



The catalytic reduction of calcium sulfate
by Thomas William Zadick

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of
MASTER OF SCIENCE in Chemical Engineering
Montana State University
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Abstract:

In several processes for obtaining elemental sulfur from gypsum the first step involves the reduction of calcium sulfate to calcium sulfide. However, these reactions require extremely high temperatures and relatively long reaction times. Very little work is reported concerning the use of a catalyst in reducing the calcium sulfate.

In this study, ferric oxide was found to have a pronounced catalytic effect on the reaction. Using this catalyst a study was made of the reduction of calcium sulfate in a fluidized bed reactor. Carbon monoxide gas was used as a reducing agent. A uni-variant search technique was employed in order to study the effect of time, temperature, weight per cent catalyst, and carbon monoxide flow rate. In addition, the auto-catalytic effect of calcium sulfide was investigated.

The optimum operating temperature was found to be 680°C. At this temperature the conversion was 97.1 per cent reduction of calcium sulfate in 45 minutes. This compares favorably with the conversion obtained using no catalyst and much higher reaction temperatures. The effect of varying the temperature was found to be relatively pronounced. This seems to indicate that the chemical rate of reaction might be controlling.

The optimum concentration of ferric oxide was found to be approximately 9 weight per cent. These runs were made at 720°C for 45 minutes. Conversion drops off sharply for concentrations below 7 weight per cent ferric oxide. Above 9 per cent concentrations the conversion is slightly smaller.

The carbon monoxide flow rate had little effect on conversion, indicating that the controlling mechanism is not film diffusion.

Runs made at 660°C showed definite reproducible oscillations when plotting the conversion of calcium sulfate with time. It was postulated that these oscillations were probably the result of a complex autocatalytic mechanism since an autocatalyzed reaction will behave in this manner under exceptional conditions. However, this behavior was not investigated further because a more elaborate reactor would be required.

Calcium sulfide was found to autocatalytically favor its own rate of formation. This would suggest that a certain amount of re-cycle of products would be desirable in the actual process design.

At 720°C for a 10-minute run it was possible to increase the conversion by about 30 per cent by adding calcium sulfide to the reactants.

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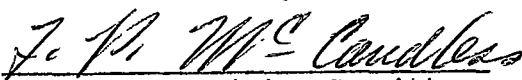
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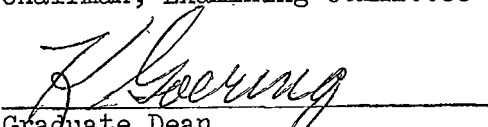
in

Chemical Engineering

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MONTANA STATE UNIVERSITY
Bozeman, Montana

March, 1971

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ACKNOWLEDGMENTS

The author wishes to thank the entire faculty of the Chemical Engineering Department at Montana State University for their encouragement and suggestions. In particular, the author is indebted to Dr. F. P. McCandless, whose direction and assistance aided him in the completion of this project. Also, special thanks must be given to Mr. James Tillery and Mr. Cyrus Huso for their help in constructing and repairing the apparatus used in this study.

The author was awarded a National Defense Graduate Fellowship under Title IV of the National Defense Education Act of 1958, and the majority of his work was supported by this grant.

Finally, the author wishes to thank his family, his wife, Linda, and his son, Tommy, for their sacrifices and encouragement.

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ABSTRACT

In several processes for obtaining elemental sulfur from gypsum the first step involves the reduction of calcium sulfate to calcium sulfide. However, these reactions require extremely high temperatures and relatively long reaction times. Very little work is reported concerning the use of a catalyst in reducing the calcium sulfate.

In this study, ferric oxide was found to have a pronounced catalytic effect on the reaction. Using this catalyst a study was made of the reduction of calcium sulfate in a fluidized bed reactor. Carbon monoxide gas was used as a reducing agent. A univariant search technique was employed in order to study the effect of time, temperature, weight per cent catalyst, and carbon monoxide flow rate. In addition, the auto-catalytic effect of calcium sulfide was investigated.

The optimum operating temperature was found to be 680°C. At this temperature the conversion was 97.1 per cent reduction of calcium sulfate in 45 minutes. This compares favorably with the conversion obtained using no catalyst and much higher reaction temperatures. The effect of varying the temperature was found to be relatively pronounced. This seems to indicate that the chemical rate of reaction might be controlling.

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Runs made at 660°C showed definite reproducible oscillations when plotting the conversion of calcium sulfate with time. It was postulated that these oscillations were probably the result of a complex autocatalytic mechanism since an autocatalyzed reaction will behave in this manner under exceptional conditions. However, this behavior was not investigated further because a more elaborate reactor would be required.

Calcium sulfide was found to autocatalytically favor its own rate of formation. This would suggest that a certain amount of recycle of products would be desirable in the actual process design. At 720°C for a 10-minute run it was possible to increase the conversion by about 30 per cent by adding calcium sulfide to the reactants.

INTRODUCTION

Gypsum is a mineral that occurs in large deposits throughout the world. Chemically, gypsum is hydrated calcium sulfate, with the formula $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. Gypsum is also produced as a by-product from the wet-process phosphoric acid and fertilizer manufacture.¹ When gypsum is heated to about 120 to 150°C with constant agitation to maintain a uniform temperature, it is calcined to the hemihydrate form, $\text{CaSO}_4 \cdot 1/2 \text{H}_2\text{O}$, and is known as first settle plaster. If it is heated further to a temperature of 190°C, it is calcined to the anhydrite form, CaSO_4 , and is known as second settle plaster.¹

Practically all the gypsum plaster sold is in the form of first settle plaster mixed with asbestos, wood pulp, or sand as a filler. Second settle plaster is used in the manufacture of plasterboard and other gypsum products. However, a good percentage of the gypsum which occurs naturally or as a by-product is not pure enough to be calcined for these industries. As a result, it is not being used.

In times of short sulfur supply, gypsum could become an important source of elemental sulfur. Natural deposits of gypsum might be mined to recover the mineral. Even more desirable would be the reduction of the by-product gypsum from the wet-process phos-

phoric acid and fertilizer manufacture. In the past these industries have encountered a problem of waste disposal for this mineral. Reduction of the gypsum to elemental sulfur would eliminate this disposal problem as well as provide a desirable source for sulfuric acid which could be recycled back to manufacture the phosphoric acid.

