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THE KINETICS AND MECHANISM OF DISSOLUTION OF COPPER IN FERRIC CHLORIDE SOLUTIONS

By

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ABSTRACT

The objective of this investigation was to determine the kinetics and mechanism of dissolution of copper in ferric chloride solutions. The reaction was studied as a function of metallic variables in addition to the solution variables that are usually studied. Kinetic data for the dissolution of copper single crystals as a function of the ferric chloride concentration; the ion contents of chloride, ferric, cuprous, ferrous, and hydrogen; the dissolved oxygen content; and the metallic variables, crystallographic orientation and surface finish, were obtained. Mechanisms describing the reactions which are in agreement with the kinetic data are presented.

The copper used throughout the experiments was a high-purity, vacuum-melted material and studies were made on selected crystal faces. Single crystals were grown from the melt by the controlled solidification and seed crystal technique and samples having (100), (110), and (111) planes parallel to the surface were prepared from the ingot.

The experimental apparatus consisted of a constant temperature reservoir from which the solution was pumped through the reaction chamber which contained the sample. The apparatus was specially designed for handling single crystals having a flat surface of known orientation. The kinetics of the reaction were measured by analysis for the cupric ion content in solution. The analysis was made by a spectrophotometric technique utilizing the strong absorption characteristics of the colored cupric

chloride ion complex.

Results showed that the rate of dissolution of copper is directly proportional to the ferric chloride concentration up to 1.0 molar concentration. Thereafter the rate increases more slowly, reaching a maximum in the vicinity of 2.2 molar, and then decreases. The decrease in dissolution rate which occurs at high ferric chloride concentrations was attributed to the presence of large amounts of undissociated $FeCl_3$.

The rate of dissolution of copper in ferric chloride solutions is greatly increased by the presence of chloride ions, but is independent of the dissolved oxygen and hydrogen ion concentration. Electron diffraction studies of a film which exists on the copper surface during the reaction detected a layer of insoluble cuprous chloride which is present as an intermediate reaction product.

Analysis of the results showed that the reaction is a diffusion-controlled process at temperatures above 7°C., and partially diffusion and partially chemically-controlled at lower temperatures. In the diffusion-controlled region the reaction is practically independent of the metallic characteristics, however, in the low temperature region the reaction is a function of the crystallographic orientation and the surface finish of the metal. In this partially chemically-controlled region it was found that the (100) plane is the most stable, i.e., it is the orientation which dissolves at the slowest rate. The (110) and the (111) orientations dissolve 12% and 20% more rapidly, respectively. The initial dissolution rate of

cold-worked surfaces is higher than surfaces which are chemically-polished.

The following mechanisms which describe the reactions are presented. At temperatures above 7°C., the rate is determined by the simultaneous diffusion rates of chloride ions to the cuprous chloride film, and of Fe^{+3}, $FeCl_2^+$ ions to the copper metal. At low temperatures, below 7°C., the reaction between chloride ions and cuprous chloride is chemically-controlled. Hence, the rate is controlled simultaneously by the chemical reaction involving chloride ions with cuprous chloride and the diffusion of Fe^{+3} and $FeCl_2^+$ ions to the copper surface.

To My Parents

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INTRODUCTION

The dissolution reaction of metals and alloys in corrosive environments is an extremely complex process, influenced by so many factors that a study of metals and alloys in their commercially usable state affords little information concerning the basic nature of the process. The fundamental dissolution or corrosion characteristics of metals can best be determined by a study of the least complex form of the metal and of the environment. In metals, the least complex state is of the form of a single crystal of a high purity material having a low density of imperfections. In solutions, the least complex form is a high purity solution of simple composition having carefully controllable and accurately known external variables. By employing single crystals and carefully controllable environments, many of the dissolution-influencing characteristics of polycrystalline materials and of unknown solution variables are eliminated, or at least minimized, and the basic behavior of the process may be studied.

It is only within recent years that any real attempt has been made to study the basic mechanisms of dissolution reactions. Most of these studies have been concerned with solution variables and little attention has been given to the metallic variables. On the other hand, the importance of crystal orientation in controlling rates of chemical reactions has been clearly demonstrated. Unfortunately, the majority of such

investigations have been qualitative in nature and only limited quantitative information is available. The difference in dissolution rates of different orientations varies greatly with the environment.

It should be emphasized at this point that in heterogeneous reactions between metals and solutions the physical and chemical characteristics of the solution are always of importance. This, however, is not always true with regard to the metal. Whether the reaction is dependent on the characteristics of the metal is a function of the controlling mechanism of the reaction. If the overall reaction is controlled by transport of reactants or products either toward or away from the surface, the reaction is independent of the physical characteristics of the metal. Thus, knowledge concerning the mechanism of a reaction must be obtained before a detailed understanding of the basic process is achieved.

The reaction between copper and ferric chloride has been of great industrial importance for many years. It has been utilized extensively in the photoengraving industry to produce etched "copper plates" which, in turn, are used by printers to reproduce colored illustrations for magazines and brochures. This process has, in recent years, assumed even greater industrial importance as it is currently being employed extensively to produce "printed electrical circuits" in the electronics and electrical industries. Since this dissolution process is of considerable industrial importance, the photoengravers have

studied the reaction to a considerable extent (1, 2, 3); however, their work has not been definitive. No complete understanding of the effect of the physical and chemical characteristics of copper on the reaction is known. Furthermore, the kinetics of the reaction have never been thoroughly studied, and no mechanism for the reaction has ever been presented.

Thus, the primary objective of this investigation was to determine the rates at which copper dissolves in ferric chloride solutions and to determine the mechanism or mechanisms by which the reactions occur.

SURVEY OF THE LITERATURE

General Theory of Heterogeneous Reactions

A general theory of the kinetics of heterogeneous reactions in solutions was first proposed by Nernst in 1904 (4). This theory postulated that chemical reactions in hetergeneous systems occur very rapidly because an extremely high chemical potential exists at a solid-liquid interface. This potential depletes the liquid in the immediate vicinity of the surface of reactant and causes the reaction to be controlled by the rate of transport of reagent to the interface, either by convection or diffusion, or of products away from the interface by the same mechanisms.

Langmuir presented a similar argument in a somewhat different form when he showed that in order for diffusion to be the slow step in a reaction, it would be necessary to postulate a very thick diffusion layer on the surface (5, 6). He realized that the convective movement of liquid decreases near a solid surface; and as later experimentally demonstrated by Fage and Townsend, the component of turbulent motion perpendicular to the surface practically vanishes within a few microns of the interface (7). Thus, the dissolution will be governed by the rate of diffusion from the point at which convective transport becomes negligible. The reaction should be first order with respect to the reactant and the rate of reaction should be equal to the velocity of diffusion of the reactant. Van Name and

Hill (8) reasoned that if this theory were correct, all metals should dissolve in a given reagent at the same rate (8). Their data confirmed this for a number of metals in ferric-alum solutions, but copper and silver dissolved at somewhat slower rates. These authors recognized that all heterogeneous reactions do not follow the diffusion rate theory, and, as later pointed out by Moelwyn-Hughes, even unimolecular behavior may be explained in other ways (9).

It is now known that chemical reactions that occur in heterogeneous systems between metals and solutions are complicated by interfacial effects that operate at the boundary of the phases. These interfacial effects may influence the rate of the reaction and may in certain suitably rapid chemical reactions be the rate controlling factor. It is necessary in these systems for the solute molecule to approach the surface and be adsorbed on the surface before the reaction can occur. The adsorption may occur through a polar bond or more loosely by attractive forces which are physical in nature. After the reaction occurs, desorption of the reaction product, or products, must occur. Thus, such interfacial effects as adsorption and desorption must be considered in addition to the diffusion and specific chemical effects which are also of importance in homogeneous reactions. There are, then, five distinct processes occurring:

1. Diffusion of the reacting ions or molecules to the surface.
2. Adsorption of the reactants on the surface.

3. Chemical reaction on the surface, electron transfer.

4. Desorption of the products from the surface.

5. Diffusion of reaction products away from the surface.

The slowest of the above processes will determine the rate of reaction.

Generally, when the transport of material is the rate-determining step, either of reactants toward solid surface or products away from surface, the process is termed "diffusion-controlled." The processes of adsorption or desorption are more likely to be the slow steps in a heterogeneous reaction, since both involve appreciable energies of activation. The activation energies for desorption are particularly high, and it is likely that in very many reactions the desorption of the products is the rate-determining step. In practice, however, it is usually difficult to separate steps two, three and four because knowledge of the rates of adsorption or desorption are usually not known. It is usual, therefore, to combine these three steps and regard them as a single step, and reactions which are controlled by any one of the three steps are commonly referred to as "chemically-controlled" reactions. However, strictly speaking, this terminology should refer only to those cases in which the rate determining step is the actual chemical reaction. There is as yet no proven case of a chemically-controlled reaction (10). Cases where the slowest or rate-determining step is the removal of material from physical contact with the surface should be considered

as "desorption-controlled" reactions. At least two clear-cut cases of this behavior have been reported and many others are believed to be of the same classification (11, 12, 13).

In this thesis, the usual terminology of either diffusion-controlled or chemically-controlled reactions will be used.

Salzburg et al. suggested that if there is a large difference in the standard oxidation-reduction potential of the system, the reaction would be controlled by diffusion, while if the difference was small, it would be controlled by the chemical reaction (10). The ferric ion-silver couple was mentioned as a possible limiting case. The reactions of silver with ferric sulfate solutions and with ferric perchlorate solutions were shown to be controlled by the rates at which products were desorbed from the surface of the metal (12, 13). The potential of the ferric ion-copper system which is of importance in this investigation is just large enough to suggest that the reaction is diffusion-controlled. However, the reaction of zinc with chromic chloride is not strictly diffusion-controlled although the potential of the system is large (14). The reaction of cadmium with chromic chloride is diffusion-controlled although the potential of the system is small (15). Therefore, generally speaking, the difference in oxidation-reduction potential of the system is often a good indication of whether the reaction is diffusion-controlled or chemically-controlled; however, it is sometimes misleading since other factors such as adsorption and desorption characteristics, complex ion formation, etc.,

can be of considerable importance.

A discussion of the characteristics of diffusion-controlled, chemically-controlled, and intermediate type reactions, those which are partly diffusion-controlled and partly chemically-controlled, is presented below.

Diffusion-Controlled Reactions

Since Nernst first postulated the chemical theory for the kinetics of dissolution of solids in aqueous solutions, many examples of diffusion-controlled processes have been found (16). The generally accepted criteria for these diffusion-controlled reactions were discussed by King and recently summarized by Salzberg et al (10, 17, 18, 19, 20).

(a) Different metals dissolve at nearly the same rate in the same reagent under identical conditions of temperature, agitation, etc.

(b) The rate of agitation of the solution past the metal surface has a great effect. The greater the agitation, the greater the dissolution rate.

(c) The dissolution rates as determined with a series of reagents of varying concentration are proportional to a fractional power of the diffusion coefficients, about 0.75.

(d) The dissolution rate is inversely proportional to the viscosity.

(e) The dissolution rate increases with increasing concentration of reagent, the curve being linear.

(f) The temperature coefficients of diffusion-controlled reactions are lower than for homogeneous or chemically-controlled reactions, usually between 1.1 and 1.5 per ten-degree rise in temperature.

(g) The previous condition of the surface has only a very minor effect on the dissolution rate.

(h) All crystallographic orientations of the metal dissolve at the same rate.

(i) Diffusion-controlled rates are generally higher than non-diffusion-controlled rates.

The over-all equation for a diffusion-controlled process may be expressed as

$$-\frac{dx}{dt} = K\,A\,(a - x)/V \qquad (1)$$

where "A" is the surface area in square centimeters of the metal being dissolved, "a" is the original concentration of reactant in gram-ions per liter, "x" is either the concentration of product being formed or the concentration of reagent that has disappeared during the course of the reaction, and "V" is the volume, expressed in liters. "K" is the specific rate constant expressed in cm - min^{-1} and is a function of the temperature, stirring speed, viscosity, and the particular metal involved.

Equation (1) is also often seen in its integrated form. It is readily integrated after first multiplying by dt and dividing by (a-x) to separate the variables.

$$-\frac{dx}{(a - x)} = \frac{K\,A\,dt}{V}$$

$$-\int_{0}^{a-x} \frac{dx}{(a - x)} = \frac{K\,A}{V} \int_{0}^{t} dt$$

$$\ln \frac{a}{(a - x)} = \frac{K A}{V} t$$

Rearranging $K = \frac{2.3 V}{A t} \log \frac{a}{a - x}$ (2)

From Equation 1, it is obvious that diffusion-controlled reactions are usually first order reactions.

Chemically-Controlled Reactions

As previously mentioned, non-diffusion-controlled reactions are usually referred to as "chemically-controlled" reactions. The criteria for chemically-controlled reactions are as follows:

(a) Different metals dissolve at different rates in the same solution under identical conditions.

(b) The rate of agitation of the solution past the metal surface has a slight effect on dissolution rate, but not nearly as pronounced as in diffusion-controlled reactions.

(c) The dissolution rates are completely independent of the diffusion coefficients of the reacting ions.

(d) The dissolution rate is independent of the viscosity of the solution.

(e) The dissolution rate increases with increasing concentration of reagent in a nonlinear fashion, slowly and reaching a maximum.

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

(g) The previous condition of the surface has a very marked effect on the rate; a polished surface has a higher initial dissolution rate than a non-polished surface.

(h) Different crystallographic orientations dissolve at different rates.

(i) Non-diffusion controlled rates are in general slower than diffusion-controlled rates.

Chemically-controlled reactions may be of first order, similar to diffusion-controlled reactions, but the value of the rate constant must be smaller. Small first order constants may be obtained if reagent, product, or other material is strongly adsorbed and completely covers the metal surface. If a reaction product or intermediate compound is weakly adsorbed and does not cover the entire surface, more of the surface will become covered as the concentration of this material increases, and the rate will not be of the first order.

Intermediate-Type Reactions

In addition to pure chemically-controlled and pure diffusion-controlled rates, there are reactions which may be intermediate between these two types. Van Name and Hill found that zinc, cadmium, iron, nickel, and tin dissolved at approximately the same rate in ferric-alum solutions containing sulfuric acid (8). However, copper dissolved at a slightly slower rate and silver dissolved much more slowly. Their results showed that the dissolution of copper in ferric alum solutions was not quite entirely diffusion-controlled. Similarly, King and Hochberg found the reaction of copper in acetic acid to be first order throughout the limited range tested; but, it was neither rapid enough to be entirely diffusion-controlled nor slow enough to be entirely chemically-controlled (21).

An equation for intermediate cases may be derived as follows:

Allow C to be the concentration of reactant in the bulk of the solution and C_s to be the concentration at the metal surface. The rate of the chemical reaction in this intermediate case is approximately the same as the rate of diffusion through the gradient $(C - C_s)$. Therefore, these two rates may be equated:

$$\frac{dx}{dt} = k_1 A C_s = k_2 A (C - C_s)$$

where k_1 is the chemical constant, k_2 the overall diffusion constant:

$$\frac{dx}{dt} = \frac{k_1 k_2 A C}{k_1 + k_2} = k A C \qquad (3)$$

Thus, the rate for this type of reaction is a function of the chemical constant k_1 and the diffusion constant k_2 and has a value which is intermediate between these two.

Role of the Metallic Surface on Dissolution Reactions

In chemically-controlled reactions, the physical and chemical nature of metallic surfaces in contact with solutions is of great importance not only from a theoretical viewpoint but also from an industrial viewpoint. The most important example of this is corrosion where the characteristics of the metal surface can greatly influence the longevity of a part in

service. In other industries such as photoengraving, the characteristics of the metallic surface can greatly influence the quality of product produced.

Metallic surfaces are usually complex in structure and, accordingly, it is not too surprising to find that spontaneous chemical reactions involving these surfaces are often structure dependent. The metallic variables which are especially important in these structure dependent reactions fall into three categories: crystallographic orientation, microstructure, and surface finish.

Crystallographic Orientation

Crystallographic orientation exerts a surprisingly large effect on the rate of dissolution of metals in acids or other reactants. Qualitatively, this effect has been known for many years in metallography where various etching reagents are used to differentiate grains varying only in their orientation relative to the surface.

Quantitatively, the chemical anisotropy of crystalline solids was first observed on ionic crystals (22-24). Aminoff and Straumanis both observed the stability of the basal plane in zinc as indicated by oxidation, vaporization, and solution studies (25, 26). These authors suggested that the stability of a crystal plane could be directly associated with the atomic configuration; higher atomic densities being the more stable. Glauner and Glocker, working with single crystals in the form of spheres, studied the relative rates of corrosion of different faces

in 20 different organic and inorganic solutions (27). Their results clearly showed that the relative chemical reaction rates of various crystal faces depend on the environment, so that it cannot be said that a certain crystal face is more resistant than others unless the corresponding environment is also named. For example, in acetic acid the (111) face was more reactive than the (100) face; however, in propionic acid, the reverse was true. They obtained differences in relative corrosion rates on one face compared with another as much as 3 to 1. Glauner later attempted to explain the dependency of the stability of crystal upon the environment in terms of lattice forces, but was unsuccessful (28).

More recently, Gwathmey et al. studied the directional reactivities of single crystals of copper in gases and in solutions. They found that the potential difference which existed between planes could be varied and actually reversed by the presence or absence of air in the electrolyte (29-33).

Several other studies of the dissolution of metal monocrystals in acids have been made. Yamamato and Watanabe studied the solution rate of zinc crystals in nitric and hydrochloric acids (34). The dissolution rate in nitric acid was found to be isotropic, whereas the dissolution rate in hydrochloric acid was anisotropic. Bolognesi studied the dissolution of aluminum, zinc, and lead in 5N and 1N hydrochloric acid; however, this study was aimed primarily at an industrial application and contains little valuable scientific information (35). A study of the etching

rate of germanium single crystals in hydrofluoric acid solutions by Camp yields some interesting information (36). His results showed that at temperatures above 25°C. the rate was greatest for the (110) orientation and least for the (111) orientation. However, below 25°C. there occurred a reversal of order of rates for the (100) and (111) surfaces and the rate was the least for the (100) plane. The author was unable to explain the reversal. Gwathmey recently completed a study of the dissolution of copper in solutions of copper sulfate and sulfuric acid (37). He found that etching characteristics of the different faces varied with the pH of the solution. The data again emphasized the importance of slight changes in environment on the relative solution of different crystal faces. A study of the corrosion of single crystals of iron in citric acid by Buck and Leidheiser showed the (100) face to be more stable than the (321) face (38). Conversion of the iron crystals to polycrystals by recrystallization resulted in a considerably increased corrosion rate.

All of the above work of corrosion as a function of orientation indicates that certain crystal planes are more stable than others. However, identification of the thermodynamically stable configuration cannot be obtained from kinetic measurements since a given plane may be the most stable configuration in a given environment whereas another plane will be more stable in another environment. Tragert and Robertson studied cells of the form:

$$Cu_{(h,k,l)} \mid CuSO_4 \mid Hg_2SO_4 \mid Hg$$

and determined that the only stable configuration of atoms is that of the close-packed octahedral planes (39). All other crystal planes were unstable and approached the (111) figure by an etch faceting process. Although the (111) plane is the most stable one from a thermodynamic viewpoint, dissolution experiments with copper have shown the (100) to be stable as frequently as the (111) plane (27).

Microstructure

Although a discussion of the effect of microstructure on dissolution reactions is beyond the scope of this investigation, it suffices to mention that microstructure can be of considerable importance in chemically-controlled reactions. An excellent review of this subject has been presented by Uhlig (40).

The importance of microstructure in structure dependent reactions is evidenced every time a sample is etched for metallographic examination. In addition to orientational differences, the rate of dissolution of the metallic surface may be a function of such factors as impurities, grain boundaries, composition variations, strain gradients, etc. The dissolution of a multiphase or inhomogeneous metal is usually more rapid than for a pure or single-phase homogeneous metal since the former process is essentially electrochemical in nature. The electrochemical reaction results from a difference in potential between the phases when the metal is placed in the etching reagent.

The etching of pure metals and homogeneous single-phase

alloys differs considerably from that associated with multi-phase alloys. Since essentially only one phase exists in these metals, an operative dissolution mechanism governed by an electrochemical mechanism is hardly tenable. The reaction in this case is a direct chemical attack. There is, however, a slight difference in potential between the base metal and impurities, between grain boundaries and grains, and between strained areas and unstrained areas which results in slight differences in corrosion rates.

Surface Finish

When the surface of a crystalline material is ground, polished, or mechanically worked in any way, the structure of the crystal adjacent to the worked surface is distorted. The nature of the distortion may have a great influence on the initial stages of dissolution reactions.

