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KINETIC STUDIES OF THE DISSOLUTION OF COPPER IN FERRIC CHLORIDE SOLUTIONS

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LIST OF SYMBOLS

k	Rate constant (moles per liter - min. - cm^2)
K	Equilibrium constants
$[\;]$	Concentrations in moles per liter
$[\;]_o$	Initial concentrations in moles per liter
μ	Ionic strength
Z	Ionic charge
a	Average effective diameter
Å	Angstrom units

ABSTRACT

The purpose of this study was to determine the rate at which metallic copper dissolves in ferric chloride solutions and to offer a mechanism by which the reaction occurs. The problem was approached by considering the effects of the reaction variables such as temperature, ionic strength, and concentration upon the rate of reaction. The direction and magnitude of these effects were correlated to a possible mechanism of the reaction.

The experimental apparatus consisted of a copper sample enclosed in a reaction cell mounted perpendicular to the flow of the solution. The solution flowed through the reaction cell and returned to the solution's reservoir from which samples were withdrawn at regular time intervals. This apparatus was especially designed to minimize the physical effects of stirring.

A direct correlation was found between absorption of light of a wave length of 970 millimicrons and the concentration of copper in solution. The increase in the concentration of copper in the solution as a function of time was a direct measure of the rate of reaction.

A series of experiments were made in which the concentration of ferric chloride was varied from dilute solutions to a concentrated solution of 3.0 molar. The reaction rate was found to increase in direct proportion to the ferric chloride concentration until a maximum rate was reached, after which the rate decreased. In similar experiments using dilute solutions of ferric sulfate, the rate was found to be 41 per cent slower than the corresponding rate in ferric chloride.

It was shown in a series of studies designed to determine the effect of the chloride ion upon the reaction that the rate increases proportionally to the square of the chloride concentration in dilute solutions. In concentration solutions the rate decreases in proportion to the cube of the chloride concentration.

The effect of temperature upon the rate was found to be much less than is normal for this type of reaction. A 10° C increase caused only an 8 per cent increase in the rate whereas a 50 to 100 per cent increase is expected for comparable reactions.

At the concentrations of ferric chloride used in this investigation there exist three distinct ferric chloro complexes: $FeCl^{+}$, $FeCl_2^{+}$, and $FeCl_3$. From an extension of the values given in the literature of the equilibrium constants for these complexes, the amount of each species present in each ferric chloride concentration was calculated and a correlation to the rate of reaction was found.

From a consideration of experimental rate equations, the following mechanism for the reaction was proposed. The three species Fe^{+3}, $FeCl^{+}$, and $FeCl_2^{+}$ each react with the copper metal, and at the copper surface the three react simultaneously at a rate which is determined by the rate at which the species diffuse through the body of the solution to the surface. The rate of diffusion to the surface is directly proportional to the concentration of the species in the bulk of the solution and inversely proportional to the charge on the ion. The species $FeCl_3$ is unreactive and inhibits the reaction by increasing the diffusion barrier at the copper surface.

Increasing the temperature increases the rate at which each species reacts but at the same time increased temperature would decrease the stability of the complexes and thereby reduce the relative amounts of the more reactive species.

CHAPTER I

INTRODUCTION

Chemical reactions that occur in heterogeneous systems are complicated by interfacial effects that operate at the boundary of the phases in addition to specific chemical effects. These interfacial effects may influence the net rate of the reaction and in suitably rapid chemical reactions may be the rate controlling influence.

In heterogeneous systems consisting of a solid and a solution, the solute molecule or ion must approach the surface of the solid before reaction can occur. The solute molecule or ion is then adsorbed on the surface of the solid through a polar bond or more loosely by attractive forces not necessarily chemical in nature. It is this adsorbed molecule or ion that is the reaction intermediate. These effects may be treated by an intermediate complex theory but the chemical reaction is a composite of the true chemical reaction together with adsorption and desorption. There are, then, three distinct processes occurring: a) diffusion of the reactant to the surface, b) chemical reaction, and c) diffusion of the product into the bulk of the solution. Any of these steps may be the slowest and therefore the rate controlling step.

The rate of the heterogeneous reaction of copper with dilute ferric chloride solutions is reported by Pletenev and Pavlov (1) and by King and Weidenhammer (2) as being controlled by the rate at which the ferric ion diffuses to the surface of the metal.

The present investigation was undertaken to determine if the same mechanism would apply to higher concentrations of ferric chloride. In particular, the effects of changes in temperature, concentration and ionic strength of the solutions upon the rate of reaction were determined.

CHAPTER II

HISTORICAL DISCUSSION

A general theory of the kinetics of heterogeneous reactions in solutions was proposed by Nernst in 1904 (3). This theory postulated that the chemical reaction at the surface is rapid and that the liquid in the immediate vicinity of the interface becomes depleted of reactant, hindering further reaction. The reactant then slowly diffuses to the surface with a velocity which is smaller than the velocity of the chemical reaction. Thus, 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 (4) reasoned that if this theory were correct, all metals should dissolve in a given reagent at the same rate. Their data confirmed this for a number of metals in ferric chloride; however, copper and silver dissolved at a somewhat slower rate.

The generally accepted criteria of the diffusion rate theory have been given by Salzberg _et al_. (5) in the following conclusions:

(1) The speed of stirring has a large effect.
(2) The rate of reaction is inversely proportional to the viscosity of the solution.
(3) The previous treatment of the surface has only a small effect, if any.
(4) The temperature coefficients are small compared to the chemical reactions.

All heterogeneous reactions, however, do not follow the diffusion rate theory and, as pointed out by Moelwyn-Hughes (6), unimolecular behavior may be explained in other ways. King and Braverman (7) concluded that the reaction of zinc with acids was controlled by the diffusion rate of the acid. Kilpatrick and Rushton (8), studying the same reaction, maintained that the rate was controlled by the chemical reaction at the surface. Their experimental data might be explained on the basis of a diffusion theory in which a molecular species as well as the hydrogen ion diffuse to the surface and two reactions subsequently take place.

Salzburg *et al*. (5) suggested that if there is a large difference in the standard oxidation-reduction potential of the system, the reaction would be controlled by diffusion, or would be controlled by the chemical reaction if the potential were small. The ferric ion-silver couple was mentioned as a possible limiting case. The reactions of silver with ferric sulfate solutions (9) and with ferric perchlorate solutions (10) were shown to be controlled by the rate at which the products were desorbed from the surface of the metal. The potential of the ferric ion-copper couple is large enough to suggest that the reaction is diffusion controlled. However, the reaction of zinc with chromic chloride (11) is not strictly diffusion controlled although the potential of the system is large.

Since an extensive treatment of heterogeneous reactions is beyond the scope of this investigation, the reader is referred to the works of Moelwyn-Hughes (6) and Amis (12) for a more general picture of the field.

