrolyte. It was thought that a kinetic study of zinc in amine solutions would be preliminary to an extensive kinetic investigation of zinc under the conditions experienced with the $Zn-Ag_2O$ battery.

Scope of the Present Investigation

It was the purpose of this investigation to determine the kinetics of the dissolution of zinc in aqueous ammonia and ethylenediamine, a comparable organic amine.

The behaviour of zinc in the above solutions has been studied in respect to the effect of oxygen pressure, concentration of the amine stirring rate, presence of ammonium ion, and the area of the zinc sample.

EXPERIMENTAL

Preparation of the Zinc Samples

The zinc used in all the recorded experiments was supplied by the Consolidated Mining and Smelting Company of Canada Limited. They report a total impurity content of 4 parts per million (2 ppm Cu, 1 ppm of Cd and Pb). It was supplied in the form of round bar stock, approximately $\frac{3}{4}$ inch in diameter and 8 inches long. The bars were machined in a lathe to remove outer layer irregularities and cut into cylinders $\frac{1}{2}$ inch in diameter and $\frac{1}{2}$ inch in length. Three such cylinders were mounted in lucite in a metallographic specimen mounting press. Four such specimens were prepared and used throughout the whole series of experiments. In each, the area of zinc metal exposed to reaction was 2.80 cm.^{2}. This surface consisted of long dendritic crystals radiating out from the centre. No modification of this crystal structure was attempted in order to assure no impurity contamination of the high-purity zinc.

Before each dissolution experiment, the zinc specimen was polished, a 2/0 polishing paper being the final paper used. This was followed by etching with a 9 to 1 ethanol and nitric acid etchant.[12] Etching times of 3 minutes were required to remove the outer stressed layers of zinc.

Preparation of Solutions

1. Dissolution Solutions

Solutions of known ammonia concentration were prepared by diluting measured amounts of Nichols C.P. Ammonium Hydroxide up to the required 2 litres, by the addition of distilled water. Sodium perchlorate added to the dissolution solution was supplied by the G. Frederick Smith Chemical Co. This was added in the form of a 100 ml. aliquot of a 2 M. sodium perchlorate solution.

Ethylenediamine solutions were prepared similarly using Carbide and Carbon Chemical supplied ethylenediamine (98.7% en, remainder water).

The base concentration of each solution was determined by titration against standard 0.5 N HCl using methyl red as an indicator with the ammonia solutions and methyl orange with the en solutions. Potential titrations with a glass electrode were made in each case to determine the pH of the end point, which would act as a guide to the choice of indicator.

2. Polarographic Solutions

The required ammonium hydroxide and ammonium chloride solutions were prepared from Nichols C.P. Ammonium Hydroxide and Nichols C.P. Hydrochloric Acid. Gelatin and sodium sulphite solutions, prepared daily, utilized Baker and Adamson chemicals. In all cases distilled water was used to dilute the solutions to the required concentration.

Apparatus

The series of experiments necessary for this investigation was conducted in an autoclave with a maximum working pressure of 8 atmospheres.

The autoclave was fabricated from 316 stainless steel. All parts that actually entered the solution were made of titanium (see Figure 1). However, because zinc is strongly anodic to both commercial grade titanium and steel, it was necessary to coat all interior parts of the autoclave with a chemically inert material. An air-drying heresite primer supplied by Industrial Coatings, Vancouver, B.C., was used. This coating had to be renewed approximately every 4 days to assure a complete and unbroken cover. A polyethelene liner was used to contain the solution. The lucite mounted zinc specimen was held by means of a stainless steel rod screwed into the autoclave cover plate.

Agitation of the solution was provided by two four-bladed impellers mounted on a single shaft sweeping out a cylinder 3 inches in diameter. The rotational speed of the impeller throughout the series of experiments was 860 rpm. A second speed of 575 rpm was used for a few experiments as will be indicated later within the thesis. The zinc specimen was mounted such that the corrosion face was tangential to the swept-out cylinder and was spaced 1/8 inch from the circumference of this cylinder.

Oxygen and nitrogen, supplied by the Canadian Liquid Air Company, were delivered from standard 2000 psig bottles through standard two stage pressure regulators. As a further check, a 0-100 psi pressure gauge was set in the delivery line.

Temperature control was maintained by means of a heating coil immersed in the autoclave solution and connected with a thermostatically controlled water bath. Water at the required temperature was forced through the heating coil by means of a centrifugal pump. A mercury control thermo-regulator set in a well of the autoclave cover was used to maintain control of the temperature of the water bath. The temperature in all experiments
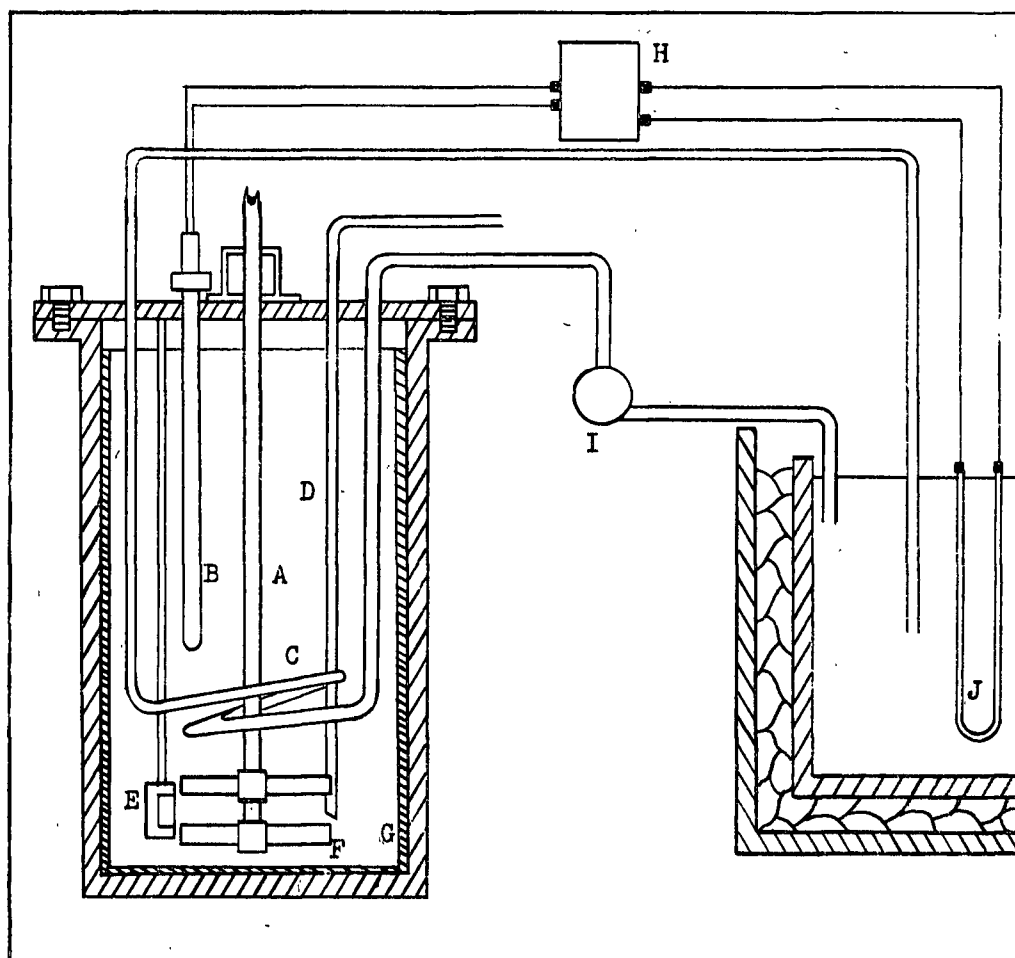
A. Shaft
B. Thermoregulator well
C. Heating coil
D. Sampling Tube
E. Zinc sample

F. Impeller
G. Autoclave Liner
H. Relay
I. Pump
J. Heater

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

was maintained at $25 \pm 0.1^{\circ}C.$

Experimental Procedure

In all experiments an autoclave solution volume of 2 litres was used. Measured amounts of ammonium hydroxide or ethylenediamine and sodium perchlorate solution were diluted to this volume and charged into the auto-clave. The solution was brought up to temperature, the zinc specimen was affixed in place and the autoclave cover bolted down. The impeller was then rotated at its fixed speed, the autoclave was flushed three times with oxygen and the desired oxygen pressure applied. An initial 50 ml. aliquot was removed from the solution to be used for base concentration and pH determinations. A further 40 ml. sample was withdrawn for zinc determination. Withdrawal of the second sample constituted zero time. Further 40 ml. samples were withdrawn at suitable time increments during the course of the run, which generally lasted for 90 minutes.

Analytical Procedure

All analyses for zinc content during the course of dissolution were made using a Sargent Polarograph Model XXI fitted with a dropping mercury electrode cell.[14] Volume of the cell was 20 ml. and drop time was constant at 3.5 seconds.

The polarographic sample solution for determination of zinc in ammonia solutions consisted of:

  i) 25 mls.   1N NH_4Cl

  ii) 10 mls.   1N NH_4OH

  iii) 10 mls.   unknown Zn^{++} sol'n drawn from 40 ml. sample

  iv) 2 mls.   0.2% gelatin (by weight)

  v) 4 mls.   2M Na_2SO_3

Experimentation proved that this was the most suitable polarographic solution.

This concentration of gelatin completely removed the very large polarographic

wave maxima normally observed with zinc. The use of Na_2SO_3[15] was found to

remove oxygen from the polarographic solution more completely and more

rapidly than did the use of nitrogen bubbled through the solution. The

resulting solution was allowed to stand for 15 minutes to allow for complete

removal of dissolved oxygen.

The supporting electrolyte for determination of zinc in en solutions

had to be modified slightly. Use of the above solution gave rise to a

three-step polarographic wave for zinc, indicating in all probability the

step-wise reduction of the triamine complex. After lengthy experimenting,

it was found that the most suitable solution for polarographic use was

obtained if 2N NH_4Cl and 2N NH_4OH were used in the same proportions as above.

Separate plots of polarographic wave height versus zinc contained

within a 10ml. sample are shown in Figures 2 and 3.

RESULTS

Preliminary Experiments

In order to determine the possible extent of electrochemical

decomposition of water, the first experiments in this investigation were

carried out at atmospheric pressure in a glass beaker with agitation by

a Teflon covered magnetic stirrer. The zinc used was 99.9% Zn and had

been melted under a reducing flame and cast into cylinders in a graphite

mold. The resulting cylinders, $\frac{3}{4}$ inch in diameter, were mounted in bakelite

