CIRCULAR 112

The Dissolution of Chalcocite in Oxygenated Sulfuric Acid Solution

by WALTER W. FISHER and RONALD J. ROMAN,

STATE BUREAU OF MINES AND MINERAL RESOURCES
NEW MEXICO INSTITUTE OF MINING AND TECHNOLOGY
CAMPUS STATION SOCORRO, NEW MEXICO

NEW MEXICO STATE

BUREAU OF MINES AND MINERAL RESOURCES

Don H. Baker, Jr., *Director*

A Division of

NEW MEXICO INSTITUTE OF MINING & TECHNOLOGY

Stirling A. Colgate, *President*

PRINTED 1971

For sale by the New Mexico Bureau of Mines and Mineral Resources
Campus Station, Socorro, N. Mex. 87801—Price $0.50

ABSTRACT

In the oxidative dissolution of chalcocite (Cu_2S) in oxygenated sulfuric acid solution under ambient conditions, the only reaction found in the dissolution process is

$$Cu_2S + 1/2\ O2 + 2H^+ = CuS + Cu^2 + H_20$$

where CuS is a stable reaction product. The rate law governing the reaction is

$$R = k(P_{02})(H^+)(SO_4^{-2})^{-1.18}$$

The rate of reaction in the presence of NO_3^- and $C10_4^-$ ions is higher relative to the rate in SO_4^{-2} solutions. The presence of Cl^- and Br^- ions causes a 100-fold increase in rate relative to the rate in SO_4^{-2} solutions.

Reaction rate is a function of stirring speed up to 700 rpm. Surface area has a first-order effect on the reaction rate.

A proposed reaction mechanism consistent with the experimental results includes both physical and chemical processes, but the rate-controlling step is thought to be chemical.

INTRODUCTION

Although the dissolution of chalcocite in a variety of lixivants has been studied by many investigators (Sullivan, 1930; Warren, 1958; Stanczyk and Rampacek, 1966), none of the studies has completely defined the chemistry and mechanism of chalcocite dissolution, and in particular, the mechanism of dissolution in oxygenated acid solution has not been resolved. The importance of chalcocite as an ore mineral in copper leach dumps justifies a detailed study of its dissolution in oxygenated acid solution.

Sullivan (1930) studied the dissolution of chalcocite in acidified ferric sulfate and in oxygenated sulfuric acid solution under ambient conditions at several acid and ferric ion concentrations. He found that chalcocite is oxidized by acidified ferric sulfate in two distinct stages. Although he did not identify the secondary product, he proposed that chalcocite is oxidized to covellite and that the covellite oxidizes further to form free sulfur. Sullivan identifies free sulfur as the final solid reaction product. The dissolution of the intermediate product is slower than that of the original chalcocite. Sullivan's work on chalcocite dissolution in oxygenated sulfuric acid solution indicates that the rate of dissolution is much slower than the rate of dissolution in ferric sulfate.

Warren (1958) studied the leaching of chalcocite in oxygenated sulfuric acid solution in an autoclave at elevated oxygen pressures and temperatures. Like Sullivan, he found that chalcocite reacts in two distinct stages. He did not postulate a reaction sequence.

Stanczyk and Rampacek (1966) investigated the leaching of various copper sulfides in an autoclave at elevated temperature and oxygen pressure. They found by microscopic examination that leached chalcocite particles are coated with covellite. They proposed that chalcocite reacts in two stages in oxygenated acid solution and that covellite is the intermediate product.

Gerlach and Pawlek (1968) studied the leaching of several sulfide minerals in oxygenated sulfuric acid solution, and found that chalcocite leaches in two stages.

Kuxmann and Biallab (1969) studied the electrode potential and electrolytic dissolution of chalcocite. They suggested that CuS is the intermediate product of either electrolytic or chemical dissolution of chalcocite. Sato (1960) studied the dissolution of sulfide minerals using electrode potential measurements. He suggested that covellite is an intermediate in chalcocite oxidation.

The investigations of chalcocite dissolution show that chalcocite is oxidized and dissolved in two steps, although the reaction sequence has not been established and CuS has not been positively identified. The intermediate product of the oxidation is proposed to be CuS.

This study is to determine the reaction for the dissolution of chalcocite in oxygenated sulfuric acid solution, establish a general rate equation for this reaction, and describe a mechanism of chalcocite dissolution, based on a combination of thermodynamic, chemical, kinetic and physical studies.

ACKNOWLEDGMENTS

The authors are indebted to Drs. Clifford Keizer and Jacques Renault for their valuable suggestions and help during the preparation of the manuscript. This manuscript is a condensation of Dr. Walter Fisher's dissertation which was financially supported by the New Mexico Bureau of Mines and Mineral Resources.

THEORETICAL CONSIDERATIONS

The dissolution of chalcocite in an oxygenated aqueous environment can theoretically be accomplished by several different reactions represented by the equations

$$Cu_2S + \tfrac{1}{2}O_2 + 2H^+ = CuS + Cu^{+2} + H_2O \tag{1}$$

$$Cu_2S + O_2 + 4H^+ = 2Cu^{+2} + S^0 + 2H_2O \tag{2}$$

$$Cu_2S + 2\tfrac{1}{2}O_2 + 2H^+ = 2Cu^{+2} + SO_4^{-2} + H_2O \tag{3}$$

$$Cu_2S + O_2 + 2H^+ = CuO + Cu^{+2} + S^0 + H_2O \tag{4}$$

$$Cu_2S + \tfrac{1}{2}O_2 + 2H^+ = Cu^{+2} + Cu^0 + S^0 + H_2O \tag{5}$$

and

$$CuS + \tfrac{1}{2}O_2 + 2H^+ = Cu^{+2} + S^0 + H_2O \tag{6}$$

which are all thermodynamically feasible. Reaction products such as CuS, CuO, Cu , and are thermodynamically unstable in this system. However, thermodynamic stability is usually subject to kinetic restrictions, and reaction products that are unstable persist because their rate of reaction toward more stable products is slow. For this reason, a reaction equation should be based on thermodynamics, chemical stoichiometry, and identification of products.

Reaction Mechanism

Oxidation and dissolution of chalcocite in any oxygenated aqueous solution must account for both the reduction of oxygen and the oxidation of the mineral. Since the dissolution involves an aqueous solution-solid surface reaction, sorption and solid-state transformations must also be considered as part of the dissolution process.

The chemical studies of Sullivan (1930) and Warren (1958), the electrochemical investigations of Kuxmann and Biallab (1969), and Sato (1960), and the microscopic study of Stanczyk and Rampacek (1966), suggest that the dissolution of chalcocite occurs in the two steps given by equations (1) and (6). Since CuS or a CuS-like compound is observable, the rate of dissolution of the intermediate, CuS, must be slower than the rate of dissolution of Cu S. The rate of CuS dissolution may be slow enough to be considered negligible in this system, and therefore, it is postulated that the only reaction of importance is given by equation (1).

Latimer (1952), and Huffman and Davidson (1956) suggest that oxygen is reduced by ferrous iron through the reaction sequence given by the equations

$$\mathrm{Fe^{+2} + O_2 + H^+ = Fe^{+3} + HO_2} \tag{7}$$

$$\mathrm{Fe^{+2} + HO_2 + H^+ = Fe^{+3} + H_2O_2} \tag{8}$$

$$\mathrm{Fe^{+2} + H_2O_2 + H^+ = Fe^{+3} + OH + H_2O} \tag{9}$$

$$\mathrm{Fe^{+2} + OH + H^+ = Fe^{+3} + H_2O} \; . \tag{10}$$

It seems reasonable to assume that the reduction sequence of oxygen will be the same for both the oxidation of chalcocite and the oxidation of ferrous ion. Therefore, the oxygen-reduction sequence will be included in the chalcocite oxidation mechanism.

Using equation (1), sorption of oxygen on the mineral surface, the oxygen-reduction reaction sequence, and solid-state reactions, the reaction sequence given by equations (11) through (22) is proposed for the dissolution of chalcocite.

$$\mathrm{Cu_2S}\wr \;\xrightleftharpoons{\text{fast}}\; \mathrm{Cu_{2-x}S}\wr\,\mathrm{Cu^{+1}} \tag{11}$$

$$\mathrm{Cu_{2-x}S}\wr\,\mathrm{Cu^{+1}} + \mathrm{O_{2(aq)}} \;\xrightleftharpoons{\text{fast}}\; \mathrm{Cu_{2-x}S}\wr\,\mathrm{Cu^{+1}\text{--}O_2} \tag{12}$$

$$\mathrm{Cu_{2-x}S}\wr\,\mathrm{Cu^{+1}\text{--}O_2} + \mathrm{H^+} \;\xrightarrow{\text{slow}}\; \mathrm{Cu_{2-x}S}\wr\,\mathrm{Cu^{+2}\text{--}HO_2} \tag{13}$$

$$\mathrm{Cu_2S\;\;Cu_{2-x}S}\wr\,\mathrm{Cu^{+2}\text{--}HO_2} \;\xrightleftharpoons{\text{fast}}\; \mathrm{Cu_2S\;\;CuS}\wr\,\mathrm{Cu^{+1}\text{--}HO_2} + \mathrm{Cu^{+2}} \tag{14}$$

$$\mathrm{Cu_2S\;\;CuS}\wr\,\mathrm{Cu^{+1}\text{--}HO_2} + \mathrm{H^+} \;\xrightarrow{\text{fast}}\; \mathrm{Cu_2S\;\;CuS}\wr\,\mathrm{Cu^{+2}\text{--}H_2O_2} \tag{15}$$