Having reviewed the basic theories of heterogeneous reactions in general, we may proceed to a discussion of the reaction with which this thesis is concerned.

As mentioned in the introduction, Pletenev and Pavlov (1) have studied the behavior of copper in dilute solution of ferric chloride. Their results showed, that up to a ferric chloride concentration of 0.05 molar, the reaction rate was controlled by the rate of diffusion of ferric ion. At higher concentrations of ferric chloride, however, the reaction rate decreased, a fact which 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 of ferric ions by coating the copper surface with different thicknesses of gelatin. This technique demonstrated that the velocity of reaction decreased proportionately to the thickness of the layer.

King and Weidenhammer (2) investigated the dissolution of copper in both ferric chloride and ferric nitrate by rotating a copper cylinder in these reagents and measuring the weight loss of copper as a function of time. They found that the kinetics of the reaction were first order with respect to ferric chloride up to a concentration of 0.15 molar and that the rate was directly proportional to the speed at which the cylindrical copper sample was rotated in the solution. These investigators found that the rate of reaction in ferric chloride was thirty per cent higher than in ferric nitrate, a fact which was thought to be due to the formation of iron-chloride complex ions. The speed of rotation of the copper sample also proved to be important. At high rotational speeds the copper remained bright, but at low speeds a red film resembling cuprous oxide formed even when there was considerable hydrochloric acid present. The addition of hydrochloric acid or potassium chloride had less effect on the reaction in ferric nitrate than in ferric chloride, a fact which gives added credence to the theory of the formation of iron-chloride complexes mentioned above. Some indication of a slight autocatalytic effect due to dissolved copper ions can be deduced from the fact that the zero order reaction rate increased some seven per cent over a twelve-minute period. A decrease in direct proportion to the increase in viscosity of the solution, an increase which was effected by the addition of cane sugar. These same authors also found a very low temperature coefficient for the reaction. From these data they concluded that the rate of dissolution of copper in ferric ion solutions is largely controlled by the diffusion of the ferric ion to the copper surface. These same authors, from their values of the rate constant of the reaction and the value of the diffusion coefficient for the ferric ion, calculated a value for the thickness of the so-called Nernst diffusion layer. The value of 4.6 microns, thus arrived at, is somewhat unreasonable, if one takes into account the rotational speeds of 1500 revolutions per minute used in these experiments.

Szabo (13) has suggested that, in an oxidizing environment, the dissolution of copper in acids would proceed at a speed dependent upon the rate at which the adsorbed cuprous ion would oxidize at the copper surface. He derived equations based on this mechanism which would relate the increase in reaction with the concentration of hydrogen and chloride ions and also with the concentration of cupric ions produced. Unfortunately, Szabo gives very little experimental data to support this mechanism.

Gokhale (14) reports 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. However, this was not a strictly kinetic study.

The above summary practically exhausts those references which specifically mention the copper-ferric chloride reaction. However, if one assumes that this reaction has a mechanism comparable to that of other similar reactions, other literature references which will aid in determining the character of the copper-ferric chloride reactions can then be cited.

Hochberg and King (15) present the results of a survey of the action of various quinones and dyes as reagents in acid solution upon the dissolution of cadmium, zinc, and copper. They maintain that the reaction of copper in acetic acid, utilizing benzoquinone as a depolorizing agent, is neither rapid enough to be diffusion controlled nor slow enough to be chemically controlled. They found that the reaction was first order with respect to benzoguinone concentration and described the reaction as being both diffusion and chemically controlled.

Halpern (16) investigated the kinetics of the reaction of copper in aqueous ammonia over a wide range of ammonia and ammonium ion concentrations as well as oxygen pressures and stirring velocities. At low oxygen pressure, the rate was determined by the rate of transport of oxygen to the surface, but when the oxygen pressure was increased, the chemical reaction at the surface became the rate controlling step. At this point, two reactions were found to proceed simultaneously and with independent rates, which were first order with respect to the concentrations of ammonia and ammonium ions. At high oxygen pressures, no dependence upon the stirring velocity was found.

Hill (17) studied the kinetics of the initial rate of dissolution of copper in aqueous solutions of potassium chloride at a pH of about 8.5 and found that in solutions more acidic that a pH of 7.0 the reaction product dissolved from the surface as fast as was formed. At a higher pH, an impervious film formed. However, if acetate ions were added, they were preferentially adsorbed on the copper and thus prevented the formation of the film.

The reaction of copper with sulfuric acid solutions was studied by Benjamin et al. (18), and a mechanism was proposed in which the rate controlling step was the oxidation of cuprous ions at the solution-copper interface. The variation of rate with stirring speed was only eight per cent from 250 to 4800 revolutions per minute, which seemed to eliminate the possibility that the rate was controlled by the removal of cupric ions by diffusion. These workers also showed that the acidity of the solution had little effect on the rate of reaction for any pH less than one.

The reaction of copper with ferric ions could be regarded as a reaction between ions of like charge if diffusion effects are not significant, since the metallic copper would acquire a positive charge during the course of the reaction. It is interesting to note that Duke and Pinkerton (19) used a similar treatment to that used in this work to explain the homogeneous reaction of iron (III) and tin (II) in the presence of chloride ions.

Perhaps more closely related to the present investigation is the exchange reaction of iron (III) with iron (II). Dodson and Silverman (20), using a technique involving isotopes of iron to study this reaction, found that the iron (III) dichloro-complex reacted more rapidly than did the iron (III) monochloro-complex. They suggested an activated complex consisting of a chlorine bridge between the iron (III) and iron (II) ions and that the reaction path involved a halogen transfer rather than an electron transfer. They cite the principle of microscopic reversibility as a strong argument for the reaction's proceeding by atom transfer in this case. However, the rate law of a reaction can determine the composition of the activated complex but cannot distinguish between an atom transfer or an electron transfer mechanism.