There are several processes for the winning of elemental sulfur from gypsum. The details of these reactions are discussed in the literature survey. In general, these processes involve three principal steps. They are:

1. The reduction of the gypsum to calcium sulfide using a convenient reducing material.
2. The conversion of the calcium sulfide to hydrogen sulfide.
3. The liberation of elemental sulfur from hydrogen sulfide by the conventional Claus-Chance Process.

The reduction of the gypsum to calcium sulfide requires extremely high reaction temperatures and relatively long reaction times. The design, construction, and operation of a high temperature reactor capable of satisfying these restrictions would understandably tax the economic feasibility of such a process. And, in fact, before gypsum can be used as a source for elemental sulfur, the economics of the process must improve.²

Since high temperature reactors are expensive to build and operate, the economics would improve if the temperature and processing time could be reduced. This raises the question of the use of a catalyst or a more active reducing agent in this process.

Very little work is reported in the literature involving the use of a catalyst in the reduction of gypsum. One article³ mentions the use of a chromium trioxide catalyst with a reducing agent of peat. The chromium trioxide reportedly enabled a lower reaction temperature to be used. This suggests the possibility of investigating other compounds for catalytic activity.

Significant success was reported by H. R. Appell and I. Wender⁴ in using nascent hydrogen in the hydrogenation of coal. The active hydrogen reducing gas was formed at the bed by the reaction of carbon monoxide and water. Using this reducing gas, the required time for hydrogenation of the coal was shortened. Therefore, this reducing gas might permit the reduction of calcium sulfate at lower temperatures and shorter processing times.

Thus, the objective of this research was twofold. First, nascent hydrogen must be investigated as a potentially more active reducing gas. Second, the catalytic activity of several compounds must be studied. Based on these results, the economics of this process might be improved.

SURVEY OF PREVIOUS WORK

From the literature it appears that several interesting studies have been made concerning the production of sulfur from gypsum. In general, three reaction steps are involved in the complete conversion of gypsum to elemental sulfur. These are:

1. The reduction of the calcium sulfate to calcium sulfide using some convenient reducing gas.
2. The conversion of the calcium sulfide to hydrogen sulfide.
3. The liberation of elemental sulfur from hydrogen sulfide using the conventional Claus-Chance Process.

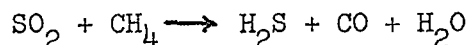
The first of these reactions is limiting the economic feasibility of this process.² In order to convert gypsum to calcium sulfide, the reaction requires extremely high temperatures and relatively long holding times. The primary goal of this research was to attempt to improve the reaction conditions for this first step. As a result, this survey will be primarily concerned with the previous work reported in the literature dealing with the reduction of calcium sulfate to calcium sulfide.

Several of these articles discuss the production of calcium sulfide from calcium sulfate with no further processing mentioned to obtain hydrogen sulfide or elemental sulfur. S. M. Ali and others⁵ report the use of a hydrogen reducing gas at temperatures

of 870-920°C in order to reduce the calcium sulfate. A process in which coal was used as a reducing agent at 900°C was studied by P. P. Reddy.⁶ Work involving the use of non-coking coal was done by Lisouskii.⁷ In this process the reaction was carried out in an arc furnace at a temperature of 950-1050°C with the gypsum being introduced in the form of briquets. Other reactions reported include the use of a natural gas reducing agent at 800-1050°C,⁸ the use of coal, carbon monoxide, or hydrogen at 950-1000°C,⁹ and the use of peat along with a chromium trioxide catalyst to lower the reaction temperature to 900°C.³

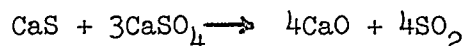
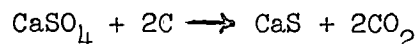
Several of the articles investigated were involved with the entire process for producing sulfur from gypsum. These articles will be briefly discussed with emphasis placed on the conversion of gypsum to calcium sulfide.

One article discussed the production of hydrogen sulfide and sulfur from sulfur dioxide and methane.¹⁰ The principal reaction appeared to be:

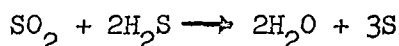
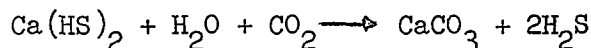
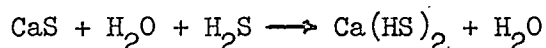
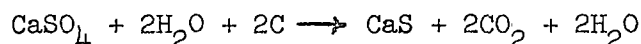


although CS₂, COS, and S₂ were also produced. In this article, the effect of the ratio of reactants, temperature, and space velocity on the yield of hydrogen sulfide were determined. This work is

interesting since gypsum can be reduced to produce sulfur dioxide via the Müller-Kuhne reactions:¹¹

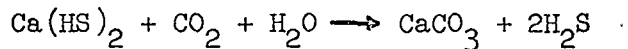
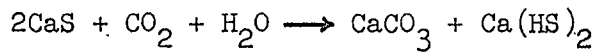


Three French patents also deal with the production of sulfur from gypsum.¹² These produce sulfur by the following reactions:



A process which is very similar to this French Process was developed by the U. S. Bureau of Mines.¹³ In this process the gypsum is reduced to calcium sulfide using any one of a number of suitable reducing agents. These include coal, coke, natural gas, carbon monoxide, or hydrogen. The reactions are carried out in a rotary kiln, fluidized bed, or other suitable reactor to produce calcium sulfide. The reaction using coal can attain 94 to 98 per cent conversion at temperatures between 900 to 950°C. Next a slurry of calcium sulfide is contacted with the carbon dioxide rich off-gas

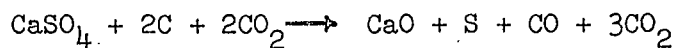
from the reduction reactor. This results in the precipitation of calcium carbonate and the evolution of hydrogen sulfide:



Bureau of Mines personnel predict 95 per cent conversion of the calcium sulfide can be attained at near stoichiometric use of the carbon dioxide. The hydrogen sulfide is then converted to elemental sulfur by the Claus-Chance Process.

Another process which the Bureau of Mines has investigated produces sodium carbonate and calcium chloride as by-products.¹³ However, the reduction of gypsum to calcium sulfide occurs in the same manner as before. The process differs in its treatment of the calcium sulfide to obtain these end products, and is of no further interest to this study.

