RATE STUDY ON THE DISSOLUTION OF COPPER IN FERRIC CHLORIDE USING THE ISOTOPE COPPER-64

A THESIS

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SUMMARY

The dissolution of metals is a typical example of a heterogeneous process. Reactions of this nature, which occur at an interface, are controlled either by the rate of diffusion of the reactant to the interface ("diffusion control") or by the rate of the chemical reaction at the interface ("chemical control"). The purpose of this study was to determine the controlling mechanism for the reaction between copper and ferric chloride and to compare the experimental results with previous findings of other investigators.

The kinetics of the reaction was studied by varying the ferric chloride concentration and temperature. Runs were made at 25°, 35° and 45° C and with ferric chloride solutions ranging from 0.5 to 3.5 molar.

The actual experimental runs were performed in equipment which was specially designed for this investigation. The apparatus consisted of a reaction cell, solution reservoir, pump, and heating mantle. Strips of radioactive copper were placed in the reaction cell where they came in contact with the circulating ferric chloride solution. In order to study the rate of the reaction, sample aliquots were withdrawn from the solution reservoir at six minute intervals. These samples were discharged onto watch glasses, placed on a hot plate, and dried by infrared lamps which were mounted over the hot plates.

Once the samples were dry they were counted by a Geiger-Muller Counting Tube to determine the amount of copper-64 activity in each sample. The experimental data obtained from the various runs were in terms of

counts per minute which indicated the concentration of copper-64 present in the solution when the sample was withdrawn. In order to convert this data to the amount of dissolved copper in solution, a special technique involving the use of small accurately weighed irradiated copper samples was developed. This technique provided a mathematical factor for converting experimental data to grams of dissolved copper in solutions.

The copper samples used in this study were irradiated to the copper-64 form in the ORNL Graphite Reactor which is located at the Oak Ridge National Laboratory.

Results of this investigation indicate that the dissolution rates for the system follow a parabolic dependency upon the ferric chloride concentration. Dissolution rate curves show that the reaction rate increases linearly with respect to the ferric chloride solution up to a concentration of about 1.0 molar. Above one molar the rate increases more slowly reaching a maximum between a concentration of 2.0 and 2.5 molar and then decreases with increasing concentrations. These results agree in general with the data reported by Brooks and Ferrari.

Conclusions reached as a result of this investigation are as follows:

(1) The dissolution of copper in ferric chloride solutions follows a zero-order rate relationship.

(2) Maximum dissolution rates occur in ferric chloride concentrations ranging between 2.0 and 2.5 molar.

(3) The reaction is diffusion controlled as is indicated by the low temperature coefficients and activation energies obtained.

CHAPTER I

INTRODUCTION

Chemical reactions fall into two categories: homogeneous and heterogeneous. Homogeneous reactions take place in a single phase while heterogeneous reactions occur at an interface.

Heterogeneous reactions are usually classified as complex reactions. In this sense, a complex reaction may be defined as a reaction in which the chemical rate depends on the concentrations of not only the reactants and the final products but also of the intermediate products formed during the course of the reaction. The dissolution of metals, which is a heterogeneous process, falls within this type of reaction.

The rate of a heterogeneous reaction is measured in terms of the amount of substance reacting on a unit surface area per unit time. It is not directly linked with the change of concentration of the reactants in solution as is the case of homogeneous reactions. However, the rate is nevertheless a function of the temperature and of the concentrations of the reactants.

In heterogeneous systems there are three distinct steps that must occur for the reaction to be complete. These steps are as follows:

(1) Transport of the reactant to the interface through molecular or convective diffusion.

(2) Chemical reaction on the surface.

(3) Desorption of the products from the surface into the solution.

The slowest of these steps is the rate-controlling step of the reaction.

The dissolution of copper in ferric chloride was first studied in detail by King and Weidenhammer (1) and Pletenev and Pavlov (2). These investigators, working with dilute solutions of ferric chloride, reported that the reaction was controlled by the transportation or diffusion of the ferric ion to the copper surface. In more recent years Brooks (3) and Ferrari (4) investigated the mechanism of the system over a much wider range of ferric chloride concentration than was previously reported. These authors also reported that the kinetics of the reaction was controlled by a diffusion mechanism.

This present investigation was undertaken to verify and expand the data reported by Brooks and Ferrari by the use of a radioisotope tracer technique. In particular, this work investigated the mechanism and kinetics of the reaction as affected by increasing temperature. Experimental runs were performed at 25°, 35°, and 45° C and with varying ferric chloride concentrations. The controlling mechanism for the reaction was determined from observed temperature coefficients and activation energies of the system.

CHAPTER II

HISTORICAL DISCUSSION

A theory on the kinetics of heterogeneous reactions was first proposed by Nernst (5) in 1904. In this theory, Nernst postulated that under certain conditions reaction velocities in heterogeneous systems could be reduced to diffusion velocities. Nernst based his postulation on the fact that in the immediate vicinity of the solid surface the chemical reaction is extremely rapid and thus the reactant in the immediate area becomes quickly depleted. As a result, the rate of which the reactant diffuses to the solid interface will be the controlling factor in the reaction. Van Name and Hill (6) concluded that if this theory was correct, all metals would dissolve in a given reactant at the same rate. However, their experimental results indicated that there are three possible types of kinetic reaction controls. The first type agreed with Nernst's theory, in that the rate of reaction was determined by diffusion of the reactant to the metal interface. On the other hand, they found that certain reactions were controlled by the actual chemical rate while others were controlled by the simultaneous effect of both the diffusion and chemical rates.

In more recent years King (7) has developed a general theory in which he states five criteria that characterize diffusion controlled reactions.

(1) Different solids dissolve at nearly the same rate in the same reagent, under similar conditions.

(2) The dissolution rate is approximately inversely proportional to the viscosity, with other physical and chemical factors being constant.

(3) The speed of stirring has a large effect, the exact nature of which depends on the type of stirring used.

(4) The dissolution rates with a series of reagents are proportional to a fractional power of the diffusion coefficients.

(5) The temperature coefficients are lower than for homogeneous reactions, usually between 1.1 to 1.5 per 10° C rise at room temperature.

Salzberg, Knoetgen and Molless (8) expanded King's criteria by postulating that desorption and chemically controlled reactions must behave in the following manner:

(1) Different solids dissolve at different speeds in the same solution, under the same conditions.

(2) Temperature coefficients are much higher than in diffusion control, the value being anywhere between 2 and 4 per ten-degree rise in temperature.

(3) The dissolution rates increase with reagent concentration in a non linear fashion, slowly reaching a maximum.

(4) Desorption controlled rates should be, in general, slower than diffusion controlled rates.

Salzberg further postulated that a large difference in oxidation potential, in excess of 10 volts, between the metal and the solution facilitates diffusion control, while a small difference results in a chemical controlled reaction.

The above criteria of King and Salzberg represent the present generally accepted theories on heterogeneous dissolution reactions.

A survey of the literature has revealed that certain heterogeneous reactions are chemically controlled while others fall into the diffusion controlled class. However, as previously expressed, in some cases a reaction may be both chemically and diffusion controlled. For example, Durdin and Markevich (9) observed this feature in their study on the solution rate of chromium in hydrochloric and sulfuric acid. These authors observed that the dissolution rate of chromium in hydrochloric and sulfuric acid up to 8 and 10 normal, respectively, was independent of the rate at which the solution was stirred. This provides a basis for the conclusion that the chromium dissolution rate in these acids is chemically controlled. This result agrees with the high temperature coefficients, greater than 2.0, reported by the authors for this reaction. However, in solutions of higher acid concentrations, stirring had a marked effect upon the rate of the reaction. Durdin and Markevich explained this effect by suggesting that a mechanism change from a chemical to a diffusion controlled system occurs at high acid concentrations.

King and Hillner (10) in their study on the cadmium-chromic chloride system found that in violet solutions of chromic chloride the rate of cadmium dissolution was unaffected by stirring and exhibited comparatively high temperature coefficients. These mechanisms definitely indicate a chemical controlled reaction. However, when green solutions of chromic chloride were used as the dissolving reagent, the authors experienced an increase in the dissolution rate with stirring and low temperature coefficients. These results indicate a diffusion controlled reaction. King and Mayer (11) also investigated this reaction and concluded that it was controlled by the actual chemical rate at the metal surface.

Weaver and Lynch (12) investigated the rate of dissolution of cadmium in dilute aqueous hydrochloric acid solutions. They reported that the kinetic rate was zero order as indicated by a linear dissolution increase with respect to time. Diffusion of the reactant seemed to be the rate controlling step, as the effect of stirring produced a considerable increase in cadmium dissolution.

The rate of solution of magnesium in acids was studied by Kilpatrick (13) who proposed that in weak acids the velocity constant of chemical controlled systems is proportional to the concentration of the acid present and independent of the H_3O^+ ion concentration. His results show a linear relationship between the logarithm of the velocity constants and the logarithm of the acid strength. This, along with his reported high temperature coefficients, denotes a chemically controlled process.

