THE REACTION OF COPPER-GOLD ALLOYS IN AQUEOUS AMMONIA UNDER OXYGEN PRESSURE

by

JAMES IRWIN FISHER

A THESIS SUBMITTED IN PARTIAL FULFILMENT OF
THE REQUIREMENTS FOR THE DEGREE OF
MASTER OF APPLIED SCIENCE

in the Department
of
MINING AND METALLURGY

We accept this thesis as conforming to the standard required from candidates for the degree of MASTER OF APPLIED SCIENCE

Members of the Department of
Mining and Metallurgy

THE UNIVERSITY OF BRITISH COLUMBIA

September, 1953

ABSTRACT

An investigation was conducted of the corrosion of copper-gold alloys in ammonia solutions under oxygen pressure. The reaction, which took place in an autoclave, was followed by sampling and analysis of the solutions. It was found that only copper was dissolved from the alloys, the gold being left behind in a film on the surface of the corroding specimen.

The reaction of pure copper as well as of four alloys ranging in gold content from 2 to 15 atomic percent were studied. Other variables examined include the concentrations of NH_3 and NH_4^+ in the solution, the oxygen pressure and the temperature.

It was found that while the rate curves for the dissolution of pure copper were linear, those for the alloys were generally parabolic in shape. The rate of dissolution of copper from the alloys appears to be determined by the transport of reactants and products through the gold rich films. Some copper oxide may also be precipitated in the pores of the film or in the region between the film and the underlying metal, further impeding the transport processes and contributing to the lowering of the rate.

ACKNOWLEDGEMENT

The author is indebted to the National Research Council of Canada for the financial aid which enabled this project to be carried out.

The author is grateful to the members of the Department of Metallurgy for their assistance throughout this work, and is especially grateful to Dr. J. Halpern, who ably directed this investigation.

TABLE OF CONTENTS

	Page
Introduction	1
Previous Work on the Corrosion of Similar Alloy Systems	2
Object and Scope of the Present Investigation	4
Experimental	5
A. Preparation of the Alloys	5
B. Apparatus	7
C. Chemical Reagents and Solutions	7
D. Measurement of the Rates of Dissolution	9
E. Analytical Procedures	9
(1) Copper	9
(2) Gold	10
(3) Ammonia	12
Results and Discussion	13
Nature of the Reactions and Rate Curves	13
Effect of NH_3 Concentration	16
Effect of $(NH_4)_2SO_4$	24
Effect of Varying NH_3 in the Presence of Constant NH_4^+	34
Effect of Oxygen Partial Pressure	41
Effect of Temperature	46
Structure and Composition of the Films	50
Conclusions	59
Summary of Experimental Results	59
Interpretation of the Results	61

TABLE OF CONTENTS (continued)

	Page
Appendix I	65
Appendix II	66
References	67

LIST OF FIGURES

Figure No.		Page
1.	Diagram of Pressure Vessel	8
2.	Calibration Curve for Copper Carbamate	11
3.	Typical Rate Curves for Copper and Alloy 5 in NH_3	14
4.	Rate Curves for Copper in NH_3	17
5.	Rate Curves for Alloy 5 in NH_3	18
6.	Parabolic Plots for Alloy 5 in NH_3	19
7.	Comparative Rate Curves for the Alloys in NH_3	20
8.	Effect of NH_3 on the Rate of Copper Dissolution	21
9.	Effect of Gold on the Rate of Copper Dissolution in Solutions containing NH_3 Alone	22
10.	Rate Curves for Pure Copper with NH_3 Constant and NH_4^+ Varying	25
11.	Rate Curves for Alloy 10 with NH_3 Constant and NH_4^+ Varying	26
12.	Parabolic Plots for Alloy 10 with NH_3 Constant and NH_4^+ Varying	27
13.	Comparative Rate Curves for Alloys with Constant NH_3, Constant NH_4^+	28

LIST OF FIGURES (continued)

Figure No.		Page
14.	Effect of NH_4^+ on the Rate of Copper Dissolution at Constant NH_3	31
15.	Effect of Gold on the Rates of Copper Dissolution with NH_3 Constant and NH_4^+ Varying	32
16.	Rate Curves for Copper with NH_4^+ Constant and NH_3 Varying	35
17.	Rate Curves for Alloy 5 with NH_4^+ Constant and NH_3 Varying	36
18.	Rate Curves for Alloy 10 with NH_4^+ Constant and NH_3 Varying	37
19.	Parabolic Plots for Alloy 10 with NH_4^+ Constant and NH_3 Varying	38
20.	Effect of NH_3 in Solutions Containing Constant NH_4^+	39
21.	Effect of Gold on the Rates of Copper Dissolution with NH_4^+ Constant and NH_3 Varying	42
22.	Rate Curves for Copper at Various Oxygen Pressures	43
23.	Rate Curves for Alloy 10 at Various Oxygen Pressures	44
24.	Rate Curves for Copper at Various Solution Temperatures	47
25.	Rate Curves for Alloy 2 at Various Solution Temperatures	48

LIST OF FIGURES (continued)

Figure No.		Page
26.	Surface Structure of Alloy 2	51
27.	Surface Structure of Alloy 2	51
28.	Surface Structure of Alloy 5	52
29.	Surface Structure of Alloy 10	52
30.	Surface Structure of Alloy 10	53
31.	Surface Structure of Alloy 10	53
32.	Surface Structure of Alloy 15	54
33.	Surface Structure of Alloy 15	54

LIST OF TABLES

Table No.		Page
I	Data on Experiments with Solutions Containing NH_3 Alone	23
II	Data on Experiments with Solutions in which NH_4^+ was Varied and NH_3 Held Constant	29
III	Data on Experiments with Solutions in which NH_3 was Varied and NH_4^+ Held Constant	40
IV	Data on Experiments in which Oxygen Pressure was Varied	45
V	Data on Experiments in which Temperature was Varied	49
VI	Analyses of Films	55

THE REACTION OF GOLD-COPPER ALLOYS WITH AQUEOUS AMMONIA UNDER OXYGEN PRESSURE

INTRODUCTION

This study of the kinetics of the dissolution of copper-gold alloys in aqueous ammonia and ammonium salt solutions under oxygen pressure had its inception in a similar study on the kinetics of the dissolution of copper recently conducted in this laboratory (1). In the course of the latter investigation, it was shown that the total rate of dissolution of copper in ammonia solutions was the sum of the rates of two independent reactions, first order in relation to the concentrations of ammonia and ammonium ion respectively. These rates were found to be independent of the oxygen concentration, provided the oxygen was present in excess so that its transport to the copper surface did not limit the rate of the reaction. It was also found that the rates were independent of the concentrations of hydrogen ion and dissolved copper. On the basis of these results, the following mechanism for the dissolution of copper was proposed:

(i) Adsorption of dissolved oxygen onto the copper surface:

$$Cu + 1/2\ O_2 \xrightarrow{\text{fast}} Cu....O \qquad .....(1)$$

(ii) Reaction of an ammonia molecule or ammonium ion with the copper-oxygen complex on the surface:

$$Cu....O + NH_3 \xrightarrow{slow} {}^{++}Cu\begin{matrix}\diagup NH_3 \\ \diagdown\ O^{--}\end{matrix} + HOH \xrightarrow{fast} Cu(NH_3)^{++} + 2OH^- \qquad .....(2)$$

$$Cu....O + NH_4^+ \xrightarrow{slow} {}^{++}Cu\begin{matrix}\diagup NH_3 \\ \diagdown\ H^+ \\ \quad O^=\end{matrix} + OH^- \xrightarrow{fast} Cu(NH_3)^{++} + 2OH^- \qquad .....(3)$$

Following this work on copper, it seemed of interest to examine the effect on the dissolution reaction of varying the composition of the metal phase by suitable alloying, copper remaining the principal or only dissolving metal. Gold was chosen as the alloying metal because:

(a) it is inert to attack by all the reagents contemplated.

(b) it forms a continuous solid solution with copper, and the structural properties of this system have been extensively investigated.

(c) there appeared to be some possibility of studying the effect of ordering on the corrosion properties of the alloy.

Previous Work on the Corrosion of Similar Alloy Systems.

The corrosion properties of copper-gold alloys have been studied by Tammann (2) and Muller, Freissler and Plettinger (3). However, their work was mainly restricted to establishing parting limits* of the alloys in various corroding media. Landau and Oldach (4) have compiled a comprehensive summary of qualitative and quantitative data on the corrosion properties of various solid solution alloys, and have noted several interesting correlations. In particular, they

---

* The parting limit of an alloy may be defined as the maximum concentration of the less noble element of an alloy at which selective oxidation can occur. Beyond this limit the alloy behaves like the pure noble metal (5).

emphasized the importance of passivity limits*, and noted the existence of minima in the corrosion rate - composition curves of certain alloy systems.

Several theories relating to the corrosion of alloys have been proposed and, although the present work was not undertaken with the idea of applying or confirming any particular one of these theories, it may be useful to refer briefly to some of them. In 1921 Tammann (2) proposed a correlation between parting limits and the atomic ratio of the metals in the alloy, noting certain exceptions and explaining these in terms of space-lattice isomerides. Russell (6) noted a somewhat similar correlation between alloy structure and passivity. Uhlig and Wulff (8), extending Russell's ideas, proposed the Electron Configuration Theory in which passive metals are characterized by unfilled d energy bands. These passive metals are able to transmit their characteristics to other less passive metals in alloys by electron sharing. Landau (9), treating theories based on alloy structure with considerable reserve, extended the local cell theory for the corrosion of pure metals to alloys.

It should be noted here that most alloy corrosion theories treat passivity rather than parting. Since in the present system the alloying metal (gold) is thermodynamically immune to corrosion in the media used, the concept of parting is of greater significance than

---

* Uhlig and Mears (7) give the following definition of passivity: "a metal or alloy is passive if it substantially resists corrosion in an environment where thermo-dynamically there is a large free energy decrease associated with its passage from the metallic state to appropriate corrosion products''.

that of passivity.

Object and Scope of the Present Investigation

This study was undertaken with the object of establishing the effect of alloying copper with an inert metal on the dissolution kinetics of the former. Specimens of copper-gold alloys were exposed to ammonia solutions in an autoclave maintained under controlled temperature and pressure conditions, and the rate of dissolution of copper determined by periodic sampling and analysis of the solution. The variables examined included alloy composition, NH_3 and NH_4^+ concentrations, oxygen pressure and temperature. The experimental procedures used and the results obtained are described and discussed below.

EXPERIMENTAL

A. Preparation of the Alloys:

The copper used in this work was supplied as half-inch rods by Ellett Copper and Brass Company. The gold was supplied as fine gold shot by Birks Limited. Spectrochemical analyses* of these metals and of the alloys are given in Appendix I.

At the outset, it was thought that three alloys at 5 atomic percent intervals (i.e. corresponding to 5, 10 and 15 atomic percent gold) would be sufficient to establish a pattern of results which would suggest what other alloys should be prepared and studied. The metal constituents for these alloys were carefully weighed, and then degassed and melted by induction heating in a carbon crucible under 150 microns of argon pressure. On cooling, a cylindrical ingot about 1.25 inches in diameter and weighing about 25 grams was obtained. It was subsequently decided to prepare and study another alloy containing 2 atomic percent gold. Since a carbon crucible was not easily obtainable at that time, an alundum crucible was used in preparing this alloy.

It was also desired to conduct some comparative dissolution experiments on pure copper, and a sample of pure copper was melted and heat treated under the same conditions as the alloys.**

---

* Kindly carried out by the Department of Mines, Victoria, B.C.

** Henceforth the alloys will be referred to as alloy 2, alloy 5, etc., where the number corresponds to the gold content in atomic percent.

All the alloys were homogenized in an argon atmosphere at 850°C. for periods ranging between 60 and 75 hours. They were then furnace cooled to 500°C. and water quenched. This treatment was designed to produce disordered structures for, if studies were to be made on the effects of order on the dissolution rates of the alloys, it was decided to treat disordered alloys first. Although ordering is most significant in a 25 atomic percent gold alloy, a consistent treatment for all the alloys was desirable. The critical temperature for the order-disorder transformation in a 25 atomic percent alloy is 391°C.

The ingots were turned on a lathe to a uniform diameter which was measured with a micrometer. They were then sawed in half through a plane perpendicular to the cylindrical axis, and mounted in bakelite with the circular face exposed. Samples from the saw cuttings and from drillings, which were taken at the completion of the work, were assayed for gold. The assays were found to correspond very closely to the intended compositions (see Appendix II). Metallographic tests failed to show any evidence of coring or inhomogeneity in the ingots, but in some cases interdendritic shrinkage cavities were observed toward the upper end. It was assumed that this shrinkage did not affect the surface area appreciably.

Prior to each experiment the mounted alloy samples were refaced in a lathe to remove any film or surface inconsistencies in composition which might have resulted from the previous experiment. About 3/1000 inches were machined from the exposed surfaces of the alloys, which were then polished using standard techniques and stored

in a dessicator for subsequent experiments.

B. Apparatus:

The experiments were conducted in a stainless steel autoclave (see Figure 1) designed for working pressures up to 150 psig. The bakelite mount (which also served as electrical insulation) containing the metal specimen was held by a stainless steel rod, tapped into the lid of the autoclave, so that the surface of the alloy was exposed to the solution about 0.25 inches above the blades of the impeller. Fresh solution was forced against the face of the alloy by the impeller, which was 10.9 cm. in diameter and rotated at 720 RPM. The temperature of the solutions was regulated by a Wheelco controller coupled to a platinum resistance thermometer, which was placed in a stainless steel well extending from the lid of the autoclave into the solution. The thermometer leads were connected in the controller across a double pole, single throw microswitch which activated solenoid valves on gas and water lines. The gas was fed to a ring burner mounted under the autoclave, and the water line was connected to cooling coils running through the corroding solution. A cyclic temperature variation resulted which could be held to within $\pm$1°F. at 77°F. (25°C.) and $\pm$3°F. at 132°F. (50°C.). Pressure was controlled by a standard pressure regulator on the oxygen cylinder.

C. Chemical Reagents and Solutions:

Chemically pure grade ammonium hydroxide and ammonium sulphate, supplied by the Nichols Chemical Company, were used. Oxygen was supplied in cylinders by the Canadian Liquid Air Company,

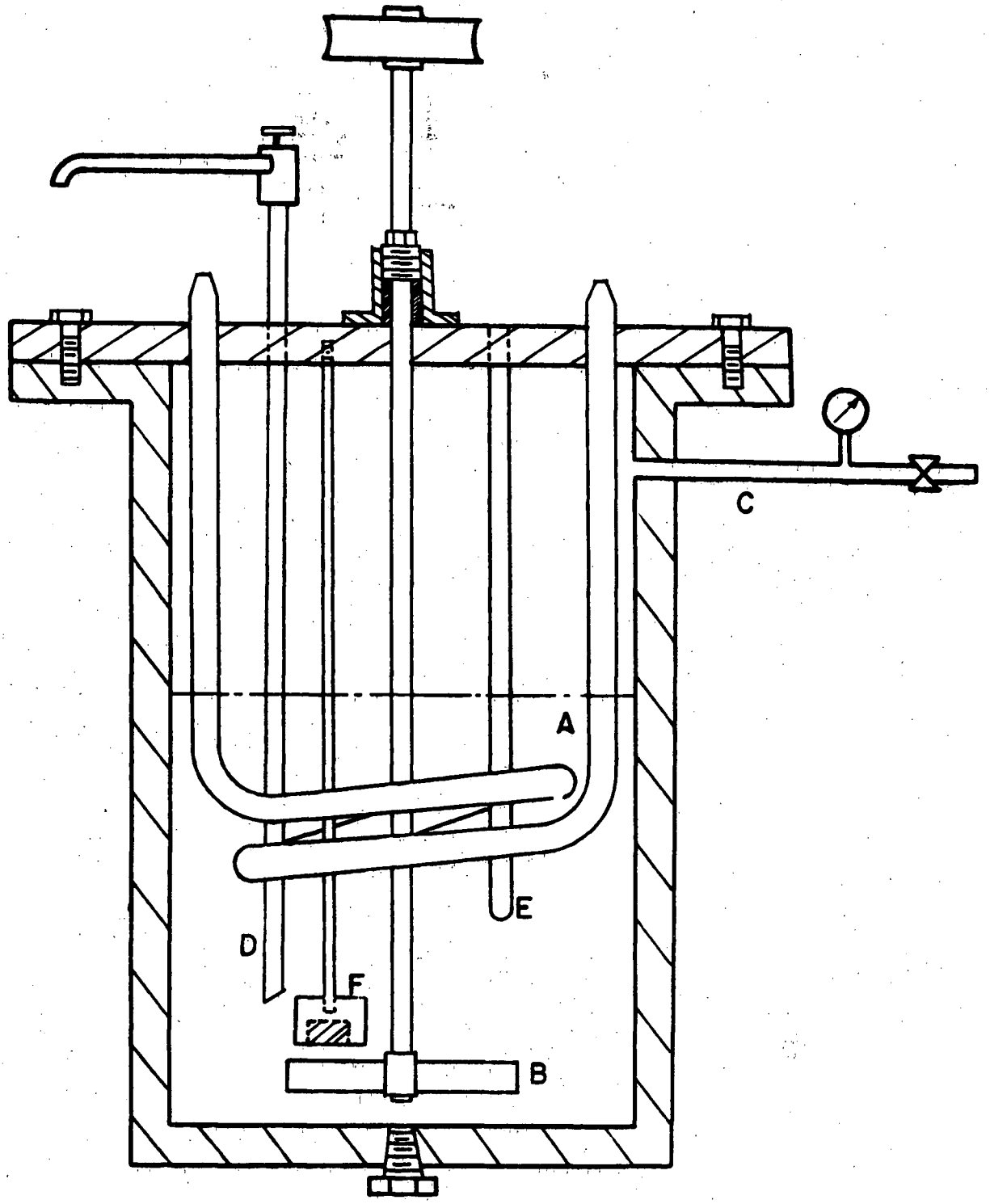

Figure 1. Diagram of Stainless Steel Pressure Vessel and Internal Parts.

A - Cooling Coil
B - Impeller
C - Gas Inlet Tube
D - Sampling Tube
E - Thermometer Well
F - Metal Specimen in Bakelite Mount

and was used without further purification.

Solutions were prepared by diluting a measured volume of ammonium hydroxide to 3.0 litres with distilled water. Ammonium sulphate was weighed and added to the solution in the autoclave.

D. Measurement of the Rates of Dissolution:

After the desired specimen and solution were placed in the autoclave, the latter was sealed and the solution brought to temperature. When the correct temperature was attained, the oxygen was introduced and maintained at the desired value. The first sample of the solution was taken within one minute of the pressure increase. To follow the rate of the reaction 25 ml. samples were withdrawn through the sample tube shown in Figure 1 at 30 minute intervals and analysed for copper. Since the surface area of the alloy and the volume of solution were known, the amount of copper dissolved per unit area could be calculated.

E. Analytical Procedures:

(1) Copper:

Copper concentrations were determined spectrophotometrically by the Carbamate method (11). Sodium diethyldithiocarbamate forms a stable, colored chelate compound with cupric ions, showing a maximum light absorption at 437 millimicrons. A Beckman model DU spectrophotometer was used to determine the optical density of the solutions at this wavelength. The optical density was found to be proportional to the copper concentration. (A calibration curve for this analytical

procedure is given in Figure 2). To prepare the samples for analysis, 7 ml. of a carbamate solution* were added to an aliquot of the sample taken from the autoclave, and the mixture diluted with distilled water to 50 ml. in a volumetric flask. The aliquot used varied from 1 to 5 ml. depending on the copper concentration. Since the stability of the copper carbamate complex is affected by daylight (11), analytical solutions were prepared in an artificially lit room. With careful technique, results obtained by this method could be duplicated within 1 percent.

