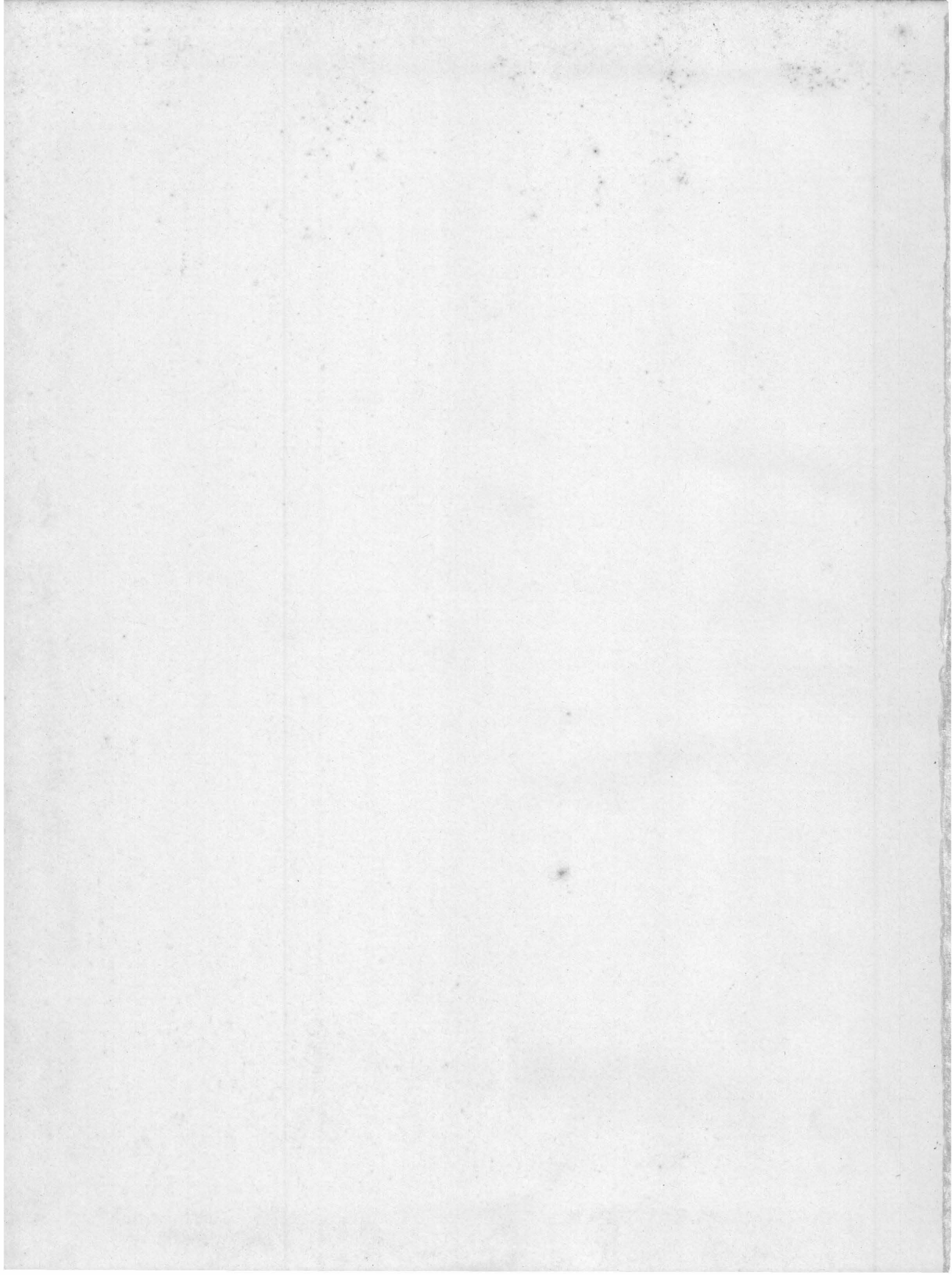




To Dr. Naughton

With best regards.

Francis T. Tanaka



A STUDY OF THE  
CATALYTIC EFFECT OF IRON OXIDE ON  
THE OXIDATION OF HYDROGEN SULFIDE

A Thesis Submitted to the Graduate School of the  
University of Hawaii in Partial Fulfillment  
of the Requirements for the Degree of  
Master of Science

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## I. INTRODUCTION

### A. Hydrogen Sulfide in Manufactured Gas.

Processes which are evolved empirically are frequently encountered in manufacturing. A processing step developed in this manner is often imperfectly understood. A good example of such a system is the removal of hydrogen sulfide from manufactured domestic fuel gas.

Hydrogen sulfide, an obnoxious gas, is poisonous in concentrations above 20 parts in a million parts of gas. Its combustion product, sulfur dioxide, is equally unpleasant with a maximum allowable concentration in air of 10 parts per million. Concentrations of 400 parts per million may cause immediate death.<sup>1</sup> Besides being dangerous to life both gases, on dissolving in water, form corrosive acids.

All raw fuel gases contain hydrogen sulfide which must be removed before they can be used domestically. The extent of their removal is usually governed by law, which states that all gases must pass the "referee's test".<sup>2</sup> This test consists of exposure of a lead acetate solution to a stream of gas for one minute. If hydrogen sulfide is present in excess, the formation of lead sulfide will give a brownish color to the solution. The sensitivity of the "referee's test" is one part per million for the detection of hydrogen sulfide.

One of the time-tested methods for removal of hydrogen sulfide from such a gas is to pass the gas through a bed of iron oxide. A study of the reactions and kinetics of the removal of hydrogen sulfide in this process is the basis of this research.

## B. Brief History

As far back as 1802, the foul atmosphere caused by the combustion of fuel gas was of concern to both the manufacturer and the public. At this time in a gas manufacturing plant in Soho, England, Murdock used lime in the water of his gas holder and the purification was quite acceptable. In 1817, slaked lime was used in solid form. Lime also removed carbon disulfide and some organic sulfur compounds. The laws controlling obnoxious sulfur compounds in the fuel gas were formulated with this purification process in mind and therefore stipulated the total sulfur content allowable in the gas.<sup>3</sup>

In 1817, the iron oxide process was suggested as a method of purification. This method did not remove the carbon disulfide in the gas and therefore did not purify the gas to the maximum total sulfur level as required by the laws of that period. However, in 1849, despite the law, the first iron oxide purification system was tried. It was not until 1905, after the laws were changed, that the transition from lime to iron was completed.

The practice at that time was to let the raw gas react with the iron oxide until it no longer performed its function of removing hydrogen sulfide. This fouled oxide was then removed from the unit and allowed to oxidize in air.

By 1919, the water gas manufacturers had adopted the method of oxidation in situ.<sup>4</sup> This was accomplished by adding about one percent oxygen to the raw gas stream, which would oxidize the fouled iron oxide without having to remove the iron oxide from the gas stream. Because of the lower oxygen content and the slower rate of oxidation, the size of the beds had to be quadrupled by adding units in series. Two units would be oxidizing,

one unit would be sulfiding, and one would be kept as a "catch box." The units could be rotated when the sulfiding box was completely fouled.

Although the dry box iron oxide purification system is fast being replaced by fluidized systems, developments and improvements in the system are still being made. This is particularly so in areas where natural gas is not available. Honolulu Gas Company, by developing a system using iron powder instead of prepared oxide, has reduced its cost for purification from \$100,000 to \$50,000 a year.<sup>5</sup> Northshore Gas Company in Australia similarly has reduced its cost on dry box purification by 90% after adopting the iron powder system known as the "low density sponge".<sup>6</sup>

### C. Review of Pertinent Literature

A process that has been in use for over a hundred years accumulates a considerable amount of technical literature. This is certainly true of oxide purification process, although most of the information in this literature was derived through a trial and error method. A review will provide a summary of the type of problems encountered and the variables which must be controlled in the purification process.

1. Water: As early as 1869 it was noted that water was essential for hydrogen sulfide to react with iron oxide.<sup>7</sup> Several different conclusions were reached as to the exact amount of water needed. Dunkley,<sup>8</sup> Weyman,<sup>9</sup> and Huttig<sup>10</sup> decided that each oxide required a different amount of water. The participants at a meeting of the Gas Engineers Institute of London, during December 1949, agreed that water was needed in purification and that the hardening of the oxide was caused by the lack of water.<sup>11</sup> Marshall<sup>12</sup> thought the water content should be from 15% to 20% by weight, Clayton<sup>13</sup> felt it should be from 35 to 49% by weight. Cook<sup>14</sup> decided that the oxide should be steamed regularly to moisten it. Sperr Jr.<sup>15</sup> went to

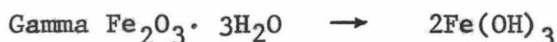
the extreme and added the iron to water and formed a very effective fluidized system known as the "Ferrox Process." Milborne<sup>16</sup> concluded that water was necessary for oxidation but was not needed for sulfiding.

The hardening of the oxide, the migration of iron, the regulation of temperature, and the inactivity of the oxide are all believed to be direct functions of moisture content of the iron oxide. Yet, presently, there is no control for moisture, nor even any indicator to determine the amount of water in a reacting iron oxide system. If it is suspected that the iron oxide is inactive because of lack of water, the unit is flooded until the water covers the iron oxide bed. Although much work has been published which points to the necessity of water, none of the investigators have formulated a mechanism involving water.

2. Oxygen: The need for oxygen commonly has been explained in the oxidation of the sulfide proceeding through the following mechanism:<sup>17</sup>



Clayton<sup>18</sup> gave iron hydroxide as the final product, which can also be iron oxide hydrate. Both are known as lepidocrite:



Milborne<sup>19</sup> suggested that the reaction may be the reaction of water with sulfide:



The sulfide would react with air without the iron entering into the oxidation reaction.

In order to have enough to revive the oxide in situ, it was found that double the stoichiometric amount of oxygen was needed, based on the oxidation of hydrogen sulfide.<sup>20-22</sup> Goldsmith<sup>23</sup> found that in a solution

reaction he needed air in quantities of four times the volume of gas processed, or three hundred times the stoichiometric amount of hydrogen sulfide. He concluded that it would be cheaper to discard the fouled iron oxide than to provide the air.

In the experiments of these workers, the uptake of oxygen could not be determined accurately and the results of the oxidation were measured in terms of hydrogen sulfide being removed. A direct and accurate measurement of oxygen would be necessary to determine in detail its part in the mechanism of the reaction.

3. Temperature: The degree of hydration was known to be a function of the temperature of the iron oxide. It was reported that at 15° a mole of iron oxide was stable with five moles of water of hydration; at 55° three, and between 100° and 400°, one.<sup>24</sup>

Evans<sup>25</sup> reported that hydrogen sulfide was formed at 100°C by the passage of steam over iron sulfide. The temperature range was therefore limited to an upper value of about 100°C where dehydration occurred and hydrogen sulfide formed, and a lower limit where the reaction rate lessened.

No rate determinations nor detailed laboratory analysis of the temperature factor have been reported in the literature. The effect of temperature evidently is another aspect in the mechanism that could be further explored with profit.

4. PH: It is a practice to keep the pH above 7.0<sup>26</sup> to 8.0<sup>27</sup>. Alkali carbonates and ammonia<sup>28</sup> were added to maintain the high pH. Sodium hydroxide was never mentioned in the literature as a possible means of pH control. At the Honolulu Gas Company, the practice of adding ammonia to the iron oxide was continued until 1959. A laborer regulated the amount

of gaseous ammonia added to the iron oxide beds by the smell of the manufactured gas leaving the beds. The purpose of adding ammonia was not fully understood by the technical staff. Gaseous ammonia became unavailable and rather than convert to ammonia solution, the addition was discontinued on a trial basis. The iron oxide reacted as well without the ammonia, showing that the original addition of sodium carbonate was sufficient for the life of the iron oxide.<sup>29</sup> Also, cyanide poisoning of the oxide, which gave it a blue color, was no longer evident.

5. Migration: As the iron oxide removes hydrogen sulfide from the fuel gas and after oxidation converts it into sulfur crystals, it would be expected that the surface area would decrease and the iron oxide would become less active. Avery<sup>30</sup> used a series of iron oxides and reacted them alternately with hydrogen sulfide and air. After 12 cycles of fouling and reviving, the volume of hydrogen sulfide that reacted with the oxide was the same as the first cycle. The oxide showed no loss of activity. The crystals were sectioned and the interior was found to be free from iron oxide. The iron oxide was found on the outer surfaces in a thin layer. The alpha and gamma iron oxide hydrates were considered to be most active.<sup>33,34</sup> The presence of these oxides was somehow believed to be necessary in order to keep the iron oxide on the outer layers of the sulfur crystals. The process is commonly known as "iron migration."

A mechanism whereby the iron sulfide or iron hydroxide would play a part in the migration of the iron oxide was considered unacceptable because these substances were considered too insoluble in water. Iron sulfide has a solubility of 6.1 ppm and iron hydroxide, 3.7 ppm in water. Other mechanisms such as sulfur migration<sup>33</sup> were mentioned as a more

sensible possibility.

Since the iron migration occurred in the single grains, it was reasoned that the iron would also migrate in the oxide bed toward the point of first contact with the raw gas. This layer would be very active because of the high iron content and would remove the sulfide at a very high rate. The sulfur would then precipitate preferentially at this topmost layer and plug the iron oxide bed, a reaction called "hardening." The correctness of this mechanism on the hardening process has never been investigated and would be another fruitful subject for research.

From the literature one gets a disjointed picture of all the parameters involved in the iron oxide purification system. The experimenters used a variety of iron oxide samples and got a variety of results which were often confusing and conflicting. The results could in no way be related to the form or state of the iron oxide, and a method of pre-determining the activity of the oxide has not been available.

## II. STATEMENT OF PROBLEM

Because of the inadequacies of the mechanism which has been proposed, improvements on the iron oxide dry box purification system have been achieved mostly through the trial and error method. The regulation of such a system develops into an art of process control. This art provides no hint as to methods of improvement once the various parameters of the system have been explored. The maximum and minimum of the parameters through which the process will function are established, and the process is allowed to fluctuate within these limits. All the deficiencies of the system are accepted and made as harmless as possible.

The problem then is to explain at least to some degree the reactions and the kinetics of the iron oxide catalyst system. Once some understanding is achieved, it may be possible to suggest improvements which may again render the process competitive in cost and reliability with other methods of purification.



### III. EXPERIMENTAL

In an attempt to achieve a solution to the problem as stated, the following experiments were carried out:

1. The study of the kinetics of the reaction and the effects of the following variables on the kinetics
  - a. Water
  - b. Oxygen
  - c. Temperature
  - d. Surface Area (qualitative)
  - e. pH effect

2. A study of the effect of the reaction on the iron oxide, and the determination of the reaction products.

3. The study of the regeneration of the iron oxide. During the work, the role of the aqueous phase became evident and studies were made on the equilibrium reactions occurring in solutions.

#### A. Kinetics of Reaction and Effect of the Variables

1. Warburg Oxide Pellets: A Warburg apparatus was used to study the reaction rates by measuring the change in volume per unit time of a reacting gaseous mixture. The Warburg has been used quite successfully in studying catalytic reactions in biochemistry where one product was a gas. The usefulness of the method was somewhat limited primarily because reactions are usually sufficiently complicated so that the measurement of the rate of volume change of the gaseous components gave little conclusive information. To minimize this inconclusiveness, reactions were carried out in an inert atmosphere, and where other complications were observed, different experimental methods were used.

The Warburg apparatus consisted of two sections as illustrated in Figure 1. The manometer section had a differential manometer of capillary tubing with mm. scales on both arms. The apparatus was calibrated so a differential of 10,000mm. of Brodie solution equaled 760mm. of mercury.<sup>34</sup> In place of the Brodie solution, a 20% sodium sulfate - 5% sulfuric acid solution with the same differential was used. Methyl red coloring was added to aid in reading the liquid levels.