The depth to which the metal is disturbed by the applied cold work is dependent on the coarseness of the abrasive and the applied pressure. This depth may be as much as 10,000 Å in many cases. Many of the experiments to determine the depth of penetration of the distorted layer have been carried out by successively etching away the outer layers of the surface, and examining the electron-diffraction patterns obtained at each stage. Using this technique, it has been found that the degree of misorientation decreases with depth, and even with extremely light polishing as much as 1,000 Å has to be removed before the perfect single-crystal pattern is again obtained (41).

The following general conclusions about the state of metallic surfaces after abrasion may be drawn from studies by Finch (42-44), Raether (45, 46) and others (47, 48):

a. A ground surface contains highly misoriented material, the degree of misorientation increasing with increasing abrasion.

b. The penetration of the distortion into the crystal is limited.

c. Small particles are formed during the deformation.

d. The distorted layer on a highly polished surface has the properties of an amorphous layer.

The dependency of the dissolution rate of copper on the arrangement of crystallites was observed by DuBois (49). He found that cold working a surface produces differences in corrosion-resistance. He concluded that the corrosion rate increased with increasing degree of cold work.

It is to be expected that the initial corrosion rate of a worked metallic surface would be greater at the start, since the surface is highly strained. Conversely, it would be possible to measure the depth of the worked surface by accurately determining the dissolution rate as a function of time, and assuming that the surface has been completely dissolved at the time when the dissolution rate reaches a constant value.

Dissolution of Copper in Ferric Chloride

Having reviewed the basic theories and characteristics of dissolution reactions in general, we can proceed to a discussion of the reaction with which this thesis is concerned.

The rate of dissolution of copper in ferric salts was first studied by Van Name and Hill (8). They found that the addition of 0.5 M HCl to 0.05 M Fe^{+3} salts increased the rate.

King and Weidenhammer investigated the rate of dissolution of copper in both ferric chloride and ferric nitrate solutions (50). Their work was confined to very low ferric concentrations. They rotated cylinders of copper in these reagents and measured the loss in weight of the copper as a function of time. The kinetics of the reaction were first order with respect to the ferric chloride solution up to a concentration of 0.15 molar. These investigators also found that the rate of reaction in ferric chloride solution was approximately thirty per cent higher than in ferric nitrate solutions. The higher rate with ferric chloride solution was attributed to the formation of iron-chloride complex ions (51). Some experiments were performed in which NaOH, KCl, and HCl were added to 0.015 molar ferric chloride solution. The rates decreased with the addition of NaOH since some of the ferric ions were probably converted to hydroxyl ions. With increasing amounts of KCl, the rates showed a slight decrease and then an increase until a

plateau was reached. Further additions of KCl up to 0.4M resulted in no change in reaction rate. With HCl, the authors interpreted the results to mean that a continual increase in rate occurred with increasing HCl content. The authors were unable to explain most of these effects.

Pletenev and Pavlov also investigated the behavior of copper in dilute ferric chloride solutions (52). Their work was also confined to low concentrations. Their results showed, that up to a concentration of 0.05 M, the reaction rate was controlled by the rate of diffusion of some reacting species. The authors assumed the species to be ferric ions. At higher concentrations of ferric chloride, however, they found the reaction rate decreased, a fact they attributed to a decrease in activity coefficients and an increase in the viscosity of the solution. The authors showed that the rate was controlled by diffusion by coating the copper surface with different thicknesses of gelatin. This technique clearly demonstrated that the rate of reaction decreased directly with the thickness of the layer.

Concurrently with this investigation, Brooks surveyed the reaction of copper with ferric chloride (53). He hypothesized that the reaction was controlled by the rates at which ferric-chloro species diffuse to the copper surface.

King and Appleton dissolved a sphere of a single crystal of copper in a 0.1 M ferric chloride and 0.1 M hydrochloric acid solution (54). The diameter was reduced, but the crystal

remained a perfect sphere. This clearly indicated that the reaction in the above solution was diffusion-controlled.

Most of the above work indicates that the dissolution of copper in ferric chloride is a diffusion-controlled reaction. However, there are several indications that the reaction is not completely diffusion-controlled. Photoengravers have observed that copper is sometimes highly structure sensitive when etched with ferric chloride (2). These results indicate that the reaction is at least partially chemically-controlled under certain conditions.

Reaction Mechanisms for Analogous Dissolution Studies

A three step mechanism has been proposed by Szabo for the dissolution of copper in acids in an oxidizing environment (55). He postulated that the first step is the oxidation of copper to cupric ions. The cupric ions then react with copper, forming adsorbed cuprous ions which are then oxidized to cupric ions. The rate dependent step was believed to be the rate at which the adsorbed cuprous ions were oxidized at the copper surface. Szabo derived equations based on this mechanism which related the rate of dissolution to the concentration of hydrogen, chloride, and cupric ions available, and also upon the concentration of oxygen dissolved in the reactant solution. Unfortunately, Szabo presents very little experimental work to support his mechanism.

Other mechanisms involving hydrogen and oxygen

concentrations have been proposed for dissolution reactions of copper in various aqueous solutions. Halpern found that copper reacts with aqueous ammonia in the presence of oxygen by a reaction which is determined by the transport of dissolved oxygen to the surface at low oxygen pressures, and by the chemical reaction which again involves oxygen at high oxygen pressures (56). The dissolution of copper in acids also is dependent on oxygen and hydrogen concentrations as found by Lu and Graydon for sulfuric acid and by Weeks and Hill for hydrochloric acid (57, 58).

Salzberg and King stated that metals down to copper in the EMF series dissolve in ferric salt solutions at maximum diffusion-controlled rates with the quantitative reduction of ferric to ferrous ions (11). They found, however, that silver reaches an equilibrium with only partial reduction of ferric ion, and the dissolution rate is smaller than with more reactive metals. Further work by King and Lang showed that silver dissolves much more slowly in ferric perchlorate solutions than in ferric sulfate solutions (13). The reasons advanced by the authors to explain this difference was that silver perchlorate is more strongly adsorbed on silver than silver sulfate and also a sulfo-ferric complex ion reacts more rapidly than the normal hydrated ferric ion.

Gokhale reported that, in the reaction of copper with cupric chloride, the rate increases in proportion to the concentration of cupric chloride and is also enhanced by the

addition of sodium chloride (59). Thus, it appears that the chloride ions are of importance in this reaction.

From the above discussion it appears that the reaction of copper with ferric chloride may be a function of any of the following variables: hydrogen, oxygen, ferric, cupric, or chloride ions.

EXPERIMENTAL PROCEDURES

Analysis of Experimental Problem

In this investigation of the mechanism and kinetics of dissolution of copper in ferric chloride solutions, the reaction was to be studied as a function of both the metallic and the solution variables. The first experimental step was to produce single crystals of high purity copper for the experiments. After the crystals were produced, appropriate samples from the crystals for kinetic measurements were prepared. A suitable experimental apparatus for measuring the kinetics of dissolution as a function of such solution variables as temperature, agitation, and composition was fabricated. An accurate and rapid analytical technique was also developed for the kinetic measurements. In addition to these measurements other experimental techniques, such as electron diffraction, proved to be valuable in studying intermediate reaction products and thus gave a further insight to the mechanism of the reaction.

After all the kinetic data and other information were compiled, a mechanism for the reaction which fit these kinetic data was developed.

Production of Copper Single Crystals

Since single crystals of the greatest perfection were required, the strain-anneal method was first used. It has been

claimed that crystals grown in this manner have the smallest amount of imperfections (60). The inception of the strain-anneal technique occurred in 1918 when Hanson, incidental to a study of recrystallization of several nonferrous metals, found that grain growth is extremely rapid when slightly strained crystals are annealed at appropriately high temperatures (61). Hanson's findings led him to formulate the following law: "For every degree of deformation there is a critical recrystallization temperature at which crystal growth is extremely rapid, and the size of the crystals produced by the rapid growth is greater the smaller the amount of deformation preceding such annealing." Since that time, many large crystals of metals have been produced; metals such as iron, zinc, aluminum, tungsten, and aluminum alloys have been made, but no reference could be found for the growth of large copper crystals by this technique (60).

The material used for production of single crystals was a commercial grade of vacuum-melted high purity copper, the analysis of which is given in Table I, page 32. The copper was rolled into a thin sheet approximately 3/32 inch thick and cut into specimens, 1/2 inch by 3-1/2 inches long. The specimens were annealed at 850°C. for 24 hours in a purified argon atmosphere. After annealing, the specimens were strained approximately 1% by subjecting them to a tensile force. The specimens were then slowly lowered through a vertical furnace at a rate of 1/2 inch per hour. The furnace had a 50°C. temperature

gradient over a two inch zone. The desired gradient was produced by means of a cooling coil which was placed in the tube of the furnace. Various degrees of straining in conjunction with different combinations of furnace temperatures were used but little success was obtained. Although some fairly large crystals were produced, they were somewhat difficult to reproduce. This in conjunction with the fact that the crystals produced contained twins made it necessary to try other methods.

Several attempts to grow large crystals of copper in the solid state by the secondary recrystallization method were made. Previous work by Cook and MacQuarrie had shown that very large crystals of copper could be produced by imparting a large amount of cold work followed by a high temperature anneal (62). It was found that very large grains could be produced if the material was cold-worked 99-1/2% or more, but this resulted in a sheet which was too thin for subsequent etching experiments.

While the above research was being conducted, a paper was published by Noggle and Koehler which showed that single crystals could be produced from the melt which had the same degree of perfection as crystals grown from the solid state (63). Thus, the solid state methods were discarded and all efforts were concentrated on the growth of single crystals from the melt by the controlled solidification and seed crystal technique.

Essentially, this process consists of the use of a single crystal as a seed for nucleating solidification. The equipment utilized for crystal growth was similar to that employed by

Yukawa (64) and Upthegrove (65) for the growth of copper and nickel bicrystals. The charge metal is placed in a horizontal boat which contains a seed at one end of the boat. A schematic drawing of the graphite boat is shown in Figure 1. The charge metal is melted and allowed to fuse onto the seed crystal. The heat source is then moved away from the seed at a very slow rate, causing progressive solidification of the single crystal which has the same orientation as the initial seed.

A schematic drawing of the crystal growing equipment is shown in Figure 2. The essential components are a graphite boat within a graphite cylinder (heat susceptor) which fits in a sealed Pyrex glass tube, and a movable induction coil.

Sample Preparation

The determination of the orientation of the single crystals was initially performed by the x-ray back reflection Laue picture technique described by Barrett (66). It then became apparent that an etchpit technique would be much more rapid, so this method was adopted when it proved to be almost as accurate as the x-ray technique. The process consisted of etching the copper in an appropriate reagent for 10 minutes, placing the etched crystal in an optical goniometer, and determining the reflections from the base of the etch pits. The reagent described by Barrett was not completely satisfactory (66). The recommended etchant to develop etch pits in copper is a 50% HCl solution

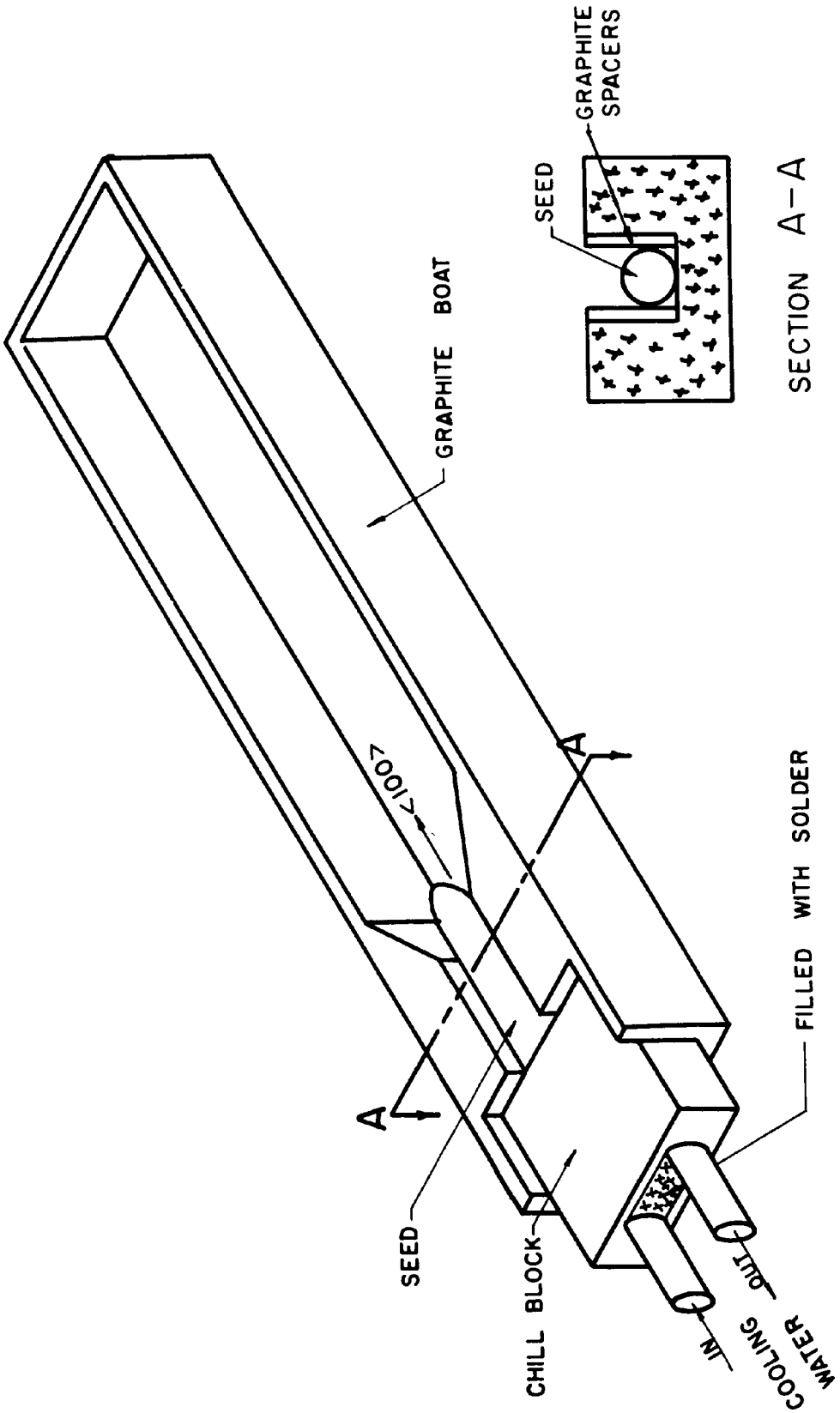
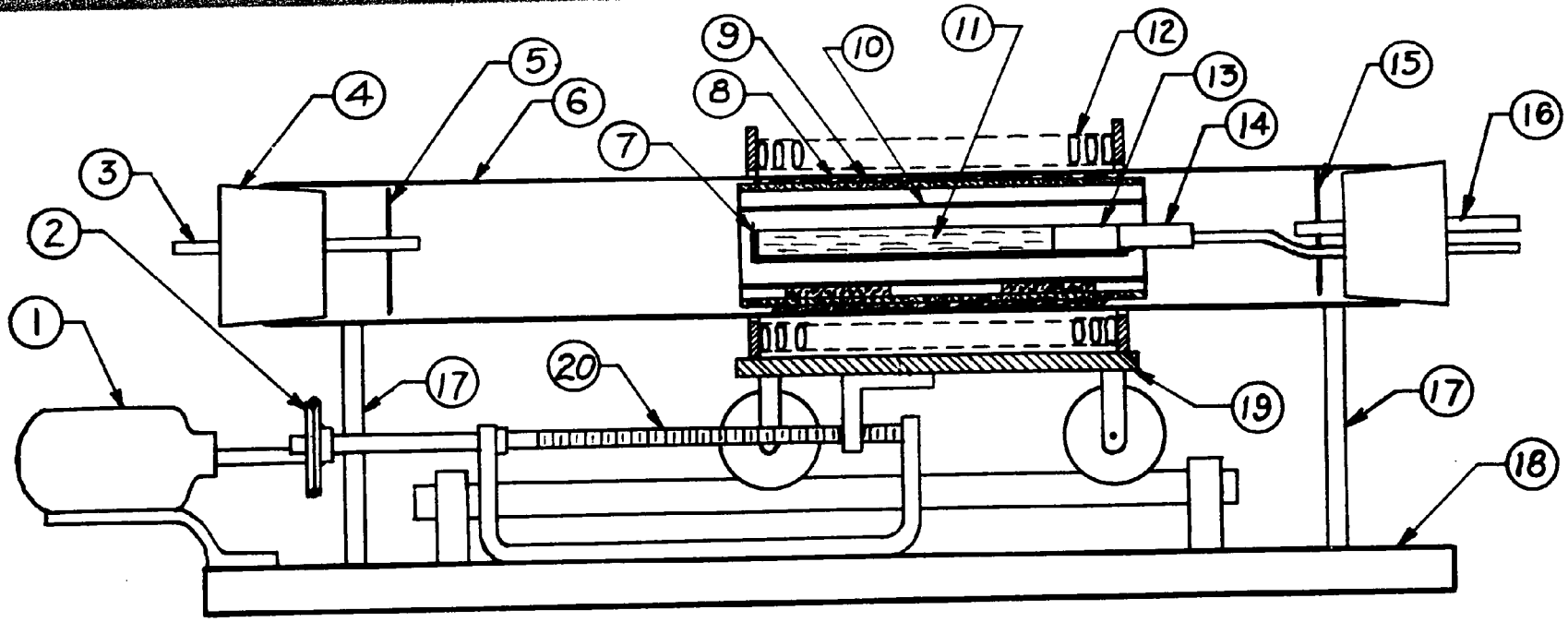


Figure 1 - Detailed Drawing of Chill Block and Boat Used for Growing Copper Single Crystals



KEY TO FIGURE

1. Drive motor
2. Speed-reduction pulley
3. Argon exit
4. Rubber stopper
5. Radiation shield
6. Pyrex glass tube
7. Graphite boat
8. Fiberfrax insulation
9. Ceramic cylinder
10. Graphite cylinder
11. Copper charge
12. Induction coil
13. Seed crystal holder
14. Water-cooled graphite block
15. Radiation shield
16. Argon inlet
17. Pyrex tube supports
18. Baseboard
19. Traveling carriage
20. Drive screw

Figure 2.

Equipment for Producing Copper Single Crystals

saturated with $FeCl_3 \cdot 6 H_2O$. A reagent described by Yukawa (64) was then tried, and the results were excellent. This latter reagent consists of 50% HCl saturated with $FeCl_3 \cdot 6 H_2O$ which has been diluted with an equal volume of 50% HCl. This etchant primarily develops the (100) planes although some (110) planes were in evidence.

After the orientation of the crystal was determined, the crystal was cut into slices approximately 1/8 inch thick, each having the desired orientation. Most samples were cut so that the surface represented the (100) plane. These cuts were made with a very thin resinoid-bonded silicon carbide cut-off wheel such as is used for glass cutting. It was found that a very slow cutting speed was necessary to minimize surface distortion. The samples were then trimmed and rough ground to the approximate final specimen size of 3/4 x 3/8 x 1/8 inch. The specimens were etched in the HCl-$FeCl_3$ solution used for etch pit analysis for a period of 20 minutes. The purpose of the etching was twofold: first, to relieve the strained surface, and second, to form etch pits for orientation analysis. The orientations of the surfaces were then determined on the optical goniometer. If slight errors in the initial cutting were observed, the surfaces were mechanically abraded on 1/0 emery paper to correct errors and to bring the desired crystal plane to within 1.5° of coincidence with the surface. Usually one or two successive cycles of polishing, etching and orientation determination were required to produce the desired sample.

Final specimen preparation consisted of abrasion on 2/0 and 3/0 emery paper followed by chemical polishing. Chemical polishing was found to work very satisfactorily for the high purity copper used in this investigation. Several solutions were tried and the best results were obtained using a solution recommended by Schadler and Burke -- a mixture of 1 part glacial acetic, 1 part phosphoric, and 2 parts nitric acids (67). The samples were suspended in the solution with the surface down, at 80°C. The reaction was very rapid and a time of 2-1/2 to 3-1/2 minutes was sufficient to produce a brightly polished surface. The samples were washed in cold flowing water, rinsed in alcohol, and dried. A photomicrograph of a copper sample which has been chemically-polished is shown in Figure 3.

