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THE KINETICS OF THE DISSOLUTION REACTIONS OF  
COPPER AND COPPER-IRON SULFIDE MINERALS  
USING FERRIC SULFATE SOLUTIONS

By

Donald Frank Lowe

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A Dissertation Submitted to the Faculty of the  
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For the Degree of

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WITH A MAJOR IN METALLURGY

In the Graduate College  
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GRADUATE COLLEGE

I hereby recommend that this dissertation prepared under my direction by Donald F. Lowe entitled The Kinetics of the Dissolution Reactions of Copper and Copper-Iron Sulfide Minerals Using Ferric Sulfate Solutions be accepted as fulfilling the dissertation requirement of the degree of Doctor of Philosophy

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27 Dec. 1969  
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Donald Frank Lowe

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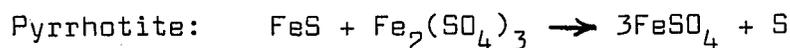
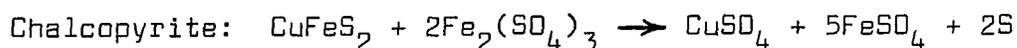
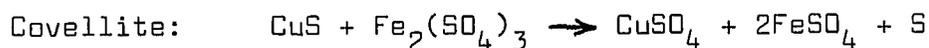
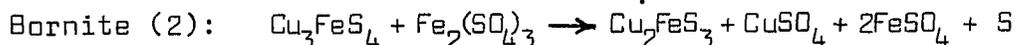
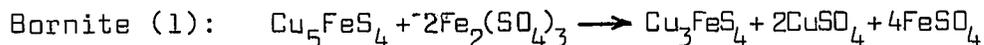
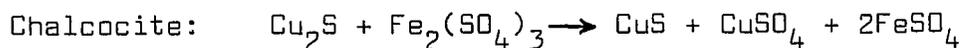
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## ABSTRACT

Leaching by bacterial oxidation of copper, copper-iron, and iron sulfide minerals in mine-waste rock is being conducted at several mining properties in the United States. Two reaction systems are involved in the bacterial leaching. These are the direct bacterial oxidation of sulfides and of ferrous iron and the ferric-sulfate leaching of sulfides.

The ferric-sulfate leaching rates of chalcocite, covellite, bornite, chalcopyrite, and pyrrhotite were measured to develop kinetic rate expressions and to propose the reaction mechanism for each mineral. The measured data involved the initial 24 to 72 hours of leaching. The variables examined were ferric sulfate concentration, sulfuric acid concentration, and reaction temperature.

Stoichiometric relations involved in the ferric-sulfate leaching of these sulfides were previously examined from which the following initial reactions were proposed:



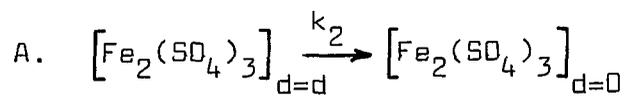
Mounted single specimens of chalcocite, bornite, covellite, and pyrrhotite were leached under a nitrogen atmosphere in an agitation cell. Ground and sized samples of chalcopyrite were leached under nitrogen in a continuous-flow reactor cell. The rate of consumption of ferric sulfate in moles per liter-min.-cm.<sup>2</sup>, was measured at various time intervals.

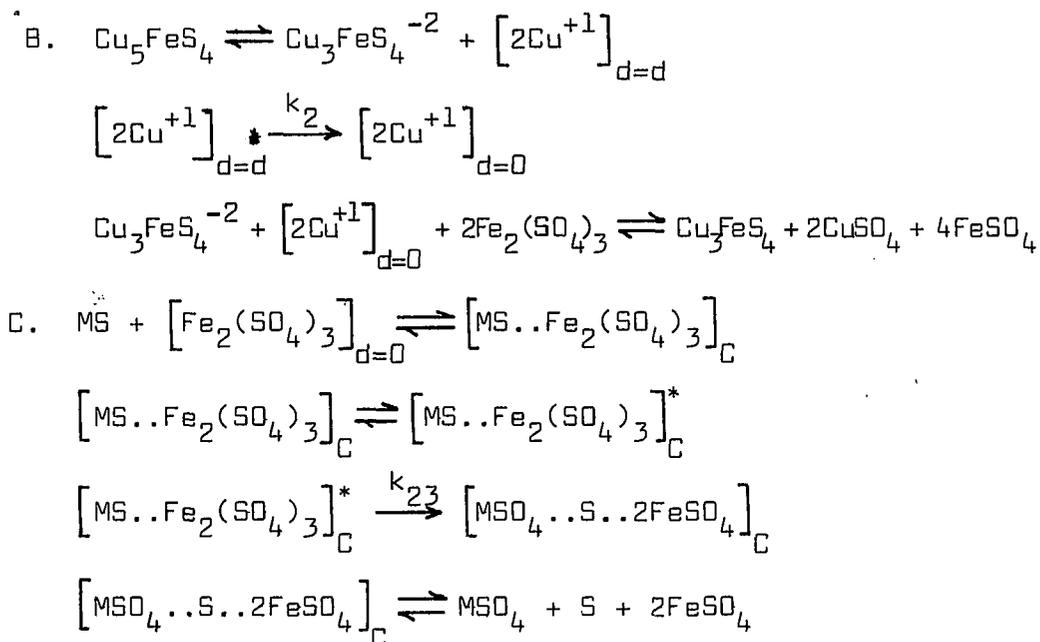
The rate equations obtained for each mineral were compared to theoretical equations determined for the mechanistic processes of

1. Aqueous diffusion of ferric sulfate,
2. Solid-state diffusion of the cuprous ions in the sulfide,
3. Chemisorption reactions, and
4. Electrode reactions.

Aqueous ferric sulfate diffusion was the only mechanistic step determined for chalcocite. The effect of sulfuric acid additions to the ferric sulfate leach solution supported this observation.

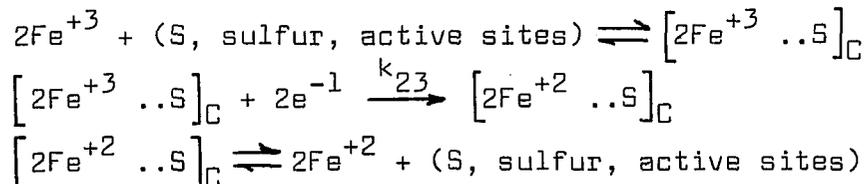
The proposed mechanism for ferric sulfate leaching of bornite was complex. At various stages of dissolution of bornite one of several processes controlled the reaction rate. These were ferric sulfate diffusion, step A, a possible solid-state diffusion of cuprous ions within the sulfide, step B, and chemisorption reactions with the metal sulfide (MS), step C.





Surface-reaction-controlled chemisorption was the dominant mechanism for covellite and chalcopyrite leaching (refer to mechanism C in the above bornite discussion). The addition of sulfuric acid to the ferric sulfate leach solution didn't alter the leaching rate. This supported the chemisorption theory.

The electrode reaction mechanism was proposed for the surface-reaction-controlling step for chemisorption. The proposed mechanism was



The results for pyrrhotite leaching were inconclusive. The variation of ferric sulfate concentrations indicated a chemisorption mechanism. However, increasing reaction temperatures and adding sulfuric acid reduced the rate of leaching.

Competing reactions between ferric sulfate and the mineral and sulfuric acid and the mineral were proposed as one reason for these results.

## CHAPTER I

### INTRODUCTION

Numerous low-grade copper sulfide ore deposits are being mined in the United States. The average sulfide copper content of the ore mined from thirty of these deposits is 0.83 percent. The ore is treated by the combined processes of flotation and smelting. In the flotation process the resulting tailing contains an average copper content of 0.14 percent. The average copper recovery by these processes is about 80 percent (Fuerstenau 1962, pp. 70-71).

The usual sulfide copper content of waste rock mined from open-pit properties is below 0.4 percent. Therefore, copper-bearing rock which contains less than 0.4 percent sulfide copper cannot be mined, milled, and smelted economically by conventional methods. The cutoff grade also results in considerable waste materials at operating mine sites. These materials are placed into waste dumps. The overall dump grade usually averages 0.3 percent sulfide copper (Argall 1963a, p. 24).

Bacterial action on copper and copper-iron sulfide materials has been used to extract copper into aqueous solutions (Jameson 1957; Bryner and Anderson 1957, pp. 721-724). The action of the bacteria in oxidizing copper and copper-iron sulfides

to copper sulfate has been applied to commercial leaching of waste materials at various operating mines (Argall 1963a, pp. 22-27; Argall 1963b, pp. 20-24; Malouf and Prater 1962, pp. 82-85). The overall leaching and copper recovery process involves oxidation of the sulfide minerals in the waste rock, precipitation of the copper from solution by metallic iron in either a launder or a cone plant, and recirculation of the ferrous-sulfate-bearing solution to the waste material for additional leaching.

The magnitude of leaching of mine waste material by bacterial action is considerable. One mining property in the United States has over a billion tons of waste rock deposited in waste-dump areas. These waste dumps contain on the average 0.3 percent sulfide copper. Leaching of these dumps yields about 200 tons of copper powder per day. At this one property mining of the ore-grade material, flotation of the copper and copper-iron sulfides to form concentrates, and smelting of the concentrates results in about 600 tons of copper metal per day. Thus one-quarter of the total copper produced per day is obtained by the bacterial leaching of sulfide minerals in the waste material.

Two possible reaction systems are involved in the process of bacterial leaching of copper and copper-iron sulfides. These systems are bacterial leaching of the sulfide minerals resulting in soluble sulfates and ferric sulfate leaching of the minerals to form soluble sulfates and a sulfur residue. The problems involved in ferric-sulfate-bacterial oxidation of sulfides has been

considered by many investigators (Razzell 1962, pp. 190-191; Beck 1959, pp. 502-509).

Due to the growing importance of ferric-sulfate-bacterial leaching of copper and copper-iron sulfide minerals, the need for understanding the mechanisms involved in the ferric-sulfate-oxidizing reactions and in the bacteria-oxidizing reactions is necessary. The bacteria oxidizes the ferrous sulfate in the leach solutions to ferric sulfate in addition to direct oxidation of the sulfide minerals by the bacteria. The ferric sulfate reacts with the sulfide minerals at sites of bacterial action and in areas where little bacterial action exists. Therefore, in order to understand the overall mechanism of the ferric-sulfate-bacterial reactions, the processes of ferric sulfate leaching and of direct bacterial action must be isolated from each other.

A kinetic study of ferric sulfate leaching of several sulfide minerals was undertaken to develop the rate expressions and the probable mechanisms for each reaction. The heterogeneous kinetics of each reaction involving aqueous ferric sulfate solutions and the minerals chalcocite ( $\text{Cu}_2\text{S}$ ), covellite ( $\text{CuS}$ ), bornite ( $\text{Cu}_5\text{FeS}_4$ ), chalcopyrite ( $\text{CuFeS}_2$ ), or pyrrhotite ( $\text{FeS}$ ) were determined. In each case the rate of consumption of ferric sulfate was measured. The rates of reaction were determined for the initial periods of leaching, that is, one to three days of leaching. This was done to avoid changes in the exposed surface area of the sulfide minerals.

The kinetic expressions for the dependencies of the rate on the ferric sulfate concentration and of the rate constant on the reaction temperature were determined. The effects of variable solution pH by the addition of sulfuric acid were also sought. These expressions were compared and interpreted in view of several theoretical kinetic processes. From this comparison the mechanistic steps involved in the observed leaching reaction for each mineral was proposed.

## CHAPTER II

### LITERATURE SURVEY

The basic aspects of the physical chemistry of hydro-metallurgy were discussed by J. Halpern (1957, pp. 280-289). The discussion involved heterogeneous processes between aqueous solutions and solid minerals or metals. Halpern presented the following steps for heterogeneous leaching reactions:

1. Absorption of gaseous reactants, if any, by the solution.
2. Transport of the dissolved reactants from the main body of the solution to the solid-solution interface. The depth of the diffusion zone between the bulk solution and a solid surface was proposed to be 0.050 centimeters for unstirred systems and 0.001 centimeters for vigorously agitated systems.
3. Diffusion of the reactants through a passivating layer.
4. Adsorption of reactants on the solid surface.
5. Reaction on the surface of the solid.
6. Desorption of the soluble products from the surface.
7. Diffusion of the products through the passivating layer.
8. Transport of the products from the solid-solution interface to the main body of the solution.

The passivating layer in steps 3 and 7 was described as the solid products of the reaction such as sulfur or another sulfide mineral. Halpern stated that the diffusion of reactants was usually slower through the passivating layer than through the main body of the solution to the solution-mineral interface.

The leaching reactions involving sulfide minerals and ferric sulfate solutions were examined by J. D. Sullivan. The experimental results were stoichiometric relationships from which little kinetic information was obtained. The minerals examined were chalcocite (Sullivan 1930a); bornite (Sullivan 1930b); covellite (Sullivan 1930c); and chalcopyrite (Sullivan 1933, pp. 531-532). These leach tests were conducted in bottles which were placed on a roller mill to continuously mix the mineral and solution. The mineral feed was ground and sized. The temperature of the leach solution was maintained at 35°C. The ferric sulfate concentration was either 25 or 50 grams ferric-iron per liter. Sulfuric acid was not added to the leach solutions.

Summaries of the pertinent data obtained by Sullivan for the ferric sulfate leaching of chalcocite, bornite, covellite, and chalcopyrite are given, respectively, in Tables 1, 2, 3, and 4. The percentages reported are the fractions of the initial copper and iron which were dissolved and of the total sulfur formed as a residue.

TABLE 1

SULLIVAN'S RESULTS PERTAINING TO FERRIC SULFATE LEACHING  
OF CHALCOCITE MINERAL

TIME Hours	TOTAL COPPER DISSOLVED Percent	SULFUR IN RESIDUE DISSOLVED By CS <sub>2</sub> Percent	RESIDUE ATOM RATIO	
			Cu	S
0	0	0	-	-
1	37	2	1.1	1.0
6	43	4	1.0	1.0
12	46	6	1.0	1.0
24	53	17	1.0	1.0
96	77	60	1.0	1.0
312	90	93	0.8	1.0

TABLE 2

SULLIVAN'S RESULTS PERTAINING TO FERRIC SULFATE LEACHING  
OF BORNITE MINERAL

TIME Hours	TOTAL COPPER DISSOLVED Percent	TOTAL IRON DISSOLVED Percent	SULFUR IN RESIDUE DISSOLVED By CS <sub>2</sub> Percent	RESIDUE ATOM RATIO		
				Cu	Fe	S
0	0	0	0	5.6	1.0	4.2
1	30	5	2	4.2	1.0	4.6
6	32	8	2	4.2	1.0	4.6
24	46	1	5	3.1	1.0	3.7
72	65	5	22	2.2	1.0	3.7
168	78	26	48	1.9	1.0	3.2

TABLE 3

SULLIVAN'S RESULTS PERTAINING TO FERRIC SULFATE LEACHING  
OF COVELLITE MINERAL

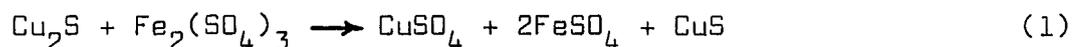
TIME Hours	TOTAL COPPER DISSOLVED Percent	SULFUR IN RESIDUE DISSOLVED By CS <sub>2</sub> Percent	RESIDUE ATOM RATIO	
			Cu	S
0	0	0	1.0	1.0
24	49	47	1.0	1.0
38	78	77	1.0	1.0

TABLE 4

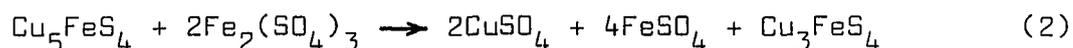
SULLIVAN'S RESULTS PERTAINING TO FERRIC SULFATE LEACHING  
OF CHALCOPYRITE MINERAL

TIME Days	TOTAL COPPER DISSOLVED Percent	SULFUR IN RESIDUE DISSOLVED By CS <sub>2</sub> Percent	RESIDUE ATOM RATIO		
			Cu	Fe	S
0	0	0	1.0	1.2	2.2
1	8	5	1.0	1.2	2.2
7	15	10	1.0	1.2	2.2
14	22	10	1.0	1.2	2.2
21	26	20	1.0	1.2	2.2
42	30	23	1.0	1.2	2.2

Since the present kinetic examination of ferric sulfate leaching of the four sulfide minerals concerned the early stages of leaching, the initial data in the four tables were examined to determine stoichiometric relations. After twelve hours of chalcocite leaching 46 percent of the copper was dissolved from the mineral. Little sulfur residue was produced. The residue atom ratio was Cu/S = 1.0/1.0. The residue was a pseudo-covellite mineral. Therefore, the stoichiometric reaction occurring during the first twelve hours of leaching was postulated to be:



After twenty-four hours of leaching the bornite mineral, 46 percent of the initial copper content was dissolved. Little sulfur residue and soluble iron was formed during the leaching. At this point of leaching the residue atom ratio was measured to be Cu/Fe/S = 3.1/1.0/4.2. The observed atom ratio was close to the chemical formula  $\text{Cu}_3\text{FeS}_4$ . Therefore, the proposed chemical reaction was

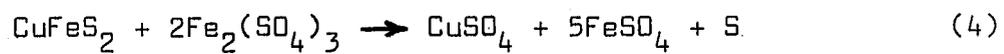


Covellite oxidized during the leaching test yielded equal moles of soluble copper and of sulfur residue. The atom ratio of the residue was Cu/S = 1.0/1.0 from which the following chemical reaction was proposed:



The results obtained from the leaching of chalcopyrite mineral indicated dissolution of the mineral to soluble copper

and iron sulfates and a sulfur residue. The proposed chemical reaction was:



## CHAPTER III

### THEORETICAL CONSIDERATIONS

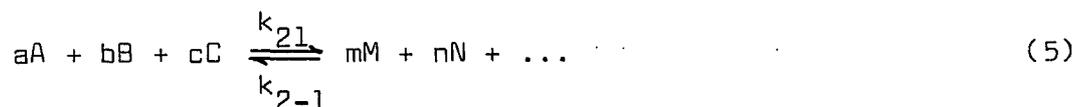
The principle functions of reaction kinetics are (Walas 1959, p. 2)

1. Collecting experimental data,
2. Correlating rate data by mathematical equations or otherwise,
3. Establishing the chemical mechanism of the reaction,
4. Designing suitable reactors, and
5. Specifying operating conditions, methods of control, and auxiliary equipment.

The theoretical considerations involving steps 2 and 3, the determining of the mathematical equations and the establishing of the possible chemical mechanism, are considered in the following discussions.

#### Reaction Rate and Rate Expression

The reaction rate is defined as the number of units of mass of some participant that is formed or transformed per unit of time per unit of volume of the system (Walas 1959, p. 5). For the general reversible reaction



the rate expression for the decrease in component (A) is given by

$$r_A = -k_{21} C_A^p C_B^q C_C^r + k_{2-1} C_M^s C_N^t \dots \quad (6)$$

C is the concentration of each component in moles per liter, and  $k_{21}$  and  $k_{2-1}$  the specific rate constants. The value of  $r_A$  is defined

$$r_A = \left(\frac{1}{V}\right) \left(\frac{dn_A}{dt}\right) = \left(\frac{1}{\text{Liters}}\right) \left(\frac{\text{Moles of A}}{\text{Unit of Time}}\right) \quad (7)$$

Eq. 7 can also be defined by

$$r_A = \frac{dC_A}{dt} = \frac{\text{Moles of A/liter}}{\text{Unit of Time}} \quad (8)$$

If the equilibrium constant, (K), for the reaction, Eq. 5,

is

$$K = \frac{k_{21}}{k_{2-1}} = \frac{C_M^s C_N^t \dots}{C_A^p C_B^q C_C^r} \quad (9)$$

and if the value of K is very large, Eq. 6 can be expressed as

$$r_A = -k_{21} C_A^p C_B^q C_C^r; \text{ for } K \text{ very large} \quad (10)$$

the sum (p + q + r) is defined as the order of the reaction. The equivalent rates of the other participants in the reaction to the rate of consumption of component (A) is given by

$$\frac{r_A}{a} = \frac{r_B}{b} = \frac{r_C}{c} = -\frac{r_M}{m} = -\frac{r_N}{n} = \dots \quad (11)$$

where a, b, c, m, n, ..., are the moles of the components A, B, C, M, N, ..., participating in the reaction.

### Theory of Absolute Reaction Rates

The theory involves the hypothesis that even when the reactants and products of a reaction are not at equilibrium with each other, the activated complex is at equilibrium with the reactants (Barrow 1961, pp. 364-371). The activated complex is a "transition state" component of the reactants which occurs before the products of the reaction are formed.

#### Derivation of the Rate Expression and the Specific Reaction Rate Constant

The chemical reaction for a system involving reactants A and B is expressed as,  $A + B \rightleftharpoons (X)^* \rightarrow \text{Products}$ , where  $(X)^*$  is the activated complex. The rate expression for this reaction as determined by the absolute rate theory is

$$r_A = \left(\frac{kT}{h}\right) \left(\frac{F^*}{F_A F_B}\right) (e^{-E_0/RT}) C_A C_B \quad (12)$$

where the "F" values are the partition functions for the reactants and the activated complex.

The energy required to activate the reactants to the activated complex state,  $(X)^*$ , is  $E_0$ . Comparing Eq. 12 to Eq. 10, an expression for the specific rate constant,  $k_2$ , is obtained

$$\frac{k_2}{T} = \left(\frac{k}{h}\right) \left(\frac{F^*}{F_A F_B}\right) e^{-E_0/RT} \quad (13)$$

#### Experimental Energy of Activation

The hypothetical energy of activation,  $E_0$ , as defined by Laidler (1950, p. 67) is

...the difference between the zero-point energy per mole of the activated complexes and that of the reactants. Since this energy is the amount of energy that the reactants must acquire at 0° K before they can react,  $E_0$  is the energy of activation at that temperature.

The relationship between  $E_{EXP}$ , the experimental energy of activation, and  $E_0$  can be stated by Eq. 14, (Laidler 1965, p. 76 and pp. 87-88).

$$E_{EXP} = E_0 + nRT \quad (14)$$

The term  $n$  is the total increase in moles of the reacting system. If  $n$  is small and  $E_0$  large, the value of  $E_{EXP}$  approximately equals  $E_0$ .

#### Thermodynamic Formulation of Specific Rate Constant

Thermodynamic functions can be applied to the specific rate constant expression to present it in a convenient form (Laidler 1965, pp. 88-90). The expression for  $k_2/T$ , which results, is

$$\frac{k_2}{T} = \left(\frac{k}{h}\right) e^{-(\Delta F)^*/RT} = \left(\frac{k}{h}\right) (e^{(\Delta S)^*/R}) (e^{-(\Delta H)^*/RT}) \quad (15)$$

The terms  $(\Delta F)^*$ ,  $(\Delta S)^*$ , and  $(\Delta H)^*$  are, respectively, the free energy, the entropy, and the enthalpy of activation. The experimental energy of activation can be compared to the enthalpy of activation

$$E_{EXP} = (\Delta H)^* - p (\Delta V)^* + RT \quad (16)$$

For the reactions in solution  $(\Delta V)^*$  is small. Therefore, the experimental energy of activation becomes.

$$E_{EXP} = (\Delta H)^* + RT \quad (17)$$

The value of the specific rate constant for reactions in solution is determined by

$$\frac{k_2}{T} = (e) \left(\frac{k}{h}\right) (e^{(\Delta S)^*/R}) (e^{-E_{EXP}/RT}) \quad (18)$$

### The Temperature Dependency of the Specific Rate Constant, $k_2$

The Arrhenius equation (Laidler 1965, p. 87) for temperature dependence of the rate constant,  $k_2/T$ , is

$$\frac{k_2}{T} = A' e^{-E_{EXP}/RT} \quad (19)$$

Comparing Eq. 19 to Eqs. 13 and 18, the value of  $A'$ , the "frequency factor," is calculated by

$$A' = \left(\frac{k}{h}\right) \left(\frac{F^*}{F_A F_B}\right) = e \left(\frac{k}{h}\right) e^{(\Delta S)^*/R} \quad (20)$$

### Diffusion Rates

#### Fick's First Law of Diffusion

Fick's equation states that species A in a mixture of A and B diffuses (moves relative to the motion of the mixture) in the direction of decreasing mole fraction of A (Bird, Stewart, and Lightfoot 1960, p. 502).

$$J_A^* = -D_{AB} \nabla c_A \quad (21)$$

When the diffusion flux is taken relative to a stationary coordinate system, Eq. 21 reduces to Eq. 22.

$$N_A - x_A (N_A + N_B) = -D_{AB} \nabla c_A \quad (22)$$

Where  $N_A$  is the total flux of A across any given boundary, and  $x_A (N_A + N_B)$  is the flux due to bulk flow of A. If  $x_A (N_A + N_B)$  is

assumed to be zero, Eq. 23 is obtained.

$$N_A = -D_{AB} \nabla C_A = \frac{\text{Moles of A per unit area}}{\text{Unit Time}} \quad (23)$$

A specific case of the first law was presented by Halpern (1957, p. 285) in which diffusion was considered to occur along the X-axis.

$$N_{AX} = D_{AB} \frac{\delta C_A}{\delta x} = \frac{\text{Moles of A per unit area}}{\text{Unit Time}} \quad (24)$$

By assuming a linear concentration gradient Eq. 25 was obtained (Burkin 1966, pp. 34-39)

$$N_{AX}^S = \left( \frac{D_{AB}^S}{d} \right) (C_A - C_{A0}) = \frac{\text{Moles of A}}{\text{Unit Time}} \quad (25)$$

where  $c$  was the concentration in moles per cubic centimeter, or

$$r_A = \frac{N_{AX}^S}{V} = \left( \frac{D_{AB}^S}{Vd} \right) (C_A - C_{A0}) = \frac{\text{Moles of A per liter}}{\text{Unit Time}} \quad (26)$$

where  $C$  was the concentration in moles per liter.

### Unsteady-State Expression for Diffusion

Fick's second law of diffusion, the general expression for unsteady-state diffusion with no chemical reaction, is given in Eq. 27 (Bird, Stewart, and Lightfoot 1960, pp. 554-558).

$$\frac{\delta C_A}{\delta t} = D_{AB} \nabla^2 C_A \quad (27)$$

If diffusion is considered to proceed along the X-axis, the second law becomes

$$\frac{\delta C_A}{\delta t} = D_{AB} \frac{\delta}{\delta x} \left( \frac{\delta C_A}{\delta x} \right) \quad (28)$$

Eq. 28 predicts the variation in the concentration gradient ( $\delta^c A / \delta x$ ) with time and distance,  $x$ , from which the resulting diffusion flux can be calculated at any particular time.

### Theories of Diffusion

One theory was presented by Glasstone (Glasstone, Laidler, and Eyring 1941, pp. 516-521). It was assumed that a molecule of solute and a molecule of solvent must slip past each other in order to obtain the diffusion of the solute. The distance between successive equilibrium positions was designated by  $\lambda$ . It was also assumed that the free energy barrier was symmetrical. From these basic assumptions the expression concerning the diffusivity,  $D^\circ$ , at infinite dilution was calculated.

$$\frac{D^\circ}{T} = \lambda^2 k_2 = e \lambda^2 \left(\frac{k}{h}\right) e^{(\Delta S)^*/R} e^{-E_{EXP}/RT} \quad (29)$$

The frequency factor was given by

$$A'' = e \lambda^2 \left(\frac{k}{h}\right) e^{(\Delta S)^*/RT} \quad (30)$$

If the entropy of activation for the diffusion process was assumed to be zero, Eq. 31 resulted.

$$\lambda = \sqrt{A''}, \text{ in Angstroms} \quad (31)$$

A special case of the Glasstone theory was postulated (Glasstone, Laidler, and Eyring 1941, pp. 519-520).

When a large molecule or ion diffuses or migrates electrically in a solvent consisting of relatively small molecules, it is unlikely that the rate-determining step will be the jump of the solute molecule from one equilibrium position to the next, since the work required to produce the necessary space would be very large. It is

much more probable, therefore, that the jump of the solvent in one direction is the rate-determining process; then the large molecule of solute moves in the opposite direction into the space left vacant as a result of the motion of the solvent molecule. ...It is clearly the movement of the solvent molecules that determines the rate of diffusion of the solute in these instances.

The relationship between the diffusion coefficients of the large molecule,  $D_1$ , and the small molecule,  $D_s$ , was given by Glasstone as

$$D_1 = D_s \left( \frac{\lambda}{a\pi r} \right) \quad (32)$$

The value of  $\lambda$  was defined as the distance between successive equilibrium positions of the solvent molecule,  $r$  as the radius of the large diffusing molecule, and "a" as a factor of the order of unity which allows for the fact that the small molecule may not take the shortest path in its journey around the large molecule.

A second theory of diffusion was postulated by Robinson and Stokes (1955, pp. 292-297). This theory is founded on the similarities of diffusion to ionic conductance, on the chemical potential gradient, and on the assumption that diffusion was a slow process in which departures from equilibrium were small as compared with a chemical process. From the basic theory and their related formulas, the expression for the diffusivity at infinite dilution was calculated as

$$\frac{D^0}{T} = \left( \frac{R(v_1 + v_2)}{F_e^2 v_1 z_1} \right) \left( \frac{\lambda_1^0 \lambda_2^0}{\lambda_1^0 + \lambda_2^0} \right) \quad (33)$$

For the condition of concentrated solutions of polyvalent solutes an expression, which approximated the diffusivity, was given as

$$\frac{D}{T} = \left(\frac{D^0}{T}\right) \left(1 - m \frac{d \ln \gamma_{\pm}}{dm}\right) (1 - 0.018m) \left(\frac{3D^*}{D} - H_n\right) (N^0/N) \quad (34)$$

### Estimation of the Activity Coefficients for Ionic Species

The activity coefficient of an ionic species may be estimated by one of the equations developed from the Debye-Hückel theory (Robinson and Stokes 1959, pp. 229-232). One of these equations is

$$-\log \gamma_i = \frac{Az_i^2 \sqrt{I}}{1 + Ba \sqrt{I}} + bI \quad (35)$$

The values of A, B, and b are constant at a particular temperature. The constants A and B are listed in Table 5 (Klotz 1964, p. 416).

TABLE 5

A AND B CONSTANTS FOR THE DEBYE-HÜCKEL EQ. 35  
AT SEVERAL SOLUTION TEMPERATURES

TEMPERATURE °C	A	B
20	0.5046	0.3276
25	0.5091	0.3286
30	0.5139	0.3297
35	0.5189	0.3307
40	0.5241	0.3375
45	0.5295	0.3330
50	0.5357	0.3342

The ionic strength, I, is calculated by Eq. 36.

$$I = \frac{1}{2} \sum C_i z_i^2 \quad (36)$$

The mean activity coefficient of ferric sulfate in solution is calculated by Eq. 37.

$$\gamma_{\pm} = (\gamma_{\text{Fe}^{+3}}^2 \gamma_{\text{SO}_4^{-2}}^3)^{\frac{1}{5}} \quad (37)$$

#### Aqueous Ferric Sulfate Diffusivities

Utilizing Eqs. 33 and 34 the diffusivity of ferric sulfate,  $\text{Fe}_2(\text{SO}_4)_3$ , was calculated. The value of  $(N^\circ/N)$  in Eq. 34 was estimated by Eq. 38.

$$(N/N^\circ) = (1 + A_2 m) \quad (38)$$

The various values utilized in the calculation of the diffusivities of ferric sulfate are given in Tables A-1, A-2, and A-3, Appendix A. Table A-1 lists the limiting ionic conductivities,  $\lambda_i^\circ$ , for various ions versus the temperature of the aqueous solution. Table A-2 gives the activity coefficients for aluminum, indium, and ferric sulfate in water versus the concentration of the solute. Table A-3 lists the values of  $A_2$  for Eq. 38 at various temperatures.

The ionic conductivities for ferric ions,  $\text{Fe}^{+3}$ , and lanthanum ions,  $\text{La}^{+3}$ , at 25°C were listed in Table A-1 as 68.0 and 72.0, respectively. Because of this near equivalency at 25°C, the ionic conductivities for ferric ions, through the temperature range 0° to 128°C, were assumed to be equal to the ionic conductivities for lanthanum ions.

The activity coefficients of ions in aqueous solutions are dependent on ionic strength, effective diameter of hydrated

ions, and ion-solvent interactions (Klotz 1964, pp. 415-419; Robinson and Stokes 1959, pp. 238-248). These values are nearly equivalent for ferric ions,  $\text{Fe}^{+3}$ , indium ions,  $\text{In}^{+3}$ , and aluminum ions,  $\text{Al}^{+3}$ , in aqueous solutions. Therefore, the activity coefficients for ferric sulfate were assumed to be equivalent to the coefficients for indium and aluminum sulfates. Because of similar electrochemical behavior between cerrous ions,  $\text{Ce}^{+3}$ , and ferric ions (Gurney 1953, pp. 159-171), the values of  $A_2$  for ferric ions were assumed to be equivalent to the  $A_2$  values for cerrous ions.

The results of the estimated diffusivity calculations are given in Table 6. The diffusivities of ferric sulfate in square centimeters per minute at various solution temperatures and for increasing ferric sulfate concentrations in moles per liter are listed.

TABLE 6  
 DIFFUSIVITIES OF FERRIC SULFATE IN WATER  
 AT VARIOUS TEMPERATURES AND  
 CONCENTRATIONS

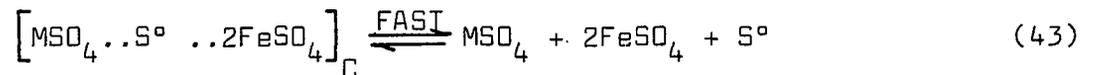
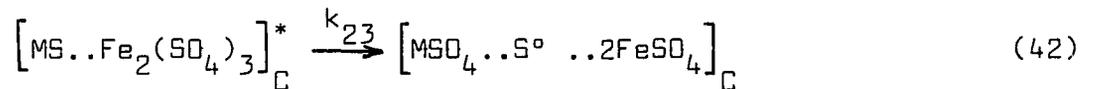
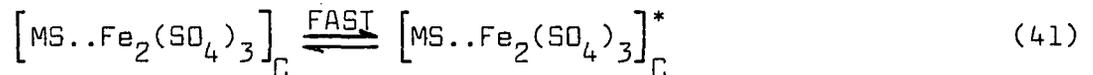
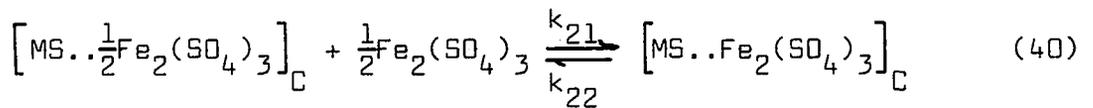
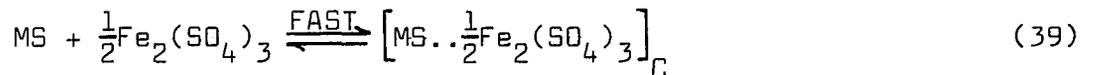
FERRIC SULFATE Moles per Liter	DIFFUSIVITY, $D \times 10^4$ , square centimeters per minute				
	25°C	28°C	38°C	52°C	68°C
0.000	4.84	5.44	6.90	9.16	12.3
0.010	1.83	2.05	2.62	3.48	4.66
0.020	1.82	2.04	2.59	3.44	4.62
0.050	1.58	1.78	2.25	2.99	4.01
0.100	1.55	1.74	2.20	2.93	3.93
0.200	1.21	1.36	1.72	2.29	3.07
0.300	1.24	1.39	1.76	2.34	3.15
0.400	1.62	1.82	2.31	3.06	4.11
0.500	1.91	2.14	2.71	3.61	4.85
0.600	1.86	2.08	2.64	3.52	4.72
0.700	2.14	2.40	3.04	4.04	5.44

#### Chemical Reaction at the Surface of a Mineral

A process similar to the chemisorption of a gas at an active site on a solid catalyst surface (Laidler 1965, pp. 256-320) could exist between an ion in solution and the surface of a mineral. Sulfides, such as chalcocite, bornite, covellite, and chalcopyrite, consist of the basic tetrahedral sulfur structure with the various cations situated in specific spaces between the sulfur atoms (Bragg, Claringbull, and Taylor 1965, pp. 45-83;

Lundquist and Westgren 1936, pp. 3-5). The active sites could be at certain crystallographic positions of the sulfur tetrahedra.