The difference in height of the liquid meniscus in the manometer was proportional to the change in pressure at constant volume when the level of liquid was kept at the same mark in the arm connected to the reaction vessel. The liquid level was raised or lowered by manipulation of the manometer leveling clamp.

The reaction vessel had an inner well, an outer annular well, and a side arm. This allowed mixing of solid and liquid reactants at any time during an experiment of isolation of reactants. The volume of the reaction vessel was 20 c.c., and a ground glass joint provided easy detachment from the manometer.

A water bath kept the reaction vessel at constant temperature. This bath had a twelve liter capacity with a stirrer for circulation of the water. A bi-metallic temperature sensing device controlled 100 and 500 watts submersible heater elements, keeping the temperature of the bath constant to  $\pm 0.1$  degree.

The stopcock on the reaction vessel was used to allow inert gases to be admitted into the vessel. For purging, the gases were allowed to flow through the vessel and out through the manometer stopcock. For experiments requiring an inert atmosphere, the liquid and solid reactants were placed in the reaction vessel and the vessel purged for half an hour in the water

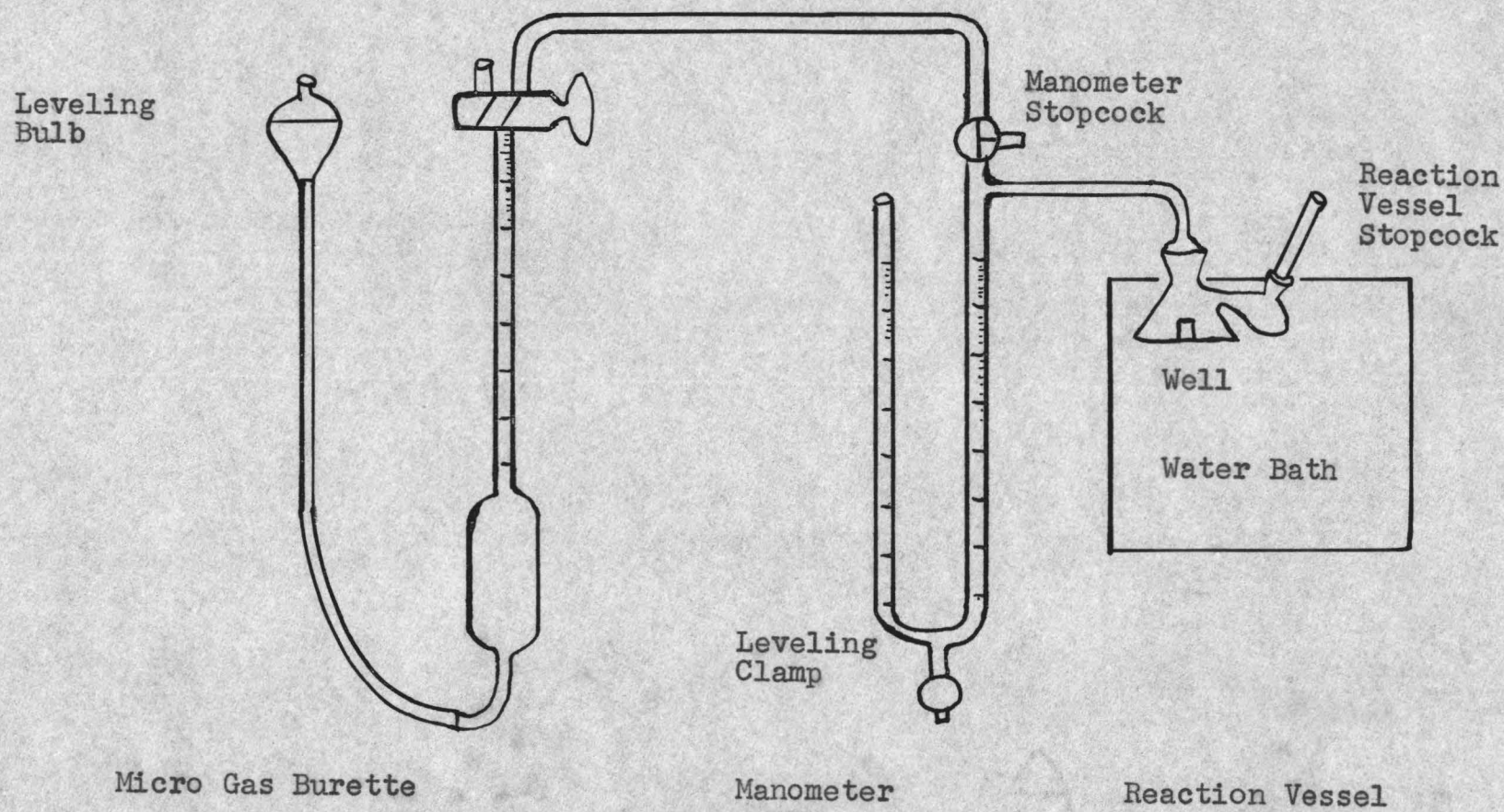
The Warburg apparatus consisted of two sections as illustrated in Figure 1. The manometer section had a differential manometer of capillary tubing 1.5 mm. scales on both arms. The apparatus was calibrated as a differential of 10,000 mm. of Brodie solution equal to 1 mm. of mercury. In place of the Brodie solution, a 10% sodium sulfate - 5% sulfuric acid solution with the same differential was used. Methyl red coloring was added to aid in reading the liquid levels.

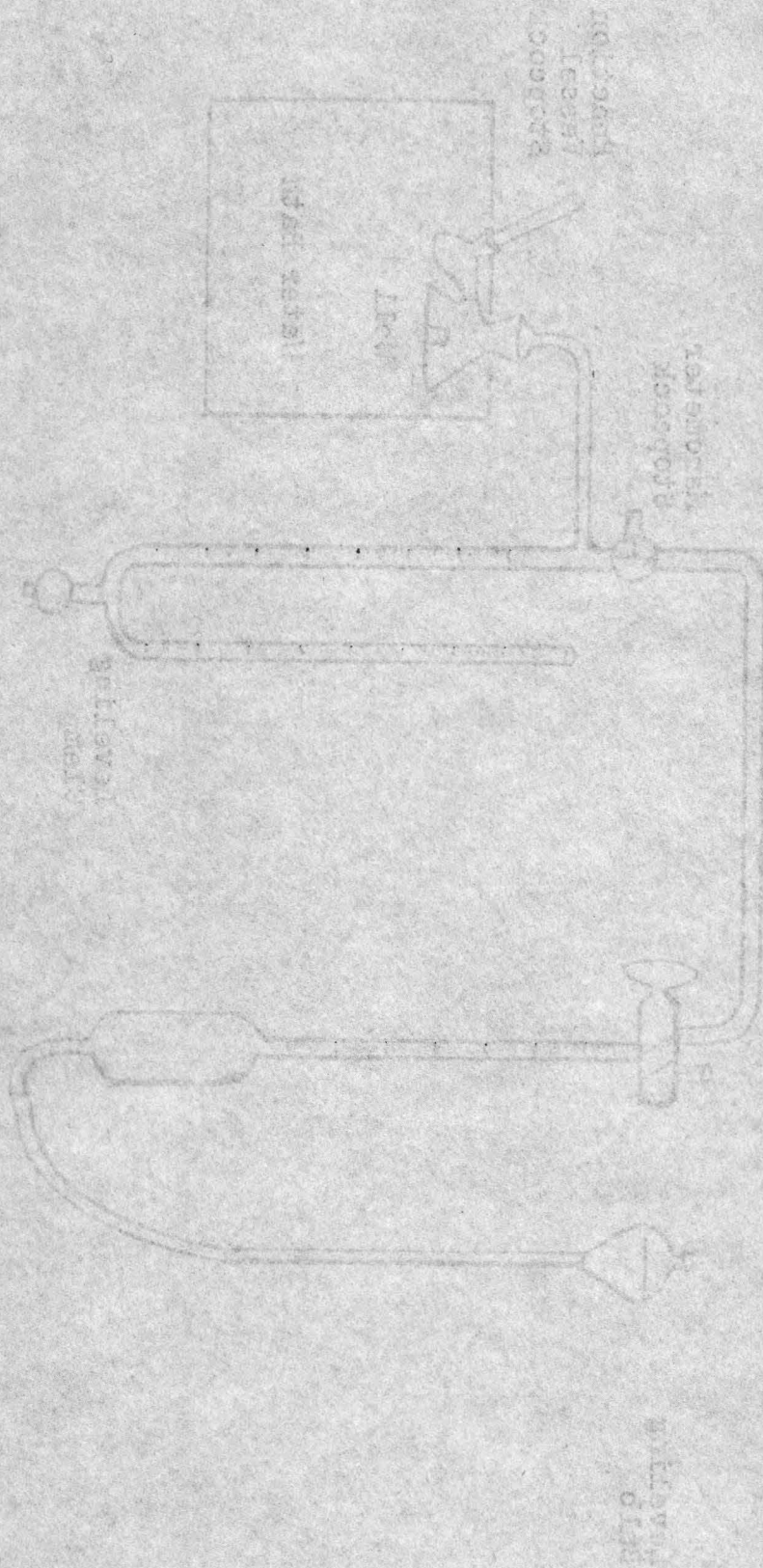
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The reaction vessel had an inner well, an outer annular well, and a side arm. This allowed mixing of solid and liquid reactants at any time during an experiment of isolation of reactants. The volume of the reaction vessel was 10 c.c., and a ground glass joint provided easy detachment from the manometer.

A water bath kept the reaction vessel at constant temperature. This was a 250 c.c. glass beaker with a stirrer for circulation of the water. The reaction vessel was connected to the manometer by a glass tube.

FIGURE 1. WARBURG APPARATUS





bath. Both stopcocks were then closed and the reactant gas added.

To add reactant gas to the reaction vessel, the following procedure was followed. A gas micro-burette was filled with acid salt solution and fitted to the manometer stopcock as shown in Figure 1. The compressed reactant gas, admitted to the micro-burette through the two-way stopcock, displaced the salt solution into the leveling bulb reservoir. This gas was then moved by displacement into the connecting manifold, moving the gas already in the manifold out the three-way stopcock, thus filling it with reactant gas up to the manometer stopcock. The procedure was repeated, finally leaving the required amount of gas in the micro-burette. Both stopcocks of the Warburg apparatus were then opened and the measured amount of reactant gas was displaced into the vessel. Both stopcocks of the Warburg were closed and the liquid level set to take the first reading of the pressure in the reaction vessel. This reading took 15 seconds and subsequent readings were 15 seconds apart.

a. Reagents: The studies were carried out using chemically pure solids that met American Chemical Society requirements for Reagent Grade chemicals. The hydrogen sulfide was a purified grade furnished compressed in steel cylinders with a certified purity of 99.5%. Sulfur dioxide was a commercial grade compressed in lecture bottles with a certified purity of 99.9%. Both gases were purchased from Matheson Company, East Rutherford, New Jersey. Oxygen, argon, helium, hydrogen and carbon dioxide were secured from Gaspro Limited, Honolulu, Hawaii. The commercial iron oxide samples were donated by Honolulu Gas Company, Honolulu, Hawaii.

b. Description of Experiments:

Kinetic Studies: Reaction observed in the Warburg apparatus on the attached manometer are indicated by pressure change and can be a

manifestation of a series of complex reactions and phase changes. For the reactants involved in this study, which are hydrogen sulfide, air, water, and iron oxide, the changes might be (a) a solution or an absorption of any of the gases present; (b) a chemical reaction of hydrogen sulfide with the substrate iron oxide; (c) the reaction of iron sulfide subsequent to b; (d) the evolution of gaseous products; (e) the slow removal by diffusion of reaction products or reactants. A variety of experiments were tried in an attempt to characterize the overall reaction.

Preparation of Oxide Pellets: It was decided to perform the first experiments with the iron oxide compressed into the form of pellets. Preparation involved pressing the oxide into a mold. A tool steel die with a ramrod was used to press the pellets under a pressure of 2000psi in a hydraulic press. The bottom of the die was removed and the ramrod used to push the pellet out of the die. The pellet was one quarter inch in diameter with a smooth surface. A single pellet fitted snugly into the center well of the reaction vessel.

Warburg Blanks: Three c.c. of hydrogen sulfide were introduced into the reaction vessel with the gas micro-burette. The vessel contained air only and was maintained at 30°C in the water bath. No reaction was observed over a ninety minute period. This procedure was repeated with one c.c. of water, two c.c. of 0.05 N. borax and one c.c. 6N sodium hydroxide in the reaction vessel. Water reached equilibrium after 24 hours when 0.4 c.c. of gas had reacted. Borax solution reacted with an equal amount of gas in one hour and sodium hydroxide took one and a half minutes to react with this amount of gas. These latter experiments illustrated the expected reaction of an acid gas with a basic solution.

The Role of Water in the Oxide Reaction: Four samples of commercial

oxides and chemically pure ferric oxide were pressed into pellets. A pellet of ferric oxide was placed in a dessicator with calcium chloride for seven days thus bringing it to equilibrium with a partial pressure of water vapor of about 0.2 mm. and effectively "drying" it of free water. Then it was quickly placed into the vessel and reacted with two c.c. of hydrogen sulfide. There was no reaction which could be measured by a change in gas volume in this apparatus.

Variation of Commercial Oxides: To reproduce the amount of water in each case, 0.1 c.c. of water was added to the pellets of commercial oxides. The pellet was placed in the center well and the water filled the area between the well wall and the pellet. Two c.c. of hydrogen sulfide were reacted with air and the wet oxide. Table 1 contains the change in manometer readings per change in time of one typical experiment with the commercial oxides. When the log of the concentration is plotted against time and a linear relationship is found the reaction concerned is considered to be first order. A plot of gas volume change for the first 120 seconds shows first order kinetics. The results are plotted as log c.c. versus time in Figure 2, where c.c. is the volume of the gas in the reaction vessel. The slope of the first order lines are equal to  $-k/2.3$ , where  $k$  is the reaction constant for the different samples. The slope for the commercial oxides are listed in Table 2.