$$\mathrm{Cu_2S\;\;CuS}\wr\,\mathrm{Cu^{+2}\text{--}H_2O_2} \;\xrightleftharpoons{\text{fast}}\; \mathrm{Cu_{2-x}S\;\;CuS}\wr\,\mathrm{Cu^{+1}\text{--}H_2O_2} + \mathrm{Cu^{+2}} \tag{16}$$

$$\mathrm{Cu_{2-x}S\;\;CuS}\wr\,\mathrm{Cu^{+1}\text{--}H_2O_2} + \mathrm{H^+} \;\xrightarrow{\text{fast}}\; \mathrm{Cu_{2-x}S\;\;CuS}\wr\,\mathrm{Cu^{+2}\text{--}OH} + \mathrm{H_2O} \tag{17}$$

$$\mathrm{Cu_2S\;\;Cu_{2-x}S\;\;CuS}\wr\,\mathrm{Cu^{+2}\text{--}OH} \;\xrightleftharpoons{\text{fast}}\; \mathrm{Cu_2S\;\;CuS\;\;CuS}\wr\,\mathrm{Cu^{+1}\text{--}OH} + \mathrm{Cu^{+2}} \tag{18}$$

$$\mathrm{Cu_2S\;\;CuS\;\;CuS}\wr\,\mathrm{Cu^{+1}\text{--}OH} + \mathrm{H^+} \;\xrightarrow{\text{fast}}\; \mathrm{Cu_2S\;\;CuS\;\;CuS}\wr\,\mathrm{Cu^{+2}} + \mathrm{H_2O} \tag{19}$$

$$\mathrm{Cu_2S\;\;CuS\;\;CuS}\wr\,\mathrm{Cu^{+2}} \;\xrightleftharpoons{\text{fast}}\; \mathrm{Cu_{2-x}S\;\;CuS\;\;CuS}\wr\,\mathrm{Cu^{+1}} + \mathrm{Cu^{+2}} \tag{20}$$

$$Cu_{2-x}S \quad CuS \quad CuS\wr Cu^{+1} + O_{2(aq)} \xrightleftharpoons{fast} Cu_{2-x}S \quad CuS \quad CuS\wr Cu^{+1}--O_2 \qquad (21)$$

$$\vdots$$

$$CuS \quad CuS \quad CuS \quad CuS\wr Cu^{+2} \xrightleftharpoons{fast} CuS \quad CuS \quad CuS \quad CuS\wr + Cu^{+2} \qquad (22)$$

The reaction mechanism implies that Cu^{+1} atoms diffuse from the interior of the Cu_2S particle, creating the physical situation shown in Figure 1. As the atoms diffuse out of the Cu_2S lattice and are oxidized to $Cu+^2$, a nonstoichiometric chalcocite of the form $Cu_{2-x}S$ is created. The factor x goes from 1 at the mineral surface to 0 at the unreacted Cu_2S boundary. This physical picture of the dissolution process is proposed on the basis of the existence of CuS as a stable reaction product.

Dutrizac, MacDonald, and Ingraham (1970) showed that when bornite is leached in acidified ferric sulfate solution, a non-reactive, bornite layer of the form $Cu_{5-x}FeS_4$ forms. Their electron microprobe examination of the edge of a leached bornite disk produced a picture similar to Figure 1 with CuS replaced by $Cu_{5-x}FeS_4$. They found a value of about 1. 2 for x.

Rate Equation

A reaction mechanism is not complete until the relative reaction velocities for each reaction in the sequence are established and a rate law consistent with experimental data has been derived from the mechanism. A reaction mechanism is made up of elementary reactions so that the stoichiometric coefficients of the reactants are the same as the order of the reaction with respect to each reactant. A theoretical rate equation can be derived from these elementary reactions by assigning relative reaction velocities to each step in the mechanism sequence.

If reactions (11) and (12) establish rapid equilibria and reaction (13) is rate controlling, the rate law governing the reaction is given by

$$R = k_{21}(H^+)(Cu_{2-x}S\wr Cu^{+1}--O_2) . \qquad (23)$$

The equilibrium relations for reactions (11) and (12) are given by

$$K_{11} = \frac{k_{11}}{k_{-11}} = \frac{(Cu_{2-x}S\wr Cu^{+1})}{(Cu_2S\wr)} \qquad (24)$$

and

$$K_{12} = \frac{k_{12}}{k_{-12}} = \frac{(Cu_{2-x}S\wr Cu^{+1}--O_2)}{(O_2)(Cu_{2-x}S\wr Cu^{+1})} \qquad (25)$$

Combination of equations (23), (24) and (25) yields the rate law

$$R = \frac{k_{11}\, k_{12}\, k_{13}}{k_{-11}\, k_{-12}} (O_2)(H^+) \tag{26}$$

where the surface activity is assumed to be one.

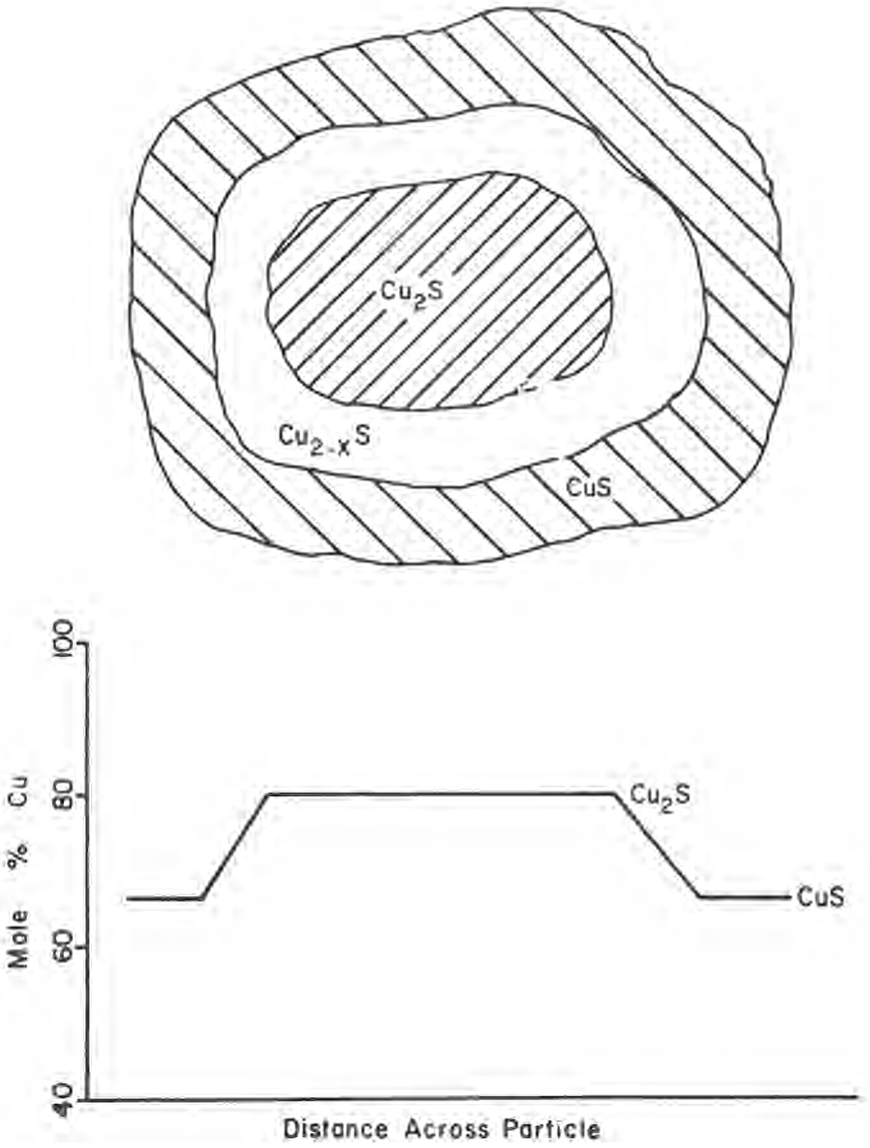

Figure 1. The stoichiometry of a partially leached chalcocite particle.

EXPERIMENTAL PROCEDURE

The samples of chalcocite used in this study were obtained from the New Cornelia Mine, Ajo, Arizona, through the Southwest Scientific Company. The samples were massive pieces of chalcocite bounded on one or more sides by quartz and contained some quartz inclusions.

The chalcocite is prepared for leaching by breaking the massive pieces of mineral with a hammer. Most of the quartz is rejected and the small pieces of chalcocite are crushed with an agate mortar and pestle. The crushed material is sized with a series of Tyler screens to yield the size fractions -48+65, -65+100, +100-150, -150+200 and -200 mesh, and stored in stoppered glass bottles.

Chalcocite Analysis

An x-ray diffraction examination of a -48+65 mesh sample of chalcocite identified the minerals present as chalcocite and quartz.

A sample of the mineral was examined by an emission spectrograph to determine the impurities present. The major elements were copper, silicon and iron, with aluminum, calcium, and silver in minor amounts and magnesium, manganese, arsenic, tungsten, cobalt, and molybdenum in trace amounts.

On the basis of the emission spectrograph report, a chemical analysis of the chalcocite determined the amount of copper, iron, sulfur, and quartz present. The sample contained 71.48% copper, 0.55% iron, 20.03% sulfur and 7. 94% quartz. Copper and iron were determined as aqueous ions, quartz as the weight of insoluble material, and sulfur by weight difference.