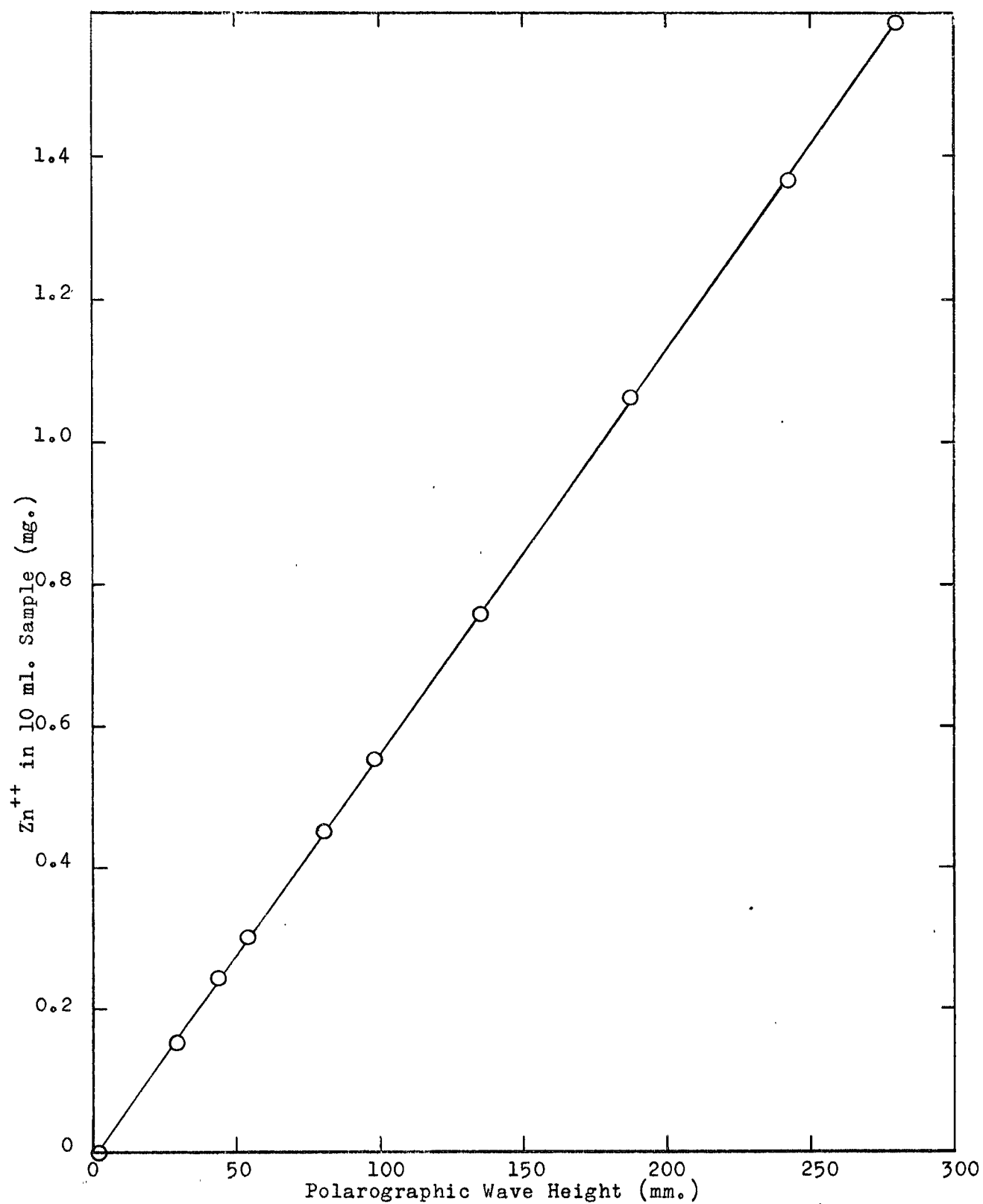and immersed in the ammoniacal solution (1.0N NH_4OH). Rates of dissolution

<u>Figure 2.</u> Calibration curve for determination of zinc in ammonia
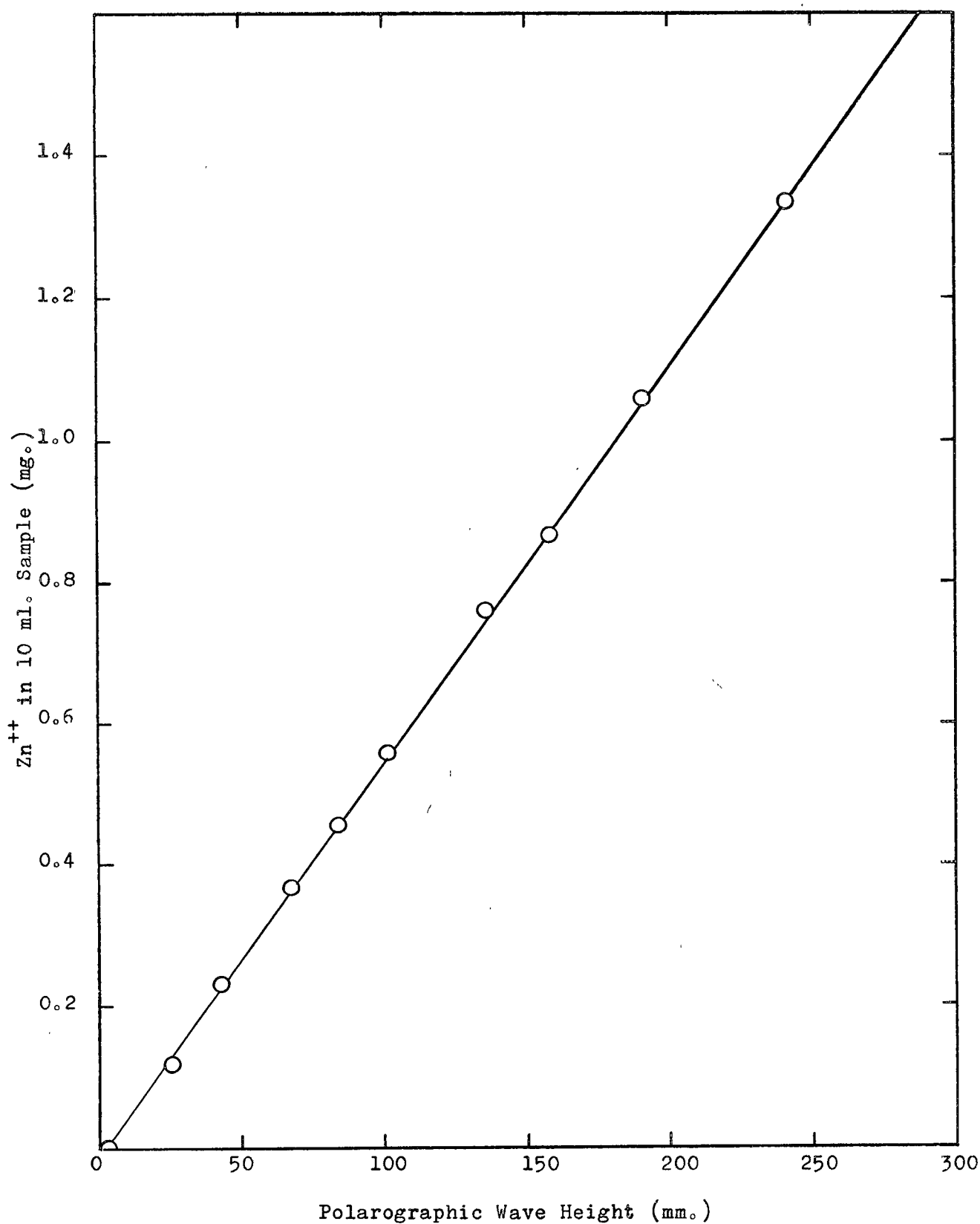solutions.

<u>Figure 3</u>. Calibration curve for determination of zinc in
ethylenediamine solutions.

were very slow but varied widely from one run to the next. The surface of
the zinc showed etch pits and preferential corrosion at grain boundaries.
It would appear that galvanic cells were active in the dissolution process,
and as a result of melting and casting, grain boundaries, through the col-
lection of impurities, were anodic to the bulk of the grains.

The next experiments were carried out under oxygen pressure in
the autoclave using a titanium liner and direct immersion of the titanium
and stainless steel parts of the autoclave in the reaction solution.
To avoid the preferential grain boundary dissolution, high purity C.M. and S.
zinc (99.9996% Zn) was used in the as-received condition since it was felt
that any melting process would add to the impurity content or at least
cause local concentration of impurities already present. Studies were
carried out in 0.5M and 1.0M NH_4OH and again rates were observed which
varied widely from run to run. An examination of the zinc surface showed
that preferential grain boundary dissolution had almost disappeared but
etch pits were common.

Although corrosion pits are not positive evidence of galvanic
cells, it was considered advisable to minimize the possibility of such by
exclusion of stainless steel and titanium surfaces from the solution,
therefore taking full advantage of the high hydrogen overvoltage of zinc.

This was done by covering all metal parts in contact with the
solution with a chemically inert layer. A heresite primer was painted on
all the autoclave parts and was found to be completely satisfactory. To
contain the solution, a glass autoclave liner was first tried but proved
to be too fragile. A polyethylene 4 litre beaker was found to be satis-
factory, showing no corrosion when used with the ammoniacal solutions or

physical damage on repeated insertion and removal from the autoclave.

Under these conditions, pitting and grain-boundary corrosion of the zinc surface were no longer observed and kinetic studies now gave reproducible results.

It should be noted, however, that inspection of the heresite layer was necessary after each run. Pin-hole flaws did develop but their presence could be detected easily at the end of an experimental run by the appearance of the zinc sample which would show many small corrosion pits. When breaks in the coating developed, the autoclave parts were repainted and allowed to air-dry for 12 hours. Drying in a warm-air blast was found to leave the coating in a brittle condition which resulted in breakage at the corners of the impeller. Drying at room temperature was found to be more satisfactory.

Reproducibility of Experimental Results

A series of experiments was carried out at constant ammonia concentration, oxygen pressure, stirring rate, and temperature in order to determine the reproducibility of the experimental technique. The results of these tests are shown in Table II.

TABLE II

Determination of Reproducibility

Run No.	Rate of Dissolution $(mgZn/cm.^2/hr.)$	Deviation $\%$
1	45.1	-1.95
2	47.0	+2.17
3	46.1	+0.22
4	45.8	-0.44
Average	46.0	

Conditions: Temperature $25^{\circ}C$, stirring rate 860 rpm., oxygen pressure 5.1 atm., NH_4OH 1.0M, $NaClO_4$ 0.1M

Reproducibility for duplicate experiments was considered to be of the order of 4%. If, during a series, deviations from the experimental curve were greater than 5%, the heresite coating on the autoclave was replaced and the experiment repeated.

Effect of Surface Area

Another series of tests was carried out in the initial stages of this investigation to check on the effect of the surface area of zinc exposed to the reaction solution. The results are shown in Table III and demonstrate that surface area has no effect on the rate. In all further experiments, the zinc sample had a surface area of 2.80 cm.^{2}

TABLE III

Effect of Surface Area on Rate of Dissolution of Zinc

Surface Area of Zinc ($cm.^2$)	Rate of Dissolution ($mgZn/cm.^2/hr.$)	Deviation %
2.80	6.9	-1.4
2.80	7.1	+1.4
2.01	7.0	0
2.01	6.9	-1.4
Average	7.0	

Conditions: Temperature 25°C, stirring rate 860 rpm., oxygen pressure 6.4 atm, NH_4OH 0.3M, $NaClO_4$ 0.1M.

This series of tests also served as a further check on the reproducibility of rates.
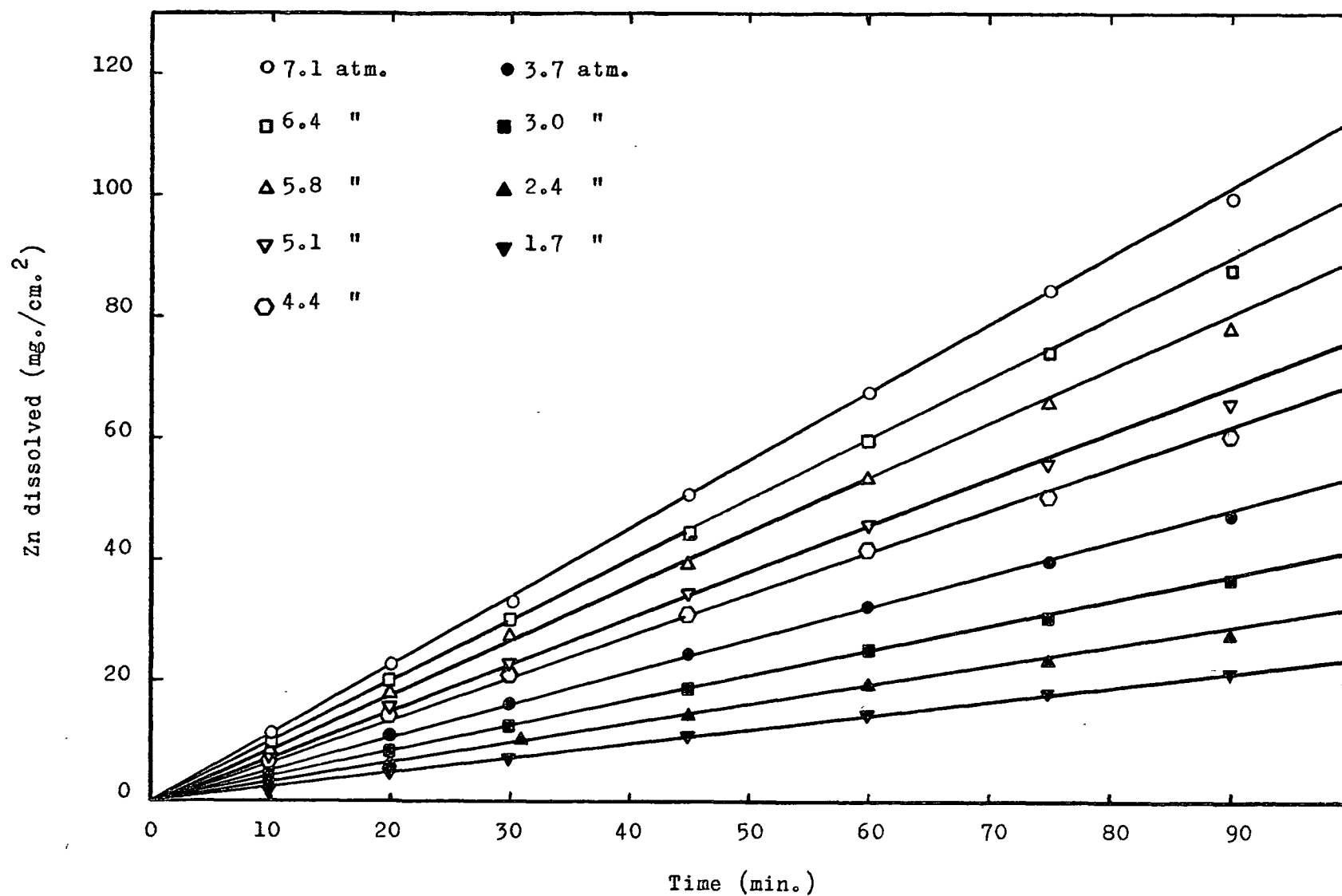
Ammonia System