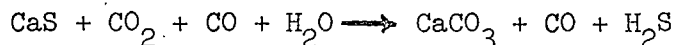
A recent patent discloses a process for the production of sulfur from metal sulfates in a one-step process.¹⁴ This is done by mixing the sulfate with carbon and contacting the resulting mixture with hot gases containing carbon dioxide. The resulting reaction forms elemental sulfur and the corresponding metal oxide:



The reaction is carried out in a fluidized bed with the hot fluidizing gases containing at least 15% carbon dioxide. The reactor is maintained at about 870°C. This reaction appears to have great potential since it is a one-step process.

Another U. S. patent also deals with the production of hydrogen sulfide from gypsum.¹⁵ In this process powdered gypsum is heated to 900-1000°C in a stream of reducing gases (a mixture of hydrogen, natural gas, or a mixture of hydrocarbons) and steam. Hydrogen sulfide is produced in the reaction and the solid product is cooled in the absence of air to yield lime.

Finally, a French patent deals with the production of high grade sulfur from calcium sulfate.¹⁶ The calcium sulfate is reduced in a closed retort in the presence of carbon. The resulting calcium sulfide is then treated in an aqueous suspension with a gaseous mixture of carbon dioxide and carbon monoxide. The carbon dioxide reacts with the calcium sulfide to form hydrogen sulfide:



The hydrogen sulfide and carbon monoxide are then passed through a closed retort containing calcium sulfate to form a mixture of water and free sulfur.

In general, the reduction of calcium sulfate to calcium sulfide is a process characterized by extremely high temperatures and relatively long reaction times. Temperatures from 900 to 1000°C are common, and processing times of three to four hours are not unusual in order to affect a high percentage reduction of the calcium sulfate. In spite of these extreme conditions, very little work is reported concerning the catalytic reduction of calcium sulfate.

One article³ mentions the use of a chromium trioxide catalyst. In this process peat was used as a reducing agent. The reaction temperature was lowered upon addition of the catalyst.

Although this is the only article which mentions the use of a catalyst in the reduction of calcium sulfate, the reported success might indicate that the reaction could be affected by the addition of a catalyst. Because the catalytic mechanism is not completely understood, the development or promotion of a catalyst is largely an art. The use of a catalyst in reduction processes is not a novel idea. Some work has been done concerning the catalytic reduction of sodium sulfate,^{17,18} and this work is closely related to this project.

In these studies the reduction of sodium sulfate to sodium sulfide has been investigated at temperatures ranging from 500 to

900°C. The catalysts tested were compounds of iron, nickel, copper, platinum, and sodium. Using a hydrogen reducing gas, the most effective catalysts were found to be iron compounds added as either an oxide or a sulfate. Using coal as a reducing agent, the most effective catalysts were compounds of iron and copper. Nickel compounds were reported to produce some catalytic effect, although this activity was not as pronounced as those of copper and iron. Sodium sulfide was also reported to exhibit a slight effect on its own rate of formation.

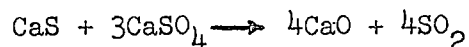
A majority of the work reported on the reduction of calcium sulfate investigates various reducing agents for their potential activity. A more active reducing gas might succeed in reducing the extreme conditions required for conversion. In the hydrogenation of coal, researchers have reported significant success by reacting carbon monoxide and water to form nascent hydrogen at the reduction site. The time required to affect a 90 per cent conversion using carbon monoxide and water was 10 minutes. Using a hydrogen reducing gas, 80 per cent conversion was attained in 2 hours.⁴ The carbon monoxide-water reducing gas might possibly activate the reduction of calcium sulfate in a similar manner. This might permit a reduction in the operating temperature and the processing time.

THERMODYNAMIC STUDY

A brief thermodynamic study¹⁹ was made for the different processes mentioned in the literature survey. The results of this study are summarized in Tables I and II. Table I shows the estimated change in free energy at various temperatures for the reactions of interest. Table II summarizes the heats of reaction for these processes.

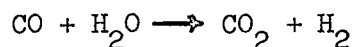
Several interesting conclusions can be drawn from these tables. The reduction reactions for various reducing agents are all endothermic except for the carbon monoxide and hydrogen reducing gases. Also, a favorable change in free energy was calculated for temperatures above 227°C for all of the reducing reagents. However, for carbon monoxide and hydrogen the change in free energy is favorable even at room temperatures. From this point of view, the carbon monoxide or hydrogen reducing gases might have a slight advantage over the others.

Another important point is that at higher temperatures, near 1500°K, the reaction



becomes thermodynamically favorable. Therefore, if calcium sulfide is the desired product, a temperature much above 1000°C should be avoided to eliminate this reaction.

A thermodynamic study investigating the reduction of calcium sulfate in a nascent hydrogen atmosphere was not made since no thermodynamic data was available on nascent hydrogen. Assuming the properties are not too different than molecular hydrogen, a simple study was made. For the following reactions:



a few general conclusions were reached. The formation of the activated hydrogen was thermodynamically favorable over a temperature range from 0 to 700°C. The reduction of calcium sulfate was favorable for any temperatures. And finally, the overall reactions appeared to have favorable thermodynamics for the temperatures from 0 to 700°C.

Nothing can be said about the kinetics of these reactions at this time. The kinetic relationships can be determined only by experiment. In general, the kinetics of these reactions appear to be limiting the conversion since these reactions require extremely high temperatures and relatively long reaction times in order to react to equilibrium.

