A KINETIC STUDY OF THE OXIDATION OF PYRITE IN AQUEOUS SUSPENSION

by

DONALD RODERICK McKay

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We accept this thesis as conforming to the required standard

Members of the Department of Mining and Metallurgy

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This thesis describes a kinetic study of the oxidation of pyrite in aqueous suspension by molecular oxygen. The reaction is found to proceed by several simultaneous paths, the direct dissociation by molecular oxygen being predominant, i.e.,

\[
\text{FeS}_2 + O_2 (aq) \xrightarrow{\text{fast}} \text{FeS}_2 \cdot O_2
\]

\[
\text{FeS}_2 \cdot O_2 + O_2 (aq) \xrightarrow{\text{slow}} \text{FeS}_2 \cdot 2O_2 \xrightarrow{+} \text{FeSO}_4 + S^0.
\]

In accord with this mechanism the overall rate of oxidation is found to be proportional to the pyrite surface area and to the oxygen partial pressure and independent of the solution composition. The rate constant \( k_3 = 0.125 \exp \left( -13,300/RT \right) \text{ m. cm.}^{-2} \text{ atm.}^{-1} \text{ min.}^{-1} \). The products of oxidation were found to be both ferrous and ferric sulphate, sulphuric acid and elemental sulphur. Solution composition did affect the distribution of products. High temperatures and low acidities favoured the formation of sulphuric acid while the opposite conditions favoured the formation of elemental sulphur.

A separate study of the aqueous oxidation of ferrous sulphate by molecular oxygen revealed a second order dependence on ferrous ion and a first order dependence on molecular oxygen, i.e.,

\[
\frac{d}{dt} \left[ \text{Fe}^{2+} \right] = k \left[ \text{Fe}^{2+} \right]^2 \left[ O_2 \right]
\]
This reaction was found to be catalyzed by small amounts of cupric ion according to the following observed kinetics:

\[
\frac{\text{d} [\text{Fe}^{3+}]}{\text{d} t} = k_1 [\text{Fe}^{2+}]^2 [\text{O}_2] + k_2 [\text{Fe}^{3+}]^2 [\text{O}_2][\text{Cu}^{2+}]^{1/2}
\]

\[k_2 = 45.5 \, \text{L}^{1/2} \, \text{m}^{-1/2} \, \text{atm}^{-1} \, \text{hr}^{-1} \text{ at } 100^\circ \text{C}\]

Although ferric sulphate was found to be an adequate oxidizing agent for pyrite, the contribution of this reaction to the over-all dissociation of pyrite in the presence of molecular oxygen was not significant since the rate of reoxidation of ferrous sulphate was found to be comparatively slow.
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Department of Mining & Metallurgy

The University of British Columbia, Vancouver 8, Canada.

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INTRODUCTION

SCOPE OF INVESTIGATION

The aqueous acid oxidation of pyrite by molecular oxygen has been studied to determine both the probable mechanism of the reaction, and the effect of most of the likely variables on the reaction rate. The homogeneous oxidation of ferrous sulphate by molecular oxygen was investigated first, followed by a related study of the heterogeneous oxidation of natural pyrite.

INDUSTRIAL APPLICATION OF AQUEOUS SULPHIDE OXIDATION

In recent years much attention has been focused on hydrometallurgical processes conducted at elevated temperatures and pressures. Under these conditions, made possible by the use of autoclaves, the rate of chemical reaction is accelerated, and it is possible to employ gases which are too volatile to be otherwise used. Also, the flexibility of the control of pressure and temperature permit favourable displacement of thermodynamic equilibria. For these reasons autoclave conditions have recently proven advantageous in the extraction of a number of metals from their sulphide ores.

Early in 1954, Sherritt Gordon Mines Limited commenced operation of a plant employing the ammonia leach
process for the extraction of nickel, cobalt, and copper from a sulphide concentrate.\textsuperscript{1,2} Base metal sulphides are converted to soluble ammine complexes, such as \( \text{Cu(NH}_4\text{)}_{4}^{++} \) by aerated ammonia solutions heated to above 175°F. Seventy-five to ninety-five percent of the nickel, cobalt and copper are extracted within eight hours. Pyrrhotite is completely decomposed, while pyrite is unaltered. Advantage of the basic medium is realized by permitting certain sulphur compounds to be only partially oxidized.

Both thionates and thiosulphate can be carefully controlled to provide the necessary sulphur for subsequent copper stripping operations. Nickel and cobalt are then recovered from the copper-free solutions by precipitation with hydrogen.

Another application of the autoclave reaction has recently been initiated by Howe Sound Mining Company. They are employing the Chemical Construction Corporation's process for the leaching of cobalt-arsenic sulphide.\textsuperscript{3} The sulphide concentrate is oxidized in an aqueous medium maintained at 230°C under an oxygen partial pressure 200 p.s.i. Under these conditions the base metal sulphides are oxidized forming sulphuric acid, which rapidly dissolves much of the cobalt. At the elevated temperature employed dissolved iron is hydrolyzed to an insoluble precipitate that is filtered from the pregnant solution. The process has the further advantage of being sufficiently exothermic to be self-sustaining.
More recently a process has been developed for the acid pressure leaching of pyrite bearing uranium ores.\(^4\) Pyrite has been found readily soluble at elevated temperatures and oxygen partial pressures in aqueous solutions, forming sulphuric acid as one of the products of decomposition. Under autoclave conditions this acid rapidly leached the uranium, which is recovered by subsequent treatment.

**AQUEOUS OXIDATION OF FERROUS SULPHATE**

One product of the oxidation of pyrite is ferrous sulfate, which is further oxidized to ferric sulphate. Two plausible reactions for the oxidation of pyrite by oxygen to form ferrous sulphate are:

\[
\begin{align*}
\text{FeS}_2 + 2\text{O}_2 & \rightarrow \text{FeSO}_4 + \text{S} - - - - - - - - (1) \\
2\text{FeS}_2 + 7\text{O}_2 + 2\text{H}_2\text{O} & \rightarrow 2\text{FeSO}_4 + 2\text{H}_2\text{SO}_4 - - (2)
\end{align*}
\]

Pyrite might also be decomposed by sulphuric acid in the absence of oxygen to form ferrous sulphate.

\[
\text{FeS}_2 + \text{H}_2\text{SO}_4 \rightarrow \text{FeSO}_4 + \text{H}_2\text{S} + \text{S} - - - - - - (3)
\]

Ferrous sulphate will also be oxidized by molecular oxygen, i.e.,

\[
4\text{FeSO}_4 + \text{O}_2 + 2\text{H}_2\text{SO}_4 \rightarrow 4\text{Fe(SO}_4)_{1.5} + 2\text{H}_2\text{O} - (4)
\]

Ferric sulphate formed in this way may contribute to further oxidation of both pyrite and the hydrogen sulphide formed by reaction (3), i.e.
FeS + 8Fe(SO₄)₁.₅ + 4H₂O → 9FeSO₄ + 4H₂SO₄ + S — (5)

FeS₂ + 14Fe(SO₄)₁.₅ + 8H₂O → 15FeSO₄ + 8H₂SO₄ — (6)

H₂S + 2Fe(SO₄)₁.₅ → 2FeSO₄ + H₂SO₄ + S — — — (7)

H₂S + 8Fe(SO₄)₁.₅ + 4H₂O → 8FeSO₄ + 5H₂SO₄ — — — (8)

Hydrogen sulphide would likely also be oxidized by molecular oxygen, i.e.

2H₂S + O₂ → 2H₂O + 2S — — — — — — — (9)

H₂S + 2O₂ → H₂SO₄ — — — — — — — — — — (10)

Obviously both ferrous and ferric sulphate will be important products of the aqueous oxidation of pyrite, making a separate study of reaction (4) most desirable.

One of the earliest investigators in this field was McBain, who found that for concentrations of sulphuric acid greater than 0.1M the rate of the reaction could be expressed as:

\[- \frac{d[Fe^{++}]}{dt} = k [Fe^{++}]^2 [O₂] \] — — — — — — — (11)

Further, he observed that increasing the concentration of sulphuric acid in the range 0.1N to 0.5N retarded the reaction. Lamb and Elder observed a similar kinetic behaviour, although they disagreed with McBain's hypothesis that the rate is determined by the oxidation of minute
amounts of hydrolyzed ferrous sulphate. They claimed that the change in rate with change in acidity was not sufficient to be compatible with this theory.

Just found that in bicarbonate solutions the rate was a function of the hydrogen ion concentration, and varied directly as the ferrous ion concentration. Likewise a direct dependence on the concentration of ferrous ions was reported by A.M. Posner. The latter results supported the mechanism proposed by Weiss for the iron-catalyzed decomposition of hydrogen peroxide, involving the intermediate formation of either \( \text{HO}_2 \) or \( \text{OH} \) by a one-electron transfer reaction. Further support for a bimolecular, one electron oxidation of ferrous sulphate has been reported by Cher and Davidson, who observed also that the rate of the reaction depended on the wetted area of glass container. They felt that the results of McBain, as well as those of Lamb and Elder were at fault because of doubtful values of the activities applied to relatively concentrated solutions of ferrous sulphate (\( \text{FeSO}_4 \cdot 1\text{M} \)). They could not explain the observed heterogeneous dependence of the reaction.