The chemisorption reaction between ferric sulfate in solution and the active sites of a metal sulfide, MS, could proceed by the steps which are indicated in reaction Eqs. 39 through 43.



Reaction Eqs. 39 and 40 are the adsorption steps. Reaction Eq. 41 is the formation of the activated complex, and reaction Eq. 42 is the subsequent electron exchange between the adsorbed species,  $\text{Fe}_2(\text{SO}_4)_3$ , and the mineral, MS.

If the adsorption process controls the overall reaction, the rate of consumption of ferric sulfate in solution is expressed by Eq. 44 (Andersen, Halpern, and Samis 1953, pp. 554-558; Dresher, Wadsworth, and Fassell 1956, pp. 794-800; Ong, Wadsworth, and Fassell 1956, pp. 257-263; Pearson and Wadsworth 1958, pp. 294-299).

$$\frac{r_A}{S} = \frac{k_o k_{21}}{N_a V} f(\theta) f(C_A) \quad (44)$$

In this equation the rate is a function of the fraction of active sites covered and of the ferric sulfate concentration. If the surface reaction process controls, the rate of consumption of ferric sulfate is expressed by Eq. 45.

$$\frac{r_A}{S} = \frac{k_o k_{23}}{N_a V} f(\theta) \quad (45)$$

In this equation the rate is a function of the fraction of active sites covered.

The term,  $k_o$ , in Eqs. 44 and 45 is the total number of active sites available on the mineral surface. It is defined by Eq. 46.

$$k_o = k_{SR} k_{ACT} k', \text{ (molecules or atoms per unit area)} \quad (46)$$

The terms  $k_{SR}$ ,  $k_{ACT}$ , and  $k'$  are, respectively, the surface roughness factor, the fraction of the total number of surface sites activated, and the geometric number of molecules or atoms per unit area of surface.

If the surface reaction, Eq. 42, controls the overall chemisorption process, the number of active sites covered by ferric sulfate are determined by assuming that:

1. Eq. 40 is near equilibrium, but it is considerably slower than Eqs. 39, 41, and 43.
2. Steady state exists in which the concentration of surface reactants are considered constant for any one set of conditions.

3. The rate of formation of  $[\text{MS} \cdot \text{Fe}_2(\text{SO}_4)_3]_C$  sites, Eq. 40, is balanced by the rate at which they disappear, Eqs. 42 and 40.

Based on these assumptions, the value of  $\theta$  is determined by Eq. 47.

$$\theta = \frac{\left(\frac{k_{21}}{k_{22} + k_{23}}\right) C_A}{1 + \left(\frac{k_{21}}{k_{22} + k_{23}}\right) C_A} \quad (47)$$

If the overall reaction is controlled by Eq. 42, the rate is determined by combining Eqs. 45 and 47.

$$\frac{r_A}{S} = \frac{k_a k_b C_A}{1 + k_b C_A} \quad (48)$$

The values of  $k_a$  and  $k_b$  are defined by Eqs. 49 and 50.

$$k_a = \frac{k_o k_{23}}{N_a V} \quad (49)$$

$$k_b = \left(\frac{k_{21}}{k_{22} + k_{23}}\right) \quad (50)$$

If the value of  $k_{22}$  is considerably greater than  $k_{23}$ , reaction Eq. 40 is at equilibrium. Therefore, Eq. 48 is modified to

$$\frac{r_A}{S} = \frac{k_a k_{eq} C_A}{1 + K_{eq} C_A} \quad (51)$$

$K_{eq}$  is the equilibrium constant for reaction Eq. 40, i.e.,

$$K_{eq} = \frac{k_{21}}{k_{22}} = k_b \quad (52)$$

From Eq. 51 two cases involving the degree of covering of active sites by ferric sulfate can be determined. The first case, in

which the active sites are fully covered, and the value of  $K_{eq}$  is greater than one, is expressed by Eq. 53.

$$\frac{r_A}{S} = k_a, \text{ for } \theta \rightarrow 1 \text{ and } K_{eq} > 1 \quad (53)$$

The second case, in which the active sites are sparsely covered by adsorbed ferric sulfate, is expressed by Eq. 54.

$$\frac{r_A}{S} = k_a k_{eq} C_A, \text{ for } \theta \rightarrow 0 \text{ and } K_{eq} < 1 \quad (54)$$

If the value of  $k_{23}$  is considerably greater than  $k_{22}$ , Eq. 48 is modified to

$$\frac{r_A}{S} = \frac{k_a k_b C_A}{1 + k_b C_A} \quad (55)$$

Eq. 55 asserts that equilibrium in the adsorption process, Eq. 48, has not been attained. The value of  $k_b$  now becomes

$$k_b = \frac{k_1}{k_2} \quad (56)$$

The terms  $k_a$  and  $K_{eq}$  or  $k_b$  in the above equations can be determined from the plots of rate of consumption of ferric sulfate during leaching versus the concentration of ferric sulfate. Curves are determined at several temperatures. An example of a set of these curves is given in Figure 1. Values of  $k_a$  are calculated from the curve plateau ( $\theta \rightarrow 1$ ). Using the calculated value of  $k_a$  and another point on the same rate isotherm, the value of  $K_{eq}$  or  $k_b$  can be determined.

The constant determined,  $K_{eq}$  or  $k_b$ , will depend on the mechanism. All surface adsorption processes must be exothermic,

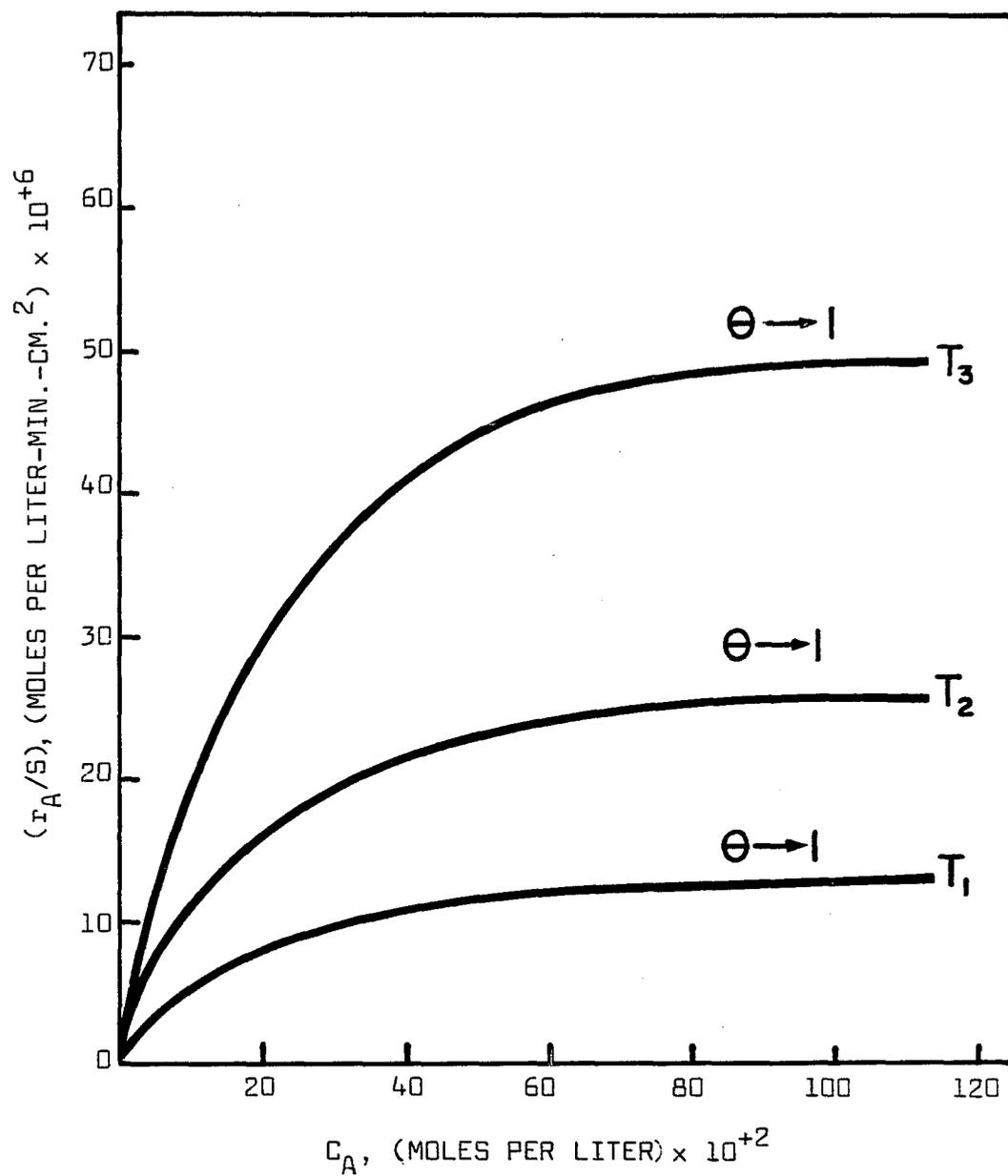
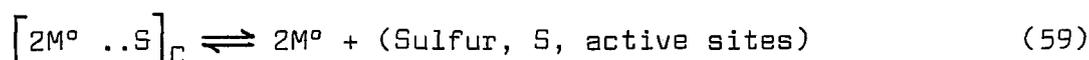
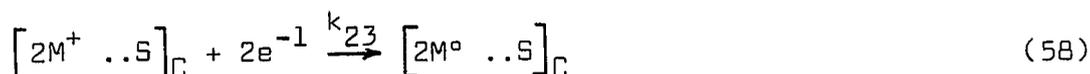
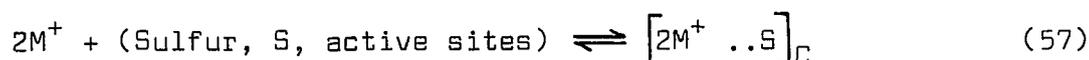


Fig. 1. Rate of reaction of species A versus the concentration of species A.

i.e., the constant decreases with increasing temperatures (Dresher, Wadsworth, and Fassel 1956, p. 799). The value calculated is  $K_{eq}$ , and Eqs. 51 through 54 will hold. If the constant increases with increasing temperature, the value calculated is  $k_b$  and Eqs. 55 and 56 will hold.

### Electrode Process

The process to be examined is the irreversible cathodic discharge of a cation at an electrode surface (Potter 1956, pp. 124-154; Young 1960, pp. 34-50; Glasstone, Laidler, and Eyring 1941, pp. 575-598). Eq. 42 showing the discharging process of the chemisorbed ferric sulfate on the sulfide surface could be such a process. A hypothetical mechanism for the cathodic discharge is given by reactions, Eqs. 57 through 59.



The term  $e^{-1}$  is the number of electrons exchanged between the ion and the electrode in going from  $M^+$  to  $M^0$ .

The degree of irreversibility is measured by the departure of the electrode potential,  $e$ , from the reversible value,  $e^0$ , under the same conditions of temperature, pressure, and concentrations (Potter 1956, p. 124). The departure is given by the polarization potential,  $e_p$ , and is related to the reversible and irreversible potentials by Eq. 60.

$$e_p = e - e^0 \quad (60)$$

The polarization potential alters the free energy of the overall process. The free energy diagram accompanying reaction Eqs. 57 through 59 is given in Figure 2. The various steps described in the diagram are

1. 'A' the chemisorbed ions  $M^0$  about to increase in charge,
2. 'B' the chemisorbed ions  $M^+$  about to decrease in charge,
- and
3. 'C' the  $M^+$  ions in the solution.

The points D and E are, respectively, the activated states of the  $M^+$  ions in solution during the chemisorption process and of the chemisorbed ions,  $[M^+ \dots S]_C$ , in the discharging process. The value of  $\alpha$  in the free energy terms  $(n\alpha e_p F_e)$  and  $(n(1-\alpha)e_p F_e)$  in Figure 2 is that fraction of the polarization potential aiding the discharging process.

If all reactions are at dynamic equilibrium, a reversible process exists. The rate of the electron exchange reaction is given by Eq. 61

$$\frac{r_{1e}}{S} = \frac{r_{2e}}{S} = \left(\frac{kT}{h}\right)(a_+)_e \text{EXP}(-\Delta F_1^*/RT) \quad (61a)$$

$$= \left(\frac{kT}{h}\right)(a_0)_e \text{EXP}(-\Delta F_2^*/RT) \quad (61b)$$

The values of  $(a_+)_e$  and  $(a_0)_e$  are the equilibrium activities of the chemisorbed  $M^+$  and  $M^0$  ions, respectively. Using Eq. 62 the

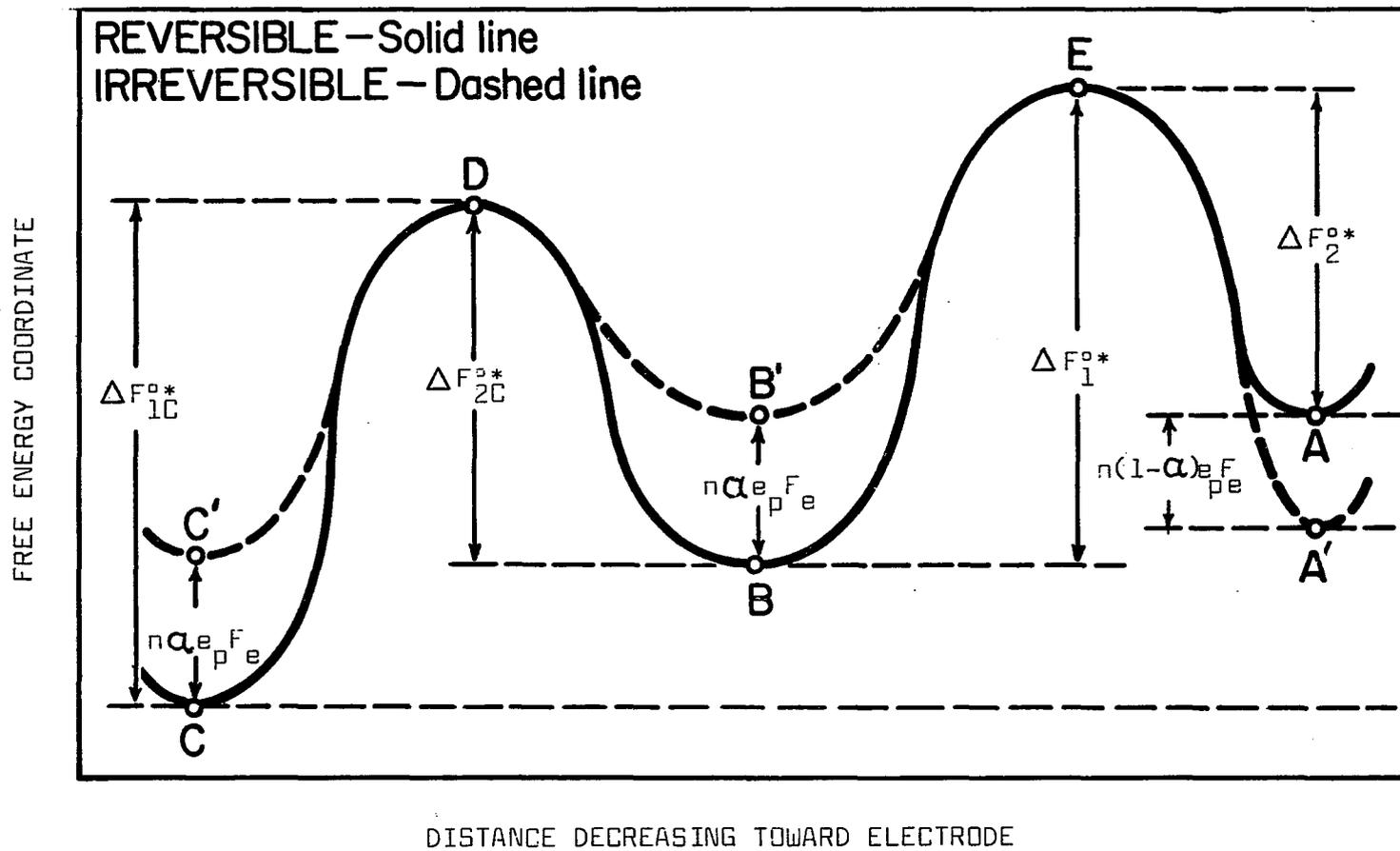


Fig. 2. Free energy diagram for reversible and irreversible electrode reactions.

standard free energy of the electrode process is obtained.

$$\Delta F^\circ = (\Delta F_1^{\circ*} - \Delta F_2^{\circ*}) = -RT \ln K_e = -RT \ln \frac{(a_o)_e}{(a_+)_e} \quad (62)$$

If all reactions but the electron exchange process, Eq. 58, are at equilibrium, an irreversible process exists. The net rate of the reaction is given by Eq. 63.

$$\frac{r_{NET}}{S} = \left( \frac{r_1 - r_2}{S} \right) = \frac{r_{1e}}{S} \left[ \text{EXP} \left( \frac{n\alpha_e F_e}{RT} \right) - \text{EXP} \left( -\frac{n(1-\alpha)_e F_e}{RT} \right) \right] \quad (63)$$

The net free energy loss due to the current flow is

$$\Delta F = (\Delta F_1^{\circ*} - n\alpha_e F_e) - (\Delta F_2^{\circ*} + n(1-\alpha)_e F_e) \quad (64)$$

If the rate of discharge of the  $M^+$  ions is much greater than the charging of the  $M^0$  ions, the net rate of reaction is given by Eq. 65.

$$\frac{r_{NET}}{S} = \frac{r_1}{S} = \left( \frac{kT}{h} \right) (a_+)_e \text{EXP} \left[ \frac{(-\Delta F_1^{\circ*} + n\alpha_e F_e)}{RT} \right] \quad (65)$$

The net rate of electron flow from the electrode surface to the discharging  $M^+$  ions is obtained by the following equation.

$$i_{NET} = \frac{r_1}{S} F_e n = n F_e \left( \frac{kT}{h} \right) (a_+)_e \text{EXP} \left[ \frac{(-\Delta F_1^{\circ*} + n\alpha_e F_e)}{RT} \right] \quad (66)$$

Eq. 66 can be rearranged to yield an expression for the polarization potential,  $e_p$ , in terms of the current  $i$ .

$$e_p = a + b \ln i \quad (67)$$

$$a = -\left( \frac{2.3RT}{\alpha n F_e} \right) \ln (I) \quad (68)$$

$$b = \left( \frac{2.3RT}{\alpha n F_e} \right) \quad (69)$$

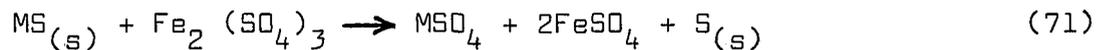
$$I = \left(\frac{kT}{h}\right)(a_+) e^{\text{EXP}\left(-\frac{\Delta F^{\circ*}}{RT}\right)} \quad (70)$$

Eq. 67 is known as the Tafel equation. It applies when the polarization potential is greater than 50 to 100 millivolts. For a given current, the polarization potential is small if I is large (Young 1960, p. 42).

#### Equations Used in the Calculation of the Results

The basic equations used in the calculation of the rate expressions from the experimental data for the reaction between a sulfide mineral and aqueous ferric sulfate are given below.

For the general reaction



the rates of consumption or production of each component are given by

$$2\frac{dMS}{dt} = 2\frac{d(Fe_2(SO_4)_3)}{dt} = -\frac{d(FeSO_4)}{dt} = -2\frac{d(MSO_4)}{dt} \quad (72)$$

The differential rate expression used in the following chapters is Eq. 73.

$$\frac{d(Fe_2(SO_4)_3)}{dt} = r_A \frac{\text{Moles per liter}}{\text{Minute}} \quad (73)$$

The expression for the dependence of the rate of reaction on ferric sulfate or sulfuric acid concentration is given by Eq. 74.

$$\frac{r_A}{S} = -k_2 C_A^p \text{ or } -k_{2B} C_B^q \frac{(\text{Moles/Liter})}{(\text{Minute})(\text{cm}^2)} \quad (74)$$

$k_2$  is the specific rate constant,  $C_A$  and  $C_B$  are the concentrations of ferric sulfate (A) and sulfuric acid (B), in moles per liter,

p and q are the orders of the reaction in respect to ferric sulfate and sulfuric acid, and S is the exposed surface area of the mineral MS in square centimeters. The value of the specific rate constant is determined by

$$\frac{k_2}{T} = \frac{(\text{Moles per Liter})^{1-p}}{(\text{Min.-Cm.}^2\text{-}^\circ\text{K})} \quad (75)$$

The Arrhenius equation for the temperature dependence of the specific rate constant is

$$\frac{k_2}{T} = A' e^{-E_{\text{EXP}}/RT} \quad (76)$$

The frequency factor (A') is in the units of (k<sub>2</sub>/T). The value of E<sub>EXP</sub>, the experimental activation energy, is in calories per mole of activated complex.

## CHAPTER IV

### EXPERIMENTAL APPARATUS

Two types of leach cells were used in the investigation. These were the AGITATION and FLOW cells.

The AGITATION cell was used to leach the samples of the readily oxidizable sulfide minerals which were chalcocite, covellite, bornite, and pyrrhotite. A single mineral specimen was used in each instance. This specimen was immersed in the ferric sulfate solution which was contained within the cell. The solution was agitated vigorously to produce a thin bulk-solution mineral-surface barrier for ferric sulfate diffusion (Halpern 1957, p. 280).

The FLOW cell was used to leach the chalcopyrite mineral samples. A large exposed mineral surface area was required because of slow dissolution rates. Therefore, the mineral was ground and sized providing the required exposed surface area. Vigorous agitation of the solution was not required because preliminary leach tests indicated that the leaching reaction between ferric sulfate solutions and chalcopyrite were not controlled by ferric sulfate diffusion. Thus the leach solutions were pumped through a bed of chalcopyrite particles contained in a

glass tube at such a rate as to produce a solution retention time between 0.01 to 0.02 minutes.

The component parts of the AGITATION cell as shown in Figure 3 and as assembled in Figure 4 were

1. Plexiglas reaction cell, four inch outside diameter,
2. Plexiglas bearing for the glass stirring rod,
3. Glass stirring rod,
4. Exhaust gas outlet tube,
5. Combination gas inlet tube and solution sampling tube assembly,
6. Thermometer,
7. Mineral specimen holder, and
8. Agitator motor.

Two assembled cells were placed into a constant temperature bath. The constant temperature bath as shown in Figure 5 consisted of the following pieces of equipment:

1. Mercury relay, normally closed (Inside box),
2. Mercury thermostat,
3. Two immersion heaters,
4. Glass aquarium tank, three gallon,
5. Bath agitator and stirring rod, and
6. "Variac" power transformer (To control the rotation speed of the two leach-cell stirring motors).

The component parts of the FLOW cell, Figure 6, consisted of

1. Reaction cell- flow tube, pump outlet tube,

2. Gorman - Rupp polyethylene pump, Number 11885,
3. Pump intake tube,
4. Three hole round bottom flask, 500 milliliter,
5. Thermometer,
6. Flow cell retainer ring,
7. Solution flow control clamp, and
8. Solution sampling tube and inert gas inlet tube assembly.

The FLOW cell was assembled as shown in Figure 7. The glass tube which contained the ground and sized mineral was constructed as drawn in Figure 8. This cell was also immersed in the constant temperature bath during the leach tests.

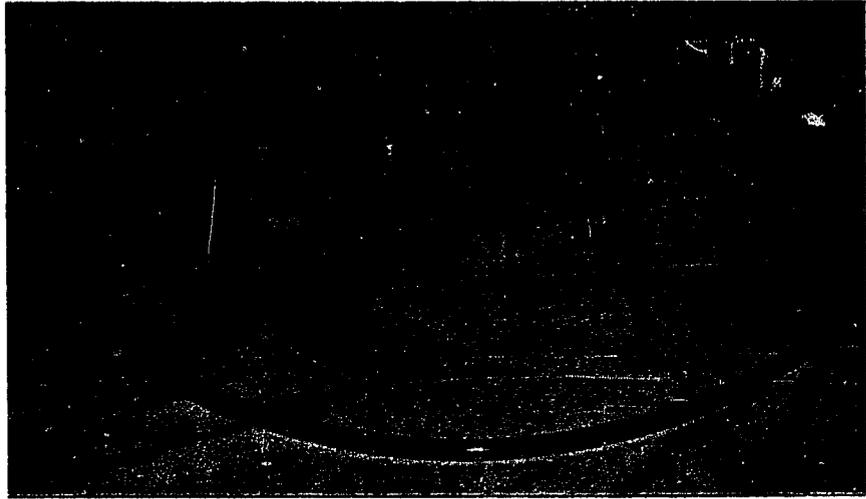


Fig. 3. Agitation-Cell Component Parts



Fig. 4. Assembled Agitation Cell

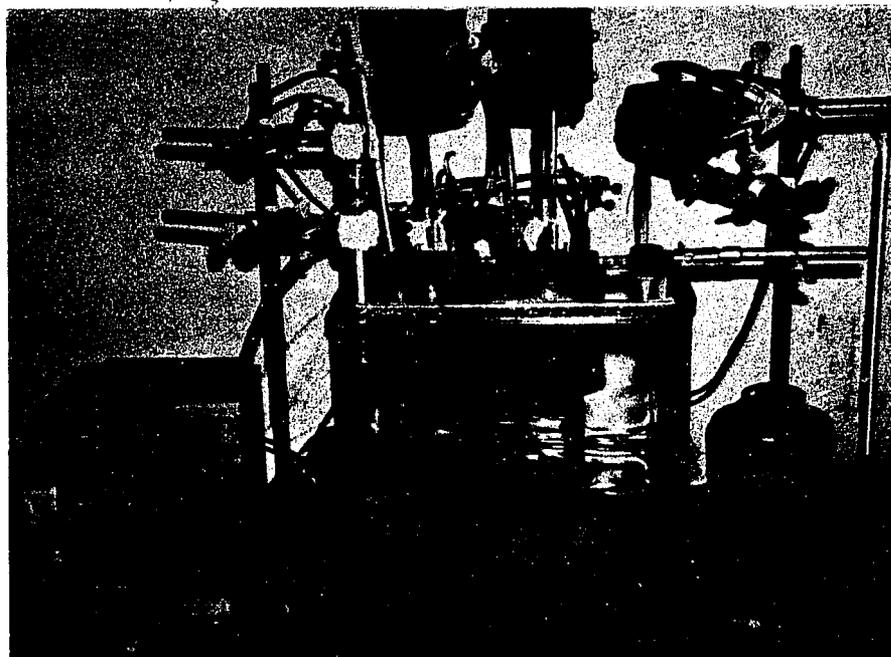


Fig. 5. Constant Temperature Bath



Fig. 6. Flow-Cell Component Parts



Fig. 7. Assembled Flow Cell

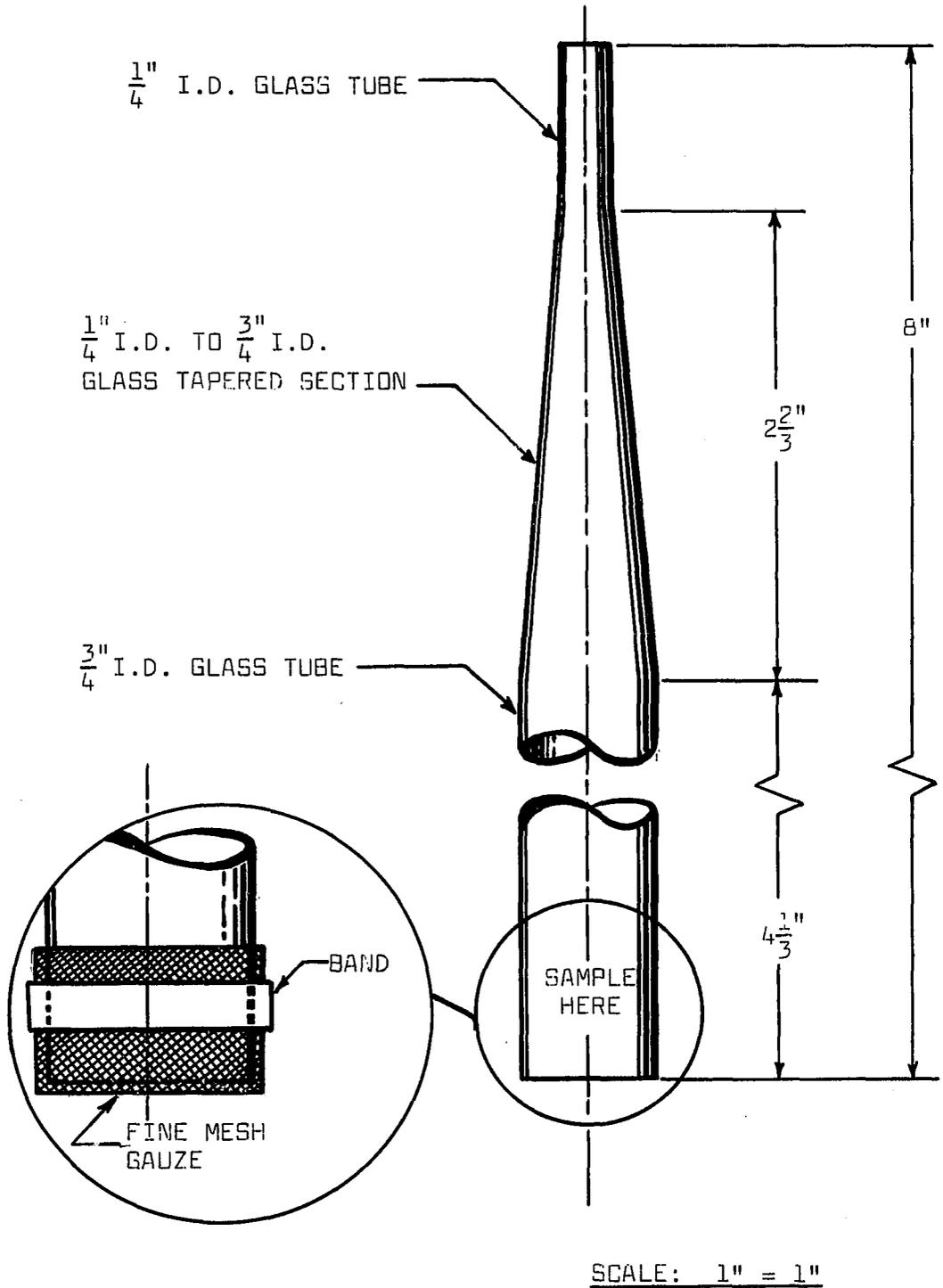


Fig. 8. Drawing of flow-reaction cell.

## CHAPTER V

### TEST PROCEDURES

The AGITATION cell was used to leach the samples of chalcocite, covellite, bornite, and pyrrhotite minerals with ferric sulfate solutions. The FLOW cell was used to leach the chalcopyrite mineral samples.

#### Preparation of Mineral Samples

All the mineral specimens which were leached were obtained from the Arizona Bureau of Mines, Tucson, Arizona, or Ward's Natural Science Establishment, Inc., Ward's of California, Monterey, California.

The mineral samples for the AGITATION cell were single specimens. The size of the specimens varied from about one-half-inch cubes to one-inch cubes. The minerals were cut to the desired shape using a diamond saw. The corners and edges were slightly rounded on a belt sander to prevent flaking of the sulfide material during leaching. Each face on a specimen was progressively sanded using coarse to fine sand paper. One of the surfaces of the mineral specimen was mounted by epoxy cement to one of the flat surfaces of a number three cork. A glass rod, four inches in length, was cemented into a small hole on the

opposite flat surface of the cork. The cork and glass rod were sealed with epoxy paint. The glass rod was then inserted into the specimen holder (Figure 3, No. 7). The specimen holder was placed into one of four holes in the cover of the plexiglas reaction cell. The exposed surface area was based on the size of the cube and on five faces exposed to the solution.

The mineral samples for the flow cell were ground and sized charges. The ground-mineral exposed surface area for chalcopyrite was estimated by the specific surface method for spherical particles (Brown 1961, pp. 21-22). The density for the chalcopyrite material leached was 3.9 grams per cubic centimeter (Palache, Berman, and Frondel 1944, p. 220). Five size ranges were selected, and the weight distribution of these ranges were held constant for all chalcopyrite leach tests. The average diameter,  $D_{AVE}$ , was the mean value obtained from the upper and the lower limits of a particular size range. The specific surface,  $(SS)_n$ , for each size range (n) was determined by Eq. 77.

$$(SS)_n = \frac{6.0}{(5.6)(D_{AVE})_n}, \text{ cm.}^2 \text{ per gram} \quad (77)$$

The total specific surface, (TSS), for the five ranges was calculated by Eq. 78.

$$(TSS) = \sum_{n=1}^{n=5} \left[ (SS)_n \left( \frac{\text{Weight Distribution, Percent}}{100} \right)_n \right] \quad (78)$$

The size distribution and exposed surface area per gram of the ground chalcopyrite samples as listed in Table 7 were held constant in all tests.

TABLE 7  
THE SIZE DISTRIBUTION AND EXPOSED SURFACE AREA  
PER GRAM FOR GROUND CHALCOPYRITE SAMPLES

MESH SIZE	WEIGHT PERCENT	AVERAGE SURFACE AREA Cm. <sup>2</sup>	SURFACE AREA Cm. <sup>2</sup> per Gram	ACCUMULATIVE SURFACE AREA Cm. <sup>2</sup> per Gram
+3	0.0	0.00	0.000	0.000
+4	6.2	2.84	0.167	0.167
+6	17.6	4.02	0.671	0.838
+8	26.8	5.68	1.45	2.29
+10	27.6	8.08	2.12	4.41
+14	21.7	11.52	2.38	6.79

The area percents of the various sulfides, such as chalcocite, chalcopyrite, covellite, bornite, pyrite, pyrrhotite, and gangue, within a particular specimen were determined from the weight percents of each sulfide. The weight percents of each sulfide contained in a specimen were calculated by micro-metric counting (Stephans 1967, pp. 1-4). The percent exposed surface areas of all sulfide minerals contained within a particular specimen were calculated by the method outlined in Table 8.