Table I. Calculated Free Energy Changes for Reactions Involved
in the Reduction of Gypsum (16)

Reaction	Free Energy Change in Kcal/mole			
	298°K	500°K	1000°K	1500°K
1. $\text{CaSO}_4 \cdot 2\text{H}_2\text{O} + 2\text{C} \rightarrow \text{CaS} + 2\text{CO}_2 + 2\text{H}_2\text{O}$	+17.4	-14.3	-92.7	-171.0
2. $\text{CaSO}_4 + 2\text{C} \rightarrow \text{CaS} + 2\text{CO}_2$	+12.9	- 4.7	-48.4	- 92.1
3. $\text{CaSO}_4 \cdot 2\text{H}_2\text{O} + 4\text{CO} \rightarrow \text{CaS} + 4\text{CO}_2 + 2\text{H}_2\text{O}$	-40.0	-54.6	-90.8	-127.0
4. $\text{CaSO}_4 + 4\text{CO} \rightarrow \text{CaS} + 4\text{CO}_2$	-44.3	-44.9	-46.4	- 47.9
5. $\text{CaSO}_4 \cdot 2\text{H}_2\text{O} + \text{CH}_4 \rightarrow \text{CaS} + \text{CO}_2 + 4\text{H}_2\text{O}$	+11.5	-21.6	-103.7	-185.8
6. $\text{CaSO}_4 + \text{CH}_4 \rightarrow \text{CaS} + \text{CO}_2 + 2\text{H}_2\text{O}$	+ 6.6	-12.7	-61.2	-109.5
7. $\text{CaSO}_4 \cdot 2\text{H}_2\text{O} + 4\text{H}_2 \rightarrow \text{CaS} + 6\text{H}_2\text{O}$	-15.7	-35.5	-92.0	-163.5
8. $\text{CaSO}_4 + 4\text{H}_2 \rightarrow \text{CaS} + 4\text{H}_2\text{O}$	-17.1	-25.9	-47.7	- 69.5
9. $\text{CaS} + 3\text{CaSO}_4 \rightarrow 4\text{CaO} + 4\text{SO}_2$	+195.8	+158.3	+65.5	- 27.3
10. $\text{CaSO}_4 + 2\text{C} \rightarrow \text{CaO} + \text{S} + \text{CO} + \text{CO}_2$	+87.4	+63.1	+ 3.1	- 57.0
11. $\text{CaSO}_4 + 1/2 \text{C} \rightarrow \text{CaO} + \text{SO}_2 + 1/2 \text{CO}_2$	+52.3	+38.6	+ 5.7	- 24.4

Table II. Calculated Heats of Reaction for the Reactions Involved
in the Reduction of Gypsum.

Reaction	Heat of Reaction in Kcal/mole 298°K
1. $\text{CaSO}_4 \cdot 2\text{H}_2\text{O} + 2\text{C} \longrightarrow \text{CaS} + 2\text{CO}_2 + 2\text{H}_2\text{O}$	+64.1
2. $\text{CaSO}_4 + 2\text{C} \longrightarrow \text{CaS} + 2\text{CO}_2$	+39.0
3. $\text{CaSO}_4 \cdot 2\text{H}_2\text{O} + 4\text{CO} \longrightarrow \text{CaS} + 4\text{CO}_2 + 2\text{H}_2\text{O}$	-18.4
4. $\text{CaSO}_4 + 4\text{CO} \longrightarrow \text{CaS} + 4\text{CO}_2$	-43.4
5. $\text{CaSO}_4 \cdot 2\text{H}_2\text{O} + \text{CH}_4 \longrightarrow \text{CaS} + \text{CO}_2 + 4\text{H}_2\text{O}$	+60.4
6. $\text{CaSO}_4 + \text{CH}_4 \longrightarrow \text{CaS} + \text{CO}_2 + 2\text{H}_2\text{O}$	+35.4
7. $\text{CaSO}_4 \cdot 2\text{H}_2\text{O} + 4\text{H}_2 \longrightarrow \text{CaS} + 6\text{H}_2\text{O}$	+20.9
8. $\text{CaSO}_4 + 4\text{H}_2 \longrightarrow \text{CaS} + 4\text{H}_2\text{O}$	- 4.1
9. $\text{CaS} + 3\text{CaSO}_4 \longrightarrow 4\text{CaO} + 4\text{SO}_2$	+251.2
10. $\text{CaSO}_4 + 2\text{C} \longrightarrow \text{CaO} + \text{S} + \text{CO} + \text{CO}_2$	+123.2
11. $\text{CaSO}_4 + 1/2 \text{C} \longrightarrow \text{CaO} + \text{SO}_2 + 1/2 \text{CO}_2$	+72.6

RESEARCH OBJECTIVES

The primary objective of this research was to develop a process by which calcium sulfate could be reduced at lower reaction temperatures and shorter holding times than those cited in the literature. Two principal areas were investigated in order to affect this change.

It was proposed to first investigate the use of a more active reducing gas. Specifically, the reaction of carbon monoxide and water to form nascent hydrogen at the reduction site might form a potentially more active reducing agent. In addition to temperature, the effect of the carbon monoxide flow rate, the water flow rate, the carbon monoxide to water ratio, and the reaction time were to be studied. In this manner the conditions for optimal conversion of the calcium sulfate could be determined. At the same time, some conclusions could be made regarding the type of controlling mechanism.

It was also proposed to investigate the possible catalytic effect of several compounds on this process using a carbon monoxide reducing gas. Although catalysts are employed in the reduction of several similar compounds, little work is reported in the literature concerning the catalytic reduction of calcium sulfate. Since the exact mechanism of catalysis is now known in all

cases, the development or promotion of a catalyst is largely an art. Therefore, no specific method was employed to determine what compounds or types of compounds should be tested for catalytic activity.

Once a relatively active catalyst was found, the effect of temperature, reactant composition, carbon monoxide flow rate, and reaction time were studied. In this manner the conditions for optimal reduction of the calcium sulfate were determined. Also, several observations regarding a controlling mechanism and chemical rate expression were made.

EXPERIMENTAL APPARATUS

In order to study the reaction as proposed, it was necessary to design an apparatus capable of several requirements. The reactor had to be heated to temperatures ranging from 350 to 1000°C. Superheated steam had to be furnished to the reactor at a measured flow rate. Carbon monoxide had to mix with the steam before entering the reactor. The excess steam had to be condensed and collected downstream from the reaction site. The carbon monoxide had to be purged from the lines before the reactor could be opened. At the same time, the reactor had to be low in cost, simple, and easily repaired. The following apparatus was constructed to satisfy these requirements. Figure 1 is a flow diagram of the reactor setup.

For certain runs, superheated steam was supplied by heating water which was being pumped to the reactor at a measured flow rate. The water was heated by using a high resistance nickel-chromium wire wrapped with ceramic beads and insulated. This system was capable of producing superheated steam at 160°C and one atmosphere pressure.