Effect of Oxygen Pressure

The effect of oxygen pressure on the rate of dissolution of zinc was investigated initially in 1.0M NH_4OH. Over a wide range of O_2 pressures, 1.7 to 7.1 atm., linearity of the family of rate curves was

good (Figure 4) and when rate was plotted versus oxygen pressure, the resulting curve showed a first order dependence of rate on O_2 pressure (Figure 8).

Experiments were next carried out in 0.5M NH_4OH over the same range of O_2 pressures. The same rates of dissolution were observed over the range of O_2 pressures 2.4 to 6.4 atm. (Figure 5). Within this range, it could then be concluded that rate of dissolution of zinc was first order in oxygen pressure and zero order in ammonia concentration.

At higher O_2 pressures, in 0.5M NH_4OH, the rate showed a sudden decrease, reaching a constant value of 11 mg $Zn/cm.^2/hr.$ The first indications of such a rate transition had been noted in the experimental run at 6.4 atm. O_2 pressure, in which the rate changed abruptly after 40 minutes but still maintained linearity. On removal from the autoclave, the surface of the zinc sample showed interference colours indicating the presence of a thin coherent film. The surface of the zinc, after runs at 6.8 and 7.1 atm., showed the presence of an opaque white film. Again, as with 1.0M NH_4OH solutions, all curves were linear.

A 0.3M NH_4OH solution was next investigated over an O_2 pressure range of 2.4 to 6.4 atm. (Figure 6) Parallel results were obtained: first order dependence on O_2 pressure from 2.4 to 4.4 atm. and a sudden decrease in rate at higher pressures. The value of the linear rate at high pressures, 7.0 mg $Zn/cm.^2/hr.$ indicated that rates in this region had become first order in NH_4OH concentration and zero order in oxygen pressure. The same break occurred in the curve for an oxygen pressure of 4.4 atm. which corresponds to the transition from one rate-controlled region to the other.

120

100

80

60

40

20

0

Zn dissolved (mg./cm.^{2})

○ 7.1 atm.   ● 3.7 atm.

□ 6.4 "   ■ 3.0 "

△ 5.8 "   ▲ 2.4 "

▽ 5.1 "   ▼ 1.7 "

⬡ 4.4 "

0   10   20   30   40   50   60   70   80   90

Time (min.)

Conditions: Temperature 25°C, stirring rate 860 rpm., NH$_4$OH 1.0M, NaClO$_4$ 0.1M.

Figure 4 Rate curves for the dissolution of Zn in 1.0M ammonia solution at various oxygen pressures.
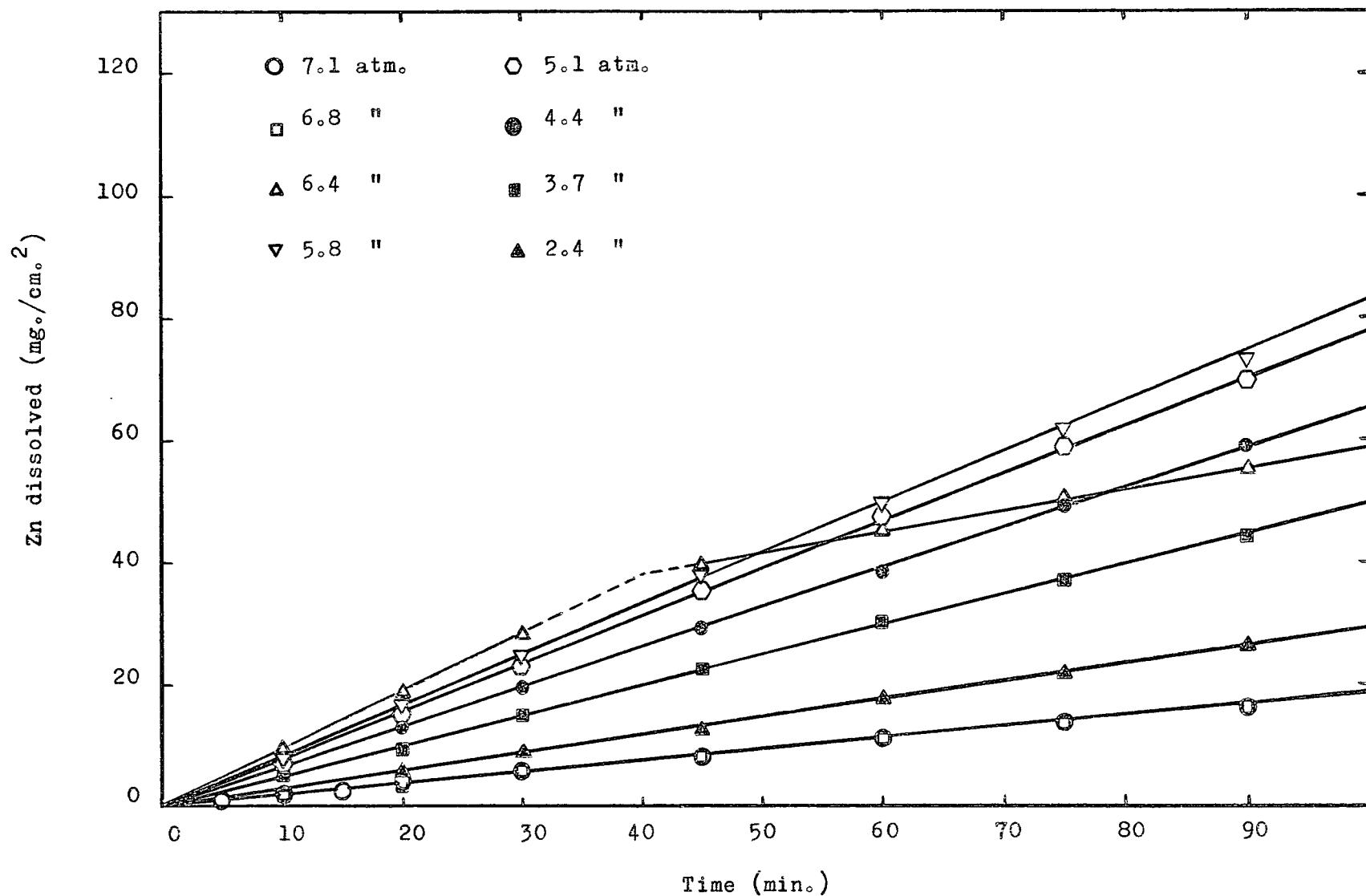
Conditions: Temperature $25^{\circ}C$, stirring rate 860 rpm., NH_4OH 0.5M, $NaClO_4$ 0.1 M

<u>Figure 5</u> Rate curves for the dissolution of Zn in 0.5M ammonia solution at various oxygen pressures.

Conditions: Temperature $25^\circ C$, stirring rate 860 rpm., NH_4OH $0.3M$, $NaClO_4$ $0.1M$