Philip George, working with a perchlorate solution and using high-pressure oxygen, observed the same rate law as McBain, i.e. reaction (11).

In the determination of this rate equation George not only observed the reaction over a greater range of ferrous ion concentrations than previous investigators had done, but he also accounted for such minor effects as the
change in solubility of oxygen with variations of ferrous salt concentration.

Huffman and Davidson in a recent investigation, observed that in sulphate media the order of reaction with respect to ferrous ion is slightly less than two.

In summary, it appears that the apparent reaction is second order with respect to ferrous ion in perchlorate, and sulphate media, and first order in bicarbonate, chloride, and phosphate solutions. The reaction rate is generally decreased by increasing acidity.

The effects of several additional ions upon the reaction have been reported. In the presence of chloride ion the apparent order of reaction in ferrous ion increased from one to two with increasing acidity. Phosphate ion increased the observed reaction rate, the increase being attributed to the complexing ability of this anion. Increased cupric ion concentrations in the range of $10^{-5}$M were observed to markedly increase the reaction rate. However, no appreciable further increases were noted upon the addition of cupric ion to solutions containing more than $10^{-3}$M cupric salt. Also, the addition of cupric ion produced an increase in the observed order of the reaction for those instances cited as first order with respect to ferrous ion.

OXIDATION OF SULPHIDES

Since the oxidation of a sulphide mineral in aqueous suspension is a heterogeneous reaction, any kinetic study of
such a system is faced with certain inherent difficulties. It will be noted in the following literature survey that heterogeneous leaching mechanisms may be classified into two categories depending on whether the reaction products are soluble or insoluble. Processes in which soluble products are formed usually lend themselves to investigations employing normal methods of chemical analyses, while the formation of insoluble reaction products often requires the adoption of more elaborate techniques. However, regardless of the reaction type the economic pressure of industrial requirements for hydrometallurgical processes has made investigation of the various parameters necessary. To this end many investigations of leaching reactions with specific minerals have recently been conducted.

Stenhouse and Armstrong studied the oxidation of pyrite powder in a basic solution under high oxygen pressures. They observed that the rate could be represented initially by the sum of two exponential curves, and latterly by a continuation of one of the exponential curves. To account for this and other observations, they proposed a mechanism in which electrons from sulphur atoms are transferred to the surface through outer oxide layers, leaving positive sulphur ions. Armstrong and Stenhouse postulated that the positive sulphur ions then diffused to the surface while oxygen atoms diffused inward.

The oxidation of galena crystals in sodium hydroxide solution was investigated by Anderson, Samis, and Halpern.
They proposed that hydration of a lead complex at the solid surface constituted the rate-controlling step. Later, Seraphim studied the oxidation of galena in ammonium acetate solution and observed the apparent rate controlling step to be diffusion through a surface coating of sulphur.15

A recent study of the oxidation of Molybdenite by Dresker, Wadsworth, and Fassell16 indicated a reaction mechanism in which oxygen is adsorbed at the solid surface prior to a configurational rearrangement. Hydroxyl ions react with the rearranged oxygen to form water-soluble molybdates. The dependence on hydroxyl ions, which they observed, is considered evidence of slow diffusion of these ions to adsorbed oxygen sites.

Downes and Bruce have studied the oxidation of pyrrhotite, which is of interest as a possible method of recovering elemental sulphur, iron oxide ore, and other base metals.17 They discovered that either natural pyrrhotite or artificial pyrrhotite, formed by the liberation of the labile sulphur atom of pyrite roasted at 700°C, would produce free sulphur and iron oxide when leached at moderate oxygen partial pressures. They observed the reaction to be almost complete after one or two hours at 110°C. The reaction was observed to be sufficiently exothermic to be self-sustaining at this temperature. In the neighbourhood of 120°C monoclinic sulphur melted to form globules of sulphur which occluded pyrrhotite particles, protecting them from further oxidation.
At 130°C, or above, pyrrhotite dissociated to form appreciable quantities of iron sulphate. Pyrite, when present, oxidized to iron sulphate and sulphuric acid over the temperatures range observed.

The oxidation of sulphides in dilute acidic chlorine solutions has been studied by Strickland. He has observed that both pyrrhotite and pyrite produce sulphate ions at room temperature. The activation energies for the oxidation of covellite, chalcocite, pyrite, and pyrrhotite are in the order of 4000 to 5000 calories per mole, which Strickland suggests to be evidence of transport controlled mechanisms. However, there is no evidence of any similarity in the fundamental reactions which occur in dilute chlorine solutions and those which occur in the presence of oxygen.
Both ferrous sulphate and pyrite were oxidized in a five litre pressurized autoclave fabricated from 316 stainless steel. Heat was supplied by a gas burner and cooling through a stainless steel, water filled, cooling coil. The temperature was controlled by a resistance thermometer actuating the gas flame and cooling mechanism through solenoid valves. In this way the temperature was maintained within ± 4°C of the set value at all times. Agitation was provided by a propellor type impeller and above it a turbine type impeller operated on the same shaft. Other details are shown on Fig. 1.

Commercial oxygen was supplied through mild steel tubes from cylinders of gas manufactured by Canadian Liquid Air Co. Pressure was controlled by a diaphragm regulating valve. Reagent grade chemicals were used for all phases of work.

A coarse portion of a pyrite concentrate prepared in our laboratory was used initially. This pyrite had the following analyses:

Pyrite A

<table>
<thead>
<tr>
<th>Element</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>44.2%</td>
</tr>
<tr>
<td>S</td>
<td>53.7%</td>
</tr>
<tr>
<td>Ins</td>
<td>1.55%</td>
</tr>
<tr>
<td>Pb</td>
<td>0.01%</td>
</tr>
<tr>
<td>Zn</td>
<td>Trace</td>
</tr>
<tr>
<td>Cu</td>
<td>0.01%</td>
</tr>
</tbody>
</table>

After the pertinent parameters had been initially investigated a pyrite sample prepared by the Department of
Figure 1. Sectional Diagram of Five Liter Autoclave.
Mines in Ottawa, Canada, was employed.

Pyrite B

Fe 46.22%  S 51.40%  Ins. 0.11%
Cu 0.01%

Each of the two pyrite lots was rolled and split into 200 gram and 400 gram samples which were carefully stored until required.

Standard Tyler screen analyses were as follows:

Pyrite A

<table>
<thead>
<tr>
<th>Mesh No. 2 Series</th>
<th>Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>+ 65</td>
<td>.05%</td>
</tr>
<tr>
<td>- 65 + 100</td>
<td>1.45%</td>
</tr>
<tr>
<td>- 100 + 150</td>
<td>18.80%</td>
</tr>
<tr>
<td>- 150 + 200</td>
<td>28.60%</td>
</tr>
<tr>
<td>- 200 + 270</td>
<td>27.50%</td>
</tr>
<tr>
<td>- 270 + 325</td>
<td>18.60%</td>
</tr>
<tr>
<td>- 325</td>
<td>5.00%</td>
</tr>
</tbody>
</table>

Pyrite B

<table>
<thead>
<tr>
<th>Mesh No. 2 Series</th>
<th>Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>+ 65</td>
<td>0</td>
</tr>
<tr>
<td>- 65 + 100</td>
<td>0.1</td>
</tr>
<tr>
<td>- 100 + 150</td>
<td>0.5</td>
</tr>
<tr>
<td>- 150 + 200</td>
<td>2.8</td>
</tr>
<tr>
<td>- 200 + 270</td>
<td>19.8</td>
</tr>
<tr>
<td>- 270 + 325</td>
<td>64.3</td>
</tr>
<tr>
<td>- 325</td>
<td>12.5</td>
</tr>
</tbody>
</table>
Additional information related to sub-sieve sizes as determined by Roller Particle Size Analyzer and microscopic measurements is given in Appendix I.

In addition to autoclave tests, some experiments were conducted in which large crystals of pyrite were placed in a flask maintained at constant temperature. Various acid concentrations were employed. Atmospheric air bubbled through the solutions not only supplied oxygen, but also provided agitation. These tests provided qualitative information regarding the microscopic surface alterations occurring during leaching.

An attempt to press pyrite powder for use in subsequent leaching tests was not successful. Pressures as high as 120,000 pounds per square inch failed to produce a product with sufficient strength.

OXIDATION OF FERROUS SULPHATE

Ferrous sulphate, sulphuric acid, and distilled water, plus any additional materials were charged to the autoclave, the lid bolted down, and the temperature controller set. Once the operating temperature had been reached the autoclave was purged three to five times with oxygen and an initial sample removed. Fifty cubic centimeter samples were removed through the sampling device at regular intervals, collected in stoppered sample bottles, and cooled. These were titrated with potassium dichromate for ferrous iron, using diphenylamine as an indicator. Values for total iron
were obtained by standard analytical methods using stannous chloride for the reduction step. Copper concentrations were determined electrolytically using small amounts of nitric acid to oxidize the ferrous ion, and phosphoric acid to complex the ferric ion. Sulphur was determined by standard gravimetric methods using barium chloride to precipitate sulphur from solution.