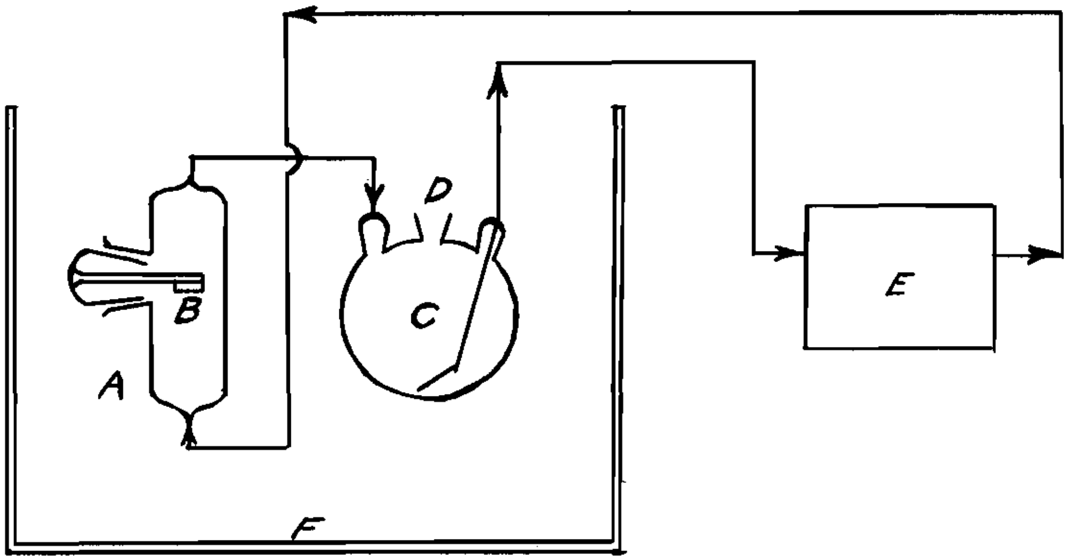
CHAPTER III

EXPERIMENTAL

Kinetic runs were made in an apparatus that was especially designed to minimize the physical effects of stirring. This apparatus differs from usual apparatus mentioned in the literature in that a circulating system was used instead of the usual practice of rotating a cylinder of the metal in the reaction solution. It was felt that a circulating system would not have the surface heat effects of the usual procedure.

The apparatus used in this work is diagrammed in Fig. 1 and consisted of a reaction cell, solution reservoir, and a circulating pump. One-quarter inch diameter gum rubber tubing was used to connect the various units and was kept as short as possible to reduce the amount of solution held in the connections. Circulation was provided by a Sigmamotor tubing pump which had a capacity of 450 milliliters per minute. At this pumping rate, the dimensions of the reaction cell were such as to provide a change in contents every half minute and a linear velocity in the cell of 19 centimeters per minute. The bottom of the cell was filled with short glass rods to distribute the flow of liquid uniformly throughout the cell. When in operation the reaction cell held a volume of 215 milliliters of solution. In all runs a copper sample of 1.61 square centimeters was used and was mounted on the sample holder with a rubber base cement.

Stock solutions of ferric chloride, ferric sulfate, and calcium chloride were prepared by accurately weighing a known amount of reagent and dissolving it in a measured volume of distilled water. All of these



A is the reaction cell enclosing the copper sample, B. The solution flows through the reaction cell and returns to the solution reservoir, C, provided with a port, D, from which solution samples were withdrawn. Circulation was provided by a Sigmamotor tubing pump at E. With the exception of the pump, the entire system was immersed in a constant temperature bath, F.

Fig. 1. Experimental Apparatus

solutions were approximately 4.0 molar. After standardization, these stock solutions were diluted to the desired concentration for each kinetic run as needed.

Stock solutions of ferric chloride and ferric sulfate were standardized by measuring the specific gravity with a Westphal balance and determining the concentrations from the data given in the Handbook of Chemistry (21). This standardization was further checked by measuring the optical density of a diluted aliquot at a wave length of 400 millimicrons in a Beckman Model DU spectrophotometer. The concentration was read directly from a previously determined calibration curve. The two methods of standardization agreed within the experimental error. Calcium chloride solutions were used as prepared with no further standardization.

Analysis for cupric ion in solution was made by a spectrophotometric method developed by Giesecke (22), which has the advantage that ferric and ferrous ions do not interfere and analysis of the reaction mixture could be made directly by a very simple procedure. The analysis makes use of the strong absorption of the colored cupric chloride complex at a wave length of 970 millimicrons which is reported to be very stable and free from interferences.

A calibration curve of the optical density of several known concentrations of cupric ions was determined by a series of dilutions of a 1.0 molar solution of cupric chloride. Preliminary dilutions were made with distilled water and the final dilution in every case was 10 milliliters of solution diluted to 50 milliliters with concentrated hydrochloric acid. The absorption of each sample was measured in a Beckman Model DU spectrophotometer at 970 millimicrons, using concentrated hydrochloric acid as a reference. The original solution of cupric chloride was made by accurately weighing one mole of $CuCl_2 \cdot 2\ H_2O$, dissolving it in distilled water, and diluting to one liter in a volumetric flask.

Samples, each ten milliliters in volume, taken from the kinetic runs, were analyzed by diluting to fifty milliliters with concentrated hydrochloric acid and measuring the optical density at 970 millimicrons without further treatment. From the measured optical density of the sample, the concentration in moles per liter was read from the calibration curve.

Kinetic runs were made under initial rate conditions. Starting with 500 milliliters of ferric chloride solution, the changes in concentration, after a typical run of eighty minutes, were at most 1.0×10^{-2} moles per liter and were insignificant compared to the total concentration.

A typical kinetic run was made by placing the ferric chloride solution in the reservoir and immersing it, together with the reaction cell, in the water bath. The copper sample was dipped into a mixture of ferric chloride and hydrochloric acid to remove any surface films, and carefully washed and dried before it was placed in the reaction cell. After thermal equilibrium was established and a ten milliliter sample of the initial solution was taken, the circulating pump was started. Timing was begun when the circulating solution first reached the surface of the copper sample. Every twenty minutes a ten milliliter sample was withdrawn in a pipette, diluted to fifty milliliters with concentrated reagent grade hydrochloric acid and saved for later analysis for cupric ions. The reaction was continued for a total of eighty minutes except that, in the few cases where it was slow, the total time was extended to one-hundred and twenty minutes.

A plot of the concentration of cupric ion in moles per liter versus the time of reaction in minutes gave a straight line in all runs. The slope of this graph divided by the area of the copper sample in square centimeters was equal to the initial rate of reaction at the given starting concentration of ferric chloride.

A series of runs was made in which the ferric ion concentration was kept 1.0 molar and the chloride concentration was varied by mixing 1.0 molar solutions of ferric chloride and ferric sulfate in the proper proportions. Calcium chloride was added to 1.0 molar solutions of ferric chloride in a few runs to obtain chloride concentrations greater than 3.0 molar.

CHAPTER IV

DISCUSSION OF RESULTS

The series of experiments in which the ferric chloride concentration was varied is summarized in Table 1. Rates are given in units of moles per liter per minute per square centimeter of surface area and correspond to the pseudo-zero-order specific rate constant shown in the second column of that table. When these rates are plotted against the total ferric chloride concentration, the points of Fig. 2 are obtained.

Table 1.

