STUDIES ON IRON PYRITE

by

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ABSTRACT

The amount of reaction between pyrite and vapor state nitric acid has been analytically determined at 130°, 145°, 160° and 175° C for one hour reaction time, and for one-half, one and two hour reaction times at 160°C. The variation of pressure with time for constant-boiling (68.2 per cent) nitric acid was studied at 130° and 160°C.

The reaction observed between pyrite and vapor state nitric acid followed the possible chain of reactions given below:

$$2 \text{HNO}_3 \rightarrow \text{H}_2\text{O} + 2 \text{NO}_2 + \frac{1}{2} \text{O}_2 \quad (1)$$

$$2 \text{HNO}_3 \rightarrow \text{H}_2\text{O} + 2 \text{NO} + \frac{3}{2} \text{O}_2 \quad (2)$$

$$2 \text{FeS}_2 + \frac{3}{2} \text{O}_2 \rightarrow \text{Fe}_2 \text{O}_3 + 4 \text{S} \quad (3)$$

$$2\text{S}_2 + 2 \text{O}_2 \rightarrow 2 \text{SO}_2 \uparrow$$

$$2 \text{H}_2\text{O} + 2 \text{SO}_3 \rightarrow 2 \text{H}_2\text{SO}_4 \quad (4)$$

$$\text{Fe}_2\text{O}_3 + 3 \text{H}_2\text{SO}_4 \rightarrow \text{Fe}_2(\text{SO}_4)_3 + 3\text{H}_2\text{O} \quad (5)$$

or

$$\text{Fe}_2\text{O}_3 + 3 \text{SO}_3 \rightarrow \text{Fe}_2(\text{SO}_4)_3 \quad (6)$$

with the possible reaction:

$$\text{Fe}_2(\text{SO}_4)_3 + \text{H}_2\text{SO}_4 \rightarrow \text{Fe}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{SO}_4$$
At 160°C the overall reaction was found to be of an apparent zero-order as was also that for the formation of ferric sulfate and ferric oxide, over the range of almost 100 per cent decomposition of the nitric acid. The maximum amount of pyrite used was about 11 per cent. Experimental results show that reactions (3), (4), (5) and (6) must all be surface reactions.

A decrease in the rates of the reactions was noted between 145° and 160°C. This was most probably caused by the change in the physical and chemical properties of sulfur in this range, and indicates that elemental sulfur has a significant retarding effect on the rate of the overall reaction.
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INTRODUCTION

In the past much work has been done on the reactions of iron pyrite. The work, in general, has been carried out with the idea of commercial use of pyrite as a source of sulfur, sulfur dioxide and iron oxides. Apart from the production of sulfur dioxide, these studies have led to a few processes such as that used by Camstock-Wescott Inc. of Niagara Falls, New York, and of Noranda Mines Ltd. at Port Colborne, Ontario. However, there has been no generally accepted process developed primarily for the production of sulfur from pyrites.

Investigators in this field have worked with carbon and its oxides (16, 24, 28, 38, 44), hydroden (12, 43), water or steam (16, 24, 27, 29, 37), sulfur dioxide (1, 35, 49, 50), chlorine, hydrochloric acid or chlorinating gases (2, 7, 11, 13, 18, 31, 42), and other miscellaneous chemicals (9, 23, 36). No evidence of any work was found on the use of nitric acid as a reagent with pyrite (except for the solution of pyrite samples for analysis (20) ), and it was the purpose of this project to investigate the mechanism of the reaction of iron pyrite with nitric acid in the vapor state through the temperature range of 130 - 175°C.
THEORY AND RELATED LITERATURE

In the literature there was found considerable confusion as to the nomenclature of the nitrogen oxides. In this thesis the following system has been used:

- $N_2O$ nitrous oxide, or nitrogen monoxide
- $NO$ nitric oxide
- $N_2O_3$ nitrogen trioxide
- $NO_2 (N_2O_4)$ nitrogen dioxide or tetroxide
- $N_2O_5$ nitrogen pentoxide

Dissociation of Nitric Acid and Nitrogen Dioxide.

In a study of the properties of nitric acid, J. Dalton (15) pointed out that when a concentrated or dilute solution was boiled at atmospheric pressure the boiling point reached 120.5°C after which the distillate did not change. H.E. Roscoe (41) found that the composition of this constant boiling mixture contained 68 weight percent nitric acid and it had a specific gravity of 1.414 at 15.5°C. However, if the solution was distilled under increased or decreased pressure the composition of the constant boiling mixture changed. H. J. Creighton and J. H. Githens (14) found that the maximum boiling point at 760 mm Hg was 121.70°C giving a solution containing 68.18 percent nitric acid; at 360 mm, 99.9°C. for a 67.15 percent nitric acid solution; and at 110 mm, 74.2°C for a 66.8 percent nitric acid solution.
When nitric acid is heated it decomposes. According to P. Braham and J. W. Gatehouse (6), and H. Bottger (5) all the nitrogen oxides as well as nitrogen and oxygen are formed. On the other hand, L. Carius (10) found that nitric acid decomposed according to the reaction:

$$4 \text{HNO}_3 \rightarrow 4 \text{NO}_2 + 2\text{H}_2\text{O} + \text{O}_2$$

being entirely decomposed at 256°C. Measuring the progress of the decomposition by vapor density methods he found:

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>D</th>
<th>a%</th>
<th>v (c.c.)</th>
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<tr>
<td>86</td>
<td>2.05</td>
<td>9.53</td>
<td>9.43</td>
</tr>
<tr>
<td>100</td>
<td>2.02</td>
<td>11.77</td>
<td>10.41</td>
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<tr>
<td>130</td>
<td>1.92</td>
<td>18.78</td>
<td>16.62</td>
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<td>160</td>
<td>1.79</td>
<td>28.96</td>
<td>26.22</td>
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<tr>
<td>190</td>
<td>1.59</td>
<td>49.34</td>
<td>43.69</td>
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<tr>
<td>220</td>
<td>1.42</td>
<td>72.07</td>
<td>63.77</td>
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<tr>
<td>250</td>
<td>1.29</td>
<td>93.03</td>
<td>82.30</td>
</tr>
<tr>
<td>256</td>
<td>1.25</td>
<td>100.0%</td>
<td>88.47 c.c.</td>
</tr>
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where D is the vapor density, a, the per cent dissociation and v, the volume of oxygen in cc. per gram of nitric acid.

M. Berthelot (3) also worked on the decomposition of nitric acid. In his experiments at 100°C he found that nitrogen dioxide and oxygen, but no nitrogen or nitrous oxide were formed. The oxide did not exist in the presence of free oxygen. He concludes from his data that nitric acid is decomposed according to the equation:

$$2 \text{HNO}_3 \rightarrow 2 \text{NO}_2 + \text{H}_2\text{O} + \frac{1}{2} \text{O}_2$$

In their thermodynamic study of nitric acid, Forsythe and Giauque (19) consider two reactions:
\[
2 \text{NO}_2 + \text{H}_2\text{O} + \frac{1}{2} \text{O}_2 \rightarrow 2 \text{HNO}_3 \quad 1
\]
\[
2 \text{NO} + \text{H}_2\text{O} + \frac{3}{2} \text{O}_2 \rightarrow 2 \text{HNO}_3 \quad 2
\]

They give values of the equilibrium constants for these reactions over a range of 275-500°K. The values of \(K_1\) and \(K_2\) from 375 to 450°K are given in graphical form, in the Appendix, for the reactions written above.

