KINETICS OF DISSOLUTION OF CUPRITE IN PHOSPHORIC ACID

by

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ABSTRACT

The kinetics of dissolution of cuprite with phosphoric acid was studied and it was found that temperature, stirring velocity, oxygen, and acid concentration have a marked effect on the rate of reaction.

The activation energy of the reaction was calculated and it was found to be +2.31 kcal $mole^{-1}$. It was also found that temperatures above 70°C and acid concentrations greater than 0.26 m/l do not affect the rate of dissolution.

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INTRODUCTION

Copper occurs in nature primarily in the form of sulphide or oxidized minerals. The principal sulfide minerals are chalcopyrite, chalcocite, coveline, whereas azurite, malachite, cuprite and chrysocolla are the most common oxidized forms. Since the mineralogy and chemistry of these species are different, different methods must be employed for efficient extraction. In some cases size reduction and flotation followed by pyrometallurgical processes will be the best extraction method. In other cases, chemical dissolution and precipitation will be employed. The latter processes fall within the field of extractive metallurgy known as hydrometallurgy.

Extraction of copper by hydrometallurgical methods has been known for many years. As far back as the 16th century copper was recovered from mine waters at Rio Tinto, Spain. Numerous solvents are available for treating oxidized copper ores, although sulfuric acid is the most commonly used. Because of its higher cost, phosphoric acid has little commercial applications. It is conceivable, however, that with new developments in production methods, the application of phosphoric acid as a solvent will become possible. Thus, this work was undertaken to provide some insight into the nature of oxidized copper-phosphoric acid reactions. Since chrysocolla, azurite and malachite are not available in highly purified form, cuprite was chosen as the initial oxidized copper form to be investigated.

PREVIOUS WORK

Although no work is reported in literature on dissolution reactions with phosphoric acid, considerable work has been done with other solvents.

A. R. Burkin[2] reported the reaction between cuprous oxide and sulfuric acid and was able to show that the cuprous ion is unstable in aqueous solutions. The proposed chemistry of the reaction was explained in detail.

F. A. Forward and V. N. Machiw[7] studied the extraction of copper, nickel and cobalt with ammonia solutions under different conditions of pressure, temperature and agitation.

M. E. Wadsworth and D. R. Wadin[17] investigated the dissolution of cuprite in sulfuric acid solutions. The reaction mechanism was studied at different values of temperatures, pH and stirring speeds. They were able to calculate the activation energy for the reaction and have established that the dissolution of cuprite in sulfuric acid results in the formation of metallic copper and cupric ion (Cu^{++}). The overall chemistry of this reaction was explained and a mechanism was suggested.

K. J. Jackson and J. D. Strickland[6] investigated the kinetics of dissolution of copper sulfides in acid-chlorine solution. They concluded that leaching of copper sulfide ores (covellite, chalcocite, and bornite) results in elemental sulfur and this reaction is governed by the transport-controlled consumption of chlorine.

D. R. McKay and J. Halpern[9] studied the kinetics of the oxidation of pyrite in aqueous suspension. From the chemistry of the reaction they concluded that elemental sulfur forms and further oxidation in the presence of water results in sulfuric acid, which affects the mechanism of the reaction. The presence of metal ions, such as Cu^{++} had an effect on the chemistry and nature of the products.

A. Vizsolyi, H. Veltmon and I. H. Warren[14] investigated the leaching of chalcopyrite with sulfuric acid under high oxygen pressure. The effects on the reaction rates of acid concentration, particle size, oxygen partial pressure and temperature were determined. The typical rate curves for oxidation of chalcopyrite under optimum conditions were plotted.

CHEMISTRY OF REACTIONS

Metals such as cobalt, iron, nickel, and copper form ionic complexes with phosphoric acid and this has been known for a number of years[13]. Orthophosphoric acid (H_3PO_4) has been shown to be a tribasic acid which is quite strong with respect to the first dissociation constant, moderately weak with respect to the second, and very weak with respect to the third. Accurate determination of the dissociation constants, and the heats and free energies of ionization have shown them to be[13]:

$$H_3PO_4 \rightleftarrows H^+ + H_2PO_4^-$$

$$K_1 = 0.7107 \times 10^{-2}$$

$$\Delta G^o = +2.90 \text{ kcal} \qquad \Delta H = -1.88 \text{ kcal}$$

$$H_2PO_4^- \rightleftarrows H^+ + HPO_4^=$$

$$K_2 = 7.99 \times 10^{-8}$$

$$\Delta G^o = +9.82 \text{ kcal} \qquad \Delta H = +0.99 \text{ kcal}$$

$$HPO_4^= \rightleftarrows H^+ + PO_4^{\equiv}$$

$$K_3 = 4.8 \times 10^{-13}$$

$$\Delta G^o = +16 \text{ kcal} \qquad \Delta H = +3.5 \text{ kcal.}$$

The first dissociation of orthophosphoric acid is exothermic, and the following two dissociations are endothermic.

Orthophosphoric acid is quite inactive at normal temperatures. Thus, it is sometimes used as a substitute[13] for sulfuric acid when the oxidizing properties of the latter are not wanted. Usually the reaction between a metal oxide and phosphoric acid is moderately active, the reaction product being the mono, di and/or tri orthophosphate salts. A dissociation diagram (Fig. 4) for phosphoric acid shows the formation of these orthophosphates. At low pH (0 - 5.0), undissociated phosphoric acid and $H_2PO_4^-$ species are present in the solution. From pH 5.0 to 11.0 only $H_2PO_4^-$ and $HPO_4^=$ species are present, and at high pH value only $PO_4^{\equiv}$ species form in solution. Therefore, depending on the pH values, different compounds of orthophosphate salts can be expected. The reaction between cuprite and phosphoric acid at a low pH (0.0-5.0) can be written as follows:

$$Cu_2O + 2H_3PO_4 \rightarrow \underset{\downarrow}{Cu^o} + Cu(H_2PO_4)_2 + H_2O. \qquad (1)$$

Three products form in this reaction: a) elemental copper, b) diorthophosphate copper complex, and c) water. The copper complex $Cu(H_2PO_4)_2$ has the following chemical composition:

Element	Percent in $Cu(H_2PO_4)_2$
Copper	24.7
Phosphorus	24.1
Hydrogen	1.6
Oxygen	49.6

This complex is completely soluble in the leach solution. Metallic copper does not dissolve in a solution of phosphoric acid in the absence of oxygen. Therefore as the reaction progresses, it will settle out at the bottom of the reaction vessel, or precipitate as a spongy layer on the surface of the rotating disc.

THE ARRHENIUS EQUATION

The Arrhenius equation relates the rate constant of a reaction to the activation energy of the reaction:

$$k = Ae^{-Q/RT} \tag{2}$$

where

k = rate constant

Q = energy of activation

A = integration constant

R = gas constant

T = absolute temperature.

Taking logarithm of equation (2) we get:

$$\ln k = \ln A - Q/RT. \tag{3}$$

This is an equation of a straight line of lnk versus 1/T, providing A and Q are constant for a given range of temperatures. The energy of activation Q can be determined readily from the slope of the graph which is equal to $-Q/R$. The intercept on the y axis gives the value of lnA. The activation energy is expressed in cal/mole or kcal/mole[5]. The energy of activation represents the energy that the molecules must acquire in order to be able to react.

EXPERIMENTAL PROCEDURE

a) Sample Preparation

Cuprite powder used for sample preparation was obtained from J. T. Baker Chemical Co., Phillipsburg, N.J. The analysis of the cuprite was 97.0 percent Cu_2O. The remaining impurities were preservative (oil), chlorine, sulfate, and iron.

Studies of the kinetics of dissolution of fine sized particles present the problem of accurate measurements of the surface areas involved. By assuming exact geometric form (either cubes or spheres) for each particle the surface area can be determined from the mean mesh size of the solids. This method, however, introduces inaccuracies inherent in the assumption. Some investigators have attempted to classify the particles according to their geometric form, by a microscopic examination. However, this method fails when it is applied to materials which have no distinct cleavage, such as cuprite, since all the particles must necessarily be classified as irregular.

To eliminate these problems disc samples, with a constant surface area were prepared. A known amount of cuprite powder was compressed in a one inch diameter stainless steel cylinder under 50,000 psi pressure applied in a hydraulic press. The result was a solid disc of cuprite with a known geometrical shape and surface area. The cuprite discs were then mounted in bakelite, and the finished briquette was attached to a glass rod (Figure 1). The exposed area of the cuprite surface was 5.067 cm^2.