(2) Gold:

It was also thought advisable to develop a method for determining gold concentrations in the corroding solutions. A colorimetric procedure was again adopted using p-dimethylaminobenzalrhodanine which forms a colored chelate complex with gold ions. A 15 ml. aliquot of the solution was made 0.1 N in HCl and 1 ml. of a 20 percent saturated solution of rhodanine in ethyl alcohol was added. The resulting solution was diluted to 50 ml. and its absorption measured in silica cells at 300 millimicrons. While it was found that this method did not give quantitatively reproducible results, it was very sensitive and made it possible to detect visually less than 1γ of gold per ml. by the purple color developed. Copper had no effect on the visual test, although it could be detected by the spectrophoto-

---

* Preparation of the carbamate solution:
Solution A: 0.4 grams carbamate in 400 ml. distilled water.
Solution B: 10 grams gum arabic and 1 ml. toluene in 1000 ml. distilled water.
Solutions A and B were mixed and filtered, and stored in the dark.

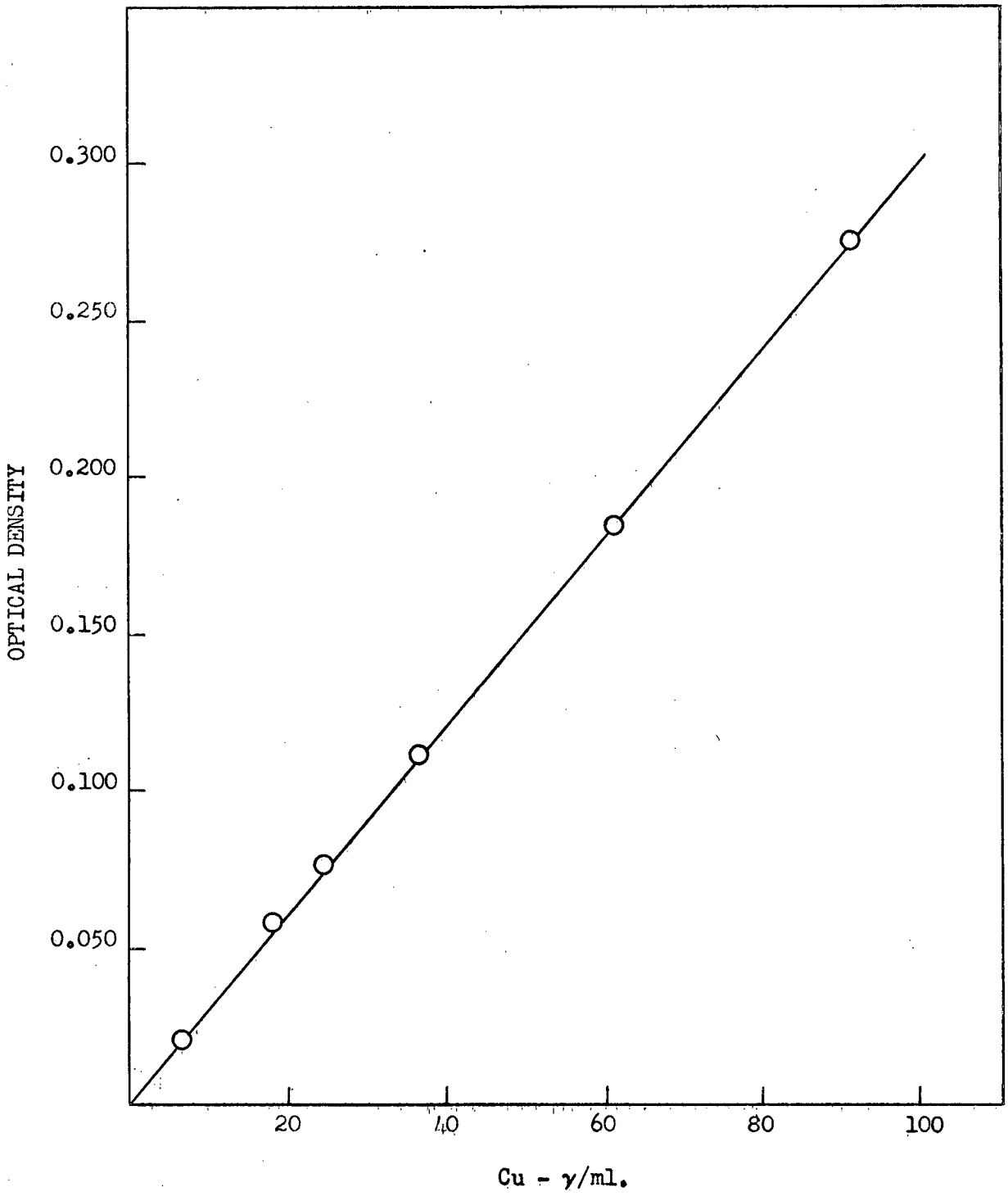

Figure 2. Calibration curve for copper carbamate.

meter. It was found that the optical densities of copper and gold rhodanine were additive.

(3) Ammonia:

Ammonia concentrations were determined by potentiometric titration with standard HCl.

RESULTS AND DISCUSSION

Nature of the Reactions and Rate Curves.

In all the experiments, specimens of copper or of a copper-gold alloy were exposed to solutions containing NH_3 (and, in some instances, $(NH_4)_2SO_4$) under oxygen pressure. In general, it was found that the specimens were corroded under these conditions and that copper was dissolved. At no time could any gold be detected in the solutions. The reaction involved thus appears to be represented by the equation:

$$Cu_{(100-n)}Au_{(n)} + y/2\ O_2 + 4yNH_3 + yH_2O \rightarrow$$

$$Cu_{(100-r)}Au_{(r)} + yCu(NH_3)_4^{++} + 2yOH^- \qquad .....(4)$$

where $r > n$, n and r being the atomic percent gold in the alloys before and after corrosion. All the results described below thus relate to measurements of the rate of dissolution of copper.

The shapes of the two rate curves, shown in Figure 3, are typical of those obtained for pure copper and for the copper-gold alloys, respectively, under most conditions. The rate plots for the dissolution of pure copper were always found to be linear, the amount of copper dissolved being proportional to the time, i.e.

$$Cu = k_1 T \qquad .....(5)$$

On the other hand, the rate of dissolution of copper from copper-gold alloys generally fell off with time, corresponding in most cases

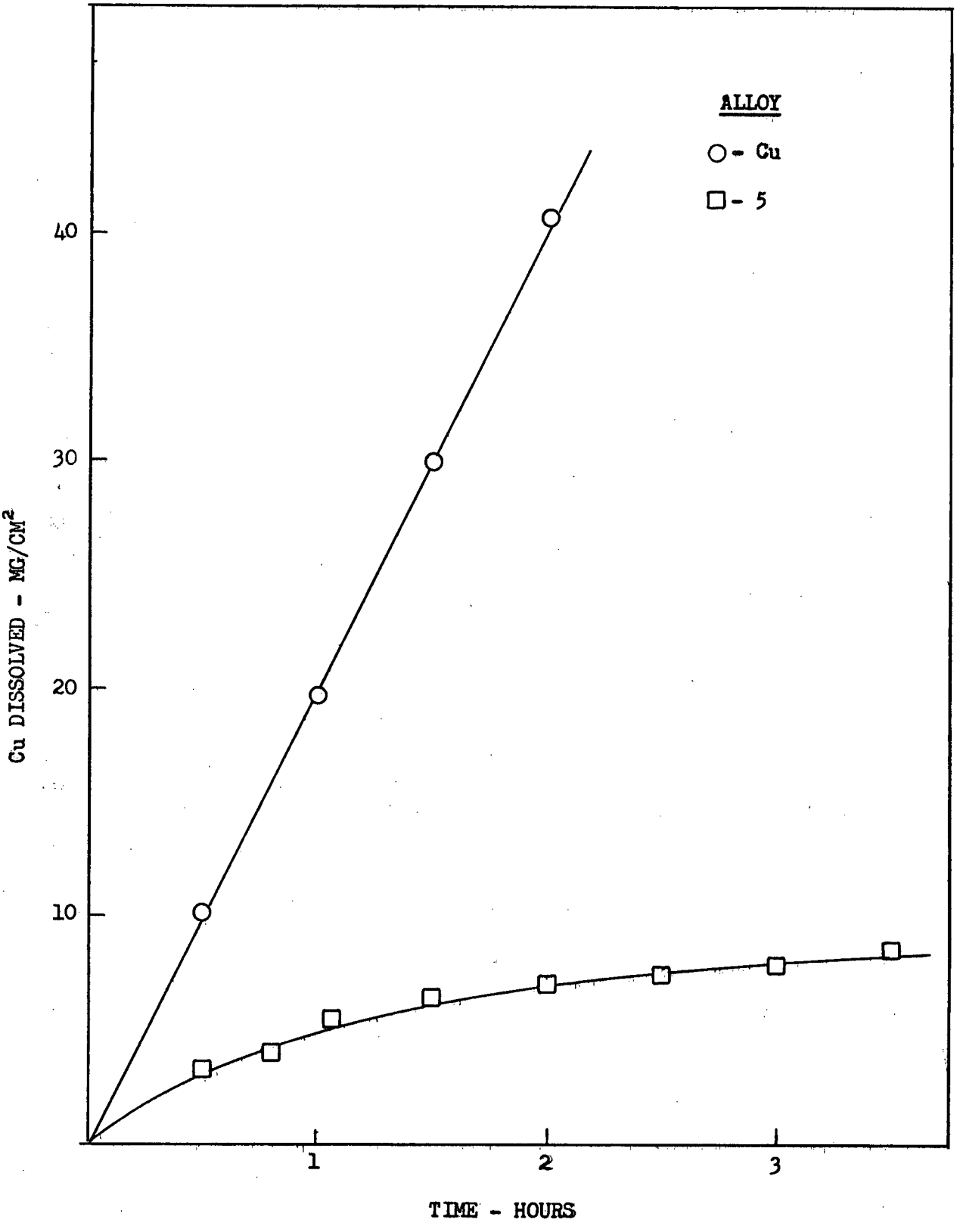

Figure 3. Typical rate curves for the dissolution of copper for pure copper and alloy 5, showing relative rates. T = 25°C; O_2 = 6.8 Atm.; NH_3 = 0.5 m/l.

to a parabolic relation, i.e.

$$[Cu]^2 = a + k_2T \qquad \text{.....(6)}$$

where Cu is the amount of copper dissolved per square centimeter of surface in time T, and k_1, k_2 and a are constants.

Such a relation usually denotes the buildup of a surface film on the corroding specimen which slows the reaction as it thickens by impeding the transfer of reactants and products. It was concluded that this film was due to the gold which was left behind at the surface of the alloy when the copper dissolved. This was confirmed by subsequent analyses of some of the films which showed them to be much richer in gold than the original alloys.

Although it was found that the rate curves obtained in most of the experiments on alloys conformed closely to a parabolic relation, there were not infrequent exceptions to this rule. This, together with the fact that the rate curves for pure copper were linear, made it impossible to compare the rates for the different specimens in terms of a uniform rate constant. For these reasons it was decided to adopt the amount of copper dissolved during the first hour of any experiment as a measure of the rate. All subsequent correlations of the effects of variables are expressed in terms of this quantity. Where possible, such correlations were compared with those based on parabolic rate constants, and in general the trends were found to be similar.

In the following sections are described the results of studies on the different variables. Unless otherwise stated, the

pressure and temperature in all the experiments were 6.8 atmospheres of oxygen and 25°C.

Effect of NH_3 Concentration.

The corrosion of copper and each of the four copper-gold alloys was investigated using a series of solutions containing different concentrations of NH_3 generally ranging from 0.15 to 2.5 m/l. No NH_4^+ salts were added to these solutions. Some typical rate curves obtained during this series of experiments are shown in Figures 4 to 7, and the results are summarized in Figures 8 and 9 and in Table I.

In general it was found that increasing the concentration of NH_3 resulted in a higher rate of dissolution of copper for the alloys as well as for pure copper. This is shown in Figures 8 and 9. Figures 4 and 5 demonstrate the rate curves obtained for copper and for an alloy with increasing NH_3 concentrations. The parabolic character of the alloy rate curves is shown in Figure 6, where the square of the amount of copper dissolved is plotted against time. It should be noted that the extrapolations of the lines in Figure 6 do not go through the origin, but intersect the ordinate, indicating a high initial rate of copper dissolution. This effect was particularly pronounced with alloy 10 (see Figure 7), and increased with increasing NH_3 concentrations. However, a falling off of the rate was always observed following this initial period, indicating that ultimately the film became rate controlling in every case.

The effect on the rate of increasing the gold content of the alloy is shown in Figures 8 and 9. Particular reference may be

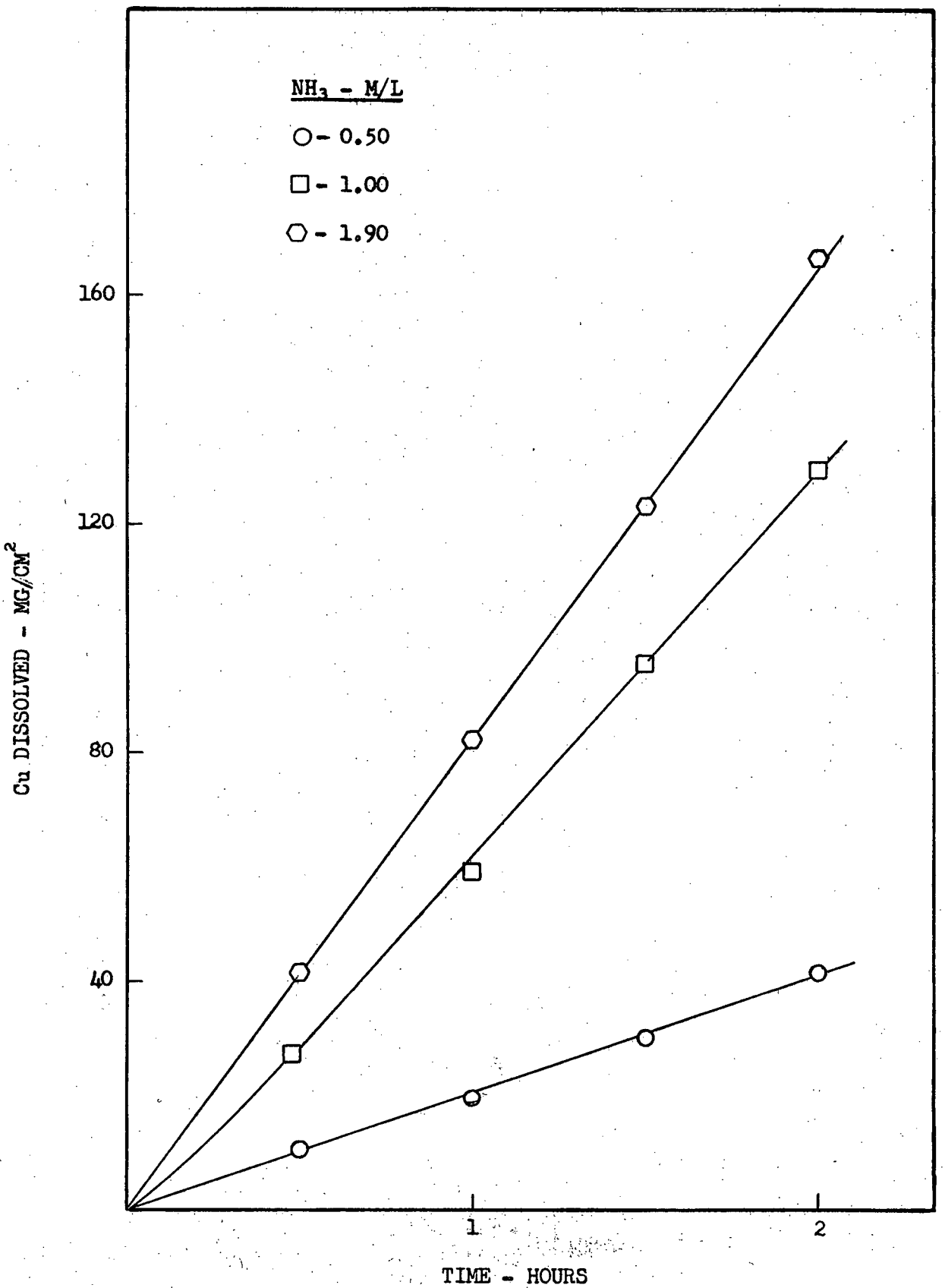

Figure 4. Rate curves for pure copper in solutions containing NH_3 alone. T = 25°C; O_2 = 6.8 Atm.

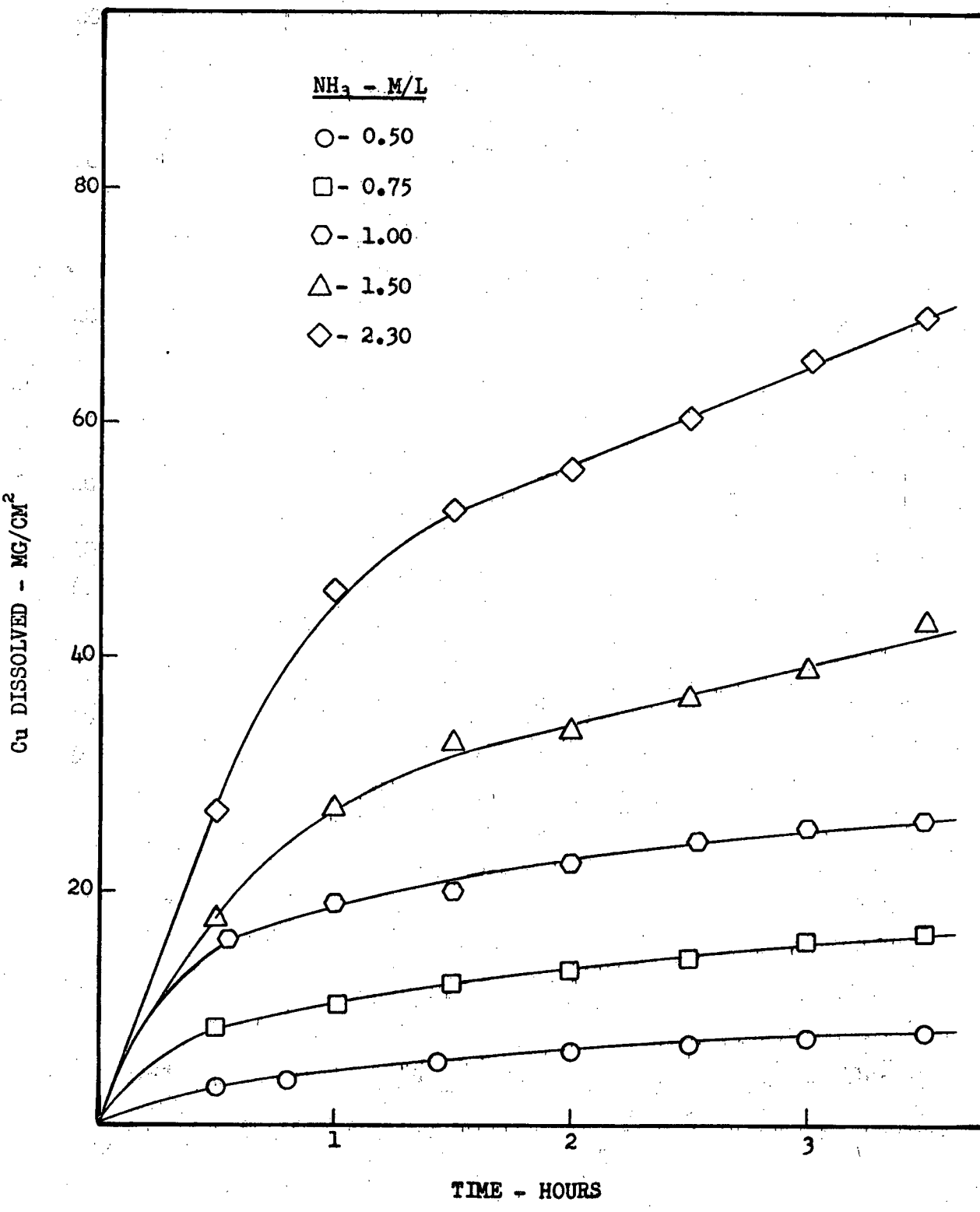

Figure 5. Rate curves for the dissolution of copper from alloy 5 in NH_3 solutions. T = 25°C; O_2 = 6.8 Atm.