Solution Preparation

All of the reagents used in this study are analytic grade chemicals supplied by the J. T. Baker Chemical Company.

Most of this study is carried out with solutions containing specific concentrations of various ions at a constant ionic strength of 0.2 M. The reagents used to prepare leach solutions are added as either stable salts or standardized stock solutions.

Solutions of 1 N H_2SO_4, $HC10_4$, HNO_3, HCl, and HBr are prepared by diluting the concentrated acid with distilled water, then standardizing the acid against a standard NaOH solution. Stock solutions of Na_2SO_4, $NaClO_4$, and $NaNO_3$ are prepared by neutralizing the acid with standard NaOH solution and diluting the neutralized mixture to a known volume. Solutions of $Cu(ClO_4)_2$, $Cu(NO_3)_2$, and $CuBr_2$ are prepared by dissolving the proper weight of CuO in $HC1O_4$, $HN0_3$, or HBr respectively. The resulting solutions are diluted to a known volume and analyzed for Cu^{+2} and H+ ions, All other reagents used in preparing leach solutions are added as the salts $CuSO_4 \bullet 5H_20$, $CuC1_2 \bullet 2H_20$, NaCl, or NaBr.

By combining predetermined quantities of salts and stock solutions and diluting the mixture to the appropriate volume each leach solution is made up volumetrically so that it is not necessary to determine the concentration of each species in the initial leach solution.

Analytic Procedures

Cupric ion in leach solutions is determined by atomic absorption spectroscopy. Each sample is diluted to the concentration range 5 to 20 ppm immediately after it is taken from the leaching system. One N HCl is added to each dilution to keep the pH of the diluted sample below a value of 1.

Hydrogen ion concentration is determined by NaOH titration. The NaOH solutions are standardized against potassium hydrogen phthalate. The end point of unknown titrations, determined with a pH meter, is set at a pH value of 4. The low endpoint pH is selected to prevent the hydrolysis of cupric ion. Since the change in hydrogen ion concentration is the important quantity being sought, no error is introduced by selecting pH 4 as an endpoint.

Sulfate ion concentration is determined by the standard $BaSO_4$ gravimetric method given by Olson, Koch, and Pimentel (1956). Oxidation of sulfur species to sulfate is accomplished by adding saturated bromine water to the hot solution. The excess bromine is boiled off prior to $BaSO_4$ precipitation.

Equipment

The reaction vessel used for this study is a 2. 5-liter Lucite pre ssure vessel with an internal, overhead, magnetic stirring device. Agitation is accomplished by a three-bladed glass impeller connected to the magnetic stirring device. The vessel is equipped with a sample outlet, four inlet-outlets for gases and solutions, and a thermometer. The sampling outlet is fitted with a glass-wool filter to prevent uptake of mineral particles, and is constructed of 0.5 mm capillary tubing to reduce the volume of solution trapped between samples. The main gas inlet is a glass frit diffuser that is used to insure good gas-solution contact. Complete details of the reaction vessel are given by Fisher (1970).

Figure 2 is a diagrammatic representation of the leaching system. The reaction vessel and a solution storage bottle are submerged in a constant temperature bath which can be controlled with an accuracy of +0. 1°C. The flow of gases and solutions is controlled by the valves and piping shown in

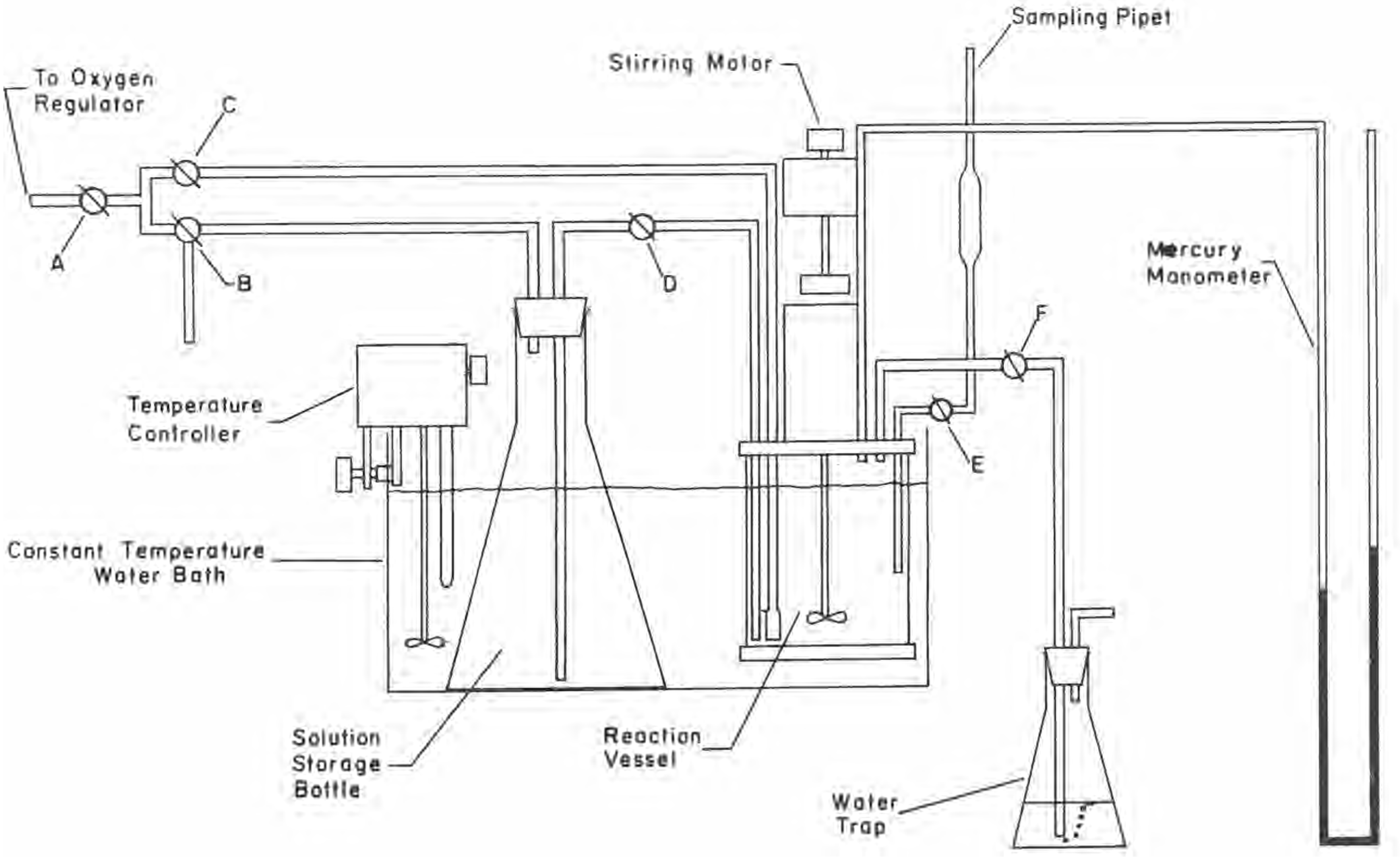

Figure 2. Schematic representation of the leaching system.

Figure 2. Samples are removed from the system through a 10 nil pipet. The system may contain other supporting equipment not shown, such as a pH meter, barometer, potentiometer, switching circuit, and timer.

Procedure

Three types of experiments were performed during this study. These included determination of the reaction stoichiometry, rate of oxygen consumption, and the rate of cupric ion production. The reaction stoichiometry was determined by finding the change in the concentration of hydrogen ion, cupric ion, and dissolved oxygen. Hydrogen and cupric ion concentrations are determined by the methods described previously. The quantity of oxygen consumed is determined from the total pressure change, system gas volume, and experimental temperature by using the ideal gas law.

By following the change in system pressure measured with a water manometer the rate of oxygen consumption is determined as a function of time.

The rate of cupric ion production is followed by finding the change in cupric ion concentration as a function of time by taking samples of the leach solution at specified times during the experiment and analyzing them for cupric ion.

The details of the experimental procedure are given by Fisher (1970).

RESULTS AND DISCUSSION

Stoichiometry

The stoichiometric coefficients of each reactant and product are by finding the number of moles of reactant or product consumed or produced in a given period of time. Table 1 is a tabulation of the stoichiometric data for seven experiments. The average mole ratios and their probable errors for H^+/Cu^{+2}, $Cu^{+2}/0_{2}$, and $H^+/0_2$ are respectively 2. 05+0. 03, 2. 02+0. 03, and 4. 09+0. 04, and can be rounded off respectively to 2, 2, and 4.

Table 1

STOICHIOMETRIC DATA FOR THE DISSOLUTION OF CHALCOCITE IN OXYGENATED ACID SOLUTION

H^+/Cu^{+2}	Cu^{+2}/O_2	H^+/O_2
1.93	2.06	3.94
2.03	2.02	4.09
2.02	2.13	4.31
1.99	2.09	4.15
2.24	2.10	4.30
2.02	1.93	3.90
2.11	1.85	3.95

Determination of these ratios does not completely solve the reaction stoichiometry, because there are several reactions that chalcocite can undergo that produce the same ratios as those given above. Reactions (1), (2), and (6) satisfy the mole ratios of 2, 2, and 4. It is possible, however, to rule out reactions (2) and (6) on the basis of additional stoichiometric work.