Kinetic Measurements

Kinetic measurements were made in an apparatus especially designed for handling single crystals of a given orientation. Since ferric chloride is very reactive and attacks almost all metals, it was necessary to construct all parts which were in contact with the solution of non-metallic materials. The apparatus used in this work is shown schematically in Figure 4. Essentially, it consisted of a reaction chamber, a solution reservoir, and a circulating pump. One-quarter inch Tygon tubing was used to connect the various units and was kept as short as possible to

TABLE I

CHEMICAL ANALYSIS OF VACUUM-MELTED COPPER

Arsenic	0.0008	Silicon	0.0025
Antimony	0.0002	Silver	0.0008
Bismuth	0.00006	Tellurium	0.0005
Iron	0.001	Tin	0.0002
Lead	0.0002	Oxygen	Less than 0.001
Nickel	0.0006	Copper	99.99+

Figure 3. Photomicrograph of a Chemically Polished Copper Sample. Unetched; 500X

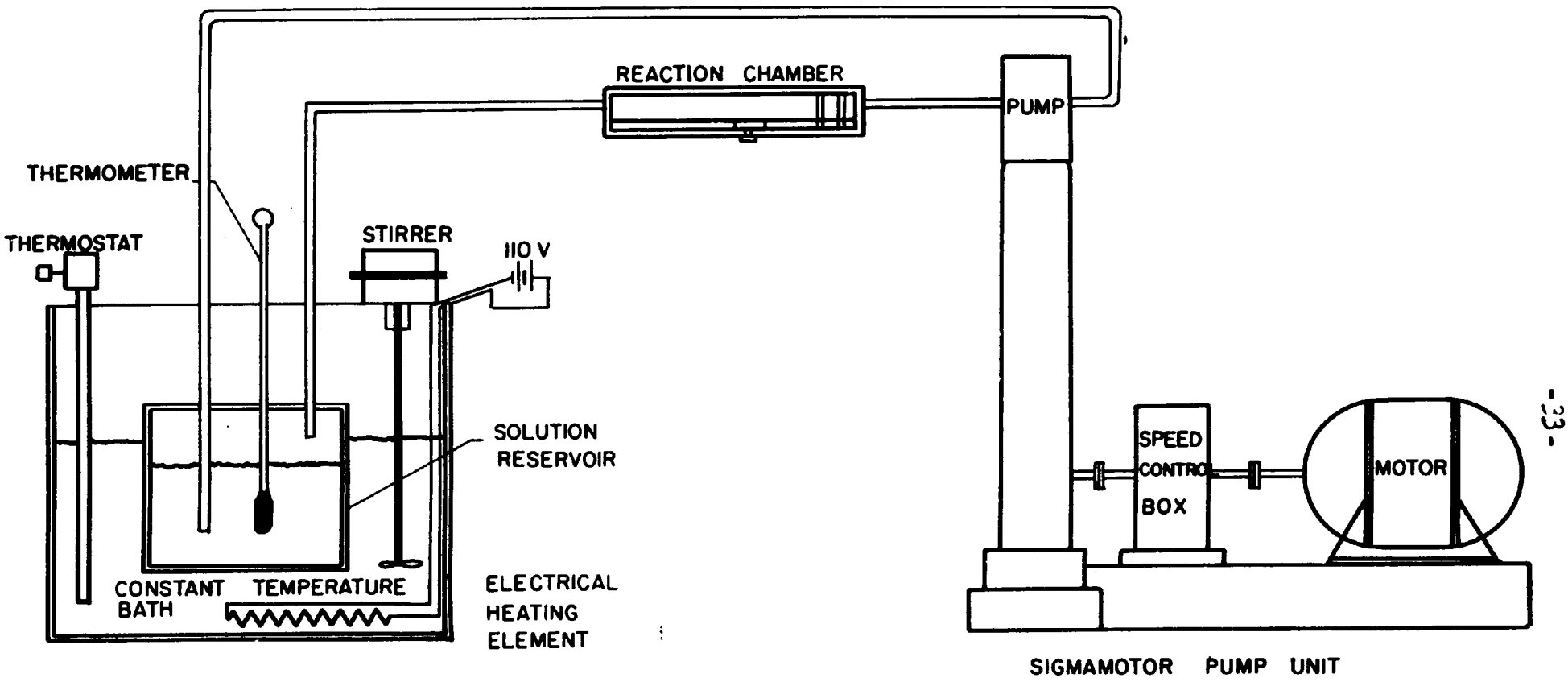
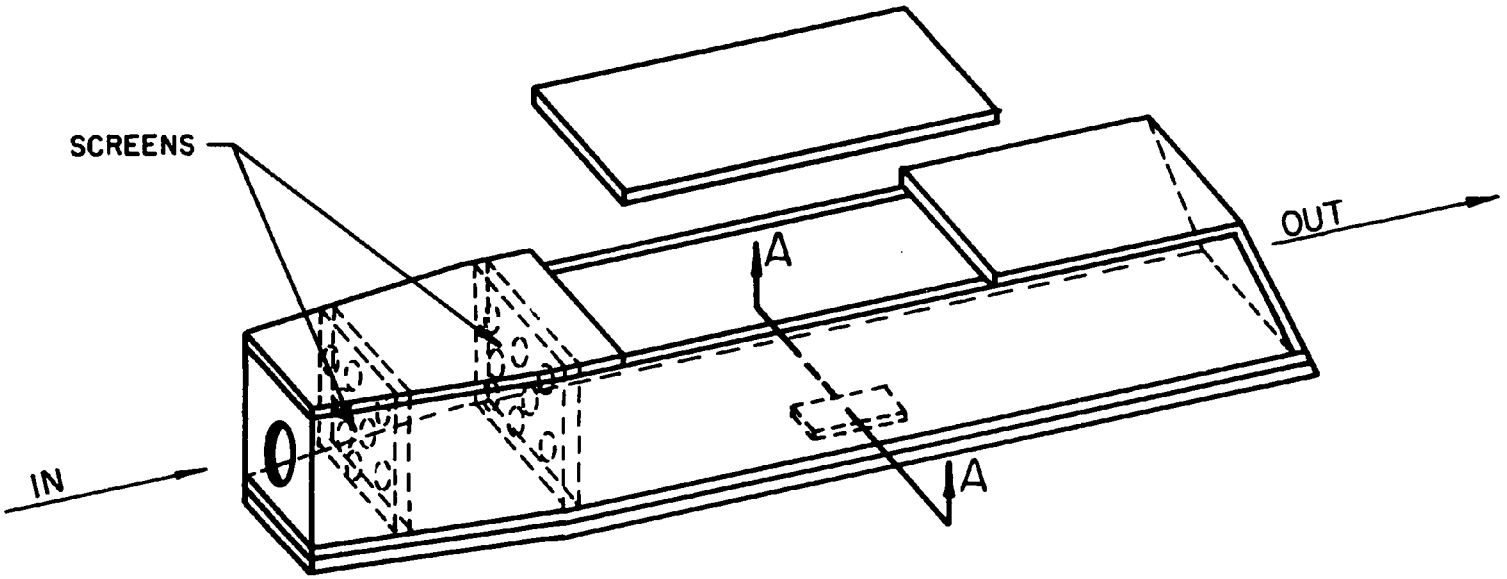


Figure 4 - Schematic Drawing of Experimental Apparatus

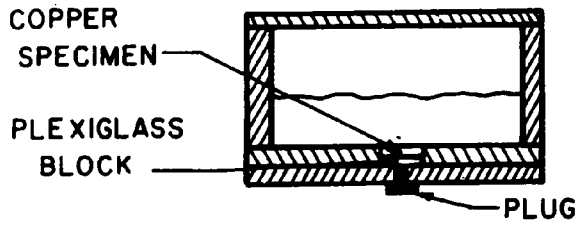
reduce the amount of solution held in the connections. Circulation was provided by means of a Sigma-motor pump. The flow rate of the solution was accurately controlled and could be varied by means of a variable speed torque converter which was attached to the pump. The circulation rate could be varied from 0 to 450 milliliters per minute. The rate which was used in the majority of these experiments was 400 milliliters per minute. This corresponded to a linear velocity in the reaction chamber past the specimen of approximately 900 centimeters per minute.

The reaction cell was constructed entirely of Plexiglas and the details of construction are shown in Figure 5. The inlet opening of the chamber was narrow, and widened as the solution progressed inwards, reaching a constant width portion before the specimen. Two screens of Plexiglas were constructed and placed near the entrance of the cell to distribute the flow of the liquid uniformly past the copper specimen. Calculations showed that turbulent flow conditions existed in the chamber. A slot was carefully milled at the bottom of the chamber and specimens having critical dimensions of length and width were placed into the slot so the surface to be attacked was flush with the bottom of the reaction cell. The height of the specimen was adjusted by placing spacers below the specimen. The slot and specimens were carefully machined so that the specimens fitted into the slot with the slight "press fit" thus prohibiting any reaction occurring on the sides of the specimens. The specimens were 1.712 square centimeters in area. The quantity of reacting solution used in all experiments was 200 milliliters.



MATERIAL: ALL PLEXIGLASS CONSTRUCTION

SCALE : APPROX FULL.



SECTION A-A

Figure 5 - Details of Reaction Chamber

If the test temperature differed from room temperature, the pump was started for a period of approximately five minutes and the solution was allowed to circulate until thermal equilibrium was established. Temperature control was held to within $\pm$ C.25°C. The specimens were then placed into the slot and the test was begun.

Since it was desirable to measure reaction kinetics by a rapid continuous method, a technique measuring the change in electrical conductivity of the solution was first used. The circuit employed was essentially an A.C. Wheatstone Bridge Circuit having a conductivity cell as one leg of the bridge. The alternating current was achieved by means of an audio oscillator generating a frequency of 1000 cycles per second. An amplifier, attached to an electronic null indicator, was used to balance the circuit. Although the equipment which was used was extremely sensitive, the change in electrical conductivity caused by cupric ions going into solution and ferric ions being reduced to ferrous ions was small compared to the high conductivity of the solution. This technique worked very well for dilute concentrations of ferric chloride but was useless at high concentrations. At high ferric chloride concentrations the change in conductivity caused by temperature fluctuations overshadowed the change which resulted from the dissolution reaction. Thus, this technique was discarded and a new technique was adopted. A spectrophotometric technique somewhat modified from that developed by Giesecke was used for the analysis of cupric ions in solution (68).

The analysis makes use of the strong absorption of the colored cupric chloride complex at a wave length of 945 millimicrons. This technique is especially desirable since ferric and ferrous ions do not interfere and the analysis of the reaction mixture can be made directly by a simple procedure. It was found that a wave length of 945 millimicrons had stronger absorption characteristics than the 970 millimicrons used by Giesecke, and this value was used.

Calibration curves of the absorption characteristics of several known concentrations of cupric ions were determined by dissolving known amounts of copper in ferric chloride. In preliminary studies dilutions were made with either distilled water or concentrated hydrochloric acid. Dilutions made with hydrochloric acid were found to work more satisfactorily; therefore this method was used in all analysis. A 3 ml sample was periodically removed from the solution with a pipette, diluted to 10 ml in a volumetric flask, and analyzed in a Beckman Model Du Spectrophotometer. A solution of concentrated hydrochloric acid was used as reference. Samples were removed every 10 minutes for the first 30 minutes and then every 30 minutes for the next hour. Most tests lasted 90 minutes.

Repeated dissolution studies of copper samples under identical conditions of temperature, agitation, and composition of the bath revealed that the results are accurate to $\pm$ 2%.

Electron Diffraction Studies

When copper is placed in a solution of ferric chloride it is possible to observe the continual formation and dissolution of a film. It was felt that a study of the nature of the film would be of importance in this investigation. Samples of copper were rapidly removed from the ferric chloride solution, washed with distilled water, triply distilled acetone, ether, and then allowed to dry. An electron diffraction pattern was made immediately thereafter on the surface of the specimen using a RCA Type EMD-2 electron diffraction apparatus. It was observed optically that the physical characteristics of the film changed during exposure to the atmosphere. Thus samples were placed in a desiccator after etching and allowed to stand for periods of 12 hours, 4 days, and 10 days before electron diffraction patterns were taken of the resulting films. Another sample was rapidly removed from the ferric chloride and immediately placed in triply distilled acetone. A layer of ferric chloride solution remained on the surface during the second the sample was transferred from the ferric chloride solution to the acetone. Thus, this sample was not exposed to air or water during the period prior to taking the diffraction photograph.

EXPERIMENTAL RESULTS AND DISCUSSION

Kinetic Studies

The rates of dissolution of copper in ferric chloride were measured as a function of time, ferric chloride concentration, flow rate of the solution past the copper, temperature, crystallographic orientation of the crystal, chloride ion concentration, ferric ion concentration, ferrous ion concentration, cupric ion concentration, dissolved oxygen concentration, and hydrogen ion concentration in order to determine the reaction mechanism.

Dissolution of Copper in a 0.25 Molar Ferric Chloride Solution

A typical curve of the total amount of copper which has dissolved in a 0.25 M. ferric chloride solution as plotted against the time of reaction is shown in Figure 6. (The data obtained from this study and all other kinetic studies are tabulated in Appendix A.) The data are typical of first order reactions obtained in diffusion-controlled reactions and show that as the reaction progresses the concentration of reacting ion decreases causing the rate, or slope of the curve, to gradually decrease. If the test were conducted to completion, the rate would gradually approach zero.

When the data are replotted as first order rates in

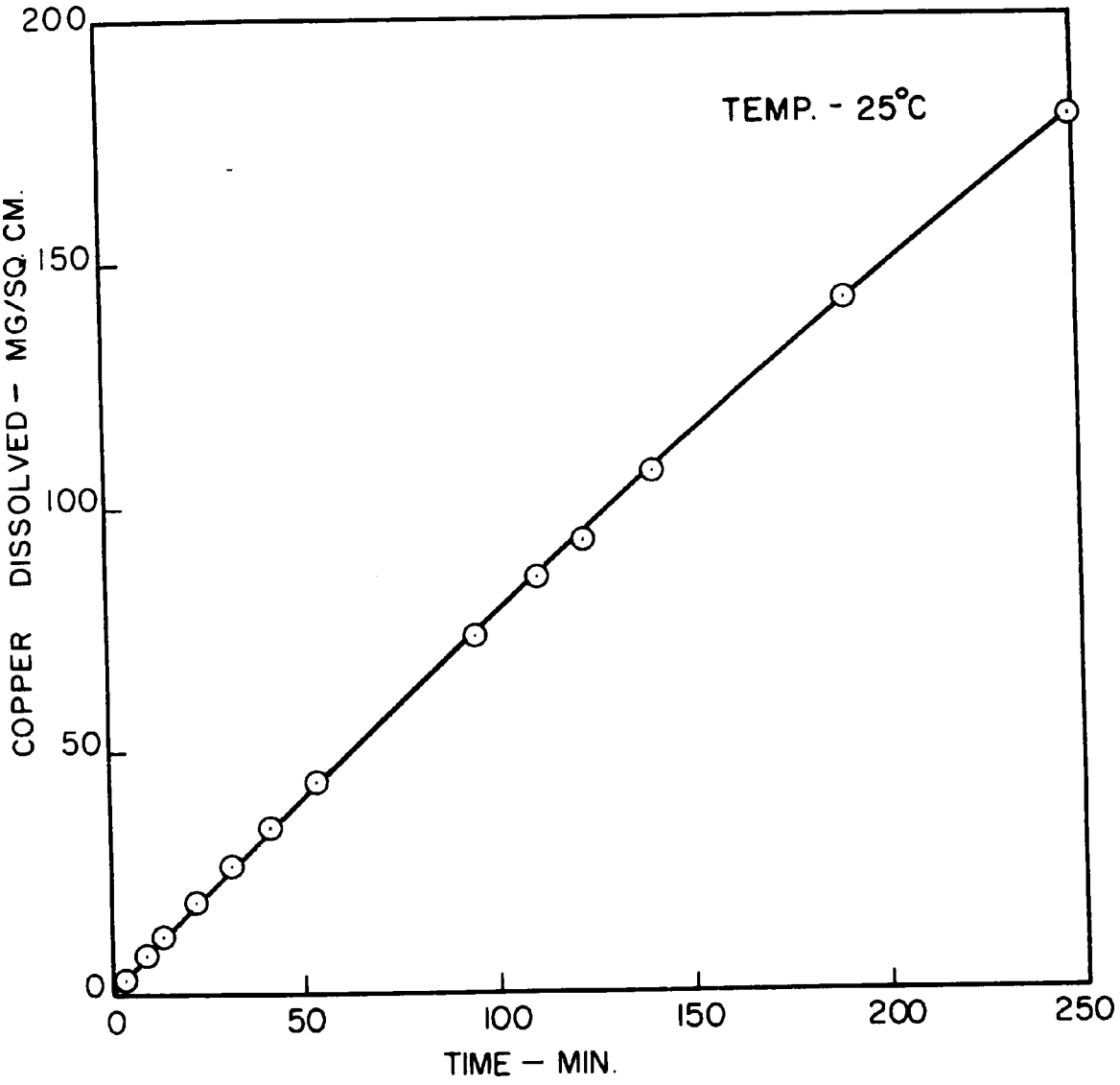


Figure 6 - Dissolution of Copper in a 0.25 Molar Ferric Chloride Solution

accordance with Equation (2) which was derived in a previous section,

$$K = \frac{2.3\ V}{A\ t} \log \frac{a}{a - x}$$

all points fall on a straight line as shown in Figure 7. This proves that the reaction is first order. A value of the first order reaction constant, K, can be obtained from the slope of the line. However, in this investigation it was not considered necessary to plot the data as shown in Figure 7 since a pseudo-zero-order specific rate constant could be obtained from the initial slope of Figure 6. Since the reactant was high in ferric ions and these ions were depleted very slowly during the reaction, the ferric ion concentration did not significantly change during the 90 minute experiment. Thus, the rate constants were taken as the slope of curves similar to Figure 6, plotted over the first 90 minutes of reaction.

Dissolution Rate Versus Ferric Chloride Concentration

The rates of dissolution of copper in various concentrations of ferric chloride were studied for concentrations varying from 0.1 molar to 3.0 molar. Rates are given in units of milligrams per minute per square centimeter of surface area which correspond to those of a pseudo-zero-order specific rate constant. When these rates are plotted against the total ferric chloride concentration, the points of Figure 8 are obtained.

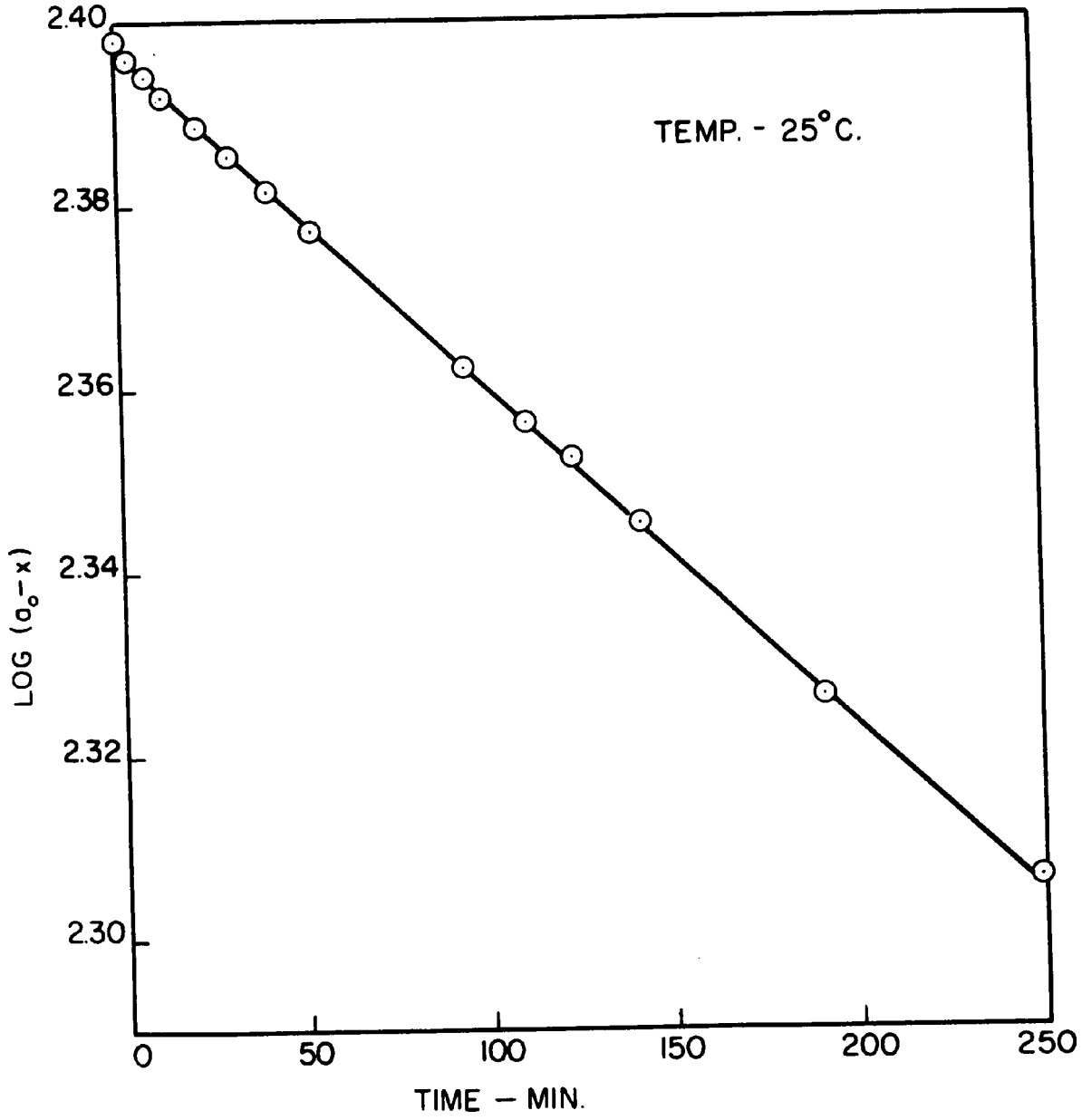


Figure 7 - Dissolution of Copper in a 0.25 Molar Ferric Chloride Solution (Plotted According to First Order Rate Equation.)