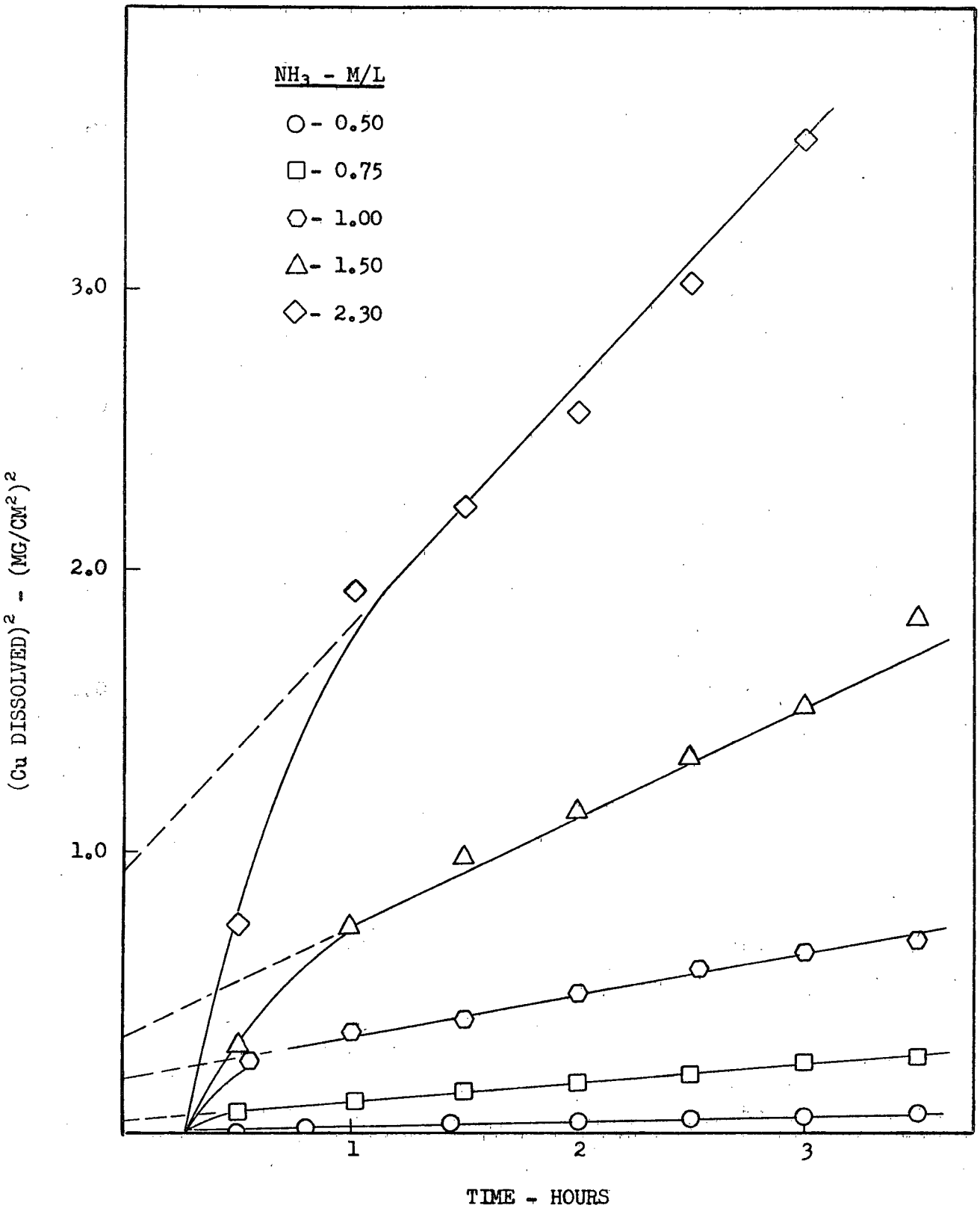

Figure 6. Parabolic plots for the dissolution of copper from alloy 5 in NH_3 solutions. T = 25°C; O_2 = 6.8 Atm.

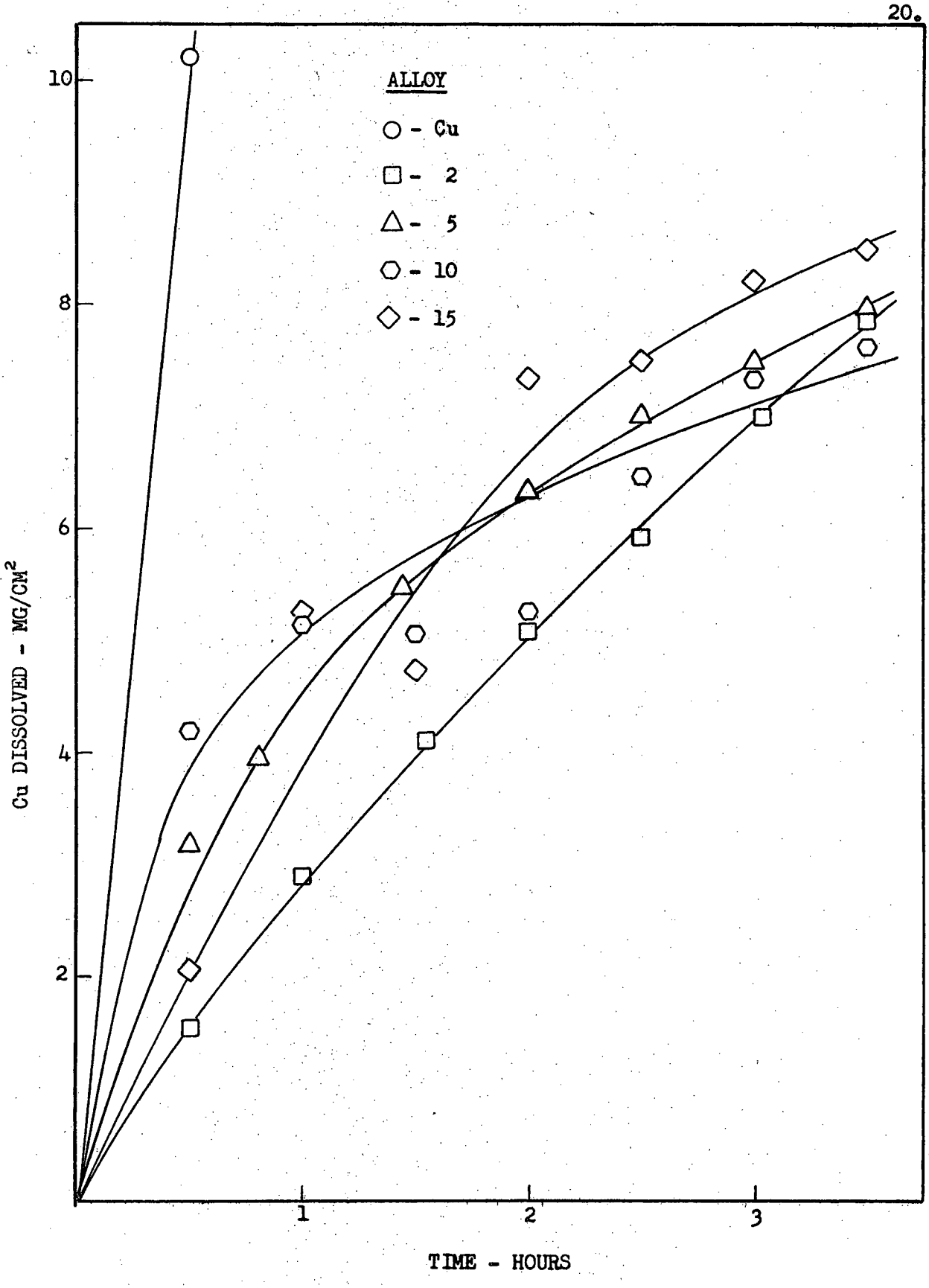

Figure 7. Comparative rate curves for the various alloys under similar corroding conditions in NH_3 solutions. NH_3 = 0.5 m/l; T = 25°C; O_2 = 6.8 Atm.

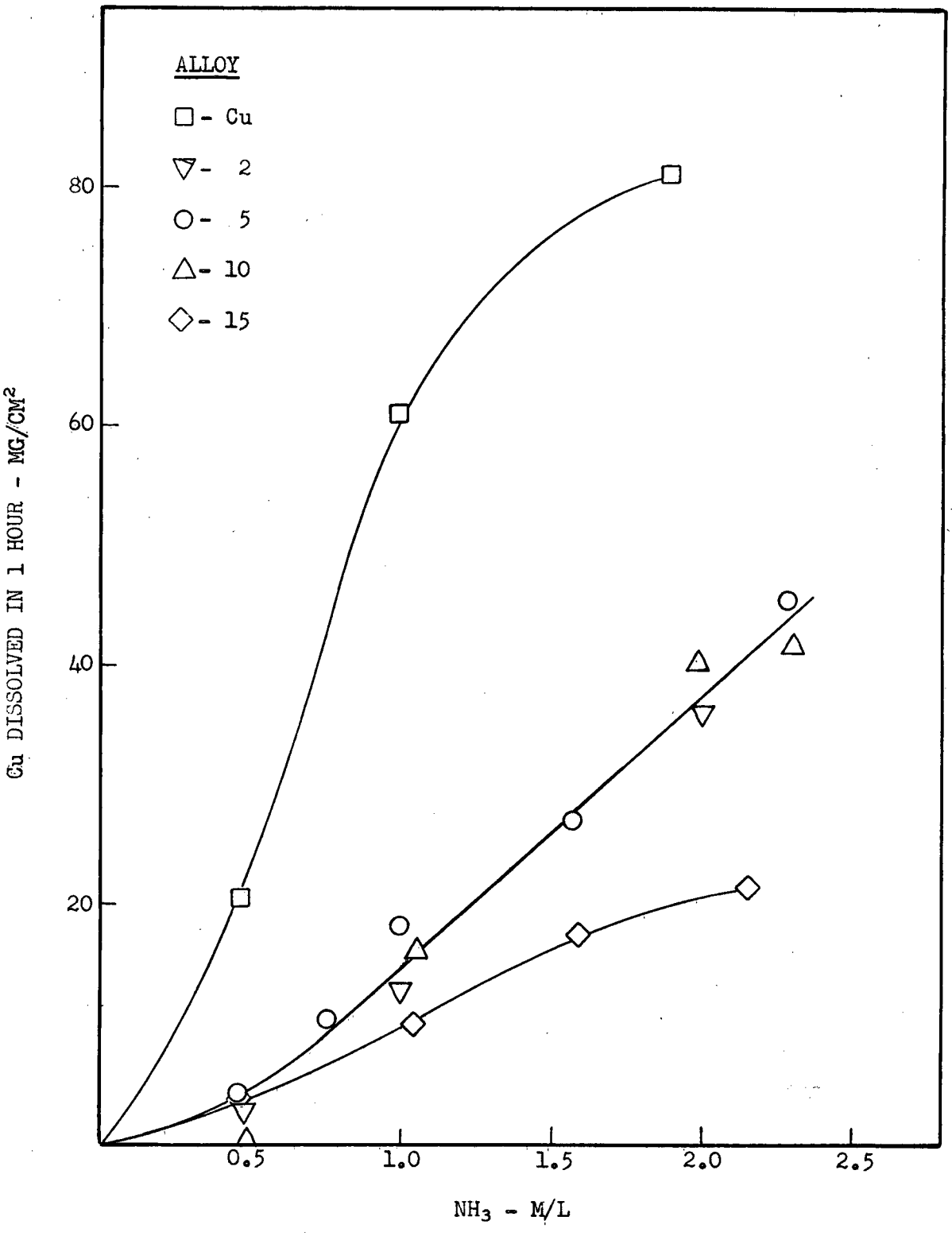

Figure 8. Effect of NH_3 on the rate of copper dissolution.
T = 25°C; O_2 = 6.8 Atm.

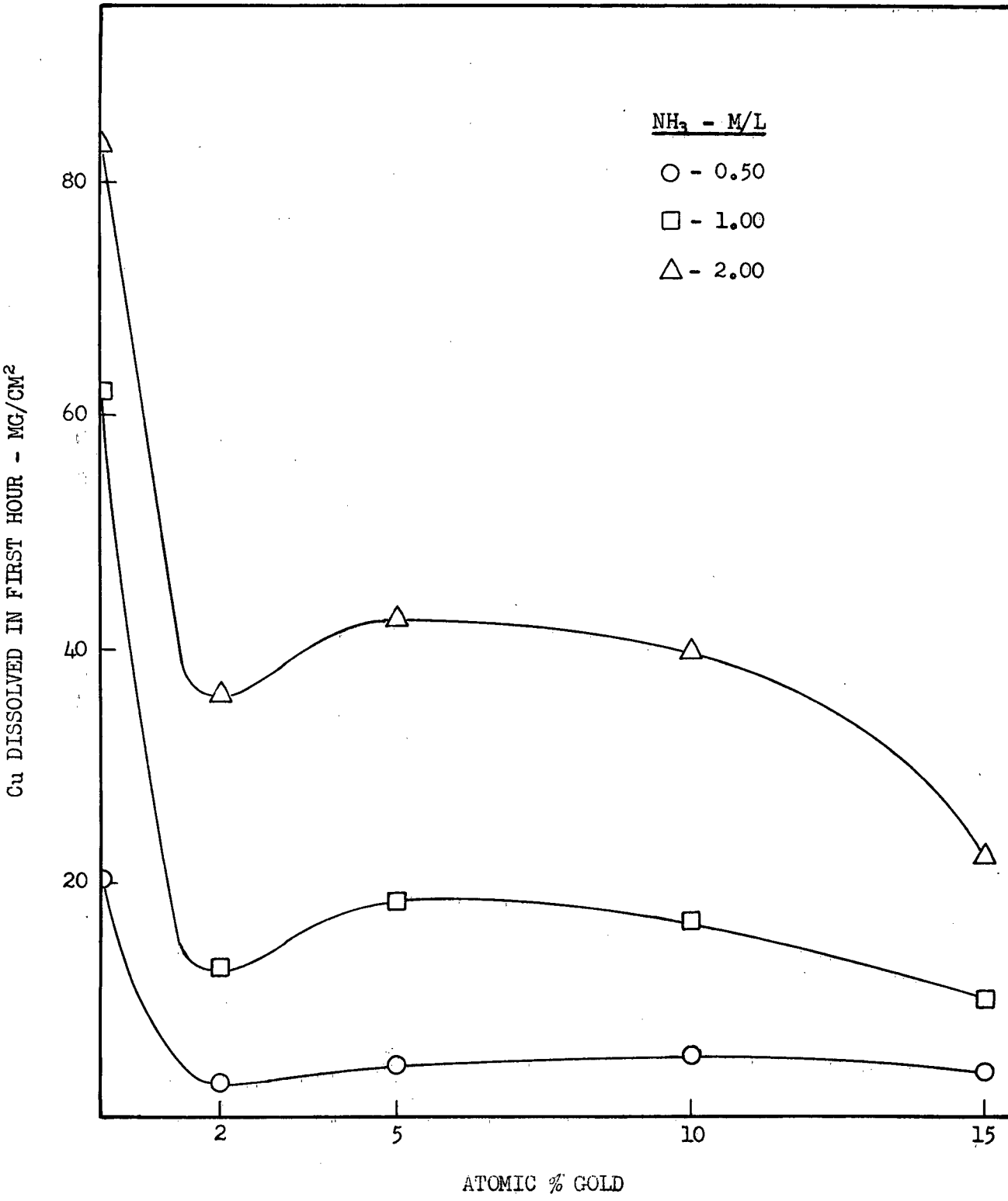

Figure 9. Effect of gold on the rate of copper dissolution in solutions containing NH_3 alone. T = 25°C; O_2 = 6.8 Atm.

TABLE I.

Data on Experiments with Solutions Containing NH_3 Alone.

Run No.	NH_3	Alloy	NH_3 Titrated	* Rate Type	*** Linear Rate	** Parab. Rate	Cu Dissolved in 1 hour
	m/l		m/l				mg
C-6	0.5	Cu	0.47	L	21.0	-	20.5
C-34	0.5	2	0.48	I	-	(0.019)	2.89
C-3	0.5	5	0.46	P	-	0.02	4.41
C-4	0.5	10	0.48	P	-	0.013	5.25
C-5	0.5	15	0.47	P	-	0.013	4.0
C-35	0.75	5	0.75	P	-	0.60	10.4
C-24	1.0	Cu	0.99	L	66.6	-	62.0
C-36	1.0	2	0.96	P	-	0.19	12.6
C-21	1.0	5	1.00	P	-	0.15	18.3
C-22	1.0	10	1.05	P	-	0.08	16.6
C-23	1.0	15	1.04	I	-	(0.11)	10.0
C-99	1.5	5	1.57	P	-	0.39	27.1
C-39	1.5	15	1.60	P	-	0.60	18.0
C-103	2.0	2	2.00				36.0
C-60	2.0	Cu	1.89	L	82.2	-	82.2
C-28	2.0	5	2.00	P	-	0.88	42.5
C-27	2.0	10	1.99	I	-	(0.34)	39.8
C-25	2.0	15	2.15	P	-	0.81	22.1
C-42	2.3	5	2.28	P	-	1.03	45.6
C-41	2.3	10	2.30	I	-	-	41.5

* Rate types: L = Linear; P = Parabolic; I = Intermediate;

** Rates in parentheses are doubtful. Units of parabolic rates are $[mgCu/cm^2]^2/hour$.

*** Units of linear rates are $mgCu/cm^2/hour$.

made to the pronounced decrease in rate which occurs when as little as 2 atomic percent gold is added to the copper. Under the conditions of these experiments (i.e. when solutions contained NH_3 but no NH_4^+ salts) further addition of gold had relatively little effect on the rate. Following a minimum at about 2 atomic percent gold, the rates appeared to increase slightly with further gold addition, reach a maximum in the region of 5 to 10 atomic percent gold, and then decrease again as the gold was increased to 15 atomic percent. Since the shapes of the rate curves for the various alloys in NH_3 are complex and differ significantly for the different alloys, the use of the amount of copper dissolved in the first hour as a measure of the rate is possibly not justified in this case. The results should therefore be interpreted with caution, since the differences involved are relatively small.