**Oxidation of Pyrite**

Pyrite samples were charged to the autoclave with sufficient distilled water and sulphuric acid. Copper, when employed, was added as aliquot portions of standardized copper sulphate solution. Operation of the autoclave was identical to that outlined previously. Samples were filtered immediately upon removal from the sampling tap. Filtrates were collected in bottles as before, while the residues were washed and dried.

Ferrous iron and total iron concentrations were determined in each instance. Total sulphur and sulphate sulphur concentrations were determined for the first six runs. Careful analyses showed that all sulphur in solution was present as sulphate. Hence, determination of total sulphur in solution was discontinued.

Residue samples were analysed for iron, total sulphur, and elemental sulphur. Iron was determined by dissolving the sample in a mixture of nitric and hydrochloric acids, precipitation with ammonium hydroxide, redissolving in hot hydrochloric acid, and titrating with standard dichromate as previously outlined.
Samples for sulphur determination were dissolved in hot bromine-bromide and nitric acid, evaporated, and redissolved in aqueous hydrochloric acid. Solutions were filtered and the filtrates analyzed for sulphur as outlined previously.

The free sulphur content of the residues were obtained by extraction from weighed samples with boiling aniline. Following the extraction, residues were washed with hot toluene, ethyl alcohol and ether. Samples were then dried and weighed to determine the percentage of elemental sulphur in the original sample as indicated by the reduced weight of the stripped residues.
RESULTS

OXIDATION OF FERROUS SULPHATE

Experiments were conducted, using the range of variables shown in Table I.

To determine whether or not the reaction is diffusion controlled two experiments were conducted with impeller speeds of 450 R.P.M. and 830 R.P.M. All other variables were maintained constant. Since the rate curves as shown in Fig. 2 are identical for both experiments, it is concluded that the reaction is not diffusion controlled if normal agitation is provided. The higher impeller speed was employed for the remainder of the experimental work.

Effect of Ferrous and Hydrogen Ion Concentrations

Data shown in Table II are representative of the information recorded for experiments related to the study of the oxidation of ferrous sulfate. These same data are recorded by the upper rate curve of Fig. 3. The rapid change of slope of this curve is indicative of a high order reaction with respect to ferrous ion. It may also be seen that the two curves in Fig. 3 intersect; i.e., their slopes at equal ferrous ion concentrations are dissimilar. This indicates a variation in the order of the reaction with respect to ferrous ion, which appears to be dependent upon the initial concentration of this ion.

The reaction rate for second order dependence upon ferrous ion concentration may be written:
<table>
<thead>
<tr>
<th>Variable</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Agitation</td>
<td>400 R.P.M. to 800 R.P.M.</td>
</tr>
<tr>
<td>2. Initial ferrous ion concentration</td>
<td>3 g/l to 15 g/l</td>
</tr>
<tr>
<td>3. Hydrogen ion concentration</td>
<td>0.025N to 0.63N</td>
</tr>
<tr>
<td>4. Oxygen partial pressure</td>
<td>1 to 4 atmospheres</td>
</tr>
<tr>
<td>5. Reaction Temperature</td>
<td>100°C to 130°C</td>
</tr>
<tr>
<td>6. Initial ferric ion concentration</td>
<td>Zero to 3 g/l</td>
</tr>
<tr>
<td>7. Cupric ion concentration</td>
<td>Zero to 1.25 g/l</td>
</tr>
<tr>
<td>8. Stainless steel surface area</td>
<td>1 to approx. 2 or 3 times that of reactor</td>
</tr>
</tbody>
</table>
Figure 2. Effect of Variation in Agitation
TABLE II

DATA RECORDED DURING THE OXIDATION OF FERROUS SULPHATE BY MOLECULAR OXYGEN

<table>
<thead>
<tr>
<th>Sample</th>
<th>Time (Minutes)</th>
<th>Titration of 20 cc sample with ( \text{Cr}_2\text{O}_7^- )</th>
<th>( \text{Fe}^{++} ) in grams/litre</th>
<th>Total Iron Content Titration (Measured at Room Temp.)</th>
<th>pH (Measured at Room Temp.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>34.8</td>
<td>8.35</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>5.5</td>
<td>29.05</td>
<td>6.98</td>
<td>46.40</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>10.5</td>
<td>25.55</td>
<td>6.14</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>20.5</td>
<td>21.10</td>
<td>5.07</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>30.0</td>
<td>18.25</td>
<td>4.38</td>
<td></td>
<td>1.5</td>
</tr>
<tr>
<td>6</td>
<td>40.5</td>
<td>16.10</td>
<td>3.86</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>60.0</td>
<td>13.40</td>
<td>3.22</td>
<td></td>
<td>1.5</td>
</tr>
<tr>
<td>8</td>
<td>90.0</td>
<td>10.80</td>
<td>2.59</td>
<td>46.10</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>120.0</td>
<td>9.45</td>
<td>2.27</td>
<td>44.5</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>151</td>
<td>8.10</td>
<td>1.95</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>180</td>
<td>7.40</td>
<td>1.78</td>
<td>43.4</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>210</td>
<td>6.65</td>
<td>1.60</td>
<td></td>
<td>1.5</td>
</tr>
<tr>
<td>13</td>
<td>240</td>
<td>6.05</td>
<td>1.45</td>
<td></td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>303.5</td>
<td>5.15</td>
<td>1.24</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

NOTES: A fine yellow precipitate of hydrated iron salts precipitated in the sample bottles. This is believed responsible for reduction of total iron content of solution.
Data from Fig. 3 may then be inserted into the integrated form of this rate expression, equation (8). Evidently at

\[
- \frac{d}{dt} \left[ \text{Fe}^{++} \right] = k_1 \left[ \text{Fe}^{++} \right]^2
\]  

(low ferrous ion concentrations the reaction rate is dependent on the square of the ferrous ion concentration. However, at higher ferrous ion concentrations both the value of \( k_1 \) and the order of the reaction increase. Evidence of this is seen in the increased slope and curvature of the line of high ferrous ion concentrations in the \( \text{PH} \) range 1.2 to 1.5 (Fig. 4). Nevertheless, by increasing the acidity the reaction can be made dependent upon the square of the ferrous ion concentration, even in concentrated solutions of this ion.

The apparent effect of hydrogen ion is to reduce the reaction rate. Unfortunately it is not possible to observe the effect of ferrous ion concentration at constant hydrogen ion concentration, as the latter is continually consumed by reaction (4) or produced by reaction (14).

\[
\text{Fe}_2(\text{SO}_4)_3 + 6\text{H}_2\text{O} \rightarrow 3\text{H}_2\text{SO}_4 + 2\text{Fe(OH)}_3
\]  

Therefore, the order of the reaction with respect to ferrous ion can only be established in conjunction with a knowledge of the effect of hydrogen ion.
Figure 3. Effect of Variation in Initial Ferrous Ion Concentration in 0.08M H$_2$SO$_4$; 100°C; 3 Atm. O$_2$
Figure 4. Second Order Plots For the Oxidation of Ferrous Sulphate in Varying Ferrous Sulphate Concentrations 100°C; 3 Atm. O₂; H₂SO₄ variable.
Although the hydrogen ion concentration cannot be held constant the range of acidity during any one experiment may easily be varied from that in other experiments. The rate curves for different ranges of hydrogen ion concentration are shown in Fig. 5. The same data have been replotted in Fig. 6 to show the effect of $p^H$ upon the reaction order in ferrous ion and the magnitude of $k_1$ in equation (12). Evidently both $k_1$ and the reaction order decrease as the hydrogen ion concentration increases until the system becomes highly acid (0.6N). In the presence of a hydrogen ion concentration of at least this magnitude the value of $k_1$ is essentially constant, for ferrous ion concentrations up to fifteen grams per litre, and the rate varies as the second power of the ferrous ion concentration.

The apparent effect of hydrogen ion has been determined by plotting the log of the reaction rate, as determined from the slopes of the plots in Fig. 6, against the log of the hydrogen ion concentration. The slope of this plot, Fig. 7, is -0.33, which is of the same order of magnitude as the value -0.23 obtained by George for the exponent of hydrogen ion concentration for the oxidation of ferrous ion in perchlorate solution (equation 15).

$$- \frac{d[Fe^{++}]}{dt} = k_{II} [Fe^{2+}]^2 [H^+]^n$$

(15)

However, George found that exponent $n$ changed signs, becoming positive when the hydrogen ion concentration reached 0.3N, while the value of the exponent is seen to be constant for
Figure 5. Rate plots for varying hydrogen ion concentrations. 100°C; 3 Atm. O₂
Figure 6. Second Order Plots For The Oxidation of Ferrous Sulphate In Varying Sulphuric Acid Concentration; 100°C; 3 Atm. O₂
Figure 7. Plot of Log k, vs Log Hydrogen Ion Concentration; 100°C; 3 Atm. O₂.
Effect of Oxygen

Rate curves for various oxygen partial pressures between one and four atmospheres are shown in Fig. 8, and curves of the reciprocal of ferrous ion concentrations vs. time are plotted in Fig. 9. Since the slopes of the plots in Fig. 9 are equal to the rate constant $k_1$ for equation (12) they have been employed in Fig. 10 to determine the effect of oxygen. Evidently the reaction rate is directly proportional to the partial pressure of the oxygen (i.e., the concentration of molecular oxygen as shown in Fig. 10). Therefore, the rate equation for the oxidation of ferrous sulphate is of the form:

$$-d\left[\text{Fe}^{++}\right]/dt = k \left[\text{Fe}^{++}\right]^2 \left[\text{O}_2\right] \quad -(11)$$

Since $k \left[\text{O}_2\right]$ equals $k_1$ the mean value of the rate constant $k$ in equation (11) is obtained by dividing any value of $k_1$ by the corresponding oxygen concentration given in Fig. 10. In this way the value of $k$ (equation 11) is found to equal $45 \times 10^{-5}$ litre gram$^{-1}$ minute$^{-1}$ atmosphere$^{-1}$, or 1.51 liter mole$^{-1}$ atmosphere$^{-1}$ hour$^{-1}$ at $100^\circ$C.