To check the uniformity of behavior of all samples, experiments were carried out under identical conditions on ten different samples. A statistical evaluation of the results by analysis of variance (see Appendix I) showed the samples to be identical, with a 95 percent confidence limit. It was, therefore, concluded that the method of sample preparation did not introduce significant variations in their behavior during the dissolution reaction.

b) Determination of Copper Ions in the Solution Samples

All determinations of copper ions in solution were made with an atomic absorption spectrophotometer manufactured by Techtron Pty. Ltd., Melbourne, Australia.

c) Equipment and Instrumentation

Figures 2 and 3 show the experimental set up. The reaction vessel is a 2000 ml cylindrical flask, placed in a constant temperature bath. The temperature is maintained constant to within ± 0.1°C. A motor driven stirrer is used to agitate the solution at a pre-determined speed of rotation. The sample is placed in solution, two inches above the surface of the stirrer surface. This difference in height was maintained constant throughout the experiments. The speed of rotation of the stirrer is regulated by means of a Variac and checked with a tachometer.

d) Procedure

One thousand ml of phosphoric acid solution at the desired pH is placed in a sealed cylindrical flask and this unit put into the constant temperature bath. After the solution has reached the desired temperature, the cuprite sample is inserted and fixed in a given position. The nitrogen gas, supplied from commercial pressure cylinders, is passed through the solution before and during the experiment to prevent any air from entering the reaction vessel.

Duration of each experiment was 5 hours. Samples of solution were removed from the reaction vessel periodically and analyzed for copper. The total copper content of the solution was used as a measure of the half reaction rate.

RESULTS AND DISCUSSION

a) Chemistry of the Dissolution Reaction

As shown in equation 1, the reaction between cuprite and phosphoric acid results in metallic copper and a soluble copper phosphate complex. Since the metallic copper formed during the reaction with the rotating disc adhered to the surface of the disc as a spongy, porous layer, it was difficult to establish its exact weight, although qualitatively it was shown to be pure copper. To determine the stoichiometric relations, tests were performed with a known quantity of cuprite powder in phosphoric acid. In this case, the metallic copper remained at the bottom of the vessel and could be weighed and the amount obtained compared to the amount of copper in solution. This is shown in Table 1.

Exp. No.	Weight of Cu in Cu_2O, gm	Weight of elemental Cu obtained, gm	Weight of Cu as Cu^{++} in solution, gm
1	0.75	0.368	0.372
2	0.102	0.466	0.495

In order to verify further the correctness of equation 1, the copper-bearing solution was evaporated and the resulting non-crystalline salt analyzed for Cu, P, H, and O. This is shown in the following table:

Element	Percent in $Cu(H_2PO_4)_2$ (theor.)	Percent in $Cu(H_2PO_4)_2$ (exper.)
Copper	24.7	26.2
Phosphorus	24.1	25.6
Oxygen	49.6	46.2
Hydrogen	1.6	2.0

The above results indicate that within the limits of experimental error any other complexes that may be formed will be in negligible amounts and the overall reaction is indeed:

$$Cu_2O + 2H_2PO_4 \rightarrow Cu + Cu(H_2PO_4)_2 + H_2O.$$

b) The Rate of the Reaction

The rate of dissolution of cuprite is shown in Figures 5, 6, and 7. The effect of acid concentration is shown in Figure 8, and the effect of temperature is shown in Figure 9. From Figure 8, it may be seen that increasing the acid concentration above 0.5 m will not result in an appreciable increase in the rate of reaction for any given temperature. This would indicate that at low acid concentrations the rate of the reaction is controlled by the diffusion of the $(H_2PO_4)^-$ species to the surface of the disc. As the temperature is increased the dissociation of H_3PO_4 into H^+ and $(H_2PO_4)^-$ ions is significantly increased (Fig. 10), and thus the initial rate of reaction increases with temperature. However, once an equilibrium is established between the rate of diffusion to the surface and the rate of reaction at the surface, the reaction becomes chemically controlled and the rate remains constant.

c) The Activation Energy

The values of the rate constants k were calculated from Figures 5, 6, and 7 for various temperatures and acid concentrations and are shown in Table VI.

The values of k can be used to calculate the energy of activation Q, based on the Arrhenius equation. This is shown in Figure 11, where log k is plotted against 1/T for various acid concentrations. The calculated values of Q are 2.312 and 2.388 which gives an average value of 2.35 kcal $mole^{-1}$.

d) Effect of Oxygen

In the presence of oxygen the rate of the reaction is increased. This is probably due to the reoxidation of the elemental copper formed during the reaction:

a. $Cu_2O + 2H_3PO_4 \rightarrow Cu + Cu(H_2PO_4)_2 + H_2O$

b. $Cu + 1/2\ O_2 \rightarrow CuO$

c. $CuO + 2H_3PO_4 \rightarrow Cu(H_2PO_4)_2 + H_2O$.

Thus, the amount of Cu^{++} in solution will depend on the rate of oxidation of metallic Cu. To ascertain the correctness of this mechanism, a series of tests were carried out to study the dissolution of Cu_2O powder in the presence of air and in the presence of nitrogen. This is shown in Figures 12 and 13, and it can be seen that in an oxidizing medium the amount of Cu^{++} in solution is greater than in a neutral atmosphere. The additional copper in solution, however, is accounted for by the rate of dissolution of copper powder under similar conditions. This would indicate that oxygen does not play any part in the dissolution of cuprite; its only effect being the reoxidation of the metallic copper formed during the reaction. The procedure used for the experiments in the presence of air was similar to that described previously except for the fact that nitrogen was not bubbled through the system. Results of these experiments are summarized in Tables VIII, IX, and X, and Figures 12 and 13.

Figure 1. Cuprite sample disc.

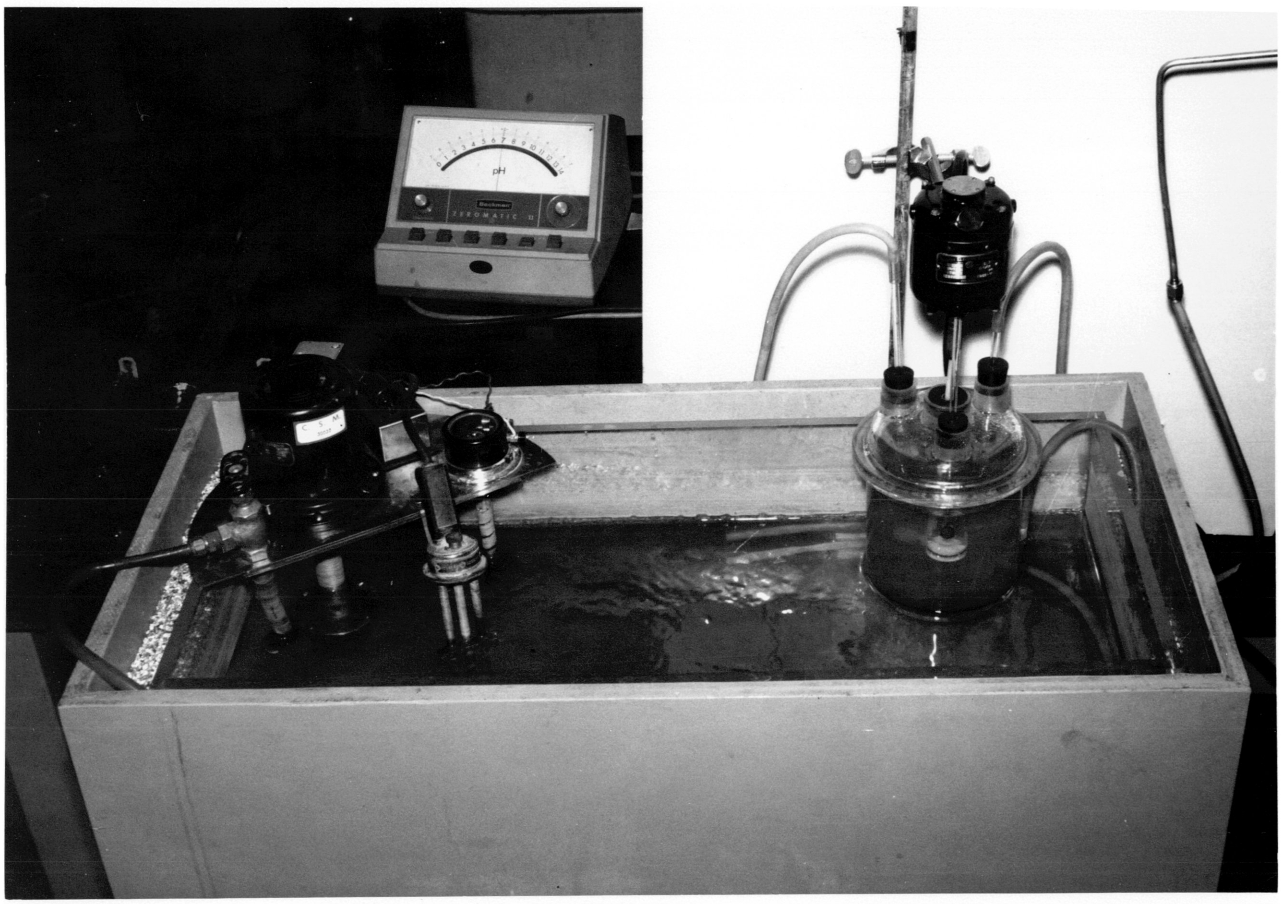

Figure 2. General layout of the apparatus.