The carbon monoxide was supplied to the reactor from a gas cylinder. After expanding the gas across a needle valve, the carbon monoxide passed through a drying tube to remove any water. The carbon monoxide flow rate was measured with a calibrated rotameter. A one-way valve prevented any steam from entering this line. The

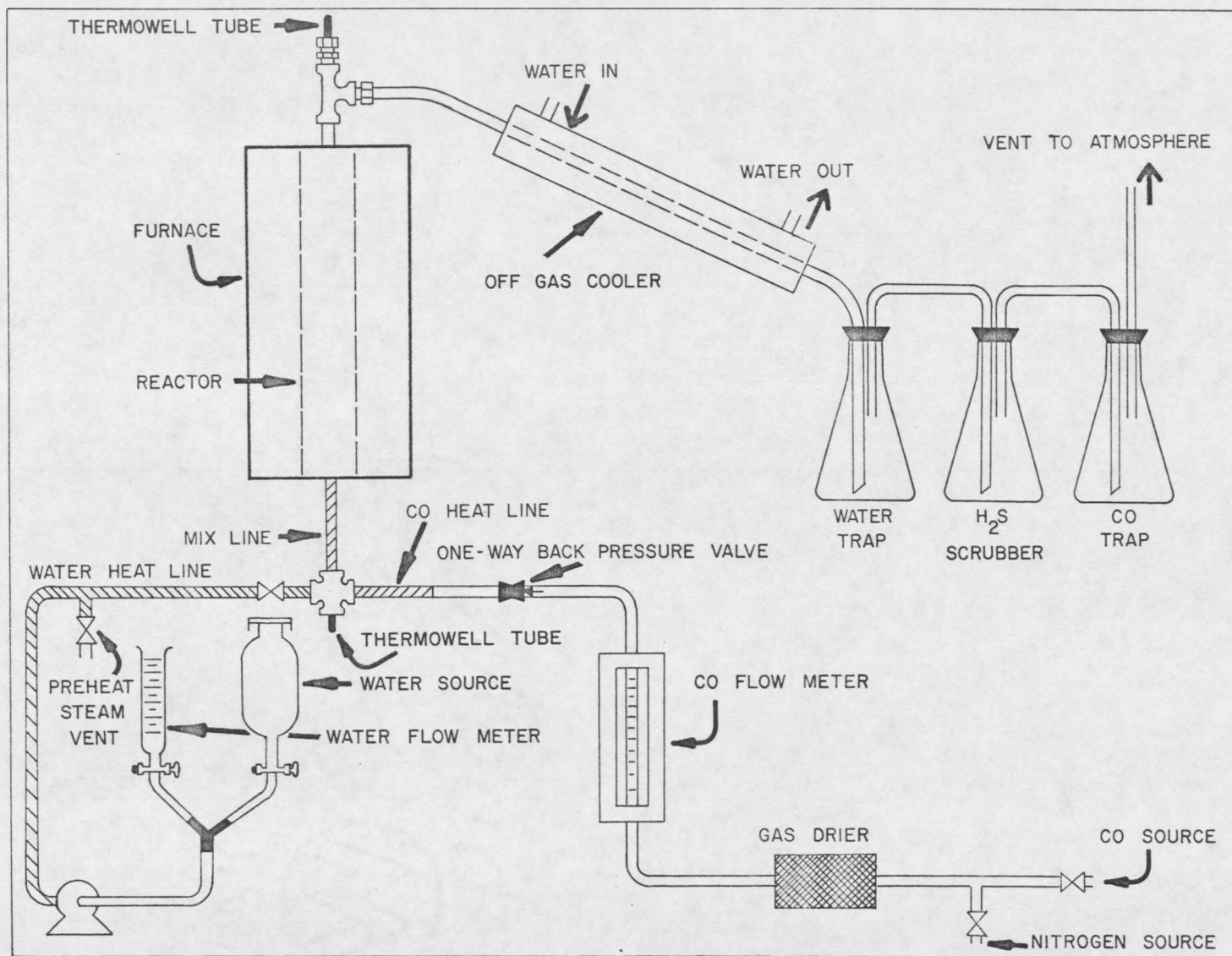


Figure 1. A Flow Scheme of the Experimental Apparatus.

carbon monoxide was preheated to 170°C using high resistance wire. Then the hot gas mixed with the superheated steam before being fed into the reactor.

The carbon monoxide could be purged from the system using nitrogen gas. Nitrogen was used since air would oxidize the product at the desired reaction temperatures. An initially inert atmosphere was also attained by clearing the lines of air before preheating the reactor.

The carbon monoxide line and the superheated steam line were joined to the "mix" line at a stainless steel cross. The mix line was an 18-inch section of 1/2-inch stainless steel pipe which led to the reactor. The fourth connection to the cross was used to position a thermowell tube up through the mix line to the reactor bed.

The reactor was constructed from a one-inch nominal stainless steel pipe. It was 12 inches in length, and it was fitted so that the reactants were introduced from the top. In order to heat the reactor, it was mounted inside of a 110-volt, 5-ampere electric furnace. The furnace was capable of heating the reaction site up to 1000°C; however, the highest temperature for any run was 850°C.

In order to increase the heat transfer to the reaction site, the first eight inches of the pipe were packed with small stainless steel rings. These rings increased the heat transfer surface area without causing a large pressure drop across the reactor. It was important to prevent a drastic increase in pressure since this might condense the steam inside of the system.

The last four inches of the pipe were the actual reaction site. The reactor was designed so that the calcium sulfate bed would be fluidized by the reducing gases. The fluidized bed was contained by two porous stainless steel plates positioned above and below the calcium sulfate. These plates were held in place by punching a small hole in their centers and force fitting them onto the respective thermowell tubes. Figure 2 shows these details.

After passing through the reactor, the product gases flowed down to a heat exchanger. Here the gases were cooled to approximately room temperature, and any condensate dropped vertically into a water trap. Next, any hydrogen sulfide formed in the reaction was scrubbed with a strong caustic solution. The carbon monoxide was scrubbed with a solution of cuprous chloride. Finally, the gases were vented to the atmosphere.