Effect of $(NH_4)_2SO_4$

It was found that solutions containing NH_4^+ salts only, with no free NH_3, did not react with copper. Apparently some free NH_3 is necessary to form the soluble cuprammine ion. The effect of the NH_4^+ ion was therefore investigated using a series of solutions in which the free NH_3 concentration was kept constant at 0.5 m/l and the concentration of $(NH_4)_2SO_4$ varied between 0.01 and 0.06 m/l (corresponding to NH_4^+ concentrations ranging from 0.02 to 0.12 m/l). This series of solutions was used to study the corrosion of copper and of each of the alloys. Some of the typical rate curves obtained in these experiments are shown in Figures 10 to 13, and all the results summarized in Table II. The rates are plotted as functions of the NH_4^+

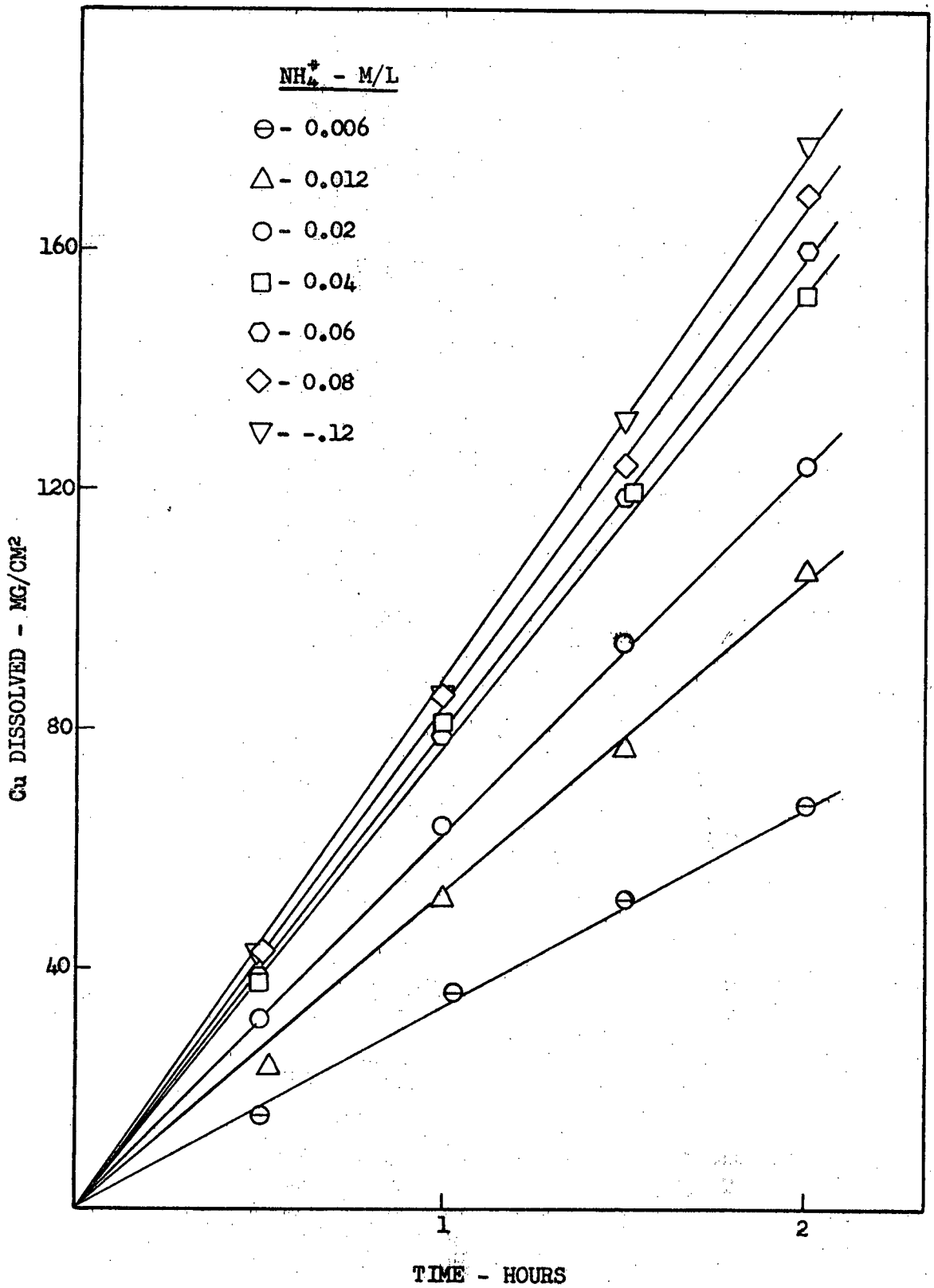

Figure 10. Rate curves for pure copper in solutions with constant NH_3 and varying NH_4^+. NH_3 = 0.5 m/l; T = 25°C; O_2 = 6.8 Atm.

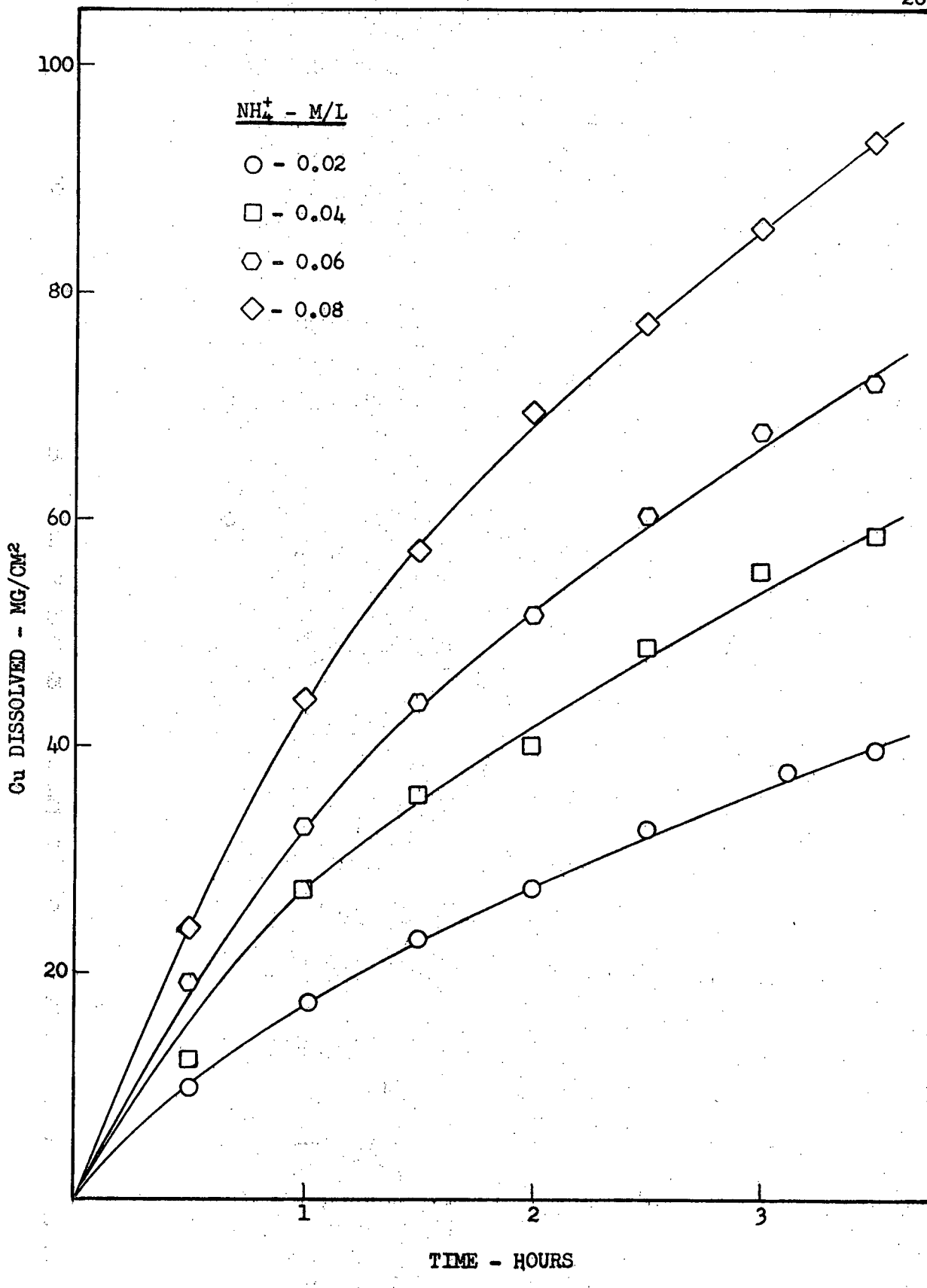

Figure 11. Rate curves for alloy 10 in solutions with constant NH_3 and varying NH_4^+. NH_3 = 0.5 m/l; T = 25°C; O_2 = 6.8 Atm.

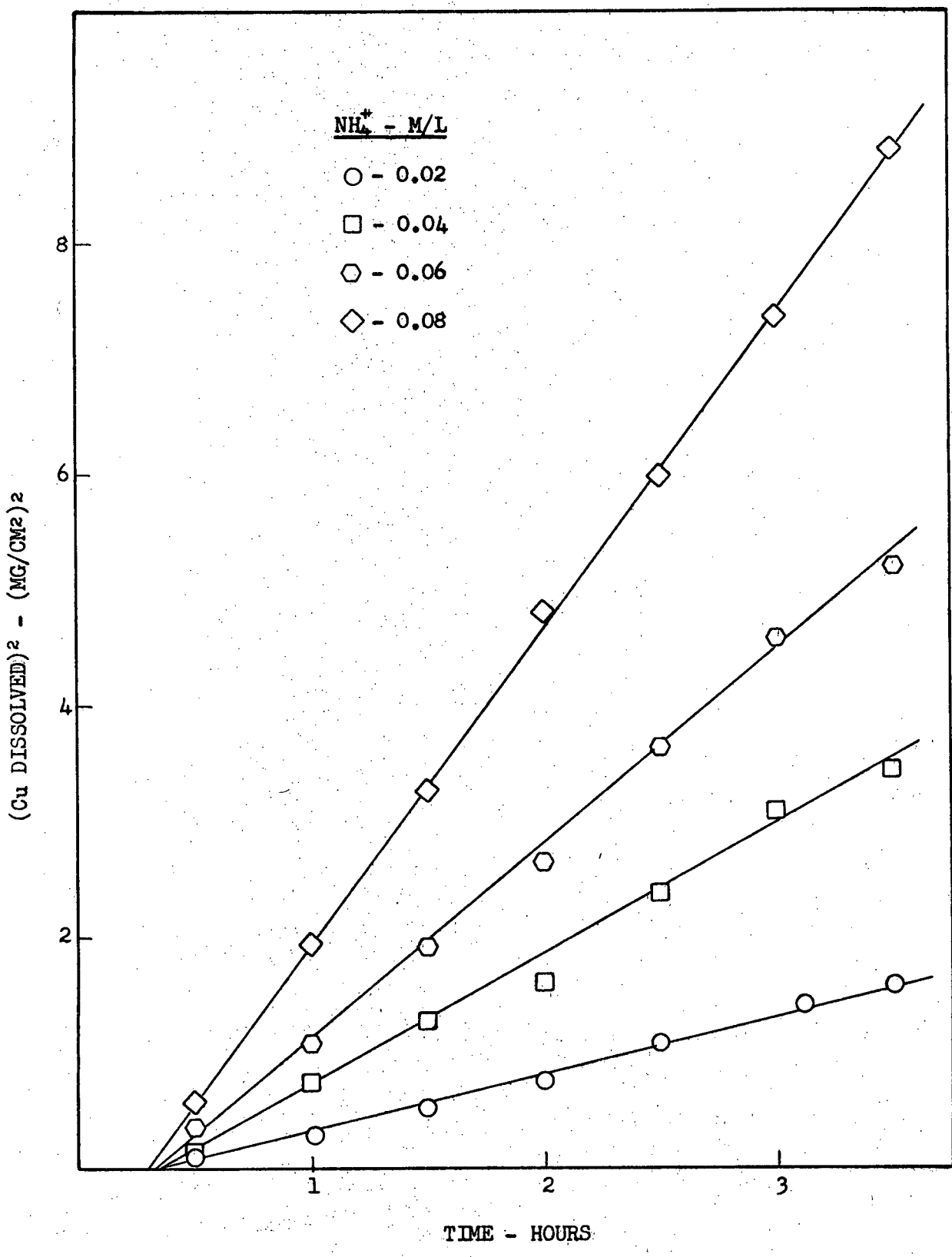

Figure 12. Parabolic plots for alloy 10 in solutions with constant NH_3 and varying NH_4^+. NH_3 = 0.5; T = 25°C; O_2 = 6.8 Atm.

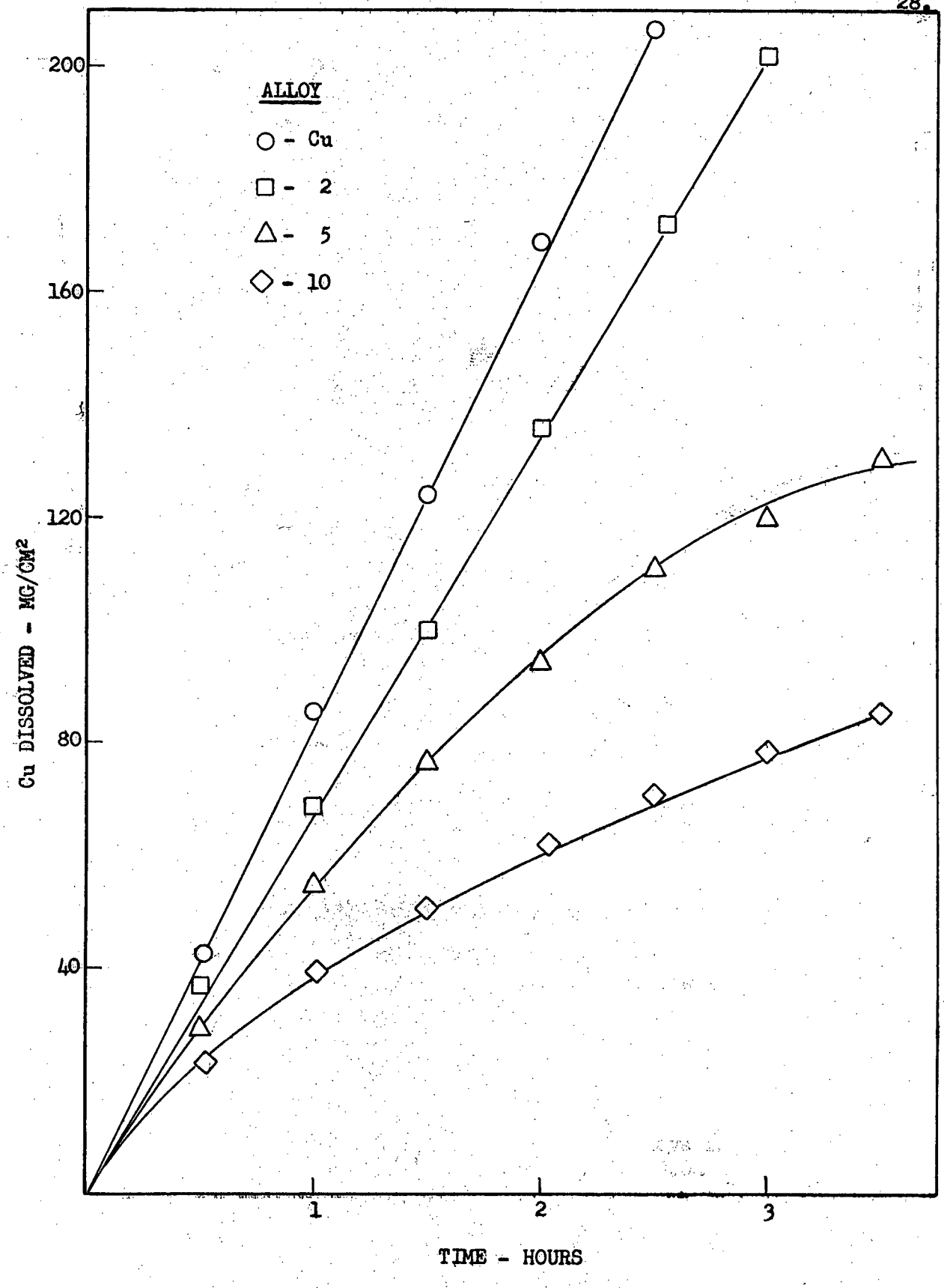

Figure 13. Comparative rate curves for the alloys in solutions with constant NH_3, constant NH_4^+. NH_4^+ = 0.04 m/l; NH_3 = 0.5 m/l; T = 25°C; O_2 = 6.8 Atm.

TABLE II.

Data on Experiments with Solutions in which NH_4^+ was Varied and NH_3 Held Constant.

Run No.	NH_4^+	NH_3	Alloy	NH_3 Titrated	Rate Type *	Linear Rate ***	Parab. Rate **	Cu Dissolved in 1 hour
	m/l	m/l		m/l				mg
C-73	0.006	0.5	Cu	0.49	L	33.3	-	33.3
C-80	0.012	0.5	Cu	0.51	L	52.5	-	52.5
C-18	0.02	0.5	Cu	0.49	L	62.2	-	62.2
C-37	0.02	0.5	2	0.50	I	-	(1.51)	31.5
C-19	0.02	0.5	5	0.50	I	-	(1.41)	28.8
C-20	0.02	0.5	10	0.48	P	-	0.53	17.2
C-17	0.02	0.5	15	0.49	-	0	0	0
C-10	0.04	0.5	Cu	0.49	L	76.8	-	76.8
C-43	0.04	0.5	2	0.53	L	60.0	-	60.0
C-8	0.04	0.5	5	0.53	P	-	3.60	45.0
C-9	0.04	0.5	10	0.50	P	-	1.14	25.5
C-11	0.04	0.5	15	0.51	-	0	0	0
C-31	0.06	0.5	Cu	0.53	L	80.8	-	80.8
C-45	0.06	0.5	2	0.50	I	68.3	-	68.3
C-14	0.06	0.5	5	0.50	P	-	5.47	55.0
C-16	0.06	0.5	10	0.51	P	-	1.72	32.8
C-13	0.08	0.5	Cu	0.52	L	83.3	-	83.3
C-46	0.08	0.5	2	0.52	L	67.8	-	67.8
C-26	0.08	0.5	5	0.49	P	-	5.64	54.8
C-15	0.08	0.5	10	0.51	P	-	2.36	37.8
C-12	0.08	0.5	15	0.51	-	0	0	0
C-56	0.10	0.5	5	0.51	P	-	6.86	61.0
C-38	0.10	0.5	10	0.52	P	-	2.74	44.0
C-44	0.12	0.5	Cu	0.51	L	89.6	-	85.5
C-59	0.12	0.5	2	0.51	I	(59.0)	-	68.0
C-29	0.12	0.5	5	0.45	P	-	7.04	59.0
C-30	0.12	0.5	10	0.49	P	-	2.67	44.9

* L = Linear; P = Parabolic; I = Intermediate;

** Rates in parentheses are doubtful. Units of parabolic rates are $[mgCu/cm^2]^2/hour$.

*** Units of linear rates are $mgCu/cm^2/hour$.

ion concentration and of the alloy composition in Figures 14 and 15, respectively.

An examination of the results reveals the following effects:

(1) All the rate curves for pure copper were again found to be linear. Most of those for the alloys (but not all) were parabolic (compare Figures 10, 11 and 12).

(2) Increasing the gold content of the alloy resulted in a lowering of the rate of dissolution (see Figures 13 and 15). The rate decreased continuously with increasing gold concentration until the reaction ceased at about 15 atomic percent gold. In no case, when the solutions contained NH_4^+ ions as well as free NH_3, could any reaction be detected with alloy 15. These results are in marked contrast to those observed with solutions containing NH_3 only and discussed earlier, where it was found that the initial addition of a small amount of gold to the copper resulted in a large decrease in the rate, while further gold addition had relatively little effect (compare Figures 9 and 15).

(3) Increasing the gold content of the alloy also tended to make the rate curves more parabolic as is shown in Figure 13. In a solution containing 0.08 m/l of NH_4^+, it was found that the rate curve for alloy 2 remained linear until a considerable amount of copper had dissolved. The rate curves for alloys 5 and 10, on the other hand, were parabolic from the start.

(4) The rates of dissolution for pure copper and for alloys 2, 5

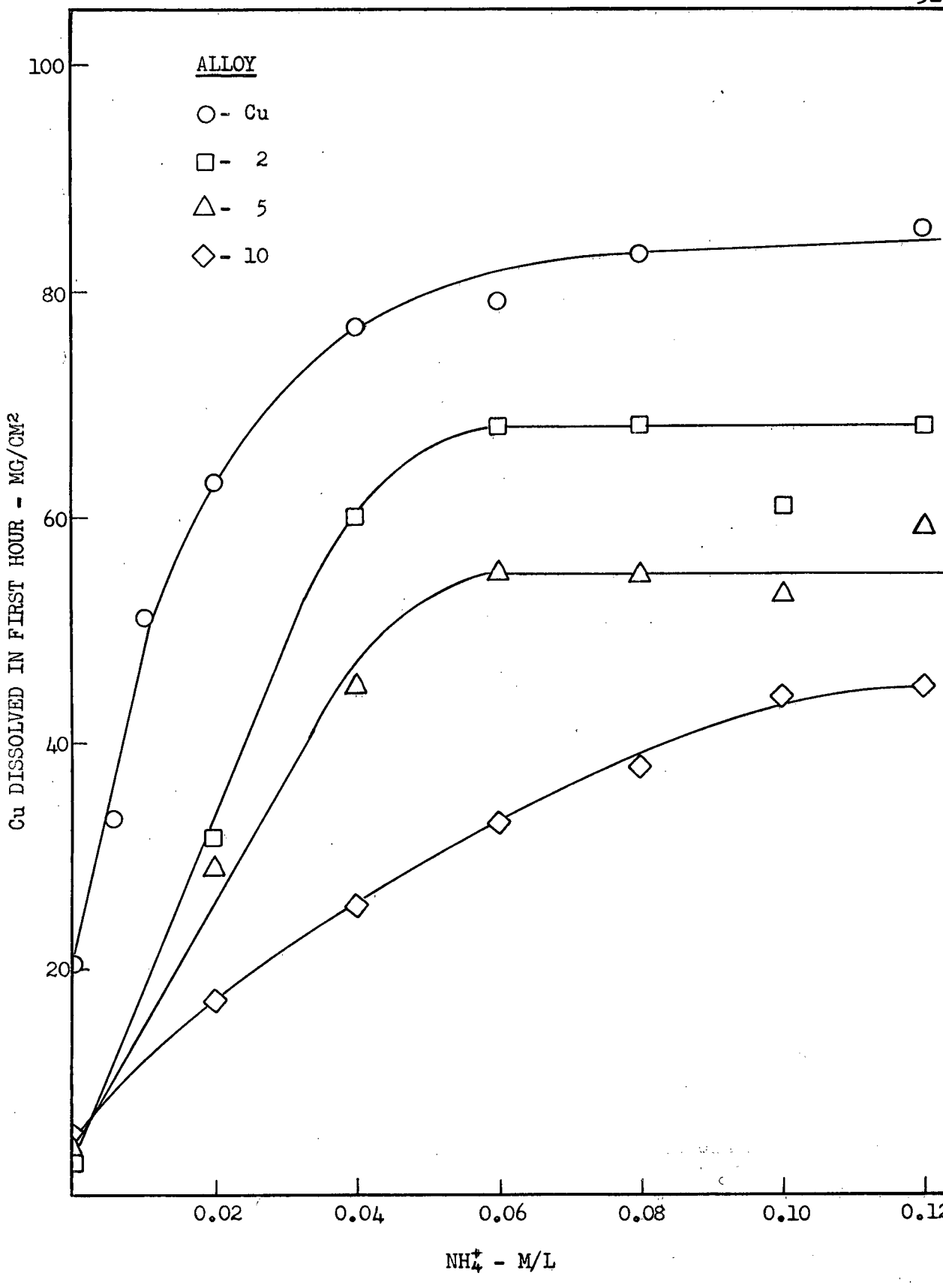

Figure 14. Effect of NH_4^+ on the rate of copper dissolution at constant NH_3. NH_3 = 0.5 m/l; T = 25°C; O_2 = 6.8 Atm.