Considering reaction 1 with a 68.2 weight per cent nitric acid and defining \(x\) as the moles of nitric acid dissociated, \(n^o\) as the moles of nitric acid originally present, \(y\) as the fractional dissociation and \(c\) as the moles of excess water present per mole of original nitric acid we have present at any time:

- moles of nitric acid: \(n^o - x\)
- moles of nitrogen dioxide: \(x\)
- moles of water: \(x + c\) \(n^o\)
- moles of oxygen: \(\frac{3}{4}\)

By definition:

\[
K_1' = \frac{(P_{\text{NO}_2})^2 (P_{\text{H}_2\text{O}}) (P_{\text{O}_2})^\frac{1}{2}}{(P_{\text{HNO}_3})^2} = \frac{1}{K_1}
\]

Assuming ideal behavior:

\[
P_A = N_A \tau' = \frac{n_A}{n_t} \tau'
\]

At equilibrium:

\[
K_1' = \frac{y^2 \left( \frac{y}{2} + c \right) \left( \frac{y}{4} \right)^{\frac{1}{2}}}{\left( 1 - y \right)^2} \left[ \frac{\tau'}{1 + \frac{3}{4} y + c} \right]^{\frac{3}{2}}
\]

For a 68.2 per cent acid, \(c = 1.644\), and at 130°C, \(K_1 = 3.00\) atm\(^{3/2}\), so that at atmospheric pressure:

\(y = 0.815\)
or that the acid is 81.5 per cent dissociated at 130°C.

Similarly for reaction 2 we find that:

$$K'_2 = \frac{y^{2}(\frac{y}{\frac{3}{4}} + c)(\frac{3}{2} y)^{\frac{3}{2}}}{(1 - y)^{2}} \left[ \frac{Y^r}{1 + \frac{3}{2} y + c} \right]^{2}$$

Upon substitution of the value of \( c = 1.644 \) and \( K_2 = 1.038 \times 10^{-7} \) atm \( 5/2 \) the equation gives at atmospheric pressure:

$$y = 0.0197$$

or that the acid is 1.97 per cent dissociated at 130°C.

Thus it can be seen that we may consider that reaction 2 has little effect on the dissociation of nitric acid at this temperature.

The dissociation of nitrogen dioxide has also been extensively studied. According to A. Richardson \( (40) \) the vapor density of nitrogen dioxide at 140°C corresponds exactly to the formula \( \text{NO}_2 \) and at higher temperatures the vapor density becomes smaller corresponding, at 619.5°C with the completion of the change:

$$2 \text{NO}_2 \rightarrow 2 \text{NO} + \text{O}_2$$

Thus as soon as the change from \( \text{N}_2\text{O}_4 \rightarrow 2\text{NO}_2 \) is nearing completion the decomposition starts. M. Bodenstein and M. Katayama \( (4) \) in their study of the decomposition obtained different values from those of Richardson. Some of their values of the per cent dissociation are listed in the following table.
Temperature  185°  222°  279°  390°  494°  619°  619.5° C
Values of Richardson
5  13.  56.5  100%
Values of Bodenstein and Katayama
- 4.17  13.10  35.05  58.71  100  - %

While there is fair agreement in their values at higher temperatures there is complete difference in the lower ones. However, it can readily be seen from the kinetic data for the formation and decomposition of nitrogen dioxide given in the International Critical Tables that the dissociation at lower temperatures would be comparatively slow. At a temperature of 590°K (319°C) a reaction velocity constant for the decomposition is given as 61.0 litres²/mole min. while the value for the formation is 670,000 litres²/mole² min. Since the values of the constant for decomposition increase with temperature the values at lower temperatures should decrease. At 470°K (197°C) a value of 791,000 is given for the reaction velocity constant of formation so that the decomposition at this temperature should be very slow.

Absorption of Nitrogen Dioxide

In the absorption of nitrogen dioxide in an aqueous solution the main reactions, according to Burdick (8), are:

\[ 3 \text{NO}_2 + \text{H}_2\text{O} \rightleftharpoons 2 \text{HNO}_3 + \text{NO} \]  
\[ 2 \text{NO} + \text{O}_2 \rightleftharpoons 2 \text{NO}_2 \]

Reaction 1 is a very rapid one but it does not go to completion, stopping at an equilibrium condition short of complete conversion of the nitrogen dioxide. The presence of nitric
oxide above a certain equilibrium concentration can prevent
the reaction of absorption and only as the nitric oxide is
re-oxidized according to reaction 2 can the process continue.
Reaction 2 is a slow reaction. Since the reaction of absorption
and oxidation progress simultaneously they are really mutually
interdependent.

The absorption of nitrogen dioxide is extensively
covered in Mellor (34). There are given the reactions:

\[ 2 \text{NO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HNO}_3 + \text{HNO}_2 \]
\[ 3 \text{HNO}_2 \rightleftharpoons \text{HNO}_3 + 2 \text{NO} + \text{H}_2\text{O} \]

for the absorption process which when summed gives the same
reaction as number 1 above. It is stated that the equilibrium
of the reaction is affected by the partial pressure of the
nitrogen dioxide and the nitric oxide which, in turn, are
influenced by the equilibrium formation of nitrogen trioxide
from nitric oxide and nitrogen dioxide which is a very rapid
reaction. The discussion continues stating that the lower
the partial pressure of nitrogen dioxide, the smaller the
concentration of its solution in water and also of its reaction
with water. A large volume of undissolved gases passing
through the solution causes a rapid evaporation of water and
nitric acid.

J. L. Gay Lussac (21), P. L. Dulong (17) and F.
Raschig (39) working on the absorption of nitrogen dioxide
in an aqueous solution of alkali hydroxides showed that the
those with
reactions were very much like with
water. With a concentrated
alkali-lye solution a mixture of alkali nitrates and nitrites
is formed with a slight evolution of nitric oxide. The primary reaction is:

\[ 2 \text{NO}_2 + 2 \text{KOH} \rightleftharpoons \text{KNO}_3 + \text{KNO}_2 + \text{H}_2\text{O} \]

Discussion of Some Iron Compounds

In the reaction of nitric acid with iron pyrite certain products such as iron nitrites, nitrates, sulfites and sulfates might be possible. Some of these compounds have been investigated as to their probability of formation.

Ferrous nitrite cannot be prepared (45) owing to its immediate decomposition upon formation to give the ferric ion and nitric oxide. Ferrous nitrate (45) is known only in the form of two hydrates which on warming decompose to form the ferric ion and nitric oxide. Ferric nitrate (45) is not known in an anhydrous state but only in the two hydrates with 6 and 9 waters. These hydrates melt at 35° and 47° C, respectively. No complex or double ferric nitrates are known. Ferric nitrite has never been prepared.

The sulfites, in general, are very reactive being easily oxidized to sulfates (47). Ferrous sulfate (48) forms hydrates of 1, 4 and 7 waters which pass through a series of transition points on warming:

\[ 7 \rightarrow 4 \rightarrow 1 \rightarrow 0 \]

56.6° C, 65.0° C, 90° C.
By heating to a higher temperature the anhydrous salt decomposes to give sulfur dioxide, basic ferric sulfate and other products. Ferric sulfate (26) is a very stable compound decomposing at about 700°C into ferric oxide and sulfur trioxide.

Heterogeneous Reactions

In the study of the kinetics of reactions of gases taking place on the surface of solids there have been discovered reactions of zero or fractional orders as well as those of apparently simple order. In some cases one of the reactants may have a retarding influence instead of an accelerating one while in others the products may act as an inhibitor. (22) Langmuir (30) states,

"In a heterogeneous chemical reaction the activity of a surface depends in general upon the nature of, the arrangement of and the spacing of the atoms forming the surface layer."