During two other chalcocite oxidation experiments, the change in sulfur species in the leach solution was followed. The analytic procedure used was such that all sulfur species from S^{-2} to SO_4^{-2} were included. In both cases, no significant change in soluble or free sulfur was detected. A carbon disulfide extraction of the leach residue (unreacted chalcocite) determined whether or not free sulfur was trapped in or on the surface of the leached chalcocite particles. Upon evaporation of the carbon disulfide, no free sulfur was visible.

A final step in the stoichiometric work involves determining the identity of the reaction product. CuS is identified as a reaction product by the color of the leached surface and by x-ray diffraction identification.

Because neither free sulfur nor any other sulfur species can be found on the chalcocite surface or in the leach solution, reactions (2) and (6) can be ruled out as possible reaction paths. The identification of CuS as a reaction product, the absence of oxidized sulfur in the system, and the mole ratios of 2, 2, and 4 for $H^+/Cu+^2$, $Cu+^2/O_2$, and H^+/O_2, respectively, firmly support equation (1) as the reaction occurring in the dissolution of chalcocite.

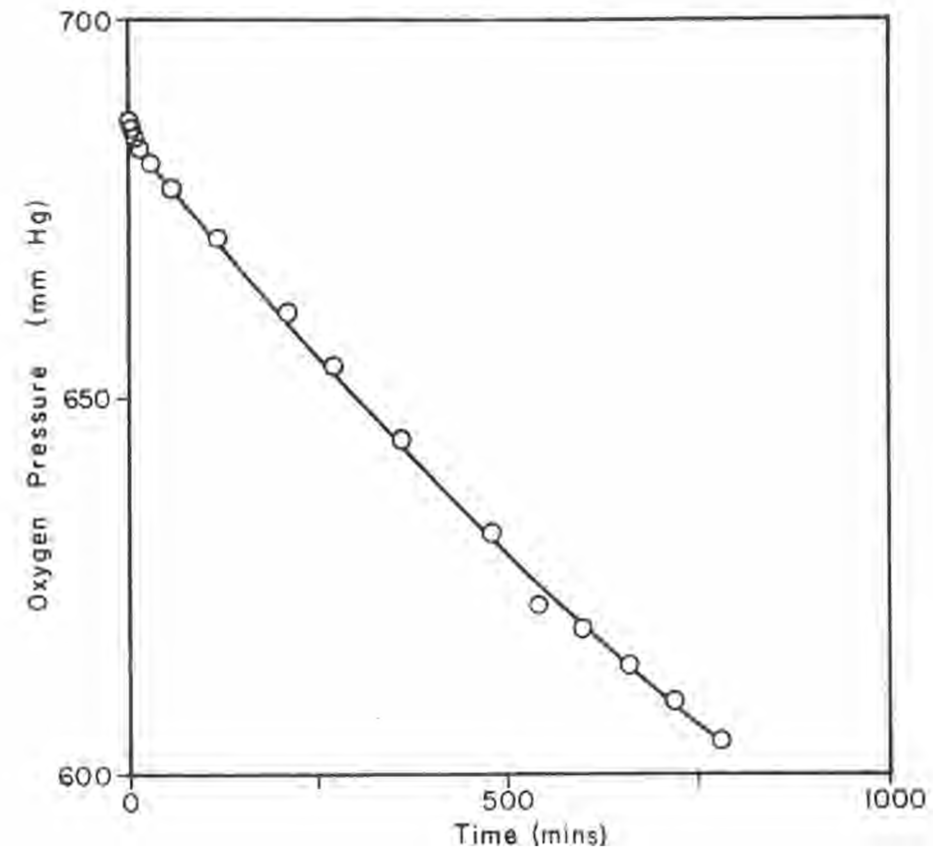

Figure 3. Oxygen partial pressure vs. time for a typical oxygen consumption experiment.

Rate of Oxygen Consumption

The purpose of this section of the study is to determine a general rate equation for the oxidation of chalcocite. The rate of reaction is followed by observing the consumption of oxygen in a closed system. Figure 3 is a plot of oxygen partial pressure vs. time for a typical oxygen consumption experiment.

Kinetic analysis of the data of Figure 3 shows that the reaction follows the rate law given by

$$\frac{d(Cu^{+2})}{dt} = -\frac{1}{2}\frac{d\,P_{O_2}}{dt} = k(H^+)(P_{O_2}) \; . \qquad (27)$$

The H^+ ion concentration can be related to the oxygen pressure through reaction stoichiometry, Henry's law, and the initial H^+ ion concentration and oxygen pressure. Equation (27) then takes the form

$$\frac{d\,P_{O_2}}{dt} = -2k(A + B\,P_{O_2})\;P_{O_2} \qquad (28)$$

where

$$A = (H^+)_0 - 222.4(P_{O_2})\,/\,HK$$

and

$$B = 222.4\,/\,HK\;.$$

The variables of equation (28) can be separated and integrated to yield

$$\ln\left[A + B(P_{O_2})\right] - \ln(P_{O_2}) = 2Akt + C \qquad (29)$$

where C is an integration constant. A plot of $\ln\left[A+B(P_{O_2})\right] - \ln(P_{O_2})$ as time will yield a straight line if equation (27) is a valid rate equation. Figure 4 illustrates the straight line relationship of $\ln\left[A+B(P_{O_2})\right] - \ln(P_{O_2})$ and time.

Rate of Cupric Ion Production

This study was designed to substantiate the general rate equation for the oxidation of chalcocite in oxygenated acid solution, determine the effect of several variables on the rate, and gain insight into the reaction mechanism. The parameters examined include agitation, surface area, oxygen pressure, temperature, and H^+, SO_4 Cl , Br^-, NO_3^-, and $C10_4$ ion concentration.

Three identical experiments were performed and compared to establish the accuracy with which an experiment could be reproduced. The average percent standard deviation from the mean is +4. 22%.

Experiments at different stirring speeds were performed to determine the rpm value above which the rate of reaction became independent of stirring speed. Above 700 rpm there was no further increase in reaction rate with increased stirring rate. All subsequent experiments at 1, 150 rpm insured that stirring was not a variable.

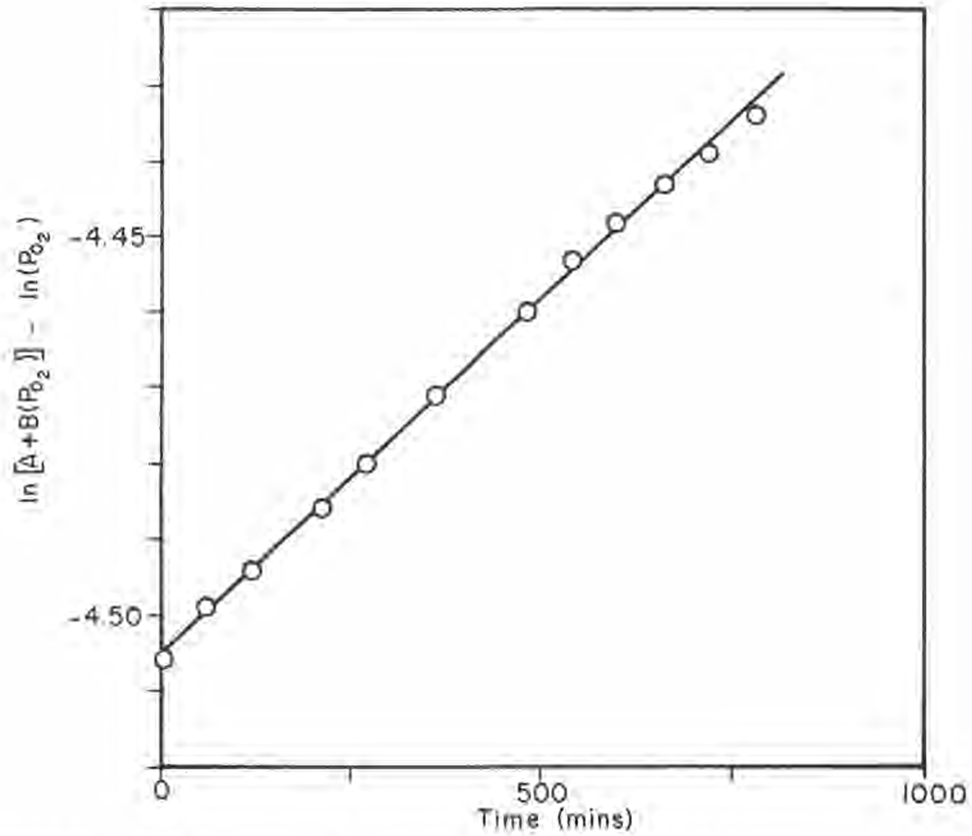

Figure 4. $\ln\left[A+B(P_{O_2})\right] - \ln(P_{O_2})$ vs. time for a typical oxygen consumption experiment.

Several experiments at constant particle size show that the rate of reaction is first order with respect to surface area.

The order of the reaction with respect to oxygen partial pressure is determined by examining the effect of oxygen while all other variables are held constant. Since all other variables are held at the same initial value, their constant effect can be included in a quasi-rate constant, k', and the rate equation for the system is represented by

$$R = k'(P_{O_2})^a \tag{30}$$

where the exponent, a, is the unknown reaction order for oxygen. The logarithmic form of the relation is given by

$$\log R = a \log R + \log k'. \tag{31}$$

A plot of log R vs. log P_{O_2} should yield a straight line of slope a.