Oxygen: To check the role of oxygen mixed with hydrogen sulfide on the sulfiding reaction, ferric oxide was reacted with hydrogen sulfide in an inert gas atmosphere (argon). An effect was evident since the reaction showed a rate with ferric oxide in air of  $13.0 \times 10^{-5} \text{ sec}^{-1}$ , and ferric oxide in an inert atmosphere when reacting with hydrogen sulfide showed a lower reaction rate of  $3.5 \times 10^{-5} \text{ sec}^{-1}$ . The kinetics remained



TABLE 1

## Reaction of Hydrogen Sulfide With Commercial Oxide

Readings are in mm. of the Warburg manometer. Temperature 30°C in air

Time second	LUX	ORR	F2	F1	Fe <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub> (argon)
15sec	45mm	58mm	80mm	60mm	34mm	
30	72	90	115	110	60	
45	105	116	145	163	73	
60	124	143	182	191	96	10
75	149	170	205	214	112	
90	171	197	236	251	140	
105	195	223	266	281	151	
120	215	240	286	299	177	42
135	239	246	310	320	190	
150	259	286	322	354	208	
165	270	300	336	392	219	
180	285	322	363	425	241	57
210			406	474	279	
240	346	388	443	515	299	70
300	380	438	532	609	356	83
360	433	492	598	674	399	93
420	480	542	647	735	439	104
480	510	584	697	788	476	114
540		624	742	837	508	123
600	571	670	781	877	528	134

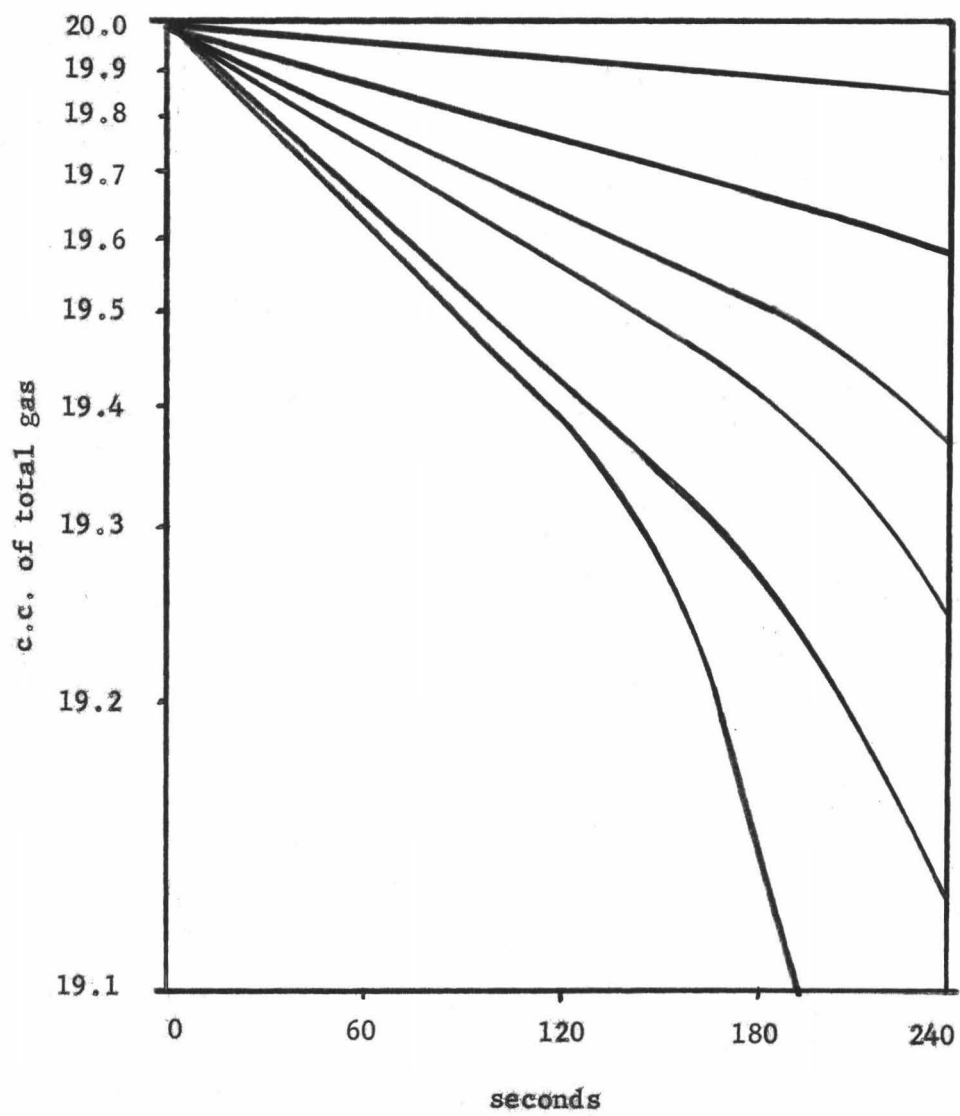


FIGURE 2. Hydrogen Sulfide Reaction With  
Commercial Oxides

first order when the reaction occurred in an inert atmosphere.

Surface: An experiment run under identical conditions with two LUX pellets, which doubled the surface area, gave the results listed in Table 3. In ten minutes one pellet in an inert atmosphere had reacted with 0.23 c.c. of gas and two pellets had reacted with 0.39 c.c. of gas.

PH Effect: In order to test the normal pH of the aqueous phase in contact with the various oxides before reaction with hydrogen sulfide, one gram of iron oxide was shaken with 100 ml. of distilled water. The resulting pH of the suspension was for F1 8.7, ferric oxide 7.2, and for LUX 6.9. There seems to be no correlation of reaction rate with the original pH of the solution in contact with the oxide.

2. Description of Experiments Using Oxide on Filter Paper: In order to achieve a greater permeation of oxide by the gases and to standardize to some extent the size and area of the surfaces, iron oxide was precipitated on filter paper by an easily reproducible technique.

Preparation of Disc: To make the required impregnated discs, filter paper was immersed in a solution of 25% by weight of hydrated ferric chloride. The excess liquid was allowed to drain from the paper after it was removed from the bath. The paper was then dipped into 6 N. ammonium hydroxide solution. An even layer of iron hydroxide was formed on the flat surfaces of the filter paper. The paper was washed twice with distilled water to remove any nonadherent oxide and was dried in an oven at 125°C. A paper punch was used to cut discs of uniform size. These had an average surface area of 7.6 mm<sup>2</sup>, and each disc contained on the average 31.5 milligrams of iron oxide hydrate. To maintain the oxide in an adherent condition, the discs were stored over water in a closed

TABLE 2

## Reaction Constant of the Commercial Oxides

Sample	Rate Constant	
ORR (Iron Oxide Corp., N.J.)	8.5 X 10 <sup>-5</sup> sec <sup>-1</sup>	
LUX (Alpha LUX Co.)	16.9	"
F2 (Dearborne Co., Japan oxide)	21.9	"
F1 (Dearborne Co., Japan oxide)	23.7	"
Ferric Oxide (C.P. Grade)	13.0	"
Ferric Oxide (argon)	3.5	"

TABLE 3

## Variation of Surface Area

Two c.c. of hydrogen sulfide reacting with iron oxide in an inert atmosphere. The readings are in mm.

Time (seconds)	One LUX pellet	Two LUX pellet
60	59	116
120	79	141
180	88	156
240	94	164
300	98	172
360	100	176
420	102	181
480	105	
540		187
600	114	190

container.

Effect of Water: In order to check the effect of moisture again, the iron oxide discs were left in a calcium chloride dessicator for seven days. The discs dried in this manner were unreactive to hydrogen sulfide in the presence of air. The storage of the disc over water prevented the iron oxide from flaking off the filter paper, as mentioned, and also regulated the water content to that in equilibrium with water saturated air at room temperature, about 28mm. of mercury, for the following experiments.

Effect of Oxygen: Iron oxide was allowed to react with hydrogen sulfide until the substrate was saturated with the gas. This fouled oxide was used to determine the reaction order of oxygen. The reaction vessel was purged with helium and one c.c. of air was displaced into the vessel with the burette. Increasing numbers of discs were used but not until 1,254 discs were added to the reaction vessel was a measureable uptake of oxygen detected. The normal plot of log concentration versus time did not give a straight line, showing that the uptake was not first order. By plotting the data listed in Table 4 as the reciprocal of concentration versus time, a straight line graph was obtained which indicated the reaction to be second order. The results are plotted in Figure 3.

Effect of Temperature: When the reaction was conducted under conditions of variable temperature, it was found in a typical experiment that at 30° the average rate was 1.22 moles c.c.<sup>-1</sup>sec<sup>-1</sup>. However a sample reacted at 50° had two reaction rates, first a 1.60 moles c.c.<sup>-1</sup>sec<sup>-1</sup> rate and after the first two minutes a faster rate of 2.19 moles c.c.<sup>-1</sup>sec<sup>-1</sup>.

The effect of temperature on the combined reaction was studied. Four discs were placed in the vessel and the vessel purged with argon.

TABLE 4

## "Fouled" Oxide Reacting With Oxygen

One c.c. of oxygen was reacted with 1254 discs which were previously reacted to hydrogen sulfide. The readings are in mm.

Time seconds	Temperature	
	30°	50°
15sec	3 mm	5mm
30	6	9
45	9	14
60	13	19
90	21	24
120	28	30
180	37	47
240	43	54
300	48	63

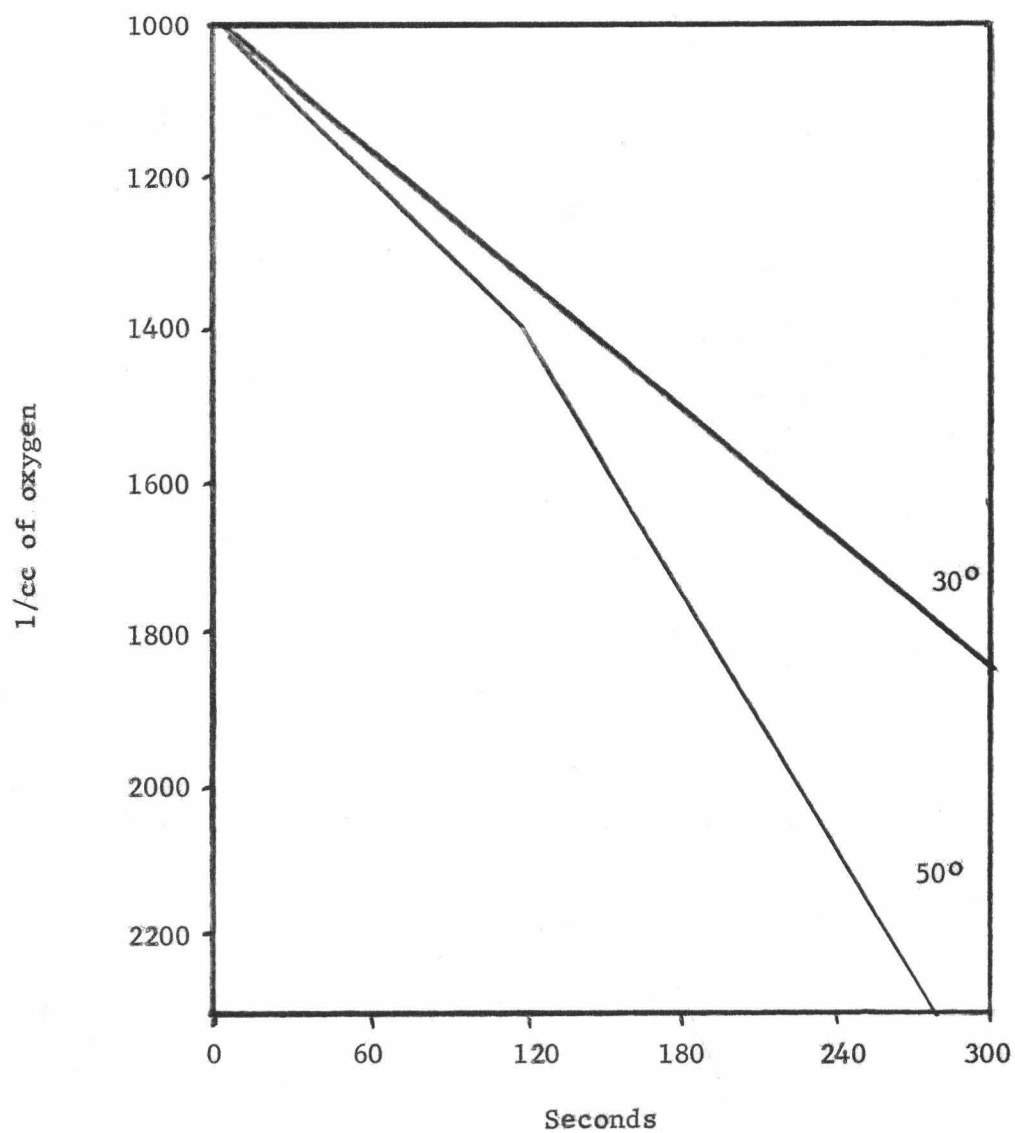


FIGURE 3. Effect of Temperature on Oxidation

The desired temperature of reaction was attained by varying the temperature of the bath containing the reaction vessel. One c.c. of air was added followed by one c.c. of hydrogen sulfide. The results are listed in Table 5 and plotted in Figure 4 log c.c. versus time.

The reaction at 0°C, 30°C and 50°C appeared to follow first order reaction kinetics. At 50°C there were two simultaneous reactions occurring as indicated by the different rates shown in Figure 4. At higher temperatures, 60°C and 70°C, the gas pressure increased instead of decreasing. This gas atmosphere was analyzed by gas chromatography and the gases evolved were found to be hydrogen and oxygen.

Iron Oxide Surface and Stoichiometry: A further study of the effect of the surface area was made. The iron oxide concentration was doubled while all other reactants were kept at a constant concentration at the start of the reaction. Two discs were placed in the reaction vessel and the vessel was purged with argon. One c.c. of air and one c.c. of hydrogen sulfide were added consecutively to the vessel. In a typical experiment the results listed in Table 6 show the change in pressure with change in time. The number of discs were doubled to 4 and the reaction rate recorded. The reactions were conducted at 30° because the industrial process is operated at that temperature.

Van't Hoff has formulated an equation which will give the reaction order of a component if the concentration of the component is changed during two different reactions while the initial concentrations of all the other components are held the same. The equation is:

$$n_b = \frac{\log (dx/dt)_1 - \log (dx/dt)_2}{\log(b)_1 - \log(b)_2}$$

where dx/dt is the rate of the reactions in subscript.

b is the concentration of the component changed and



TABLE 5

## Variation of Temperature on Sulfiding Discs

One c.c. of hydrogen sulfide and one c.c. of air over iron oxide on filter paper. The readings are in mm. The negative readings indicate an increase in pressure.

time seconds	temperature				
	0°	30°	50°	60°	70°
15sec	5mm	57mm	19mm	-15mm	- 5mm
30		77	28	-16	
45		104	37	-19	
60	8	119	41	-20	-10
90	10	139	44	-21	-13
120	11	159	47	-24	-17
180	16	174	49	-27	-23
240	16	192	52	-26	-26
300	23	204	56	-26	-30
420	36	214(360sec)	61	-23	-34
600		231(480sec)	73	-19	-37

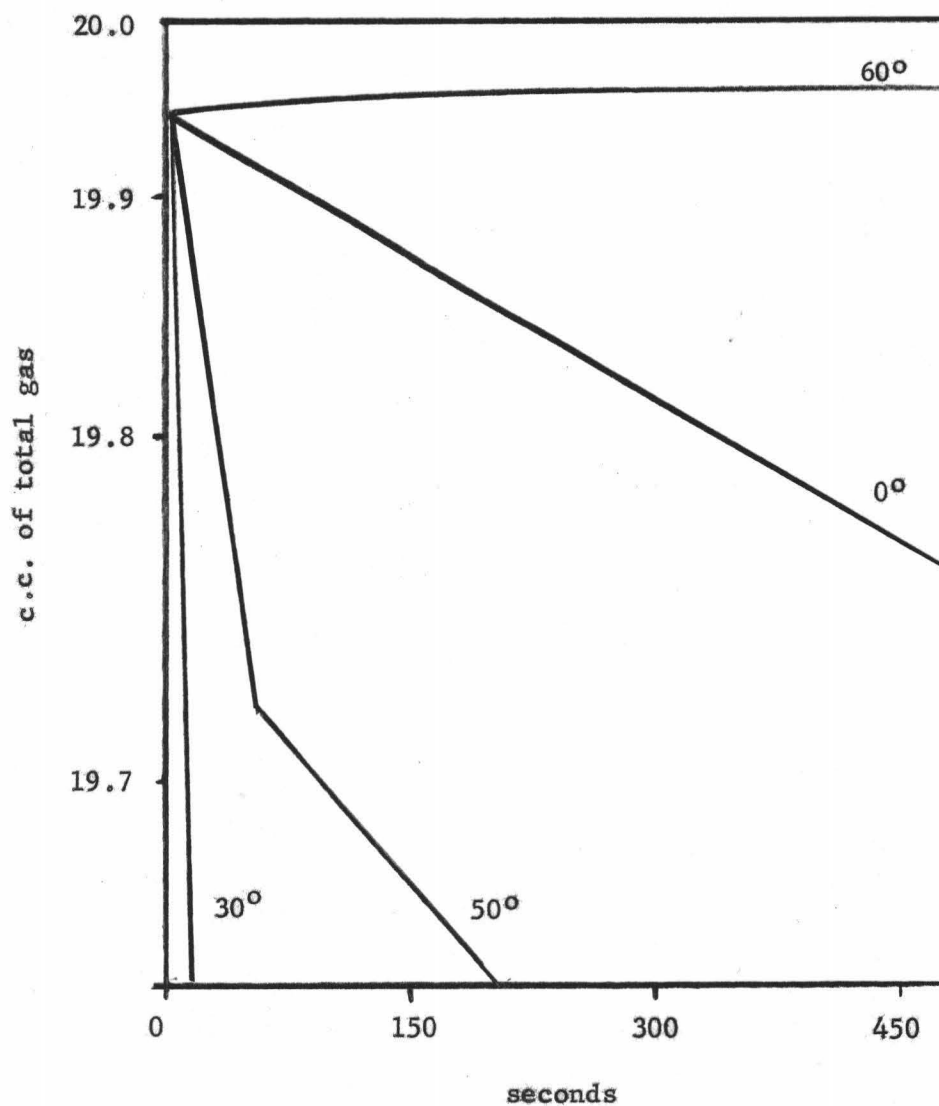


FIGURE 4. Effect of Temperature on Combination Reaction

Temperature change of hydrogen sulfide reaction in the presence of oxygen with gamma iron oxide effects reaction rate.