According to this theory the velocity of reactions, in general, is not limited by the rate of diffusion through an adsorbed film, but by the rate at which the molecules strike the surface which is activated. There are, of course, many chemical reactions which are actually limited by physical factors, such as the rate of diffusion through layers of gases or moderately thick films such as the rusting of iron and the oxidation of aluminum.

According to present theory the mechanism of heterogeneous reactions may be controlled by one or more of a sequence of steps. These steps include physical processes,
such as diffusion of reactants and products to and from the surface of a solid from and to the fluid, and chemical processes, such as adsorption and desorption of reactants and products, and the reaction of activatedly adsorbed reactants on the surface to yield products. Useful rate equations can be derived if the specific sequence of steps (the mechanism of the reaction) is known, and constants in these equations evaluated from experimental data (22) (25A).

The reaction investigated in this work may be considered irreversible and therefore rates of desorption processes and diffusion of products need not be considered. Assuming that the only component of the fluid entering into reaction with the solid on adsorption is oxygen, then the following general mechanisms may occur:

1. The rate of adsorption of oxygen is rate controlling. In this case the reaction rate will be a function of the oxygen partial pressure.

2. Surface reaction rate controls and the equilibrium amount of adsorbed oxygen is not a function of pressure. That is, all available surface sites are saturated with oxygen over the range of experimental conditions covered. In this case, a zero order may be observed.

3. The surface reaction rate controls with the equilibrium amount of adsorbed oxygen of adsorbed oxygen a function of pressure. Reactions of this type will probably be of complex order
Pyrites

Because of its high sulfur context pyrite, FeS$_2$, is commonly thought of as a ferric compound, but actually it is ferrous being the salt of the anion S$_2$$^-$. Its crystal structure may be thought of in two ways. The lattice may be described as being like that of sodium chloride with the sodium ions being replaced by iron and the chlorine by pairs of sulfur atoms (45A). The structure can also be seen as a sulfur atom surrounded tetrahedrally by three iron atoms and one sulfur atom (37A). The bonding is essentially covalent rather than ionic.

Chemically, pyrite is scarcely attacked by anything at ordinary temperatures, but on heating it reacts with many substances. It is known to burn in air forming ferric oxide and sulfur dioxide. Thus it is commonly used in the manufacture of sulfuric acid (45A). At lower temperatures pyrite in the presence of moisture will readily oxidize to ferric sulfate. In analytical procedures pyrite is oxidized by bromine followed by nitric acid and evaporation to dryness on a steam bath to give ferric sulfate (20).

Dr. Strickland (48A) in his studies of the oxidation in aqueous solution of sulfur containing ores has found that pyrite is oxidized in aqueous chlorine dioxide solution to ferric sulfate with no intermediate stage producing sulfur.
This has apparently been the experience also of other investigators working in aqueous solutions with various oxidizing agents.

Viscosity of Sulfur

The values of the viscosity of sulfur are found to vary considerably over the range of temperatures used in this thesis. The viscosity has values (25) close to ten centipoises at the lower temperatures but at 159.5° it starts a sharp increase having reached a value of 77.32 at 160.3° and 4,500 at 171.0°. These values have been plotted (see Appendix).
EXPERIMENTAL APPARATUS

The reaction apparatus, shown in figure I, consisted of three sections; the nitric acid vapor generator; the rotating reactor; and the product gas absorber. All the connections of the apparatus were of glass with the exception of those to the auxiliary manometer and water jet vacuum pump which were of rubber.

The nitric acid vapor generator consisted of a one-litre distillation flask with a thermometer well and a glass cap. In the top of the glass cap was fitted a two-way stopcock. One arm of the stopcock was connected to a single gas absorber, while the other arm was connected to the rotating reactor. The line connecting the flask and the reactor had a branch in which was fitted a glass check valve.

The rotating reactor was made of a spherical section with connectors at either end, the whole assembly rotating in ball and socket joints between two stationary end pieces. The left-hand end piece was a 20 mm. pyrex tube with a male 35/20 ball and socket joint at one end and a three-way capillary stopcock at the other. One branch of the stopcock was connected to the nitric acid vapor generator, and the other branch was connected by rubber tubing to either the water-jet vacuum pump or the cylinder of nitrogen gas. A side tube from this end piece contained a second three-way capillary stopcock, one arm of which was connected to the main mercury manometer, while the other arm was connected by rubber tubing to the auxiliary manometer.
FIGURE 1 - DIAGRAM OF APPARATUS
The rotating section was a three-litre round bottomed flask with two concave dimples which ran across it. The neck of the flask terminated in a female 35/20 ball and socket joint. A female \( \Phi \) joint was connected to the other side of the flask. To this was joined a connector tube with a male \( \Phi \) joint at one end and a male 35/20 ball and socket joint at the other. On this connector tube was fitted a meccano gear, held in place by a spring taper and a paper gasket. The paper gasket was coated with Araldite AN-103 resin after it was in position to prevent any oil from seeping under the gasket and causing slippage.

The right-hand end piece was a 20 mm. tube with a female 35/20 ball and socket joint at one end and a three-way capillary stopcock at the other. One arm of the stopcock was connected to the product gas absorber and the other arm was left open.

The flask was rotated about one-third submerged in a constant temperature both by means of the meccano gear and a Heller 6T60 motor controller and variable speed motor set. The flask and connector tube were kept hot by a film from the constant temperature bath. The oil was run over the reaction vessel by means of a pump and distributor made of bent copper tubing with small holes. The stationary end pieces of the main section and their connectors to the gas absorbers and nitric acid vapor generator were kept hot by a wrapping of electrothermal heating tape.
PROCEDURE

Reaction of Pyrites

The two gas absorbers were filled with a ten percent potassium hydroxide solution (40 ml. in the generator scrubber and 350 ml. in the product gas scrubber). A sample of pyrite (40-80 mesh) was accurately weighted out on an analytical balance and placed in the reaction vessel. The apparatus was assembled being sure that all the joints were well greased with Dow-Corning high vacuum grease. The stopcock (C) was opened to both manometers but the stopcocks (D and A) to the product gas absorber and nitric acid vapor generator were closed. The system and the connections to the generator were evacuated using the water jet vacuum pump. The system was then closed off and the rubber tube was changed from the water pump to the nitrogen tank. The system was filled with nitrogen gas, and the main manometer closed off. The heaters for the constant temperature bath were turned on and the bath brought up to temperature. The Heller motor controller was turned on, the dial set at 4 and the speed of rotation checked to give 6.7 r.p.m. (10 rev. in 89.6 sec). The electrothermal heating tapes were turned on. Next the stopcock (a) on the nitric acid vapor generator was opened to the gas absorber and the flask was gently heated with a Bunsen burner. The system and the connection to the generator were evacuated as before and the stopcock (B) closed, as was the connection to the auxiliary manometer. The main manometer connections remained filled with nitrogen.
When a good stream of vapor was coming from the generator, the system stopcock (B) was opened to the generator and the generator stopcock (A) was quickly switched from the gas absorber to the main system. When the check valve opened indicating that the contents of the reactor were at atmospheric pressure, the system stopcock (B) was closed and the generator stopcock (A) quickly switched back to the gas absorber. The main manometer was opened to the system and the initial pressure recorded. The reaction was carried on for a specified length of time and pressure recorded periodically. The heat was removed from the nitric acid vapor generator and it was allowed to cool. To stop the reaction, the system stopcock (B) was opened to the nitrogen tank and a pressure of a few mm. of Hg. was built up in the system. Then stopcock (D) was opened to the product gas absorber and the issuing gas allowed to bubble through the potassium hydroxide solution at an approximate rate of 1.5 litres per minute for two minutes and then of one litre per minute for fifty minutes. The system was then closed off; the both heaters, the electrothermal heating tapes and the motor controller were turned off. The vessel was then left to cool before extraction.