The surface area exposed of the particular mineral in a specimen under leach was determined by multiplying the total exposed surface area by the area percent of that particular mineral.

TABLE 8

DETERMINATION OF THE AREA PERCENT FOR THE SEVERAL  
SULFIDE MINERALS CONTAINED IN A LEACH SAMPLE

MINERAL	MINERAL CONTENT Weight Percent	MINERAL SPECIFIC GRAVITY	MINERAL FACTOR	MINERAL AREA Percent
$\text{Cu}_5\text{FeS}_4$	70.8	5.07	13.9	72
$\text{Cu}_2\text{S}$	22.7	5.65	4.0	21
$\text{CuFeS}_2$	3.3	3.90	0.8	4
$\text{FeS}_2$	3.2	5.02	0.7	3
TOTALS	100.0	---	19.4	100

$$\text{FACTOR} = \frac{\text{Mineral Content, Weight Percent}}{\text{Specific Gravity}} = \frac{70.8}{5.07}$$

$$\text{AREA-PERCENT} = \frac{\text{Mineral Factor}}{\text{Total Mineral Factor}} = \frac{13.9}{19.4}$$

#### Solution Analyses

The reagents used in the preparation of the leach solutions were analytical grade materials. Distilled water was used in the makeup of all solutions.

The total soluble iron in solution was determined by potentiometric titration with ceric ammonium nitrate standard solutions (Reilley and Sawyer 1961, pp. 34-38). A two-milliliter aliquot of the ferric sulfate leach solution was used in all total iron titrations.

The ferrous iron in the leach solution, both the initial and that produced during the leaching of the sulfides, was obtained by a modification of the potentiometric titration for total iron content. The ferric-iron reduction to ferrous iron as described in the above method was not included. A two-milliliter aliquot of the leach solution was taken and added to 50-milliliters of a dilute hydrochloric acid solution. The ratio of water to concentrated hydrochloric acid was ten to one. The ferrous-iron hydrochloric-acid solution was titrated with the ceric ammonium nitrate standard.

#### The Test Procedures

In all tests conducted in the AGITATION and FLOW cells a nitrogen atmosphere was maintained above the leach solution. Chemically pure grade nitrogen was used.

Prior to the initiation of each test the leach solution was added to the reaction cell to be preheated to the desired temperature. The volumes of the leach solutions which were added to the AGITATION cell and to the round bottom flask of the FLOW cell were 450-milliliters and 225-milliliters, respectively.

During the preheating of the leach solution the mounted mineral sample was also preheated to the same temperature. The sample, which was connected to the cork-glass rod assembly, was heated in a beaker containing deaerated distilled water. The beaker was partially immersed in the water bath. The ground and sized chalcopyrite sample was weighed, and then it was placed into

the reaction cell (Figure 6, No. 1) of the FLOW cell. The cell was positioned one-quarter of an inch above the leach solution in the round bottom flask. The flask was placed into the constant-temperature bath. Nitrogen gas was passed through the reaction cell and 500-milliliter flask. The mineral sample and the solution in the AGITATION-or the FLOW-cell assembly were preheated for one hour.

At the initiation of each test the mounted mineral sample was quickly immersed into the AGITATION reaction cell. The agitation of the solution was immediately started. The three-fourth-inch diameter end of the FLOW reaction cell, which contained the ground sample, was placed into the leach solution. The FLOW cell was quickly filled with the leach solution, and the recirculation of the solution from the round bottom flask through the pump back into the reaction cell was started.

The agitator speed in the AGITATION cell was maintained in all tests at 1,000 revolutions per minute. The speed was controlled by the "Variac" transformer. The solution in the FLOW cell was recirculated at the rate of 1,200 milliliters per minute. The flow was controlled by the "Variac" transformer.

The progress of the leaching reaction between the ferric sulfate solution and the sulfide mineral was followed by the potentiometric analysis of the ferrous iron produced. The ferrous iron concentration was determined at various time intervals during each test. The rate of reaction  $r_A$  was calculated by

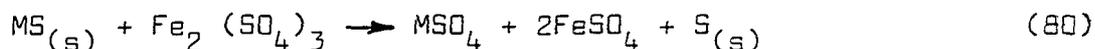
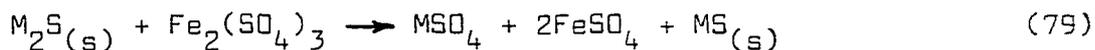
measuring the slope of a tangent line at a particular time to the curve of ferrous iron concentration versus time (Walas 1959, p. 300).

## CHAPTER VI

### EXPERIMENTAL RESULTS

#### Estimation of Leach Residue Depth

The depth of the leach residue left on the unreacted sulfide mineral specimen was estimated. The residue consisted of another sulfide material (altered product) and/or sulfur



The sulfur residue is a diffusion barrier for the ionic oxidizing agent which reacts with the sulfide mineral. The altered product  $MS_{(s)}$  in Eq. 79 also acts as a diffusion barrier to the leaching of the unaltered mineral  $M_2S_{(s)}$ . The altered product will also react with ferric sulfate as in Eq. 80 but at a much slower rate than the reactant  $M_2S_{(s)}$ . Therefore, the depth of the actual diffusion barrier will depend on the reactions and the kinetics involved in the overall leaching process of a particular mineral.

The actual depths of the sulfur and the altered sulfide residues were not measured. However, Tables 1 and 3 showed that altered mineral zones were produced during the initial stages of

ferric sulfate leaching of chalcocite and bornite. Tables 2 and 4 showed that sulfur was the only solid product made during the leaching of covellite and chalcopyrite. Therefore, altered mineral zones were assumed to be the major products formed in the leaching of chalcocite and bornite. Sulfur was assumed to be the only product formed in the leaching of covellite, chalcopyrite and pyrrhotite.

The estimation of the residue depth was based on the assumption that all the mounted mineral samples were cubes with five of the six faces exposed to the leach solution as shown in Figure 9. "D" was the length of the cube side, and "d" was the depth of the residue material. The depth, "d", was obtained by using Eq. 81.

$$d = \frac{(Fe^{+2})(V)(M.W.)}{(2)(S)(\rho)(L)} = \text{Cm.} \quad (81)$$

The symbol,  $(Fe^{+2})$ , was the ferrous-iron produced in moles per liter up to time,  $t$ ,  $(V)$  was the volume of the leach solution in liters, and  $(M.W.)$  was the molecular weight of the mineral being leached in grams per gram mole. The symbol,  $(S)$ , was the exposed surface area of the mineral in square centimeters, and  $(\rho)$  was the density of the mineral in grams per cubic centimeter. The value of  $(L)$  was the number of moles of copper sulfate stoichiometrically produced per mole of sulfide mineral leached. As an example of the latter symbol,  $(L)$  for the reaction  $Cu_2S + Fe_2(SO_4)_3 \rightarrow CuSO_4 + 2FeSO_4 + CuS$  was equal to one.

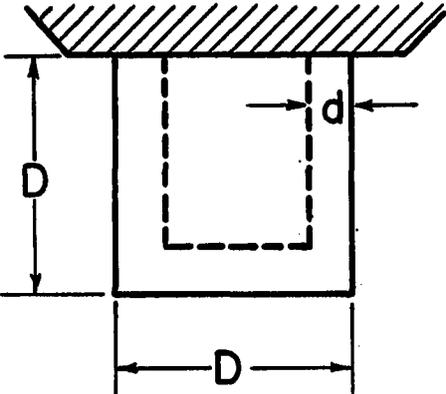


Fig. 9. Diagram of the residue diffusion barrier of a cube specimen.

### Mineral Analyses

The mineralization of each specimen series used in the kinetic studies is given in Table 9. Included in this Table are the specific mineral leached, the mineral series designation, and the percent by weight and by area of the mineralization present. The mineralization consisted of chalcocite,  $\text{Cu}_2\text{S}$ ; covellite,  $\text{CuS}$ ; bornite,  $\text{Cu}_5\text{FeS}_4$ ; chalcopyrite,  $\text{CuFeS}_2$ ; pyrite,  $\text{FeS}_2$ ; pyrrhotite,  $\text{FeS}$ ; and gangue minerals.

### The Dependence of the Rate on Exposed Mineral Surface Area

The rate of reaction,  $r_A$ , between ferric sulfate and each mineral was determined at two levels of exposed surface area.

Table 10 gives the test conditions held constant for each pair of tests. Included in this Table are the mineral leached, the temperature, the ferric sulfate concentration, and the depth of the leach residue. Table 11 gives the results for each mineral. Included in this Table are the mineral leached, the exposed surface area of the specific mineral, and the rates of reaction.

TABLE 9

MINERALIZATION OF EACH SPECIMEN SERIES USED IN THE FERRIC SULFATE LEACHING  
OF THE SEVERAL SULFIDE MINERALS IN PERCENT BY WEIGHT OR BY AREA

MINERAL SERIES		Cu <sub>2</sub> S		CuS		Cu <sub>5</sub> FeS <sub>4</sub>		CuFeS <sub>2</sub>		FeS <sub>2</sub>		FeS		GANGUE	
		WT.	AREA	WT.	AREA	WT.	AREA	WT.	AREA	WT.	AREA	WT.	AREA	WT.	AREA
Cu <sub>2</sub> S	A	94.3	89	0.1	--	0.0	--	0.0	--	0.0	--	0.0	--	5.6	--
	B	88.7	87	0.8	--	1.6	--	0.0	--	8.8	--	0.0	--	0.1	--
	C	88.7	87	0.8	--	1.6	--	0.0	--	8.8	--	0.0	--	0.1	--
CuS	A	0.0	--	82.6	82	0.3	--	0.0	--	13.7	--	0.0	--	2.8	--
Cu <sub>5</sub> FeS <sub>4</sub>	B	3.9	3	0.1	--	86.0	84	9.2	--	0.0	--	0.0	--	0.8	--
	F	6.7	6	0.1	--	79.2	77	14.0	--	0.0	--	0.0	--	0.0	--
	G	9.9	9	0.0	--	83.2	83	6.2	--	0.7	--	0.0	--	0.0	--
	I	8.7	8	0.0	--	70.4	70	10.5	--	8.4	--	0.0	--	0.7	--
CuFeS <sub>2</sub>	A	0.0	--	0.0	--	0.0	--	80.0	72	0.0	--	0.0	--	20.0	28
FeS	A	0.0	--	0.0	--	0.0	--	0.0	--	9.3	--	90.0	--	0.7	--

TABLE 10

THE TEST CONDITIONS HELD CONSTANT IN THE DETERMINATION OF THE  
DEPENDENCY OF THE RATE OF REACTION ON THE EXPOSED SURFACE AREA

MINERAL	TEMPERATURE °C	FERRIC SULFATE CONCENTRATION Moles Per Liter	DEPTH OF RESIDUE ZONE Cm.
Cu <sub>2</sub> S	38.0	0.027	0.0000
	38.0	0.027	0.0000
CuS	68.0	0.105	N.D.
	68.0	0.105	N.D.
Cu <sub>5</sub> FeS <sub>4</sub>	38.0	0.100	0.0038
	38.0	0.100	0.0038
CuFeS <sub>2</sub>	50.0	0.011	N.D.
	50.0	0.011	N.D.
FeS	38.0	0.100	N.D.
	38.0	0.100	N.D.

N.D. - Not Determined

TABLE 11

TEST RESULTS FOR THE DETERMINATION OF THE DEPENDENCY OF THE  
RATE OF REACTION ON THE EXPOSED MINERAL SURFACE AREA

MINERAL	AREA Cm. <sup>2</sup>	RATE (r <sub>A</sub> /S) × 10 <sup>6</sup>
Cu <sub>2</sub> S	4.0	12.
	8.0	13.
CuS	10.0	0.11
	19.5	0.11
Cu <sub>5</sub> FeS <sub>4</sub>	4.5	9.8
	8.0	12.3
CuFeS <sub>2</sub>	126.0	0.115
	163.0	0.120
FeS <sub>2</sub>	9.5	0.71
	16.5	0.79

Dependence of the Rate on the  
Ferric Sulfate Concentration

The kinetics of the initial reactions between aqueous ferric sulfate solutions and various sulfide minerals were examined. The effect of the variation in ferric sulfate concentration on the rate of consumption of ferric sulfate was sought for each reaction.

Example curves for each mineral of the measured rates of reaction,  $(r_A/S)$ , at several ferric sulfate concentrations are illustrated in Figures 10 through 14.

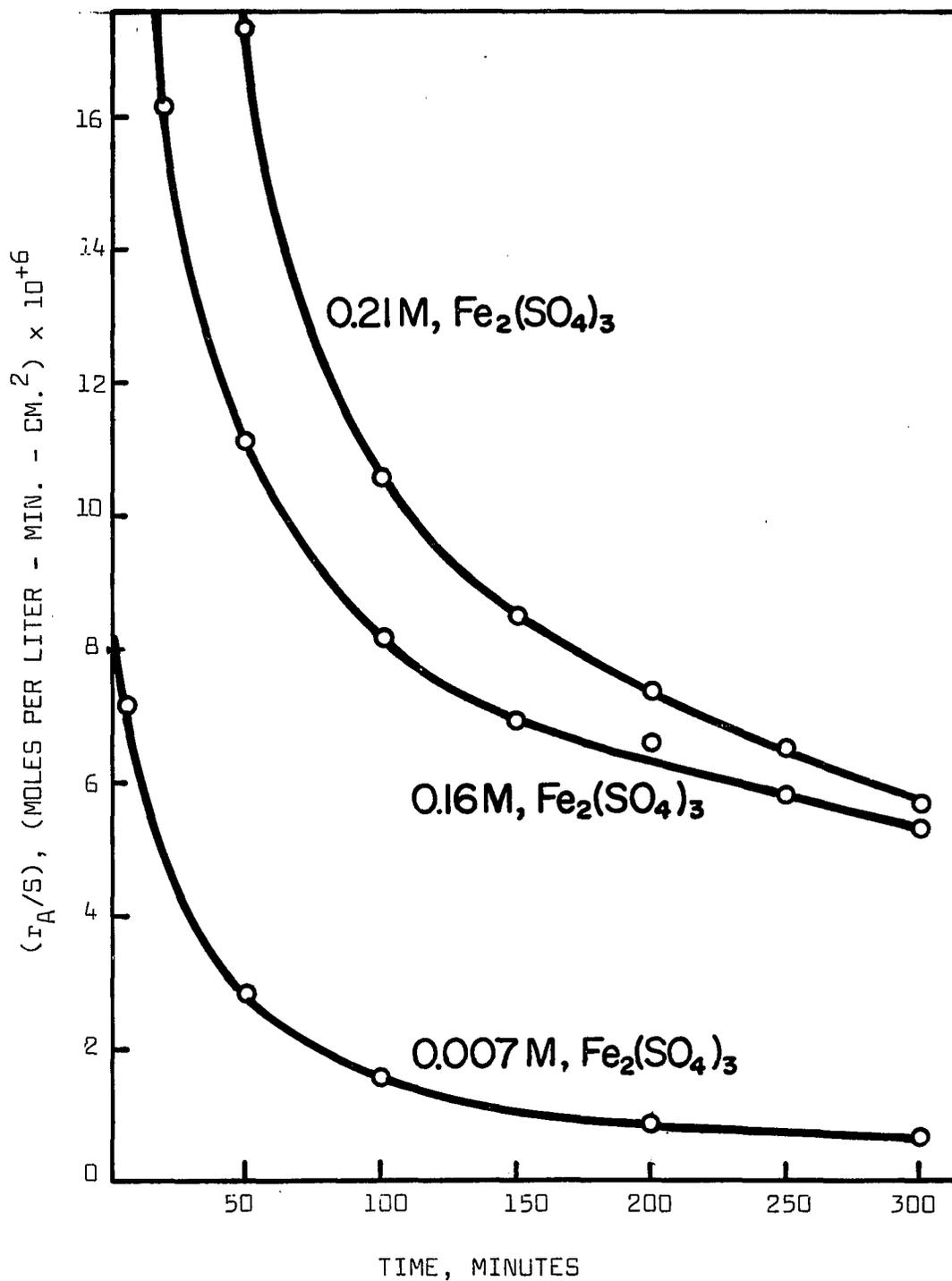
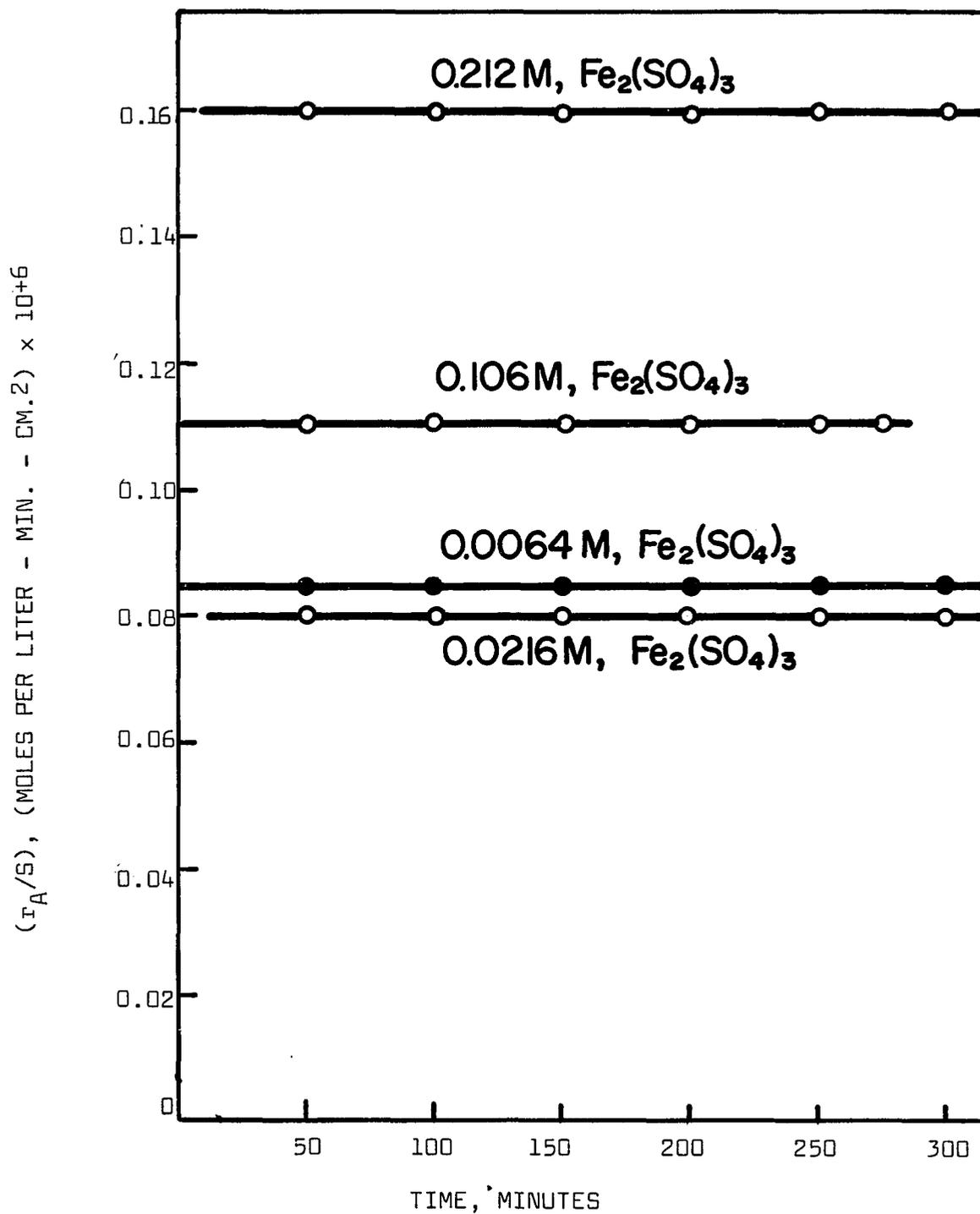


Fig. 10.  $(r_A/S)$  - time plot for chalcocite.

Fig. 11.  $(r_A/S)$  - time plot for covellite.

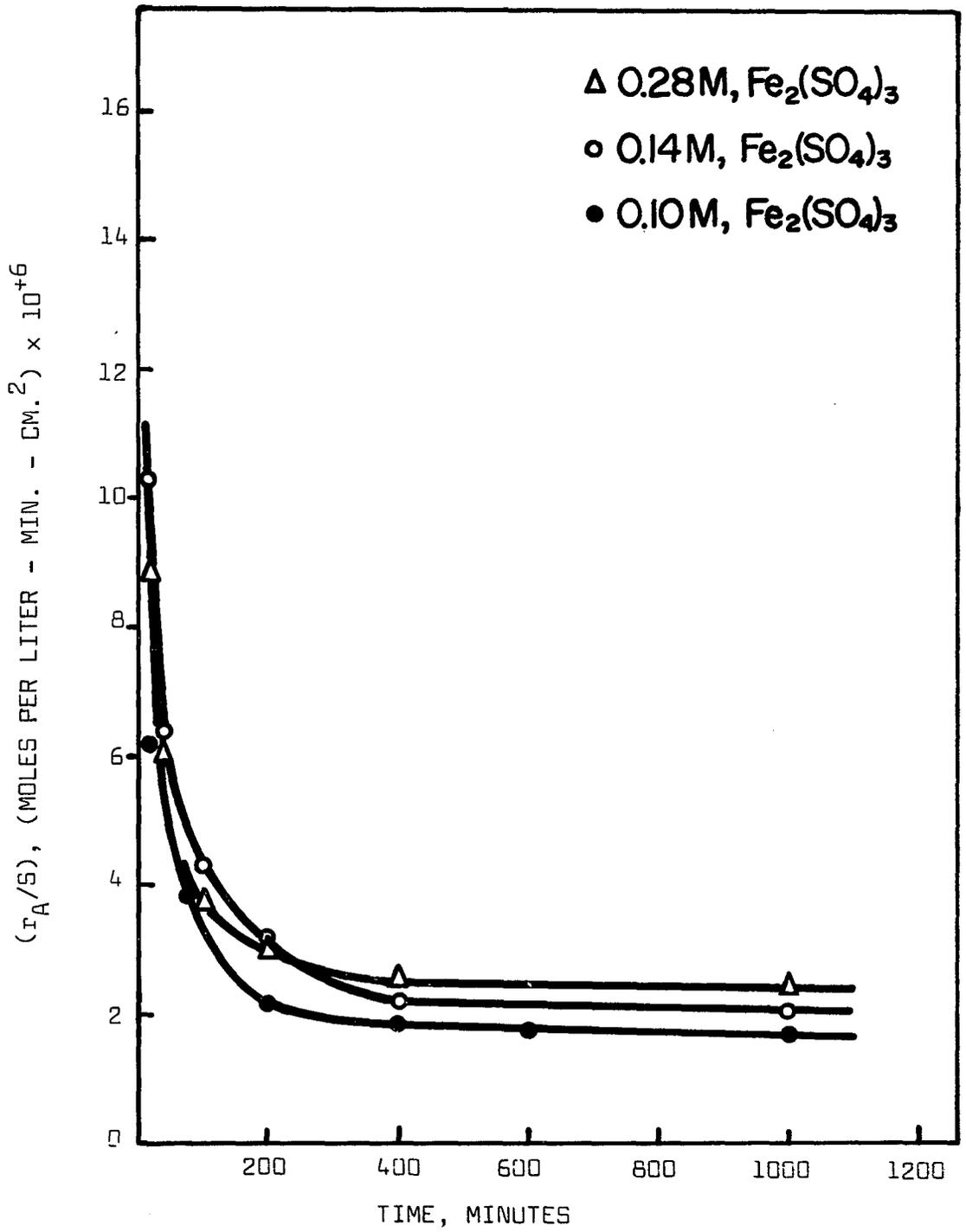


Fig. 12.  $(r_A/S)$  - time plot for barnite.

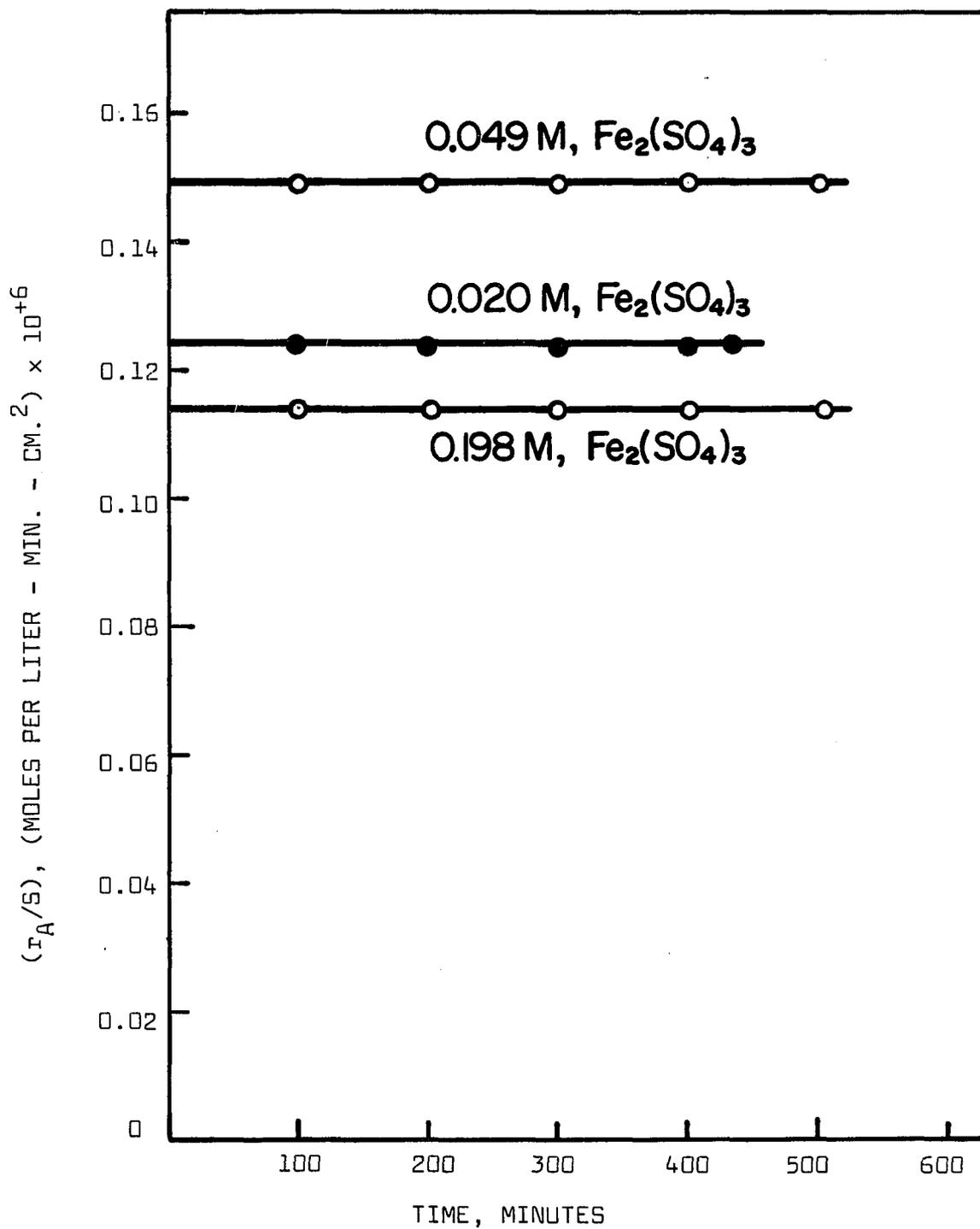


Fig. 13.  $(r_A/S)$  - time plot for chalcopyrite.

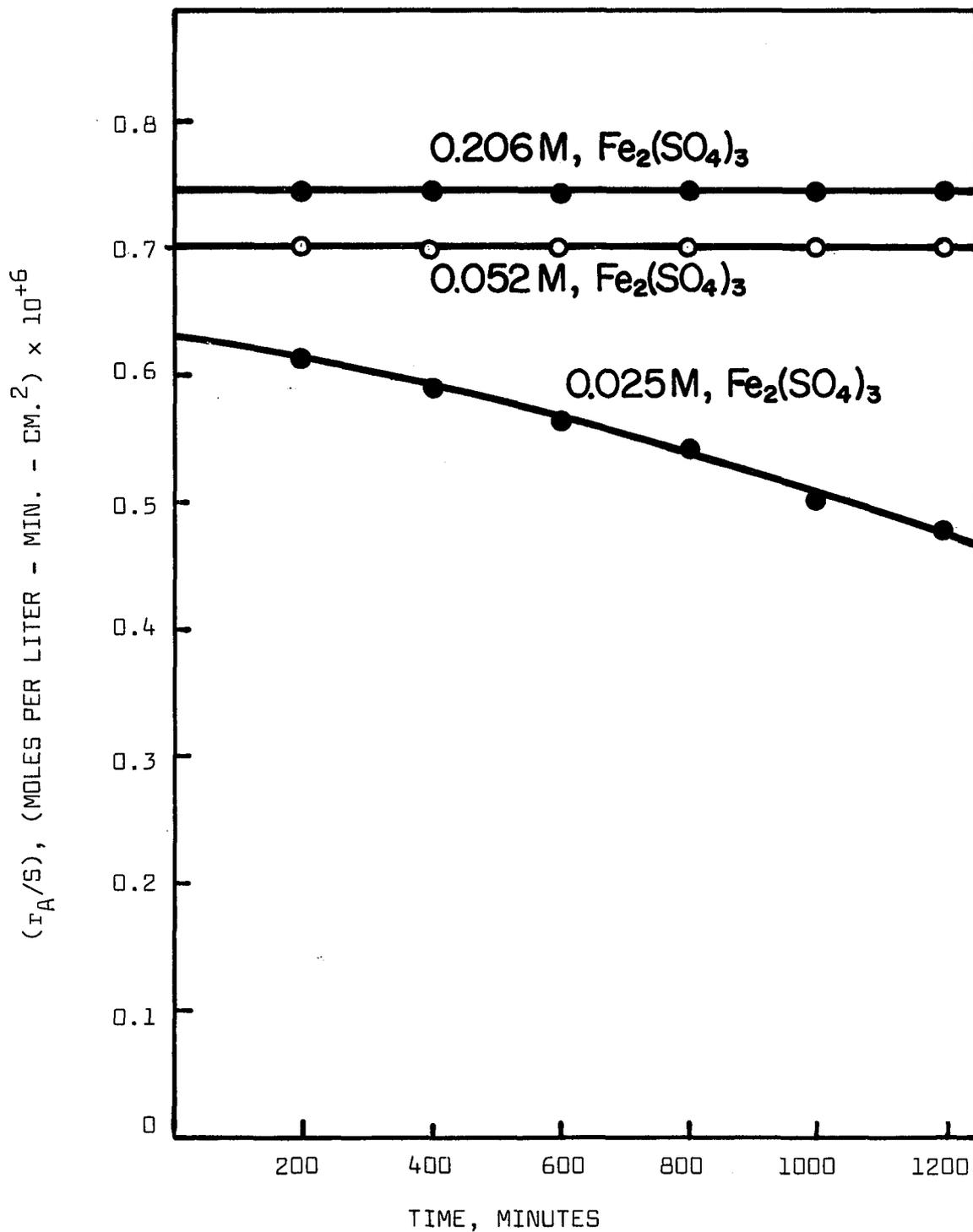


Fig. 14.  $(r_A/S)$  - time plot for pyrrhotite.

The rate of consumption of ferric sulfate did vary with time for the leaching of chalcocite, Figure 10, and of bornite, Figure 12. The rates for the other minerals were constant in all but one case, that for the 0.025 M, ferric sulfate leach of pyrrhotite. Because the rates for chalcocite and bornite leaching tests varied with time, an estimated residue depth determined at a particular time was calculated to assist the kinetic evaluation of the results.

The test conditions which were held constant for each leach study are shown in Table 12. The leach test temperature and the particular reaction examined are tabulated. The measured results for all minerals are given in Appendix B. The variations of the rates ( $r_A/S$ ), with ferric sulfate concentrations are listed, respectively, for the minerals chalcocite, covellite, bornite, chalcopyrite, and pyrrhotite.

The data from the tables in Appendix B are plotted in Figures B-1 through B-7. Plotted on the ordinate of each graph is the  $\log (r_A/S)$  and on the abscissa the  $\log C_{\text{Fe}_2(\text{SO}_4)_3}$ . The dashed line in each figure is the least-square line determined from the tabulated rate and concentration data. The solid line is the proposed result for the slope and intercept which was determined within the 95 percent confidence limit of the least-square line. The results which were calculated for the solid line using Eq. 74 are listed in Table 13. The order of the reaction,  $p$ , and the reaction rate constant,  $k_2$ , are given for the ferric sulfate concentration ranges listed.

TABLE 12

TEST CONDITIONS HELD CONSTANT IN THE FERRIC SULFATE LEACHING OF  
SULFIDE MINERALS IN WHICH FERRIC SULFATE CONCENTRATION WAS VARIED

MINERAL	TEMPERATURE °C	REACTION STUDIED
$\text{Cu}_2\text{S}$	38.0	$\text{Cu}_2\text{S} + \text{Fe}_2(\text{SO}_4)_3 \rightarrow \text{CuSO}_4 + \text{FeSO}_4 + \text{CuS}$
$\text{CuS}$	68.0	$\text{CuS} + \text{Fe}_2(\text{SO}_4)_3 \rightarrow \text{CuSO}_4 + 2\text{FeSO}_4 + \text{S}$
$\text{Cu}_5\text{FeS}_4$	38.0	$\text{Cu}_5\text{FeS}_4 + 2\text{Fe}_2(\text{SO}_4)_3 \rightarrow 2\text{CuSO}_4 + \text{Cu}_3\text{FeS}_4 + 4\text{FeSO}_4$
$\text{CuFeS}_2$	50.0	$\text{CuFeS}_2 + 2\text{Fe}_2(\text{SO}_4)_3 \rightarrow \text{CuSO}_4 + 5\text{FeSO}_4 + \text{S}$
$\text{FeS}$	38.0	$\text{FeS} + \text{Fe}_2(\text{SO}_4)_3 \rightarrow 3\text{FeSO}_4 + \text{S}$

TABLE 13  
THE ORDER OF THE REACTION FOR THE FERRIC SULFATE CONCENTRATION  
AND THE RATE CONSTANT

MINERAL	RESIDUE DEPTH Centimeters	FERRIC SULFATE RANGE Moles Per Liter FROM TO	ORDER p	RATE CONSTANT $k_2 \times 10^5$
Chalcocite	0.0154	0.0071 - 0.299	1.00	8.526
Covellite	N.D.	0.0064 - 0.212	0.06	0.0138
Bornite (d <sub>1</sub> a)	0.0038	0.0087 - 0.105	1.00	15.0
(d <sub>1</sub> b)	0.0038	0.105 - 0.280	0.00	1.36
(d <sub>2</sub> a)	0.0076	0.0067 - 0.056	0.67	3.49
(d <sub>2</sub> b)	0.0076	0.056 - 0.279	0.00	0.542
(d <sub>3</sub> )	0.042	0.090 - 0.264	0.00	0.205
(d <sub>4</sub> )	0.050	0.090 - 0.214	0.00	0.165
Chalcopyrite	N.D.	0.020 - 0.198	0.00	0.0134
Pyrrhotite	N.D.	0.025 - 0.208	0.00	0.0713

N.D. - Not Determined

See Appendix E, Table E-1, p. 156 for the measured values of order and rate constant.