Makrides and Hackerman (14) studied the dissolution of mild steel in 2.0 normal hydrochloric acid solutions containing ferric chloride. The reaction rate of the system was found to depend on the stirring velocity. Arrhenius energy of activation, calculated from experimental data, was in the range of 6,000 calories. Abramson and King (15) reported similar findings in their study on the dissolution of iron in ferric chloride and other acid media.

A considerable number of references on the dissolution of metallic zinc was found in the literature. However, due to obvious reasons, only those which are of direct interest to this study will be discussed.

Welsh and Garrett (16) studied the reaction of zinc with hydrochloric acid over temperatures ranging from 25° to -60° C. As a criteron for determining the mechanism of the reaction, the authors measured the temperature coefficients at 10° intervals from 20° to -60° C. They reported that the dissolution of zinc is a diffusion controlled reaction as indicated by temperature coefficients which ranged between 1.269 to 1.475 for the system. King and Braveman (17) reached a similar conclusion in their zinc dissolution studies. Schack and King (18) in their investigation on the same reaction attempted to study the mechanism by varying the viscosity of the system. They reported that the rate of zinc dissolution in acid solutions increased with increasing stirring speed and decreased as the viscosity of the system increased.

The reaction between copper and sulfuric acid was studied by Benjamin and Graydon (19), who proposed that the reaction rate was controlled by the rate of oxidation of the cuprous ion at the copper-solution interface. Kuzminykh _et al._ (20) investigated the same reaction by studying the effects of temperature, composition of acid and air consumption on the copper dissolution rate. They reported that the reaction rate was only slightly dependent on the sulfuric acid content. Temperature coefficients for the system varied between 1.3 and 1.5 per 10° C rise between 20° and 60° C; however, at temperatures above 60° C the coefficients were reported at values in excess of two. These results indicate a diffusion controlled reaction at low temperature with the mechanism changing to chemically controlled at higher temperatures.

Milyutin and Shultin (21) investigated the reaction of copper with nitric acid over a wide range of acid concentration. These authors stated that at moderate acid concentrations the reaction rate was controlled by the electrochemical reaction at the copper surface. However, at higher nitric acid concentrations, greater than 11.0 molar, diffusion of the oxidant to the copper surface became the controlling mechanism. Their results were based on the fact that the temperature coefficients for the system were greater than 2.0 at acid concentration below 11.0 molar, but less than 2.0 at higher concentrations. Johnson et al. (22) confirmed these results in their work on the same reaction.

The reaction of copper and silver with ammonium persulfate solutions was studied by Loshkarev and Kalevatuva (23). They suggested that the reaction followed the first order law and was controlled by a diffusion mechanism.

Perhaps more closely related to the present investigation is the work of Weeks and Hill (24). These authors made use of a radioisotope tracer technique which employed the use of copper-radioactive cobalt alloy samples to study the rate of dissolution of copper in sulfuric acid. These samples were prepared by electroplating approximately 0.001 grams of cobalt-60 on a small strip of pure copper. The strips were then coated with additional copper to bring the total sample weight to tem grams. The samples were then melted and held in a liquid state for one hour, then quenched in an oil bath. The authors felt that this procedure would produce a homogeneous alloy with properties similar to pure copper. The rate of copper dissolution was then studied by observing the appearance and the amount of radioactivity in the acid solution. Since the effect of stirring had no appreciable effect on the dissolution rate, the reaction was considered to be chemically controlled. However, since the reported results on this work were only reproducible to ±20.0 per cent, there is some question as to whether the prepared alloy samples were truly homogeneous in structure as predicted by the investigators.

The above discussion covers those references which deal with heterogeneous dissolution reactions with the exception of the copper-ferric chloride system. Since the number of references on this system is limited, this discussion was presented in order to familiarize the reader with the general mechanisms and background of rate dissolution reactions.

The first detailed experimental work to determine the rate mechanism of the copper-ferric chloride system was preformed by King and Weidenhammer (25). These authors reported that copper dissolves much slower than magnesium, zinc or cadmium in the same reactant solutions. They stated that the rate of copper dissolution in ferric slat solutions was largely controlled by the rate of diffusion of the ferric ion to the surface of the copper. Low temperature coefficients and a dissolution rate which was almost inversely proportional to viscosity seem to verify this conclusion.

Pletenev and Pavlov (26), in their investigation of the system reported that at low concentrations of ferric chloride (0.05 to 0.4 moles/liter) the rate constant of the reaction remained practically constant. However, at ferric chloride concentrations, between 0.4 and 1.55 moles/liter, the rate constants of the reaction began to decrease as a result of a decrease in the activity coefficients and due to a relatively large increase in viscosity. As another phase in their investigation, the authors covered the copper surface with a gelatin gel in order to help them in determining the controlling mechanism of the reaction. When the copper surface was covered with this gel, a sizable decrease in the dissolution rate was obwerved. From this experiment the authors concluded that the reaction between metallic copper and ferric chloride was diffusion controlled.

Szabo (27), on the other hand, stated that the rate of solution of copper is not diffusion controlled but depends on the rate at which absorbed cuprous ions oxidize at the copper surface. Szabo based his statement on the observed independence of the reaction to stirring.

Brooks (28), in work done at this school, investigated the kinetics of the reaction between copper and ferric chloride solutions by spectrophotometer means. In this study a series of experiments were made in which the concentration of ferric chloride was varied from 0.45 to 3.33 molar. Brooks shows that the reaction rate increases with increasing ferric chloride concentration until a maximum value is reached, occurring at 2.25 molar, after which a continual decrease in the rate is observed. As a conclusion to his work, he postulates that the reaction is controlled by the rate at which the reactants diffuse to the surface of the copper. In addition, he concludes that the species Fe^{+3}, $FeCl^{++}$ and $FeCl_2^{+}$ each react with the copper metal at rates determined by the individual species diffusion to the copper surface. The species $FeCl_3$, however, is unreactive and inhibits the reaction by increasing the diffusion barrier to the copper surface.

Ferrari (29), in a similar study at another university, confirmed Brooks' findings.

CHAPTER III

EXPERIMENTAL

The actual experimental runs were performed in equipment which was specially designed for this investigation. This apparatus consisted of a reaction cell, solution reservoir, pump, and a heating mantle (see Figure 1).

The reaction cell was constructed from two and a quarter inch glass tubing by glass blowing techniques. Dimensionwise, the cell was four inches long and two and a quarter inches in diameter. A Standard Taper stopcock was fitted approximately one inch from the top of the cell. This stopcock was modified by the addition of a flattened glass rod which served as the mount for the copper sample. The lower portion of the cell was filled with glass beads three millimeters in diameter to insure constant flow rates over the copper surface. As shown in Figure 1, the reaction cell was mounted so as to allow the ferric chloride solution to rise vertically in it, thus encountering the copper sample in a perpendicular manner. The solution reservoir was constructed by modifying a three-neck round bottom flask with a small Standard Taper port which was used to withdraw sample aliquots. The center neck of the flask was used as a thermometer well, while the two side necks held the inlet and outlet tubes. These tubes were placed in the flask in such a position as to provide continual agitation of the ferric chloride solution. The reservoir was heated by a mantle which was powered by a powerstat voltage control. Due