Figure 6   Rate curves for the dissolution of Zn in $0.3M$ ammonia solution at various oxygen pressures.
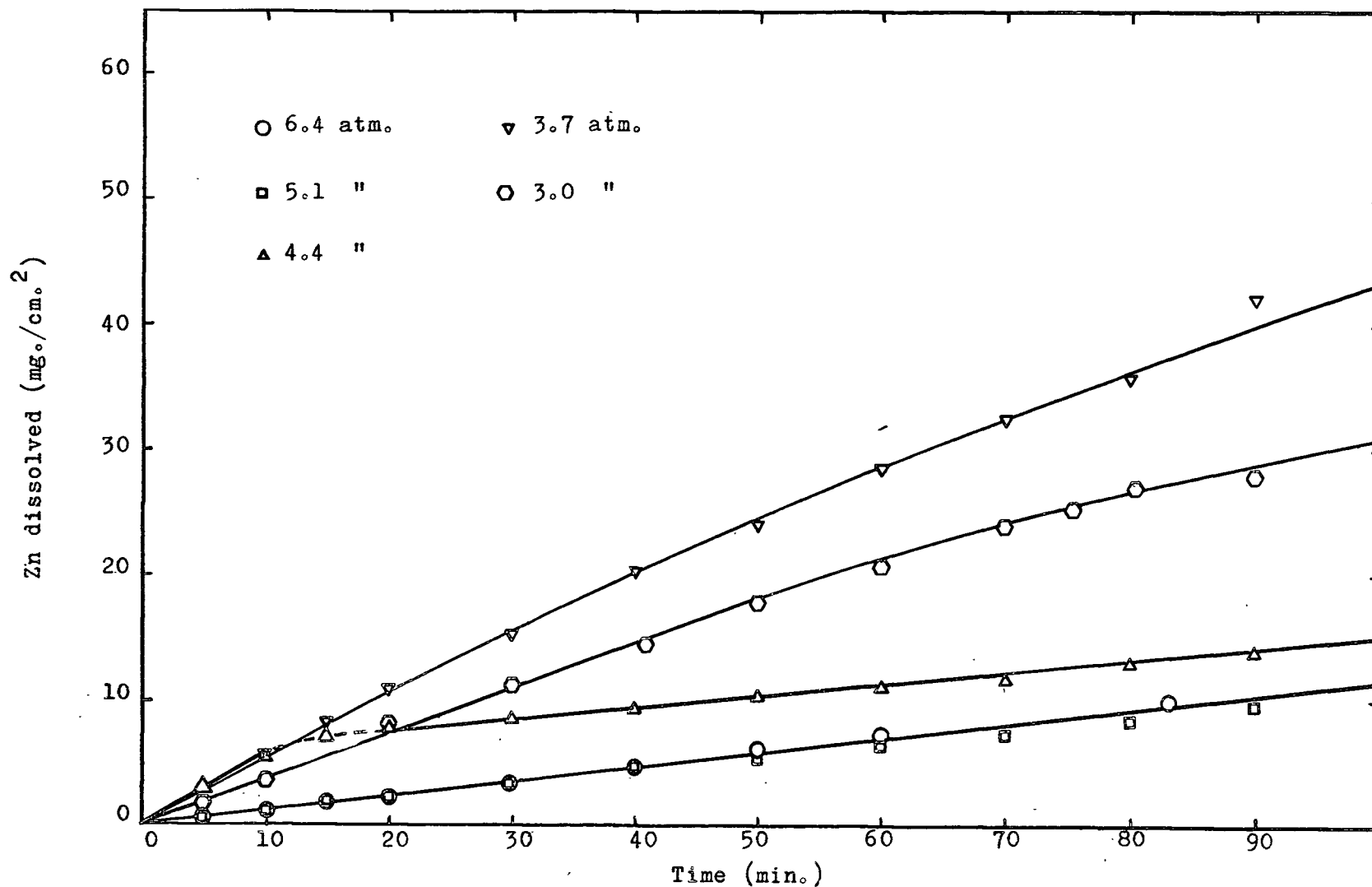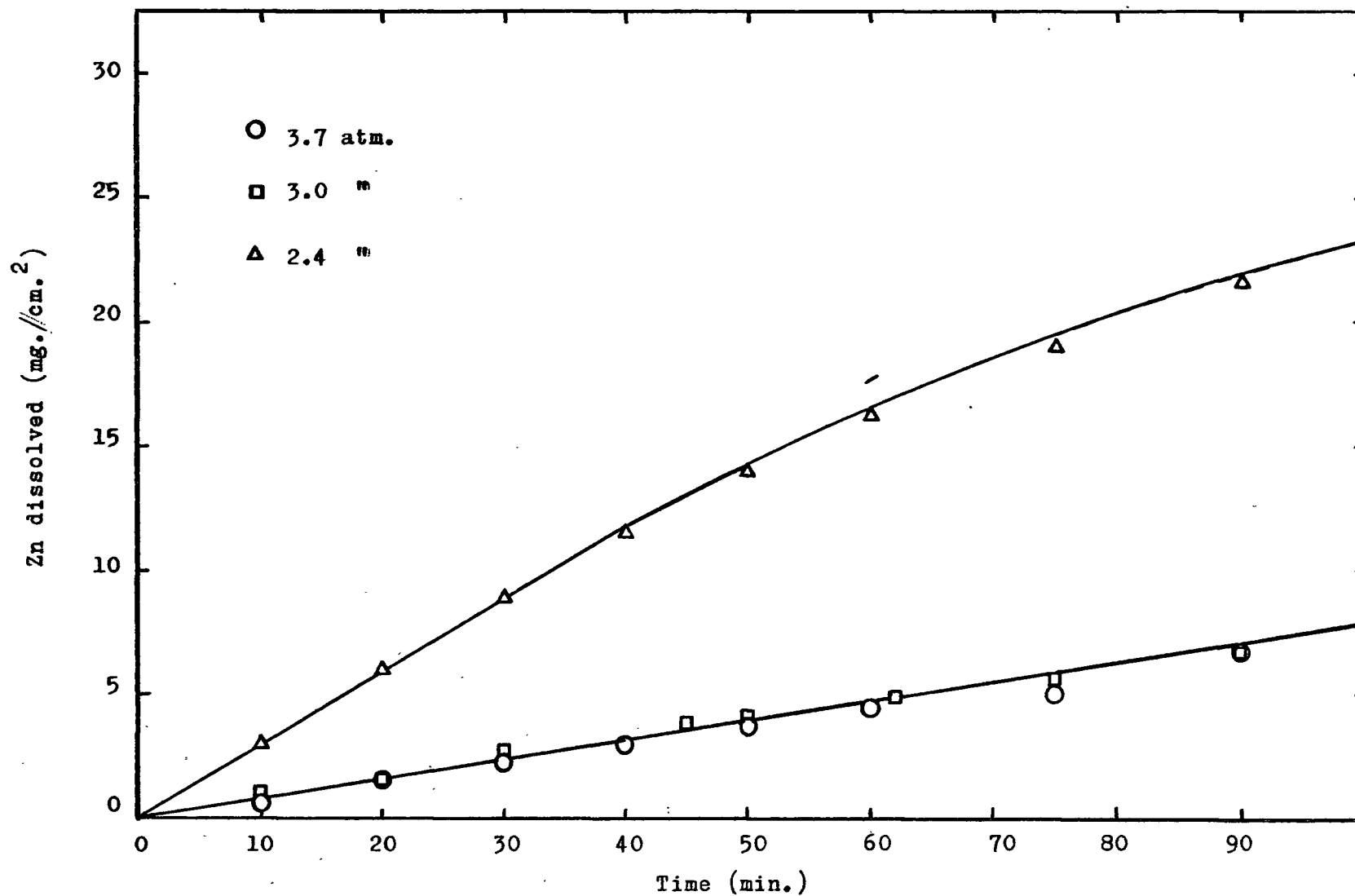
Conditions: Temperature $25°C$, stirring rate 860 rpm., NH_4OH 0.25M, $NaClO_4$ 0.1M.

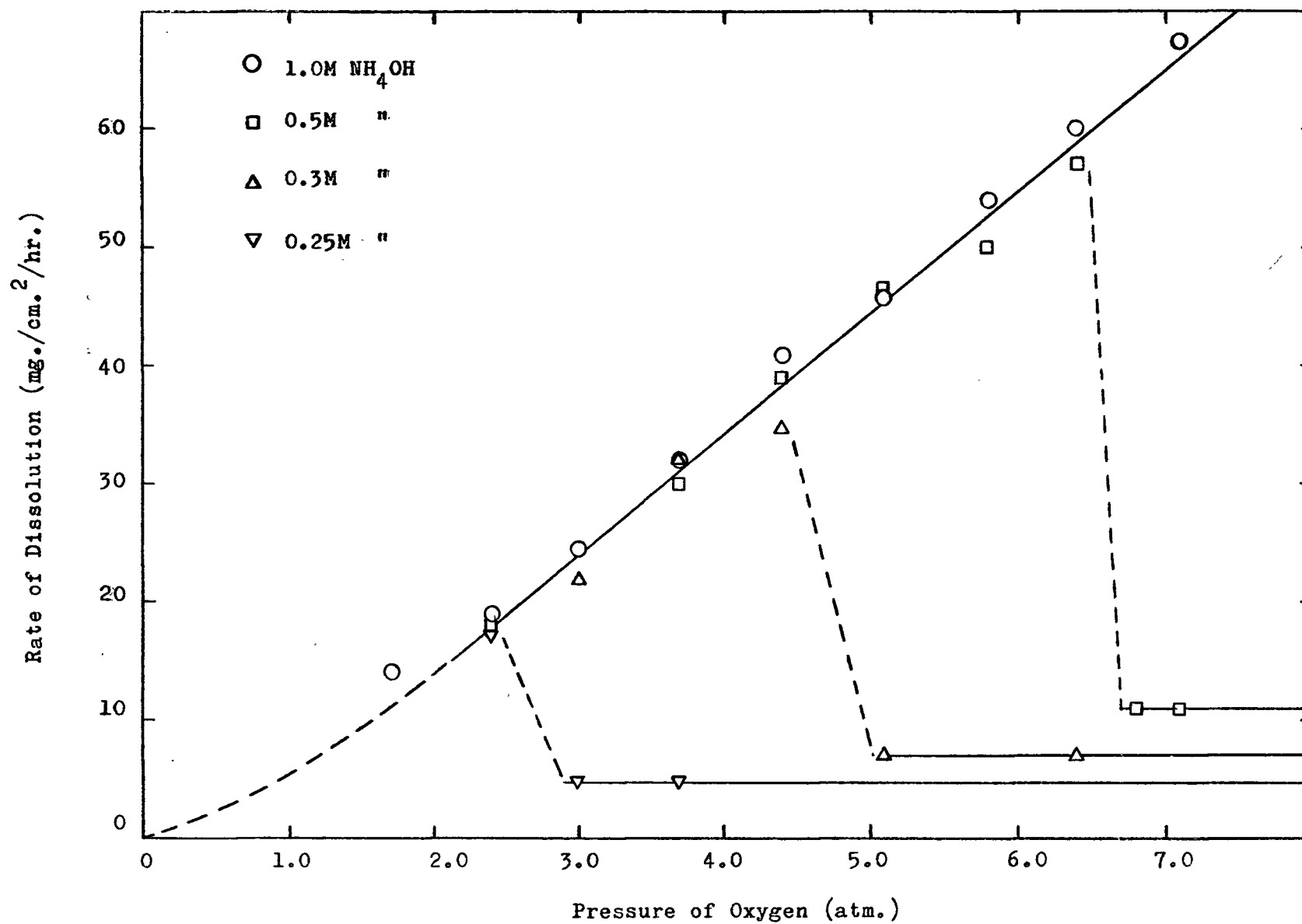**Figure 7** Rate curves for the dissolution of Zn in 0.25M ammonia solution for various oxygen pressures.

Conditions: Temperature 25°C, stirring rate 860 rpm., $NaClO_4$ 0.1M

__Figure 8__   Effect of oxygen pressure on the rate of dissolution of Zn at various ammonia concentrations.

In a subsequent experiment, the zinc sample was oxidized for 3 hours at this ammonia concentration and an O_2 pressure of 6.4 atm. The resultant film was identified by X-ray diffraction procedures as ZnO. (Appendix 1)

TABLE IV

Initial Dissolution Rates of Zinc at the Investigated Ammonia Concentrations.
($mgZn/cm.^2/hr.$)

Oxygen Pressure (atm.)	0.25M	0.30M	0.50M	1.0M
7.1			11.0	67.5
6.8			11.0	
6.4		7.0	57.0	60.0
5.8			50.0	54.0
5.1		7.0	46.5	46.0
4.4		34.5	39.0	41.0
3.7	4.7	32.0	30.0	32.0
3.0	4.7	22.0		24.5
2.4	17.8		18.0	19.0
1.7				14.0

Conditions: Temperature $25^{\circ}C$, stirring rate 860 rpm., $NaClO_4$ 0.1M

Further experiments were carried out in a 0.25M NH_4OH solution over a range of O_2 pressures. (Figure 7). These showed the same abrupt transition at an O_2 pressure of 2.4 atm. The results of these experiments are summarized in Table IV.

Effect of Ammonia Concentration

As indicated in Table IV, the range of ammonia investigated was 0.25 to 1.0M NH_4OH. In the low O_2 partial pressure region, the rates are independent of amine concentration. To further check this, runs were made in 2.0M and 5.0M NH_4OH solutions at 5.5 atm. O_2 pressure and gave rates of 50.2 and 49.0 $mgZn/cm.^2/hr.$ In the high oxygen pressure region, the rates show a first order dependence on amine concentration. A single run was made in 0.275M NH_4OH at 3.7 atm. O_2 pressure and gave a rate of 5.5 $mgZn/cm.^2/hr.$

Effect of Ammonium Ion Concentration

The NH_4^+/NH_4OH ratio was controlled by the addition of perchloric acid to the ammonia solution. The effect of added $NH_4^+(0.5M)$ was checked over the whole range of ammonia concentrations and gave rate curves (Figure 9) whose initial slopes are shown in Table V.

TABLE V

Rate of Dissolution of Zinc at Various Ammonia Concentrations in the presence of $0.5M$ NH_4^+ $(mgZn/cm.^2/hr.)$

Oxygen Pressure (atm.)	0.25M	0.40M	0.43M	0.92M
5.1	44.8	44.8		
4.4			38.4	
4.0				33.2

Conditions: Temperature $25°C$, stirring rate 860 rpm., NH_4^+ $0.5M$, $NaClO_4$ $0.1M$

The results indicate that the added NH_4^+ does not alter rates within the O_2 pressure dependent region (ie. 0.4, 0.42, 0.92M NH_3). In the case of the 0.25M NH_3 solution, at 5.1 atm. O_2 without the presence of NH_4^+ ions, oxide formation was noted. The addition of 0.5M NH_4^+ has at this NH_3 concentration prevented the formation of an oxide layer and thus the transition to slow oxide dissolution rates.