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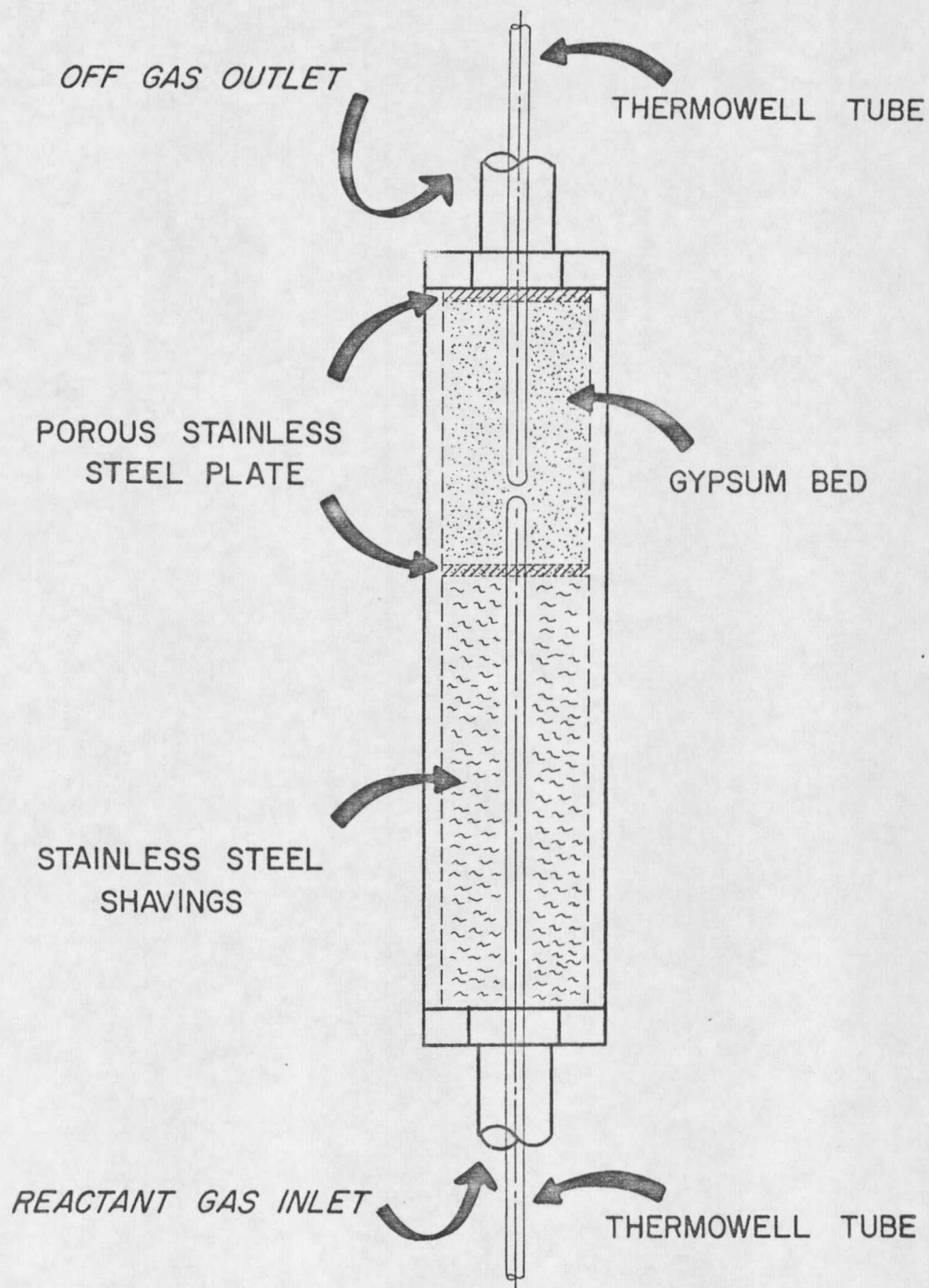


Figure 2. Front View of the Reactor Details.

Temperatures were measured in the system by using iron-constantan thermocouples and a Leeds and Northrup temperature indicator. Four principal temperatures were of interest. These are the temperature of the steam, the carbon monoxide, the mix, and the reactor.

All of the tubing used throughout the system was 1/8-inch stainless steel unless otherwise specified.

EXPERIMENTAL PROCEDURE

In order to determine the minimum fluidization velocity for the calcium sulfate bed, a glass model of the reactor was built. Since the solid reactants were very fine, a flow rate of about 0.015 gram moles per minute was sufficient to fluidize the bed.

The reactor contained sufficient voidage for approximately four grams of solid reactant, leaving enough space for the bed to freely fluidize. Therefore, a charge of approximately four grams was used in all runs. When a catalyst was used, 3.50 grams of calcium sulfate and 0.05 to 0.50 grams of catalyst were weighed on a Mettler Analytical Scale. The calcium sulfate used was reagent grade, and it was 99 weight per cent pure. An initial concentration of calcium sulfate was calculated from these measurements.

After thoroughly mixing the reactants, they were placed into the reactor. The pipe threads were coated with an anti-seizing compound, and the reactor was closed, positioned inside the furnace, and connected to the appropriate lines. Next, the reference potential on the temperature indicator was standardized. Then, the iron-constantan thermocouples were positioned inside of their respective thermowell tubes.

Once the system was fitted together, nitrogen was introduced to purge the air from the reactor. An initially inert atmosphere

was especially important if calcium sulfide was being tested as a catalyst. The oxygen in the air will oxidize the calcium sulfide to calcium sulfate at temperatures above 200°C.¹³

The Powerstat which controlled the current to the furnace was turned on in order to preheat the reactor. The carbon monoxide and mix lines were also heated at this time. If water was to be used, the steam was preheated to about 160°C. The preheat steam valve was opened to permit the steam to by-pass the reactor until it was needed. The steam flow rate was determined by timing the change in water level in the small burette. Finally, the cooling water to the heat exchanger was turned on.

When the reactor had reached the desired temperature, and the steam was superheated, the nitrogen gas was shut off. The steam line valves were regulated to permit the flow of superheated steam to the mix line. At a recorded time the carbon monoxide valve was opened, introducing the reducing gas into the system. The carbon monoxide flow rate was measured with a rotameter which had previously been calibrated as discussed in the Appendix. During the reaction the temperatures were controlled manually. After the calcium sulfate had reacted for the desired amount of time, the carbon monoxide valve was closed. Nitrogen was immediately introduced into the system to purge the lines of the reducing gas. The furnace and

the heating elements for the steam and mix lines were turned off. After the reactor had cooled to room temperature, the system was dismantled, and the reactor was opened. The product was taken from the reactor, thoroughly mixed, and placed in a weighing bottle. The product was dried for about eight hours at 190°C to insure complete drying of the calcium sulfate.