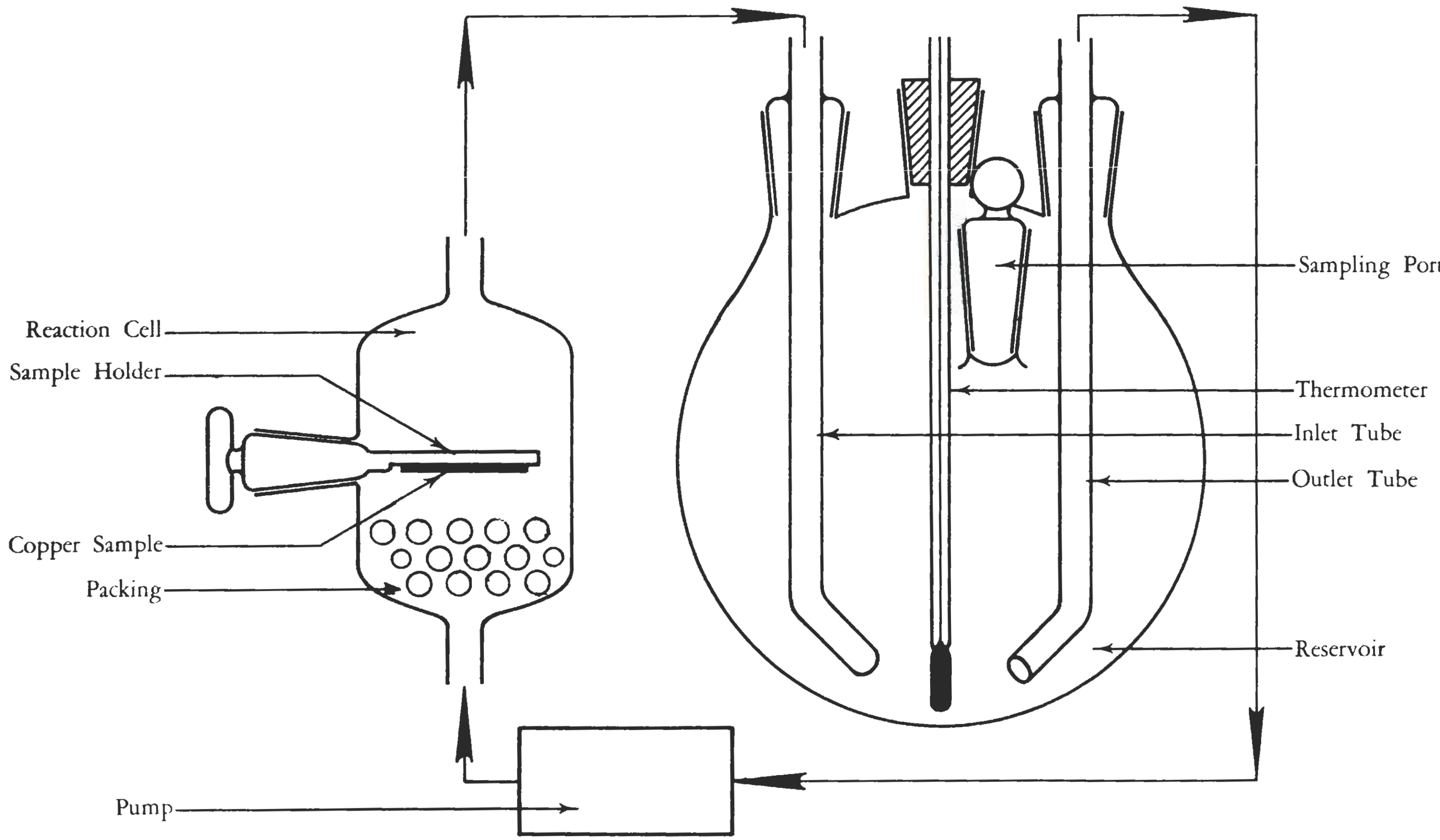

Figure 1. Reaction Cell and Accessories.

to the high flow rates through the system and the volume ratio existing between the reservoir and the system, it was felt that a uniform temperature in the reaction cell could be maintained by controlling the temperature in the reservoir. A Sigmamotor finger pump was used to circulate the ferric chloride solution and the system was connected by three-eighths inch I. D. Tygon tubing.

The experimental concentrations of ferric chloride used in this study were prepared by making a stock solution of approximately 4.0 molar. This solution was prepared by accurately weighing out a known amount of reagent grade ferric chloride and dissolving it in a measured volume of distilled water. The molarity of this solution was obtained by measuring its specific gravity with a Westphal balance and determining the concentration from the data given in Lange's Handbook of Chemistry (30). The experimental concentrations were then obtained from this stock solution by accurate dilution means. The concentrations of these diluted solutions were remeasured by the above mentioned specific gravity method.

Electrolytic copper, cut from sheets 1/32 in. thick, was used in this study. The purity of this copper, as reported from spectrographic analysis, was approximately 99.99 per cent. Small traces of silver and chromium were the only impurities found in this copper. The experimental samples used in this study were first cut slightly oversized and then machined down to precise dimensions of one by three centimeters.

At periodic intervals copper samples were sent to Oak Ridge to be irradiated in the ORNL Graphite Reactor. A series of experimental runs were performed whenever a shipment of irradiated copper was received. Each shipment contained enough copper to perform four experimental runs.

Since the half-life of copper-64 of short, approximately 12.8 hours, each series of runs was conducted over an eighteen hour period.

Before each scheduled run an irradiated copper sample was removed from the lead shielding pig and sprayed on its back surface with a resist enamel. The sample was then attached to the sample holder with rubber base cement. A typical run was made by placing 500 milliliters of ferric chloride solution in the reservoir and circulating this solution until the system reached thermal equilibrium. The irradiated copper sample was then dipped into a dilute solution of ferric chloride and placed in the reaction cell. The wetting of the copper sample was found to be necessary in order to prevent the formation of air bubbles on its surface. With the copper sample in place the circulating pump was started and the timing of the reaction began when the ferric chloride solution reached the copper surface. In order to study the rate of the reaction, sample aliquots were withdrawn from the reservoir porthole at six minute intervals. A 0.1 milliliter pipette attached to an adjustable micrometer was used to obtain these samples. The reaction was allowed to proceed for sixty minutes and thus provided ten evenly spaced sample periods. Once withdrawn, the samples were discharged onto watch glasses which were mounted on aluminum rings and placed on a hot plate. Overhead heat, which accounted for most of the evaporation, was provided by infrared lamps mounted over the hot plates.

The importance of this drying cycle cannot be overly stressed, since each sample must be evaporated to the same degree of dryness in order to obtain reliable experimental data. In order to develop this technique, a number of experiments were performed using known concentrations of P^{32} as phosphoric acid and Cu^{64} as the nitrate, in ferric chloride solutions. This work was continued until successive sampling, plating and drying of these samples produced results which did not contribute any appreciable error to the experimental procedure.

Once the samples were dry they were counted by a Geiger-Muller Counting Tube to determine the amount of copper-64 activity in each sample. The experimental data obtained from these runs were in terms of counts per minute which indicated the concentration of Cu^{64} present in the solution when the sample was withdrawn. To convert this data to the amount of dissolved copper in solution, a special technique, involving the use of small accurately weighed copper samples which were irradiated along with the experimental copper plates, was developed. Each irradiated copper shipment from Oak Ridge contained four control samples. Upon receipt of a shipment the control samples were immediately dissolved in five milliliters of aqua regia solution. One-tenth of a milliliter of these acid solutions was then withdrawn and discharged into five milliliters of the experimental ferric chloride solution. A small aliquot, one-tenth of a milliliter in size, was withdrawn from these solutions, plated, and dried in a procedure similar to that used for the experimental aliquots. The dried control solutions were then counted on the same counting equipment used for the experimental samples. The use of this control sample technique enabled the activity of the irradiated copper to be determined and also provided a mathematical factor for converting experimental data to grams of dissolved copper in solution.

In this investigation the IBM 650 computer was used to a considerable degree in calculating the results of this work. This was accomplished by writing a program which provided for all data-converting computations. This program, which consisted of several steps, applied the counting tube dead time and isotope half life correction factor to the data. It also converted the experimental data to grams of copper in solution and calculated an average result value along with the per cent deviation attached to each result. Least square fit curves for grams of copper in solution versus time and for rate constants versus ferric chloride molarity were also programmed and performed on the IBM 650.

CHAPTER IV

RESULTS AND DISCUSSION

This study investigated the kinetics of the reaction between copper and ferric chloride as affected by varying the ferric chloride concentration and temperature. The reaction was studied at 25°, 35° and 45° C and with ferric chloride solutions ranging from 0.5 to 3.5 molar. Eight experiments were conducted at each temperature interval making a total of twenty-four completed runs. The results of these runs are expressed in terms of grams of dissolved copper versus reaction time and are presented in the appendix of this paper.

By plotting the experimental data obtained from each run, a linear increase in grams of dissolved copper versus reaction time is observed. Sample plots from one run at each temperature range are given in Figures 2, 3, and 4. These plots, which are typical for all the experimental runs, show that the reaction follows a zero order rate with respect to time.

The dissolution rate constants for the kinetic runs were obtained from the slopes of these lines. These rates are expressed in milligrams of copper per minute per square centimeter and are given in Tables 1, 2, and 3.