Dependence of Rate Upon $FeCl_3$ Concentration
(Temperature - 25°C)

$FeCl_3$ Moles/Liter	$k \times 10^7$ Moles/Liter--Min.--Cm^2
0.45	2.02
0.62	2.50
0.90	3.91
1.00	4.58
1.24	5.64
1.50	6.02
1.86	6.81
2.00	6.21
2.17	6.87
2.38	6.02
2.50	7.08
3.00	5.62
3.33	4.29

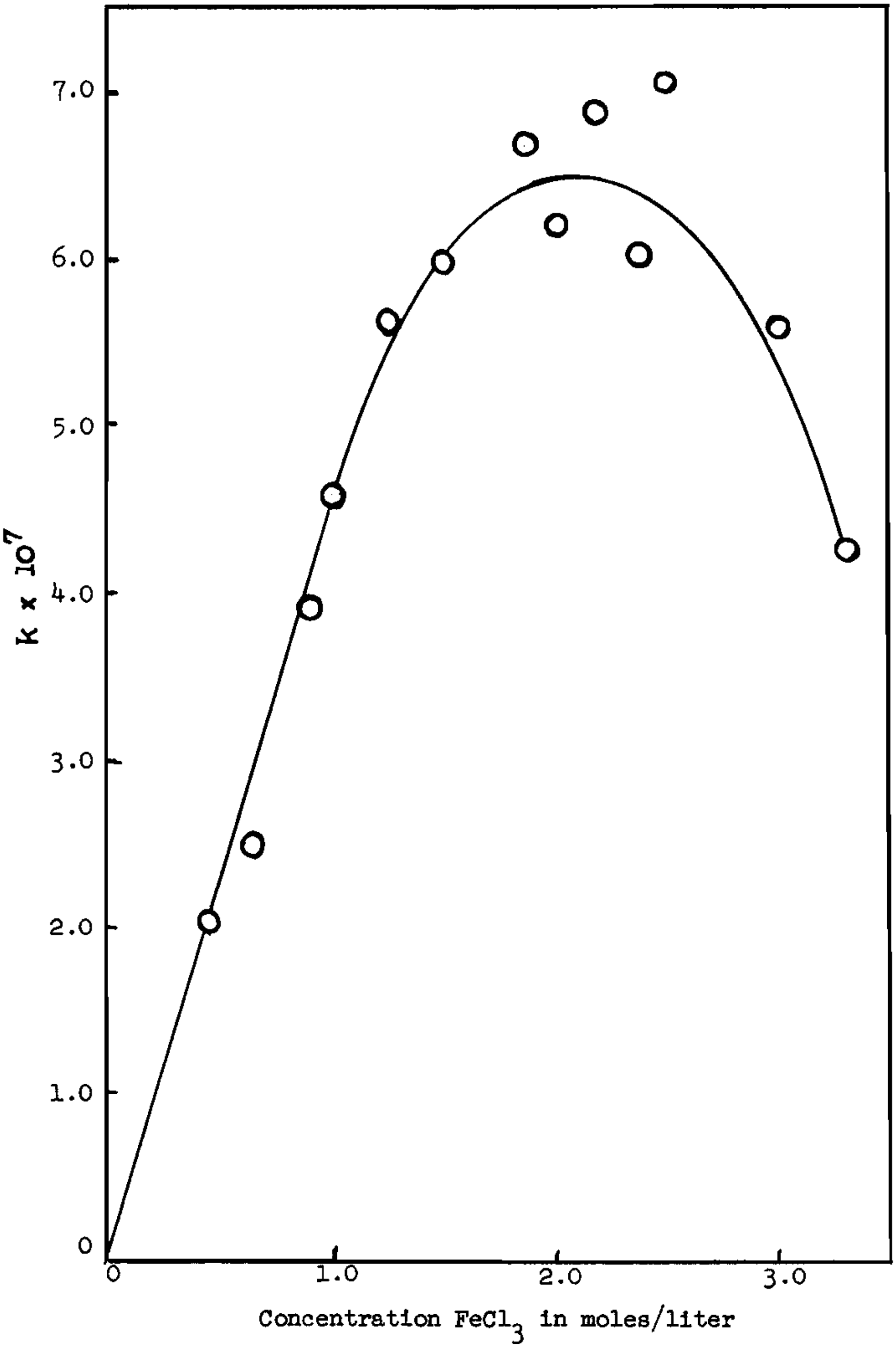


Fig. 2. Dependence of Rate Upon $FeCl_3$ Concentration

Inspection of Fig. 2 shows that the rate is first order with respect to the ferric chloride up to a concentration of 1.2 molar. At higher concentrations, the rate reaches a maximum and drops sharply with increasing concentration.

These results were interpreted to mean either that the mechanism of the reaction changes in concentrated solutions or that the reacting species is reduced by complex ion formation and changes in activity coefficient although the total concentration of ferric chloride is increased.

If the mechanism of the reaction changes as the concentration of ferric chloride increases, the energy of activation for the reaction should be different at two widely separated concentrations. The results of the change in rates with temperature are shown in Table 2 for two ferric chloride concentrations.

Table 2.

Dependence of the Rate Upon Temperature

$FeCl_3$ Moles/Liter	$k \times 10^7$ Moles/Liter--Min.--Cm^2	Temp. ^oC
1.0	4.58	25
1.0	4.72	31
1.0	5.00	38
2.5	7.08	25
2.5	7.58	38

The activation energies in the Arrhenius equation may be calculated from the overall specific rate constants given in Table 2. Their values are listed in Table 3.

Table 3.

Activation Energies

$FeCl_3$ Moles/Liter	$E_{Act.}$ Calories
1.0	1,210
2.5	990

As shown in Fig. 2, the value for the rate at 25° C. and 2.5 molar ferric chloride is considered somewhat high and a slight lowering of this value would bring the activation energy at 2.5 molar in line with the value at 1.0 molar. Therefore, the change in activation energy for the two concentrations is not considered significant enough to indicate a change in mechanism.

It is interesting to note that the value of the activation energy is even lower than the generally accepted value of 5 kilocalories predicted for a strictly diffusion controlled reaction (5).

Ferric ions are known to form a series of complexes with chloride ions and to hydrolyze in aqueous solutions. Investigation of the absorption spectra of ferric chloride solutions by Rabinowitch and Stockmayer (23) revealed that at chloride concentration of half formal an appreciable fraction of the ferric ions exist as $FeCl_2^+$ as well as $FeCl^{+2}$ and that $FeCl_3$ becomes important at higher concentrations. At the concentrations involved in the present work, all the species Fe^{+3}, $FeOH^{+2}$, $FeCl^{+2}$, $FeCl_2^+$ and $FeCl_3$ must be considered.

The above considerations lead to the rate expression:

$$\text{Rate} = k_1 \left[Fe^{+3}\right] + k_2 \left[FeOH^{+2}\right] + k_3 \left[FeCl^{+2}\right] + k_4 \left[FeCl_2^{+}\right] + k_5 \left[FeCl_3\right] \qquad (1)$$

Since sulfate ions have little tendency to form complexes with ferric ions, the rate at which copper reacts in ferric sulfate should give the overall value of k_1 and k_2 in the above rate equation.