No correction has been made for the variation in the solubility of oxygen with changes in temperature and salt concentration. MacArthur$^{19}$ found the variation in solubility of oxygen at different sulphate ion concentrations to be negligible for solutions of equal strengths to those employed for these experiments. Further, it may be seen from
Figure 8. Rate Curves Showing Effect of Varying Oxygen Partial Pressures; 100°C; 0.08M H₂SO₄.
Figure 9. Second Order Plots For Varying Oxygen Partial Pressures Between One and Four Atmospheres; 100°C; 0.08M H₂SO₄.
Figure 10. Effect of oxygen Partial Pressure Upon Reaction Rate; 100°C; 0.08M H₂SO₄
Appendix II that the solubility of oxygen is essentially constant over the temperature range 100°C to 130°C.

**Effect of Temperature**

Rate curves for varying temperatures are presented in Fig. 11. Values of the rate constant \( k_{1} \) (equation 12) have again been obtained from plots of \( \frac{1}{[\text{Fe}^{++}]} \) vs. time (Fig. 11). The results have been summarized in Fig. 13, in the form of an Arrhenius plot based on the relation:

\[
k = A e^{-E/RT}
\]

The apparent activation energy, \( E \), estimated from the slope of this plot is 16.5 ± 2 kilocalories per gram mole. This is in close agreement with the value of 16.2 ± 2.0 kilocalories per gram mole estimated by Huffman and Davidson\(^{12}\) for the portion of the mechanism which they suggest to be bimolecular.

A value for the rate constant \( k \), in equation (11), at 100°C has been previously derived (1.51 litres mole\(^{-1}\) atmosphere\(^{-1}\) hour\(^{-1}\)). The value of this rate constant at 30°C may now be obtained from the experimental value of the apparent activation energy and the Arrhenius equation.

\[
\log 1.51 = \log A - \frac{16.500}{(1.987 \times 373)} 2.3
\]

The value of \( \log A \) is thus found to be 9.93, from which the value of \( \log k \) and hence \( k \) is determined to be 0.0085 litre mole\(^{-1}\) atmosphere\(^{-1}\) hour\(^{-1}\). This is in fair qualitative agreement with the value of .0044 litre mole\(^{-1}\) atmosphere\(^{-1}\) hour\(^{-1}\) in the presence of 0.1M sulfuric acid as
Figure 11. Effect of Temperature Variation Between 100°C and 130°C; 3 Atm. O₂; 0.08M H₂SO₄
Figure 12. Second Order Rate Plots For Varying Temperatures; 3 Atm. O₂; 0.08 M H₂SO₄.
Figure 13. Arrhenius Plot For Oxidation of Ferrous Sulphate by Molecular Oxygen.
determined by Lamb and Elder. Huffman and Davidson observed the rate constant at 159° in the presence of 1N sulfuric acid to be $1.60 \times 10^{-3}$ litre mole$^{-1}$ atmosphere$^{-1}$ second$^{-1}$. The calculated value for the present experiment based on the experimental values listed above is $0.95 \times 10^{-3}$ liter mole$^{-1}$ atmosphere$^{-1}$ second$^{-1}$ in the presence of 1N H$_2$SO$_4$. The good agreement of these values, determined by entirely different procedures, has been presented here as evidence of the validity of the present work.

Other Variables

Results for experiments conducted with and without ferric sulphate addition are shown in the rate plots of Fig. 14. Obviously the ferric ion causes no inhibiting effects in this system.

Since nickel and iron are known to be good catalysts for many reactions, the possible surface effects of the stainless steel exposed to the system was investigated. Stainless steel filings, with an equivalent surface area several times as great as that of the interior of the autoclave and stirrer, were added with the charge. The apparent effect of this addition, as shown in Fig. 15, is to slightly reduce the reaction rate. However, the sample line became plugged with filings very rapidly. For this reason samples were not reliable. Nevertheless, the agreement between reaction rates in the presence of varied surface area is sufficiently good to justify assuming that
Figure 14. Effect of Variation of Initial Ferric Ion Concentration; 100°C; 3 Atm. O₂; .08M H₂SO₄
Figure 15. Effect of Variation of Surface Area; 100°C; 3 Atm. O₂; 0.08M H₂SO₄
the rate controlling mechanism is independent of surface effects.

The reaction rate was almost doubled by the addition of 0.094 grams per liter of cupric ion as shown in Fig. 16 and Fig. 17. The reaction in the presence of cupric ion was observed to deviate slightly from second order dependence on ferrous ion (Fig. 17). To determine whether this was a true indication of a different reaction or the result of a secondary effect, such as that due to $P^H$, an attempt was made to fit the kinetic data to a rate law of the form:

$$-\frac{d [Fe^{2+}]}{dt} = k [Fe^{2+}]^2 [O_2] + k_2 [Fe^{2+}]^m [O_2]^n [Cu^{2+}]^s$$

Values of the exponents $n$, $m$, and $s$ were determined from the rate curves of a number of experiments performed at varying cupric ion and molecular oxygen concentrations. The order of reaction with respect to Cu$^{2+}$ was determined from the rate plots in Fig. 16 which represent a series of experiments at constant initial FeSO$_4$ and O$_2$ concentration with various amounts of CuSO$_4$ present. As a measure of the rate of the cupric catalyzed reaction, the difference in the reciprocal of time ($1/t_x$) required for oxidation of a given percent of reaction ($x$) was used. Log ($1/t_x$) is plotted vs. log Cu$^{2+}$ for several values of ($x$)(20% and 22%) in Fig. 18. Both lines have slopes close to 0.5, suggesting that this is the value of the order of the reaction with respect to Cu$^{2+}$ (i.e. $S = 0.5$).
Figure 16. Effect of The Addition of up to 1.25 Gm/L of Cupric Ion; 100°C; 3 Atm. O₂; 0.08M H₂SO₄.
Figure 17. Second Order Plots for Variable Amounts of Cupric Ion Catalyst; 100°C; 3 Atm. \( \Phi_2 \); 0.08 M \( \text{H}_2\text{SO}_4 \).
Figure 18. Log-Log Plot For Difference in Ratio (Rate With Cupric Ion Present Minus Rate in Absence of Cupric Ion) vs Cupric Ion Concentration; 100°C; 3 Atm. O₂; 0.05M H₂SO₄.
Figure 18. Log-Log Plot For Difference in Ratio (Rate With Cupric Ion Present Minus Rate in Absence of Cupric Ion) vs Cupric Ion Concentration; 100°C; 3 Atm. O₂; 0.08M H₂SO₄
The rate constants as determined from the slopes of the curves in Fig. 17 have been plotted vs. the square root of the Cu$^{++}$ concentration in Fig. 19. It will be noted that in the presence of more than 0.35 gm/L of Cu$^{++}$ the catalyzed reaction ceases to be second order with respect to ferrous ion. The empirically observed order of reaction in cupric ion (0.5) is therefore only valid for the specific conditions of temperature, pressure, et cetera, stated in Fig. 19, and in the presence of less than 0.35 gm./l Cu$^{++}$. Unfortunately it was not possible to reexamine the system in the presence of higher acid concentrations because of the inability of the autoclave to withstand corrosive attack.

A similar procedure was used to evaluate the order of the copper catalyzed reaction with respect to O$_2$. A series of experiments was conducted with 0.34 gm./l Cu$^{++}$ present, in which the oxygen partial pressure was varied between one and four atmospheres. Rate plots for these experiments are given in Figure 20; and the log of the difference in rates, with and without cupric ion present (1/tx), vs. the log of the oxygen partial pressure is given in Fig. 21. The slope of this plot is 1.0 indicating that the catalyzed reaction is also first order in oxygen. This is in contrast to Huffman and Davidson$^{12}$ who reported the cupric ion catalyzed reaction to be zero order in oxygen.