Effect of Stirring Rate

To investigate the possibility of transport control, a reduced stirring rate was used over a range of oxygen pressures in 0.3M NH_4OH solutions. Rates were obtained which showed a parallel linearity but reduced value in the oxygen dependent region compared with rates obtained at the same ammonia concentration but at the usual stirring rate of 860 rpm. (Figures 10 and 11).
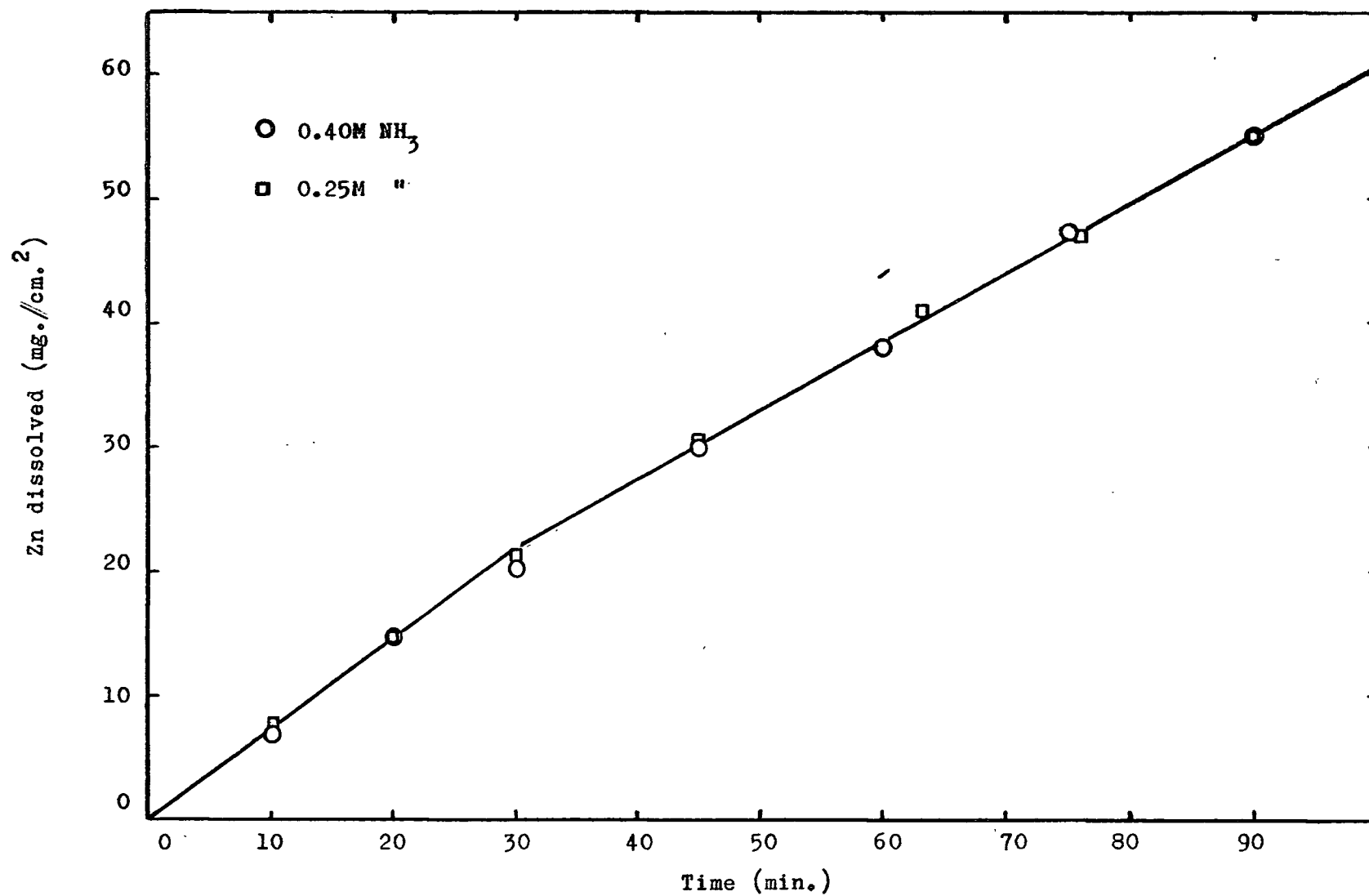
Conditions: Temperature $25^\circ C$, stirring rate 860 rpm., oxygen pressure 5.1 atm., NH_4^+ 0.5M.

Figure 9 Rate curves for the dissolution of Zn at a constant ammonium concentration.
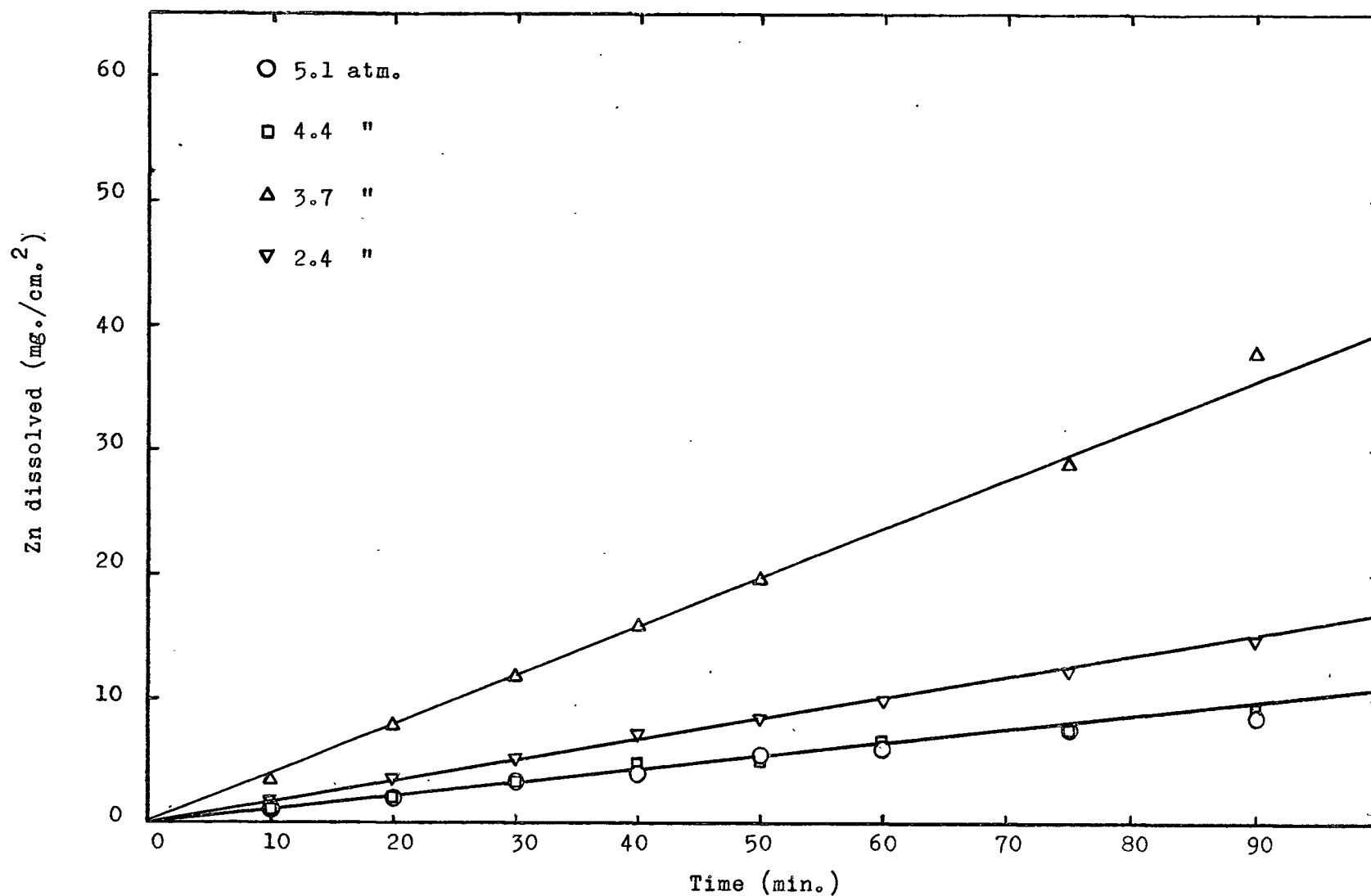
Conditions: Temperature $25^{\circ}C$, stirring rate 575 rpm., NH_4OH 0.3M, $NaClO_4$ 0.1M

<u>Figure 10</u> Rate curves for the dissolution of Zn in 0.3M ammonia solution at various oxygen pressures.
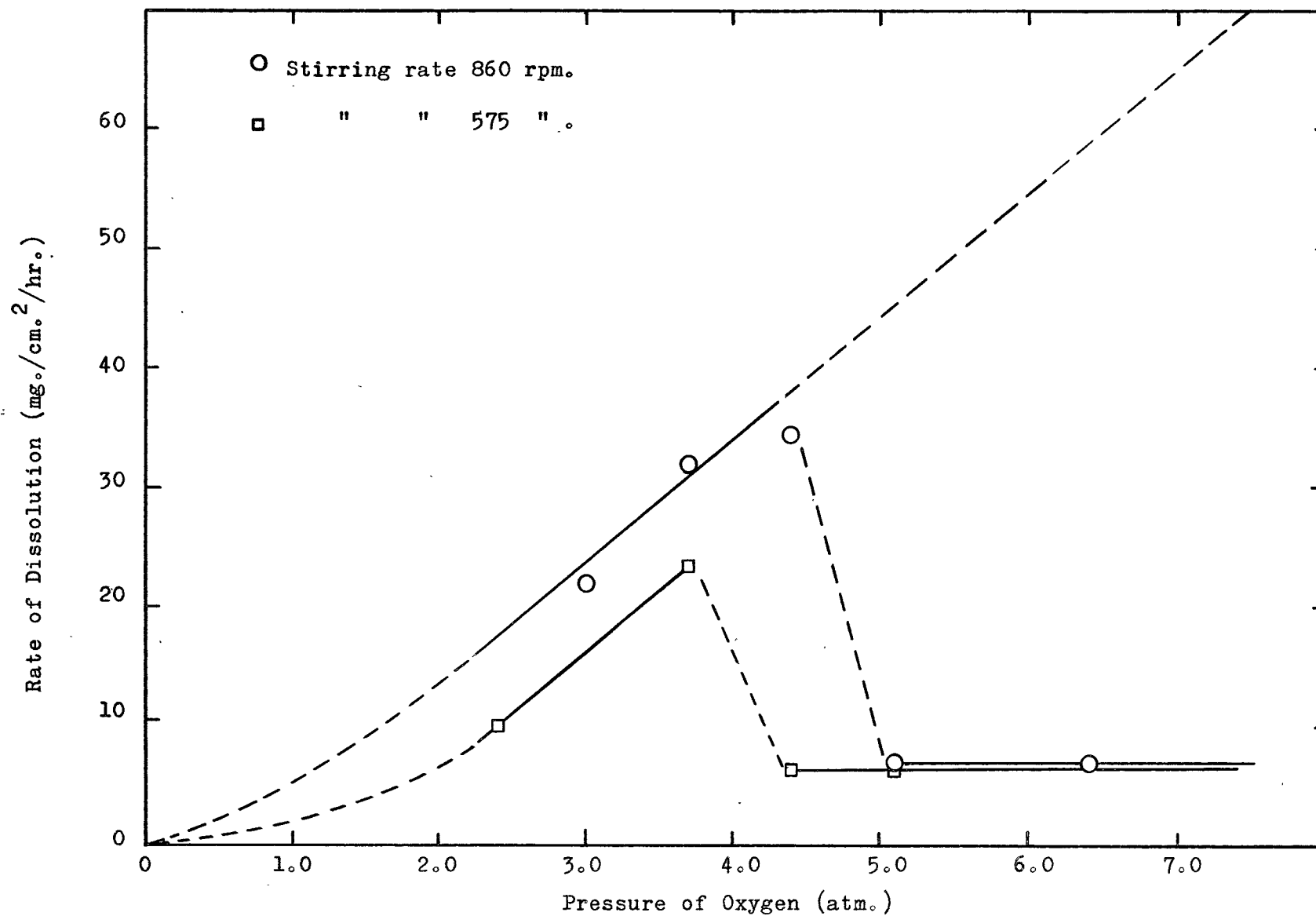
Conditions: Temperature 25°C, NH₄OH 0.3M, NaClO₄ 0.1M

Figure 11 Effect of stirring rate on the rate of dissolution of Zn at a constant ammonia concentration.

The rate in the region of oxide films remained unchanged.