Dependence of the Reaction Rate  
Constant on Temperature

The test conditions which were held constant for the studies concerning the dependence of the reaction rate constant,  $k_2$ , on the reaction temperature are listed in Table 14. In this table the ferric sulfate concentration, the residue depth, and the added sulfuric acid concentration are given for each mineral leached.

The kinetic results are given in Appendix C. Included in these tables are the reaction rate ( $r_A/S$ ), the reaction temperature, and the rate constant,  $k_2$ .

The rate constants,  $k_2$ , were determined from the values of ( $r_A/S$ ) and its corresponding ferric sulfate concentration,  $C_A$ , listed in Appendix C using Eq. 74. The value of  $p$  was obtained from Table 13.

The values of  $\text{Log}(k_2/T)$  are plotted versus the reciprocal absolute temperature ( $^{\circ}\text{K}$ ) in Figures C-1 through C-5 in Appendix C. The solid line shown on each graph is the least-square line of the data.

The experimental activation energy,  $E_{\text{EXP}}$ , and the frequency factor,  $A'$ , as calculated from the solid line in these figures using Eq. 76, are given in Table 15.

TABLE 14

CONDITIONS HELD CONSTANT IN THE FERRIC SULFATE LEACHING OF THE  
SULFIDE MINERALS IN WHICH THE REACTION TEMPERATURE WAS VARIED

MINERAL	FERRIC SULFATE Moles Per Liter	RESIDUE DEPTH Cm.	ADDED SULFURIC ACID Moles Per Liter
$\text{Cu}_2\text{S}$	0.205	0.0154	0.00
$\text{Cu S}$	0.105	N.D.	0.00
$\text{Cu}_5\text{FeS}_4$ ( $d_1a$ )	0.100	0.0038	0.50
( $d_2b$ )	0.100	0.0076	0.50
( $d_3$ )	0.100	0.0420	0.50
$\text{CuFeS}_2$	0.100	N.D.	0.40
$\text{FeS}$	0.100	N.D.	0.00

N.D. - Not Determined

TABLE 15

FERRIC SULFATE LEACHING OF VARIOUS SULFIDE MINERALS:  
THE ACTIVATION ENERGIES AND THE FREQUENCY FACTORS

MINERAL	DEPTH Centimeters	EXPERIMENTAL ACTIVATION ENERGY, $E_{EXP}$ Kilocalories Per Mole	FREQUENCY FACTOR $A'$
Chalcocite	0.0154	6.740	0.0154
Covellite	N.D.	14.200	0.487
Bornite ( $d_{1a}$ )	0.0038	6.44	0.0112
( $d_{2b}$ )	0.0076	9.62	0.104
( $d_3$ )	0.042	12.27	3.00
Chalcopyrite	N.D.	17.76	483.0
Pyrrhotite	N.D.	8.89	1.25
N.D. - Not Determined			

The Effect of Sulfuric Acid  
on the Rate of Reaction

The test conditions held constant in the study of the effect of sulfuric acid on the leaching rate ( $r_A/S$ ) of the various sulfides are given in Table 16.

For the ferric sulfate leaching of chalcocite, the effect of sulfuric acid on the rate was examined in two series of tests. The first studied the effect of increasing sulfuric acid concentration at a ferric sulfate concentration of 0.10 molar. The second test series examined the effect of increasing ferric sulfate concentration at a sulfuric acid concentration of 0.50 molar.

The tables of results for the tests conducted on chalcocite, covellite, chalcopyrite, and pyrrhotite minerals are given in Appendix D. The sulfuric acid concentration of a ferric sulfate solution to which sulfuric acid was not added, was assumed to be equal to that pH value obtained from Figure 15. The results for the leach tests conducted on bornite mineral specimens are given in Table 17. The data from the tables in Appendix D are plotted as  $\log (r_A/S)$  versus  $\log C_B$  in Figures D-1, D-3 through D-5. In Figure D-2 the  $\log (r_A/S)$  versus the  $\log C_A$  at a sulfuric acid concentration of 0.50 molar is given for the chalcocite mineral.

TABLE 16

TEST CONDITIONS HELD CONSTANT IN THE STUDY OF THE EFFECT  
OF SULFURIC ACID ON THE LEACHING RATE

MINERAL	RESIDUE DEPTH Cm.	SALT HELD CONSTANT		TEMPERATURE °C
		FERRIC SULFATE Molar	SULFURIC ACID Molar	
$\text{Cu}_2\text{S}$ (1)	0.0154	0.100	VARIED	38.0
$\text{Cu}_2\text{S}$ (2)	0.0154	VARIED	0.50	38.0
$\text{CuS}$	N.D.	0.100	VARIED	68.0
$\text{Cu}_5\text{FeS}_4$	0.042	0.100	VARIED	51.0
$\text{CuFeS}_2$	N.D.	0.100	VARIED	50.0
$\text{FeS}$	N.D.	0.100	VARIED	38.0

N.D. - Not Determined

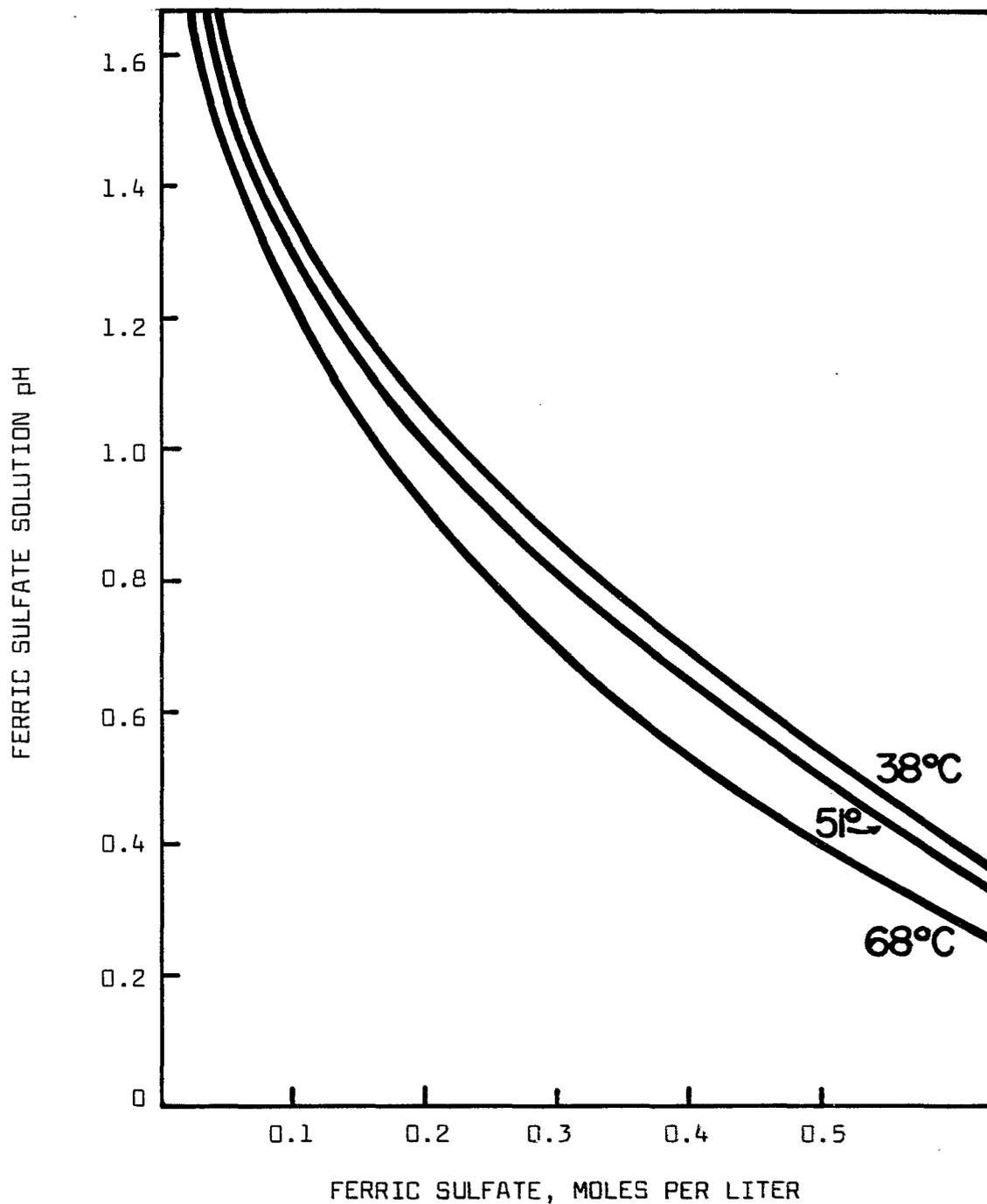


Fig. 15. Plot of ferric sulfate solution pH - ferric sulfate concentration.

TABLE 17

THE DEPENDENCE OF THE RATE ON SULFURIC ACID  
CONCENTRATION FOR THE MINERAL BORNITE

NUMBER	AREA Cm. <sup>2</sup>	Fe(SO <sub>4</sub> ) <sub>3</sub> Molar	H <sub>2</sub> SO <sub>4</sub> Molar	RATE (r <sub>A</sub> /S)×10 <sup>6</sup>
28	9.6	0.212	0.000	5.2
34	4.5	0.197	0.500	5.4
, 35	8.0	0.099	0.500	4.7

In the figures the dashed line was the least-square plot of the data given in Appendix D. The solid line was the proposed linear correlation of the data which was within the 95 percent confidence limit of the least-square line.

The kinetic data for the effects of added sulfuric acid based on the solid line plots in Figures D-1, D-3 through D-5 are given in Table 18. Reported are the mineral leached, the sulfuric acid concentration range, the order of the reaction,  $q$ , and the rate constant,  $k_2$ . The kinetic data for the effects of added sulfuric acid based on the dashed line in Figure D-1 are given in Table 19. The effect of a high sulfuric acid concentration on chalcocite leaching while the ferric sulfate concentration is increased is given in Table 20.

TABLE 18

THE EFFECT OF SULFURIC ACID ON THE RATE OF REACTION FOR CHALCOците, COVELLITE, CHALCOPYRITE, AND PYRRHOTITE

MINERAL	SULFURIC ACID RANGE		ORDER $q$	RATE CONSTANT $k_2 \times 10^5$
	FROM	TO		
Chalcocite	0.020	0.525	0.02	1.16
Covellite	0.056	0.500	0.00	0.0161
Chalcopyrite	0.050	0.780	0.00	0.0112
Pyrrhotite	0.042	0.420	0.00	0.0340

See Appendix E, Table E-3, p. 158 for the measured values of order and rate constant.

TABLE 19

EXPERIMENTAL RESULTS OF THE STUDY OF THE EFFECT OF  
SULFURIC ACID ON THE RATE EQUATION FOR CHALCOCITE

SULFURIC ACID RANGE Moles Per Liter		ORDER $\alpha$	RATE CONSTANT $k_2 \times 10^5$
FROM	TO		
0.020	0.525	0.25	1.44

TABLE 20

THE EFFECT OF 0.50 MOLAR SULFURIC ACID ON THE RATE OF REACTION  
BETWEEN FERRIC SULFATE SOLUTIONS AND THE MINERAL CHALCOCITE

FERRIC SULFATE-RANGE Moles Per Liter		ORDER $\rho$	RATE CONSTANT $k_2 \times 10^5$
FROM	TO		
0.022	0.205	1.00	12.7

## CHAPTER VII

### DISCUSSION OF RESULTS

Aqueous ferric sulfate leaching studies on several sulfide minerals were conducted. These minerals were chalcocite, bornite, covellite, chalcopyrite, and pyrrhotite. The initial rates of reduction of ferric sulfate to ferrous sulfate by the sulfide were determined under varying conditions of ferric sulfate concentration and ferric sulfate-sulfuric acid concentrations and of reaction temperatures. From the measured rates, kinetic data pertaining to each mineral were calculated. The kinetic data were compared to several possible reaction controlling processes. From the controlling process an overall reaction mechanism was proposed for the initial dissolution of each mineral.

The kinetic results for each mineral leached which were calculated in the previous chapter are summarized in Table 21.

#### Diffusion Controlled Reactions

The initial rates can be controlled by diffusion of ionic species. Two such processes are possible. The diffusion of ferric sulfate from the bulk solution to the reaction sites on the mineral. Also, the cationic species within the mineral could diffuse across an altered mineral zone to the ferric sulfate reaction sites (Peters 1968, p. 7-14).

TABLE 21

SUMMARY OF KINETIC DATA OBTAINED THROUGH THE VARIATION OF  
FERRIC SULFATE CONCENTRATION AND REACTION TEMPERATURE

MINERAL	DEPTH d, Cm.	FERRIC SULFATE		ORDER p	ACTIVATION ENERGY	FREQUENCY
		Moles Per Liter FROM	TO		$E_{EXP}$ Kcal per Mole	FACTOR A'
Chalcocite	0.0154	0.0070	0.300	1.00	6.70	0.015
Bornite (d <sub>1</sub> a)	0.0038	0.0090	0.105	1.00	6.40	0.011
(d <sub>1</sub> b)	0.0038	0.105	0.280	0.00	N.D.	N.D.
(d <sub>2</sub> a)	0.0076	0.0070	0.055	0.67	N.D.	N.D.
(d <sub>2</sub> b)	0.0076	0.055	0.280	0.00	9.60	0.104
(d <sub>3</sub> )	0.042	0.090	0.265	0.00	12.30	3.00
(d <sub>4</sub> )	0.050	0.090	0.215	0.00	N.D.	N.D.
Covellite	N.D.	0.0065	0.210	0.06	14.20	0.49
Chalcopyrite	N.D.	0.020	0.200	0.00	17.80	480.0
Pyrrhotite	N.D.	0.025	0.210	0.00	8.90	1.25

N. D. - Not Determined

### The Diffusion of Ferric Sulfate to the Reaction Sites

As expressed in Eq. 26 the diffusion of ferric sulfate to the reaction site is directly proportional to the ferric sulfate concentration in solution. Also the diffusion flux decreases as the depth of the leached residue of the mineral increases. The increase in the depth of the residue in the leaching of minerals is time dependent. Eq. 28 expresses the dependence of a varying concentration gradient on time and of the depth of the leach residue on time.

Examination of Figures 10 through 14 illustrated that the rates of reaction ( $r_A/S$ ) decreased with increasing time for chalcocite and bornite ( $d_1a$ ). The rates for the other three minerals were independent of time. Therefore, an unsteady-state process existed for the leaching of chalcocite and bornite ( $d_1a$ ) minerals. However, in the interpretation of results for these minerals a quasi-steady state at a constant concentration gradient was assumed. The assumption was based on the process proposed by Rotinyan and Drozdov (1949, pp. 1843-1852). Also examination and evaluation of unsteady-state equations for similar situations indicated errors in the calculated kinetic results would not be appreciable when quasi-steady state was assumed for slow leaching reactions (Crank 1956, pp. 99-120).

As shown in Table 21 the values of  $p$ , the order with respect to the ferric sulfate concentration, were equal to one

for chalcocite and bornite ( $d_{1a}$ ). The values of  $p$  for the minerals bornite ( $d_3$ ), covellite, chalcopyrite, and pyrrhotite were zero.

The rate Eqs. 26 and 74 were set equal to each other from which Eq. 82 resulted. In this derivation  $C_0$  was assumed to be zero, and  $p$  was assumed to be equal to one.

$$k_2 = \frac{D_{AX}}{(V)(d)} \quad (82)$$

Diffusion depths,  $d$ , for each mineral leached were calculated using Eq. 82. The values of  $k_2$  at 38°C were determined using the data given in Table 21 and Eq. 76. The values of  $D$  at 38°C were obtained from Table 6. The volume of the reaction system,  $V$ , was assumed to be 450 cubic centimeters for chalcocite, bornite and covellite and 225 cubic centimeters for chalcopyrite.

The calculated depths as determined by Eq. 82 are given in Table 22. Also shown are the experimental depth values based on Eq. 81.

The calculated depths for chalcocite and bornite ( $d_{1a}$ ) were close to the experimental depths. The calculated depths for the minerals bornite ( $d_3$ ), covellite, and chalcopyrite were approximately the same size or larger than the dimensions of the test specimens (refer to page 41).

The diffusion theories were applied to the experimental kinetic data for chalcocite and bornite ( $d_{1a}$ ). Correlations between theory and experimental results were sought.

TABLE 22

THE DIFFUSION BARRIER DEPTH AS DETERMINED FROM VALUES OF  $k_2$   
AND D AT 38°C AND COMPARED TO THE EXPERIMENTAL DEPTH

MINERAL	DIFFUSIVITY cm <sup>2</sup> /min.	RATE CONSTANT $k_2 \times 10^6$	DIFFUSION DEPTHS, Cm.	
			Eq. 82	Experimental Table 20
Chalcocite	$2.2 \times 10^{-4}$	0.92	0.0053	0.0154
Bornite ( $d_{1a}$ )	2.2	1.19	0.0041	0.0038
Bornite ( $d_3$ )	2.2	2.2	0.22	0.042
Covellite	2.2	0.016	31.0	--
Chalcopyrite	2.2	0.052	19.0	--

The Glasstone theory of diffusion was discussed on pages 17 and 18 of the "Theoretical Considerations." Eq. 30 was rearranged to yield an expression denoting the distance between successive equilibrium positions,  $\lambda$ , for the diffusion of a solute molecule past a solvent molecule such as water:

$$\lambda \sqrt{\text{EXP}(+\Delta S^*/R)} = \sqrt{\frac{A''h}{ek}} \quad (83)$$

The frequency factor,  $A''$ , was obtained by Eq. 83b.

$$A'' = d \times V \times A' \quad (83b)$$

The values of the depth,  $d$ , and the frequency factor,  $A'$ , for chalcocite and bornite ( $d_{1a}$ ) were obtained from Table 21, and were used in these equations to calculate  $\lambda$ . It was assumed that  $\Delta S^*$  was zero for the diffusion process.

The terms  $\lambda$  and  $E_{\text{EXP}}$  for the self-diffusion of water were reported by Glasstone to be, respectively,  $11.0 \text{ \AA}$  and 5.30 kilocalories per mole (Glasstone, Laidler, and Eyring 1941, p. 521). The values of  $\lambda$  for chalcocite and bornite ( $d_{1a}$ ) were  $18.3 \text{ \AA}$  and  $7.9 \text{ \AA}$ , respectively. The value of  $\lambda$  for the self-diffusion of water was of the same magnitude as the experimental  $\lambda$ 's. The values of  $E_{\text{EXP}}$  for chalcocite and bornite ( $d_{1a}$ ) were 6.7 and 6.4 kilocalories per mole, respectively, and were close to that for the self-diffusion of water.

The values for the diffusivity of ferric sulfate in aqueous solutions based on the Robinson and Stokes' theory were listed in Table 6. The diffusivities for each temperature were averaged. The average value of  $D$  at  $38^\circ\text{C}$ , was  $2.6 \times 10^{-4} \text{ cm.}^2/\text{min.}$  It was assumed that chalcocite and bornite ( $d_1a$ ) leaching were ferric sulfate diffusion controlled. Using the data in Table 21 and a solution volume of 450 cubic centimeters, experimental diffusivities for chalcocite and bornite were calculated by Eqs. 19 and 82. These results were, respectively,  $6.2 \times 10^{-4} \text{ cm.}^2/\text{min.}$  and  $2.0 \times 10^{-4} \text{ cm.}^2/\text{min.}$  The values were in the approximate range for the calculated literature value of the diffusivity.

The experimental diffusivities for chalcocite and bornite ( $d_1a$ ) and the averaged diffusivity for ferric sulfate were examined by the alternate Glasstone theory (refer to pages 17 and 18). The ferric iron ions were assumed to be the large species over which the water molecules jumped. By this process the ferric ions diffused toward the reaction site on the sulfide surface. Eq. 32 was determined for this theory.

$$D_1 = D_s \left( \frac{\lambda}{\pi r} \right) \quad (32)$$

The value of  $\lambda$ , the diameter of the water molecule, was obtained from Eq. 84.

$$\lambda = \left[ \frac{\bar{V}_{\text{H}_2\text{O}}}{N} \right]^{1/3} = \left[ \frac{\text{M.W., H}_2\text{O} / \rho_{\text{H}_2\text{O}}}{6.02 \times 10^{23}} \right]^{1/3} \quad (84)$$

$$\lambda = 3.11 \text{ \AA}$$

The diameter for the ferric-iron ions,  $r$ , was assumed to be the "effective diameter" as calculated by the Debye-Hückle theory for activity coefficients (Klotz 1964, p. 417). The diameter for the hydrated ferric iron was  $9.0 \text{ \AA}$ . The values of  $D_1$  were set equal to the experimental diffusivities for chalcocite and bornite ( $d_{1a}$ ) and the averaged ferric sulfate diffusivity at  $38^\circ\text{C}$ . Inserting these values into Eq. 32 the self-diffusion coefficient of water,  $D_s$ , for each  $D_1$  value was estimated. The self-diffusivities were, respectively,  $56 \times 10^{-4}$ ,  $18 \times 10^{-4}$  and  $23.4 \times 10^{-4} \text{ cm.}^2 \text{ per min.}$  The self-diffusion coefficient of water was reported to be  $22.4 \times 10^{-4} \text{ cm.}^2 \text{ per min.}$  (Glasstone, Laidler, and Eyring 1941, p. 524).

The self-diffusivities obtained from the bornite ( $d_{1a}$ ) data and from the averaged literature data were close to that reported by Glasstone. The experimental self-diffusivity for chalcocite was considerably greater. However, the calculations of the diffusivities,  $D_s$ , were based upon an estimated "diffusion depths,"  $d$ . The ferric sulfate diffusion depth for chalcocite could have been too large if reactions other than the leaching of chalcocite to covellite were occurring.

#### Sulfuric Acid Effect on the Leaching of Chalcocite

As shown in Figure D-1, the addition of sulfuric acid to the leach solution increased the leaching rate of chalcocite (dashed line). The experimental order,  $q$ , was estimated to be 0.25. The rate constant,  $k_2$ , was  $1.44 \times 10^{-5}$ .

Eq. 34 for the diffusivity contains the activity term  $(\frac{d \ln \gamma_{\pm}}{dm})$ . In the expression for the activity coefficient of an ionic species, Eq. 35, a term for the ionic strength of a solution is included. The ionic strength, as shown by Eq. 36, depends on all ionic species in solution. If the sulfuric acid concentration is increased at constant ferric sulfate concentration the ionic strength increases as illustrated in Figure 16.

Assuming the value of "b" in Eq. 35 was equal to 0.20, the values of  $(-\log \gamma_i)$  for ferric iron and sulfate ions were calculated at several ferric iron and sulfate concentrations. The mean activity coefficient,  $\gamma_{\pm}$ , was calculated by Eq. 37. The values of  $\gamma_{\pm}$  for aqueous ferric sulfate were plotted against the ferric sulfate concentration and the ionic strength of the solution in Figure 17. The mean activity coefficients obtained from literature data (Appendix A, Table A-2) were also plotted in this figure.

Several values of the ionic strength in Figure 16 were assumed equal to the equivalent ionic strength in Figure 17.  $(\frac{d \ln \gamma_{\pm}}{dm})$  values were determined at these points on Figure 17. The term m in Eq. 34 was held constant at 0.10 moles ferric sulfate per liter. From the new values of  $(\frac{d \ln \gamma_{\pm}}{dm})$  the diffusivities of ferric sulfate in a solution of varying sulfuric acid concentration were calculated (see Table 23) by Eq. 34.

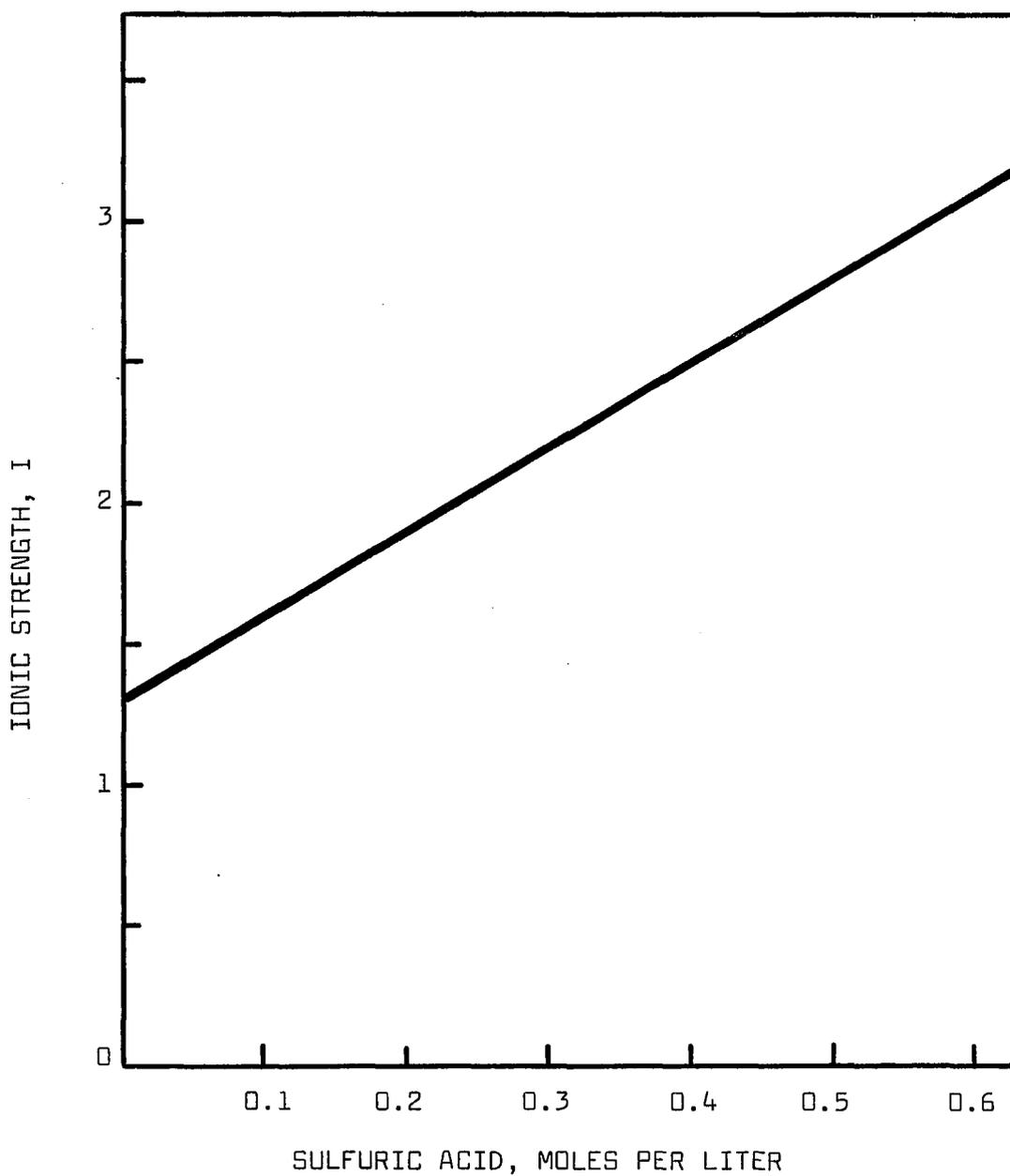


Fig. 16. Ionic strength - sulfuric acid concentration plot at 0.10 molar,  $\text{Fe}_2(\text{SO}_4)_3$ .

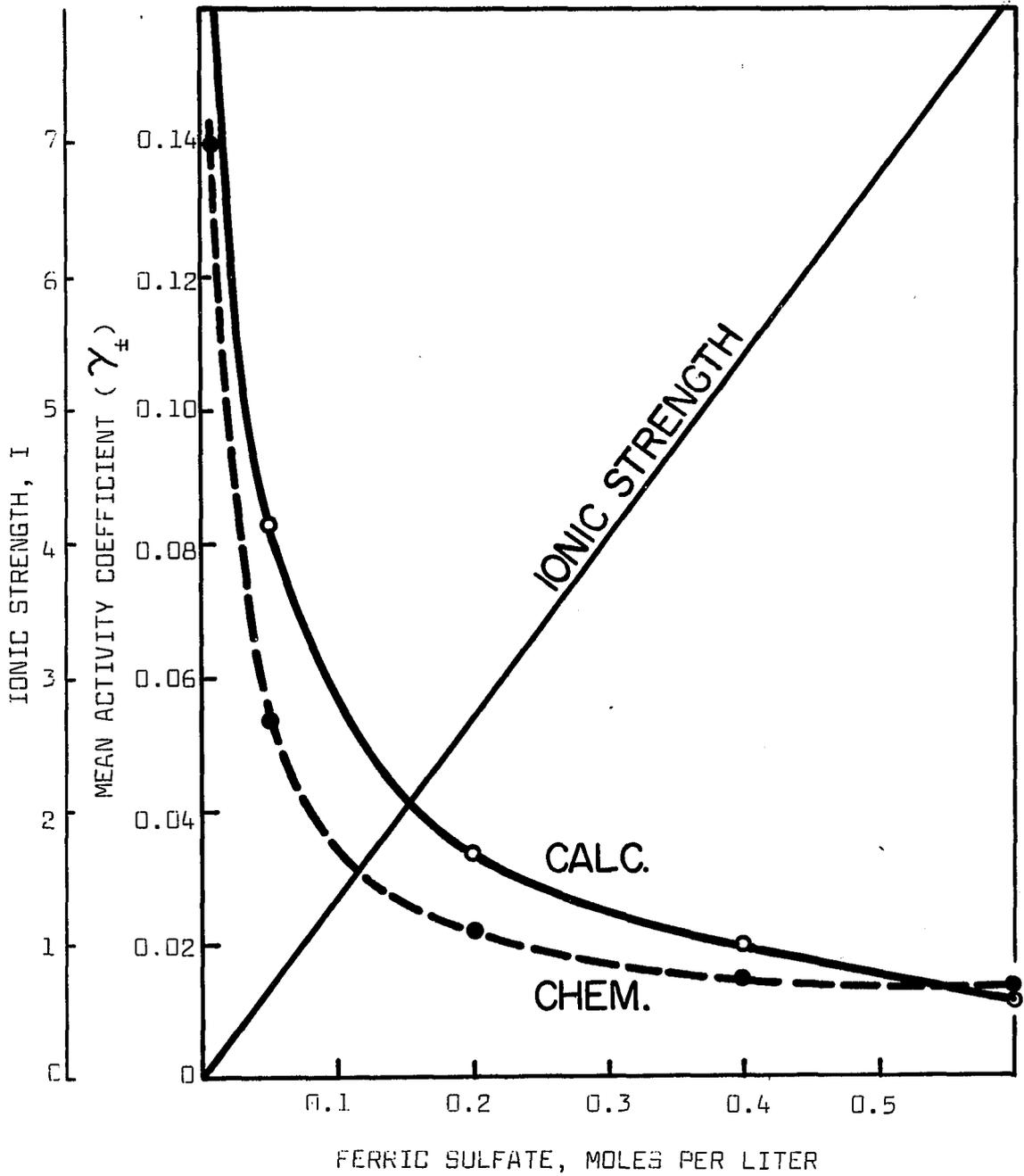


Fig. 17. Calculated and literature mean activity coefficients for  $\text{Fe}_2(\text{SO}_4)_3$ .

TABLE 23  
 THE DIFFUSIVITIES OF FERRIC SULFATE AT 38°C AT  
 CONSTANT FERRIC SULFATE CONCENTRATION AND  
 VARYING SULFURIC ACID CONCENTRATION

$\text{Fe}_2(\text{SO}_4)_3$ MOLAR	$\text{H}_2\text{SO}_4$ MOLAR	I	$D_1^{38^\circ\text{C}}$ , $\text{Cm.}^2/\text{min.}$
0.10	0.020	1.3	$2.2 \times 10^{-4}$
0.10	0.10	1.6	2.6
0.10	0.20	1.9	2.9
0.10	0.30	2.2	3.1
0.10	0.40	2.5	3.4
0.10	0.50	2.8	3.6

These calculated diffusivities, lower line, were plotted in Figure 18. The plot was compared to the experimental diffusivities, upper line, obtained from data in Table D-1. The slopes,  $q$ , of the lower and upper lines in Figure 18 were, respectively, 0.14 and 0.25. The slope of one plot was within the 95 percent confidence limit of the other plot. Therefore, sulfuric acid affected the diffusivity of ferric sulfate as predicted by theory. This comparison supported the theory that the initial leaching rate of chalcocite was controlled by the ferric sulfate diffusion process.

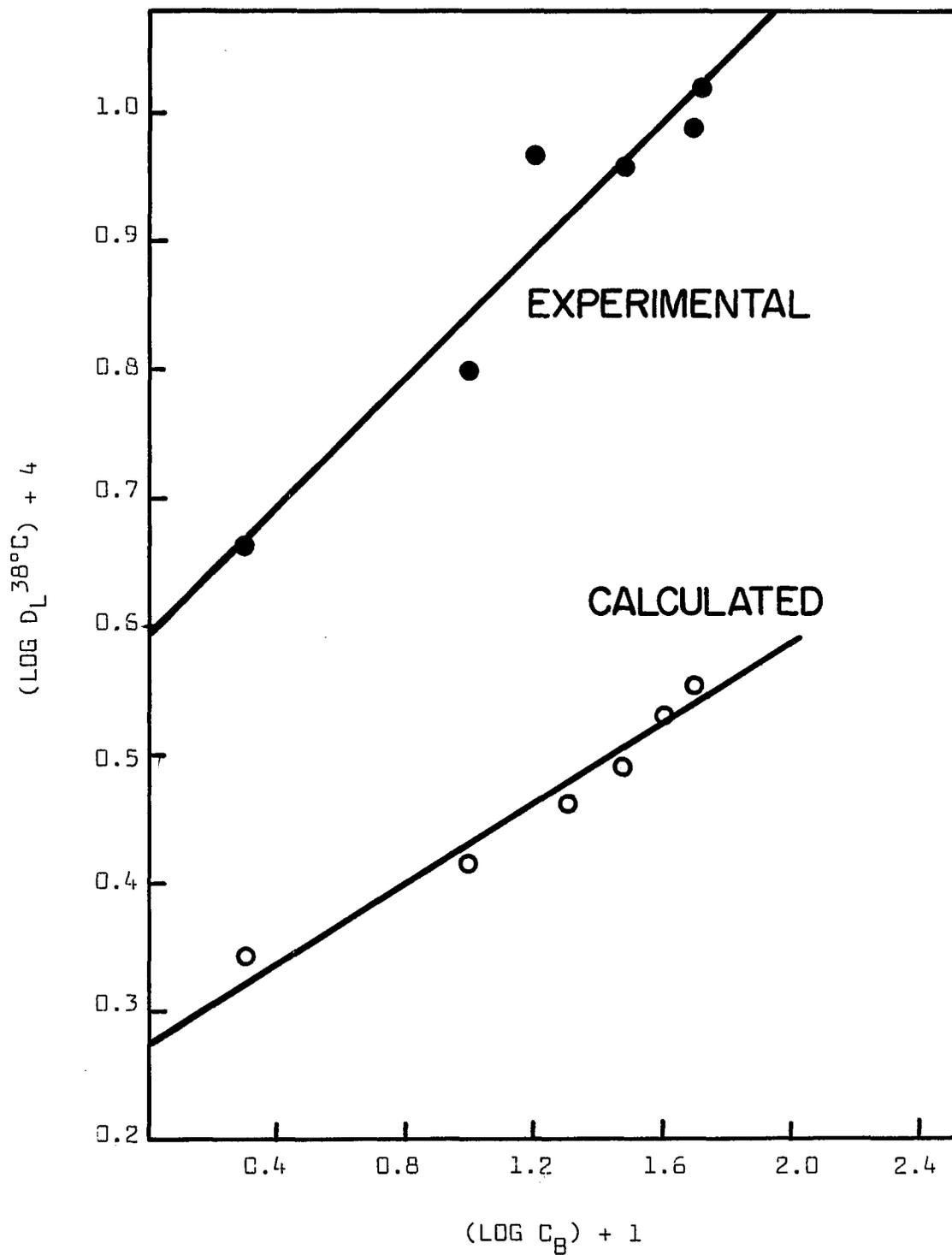


Fig. 18. Calculated and experimental diffusivities - sulfuric acid plots.