The data from Fig. 20 has been replotted in Fig. 22 as the reciprocal of the ferrous ion concentration vs. the time. Rate constants obtained from the latter have been
Figure 19. Relationship Between Square Root of Cupric Ion Concentration and Catalyzed Rate of Oxidation of Ferrous Sulphate; 100°C; 0.34 Gm/L Cu²⁺; 0.08M H₂SO₄
Figure 20. Effect of Variable Oxygen Partial Pressure Upon The Cupric Ion Catalyzed Oxidation of Ferrous Sulphate; 100°C; 0.34 Gm/L Cu²⁺; 0.08M H₂SO₄
replotted against the oxygen partial pressure in Fig. 23. Although the resulting line does not pass through the origin the correlation is sufficiently reliable to confirm a catalyzed reaction which is first order in oxygen.

The above data, within the limits outlined \((P = 1, Cu^{++} = 0.35 \text{ gms/l}, \text{Temp} = 100^\circ\text{C})\), fit an empirical equation of the form:

\[
\frac{-d[Fe^{++}]}{dt} = k \left[Fe^{++}\right]^2 \text{O}_2 + k_2 \left[Fe^{++}\right]^2[\text{O}_2][Cu^{++}]^{1/2} - - - (13)
\]

At \(100^\circ\text{C}\), \(k_2\) was found to be \(45.5\) liters\(^{1/2}\) mole\(^{-1}\) atm\(^{-1}\) hr\(^{-1}\).

DISCUSSION OF RESULTS

The results outlined above are similar to those observed by several previous investigators as mentioned in the introduction. George\(^{11}\) attempted to explain the variation in acid strength by the following mechanism:

\[
\text{Fe}^{++} + \text{O}_2 \rightleftharpoons \text{Fe}^{++}\text{O}_2 - - - - - - - - - - - (18)
\]

\[
\text{Fe}^{++}\text{O}_2 + \text{H}_2\text{O} \cdot \text{Fe}^{++} \rightleftharpoons \text{FeO}_2	ext{H}^{++} + \text{H}_2\text{OFe}^{++} - - - (19)
\]

He states that the existence of the ion pairs in equation (19), the rate controlling step, was proven by Evans, George, and Uri. The equilibria for the ion pairs, equations (20) and (21), in conjunction with equations (18) and (19), account for the reduction of molecular oxygen to hydrogen peroxide.

\[
\text{FeO}_2	ext{H}^{++} + \text{H}^{+} \rightleftharpoons \text{H}_2\text{O}_2 + \text{Fe}^{3+} - - - - - - - - - - - (20)
\]

\[
\text{Fe}^{++}\text{OH} + \text{H}^{+} \rightleftharpoons \text{H}_2\text{O} + \text{Fe}^{3+} - - - - - - - - - - - (21)
\]
Figure 21. Log-Log Plot of Cupric Ion Catalyzed Reaction vs Oxygen Partial Pressure; 100°C; 0.34 M/L Cu²⁺; 0.08 M H₂SO₄.
Figure 22. Effect of Oxygen Partial Pressure Upon Rate of Catalyzed Oxidation of Ferrous Sulphate; 0.34 Gm/L Cu^{++}; 0.08M H_{2}SO_{4}; 100°C
Figure 23. Effect of Oxygen Partial Pressure Upon Rate of Catalyzed Oxidation of Ferrous Sulphate; 0.34 Gm/L Cu\(^{++}\); 0.08M H\(_2\)SO\(_4\); 100°C
George attributes the small dependence on $H^+$ to the ionization of one of the water molecules solvating the complex. The dependence on the square of the ferrous ion concentration and the first power of the oxygen concentration, as well as the effect of hydrogen ion, are thus explained. The overall reaction may be written as follows:

$$2Fe^{++} + O_2 + 2H^+ \rightarrow 2Fe^{3+} + H_2O_2$$

This explanation satisfies all the observations of the present experiment for the uncatalyzed reaction. However, insufficient data concerning the effects of hydrogen ion and temperature was obtained to postulate a mechanism for the catalyzed reaction.

Huffman and Davidson have proposed two empirical equations to fit the results which they observed. Thus the rate is given by an equation of the form:

$$-d \left[ Fe^{++} \right] \frac{dt}{dt} + k_b \left[ Fe^{++} \right] P_2 + k_t \left[ Fe^{++} \right]^2 P_2 \rightarrow$$

The value of the bimolecular rate constant at 159°C and 1N $H_2SO_4$ media, as previously referred to, is $1.60 \times 10^{-3} \text{ M}^{-1} \text{ atm}^{-1} \text{ sec}^{-1}$, while the rate constant for the bimolecular reaction is only about one hundredth of this value ($1.93 \times 10^{-5} \text{ atm}^{-1} \text{ sec}^{-1}$). These workers also observed a slight dependence on complexing anions, with greater complexing of $Fe^{++}$ favouring the bimolecular path. Also, as stated previously they found that the copper catalyzed reaction is zero order in oxygen.
Obviously, the observations of the latter investigators are not in accord with the results of the present experiment. No significant variation in molecularity was noted when a large amount of sulphate, a known complexing anion, was added to the system. Yet, high ferrous sulphate concentrations favoured a molecularity even greater than three. On the other hand an increase of the hydrogen ion concentration was seen to decrease the observed molecularity. It therefore seems likely that the difference between the order with respect to ferrous ion as determined in the present experiment, and that determined by Huffman and Davidson, is the result of variation in the acidity of the two systems, and the mechanism proposed by George is thought to be the best explanation for the probable mechanism.

In this first part of the investigation a rate equation for the oxidation of ferrous sulphate, which is applicable under limited conditions, has been established. Also, a rate equation for the cupric ion catalyzed reaction, under even more restricted conditions than the former, has been determined. Rate constants and activation energies have been calculated and checked against previously determined values where possible. The first phase of the investigation was terminated at this point.

OXIDATION OF PYRITE

The purpose of this investigation was to establish the kinetics of the oxidation of pyrite by molecular oxygen
under commercial hydrometallurgical conditions, and to provide information from which a reaction mechanism could be elucidated. The effects of the variables shown in Table III on the kinetics of the oxidation of pyrite and the distribution of products were studied.

Throughout most of the experiments an initial concentration of \(0.075 \text{ M H}_2\text{SO}_4\) was employed. Higher acidities resulted in corrosion of the autoclave, while lower acidities contributed to hydrolysis of ferric sulphate and precipitation of ferric hydroxide or basic ferric salts.

In addition to the above tests, several large crystals of pyrite were leached in a flask containing dilute sulphuric acid (\(0.1\text{M}\)) through which air was bubbled.

**Effect of Agitation**

Difficulty was experienced initially in establishing a satisfactory impeller speed and depth of solution. The first tests revealed a distinct variation in reaction rate with agitation. This was probably a result of the excessive plastering of pyrite on the upper surfaces of the autoclave, which was noted at the higher rates of agitation. A second set of experiments was then conducted after carefully selecting new conditions which would eliminate the difficulties mentioned above as far as possible. Consistent results were obtained as the impeller speed was increased from experiment to experiment over a range of 600 R.P.M. to 1180 R.P.M. as shown in Fig. 24. All subsequent experiments were made with an impeller speed of 830 R.P.M. and pyrite "B", thus ensuring
Figure 24. Effect of Agitation Upon Oxidation of Pyrite by Molecular Oxygen; 0.25M H₂SO₄; 100°C; 4 Atm. O₂
TABLE III

VARIABLES EXAMINED DURING INVESTIGATION OF
THE OXIDATION OF PYRITE BY MOLECULAR OXYGEN

<table>
<thead>
<tr>
<th>Variable</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial Acid Concentration</td>
<td>0 to 0.15M H$_2$SO$_4$ or HClO$_4$</td>
</tr>
<tr>
<td>Stirring Velocity</td>
<td>600 to 1180 r.p.m.</td>
</tr>
<tr>
<td>Pyrite Surface Area</td>
<td>275 to 540 cm.$^2$/gm.</td>
</tr>
<tr>
<td>Pulp Density</td>
<td>2 to 8% solids (0.165 to 0.66M FeS$_2$/l.)</td>
</tr>
<tr>
<td>$O_2$ Partial Pressure</td>
<td>0 to 4 atm.</td>
</tr>
<tr>
<td>Temperature</td>
<td>100 to 130°C.</td>
</tr>
<tr>
<td>Effects of adding FeSO$_4$, Fe(SO$<em>4$)$</em>{1.5}$ and CuSO$_4$</td>
<td></td>
</tr>
</tbody>
</table>
that the reaction rate would not be controlled by oxygen diffusion.

**Distribution of Products**

Data from a typical experiment is recorded in Table IV, and the same results have been depicted in Fig. 25 by means of rate plots showing changes in the concentration of pyrite and of various oxidation products with time. Fig. 26 shows the distribution of iron and sulphur products vs. the percent pyrite oxidized. The main products of the reaction are seen to be ferrous sulphate, ferric sulphate, sulphuric acid and elemental sulphur. Certain features are evident.

1) the ratio of the molar rates of solution of sulphur and iron is two to one.

2) iron enters solution in the ferrous state, but is gradually oxidized to the ferric form.

3) the kinetics of the reaction appear to be zero order as reflected in the linearity of the rate plots.

4) the fraction of sulphur converted to elemental sulphur has decreased from about 45% to 30% as the leaching progressed.