TABLE 6

## Reaction of Air, Hydrogen Sulfide and Iron Oxide

These data changes show the effect of change in concentration of iron oxide. The reactions were conducted with one c.c. of hydrogen sulfide at 30° and the readings are in mm.

Time seconds	two discs	four discs
15 sec	6mm	57mm
30	8	77
45	13	104
60	16	119
90	21	139
120	24	155
180	31	174
240	34	192
300	37	204
360	41	214
420	47	231

TABLE 7

## Iron Oxide Concentrations for Order Determination

Reaction No.	Iron oxide initial	Gas reacted at one minute
two discs	$40 \times 10^{-5}$ mole	$21 \times 10^{-6}$ mole
four discs	$80 \times 10^{-5}$ mole	$95 \times 10^{-6}$ mole

$n$  is the reaction order of the component. This method gives the approximate order and the reaction should not cover a period where more than 10% of the component has reacted for reasonable accuracy.<sup>35</sup> The rate for the first minute and the amount of iron oxide present are tabulated in Table 7. For the typical reaction the order number  $n_p$  with respect to the iron oxide was 2.1, or the reaction order of iron oxide from the first minute is second order.

Tabulated Results: The results of the preceding experiments are summarized in Table 8.

TABLE 8

## Tabulated Summary Warburg

Kinetic studies with Warburg apparatus using pellets and disc.

	<u>Gas Present</u>	<u>Substrate</u>	<u>Results</u>	<u>Tentative Conclusion</u>
1. Blank runs	(a) H <sub>2</sub> S and air	Water	No reaction	Solution is negligible
	(b) H <sub>2</sub> S and air	Borax solution	Slight reaction	Acid gas reacting with basic substrate
	(c) H <sub>2</sub> S and air	NaOH solution	Slight reaction	Acid gas reacting with basic substrate
2. Runs with pellet iron oxide	(a) H <sub>2</sub> S and air	Dry iron oxide	No reaction	Moisture needed for reaction
	(b) H <sub>2</sub> S and air	Wet iron oxide	1st order reaction	Moisture dependent reaction is 1st order
	(c) H <sub>2</sub> S and argon	Wet iron oxide	1st order reaction	Sulfiding reaction is 1st order
	(d) H <sub>2</sub> S and argon	Variable wet iron oxide	proportional to number of pellets	Oxide directly involved in sulfiding, maybe a surface effect

TABLE 8 cont.

## Tabulated Summary Warburg

	<u>Gas Present</u>	<u>Substrate</u>	<u>Results</u>	<u>Tentative Conclusion</u>
3. Runs with discs iron oxide	(a) H <sub>2</sub> S and air	Dry oxide discs	No reaction	Moisture needed for reaction
	(b) Oxygen	Fouled oxide disc	Second order reaction	Oxidation of sulfide is slower and second order
	(c) Oxygen varied temperature	Fouled oxide disc	Second order reaction	An induction period may be a factor in reaction
	(d) H <sub>2</sub> S and air 0°, 30°, 50°	Wet iron oxide disc	1st order two reaction rates at 50°	Confirms first order kinetics for sulfiding reaction
	(e) H <sub>2</sub> S and air 60° and 70°	Wet iron oxide disc	Gas pressure increase. H <sub>2</sub> and O <sub>2</sub> released	Complex oxidation reduction at higher temperatures

### 3. Studies with Pulsed Reactor and Chromatograph

Equipment: Adsorption reactions and catalytic reactions are usually characterized by an induction time, a period of no reaction, or slow reaction, which precedes the characteristic reaction. This was not noticed in the previously discussed experimental work. If the induction period was short, then it would not have been detected in these experiments since it took 15 seconds to get the first reading on the Warburg apparatus.

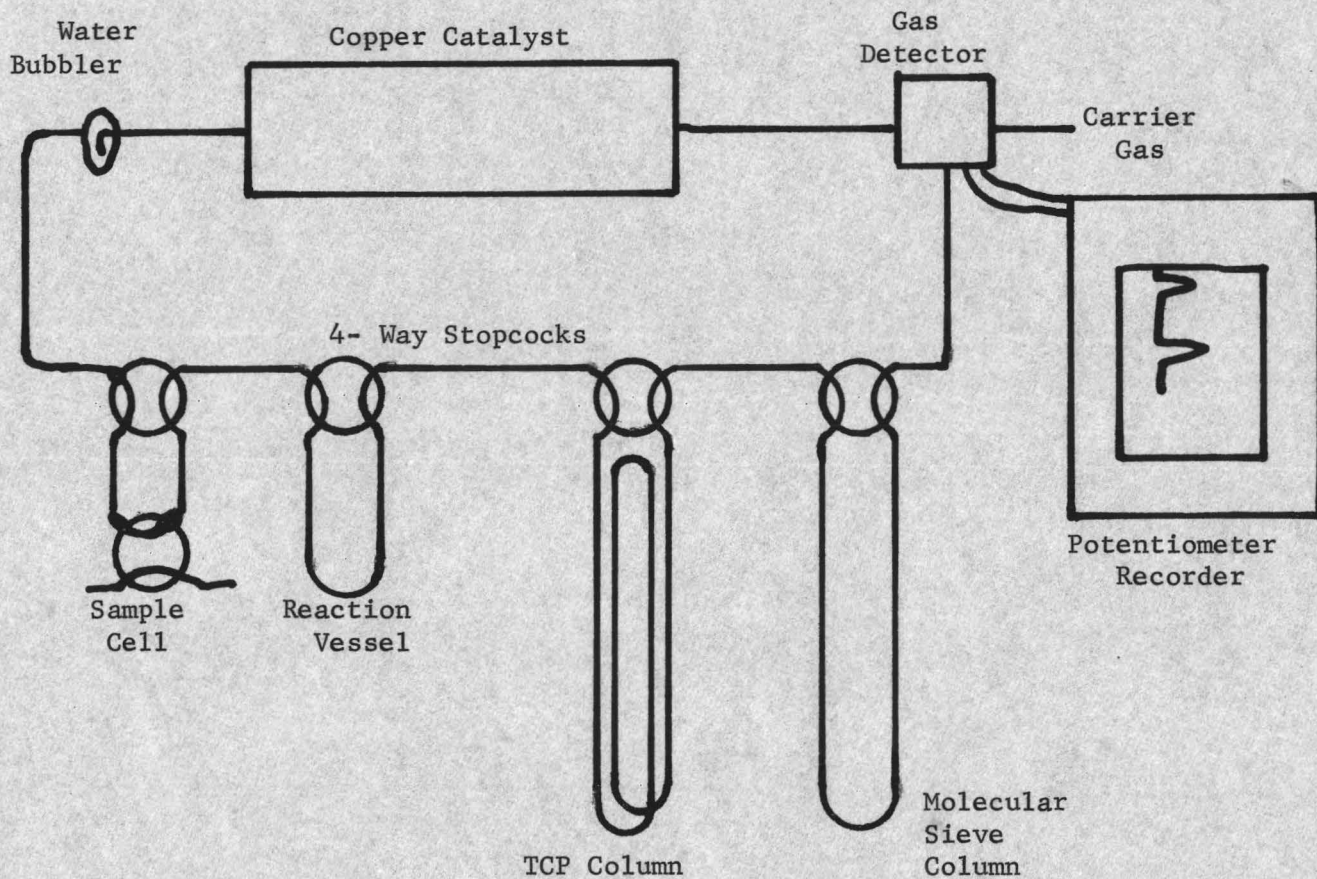
To investigate the kinetics of the first few seconds, equipment for a pulse type injection of reactant gas was developed, with an inert gas displacing the reaction gas over the catalyst and removing the product gases to be analyzed. The gaseous products were then analyzed by partition and adsorption chromatography. This technique is similar to that used by Eberly.<sup>36</sup>

Ryce and Bryce<sup>37</sup> described a gas partition column with a liquid substrate of tricresylphosphate that would separate hydrogen sulfide, disulfides and air.

Figure 5 shows a schematic diagram of the instrument. In brief, it was a gas chromatograph unit with two columns and included a reaction vessel designed for the pulse technique.

The detector was a thermal conductivity analyzer which consisted of a detector and reference electrode which were thermistor beads mounted in a stainless steel cell block, Model 9677 AEL manufactured by Gow Mac. A hot wire kovar element mounted in a brass cell was first tried, but the elements reacted with the gases used. The Gow Mac thermistor cell showed no drift for slight flow variations and ambient changes in room temperature. Two six volt dry cells furnished the 7 milliamp current required by the detector.

FIGURE 5 GAS CHROMATOGRAPH APPARATUS







The bridge circuit is illustrated in Figure 6. It was possible to adjust the zero output with two variable resistors. The signal was fed into a fixed resistor attenuator whence it was passed to a Leeds and Northrup Speedomax recorder. The recorder was equipped with a range changer that could reduce the voltage necessary for a full scale deflection from 20 millivolts to one millivolt. This control was used to increase the sensitivity once the attenuator was set on a range.

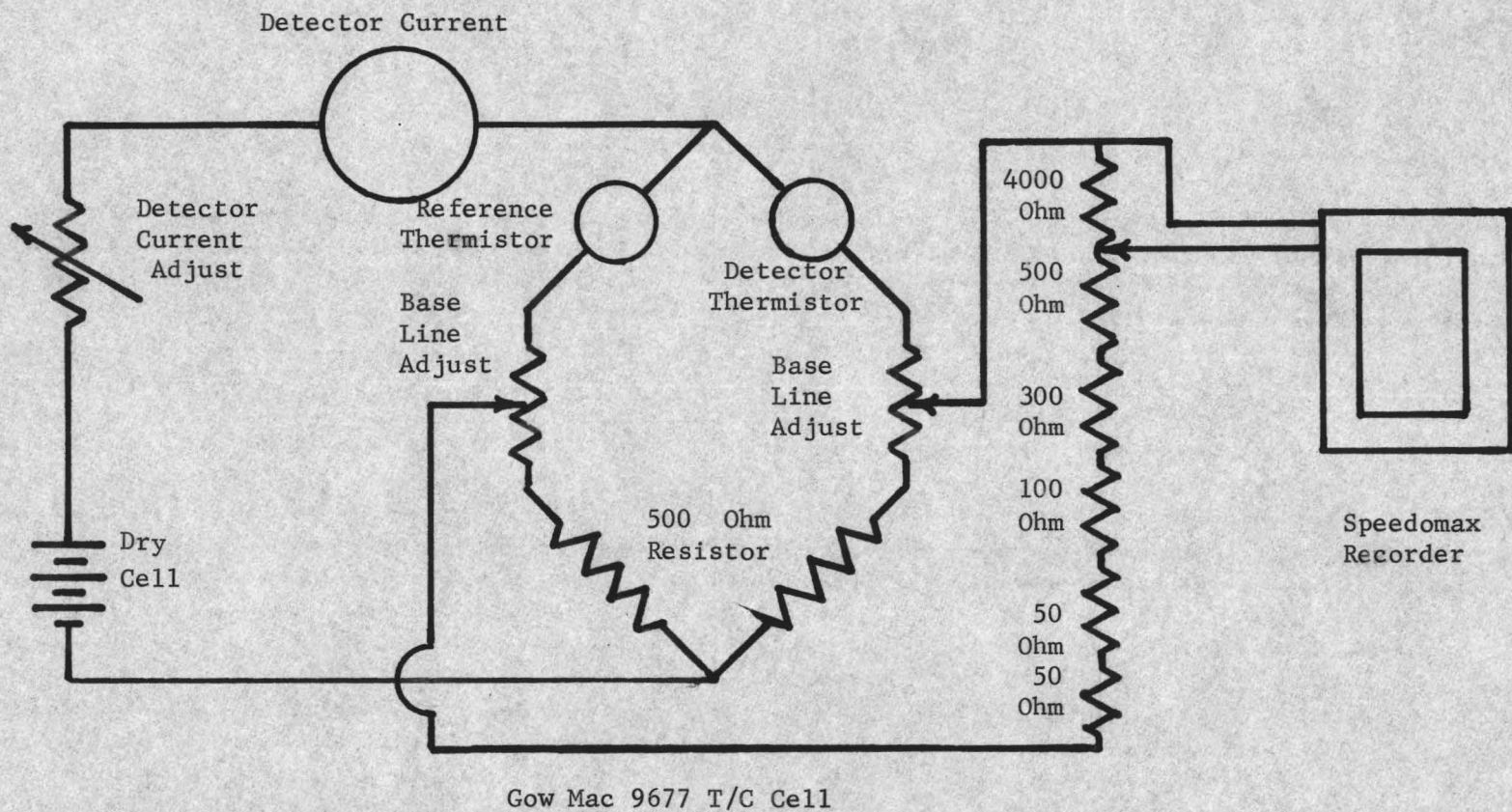
The carrier gas used was helium which was certified as 99.5% pure. Argon was used as the carrier gas for the detection of hydrogen. The carrier gas showed a trace of oxygen which was removed by passing the gas through a copper catalyst in the manner prescribed by Dodd and Robinson.<sup>38</sup> The copper catalyst was rejuvenated before every run by reaction with hydrogen.

The flow rate used was 28 c.c. per minute of helium. The flow was controlled with a pressure regulator, a surge tank, and a needle valve. Leaks were detected by having a calibrated flow meter at each end of the carrier gas flow system.

The chromatographic column was 16 feet long and was made of 8 mm. O.D. pyrex glass tubing. It consisted of four straight sections four feet in length with a U-shaped bends at the ends. The inlet and outlet were fused to a four-way stopcock. Nipples were used to fill the columns, and the filling points were sealed after the column was packed.