The condition of the surface and the change in H^+ ion concentration during the reaction could affect this determination, so the rate selected from each experiment is at the same $Cu+^2$ ion concentration (0. 002250 M), not the same time. The rate of the reaction is determined from the first derivative of a second-order polynomial curve fitted through the experimental points of Figure 5 which is a plot of Cu^{+2} ion concentration vs. time for four oxygen partial pressures. Figure 6 is a plot of log R vs. log P_{O2} for which the slope is 0.96. Therefore, the reaction order with respect to oxygen partial pressure is 1. This is in agreement with the results of the oxygen consumption experiments.

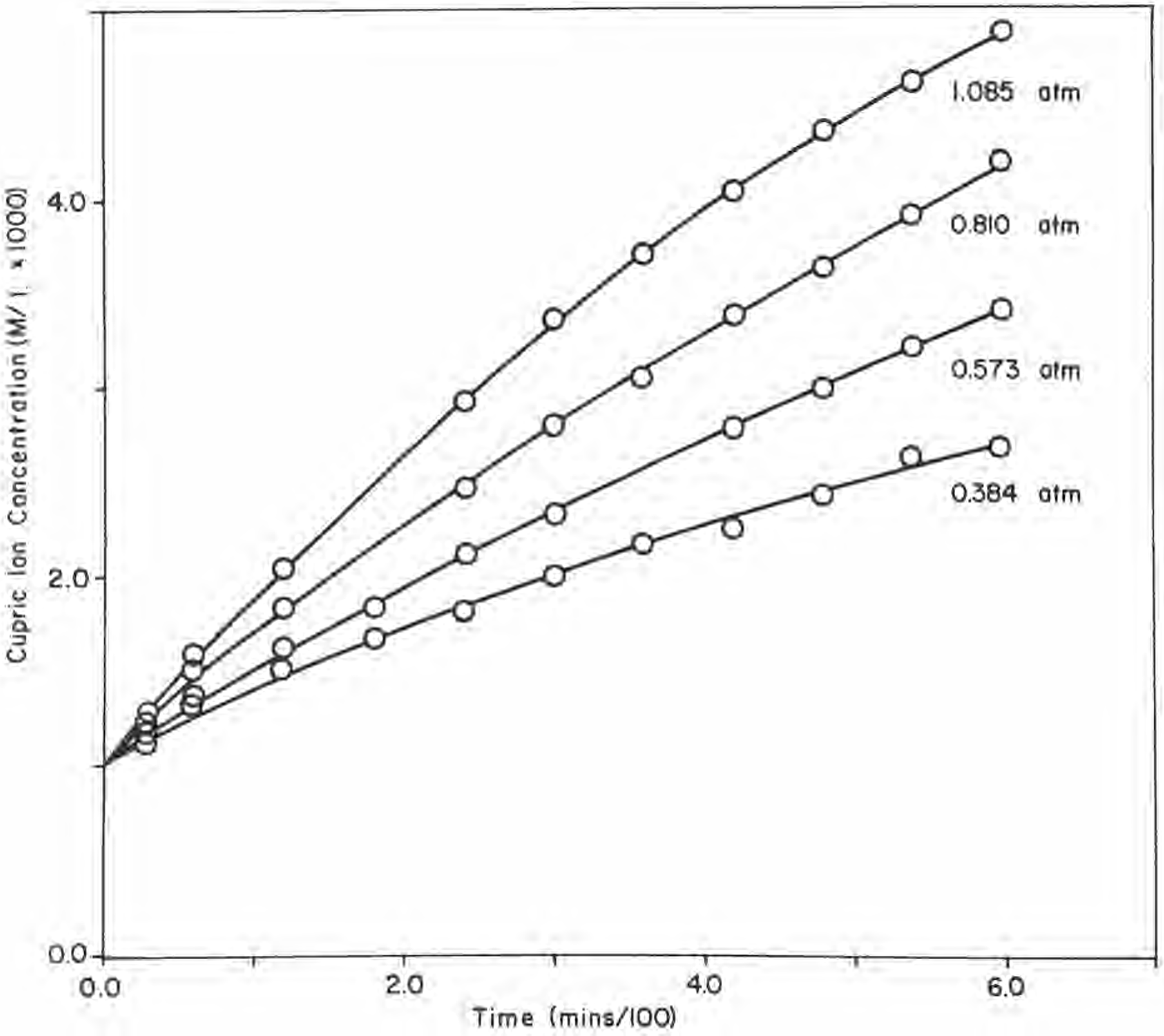

Figure 5. Cupric ion concentration vs. time for several oxygen partial pressures.

The order of the dissolution reaction with respect to H^+ ion concentration is determined by three experiments with the initial concentration of

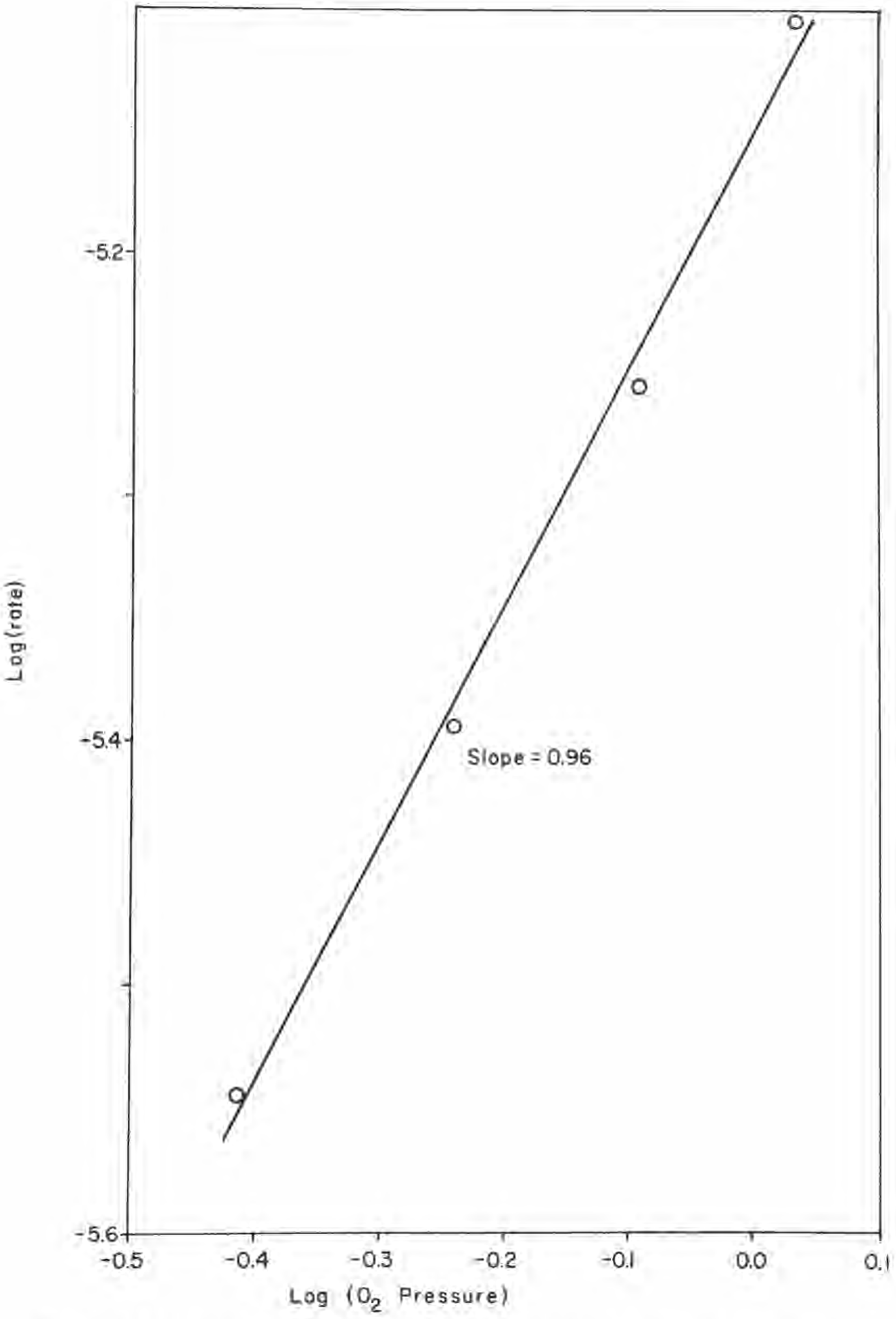

Figure 6. Log(rate vs. log(P_{O_2}). Determination of oxygen reaction order.

H^+ and SO_4^{-2} ions as variables. Hydrogen ion is consumed in the reaction and its concentration changes with time during an experiment. However, the stoichiometric study shows that the SO_4^{-2} ion concentration does not change during an experiment. Although the SO_4^{-2} ion concentration may influence the reaction rate, the effect is constant for a particular experiment and only the initial SO_4^{-2} ion concentration effects the rate of reaction.

Figure 7 is a plot of Cu^{+2} ion concentration vs. time for three different initial H^+ and SO_4^{-2} ion concentrations. Sulfate ion exerts an inverse effect on the rate of dissolution and neutralizes the effect. of H^+ ion concentration.

Since all variables except H^+ ion concentration are held constant during the course of each experiment, the rate equation for this part of the work is

$$R = k''(H^+) \tag{32}$$

where k" contains the constant effects of oxygen partial pressure and SO_4^{-2} ion concentration and the reaction order with respect to H^+ ion is assumed to be one. The H^+ ion concentration is related to Cu^{+2} ion concentration through reaction stoichiometry and the initial concentration of H^+ and Cu^{+2} ions. This allows equation (32) to be written as

$$\frac{d(Cu^{+2})}{dt} = k''\left[A - 2(Cu^{+2})\right] \tag{33}$$

where

$$A = (H^+)_o + 2(Cu^{+2})_o \, .$$

Separation of variables and integration yields

$$\ln\left[A - 2(Cu^{+2})\right] = -2k''t + C \tag{34}$$

where C is an integration constant. A plot of ln(A-2(Cu)) vs. t yields a straight line assuming the effect of H^+ ion is first order. Figure 8 is such a plot which shows that H^+ exerts a first-order effect on rate over the concentration range 0.1 to .01 M.