5) the proportion of sulphur appearing as free $\text{H}_2\text{SO}_4$ remains substantially constant at (7.5%).

These same analytical values are seen to give an excellent material balance in Appendix III.
Figure 25. Oxidation of Pyrite in 0.075M $\text{H}_2\text{SO}_4$ at 110°C; 4 Atm $\text{O}_2$
TABLE IV

TYPICAL EXPERIMENTAL DATA FOR THE
AQUEOUS OXIDATION OF PYRITE

Reaction Temp  -  110°C
Pyrite B    -  200 grams
Oxygen pressure -  60 p.s.i.
H₂SO₄    -  20 cc. (concentrated)
H₂O       -  5000 cc. distilled

<table>
<thead>
<tr>
<th>Sample</th>
<th>Time Minutes</th>
<th>% S⁰ in residue</th>
<th>Fe++ TIT/20cc gms/sample</th>
<th>S-SO₄ Wt. BaSO₄ 4 S gm/1 sample</th>
<th>Fe Total TIT/20cc gm/l</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0.54</td>
<td>1.1</td>
<td>0.28</td>
<td>3.664</td>
<td>2.57</td>
</tr>
<tr>
<td>2</td>
<td>88</td>
<td>6.5</td>
<td>10.8</td>
<td>2.72</td>
<td>0.7089</td>
<td>4.86</td>
</tr>
<tr>
<td>3</td>
<td>190</td>
<td>6.35</td>
<td>13.6</td>
<td>3.41</td>
<td>0.8767</td>
<td>6.02</td>
</tr>
<tr>
<td>4</td>
<td>280</td>
<td>8.22</td>
<td>15.2</td>
<td>3.83</td>
<td>1.0776</td>
<td>7.38</td>
</tr>
<tr>
<td>5</td>
<td>380</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>


Figure 26. Distribution of Products from Oxidation of Pyrite 0.3M FeS₂; 0.075M H₂SO₄; 110°C; 4 Atm O₂
Two of the products ($H_2SO_4$ and $S^0$) were calculated from the following stoichiometric relations:

$$\left[H_2SO_4\right] = \left[SO_4^{2-}\right]_{Total} - \left[Fe^{++}\right] - 1.5 \left[Fe^{+++}\right] - \cdots - \cdots (24)$$

$$\left[S^0\right] = \left[S\right]_{Total} - \left[SO_4^{2-}\right]_{Total} = 2\left[Fe\right]_{Total} - \left[SO_4^{2-}\right]_{Total} - \cdots - \cdots (25)$$

The values of $S^0$ calculated in this manner were checked analytically and found to be in good agreement. Since pH measurements in the range of acidities investigated are insensitive to small changes, sulphuric acid production generally could only be calculated from the stoichiometric relationship (equation 24). Where possible this method was also checked. For example in experiment 45 (Appendix III) the calculated pH change based on the stoichiometric relationship was 1.15 to 0.91 while the measured values were 1.15 and 0.97.

A minor product, a light yellow to brick red precipitate was formed under conditions of low acidity and high temperature. The composition varied, making identification difficult, although chemical analysis suggested that it was likely a basic ferric sulphate or ferric hydr-oxide with varying amounts of ferric sulphate.

**Effect of Initial Acid Concentration**

Results of four experiments in which the initial acid concentration was varied are shown in Fig. 27 and Fig. 28.
Although the acidity appears to have no consistent effect upon the rate of oxidation it has a substantial influence upon the distribution of sulphur products. In the absence of initial acid there was virtually no production of elemental sulphur. On the other hand, when the acidity was high \((H_2SO_4)\) no further acid was produced and the production of elemental sulphur accounted for nearly half of the sulphur in the oxidized pyrite. With initial \(H_2SO_4\) concentrations of 0.02 to 0.075M, intermediate sulphur product distributions were obtained. Therefore, the aqueous acid oxidation of pyrite is not an effective process for the production of sulphuric acid except in weakly acidic solutions.

The distribution of iron products shown in Fig. 28 was not substantially affected by initial acid concentrations. This is to be expected since the rate of oxidation of ferrous sulphate as mentioned previously was found to be only slightly dependent upon the acidity of the oxidizing media.

Comparison of \(H_2SO_4\) and \(HClO_4\)

An experiment was performed in which pyrite was oxidized in a solution containing 0.09 M/l perchloric acid \((HClO_4)\). This has been compared in Fig. 29 with an experiment performed under similar conditions in a solution containing 0.075M/l sulphuric acid. The total rates of oxidation and distribution of sulphur products are seen to be essentially the same. However, the ratio of ferric to ferrous ion is seen to be higher in the sulphuric acid media. This was
Figure 27. Effect of Initial Acid Concentration Upon The Oxidation of Pyrite; 110°C; 4 Atm. O₂

<table>
<thead>
<tr>
<th>INITIAL H₂SO₄</th>
<th>FINAL pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 M/L</td>
<td>1.2</td>
</tr>
<tr>
<td>0.02</td>
<td>1.2</td>
</tr>
<tr>
<td>0.075</td>
<td>1.1</td>
</tr>
<tr>
<td>0.145</td>
<td>0.8</td>
</tr>
</tbody>
</table>

![Graph showing the effect of initial acid concentration on the oxidation of pyrite.](image-url)
Figure 28. Effect of Initial Acid Concentration Upon The Distribution of Products.
to be expected since ferrous ion was noted to be more rapidly oxidized in sulphuric acid than in perchloric acid.\textsuperscript{11,12} Therefore the distribution of sulphur products noted previously is not attributable to the acid anion, but rather to the hydrogen ion.

**Effect of Oxygen Pressure**

Rate plots for a series of experiments in which the partial pressure of oxygen was varied from 0 to 4 atm. are given in Fig. 30. The rates of oxidation of pyrite, determined from the slopes of these plots, have been plotted in Fig. 31, showing a direct dependence upon the oxygen partial pressure.

Results from a further experiment performed in the absence of oxygen are shown in Fig. 32. The average rate of dissociation of pyrite over the first one hundred minutes is found to be $4.3 \times 10^{-5}$ m l$^{-1}$ min$^{-1}$. However, the rate is seen to drop off rapidly although the stoichiometric relationship only accounts for consumption of 15 percent of the acid up to this point. The effect noted above is therefore likely attributable to the decomposition of small amounts of oxidized pyrite or pyrrhotite by sulphuric acid and perhaps direct attack of pyrite by traces of oxygen dissolved in the aqueous medium. It is believed then that in spite of the obvious formation of hydrogen sulphide in the absence of oxygen (the odour of H$_2$S was easily detectable) the dissociation of pyrite by a mechanism such as equation 3.
Figure 30. Oxidation of 0.33M FeS₂ in 0.075M H₂SO₄ at 110°C and Various Oxygen Pressures.
Figure 31. Dependence of the Oxidation Rate at 110°C on the Oxygen Pressure.
Figure 32. Direct Dissociation of Pyrite by Sulphuric Acid.
does not account for a significant contribution to the overall rate of dissociation of pyrite in the presence of molecular oxygen.

**Effect of Pulp Density and Surface Area**

The effect of surface sites upon the reaction rate was measured by varying the initial pulp density of the system for a series of experiments. These tests did not account for possible reduction of both pulp density and surface area as any one reaction progressed. Since the maximum extent of dissociation was fifty percent, the probable dependence of the concentration of surface sites upon extent of reaction should be considered prior to an investigation of the effects of varying initial pulp densities.

If a particle remained a perfect sphere throughout a reaction of 40%, by weight, the overall surface area would be reduced by only 28%. As is well known the particle would not remain a perfect sphere. Such a particle would be pitted and differentially corroded, possibly even broken into smaller fractions. For this reason the number of potentially effective surface sites available for reaction is likely fairly constant for at least the initial 25% to 35% of conversion.

Plates 1, 2, and 3 show the alterations occurring on the pyrite surface as oxidation progresses at 95°C in 0.1N sulphuric acid under 0.2 atmospheres of oxygen. It will be noted that the initial corrosion is concentrated along minute scratches, followed by random pitting of the
intervening surfaces. Aside from indicating the progress of the oxidation these photographs provide evidence for the differential corrosion mentioned in the previous paragraph.

The initial pulp density was varied in a series of four experiments by the addition of different weights of pyrite powder to equal volumes of solution. Since all four charges of pyrite had similar size distributions the surface area, or concentration of surface sites was the only variable. The effects of varying the specific surface area and the pulp density are shown in Fig. 33, where the rates of oxidation correspond to the slopes of the curves. These rates have been plotted to show a direct dependence upon pyrite surface area in Fig. 34. Since the reaction thus
Plate 2. Pyrite Surface after 1½ hrs. leaching @ 95°C in .1N \( \text{H}_2\text{SO}_4 \)
\( \text{O}_2 \) partial pressure = 0.2 Atm.

Plate 3. Pyrite Surface after 15 hrs. leaching @ 95°C. in 0.1N \( \text{H}_2\text{SO}_4 \)
\( \text{O}_2 \) partial pressure = 0.2 Atm.
appears to be determined by a heterogeneous mechanism at the pyrite surface the possibility of the energy of surface sites being sufficiently altered by grinding to effect the reaction rate was investigated. Slurries with different particle size distributions, but constant pulp densities, were leached and the resulting reaction rates observed. The results of two tests have been plotted on Fig. 34, from which it is evident that the particle size distribution within the range investigated does not affect the reaction rate, i.e., the reaction rate depends only on the total surface area and not on the size of individual particles.