Three runs were made using ferric sulfate but only one was considered reliable since the copper sample dropped from its holder during the course of the first two runs. The rate of reaction appears to be first order with respect to the concentration of ferric ions. At 25° C., an overall rate constant of 1.89×10^{-7} moles per liter per minute per square centimeter was obtained at a ferric sulfate concentration of 1.0 molar. The rate is 41.2 per cent slower than the corresponding rate in ferric chloride and hence supports the assumption that the chloride ion has a specific effect upon the reaction in addition to any effects caused by its influence upon the ionic atmosphere of the reaction.

The pH was approximately 1.0 in all kinetic runs with no added acids and the concentration of hydrogen ions was considered constant. On the basis of this assumption, the first two terms of equation (1) become a function only of the ferric ion concentration and may be written as follows:

$$\left[Fe^{+3}\right] \left\{ k_1 + \frac{k_2 \; k_h}{[H^+]} \right\} = k^1 \left[Fe^{+3}\right] \qquad (2)$$

where K_h is the equilibrium constant for the species FeOH and k^1 is the overall rate constant as determined in the reaction of copper with ferric sulfate and is equal to 1.89 x 10^{-7} moles per liter per minute per square centimeter.

Equation (1) then becomes:

$$\text{Rate} = k^{1}\left[Fe^{+3}\right] + k_3\left[FeCl^{+2}\right] + k_4\left[FeCl_2^{+}\right] + k_5\left[FeCl_3\right] \qquad (3)$$

The concentrations of the ferric-chloro complexes may be replaced by terms involving only ferric and chloride ions through the use of the following equilibrium constants:

$$K_1 = \frac{\left[FeCl^{+2}\right]}{\left[Fe^{+3}\right]\left[Cl^{-}\right]} \qquad (4)$$

$$K_2 = \frac{\left[FeCl_2^{+}\right]}{\left[FeCl^{+2}\right]\left[Cl^{-}\right]} \qquad (5)$$

$$K_3 = \frac{\left[FeCl_3\right]}{\left[FeCl_2^{+}\right]\left[Cl^{-}\right]} \qquad (6)$$

Upon substitution into equation (3) and rearranging, the rate expression becomes:

$$\text{Rate} = \left[Fe^{+3}\right]\left\{k^{1} + k_3\ K_1\left[Cl^{-}\right] + k_4K_1K_2\left[Cl^{-}\right]^2 + k_5K_1K_2K_3\left[Cl^{-}\right]^3\right\} \qquad (7)$$

The equilibrium constants used in the rate expression should be obtained independently of the kinetic study. Rabinowitch and Stockmayer (23) obtained the values $K_1 = 30$, $K_2 = 4.5$, and $K_3 = 0.1$, all at an ionic strength of zero. They found that the value of K_1 was quite sensitive to changes in the ionic strength of the solution and were able to obtain an equation relating K_1 to the ionic strength. However, such an equation for the other equilibrium constants was not determined and only the other values of $K_2 = 1.3$ and $K_3 = 0.04$ at ionic strength of 1.0 were given. Since the present investigation extended to solutions of ionic strength as high as 23, the values of K_2 at high ionic strength were approximated by assuming that the same type of equation relating K_1 to the ionic strength of the solution could be used for K_2 with suitable changes in the constants of the equation. A similar assumption could be made concerning K_3; however, the best correlation was obtained by using a constant value and the value, $K_3 = 0.04$, was used in all calculations.

Rabinowitch and Stockmayer (23) gave the following equation relating K_1 to the strength:

$$\log K_1 = 1.51 - \frac{3\sqrt{\mu}}{1 + 1.5\sqrt{\mu}} + 0.295\,\mu \qquad (8)$$

Comparison of this equation with the Debye-Huckel Equation[1] below shows the two equations to be equal if the average effective diameter of the complex ion, $FeCl^{+2}$, is taken to be equal to 4.56 Å.

$$\log K = \log K_o + \frac{2AZ^+ Z^- \sqrt{\mu}}{1 + aB\sqrt{\mu}} + C\,\mu \qquad (9)$$

---

[1] As given in Glasstowe, Textbook of Physical Chemistry, D. Van Nostrand Co., New York, (1946), p. 967.

where: $A = 0.509$ for water at 25° C.
$B = 3.29 \times 10^7$ electrostatic units.
$K_o =$ Ionization constant at $\mu = 0$.
$Z =$ Ionic charge.
$a =$ Average effective diameter.
$c =$ Empirical constant.

An average effective diameter for the complex ion $FeCl_2^+$ was estimated as 7.0 Å based upon a linear (d^2 or sp) configuration and using a value of 2.44 Å for the diameter of the chloride ion as a compromise between the ionic diameter of 3.62 Å and the covalent diameter of 1.98 Å as given by Pauling (24). Using the value of 7.0 Å for the diameter and the two values of Rabinowitch and Stockmayer (23) in equation (9), 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:

$$\log K_2 = 0.653 - \frac{2\sqrt{\mu}}{1 + 2.3\sqrt{\mu}} + 0.097\mu. \qquad (10)$$

The values of K_1 and K_2 as calculated from equations (8) and (10) are shown in Table 9 in the appendix, together with the concentrations at which they are applicable.

It still remains to obtain expressions for the concentrations of ferric and chloride ions in terms of the total concentration of the solution. The concentration of ferric ions may be obtained by the following series of equations:

$$\begin{aligned}[Fe^{+3}]_o = {} & [Fe^{+3}] + [FeOH^{+}] + [FeCl^{+2}] \\ & + [FeCl_2^{+}] + [FeCl_3], \end{aligned} \qquad (11)$$

$$\left[Fe^{+3}\right]_o = \left[Fe^{+3}\right] \left\{1 + \frac{Kh}{[H^+]} + K_1 \left[Cl^-\right] + K_1K_2\left[Cl^-\right]^2 + K_1 K_2 K_3 \left[Cl^-\right]^3\right\}, \tag{12}$$

where $\left[Fe^{+3}\right]_o$ denotes the total concentration.