For packing, Johns Manville firebrick C-22 was ground to pass A.S.T.M. specification 60 mesh screen and retained by 80 mesh screen. The properly sized firebrick was acid washed. Hydrochloric acid was used first and then aqua regia. The firebrick was rinsed with water and the fines were floated off. A dilute solution of ammonia was used to neutralize any

FIGURE 6 DETECTOR CIRCUIT



Gow Mac 9677 T/C Cell

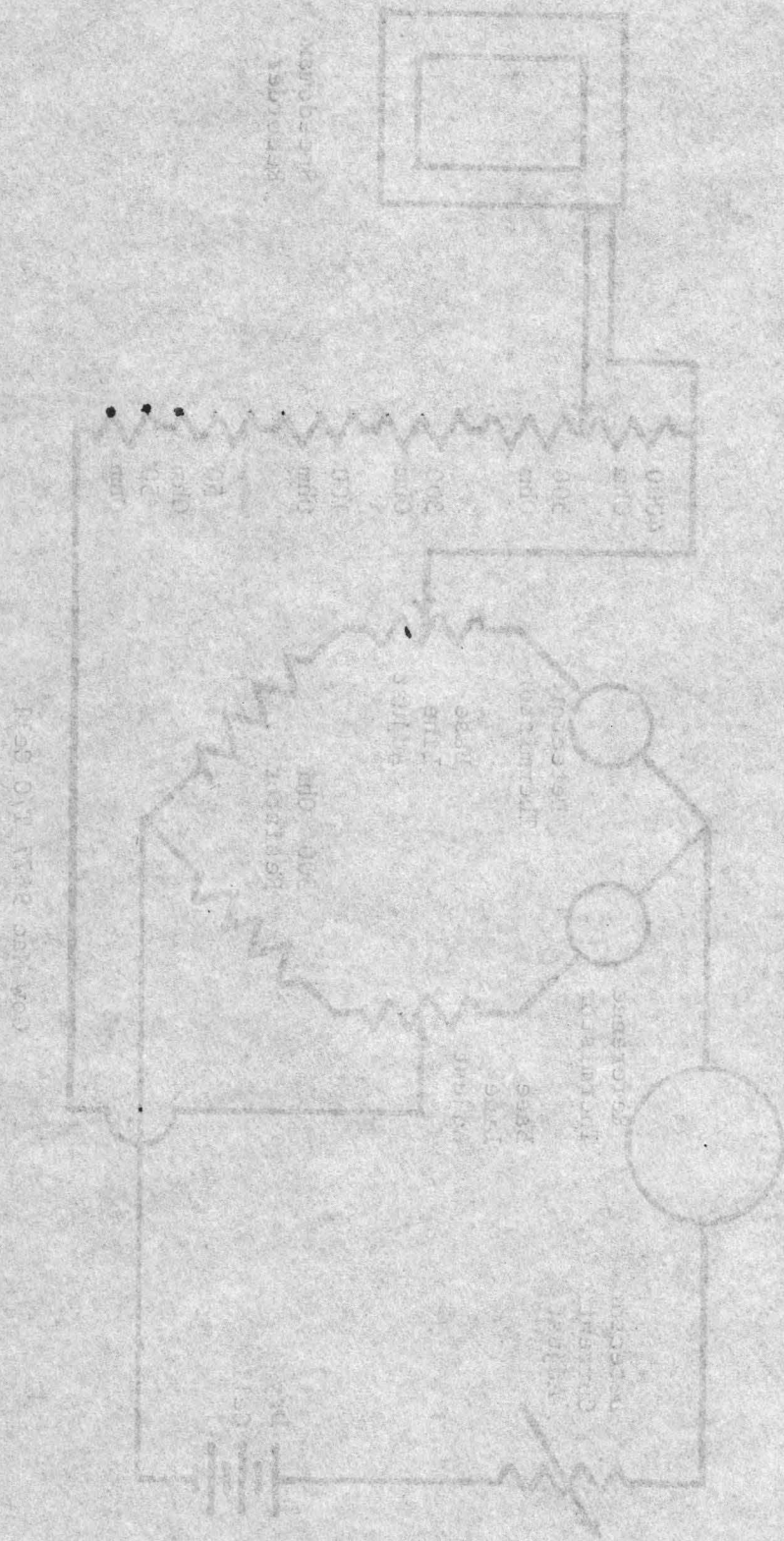


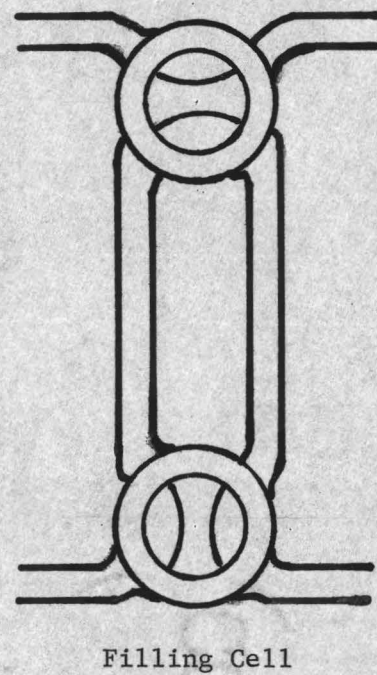
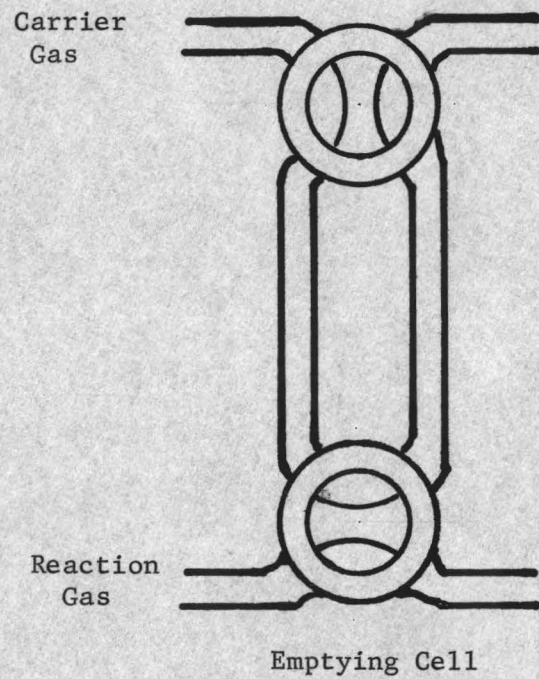
FIGURE 1. WHEATSTONE BRIDGE CIRCUIT

remaining acid on the firebrick. The firebrick was rinsed again and dried at 200°C. The dry brick was then coated with 20% by weight of tricresylphosphate (TCP) in the manner described by Keuleman.<sup>37</sup> This was then packed into the column by gentle tapping. To check possible reactions of gas with the column material, hydrogen sulfide samples were passed through the column and the recovery was compared to a sample which bypassed the column. It was found to be comparable within the 1% limit of experimental error of gas analysis by thermal conductivity methods. The TCP column also separated sulfur dioxide. Using hydrogen sulfide as the standard with a 1.00 retention time, air had a retention time of 0.69 and sulfur dioxide had a retention time of 3.5.

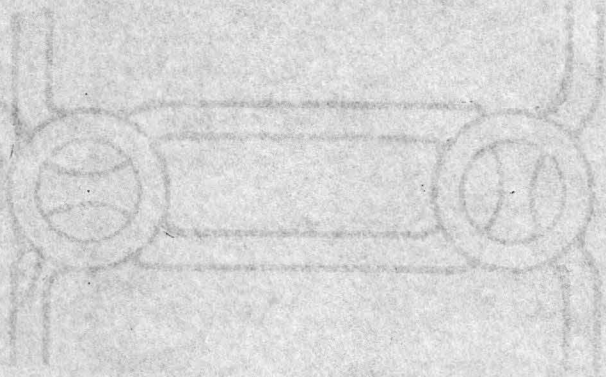
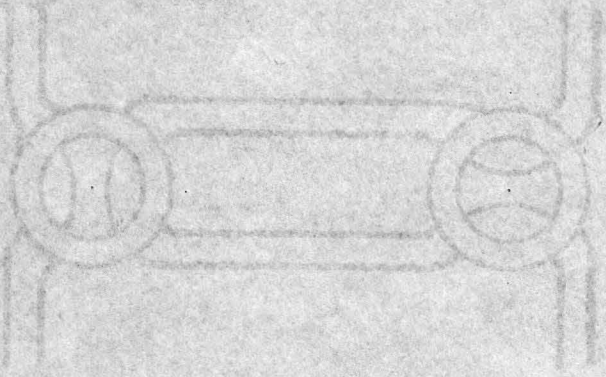
The second chromatographic column was packed with commercial 30/60 mesh 5A molecular sieve (artificial zeolite). The column was one-fourth inch O.D. copper tubing connected to a four-way stopcock with Beckman teflon unions. The molecular sieve column was contained in an oven maintained at 100°C and was used to detect hydrogen, oxygen and nitrogen.

The reacting gases could be introduced through a sampling device which consisted of two four-way stopcocks fused together as illustrated in Figure 7. The reactant gas, which was obtained compressed in cylinders, was used to purge the sample valves. The lower valve was turned one quarter turn, and a sample of gas 0.494 c.c. in volume was isolated between stopcocks. This volume measurement was made by weighing the mercury necessary to fill the sample cell. The lower stopcock would allow the reaction gas to continue into a caustic trap to remove the hydrogen sulfide. The upper stopcock allowed the carrier gas to bypass the sampling system and to continue through the apparatus. A quarter turn rotation of the upper stopcock allowed the carrier gas stream to be diverted into

FIGURE 7 SAMPLE CELL



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the sample cell and push the reaction gas contained in the sample cell through the apparatus.

The iron oxide was held in place with a glass wool in a capillary tube which was 2 mm. I.D. and 8 mm. O.D. The tubing was U-shaped and connected to a four-way stopcock with teflon unions. The reaction vessel was located downstream from the sample cell thus allowing the carrier gas to carry a sample of reactant gas to the iron oxide. As can be seen from the description of the apparatus, the reactant gas contacted only glass and teflon. The manifold containing the stopcocks was constructed of 2 mm. I.D. capillary tubing with the necessary connections of ball and socket joints. This manifold in turn was connected to the detector through teflon reducers.

Iron Oxide Preparation and Test: Industrial oxide had such a high density that it proved difficult to use in a flow through system. Iron oxide was precipitated on firebrick in a manner similar to that used in the preparation of discs for the Warburg series of experiments. However, when this iron oxide was exposed to hydrogen sulfide, the results were found to be non uniform. A few particles of iron oxide would get red while the rest of the particles became black.

Alpha, beta and gamma iron oxides are the three structural forms of ferric oxide. They were synthesized by the methods described in Inorganic Synthesis.<sup>40-41</sup> To test the effectiveness a 4.5 milligram sample of the respective iron oxides were placed in the U reaction tube. It occupied about 7 mm. of the length of the tube. Helium carrier gas was bubbled through water bubblers to insure that the catalyst was kept at a moisture content corresponding to contact with saturated carrier gas at room temperature. Pulses of 0.494 c.c. of hydrogen sulfide were passed over the iron



oxide. It took 1.1 seconds for the hydrogen sulfide pulses to pass any one spot on the iron oxide, neglecting diffusion. Thus each pulse corresponds to contact of hydrogen sulfide with the iron oxide for approximately one second. Table 9 lists the results of reacting the different forms of oxide with hydrogen sulfide by the pulse technique. The oxides were oxidized between series. Figure 8 is a plot of hydrogen sulfide removal versus pulse of the three synthesized oxides. The Figure shows the first reaction with hydrogen sulfide.

An induction period would show an increase in hydrogen sulfide removal from the removal by the previous pulse. The results show that there was an induction period for alpha iron oxide. After the fifth pulse an equivalent of 2.47 c.c. of hydrogen sulfide had passed over the iron oxide. Gamma iron oxide had absorbed 1.29 c.c., alpha iron oxide 1.46 c.c. and beta 0.30 c.c. of hydrogen sulfide. These differences may be due to different specific surface areas of the iron oxide which were not measured.

Effect of Water: A sample of gamma iron oxide was dried in acetone and momentarily heated to 200°C in a stream of dry carrier gas. The carrier gas was dried by condensing the water in a freeze out trap immersed in a bath of acetone and solid carbon dioxide. Surprisingly, the iron oxide reacted with hydrogen sulfide. The drying of the sample could have been incomplete, so a fresh sample was heated to 200°C in the stream of dried gas for half an hour. After this treatment, hydrogen sulfide was introduced into the reaction chamber. No reaction occurred. The freeze out trap for cooling the carrier gas was removed and the water saturated carrier gas was allowed to pass over the iron oxide for half an hour. It was found that the iron oxide had regained

TABLE 9

## Pulse Type Reactions

Reactions of the three forms of iron oxide. The table shows % of hydrogen sulfide not reacted with iron oxide. Numbers across the top indicate sequential reaction with air oxidation between hydrogen sulfide reactions.

Pulse (approx. seconds)	Gamma iron oxide			beta	Alpha iron oxide		
	1	2	3	1	1	2	3
1	4.3	0.0	19.8	83.1	53.6	67.2	51.9
2	8.5	0.1	24.8	6.9	86.2	75.6	79.3
3	32.8	37.9	88.6	14.4	101.2	79.6	95.7
4	76.9	70.5	93.8	35.7	100.1	94.2	99.4
5	91.2	80.3	94.2	63.5	101.8	98.4	99.5
6	97.5	100.4	95.8	90.1	100.3	97.3	101.5
7	100.4	104.5	97.3	96.1	101.3	99.3	100.5
8	95.5	109.4	96.2	97.9	97.8	97.2	101.7
9	96.2		97.3	99.1	88.9	98.8	99.6
10	96.2		99.3	100.4	99.4	98.2	101.7

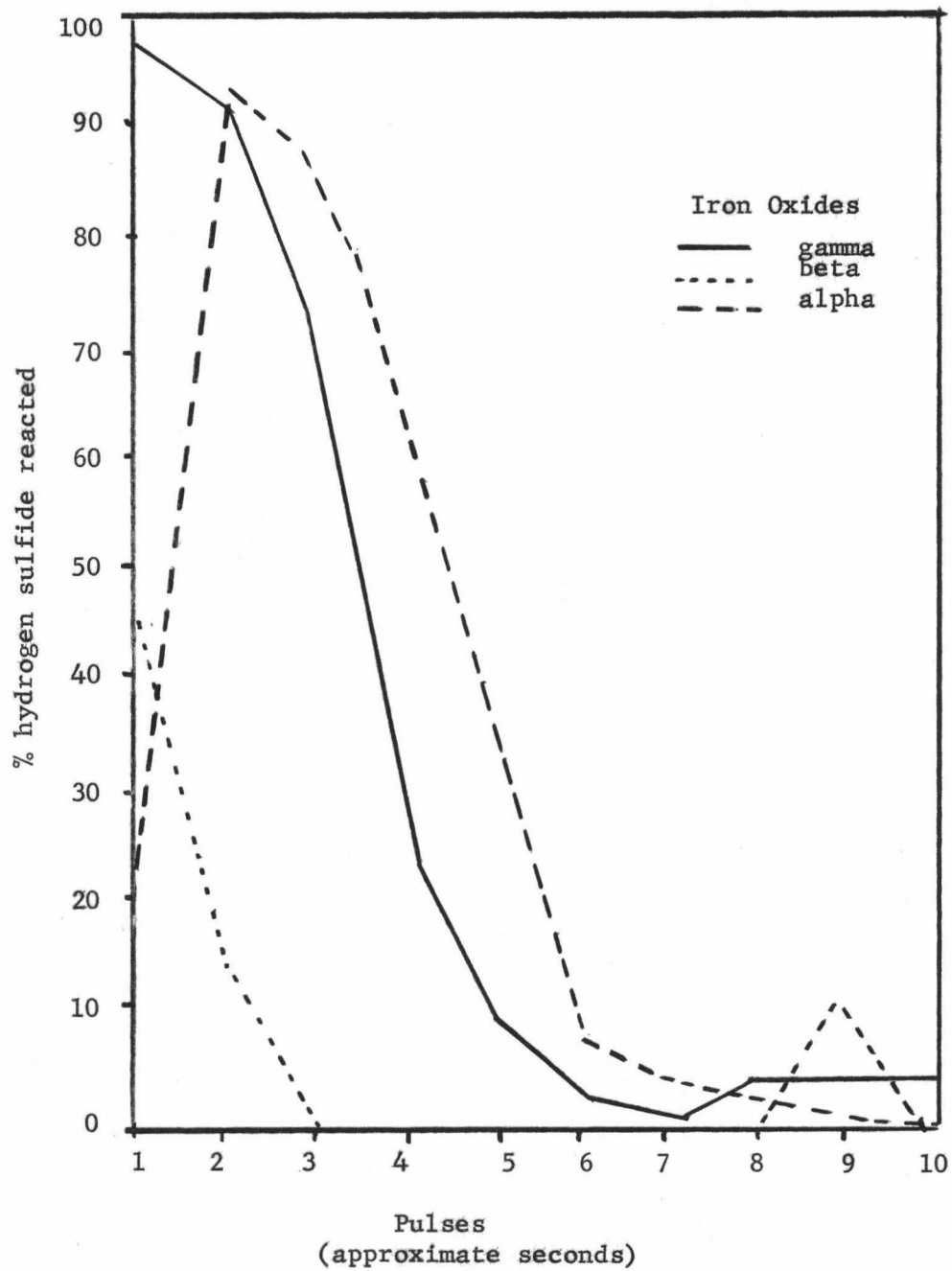


FIGURE 8. Hydrogen Sulfide Reacting With Iron Oxides

its activity. Iron oxide fouled with hydrogen sulfide and dried did not regain its activity after similar treatment.