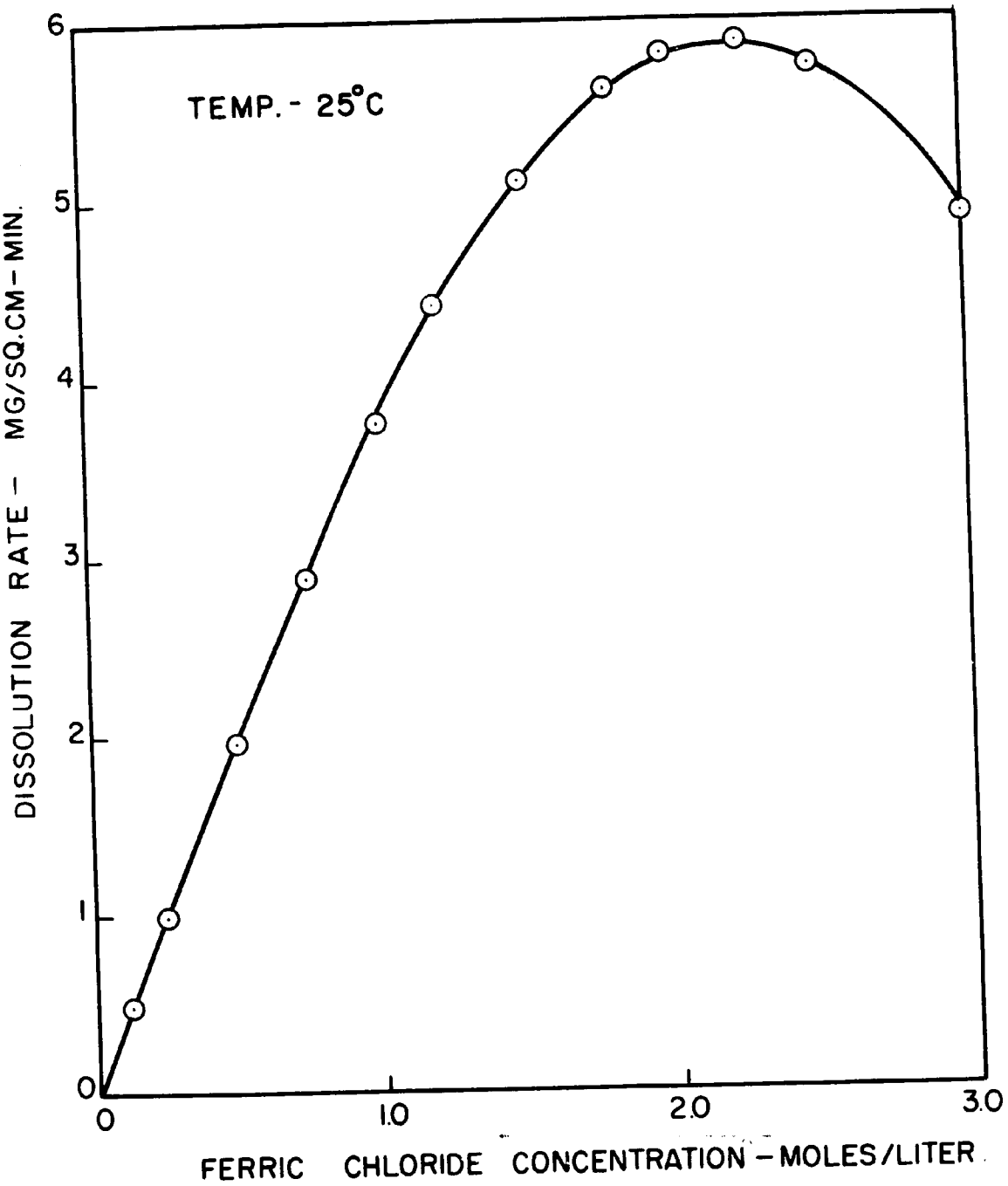


Figure 8 - Dissolution Rate Versus
Ferric Chloride Concentration

Inspection of Figure 8 shows that the rate is approximately first order with respect to the ferric chloride solution up to a concentration of approximately 1.0 molar. At higher concentrations the rate increases more slowly with increasing concentration, reaching a maximum in the vicinity of 2.2 molar and then drops rather sharply.

The initial linearity as obtained up to 1.0 molar concentration is expected since in diffusion-controlled reactions the rate of diffusion, and subsequently the rate of dissolution, is directly proportional to the concentration of reactant. The deviation from linearity after 1.0 molar and the subsequent decrease in rate which occurs were initially interpreted to mean that either the mechanism of the reaction changes or that the reacting species is reduced by complex ion formation. If the mechanism of the reaction were to change, it would be expected that the energy of activation would be different at two widely separated concentrations. However, work reported a little later clearly indicates that the mechanism must be the same at different concentrations since the energies of activation are quite similar. Thus, the explanation must involve complex ion formation. The inhibiting effect of ferric chloride which occurs at high ferric chloride concentrations may be explained by the reduction in the oxidation potential of the ferric ion through complexing with the chloride ion to the point where the potential is not sufficient to oxidize the copper. The nonreacting ferric chloride reduces the total quantity of ferric ions which are available to oxidize the copper.

Dissolution Rate Versus Flow Rate

The effect of flow rate of the etchant past the copper surface was determined for a series of ferric chloride concentrations varying from 0.25 to 3.0 molar. In all cases the rate of dissolution was directly proportional to the linear flow rate as shown in Figure 9. The data obtained under conditions of a still bath did not always correspond to the values obtained when the curves were extrapolated to zero flow rate. The still bath values were often higher; however, it is to be expected that some discrepancies would exist since the factor now involved is mostly diffusion and convective movement of the solution is no longer important.

The above data which are tabulated in Appendix A can be replotted at constant flow rate, with the ferric chloride concentration as a variable. A series of curves similar in appearance to Figure 8 are obtained and they are shown in Figure 10. These data show that the inhibiting effect which occurs at high ferric chloride concentration is present regardless of the flow rate.

The direct proportionality of the reaction rate with the flow rate again lends support to the theory that the reaction is diffusion-controlled.

Dissolution Rate Versus Temperature

The rate of dissolution of copper as a function of temperature was measured at 0.25, 1.0, 2.0, and 3.0 molar concentrations. Data were obtained for a temperature range from

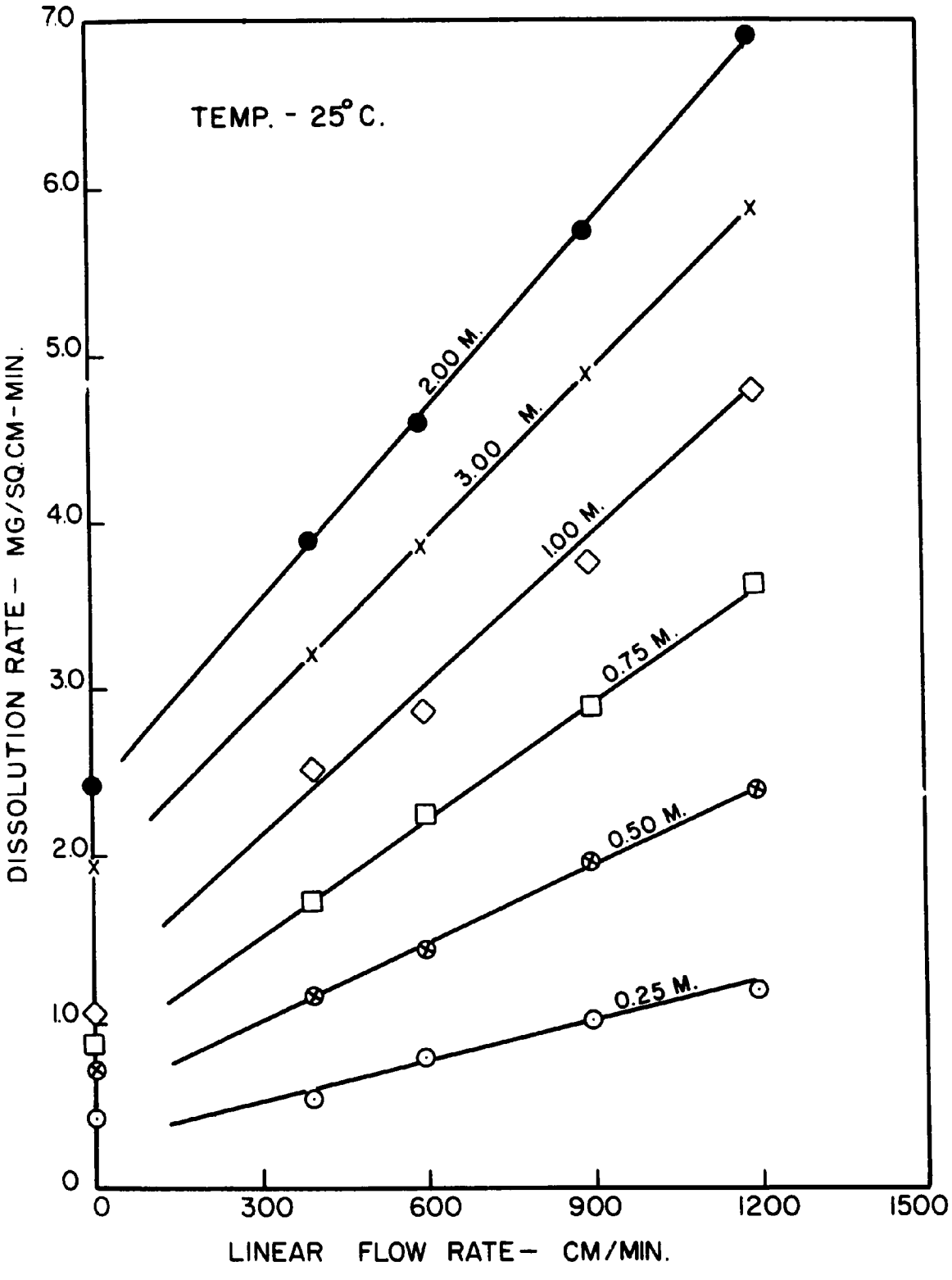


Figure 9 - Dissolution Rate Versus Solution Flow Rate

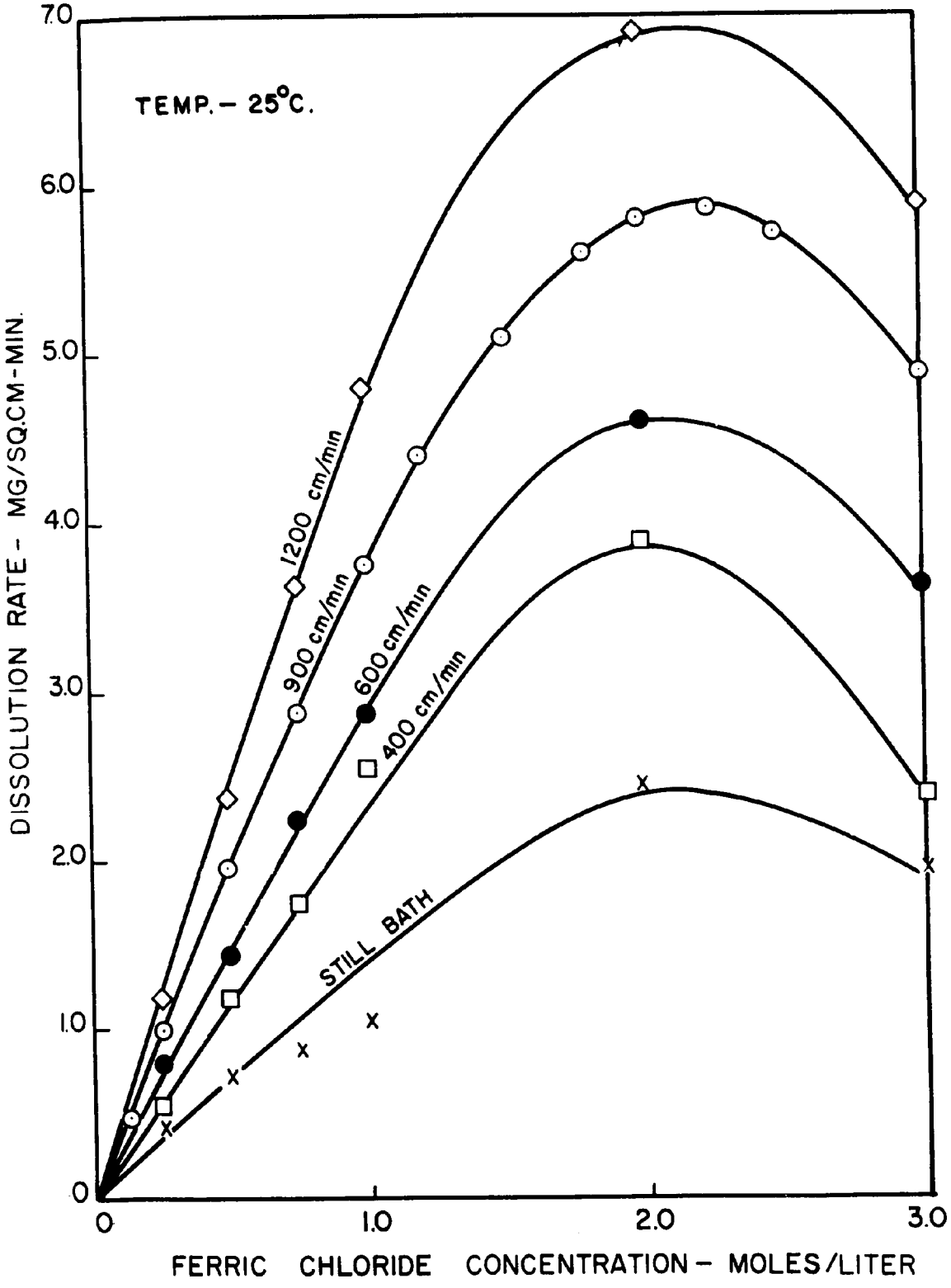


Figure 10 - Dissolution Rate Versus Ferric Chloride Concentration at Various Solution Flow Rates

5° to 50°C. The data are plotted in Figure 11 as log rate vs. 1/T, according to the Arrhenius equation:

$$K = A\, e^{-E/RT}$$

From the slope of the above plot, the activation energies for the reaction at the various concentrations were obtained. These values are given in Table II.

All values of activation energy are quite similar in magnitude, suggesting a similar mechanism is operative over these concentration ranges. The values of activation energy appear to decrease slightly with concentrations having a greater dissolution rate. Thus, the 0.25 molar concentration has the lowest dissolution rate but the greatest activation energy of the solutions tested. The values of activation energies clearly indicate that the process is controlled by diffusion of the reactants. King's criterion is that a value of 5,000 calories per mole is typical for diffusion-controlled reactions (69).

TABLE II

ACTIVATION ENERGIES FOR THE DISSOLUTION OF COPPER IN FERRIC CHLORIDE

Concentration (Moles/Liter)	Activation Energy (Calories/Mole)
0.25	4,950
1.00	4,300
2.00	4,050
3.00	4,250

It can be noted from Figure 11 that at temperatures below 7°C. there occurs a marked increase in the temperature

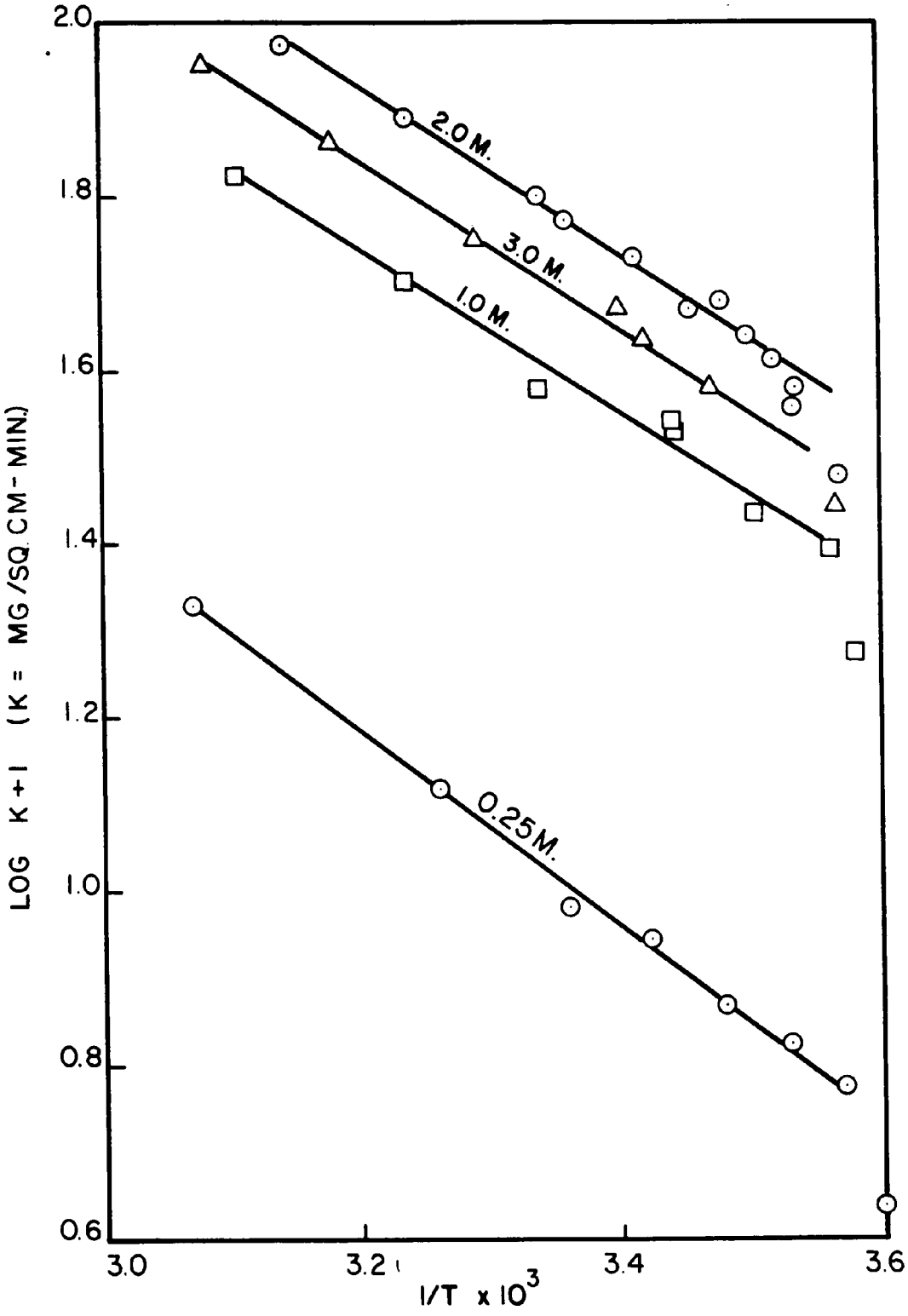


Figure 11 - Arrhenius Plot of Log Reaction Rate Versus Reciprocal of the Absolute Temperature

coefficients, suggesting that another mechanism is controlling the reaction in this range.

Dissolution Rate Versus Crystallographic Orientation

The temperature dependence of the etching rate of copper in ferric chloride was measured for three different crystallographic orientations. Data were obtained for 0.25 molar and 1.00 molar concentrations. At temperatures above approximately 7°C. all crystal faces dissolved at the same rate. However, at lower temperatures the three crystal faces dissolved at different rates. Data are plotted in Figure 12 as log rate vs. 1/T, and it can be seen that they do not lie on a single straight line. The data in the two series of curves have several interesting features. The rather abrupt change in slope which occurs around 7°C., and the apparent parallelism of the curves for different faces are particularly interesting. Unfortunately, this transition occurs at low temperatures so close to the freezing temperature of the liquid that it was impossible to obtain many data. From the limited data, activation energies for the various faces were computed. The values are given in Table III and are approximately the same for the various crystallographic faces. The differences which exist in Table III

TABLE III

ACTIVATION ENERGIES FOR THE DISSOLUTION OF COPPER IN FERRIC CHLORIDE AT TEMPERATURES BELOW 5°C.