### Reactions Controlled by Solid-State Diffusion

Various cations could diffuse through the sulfur matrix of sulfides (Smith 1963, pp. 36-69; Peters 1968, pp. 7-14; Decker 1959, pp. 60-100 and 160-182). Solid-state diffusion of cations results in a change from one thermodynamically stable mineral to another. The driving force for the diffusing species could be the electro-chemical potential between the unaltered zone and the leach solution-altered zone interface. The rate of diffusion would be equal to the rate of electrical discharge between the diffusing species and the ferric iron in solution. Therefore, the rate of solid-state diffusion would equal the rate of ferric sulfate reduction to ferrous sulfate.

Since the electrochemical potential between the unaltered zone and the leach solution-altered zone interface would be constant, the rate of diffusion would be independent of concentration. Moreover, the diffusivity and the volume of the system is usually constant. Therefore, the rate of solid-state diffusion can be given by

$$\frac{r_{ASSD}}{S} = \frac{K_3}{d} \quad (85)$$

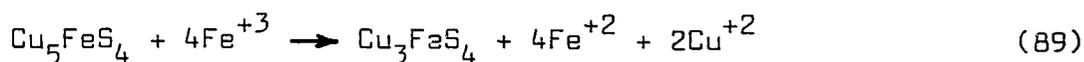
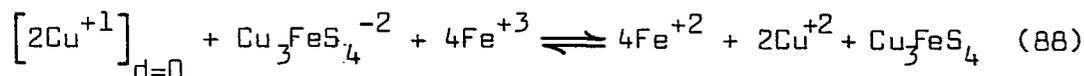
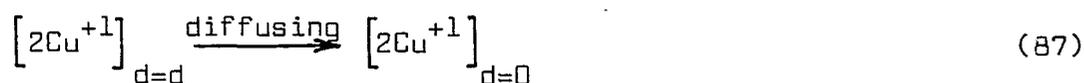
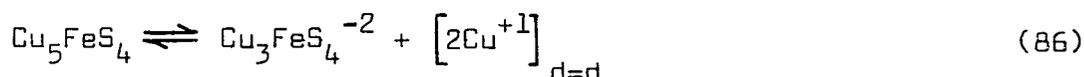
where  $K_3 = \left(\frac{D}{V}\right)$ (Concentration Gradient).

The data in Table 24 demonstrated that the rate of ferric sulfate leaching of bornite decreased as the calculated depth of the leached zone increased.

TABLE 24  
THE RATE OF REACTION FOR BORNITE DETERMINED AT 38°C

FERRIC SULFATE Moles Per Liter FROM	TO	d, Cm.	ORDER ρ	(r <sub>A</sub> /S)×10 <sup>6</sup>
0.105	0.280	0.004	0.0	13.60
0.056	0.279	0.008	0.0	5.48
0.048	0.204	0.040	0.0	2.24
0.046	0.214	0.050	0.0	1.65

Therefore, another possible process in the mechanism of ferric sulfate leaching of bornite would be solid state diffusion. As illustrated in Figure 19, the cuprous ions  $[2\text{Cu}^{+1}]$  diffused from the unaltered-altered zone interface at  $(d=d)$  through the altered zone to the reaction sites at  $(d=0)$ . The following reactions were proposed for the process:



Sullivan's data in Table 2, page 7, showed that an altered mineral formed after the removal of 40 percent of the copper ions. This altered product was earlier assumed to be  $\text{Cu}_3\text{FeS}_4$ . The continued leaching of the  $\text{Cu}_3\text{FeS}_4$  material pro-

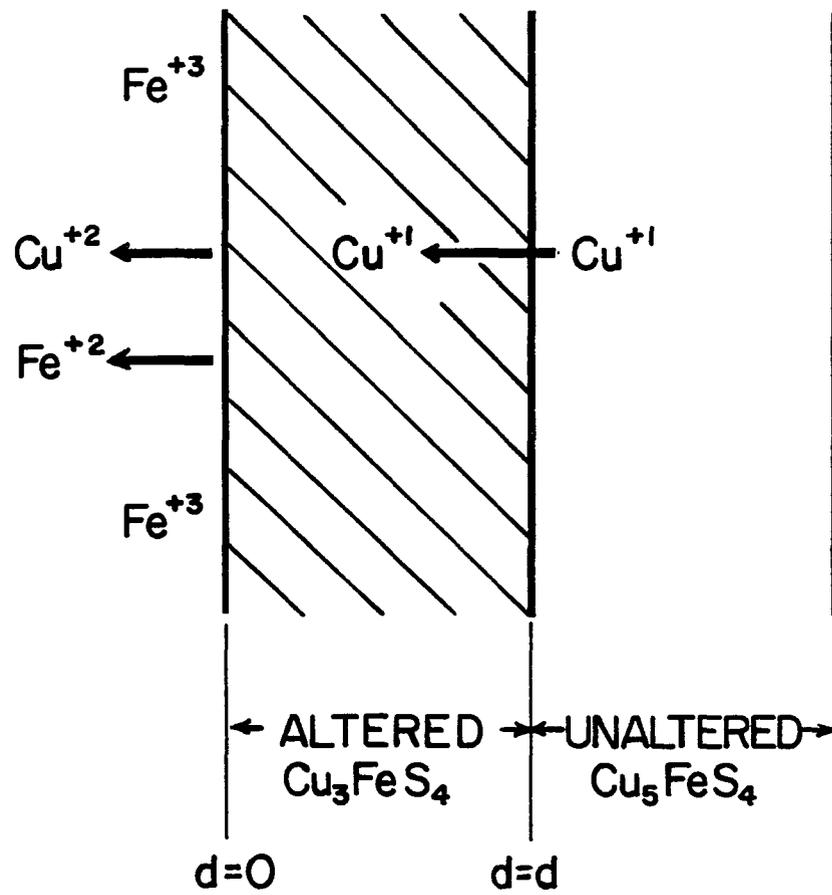
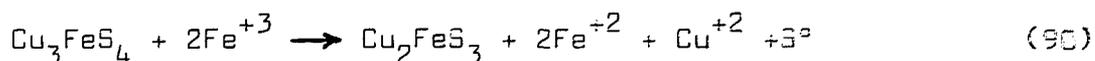


Fig 19. The altered zones occurring in the process of solid state diffusion.

duced more copper in solution, a sulfur residue, and a second altered mineral. This second product had an atom ratio of Cu/Fe/S = 2.2/2.2/3.7. Therefore, the direct attack of the initial altered zone at ( $d = 0$ ) by ferric sulfate was assumed to be the next step in the decomposition of bornite.



It was also assumed that the leaching rate of the  $\text{Cu}_3\text{FeS}_4$  mineral was independent of the variation in ferric sulfate concentration.

When the overall reaction rate was represented by  $(r_A/S)$ , the rate of solid state diffusion by  $(r_{\text{ASSD}}/S)$ , and the rate of direct ferric sulfate leaching of the altered zone by  $(r_{\text{AL}}/S)$ , the overall rate expression would be

$$(r_A/S) = (r_{\text{ASSD}}/S) + (r_{\text{AL}}/S) \quad (91)$$

The rate of solid state diffusion was expressed in terms of the overall rate and the rate of leaching of the altered zone.

$$(r_{\text{ASSD}}/S) = (r_A/S - r_{\text{AL}}/S) \quad (92)$$

The combination of Eqs. 85 and 92 resulted in equation (93).

$$\left(\frac{r_A - r_{\text{AL}}}{S}\right) = \frac{k_3}{d} = \left(\frac{r_{\text{ASSD}}}{S}\right) \quad (93)$$

The value of  $(r_{\text{AL}}/S)$  in Eq. 93 was assumed to be constant. The values of  $(r_A/S)$  and  $d$  from Table 24 were inserted into Eq. 93. The value of  $(r_{\text{ASSD}}/S)$  at each depth was determined. This calculation was repeated at several levels of  $(r_{\text{AL}}/S)$  which was increased from 0.0 to  $1.2 \times 10^{-6}$  moles per liter per minute-

square centimeter. The value of  $(r_{AL}/S)$  which resulted in a constant value for  $(r_{ASSD}/S) \times d$  was determined. The overall rate expression, Eq. 94, based on the above assumptions and calculations, was obtained.

$$(r_A/S) = \left( \frac{0.048}{d} + 0.40 \right) \times 10^{-6}, \text{ M per min.-cm.}^2 \quad (94)$$

where

$$(r_{ASSD}/S) = \left( \frac{0.048}{d} \right) \times 10^{-6} \quad (95)$$

$$(r_{AL}/S) = 0.40 \times 10^{-6} \quad (96)$$

These results indicated the possibility of a solid-state diffusion process existing in the overall reaction mechanism for the leaching of bornite. However, insufficient experimental data were collected during the leaching studies to show the existence of a solid-state diffusion process. Alteration products must be identified, and their depths from the solution-mineral surface interface must be measured. With this additional information a better comparison to solid-state diffusion would be obtained.

#### Chemisorption and Surface Reactions

The process of chemisorption was outlined on pages 22 through 28, Eqs. 39 through 43. The dependence of each rate expression on ferric sulfate concentration was based on the reactions which were at equilibrium and on the degree of adsorbed ferric sulfate coverage on the active sites.

In Table 21 the kinetic results for  $p$ ,  $A'$  and  $E_{EXP}$  were given for bornite ( $d_3$ ), covellite, and chalcopyrite, in which

the leaching rates,  $(r_A/S)$ , were not dependent on the concentration of ferric sulfate.

If an adsorption process controlled the leaching mechanism, the rate was expressed by Eq. 44.

$$(r_A/S) = \left(\frac{k_a}{N_a V}\right) k_{23} f(\theta) f(C_A) \quad (44)$$

The rate expression was a function of the ferric sulfate concentration. If the surface reaction between the mineral species and the adsorbed ferric iron controlled, the rate was expressed by Eq. 45.

$$(r_A/S) = \left(\frac{k_a}{N_a V}\right) k_{23} f(\theta) \quad (45)$$

This expression was a function of the number of active sites on the mineral surface covered by the ferric iron.

Several cases of Eq. 45 were evaluated. If the reactions, Eqs. 40 and 42, were the slow steps in the mechanism, the other reactions, Eqs. 39, 41 and 43, were at equilibrium. When the adsorption process, Eq. 40, was at equilibrium ( $K_{22} \gg k_{23}$ ), the rate expression was

$$(r_A/S) = \frac{k_a K_{eq} C_A}{1 + K_{eq} C_A} \quad (51)$$

Two special cases for Eq. 51 existed. As  $\theta$  approached one and  $K_{eq}$  was much greater than one, the rate expression was

$$(r_A/S) = k_a = \left(\frac{k_a}{N_a V}\right) k_{23} \quad (53)$$

As  $\theta$  approached zero and  $K_{eq}$  was much smaller than one, the rate became

$$(r_A/S) = k_a K_{eq} C_A \quad (54)$$

If the absorption process, Eq. 40, affected the surface reaction steps ( $k_{23} \ll k_{22}$ ), the rate was given by

$$(r_A/S) = \frac{k_a k_b C_A}{1 + k_b C_A} \quad (55)$$

Of the latter three rate expressions, Eq. 53 was the only one which was independent of the ferric sulfate concentration. Therefore, the controlling step for the proposed mechanism for ferric sulfate leaching of bornite ( $d_3$ ), covellite, and chalcopyrite was due to the surface reaction. All the remaining reactions in the mechanism were assumed to be at equilibrium.

Equating Eqs. 53 and 46, the rate can be expressed by Eq. 97.

$$(r_A/S) = k_a = k_2 = \left(\frac{k_0}{N_a V}\right) k_{23} = \left(\frac{k_{SR} k_{ACT} k'}{N_a V}\right) k_{23} \quad (97)$$

The constant,  $k_{23}$ , is the actual rate constant which is expressed by

$$\frac{k_{23}}{T} = e\left(\frac{k}{h}\right) \exp(+\Delta S^*/R) \exp(-E_{EXP}/RT) \quad (188)$$

The measured rate constant,  $k_2$ , is equivalent to  $k_a$  in the rate Eq. 96. Combining Eqs. 97 and 188 gives

$$\frac{k_a}{T} = \frac{k_2}{T} = \left(\frac{k_0}{N_a V}\right) e\left(\frac{k}{h}\right) \exp(+\Delta S^*/R) \exp(-E_{EXP}/RT) \quad (98)$$

From the kinetic data for bornite ( $d_3$ ), covellite, and chalcopyrite in Table 21, the enthalpy of activation,  $\Delta H^*$ , and the entropy of activation,  $\Delta S^*$ , were estimated. The enthalpy values were determined from Eq. 17. The entropy values were calculated from Eq. 98 in which the  $A'$  term of the Arrhenius equation was

$$A' = \left( \frac{k_0}{N_a V} \right) e \left( \frac{k}{h} \right) \text{EXP} (+ \Delta S^*/R) \quad (99)$$

The  $k_{SR}$  term in the expression for  $k_0$ , Eq. 46, was assumed to have the value of ten for bornite and covellite and the value of one-hundred for chalcopyrite (Potter 1956, p. 129). It was determined that the plane of highest atom density for these three minerals contained sulfur atoms (Lundquist and Westgren 1936, pp. 3-5; Bragg, Claringbull, and Taylor 1965, pp. 55-63). From the parameters for the lattice structure of the minerals, the  $K'$  values were calculated for the plane of highest density (see Table 25).

TABLE 25

THE LATTICE TYPE, THE PLANE OF HIGHEST ATOM DENSITY,  
AND THE NUMBER OF ATOMS PER SQUARE CENTIMETER  
ALONG THIS PLANE

MINERAL	LATTICE TYPE	PLANE OF HIGHEST ATOM DENSITY	$k' \times 10^{-15}$ ATOMS PER CM. <sup>2</sup>
Bornite	CCP	111	3.11
Chalcopyrite	CCP	111	3.41
Covellite	HCP	0001	0.80

The values of  $k_0$  were determined by rearranging Eq. 99 to give

$$k_0 = \left( \frac{A' N_a V}{e} \right) \left( \frac{h}{k} \right) \text{EXP} (-\Delta S^*/R) \quad (99B)$$

Several values of  $k_0$  were calculated at several levels of  $\Delta S^*$ . Using the assumed  $k_{SR}$  values, and the calculated  $k'$  values, the fraction of the total number of sites activated,  $k_{ACT}$ , were determined from Eq. 46.

The results are shown in Table 26. Included are the assumed entropies of activation, the  $k_0$  terms, and the calculated  $k_{ACT}$  term.

The dimensionless number  $k_{ACT}$  was plotted against the entropies of activation for the three minerals in Figure 20. The fraction of total sites activated was assumed to be 0.25 percent (Dresher, Wadsworth, and Fassell 1956, p. 800). Using this fraction, the entropies of activation were obtained from the plots.

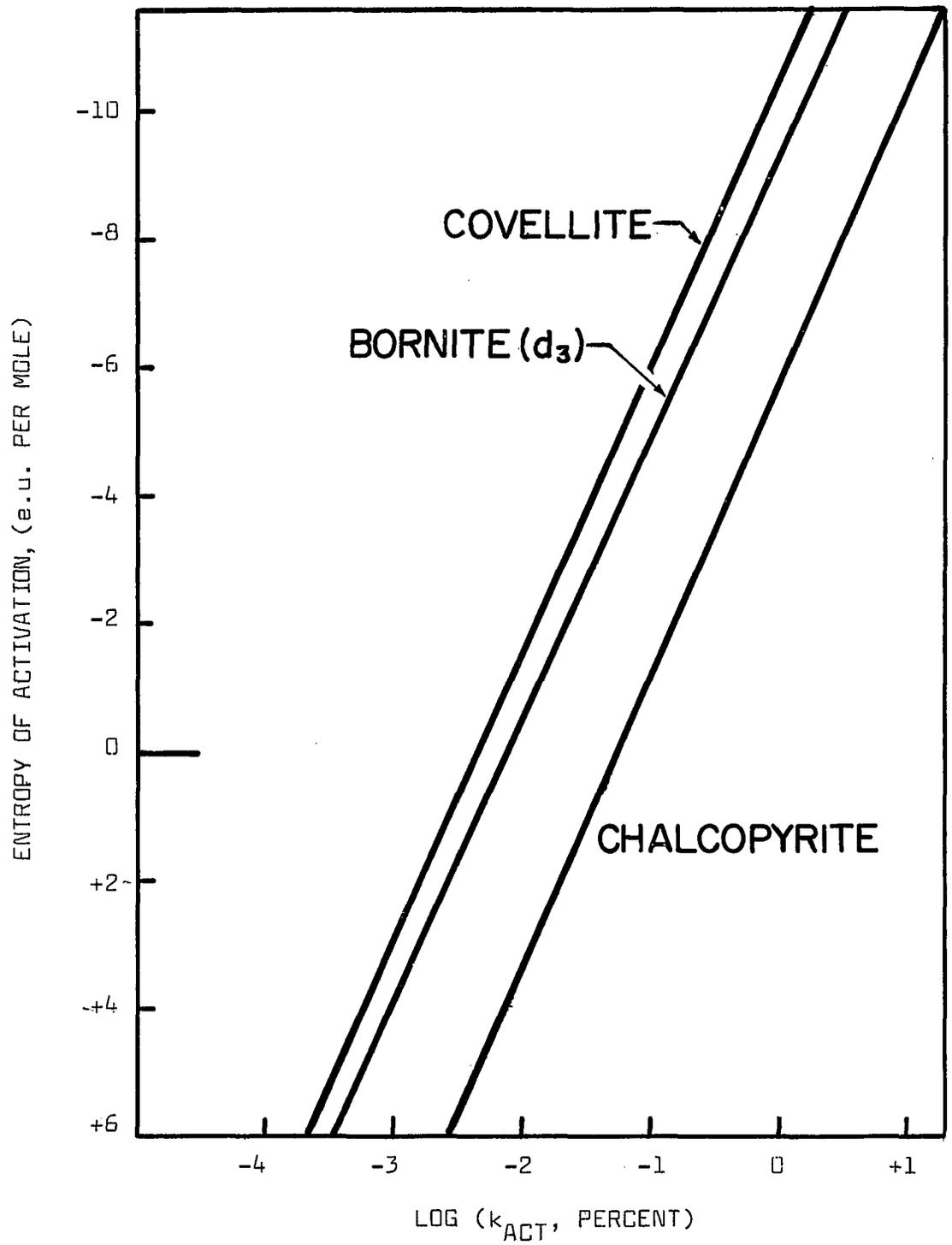


Fig. 20. Entropy of activation - LOG  $k_{ACT}$  for bornite ( $d_3$ ), covellite, and chalcopyrite.

TABLE 26

THE ASSUMED ENTROPIES OF ACTIVATION,  $k_D$ , AND  $k_{ACT}$  TERMS  
FOR THE MINERALS BORNITE ( $d_3$ ), COVELLITE AND CHALCOPYRITE

MINERAL	$\Delta S^*$ , e.u./Mole	$k_D \times 10^{-12}$ Atoms/Cm. <sup>2</sup>	$k_{ACT}$ , Percent
Bornite	+ 6.0	0.11	0.00036
	0.0	2.40	0.0077
	- 6.0	49.0	0.16
	-12.0	1,000.0	3.2
	-18.8	31,000.0	100.0
Covellite	+ 6.0	0.019	0.00024
	0.0	0.39	0.0048
	- 6.0	7.9	0.0099
	-12.0	162.0	2.02
	-18.8	8,000.0	100.0
Chalcopyrite	+ 6.0	9.4	0.0028
	0.0	193.0	0.057
	- 6.0	3,950.0	1.16
	-12.0	81,000.0	23.7
	-14.9	340,000.0	100.0

The calculated results for the enthalpies and entropies of activation are given in Table 27 for the minerals bornite ( $d_3$ ), covellite, and chalcopyrite. Also included in this table is an estimation of the free energy of activation,  $\Delta F^*$ .

TABLE 27  
THE ENTHALPY, ENTROPY, AND FREE ENERGY OF ACTIVATION FOR  
BORNITE ( $d_3$ ), COVELLITE, AND CHALCOPYRITE

MINERAL	$\Delta H^*$ , Kcal./Mole	$\Delta S^*$ , e.u.	$\Delta F^*$ , Kcal./Mole
Bornite ( $d_3$ )	+11.7	-6.7	+13.9
Covellite	+13.6	-7.8	+16.1
Chalcopyrite	+17.2	-3.0	+18.2

The negative entropy of activations values suggested a transition from a disordered process to an ordered process on the mineral surface. Concerning the disordered-ordered process Glasstone (Glasstone, Laidler, and Eyring 1941, p. 22) stated that "...when a reaction occurs between complex molecules there is a considerable rearrangement of energy among the degrees of freedom...there is a decrease of entropy in the formation of the activated complex." The ferric iron in solution was chemisorbed onto specific mineral sites. There was an electronic change in the ferric iron reduction process, and the mineral was rearranged structurally yielding a copper ion and a new solid species. Therefore a negative entropy of activation could be expected in the ferric sulfate leaching of the minerals bornite ( $d_3$ ), covellite, and chalcopyrite.

#### The Electrode Process

A possible mechanism for the surface controlling reaction in the leaching of bornite ( $d_3$ ), covellite, and chalcopyrite

would be the electrode type process. Since potential and current relations were not determined, the leaching tests did not provide a direct correlation to such a process. However, several observations were made from the above calculated results for chemisorption in Table 27 to show that the existence of such a process was possible.

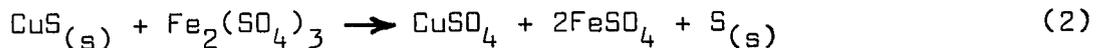
Assuming chemisorption at equilibrium and the rate of electron exchange the slow reaction step in the electrode process Eq. 65 was obtained.

$$(r_{NET}/S) = (r_1/S) = \left(\frac{kT}{h}\right) (a_+)_e \text{EXP}\left(\frac{-\Delta F_1^{\circ*} + n\alpha e_p F_e}{RT}\right) \quad (65)$$

The value of  $n$  was the number of electrons exchanged between the electrode surface and the absorbed ionic species  $M^+$ . The value of  $\alpha$  was the fraction of the over-potential,  $e_p$ , aiding the reaction from left to right, that is, the discharging of the ferric iron to the ferrous iron on the electrode surface.

For the discharging process of ferric sulfate at a sulfide surface there were two electrons exchanged per ferric sulfate molecule,  $Fe_2(SO_4)_3$ . The value of  $\alpha$  was assumed to be equal to 0.50.

The electrode potential,  $e$ , between the covellite mineral and a ferric sulfate solution was assumed to be +0.304 volts. The value of the standard electrode potential,  $e^\circ$ , for the reaction



was calculated to be +0.204 volts (Garrels and Christ 1965,

pp. 403-429; Kelley 1937, pp. 120-121; Merwin and Lombard 1937, p. 222). Therefore, the overpotential,  $e_p$ , as obtained by Eq. 60 was +0.10 volts.

If  $(a_{+e})$  in Eq. 65 equaled the number of active sites on the electrode surface, its value became  $(k_o/N_a V)$ . Therefore, the experimental free energy of activation,  $\Delta F_1^*$ , equaled the term  $(-\Delta F_1^{\circ*} + n\alpha e_p F_e)$ . The experimental free energy of activation,  $\Delta F_1^*$ , for covellite was stated in Table 27 to be +16.1 kilocalories per mole. Using the above free energy of activation equality, the value of  $\Delta F_1^{\circ*}$  was calculated to be 18.4 kilocalories per mole.

The electrode surface was assumed to be the sulfide ions in the covellite, bornite, and chalcopyrite minerals. Therefore, the free energy,  $\Delta F_1^{\circ*}$ , could be the same in all three cases. The values of the overpotential,  $e_p$ , were estimated for chalcopyrite and bornite from the  $\Delta F_1^{\circ*}$  result obtained above for covellite and the  $\Delta F_1^*$  values in Table 27.

The free energies of activation,  $\Delta F_1^*$  and  $\Delta F^{\circ*}$ , and the overpotentials for the three minerals are given in Table 28.

TABLE 28

DETERMINATION OF THE OVERPOTENTIAL FOR BORNITE ( $d_3$ )  
AND CHALCOPYRITE AS OBTAINED FROM AN  
ASSUMED VALUE FOR COVELLITE

MINERAL	FREE ENERGIES, Kcal. per Mole		$n\alpha_{Fe}$	$e_p$ , Volts
	$\Delta F_1^*$	$\Delta F_1^{o*}$		
$Cu_5FeS_4$	+13.9	+18.4	+4.5	+0.200
CuS	+16.1	+18.4	+2.3	+0.100
$CuFeS_2$	+18.2	+18.4	+0.2	+0.009

$$e_p = \left( \frac{\Delta F_1^{o*} - \Delta F_1^*}{n\alpha_{Fe}} \right)$$

The overpotential increased from the low positive value for chalcopryrite to the high positive value for bornite ( $d_3$ ). The rates of ferric sulfate leaching ( $r_A/S$ ) of these minerals at 38 degrees centigrade were determined from the data in Table 21. Assuming the roughness factors,  $k_{GR}$ , to be 10 for bornite and covellite and 100 for chalcopryrite, these values were:

Bornite ( $d_3$ ):  $2.2 \times 10^{-7}$ , moles per 1.-min.-cm.<sup>2</sup>

Covellite:  $1.6 \times 10^{-9}$ , moles per 1.-min.-cm.<sup>2</sup>

Chalcopryrite:  $5.2 \times 10^{-10}$ , moles per 1.-min.-cm.<sup>2</sup>

These results agreed reasonably with theory, that is,

$$[r_{NET}/S] \text{ is proportional to } \text{EXP}(+e_p) \quad (100)$$

### Ferric Sulfate Leaching of Pyrrhotite

For the ferric sulfate leaching of pyrrhotite the initial kinetic rate was determined to be independent of the ferric sulfate concentration. The frequency factor,  $A'$ , and the experimental energy of activation,  $E_{EXP}$ , were estimated to be, respectively, 1.25 moles per liter per minute and 8.90 kilocalories per mole.

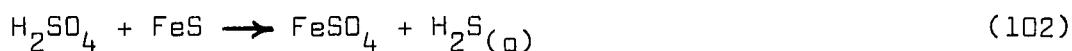
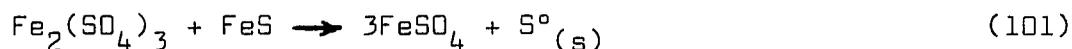
A mechanism similar to that proposed for bornite ( $d_3$ ), covellite and chalcopyrite could exist for the ferric sulfate leaching of pyrrhotite. However, the data obtained at various temperatures and at several sulfuric acid concentrations indicated departures from such a chemisorption mechanism.

As the temperature of the leach system increased from 32 to 39 degrees centigrade the rate of ferric sulfate consumption increased from 0.70 to 1.34 moles per l.-min.-cm.<sup>2</sup>. However, when the temperature increased to 50 degrees centigrade the rate decreased sharply to 0.27 moles per l.-min.-cm.<sup>2</sup>.

When sulfuric acid was added to the ferric sulfate leach solution, the rate decreased. At zero added sulfuric acid concentration the rate was, as above, 0.70 moles per l.-min.-cm.<sup>2</sup>. At an added sulfuric acid concentration of 0.042 molar the rate decreased to 0.060 moles per l.-min.-cm.<sup>2</sup>. With increasing concentrations of sulfuric acid the rate increased from the low value of 0.060 to 0.24 moles per l.-min.-cm.<sup>2</sup>.

The increasing temperatures could have broken down the chemisorption process which existed between the mineral and

ferric sulfate. Also the addition of sulfuric acid to the leach solution containing ferric sulfate could have resulted in competing reactions between the ferric sulfate and the mineral, Eq. 101, and the sulfuric acid and the mineral, Eq. 102.



Additional test data concerning the variation in ferric sulfate concentration, process temperature, and sulfuric acid concentration must be made. The effects of each alone and of their interrelationships must be sought.

#### Effects of Sulfuric Acid on the Leaching of Sulfides

The effects of sulfuric acid on the ferric sulfate leaching of chalcocite and pyrrhotite were discussed in previous sections. Sulfuric acid was added to leach solutions in several tests for each of the minerals bornite ( $d_3$ ), covellite, and chalcopyrite. The results were given in Tables 17 and 18. As indicated by the data, the increasing sulfuric acid concentrations did not have any effect on the initial leaching rates of these minerals. These results added support to the theory for the existence of a chemisorption type process since the ionic strength effect, which would modify the rate for ionic-reaction and ionic-diffusion mechanisms, was not present (Laidler 1965, pp. 229-230). Therefore, the reaction rate must have involved either a process between an ion and a neutral molecule or a chemisorption type process. The former case would be unlikely when the ionic character

of all sulfide minerals was considered. This ionic character would produce charged surfaces due to the difference in size of the cations and anions of the sulfide, and the reaction would have involved an ion-ion process which would have been dependent on ionic strength.

## CHAPTER VIII

### SUMMARY OF RESULTS

The initial rates of reaction between ferric sulfate solutions and several sulfide minerals were measured. These minerals were chalcocite, bornite, covellite, chalcopyrite, and pyrrhotite. From the rates of reaction the kinetics of the initial leaching process, in which less than ten percent of the mineral was leached were determined. From the kinetic data a mechanism for the leaching reaction of each mineral was proposed.

The mechanism for ferric sulfate leaching of chalcocite was not fully evaluated. Insufficient leaching time was allowed. Tests of considerably longer duration than those conducted in this investigation must be carried out to ascertain the complete mechanism. However, the kinetic data obtained indicated that during the initial dissolution process, ferric sulfate diffusion to the reaction sites on the mineral controlled the rate. The data also indicated agreement with the theories of Glasstone for the diffusion of water molecules over the larger hydrated ferric-iron ions and of Robinson and Stokes which was based on ionic conductance, chemical potential gradient, and quasi-equilibrium of the diffusion process.

The comparisons of experimental data to the theoretical data are shown in Table 29. Included are the experimental data for the energy of activation,  $E_{\text{EXP}}$ , the equilibrium distance,  $\lambda_{\text{EXP}}$ , and the self-diffusivity of water,  $D_{\text{EXP}}^{(1)}$ . These experimental values are compared to Glasstone's theoretical data for the self-diffusion of water, that is,  $E_{\text{H}_2\text{O}}$ ,  $\lambda_{\text{H}_2\text{O}}$ , and  $D_{\text{H}_2\text{O}}$ . Also included is the comparison between the experimental diffusivity,  $D_{\text{EXP}}^{(2)}$ , and the diffusivity,  $D_{\text{R-S}}$ , based on Robinson and Stokes' theory.

TABLE 29

SUMMARY OF EXPERIMENTAL AND THEORETICAL DATA  
FOR THE DIFFUSION CONTROLLING PROCESS IN THE  
FERRIC SULFATE LEACHING OF CHALCOCITE

GLASSTONE'S THEORY: THE SELF DIFFUSION OF WATER						DIFFUSIVITIES BASED ON ROBINSON AND STOKES' THEORY	
ENERGY OF ACTIVATION		EQUILIBRIUM DISTANCES		DIFFUSIVITIES			
$E_{\text{EXP}}$	$E_{\text{H}_2\text{O}}$	$\lambda_{\text{EXP}}$	$\lambda_{\text{H}_2\text{O}}$	$D_{\text{EXP}}^{(1)}$	$D_{\text{H}_2\text{O}}$	$D_{\text{EXP}}^{(2)}$	$D_{\text{R-S}}$
6.7	5.3	18.3Å	11.0Å	$56 \times 10^{-4}$	$22 \times 10^{-4}$	$6.2 \times 10^{-4}$	$2.6 \times 10^{-4}$

The effect of ionic strength in the leaching of chalcocite was also noted. Adding sulfuric acid to a solution at constant ferric sulfate concentration increased the dissolution rate of chalcocite. These results agreed with the theoretical correlation of ionic strength to the diffusivity of ferric sulfate which stated that as the ionic strength increased the diffusivity increased.

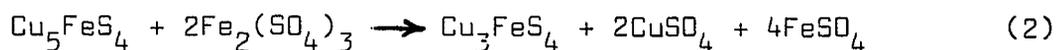
The mechanism for the ferric sulfate leaching of bornite ( $d_{1a}$ ) was evaluated. The results indicated that the initial stages of leaching at low ferric sulfate concentrations involved a diffusion controlled process. The data agreed closely to the theories of Glasstone for the self-diffusion of water and that of Robinson and Stokes' (Table 30).