The product was quantitatively analyzed for the sulfate ion using a barium sulfate precipitation technique. The procedure is discussed in detail in the Appendix. In general, two samples were analyzed for each run. If they were reasonably close in agreement, the average of the two samples was recorded as the final concentration of sulfate ion. If they did not agree, a third sample was analyzed, and a weighted average was calculated for the final concentration of sulfate ion. In almost all instances, only two samples were analyzed per run.

The product was also quantitatively analyzed for the sulfide ion using an iodimetric analysis. This is a relatively involved technique and is also discussed in the Appendix. To analyze every run for the sulfate and sulfide ion concentrations would have been very time consuming. Therefore, only the sulfate analysis was used in most instances. The percentage conversion was based on the re-

duction of the sulfate ion. For several typical runs of high conversion the product was analyzed for the sulfide ion to determine if this was the primary product of reduction.

RESULTS

It was felt that nascent hydrogen might be a more active reducing agent for the conversion of calcium sulfate to reduced products. Ideally, the nascent hydrogen would be formed at the reduction site by the reaction of carbon monoxide and water. However, positive results were not obtained using this gas mixture over the temperature range of 350 to 750°C. At a temperature of 750°C, a 14.2 per cent reduction of calcium sulfate was obtained in two hours. The carbon monoxide flow rate was 0.022 gram moles per minute, and the water flow rate was 0.045 gram moles per minute. However, this reduction cannot be definitely attributed to the formation and reaction of nascent hydrogen.

Since the carbon monoxide-water mixture was not active, several materials were investigated for catalytic activity. Figure 3 summarizes the results obtained in this study. This graph shows the relation between per cent conversion of calcium sulfate and reaction time for different possible catalytic materials. The carbon monoxide flow rate was constant at 0.022 gram moles per minute for all runs. When steam was used, its flow rate was 0.045 gram moles per minute. The solid markings represent runs made at 720°C using only carbon monoxide as a reducing gas. The open markings represent runs made using a carbon monoxide and water mixture as the

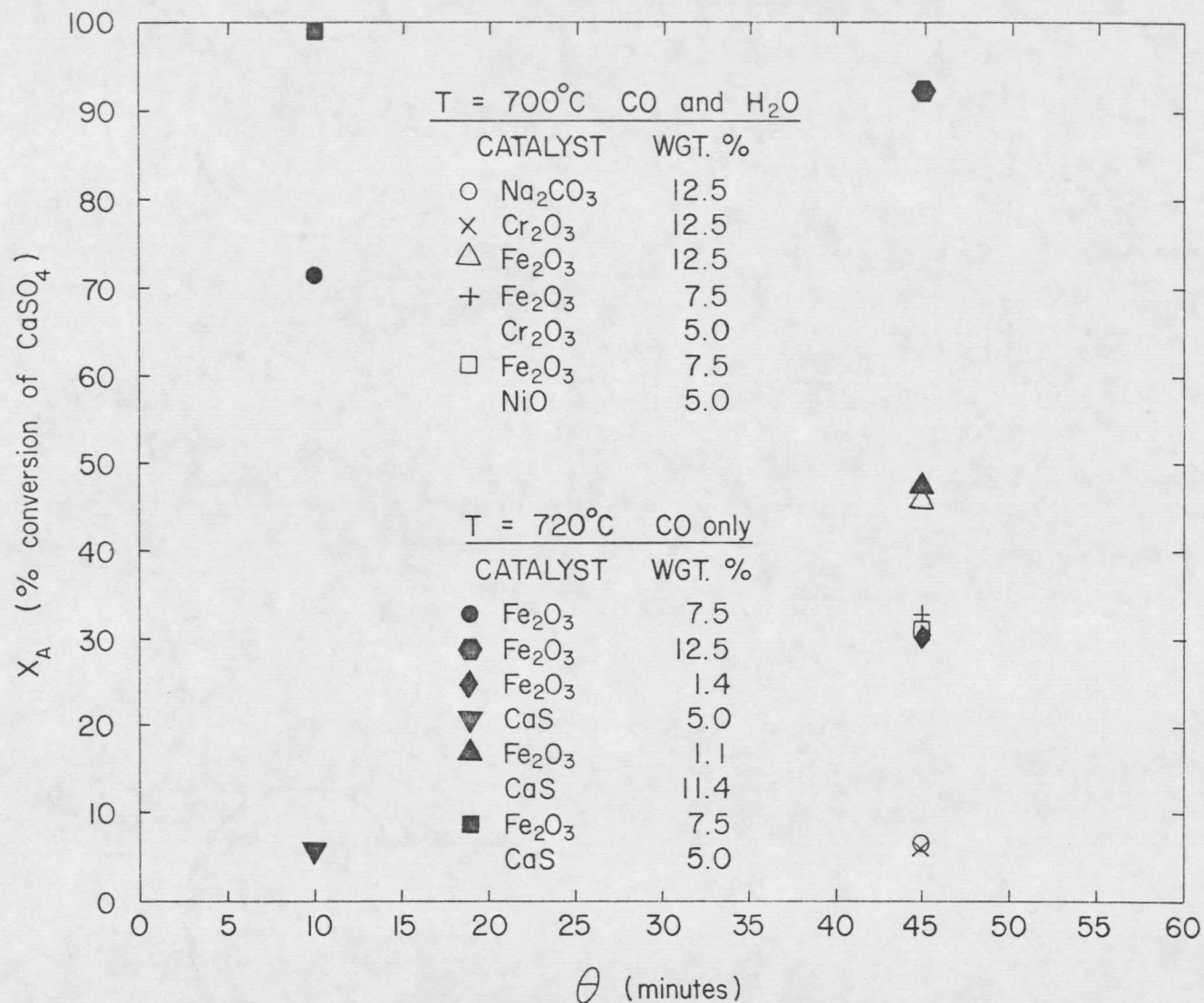


Figure 3. Per Cent Conversion of Calcium Sulfate vs Time for Various Catalytic Materials.

reducing gas at a reaction temperature of 700°C.