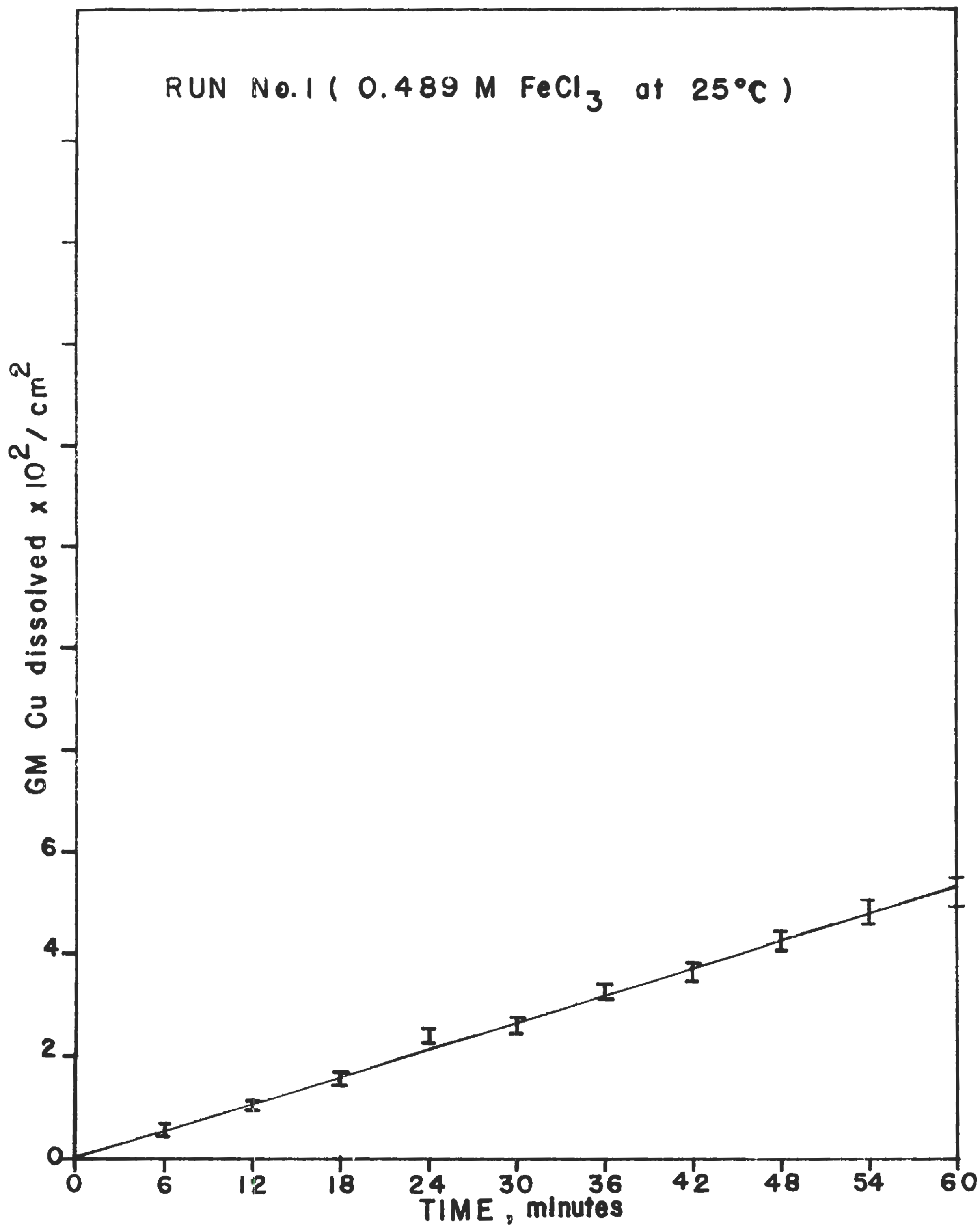

Figure 2. Sample Plot from 25°C Runs.

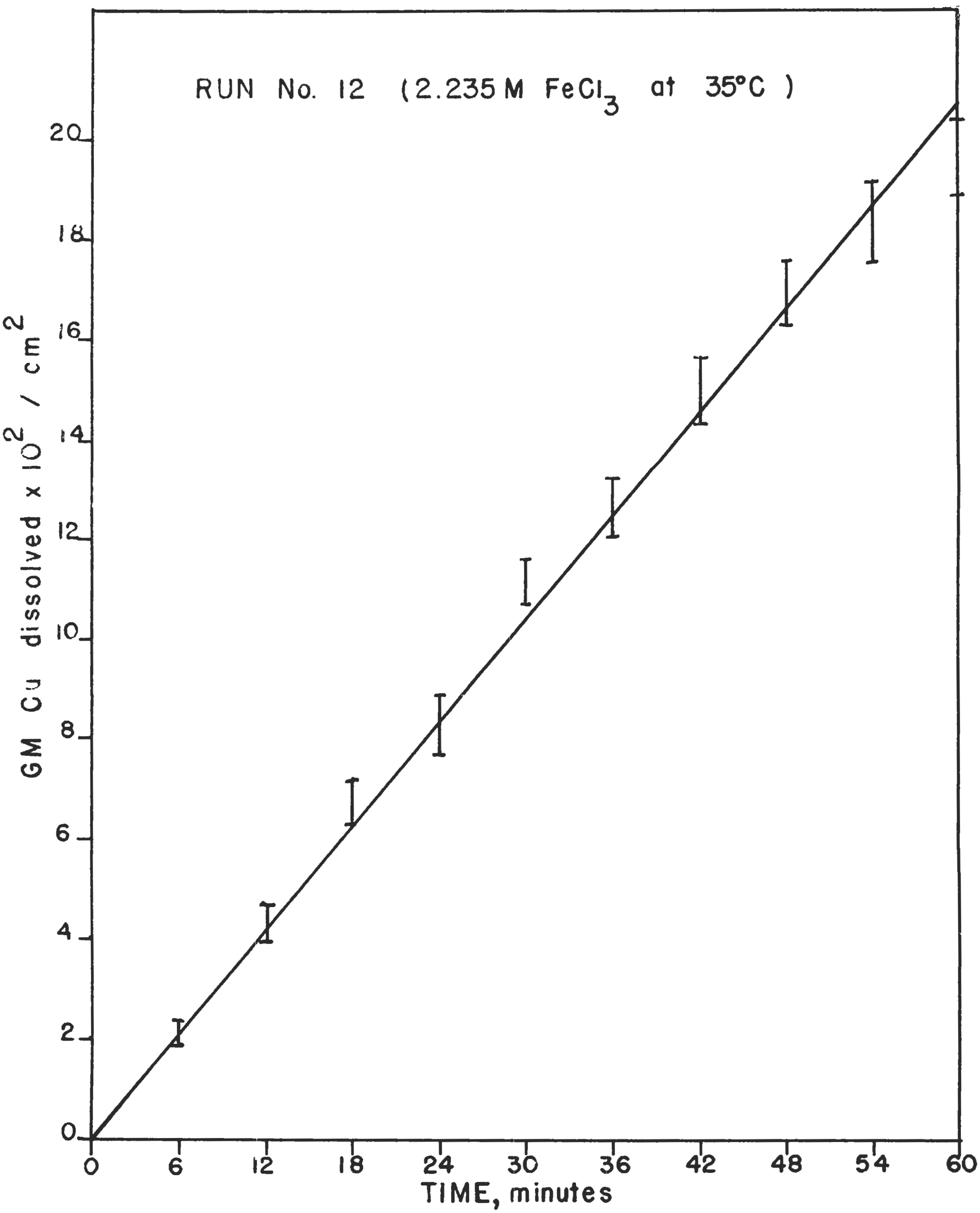

Figure 3. Sample Plot from 35°C Runs.

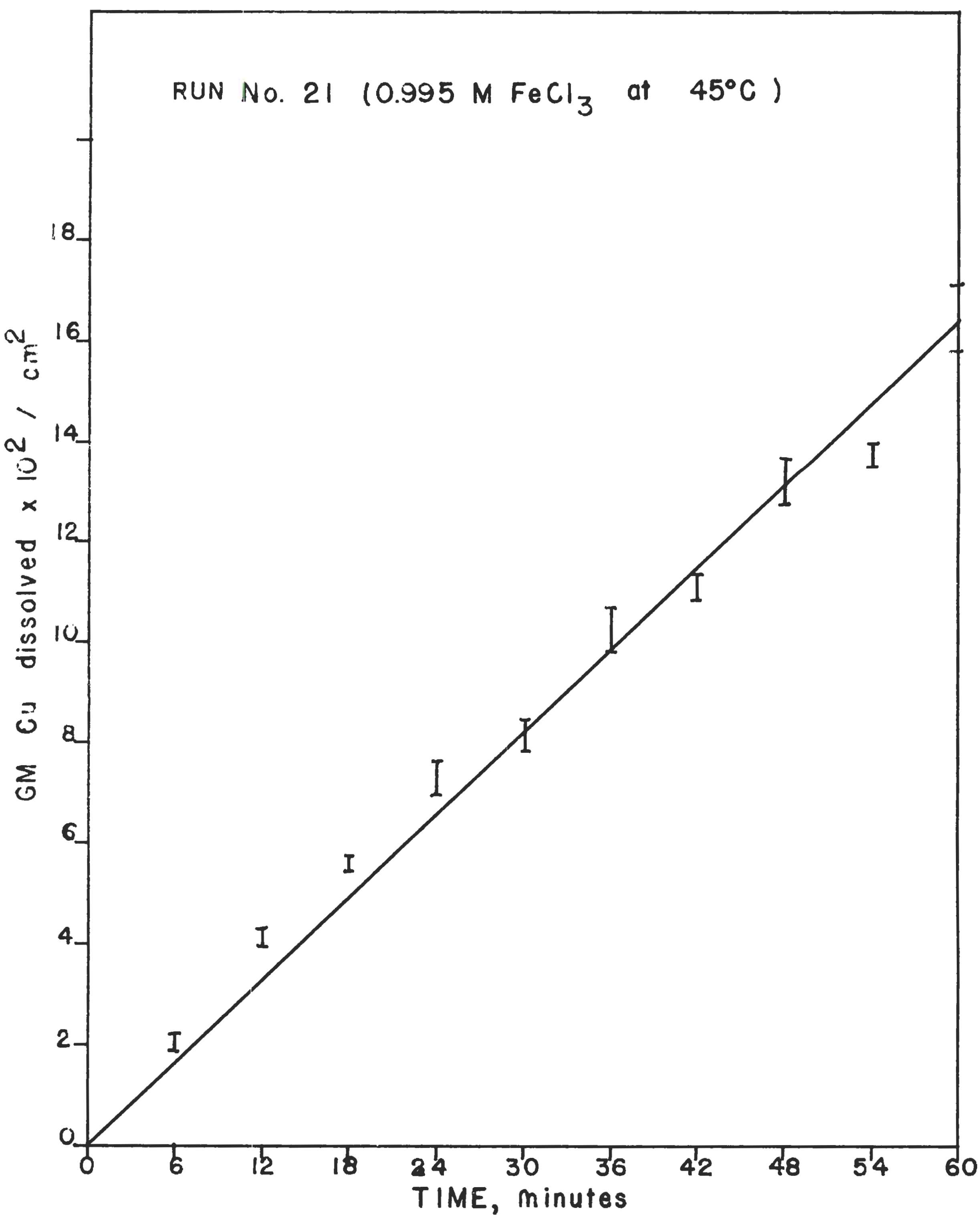

Figure 4. Sample Plot from 45°C Runs.