TABLE VI

Rate of Dissolution of Zinc at a reduced stirring rate. $(mgZn/cm.^2/hr.)$

Oxygen pressure atm.	0.3M NH_4OH 575 rpm.	0.3M NH_4OH 860 rpm.
5.1	6.7	7.0
4.4	6.7	34.5
3.7	23.5	32.0
2.4	10.0	16.0

Conditions: Temperature $25^{\circ}C$, NH_4OH 0.3M, $NaClO_4$ 0.1M

Ethylenediamine System

An investigation of the Zn-ethylenediamine system gave analogous results. Initial experiments were carried out in 0.5M en and 0.3M en. The resulting rates (Figures 12 and 13) were independent of amine concentration and showed the same first order dependence on oxygen partial pressure. A much lower en concentration was used (0.065M en) and the sharp transition to lower rates with increasing O_2 pressure was observed. (Figure 14). A final en concentration of 0.03M was investigated over a wide range of O_2 pressures (Figure 15) to verify that the rate of dissolution of Zn did, in fact, remain constant in the "high" pressure region (3.4 to 7.8 atm.). These results are summarized in Table VII.

The linearity of all curves was excellent. The plot of rate versus oxygen pressure (Figure 16) shows that at low pressures of O_2 (for each individual en concentration) the rate of dissolution is first order in oxygen pressure and independent of amine concentration. In the high pressure region, the dependence is reversed, becoming proportional to the amine concentration and zero order in oxygen pressure.
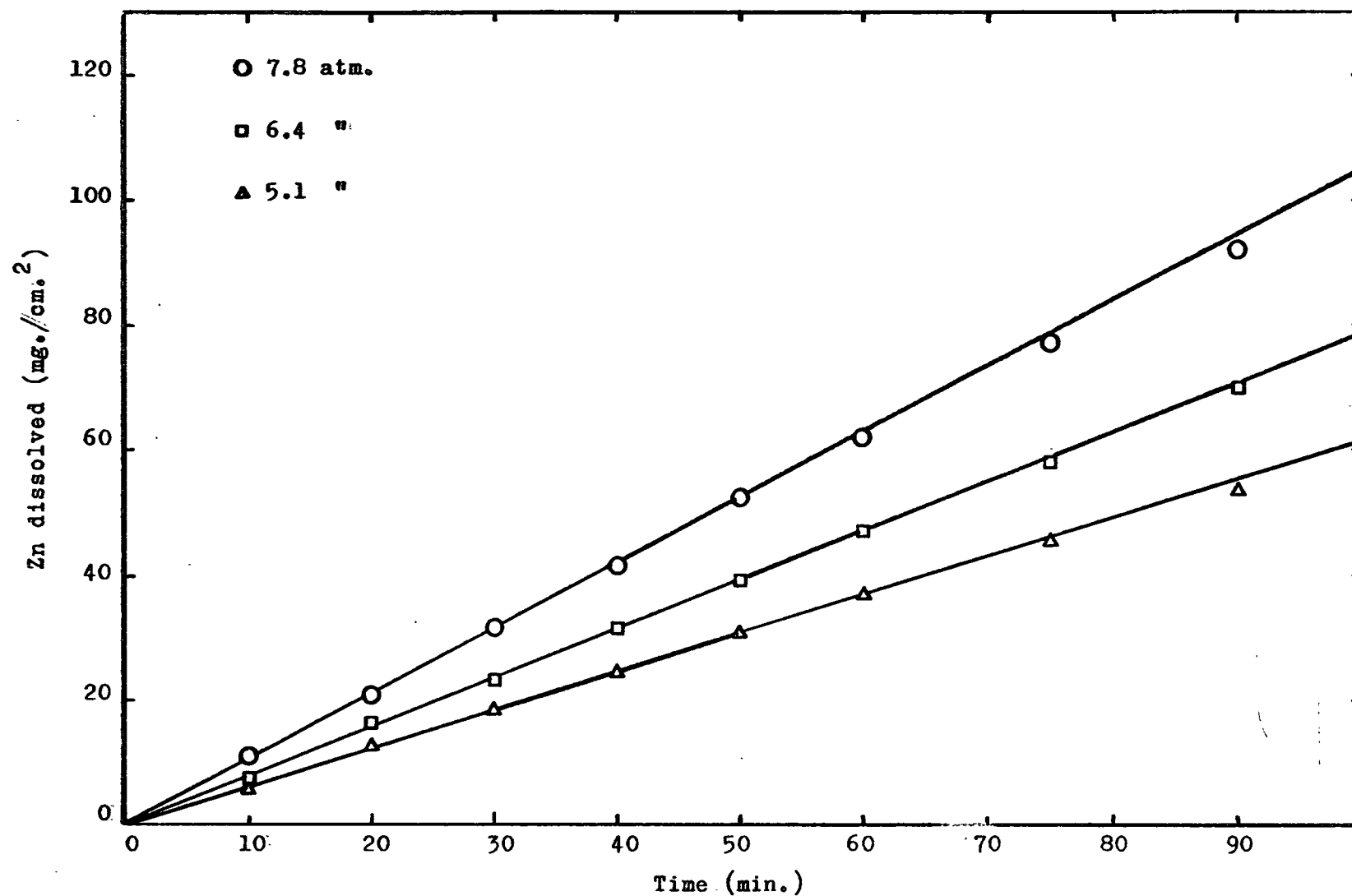
Conditions: Temperature 25°C, stirring rate 860 rpm., en 0.50M., NaClO$_4$ 0.1M

Figure 12 Rate curves for the dissolution of Zn in 0.5M ethylenediamine solution at various oxygen pressures.
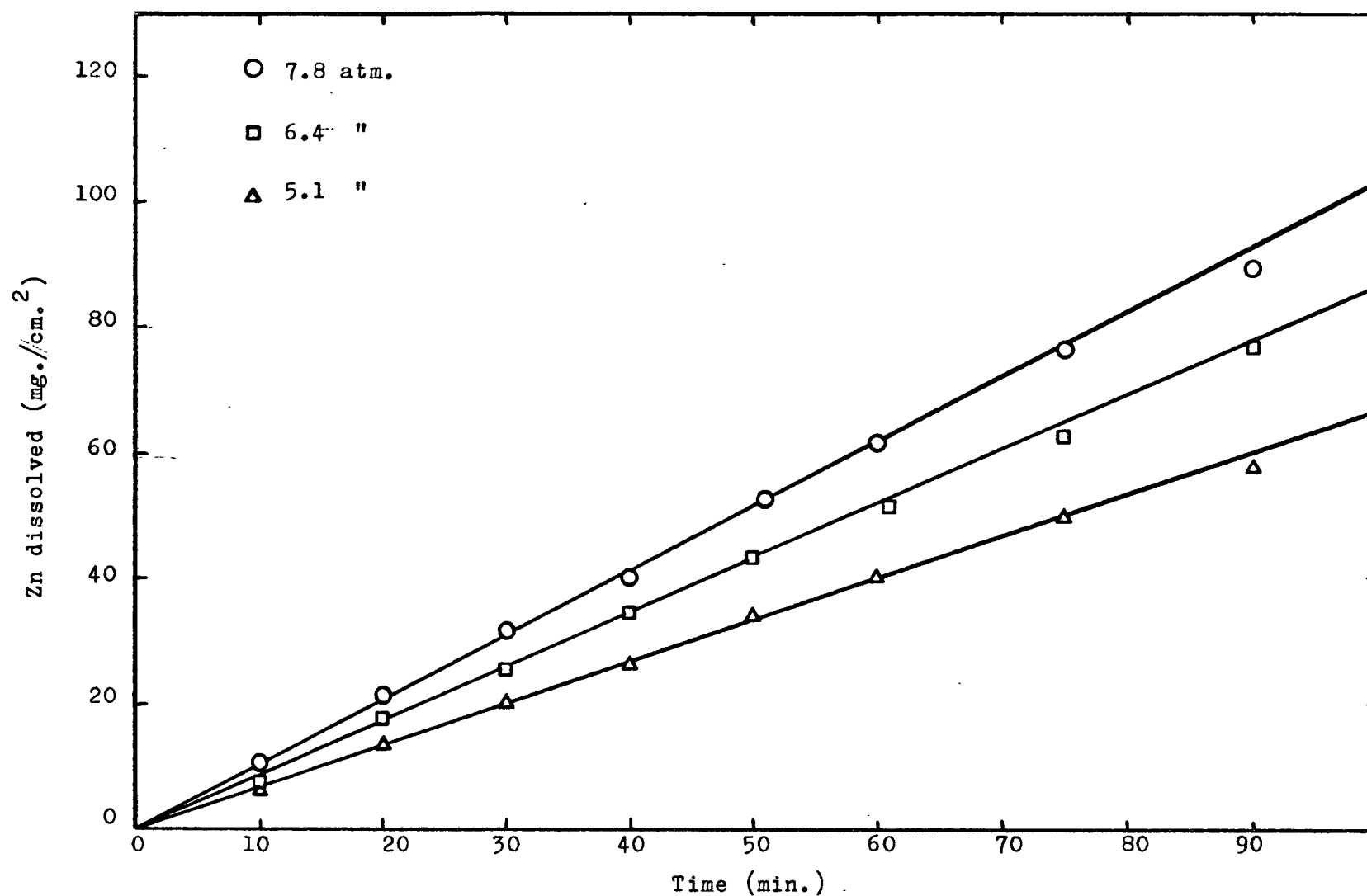
Conditions: Temperature 25°C, stirring rate 860 rpm., en 0.30M, NaClO$_4$ 0.1M

Figure 13   Rate curves for the dissolution of Zn in 0.30M ethylenediamine solution at various oxygen pressures.