In the determination of H^+ ion reaction order, the effect of sulfate is included in the quasi-rate constant since its effect is only a function of initial concentration. This is represented by

$$k'' = k(SO_4^{-2})^b \tag{35}$$

where k" is the quasi-rate constant of equation (36), k is a new rate constant containing the constant effect of oxygen and b is the unknown reaction order with respect to SO_4^{-2} ion concentration. The logarithmic form of this equation is given by

$$\log k'' = b \log(SO_4^{-2}) + \log k. \tag{36}$$

A plot of log k" vs. log (SO_4^{-2}) should yield a straight line of slope b.

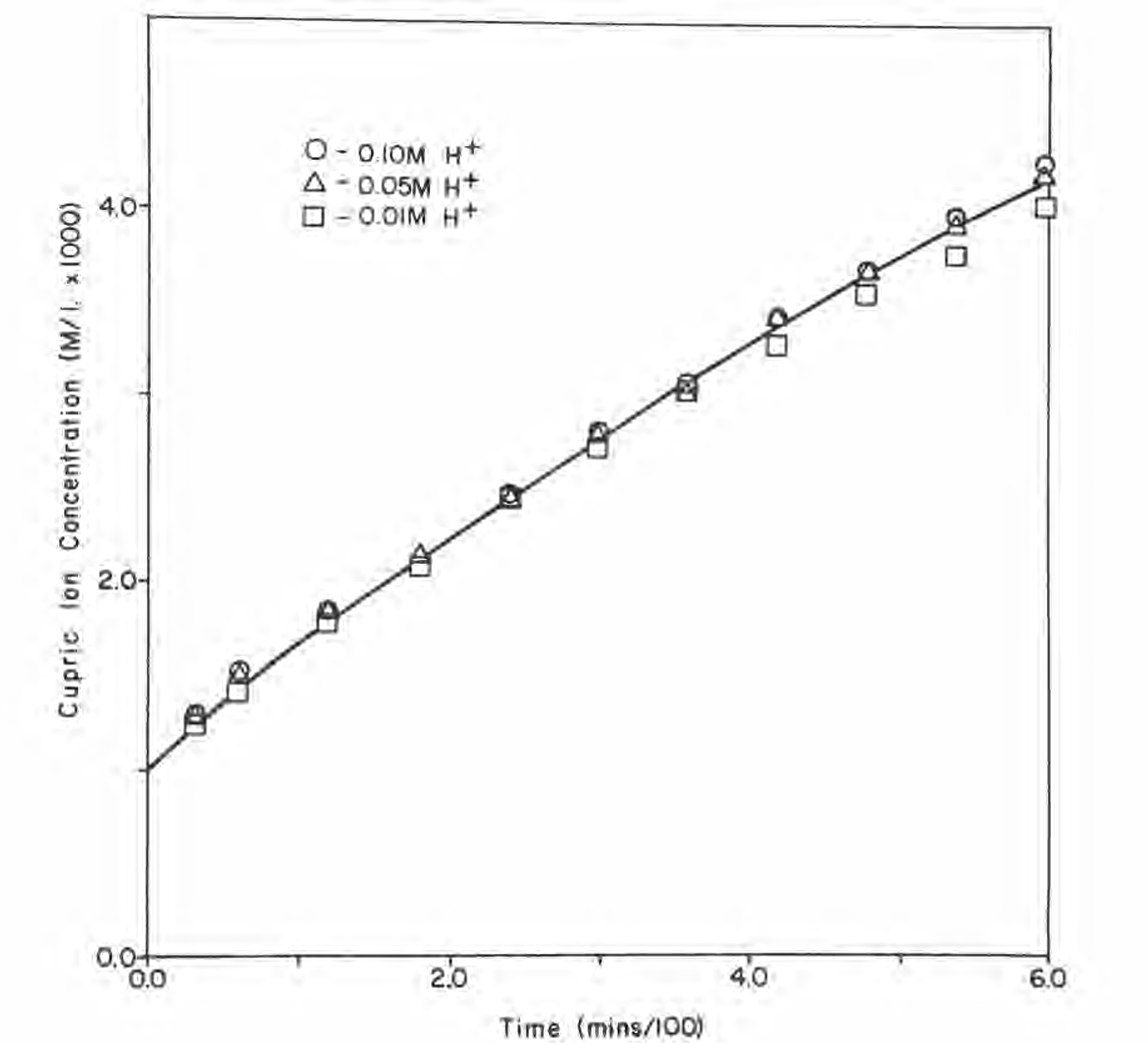

Figure 7. Cupric ion concentration vs. time for different initial hydrogen ion concentrations.

The slope of the lines in Figure 8 are equal to -2k". Figure 9 uses the k" values determined from Figure 8. The slope of the line in Figure 9 indicates that the reaction order with respect to sulfate is -1.18.

In other experiments, sulfate ion is completely replaced by perchlorate and nitrate ions. Figure 10 is a plot of Cu+ ion concentration vs. time

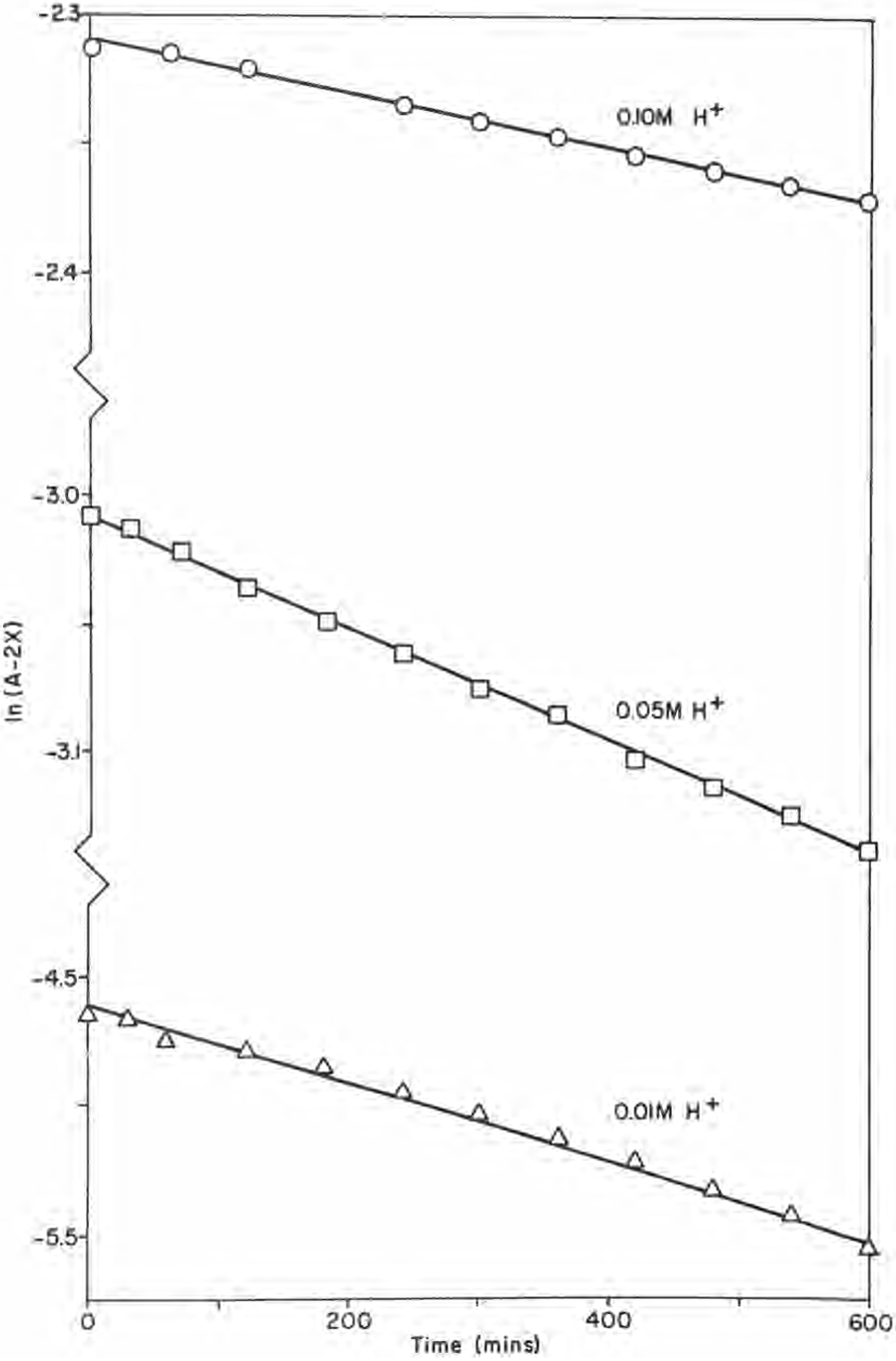

Figure 8. Ln(A-2X) vs. time for three different H^+ ion concentrations. Hydrogen ion reaction order.

showing the effects of SO_4^{-2}, , and NO_3^-
reaction rate relative to the rate in ClO_4 and NO_3 solutions.