Effect of Oxygen: It was found that after ten pulses of hydrogen sulfide, the iron oxide would not react with any more hydrogen sulfide. Oxygen was pulsed over this fouled iron oxide and the uptake of oxygen was determined. The absorption of oxygen was strangely erratic as illustrated by the results listed in Table 10. Figure 9 shows the first results of oxidation and the reaction with hydrogen sulfide immediately after this. The sequential oxidation is listed in series. Five standards were run randomly through the 1st series of pulses by bypassing the reaction vessel. The average deviation was 1.9 parts in 10,000, showing that the normal variations of measurement with the apparatus were not the cause of the erratic result. The erratic effect may have been due to uneven heating resulting from heat of reaction, which was not easily dissipated. This, however, was not investigated further. Table 10 also contains tabulated two other oxidations of fouled oxide which were carried out on the same sample in consecutive order.

After 30 pulses 0.231 c.c. of oxygen had been absorbed. Hydrogen sulfide was then pulsed over the iron oxide and in three pulses 0.421 c.c. of hydrogen sulfide was absorbed. In the isolated reactions of first hydrogen sulfide with iron oxide, and then, oxygen with sulfided oxide, it is evident that the former reaction was by far the faster.

In order to more closely simulate industrial conditions, where air is mixed with the gas containing the hydrogen sulfide, a blend was reacted with iron oxide at 30°C. The blend was made of 73.8% oxygen and 26.2% hydrogen sulfide. The ratio was kept constant by maintaining rotameter readings constant and the original gas mixture was analyzed by bypassing

TABLE 10

## Reaction of Oxygen With the "Fouled" Oxide.

Oxygen was passed over gamma iron oxide that had already reacted with hydrogen sulfide. The oxygen is expressed in % unreacted.

Pulse approx. sec.	Run Number		
	#1	#2	#3
1	99.12	98.16	97.89
2	98.50	98.35	97.63
3	98.75	98.16	98.28
4	98.44	98.55	98.54
5	98.50	98.55	98.54
6	98.19	98.48	98.54
7	98.50	98.48	98.67
8	98.13	98.48	98.67
9	98.44	98.48	98.41
10	98.25	98.55	98.74
11	98.75	98.61	98.54
12	98.44	98.30	98.67
13	98.75	98.48	98.74
14	99.25	98.55	100.06
15	98.62	98.61	99.32
16	98.99	98.55	99.52
17	99.12	98.68	99.71
18	98.12	98.55	99.71
19	98.37	98.87	99.71
20	98.19	98.81	100.04
21	98.44	98.87	99.06
22	98.31	98.81	99.52
23	98.50	98.81	99.52
24	98.19	98.68	99.91
25	98.44	98.87	99.85
26	98.19	98.87	99.91
27	98.19	98.61	99.52
28	98.13	98.81	99.85
29	98.13	98.68	99.91
30	98.13	98.81	100.17

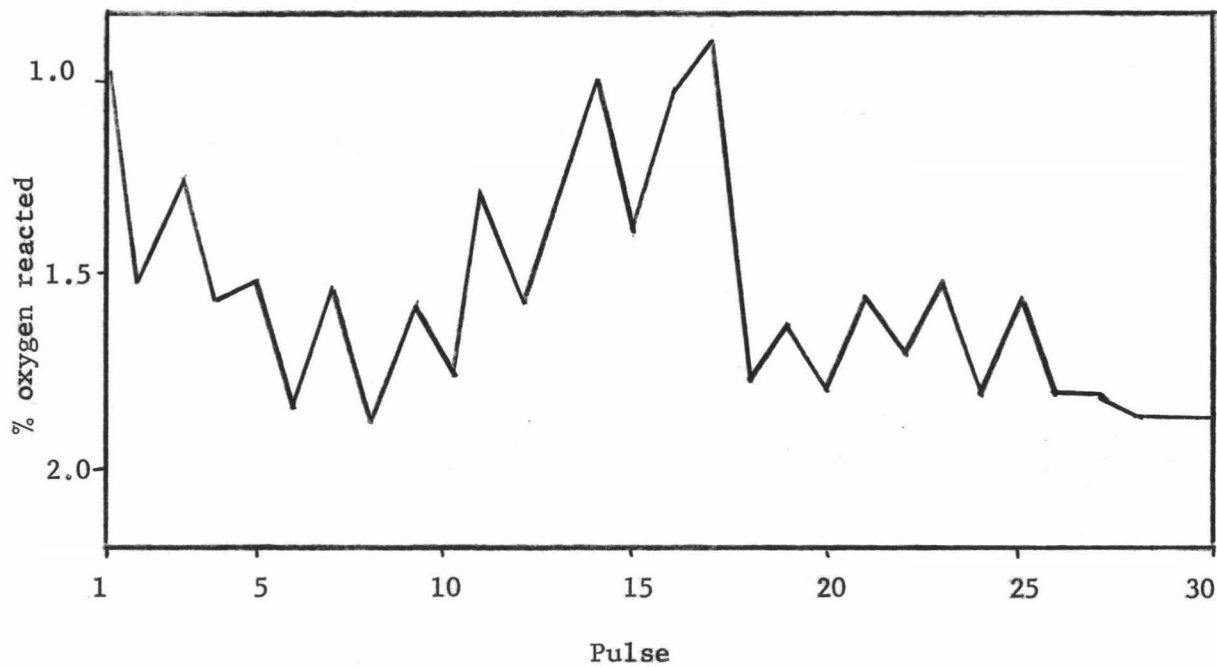
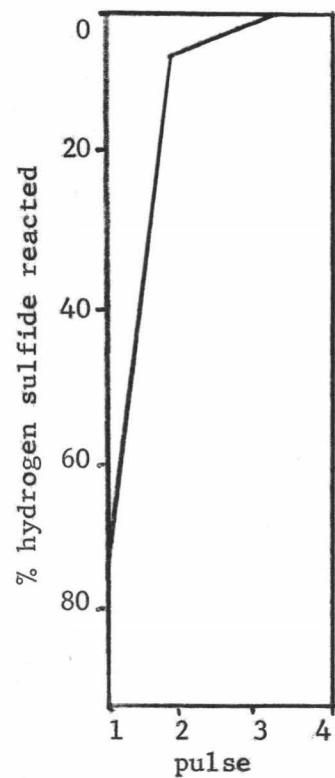


FIGURE 9. Fouled Gamma Iron Oxide Reacting With Oxygen

Above: Per Cent Oxygen Reacted With Fouled Sponge.

Right: Hydrogen Sulfide Reacting With Iron Oxide After Above Reaction.



the reaction vessel. After seven pulses over the iron oxide, 0.797 c.c. of oxygen and 0.646 c.c. of hydrogen sulfide were absorbed. Thus a total of 1.44 c.c. of gas was reacted which was similar to the amount of gas absorbed when hydrogen sulfide alone was reacted with this sample of iron oxide, where 1.43 c.c. was removed. Table 11 gives the results of this experiment and the results at 30°C are plotted in Figure 10. The gases were reported individually and plotted against pulse for the reaction at 30°C.

Effect of Temperature: Another reaction of a blend was run at 80°C. The blank showed the ratio of hydrogen sulfide to oxygen at 36.8% to 63.2%. The absorption of 0.212 c.c. of hydrogen sulfide and 0.412 c.c. of oxygen gave a total absorption of 0.624 c.c. of gas. This compared with 0.623 c.c. of hydrogen sulfide absorbed when only this gas was present as reactant. These measurements emphasize the complex nature of the mechanism involved in the reaction being studied, for no simple stoichiometry will explain this reaction behavior as illustrated later in the discussion.

Regeneration: The industrial iron oxides are known to increase in activity as they are used. This was not found to be the case for gamma iron oxide. Table 9 shows the first sulfiding, after which the oxide was left in air for twenty four hours and then re-exposed to hydrogen sulfide. These results are under series 2 for Gamma iron oxide. With the increase in the number of times the oxide had been exposed to hydrogen sulfide, the activity of the iron oxide increased but in the third series the activity decreased. The oxygen absorption, as shown in Table 10, decreased with usage. The effect of the physical barrier produced by the sulfur crystals was checked by removing the sulfur left from the first

TABLE 11

## Pulse Type Reaction Using a Gas Mixture

Hydrogen sulfide and oxygen were coadsorbed on gamma iron oxide. Data refers to the percent of gas in a pulse which was unreacted for an individual component.

Pulse No.	Temperature 30°C			Temperature 50°C		
	100% H <sub>2</sub> S	26.2% H <sub>2</sub> S	73.8% O <sub>2</sub>	100% H <sub>2</sub> S	36.8% H <sub>2</sub> S	63.2% O <sub>2</sub>
1	4.3	0.2	73.4	4.1	66.9	79.6
2	8.5	0.6	69.0	76.1	82.2	78.5
3	32.8	1.5	60.8	96.2	84.3	78.3
4	76.9	9.1	63.0	97.5	85.4	80.6
5	91.2	36.8	66.7	100.2	88.2	81.9
6	97.5	73.1	69.8	100.6	88.2	82.6
7	100.4	80.2	78.4	100.6	88.2	82.6
8	95.5	85.9	84.8			
9	96.2	85.8	95.1			
10	96.2	85.9	98.6			



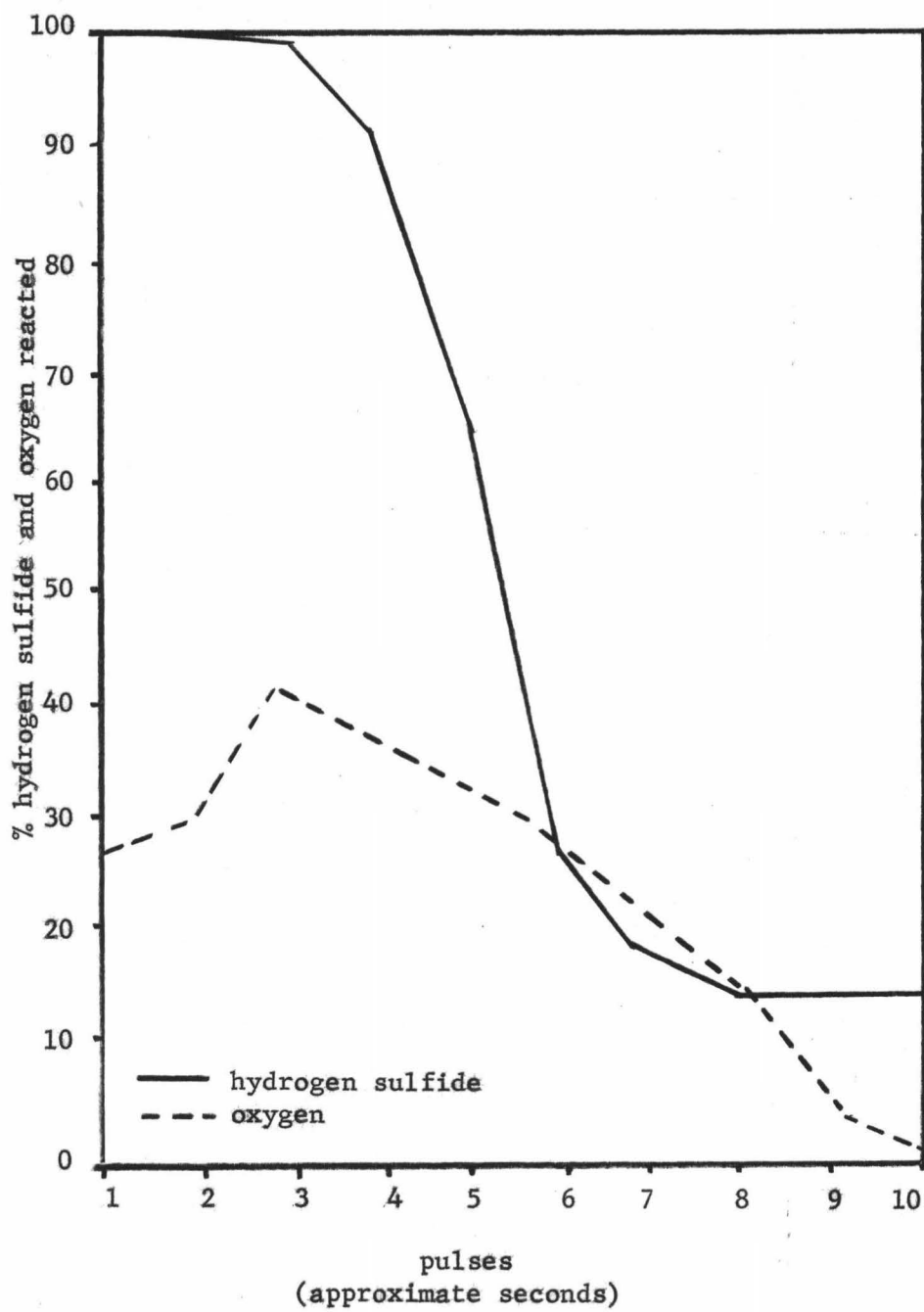


FIGURE 10. Combined Reaction With Gamma Iron Oxide

fouling by gas stripping at 200°C. This did not increase the capacity of hydrogen sulfide or oxygen absorption of the iron oxide.

Tabulated Data: The results of the pulse type experiments are tabulated in Table 12.

TABLE 12

## Summary of Results of Study

## With Flow Reactor and Chromatographic Column

	<u>Reactant</u>	<u>Substrate</u>	<u>Results</u>	<u>Tentative Conclusion</u>
(a) Test of types of iron oxides	H <sub>2</sub> S	Gamma, Alpha beta iron oxide	Gamma iron oxide most effective	Gamma ferric oxide is most effective in sulfiding
(b) Effect of moisture	H <sub>2</sub> S	Gamma iron oxide dry	No reaction when well dried	Moisture necessary for sulfiding reaction
(c) Effect of oxygen	O <sub>2</sub>	Fouled iron oxide	Erratic absorption at each pulse. 1/10 as fast as sulfiding reaction. Stoichiometry one O <sub>2</sub> : 2H <sub>2</sub> S	Oxidation of sulfided iron oxide is a slow reaction. Stoichiometry of reactions carried out in sequence is as expected for a simple chemical reaction
(d) Effect of oxygen when reactants combined	H <sub>2</sub> S	Gamma iron oxide	H <sub>2</sub> S reacted as alone. O <sub>2</sub> uptake many times faster. Stoichiometry variable	Oxide may behave as a "catalyst" under these conditions

### B. X-ray Studies of the Oxides and the Solid Reaction Product

A Philips Electronic X-ray diffraction unit with a powder diffraction camera was used for the examination of the iron oxides. The usual powder technique for X-ray identification of solids was employed. An iron target tube with a manganese filter was used to give a monochromatic X-ray beam of wave length of 1.934 angstroms. The X-ray tube was operated at 25 kilovolts and 15 milliamps. The Straumanis type powder diffraction camera had a diameter of 114.6mm.