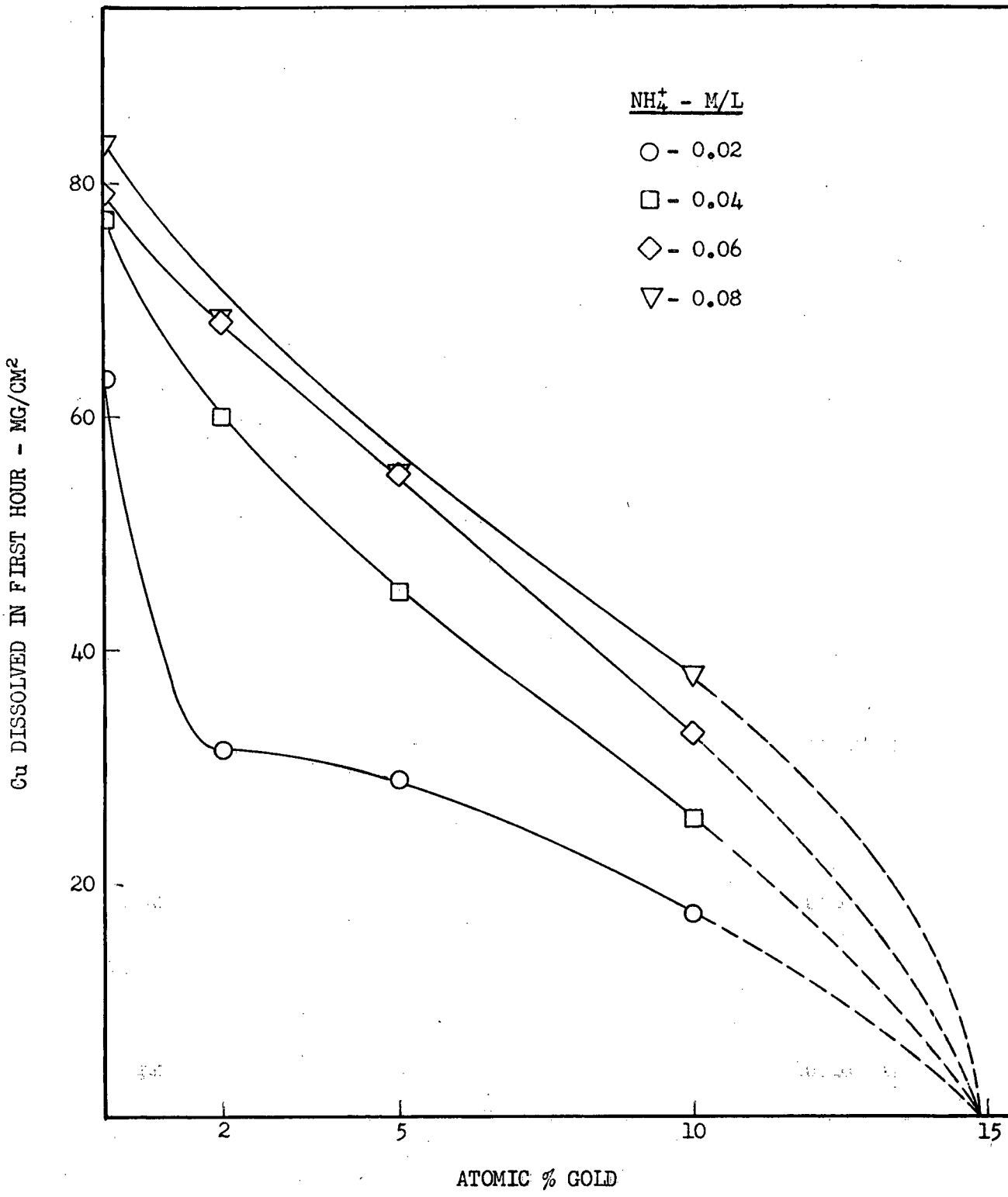

Figure 15. Effect of gold on the rates of copper dissolution in solutions with constant NH_3 and varying NH_4^+. NH_3 = 0.5 m/l; T = 25°C; O_2 = 6.8 Atm.

and 10 increased with increasing NH_4^+ concentration until the latter reached about 0.06 m/l. Further addition of NH_4^+ did not increase the dissolution rates (see Figures 14 and 15). The limiting value of the rate decreased with increasing gold concentration in the alloys, and became zero for the 15 atomic percent alloy. For pure copper, there is evidence (1) that the attainment of a limiting value of the rate is due to control by oxygen transport through the solution to the surface of the metal. With the alloys, it is apparent that other considerations are involved.

(5) With alloy 2 it was noted that the rate curves tended toward linearity when the NH_4^+ ion concentration was increased. Thus the rate curve was parabolic below 0.02 m/l of NH_4^+ ion and linear at higher concentration, but with a tendency to become parabolic in later stages of the reaction.

Without going into detailed considerations of the mechanism at this point, some general conclusions relating to the effect of NH_4^+ may be noted. The presence of NH_4^+ appears to have a large effect on alloys of low gold content. This effect is to increase the rates very markedly and to make the rate curves tend toward linearity, or in other words, to offset the effects which were observed when only NH_3 was present in the solutions and which were attributed to the presence of a film. Since it is not likely that NH_4^+ could have any effect on a film consisting only of gold or a gold-rich metallic phase, there is some suggestion here that an oxide, such as copper oxide whose stability is very sensitive to NH_4^+, is constituting part of the

film structure. It should be emphasized that this applies only to the low gold alloys. For the alloys higher in gold, NH_4^+ had a much smaller effect and in the case of alloy 15 actually inhibited the reaction.

The Effect of Varying NH_3 in the Presence of Constant NH_4^+

In view of the differences noted above between solutions containing NH_3 only and those containing both NH_3 and NH_4^+, it was decided to undertake a series of experiments on all the alloys in which the NH_4^+ concentration was held constant at 0.02 m/l and the NH_3 concentration varied between 0.25 and 1.0 m/l. Some typical results of these experiments are represented by Figures 16 to 20 and summarized in Table III.

These results present a very striking feature, namely that increasing the concentration of NH_3 in solutions containing both NH_3 and NH_4^+ has a very similar effect to that obtained by increasing the concentrations of NH_4^+ in such solutions and discussed earlier. In particular, the following points of similarity may be noted:

(1) Increasing the NH_3 concentration caused the rate curves to approach linearity. This was noted with both alloy 2 and alloy 5. It was shown earlier that increasing the NH_4^+ concentration had a similar effect.

(2) The rate increased with increasing NH_3 concentration, and reached a limiting value at 0.75 m/l of NH_3. At higher NH_3 concentrations a tendency was observed for the rate to fall off again, but the effect was small and its validity is open to question in

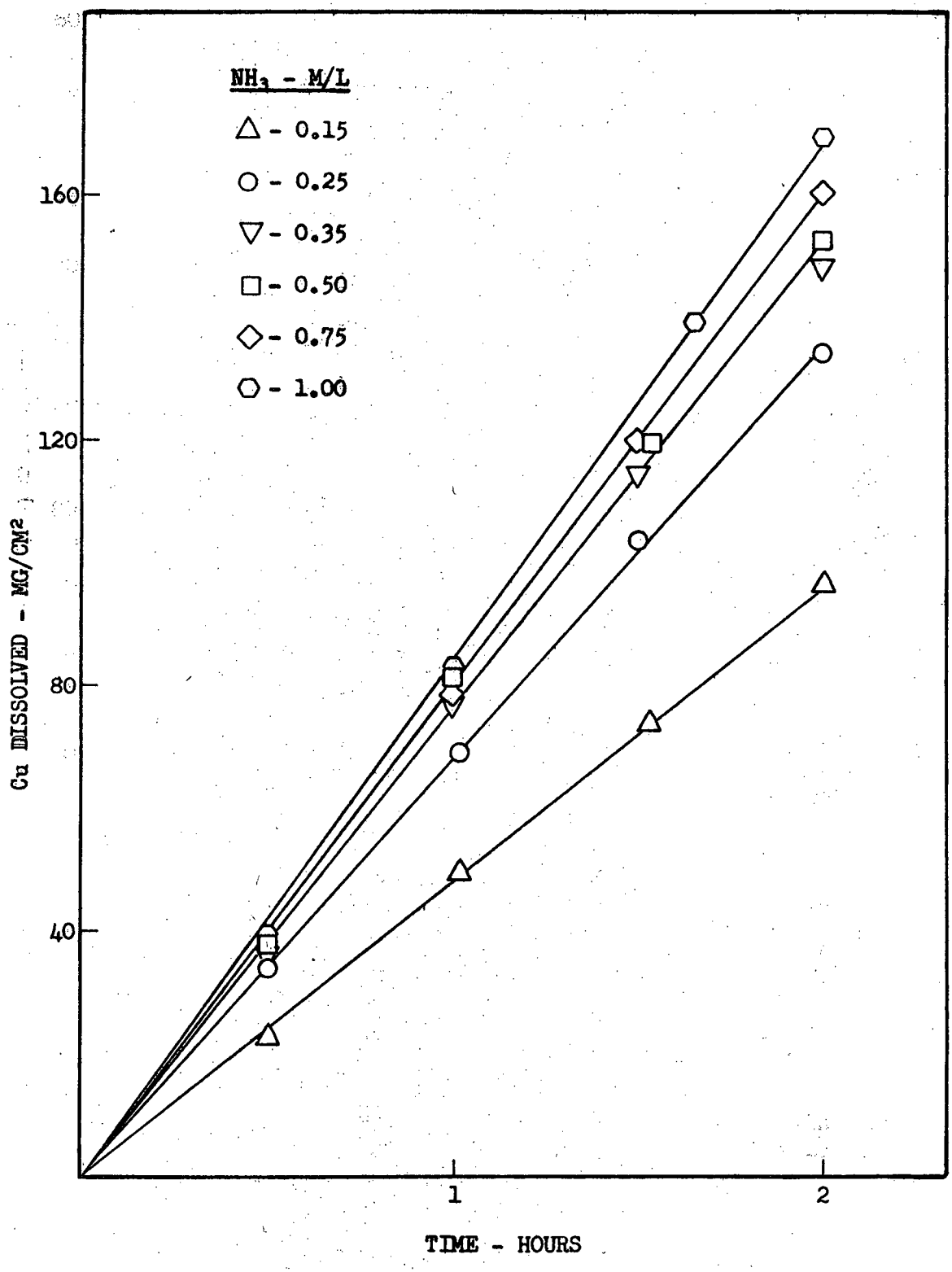

Figure 16. Rate curves for pure copper in solutions with constant NH_4^+ and varying NH_3. NH_4^+ = 0.04 m/l; T = 25°C; O_2 = 6.8 Atm.

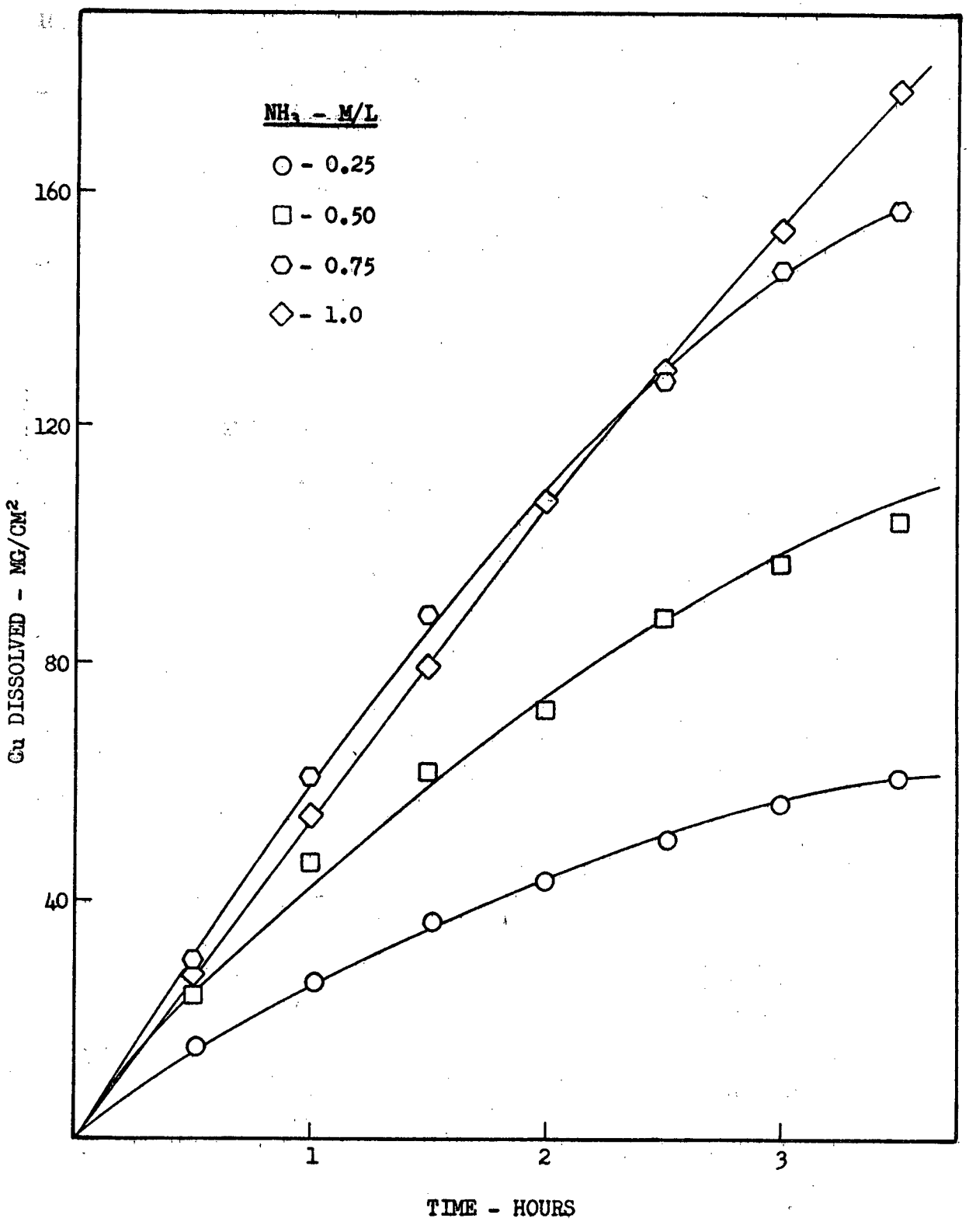

Figure 17. Rate curves for alloy 5 in solutions with constant NH_4^+ and varying NH_3. NH_4^+ = 0.04 m/l; T = 25°C; O_2 = 6.8 Atm.

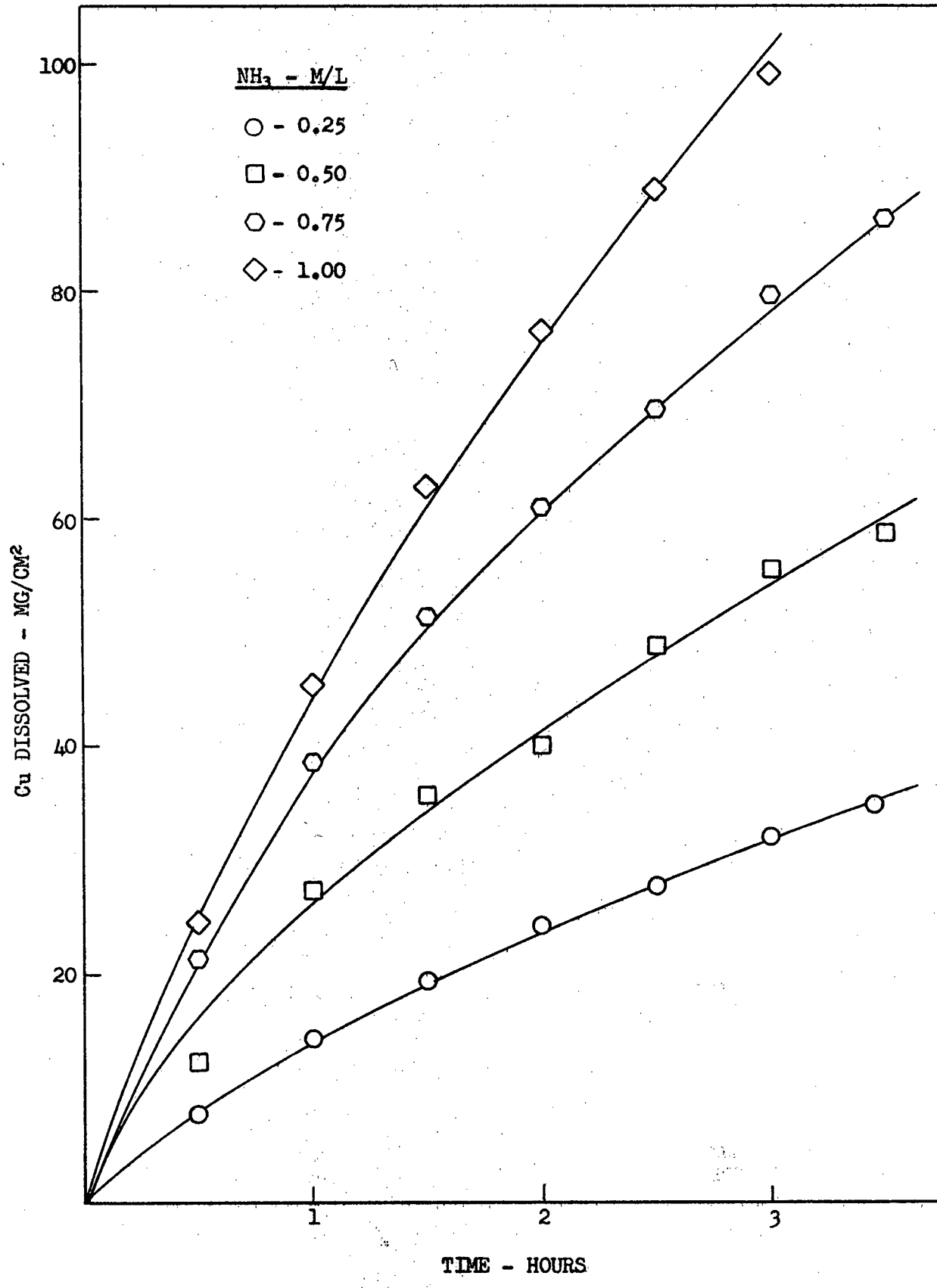

Figure 18. Rate curves for alloy 10 in solutions with constant NH_4^+ and varying NH_3. NH_4^+ = 0.04 m/l; T = 25°C; O_2 = 6.8 Atm.