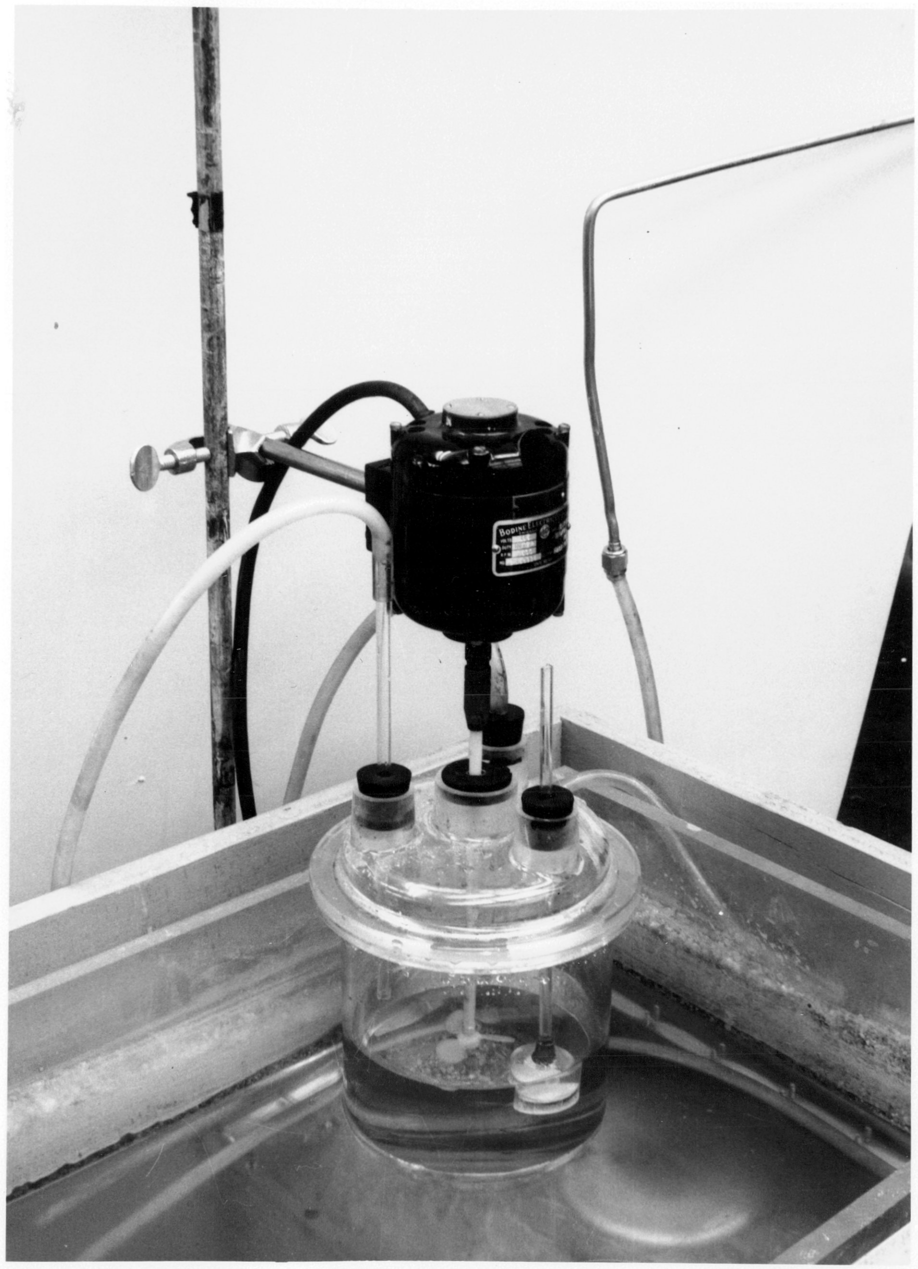

Figure 3. Details of the reaction vessel.

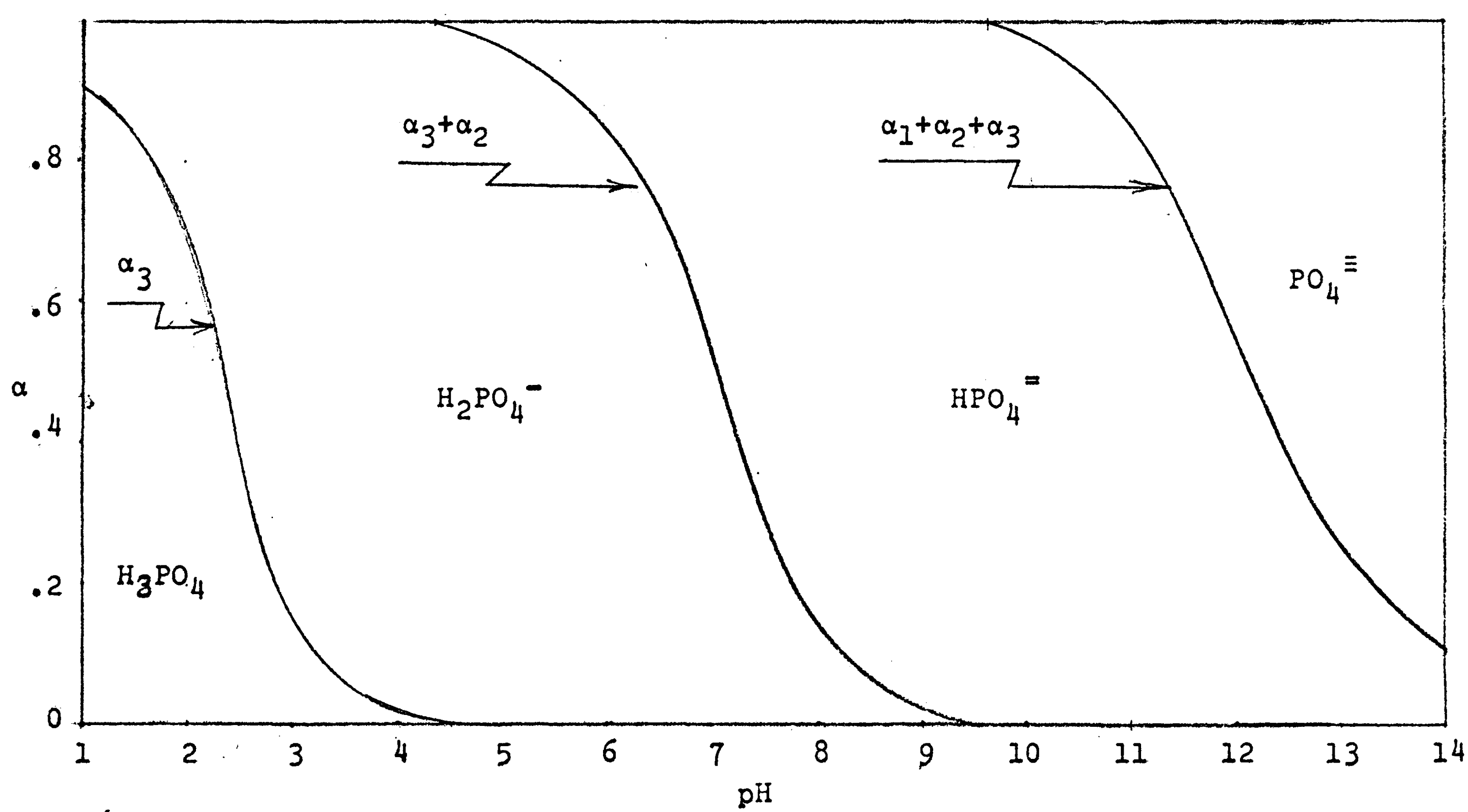

Figure 4. Dissociation diagram for phosphoric acid. After T. Butler.