TABLE 30

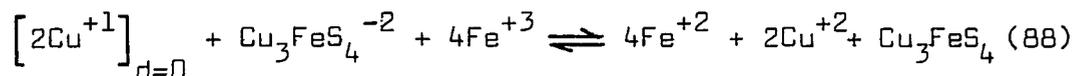
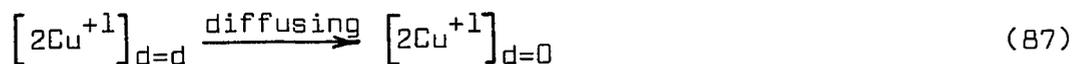
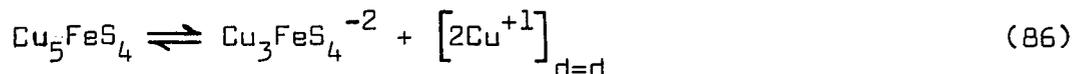
SUMMARY OF EXPERIMENTAL AND THEORETICAL DATA  
FOR THE DIFFUSION CONTROLLING PROCESS IN THE  
FERRIC SULFATE LEACHING OF BORNITE ( $d_{1a}$ )

GLASSTONE'S THEORY: THE SELF DIFFUSION OF WATER				DIFFUSIVITIES BASED ON ROBINSON AND STOKES' THEORY			
ENERGY OF ACTIVATION		EQUILIBRIUM DISTANCES		DIFFUSIVITIES			
$E_{EXP}$	$E_{H_2O}$	$\lambda_{EXP}$	$\lambda_{H_2O}$	$D_{EXP(1)}$	$D_{H_2O}$	$D_{EXP(2)}$	$D_{R-S}$
6.4	5.3	7.9 $\text{\AA}$	11.0 $\text{\AA}$	$18 \times 10^{-4}$	$22 \times 10^{-4}$	$2.0 \times 10^{-4}$	$2.6 \times 10^{-4}$

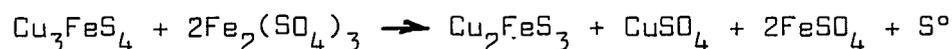
Further examination of the experimental data for ferric sulfate leaching of bornite indicated the possibility of a solid-state diffusion process. The cuprous ions were assumed to be the diffusing species. This process altered the mineral structure of bornite to an intermediate mineral,  $Cu_3FeS_4$ . Sullivan's data indicated that the initial reaction involving the dissolution of bornite was



The probable solid-state diffusion mechanism involved the following steps



The altered mineral would also be attacked by ferric sulfate yielding additional dissolved copper. The leaching reaction involving the altered product,  $\text{Cu}_3\text{FeS}_4$ , probably was



The combined rate of reaction ( $r_A/S$ ) for the solid state diffusion process and for the direct attack of the altered species was proposed to be

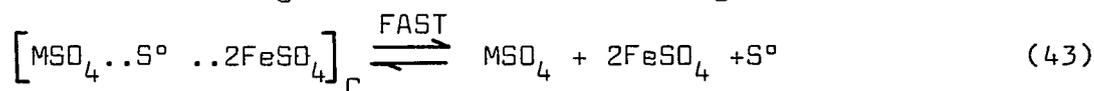
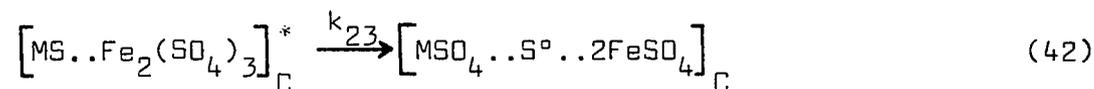
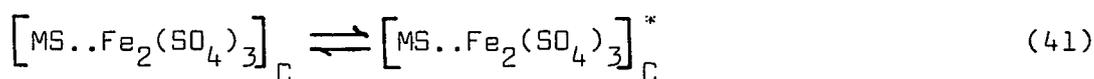
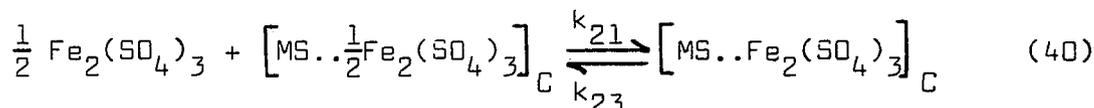
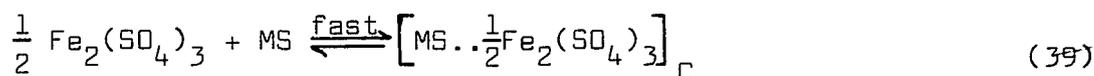
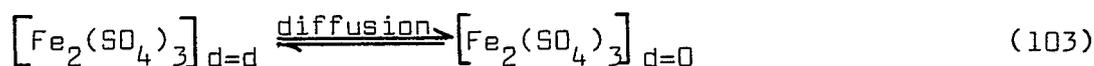
$$(r_A/S) = \left(\frac{0.048}{d} + 0.40\right)10^{-6}, \text{ (Moles/liter) per min.-cm.}^2 \quad (94)$$

Additional information concerning the process of solid state diffusion is needed. The altered minerals must be identified. Depth measurements of the unaltered zone, the altered zones, and the final leach residue must be obtained at various times during the leaching process.

The possible mechanism involved in the direct dissolution of the bornite ( $d_3$ ),  $\text{Cu}_3\text{FeS}_4$ ; covellite; and chalcopyrite was a chemisorption process with an electrode type surface reaction.

The chemisorption process assumed that the adsorption of ferric sulfate on the mineral was at equilibrium. It also

assumed that the active sites were all covered and that the controlling reaction was the oxidation process. The mechanism for the direct attack of ferric sulfate on these sulfide minerals (MS) was proposed to be



In this mechanism the surface reaction controls and the rate expression was stated by

$$(r_A/S) = k_o = \left( \frac{k_o}{N_a V} \right) k_{23} = k_2 \quad (53)$$

From the crystal chemistry data for the minerals, the kinetic data, the assumed surface roughness factors, and the assumed fraction of adsorption sites covered by ferric sulfate to be 0.25 percent, the free energies of activation were estimated. These values were 13.9, 16.1, and 18.2 kilocalories per mole of activated complex for bornite ( $d_3$ ), covellite, and chalcopyrite, respectively. The values correspond to the meas-

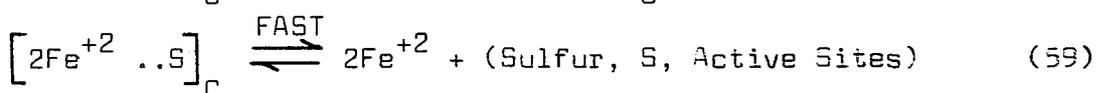
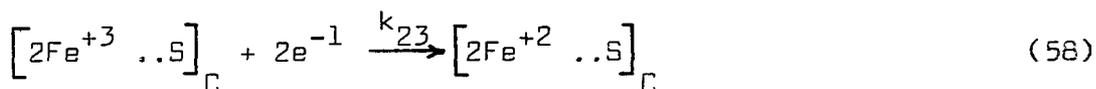
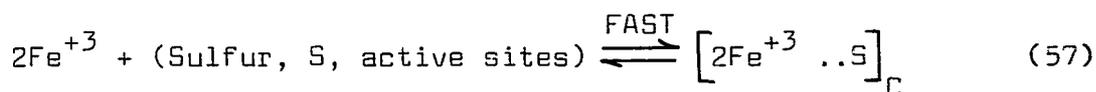
ured order of reactivity at 38 degrees centigrade between these sulfides and ferric sulfate:

Bornite:  $(r_A/S) = 2.2 \times 10^{-7}$ , moles per l.-min.-cm.<sup>2</sup>

Covellite:  $(r_A/S) = 1.6 \times 10^{-9}$ , moles per l.-min.-cm.<sup>2</sup>

Chalcopyrite:  $(r_A/S) = 5.2 \times 10^{-10}$ , moles per l.-min.-cm.<sup>2</sup>

A possible process which involves the surface reactions between chemisorbed ferric sulfate and bornite ( $d_3$ ), covellite, or chalcopyrite was the electrode mechanism. The chemisorption process was assumed to be at equilibrium. The surface reaction involving the electron exchange between the adsorbed ferric ions and the sulfur active sites of the sulfide mineral was assumed to be the slow process. The proposed mechanism involved



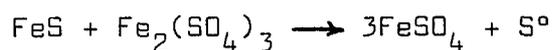
Copper ions were assumed to be released upon the electron exchange to maintain electrical neutrality. The overpotential,  $e_p$ , which decreased the free energy of activation barrier was estimated for each mineral. The overpotentials were calculated to be +0.20, +0.10, and 0.01 volts, respectively, for bornite ( $d_3$ ), covellite, and chalcopyrite. A correlation between measured rates, as shown above, and the overpotential existed. As the overpotential increased the rate of reaction between ferric

sulfate and the sulfide increased in accordance with the theoretical aspects of the process.

However, these overpotentials were based on kinetic experiments which were not designed to obtain potential-current relationships. Moreover, the overpotentials were based on an assumed measured potential for covellite.

Addition of sulfuric acid to the ferric sulfate leach solutions did not affect the kinetics of the dissolution of bornite ( $d_3$ ), covellite, and chalcopyrite. These results substantiated the possible existence of a mechanistic process which was not controlled by the diffusion of ferric sulfate.

The kinetic data for the ferric sulfate leaching of pyrrhotite changed as the reaction temperature and added sulfuric acid varied. The data concerning the rate ( $r_A/S$ ) dependency on ferric sulfate concentration indicated mechanisms similar to that proposed for bornite ( $d_3$ ), covellite, and chalcopyrite. However, the ( $k_2/T$ ) - reaction temperature and the ( $r_A/S$ ) - added sulfuric acid concentration data indicated a sharp decrease in the rate of reduction of ferric sulfate to ferrous sulfate, ( $r_A/S$ ). These conditions were probably due to temperature-adsorption effects and the competing reactions:



APPENDIX A

LITERATURE DATA FOR THE CALCULATION  
OF FERRIC SULFATE DIFFUSIVITIES

TABLE A-1  
 LIMITING IONIC CONDUCTIVITIES OF VARIOUS IONS  
 AT SEVERAL TEMPERATURES

Ion	0°C	18°C	25°C	50°C	75°C	100°C	128°C
$1/2 \text{Fe}^{+2}$	31.5	53.0	62.5	101	145	196	257
$1/3 \text{La}^{+3}$	35.0	61.0	72.0	119	173	235	312
$1/3 \text{Fe}^{+3}$	-	-	68.0	-	-	-	-
$1/3 \text{Al}^{+3}$	-	-	63.0	-	-	-	-
$1/3 \text{Cr}^{+3}$	-	-	67.0	-	-	-	-
$1/3 \text{Ce}^{+3}$	-	-	69.9	-	-	-	-
$\text{Cl}^{-1}$	41.1	64.5	75.5	116	160	207	264
$\text{OH}^{-1}$	105.0	172.0	192.0	284	360	439	525
$1/2 \text{SO}_4^{-2}$	41.0	68.0	79.0	125	177	234	303
$\text{H}^{+1}$	240.0	314.0	350.0	465	565	644	722

SOURCE: Hodgman 1956, p. 2379.

TABLE A-2  
ACTIVITY COEFFICIENTS FOR  $Al_2(SO_4)_3$  AND  $In_2(SO_4)_3$

$M_2(SO_4)_3$ Molality	$Al_2(SO_4)_3$ $\gamma_{\pm}$	$In_2(SO_4)_3$ $\gamma_{\pm}$	$Fe_2(SO_4)_3$ $\gamma_{\pm}^*$
0.01	-	0.142	0.142
0.02	-	0.092	0.092
0.05	-	0.054	0.054
0.10	0.0350	0.035	0.035
0.20	0.0225	0.022	0.022
0.30	0.0176	-	0.018
0.40	0.0153	-	0.015
0.50	0.0143	-	0.014
0.60	0.0140	-	0.014
0.70	0.0142	-	0.014
0.80	0.0149	-	0.015
0.90	0.0159	-	0.016
1.00	0.0175	-	0.018

\*Assumed to be the same as  $\gamma_{\pm}$  for  $Al_2(SO_4)_3$  and  $In_2(SO_4)_3$

SOURCES: Hodgman 1956, p. 2380.

Robinson and Stokes 1955, p. 488.

Conway 1952, p. 64.

TABLE A-3  
 $A_2$  VALUES FOR EQ. 36

Ion	15°C	25°C	35°C	42.5°C
$\text{Fe}^{+2}$	0.4372	0.4160	0.3955	0.3950
$\text{La}^{+3}$	-	0.588	-	-
$\text{Ce}^{+3}$	0.5841	0.5765	0.5573	0.5427
$\text{Cl}^{-1}$	-0.0200	-0.0070	+0.0049	+0.0121
$\text{SO}_4^{-2}$	0.1889	0.2085	0.2277	0.2399

Example Calculation of  $A_2$  for a Compound:

$\text{La}_2(\text{SO}_4)_3$  at 25°C

$$A_2 = (2) (0.588) + (3) (0.2085) = 1.802$$

SOURCE: Robinson and Stokes 1955, p. 517

APPENDIX B

MEASURED DATA FOR THE RATE ( $r_A$ /S) DEPENDENCY  
ON FERRIC SULFATE CONCENTRATION,  $C_A$

TABLE B-1

MEASURED RATE DATA FOR CHALCOHITE WITH THE  
FERRIC SULFATE CONCENTRATION VARIED

TEST NUMBER	SPECIMEN	CHALCOHITE AREA, Cm. <sup>2</sup>	FERRIC SULFATE CONCENTRATION Moles Per Liter	RATE (r <sub>A</sub> /S)×10 <sup>6</sup>
29	B10	5.3	0.0071	0.550
5	B1	4.8	0.0224	1.37
3	A2	6.5	0.0449	3.74
8	C3	5.1	0.0744	5.72
4	A5	5.4	0.0957	6.68
1	A1	4.4	0.153	19.6
14	C2	5.2	0.155	14.3
13	C1	3.2	0.156	17.3
9	C4	6.1	0.159	12.8
6	B3	4.5	0.208	17.7
2	A4	6.3	0.299	21.7

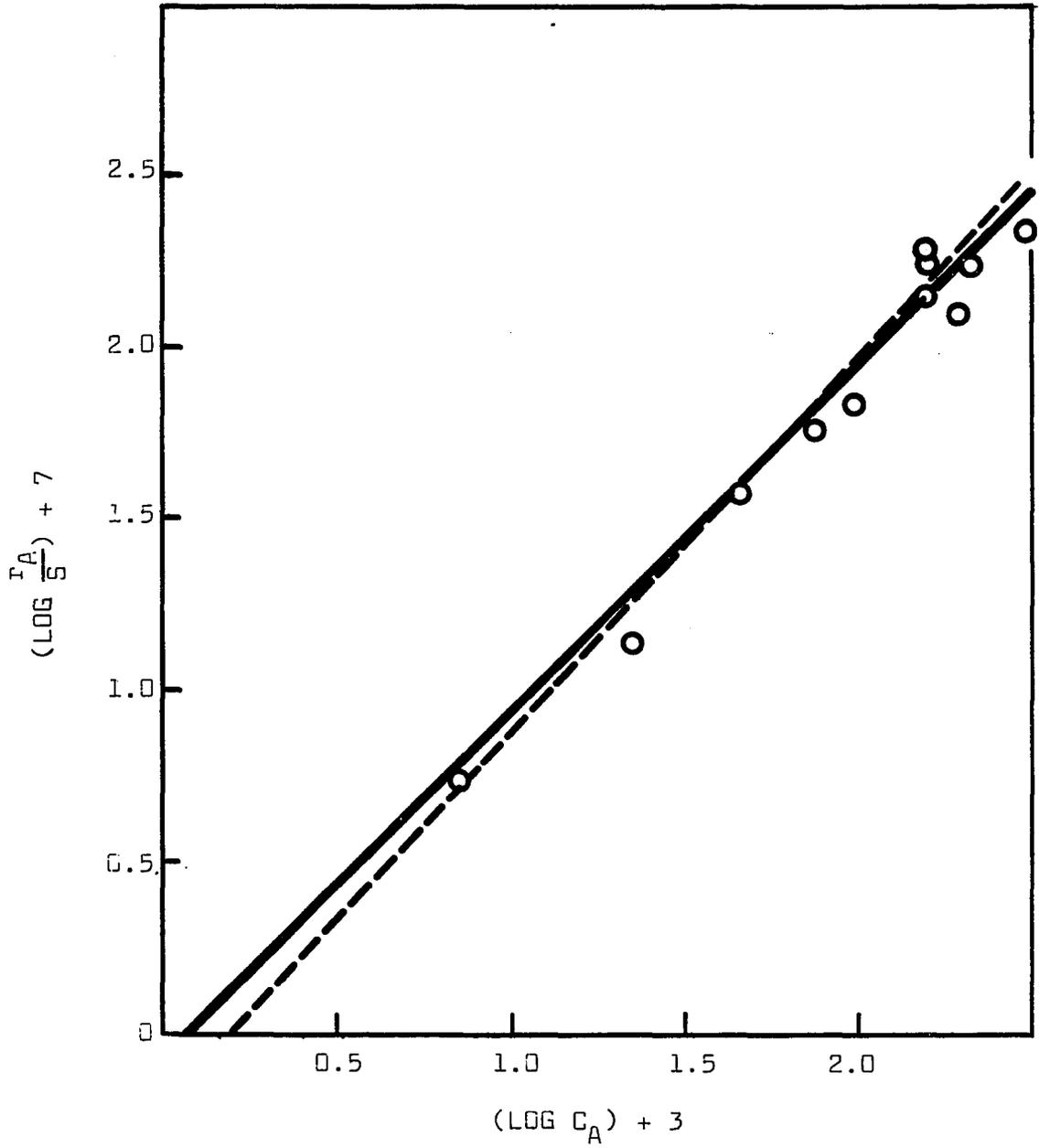


Fig. B-1.  $\text{LOG } (r_A/S)$  versus  $\text{LOG } C_A$  for  $\text{Cu}_2\text{S}$ .

TABLE B-2

MEASURED RATE DATA FOR COVELLITE WITH THE  
FERRIC SULFATE CONCENTRATION VARIED

TEST NUMBER	COVELLITE AREA, Cm. <sup>2</sup>	FERRIC SULFATE CONCENTRATION Moles Per Liter	RATE ( $r_A/S$ ) $\times 10^6$
24	17.0	0.0064	0.086
14	19.0	0.0216	0.080
6	11.0	0.0214	0.094
11	20.0	0.107	0.111
7	10.0	0.106	0.111
8	9.7	0.157	0.171
12	13.0	0.212	0.160

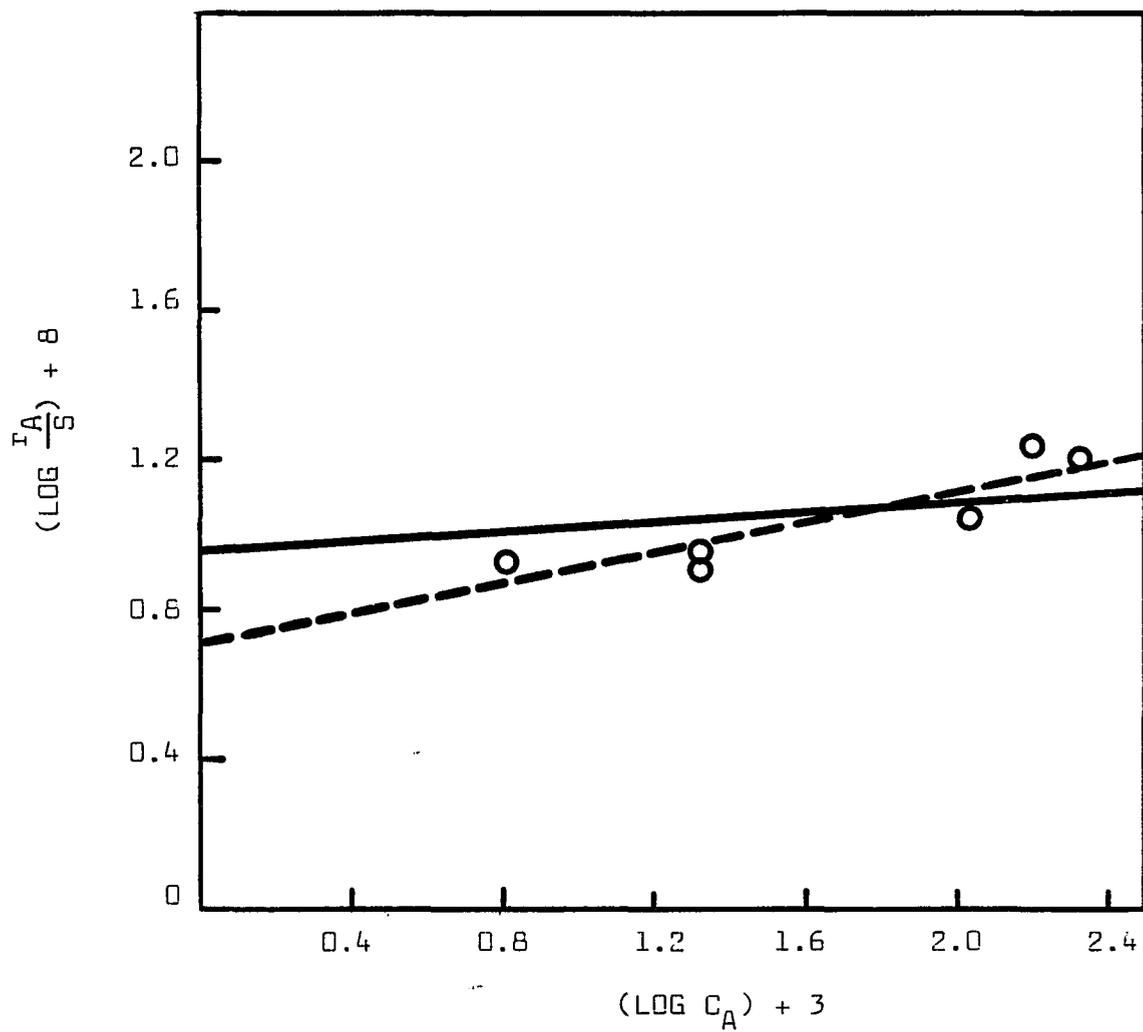


Fig. B-2.  $\text{LOG } (r_A/S)$  versus  $\text{LOG } C_A$  for  $\text{CuS}$ .

TABLE B-3

MEASURED RATE DATA FOR BORNITE DETERMINED  
AT  $d = 0.0038$  CM. WITH THE  
FERRIC SULFATE CONCENTRATION VARIED

TEST NUMBER	BORNITE AREA, Cm. <sup>2</sup>	FERRIC SULFATE CONCENTRATION Moles Per Liter	RATE ( $r_A/S$ ) $\times 10^6$
37	5.7	0.0087	2.4
29	5.3	0.0102	2.3
20	5.2	0.0570	8.5
22	7.0	0.0980	7.0
26	8.0	0.105	12.4
19	4.7	0.105	14.9
15	10.2	0.139	10.6
12	8.5	0.141	11.1
25	5.3	0.212	15.9
21	4.9	0.209	14.1
14	7.6	0.231	16.1
18	9.7	0.238	13.1
13	9.4	0.280	14.9

TABLE B-4  
MEASURED RATE DATA FOR BORNITE DETERMINED  
AT  $d = 0.0076$  CM. WITH THE  
FERRIC SULFATE CONCENTRATION VARIED

TEST NUMBER	FERRIC SULFATE CONCENTRATION Moles Per Liter	RATE $(r_A/S) \times 10^6$
37	0.0067	1.23
29	0.0093	1.52
20	0.0560	5.05
22	0.096	5.9
26	0.103	5.4
19	0.104	6.0
15	0.137	5.5
12	0.140	6.4
25	0.210	5.2
21	0.207	4.9
14	0.229	5.0
18	0.237	5.1
13	0.279	4.9

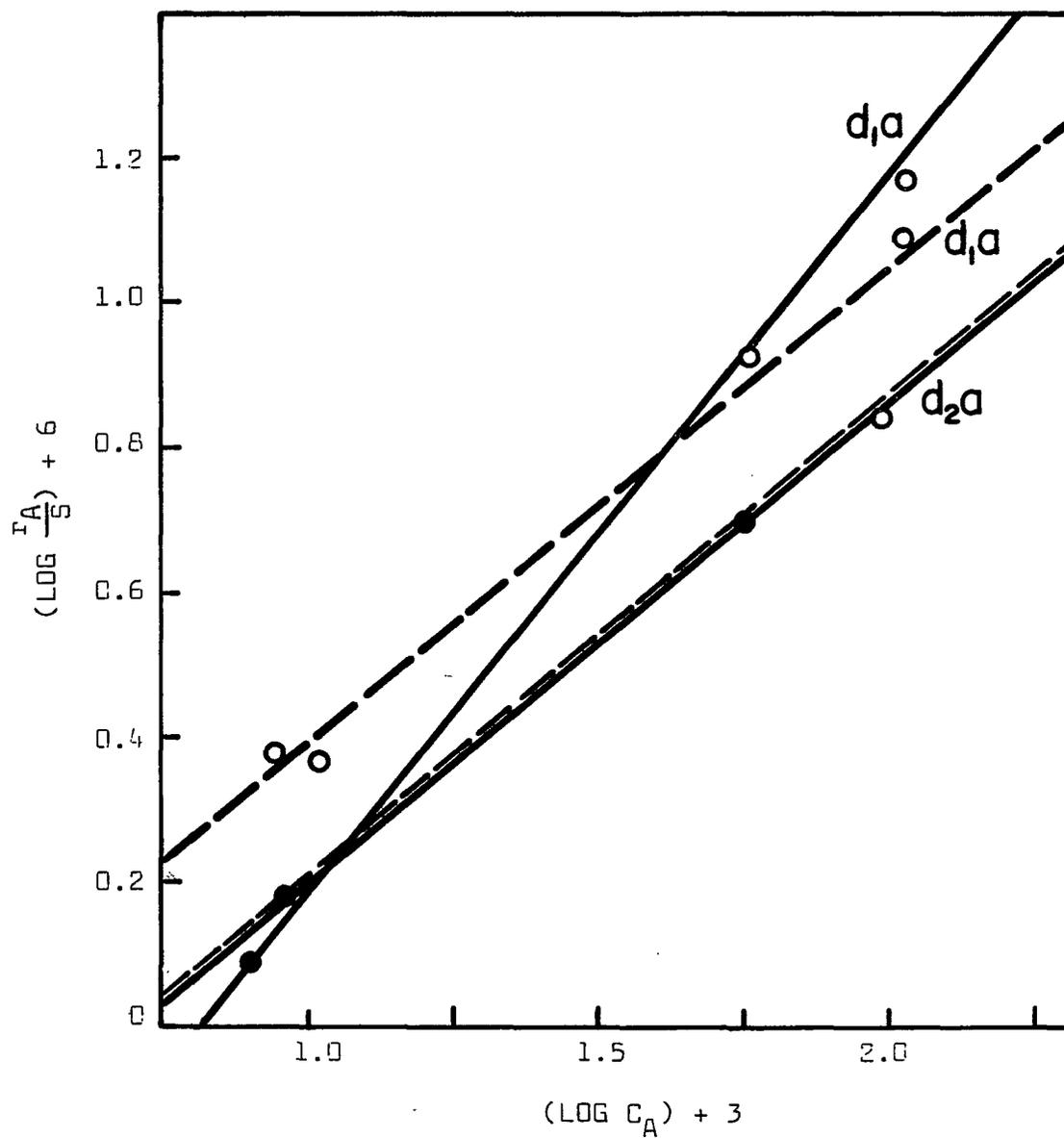


Fig. B-3.  $\text{LOG } (r_A/S)$  versus  $\text{LOG } C_A$  for  $\text{Cu}_5\text{FeS}_4$ .

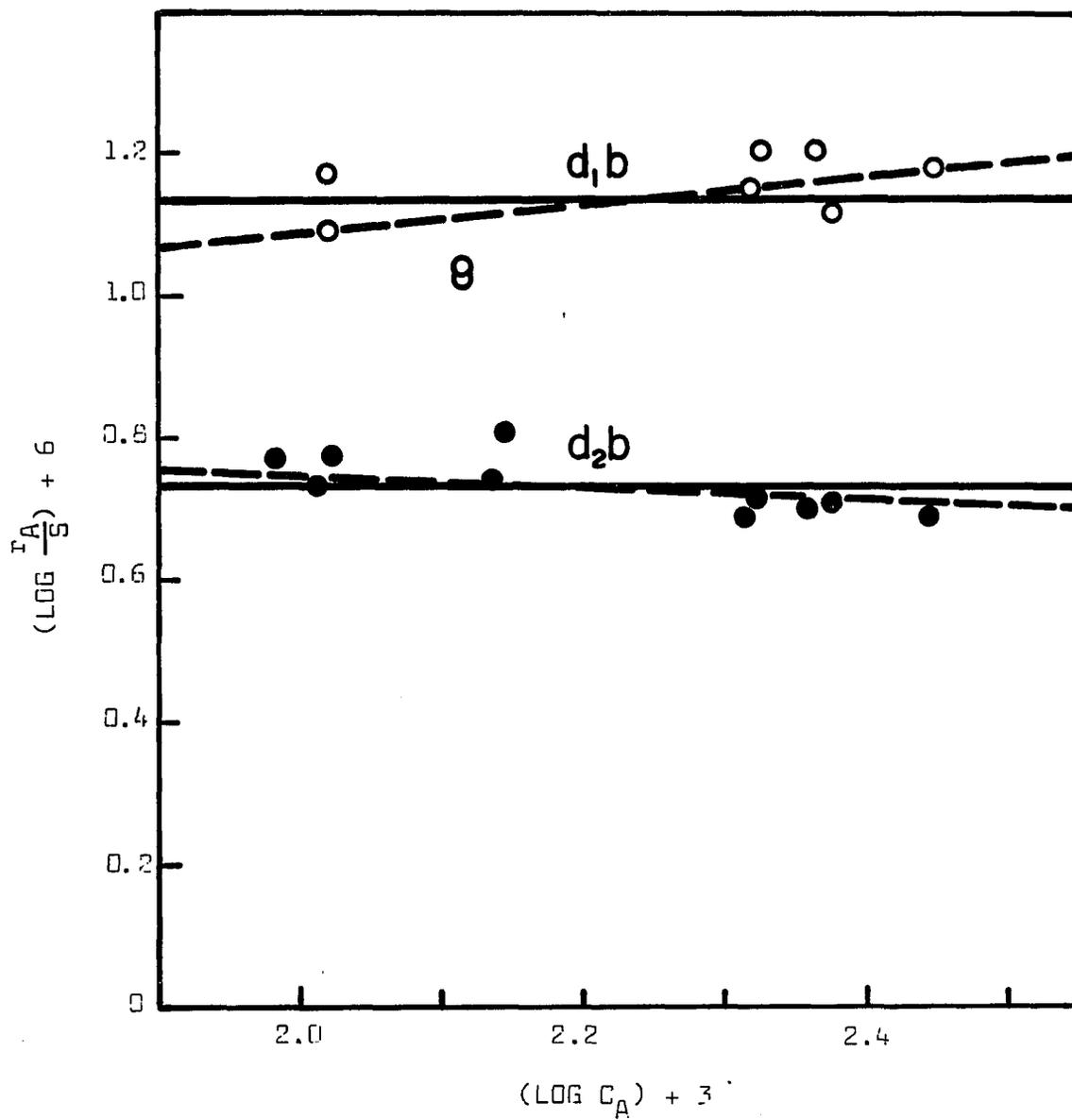


Fig. B-4.  $\text{LOG } (r_A/S)$  versus  $\text{LOG } C_A$  for  $\text{Cu}_5\text{FeS}_4$ .

TABLE B-5  
MEASURED RATE DATA FOR BORNITE DETERMINED  
AT  $d = 0.042$  CM. WITH THE  
FERRIC SULFATE CONCENTRATION VARIED

TEST NUMBER	FERRIC SULFATE CONCENTRATION Moles Per Liter	RATE $(r_A/S) \times 10^6$
26	0.091	1.97
19	0.097	1.75
15	0.121	1.44
12	0.126	2.02
25	0.202	2.57
14	0.217	1.76
18	0.221	2.51
13	0.264	2.40

TABLE B-6

MEASURED RATE DATA FOR BORNITE DETERMINED  
AT  $d = 0.050$  CM. WITH THE  
FERRIC SULFATE CONCENTRATION VARIED

TEST NUMBER	FERRIC SULFATE CONCENTRATION Moles Per Liter	RATE $(r_A/S) \times 10^6$
19	0.095	1.75
15	0.117	1.44
14	0.214	1.76

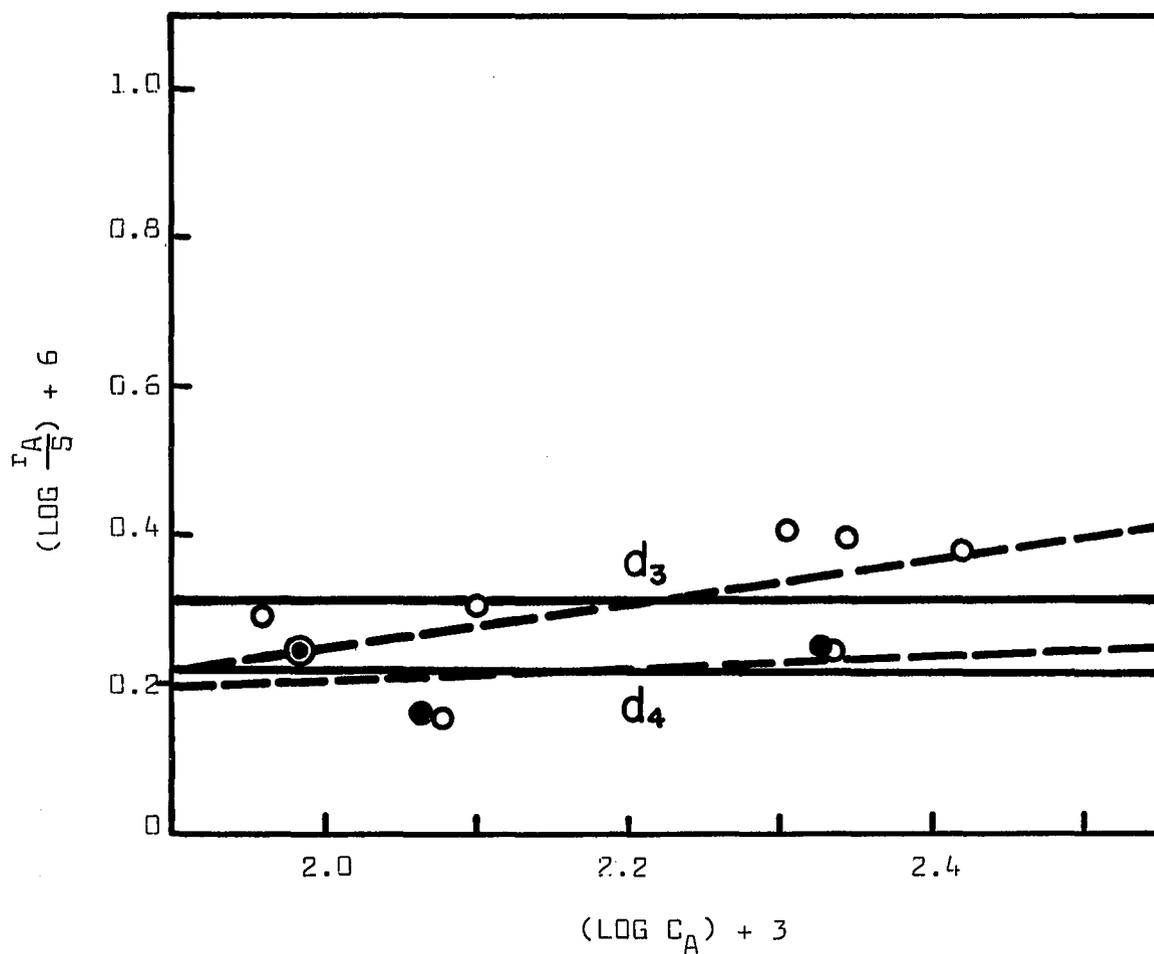


Fig. B-5.  $\text{LOG } (r_A/S)$  versus  $\text{LOG } C_A$  for  $\text{Cu}_5\text{FeS}_4$ .