Analytical Procedure

In the analysis of the reaction products, three extracts were made. The cooled reaction vessel was removed from the constant temperature bath and wiped free of oil. Care was taken to remove all the lubricating grease from the
ball and socket joints. The main portion of the reaction products was transferred to a 250 ml. beaker and the vessel and connection tubes were rinsed with 100 ml. of warm distilled water. The rinse water was then mixed with the main mass of the reaction product. This mixture was filtered through a tared Gooch crucible. The filtrate was rewarmed and passed through the reaction vessel repeating the process. This was done a third time. The vessel and beakers were then rinsed with 100-150 ml. of room-temperature distilled water in small portions and passed through the residue in the Gooch crucible. The above procedure was repeated with warm 4 N HCl. and then with hot potassium hydroxide solution (50 g KOH in 100 ml. of distilled water). The volumes of the three extracts and their washes were recorded and then they were set aside for analysis.

The water extract was analysed for its ferric ion, ferrous ion, and sulfate ion content. The quantity of ferric ion and ferrous ion was determined in the acid extract and a sulfate determination was carried out on the base extract after oxidation with hydrogen peroxide. The analytical methods used were modifications of those given in Scott's Standard Methods of Chemical Analysis (20). Detailed procedures are given in Appendices A, B, C and D.

Other Tests

In the first runs the complete analysis was not made, but a series of spot tests for various ions were performed on
the extracts. The water extract was subjected to the following
tests: the potassium thiocyanate test for ferric ion; the
potassium ferricyanide test for ferrous ion; the permanganate
test for nitrite and sulfite ions; and the barium chloride
test for sulfate ion. The potassium thiocyanate and potassium
ferricyanide tests were run on the acid extract, also. After
oxidation with hydrogen peroxide the basic extract was acidified
and then tested with a barium chloride solution.

At various times certain other checks were performed
on the extracts. The complete extraction and test procedure
was carried out on an unreacted sample of pyrite to be sure
that the pyrite itself did not interfere in the analytical
procedures. A sulfate ion test was run on the acid extract.

A check of the scrubber solution was made by titrating
the original and resultant solutions against a standardized
sulfuric acid solution. With the aid of this check and the
loss in weight of the nitric acid vapor generator a balance
for the nitric acid was made.

The temperature of the vapor from the vapor generator
to the reactor flask was measured with the electrothermal
heating tape turned on. A plastic coated thermocouple was
inserted into the line through the glass joint of the reactor
flask and placed close to the capillary section of the flask
stopcock (B).

The sulfur to iron ratio of the pyrite sample and
of the residue of run number 11 was determined by the method
outlined in Appendix A. The two ratios were compared.
The volume of the apparatus was found by completely filling the assembled apparatus with water and measuring the volume of water in a graduated cylinder.

A study of the variation of pressure over a time interval was made for nitric acid at 130° and 160°C. The measurements were made by carrying out the reaction procedure without the use of pyrite. The manometer was read at ten minute intervals until a constant pressure was obtained.
DATA AND RESULTS

In the experimental work a series of runs were done at a reaction time of one hour with varying temperature. There were duplicate runs made at 130°C and single runs at 145°, 160° and 175°C. Another series of runs were made at 160° for reaction times of 30, 60 and 120 minutes. Data on these two series of runs are presented in Table I and the variations in the total pressure with time in each run are given in Table II and shown in Figures 4 and 4A.

The amounts of each product formed are shown on Figure 2 for the runs at varying temperatures and in Figure 3 for the runs at 160° and varying reaction time.

Data on the runs using nitric acid only are given in Table III and shown graphically in Figures 5 and 6.
# TABLE I - Reaction Data

<table>
<thead>
<tr>
<th>Run No.</th>
<th>1</th>
<th>4</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature°C</td>
<td>140</td>
<td>185</td>
<td>130</td>
<td>130</td>
<td>130</td>
<td>130</td>
</tr>
<tr>
<td>Evacuated to: mm. Hg</td>
<td>732</td>
<td>740</td>
<td>742</td>
<td>739</td>
<td>739</td>
<td>732</td>
</tr>
<tr>
<td>Gas used:</td>
<td>NO₂</td>
<td>NO₂</td>
<td>HNO₃</td>
<td>HNO₃</td>
<td>HNO₃</td>
<td>HNO₃</td>
</tr>
<tr>
<td>Length of run Hr.</td>
<td>9.834</td>
<td>5.25</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>Wt. of pyrite used g.</td>
<td>19.93</td>
<td>9.49</td>
<td>9.38</td>
<td>7.63</td>
<td>6.2966</td>
<td>8.4313</td>
</tr>
<tr>
<td>Wt. of residue g.</td>
<td>-</td>
<td>-</td>
<td>8.14</td>
<td>7.03</td>
<td>5.7443</td>
<td>7.8742</td>
</tr>
<tr>
<td>Amt. reacted</td>
<td>-</td>
<td>-</td>
<td>1.24</td>
<td>0.60</td>
<td>0.5523</td>
<td>0.5571</td>
</tr>
<tr>
<td>Fe---</td>
<td>V.F.</td>
<td>V.F.</td>
<td>0.314</td>
<td>0.117</td>
<td>0.2536</td>
<td>0.2349</td>
</tr>
<tr>
<td>Fe---</td>
<td>N.</td>
<td>N.</td>
<td>0.0126</td>
<td>T.</td>
<td>T.</td>
<td>T.</td>
</tr>
<tr>
<td>H₂O Ext. Permanganate test</td>
<td>N.</td>
<td>N.</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SO₄---</td>
<td>V.F.</td>
<td>V.F.</td>
<td>0.969</td>
<td>0.643</td>
<td>0.7734</td>
<td>0.7504</td>
</tr>
<tr>
<td>S</td>
<td>-</td>
<td>-</td>
<td>0.324</td>
<td>0.215</td>
<td>0.2580</td>
<td>0.2504</td>
</tr>
<tr>
<td>Fe---</td>
<td>F.</td>
<td>F.</td>
<td>0.0186</td>
<td>0.0165</td>
<td>0.00671</td>
<td>0.02259</td>
</tr>
<tr>
<td>4NHCl Ext. Fe---</td>
<td>N.</td>
<td>N.</td>
<td>T.</td>
<td>T.</td>
<td>T.</td>
<td>T.</td>
</tr>
<tr>
<td>KOH Ext.</td>
<td>F.</td>
<td>F.</td>
<td>-</td>
<td>0.00305</td>
<td>0.007211</td>
<td>0.009126</td>
</tr>
<tr>
<td>Amt. reacted by analysis</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.3516</td>
<td>0.5255</td>
<td>0.5170</td>
</tr>
<tr>
<td>% error</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>41.4</td>
<td>4.85</td>
<td>7.20</td>
</tr>
</tbody>
</table>

Note: Runs No. 2 and 3 had to be shut down due to fluctuations in temperature. Runs No. 5, 6, 7, 12, and 13 had to be shut down due to condensation in the reactor flask.