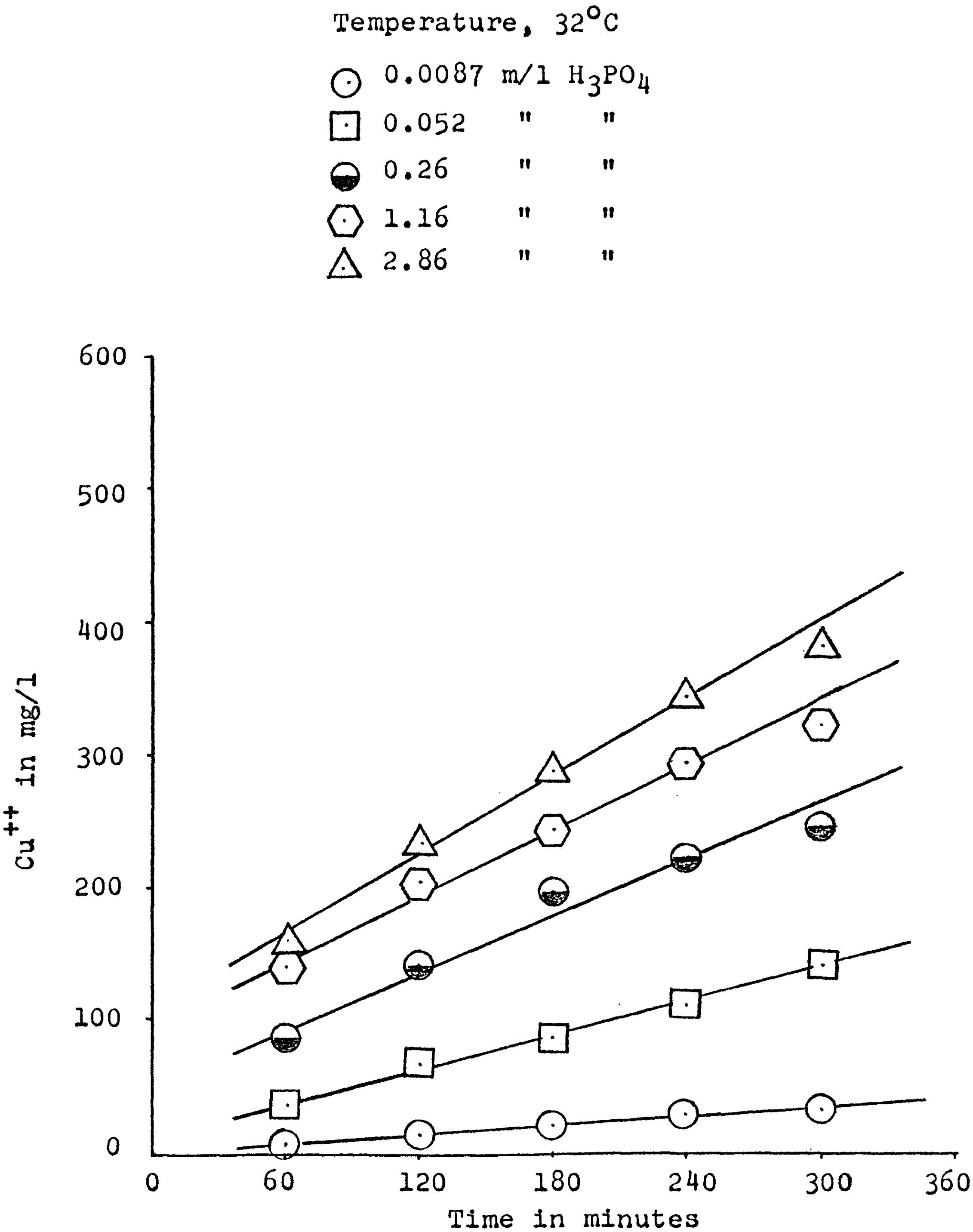

Figure 5. Rate of dissolution of cuprite in phosphoric acid.

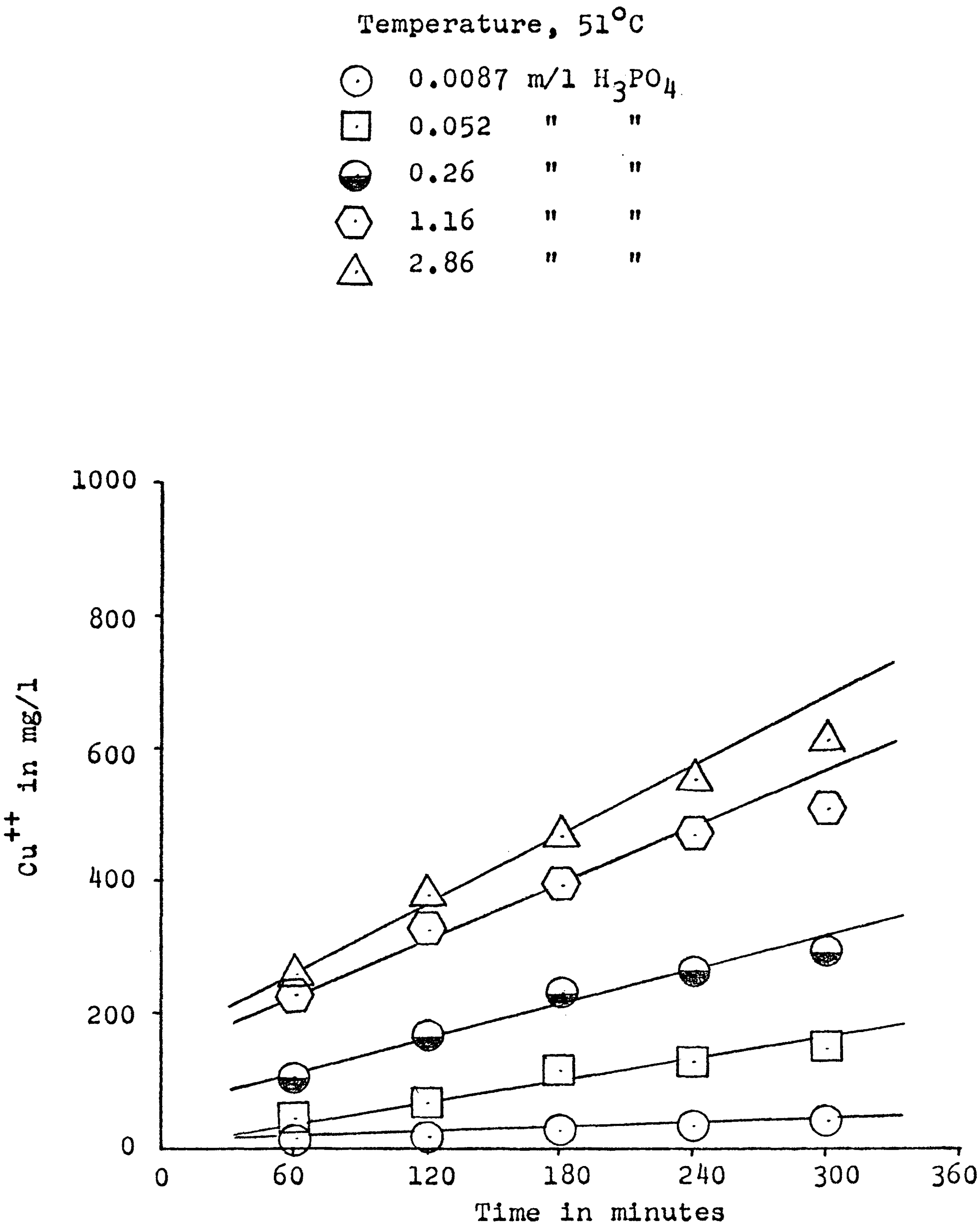

Figure 6. Rate of dissolution of cuprite in phosphoric acid.