The empirical rate constant for the oxidation of pyrite shown in equation 26 may now be calculated at 110°C.

\[ - \frac{d[\text{FeS}_2]}{dt} = k_3 A_{\text{FeS}_2} [\text{PO}_2] \quad (26) \]

The average rate of oxidation of pyrite is equal to the slope of the plot in Fig. 34. This is \(1.47 \times 10^{-8}\) moles \(\text{min}^{-1} \text{cm}^{-2}\) at 110°C and 4 atm. oxygen partial pressure.

The distribution of reaction products is shown in Fig. 35. The distribution of sulphur products is essentially constant, but the ratio of ferric to ferrous ions, while independent of specific surface area, increases with increased pulp density. This may be explained by the fact that the rate of oxidation of ferrous to ferric ion is second order in

\* \(\text{FeS}_2\) is "concentration" of pyrite in m/l.

\(A_{\text{FeS}_2}\) is the apparent surface area of pyrite.

\(\text{PO}_2\) is partial pressure of oxygen in atm.
Figure 33. Effect of Pulp Density and Surface Area of the Oxidation of Pyrite. 0.075M H₂SO₄; 110°C; 4 Atm. O₂
Figure 34. Dependence of the Rate of Oxidation at 110°C, 4 Atm O₂ on The Pyrite Surface Area.
ferrous; therefore, higher concentrations of the latter favour the formation of ferric ion.

**Effect of Temperature**

Increasing the temperature resulted in considerably increased reaction rates as shown in Fig. 36. The temperature coefficient of the rate, as shown in Fig. 37, corresponds to an activation energy of 13.3 (± 2) k cal./mole. Warren found the activation energy for the oxidation of pyrite to be 20 k cal./mole, which is appreciably higher, although the discrepancy is not surprising. His experiments were performed in a much higher temperature range (130 to 210 °C) where the significance of the direct attack by molecular oxygen might be appreciably different. However, both values indicate that the rate controlling step is a chemical reaction rather than a diffusion process.

The experimental values for temperature, pyrite surface area, and oxygen partial pressure give the following value for $k_3$ in equation (26):

$$k_3 = 0.125 \exp\left(-\frac{13,300}{RT}\right) \text{ m. cm.}^{-2} \text{ atm.}^{-1} \text{ min.}^{-1}$$

The variation of temperature had a considerable effect upon the distribution of products, especially sulphur. Fig. 38 shows the marked increase in percentage sulphur converted to sulphuric acid at the expense of elemental sulphur as the temperature is increased. This is likely why Warren did not observe any sulphur during his investigation. The ferric to ferrous ratio increases slightly with temperature.
Figure 35. Effect of Pulp Density And Surface Area on The Distribution of Products. O 0.75M H₂SO₄; 110°C; 1 Atm. O₂.
Figure 36. Oxidation of 0.33M FeS$_2$ in 0.075M H$_2$SO$_4$
By 4 Atm. O$_2$ at Various Temperatures.

TEMPERATURE
- ▲ 100 °C
- □ 110
- ○ 120
- △ 130

TIME - MINUTES

OXIDIZED

FeS$_2$

PERCENT

OxIDIZED

FeS$_2$
Figure 37. Arrhenius Plot For The Oxidation of Pyrite in 0.075M \( \text{H}_2\text{SO}_4 \) by 4 Atm. Oxygen in The Temperature Range 100°C - 130°C.
Figure 38. Effect of Temperature on the Distribution of Oxidation Products. 0.33M FeS₂; 0.75M H₂SO₄; 4 Atm. O₂
as would be expected in view of the results of the study of this ratio made in the absence of pyrite.

**Effect of Ferrous and Ferric Sulphates**

It has been previously indicated in equations (5) and (6) that ferric ion may contribute substantially to the oxidation of pyrite. Therefore the effect of both ferrous and ferric sulphate, which accumulate in the solution, must be considered. The results of an experiment in which 0.33 m/l of pyrite was leached at 110°C in the absence of oxygen in a solution containing 0.075 M sulphuric acid and 0.055 M ferric sulphate are depicted in Fig. 39. The ferric ion is seen to be rapidly reduced with the accompanying decomposition of a small amount of pyrite. The initial rate of oxidation of pyrite may be appreciable but the effective rate over a period of time is small compared with that resulting from direct decomposition by molecular oxygen for two reasons:

1) the stoichiometric requirements of ferric sulphate are adverse to the decomposition of appreciable amounts of pyrite.

2) the rate of re-oxidation of ferrous sulphate to ferric sulphate is comparatively low.

Therefore, the catalysis of the oxidation of pyrite in the temperature range considered (100°C to 130°C) by ferrous and ferric sulphate is not significant. This agrees with experimental results in which the initial concentration of
Figure 39. Oxidation of Pyrite by 0.075M Sulphuric Acid solution containing 0.1055M Ferric Sulphate at 110°C in The Absence of Oxygen.
iron sulphates was increased in the presence of several atmospheres of molecular oxygen and no apparent increase in rate noted.

The comparatively high apparent rate of oxidation of pyrite by ferric ion observed initially may also be partially attributed to the presence of small amounts of oxidized material or pyrrhotite which are easily decomposed.

Effect of Copper Sulphate

Cupric ion as copper sulphate was added in various amounts up to 0.077M to the leaching solution. As shown in Fig. 40 the apparent rate appeared to be reduced initially, but increased slightly as each experiment progressed. Since the magnitude of the effect is slight and no consistent trend is evident this observed decrease in rate in the presence of cupric ion may be the result of experimental error. On the other hand this effect may be possibly attributed to the increase in the rate of oxidation of ferrous sulphate which might compete with the direct decomposition of pyrite by molecular oxygen in the region of the pyrite surface. The slight increase in the rate of decomposition of pyrite as the reaction proceeds would then be the result of a small but significant contribution to oxidation by ferric ion. No change in the distribution of sulphur products could be noted although a definite trend towards increased ferric to ferrous ion was evident (Fig. 41). This was to be expected since the oxidation of ferrous ion was found to be catalyzed by cupric ion. Therefore, in the presence of cupric
Figure 40. Effect of Copper Sulphate on The Oxidation of 0.33M Pyrite in 0.075M Sulphuric Acid at 110°C, 4 Atm. O₂
Figure 41. Effect of Cupric Sulphate on the Ferric Ion to Ferrous Ion Product Ratio.

0.33M FeS$_2$; 0.075M H$_2$SO$_4$; 110 ℃; 4 Atm. O$_2$. 
ion the catalysis of the oxidation of pyrite by the cyclic oxidation of ferrous ion and reduction of ferric ion may be just significant. However, since both the distribution of sulphur products and the overall rate of pyrite oxidation are not significantly altered by additions of cupric ion it may be assumed that the direct decomposition of pyrite by molecular oxygen is not catalyzed. This is of interest as it had been suggested previously that cupric ion catalyzes the decomposition of pyrite by a mechanism of the form shown in equation (27).

**Formation of Elemental Sulphur**

The formation of elemental sulphur during the oxidation of pyrite is of interest for several reasons, the more important of these being the ability of molten sulphur to occlude sulphides, protecting them from further leaching. Of lesser importance is the possible economic value of free sulphur produced by this method.

Downes and Bruce observed that pyrite is oxidized almost entirely to iron sulphates and sulphuric acid. On the other hand the present work has revealed that as much as 50% of the sulphur can be liberated in the elemental form. Further values for the extraction of elemental sulphur are given in Appendix III.

The above results indicate that elemental sulphur is produced primarily by reaction (1) and that equations (3) (5) (7) and (9) do not contribute significantly. This
is in accord with the observed result that as much as 50% of the sulphur leached may be found in the elemental form. Also, it is in agreement with the observed results that the ferrous ion, ferric ion, cupric ion, hydrogen ion, and sulphate ions do not materially affect the rate of decomposition of pyrite in the presence of appreciable oxygen, (i.e., pyrite is substantially decomposed by direct combination with molecular oxygen).

The above results also indicate that the formation of elemental sulphur is favoured by high acidities and low temperatures.
DISCUSSION

The observed kinetics of the oxidation of ferrous ion in acid (.1N) sulphate media by molecular oxygen are satisfied by an equation of the form:

\[-d\left[\text{Fe}^{++}\right]/dt = k \left[\text{Fe}^{++}\right]^2 \left[O_2\right]\]

The constant k is equal to \(6 \times 10^7 \exp(-16,500/RT)\) l.m.\(^{-1}\) atm.\(^{-1}\) min.\(^{-1}\). The reaction shows a slight dependence on hydrogen ion concentration which may be expressed empirically in the range (.1N - .6N) by the factor \(H^+ - .33\). The best explanation for this \(p_H\) dependence is that one of the ferrous ions in the rate controlling step is coupled with a water molecule, and it is the ionization of this molecule that is affected by changes in acidity. The oxidation of \(\text{Fe}^{++}\) has been found to be catalyzed by small amounts of cupric ion. For limited conditions (.1NH\(^+\), Cu\(^{++}\) .35 gm/l, 100°C) the reaction fits an empirical rate equation of the form:

\[-d\left[\text{Fe}^{++}\right]/dt = k \left[\text{Fe}^{++}\right]^2 \left[O_2\right] + k_2 \left[\text{Fe}^{++}\right]^2 \left[O_2\right] \left[Cu^{++}\right]^{1/2}\]

The value of \(k_2\) was determined to be \(45.5 l^{1/2} m^{1/2} atm.^{-1} hr.^{-1}\).