N = no test; F = faint test; V.F. = very faint test; T = traces
### TABLE I - Reaction Data (continued)

<table>
<thead>
<tr>
<th>Run No.</th>
<th>14</th>
<th>15</th>
<th>16</th>
<th>17</th>
<th>18</th>
<th>19</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature°C</td>
<td>130</td>
<td>145</td>
<td>160</td>
<td>175</td>
<td>160</td>
<td>160</td>
</tr>
<tr>
<td>Evacuated to: mm.Hg</td>
<td>726</td>
<td>736</td>
<td>732</td>
<td>726</td>
<td>745</td>
<td>739</td>
</tr>
<tr>
<td>Gas used:</td>
<td>HNO₃</td>
<td>HNO₃</td>
<td>HNO₃</td>
<td>HNO₃</td>
<td>HNO₃</td>
<td>HNO₃</td>
</tr>
<tr>
<td>Length of run hr.</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>0.50</td>
<td>2.00</td>
</tr>
<tr>
<td>Wt. of pyrite used g.</td>
<td>8.1797</td>
<td>8.1440</td>
<td>8.1263</td>
<td>8.1000</td>
<td>8.0561</td>
<td>8.0876</td>
</tr>
<tr>
<td>Wt. of residue g.</td>
<td>7.7104</td>
<td>7.6417</td>
<td>7.7946</td>
<td>7.7734</td>
<td>7.8948</td>
<td>7.4451</td>
</tr>
<tr>
<td>Amt. reacted Fe</td>
<td>0.4693</td>
<td>0.5023</td>
<td>0.3317</td>
<td>0.3266</td>
<td>0.1613</td>
<td>0.6425</td>
</tr>
<tr>
<td>H₂O Ext. Permanganate test</td>
<td>0.2093</td>
<td>0.1988</td>
<td>0.1374</td>
<td>0.1328</td>
<td>0.06406</td>
<td>0.2519</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>0.6029</td>
<td>0.6044</td>
<td>0.3755</td>
<td>0.3755</td>
<td>0.1790</td>
<td>0.8594</td>
</tr>
<tr>
<td>S</td>
<td>0.2012</td>
<td>0.2017</td>
<td>0.1353</td>
<td>0.1253</td>
<td>0.05973</td>
<td>0.2867</td>
</tr>
<tr>
<td>Fe³⁺</td>
<td>0.02716</td>
<td>0.04054</td>
<td>0.02974</td>
<td>0.02869</td>
<td>0.01492</td>
<td>0.05036</td>
</tr>
<tr>
<td>4HCl Ext. Fe²⁺</td>
<td>0.008043</td>
<td>0.007698</td>
<td>0.00723</td>
<td>0.004462</td>
<td>0.004952</td>
<td>0.006174</td>
</tr>
<tr>
<td>Amt. reacted by analysis 2</td>
<td>0.4457</td>
<td>0.4487</td>
<td>0.2996</td>
<td>0.2913</td>
<td>0.1437</td>
<td>0.5913</td>
</tr>
<tr>
<td>% error</td>
<td>2.90</td>
<td>10.67</td>
<td>9.68</td>
<td>10.84</td>
<td>10.91</td>
<td>7.97</td>
</tr>
</tbody>
</table>

Note: Runs No. 2 and 3 had to be shut down due to fluctuations in temperature. Runs No. 5, 6, 7, 12, and 13 had to be shut down due to condensation in the reactor flask.

N = no test; F = faint test; V.F. = very faint test; T = traces
FIGURE 2 - WEIGHT REACTED VS. TEMPERATURE FOR ONE HOUR REACTION TIME

- □ BY WT. DIFF.  □ TOTAL WT. CURVE
- ○ BY ANALYSIS  ○ IRON AS FERRIC SULFATE
- △ IRON AS FERRIC OXIDE  × IRON AS FERRIC OXIDE
FIGURE 3 - WT. REACTED VS. TIME AT 160°
TABLE II - Pressure Variation for Indicated Runs

<table>
<thead>
<tr>
<th>Run No.</th>
<th>10</th>
<th>11</th>
<th>14</th>
<th>15</th>
<th>16</th>
<th>17</th>
<th>18</th>
<th>19</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>130</td>
<td>130</td>
<td>130</td>
<td>145</td>
<td>160</td>
<td>175</td>
<td>160</td>
<td>160</td>
</tr>
<tr>
<td>Pressure at start</td>
<td>776</td>
<td>770</td>
<td>783</td>
<td>777</td>
<td>820</td>
<td>747</td>
<td>664</td>
<td>660</td>
</tr>
<tr>
<td>10 min.</td>
<td>776</td>
<td>772</td>
<td>783</td>
<td>777</td>
<td>822</td>
<td>759</td>
<td>712</td>
<td>712</td>
</tr>
<tr>
<td>20 min.</td>
<td>773</td>
<td>772</td>
<td>785</td>
<td>807</td>
<td>820</td>
<td>778</td>
<td>808</td>
<td>719</td>
</tr>
<tr>
<td>30 &quot;</td>
<td>777</td>
<td>785</td>
<td>781</td>
<td>823</td>
<td>820</td>
<td>797</td>
<td>828</td>
<td>735</td>
</tr>
<tr>
<td>40 &quot;</td>
<td>777</td>
<td>785</td>
<td>783</td>
<td>831</td>
<td>820</td>
<td>814</td>
<td>-</td>
<td>765</td>
</tr>
<tr>
<td>50 &quot;</td>
<td>777</td>
<td>771</td>
<td>785</td>
<td>781</td>
<td>820</td>
<td>828</td>
<td>-</td>
<td>781</td>
</tr>
<tr>
<td>60 &quot;</td>
<td>775</td>
<td>777</td>
<td>785</td>
<td>777</td>
<td>820</td>
<td>836</td>
<td>-</td>
<td>781</td>
</tr>
<tr>
<td>70 &quot;</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>761</td>
</tr>
<tr>
<td>80 &quot;</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>777</td>
</tr>
<tr>
<td>90 &quot;</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>786</td>
</tr>
<tr>
<td>100 &quot;</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>797</td>
</tr>
<tr>
<td>110 &quot;</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>797</td>
</tr>
<tr>
<td>120 &quot;</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>785</td>
</tr>
</tbody>
</table>
FIGURE 4 - PRESSURE VS TIME FOR THE REACTION RUNS

- - - - - RUN 10, 11, 14 - 130\degree
- - - - - RUN 15 - 145\degree
- - - - - RUN 16 - 160\degree
- - - - - RUN 17 - 175\degree
FIGURE 4A - PRESSURE VS TIME FOR THE REACTION RUNS AT 160°
<table>
<thead>
<tr>
<th>Run No.</th>
<th>20</th>
<th>21</th>
<th>22</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt. of Pyrite</td>
<td>none</td>
<td>none</td>
<td>none</td>
</tr>
<tr>
<td>Temperature</td>
<td>160°</td>
<td>130°</td>
<td>130°</td>
</tr>
<tr>
<td>Evacuated to (mm Hg.)</td>
<td>739</td>
<td>740</td>
<td>720</td>
</tr>
<tr>
<td>Pressure at start</td>
<td>638</td>
<td>698</td>
<td>760</td>
</tr>
<tr>
<td>10 min.</td>
<td>655</td>
<td>686</td>
<td>734</td>
</tr>
<tr>
<td>20 min.</td>
<td>653</td>
<td>662</td>
<td>713</td>
</tr>
<tr>
<td>30 min.</td>
<td>654</td>
<td>631</td>
<td>704</td>
</tr>
<tr>
<td>40 min.</td>
<td>647</td>
<td>623</td>
<td>692</td>
</tr>
<tr>
<td>50 min.</td>
<td>639</td>
<td>621</td>
<td>680</td>
</tr>
<tr>
<td>60 min.</td>
<td>631</td>
<td>611</td>
<td>663</td>
</tr>
<tr>
<td>70 min.</td>
<td>-</td>
<td>603</td>
<td>656</td>
</tr>
<tr>
<td>80 min.</td>
<td>631</td>
<td>589</td>
<td>649</td>
</tr>
<tr>
<td>90 min.</td>
<td>629</td>
<td>580</td>
<td>647</td>
</tr>
<tr>
<td>100 min.</td>
<td>631</td>
<td>572</td>
<td>649</td>
</tr>
<tr>
<td>110 min.</td>
<td>629</td>
<td>568</td>
<td>649</td>
</tr>
<tr>
<td>120 min.</td>
<td>631</td>
<td>567</td>
<td>649</td>
</tr>
</tbody>
</table>
Figure 5 - Pressure vs Time for HNO₃
Run Number 22 - 130°C
Figure 6 - Pressure vs Time for HNO₃. Run Number 20 - 160°C
Additional Tests

The extracts of the unreacted pyrite gave no results for the analytical spot tests.