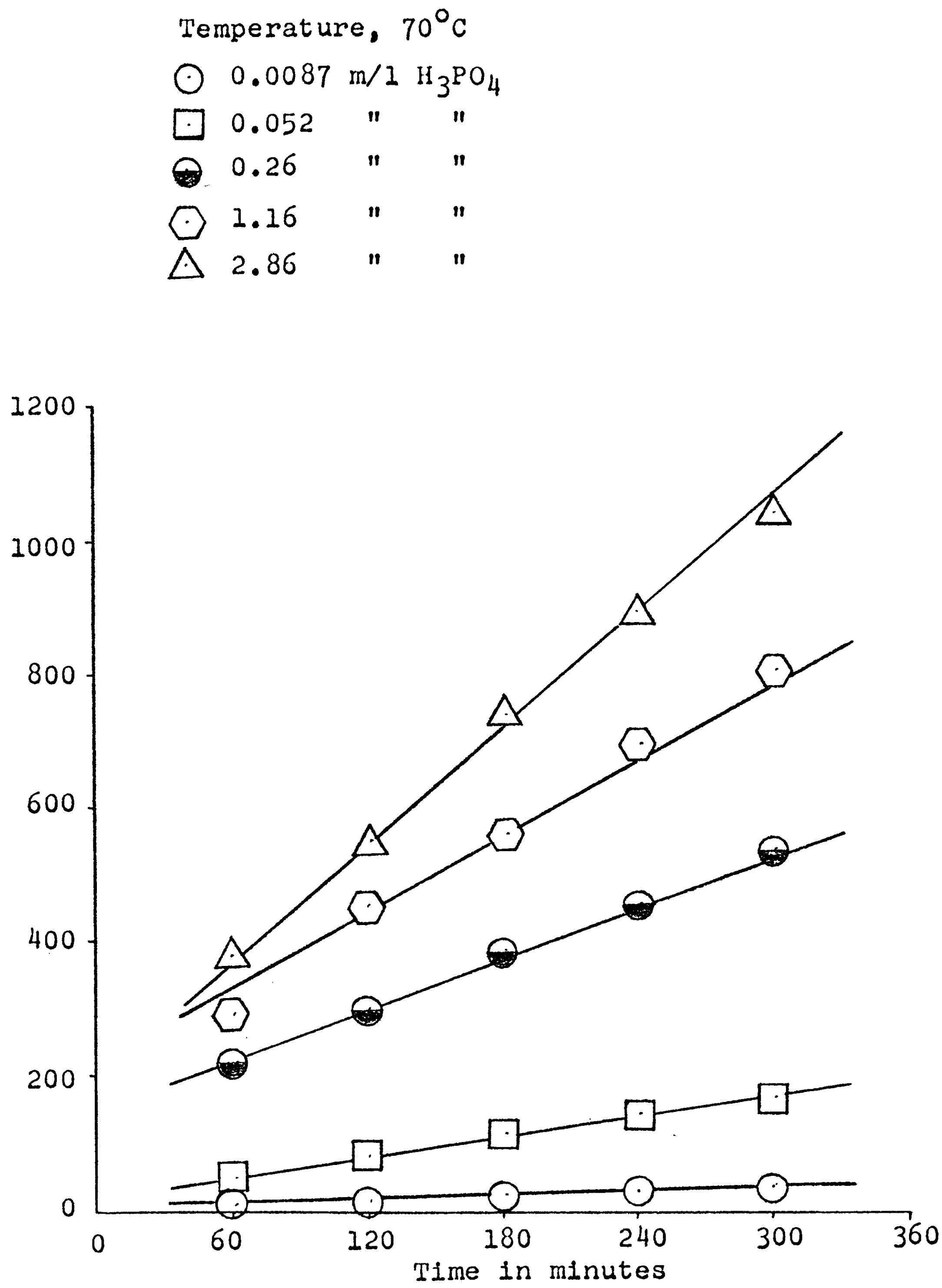

Figure 7. Rate of dissolution of cuprite in phosphoric acid.

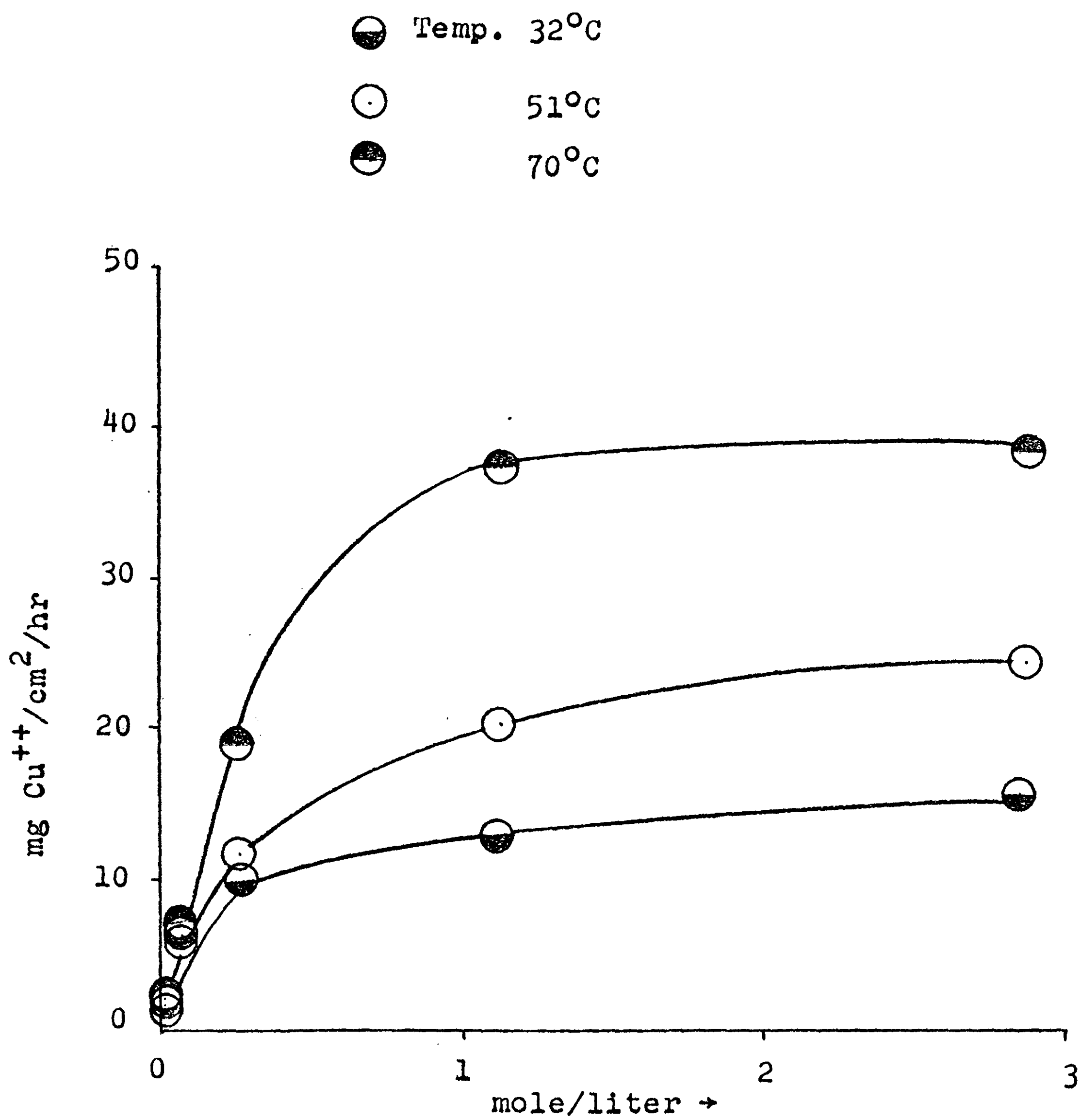

Figure 8. Effect of the concentration of H_3PO_4 on the dissolution of cuprite at different temperatures.