Table 1.

Dissolution Rate Constants at 25° C

Ferric Chloride Concentration Moles/Liter	Reaction Rate Constants Mg./Sq. Cm. - Min.
0.489	0.898
1.026	2.01
1.499	2.36
2.079	2.79
2.243	2.73
2.601	3.56
2.977	2.68
3.647	2.16

Table 2.

Dissolution Rate Constants at 35° C

Ferric Chloride Concentration Moles/Liter	Reaction Rate Constants Mg./Sq. Cm. - Min.
0.4805	1.28
1.018	2.46
1.497	3.25
2.036	4.05
2.235	3.47
2.532	3.81
2.953	3.10
3.509	2.46

Table 3.

Dissolution Rate Constants at 45° C

Ferric Chloride Concentration Moles/Liter	Reaction Rate Constants Mg./Sq. Cm. - Min.
0.508	1.85
0.995	2.72
1.504	3.88
2.010	4.35
2.260	4.85
2.506	5.12
3.027	4.98
3.490	3.59

By plotting the dissolution rate constants at each temperature, a parabolic dependence upon the ferric chloride concentration is observed. Of the various least square fits tried, the third order fit best represents this dependency. This is illustrated by the curves in Figures 5, 6, and 7, which are third order fits of the data presented in Tables 1, 2, and 3.

Inspection of these figures shows that the dissolution rate curves increase linearly with respect to the ferric chloride solution up to a concentration of about 1.0 molar. Above one molar the rate increases more slowly, reaching a maximum between a concentration of 2.0 and 2.5 molar and then decreasing with increasing concentrations.

It is interesting to note that the dissolution rate curves reported in Figures 5, 6, and 7 are in general agreement with the data reported by Brooks (31) and Ferrari (32). Both of these investigators reported similar dissolution curves with maximum values occurring between 2.0 and 2.5 molar solutions of ferric chloride. However, the works of these investigators were confined to temperatures at and below 25° C.

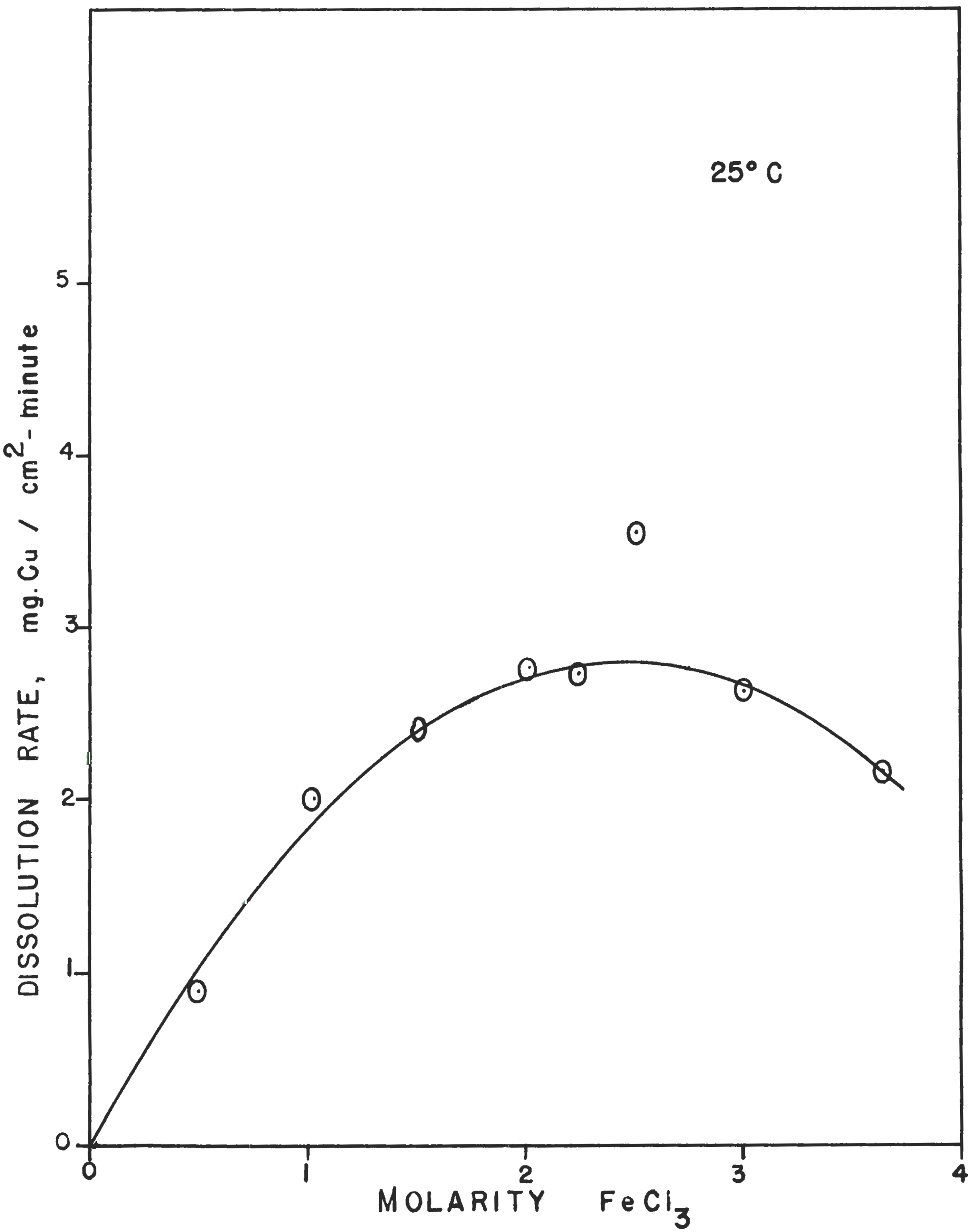

Figure 5. Plot of Dissolution Rate Against Concentration at 25°C.