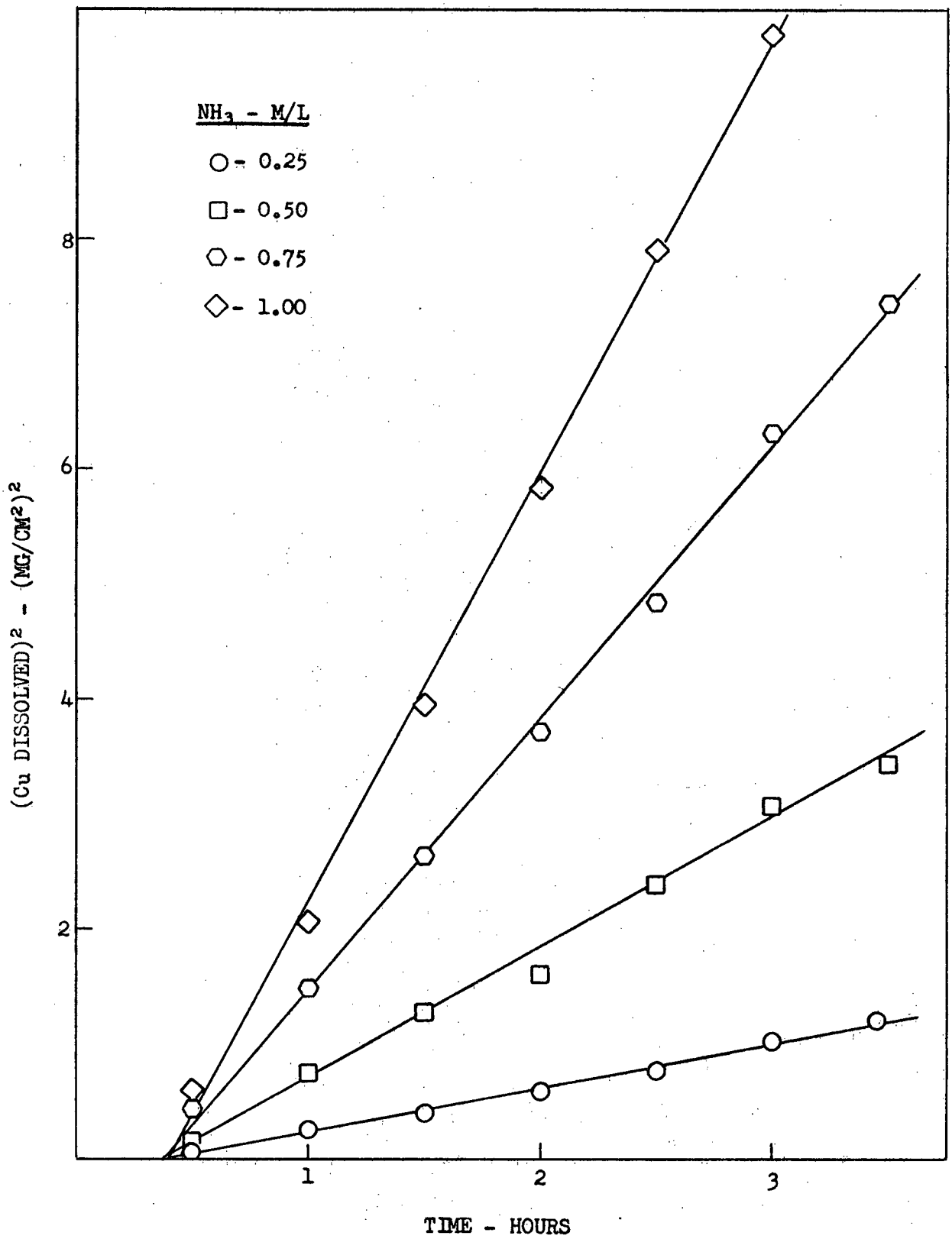

Figure 19. Parabolic plots for alloy 10 in solutions with constant NH_4^+ and varying NH_3. NH_4^+ = 0.04 m/l; T = 25°C; O_2 = 6.8 Atm.

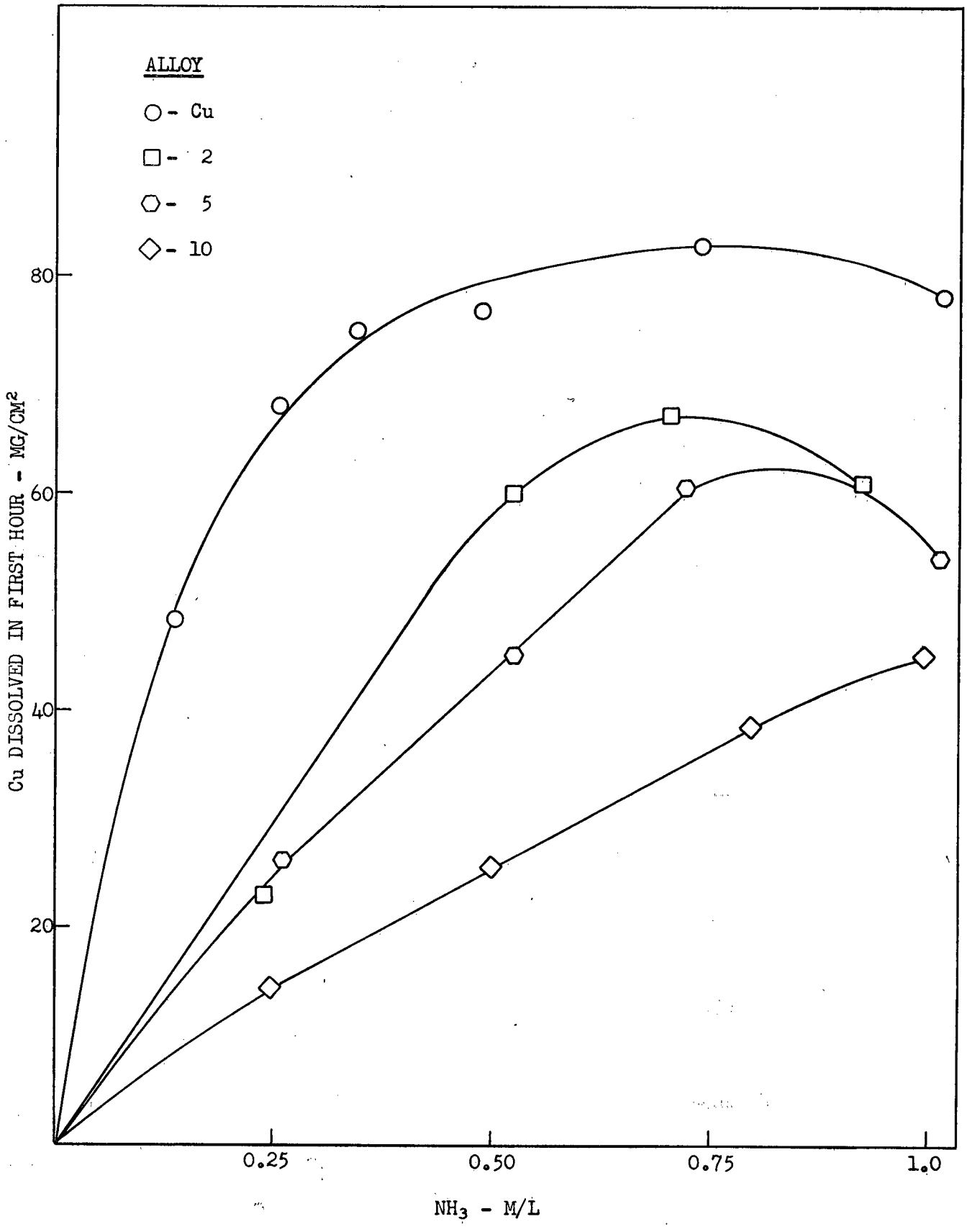

Figure 20. Effect of NH_3 in solutions containing constant NH_4^+.
NH_4^+ = 0.04 m/l; T = 25°C; O_2 = 6.8 Atm.

TABLE III.

Data on Experiments with Solutions in which NH_3 was Varied and NH_4^+ Held Constant.

Run No.	NH_4^+	NH_3	Alloy	NH_3 Titrated	Rate Type *	Linear Rate ***	Parab. Rate **	Cu Dissolved in 1 hour
	m/l	m/l		m/l				mg
C-63	0.04	0.15	Cu	0.14	L	48.2	-	48.2
C-51	0.04	0.25	Cu	0.26	L	68.4	-	68.4
C-62	0.04	0.25	2	0.24	I	-	-	22.8
C-47	0.04	0.25	5	0.26	P	-	1.21	26.1
C-50	0.04	0.25	10	0.25	P	-	0.42	14.3
C-97	0.04	0.35	Cu	0.35	L	75	-	75
C-10	0.04	0.5	Cu	0.49	L	76.8	-	76.8
C-43	0.04	0.5	2	0.53	L	60.0	-	60.0
C-8	0.04	0.5	5	0.53	P	-	3.60	45.0
C-9	0.04	0.5	10	0.50	P	-	1.14	25.5
C-11	0.04	0.5	15	0.51	-	0	0	0
C-52	0.04	0.75	Cu	0.74	L	86.6	-	82.8
C-68	0.04	0.75	2	0.71	I	67.2	-	67.2
C-49	0.04	0.75	5	0.72	P	-	8.29	60.5
C-53	0.04	0.75	10	0.80	P	-	2.36	38.5
C-58	0.04	1.0	Cu	1.02	L	80.9	-	78.3
C-70	0.04	1.0	2	0.92	I	-	-	61.0
C-54	0.04	1.0	5	1.02	I	(54.0)	-	54.0
C-55	0.04	1.0	10	1.00	P	-	3.72	45.0
C-48	0.04	1.0	15	0.99	-	0	0	0
C-56	0.12	0.12	10	0.12	P	-	0.50	17.5
C-61	0.12	0.20	10	0.21	P	-	0.91	24.5
C-62	0.12	0.25	10	0.24	I	-	-	26.0
C-30	0.12	0.5	10	0.49	P	-	-	44.5
C-64	0.12	1.0	10	0.93	I	-	-	47.0

* L = Linear; P = Parabolic; I = Intermediate;

** Rates in Parentheses are doubtful. Units of parabolic rates are $[mgCu/cm^2]^2/hour$.

*** Units of linear rates are $mgCu/cm^2/hour$.

view of the errors involved in both the measurements and the method used to estimate the rate. More significant is the fact that the limiting rates obtained on increasing the NH_3 concentration were very close to those which resulted on increasing the NH_4^+ concentration. The value of this limiting rate thus appears to be characteristic only of the composition of the alloy. It might also be noted that the effect of NH_3, while qualitatively similar to that of NH_4^+, was smaller, considerably higher concentrations of NH_3 being required to achieve the limiting rate (see Figures 14 and 20).

(3) At very low NH_3 concentrations the pronounced initial decrease in rate on addition of a small amount of gold to the copper was again observed, with an apparent minimum in the rate occurring at about 2 atomic percent gold (see Figure 21). A similar effect has already been noted for solutions very low in NH_4^+.

Effect of Oxygen Partial Pressure.

The effects of varying the partial pressure of oxygen from 1.7 to 6.8 atmospheres were investigated for copper and for each of the alloys. In this series of experiments the compositions of the solutions were held constant at 0.5 m/l NH_3 and 0.02 m/l NH_4^+. The rates were thus well below the limiting values attained at higher NH_3 or NH_4^+ concentrations. Some typical rate curves depicting the effects of varying the oxygen pressure on pure copper and on one of the alloys (the effects for the other alloys were similar), are shown in Figures 22 and 23. The results for this series of experiments are summarized in Table IV.

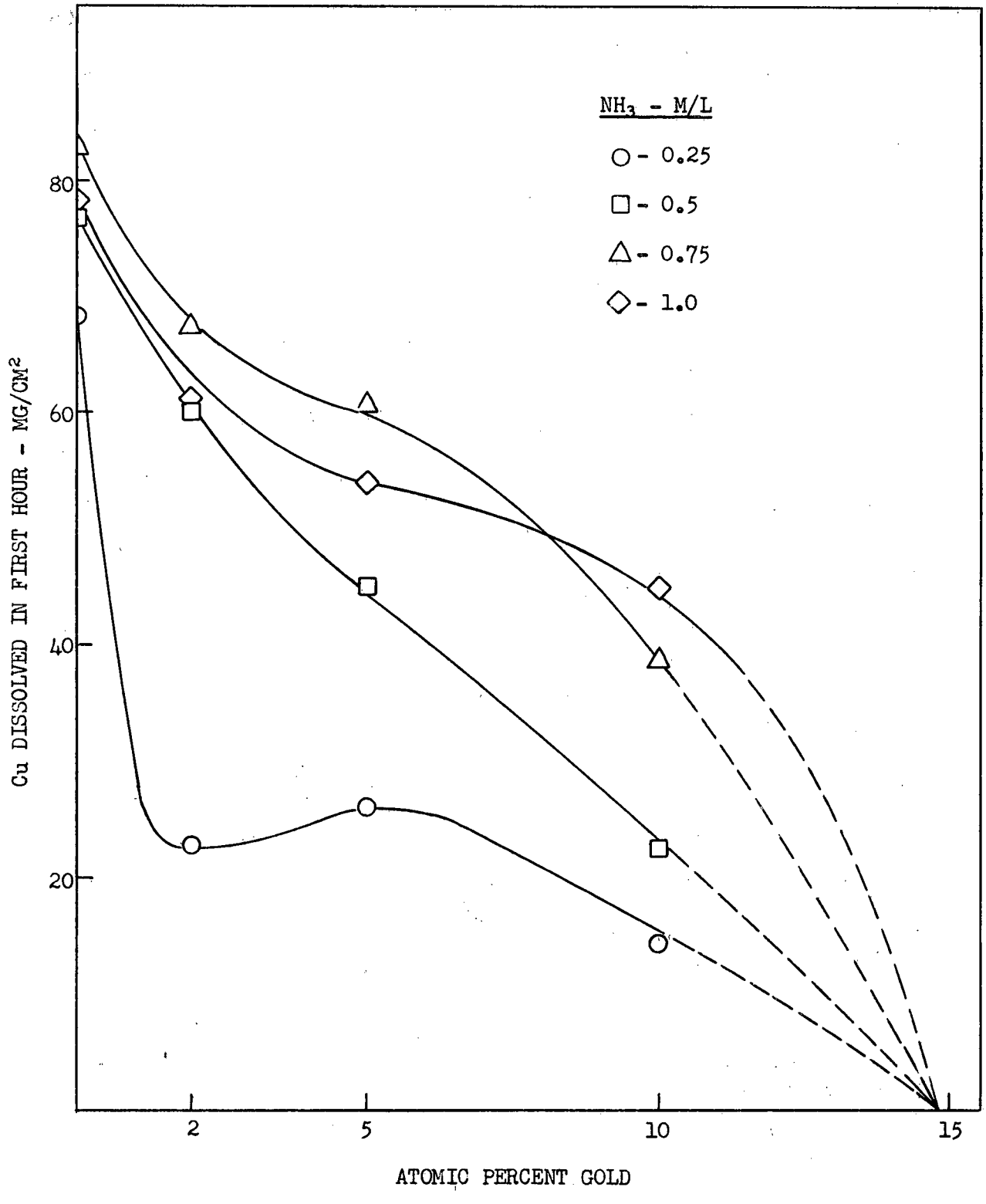

Figure 21. Effect of gold on the rates of copper dissolution in solutions with constant NH_4^+ and varying NH_3. NH_4^+ = 0.04 m/l; T = 25°C; O_2 = 6.8 Atm.

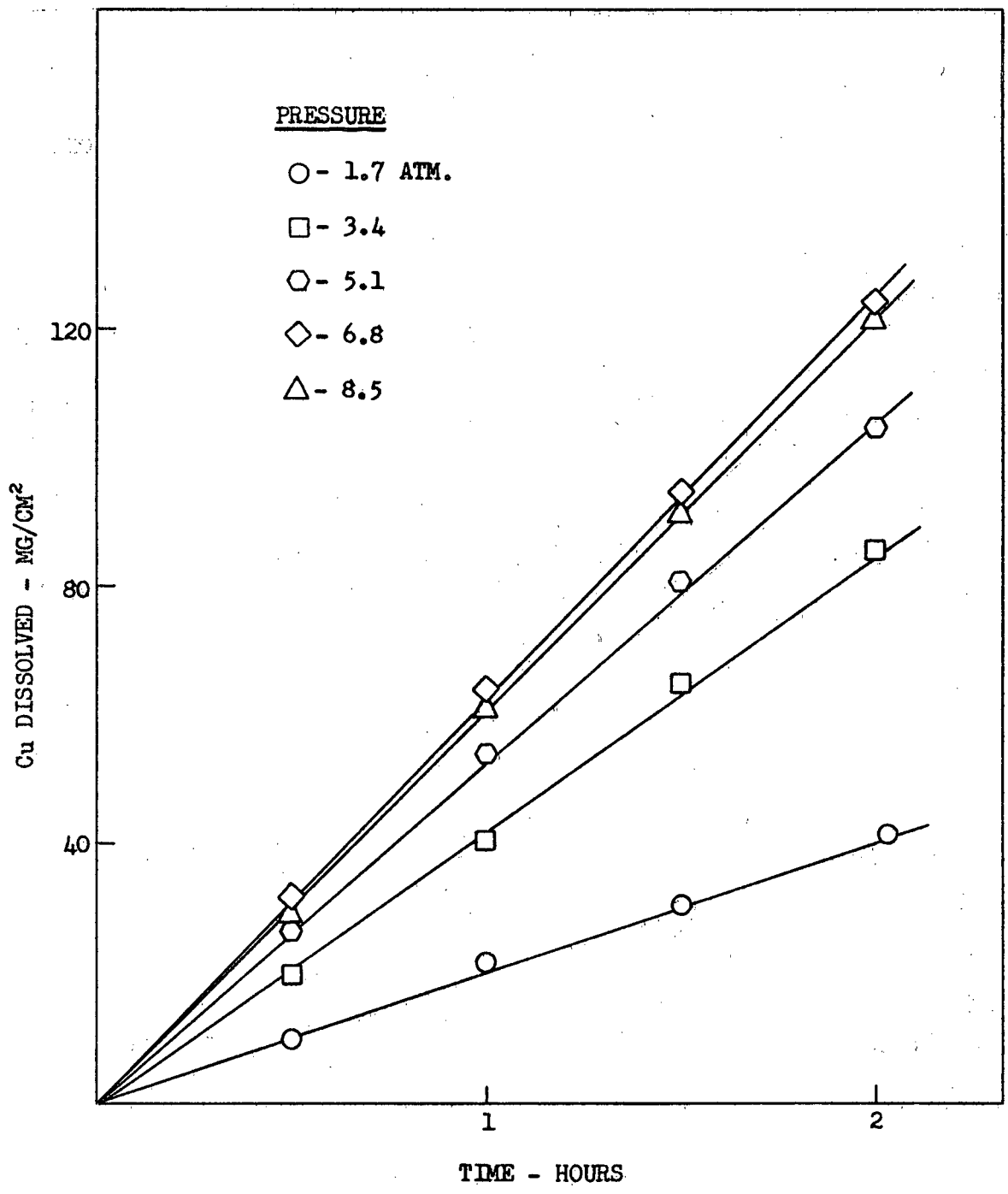

Figure 22. Rate curves for pure copper at various oxygen pressures. NH_3 = 0.5 m/l; NH_4^+ = 0.02 m/l; T = 25°C.