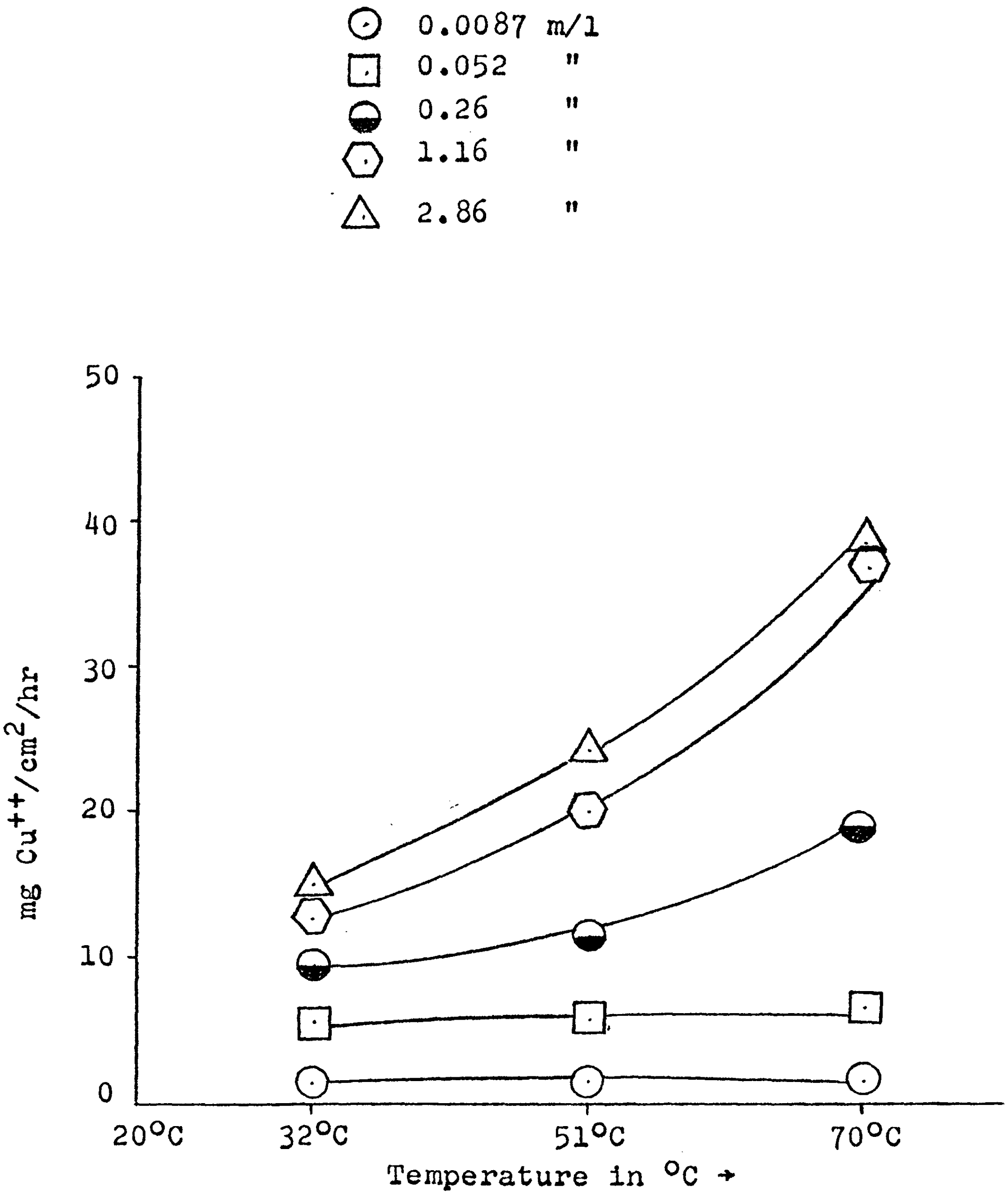

Figure 9. Effect of temperature on the dissolution of cuprite at different concentrations of H_3PO_4.

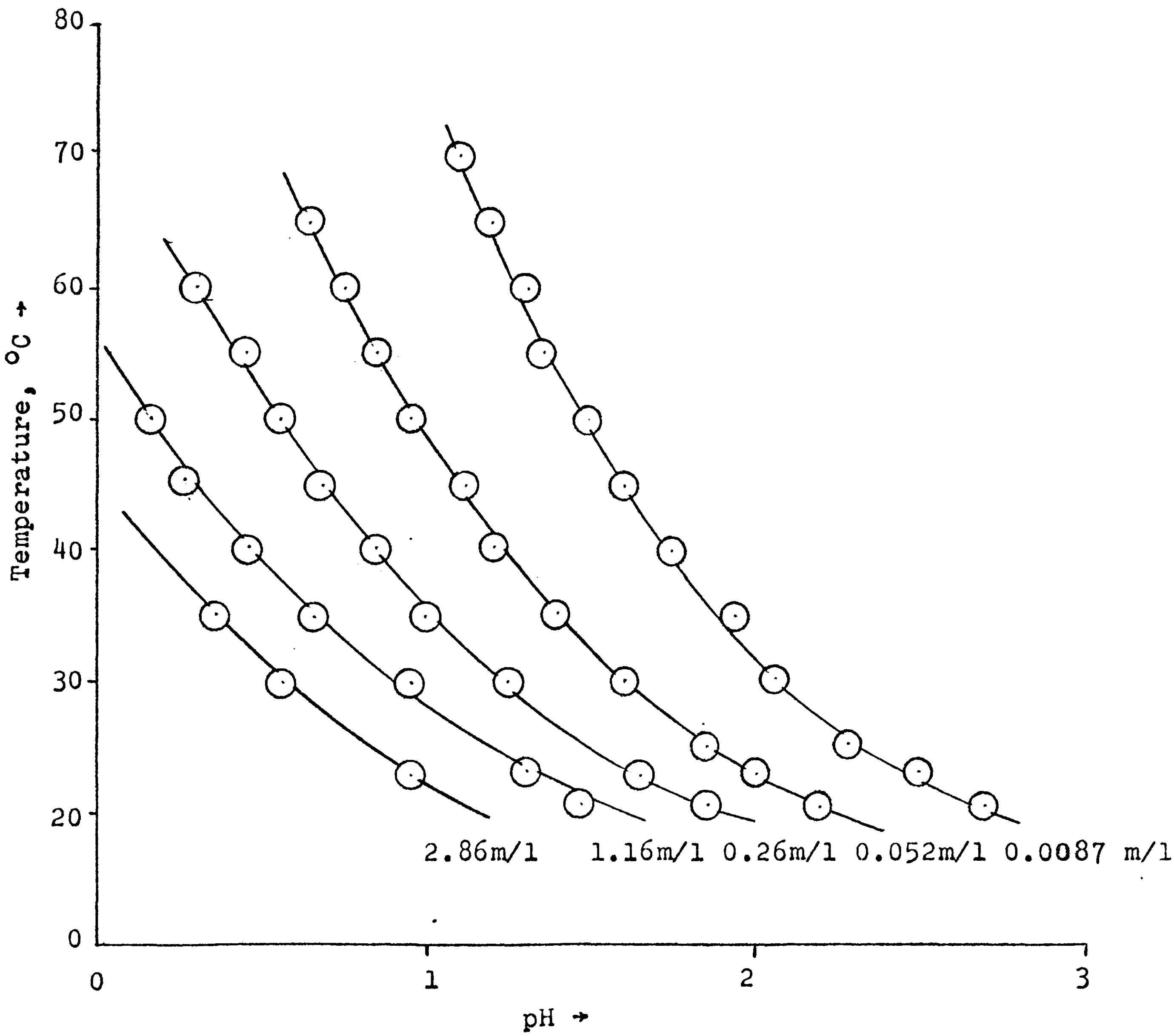

Figure 10. Effect of temperature on the dissolution of H_3PO_4 at different initial concentrations.

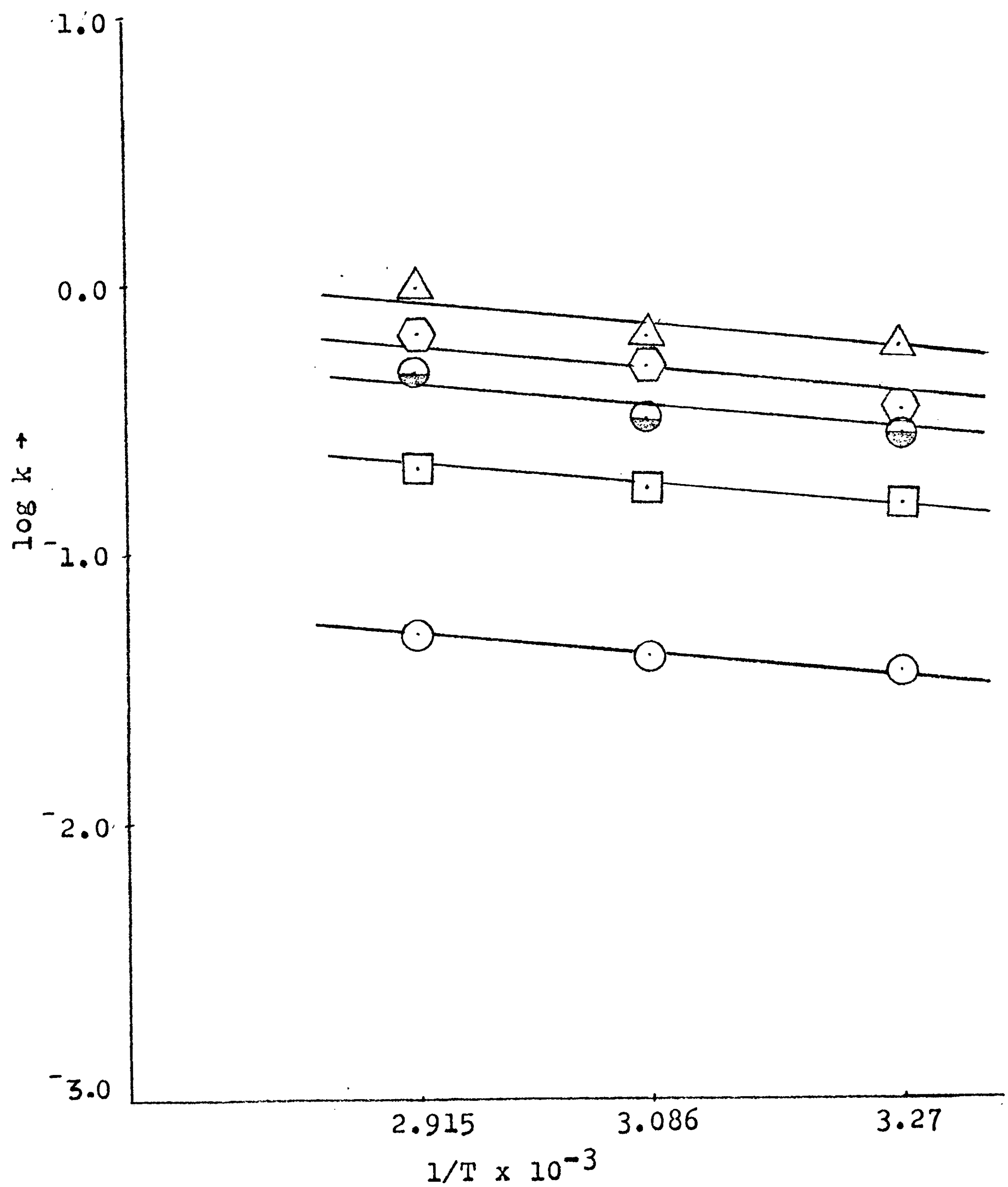

Figure 11. The Arrhenius Curves.