No sulfate ion was found in the acid extracts.

In the product gas scrubber solution there was no or little sulfate ion (no precipitate, but occasionally a slightly milky test).

The balance attempted on the nitric acid solution did not give satisfactory results.

The temperature of the vapor issuing into the flask after passing through the heated connector tube was found to be 139.5°C.

The average sulfur to iron weight ratio of a fresh pyrite sample was found to be 1.1634 which agreed well with the value of 1.1633 found for the residue.

The volume of the apparatus was found to be 3.135 litres.
SAMPLE CALCULATIONS AND CALCULATED RESULTS

Estimation of the Amount of Nitric Acid Present in the Reactor Flask.

If it is assumed that the reaction taking place in the runs using nitric acid alone is:

\[ 2 \text{HNO}_3 \rightarrow \text{H}_2\text{O} + 2 \text{NO}_2 + \frac{1}{2} \text{O}_2 \]

Then the equilibrium constant can be used as before:

\[ K' = \frac{y^2 (y + c)(\frac{y}{4})^{\frac{1}{2}}}{(1 - y)^2} \left[ \frac{\pi}{1 + \frac{y}{2} + c} \right]^{\frac{3}{2}} \]

At 130° the value of \( K' \) is 3.00 atm \( \frac{3}{2} \) and the value of \( c \) is 1.644 for a 68.2 per cent nitric acid. If it is assumed that when the nitric acid attained constant pressure the reaction has reached equilibrium then the equilibrium pressure from Figure 5 is 0.853 atm. Substitution of these values in the equation for \( K' \) gives:

\[ y = 0.831 \]

Assuming an ideal gas then:

\[ n_t = \frac{\pi V}{RT} = \frac{0.853 \times 3.135}{0.082 \times 403} = 0.0809 \text{ moles} \]

Also

\[ y = \frac{x}{n_0} \]

\[ n_{\text{HNO}_3}^0 \]

and

\[ n_t = n_{\text{HNO}_3}^0 + \frac{3}{4} x + c n_{\text{HNO}_3}^0 \]
Solving these equations for \( n^{°} \) \(_{\text{HNO}_3} \) we obtain:

\[
\frac{n^{°}}{\text{HNO}_3} = 0.0247 \text{ moles}
\]

Oxygen Available and Per Cent Used

Since in the runs using both nitric acid and pyrite the oxygen is being removed the equilibrium of the reaction:

\[
2 \text{HNO}_3 \rightarrow 2 \text{NO} + \text{H}_2\text{O} + \frac{3}{2} \text{O}_2
\]

will be shifted considerably to the right. Thus, it may be considered that the total amount of oxygen available for the oxidation of the pyrite is given by this reaction. Considering run number 11 at 130°C the amount of available oxygen is:

\[
0.0247 \times \frac{3}{4} \times 32.0 = 0.593 \text{ g.}
\]

Oxygen found by analysis:

\[
\begin{align*}
\text{SO}_4^2- &: \quad \frac{0.7504}{98.06} \times 64.0 = 0.500 \\
\text{Fe}_2\text{O}_3 &: \quad \frac{0.0226}{111.7} \times 48.0 = \frac{0.00973}{0.50973 \text{ or } 0.510 \text{g } \text{O}_2} \\
\end{align*}
\]

Therefore per cent available oxygen used: \( \frac{0.510(100)}{0.593} = 86.0\% \)

<table>
<thead>
<tr>
<th>Run No.</th>
<th>11</th>
<th>16</th>
<th>18</th>
<th>19</th>
</tr>
</thead>
<tbody>
<tr>
<td>Available ( \text{O}_2 ), g.</td>
<td>0.593</td>
<td>0.521</td>
<td>0.521</td>
<td>0.521</td>
</tr>
<tr>
<td>( \text{O}_2 ) by Analysis, g.</td>
<td>0.510</td>
<td>0.263</td>
<td>0.125</td>
<td>0.594</td>
</tr>
<tr>
<td>Per cent ( \text{O}_2 ) used:</td>
<td>86.0%</td>
<td>50.4%</td>
<td>24.0%</td>
<td>114%</td>
</tr>
</tbody>
</table>
Per Cent Excess Sulfate in Water Extract

If in the analysis of the water extract we take the ferric iron analysis as correct and the iron present as ferric sulfate we can calculate the amount of sulfate ion which should be present. Considering run number 11 we find the amount of sulfate which should be present is:

\[
\frac{0.2349 \times 3(96.06)}{2(55.84)} = 0.607 \text{ g. } \text{SO}_4^{2-}
\]

The amount of sulfate found by analysis: 0.7504 g \text{SO}_4^{2-}

Per cent excess sulfate: \[
\frac{0.7504 - 0.607}{0.7504} \times 100 = 19.1%
\]

Run No. 11 15 16 17 18 19
Theoretical \text{SO}_4^{2-}, \text{g.} 0.609 0.515 0.356 0.344 0.166 0.652
\text{SO}_4^{2-} \text{ by Analysis, g.} 0.7504 0.6044 0.3755 0.3755 0.1790 0.8594
Per cent Excess 19.1% 14.8% 5.19% 8.40% 7.25% 24.1%
DISCUSSION OF RESULTS

In the preliminary runs the extracts of the reaction products were given tests for various ions. The water extract was found to contain ferric ion, traces of ferrous ion and sulfate ion, but nitrite, nitrate or sulfite tests were negative. The ferric ion and traces of ferrous ion, but no sulfate ion were found in the acid extract. The basic extract contained sulfur which was detected as sulfate after oxidation of the extract with hydrogen peroxide. These tests indicated that the water contained ferric sulfate; the acid extract, ferric oxide; and the basic extract, elemental sulfur.

A search of the literature eliminated the possibility of the formation of ferrous or ferric nitrites and nitrates and made the formation of ferrous or ferric sulfite and ferrous sulfate doubtful. Ferric sulfate was found to be a very stable compound.

In the investigation of the decomposition of nitric acid two reactions were found:

\[
2 \text{HNO}_3 \rightleftharpoons \text{H}_2\text{O} + 2 \text{NO}_2 + \frac{1}{2} \text{O}_2 \quad (1)
\]
\[
2 \text{HNO}_3 \rightleftharpoons \text{H}_2\text{O} + 2 \text{NO} + \frac{3}{2} \text{O}_2 \quad (2)
\]

The equilibrium constants of these two equations show a dissociation of 81.5 per cent and 1.97 per cent respectively at 130° and atmospheric pressure. Since the oxygen will be removed by the reaction with the pyrite the
equilibrium will be shifted considerably to the right. Thus both equations must be considered as the source for the oxygen consumed in the reaction.