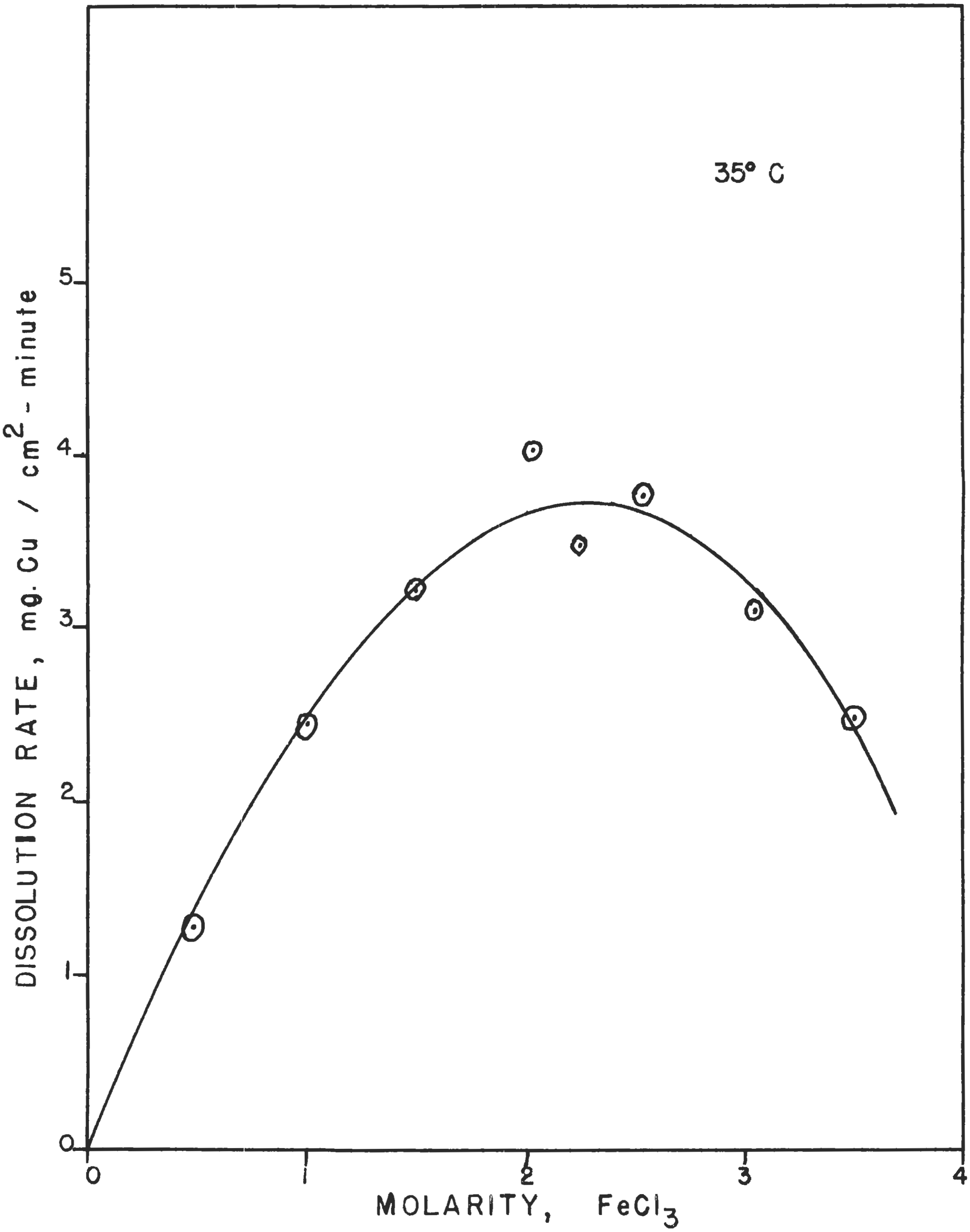

Figure 6. Plot of Dissolution Rate Against Concentration at 35°C.

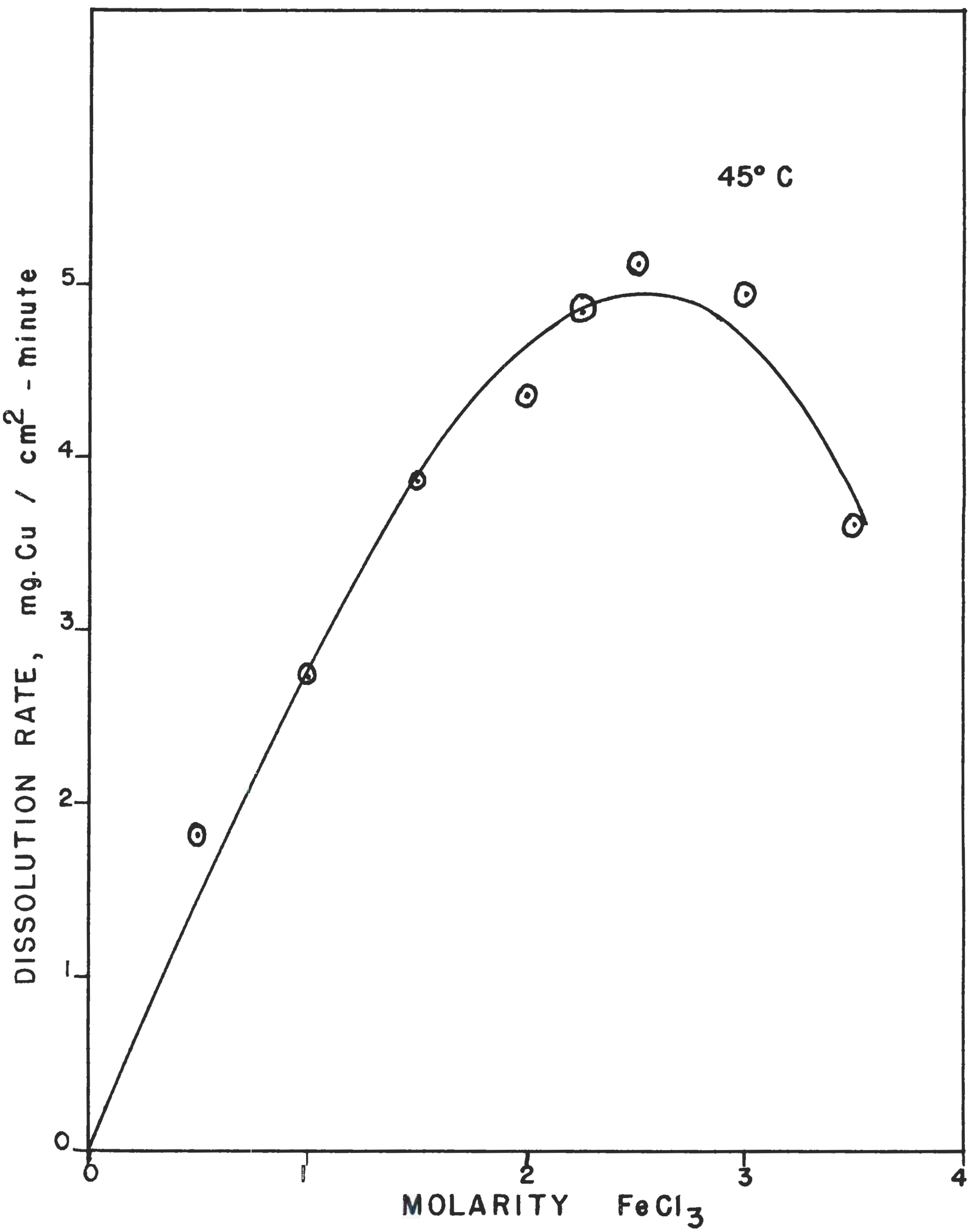

Figure 7. Plot of Dissolution Rate Against Concentration at 45°C.

Further inspection of the dissolution plots shows that some points are farther from the curves than would normally be expected with routine experimental error. This is particularly true in the maximum region of the 25° and 35° C rate curves. A possible solution to this can be traced to the Sigmamotor pump used in this study. This pump circulated ferric chloride through the system by means of a pulsing action on the three-eighths inch tubing drawn through it. Since an experimental run lasted for sixty minutes, it is suspected that during some runs the walls of the tubing in the pump weakened, thus changing the flow rate of the system. This, in turn, affected the copper dissolution rate. This point seems to be illustrated by Figure 3 where a variation in the linear dissolution rate is observed near the end of the run.

The main purpose of this work was to determine the controlling mechanism of the copper-ferric chloride reaction. In order to study the mechanism, use was made of the previously mentioned temperature coefficient criterion. The dissolution rate for the reaction at various temperatures and concentrations have already been reported in Tables 1, 2, and 3. Temperature coefficients, which are easily calculated from these values are presented in Table 4.

As shown in this table, temperature coefficients for the reaction vary between 1.07 and 1.60. These results strongly indicate a diffusion controlling mechanism. In addition, since the above coefficients cover the entire experimental range of this study, it may be stated that the reaction is controlled by a diffusion mechanism over the entire scope of this investigation.

Table 4.

Temperature Coefficients for the Dissolution of Copper in Ferric Chloride

Ferric Chloride Concentration Moles/Liter	$K_{35°}/K_{25°}$	$K_{45°}/K_{35°}$
0.5	1.43	1.45
1.0	1.22	1.11
1.5	1.38	1.19
2.0	1.45	1.07
2.25	1.27	1.40
2.5	1.07	1.34
3.0	1.15	1.60
3.5	1.14	1.46

Further proof that the reaction is controlled by a diffusion mechanism is given by the low energies of activation exhibited by the system. Abramson and King (33) have shown that activation energies in the range of 5,000 calories per mole are typical for diffusion controlled reactions. By using the basic Arrhenius Energy Equation, activation energies for the copper-ferric chloride system studied in this investigation were obtained. The Arrhenius Equation is represented as follows:

$$\text{Ln } K = \text{Ln } A - E_A/RT,$$

where E_A is the activation energy for the reaction, K is the dissolution rate, R is the gas constant, T is the absolute temperature and A is the reaction constant.

Activation energies were obtained by plotting the logarithm of the dissolution rate canstant against the reciprocal of the absolute temperature.

The slope of this line multiplied by the gas constant R (1.9869 calories per degree) gives the value of activation energy. These values expressed in terms of calories per mole are presented in Table 5. Illustrations of the activation energy plots are given in Figure 8.

Table 5.

Activation Energies for the Dissolution of Copper in Ferric Chloride Solutions

Ferric Chloride Concentration Moles/Liter	Activation Energy Calories/Mole
0.5	4583
1.5	4426
2.0	4877
2.25	5148
2.5	5148
3.0	5057
3.5	4968

From inspection of the activation energies reported in Table 5 two important conclusions can be reached. First, since the values of the activation energies for the reaction lay close to 5,000 calories per mole, a diffusion controlled mechanism is suggested. Secondly, since the values of the activation energies are approximately equal in magnitude, a similar mechanism over the entire experimental range is indicated.

It is also interesting to note that the activation energies found in this study agree in general with those reported by Ferrari (35).