Face	0.25 Molar $FeCl_3$	1.00 Molar $FeCl_3$
(100)	16,000	17,000
(110)	15,500	16,000
(111)	15,000	17,000

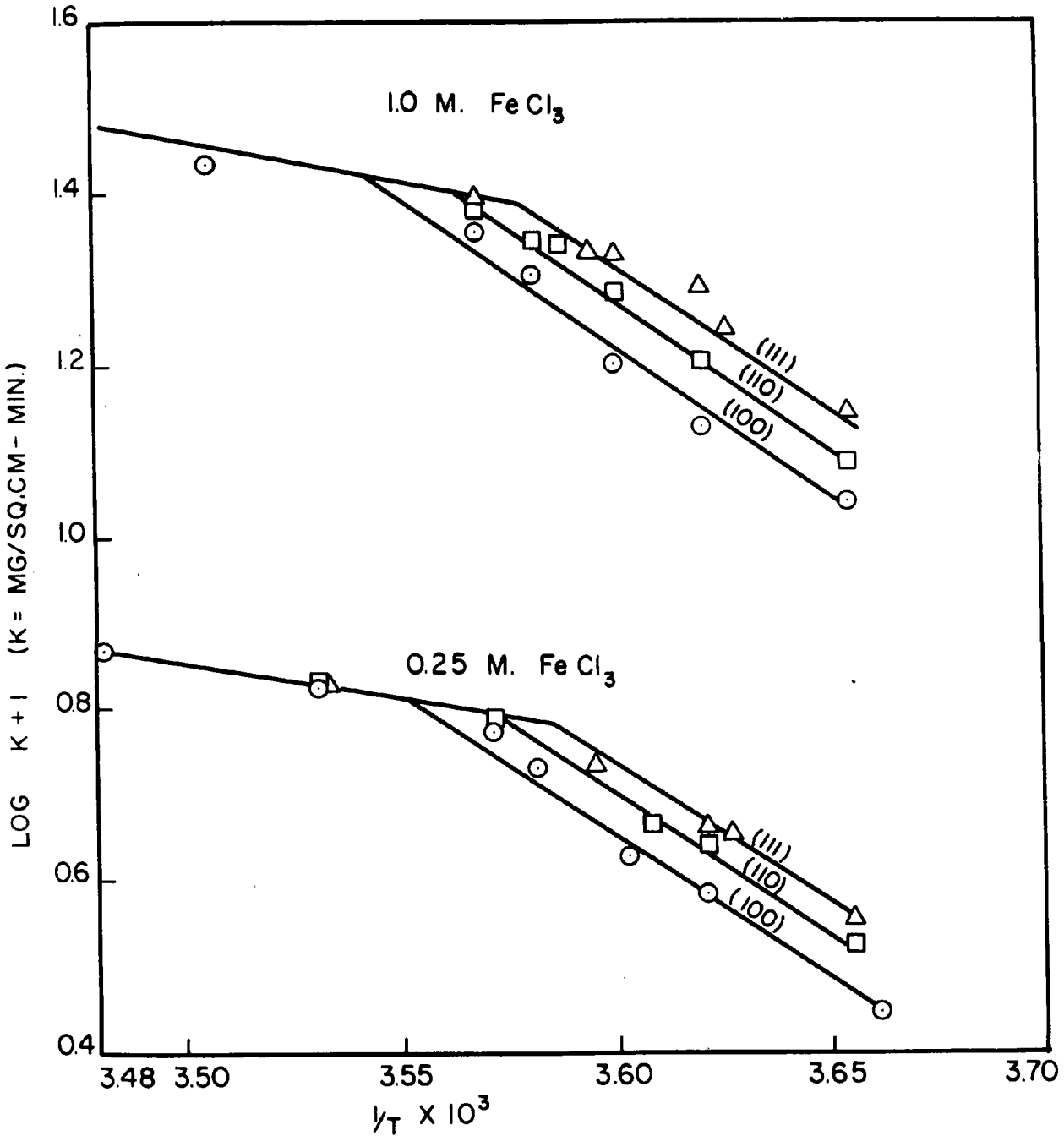


Figure 12 - Arrhenius Plot of Log of Reaction Rate Versus the Reciprocal of Absolute Temperature For Different Crystallographic Orientations

between different orientations are not believed to be significant. Only the magnitude of these values is of importance. These values of activation energies are somewhat lower than the value of approximately 30,000 calories per mole which is usually obtained in chemically-controlled reactions.

There is, however, much valuable information which can be obtained from these data. First, it is apparent that the (100) plane is the most stable of the three orientations studied. Secondly, the (111) plane is the most reactive. The dissolution rates of the different planes can be presented as definite ratios. These ratios which are valid for both the 0.25 molar and 1.00 molar concentrations are as follows:

(111)/(110)/(100) : : 1.00/0.88/0.80

Thus, there is approximately a 20% difference in rates between the slowest etching plane (100) and the (111).

It is apparent that at temperatures above 7°C., a diffusion mechanism is operative, and at temperatures below 5°C., a chemically-controlled mechanism is operative. At temperatures between these two regions, a transition zone occurs. It is conceivable, however, that the region below 5°C. is not totally a chemically-controlled region but a composite of chemical and diffusion-controlled mechanisms.

The variation of diffusion rates with temperature can be equated by the following well-known logarithmic expression:

$$D = D_o \, e^{-E_d/RT}$$

where E_d is the activation energy for the diffusion process.

The variation in chemical reaction rate can also be equated to temperature by a comparable expression:

$$K = A\ e^{-E_c/RT}$$

where E_c is the activation energy for the chemical reaction. Since E_c is greater than E_d, the rate of chemical reaction varies more rapidly with temperature than the rate of diffusion, thus, it is expected that a diffusion-controlled mechanism would be operative at high temperatures whereas a chemically-controlled mechanism would be operative at low temperatures.

Dissolution Rate Versus
Chloride Ion Concentration

A series of experiments was performed in which the ferric ion concentration was kept constant at 0.25 molar concentration and the chloride concentration was varied by mixing solutions of ferric chloride and ferric nitrate in the proper proportions. Potassium chloride was added to 0.25 molar solutions of ferric chloride in a few runs to obtain chloride concentrations greater than 0.75 molar. The results are shown in Figure 13. The rate of dissolution increases with chloride ion concentration up to 1.5 molar concentration, reaching a plateau whereby further increases in chloride ions result in no further increase in etching rate.

The results may be interpreted as either indicating that the chloride ions are directly of importance in the reaction or that the chloride ions increase the quantity of reactive ferric

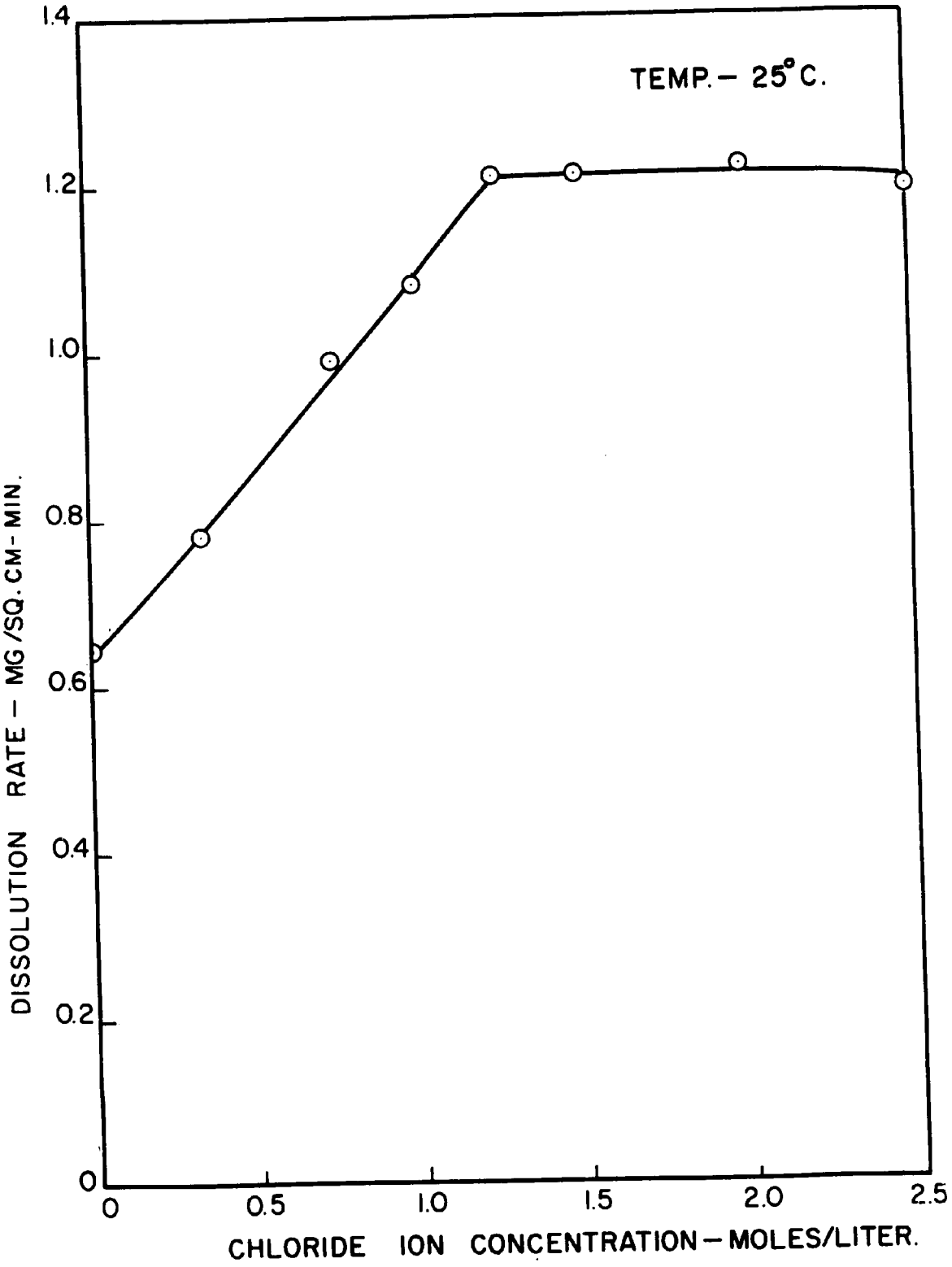


Figure 13 - Dissolution Rate Versus Chloride Ion Concentration (0.25 M. Ferric Ion Concentration)

or ferric-chloro ions by complex ion formation. Further, the data indicate that after a certain amount of chloride ions are added to the solution, the addition of more chloride ions does not either increase or decrease the rate. These results are in partial agreement with those obtained by King and Weidenhammer who also observed a plateau when chloride ions were added to 0.015 M. ferric solutions (50). These authors claimed that the rate first decreased and then increased with chloride ions; however, it is believed that the decrease which they attributed on the basis of only one data point was probably due to experimental error.

Another interesting observation was noted at the point where further increases in chloride ion concentration do not affect the rate. It was noticed that the film which exists on the copper surface during the reaction disappeared entirely in the vicinity of the plateau.

Dissolution Rate Versus Ferric Ion Concentration

The dissolution of copper in other solutions containing ferric ions was studied to obtain the rate due to the ferric ion alone. It has been demonstrated from the change in color of ferric nitrate solutions on adding nitric acid that these ions do not form complexes (70). Salzberg and King concluded from their studies of the dissolution of silver in ferric sulfate that ferric sulfate solutions do form complexes in solution (11). Hence, the rates of dissolution of copper were studied

in ferric nitrate and ferric sulfate solutions in various concentrations up to 1 molar to determine ferric ion effects. The results are shown in Figure 14. Also shown, for comparative reasons, are the ferric chloride data. The dissolution rates in ferric nitrate and ferric sulfate solutions are comparable at low concentrations and have values which are approximately 33% slower than those obtained with ferric chloride solutions. At concentrations above 0.50 molar, the ferric-sulfate complexes which form must in this case inhibit the reaction.

Another test which was performed consisted of adding varying amounts of ferric nitrate to a 0.25 molar ferric chloride solution. The results in Figure 15 show that the rate does not increase as rapidly as with ferric chloride but increases at the same rate as the ferric nitrate in Figure 14. The rate of dissolution of copper in ferric nitrate is due entirely to the ferric ions. Thus, it appears that the rate of dissolution of copper in ferric chloride is a function of both the ferric ions and the chloride ions or that the rate is a function of the ferric ions which in turn is a function of the chloride ions.

$$\text{Rate} = f(Fe^{+3}) + g(Cl^{-})$$

$$\text{or Rate} = f(Fe^{+3}) \quad \text{where} \quad (Fe^{+3}) = g(Cl^{-})$$

Another test which was performed consisted of adding varying amounts of sodium nitrate to ferric nitrate to determine the effect of nitrate ions on the dissolution rate. Results showed that the addition of sodium nitrate had no effect on the

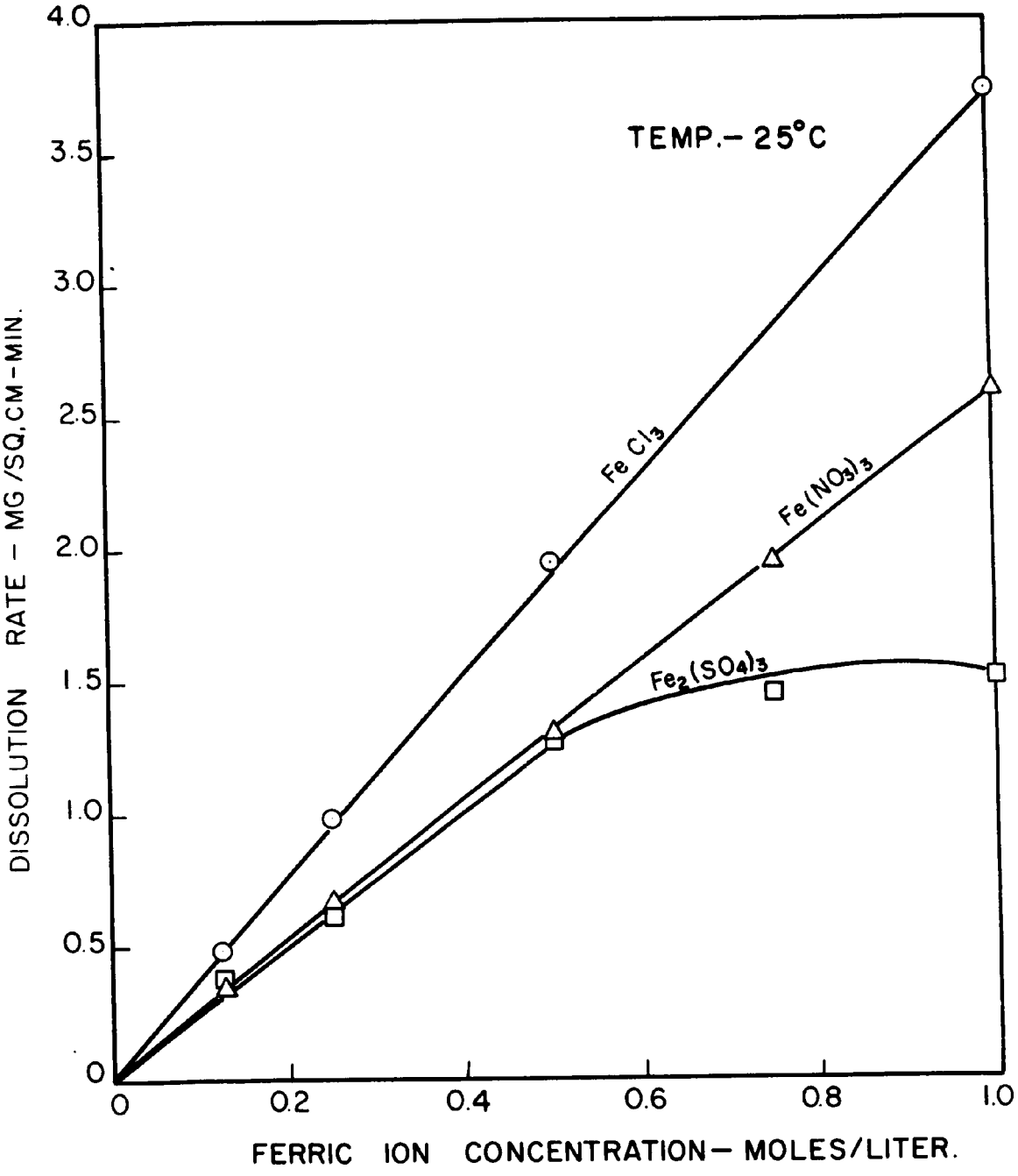


Figure 14 - Dissolution Rate Versus Ferric Ion Concentration

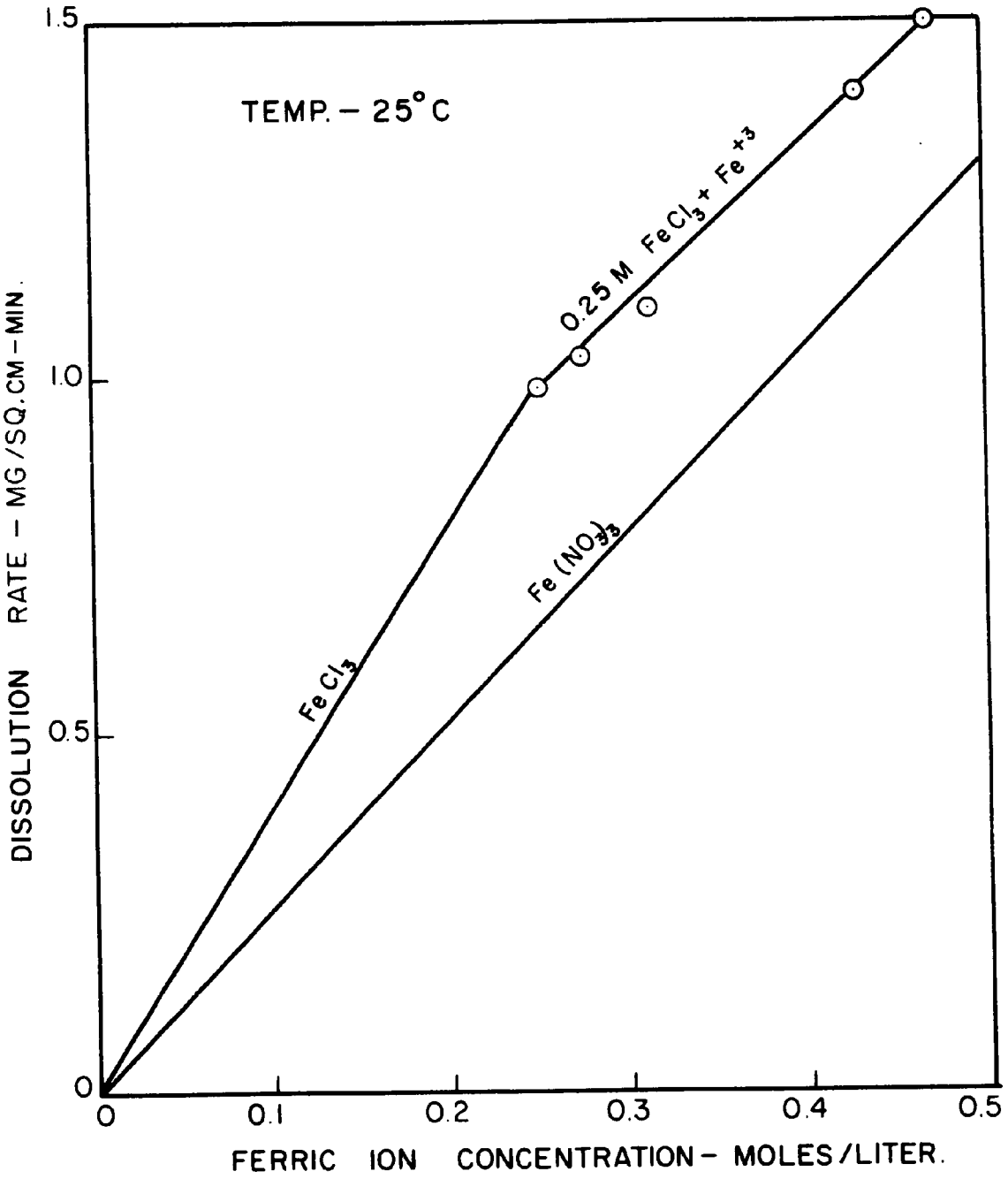


Figure 15 - Dissolution Rate In A 0.25 Molar Ferric Chloride Solution Versus Varying Amounts of Ferric Ions

dissolution rate. (Appendix A) These results were expected since it was known that ferric nitrate does not form complexes in solution.

Other tests were performed to determine the effect of sulfate ions on the dissolution of copper in ferric sulfate. Various concentrations of sodium sulfate were added to a 0.25 molar ferric sulfate solution. Results showed that the addition of sodium sulfate up to 0.5 molar concentrations had no effect on the rate.

From the above data, it is apparent that chloride ions are instrumental in increasing the dissolution rates of ferric ions whereas nitrate and sulfate ions have no effect.