Dissolution of Cu_2O powder in the presence of air

Dissolution of Cu_2O powder in the presence of nitrogen

Dissolution of Cu powder in the presence of air

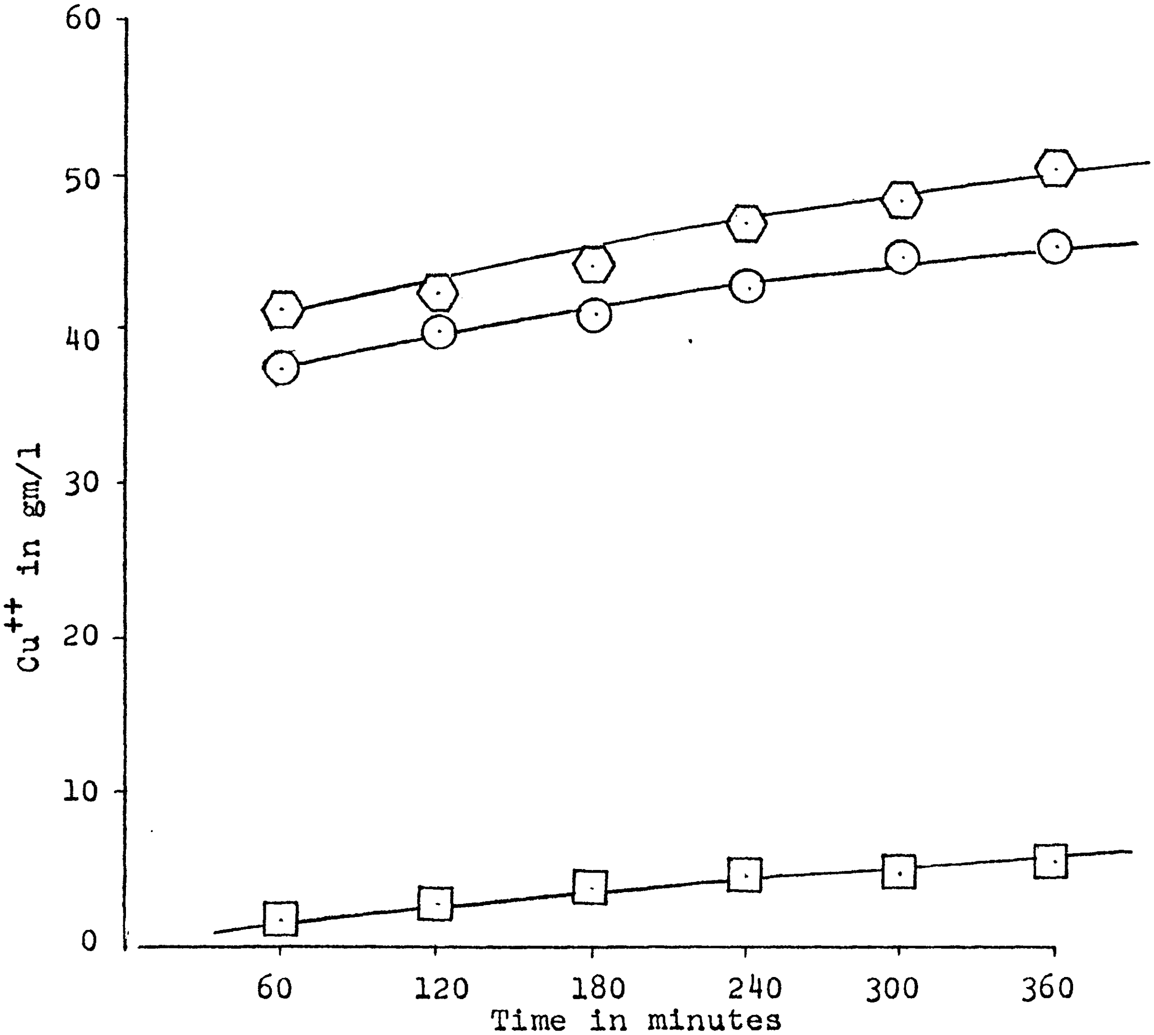

Figure 12. Dissolution of Cu_2O and Cu powders in 1.16 m/l H_3PO_4 at 32°C, in the presence of air and nitrogen.

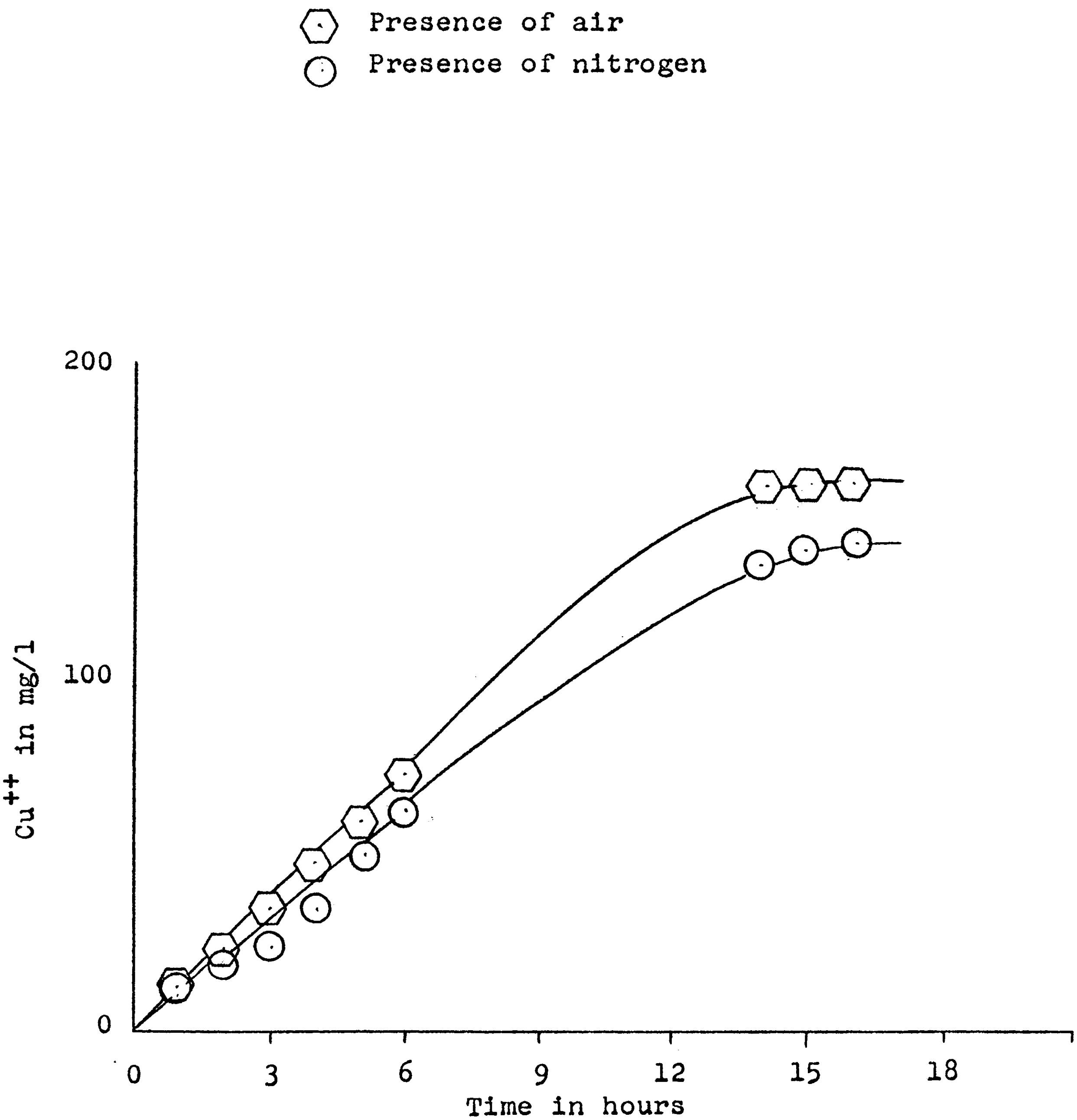

Figure 13. Dissolution of Cu_2O disc in 0.0087 m/l H_3PO_4 at 70°C in the presence of air and nitrogen.