Brooks (36), in his investigation of the copper-ferric chloride system postulated that the reaction was controlled by the diffusion of the various ferric-chloro species to the copper surface. He also stated that

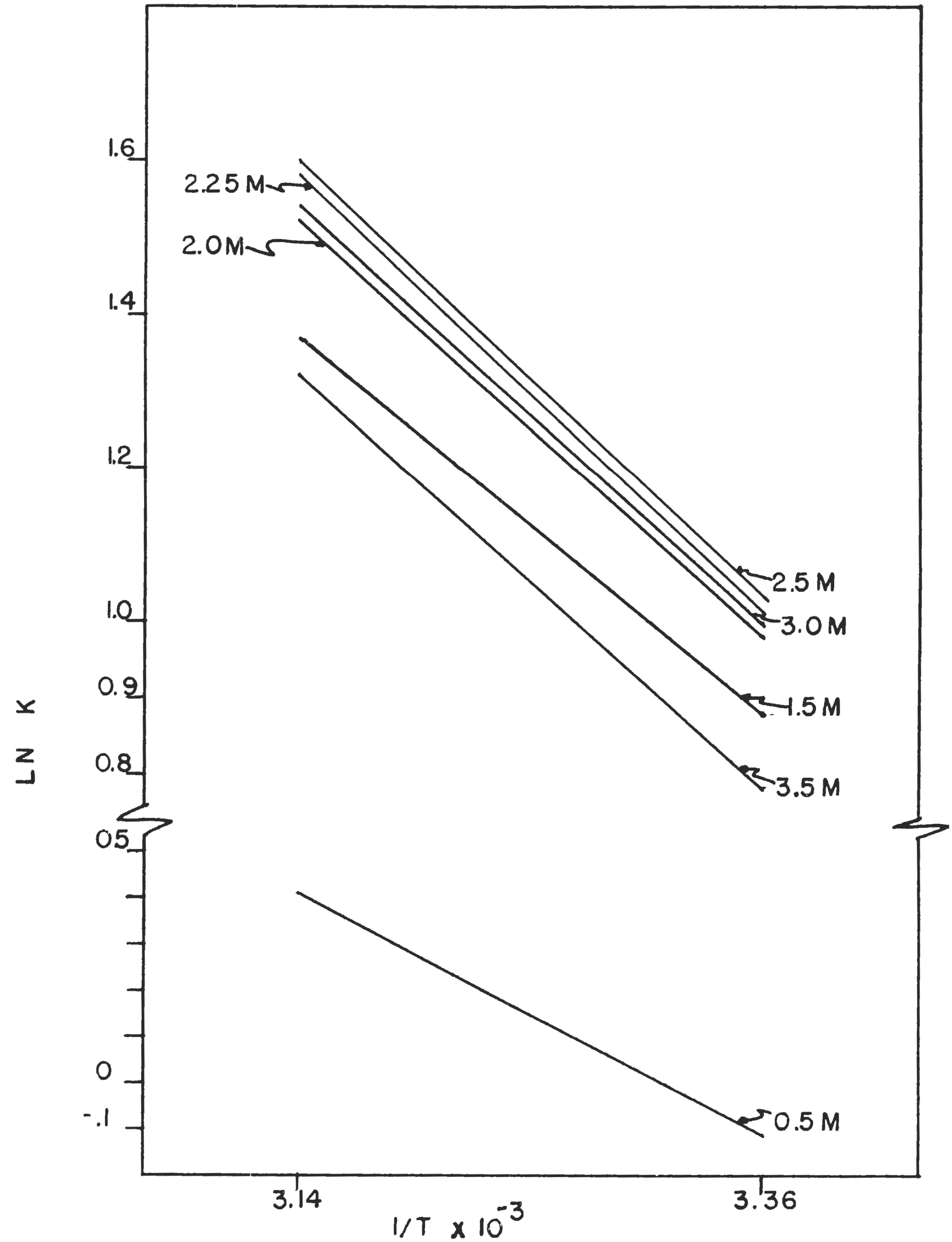

Figure 8. Activation Energy Plots.

the reaction was hindered by ferric chloride itself which acted as a diffusion barrier. It is in the light of this theory that the dissolution rate curves for this reaction will be discussed.

In aqueous solutions ferric chloride, to a certain extent, undergoes hydrolysis. This reaction may be visualized by the following overly simplified equation:

$$FeCl_3 + HOH = Fe^{+3} + FeCl^{+2} + FeOH^{+2} + FeCl_2^{+}$$

The ferric-chloro species on the right hand side of the equation are the active species in that they diffuse to the copper surface and react or oxidize the copper. However, ferric chloride itself is unreactive and thus inhibits the reaction by causing a diffusion barrier to the reactive species. At low concentrations equilibrium seems to favor the formation of the ferric-chloro species and the rate of copper dissolution increases linearly as shown by Figures 5, 6, and 7. Above one molar ferric chloride concentration the dissolution rate increases more slowly, which indicates the beginning of an equilibrium change toward the left side of the equation. At concentrations greater than three molar the reaction rate drops sharply, thus indicating an equilibrium shift in the direction of the ferric chloride species. This trend becomes more pronounced with increasing ferric chloride concentrations. This equilibrium shift results in a decrease in the amount of active ferric-chloro species in solution and causes an increase in the ferric chloride species. As the ferric chloride species builds up, it produces an inhibiting effect upon the reaction and reduces the amount of active species available to oxidize the copper.

It should be mentioned that the experimental results and conclusions of this investigation represent only basic kinetic data for the copper-ferric chloride system, particularly since temperature and concentration were the only variables investigated. Further work on the system should involve a study on the effects of dissolved oxygen and the addition of chloride and ferric ions on the dissolution rate. Experiments which study the system as affected by variations in linear velocity would also be of value in determining the mechanism of the reaction. It is felt that only through such an extensive investigation can a clear and complete understanding on the kinetics and mechanisms of the copper-ferric chloride system be obtained.

CHAPTER V

CONCLUSIONS

The dissolution of copper in ferric chloride solutions follows a zero-order rate relationship with respect to reaction time. Results show that the dissolution rate curves follow a parabolic dependency upon the ferric chloride concentration. These curves are linear with respect to the ferric chloride concentration up to about 1.0 molar. Above one molar the rate increases more slowly, reaching a maximum between 2.0 and 2.5 molar and then decreasing with increasing ferric chloride concentration.

The reaction is controlled by a diffusion mechanism. This is indicated by the low temperature coefficients (1.1 to 1.6) and activation energies (4426 to 5148 calories per mole) obtained in this investigation.

APPENDIX

TABLE 6
EXPERIMENTAL RESULTS AT 25°C

Run No.		1		2		3		4	
Conc. of $FeCl_3$, M		0.489		2.977		1.499		2.243	
Sample No.	Time (Min)	Cu Dissolved (GM x 10^{-2})	Dev. (%)	Cu Dissolved (GM x 10^{-2})	Dev. (%)	Cu Dissolved (GM x 10^{-2})	Dev. (%)	Cu Dissolved (GM x 10^{-2})	Dev. (%)
1	6	.588	7.8	1.37	9.1	1.44	2.0	1.71	10.9
2	12	1.08	6.0	2.70	5.4	2.94	2.9	3.46	7.7
3	18	1.58	3.9	4.36	4.9	4.04	3.9	5.48	6.3
4	24	2.28	2.3	5.87	8.3	5.60	3.5	6.73	5.6
5	30	2.70	2.8	7.47	4.8	8.12	5.5	8.35	6.3
6	36	3.30	2.7	9.51	6.9	8.90	3.1	10.9	6.6
7	42	3.71	2.9	11.2	4.8	10.1	4.0	12.3	5.2
8	48	4.34	2.5	14.2	6.6	11.8	4.7	13.0	6.8
9	54	4.87	2.9	15.9	5.8	12.8	3.3	14.2	8.4
10	60	5.31	2.2	14.6	4.9	12.9	2.0	15.4	6.8

Run No.		5		6		7		8	
Conc. of $FeCl_3$, M		3.647		1.026		2.601		2.079	
Sample No.	Time (Min)	Cu Dissolved GM x 10^{-2})	Dev. (%)	Cu Dissolved (GM x 10^{-2})	Dev. (%)	Cu Dissolved (GM x 10^{-2})	Dev. (%)	Cu Dissolved (GM x 10^{-2})	Dev. (%)
1	6	1.37	5.6	1.35	7.9	2.10	10.0	1.70	6.7
2	12	2.54	7.4	2.68	2.4	4.02	10.6	3.29	3.9
3	18	4.12	6.4	3.87	5.1	6.04	8.7	4.99	1.0
4	24	4.87	6.0	5.06	2.6	8.79	3.5	6.65	6.1
5	30	6.21	6.1	6.17	2.8	10.9	5.1	8.16	4.4
6	36	7.16	6.3	7.39	2.1	13.9	3.0	10.1	6.9
7	42	8.39	9.2	8.29	2.9	13.8	5.0	12.0	2.8
8	48	9.63	14.5	9.27	4.0	16.2	4.6	14.1	3.4
9	54	12.2	6.8	10.6	2.8	19.2	10.2	14.8	3.3
10	60	14.2	8.7	12.2	2.4	22.2	4.7	16.4	3.3