Dissolution Rate Versus Cupric and Ferrous Ion Concentrations

The effect of dissolved cupric and ferrous ions on the rate of dissolution was studied. Cupric nitrate or ferrous nitrate was added in varying amounts to a 0.25 molar ferric chloride solution. The results, given in Appendix A, show there is a definite decrease in dissolution with increasing cupric or ferrous ions. The cupric ions appear to decrease the rate much more than the ferrous ions. It was suspected that the decrease was due to complexing with the chloride ions, thus an experiment was performed whereby cuprous and ferrous ions were added to ferric nitrate, and when the results showed practically no change in rate it supported this conclusion.

Dissolution Rate Versus Dissolved Oxygen Concentration

Since oxygen is quite often a very important species in the dissolution of metals in aqueous solutions, it was necessary to study the effect of oxygen on the dissolution rate. Various known mixtures of oxygen and nitrogen were bubbled into a 0.25 molar ferric chloride solution to determine if oxygen had an effect on the rate of dissolution of copper. The concentration of dissolved oxygen in the solution was considered from Henry's Law to be equal to the fractional pressure of oxygen in the gas mixture times the solubility of pure oxygen at the prevailing temperature of 25°C. The results, Appendix A, showed that the dissolution rate was independent of the dissolved oxygen concentration in the solution.

Dissolution Rate Versus Hydrogen Ion Concentration

Various concentrations of hydrogen ions were added in the form of nitric acid to a 0.25 molar ferric chloride solution. The results, Appendix A, show that the reaction is entirely independent of the hydrogen ion concentration up to a concentration of 1.00 molar. However, when hydrochloric acid was added to the solution, the rate increased - this increase was due to the chloride ions and not the hydrogen ions.

Low Temperature Dissolution Rate Versus Chloride Ion Concentration

The rate of dissolution of copper in ferric chloride was studied as a function of chloride ion concentration at 0°C.,

i.e., in the region where the reaction is believed to be chemically-controlled, to ascertain if any differences existed from those of the diffusion-controlled region. Various concentrations of chloride ions were prepared by mixing solutions of ferric chloride and ferric nitrate in the proper proportions. Potassium chloride was added to 0.25 molar solutions of ferric chloride in a few runs to obtain chloride concentration greater than 0.75 molar. The results are shown in Figure 16.

Again, the dissolution rate increases with increasing chloride concentration reaching a plateau; however, the increase deviates from linearity to a greater extent. This deviation is often found in reactions which are chemically-controlled. Thus, it appears that the reaction changed from one which was controlled by the diffusion of chloride ions to one which is controlled by the chemical reaction involving chloride ions.

Low Temperature Dissolution Rate Versus Ferric Chloride Concentration

The rate of dissolution of copper in various concentrations of ferric chloride was also studied in the chemically-controlled region. The tests were again conducted at 2°C. The results which are shown in Figure 17 are similar to those obtained in the diffusion-controlled region.

Dissolution Rate of Iron in Ferric Solutions

The rate of dissolution of another metal, pure iron, was determined as a function of ferric chloride concentration and

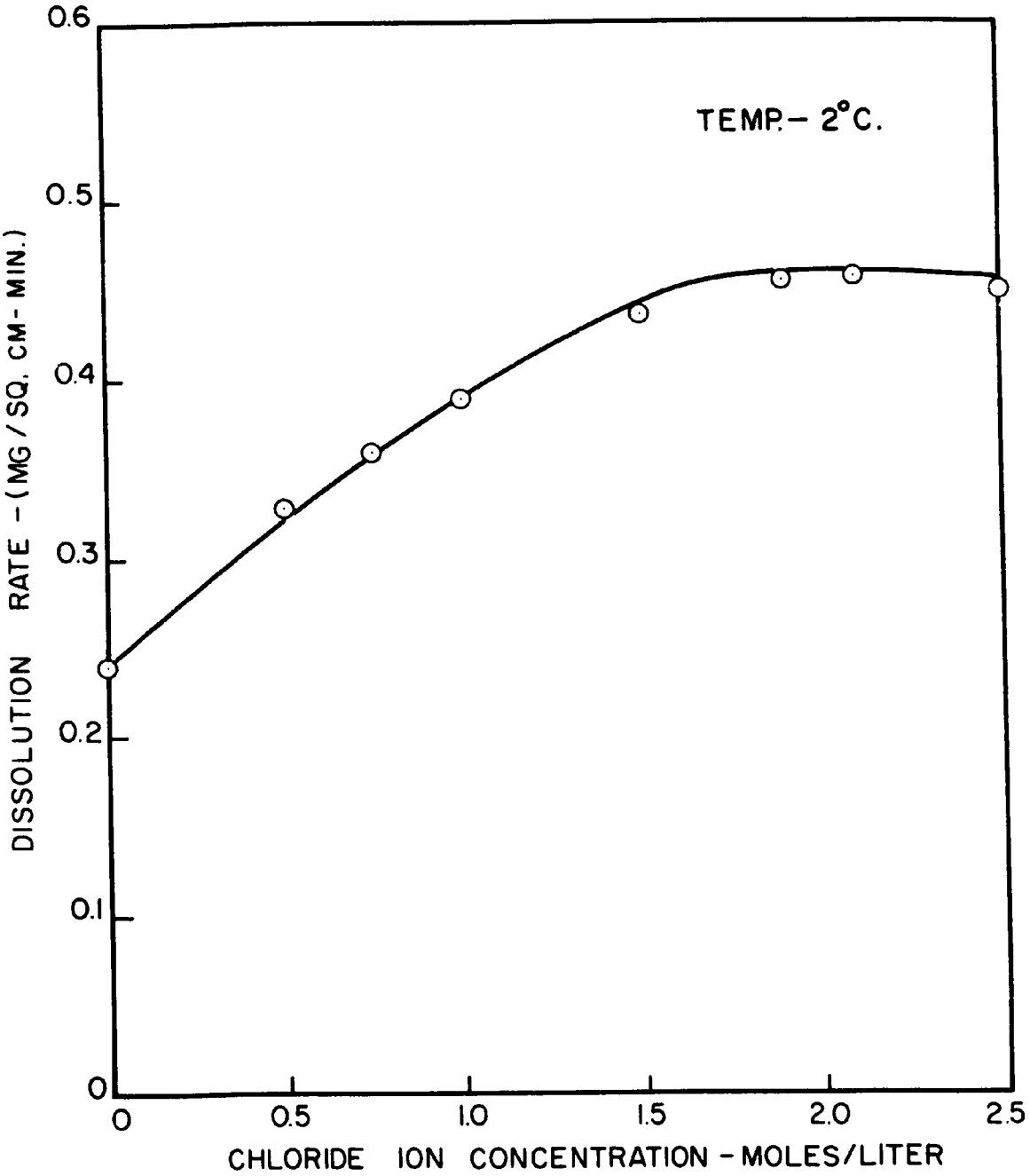


Figure 16 - Low Temperature Dissolution Rate Versus Chloride Ion Concentration (0.25 M. Ferric Ion Concentration)

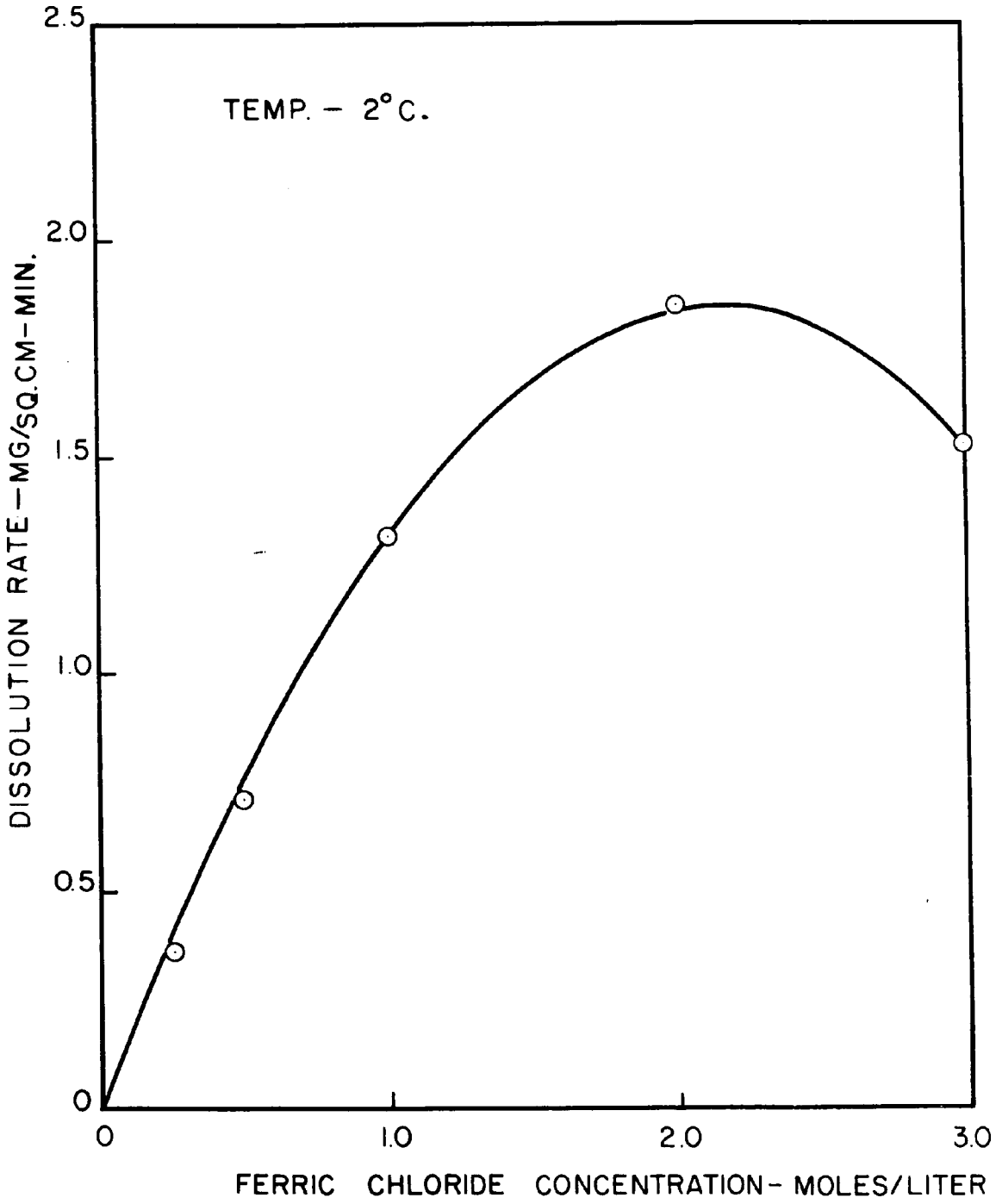


Figure 17 - Low Temperature Dissolution Rate Versus Ferric Chloride Concentration

as a function of ferric nitrate concentration. The dissolution rates were determined at 0.25, 0.50, and 1.00 molar concentrations. The rates increased linearly with concentration and were equal in magnitude in each solution. Thus, it appears that the addition of chloride ions to ferric ions does not increase the dissolution rate of iron as is the case with copper. The dissolution rate of iron in ferric solutions is approximately equal in magnitude to the dissolution rate of copper in ferric nitrate.

Dissolution Rate as a Function of Surface Finish

The rate of dissolution of copper in ferric chloride was studied as a function of surface finish at 25°C. and at 2°C. to determine if any discernible differences occurred in these two different regions. Only four different surface finishes were compared - a rough ground sample, a sample polished on 1/0 metallographic paper, a metallographically polished sample, and a chemically polished sample. The concentration of ferric chloride used in these experiments was 0.25 molar. The results are plotted as rate vs. time in Figure 18. It can be seen from this that even at 25°C., a diffusion-controlled region, that there is a slight difference in the initial corrosion rates of the more roughly-finished samples as compared to the rate after the cold-worked surface has been dissolved. These results are contrary to the popular concept that the dissolution rate is unaffected by surface finish in diffusion-controlled reactions. However, this can be explained by the fact that the cold-worked samples

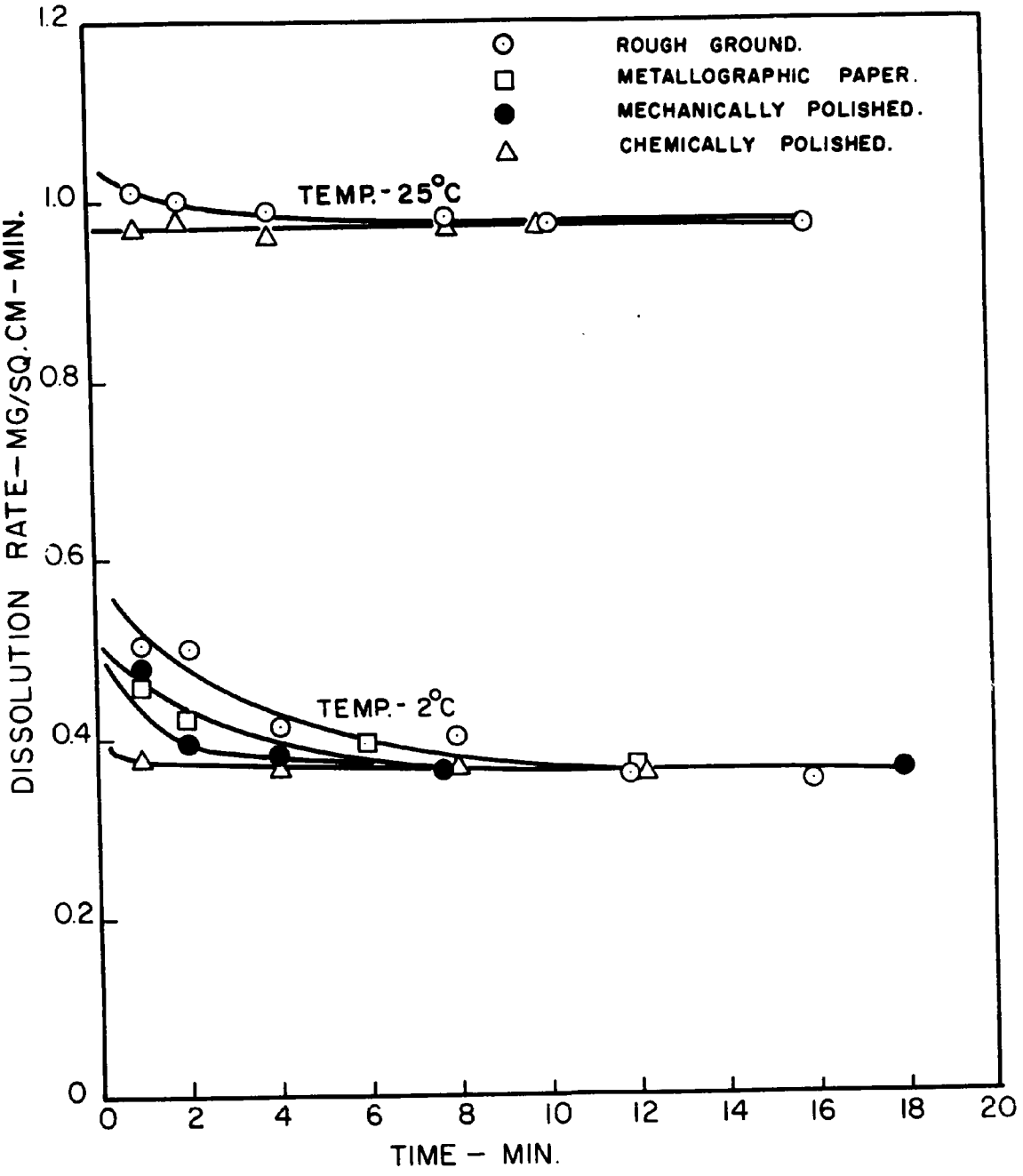


Figure 18 - Dissolution Rate Versus Surface Finish

have more small particles or crystallites on the surface, thus they probably have a larger exposed surface area. The curves at the low temperature regions illustrate the importance of surface finish on the initial dissolution rate. Thus, it is especially important when dealing with chemically-controlled reactions to carefully control surface conditions.

Electron Diffraction Studies

The characteristics of the thin film which exists on the copper during dissolution with ferric chloride were studied with an electron diffraction unit. Figure 19 is an electron diffraction pattern of a sample which was rapidly removed from the ferric chloride solution, washed with distilled water, washed with triply-distilled acetone, and allowed to dry in air. Analysis of the diffraction pattern shows that the film consisted of a mixture of cuprous chloride and cuprous oxide. Figures 20 and 21 are patterns of samples which were removed from the etching solution and allowed to stand in a desiccator for periods of 12 hours, and 4 days, respectively, before the pattern was taken. It was impossible to obtain sharp lines for a sample which was allowed to stand for 10 days. The film which exists when the copper is immediately removed from the etching solution had a pinkish-white appearance. The color darkened on standing in air and was dark grey in 4 days and very black after 10 days.



Fig. 19. Electron Diffraction Pattern of Film on Copper Surface. (Pattern taken immediately after sample was removed from $FeCl_3$, washed in water and washed in acetone.)

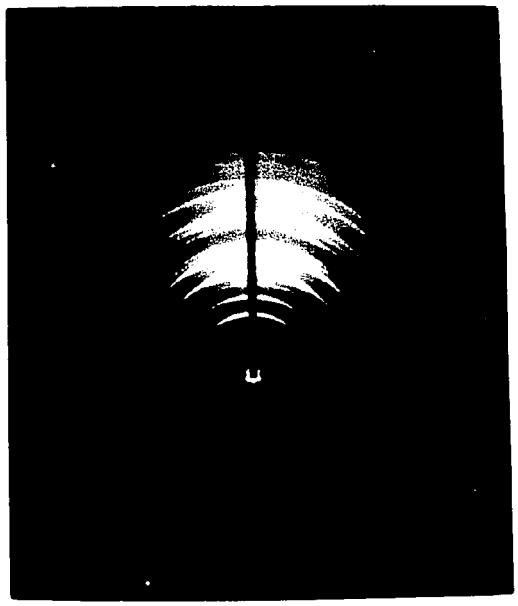


Fig. 20. Electron Diffraction Pattern of Film on Copper Surface. (Pattern taken after sample was removed from $FeCl_3$, washed in water, washed in acetone, and allowed to stand for 12 hours in a desiccator.)



Fig. 21. Electron Diffraction Pattern of Film on Copper Surface. (Pattern taken after sample was removed from $FeCl_3$, washed in water, washed in acetone, and allowed to stand for 4 days in a desiccator.)

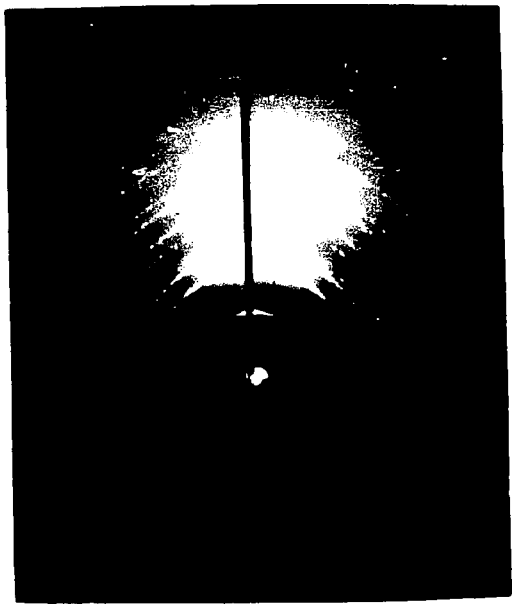


Fig. 22. Electron Diffraction Pattern of Film on Copper Surface. (Pattern taken immediately after sample was removed from $FeCl_3$ and rapidly plunged into acetone bath.)

The results indicate that a cuprous chloride-cuprous oxide mixture was first formed and upon standing the cuprous oxide disappeared. Apparently, the cuprous oxide reacts on exposure to air to form cupric oxide and possibly other reaction products.

After several more diffraction patterns were taken, it was noticed that the relative intensities of the lines for the cuprous chloride and the cuprous oxide as obtained after etching and washing varied; thus, it was suspected that the amount of cuprous oxide present was a function of the length of time the sample was washed and exposed to air after etching. A sample was then rapidly removed from the etching solution and placed directly into the triply distilled acetone. The electron diffraction pattern obtained from this sample is shown in Figure 22. The film consisted only of cuprous chloride. The sample was removed from the etching solution and placed into the acetone bath in such a manner as not to expose the sample to the atmosphere. Two more samples were taken in a similar manner and gave the identical results. Thus, it was concluded that the film consists only of cuprous chloride which is readily oxidized when brought out into contact with air and washed with water.

In the study of the anodic behavior of copper in 2N HCl, Stephenson and Bartlett observed the formation of a film on the copper surface (71). The film was believed to be cuprous chloride. Thus, the existence of a cuprous chloride film on the surface of the copper probably occurs quite frequently in chloride solutions.