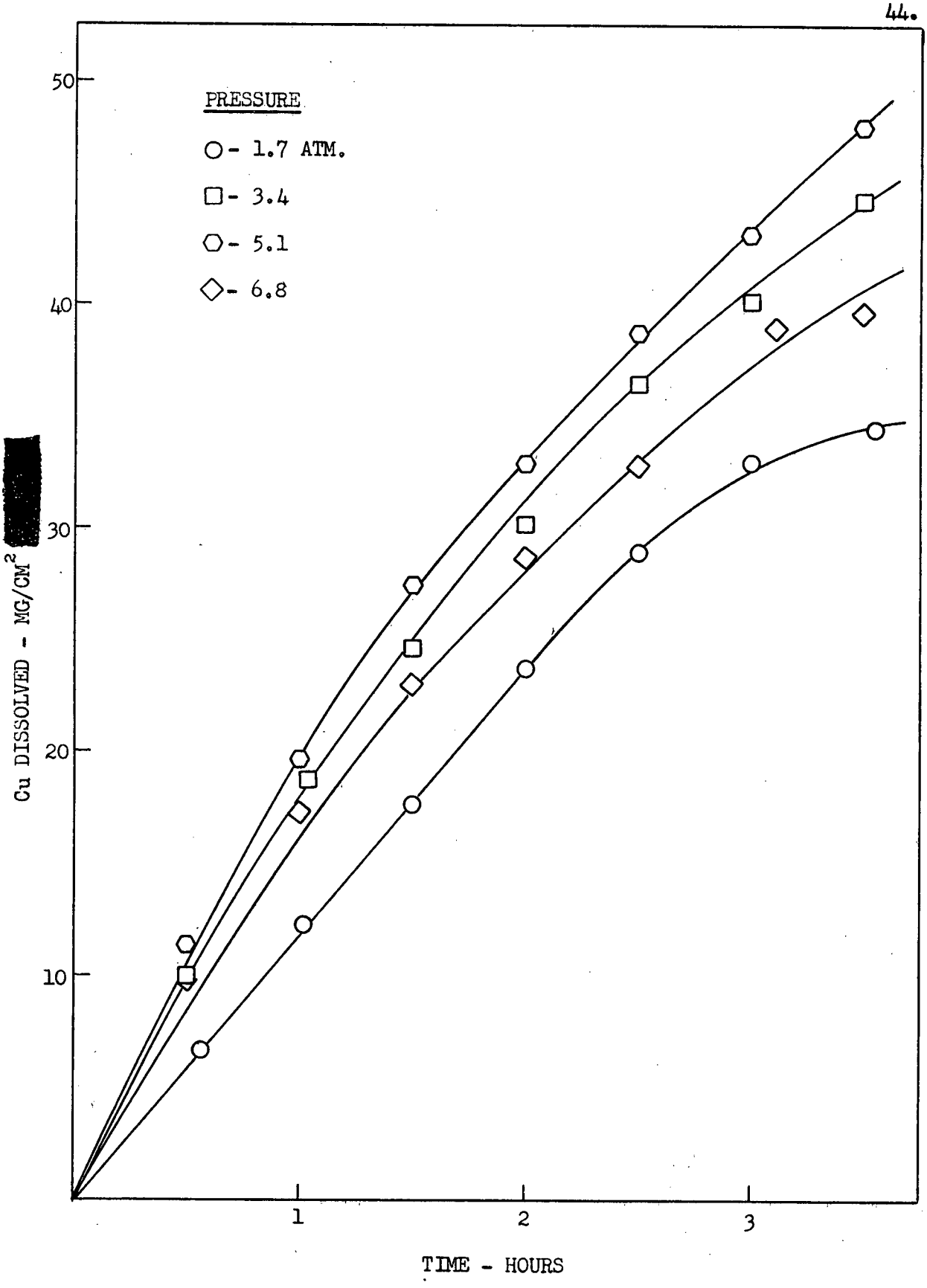

Figure 23. Rate curves for alloy 10 at various oxygen pressures. NH_3 = 0.5 m/l; NH_4^+ = 0.02 m/l; T = 25°C.

TABLE IV.

Data on Experiments in which Oxygen Pressure was Varied.

Run No.	Alloy	Pressure	Temp.	NH_3	NH_4^+	NH_3 Titrated	Rate Type *	Linear Rate ***	Parab. Rate **	Cu Diss. in 1 hr.
		Atm.	°C.	m/l	m/l	m/l				mg.
C-88	Cu	1.7	25	0.5	0.02	0.49	L	20.0	-	20.0
C-83	2	1.7	25	0.5	0.02	0.51	I	-	-	25.5
C-69	10	1.7	25	0.5	0.02	0.50	I	-	-	12.2
C-92	Cu	3.4	25	0.5	0.02	0.49	L	42.0	-	42.0
C-89	2	3.4	25	0.5	0.02	0.50	I	-	-	31.4
C-71	10	3.4	25	0.5	0.02	0.49	P	-	0.69	18.7
C-96	Cu	5.1	25	0.5	0.02	0.47	L	53.9	-	53.9
C-94	2	5.1	25	0.5	0.02	0.49	P	-	2.0	39.0
C-74	10	5.1	25	0.5	0.02	0.50	P	-	0.78	19.6
C-18	Cu	6.8	25	0.5	0.02	0.49	L	62.2	-	62.2
C-37	2	6.8	25	0.5	0.02	0.50	I	-	(1.51)	31.5
C-19	5	6.8	25	0.5	0.02	0.50	I	-	(1.41)	28.8
C-20	10	6.8	25	0.5	0.02	0.48	P	-	0.53	17.2
C-101	Cu	8.5	25	0.5	0.02	0.50	L	61.1	-	61.1
C-79	10	1.7	15	0.5	0.02	0.52	I	-	-	11.1
C-85	10	3.4	15	0.5	0.02	0.51	P	-	0.64	16.8
C-76	10	6.8	15	0.5	0.02	0.50	P	-	0.54	17.7
C-87	10	1.7	35	0.5	0.02	0.48	I	-	-	15.4
C-91	10	3.4	35	0.5	0.02	0.48	P	-	0.98	24.7
C-93	10	5.1	35	0.5	0.02	0.49	I	-	-	21.7
C-78	10	6.8	35	0.5	0.02	0.49	I	-	-	22.4

* Rate types: L = Linear; P = Parabolic; I = Intermediate;

** Rates in parentheses are doubtful. Units of parabolic rates are $[mgCu/cm^2]^2/hour$.

*** Units of linear rates are $mgCu/cm^2/hour$.

For pure copper it was found that the rate increased with the oxygen pressure and levelled off at a constant value when the pressure was increased beyond 6.8 atmospheres. The significance of this has been discussed elsewhere (1). At low oxygen pressures the rate is determined by the transport of oxygen to the metal surface and is therefore proportional to the oxygen pressure. At higher oxygen pressures, the chemical reaction at the metal surface becomes rate controlling and the rate becomes independent of the oxygen pressure.

With the alloys, however, the effect of varying the oxygen pressure was found to be somewhat different. The rate increased with the oxygen pressure up to a maximum value, generally at about 5.1 atmospheres, and then fell again as the oxygen pressure was further increased (see Figure 23). This was the case for all the alloys.

Effect of Temperature.

The effect of temperature on copper and on alloys 2 and 10 was investigated using solutions of the same composition as those used in the investigation on pressure (i.e. 0.5 m/l NH_3 and 0.02 m/l NH_4^+). The effect of temperature on alloy 5 was investigated using solutions containing 0.5 m/l NH_3, but without NH_4^+. The temperature was varied between 15 and 50°C with the pressure held constant at 6.8 atmospheres. Typical rate curves for copper and for an alloy are shown in Figures 24 and 25 and the results are summarized in Table V.

While increasing temperature was found to increase the rate

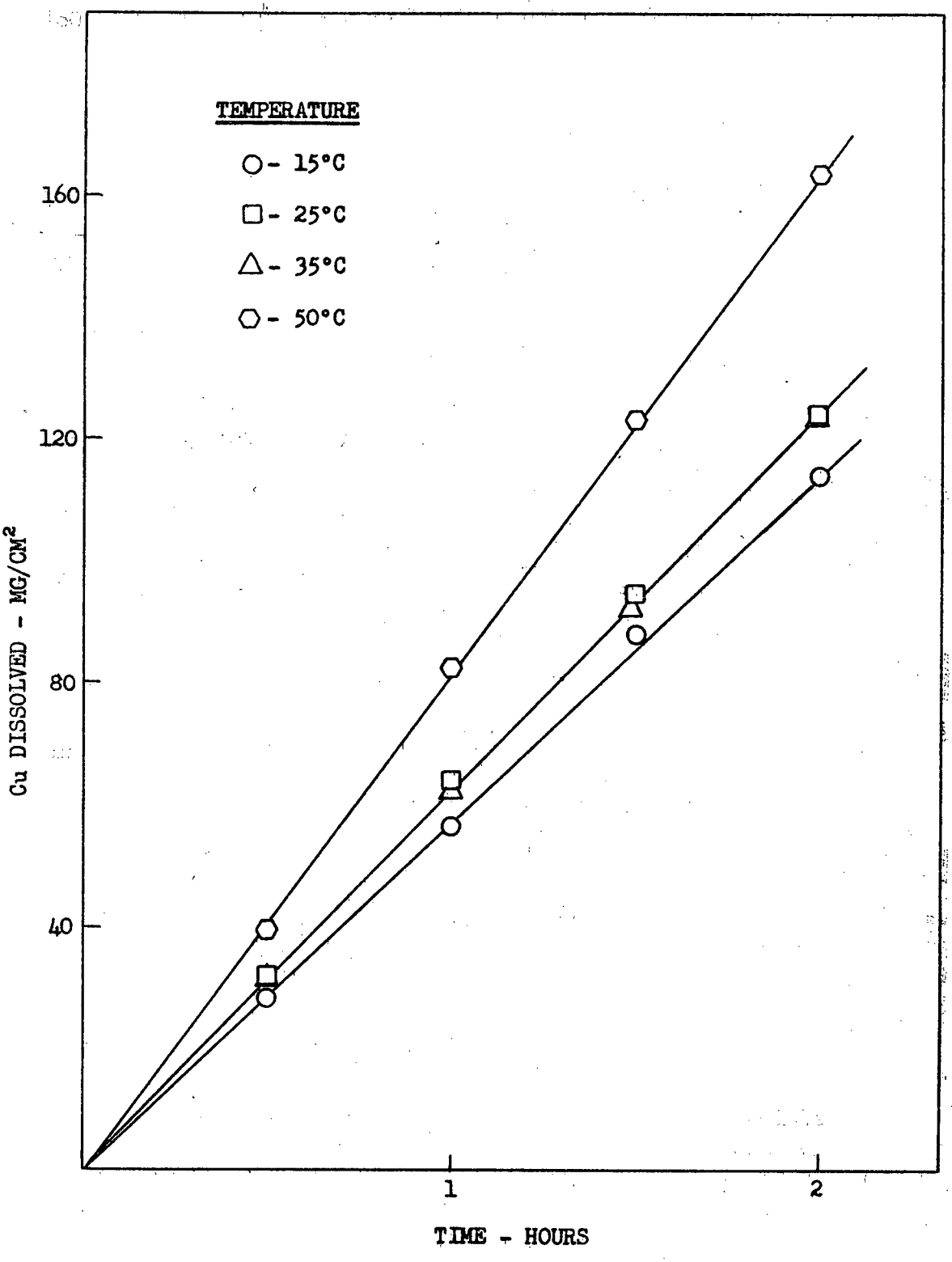

Figure 24. Rate curves for pure copper at various solution temperatures. NH_3 = 0.5 m/l; NH_4^+ = 0.02 m/l; O_2 = 6.8 Atm.

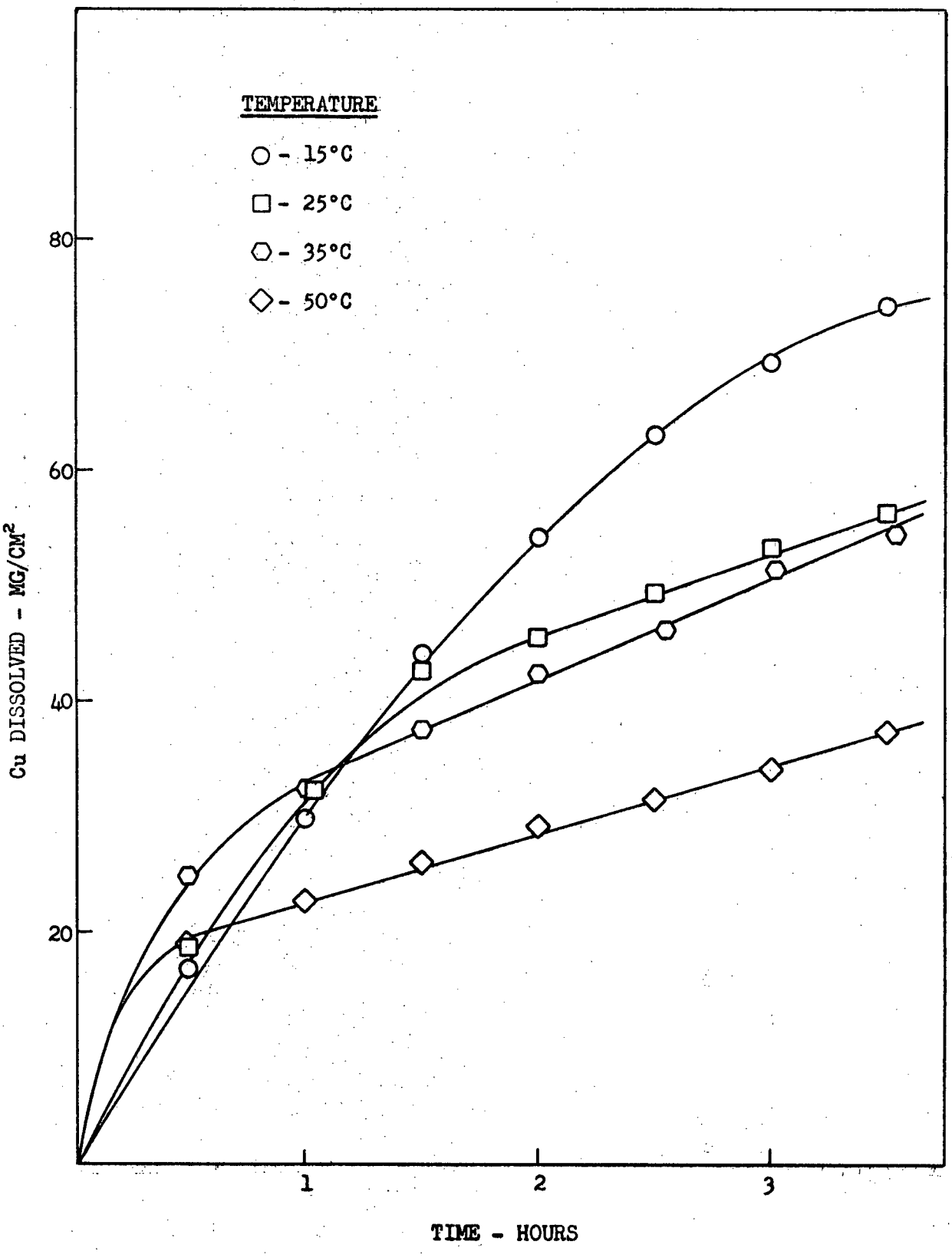

Figure 25. Rate curves for alloy 2 at various solution temperatures. NH_3 = 0.5 m/l; NH_4^+ = -.-2 m/l; O_2 = 6.8 Atm.

TABLE V.

Data on Experiments in which Temperature was Varied.

Run No.	Alloy	Temp. °C.	Pressure Atm.	NH_3 m/l	NH_4^+ m/l	NH_3 Titrated m/l	Rate Type*	Linear Rate***	Parab. Rate**	Cu Diss. in 1 hr. mg.
C-77	Cu	15	6.8	0.5	0.02	0.50	L	56.2	-	56.2
C-75	2	15	6.8	0.5	0.02	0.52	I	-	-	29.8
C-76	10	15	6.8	0.5	0.02	0.50	P	-	0.54	17.7
C-18	Cu	25	6.8	0.5	0.02	0.49	L	62.2	-	62.2
C-37	2	25	6.8	0.5	0.02	0.50	I	-	(1.51)	31.5
C-20	10	25	6.8	0.5	0.02	0.48	P	-	0.43	17.2
C-84	Cu	35	6.8	0.5	0.02	0.51	L	61.6	-	61.6
C-81	2	35	6.8	0.5	0.02	0.51	P	-	0.75	32.5
C-78	10	35	6.8	0.5	0.02	0.49	I	-	-	22.4
C-98	Cu	50	6.8	0.5	0.02	0.49	L	82.2	-	82.2
C-95	2	50	6.8	0.5	0.02	0.48	P	-	0.33	22.7
C-82	10	50	6.8	0.5	0.02	0.51	P	-	0.19	15.4
C-79	10	15	1.7	0.5	0.02	0.52	I	-	-	11.1
C-85	10	15	3.4	0.5	0.02	0.51	P	-	0.48	16.8
C-86	10	15	5.1	0.5	0.02	0.49	I	-	-	14.2
C-99	5	25	6.8	1.5	-	1.57	I	-	-	27.1
C-100	5	35	6.8	1.5	-	1.51	I	-	-	20.5
C-102	5	50	6.8	1.5	-	1.51	I	-	-	13.3

* Rate types: L = Linear; P = Parabolic; I = Intermediate;

** Rates in parentheses are doubtful. Units of parabolic rates are $[mgCu/cm^2]^2/hour$.

*** Units of linear rates are $mgCu/cm^2/hour$.

for pure copper, the effect was slight (corresponding to an activation energy of the order of 320 cal/mole). This indicates some measure of rate control by transport of oxygen under these conditions.

For the alloys, the effect of temperature was strikingly different. Here it was found that, with the possible exception of a short initial period, the rate generally decreased with increasing temperature.

These results suggest that as the temperature is increased the influence of the films in retarding the reaction becomes more pronounced. This is supported by the results of physical examinations of the films, which indicate that the films formed at higher temperatures are denser and would therefore be expected to be less permeable to reactants or products.

Structure and Composition of the Films.

Following most of the experiments, the surfaces of the alloy specimens were examined microscopically and in some cases the films which had formed during the reaction were removed for analysis. A soft lead spatula was used to remove the films, which were very fragile and, when scraped from the underlying metal, broke up into a fine apparently metallic powder.

Photomicrographs of typical films are shown in Figures 26 to 33, and the results of chemical analyses of some of the films are listed in Table VI. Several attempts were made to determine the crystal structure of the film particles using X-ray diffraction methods, but due either to very fine particle size or imperfect crystal

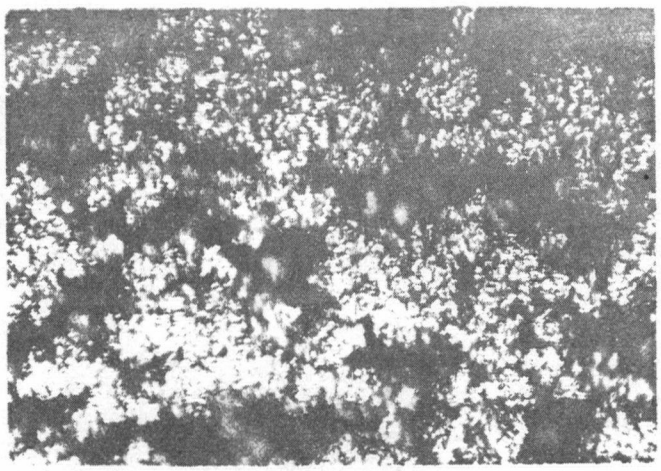

Figure 26. Surface structure of alloy 2.
Experimental conditions:
NH_3 = 0.5 m/l; NH_4^+ = 0.06 m/l;
T = 25°C; O_2 = 6.8 Atm.
Magnification X75.

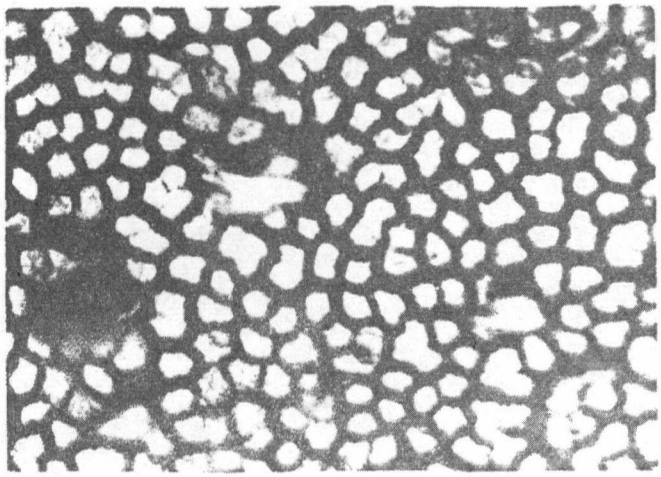

Figure 27. Surface structure of alloy 2.
Experimental conditions:
NH_3 = 0.5 m/l; NH_4^+ = 0.02 m/l;
T = 50°C; O_2 = 6.8 Atm.
Magnification X600.