The quantity $\frac{Kh}{[H^+]}$ is considered negligible at the pH of the solutions used in this work since the value of the constant, K_h, is equal to 6×10^{-3} (23). Corresponding to this assumption, the final expression for the concentration of the ferric ion is

$$\left[Fe^{+3}\right] = \frac{\left[Fe^{+3}\right]_o}{1 + K_1 \left[Cl^-\right] + K_1K_2 \left[Cl^-\right]^2 + K_1K_2K_3 \left[Cl^-\right]^3} . \tag{13}$$

An expression for the concentration of the chloride ion may be obtained by a similar treatment to give

$$\left[Cl^-\right]_o = \left[Cl^-\right] + \left\{\frac{1 + 2\,K_2 \left[Cl^-\right] + 3\,K_2K_3 \left[Cl^-\right]^2}{1 + K_2 \left[Cl^-\right] + K_2K_3 \left[Cl^-\right]^2}\right\}\left[Fe^{+3}\right]_o \tag{14}$$

where $\left[Cl^-\right]_o$ denotes the total concentration. The actual free chloride ion concentration is found by a successive approximation method from equation (14).

Calculated values for the free chloride ion concentration at various total concentrations are listed in Table 10 in the Appendix.

Upon substituting the expression for the ferric ion concentration, the rate equation becomes

$$R = \left[Fe^{+3}\right]_o \left\{ \frac{k^1 + k_3K_1\left[Cl^-\right] + k_4K_1K_2\left[Cl^-\right]^2 + k_5K_1K_2K_3\left[Cl^-\right]^3}{1 + K_1\left[Cl^-\right] + K_1K_2\left[Cl^-\right]^2 + K_1K_2K_3\left[Cl^-\right]^3} \right\}. \tag{15}$$

Denoting by G the following expression, which contains only measured or calculable quantities,

$$G = \frac{R\left\{1 + K_1\left[Cl^-\right] + K_1K_2\left[Cl^-\right]^2 + K_1K_2K_3\left[Cl^-\right]^3\right\} - k^1\left[Fe^{+3}\right]_o}{K_1\left[Cl^-\right]\left[Fe^{+3}\right]_o} \tag{16}$$

We obtain the final rate equation

$$G = k_3 + k_4K_2\left[Cl^-\right] + k_5K_2K_3\left[Cl^-\right]^2 . \tag{17}$$

At low chloride ion concentrations, the $k_5K_2K_3\left[Cl^-\right]^2$ term in equation (17) should be small since K_3 is small and, hence, a graph of the function, G, plotted against $K_2\left[Cl^-\right]$ should be linear with an intercept equal to k_3. In Table 4, the values of G and $K_2\left[Cl^-\right]$ up to a ferric chloride concentration of 1.0 molar are summarized and these values are plotted in Fig. 3. From the intercept of Fig. 3, k_3 was found to be 3.2×10^{-7}.

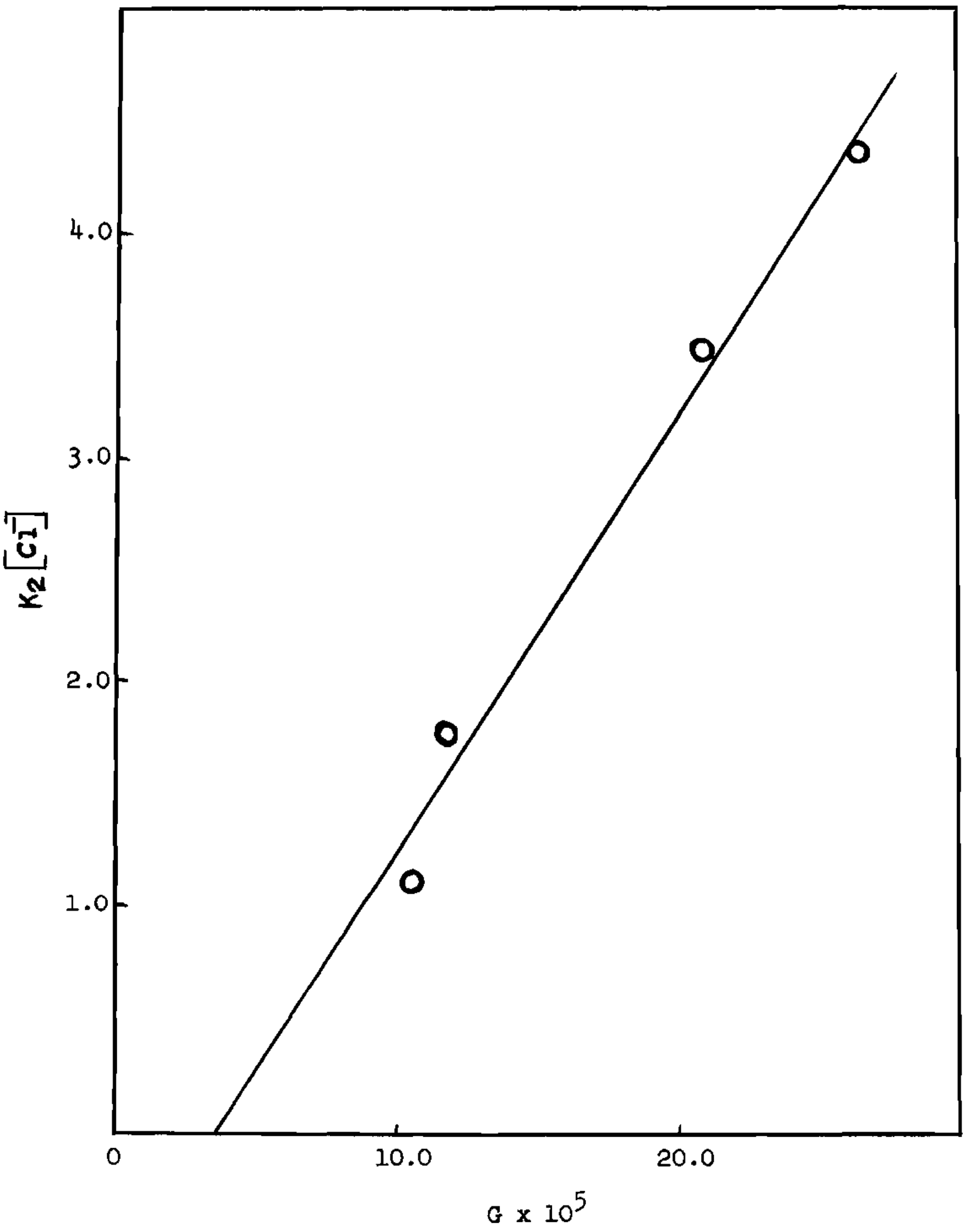


Fig. 3. Dependence of the Function, G, Upon $K_2\left[Cl^-\right]$

Table 4.

Dependence of the Function, G, Upon $K_2 \left[Cl^-\right]$

$FeCl_3$ Moles/Liter	$K_2 \left[Cl^-\right]$	$G \times 10^7$
0.45	1.18	10.3
0.62	1.78	11.6
0.90	3.47	20.1
1.00	4.38	25.6

Using this value of the constant, k_3, and denoting by F the following expression,

$$F = \frac{G - k_3}{K_2 \left[Cl^-\right]} = k_4 + k_5 K_3 \left[Cl^-\right] \qquad (18)$$

the values of the two remaining constants, k_4 and k_5, were determined by plotting the function, F, against the chloride concentration. The calculated values for F together with the corresponding concentrations of ferric chloride and free chloride ion are presented in Table 5 and are plotted in Fig. 4.