Etch Pattern Studies

As previously mentioned, when a metal is dissolved in a solution and the reaction is chemically-controlled, crystallographic orientation is of the utmost importance. Thus, when the single crystals of copper were etched at low temperatures in the chemically-controlled region, different crystallographic orientations dissolved at different rates. Attempts were made to understand and interpret the quantitative studies with no success. Thus, it was believed that a qualitative discussion would yield some interesting information.

Data previously obtained showed that the (100) plane was the slowest etching and, thus, the most stable plane while the (111) plane was the most rapid etching of the planes studied. An examination of the etched structure revealed that only the cubic planes were exposed as the result of the attack. The same results were obtained regardless of which initially oriented single crystal was chosen. The etch pits in the plane having the surface parallel to the (100) plane have the expected fourfold symmetry details as shown in Figure 23. When a photomicrograph of an etched sample having its surface parallel to the (110) plane is taken, the results should show an etch pit having twofold symmetry. However, no well-defined etch pits could be obtained. Perhaps, the difference in etching rates between the (110) and the stable (100) was not great enough to produce any visible effects. However, when a (111) plane is etched, etch pits

having threefold symmetry are easily produced, as shown in Figure 24.

The observation that the (100) plane is the slowest etching plane of copper in ferric chloride at low temperatures is apparent since this face remains after prolonged etching. However, it has not been definitely shown that the (111) plane is the most rapid etching plane since the results merely showed that it was the fastest etching of the 3 planes studied. However, it has been observed by Kostron, et.al. (72) and also by Orem (73) that when aluminum is subjected to a corrosive medium which exposes the cubic planes only, the rate of corrosion is fastest in a direction normal to the octahedral planes, slowest in a direction normal to the cubic planes, and at some intermediate rate in a direction normal to the dodecahedral planes. Since aluminum and copper are both face-centered cubic materials, having the same relative atomic densities along the same direction, it could be hypothesized that the etching characteristics of single crystals of these two metals are probably similar in certain respects. Thus, it is likely that the (111) plane is the fastest etching plane.

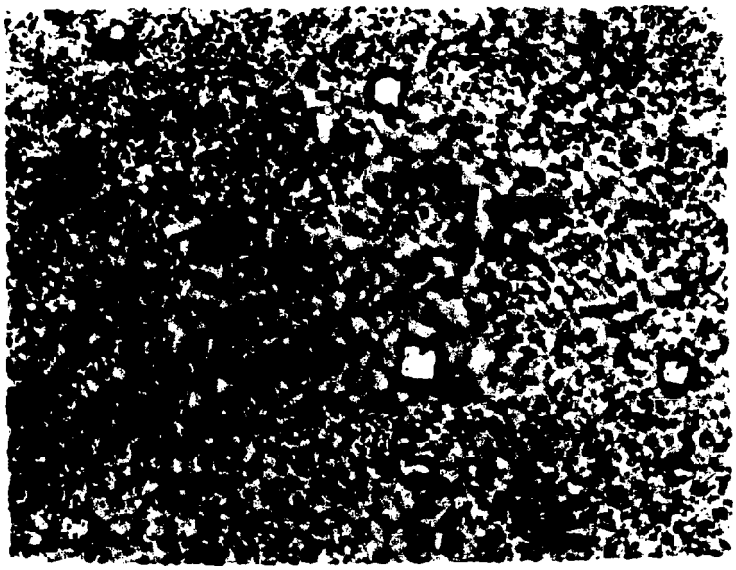


Fig. 23. Photomicrograph of (100) plane showing etch pits. Sample etched in 0.25 M. $FeCl_3$ at 0°C.; 500 x.

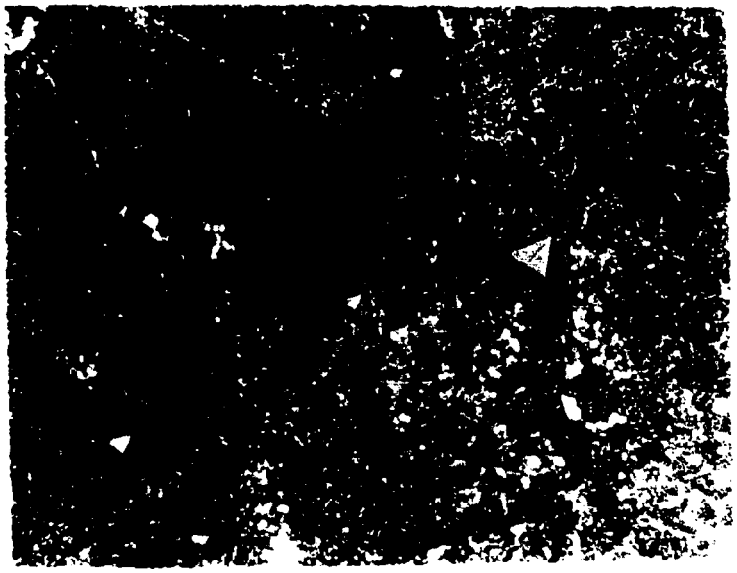


Fig. 24. Photomicrograph of (111) plane showing etch pits. Sample etched in 0.25 M. $FeCl_3$ at 0°C.; 500 x.

ANALYSIS

Complex Ion Formation

Ferric ions are known to form a series of complexes with chloride ions and to hydrolyze in aqueous solutions. The depressing effect of chloride ions on E° in the oxidation-reduction potentials of the Fe^{+3}/Fe^{+2} system was attributed to the formatiom of complex ionic species (74, 75). Investigation of the absorption spectra of ferric solutions to which chloride ions had been added revealed that an appreciable fraction of the ferric ions in a solution of ferric chloride exist as $FeCl_2^+$, $FeCl^{+2}$, $FeOH^{+2}$, $FeCl_3$ in addition to the Fe^{+3}. At the concentrations and pH's encountered in the present study, all the above species with the exception of the $FeOH^{+2}$ must be considered.

It is desirable to obtain values for the concentration of each of the above species in the solutions employed. The total concentration of ferric ions, denoted by $(Fe^{+3})_o$ may be represented as the sum of the individual species:

$$(Fe^{+3})_o = (Fe^{+3}) + (FeCl^{+2}) + (FeCl_2^+) + (FeCl_3) \quad (5)$$

It is possible to replace the concentrations of the ferric-chloro complexes by terms involving only ferric and chloride ions through the use of the following thermodynamic equilibrium constants:

$$Fe^{+3} + Cl^- \rightleftharpoons FeCl^{+2} \quad (6)$$

$$K_1 = \frac{(FeCl^{+2})}{(Fe^{+3})(Cl^-)} \quad (7)$$

$$FeCl^{+2} + Cl^- \rightleftharpoons FeCl_2^+ \quad (8)$$

$$K_2 = \frac{(FeCl_2^+)}{(FeCl^{+2})(Cl^-)} \quad (9)$$

$$FeCl_2^+ + Cl^- \rightleftharpoons FeCl_3 \quad (10)$$

$$K_3 = \frac{(FeCl_3)}{(FeCl_2^+)(Cl^-)} \quad (11)$$

Substitution of the above quantities into Eq. (5) yields:

$$(Fe^{+3}) = \frac{(Fe^{+3})_o}{1 + K_1(Cl^-) + K_1K_2(Cl^-)^2 + K_1K_2K_3(Cl^-)^3} \quad (12)$$

It can readily be seen from Equation (12) that the concentration of (Fe^{+3}) decreases as the chloride ion concentration increases.

In a similar manner, an expression for the total concentration of chloride ions, $(Cl^-)_o$, may be expressed in terms of the various species:

$$(Cl^-)_o = (Cl^-) + (FeCl^{+2}) + 2(FeCl_2^+) + 3(FeCl_3) \quad (13)$$

Substituting Eqs. (7), (9), (11), and (12) into the above equation yields:

$$(Cl^-)_o = (Cl^-) + \frac{K_1(Cl^-)+2K_1K_2(Cl^-)^2+3K_1K_2K_3(Cl^-)^3}{1+K_1(Cl^-)+K_1K_2(Cl^-)^2+K_1K_2K_3(Cl^-)^3}(Fe^{+3})_o \quad (14)$$

Values for the equilibrium constants K_1, K_2, and K_3 were obtained independently by Rabinowitch and Stockmayer (76). They obtained values of $K_1 = 4.2$, $K_2 = 1.3$, and $K_3 = 0.04$ all at an ionic strength of 1.0. Ionic strength, μ, is defined as one-half the sum of the terms obtained by multiplying the concentration of each ion in solution by the square of its valency; that is,

$$\mu = 1/2 \sum (c\ Z^2)$$

where Z is the valency of the particular ion of concentration c. This quantity μ is really a measure of the intensity of the electrical field existing in a solution. They also found that the equilibrium constants varied greatly with ionic strength, thus, they obtained an expression relating K_1 with ionic strength. Unfortunately, little data were obtained for K_2 and K_3 and no similar expression relating these quantities with ionic strength was obtained. Since this investigation involved ionic strengths as high as 18, it was necessary to calculate values for different ionic strengths. Values for K_1 were calculated from Rabinowitch and Stockmayer's equation:

$$\log K_1 = 1.51 - \frac{3\sqrt{\mu}}{1 + 1.5\sqrt{\mu}} + 0.295\ \mu \qquad (15)$$

Equations relating K_2 and K_3 were obtained on the assumption that they could be expressed by a similar relationship. Values of K_2 and K_3 were calculated from these expressions. (See Appendix B for a detailed discussion on the derivation of an expression for K_2 and K_3.) Values for K_1, K_2, and K_3 calculated for a total ferric concentration of 0.25 molar and for variable total chloride ion

concentrations are given in Table IV.

TABLE IV

CONCENTRATIONS OF FERRIC-CHLORO COMPLEXES PRESENT IN A 0.25 MOLAR FERRIC SOLUTION WITH VARYING AMOUNTS OF CHLORIDE IONS (Temperature 25°C)

K_1	K_2	K_3	$(Cl^-)_o$	(Cl^-)	(Fe^{+3})	$(FeCl^{+2})$	$(FeCl_2^+)$	$(FeCl_3)$
4.20	1.40	.0410	0.0	0.0	0.25	0.0	0.0	0.0
4.56	1.44	.0423	0.25	0.13	0.146	0.0868	0.0163	8.9×10^{-5}
4.94	1.475	.0437	0.50	0.28	0.085	0.117	0.0485	5.0×10^{-4}
5.50	1.518	.0451	0.75	0.45	0.0764	0.1158	0.0573	0.00103
6.17	1.57	.0468	1.0	0.61	0.0466	0.1137	0.0899	0.00216
7.82	1.70	.0502	1.50	1.08	0.0212	0.0941	0.1322	0.00528

Also given in Table IV are calculated values for the (Cl^-), (Fe^{+3}), $(FeCl^{+2})$, $(FeCl_2^+)$. and $(FeCl_3)$. The ferric ion concentration was calculated from Eq. (12), and the free chloride ion concentration was obtained by a successive approximation method from Eq. (14). The values of $(FeCl^{+2})$, $(FeCl_2^+)$, $(FeCl_3)$ were then obtained from Eqs. (7), (9), and (11), respectively. The various concentrations of the ferric-chloro complexes are also plotted as a function of total chloride ion concentration in Figure 25. This graph clearly shows that the concentration of ferric ions decreases as the chloride ion concentration is increased, while the $(FeCl_2^+)$ and $(FeCl_3)$ complexes increase. The $(FeCl^{+2})$ complex increases to a maximum, and then decreases.

In a similar manner, it is possible to compute the approximate quantities of each complex ion in the ferric chloride solution at various concentrations. The various quantities of each

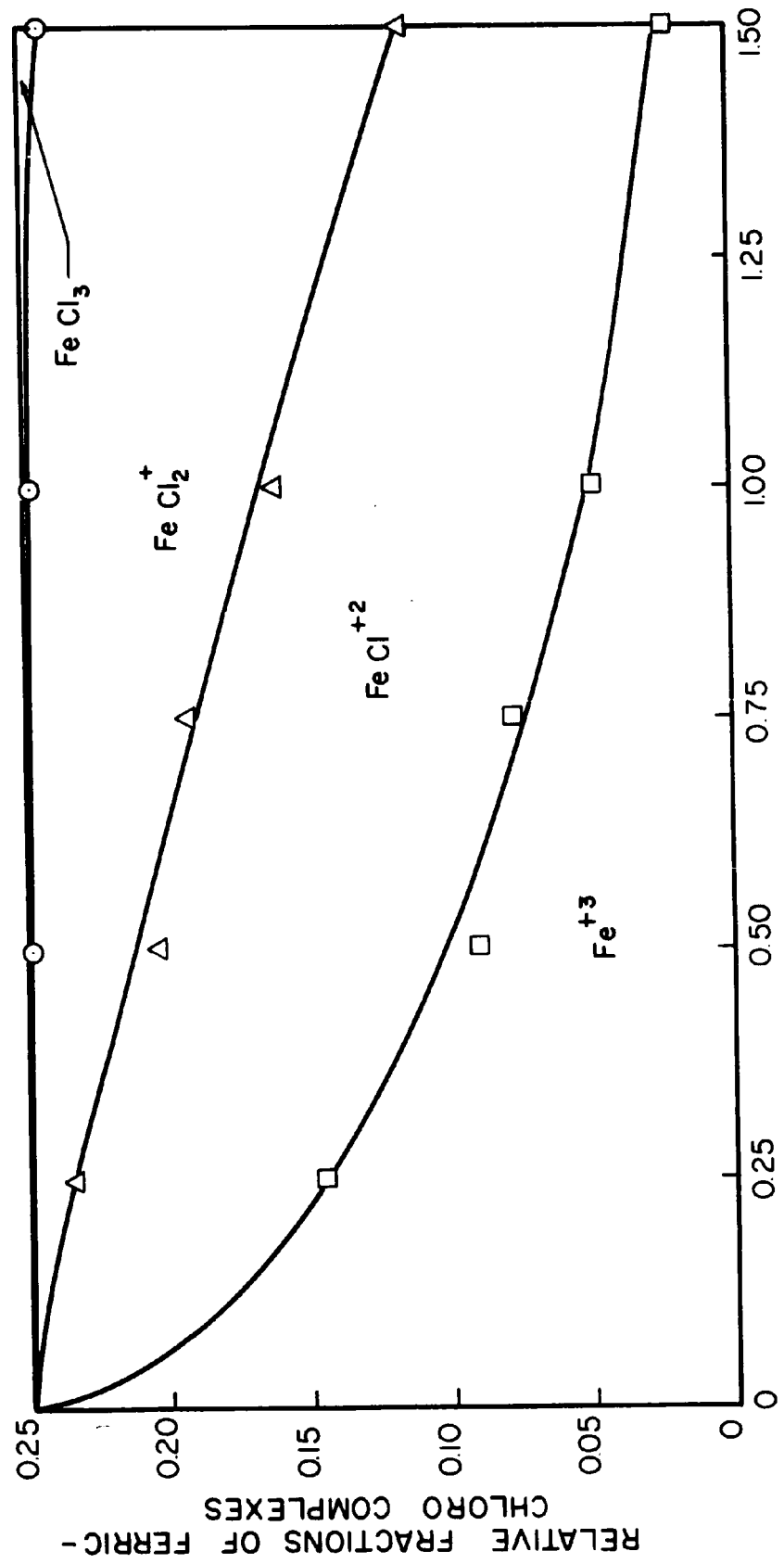


Figure 25 - Concentrations of Ferric-Chloro Complexes Present in A 0.25 M. Ferric Solution at Various Chloride Concentrations

species at different ferric chloride concentrations are given in Table V. Again, it can be seen that the relative quantity of (Fe^{+3}) decreases as the ferric chloride concentration is increased. The ($FeCl^{+2}$) again increases, reaches a maximum, and then decreases. The ($FeCl_2^+$) increases and also reaches a maximum; however, this occurs at very high values of ferric chloride concentrations. At these high values of ferric chloride concentrations, the presence of undissociated ($FeCl_3$) becomes of considerable importance. It is this undissociated ($FeCl_3$) which causes the reaction rate to decrease at high ferric chloride concentrations as shown in Figure 8.

Mechanism of the Reaction

The overall reaction between copper and ferric chloride is usually written in the following stoichiometric form:

$$Cu + 2\,FeCl_3 \longrightarrow CuCl_2 + 2FeCl_2 \qquad (16)$$

This oxidation-reduction reaction involves two moles of ferric chloride for each mole of copper metal with the copper metal being oxidized to the cupric state and the ferric ions being reduced to ferrous ions.

The data have shown that the above reaction is a diffusion-controlled process at ordinary temperatures, and at least partially chemically-controlled at temperatures below 7°C. The exact mechanism of a reaction usually cannot be obtained in a diffusion-controlled zone, since the effect of a given species on a reaction

TABLE V

CONCENTRATIONS OF FREE CHLORIDE IONS, AND FERRIC-CHLORO COMPLEX IONS PRESENT AT VARIOUS FERRIC CHLORIDE CONCENTRATIONS
(Temperature 25°C.)

$(Fe^{+3})_o$	$(Cl^-)_o$	K_1	K_2	K_3	Cl^-	Fe^{+3}	$FeCl^{+2}$	$FeCl_2^+$	$FeCl_3$
0.	0.	32.4	4.498	.15	0.	0.	0.	0.	0.
.25	.75	4.544	1.4346	.0422	.473	5.4×10^{-2}	.116	.0788	.00157
.50	1.50	8.931	1.7723	.0527	.748	.0296	.197	.262	.01032
.75	2.25	20.69	2.3327	.0679	.909	.01207	.227	.481	.0297
1.00	3.00	50.21	3.1308	.0885	1.13	.00358	.204	.721	.071
1.50	4.50	337.8	5.8414	.1485	1.40	2.93×10^{-4}	.1388	1.131	.234
2.00	6.00	2,383.	11.1	.258	1.53	2.23×10^{-5}	.0812	1.1378	.544
2.50	7.50	16,930.	21.2	.429	1.57	1.66×10^{-6}	.0441	1.47	.99
3.00	9.00	120,700.	40.83	.803	1.64	9.72×10^{-8}	.0192	1.285	1.693

is sometimes masked because of the diffusion process. However, in this case, much valuable information can be obtained from the kinetic and electron diffraction studies. Since the reaction is diffusion-controlled, the slow step could be either the diffusion of reactants to the surface or of products away from the surface. If the reaction were controlled by the rate of diffusion of products away from the surface, it would probably be expected that different metals would dissolve at different rates in ferric solutions since the diffusion of different reaction products would probably differ; however, Van Name and Hill (8) found that zinc, cadmium, iron, and tin dissolve at the same rate in ferric-alum solutions. Therefore, it appears that the rate is controlled by the rate of diffusion of a common ion, ferric ions, to the surface of the metal.

The kinetic data have shown that chloride ions greatly increase the dissolution rate of copper in ferric solutions, and it also has been shown that the addition of chloride ions to ferric solutions form ferric-chloro complexes. It would appear then that the increased reaction rates are caused by the faster diffusion of these complex ions. The rate of reaction could then be represented as

$$R = K_1(Fe^{+3}) + K_2(FeCl^{+2}) + K_3(FeCl_2^{+}) \qquad (17)$$

where K_1, K_2, and K_3 would be proportional to the diffusion coefficients of the various ions. However, if this were the case, the dissolution of other metals such as iron would be more rapid in ferric chloride than in ferric nitrate - which

is not true. Furthermore, if the diffusion of the various species differed, no plateau would be reached in the dissolution rate versus chloride ion concentration curve, since the relative amounts of the complexes are still changing when the plateau is reached. Therefore, it appears that all of the ferric-chloro complexes must diffuse at approximately the same rate. Also, it is apparent that the addition of chloride ions to ferric solutions must increase the rate by some mechanism which is peculiar to copper.

The electron diffraction studies have shown that cuprous chloride is an intermediate reaction product which exists on the copper surface during the chemical reaction. It would be expected that the presence of a film would decrease the diffusion rates of the ferric and ferric-chloro complex ions thus decreasing the reaction rate; however, the rate increases in ferric solutions containing chloride ions. Hence, it appears that the film is either extremely thin or discontinuous so as not to greatly inhibit the diffusion of reacting ions, and that this effect is completely overshadowed by another more important effect which increases the rate.

Since a cuprous chloride film is observed on the copper during the reaction, the slow diffusion step must involve the diffusion of reactants to the film to dissolve it. Since the reaction is a function of chloride ions, and since no film is present at high chloride concentrations, it appears that a reaction between the cuprous chloride and chloride ions occurs to form a soluble cuprous chloride complex:

$$CuCl_s + Cl^- \longrightarrow CuCl_2^- \qquad (18)$$

Considerable evidence for the reaction of cuprous chloride with chloride ions to form a soluble complex, $CuCl_2^-$, was found in the literature (77). The solubility of cuprous chloride in chloride solutions was studied by Chaltykyan (78) who found that the reaction occurred by the formation of soluble complex ions, $CuCl_2^-$, $CuCl_3^{-2}$, and $Cu_2Cl_3^-$. This reaction step was also used by Gauvin and Winkler to explain the effect of chloride ions on copper deposition (79). Further proof is that the addition of chloride salts was used for preventing the formation of cuprous chloride in the hydrometallurgy of copper (80, 81). Thus, it appears that the addition of chloride ions increases the formation of $CuCl_2^-$ by the reaction represented by Eq. 18, until a point is reached at which the cuprous chloride is being dissolved as rapidly as it is being formed and it no longer is visible on the copper surface.