The three synthesized iron oxides and the reaction product produced after five minutes exposure to hydrogen sulfide were used as samples. The samples were placed in lithium borate capillary tubes which are made especially for this purpose. The original oxides were exposed to the X-ray beam for four hours and the reacted iron oxides for eight hours. Also, a new method of holding the sample in place was attempted. A lucite rod one-eighth inch in diameter was used. A 78 gauge drill was used to bore a hole through the center of the rod. The rod was then cut to the required length to fit the mounting bracket and to reach the X-ray beam in the camera but not enter into the path. The sample to be run was ground to pass a 300 A.S.T.M. standard screen. It was then filled in the center hole of the lucite rod and tapped firmly with a wire rod. The sample was pushed out the end so that it protruded 2mm. This protrusion fell into the path of the X-ray beam and the photograph produced was of pure sample with no complications of absorption and refraction by a container. This method seemed less delicate in the manipulations involved, than using the fragile capillary tubes.

The positions of the diffractions maxima were measured on the developed film and with the use of the Bragg equation the following interplaner

openings were computed. The results are listed in Table 13 in order of decreasing intensity. The A.S.T.M. values are also listed.<sup>42</sup>

Only gamma iron oxide mono-hydrate was identified. If alpha iron oxide were present, it could not be identified. Also, the lines for beta oxide did not agree with the standard values given in A.S.T.M. cards.

The beta iron oxide reaction product was found to be the only product that appeared to have retained some spacings similar to the starting oxide. In any case, the reaction products did not correspond with the results found in the work reported by Banjeree.<sup>43</sup>

#### C. Microscopic Examination

Microscopic examination of the iron oxide was carried out with the type of microscope which employs reflected light (a metallurgical microscope). The different industrial oxide pellets were observed both before and after the reaction with hydrogen sulfide. Red dots were found on the surfaces of the iron oxide pellets. These were noted to be bright red as compared to the overall color of black or brown. Upon exposure to hydrogen sulfide these dots became black. Reoxidation was achieved by leaving the pellets in air for several hours whereupon it was noted that the dots became red again. However, the number of dots increased in number and size. Sulfur crystals had formed at certain points on the pellet surface and at the edges of the pellets. The crystals of sulfur were often stacked in such a way that it appeared as if one crystal had grown to a certain extent and the second crystal had appeared later beneath it, pushing the original away from the pellet. The peculiar formation of the sulfur crystals at point sites on the oxide might indicate that a crystalline defect or active center was a point about which chemical activity of catalysis centered.

TABLE 13

## Interplaner Openings of Iron Oxide Samples

Alpha Iron Oxide			Beta Iron Oxide			Gamma Iron Oxide		
Rel. d int. A <sup>o</sup>	d A <sup>o</sup>	A.S.T.M.	Rel. d int. A <sup>o</sup>	d A <sup>o</sup>	A.S.T.M.	Rel. d int. A <sup>o</sup>	d A <sup>o</sup>	A.S.T.M.
d	3.67	2.69	dw	7.39	3.33	d	6.32	6.32
d	2.51	2.51	dw	3.32	3.29	d	3.29	3.30
m	2.70	1.69	m	4.74	2.47	mw	2.45	2.48
m	2.21		m	2.29		mw	1.92	
m	1.69		mw	1.64				

The reaction products of all oxides with hydrogen sulfide gave very diffused powder photographs and are listed in the order of decreasing opaqueness of the lines on the powder diagram.

Alpha	Beta	Gamma
1. 4.19 A <sup>o</sup>	1. 7.38	1. 3.85
2. 3.43	2. 3.31	2. 3.20
3. 3.68	3. 2.30	3. 2.53
4. 3.30	.	4. 3.43

An examination of the iron oxide removed from a plant process stream showed numerous yellow crystals of sulfur. The oxide removed was very wet and as the solution evaporated, more crystals were noted to form. Finally, when only a thin layer of water was left, the crystals changed from a yellow color to a brownish red color of iron oxide or hydroxide. The brownish material readily turned black upon exposure to hydrogen sulfide and dissolved in hydrochloric acid. This behavior had previously been noticed by Avery.<sup>44</sup>

Alpha iron oxide which was covered with a thin film of water reacted only slightly with hydrogen sulfide and became a little more brown in color. When the adherent moisture was made basic with ammonia or sodium carbonate, the oxide became black immediately upon being exposed to hydrogen sulfide. The effect seemed to be a surface effect. The lower layers as observed from the bottom of the glass slide did not undergo reaction as evidenced by change of color.

#### D. Liquid Phase Studies

Equilibrium: All previous work tends to emphasize the important role played by water in the reaction being studied. In addition, it has been shown that in the mixed system both the sulfiding and the oxidizing reactions are completed within a very few seconds or minutes when all reactants have free access to each other. Other slow processes involving diffusion in the solid or liquid media may become important under industrial conditions, but can be neglected in a study of the basic chemical reactions. One might consider, then, reactions in aqueous media which are essentially complete. It would seem to be logical to extend the study one step beyond the kinetics, to the equilibrium condition toward which the reactions involved will tend to go.

Recently, equilibrium studies have been made by Garrels<sup>45</sup> on mineral systems involving the aqueous phase. The phases and components to be expected theoretically at thermodynamic equilibrium under various conditions are given by this author in charts plotting Eh against pH. Eh is a factor expressing the oxidation condition of the system and is defined as the electromotive force or the EMF of the system versus a saturated calomel electrode. One such system studied was that of sulfur-oxygen-iron-water. It would be instructive to see how closely the system under study in this work approaches the theoretical, and whether the phases involved in the industrial system exist within the theoretical diagrams.

1. Experimental Eh-pH: The studies involved measurements of Eh-pH on systems which contained components of interest in this study. A Beckman Zeromatic pH meter was used for the determination. A glass electrode and a saturated calomel electrode were used for the pH readings, and the saturated calomel electrode and a platinum wire electrode were used for the Eh readings. The electrodes were checked before use with two pH buffers and a standard solution of known value of Eh.<sup>46</sup> It was found that the electrodes had to be cleaned after every series of experiments and that it was necessary to change the saturated calomel solution in the reference cell at every session.

The first step was to find out if mixtures containing known components would easily come to equilibrium and would exist within the expected areas of the Eh-pH diagrams. For the first experiment, pyrite ( $\text{FeS}_2$ ) powder was suspended in water by a magnetic stirrer and Eh-pH readings were taken. It was found that by measurements of the change of readings with time, a fifteen minute mixing period was sufficient to attain constancy, or "equilibrium", for the components in contact. Typical examples of



these measurements are shown in Table 14 and the variation of pH with Eh can be followed on Figure 11.

To check the approach to equilibrium from the other direction, ferric hydroxide was precipitated by mixing correct amounts of ferric chloride and sodium hydroxide. This was deaerated with nitrogen and reacted successively with hydrogen sulfide and air. PH-Eh measurements were taken after equilibrium had been attained at each of these steps. The results are listed in Table 15 and the points can be followed on Figure 12.

The behavior of the industrial materials were tested in a similar manner. The results are listed in Table 16 and the behavior can be seen on Figure 13.

It is interesting to note, that in the oxide used in plant practice, it was found that by placing the electrodes in the moist iron oxide sponge stable readings of Eh-pH could be made. The oxide was made with equal weights of iron and sodium carbonate mixed on wood chips.

2. Liquid Phase Purifications: In order to utilize some of the information gained in this work and to apply it to the industrial gas system, laboratory purifiers involving reactants suspended in a liquid phase were constructed and tested under various conditions. The effect of the different alkali salts was investigated to determine their influence on the reaction. Unpurified illuminating gas containing 0.4% hydrogen sulfide and 1% oxygen was passed through gas washing bottles. The washing bottles had coarse sintered glass discs which dispersed the gas stream into fine bubbles. The removal of hydrogen sulfide was measured by Tutweiler apparatus and standardized iodine solution.<sup>48</sup> The alkalis were added in mole equivalents to a ferric sulfate solution and the results are tabulated in Table 17. This table again emphasizes that the reaction of hydrogen sulfide

TABLE 14

## Variation of Eh-pH Readings of Pyrite

A solution was treated with sodium hydroxide and hydrogen sulfide and changes in Eh-pH readings are listed. The Eh is in millivolts.

Number	Sample	pH	Eh
1	Pyrite and water mixture	1.8	.73
2	Added hydrogen sulfide	1.4	.17
3	Added sodium hydroxide	3.6	.15
4	Added hydrogen sulfide	2.6	-.15
5	Added Sodium hydroxide	3.9	-.20
6	Added hydrogen sulfide	3.6	-.00
7	Added sodium hydroxide	6.1	-.19
8	Added hydrogen sulfide	4.0	-.26
9	Added sodium hydroxide	8.1	-.28
10	Added hydrogen sulfide	6.8	-.17
11	Added sodium hydroxide	11.7	-.33
12	Added hydrogen sulfide	7.1	-.36

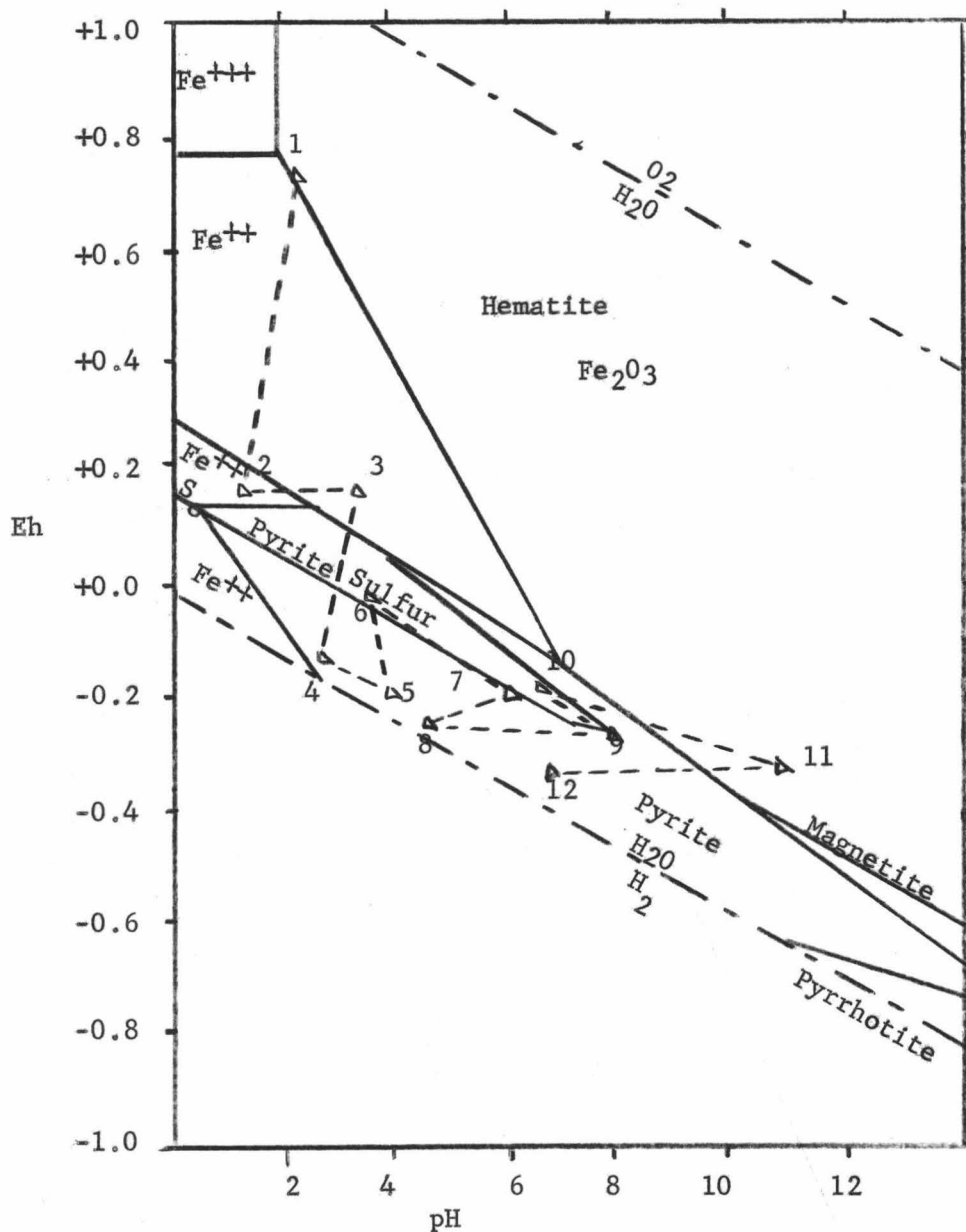


Figure 11. Stability Relations of Pyrite System

Stability relations of iron oxides and sulfides in water at 25°C and 1 atmosphere total pressure at an activity of dissolved sulfur of  $10^{-1}$ . Boundaries between ions and solids are at an activity of  $10^{-6}$  of dissolved iron specie. Reprinted from Garrels p 154. Superimposed are the results of actual Eh-pH measurements. See Table 14.

TABLE 15

## Variation of Eh-pH Readings of Ferric Hydroxide

Number	Sample	pH	Eh
1	Ferric hydroxide	11.2	.70
2	Added nitrogen	11.2	.02
3	Added hydrogen sulfide	4.4	-.01
4	Added air	6.2	-.04

TABLE 16

## Variation of Eh-pH Readings of Commercial Oxide

Number	Sample	pH	Eh
1	Fresh iron oxide commercial	10.0	.20
2	"Street gas" passed through	9.4	.18
3	Added hydrogen sulfide and gas	8.9	-.31
4	Added hydrogen sulfide 12 hours	8.2	-.26
5	Added hydrogen sulfide 24 hours	8.3	-.10
6	Added air	10.3	-.10
7	Dead oxide #8 purifier Hon. Gas	4.9	.20
8	Added hydrogen sulfide 20 min.	4.2	.13
9	Dead oxide #4 purifier Hon. Gas	5.5	.30
10	Added hydrogen sulfide 20 min.	4.3	.14

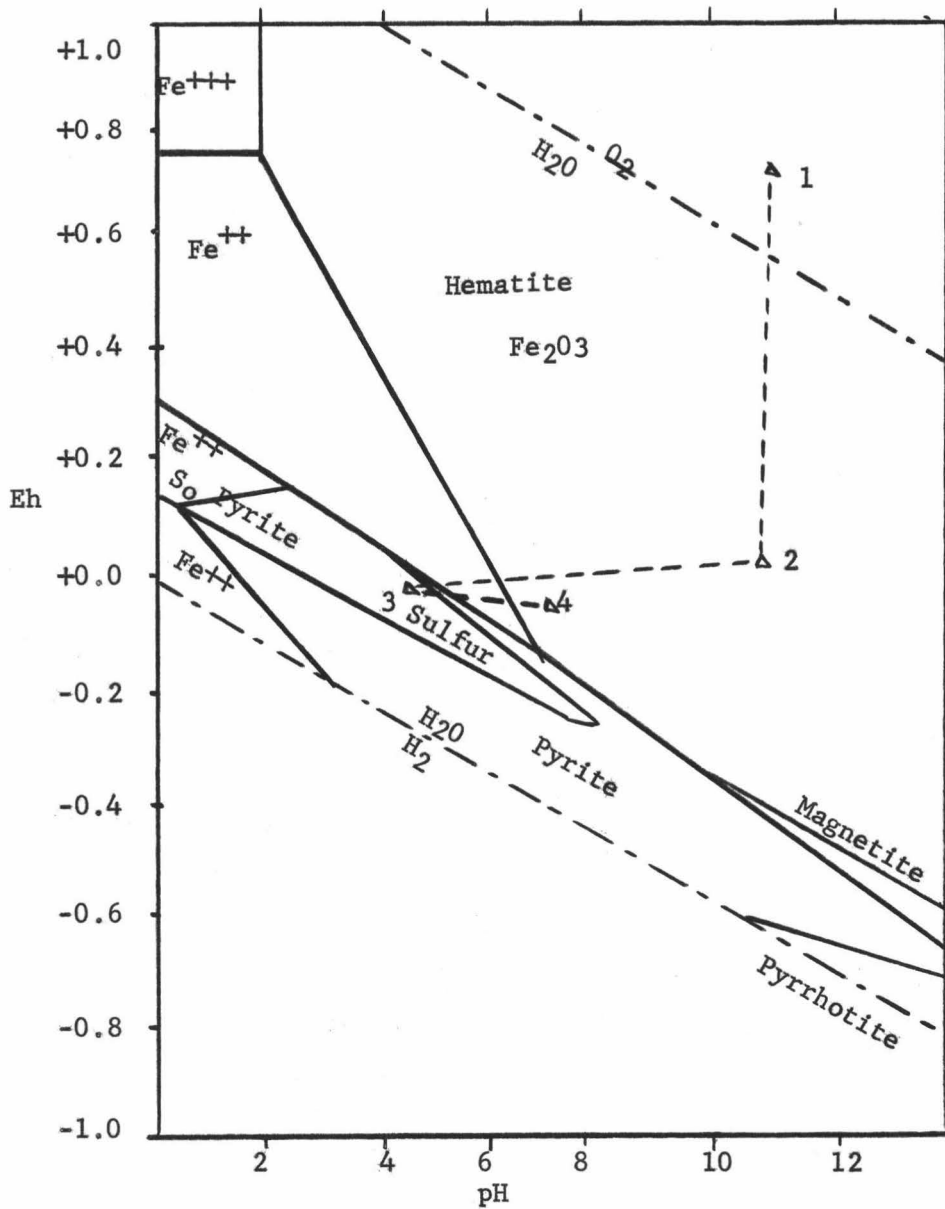


Figure 12. Ferric Hydroxide Reaction With Hydrogen Sulfide

See Table 15 for explanation of points. Reprinted from Garrels p154.