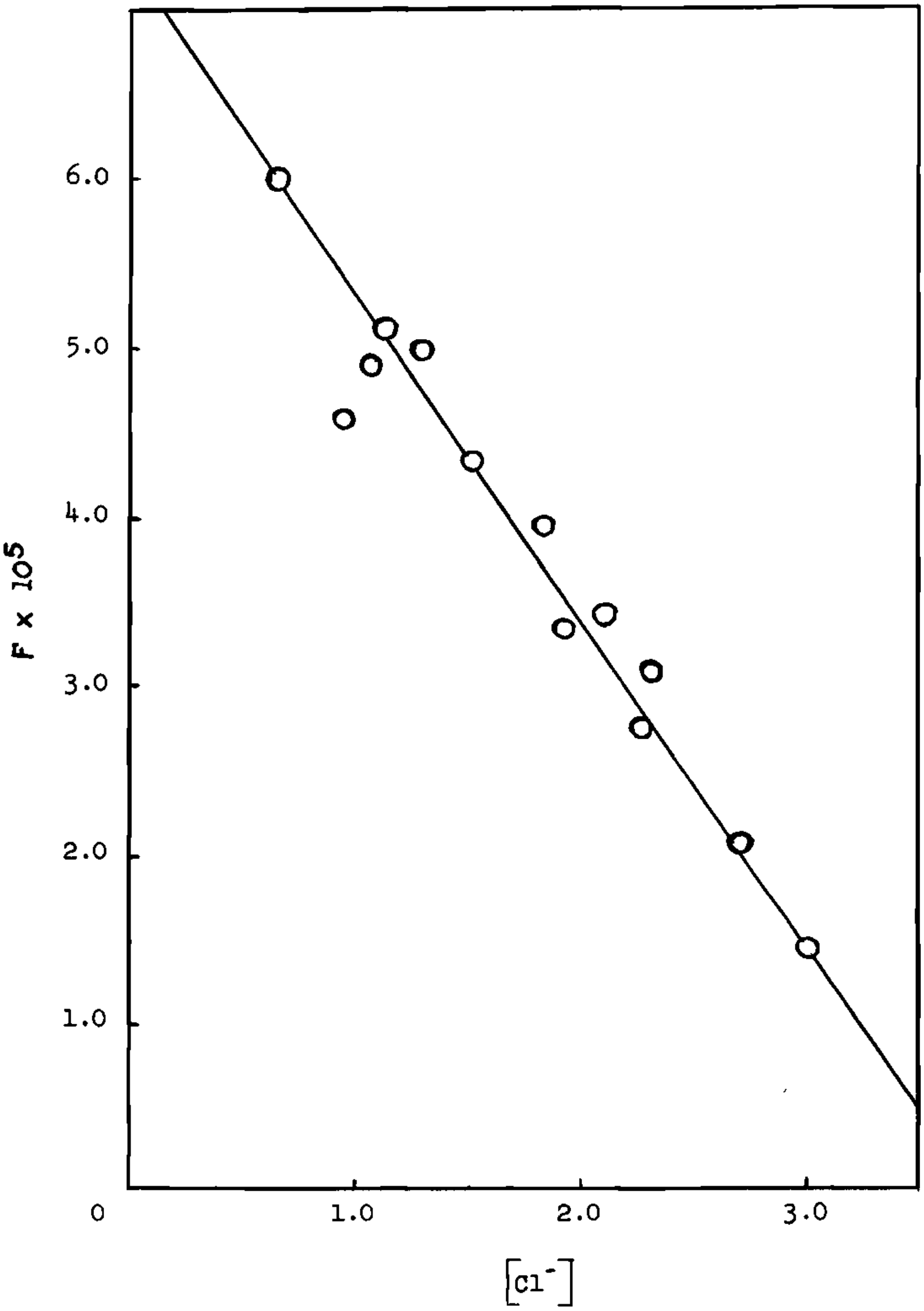


Fig. 4. Dependence of the Function, F, Upon the Chloride Ion Concentration

Table 5.

Dependence of the Function, F, Upon the Chloride Ion Concentration

$FeCl_3$ Moles/Liter	$[Cl^-]$ Moles/Liter	$F \times 10^7$
0.45	0.65	6.02
0.62	0.79	4.72
0.90	1.05	4.87
1.00	1.15	5.12
1.24	1.31	4.97
1.50	1.50	4.33
1.86	1.80	3.94
2.00	1.90	3.34
2.17	2.10	3.43
2.38	2.25	2.75
2.50	2.30	3.09
3.00	2.70	2.07
3.33	3.00	2.44

From the intercept of Fig. 4, k_4 was found to be equal to 7.2×10^{-7} and from the slope, k_5 was calculated to be -48.7×10^{-7}.

This gives the final equation

$$\begin{aligned} k = 1.89 \times 10^{-7} [Fe^{-3}] + 3.2 \times 10^{-7} [FeCl^{+2}] \\ + 7.2 \times 10^{-7} [FeCl_2^+] - 48.7 \times 10^{-7} [FeCl_3] \end{aligned} \tag{19}$$

from which the overall specific rate constant may be obtained. The concentrations of each reacting species in the above equation are summarized in Table 6 and were calculated from the values of the equilibrium constants in Table 9 and from the values of the ferric and chloride ion concentrations in Table 10. The calculated rate constants so obtained are listed in Table 7 for comparison with the corresponding experimental rate constants.

Table 6.

Concentration of Reacting Species at Various Ferric Chloride Concentrations
(Temperature - 25° C)

Total Concentration $FeCl_3$ Moles/Liter	$FeCl^{+2}$ Moles/Liter	$FeCl_2^{+}$ Moles/Liter	$FeCl_3$ Moles/Liter
0.45	0.195	0.223	.005
0.62	0.214	0.381	.012
0.90	0.194	0.673	.028
1.00	0.180	0.790	.036
1.24	0.146	1.04	.054
1.50	0.110	1.31	.079
1.86	0.068	1.67	.120
2.00	0.057	1.80	.137
2.17	0.043	1.97	.165
2.38	0.032	2.15	.194
2.50	0.028	2.27	.209
3.00	0.013	2.70	.291
3.33	0.008	2.97	.356

Table 7.