It also has been shown that the addition of ferric ions to a ferric chloride solution also increases the rate of reaction. Thus, it appears that the reaction is determined by the rates of diffusion of chloride ions to the cuprous chloride film and also by the ferric ions to the copper surface through the cuprous chloride film. The probable reaction between copper and ferric ions is a simple electron transfer process:

$$Fe^{+3} + Cu_s \longrightarrow Cu^+ + Fe^{+2} \qquad (19)$$

On the other hand it is more likely that the reactions between the $FeCl_2^+$ and $FeCl^{+2}$ complexes with copper proceed by the transfer

of chloride ions as opposed to electron transfer mechanisms. Possible reactions involving these complexes may proceed as follows.

$$FeCl_2^+ + Cu_s \longrightarrow CuCl_2^- + Fe^{+2} \qquad (20)$$

$$FeCl^{+2} + Cu_s \longrightarrow CuCl + Fe^{+2} \qquad (21)$$

These reactions are quite probable since if the reaction were to proceed by electron transfer, it would necessitate the formation of iron (II) in the form of the unlikely species $FeCl_2$ and $FeCl^+$. Dodson and Silverman also postulated a mechanism involving a halogen transfer to explain the exchange reaction between iron (III) and iron (II), (82).

Since the reaction between the ferric monochloro complex with copper yields insoluble cuprous chloride and since this film is visible, it is obvious that this step must be faster than the diffusion step involving chloride ions to the cuprous chloride film. Therefore, an empirical relationship relating the rate of dissolution of copper as a function of the reacting ions should involve chloride ions instead of the ferric monochloro complex. An empirical relationship would then involve the following species:

$$R = K_1(Fe^{+3}) + K_2(FeCl_2^+) + K_3(Cl^-) \qquad (22)$$

Since the dissolution of iron in ferric nitrate was shown to be the same as in ferric chloride, diffusion of the ferric-chloro complexes must be the same as for the ferric ions; therefore, K_2 must be equal to K_1. Furthermore, if the values of K_1 and K_2

are assumed to be equal to the values obtained for the reaction of copper with ferric ions in ferric nitrate, then

$$K_1 = K_2 = 2.6$$

The value of K_3 can be obtained from the data of Table IV, and a value of 1.48 fits the data well. Thus, the final rate expression can be represented as follows:

$$R = 2.6(Fe^{+3}) + 2.6(FeCl_2^+) + 1.48(Cl^-) \quad (23)$$

Using the above expression, values for the rate of dissolution were computed at various concentrations of ferric chloride. The computed results are shown in Table VI along with the experimental results. Some discrepancies were expected since the concentrations of the various species as obtained from the equilibrium constants are not exact, since the equilibrium constants,

TABLE VI

COMPARISON OF EXPERIMENTAL AND CALCULATED RATE CONSTANTS

$FeCl_3$ Moles/Liter	k (mg/sq.cm. - min) Experimental	Calculated	Per Cent Deviation
0.25	0.99	1.02	+ 3.0
0.50	1.96	1.89	- 3.6
0.75	2.86	2.64	- 4.2
1.00	3.74	3.58	- 4.3
1.50	5.10	4.98	- 2.4
2.00	5.80	5.81	+ 1.7
2.50	5.74	6.12	+ 6.6
3.00	4.88	5.64	+15.5

especially K_2 and K_3, are only approximations. Furthermore, it is to be expected that the calculated values at high ferric chloride concentrations would be higher than the experimental values because no account was taken of the increased viscosity of the solution which occurs at high concentrations, thus decreasing the diffusion rate of the reacting species.

Another reaction which probably is occurring is one between the cupric chloride which is formed and the copper metal, to form cuprous chloride. The reaction of copper with cupric chloride was studied by Gokhale, who found that the reaction is enhanced by chloride ions (59). Therefore, it is not improbable that some of the cupric ions which are formed and are in contact with the copper should react with it.

At temperatures below 5°C., it has been shown that the mechanism of the reaction changes from a diffusion-controlled process to one which is partially or fully chemically-controlled. Most of the evidence supports the theory that it is only partially chemically and partially diffusion-controlled at these low temperatures. The change in shape of the dissolution rate versus chloride ion concentration curve at low temperatures, although not very pronounced, seems to indicate that the slow step in the reaction of cuprous chloride and chloride ions is the chemical reaction and no longer the diffusion of the chloride ions. The relatively low activation energy as compared to usual chemically-controlled reactions is another indication that the reaction is not completely chemically-controlled at these low temperatures. Although the variation

of dissolution rate with flow rate was not actually recorded in this investigation at these low temperatures, it was noted that the reaction still was a definite function of flow rate; thus, the reaction must be at least partially diffusion-controlled at these temperatures.

CONCLUSIONS

The dissolution of copper in ferric chloride solutions is a diffusion-controlled reaction at temperatures above 7°C., and an intermediate type reaction, partially chemically and partially diffusion controlled, at temperatures below 7°C.

General

1. The rate of dissolution is directly proportional to the ferric chloride concentration up to 1.0 molar concentration. Thereafter the rate increases more slowly, reaching a maximum in the vicinity of 2.2 molar, and then decreases.

2. The rate of dissolution of copper in ferric solutions is increased by chloride ions.

3. The rate of dissolution is independent of the dissolved oxygen and hydrogen ion concentration.

4. A layer of insoluble cuprous chloride exists on the surface of the copper during the reaction, as an intermediate reaction product.

5. Three distinct ferric-chloro complexes: $FeCl^{+2}$, $FeCl_2^+$, and $FeCl_3$ exist in ferric chloride solutions. The decrease in dissolution rate which occurs at high ferric chloride concentrations was attributed to the presence of large amounts of undissociated $FeCl_3$ complex.

Diffusion-Controlled Region

1. The rate of reaction is directly proportional to the linear flow rate of the solution past the metal surface.

2. The rate of reaction is independent of the metallic characteristics as shown from studies of different crystallographic orientations.

3. The rate of reaction is determined by the rate at which the ferric and ferric dichloro complex ions diffuse to the copper surface and by the rates at which chloride ions diffuse to the cuprous chloride film.

Partially Chemically-Partially Diffusion-Controlled Region

1. The dissolution rate is dependent on metallic characteristics. The dissolution rate was the greatest for the (111) orientation and least for the (100) orientation. The (110) direction of the crystal dissolved at an intermediate rate.

2. The rate of reaction is determined by the rate at which the ferric and ferric dichloro complex ions diffuse to the copper surface and also by the chemical reaction between the chloride ions and the cuprous chloride film.

APPENDICES A and B

APPENDIX A

Tabulation of Kinetic Data Results

TABLE I

DISSOLUTION OF COPPER IN A 0.25 MOLAR FERRIC CHLORIDE SOLUTION, 100 ml, 25°C.

Time (min.)	Total Copper Dissolved (8 Hrs.)	Copper Dissolved (mg/cm^2)	Copper Dissolved (Milli-moles)	$(a_o - x)$	log $(a_o - x)$
0	0	0	0	256.	2.39794
4	.0061	3.56	0.962	249.04	2.39627
9	.0148	8.64	2.30	247.70	2.39393
13	.0207	12.08	3.26	246.74	2.39224
22	.0331	19.32	5.22	244.78	2.38877
31	.0453	26.45	7.13	242.87	2.38537
41	.0584	34.11	9.19	240.81	2.38168
53	.0737	43.05	11.60	238.40	2.37731
95	.1260	73.60	19.85	230.15	2.36201
111	.1462	85.48	23.00	227.00	2.35603
124	.1582	92.46	24.90	225.10	2.35238
142	.1819	106.10	28.60	221.40	2.34518
191	.2421	141.20	38.10	211.90	2.32613
249	.3032	178.10	47.80	202.20	2.30578

a_o = 0.25 moles = 250 millimoles

TABLE II

DISSOLUTION RATE VERSUS FERRIC CHLORIDE CONCENTRATION, 25°C.

Conc.-Moles/Liter	Rate - Mg/sq.cm. - Min.
.125	0.49
.25	0.99
.50	1.96
.75	2.86
1.00	3.74
1.20	4.40
1.50	5.10
1.80	5.60
2.00	5.80
2.25	5.86
2.50	5.74
3.00	4.88

TABLE III

DISSOLUTION RATES VERSUS FLOW RATE, 25°C.

Conc.-Moles	Still Bath	400 cm/min	600 cm/min	900 cm/min	1200 cm/min
0.25	0.41	0.54	0.79	0.99	1.19
0.50	0.71	1.17	1.43	1.96	2.37
0.75	0.86	1.73	2.24	2.88	3.62
1.00	1.04	2.52	2.86	3.74	4.78
2.00	2.43	3.88	4.58	5.74	6.90
3.00	1.94	3.21	3.85	4.88	5.88

TABLE IV

DISSOLUTION RATE VERSUS TEMPERATURE

Temp. - °C.	$1/T \times 10^3$	Rate (k) $\frac{mg}{sq.cm.-min}$	Log k + 1
1/4 Molar $FeCl_3$			
53	3.07	1.355	1.33
34	3.26	1.315	1.12
25	3.36	0.96	0.982
19	3.42	0.87	0.940
14	2.482	0.74	0.870
10	3.5328	0.673	0.828
6.5	3.572	0.598	0.799
4.5	3.601	0.430	0.634
1 Molar $FeCl_3$			
49	3.105	6.66	1.825
36	3.238	4.99	1.701
26	3.340	3.78	1.580
19	3.423	3.46	1.539
19	3.423	3.42	1.536
12	3.507	2.72	1.436
7	3.569	2.45	1.391
6	3.582	1.88	1.274
2 Molar $FeCl_3$			
45	3.145	9.33	1.971
36	3.236	7.73	1.89
26	3.340	6.28	1.80
25	3.358	8.93	1.725
20	3.415	5.35	1.73
16	3.457	4.66	1.67
13	3.490	4.77	1.68
12.5	3.500	4.35	1.64
12	3.510	4.10	1.615
10	3.535	3.78	1.58
10	3.535	3.62	1.56
7	3.570	2.94	1.48
3 Molar $FeCl_3$			
50	3.08	8.90	1.951
41	3.18	7.32	1.866
31	3.29	5.65	1.746
21	3.40	4.66	1.671
19	3.42	4.28	1.634
15	3.47	3.78	1.579
7	3.57	2.74	1.44

TABLE V

DISSOLUTION RATE VERSUS TEMPERATURE FOR (100), (110), AND (111) CRYSTALLOGRAPHIC ORIENTATIONS, 0.25 Molar $FeCl_3$

Temp. °C	$1/T \times 10^3$	Rate (k) mg/sq.cm.-min.	Log k + 1
(100) Plane			
10. °	3.5318	0.671	0.827
6.5	3.5718	0.594	0.774
6.0	3.5818	0.538	0.732
4.5	3.6013	0.425	0.629
3.0	3.6208	0.384	0.586
0.0	3.6616	0.280	0.448
(110) Plane			
10. °	3.5318	0.677	0.831
6.5	3.5718	0.609	0.785
4.0	3.6079	0.452	0.665
3.0	3.6208	0.438	0.642
0.5	3.6550	0.332	0.522
(111) Plane			
10. °	3.5318	0.673	0.828
5.	3.5948	0.541	0.734
3.	3.6200	0.460	0.663
2.5	3.6274	0.446	0.651
0.5	3.6550	0.362	0.558

TABLE VI

DISSOLUTION RATE VERSUS TEMPERATURE FOR (100), (110), AND (111) CRYSTALLOGRAPHIC ORIENTATIONS, 1.0 Molar $FeCl_3$

Temp. °C	$1/T \times 10^3$	Rate (k) mg/sq.cm.-min.	Log k + 1
(100) Plane			
19. °	3.423	3.42	1.536
7.	3.5691	2.28	1.358
6.	3.5819	2.03	1.308
4.5	3.6013	1.590	1.202
3.	3.6208	1.349	1.130
0.5	3.6550	1.098	1.041
(110) Plane			
19. °	3.423	3.40	1.533
7.	3.5691	2.41	1.383
6.	3.5819	2.22	1.347
5.	3.5880	2.18	1.339
4.5	3.6013	1.93	1.286
3.	3.6209	1.61	1.207
0.5	3.6550	1.227	1.089
(111) Plane			
10. °	3.423	3.52	1.548
7.	3.5691	2.49	1.396
5.	3.5948	2.17	1.337
4.5	3.6013	2.14	1.330
3.0	3.6208	1.96	1.292
2.5	3.6274	1.76	1.245
0.5	3.6550	1.38	1.146

TABLE VII

DISSOLUTION RATE VERSUS CHLORIDE ION CONCENTRATION
0.25 Molar Ferric Solution, 25°C.

(Cl^-) Concentration Moles/Liter	Rate mg/cm^2-min
0.	0.64
0.375	0.78
0.75	0.99
1.00	1.08
1.25	1.21
1.50	1.21
1.75	1.20
2.00	1.22
2.50	1.69

TABLE VIII

DISSOLUTION RATE VERSUS FERRIC ION CONCENTRATION
25°C.

Concentration Moles/Liter	$Fe_2(SO_4)_3$ Rate - mg/sq.cm.-min	$Fe(NO_3)_3$ Rate - mg/sq.cm.-min
0.125	0.39	0.34
0.250	0.65	0.68
0.500	1.31	1.31
0.750	1.46	1.96
1.000	1.51	2.60

TABLE IX

EFFECT OF ($NaNO_3$) CONCENTRATION ON THE DISSOLUTION RATE OF 0.25 Molar Ferric Nitrate, 25°C.

($NaNO_3$) Concentration Moles/Liter	Rate mg/sq.cm. - min
0.	0.68
0.125	0.65
0.250	0.66
0.500	0.64

TABLE X

EFFECT OF (Na_2SO_4) CONCENTRATION ON THE DISSOLUTION RATE OF 0.25 MOLAR FERRIC IONS $Fe_2(SO_4)_3$, 25°C.

(Na_2SO_4) Concentration Moles/Liter	Rate mg/sq.cm.-min.
0.00	0.65
0.125	0.66
0.250	0.64
0.500	0.63

TABLE XI

DISSOLUTION RATE OF 0.25 MOLAR FERRIC CHLORIDE SOLUTION WITH ADDED FERRIC IONS, 25°C.

Moles/Liter of Fe^{+3} Added	Rate
0.00	0.99
0.025	1.03
0.0559	1.10
0.1802	1.40
0.221	1.50

TABLE XII

DISSOLUTION RATE VERSUS FERROUS AND CUPRIC ION CONCENTRATIONS, 0.25 MOLAR FERRIC CHLORIDE, 25°C.

Moles/Liter	Rate
0.00 Fe^{++}	0.98
0.0663 Fe^{++}	0.96
0.520 Fe^{++}	0.92
0.811 Fe^{++}	0.86
0.00	0.98
0.181 Cu^{++}	0.87
0.57 Cu^{++}	0.62
0.902 Cu^{++}	0.39
Cu^{++} added as $Cu(NO_3)_2$	Fe^{++} added as $Fe(NO_3)_2$

TABLE XIII

DISSOLUTION RATE VERSUS DISSOLVED OXYGEN CONCENTRATION, 0.25 MOLAR FERRIC CHLORIDE, 25°C.

Dissolved O_2	Rate mg/sq.cm. - min
(Pure N_2 bubbled through solution)	0.97
50% mixture of O_2 and 50% and 50% N_2 bubbled through solution	0.97
Pure O_2 bubbled through solution	0.98

TABLE XIV

DISSOLUTION RATE VERSUS HYDROGEN ION CONCENTRATION, 0.25 MOLAR FERRIC CHLORIDE 25°C.

Hydrogen Ion Concentration Moles /Liter	Rate mg/sq.cm.-min.
0.	0.99
0.25	0.98
0.50	0.99
0.75	1.02

H^+ added as HNO_3

TABLE XV

LOW TEMPERATURE DISSOLUTION RATE VERSUS CHLORIDE ION CONCENTRATION, 0.25 MOLAR FERRIC ION, 2°C.

(Cl^-) Moles/Liter	Rate mg/cm^2 - min
0.	0.241
0.50	0.328
0.75	0.359
1.00	0.385
1.50	0.436
1.8	0.454
2.2	0.457
2.5	0.450

TABLE XVI

LOW TEMPERATURE DISSOLUTION RATE VERSUS FERRIC CHLORIDE CONCENTRATION, 2°C.

$FeCl_3$ Moles/Liter	Rate mg/cm^2 - min
0.	0.
0.25	0.359
0.50	0.709
1.00	1.32
2.00	1.85
3.00	1.54

TABLE XVII

DISSOLUTION RATE VERSUS SURFACE FINISH
(100) SINGLE CRYSTAL

Temp.	Time (min.)	Rate - mg/sq.cm. - min.			
		Rough ground	1/0 metallographic paper	Mechanically polished	Chemically polished
25°C.	1	1.01	--	--	0.97
	2	1.00	--	--	0.98
	4	0.99	--	--	0.96
	8	0.98	--	--	0.97
	10	0.97	--	--	0.97
	16	0.97	--	--	0.98
2°C.	1	0.51	0.46	0.48	0.39
	2	0.50	0.42	0.39	--
	4	0.42	--	0.38	0.37
	6	--	0.39	--	--
	8	0.40	--	0.37	0.37
	10	--	--	--	--
	12	0.36	0.36	--	0.36
	14	--	--	--	--
	16	0.35	0.36	--	--
	18	--	--	0.35	--

TABLE XVIII

DISSOLUTION RATE OF IRON IN FERRIC SOLUTIONS, 25°C

$Fe(NO_3)_3$ Moles/Liter	Rate mg/sq.cm. - min.
0.	0.
0.25	0.58
0.50	1.16
1.00	2.25
$FeCl_3$ Moles/Liter	Rate mg/sq.cm. - min.
0.	0.
0.25	0.59
0.50	1.15
1.00	2.29

APPENDIX B

CALCULATION OF EQUILIBRIUM CONSTANTS K_1, K_2, and K_3

Rabinowitch and Stockmayer (76) gave the following equation relating K_1 to the ionic strength:

$$\log K_1 = 1.5 - \frac{3\sqrt{\mu}}{1 + 1.5\sqrt{\mu}} + 0.295\,\mu \qquad (1b)$$

Comparison of the above equation with the Debye-Huckel Equation (83) below shows the two equations to be equal if the average effective diameter of the complex ion, $FeCl_2^+$, is taken as 4.56 Å.

$$\log K = \log K_o + \frac{2\,AZ^+Z^-\sqrt{\mu}}{1 + aB\sqrt{\mu}} + c\,\mu \qquad (2b)$$

where:

A = 0.509 for water at 25°C.

B = 3.29×10^7 electrostatic units.

K_o = Ionization constant at $\mu = 0$.

Z = Ionic Charge

a = Average effective diameter

C = Empirical Constant

μ = Ionic Strength

An average effective diameter for the complex ion $FeCl_2^+$ was estimated as 7.0 Å. This value was obtained by assuming a linear configuration and a value of 2.44 Å for the diameter of the chloride ion which is a compromise between the ionic diameter of 3.62 Å and the covalent diameter of 1.98 Å. Using the value of 7.0 Å for the diameter and the two values of Rabinowitch and Stockmayer (76)

in Eq. (2b), the constant, C, was calculated to be equal to 0.097. Thus the final equation used to calculate K_2 as a function of the ionic strength is:

$$\log K_2 = 0.653 - \frac{2\sqrt{\mu}}{1 + 2.3\sqrt{\mu}} + 0.97\,\mu \qquad (3b)$$

In a similar manner, it is possible to obtain an expression relating K_3 with ionic strength. An average effective diameter for the complex $FeCl_3$ was estimated to be 7.0 Å which is the same value used for the $FeCl_2^+$ complex. Since a linear configuration for the $FeCl_2^+$ complex was used by Rabinowitch and Stockmayer (76), this assumes that the chloride ions are on opposite extremities of the ferric ion; therefore, any additional chloride ion will not increase the effective diameter.

Using the average value of 0.04 at $\mu = 1$, a value of 0.15 for $\mu = 0$, and the value of 7.0 Å for the effective diameter, the constant, C, in Eq. (2b) was calculated to be 0.082. The value of 0.15 was the high limit of the values obtained by Rabinowitch and Stockmayer. This value was used because it much more closely corresponded to the expectation that the solution is half-saturated at a chloride concentration of approximately 6.5 Molar. The final equation used to calculate K_3 is:

$$\log K_3 = -1.176 - \frac{\sqrt{\mu}}{1 + 2.3\sqrt{\mu}} + 0.082\,\mu \qquad (4b)$$

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