Considering these facts it was possible to postulate the mechanism as follows:

\[ 2 \text{HNO}_3 \rightarrow \text{H}_2\text{O} + 2 \text{NO}_2 + \frac{1}{4} \text{O}_2 \]  
(1)

\[ 2 \text{HNO}_3 \rightarrow \text{H}_2\text{O} + 2 \text{NO} + \frac{3}{2} \text{O}_2 \]  
(2)

\[ 2 \text{FeS}_2 + \frac{3}{2} \text{O}_2 \rightarrow \text{Fe}_2 \text{O}_3 + 4 \text{S}_2 \]  
(3)

\[ 2 \text{S}_2 + 2 \text{O}_2 \rightarrow 2 \text{SO}_2 \]  

\[ 2 \text{H}_2\text{O} + 2 \text{SO}_3 \rightarrow 2 \text{H}_2\text{SO}_4 \]  
(4)

\[ \text{Fe}_2\text{O}_3 + 3\text{H}_2\text{SO}_4 \rightarrow \text{Fe}_2(\text{SO}_4)_3 + 3 \text{H}_2\text{O} \]  
(5)

It may be considered that reaction (4) will stop at the formation of sulfur trioxide and that reaction (5) should be written

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

However, it has been noted that there was no sulfate or mere traces of sulfate ion in the product gas scrubber solutions. This indicated that there were practically no sulfur oxides in the product gases. It was also found that there was always an excess of sulfate ion (5-24 per cent) compared to the idea that either free sulfuric acid was present or a molecule of sulfuric acid or sulfur trioxide had been absorbed into the ferric sulfate molecule or was strongly adsorbed by
the solid surface. Thus it seemed most probable that reactions (4) and (5) proceeded as given, or by reaction (6) proceeding exclusively on the solid surface, with an additional possible reaction:

$$\text{Fe}_2(\text{S}_4\text{O}_6)_3 + \text{H}_2\text{SO}_4 \rightarrow \text{Fe}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{SO}_4$$

If nitric acid was taken as the limiting reactant such that it could be considered that reaction (2) went to completion the equations were found to total as follows:

$$4 \text{FeS}_2 + 16 \text{HNO}_3 \rightarrow 8 \text{H}_2\text{O} + 16 \text{NO} + 2\text{S}_2 + 2 \text{Fe}_2(\text{SO}_4)_3$$

Since in the reaction products there was found ferric oxide and excess sulfate ion it can be seen that the overall mechanism did not follow a stoichiometric reaction, but acted as a sequence of reactions of varying rates.

The results of the runs could best be seen from the plots of the data. In the plot of weight reacted versus time at 160°C, Figure 3, the data points were found to lie on straight lines which passed through the origin. This showed that the rate of reaction was a constant; i.e.,

$$\frac{dx}{dt} = \text{constant}$$

Therefore the reaction was of apparent zero-order with respect to nitric acid (or oxygen) at 160° not only on an overall basis but for the formation of ferric sulfate and ferric oxide as well. Thus the reaction was completely independent of the
pressure and the surface of the particles, and according to Langmuir's theory, was almost completely covered at all times with reacting molecules. The maximum amount of pyrites reacted in any run was about 11 per cent. Therefore, the pyrites were present in large excess, and the nitric acid was the limiting reactant.

The curves given in the plot of weight reacted versus temperature for one hour, Figure 2, showed a marked decrease in the amount of reaction between 145° and 160° for the total weight curve and the curve representing the amount of iron as ferric sulfate. The curve for the iron as ferric oxide stayed approximately constant. Since the reaction at 160° was of zero order a surface reaction was indicated. This marked decrease could be caused by a change in the properties of the surface and its consequent deactivation. As the amount of ferric oxide remained essentially constant and as the amount of ferric sulfate decreased the rate of reaction (3) of the mechanism must have been disturbed by the increase in temperature.

In surface reactions the reaction rate can be inhibited by a reactant or product, or by a general change in surface activity. It was noted that at about 159.5°C the viscosity of sulfur started a sharp increase from about 10 cp. at the lower temperatures to 4,500 cp. at 171°C. This marked change in the viscosity, and consequently other physical properties, of sulfur could change the surface layer properties giving a deactivation as shown by the curves of Figure 2.
In the runs using nitric acid alone the pressure of the gases was measured at intervals. From the plots of the data for runs 20 and 22, Figures 6 and 5 respectively, it can be seen that in general the pressure decreases from the initial pressure to some equilibrium value. The plot for 160° shows an initial increase in pressure then the descent to the equilibrium value. Since the nitric acid vapor was found to enter the flask at a temperature of 139.5°C, the increase would be due to the warming of the gases to 160°C.

The decrease in pressure to an equilibrium value can be readily understood by examination of the equilibrium constant.

\[ K' = \frac{y^2 \left( \frac{y}{2} + c \right) \left( \frac{y}{4} \right)^{\frac{1}{2}}}{(1 - y)^2 \left[ \frac{v}{1 + \frac{v}{2} y + c} \right]^{\frac{3}{2}}} \]

At 130°C, it has been found by this equation that 68.2 per cent nitric acid was 81.5 per cent dissociated at one atmosphere, and 83.1 per cent dissociated at 0.853 atmospheres. In other words as the pressure decreased the per cent dissociation increased. As the reactor flask was evacuated to within 20-40 mm Hg. in order to fill the flask with nitric acid vapor, it can be seen that the initial vapors were entering into a very low pressure and that this pressure would build up as the flask was filled. Since the flask filled slowly (about one minute) the vapors initially were more dissociated than they should have been for equilibrium. As the dissociation comes back to its equilibrium value the pressure will decrease due to the shifting to the lesser number of moles.
The pressure curves for the reaction runs, shown in Figures 4 and 4A, were found generally to increase. There were some deviations from this but they did not seem to be serious ones. At 160° for runs 18 and 19 there were found definite increases in pressure. Since the nitric acid vapor entered the flask at a lower temperature, part of this increase would be due to the warming up of the gases. Also as the oxygen was being removed by the reaction with pyrite then the gases would become more dissociated thus causing a greater increase in pressure. It should be noted that in run 16 the pressure appeared to remain constant. This entirely disagreed with runs 18 and 19 and showed that it may be in error. Since the pressure was so very constant it was most probably due to a clogged manometer stopcock. Run 17 can be explained in the same manner as runs 18 and 19. At the lower temperatures there was found a somewhat different behaviour. In run 11 at 130°C the pressure was found to remain fairly constant rising slightly in the middle and falling again. Since the acid vapor entered the flask at a temperature above that of the flask the cooling of the vapors would compensate for the changes made by the shifting of the equilibrium keeping the pressure relatively constant. For run 17 at 145°C the pressure was found to rise considerably then to fall back to the original pressure. The rise must be due to the increase in temperature and the shifting of the equilibrium which must eventually have caused the pressure to fall to its original value.
It was noted that in the calculation of the percentage oxygen for run 19 (160°C for 2 hours) that 114 per cent of the available oxygen was used up. The amount of available oxygen was calculated from the amount of nitric acid originally placed in the reactor flask. This value for the nitric acid was only an approximation having been calculated from equilibrium data which, in turn, was based on thermodynamic data. In the calculation of this value there were made such assumptions as ideal behaviour of the gases. Thus, if the gases actually deviated to some measurable degree from ideality and if the equilibrium data was accurate to within say only ten per cent, then there would be considerable error in the amount of original nitric acid and, consequently, of the available oxygen. The nitric acid value was only an approximation and was intended to show the relative amount of reaction that had taken place with respect to the nitric acid. Also the values would show if the limit of the reaction, due to the lack of further oxygen, had been reached. Since the amount used in run 19 gave a value greater than the calculated amount it could be assumed that the reaction at this point approached the limit.
CONCLUSIONS