TABLE 7
EXPERIMENTAL RESULTS AT 35°C

Run No.		9		10		11		12	
Conc. of $FeCl_3$, M		0.4850		2.953		1.497		2.235	
Sample No.	Time (Min)	Cu Dissolved (GM x 10^{-2})	Dev. (%)	Cu Dissolved (GM x 10^{-2})	Dev. (%)	Cu Dissolved (GM x 10^{-2})	Dev. (%)	Cu Dissolved (GM x 10^{-2})	Dev. (%)
1	6	0.822	2.5	1.84	4.9	2.25	5.0	2.05	7.1
2	12	1.64	3.2	3.94	4.0	4.50	5.4	4.08	5.7
3	18	2.32	3.1	5.71	4.1	6.44	3.2	6.63	4.8
4	24	3.17	1.8	8.11	3.9	8.26	4.5	8.38	5.9
5	30	3.82	2.3	9.31	2.4	10.1	3.3	11.0	4.0
6	36	4.74	2.1	11.7	3.7	11.5	4.5	12.8	4.9
7	42	5.37	2.3	12.5	1.7	14.3	5.0	15.0	4.1
8	48	6.16	0.9	14.9	3.0	15.3	7.6	17.2	4.4
9	54	6.74	3.2	16.8	2.9	17.4	2.5	18.3	4.2
10	60	7.67	1.6	18.3	3.5	18.8	5.0	19.7	5.3

Run No.		13		14		15		16	
Conc. of $FeCl_3$, M		1.018		3.509		2.036		2.532	
Sample No.	Time (Min)	Cu Dissolved (GM x 10^{-2})	Dev. (%)	Cu Dissolved (GM x 10^{-2})	Dev. (%)	Cu Dissolved (GM x 10^{-2})	Dev. (%)	Cu Dissolved (GM x 10^{-2})	Dev. (%)
1	6	1.59	5.3	1.57	7.8	2.40	1.9	2.03	4.3
2	12	3.31	1.9	2.77	2.5	5.18	3.0	4.67	2.6
3	18	5.08	3.6	4.32	4.3	7.21	2.4	6.64	4.5
4	24	6.65	2.1	5.84	1.2	10.8	3.8	9.19	2.7
5	30	8.28	3.5	7.32	2.8	12.6	2.0	11.1	10.8
6	36	9.22	2.1	8.90	4.3	16.8	7.7	14.8	5.0
7	42	10.7	3.1	9.63	2.5	17.1	1.9	15.8	5.5
8	48	11.1	1.8	11.2	6.0	19.7	4.2	19.7	3.6
9	52	12.4	4.2	13.4	4.1	19.5	3.8	17.8	5.5
10	60	14.5	3.5	15.7	1.6	24.1	10.4	24.0	2.8

TABLE 8
EXPERIMENTAL RESULTS AT 45°C

Run No.		17		18		19		20	
Conc. of $FeCl_3$, M		0.508		3.027		1.504		2.260	
Sample No.	Time (Min)	Cu Dissolved (GM x 10^{-2})	Dev. (%)	Cu Dissolved (GM x 10^{-2})	Dev. (%)	Cu Dissolved (GM x 10^{-2})	Dev. (%)	Cu Dissolved (GM x 10^{-2})	Dev. (%)
1	6	1.11	5.8	3.39	6.3	2.73	6.1	3.08	3.6
2	12	2.44	5.8	6.47	5.2	5.00	4.0	6.10	4.7
3	18	3.42	2.4	9.26	9.2	7.68	3.2	10.7	2.2
4	24	4.76	3.4	11.7	1.7	9.76	4.4	13.0	5.7
5	30	5.48	1.8	15.08	6.1	12.6	3.7	16.2	3.4
6	36	6.89	4.3	18.06	1.7	13.1	5.0	17.9	3.4
7	42	7.60	1.8	21.5	6.0	17.0	4.4	23.8	5.5
8	48	9.17	4.0	23.2	1.9	17.3	3.9	22.3	3.8
9	54	9.62	1.2	27.8	6.0	23.2	2.9	26.3	3.0
10	60	10.9	3.4	28.9	2.3	21.3	2.7	25.0	3.8

Run No.		21		22		23		24	
Conc of $FeCl_3$, M		0.995		3.490		2.010		2.506	
Sample No.	Time (Min)	Cu Dissolved (GM x 10^{-2})	Dev. (%)	Cu Dissolved (GM x 10^{-2})	Dev. (%)	Cu Dissolved (GM x 10^{-2})	Dev. (%)	Cu Dissolved (GM x 10^{-2})	Dev. (%)
1	6	1.74	1.6	1.80	9.1	3.03	2.8	2.81	6.1
2	12	3.78	3.4	3.98	8.1	6.54	4.4	5.97	8.0
3	18	5.39	1.7	5.86	5.2	9.45	4.7	9.67	5.1
4	24	7.35	3.3	8.36	5.3	12.9	5.4	12.8	4.3
5	30	8.01	4.2	10.6	4.6	14.3	3.6	16.2	6.7
6	36	10.3	4.3	12.9	3.5	17.0	5.4	17.9	4.0
7	42	11.1	2.3	15.2	4.9	18.8	6.1	20.9	4.9
8	48	13.1	4.2	18.7	3.5	20.0	4.4	20.9	9.6
9	54	13.7	1.7	18.4	5.2	22.1	7.2	21.7	4.9
10	60	16.6	3.6	21.7	8.4	24.4	5.2	24.1	4.9

BIBLIOGRAPHY

Literature Cited

1. King, C. V., and L. Weidenhammer, Journal of the American Chemical Society, 58, 602 (1936).

2. Pletenev, S. A., and S. A. Pavlov, Zhurnal Prikladoni Khimii, 10, 1957 (1937).

3. Brooks, R. E., Kinetic Studies of the Dissolution of Copper in Ferric Chloride Solutions, Unpublished M. S. Thesis, Georgia Institute of Technology, 1958

4. Ferrari, H. M., The Kinetics and Mechanism of Dissolution of Copper in Ferric Chloride Solutions, Unpublished Ph. D. Thesis, University of Michigan, 1958.

5. Nernst, W., Zeitschrift fur Physikalische Chemie, 47, 52 (1904).

6. Van Name, E. A., and D. V. Hill, American Journal of Science, 42, (4), 307 (1916).

7. King, C. V., Transactions of the New York Academy of Science, 10, 262 (1948).

8. Salzberg, H. W., H. Knoetgen, and A. M. Molless, Journal of the Electrochemical Society, 98, 31 (1951).

9. Durdin, Y. V., and A. M. Markevich, Journal of General Chemistry (U.S.S.R.), 19, No. 12a, 605 (1949).

10. King, C. V., and E. Hillner, Journal of the Electrochemical Society, 103, 203 (1956).

11. King, C. V., and N. Mayer, Journal of the Electrochemical Society, 100, 473 (1953).

12. Weaver, H., and C. C. Lynch, Corrosion, 14, 13t (1958).

13. Kilpatrick, M., Journal of Physical Chemistry, 38, 269 (1934).

14. Makrides, A. C., and N. Hackerman, Journal of the Electrochemical Society, 105, 156 (1958).

15. Abramson, M. B., and C. V. King, Journal of the American Chemical Society, 61, 2290 (1939).

16. Welsh, J. Y., and A. B. Garrett, Journal of Physical Chemistry, 56, 727 (1952).

17. King, C. V., and M. M. Braverman, Journal of the American Chemical Society, 54, 1744 (1932).

18. King, C. V., and M. Schack, Journal of the American Chemical Society, 57, 1212 (1935).

19. Benjamin, C. Y. Lu, and W. F. Graydon, Canadian Journal of Chemistry, 32, 1953 (1954).

20. Kuzminykh, I. N., E. L. Yakhantova, and M. D. Babushkina, Journal of Applied Chemistry (U.S.S.R.), 26, 315 (1953).

21. Milyutin, N. N., and A. I. Shultin, Journal of Applied Chemistry, 30, 57 (1957).

22. Johnson, R. L., M. Hobson, and J. H. Weber, Industrial and Engineering Chemistry, 50, 1194 (1958).

23. Loshkarev, A. G., and V. S. Kalevatova, Zhurnal Prikladoni Khimii, 21, 954 (1948).

24. Weeks, J. R., and G. R. Hill, Journal of the Electrochemical Society, 103, 203 (1956).

25. King and Weidenhammer, op. cit.

26. Pletenev and Pavlov, op. cit.

27. Szabo, Z., Journal of the American Chemical Society, 71, 1511 (1949).

28. Brooks, op. cit.

29. Ferrari, op. cit.

30. Lange, N. A. (Editor), Handbook of Chemistry, Handbook Publishers Incorporated, Sandusky, Ohio, (1952), p. 1129.

31. Brooks, op. cit., p. 16.

32. Ferrari, op. cit., p. 43.

33. Abramson and King, op. cit.

34. Moelwyn-Hughes, E. A., The Kinetics of Reactions in Solutions, Oxford University Press, London, (1933), p. 3.

35. Ferrari, op. cit., p. 48.

36. Brooks, op. cit.