Comparison of Experimental and Calculated Rate Constants

$FeCl_3$ Moles/Liter	$k \times 10^7$ Exper.	$k \times 10^7$ Calc.	Per Cent Deviation
0.45	2.02	2.04	0.98
0.62	2.50	2.87	1.29
0.90	3.91	4.12	0.51
1.00	4.58	4.52	-0.01
1.24	5.64	5.31	-0.62
1.50	6.02	5.95	-0.01
1.86	6.81	6.42	-0.62
2.00	6.21	6.50	0.46
2.17	6.87	6.26	-0.96
2.38	6.02	6.15	0.21
2.50	7.08	6.25	-1.33
3.00	5.62	5.29	-0.62
3.33	4.29	4.05	-0.59

The values for the specific rate constants in the series of kinetic runs in which the ferric concentration was held constant at 1.0 molar and the chloride concentration varied are listed in Table 8.

Table 8.

Dependence of Rate Upon Chloride Ion Concentration
(Fe^{+3} = 1.0 molar)

Free Chloride Ion Moles/Liter	$k \times 10^{+7}$
0.16	2.57
0.45	4.09
1.15	4.58
2.00	4.81
2.50	5.38
2.70	5.07
2.90	4.24

These data could not be correlated with the previous rate equation. However, if a value of $k_3 = 4.0 \times 10^{-7}$ and $k_5 = 20.0 \times 10^{-7}$ were used in the rate expression, a fair agreement of the data with the calculated values can be obtained.

It should be mentioned that a close agreement of this series of experiments to the rate equation for ferric chloride alone was not expected for several reasons. In order to keep the ferric ion constant and vary the chloride ion concentration, ferric chloride was added to ferric sulfate to obtain chloride concentrations less than 3.0 molar and calcium chloride was added to ferric chloride to obtain chloride concentration above 3.0 molar. Hence, in addition to ferric and chloride ions, sulfate ions were present in some solutions while calcium ions were present in others. These ions would influence the ionic atmosphere of the reaction by an inert salt effect. In addition, King and Lange (10) reported a shift in the absorption spectra of ferric perchlorate solutions upon the addition of sulfate ions, suggesting a possible complex ion formation. Such a complex would have to be considered in any rate expression. Secondly, it was tacitly assumed in the derivation of equation (19) that the specific rate constants did not change with a change in the ionic strength of the solution. In general this change is small compared to other effects; however, the rates in two different experiments should not be compared if the ionic strength of the solutions were different even though the concentration of the reacting species were the same.

As mentioned in the historical discussion, Dodson and Silverman (20) used a similar treatment to explain the exchange reaction between iron (III) and iron (II) and postulated a mechanism involving a halogen transfer.

In the present work, the greater reactivity of the $FeCl_2^+$ compared to $FeCl^{+2}$ and Fe^{+3} and the second order dependence on chloride ion at some concentrations was taken to mean that the intermediate complex involves two chloride ions. If the reaction proceeds by an electron transfer, the iron (II) would be in the form of the unlikely species $FeCl_2$. Also the cuprous ion formed in the presence of chloride ion would precipitate as the insoluble cuprous chloride which would retard the reaction. On the other hand, if the complex involves a chlorine bridge and the reaction proceeds through the transfer of a species, Cl_2^-, the soluble complex $CuCl_2^-$ would be immediately formed. At the same time, the atom transfer path would require no association of iron (II) and chloride ions in an unlikely complex. The postulation of a chlorine transfer does not require the production of a species, Cl_2^-, in the solution, an event which would be unlikely from an energy consideration. Therefore, from these arguments, the reaction path in which a species, Cl_2^-, is transferred does not seem improbable.

The inhibiting effect of $FeCl_3$ may be explained by the reduction in the oxidation potential of the ferric ion through complexing with the chloride ion to the point reached in $FeCl_3$ where the potential is not sufficient to oxidize copper. The nonreacting $FeCl_3$ accummulates at the phase boundary increasing the diffusion barrier through which the reacting species must diffuse. It should also be remembered that the concentration of $FeCl_3$ is increased at the expense of reducing the relative concentrations of the reacting species $FeCl_2^+$ and $FeCl^{+2}$.

The low value for the activation energy of the reaction supports the idea that there is a diffusion controlled mechanism. Activation energies for chemically controlled reactions are in general of the order of thirty kilocalories while those for a diffusion process are of the order of five kilocalories. The value of one kilocalorie for the present work is not strictly an energy of activation but is a composite term which includes the effect of temperature upon the equilibrium constants of the complex ions. Without further information about the effect of temperature upon the equilibrium constants, the terms may not be separated and the true activation energy for the reaction, therefore, is not known.

CHAPTER V

CONCLUSIONS

The reaction of copper with ferric chloride solutions was found to be controlled by the rate at which the reactants diffuse to the surface of the copper. Ferric-chloro complexes, $FeCl^{2}$ and $FeCl_2$, were found to react independently at different rates, while the complex $FeCl_3$ produced an inhibiting effect. An activation energy for the reaction of 1.0 to 1.2 kilocalories was obtained. In the presence of sulfate and calcium ion, the reactant did not follow the same rate law as in ferric chloride alone. The experimental data was correlated by the following rate equation:

$$k = 1.89 \times 10^{-7}\left[Fe^{+3}\right] + 3.2 \times 10^{-7}\left[FeCl^{+2}\right] + 7.2 \times 10^{-7}\left[FeCl_2^{+}\right]$$

$$- 48.7 \times 10^{-7}\left[FeCl_3\right].$$

APPENDIX

Table 9.

Values of the Equilibrium Constants, K_1 and K_2

$FeCl_3$ Moles/Liter	K_1	K_2
0.45	9.48	1.81
0.62	1.86×10^1	2.25
0.90	5.89×10^1	3.30
1.00	9.12×10^1	3.81
1.24	2.63×10^2	5.41
1.50	8.51×10^2	7.94
1.86	4.37×10^3	1.36×10^1
2.00	8.13×10^3	1.68×10^1
2.17	1.82×10^4	2.17×10^1
2.38	4.68×10^4	2.96×10^1
2.50	6.46×10^4	3.57×10^1
3.00	8.51×10^4	7.68×10^1
3.33	3.80×10^5	1.27×10^2

Table 10.

Concentrations of Free Ferric and Chloride Ions.

$FeCl_3$ Moles/Liter	Fe^{+3} Moles/Liter	Cl^- Moles/Liter
0.45	3.08×10^{-2}	0.65
0.62	1.53×10^{-2}	0.79
0.90	3.14×10^{-3}	1.05
1.00	1.72×10^{-3}	1.15
1.24	4.25×10^{-4}	1.31
1.50	8.63×10^{-5}	1.50
1.86	8.68×10^{-6}	1.80
2.00	3.66×10^{-6}	1.90
2.17	1.13×10^{-6}	2.10
2.38	3.07×10^{-7}	2.25
2.50	1.86×10^{-7}	2.30
3.00	5.66×10^{-8}	2.70
3.33	6.83×10^{-8}	3.00

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