The oxidation of pyrite by molecular oxygen in acid media may be effected by at least three parallel reactions. The predominant of these is the direct oxidation of sulphur atoms by molecular oxygen as suggested by the following mechanism.
(1) \( \text{O}_2 \) is chemisorbed rapidly on the pyrite surface, which is thus always covered by a mono-layer of oxygen, comprised of one \( \text{O}_2 \) molecule at each \( \text{FeS}_2 \) site, i.e.

\[
\text{FeS}_2 + \text{O}_2 \text{(aq)} \xrightarrow{\text{fast}} \text{FeS}_2\text{O}_2 - - - - - - (28)
\]

(ii) The slow step in the reaction is the attack of a second \( \text{O}_2 \) molecule on an \( \text{O}_2^- \) covered site, i.e.

\[
\text{FeS}_2 \text{O}_2 + \text{O}_2 \text{(aq)} \xrightarrow{k_3 \text{ slow}} \text{FeS}_2\text{O}_2 \text{O}_2 \xrightarrow{+} \text{FeSO}_4 + \text{S}^0 - - (29)
\]

This accounts for the observed dependence of the reaction rate on both the pyrite surface area and the concentration of molecular oxygen in solution. The overall apparent activation energy of \( 13 \pm 3 \) kilocalories and a frequency factor corresponding to an apparent entropy of activation of about \(-18 \text{ cal/mole } ^\circ \text{C} \) (the standard state of \( \text{O}_2 \) being taken as the dissolved molecule at a concentration of 1 m/l) are both plausible for the proposed mechanism (see Appendix IV for entropy calculation).

Both sulphuric acid and ferric sulphate contribute to the observed oxidation of pyrite, at least in the initial stages of decomposition. However, whether this is a true oxidation of pyrite or an attack of small amounts of surface oxidized material or pyrrhotite was not determined. The results have shown that in the presence of moderate oxygen pressures these reactions do not contribute substantially to the overall decomposition of pyrite, i.e., reactions represented by equations (3) (5) (6) (7) (8) (9) and (10) are
not significant.

Cupric ion has been found to increase the ratio of ferric to ferrous ion without substantially altering either the rate of oxidation of pyrite or the distribution of sulphur products.

Low acidities and high temperatures have been found to favour the formation of sulphuric acid. The opposite conditions favour the production of elemental sulphur.

According to the above results sulphuric acid may be produced in one of two ways.

(i) Elemental sulphur is oxidized according to equation (30).

\[ 2 \text{S} + 3\text{O}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{H}_2\text{SO}_4 \] (30)

This reaction must be favoured by low acidities and high temperatures.

(ii) Elemental sulphur may not be an intermediate in the formation of sulphuric acid. Sulphuric acid and elemental sulphur may be formed by simultaneous competing reactions corresponding to equations (1) and (2) from the intermediate formed in the rate determining step equation (29).

These results suggest that separate investigations of the oxidation of elemental sulphur and pyrrhotite by molecular oxygen should be most enlightening.
BIBLIOGRAPHY


APPENDIX I

Relationships between particle size and surface area have been determined using solution methods and reported by Gross of the U.S. Bureau of Mines. This data has been used as presented by Brown who has given the values of surface area as a function of the average diameter of particles able to pass through a given Tyler screen opening.

A sample of the pyrite used in this investigation was analyzed with Tyler standard \( \sqrt{2} \) series screens from #65 to 270 mesh. The -270 mesh material was further analyzed by elutriation methods employing a Roller analyzer. All fractions were mounted, polished and examined under the microscope. The largest particle diameters were determined for each fraction and have been plotted in Fig. 42. The diameters of openings of Tyler screens have also been plotted on the same graph. Based on the assumption that the shape factor is constant for different sizes of particles, the line representing Tyler screen sizes has been extended to permit conversion of measured largest diameters observed into equivalent screen sizes. The average diameter for any fraction has been taken as the dimension midway between the largest equivalent Tyler screen diameter of the fraction considered and the largest equivalent Tyler screen diameter of the next smaller size range. The specific surface area based on this average diameter has been multiplied by the mass of the fraction to give the surface area of that fraction. The following values were obtained on the basis of 100 grams of pyrite "B".
Figure 42. GRAPH TO CONVERT MEASURED MAX DIAMETERS TO EQUIVALENT MAX DIAMETERS OF SCREEN OPENING FOR PYRITE
The average specific area for pyrite B is therefore 533 cm.\(^2\) per gram.
PARTIAL PRESSURE OF OXYGEN IN ATMOSPHERES EQUALS THE MOLE FRACTION OF OXYGEN IN WATER $x^O_2$.

APPENDIX II

SOLUBILITY OF OXYGEN IN WATER AT VARYING TEMPERATURES
APPENDIX III

The material balances tabulated here have been calculated on the basis of an iron balance. Since five 75 cc samples were removed during the course of each run, the final analyses have been applied to an arbitrary mean value of 4800 cc. The weight of iron dissolved has been calculated from solution analyses for total iron and deducted from the weight of iron in the original pyrite to obtain the weight of iron in the residue. From this value, and analyses of the residue have been calculated the weights of the residue products.

The sulphate analysis has been corrected for sulphuric acid added initially.
<table>
<thead>
<tr>
<th>PYRITE</th>
<th>IN</th>
<th>SOLID</th>
<th>SOLUTION 4800 cc.</th>
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<td>ASSAY</td>
<td>GMS.</td>
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<td></td>
<td>Fe</td>
<td>S</td>
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<tr>
<td>200 gms</td>
<td>46.2</td>
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APPENDIX IV

Determination of Entropy of Activation

\[ - \frac{d}{dt} \left[ \text{FeS}_2 \right] = k_4 \left[ A_{\text{FeS}_2} \right] [O_2] \]

where \( \left[ A_{\text{FeS}_2} \right] \) is the macroscopic surface area of pyrite in cm.\(^2\) l\(^{-1}\),

and \([O_2]\) is concentration of oxygen in ml\(^{-1}\)

with \( \left[ A_{\text{FeS}_2} \right] \) and \([O_2]\) in the above standard states

\[ - \frac{d}{dt} \left[ \text{FeS}_2 \right] \text{ is in moles cm}^{-2} \text{ sec}^{-1} \]

\[ E_a = RT + \Delta H^\pm \text{ and } E_a = 13,300 \text{ cal. m}^{-1} \]

\[ \Delta H^\pm = 13,300 - 383 (1.98) = 12,500 \text{ cal. m}^{-1} \]

\[ [O_2] = 324 \times 10^{-5} \text{ ml}^{-1} @ 383^\circ \text{K; 4 atm. O}_2 \]

\[ - \frac{d}{dt} \left[ \text{FeS}_2 \right] = \text{ moles Fe}^{++} \text{ cm}^{-2} \text{ sec}^{-1} \]

\[ = \frac{6.2 \times 4.8 \times 1}{(55.85) (380) (60) (106,700)} = 2.2 \times 10^{-10} \text{ mm cm}^{-2} \text{ sec}^{-1} \]

The density of pyrite given in Dana is approximately 5.0.\(^{21}\) The number of molecules of pyrite per cm.\(^3\) is then

\[ \frac{5}{119.85} \times 6.02 \times 10^{23} = 2.51 \times 10^{22} \]
Therefore, the average dimension of molecule equals

\[
\frac{1}{2.51 \times 10^{22}} = 3.42 \times 10^{-8} \text{ cm.}
\]

molecules cm\(^{-2}\) = \frac{1}{(3.42 \times 10^{-8})^2} = 0.0855 \times 10^{16}

moles cm\(^{-2}\) = \frac{8.55 \times 10^{14}}{6.02 \times 10^{23}} = 1.42 \times 10^{-9}

Inserting the above values into the following equation permits a solution of \(\Delta S^+\).

\[
- \frac{d \left[ \text{FeS}_2 \right]}{dt} = \frac{kT}{h} e^{\frac{\Delta S^+/R}{e^{\frac{\Delta H^+/RT}{[\text{FeS}_2][O_2]}}}}
\]

\[
2.2 \times 10^{-10} = \frac{(1.38 \times 10^{-16})(383)}{6.624 \times 10^{-27}} e^{\frac{\Delta S^+}{2.3} e^{\frac{-12.500}{(1.90)(383)}}}
\]

\[
(324 \times 10^{-5})(1.42 \times 10^{-9})
\]

\(\Delta S^+ = -18.4 \text{ cal. m}^{-1} \text{oC}^{-1}\)