Conditions: Temperature $25°C$, stirring rate 860 rpm., en 0.065M NaClO$_4$ 0.1M

Figure 14 Rate curves for the dissolution of Zn in 0.065M ethylenediamine solution at various oxygen pressures.
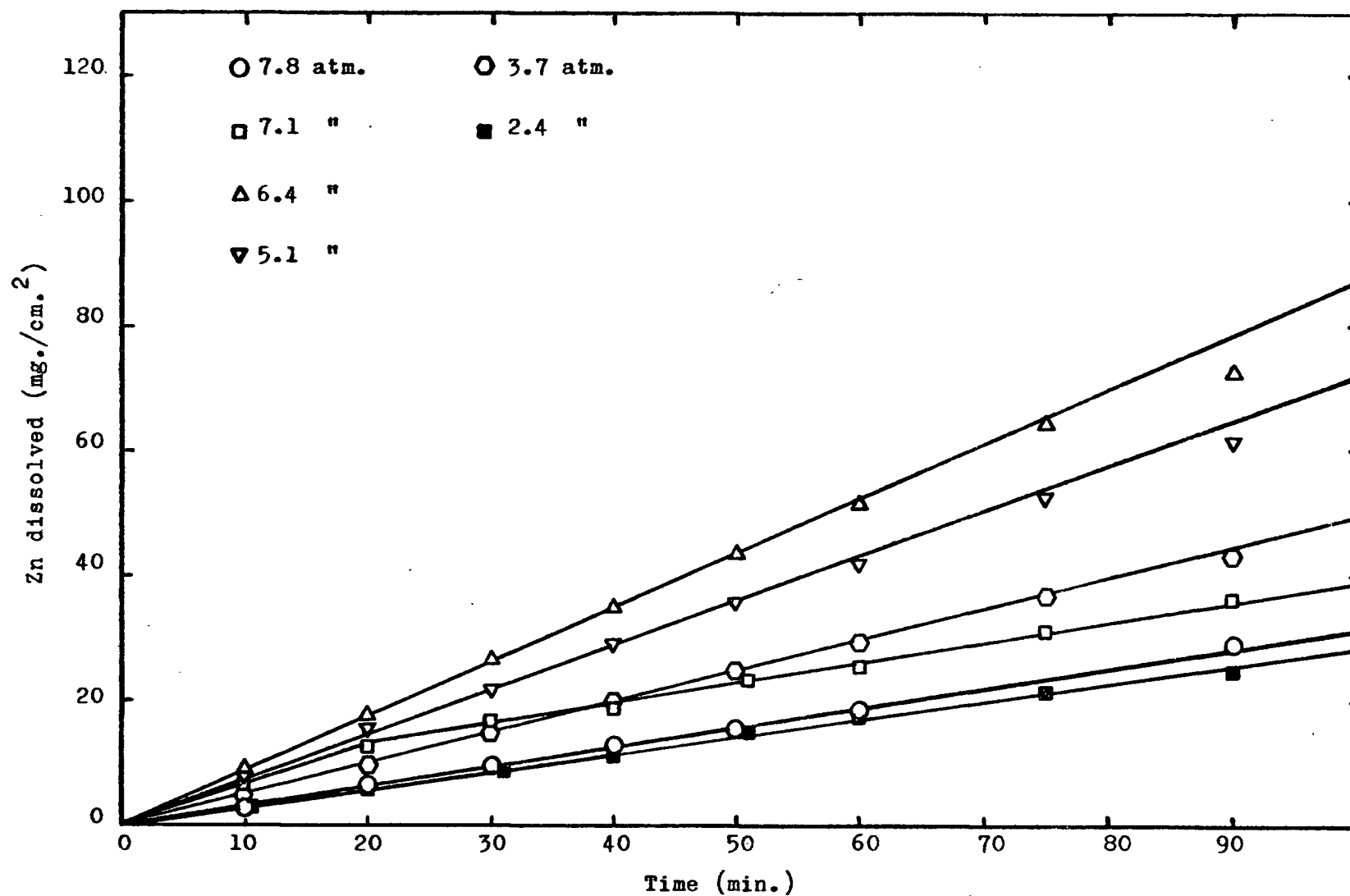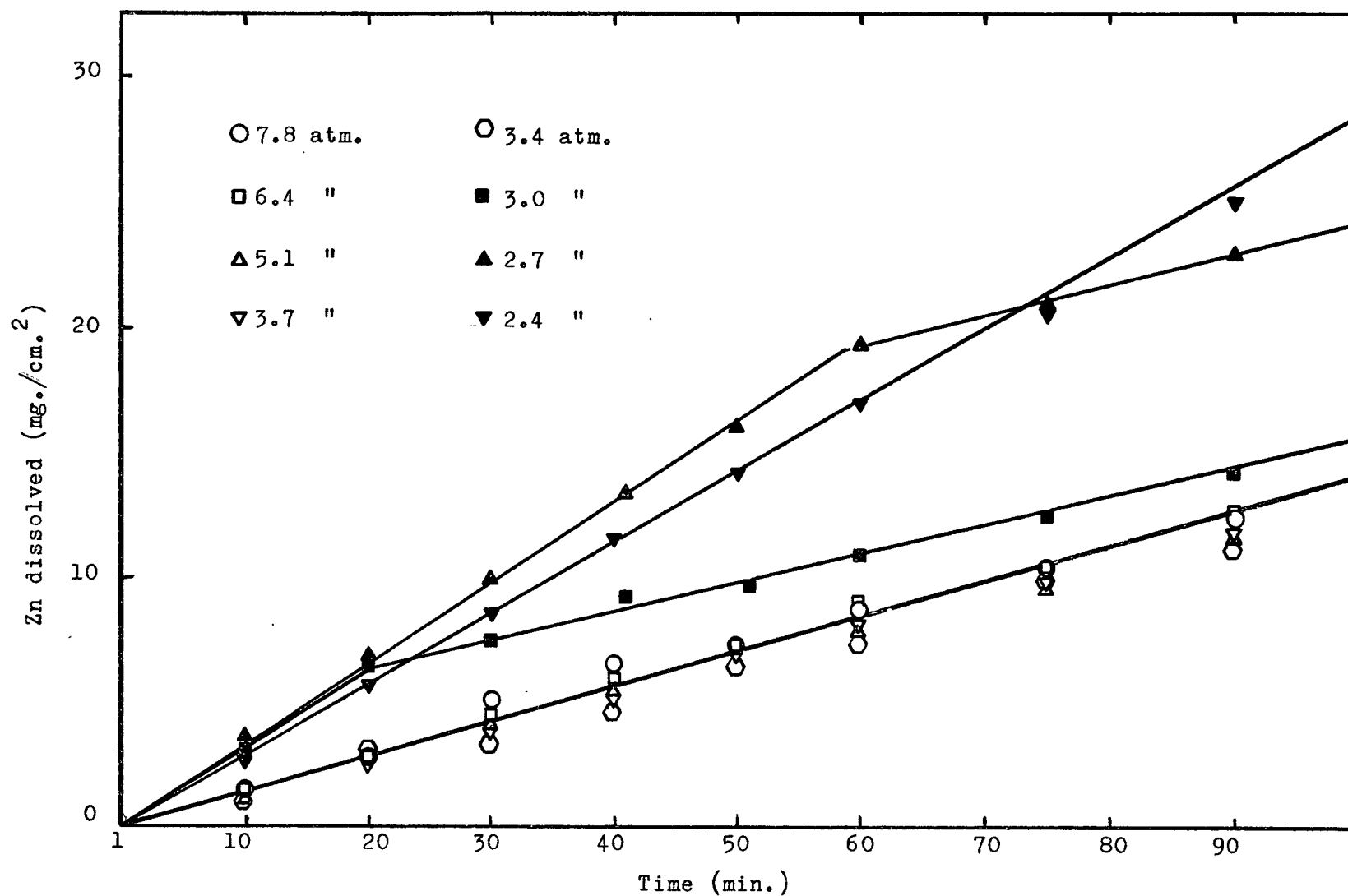
Conditions: Temperature 25°C, stirring rate 860 rpm., en 0.03M NaClO$_4$ 0.1M

Figure 15   Rate curves for the dissolution of Zn in 0.03M ethylenediamine solution at various oxygen pressures.
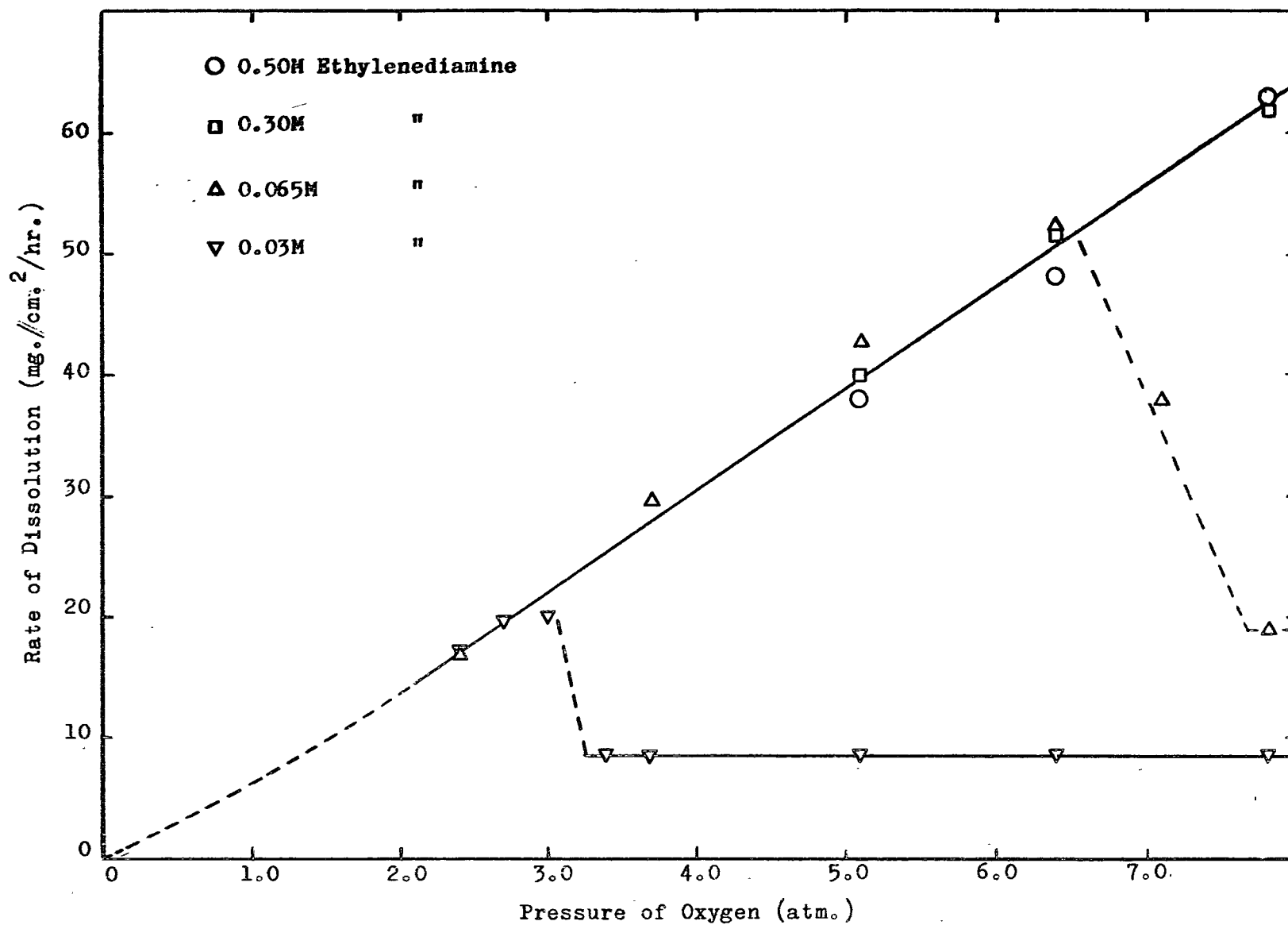
Conditions: Temperature $25^{\circ}C$, stirring rate 860 rpm., $NaClO_4$ 0.1M

Figure 16   Effect of oxygen pressure on the rate of dissolution of Zn at various
ethylenediamine concentrations.

TABLE VII

Rate of Dissolution of Zinc at the Investigated
Ethylenediamine Concentrations ($mgZn/cm.^2/hr.$)

Oxygen pressure (atm.)	0.03M	0.065M	0.3M	0.5M
7.8	8.4	19.0	62.0	63.0
7.1		38.0		
6.4	8.4	52.5	52.0	47.0
5.1	8.4	43.5	40.0	37.0
3.7	8.4	30.0		
3.4	8.4			
3.0	19.5			
2.7	19.5			
2.4	17.0	17.0		

Conditions: Temperature $25^{\circ}C$, stirring rate 860 rpm., $NaClO_4$ 0.1M.

DISCUSSION

Zinc, due to its electropositive character, dissolves rapidly
in ammonia and ethylenediamine solutions under oxidizing conditions according
to equations 1 and 2.

$$Zn + \tfrac{1}{2}O_2 + 4NH_4OH \longrightarrow Zn(NH_3)_4^{++} + 2OH^- + 3H_2O \qquad (1)$$

$$Zn + \tfrac{1}{2}O_2 + 3en + H_2O \rightarrow Zn(en)_3^{++} + 2OH^- \qquad (2)$$
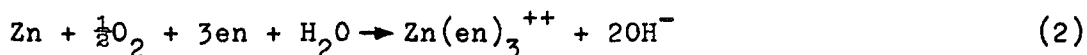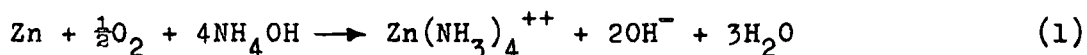
The experimental results show that there are two definite regions
of rate control. The low oxygen pressure region shows a first order depen-
dence on oxygen pressure and zero dependence on concentration of complexing
agent. This indicates control of the rate of dissolution of zinc either
by transport of oxygen within the solution to the metal surface or by
adsorption of oxygen to the surface. That transport of oxygen to the
interface is the correct alternative is indicated by decreased rates when
slower speeds of agitation are used. Such a region has been shown to
exist for copper and is known to occur with iron in alkaline solutions.[18]

There appears to be a competing reaction operative at oxygen pressures immediately before the transition from one region to the other. This is clearly shown by the levelling off of the rate curves in 0.25M and 0.3M NH$_4$OH (Figures 6 and 7) and the slight deviation from linearity for the curves of 0.03M and 0.065M en (Figures 14 and 15). Such a change in rate, approaching a parobolic rate relation, is indicative of film formation. In this case it could indicate partial coverage of the zinc surface by a thin adherent film.