TABLE B-7

MEASURED RATE DATA FOR CHALCOPYRITE WITH THE  
FERRIC SULFATE CONCENTRATION VARIED

TEST NUMBER	WEIGHT SAMPLE gms.	TOTAL AREA Cm. <sup>2</sup>	CuFeS <sub>2</sub> AREA Cm. <sup>2</sup>	FERRIC SULFATE CONCENTRATION Moles Per Liter	RATE (r <sub>A</sub> /S)×10 <sup>6</sup>
14	23.5	160	115	0.020	0.123
7	33.0	231	166	0.025	0.123
6	25.2	171	123	0.049	0.149
13	23.6	161	116	0.097	0.162
5	25.3	172	124	0.095	0.132
8	12.4	84	60	0.198	0.114

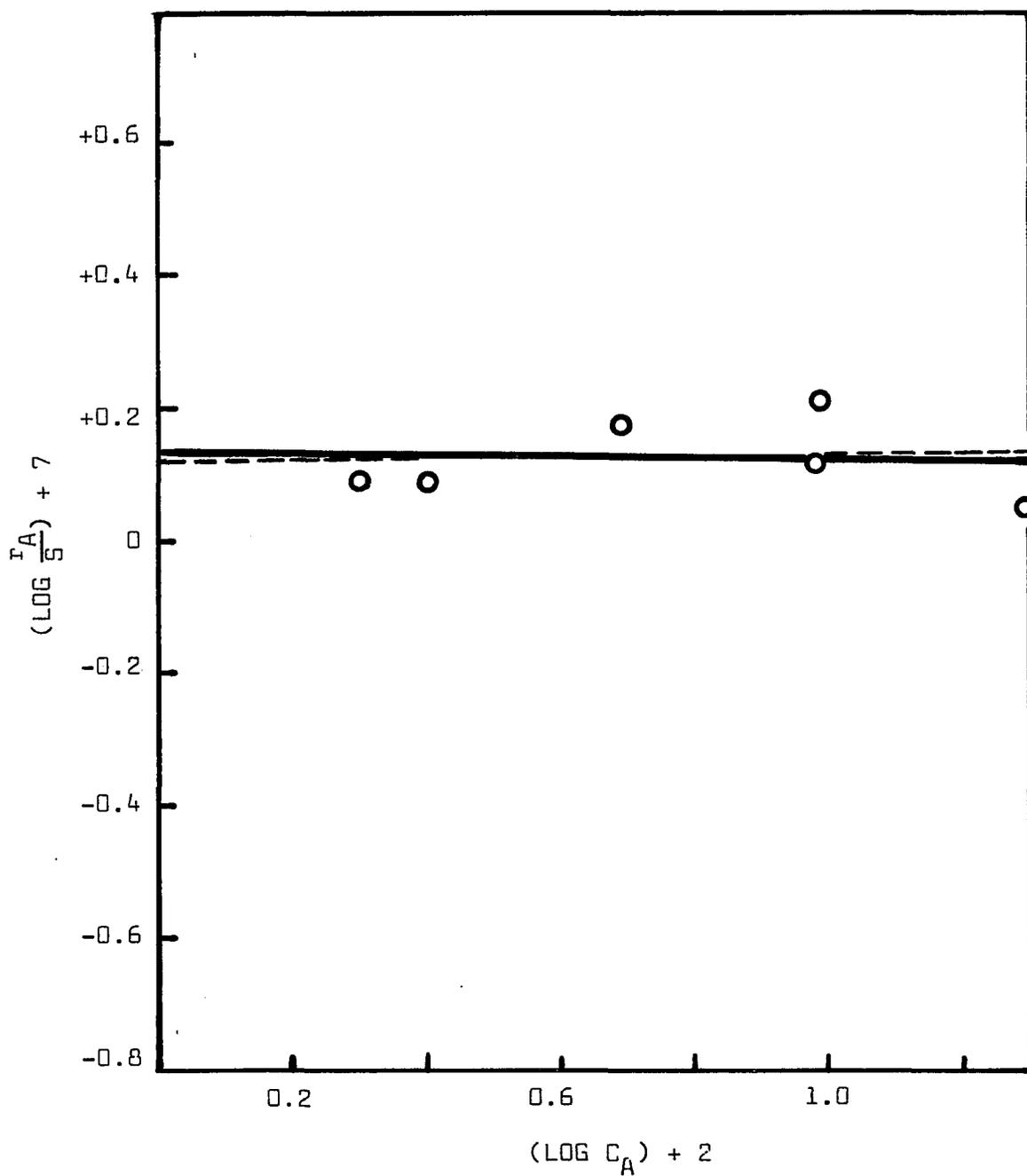


Fig. B-6.  $\text{LOG } (r_A/S)$  versus  $\text{LOG } C_A$  for  $\text{CuFeS}_2$ .

TABLE B-8

MEASURED RATE DATA FOR PYRRHOTITE WITH THE  
FERRIC SULFATE CONCENTRATION VARIED

TEST NUMBER	PYRRHOTITE AREA Cm. <sup>2</sup>	FERRIC SULFATE CONCENTRATION Moles Per Liter	RATE (r <sub>A</sub> /S)×10 <sup>6</sup>
3	9.7	0.025	0.60
4	9.7	0.052	0.70
2	12.1	0.102	0.69
11	9.5	0.105	0.70
17	16.2	0.096	0.81
1	8.0	0.206	0.79
14	8.7	0.208	0.70

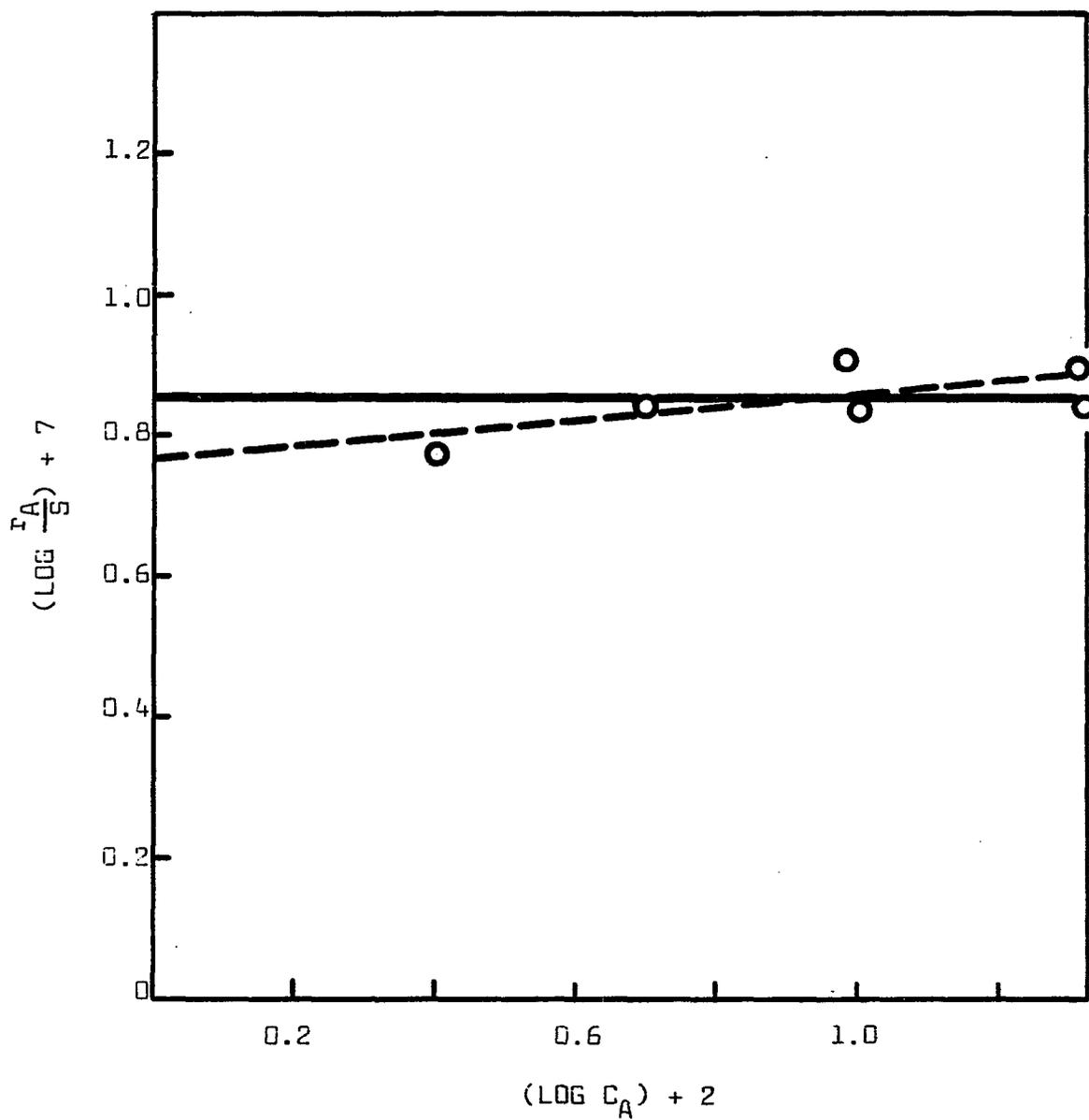


Fig. B-7.  $\text{LOG } (r_A/S)$  versus  $\text{LOG } C_A$  for FeS.

APPENDIX C

THE MEASURED RATE CONSTANT,  $k_2$ , WITH THE  
REACTION TEMPERATURE VARIED

TABLE C-1  
THE EFFECT ON  $k_2$  OF VARYING THE REACTION  
TEMPERATURE FOR CHALCOHITE MINERAL

TEST NUMBER	RATE ( $r_A/S$ ) $\times 10^6$	REACTION TEMPERATURE $^{\circ}C$	RATE CONSTANT $k_2 \times 10^{+5}$
31	12.2	28.0	6.01
6	18.0	38.0	8.80
7	20.4	38.1	9.95
25	22.8	50.9	11.1
19	61.2	70.0	29.9

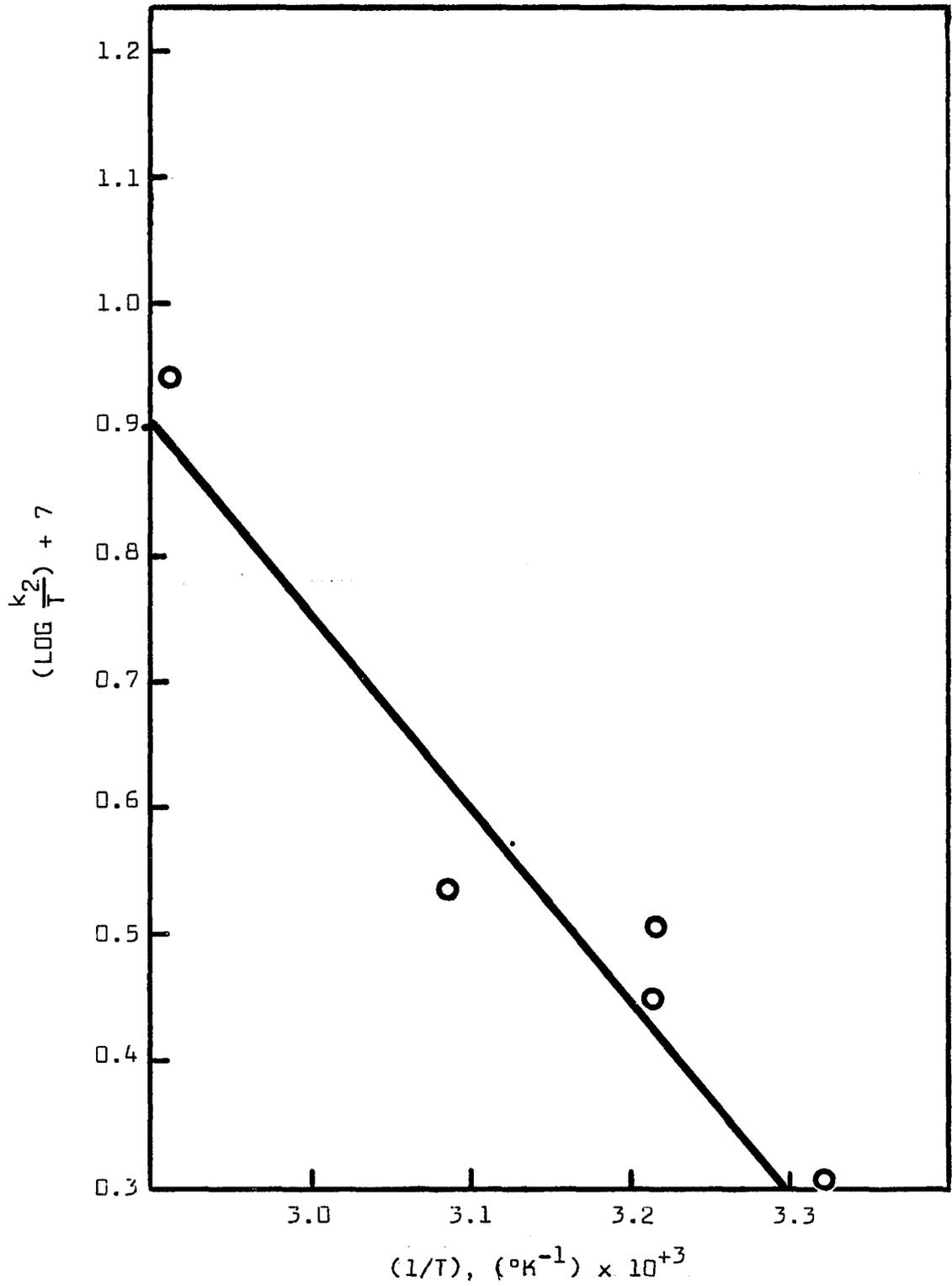


Fig. C-1.  $\text{LOG } (k_2/T) - (1/T)$  plot for  $\text{Cu}_2\text{S}$ .

TABLE C-2  
THE EFFECT ON  $k_2$  OF VARYING THE REACTION  
TEMPERATURE FOR COVELLITE MINERAL

TEST NUMBER	RATE ( $r_A/s$ ) $\times 10^6$	REACTION TEMPERATURE $^{\circ}\text{C}$	RATE CONSTANT $k_2 \times 10^5$
15	0.0147	39.2	0.0169
10	0.0387	52.6	0.0443
11	0.113	68.0	0.130
7	0.111	68.5	0.127

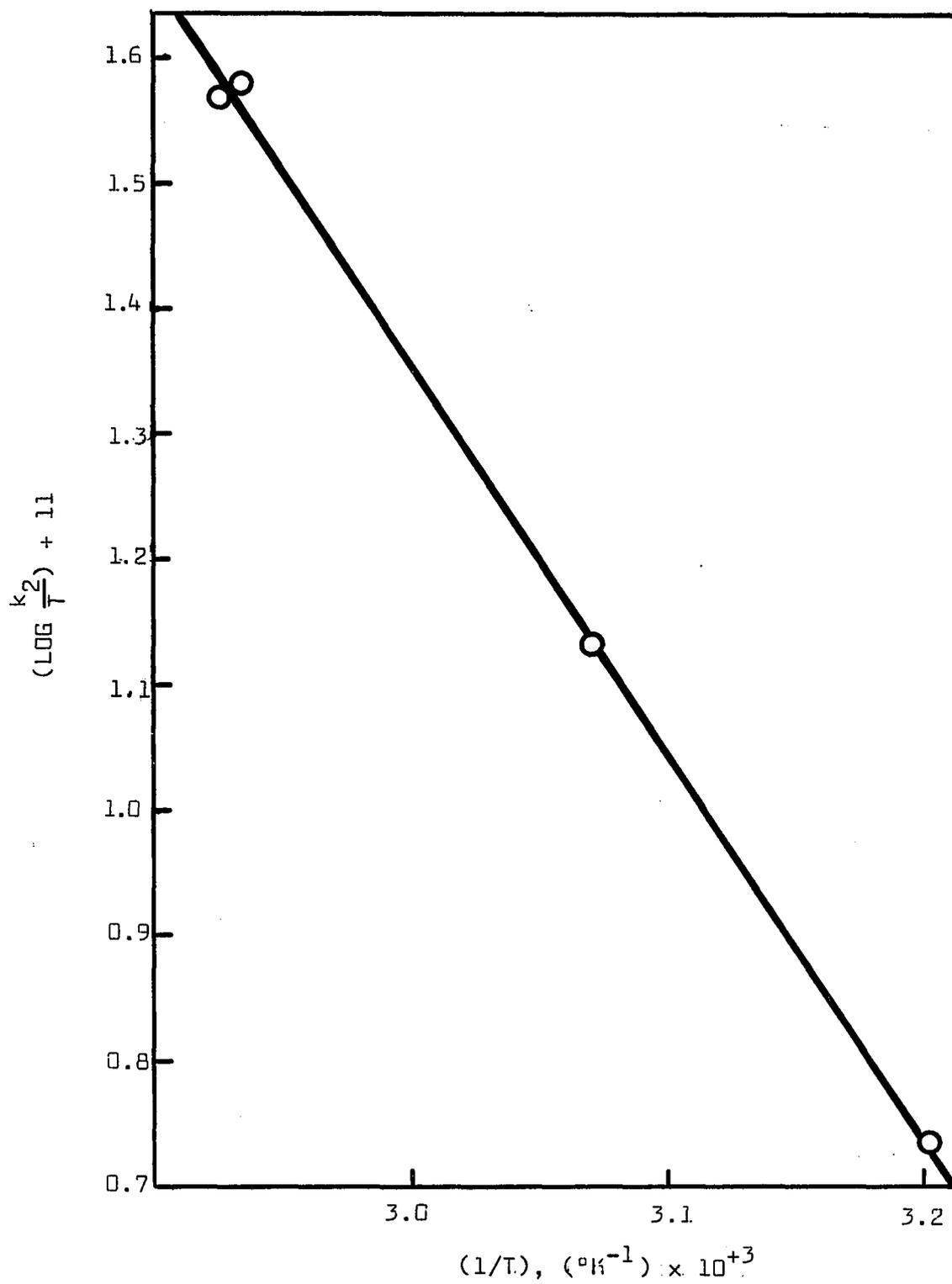


Fig. C-2.  $\text{LOG } (k_2/T) - (1/T)$  plot for CuS.

TABLE C-3

THE EFFECT ON  $k_2$  OF VARYING THE REACTION TEMPERATURE FOR  
BORNITE MINERAL DETERMINED AT VARIOUS RESIDUE DEPTHS

TEST NUMBER	RESIDUE DEPTH, Cm.	RATE (r /S) $\times 10^6$	TEMPERATURE $^{\circ}$ C	RATE CONSTANT $k_2 \times 10^6$
38	0.0038	9.3	28.0	95.8
22		7.0	38.0	72.1
35		14.7	50.0	150.0
29		58.0	70.0	344.0
38	0.0076	3.7	28.0	3.7
22		5.9	38.0	5.9
35		7.5	50.0	7.5
29		31.8	70.0	31.8
38	0.0420	1.15	28.0	1.15
22		2.18	38.0	2.18
35		4.73	50.0	4.73
29		15.90	70.0	15.9

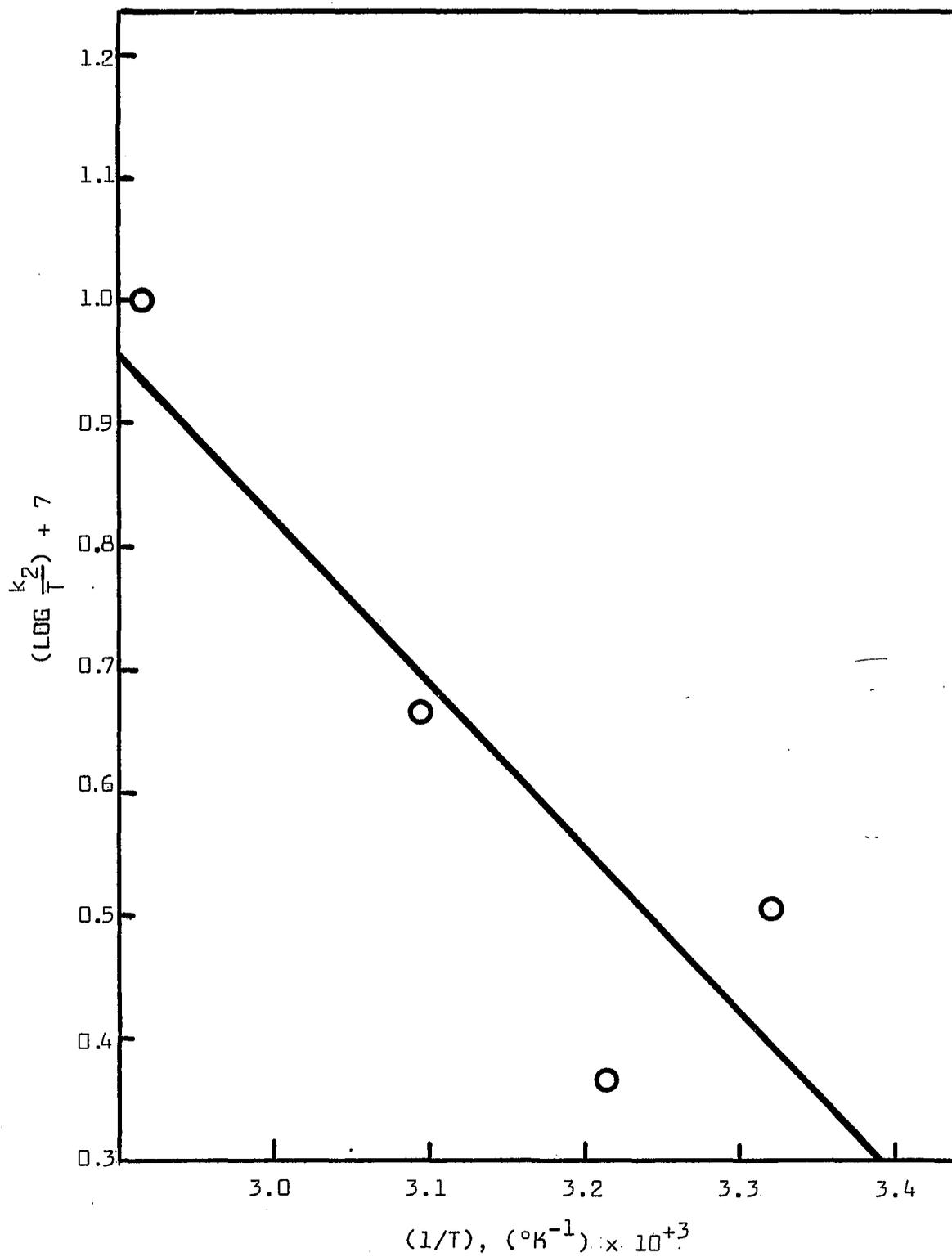


Fig. C-3.  $\text{LOG } (k_2/T) - (1/T)$  plot for  $\text{Cu}_5\text{FeS}_4$ .

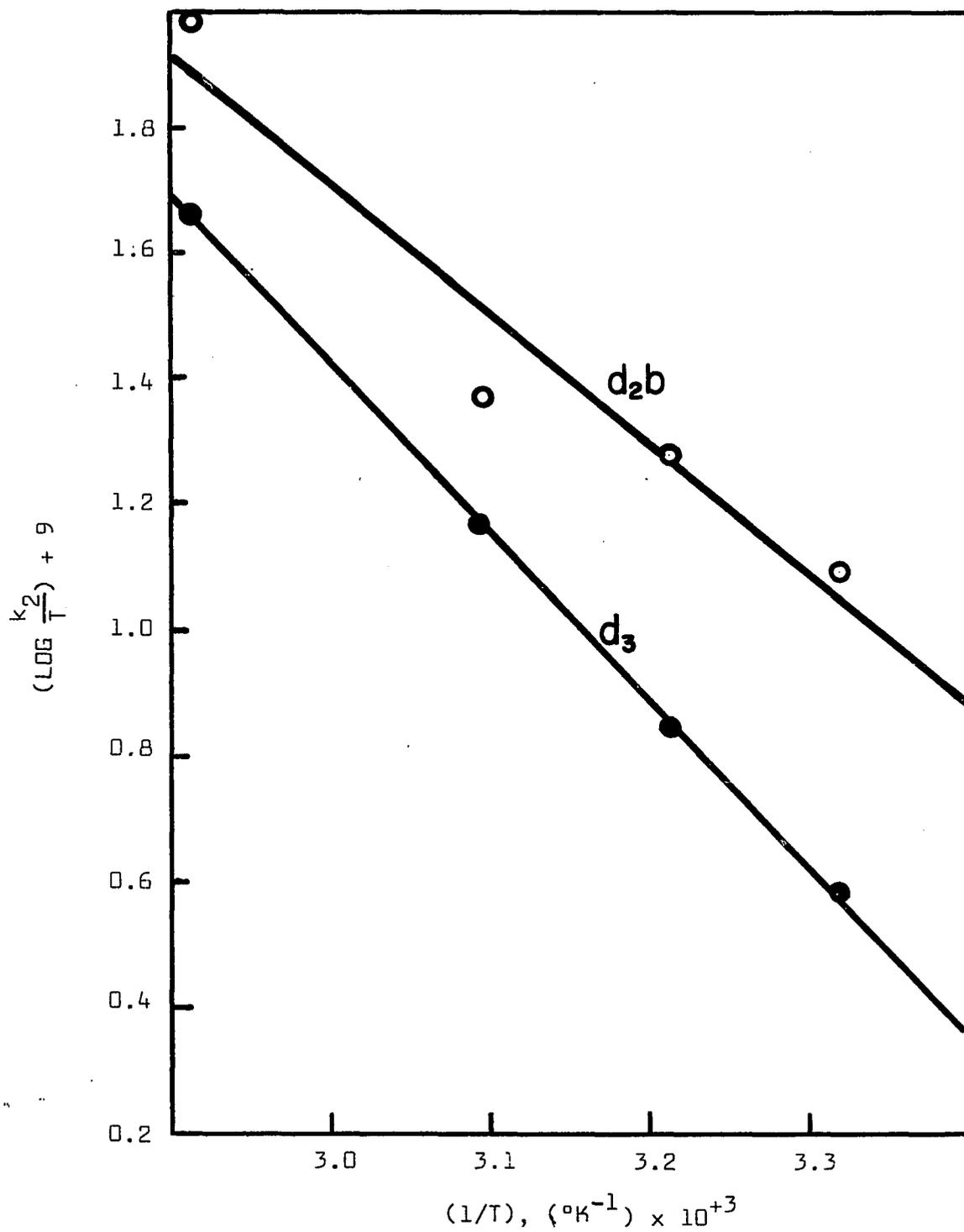


Fig. C-4.  $\text{LOG } (k_2/T) - (1/T)$  plot for  $\text{Cu}_5\text{FeS}_4$ .

TABLE C-4  
THE EFFECT ON  $k_2$  OF VARYING THE REACTION  
TEMPERATURE FOR CHALCOPYRITE MINERAL

NUMBER	RATE ( $r_A/s$ ) $\times 10^6$	TEMPERATURE $^{\circ}C$	RATE CONSTANT $k_2 \times 10^6$
16	0.0290	32.4	0.0290
4	0.0543	38.8	0.0543
13	0.162	50.0	0.162
5	0.132	49.6	0.132

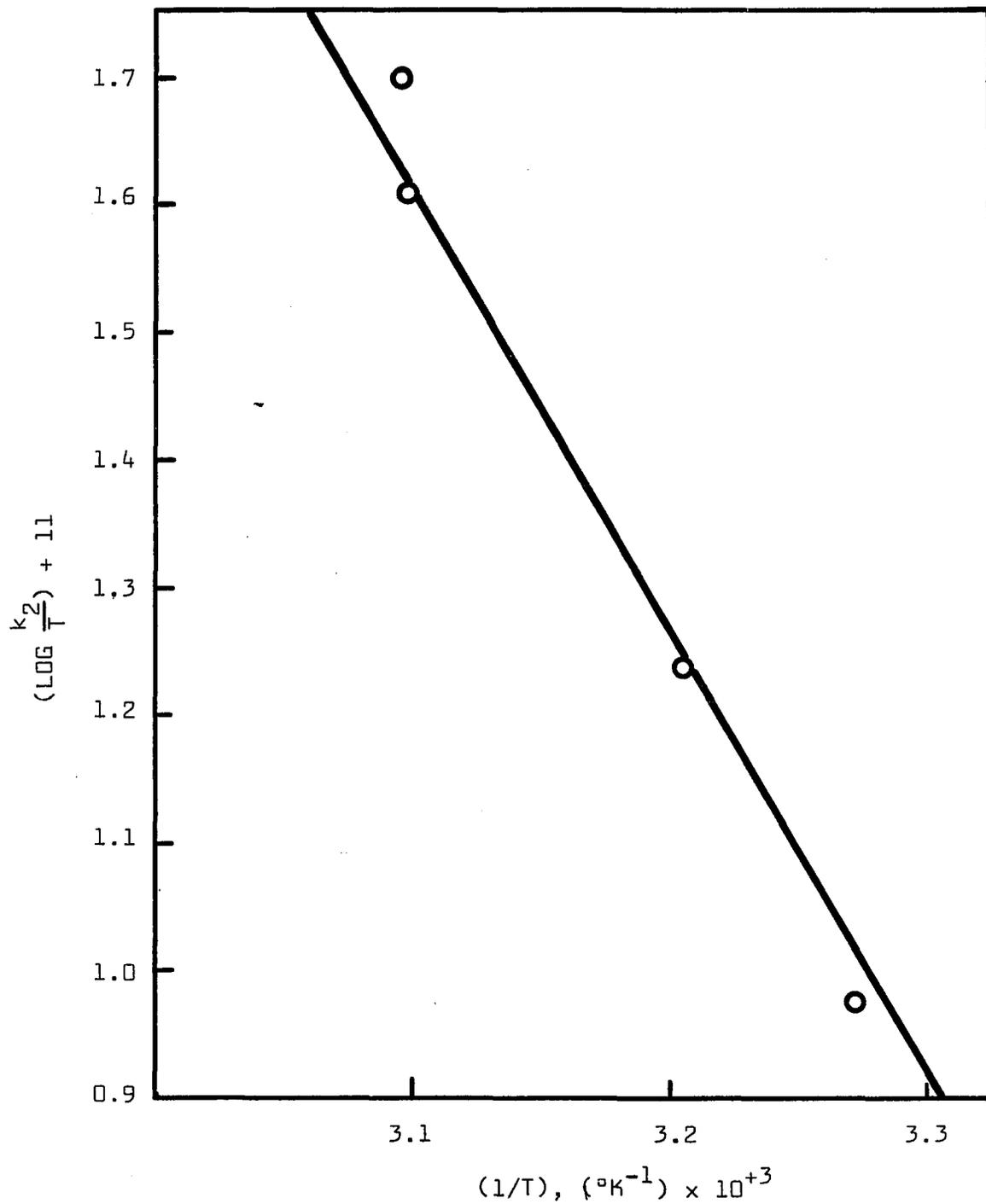


Fig. C-5.  $\text{LOG } (k_2/T) - (1/T)$  plot for  $\text{CuFeS}_2$ .

TABLE C-5  
THE EFFECT ON  $k_2$  OF VARYING THE REACTION  
TEMPERATURE FOR PYRRHOTITE MINERAL

TEST NUMBER	RATE ( $r_A/s$ ) $\times 10^{+6}$	TEMPERATURE $^{\circ}C$	RATE CONSTANT $k_2 \times 10^{+6}$
2	0.69	37.8	0.69
11	0.70	37.5	0.70
16	1.34	52.7	1.34
20	0.27	67.5	0.27

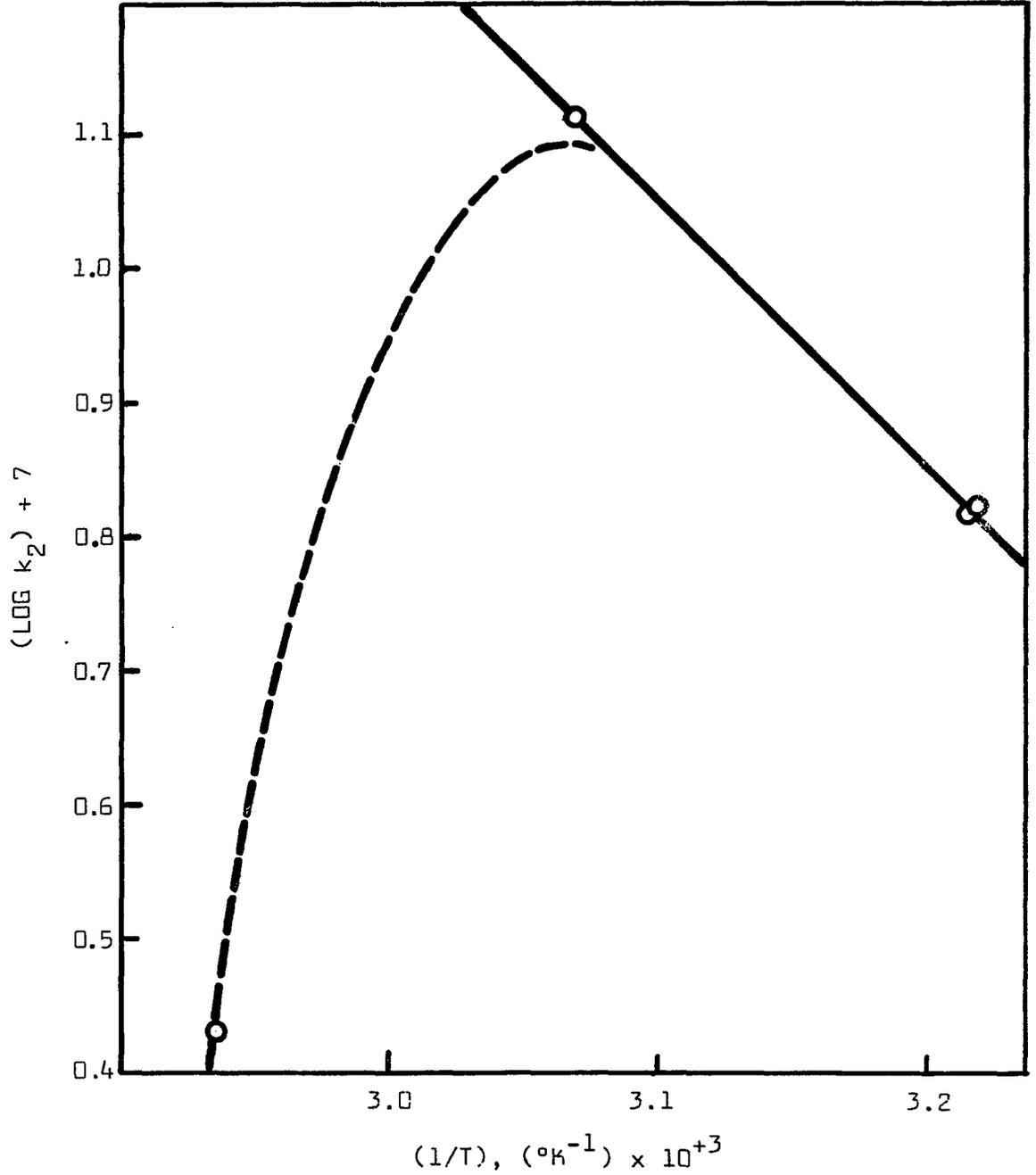


Fig. C-6.  $\text{LOG } (k_2) - (1/T)$  plot for FeS.