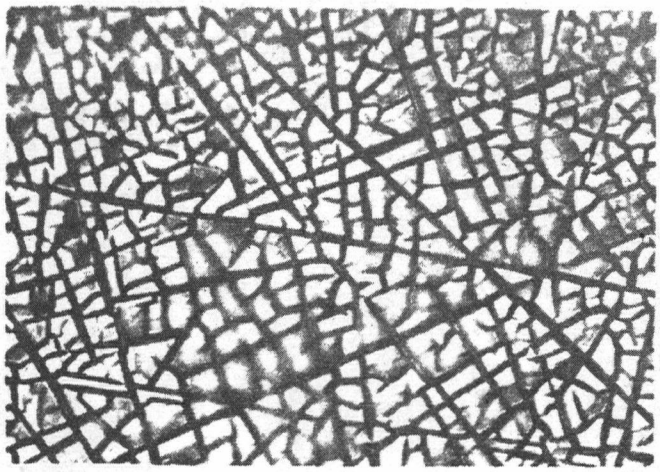

Figure 28. Surface structure of alloy 5.
Experimental conditions:
NH_3 = 0.5 m/l; T = 25°C;
O_2 = 6.8 Atm.
Magnification X1000.

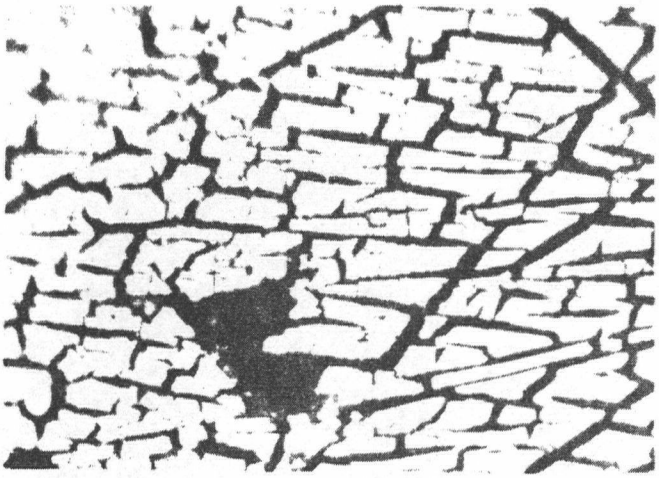

Figure 29. Surface Structure of alloy 10.
Experimental conditions:
NH_3 = 0.5 m/l; T = 25°C;
O_2 = 6.8 Atm.
Magnification X1000.

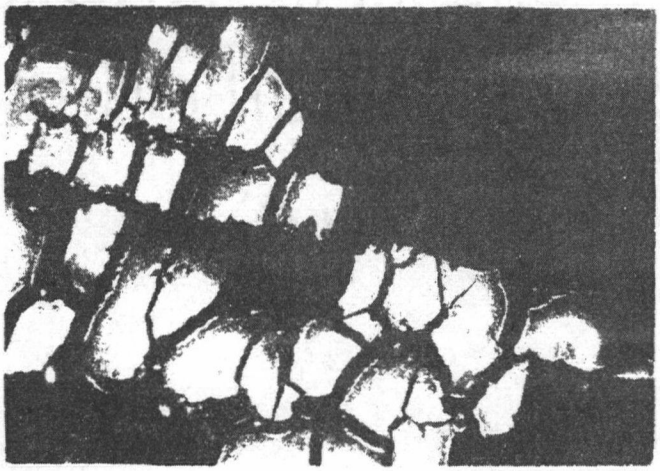

Figure 30. Surface structure of alloy 10.
Experimental conditions:
NH_3 = 0.25 m/l; NH_4^+ = 0.04 m/l;
T = 25°C; O_2 = 6.8 Atm.
Magnification X75.

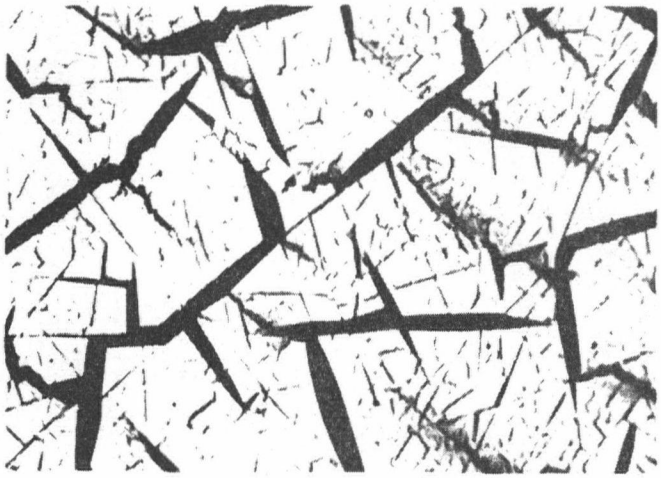

Figure 31. Surface structure of alloy 10.
Experimental conditions:
NH_3 = 0.5 m/l; NH_4^+ = 0.02 m/l;
T = 35°C; O_2 = 6.8 Atm.
Magnification X500.

Figure 32. Surface structure of alloy 15.
Experimental conditions:
NH_3 = 1.5 m/l; T = 25°C;
O_2 = 6.8 Atm.
Magnification X85.

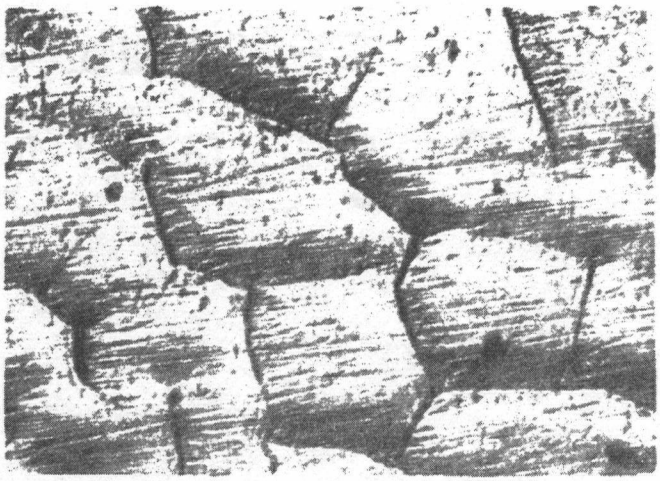

Figure 33. Same specimen as in Figure 32 with surface film removed.

TABLE VI.

Analyses of Films.

Run No.	Alloy	Sample wt.-mg	wt. % Copper
C-8	5	23.88	11.05
C-9	10	35.02	10.45
C-3	5	23.78	10.95
C-14	5	28.74	9.50
C-16	10	40.90	9.98
C-15	10	50.56	8.82
C-20	10	19.78	10.72
C-56	5	30.40	8.32
C-49	5	24.62	11.50
C-54	5	43.40	12.91
C-55	10	60.44	9.12
C-48	2	21.52	8.50
C-46			
C-57	10	25.86	9.60*
C-61			
C-81	2	18.46	37.0
C-83			

* This was a sample of the unusual film mentioned in connection with Figure 30.

structure, no interpretable results were obtained.

It is not possible at present to explain in any detail the structures that are represented in Figures 26 to 33, and the reasons for the variations observed, but a few features of interest may be noted. In Figure 26 is shown the surface of alloy 2 after it had been exposed to a corroding solution at 25°C. For this alloy the surface structure was the same whether the solutions contained NH_4^+ or not. This is perhaps surprising in view of the very large effect of NH_4^+ on the rate for this alloy. The surface appears to be porous and coarse. Figure 27 shows the surface of the same alloy following reaction at 50°C. This film was observed to be much thinner and denser than those formed at lower temperatures and can be seen to have a very different surface structure. This could account for the inverse temperature effect on the rate of dissolution of copper from the alloys which was noted earlier.

The surface structures of alloys 5 and 10 after reaction in solutions containing only NH_3 at 25°C,, are shown in Figures 28 and 29. These are seen to be very similar to each other, but markedly different from the typical structures for either alloy 2 (Figure 26) which appears to be much more porous, or alloy 15 (Figure 32) which seems much more dense.

In contrast to the observations for alloy 2, it was found that the presence of NH_4^+ in the solution had a considerable effect on the appearance of the surfaces of the higher gold alloys. This can be seen in Figures 30 and 31, which show surface structures of alloy 10 after exposure to solutions containing both NH_3 and NH_4^+.

Figure 30 illustrates an interesting effect which was often observed with the higher gold alloys, particularly after they had been exposed to reaction conditions which gave a low rate (i.e. low NH_3 concentrations, oxygen pressures or temperatures). In these instances, after the specimens were removed from the reaction vessel, their surfaces appeared to be uncorroded except for a very thin tarnished film. However, after a short exposure to the atmosphere, cracks developed in this film and fragments of a surface layer, about 1/1000 inches thick, and metallic in appearance, separated from the underlying material. An example of such a specimen is shown in Figure 30. The removal of this surface film, which analysis showed to be very high in gold, exposed another very thin layer of a black material which could readily be removed as a very fine powder to disclose the unattacked metal. It was not found possible to collect a sufficient amount of this powder for analysis, but its appearance suggested that it could be an oxide rather than a metal.

Figure 32 shows a photomicrograph of the surface of an alloy 15 specimen which had been corroded in a solution containing NH_3 alone. After the reaction, the surface appeared to the eye to be only slightly tarnished. Under the microscope the surface film appeared to be very compact, showing fewer cracks than the films of alloys lower in gold content. When the tarnished layer was removed by polishing, the underlying surface, shown in Figure 33, was observed to be metallic and obviously very rich in gold. Further, when this gold-rich layer was removed by machining, the shavings were found to contain a fine black powder.

No evidence of any surface changes, such as tarnishing or film formation, could be observed either visually or under the microscope, on specimens of alloy 15 which had been exposed to solutions containing both NH_3 and NH_4^+.

Table VI lists the results of the copper analyses which were carried out on some of the surface films formed during corrosion experiments. Most of the films are seen to contain about 10 percent by weight of copper, corresponding to about 25 atomic percent copper if the film material is assumed to consist of a copper-gold alloy. Qualitative tests confirmed that all the films were very rich in gold. The apparent constancy of the compositions of the films is perhaps surprising in view of the wide differences in their physical appearance and in the compositions of the alloys from which they were formed.

It is clear from the above discussion that while the formation of surface films is an essential feature of the corrosion of the copper-gold alloys, the films which are formed are very complex in nature, often consisting of more than one layer or component. Despite an apparent constancy of the composition (as reflected in the copper content) of these films, their detailed chemical and physical structures have not been determined. Nor has it been possible to relate their observable properties in any simple way to the compositions of the alloys, the conditions of the reactions or the reaction rates.

CONCLUSIONS

Summary of Experimental Results

The general pattern of the experimental results which were obtained in the course of this investigation may be summarized as follows:

(1) All the rate curves for the dissolution of pure copper were linear. In general the results obtained on pure copper were in good agreement with those found in earlier studies (1).

(2) Most of the rate curves for the alloys showed a decrease in the rate with time. In many cases the shapes of the rate curves conformed to a parabolic relation, but sometimes they were more complex, showing a greater or smaller tendency for the rate to fall off with time.

(3) In general, increasing the gold content of the alloys resulted in lower rates of dissolution of copper and in a greater tendency for the rates to decrease with time. This was particularly apparent in solutions high in NH_3 and NH_4^+. In solutions low in NH_3 and NH_4^+, the rates for all the alloys were still much smaller than for pure copper, but the rate appeared to be less sensitive to the gold content of the alloy.

(4) Increasing the concentration of NH_3 in the solution (in the presence of constant NH_4^+) resulted in higher dissolution rates for all the alloys. The rates increased up to a maximum value beyond which further NH_3 addition had little effect. The

limiting rates were inversely dependent on the gold content of the alloys. Increasing the NH_3 concentration also tended to make the rate curves, particularly for the lower gold alloys, more nearly linear in shape.

(5) Increasing the concentration of NH_4^+ in the solution (in the presence of constant NH_3) had a very similar effect. The rate increased with the concentration of NH_4^+, approaching a limiting value which was the same in the case of each alloy, as that reached by increasing the NH_3 concentration. Much smaller amounts of NH_4^+ than of NH_3 were required to produce a comparable effect.

(6) The rates for the low gold alloys (i.e. alloy 2) were particularly sensitive to the NH_4^+ concentration. Those for the higher gold alloys showed a smaller dependence, and for alloy 15 the dependence was actually reversed, no reaction taking place in the presence of NH_4^+ salts.

(7) The rates for all the alloys were found to increase with the oxygen partial pressure up to a maximum at about 5 atmospheres. At higher oxygen pressures the rates fell off again.

(8) While the rates for pure copper increased with temperature, those for all the alloys showed an inverse dependence, falling off as the temperature was raised.

(9) It was found for all the alloys that the reaction was accompanied by the formation of films, generally very rich in gold, on the surface of the corroded specimens. It was not possible to establish the detailed structure of these films.

Interpretation of the Results

From the nature of these results it is apparent that the system involved is of such complexity and the number of variables so great, that a far more extensive study than the present one would be required to elucidate fully the reactions which take place and their mechanisms. The investigation which has been carried out can therefore be considered to be only of an exploratory nature, intended to reveal the general features of the system. Many aspects remain to be studied in greater detail. Nevertheless, the results which have been obtained form a sufficiently complete and consistent pattern that it is possible to account for some of the observed effects and to draw some conclusions, of a general nature at least, concerning the kinetics and mechanisms of the reactions involved in the attack of ammonia solutions on copper-gold alloys.

(1) With pure copper the reaction has been shown to proceed by chemical attack of NH_3 and NH_4^+ on the metal surface, following the rapid adsorption of oxygen, and resulting in the dissolution of copper as the cuprammine ion. The surface of the corroding copper remains essentially unchanged, with no indication of any film formation. Consequently, the rate curves for copper are linear.

(2) With the alloys there is some indication that the initial attack and dissolution of copper proceeds in a somewhat similar fashion, except that some electrochemical reaction due to the presence of regions of different composition (i.e. gold content) on the metal surface may also be involved. This might account for the fact

that under certain conditions, slightly higher initial rates were observed with increasing gold content of the alloy.

(3) As the corrosion of the alloy proceeds, a film is soon formed on its surface. This film appears to be due to the accumulation of gold, as the copper in the surface region dissolves, resulting in the formation of a gold rich deposit which is itself relatively inert to attack and which retards the reaction by presenting a barrier to the transfer of reactants and products between the underlying metal and the solution. This film thickens as the reaction proceeds, accounting for the parabolic shape of the rate curves (i.e. for the fact that the rate for the alloys falls off with time).

(4) There is some indication, both from examination of the specimen surfaces after corrosion and from the nature of the kinetic results, that a deposit of oxide (either Cu_2O or CuO) may also form on the surface of the corroding alloys and that this deposit contributes in the same way as the gold film itself to the slowing down of the reaction. Such a deposit might be expected to accompany or to result from the formation of the initial gold rich film, since such a film would give rise to stagnant regions (i.e. in the pores of the film or between the film and the underlying metal) in which the solution would be deficient in NH_3 and NH_4^+ and in which the reaction products (Cu^{++} and OH^-) would accumulate. These conditions would favour the precipitation of CuO and Cu_2O. This picture is supported by the results of experiments made at low NH_3 and NH_4^+ concentrations, in which it was

found that the rates for the low gold alloys were very low (comparable to those for the higher gold alloys) despite the fact that the gold film was apparently very porous.

(5) The fact that the rate passes through a maximum with increased oxygen pressure and then falls off again might also find an explanation in the above picture. At low oxygen pressures, the transport of oxygen through the film may control in part the rate of the reaction. However, as the oxygen pressure is increased, the rate is increased to a point where there is insufficient NH_3 and NH_4^+ to prevent the accumulation of Cu^{++} and OH^-. The resulting precipitation of copper oxides thus causes the rate to drop again. This is comparable to the well known system involving the corrosion of iron in contact with an aqueous solution, where increasing the concentration of oxygen may first accelerate corrosion, but at high enough oxygen concentrations a passivating film of iron oxides is formed and corrosion inhibited.

(6) The inverse effect of temperature on the rates of reaction of the alloys may be similarly explained. At higher temperatures the formation of denser film structures would be favoured by mechanical failure, as would certainly the precipitation of copper oxides.

(7) The increase of the rate with NH_3 and NH_4^+ concentrations may be due to a higher rate of transport of these reactants through the films to the underlying metal which is dissolving. At the same time higher NH_3 and NH_4^+ concentrations would reduce the

tendency for copper oxides to precipitate, and this would also cause the rates to increase. Ultimately the rate must become controlled by the transport of oxygen through the gold film which is always present, and whose thickness and permeability depend primarily on the composition of the alloy. This would correspond to the limiting rate region, in which further increases in the NH_3 or NH_4^+ concentrations are without effect. It might be expected that in this region the rate would increase with the oxygen pressure.

(8) No explanation can be offered at this point for the fact that the alloy containing 15 atomic percent gold did not corrode in solutions containing both NH_3 and NH_4^+, while it did undergo reaction in solution containing NH_3 only.

APPENDIX I.

Spectrochemical Analyses of Metals and Alloys Used.

	Pure Copper	Pure Gold	Alloy 5	Alloy 10	Alloy 15
Cu	Major component	0.001-0.005	Major component	Major component	Major component
Au	-	Major component	Major component	Major component	Major component
Si	0.001-0.01	0.001-0.01	0.001-0.01	0.001-0.01	0.001-0.01
Mg	0.001-0.01	0.001-0.01	0.001-0.01	0.001-0.01	0.001-0.01
Ca	0.001-0.01	0.001-0.01	0.001-0.01	-	0.001-0.01
Ag	0.001-0.01	0.001-0.01	0.005-0.01	0.005-0.01	0.001-0.01
Fe	0.0001-0.001	-	0.001-0.01	0.001-0.01	0.005-0.01
Cr	0.0001-0.001	-	0.0001-0.001	0.001-0.01	0.0001-0.01
V	-	-	-	0.001-0.005	-
Ti	-	-	-	0.001-0.005	-
Mo	-	-	-	0.0001-0.001	-

The above figures are percent.

Due to the wide variations in the compositions of the samples, even the percentage ranges quoted for the impurities can only be regarded as giving the approximate order of magnitude of the concentrations present.

APPENDIX II

Assays for Gold on Copper-Gold Alloys.

Alloy No.	Cuttings	Drillings	Average	Atomic % Au
	Wt. % Au	Wt. % Au	Wt. % Au	
2	-	6.00	6.00	2.02
5	13.99	14.12	14.05	5.01
10	25.73	25.64	25.69	10.00
15	35.56	35.56	35.56	15.11

REFERENCES

1. J. Halpern, J. Electrochem. Soc., in press.

2. G. Tammann, Z. anorg. allgem. Chem., 142, 61-72 (1925).

3. W.J.Muller, H. Freissler, and E. Plettinger, Z. Elektrochem., 42, 366-71 (1936).

4. R. Landau and C.S.Oldach, Trans. Electrochem. Soc., 81, 521-558 (1942).

5. U.R.Evans, "Metallic Corrosion, Passivity and Protection", Arnold, p. 229.

6. A.S.Russell, Nature 115, 455-6 (1925); 117, 47-8 (1928), J. Chem. Soc., 1872-81 (1926).

7. H.H.Uhlig, "Corrosion Handbook", John Wiley and Sons, p. 21.

8. H.H.Uhlig and J.Wulff, Trans., A.I.M.E., 135, 494-521 (1939).

9. R. Landau, Trans. Electrochem. Soc., 81, 559-571 (1942).

10. C.Sykes and F.W.Jones, Proc. Roy. Soc. Lon., A 157, 213-233 (1936).

11. E.B.Sandell, "Colorimetric Determination of Traces of Metals", Interscience, (1950).