A suggested mechanism for the reaction of pyrite with vapor state nitric acid may be written as follows:

\[ 2 \text{HNO}_3 \rightarrow \text{H}_2\text{O} + 2 \text{NO}_2 + \frac{1}{2} \text{O}_2 \]  
\[ (1) \]

\[ 2 \text{HNO}_3 \rightarrow \text{H}_2\text{O} + 2 \text{NO} + \frac{3}{2} \text{O}_2 \]  
\[ (2) \]

\[ 2 \text{FeS}_2 + \frac{3}{2} \text{O}_2 \rightarrow \text{Fe}_2\text{O}_3 + 4 \text{S} \]  
\[ (3) \]

\[ 2\text{S}_2 + 2 \text{O}_2 \rightarrow 2 \text{SO}_2 \]  
\[ + \]
\[ 2 \text{H}_2\text{O} + 2 \text{SO}_3 \rightarrow 2 \text{H}_2\text{SO}_4 \]  
\[ (4) \]

\[ \text{Fe}_2\text{O}_3 + 3 \text{H}_2\text{SO}_4 \rightarrow \text{Fe}_2(\text{SO}_4)_3 - 3 \text{H}_2\text{O} \]  
\[ (5) \]

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

with the possible reaction:

\[ \text{Fe}_2(\text{SO}_4)_3 + \text{H}_2\text{SO}_4 \rightarrow \text{Fe}_2(\text{SO}_4)_3 + \text{H}_2\text{SO}_4 \]

The weight reacted versus time curve for 160 ° showed that the reaction was of zero-order at this temperature. Since the zero order would indicate strong oxygen adsorption and no sulfur oxides appeared in the gases the reactions (3), (4), (5) and (6) must all be surface reactions. A change in the nature of the reaction may be indicated by the marked dip in the weight reacted versus temperature curve for one hour of reaction.
The oxygen balance serves as only an approximate indication of the limit of the reaction due to the removal of the available oxygen.
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34. Ibid. 500.


45A. Ibid. 1330.

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48. Ibid. 1334.


APPENDIX A

Analysis of Pyrite and Extract Residue.

The sample was ground to pass an 80-mesh screen and dried for one hour at 100°C. Approximately 1.373 g. of the sample was weighed out accurately and placed in a 400-ml beaker. Ten ml. of bromine-carbon tetrachloride reagent (carbon tetrachloride saturated with bromine) was added, the beaker covered with a watch glass and the mixture left to stand for 15 minutes in a cold bath with occasional shaking. Next, 15 ml. of concentrated nitric acid was added and the mixture was allowed to stand for 15 minutes at room-temperature. The mixture was then warmed on an asbestos board on a steam bath with the watch glass cover raised by glass riders. When the reaction had ceased and all the bromine had been vaporised the mixture was evaporated to dryness on a steam bath. Once the residue was dry ten ml. of concentrated hydrochloric acid was added and the mixture again evaporated to dryness. Then there was added 4 ml. of concentrated hydrochloric acid and the mixture left to stand for 5 minutes. Next 100 ml. of hot distilled water was added and the mixture boiled for 5 minutes. At this point all of the sample except for the silicious materials was in solution. Twenty ml. of concentrated ammonium hydroxide was added and the precipitate filtered to dryness using suction. The precipitate was redissolved in 20 ml. of 4 N HCl and reprecipitated with concentrated ammonium hydroxide. The precipitate was again
filtered off, washed with distilled water and sucked to dryness. The ammoniacal filtrates were combined for a sulfate analysis (Appendix D). The iron precipitate was dissolved with 20 ml. of 4 N hydrochloric acid and the filter paper rinsed with distilled water. A ferric analysis (Appendix B) was run on the solution.
APPENDIX B

Analytical Method for Ferric Ion

In the analysis for ferric ion a sample of the extract (20 ml) was pipetted into a 250-ml. Erlenmeyer flask and 4 ml. of 4 N HCl was added. Next 2 g. of KI was weighed out and dissolved in 10 ml. of distilled water. The potassium iodide solution was added to the acidified sample and let stand for three minutes. The mixture was titrated with a standardized 0.1 N thiosulfate solution. Five ml. of starch solution was added near the end point and the titration completed to the disappearance of the deep iodo-blue color. The sample was then titrated to a deep blue end-point with a 0.1 N iodine solution which had been compared to the thiosulfate solution. The necessary calculations were then made to determine the ferric ion content using a multiplication factor to find the total ferric ion in the extract.
APPENDIX C

Analytical Method for Ferrous Ion

For the ferrous ion determinations a sample of the extract (20 ml.) was taken and 15 ml. of sulfuric-phosphoric acid mixture (150 ml. $\text{H}_3\text{PO}_4$ - 150 ml. $\text{H}_2\text{SO}_4$ diluted to 1 litre.) were added. The sample was then diluted to 100 ml. with distilled water and three drops of diphenylamine indicator added. The mixture was titrated with a standardised 0.1 N dichromate solution to a very deep violet-blue end point adding the last few ml. drop by drop.
APPENDIX D

Analytical Method for Sulfate Ion

Since for the sulfate analysis ferric ion interfered it had to be removed. Also any sulfur, in a lower oxidation state than the sulfate ion, had to be oxidized to the sulfate state with hydrogen peroxide. In the following analysis there has been given steps to remove the ferric ion and to oxidize the sulfur to the sulfate state, but these steps have been left out in any analysis in which they did not apply.

A sample of the extract (50-150 ml. depending on the strength of the extract) was taken and the iron precipitated out with an excess (5-10 ml.) of concentrated ammonium hydroxide. The precipitate was filtered to dryness using suction. The residue was then dissolved with hydrochloric acid and the iron reprecipitated with an excess of ammonium hydroxide. The precipitate was again filtered off and washed with distilled water. The filterates were then combined. Next the lower forms of sulfur were oxidized to sulfate ion by adding hydrogen peroxide and leaving to stand in a covered beaker. The solution was then brought to a boil to expel any excess oxygen. The solution was then cooled and then neutralized with 4 N HCl using a methyl orange indicator.

Two hundred ml. of 10% Ba Cl₂ solution was made up, acidified with 8 ml. of 3 N HCl and heated to boiling. The neutralized sample was added to the hot Ba Cl₂ solution drop by drop with
continuous stirring. The mixture was digested an hour or near the boiling point for one hour. The mixture was allowed to stand in order to cool and to settle out the precipitate. The mixture was filtered through a tared Gooch crucible washing the precipitate by decantation with water. The precipitate was then heated in a Fisher burner for one hour and subsequent fifteen minute periods to constant weight.
APPENDIX E

Miscellaneous Graphs
\begin{align*}
(1) \quad 2\text{NO}_2 + \text{H}_2\text{O} + \frac{1}{2}\text{O}_2 & \rightarrow 2\text{HNO}_3 \\
(2) \quad 2\text{NO} + \text{H}_2\text{O} + \frac{3}{2}\text{O}_2 & \rightarrow 2\text{HNO}_3
\end{align*}

\textbf{FIGURE 7 - K VALUES FOR THE ASSOCIATION OF NITRIC ACID}

FIGURE 8 - VISCOSITY OF LIQUID SULFUR

HANDBOOK OF CHEMISTRY AND PHYSICS. CHEMICAL RUBBER PUBLISHING CO. 1735 (1948)