CONCLUSIONS

1. The rate of dissolution of cuprite in phosphoric acid increases with acid concentration up to a concentration of 0.5 m/l. Above that value, the dissolution rate is not affected by a further increase in concentration.

2. The rate of dissolution is increased by an increase in temperature. This is due to the enhanced dissociation of H_3PO_4 at elevated temperatures as well as to the increased rate of reaction at the surface.

3. The activation energy for the reaction was calculated to be 2.31 kcal $mole^{-1}$.

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Table I. Dissolution of cuprite in 0.0087 m/1 phosphoric acid.

Time in minutes	Cu^{++} in solution mg/1 32°C	51°C	70°C
60	9.2	15.84	16.2
120	15.4	22.96	21.8
180	23.23	27.76	29.5
240	31.6	34.84	37.6
300	35.34	40.39	42.8
Rate Constants	k = 0.0394	k = 0.0438	k = 0.0526

Table II. Dissolution of cuprite in 0.052 m/l phosphoric acid.

Time in minutes	Cu^{++} in solution mg/l 32°C	51°C	70°C
60	38.33	44.4	47.52
120	69.19	73.79	86.74
180	89.76	119.31	125.13
240	124.35	131.25	147.6
300	143.99	149.1	168.3
Rate constant	k = 0.1639	k = 0.180	k = 0.215

Table III. Dissolution of cuprite in 0.26 m/l phosphoric acid.

	Cu^{++} in solution mg/l		
Time in minutes	32°C	51°C	70°C
60	88.82	104.97	196.54
120	142.92	171.27	300.69
180	199.15	235.36	390.23
240	224.4	265.2	460.65
300	248.71	293.93	540.74
Rate constant per unit area	k = 0.3068	k = 0.339	k = 0.503

Table IV. Dissolution of cuprite in 1.16 m/l phosphoric acid.

Time in minutes	Cu^{++} in solution mg/l 32°C	51°C	70°C
60	141.76	228.22	297.57
120	204.33	338.95	456.27
180	245.52	395.25	562.07
240	294.62	474.3	700.94
300	324.72	511.27	773.68
Rate constant	k = 0.372	k = 0.547	k = 0.71

Table V. Dissolution of cuprite in 2.867 m/l phosphoric acid.

Time in minutes	32°C	51°C	70°C
60	161.56	260.1	383.53
120	236.80	381.22	555.46
180	290.66	467.92	748.31
240	346.89	558.45	886.90
300	381.74	614.55	1040.67
Rate constant	k = 0.378	k = 0.5979	k = 1.184

Table VI.

Acid Conc. m/1	Temp. °C	k mg cu min^{-1} cm^{-2}
0.0087	32	0.0394
0.052	32	0.1639
0.26	32	0.3068
1.16	32	0.372
2.862	32	0.563
0.0087	51	0.0438
0.052	51	0.180
0.26	51	0.339
1.16	51	0.547
2.862	51	0.6979
0.0087	70	0.0526
0.052	70	0.215
0.26	70	0.503
1.16	70	0.71
2.862	70	1.184

Table VII. Effect of Temperature on the pH of a H_3PO_4 Solution.

Temperature °C	Initial Acid Concentration, m/l .0087	0.052	0.26	1.16	2.862
21	2.65	2.2	1.85	1.47	0.95
23	2.50	2.05	1.65	1.30	0.90
25	2.25	1.85	1.55	1.25	0.80
30	2.05	1.6	1.25	0.95	0.55
35	1.85	1.40	1.0	0.65	0.35
40	1.65	1.20	0.85	0.45	0.05
45	1.60	1.12	0.68	0.25	0.00
50	1.50	0.95	0.55	0.15	0.00
55	1.35	0.85	0.45	0.00	
60	1.28	0.75	0.30	0.00	
65	1.20	0.65	0.20		
70	0.90	0.35	0.00		

Table VIII. Effect of oxygen on the dissolution of Cu_2O powder in 1.16 m/l phosphoric acid at 32°C.

Time in minutes	gms Cu^{++} in Solution	
	In Air	In Nitrogen
60	4.15	3.75
120	4.24	4.01
180	4.44	4.12
240	4.71	4.30
300	4.88	4.50
360	5.08	4.57

Table IX. Dissolution of copper powder in 1.16 m/l phosphoric acid in the presence of air at 32°C.

Weight of copper powder = 5.0 gms

Time in Hours	Cu^{++} in gms/l
1	0.21
2	0.32
3	0.40
4	0.46
5	0.48
6	0.55

Table X. Dissolution of cuprite disc in 0.0087 m/l phosphoric acid in presence of air and nitrogen at 70°C.

	Cu^{++} in mg/l	
Time in Hours	Presence of Air	Presence of Nitrogen
1	16.30	16.2
2	24.34	21.8
3	37.28	29.5
4	51.42	37.6
5	63.41	52.4
6	77.86	67.2
14	165.45	140.5
15	165.45	144.25
16	165.45	145.63

APPENDIX I

Analysis of Variance to Determine Reliability of Procedures Used in Sample Preparation

	1	2	3	4	5	6	
1.	17.03	35.62	49.56	62.34	78.98	88.67	
2.	17.03	33.29	46.07	60.01	77.82	85.95	
3.	17.81	36.29	48.40	60.01	75.11	84.40	
4.	15.00	33.46	46.07	60.01	77.82	88.66	
5.	15.87	34.39	47.62	62.34	78.98	87.12	
6.	16.76	35.62	52.72	60.01	80.53	87.12	
7.	17.81	36.39	48.40	58.85	80.53	85.95	
8.	15.87	34.46	46.09	59.69	84.40	88.66	
9.	19.74	38.3	48.4	60.01	82.09	85.95	
10.	17.81	35.62	47.52	57.69	80.53	85.95	
Sample Size	10	10	10	10	10	10	N = 60
Sample Total	170.73	353.44	480.95	600.95	796.79	868.43	T = 3271.29
Sample Means	17.073	35.344	48.095	60.095	79.679	86.843	x = 54.52
SS_i	1402.0	367.7	41.41	31.08	632.97	1044.77	= 3519.93

$SS_{i(j)}$ = 35317.93

$M_{SB}=\frac{ss_i}{j-1}$ = 703.98

$MS_W=\frac{ss_{i(j)}}{N-j}$ = 654.03

$F = \frac{MS_B}{MS_W}$ = 1.08

$F_{.95}$ = F values from the statistical analysis table 3.22

APPENDIX II

Sample Calculation of the Specific Rate Constant

The rate constant per unit area is equal to

$$= \frac{\frac{dc}{dt}}{A}$$ and, therefore, the rate constant for Reaction 1

is:

$$k = 2 \times \frac{dc}{dt} \times \frac{1}{A} \text{ mg cm}^{-2} \text{ min}^{-1}$$

as explained on page 6.

From Fig. 5,

$$\frac{dc}{dt} = \frac{1}{10}$$

$$A = 5.07 \text{ cm}^2$$

$$\frac{k}{2} = \frac{1}{10} \times \frac{1}{5.07}$$

or $$k = \frac{1}{10} \times \frac{1}{5.07} \times 2 = \underline{\underline{0.0394}} \text{ mg cm}^{-2} \text{ min}^{-1}$$

APPENDIX III

Calculation of Activation Energy

From Figure 11 the slope of the curve is equal to

$$-\frac{Q}{2.303 \times R}$$

where Q is the activation energy, and R is the gas constant = 1.98 cal./degree. Therefore,

$$-\frac{Q}{2.303 \times R} = \frac{2.74 - 2.56}{2.915 - 3.27} = \frac{.18}{-.355}$$

where $2.915 = 1/T_3 \times 10^{-3} = \frac{1}{273 + 70} \times 10^{-3}$

$$3.27 = 1/T_1 \times 10^{-3} = \frac{1}{273 + 32} \times 10^{-3}$$

$$\therefore \quad -\frac{Q}{2.303 \times 1.98} = \frac{0.18}{-0.355}$$

and $Q = 2.312 \text{ kcal mole}^{-1}$.