Summary of Kinetic Analysis

The analysis of the oxygen consumption experimental data indicates that the chalcocite oxidation reaction is first order with respect to H^+ ion concentration and oxygen partial pressure and zero order with respect to Cu^{+2} ion concentration. Experiments at several constant oxygen partial pressures indicate that the oxidation reaction is first order with respect to oxygen pressure. Other experiments at various initial H^+ ion concentrations

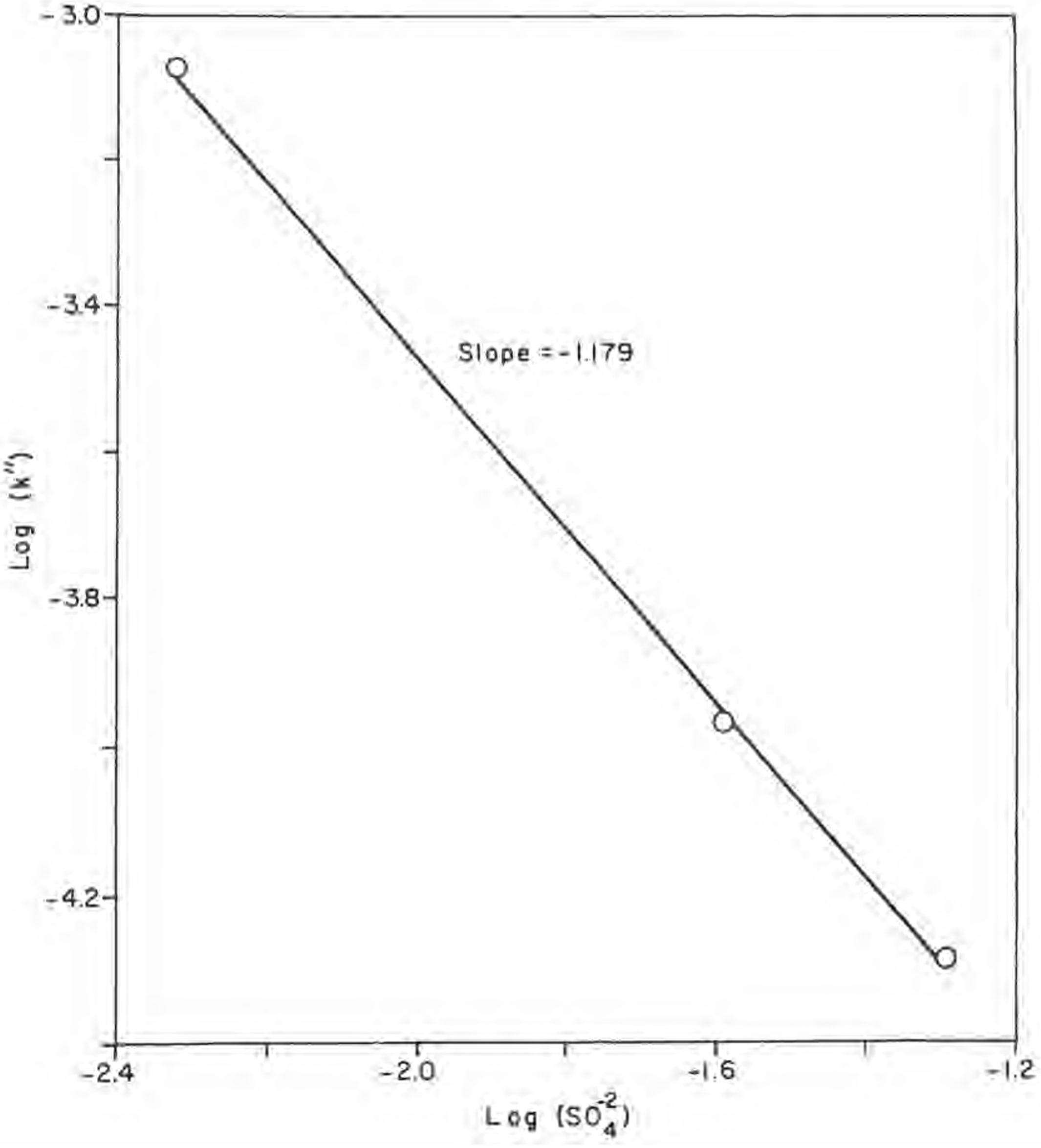

Figure 9. Sulfate ion reaction order.

indicate that the reaction is first order with respect to H^+ ion concentration. The same H^+ ion experiments indicate that the reaction order with respect to sulfate ion is -1.18. These results support 'the rate law given by

$$R = k(P_{O_2})(H^+)(SO_4^{-2})^{-1.18} , \qquad (37)$$

This rate expression is valid over the H^+ ion concentration range 0..1 to 0.01 M, the SO_4^{-2} ion concentration range 0.005 to 0.05 M,' and the oxygen pressure range 1.085 to 0.384 atmospheres.

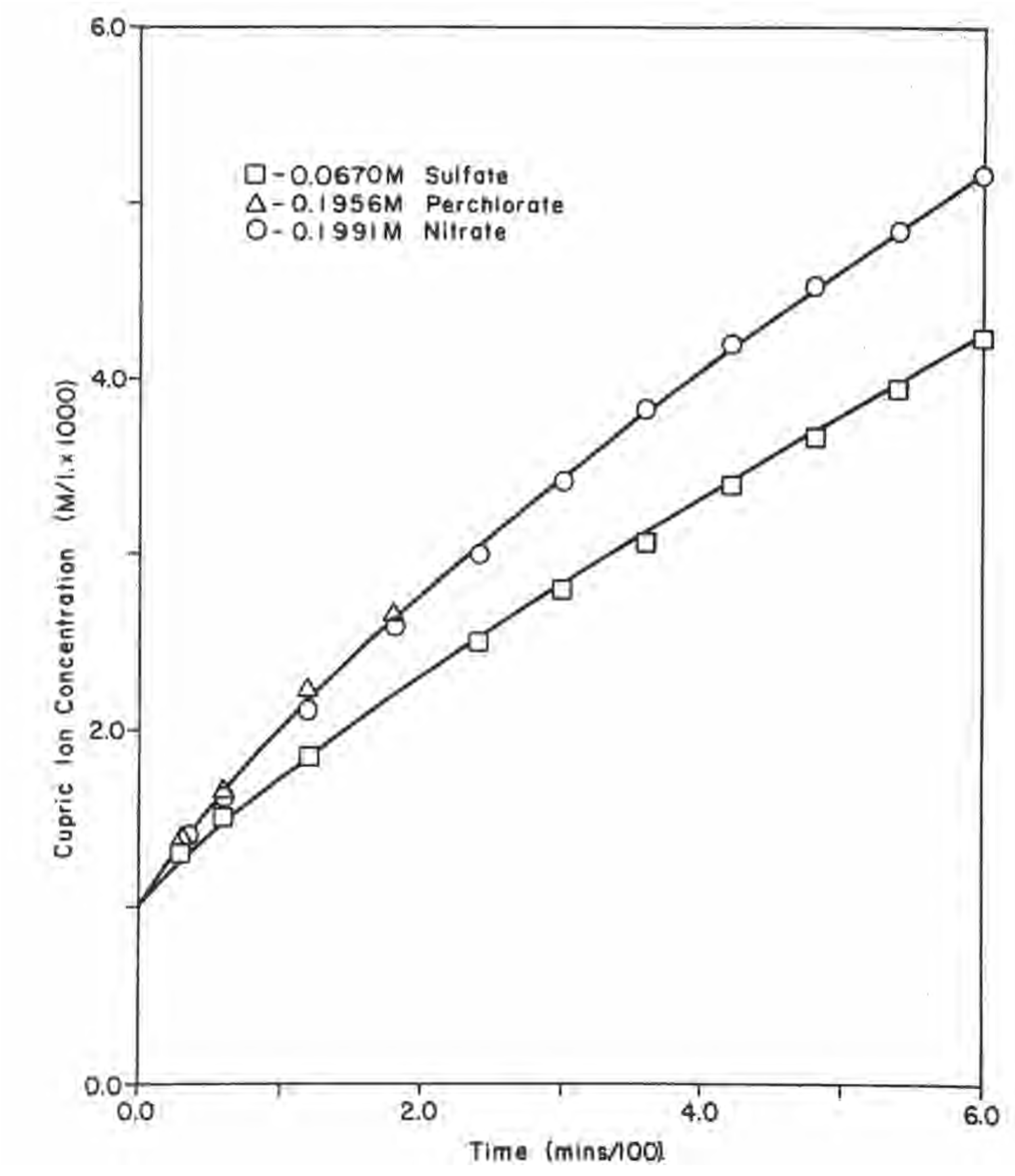

Figure 10. Cupric ion concentration vs. time for solutions containing sulfate, nitrate and perchlorate ions.

the sulfated -ion concentration does not vary from one experiment to another, then the rate law given by equation (27) is valid and the constant effect of $SO4-_2$ ion concentration is included in the rate constant. When the rate-controlling reaction of the mechanism is the first reduction step for 0_2 the rate law is given by equation (26). This rate law is the same as equation (27) with $k = k = \frac{k_{11}\, k_{12}\, k_{13}\; 55.6}{k_{-11}\, k_{-12}\, HK}$. The correspondence between the experimental and theoretical rate equations indicates that the proposed reaction mechanism is in agreement with the experimental results.