APPENDIX D

THE RATE OF REACTION ( $r_A/S$ ) VARIATION  
WITH SULFURIC ACID CONCENTRATION,  $C_B$

TABLE D-1  
 THE DEPENDENCE OF  $(r_A/S)$  ON THE VARIATION OF ADDED  
 SULFURIC ACID FOR CHALCOCITE MINERAL LEACHING

TEST NUMBER	AREA, Cm. <sup>2</sup>	H <sub>2</sub> SO <sub>4</sub> Molar	Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> Molar	RATE ( $r_A/S$ ) × 10 <sup>+6</sup>
4	5.4	0.020	0.10	6.66
11	4.3	0.100	0.10	9.15
18	6.2	0.160	0.10	13.4
12	5.4	0.240	0.10	13.1
10	6.8	0.500	0.10	14.1
17	5.8	0.525	0.10	15.3
15	7.9	0.50	0.022	3.91
10	6.8	0.50	0.093	14.1
16	6.6	0.50	0.152	14.7
7	4.6	0.50	0.205	20.5

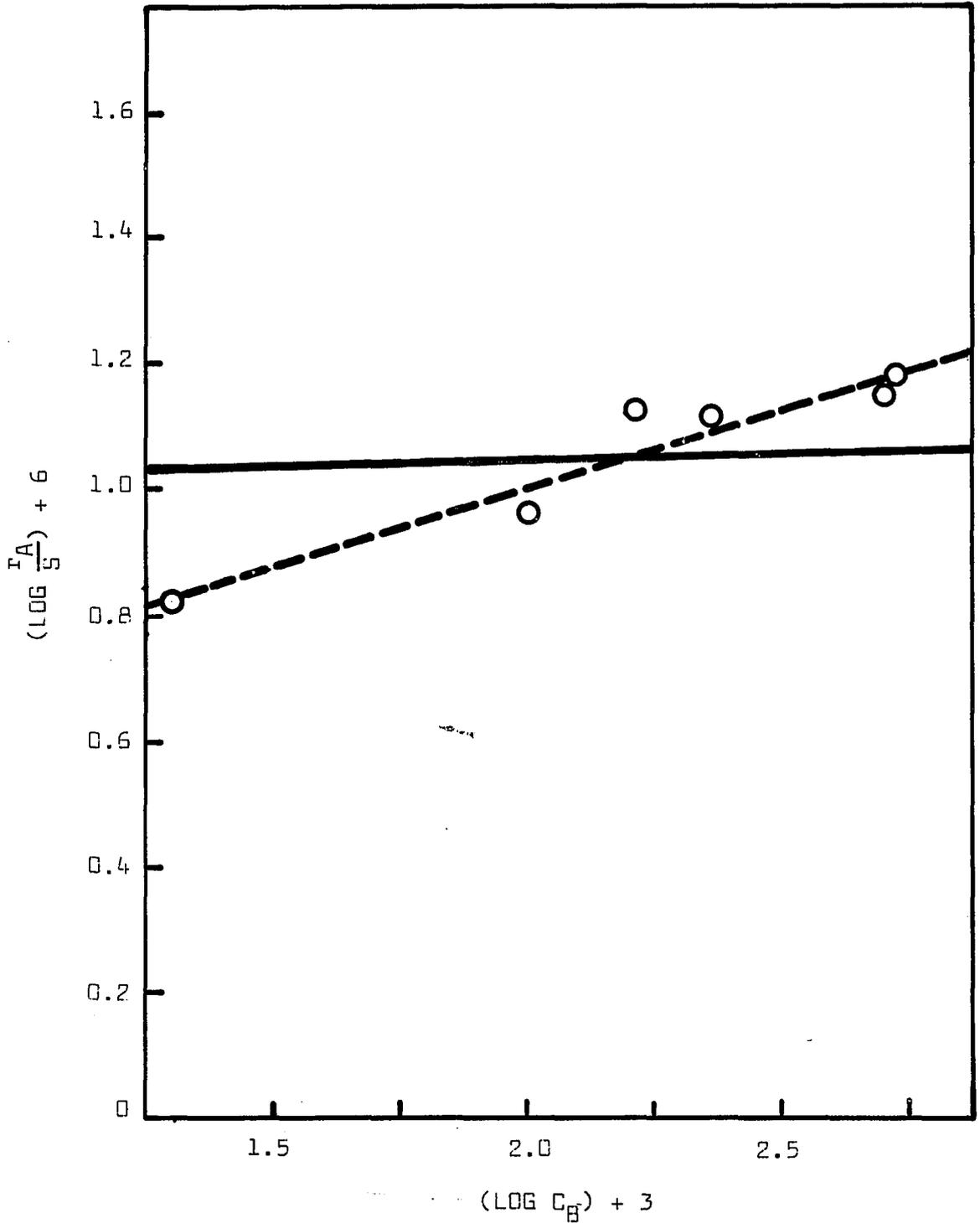


Fig. D-1.  $\text{LOG } (r_A/S)$  versus  $\text{LOG } C_B$  at 0.10M,  $\text{Fe}_2(\text{SO}_4)_3$  for chalcochite.

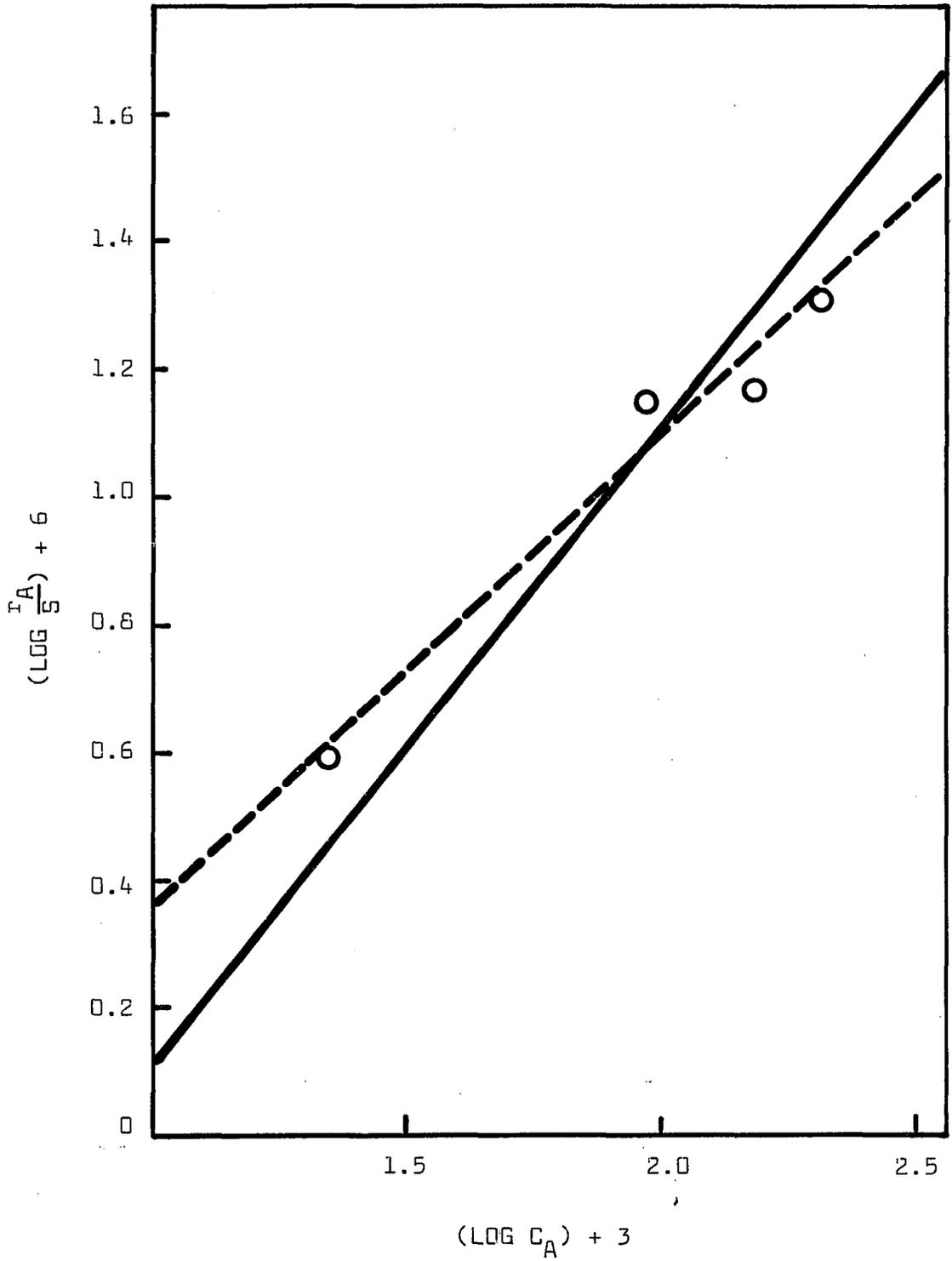


Fig. D-2.  $\text{LOG } (r_A/S)$  versus  $\text{LOG } C_A$  at 0.50 M,  $\text{H}_2\text{SO}_4$  for chalcocite.

TABLE D-2

THE DEPENDENCE OF ( $r_A/S$ ) ON THE VARIATION OF ADDED  
SULFURIC ACID FOR COVELLITE MINERAL LEACHING

TEST NUMBER	AREA, Cm. <sup>2</sup>	H <sub>2</sub> SO <sub>4</sub> Molar	RATE ( $r_A/S$ ) × 10 <sup>+6</sup>
9	14.0	0.086	0.195
21	11.0	0.20	0.182
22	11.0	0.25	0.160
13	13.0	0.39	0.148
23	6.7	0.50	0.170

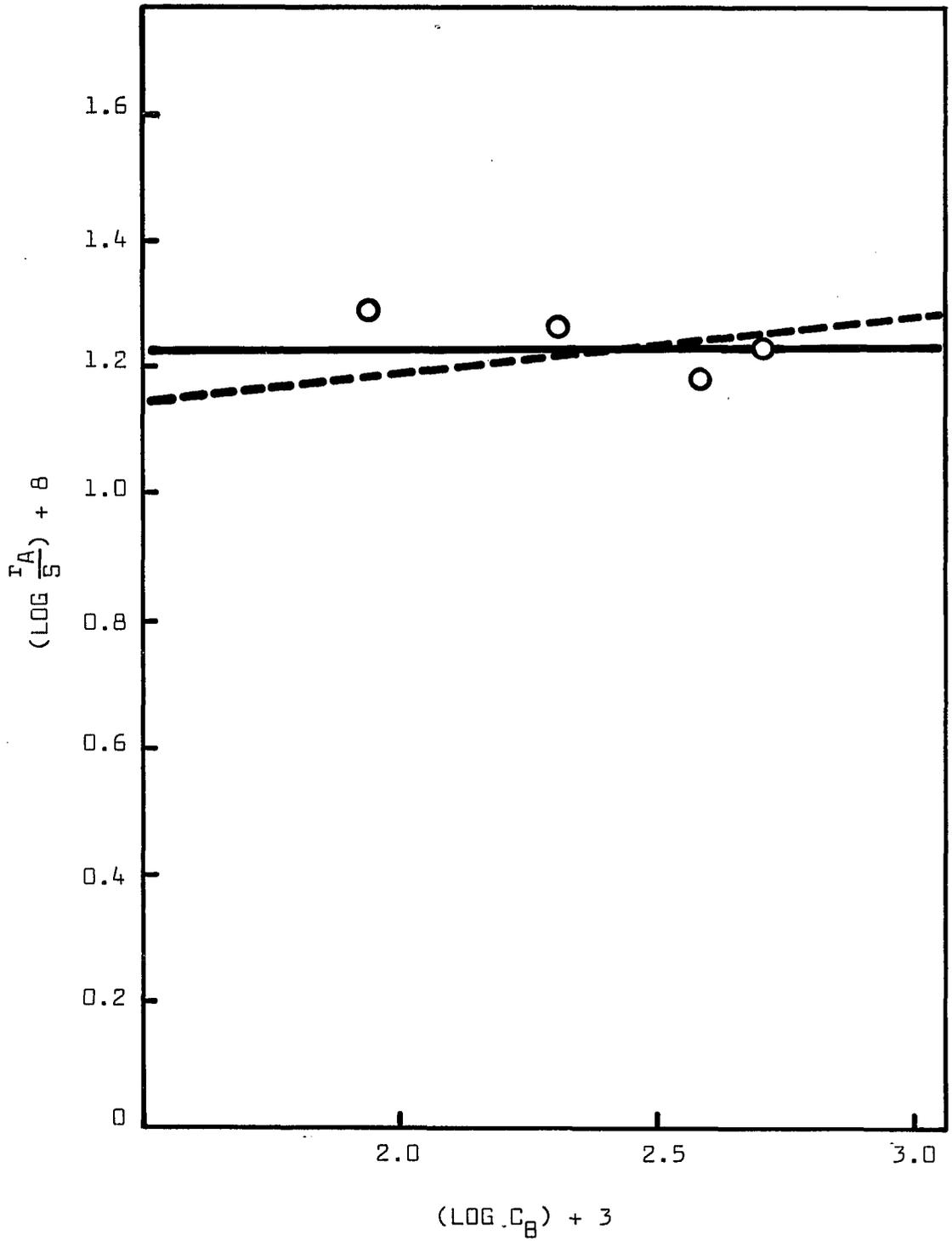


Fig. D-3.  $\text{LOG } (r_A/S)$  versus  $\text{LOG } C_B$  at 0.10M,  $\text{Fe}_2(\text{SO}_4)_3$  for covellite.

TABLE D-3  
THE DEPENDENCE OF ( $r_A/S$ ) ON THE VARIATION OF  
ADDED SULFURIC ACID CONCENTRATION  
FOR CHALCOPYRITE LEACHING

TEST NUMBER	AREA, Cm. <sup>2</sup>	H <sub>2</sub> SO <sub>4</sub> Molar	RATE ( $r_A/S$ ) × 10 <sup>+6</sup>
9	121	0.050	0.0983
11	228	0.100	0.0995
13	116	0.400	0.118
5	124	0.390	0.139
10	117	0.780	0.121
12	228	0.780	0.107

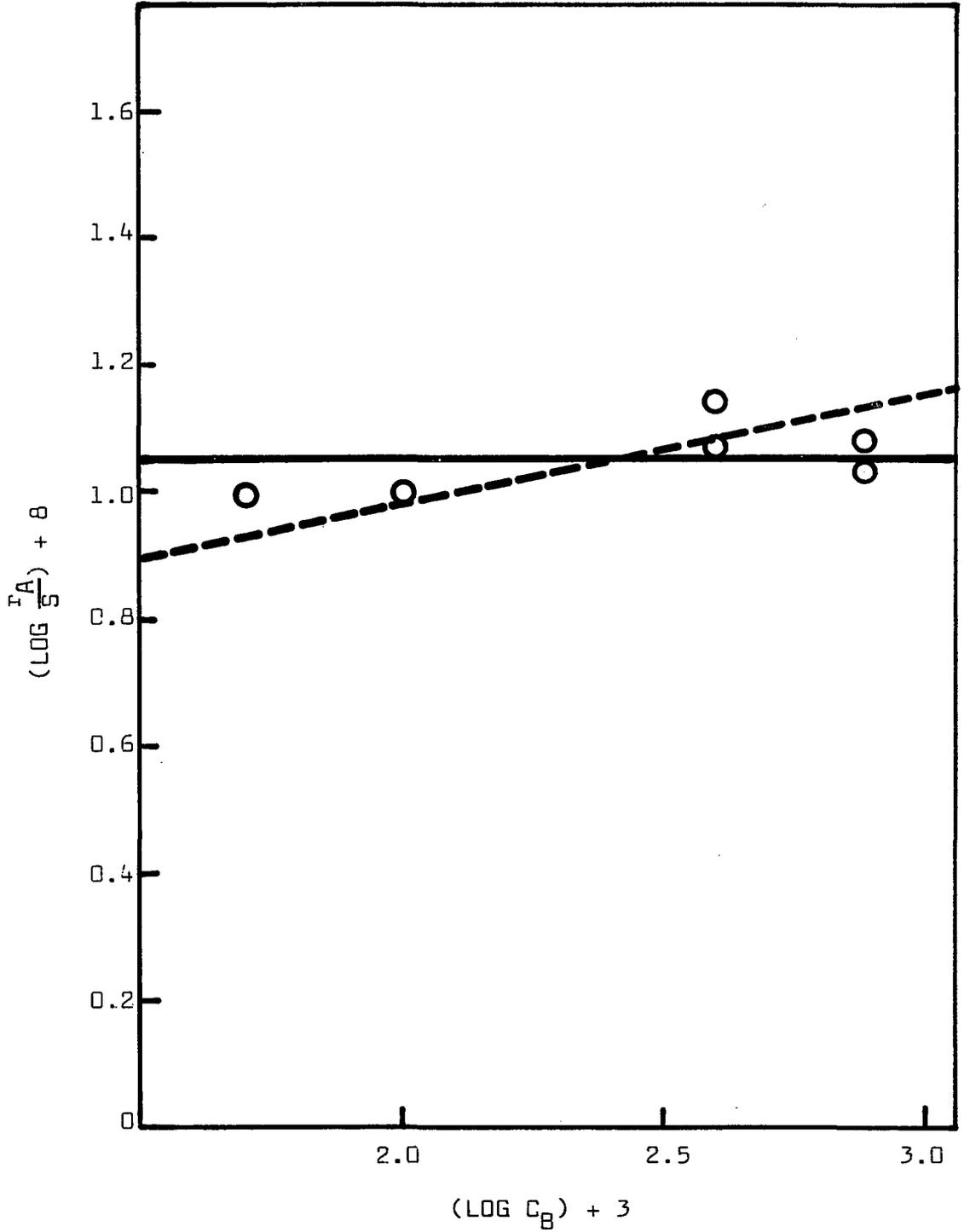


Fig. D-4.  $\text{LOG } (r_A/S)$  versus  $\text{LOG } C_B$  at 0.10M,  $\text{Fe}_2(\text{SO}_4)_3$  for chalcopyrite.

TABLE D-4

THE DEPENDENCE OF  $(r_A/s)$  ON THE VARIATION OF  
ADDED SULFURIC ACID FOR PYRRHOTITE LEACHING

TEST NUMBER	AREA, Cm. <sup>2</sup>	H <sub>2</sub> SO <sub>4</sub> Molar	RATE ( $r_A/s$ ) × 10 <sup>+6</sup>
2	12.1	0.030	0.690
10	12.9	0.042	0.060
5	8.7	0.188	0.148
6	4.7	0.422	0.238

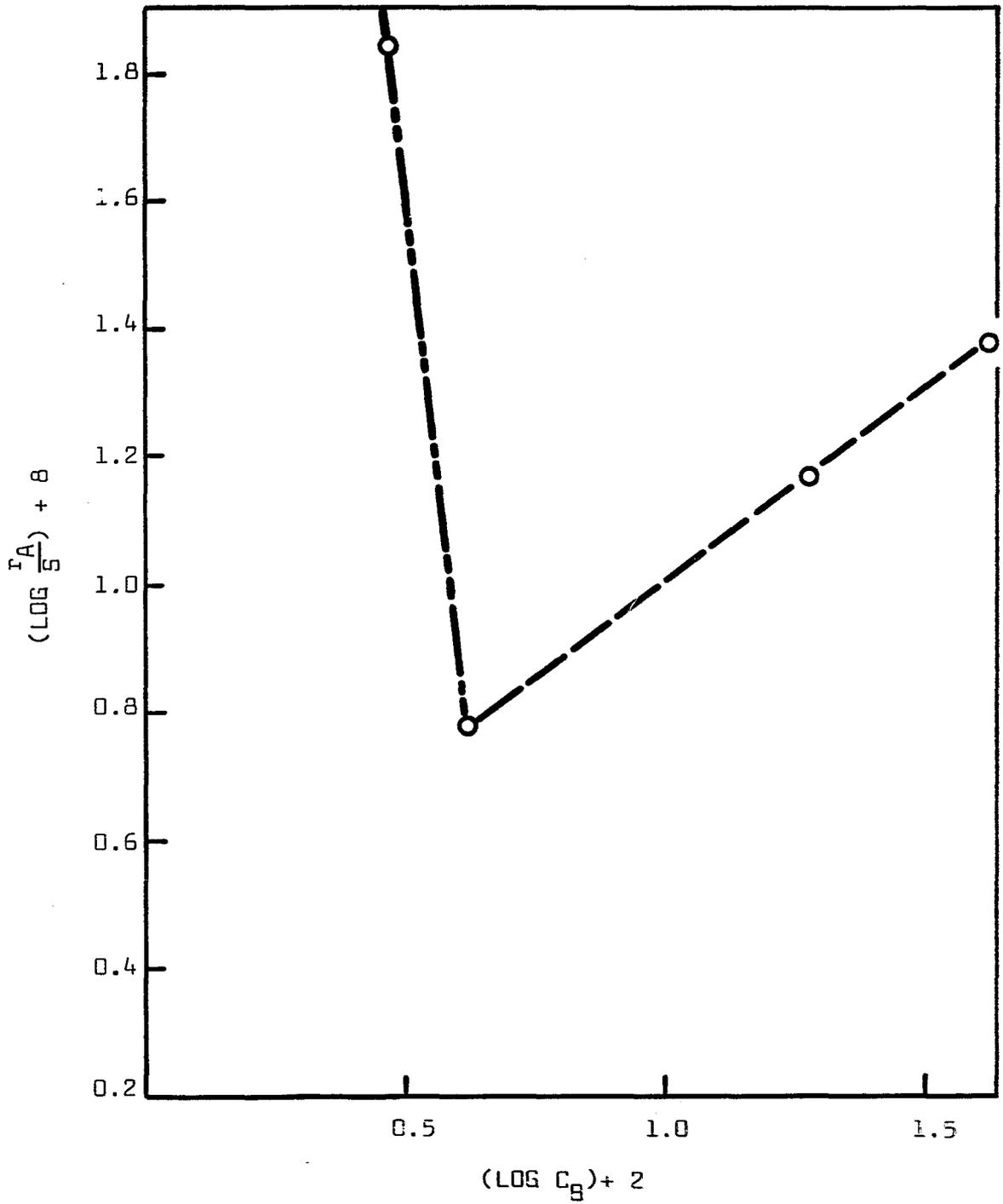


Fig. D-5.  $\text{LOG } (r_A/S)$  versus  $\text{LOG } C_B$  at 0.10M,  $\text{Fe}_2(\text{SO}_4)_3$  for pyrrhotite.

APPENDIX E  
LEAST-SQUARE STATISTIC

The least-square-line determinations were based on the method given by Walas (1958, pp. 224-295). The equation for the line was

$$\hat{y} = a + bx \quad (\text{E-1})$$

The " $\hat{y}$ " term was the estimated value of the observed value of  $y$  obtained for an observed value of  $x$ , the term " $a$ " was the intercept giving an estimated value of  $y$  at  $x$  equal zero, and the term " $b$ " the slope of the least-square line.

The results for the least-square lines obtained for the data given in the tables of Appendices B, C, and D were defined by equating the various terms in the kinetic equations to the terms in the least-square line equation. The rate ( $r_A/S$ ) was related to concentration in Appendices B and D by

$$(r_A/S) \times 10^{-u} = k_2(C_A \times 10^{-v})^q \quad (\text{E-2})$$

The least-square lines for the log-log plots of rate, ( $r_A/S$ ), versus concentration,  $C_A$  or  $C_B$ , were obtained from the measured data by using

$$\log(r_A/S) = (\log k_2 + u - qv) + q \log C_A \quad (\text{E-3})$$

where  $\hat{y}$  was given by  $\log(r_A/S)$ ,  $(\log k_2 + u - qv)$  the intercept,  $q$  the slope of the line, and  $\log C_A$  the observed  $x$  value. The reaction rate constant,  $k_2$ , was related to the absolute temperature,  $T$ , in Appendix C by

$$(k_2/T) \times 10^{-w} = A'e^{-\left(\frac{E_{\text{EXP}}}{RT}\right)} \quad (\text{E-4})$$

The least-square lines for the data plotted in the figures of Appendix C were obtained by

$$\log(k_2/T) = (\log A' + w) - \left(\frac{E_{\text{EXP}}}{2.303 RT}\right) \left(\frac{1}{T}\right) \quad (\text{E-5})$$

where  $\log(k_2/T)$  was the  $\hat{y}$  term,  $(\log A' + w)$  the intercept,  $(E_{\text{EXP}}/2.303 RT)$  the slope, and  $(1/T)$  the x term.

The least-square-line statistics for the data given in Appendices B, C and D are shown in Tables E-1, E-2, and E-3, respectively. The terms (Walas 1958, pp. 225-241) given in these tables are defined as

1. N - the number of points plotted,
2.  $t_{95, N-2}$  - the t-table value at the 95 percent confidence level and at the degrees of freedom of (N-2),
3. r - the correlation coefficient,
4. a - the intercept,
5. b - the slope of the line,
6.  $\bar{x}$  - the mean of the measured x values,
7.  $\bar{y}$  - the mean of the measured y values,
8.  $s(\bar{y})$  - the square root of the variance of  $\bar{y}$ ,
9.  $s(b)$  - the square root of the variance of the slope, and
10.  $s(\hat{y})_i$  - the square root of the variance of the average estimated value  $\hat{y}_i$  at  $(i = 1)$  and  $(i = 2)$ .

TABLE E-1  
THE LEAST SQUARE LINE RESULTS FOR  
THE DATA IN APPENDIX B

MINERAL	°C	FERRIC SULFATE Moles per Liter		N	$t_{95, N-2}$	r	a	b	$\bar{x}$	$\bar{y}$	s( $\bar{y}$ )	s(b)	s( $\hat{y}$ ) <sub>i</sub>	
		(i=1)	(i=2)										(i=1)	(i=2)
Chalcocite	38	0.0070	0.300	11	2.262	0.9868	-0.2147	1.0692	1.936	1.855	0.020	0.0585	0.067	0.037
Covellite	68	0.0065	0.210	7	2.571	0.8570	+0.7076	0.1964	1.721	1.046	0.026	0.0530	0.057	0.041
Bornite (d <sub>1a</sub> )	38	0.0090	0.105	6	2.776	0.9542	-0.2603	0.6519	1.622	0.797	0.055	0.1020	0.088	0.069
(d <sub>1b</sub> )	38	0.105	0.280	9	2.365	0.4816	+0.6890	0.1975	2.240	1.132	0.021	0.1360	0.036	0.035
(d <sub>2a</sub> )	38	0.0070	0.055	3	12.706	1.0000	-0.4643	0.6675	1.181	0.324	0.000	0.0000	0.000	0.000
(d <sub>2b</sub> )	38	0.055	0.280	11	2.262	0.4382	+0.9006	0.0784	2.169	0.730	0.011	0.0547	0.026	0.019
(d <sub>3</sub> )	38	0.090	0.265	8	2.447	0.5984	-0.3354	0.2918	2.192	0.304	0.027	0.1600	0.047	0.046
(d <sub>4</sub> )	38	0.090	0.215	3	12.706	0.2986	+0.0488	0.0787	2.125	0.216	0.038	0.2550	0.058	0.065
Chalcopyrite	50	0.020	0.200	6	2.776	0.0641	+0.1159	0.0095	0.775	0.123	0.026	0.0744	0.044	0.047
Pyrrhotite	38	0.025	0.210	7	2.2571	0.6985	+0.7648	0.0894	0.965	0.851	0.012	0.0411	0.027	0.019

TABLE E-2  
 THE LEAST SQUARE LINE RESULTS FOR  
 THE DATA PLOTTED IN APPENDIX C

MINERAL	FERRIC SULFATE Moles per Liter	TEMP., °C.		N	$t_{95, N-2}$	r	a	b	$\bar{x}$	$\bar{y}$	s( $\bar{y}$ )	s(b)	s( $\hat{y}$ ) <sub>i</sub>	
		(i=1)	(i=2)										(i=1)	(i=2)
Chalcocite	0.10	28	70	5	3.182	0.9640	5.1884	-1.4740	3.149	0.546	0.033	0.2354	0.056	0.093
Covellite	0.10	39	68	4	4.303	1.0025	10.6876	-3.1109	3.032	1.254	0.018	0.1554	0.032	0.024
Bornite (d <sub>1a</sub> )	0.10	28	70	4	4.303	0.8948	5.0492	-1.4079	3.138	0.634	0.024	0.4968	0.118	0.133
Bornite (d <sub>2b</sub> )	0.10	28	70	4	4.303	0.9656	8.0173	-2.1022	3.138	1.425	0.061	0.4650	0.105	0.120
Bornite (d <sub>3</sub> )	0.10	28	70	4	4.303	1.0016	9.4780	-2.6830	3.138	1.065	0.016	0.1072	0.026	0.029
Chalcopyrite	0.10	32	50	4	4.303	1.0025	13.6840	-3.8832	3.168	1.382	0.014	0.1909	0.025	0.020

TABLE E-3  
 THE LEAST SQUARE LINE RESULTS FOR  
 THE DATA IN APPENDIX D

MINERAL	°C	FERRIC SULFATE		SULFURIC ACID		N	$t_{95, N-2}$	r	a	b	$\bar{x}$	$\bar{y}$	s( $\bar{y}$ )	s(b)	s( $\hat{y}$ ) <sub>i</sub>	
		Moles Per Liter (i=1)	Moles Per Liter (i=2)	Moles Per Liter (i=1)	Moles Per Liter (i=2)										(x=1)	(x=2)
Chalcocite	38	Constant = 0.10	0.020	0.525	6	2.776	0.9575	+0.5024	0.2517	2.217	1.060	0.040	0.0820	0.085	0.057	
Chalcocite	38	0.022	0.205	Constant = 0.500	4	4.303	0.9832	-0.3600	0.7253	1.951	1.055	0.050	0.1340	0.096	0.070	
Covellite	68	Constant = 0.10	0.086	0.500	5	3.182	0.7715	+1.5182	-0.1204	2.385	1.231	0.016	0.0604	0.032	0.025	
Chalcopyrite	50	Constant = 0.10	0.050	0.780	6	2.776	0.6321	+0.8764	0.0723	2.441	1.053	0.018	0.0450	0.038	0.027	

## NOMENCLATURE

A	Constant for a given solvent and a specified temperature for the Debye-Hückel equation for activity coefficients
A'	Frequency factor for the Arrhenius equation
A''	Modified frequency factor, $A'' = dxVxA'$
$A_2$	The B- coefficient for the relative viscosity, $(N/N^0)$
$\dot{a}$	"Effective diameter" of an ion in solution
$(a_+)_e$	Equilibrium activity of the chemisorbed $M^+$ ion
$(a_0)_e$	Equilibrium activity of the chemisorbed $M^0$ ion
B	Constant for a given solvent and a specified temperature for the Debye-Hückel equation for activity coefficient
b	A constant in the Debye-Hückel activity coefficient equation which depends on the charge type and interaction coefficient for the electrolyte
C	Concentration, moles per liter
$C_A$	Concentration of species A, moles ferric sulfate per liter
$C_{AD}$	Bulk solution concentration of species A, moles ferric sulfate per liter
$C_B$	Concentration of species B, moles sulfuric acid per liter
c	Concentration, moles per cubic centimeter
$c_A$	Concentration of species A, moles ferric sulfate per cubic centimeter
$c_{AD}$	Bulk concentration of species A, moles ferric sulfate per cubic centimeter
D	Diffusivity, (centimeters) <sup>2</sup> per minute
$D_{AB}$	Diffusivity of species A in solvent B, (centimeters) <sup>2</sup> per minute

$D^\circ$	Diffusivity at infinite dilution, (centimeters) <sup>2</sup> per minute
$D^*$	Self-diffusion coefficient, (centimeters) <sup>2</sup> per minute
$D_{AVE}$	Average diameter of sized particles, centimeters
$d$	Calculated depth of leached residue zone, centimeters
$E_{EXP}$	Experimental energy of activation, kilocalories per mole of activated complex.
$E_o$	The energy difference between the zero-level energy and that of the reactants per mole of activated complex
$e$	A constant equal to 2.718+
$e$	Electrode potential, volts
$e_p$	Polarization potential, volts
$e^\circ$	Standard electrode potential, volts
$F^*$	The complete kinetic partition function per unit volume, also $F_A$ and $F_B$ .
$F_e$	The Faraday
$\Delta F$	Free energy, kilocalories per mole
$\Delta F^\circ$	Standard free energy, kilocalories per mole
$\Delta F^*$	Free energy of activation, kilocalories per mole of activated complex
$\Delta F^{\circ*}$	Standard free energy of activation, kilocalories per mole
$f(\theta)$	A function of the fraction of active sites covered
$f(C_A)$	A function of the ferric sulfate concentration
$H_n$	Hydration number
$\Delta H^*$	The enthalpy of activation, kilocalories per mole of activated complex
$h$	Planck's constant
$I$	Ionic strength

$i$	Current density, amps per square centimeter
$J_A^*$	The molar diffusion flux of species A relative to the molar-average velocity, $v^*$ , in gram-moles per minute - square centimeter
$K$	Equilibrium constants, also $K_{eq}$
$k$	Boltzmann's constant
$k_2$	Specific rate constant, also $k_{21}$ , $k_{2-1}$ , $k_{22}$ , $k_{23}$ , $k_a$ , and $k_b$
$k_0$	The number of active sites per unit area of mineral exposed to the solutions, molecules or atoms per square centimeter
$k_{SR}$	Surface roughness factor
$k_{ACT}$	The fraction of the total number of surface sites activated
$k'$	The geometric number of molecules or atoms per unit area of crystal surface, molecules or atoms per square centimeter
(L)	Number of moles of copper extracted from the sulfide per mole of ferrous iron produced from ferric iron
$M$	Molarity, moles per liter
(M.W.)	Molecular Weight of the particular sulfide mineral
$m$	Molality, moles of solute per kilogram of solvent
$N_A$	Flux of species A, moles of A per unit area per unit
$N_a$	Avogadro's number
( $N^0/N$ )	Relative viscosity
$n$	Number of electrons for stoichiometric electrode reaction, or the total increase in moles of the reacting system, or size range number
$p$	Order of reactions for ferric sulfate concentration
$q$	Order of reactions for sulfuric acid concentration
$R$	Gas constant

$r_A$	The rate of consumption of the ferric sulfate species, (moles per liter) per minute
$S$	Exposed mineral area to the aqueous solution, square centimeters
$(SS)_n$	Specific surface of size range $n$ , square centimeters per gram
(S.G.)	Specific gravity
$\Delta S^*$	Entropy of activation, e.u. per mole of activated complex
$T$	Temperature, °K
(TSS)	Total specific surface of all size ranges, square centimeters per gram
$t$	Time, minutes
$V$	Volume, liter
$v_i$	The number of moles of cations ( $i=1$ ) and anions ( $i=2$ ), respectively, formed from one mole of electrolyte
$v^*$	Molar average velocity
	$v^* = \frac{\sum_{i=1}^n c_i v_i}{\sum_{i=1}^n c_i}$
$v_i$	Velocity of species ( $i$ ) relative to stationary coordinates
$x_A$	Mole fraction
$z_i$	Algebraic valencies of cations ( $i=1$ ) and anions ( $i=2$ )
$\nabla$	Operator $(\frac{\partial}{\partial X} + \frac{\partial}{\partial Y} + \frac{\partial}{\partial Z})$
$\alpha$	Fraction of overpotential assisting one direction of electrode reaction
$\gamma_{\pm}$	Mean activity coefficient
$\gamma_i$	Activity coefficient of cation ( $i=+$ ) and anion ( $i=-$ )
$\theta$	Fraction of active sites covered
$\lambda_i$	Ionic equivalent conductivities for the cation ( $i=1$ ) and anion ( $i=2$ )

$\lambda$  Distance between successive equilibrium positions, Å  
 $\rho$  Density, grams per cubic centimeter

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