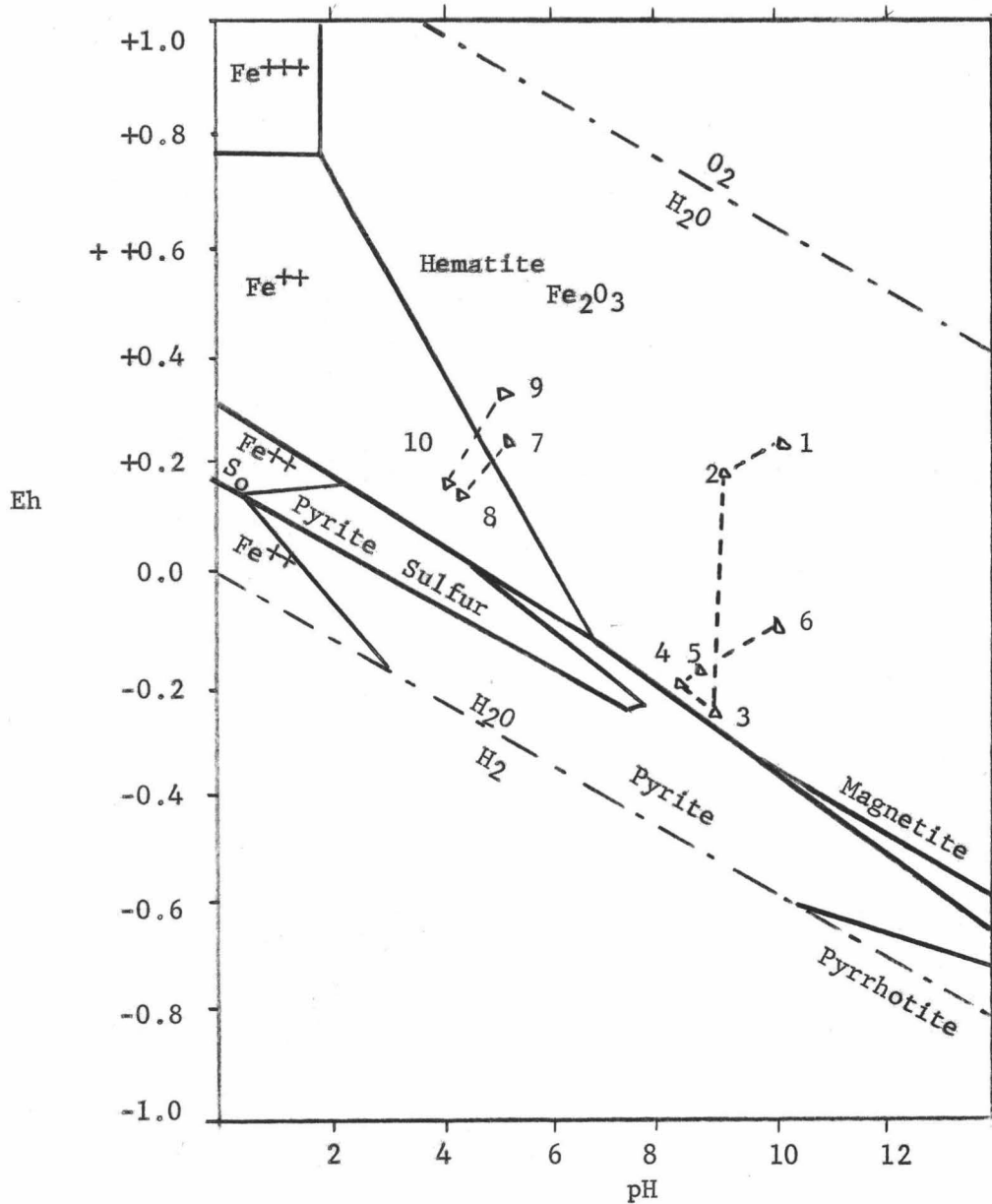


Figure 13. Industrial Oxide Reaction With Hydrogen Sulfide

See Table 16 for explanation of points. Reprinted from Garrels p154.

TABLE 17

## Liquid Phase Efficiency of Various Salts

Solution	% removal of H <sub>2</sub> S after 1cf
Sodium carbonate and ferric sulfate	99%
Potassium carbonate and ferric sulfate	88
Potassium hydroxide and ferric sulfate	84
Sodium hydroxide and ferric sulfate	54
Sodium hydroxide alone	0
Ferric sulfate alone	0

and iron oxide in the liquid phase was not a simple acid base reaction.

A more elaborate liquid type purifier was constructed to investigate further the reactions in the liquid phase. The reaction vessel was a glass tube one and a half inches in diameter and two feet long. The tube was filled with glass column packing, and the liquid was pumped to the top and allowed to flow by gravity over the packing. The gas was fed to the bottom and purified by counter current scrubbing action. The liquid was allowed to drip into a Waring blender, which acted as the oxidizing unit. Air bubbles were introduced below the blender blade so that the blades severed the rising bubbles and increased the oxidation rate. The oxidized solution was pumped from the bottom of the blender and recirculated. A solution of 12 grams of iron and 5 grams of sodium carbonate in 700 c.c. of water was used in the system. The equipment completely removed the 0.4% hydrogen sulfide in the gas stream. The starting pH was 11.1 which became progressively lower during the run resulting in a loss of efficiency of hydrogen sulfide removal. At a pH of 6.8 hydrogen sulfide started to evolve from the oxidation vessel. When the flow of hydrogen sulfide containing gas was stopped and the oxidation continued in the

blender, the pH became higher ending at a value of 10.8.

The addition of water, sodium carbonate, and potassium dichromate all increased the efficiency of hydrogen sulfide removal. The addition of an equal amount of such substances did not have the same effect on repeated application, but rapidly diminished in effect.



## IV. DISCUSSION

The overall reaction under investigation can be written:



In the past many investigators have postulated that this reaction occurred in the following steps:



The necessity of assuming a role for  $\text{Fe}_2\text{S}_3$ , a sulfide of iron which has never been prepared or observed, casts some doubt on this series of reactions.

Seil<sup>47</sup> divided the mechanism into two separate parts. He stated that both reactions occurred simultaneously and that the first was a theoretical reaction explained by equations (2), (3) and (4), and the other a catalytic reaction explained by equation (1).

The experimental results reported in this work fail to give any clear-cut answer to this question of the mechanism, or pathway, of the reaction. However, certain facts about the system which were already known have been verified, and certain new features with some tentative conclusions can be pointed out.

To summarize, the experiments with the Warburg apparatus lead us to the following conclusion: that an aqueous phase is essential, that the sulfiding reaction is first order, that oxidation reaction is slower and second order, and that at a higher temperature reaction may be very complex giving rise to unexpected products, hydrogen and oxygen.

The measurements with the flowing system, using the pulsing technique, demonstrated that gamma ferric oxide is the most effective form

of oxide in the sulfiding reaction, again, that moisture is necessary, that the stoichiometry of sulfiding and oxidation carried out in sequence is simple and expected, and that the stoichiometry and kinetics indicate that the combined reaction may be entirely different in nature.

The X-ray experiments were inconclusive, but did show that the solid reactants and products in this system have a low order of crystallinity or give products on which there is insufficient X-ray diffraction information to make identification.

Kinetic data indicated that the reactions being considered were of such velocity that they are completed within a few seconds or minutes, so that the reactions taking place within large industrial systems with long residence times might be considered as taking place at equilibrium. As mentioned in an earlier section, the equilibrium in the iron-oxygen-sulfur system has been studied by Garrels and Eh-pH diagrams representing the phases to be expected thermodynamically have been constructed. Studies on this system have been made in this work approaching the equilibrium from the pyrite ( $\text{FeS}_2$ ) side and from hematite ( $\text{Fe}_2\text{O}_3$ ) side. These indicated that the phases of the measured system appear in, or close to, the expected areas of the Eh-pH diagram, and that the experimental system, in fact, approaches equilibrium.

Applying the equilibrium measurements to the industrial system, we can see that the changes which take place again are in accord with the equilibrium diagram.

By study of Garrels' equilibrium diagram, it may be noted that certain correlations hold between the oxides and sulfides of iron and the dissolved form of molecular sulfur species which can be presumed to co-exist with them.

(1) In the field of hematite, sulfate ion is the stable form of dissolved sulfur. In this work, this ion has been detected in solutions drained from revived oxide.

(2) At pH's above 7, pyrite is stable with bisulfide ( $\text{HS}^-$ ) as the stable dissolved form of sulfur. Below pH 7, this latter becomes molecular  $\text{H}_2\text{S}$ .

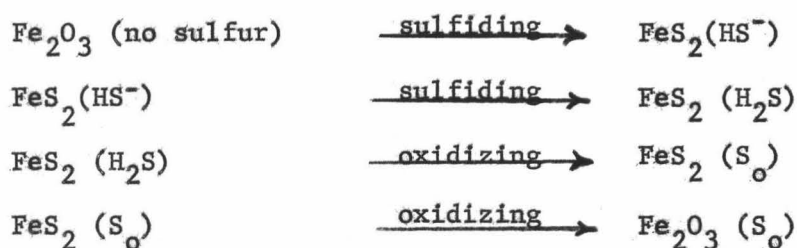
(3) Under greater oxidizing conditions at pH's below 7, molecular sulfur is the stable form of sulfur.

It should be noted that in constructing the equilibrium diagrams, Garrels has made certain assumptions:

(a) He has assumed that only sulfate ion, bisulfate, native sulfur, hydrogen sulfide, bisulfide ion and sulfide ion are present in appreciable quantities at room temperature. More than 40 other ionic and molecular species containing sulfur, he states, have been shown to be present in negligible amounts.

(b) Other sulfides of iron exist, such as marcasite, which cannot be fitted to the diagrams because of lack of thermodynamic data. It can be seen, then, that the equilibrium diagrams might be altered somewhat if all species were to be included. Thus it is not surprising if measurements on actual systems are found to give points situated slightly outside of the expected areas in these theoretical diagrams.

The reactions observed for the industrial sponge could be written as follows:



As has been pointed out, there is a multitude of sulfur species present, of indefinite character, some in minor amounts, so that formulation of exact equations for the reactions taking place could be attempted only with some hesitancy. For example, one could attempt to simplify and write for the sulfiding reaction



but this would require an increase in pH, which is contrary to the observed behavior in the system. One could also write for the oxidation of  $\text{FeS}_2$



but this fails to account for the increase of pH actually noted during oxidation. It can be concluded only that the reactions are more complicated than simple equations would indicate.

The complex nature of the actual reactions also has been brought out in (a) the complicated products of reactions found in the Warburg experiments, and (b) the irrational stoichiometry noted in the pulsed reactions and the different kinetics noted in the reaction with mixed reactants ( $\text{O}_2$  and  $\text{H}_2\text{S}$ ) when compared to the same reactions performed in sequence.

Application of Results to Industrial Practice: The information gained in this work can be applied to dry box purification of gas on the commercial scale. In the absence of reviving air in the gas to be processed, the iron oxide would follow the path of Eh-pH measurements listed in Table 16. Depending on the total amount present, the iron oxide would be converted to pyrite as the stable form. The iron oxide would then be "fouled". This product could be revived by exposure to air or oxygen which is a much slower process as revealed by kinetic studies. This sequential operation

was the procedure used in the early applications of iron oxide for the removal of hydrogen sulfide from illuminating gas.

In later practice, the addition of 0.5% or more reviving oxygen to the gas stream before it came in contact with the iron oxide became the common practice. Effectively, the rapid combined reaction is involved for a period of time depending on the amount of iron present. The iron oxide substrate gradually decreased in pH and the rate is lowered considerably. It would be deduced from this study that both sulfiding and oxidation could continue despite the drop in rate of the sulfiding reaction. This was also noted in plant practice, and the oxide boxes would not be rotated for periods up to several weeks. The efficiency of the oxide slowly decreased and when the oxide was no longer effective the boxes were rotated.

Another operating procedure was also found to be very effective. The period of rapid combined reaction was found to be about twelve hours long for the amount of iron oxide in the process stream at Honolulu Gas Company. Shortening the rotation period to twelve hours allowed a greater usage of the oxide and by such a change, Honolulu Gas Company was able to reduce the amount of iron oxide necessary to 50% of the original. During this rapid reaction the oxygen and the hydrogen sulfide were co-adsorbed and the Eh-pH readings indicate that the iron oxide never leaves the area where it is most stable as hematite.

As has been shown in this work, Eh-pH measurements can be easily made on the iron oxide sponge as it exists in the process stream. This would enable the activity of the oxide to be measured, and this could be used in rotation control and in anticipating the life of the oxide.

The gas chromatograph with a tricresylphosphate column could also be

used to study catalytic reaction rates in plant practice and to determine how the variables could be changed to achieve greater capacity and oxide effectiveness. It may also be used as an analytical method to measure hydrogen sulfide in the process stream instead of the Tutweiler apparatus which is now favored.

## V. CONCLUSIONS

The overall conclusions which can be reached for removal of hydrogen sulfide in the iron oxide system and the subsequent or concurrent oxidation, may be summarized as follows:

1. The reactions of sulfiding and oxidation require the presence of aqueous phase.
2. The rate of reaction in the system involving both sulfiding and oxidation, as in the industrial system, is relatively rapid.
3. No simple equation can be written for the reactions involved in sulfiding or oxidation which will account for the stoichiometry and the pH changes observed.
4. The system can be treated as an equilibrium situation which is approximated in the theoretical equilibrium diagrams of Garrels. However, until diagrams can be constructed based on experimental data, which give a complete picture of all components and phases present no certain reaction scheme can be deduced from such studies. It is believed that the greatest possibility for progress in future studies on these reactions will come about through the study of equilibrium, using diagrams which have been deduced from actual measurements.

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