Activation Energy

The rate constant for a reaction is related to temperature through the Arrhenius equation given by

$$\frac{d \ln k}{dT} = \frac{E^*}{RT^2} \tag{38}$$

where k is the rate constant, T is absolute temperature, R is the gas constant, and E* is the activation energy of the reaction. The integrated form of this equation is given by

$$\ln k = \frac{-E^*}{RT} + \ln A \tag{39}$$

A plot of In k vs. 1/T should give a straight line of slope -E*/R.

Figure 11 is a plot of cupric ion concentration vs. time for three different temperatures. Figure 12 is a plot of Ink k vs. 1/T for these three experiments. The rate selected from each experiment is taken at the same concentration (.004000 M), not the same time. The slope of the line gives an activation energy of 6. 59 kcal/mole. Warren (1958) found an activation energy of 6. 6 kcal/mole for the first stage of chalcocite dissolution at an oxygen pressure of 40 psi over the temperature range 100^{o} to 200° C. The significance of the activation energy is not clear. Burkin {1966) suggests that diffusion-controlled reactions have activation energies of about 4 kcal/mole. A value of 6.6 kcal/mole could indicate either diffusion or chemical rate control.

The Effect of Halide Ions

The effect of chloride and bromide ions on the dissolution of is determined to gain insight into the reaction mechanism. The reaction mechanism involves the existence of Cu$+^{1}$ ion as an intermediate. The cuprous ion normally undergoes spontaneous disproportionation to form Cu^{11} and metallic copper, and therefore, the Cu^{11} ion equilibrium concentration in solution is small. The halide ions all have the ability to selectively complex

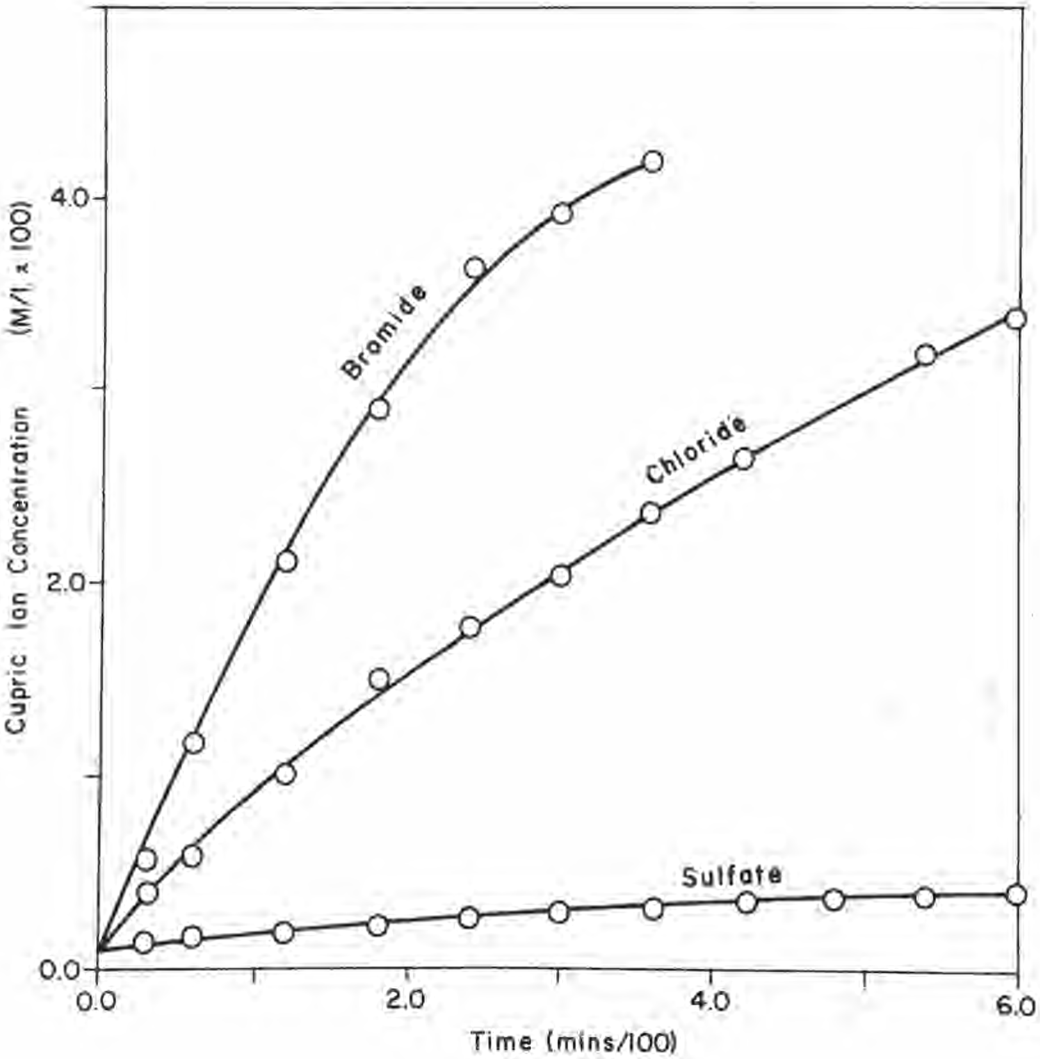

Figure 13. Cupric ion concentration vs. time for several different anions.

concentration vs. time for three experiments showing the effect of chloride, bromide, and sulfate ions. The presence of halide ions increases the reaction rate by a factor of about 100. This result is consistent with the proposed reaction mechanism.

SUMMARY AND CONCLUSIONS

The reaction accompanying the dissolution of chalcocite in oxygenated sulfuric acid solution is given by equation (l). The dissolution process is governed by the rate law represented by equation (37). This rate law is valid over the H^+ ion concentration range 0. 01 to 0.l M, the initial SO_4^{-2} ion concentration range 0.0005 to 0.05 M, and the oxygen pressure range of 1. 085 to 0.384 atmospheres. The activation energy for the dissolution reaction is 6.6 kcal/mole. The rate-controlling step is considered to be chemical in nature.

The reaction rate is first order with respect to surface area. Sulfate ion depresses the reaction rate relative to the rate in perchlorate or nitrate solutions. The presence of chloride or bromide ion in the solution causes a 100-fold increase in reaction rate relative to the rate in SO_4^{-2}, NO_3^-, or ClO_4^- solutions. The reaction mechanism consistent with all of the experimental findings is given by equations (11) through (22).

Some of the conclusions of this study can be related to commercial copper leaching. First, since the only reaction accompanying the dissolution of chalcocite in oxygenated acid solution is that represented by equation (l), only half of the copper can be recovered from chalcocite. The implications of the first-order effect of oxygen-partial pressure are obvious. However, the first-order effect of hydrogen-ion concentration is not as it first appears. Since most commercial leaching operations use sulfuric acid for pH adjustment or sulfuric acid is produced as a result of leaching, the first-order effect of increased concentration is nearly offset by the sulfate ion that accompanies acid additions. If ion can be added through another acid, then the beneficial first order ion effect can be realized. If sulfuric acid can be replaced by hydrochloric acid, this has the dual effect of removing sulfate so that the effect of H^1 is not suppressed and introducing CF ion which enhances the rate by a factor of almost 100. Although it was not attempted in this study, addition of chloride in the presence of sulfate may have the same effect as replacing sulfate with chloride.

REFERENCES

Burkin, A. R. , 1966, The chemistry of hydrometallurgical processes: Princeton, New Jersey, D. Van Nostrand, Inc., 157 p.

Dutrizac, J. E., MacDonald, R. C. J., and Ingraham, T. R., 1970, The kinetics of dissolution of bornite in acidified ferric sulfate solutions: Met. Trans. , v. l, p. 125-131.

Fisher, W. W. , 1970, A leaching mechanism for chalcocite: Ph. D. dissertation, N. Mex. Inst. Mining Technology, Socorro, New Mexico, 107 p.

Gerlack, J., and Pawlek, F., 1968, On the kinetics of pressure leaching metal sulfides and ores: Annual Meeting of the AIME, Paper, New York, Feb. 25-29, 15 p.

Huffman, R. E., and Davidson, N., 1956, Kinetics of the ferrous iron-oxygen reaction in sulfuric acid solution: Jour. Amer. Chem. Soc., v. 78, p. 4836-4842.

Kuxmann, V. U., and Biallab, H., 1969, Studies on copper matte electrolysis: Erzmetall, v. 22, #2, p. 53-64.

Latimer, W. M., 1952, Oxidation potentials: Englewood Cliffs, New Jersey, Prentice-Hall, Inc. , 392 p.

Olson, A. R., Koch, C. H., and Pimentel, G. C., 1956, Introductory quantitative analysis: San Francisco, W. H. Freeman and Co. , 470 p.

Sato, M. , 1960, Oxidation of sulfide ore bodies, II. Oxidation mechanisms of sulfide minerals at 25°C: Econ. Geology, v. 55, p. 1202-1231.

Stanczyk, M. H., and Rampacek, Carl, 1963, Oxidation leaching of copper sulfides in acidic pulps at elevated temperatures and pressures: U. S. Bur. Mines, Rept. Inv. 6193, 15 p.

Sullivan, J. D. , 1930, Chemistry of leaching chalcocite: U. S. Bur. Mines, Tech. Paper 473, 24 p.

Warren, I. H., 1958, Acid pressure leaching of chalcopyrite, chalcocite and covellite: Aust. Jour. Appl. Science, v. 9, p. 36-51.

Yatsimirskii, K. B., and Vasil'ev, V. P., 1960, Instability constants of complex compounds: New York, Consultants Bureau, 214 p.