At high oxygen pressures, the decreased rates indicate the presence of a passivation film, according to the reactions as given by equations 3 and 4

$$Zn(NH_3)_4^{++} + 2OH^- + 3H_2O \rightleftharpoons ZnO + 4NH_4OH \qquad (3)$$
$$Zn(en)_3^{++} + 2OH^= \rightleftharpoons ZnO + 3en + H_2O \qquad (4)$$
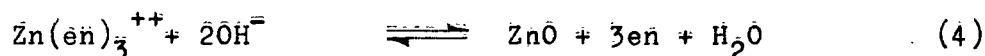
As well, visual evidence is available as to its presence and positive identification of this film as ZnO has been made by X-ray diffraction analysis of powdered surface scrapings.

Formation of the film on the attainment of a critical surface concentration of OH$^-$ is supported by the results when dissolution was carried out in ammonia solutions containing ammonium (NH$_4^+$) ion. The effect of this acid radical would be to neutralize the OH$^-$ released as the zinc is oxidized. This was shown by the prevention of film formation in a 0.25M NH$_3$ solution at 5.1 atm. O$_2$ pressure by the addition of 0.5M NH$_4^+$. Without the presence of NH$_4^+$ ions, film formation had been observed for that concentration of NH$_3$ at the particular O$_2$ pressure.

The oxide film passivates but does not completely protect the zinc metal beneath since the oxide dissolves slowly in ammonia and ethylenediamine. The rate of dissolution of zinc at this stage is first order in

amine concentration and independent of stirring rate. Hence the rate is
now chemically controlled by dissolution of the ZnO, probably at the film-
solution interface. A steady-state condition would be reached in which the
ZnO film enters solution at the same rate at which it is being restored.

An attempt was made to determine the rate of dissolution of the
oxide film under nitrogen pressure. A film was grown, the sample was
removed from the autoclave and charged into a fresh ammonia solution under
nitrogen pressure. After removal of the first zinc sample no further change
in zinc concentration was observed, indicating that the oxide had dissolved
during the time required for removing and replacing the autoclave cover
at which time the solution was not under oxygen pressure. A comparison
of rates of oxide dissolution from the kinetic experiments and the time
elapsed (approximately 14 minutes) shows that the film could have completely
dissolved during this period of time.

Rates of dissolution of zinc in ammonia and ethylenediamine solutions
are similar within the region of oxygen transport control, as would be expected,
but much higher for the en solutions in the chemically controlled region
where the concentration of amine is rate controlling. Assuming linear
dependence (necessary because of the scarcity of experimental points) rate
constants for the two systems have been obtained from Figure 17 and have
the values:

$$K^{exp}_{NH_3 \ T} = 21.6 \ mg.Zn/cm.^2/hr./M/l$$

$$K^{exp}_{en \ T} = 294 \ mg.Zn/cm.^2/hr./M/l$$

A comparison of formation constants for $Zn(NH_3)_4^{++}$ and $Zn(en)_3^{++}$ (Table 1)
would indicate that the experimentally obtained rate constants are in
accord with the thermodynamic equilibrium constants.
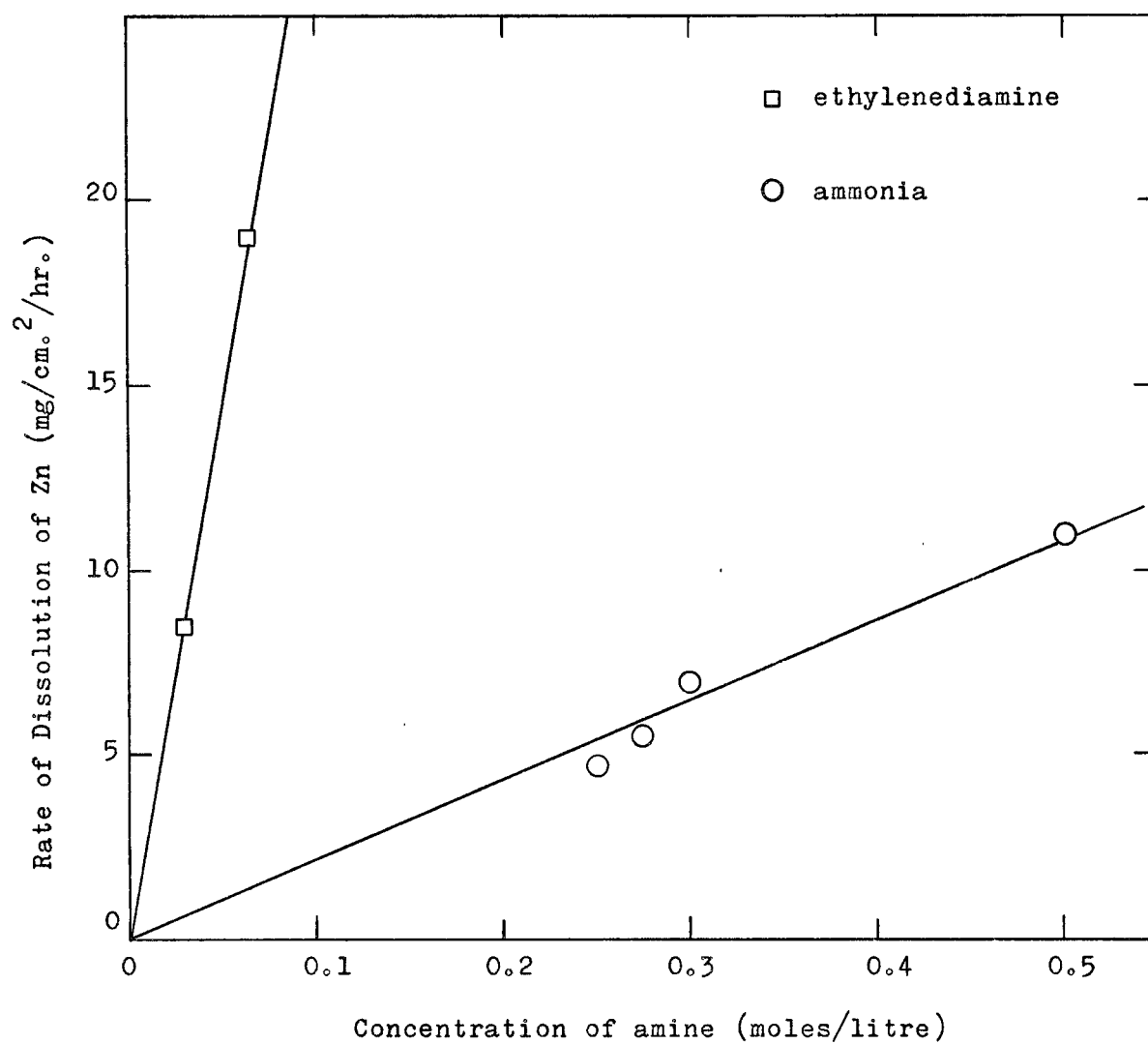
Conditions: Temperature 25°C, stirring rate 860 rpm.

Figure 17 Plot of rate of Zn dissolution versus amine concentration within region of oxide formation.

A comparison with the results obtained in the copper-ammonia and copper-ethylenediamine systems as reported by Milants[10], but for a region that showed no oxide-film formation, demonstrates considerable similarity in the order of magnitude. Rate constants and formation constants are shown for both the Zn and Cu systems in Table VIII.

<div align="center">

TABLE VIII

Comparison of Rate* and Formation Constants for Zn and Cu
in the ammonia and ethylenediamine systems.

</div>

	Formation Constant (Log K)	Rate Constant* (mg. Metal/cm.^{2}/hr./$M/1$)
$Zn(NH_3)_4^{++}$	9.46	21.6
$Zn(en)_3^{++}$	12.09	294
$Cu(NH_3)_4^{++}$	13.32	61.0
$Cu(en)_2^{++}$	19.60	245

* The rate constant in the zinc-amine systems is for dissolution of oxide present as a visible film, while in the copper-amine systems the rate constants are postulated as those for attack of a surface $Cu^{++}O$ complex.

This agreement is most surprising since in neither case are solution transport processes rate controlling. It might be inferred that the rate determining step involved the breaking up of an oxide lattice by the complexing agent. Even under these conditions it would be anticipated that the rates for copper should be the greater because of the lower stability of the oxide and the higher formation constant for the soluble complex ion.

<div align="center">

CONCLUSIONS

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A kinetic study of the zinc-ammonia and zinc-ethylenediamine systems has shown an analogous behaviour for the two systems. At low oxygen pressures,

transport of O_2 through the solution is rate-limiting and hence, the corrosion rate increases with O_2 pressure. Transport control of the rate has been verified by the results obtained at different speeds of agitation of the reaction solution.

Accumulation of hydroxyl ion in the surface region results in the formation of a passivating film. This film has been positively identified as ZnO. Rates of dissolution are decreased in the region of film formation, reaching a constant value which is dependent only on amine concentration. There exists, then, a certain critical oxygen pressure, for each concentration of amine, beyond which the reaction is limited by the rate of dissolution of the oxide.

RECOMMENDATIONS FOR FURTHER WORK

An investigation of these systems has indicated some regions where further amplification is desirable.

1) The effect of ammonium ion concentration should be studied. Those additions reported in the thesis always increased the rate to the region of control by oxygen transport. It is possible, however, that by use of small increments, some further details of the effect of NH_4^+ may be obtained.

2) The position and shape of the curve at the transition from transport control to chemical control, if studied in a more detailed fashion, may give information about the formation and nature of the oxide film.

3) The addition of OH^- to the solutions, in the form of NaOH, would

corroborate the suggested hydroxyl ion effect. This, however, should be preceded by a study of the Zn-NaOh system.

APPENDIX I

TABLE IX
Data from Film No. 1529

Line No.	I/I_1	$d\overset{\circ}{A}$(obs'd)	Line No.	I/I_1	$d\overset{\circ}{A}$(obs'd)
1	5	3.334	15	5	1.383
2	30	2.808	16	5	1.341
3	20	2.602	17	5	1.330
4	50	2.464	18	5	1.281
5	5	2.372	19	10	1.207
6	20	2.302	20	10	1.159
7	100	2.085	21	10	
8	10	1.987	22	5	
9	5	1.904	23	5	
10	5	1.814	24	5	0.9451
11	5	1.750	25	5	0.9068
12	10	1.691	26	10	0.8582
13	10	1.627	27	5	0.8312
14	10	1.479	28	5	0.8224

Film No. 1529 is an X-ray diffraction powder picture of the surface layer formed on a zinc specimen when reacted with a 0.3N NH_4OH solution under an oxygen pressure of 6.4 atmospheres. The thin adherent layer was scraped off mechanically and as a result, some zinc metal was removed with the layer.

Determination of the composition of this layer has been made by comparison of the above data with the A.S.T.M. standard X-ray diffraction data cards for zinc (No. 4-0831) and ZnO (No. 5-0664).

TABLE X

Comparison of ASTM Standard Zn and ZnO with sample layer

Zinc St'd.		Sample Layer			ZnO St'd.		Sample Layer		
$d\text{Å}$	I/I_1	Line No.	$d\text{Å}$	I/I_1	$d\text{Å}$	I/I_1	Line No.	$d\text{Å}$	I/I_1
2.473	53	4	2.464	50	2.816	71	2	2.808	60
2.308	40	6	2.302	20	2.602	56	3	2.602	40
2.091	100	7	2.085	100	2.476	100	4	2.464	100
1.687	28	12	1.691	10	1.911	29	9	1.904	10
1.342	25	16	1.341	5	1.626	40	13	1.627	20
1.332	21	17	1.330	5	1.477	35	14	1.479	10
1.237	2				1.407	6			
1.1729	23				1.379	28	15	1.383	10
1.1538	5				1.359	14			
1.1236	17				1.301	3			
1.0901	3				1.225	5			
1.0456	5				1.1812	3			
0.9454	8	24	0.9451	5	1.0929	10			
.9093	6				1.0639	3			
.9064	11	25	.9068	5	1.0422	10			
.8722	5				1.0158	5			
.8589	9	26	.8582	10	0.9848	4			
.8437	2				.9764	7			
.8245	1				.9555	1			
.8225	9				.9382	4			
					.9069	12	25	0.9068	10
					.8826	6			
					.8675	1			
					.8369	6			

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