Sodium carbonate, chromic oxide, and nickel oxide exhibited no apparent catalytic activity while ferric oxide showed a definite catalytic effect on the reaction. Without a catalyst the percentage reduction of calcium sulfate was about four per cent. Using a reactant which was 12.5 weight per cent ferric oxide, the conversion was 45.4 per cent at 700°C. Both of these runs were made using the carbon monoxide-water mixture. For the carbon monoxide reducing gas alone the conversion was 92.1 per cent at 720°C with a 12.5 weight per cent catalyst.

It was necessary to investigate the autocatalytic activity of the calcium sulfide. Using only calcium sulfide as a catalyst, a 5.9 per cent conversion was obtained in 10 minutes. This run was made at 720°C using the carbon monoxide reducing gas. Under these conditions the conversion increased to 71.3 per cent for a reactant initially 7.5 weight per cent ferric oxide and 92.5 weight per cent calcium sulfate. For a reactant composition of 7.5 weight per cent ferric oxide, 5.0 weight per cent calcium sulfide, and 87.5 weight per cent calcium sulfate, the conversion was 99.4 per cent at these same conditions.

Based on these results the following two conclusions were made. First, ferric oxide exhibited a definite catalytic effect

on the reaction. Second, calcium sulfide autocatalytically favored its own rate of formation.

Figure 4 shows the relationship between per cent conversion of calcium sulfate and temperature. The open circles represent runs made using both carbon monoxide and water as the reducing gas while the solid circles represent runs made using only carbon monoxide. The carbon monoxide flow rate was 0.022 gram moles per minute, and the catalytic concentration was 12.5 weight per cent ferric oxide. A comparatively higher temperature was required to achieve the same conversion when using the carbon monoxide-water mixture. These results indicated that the presence of water in the reducing gas had an adverse effect on the catalytic activity.

Using an iodimetric analysis, the products of these experiments were analyzed for the sulfide ion. This procedure is discussed in the Appendix. For a run which measured 99.9 per cent reduction of the calcium sulfate, the sulfide ion concentration was 32.0 weight per cent. This run was made using the carbon monoxide-water mixture as a reducing agent. For a run which measured 99.8 per cent reduction of calcium sulfate, the sulfide ion concentration was 38.8 weight per cent. This run was made using only carbon monoxide as a reducing agent. If all of the calcium sulfate were reduced to calcium sulfide, the sulfide ion concentration would be

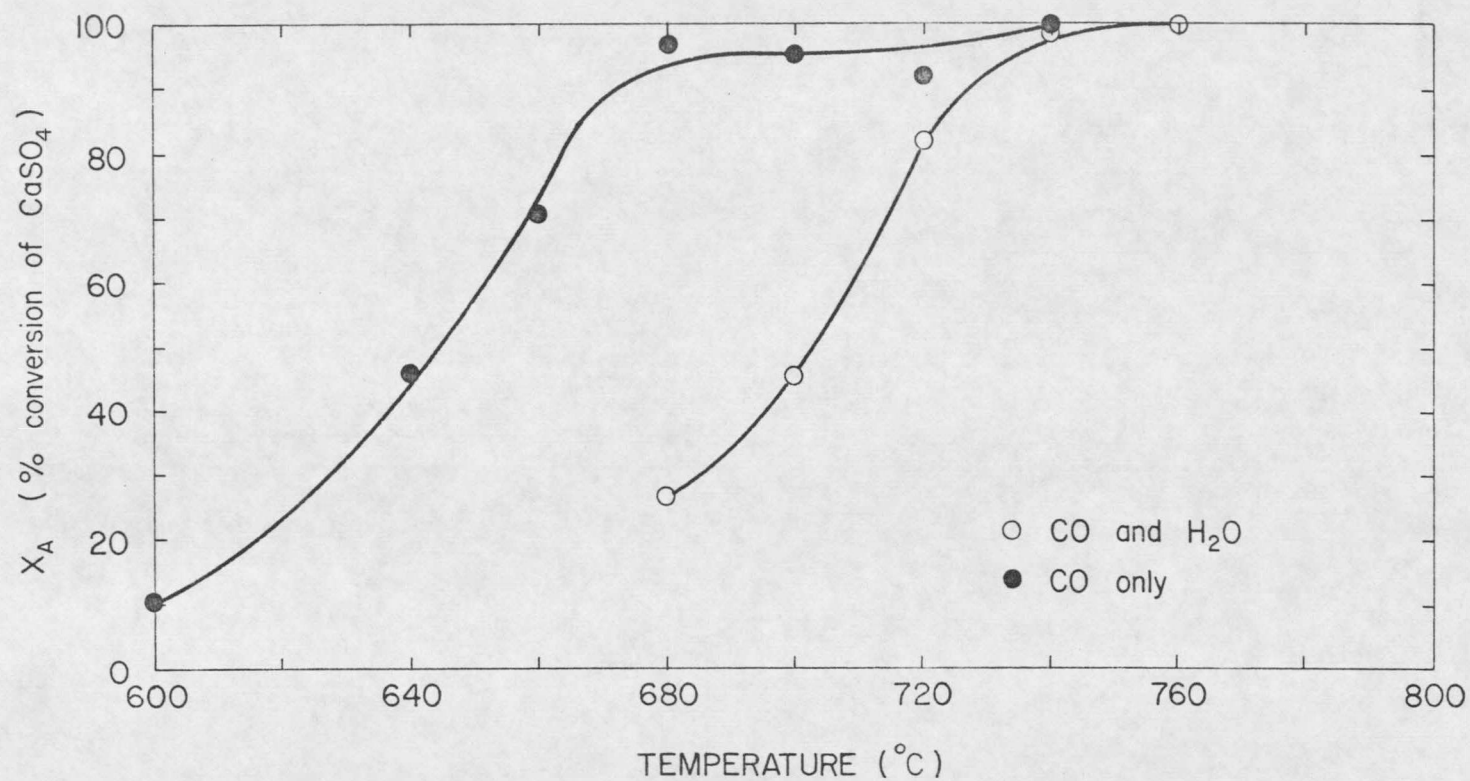


Figure 4. Per Cent Conversion of Calcium Sulfate vs Temperature for the Carbon Monoxide-Water Reducing Gas and the Carbon Monoxide Reducing Gas. Ferric Oxide was used as a catalyst.

approximately 38.9 weight per cent. These results indicate that all of the calcium sulfate was reduced to calcium sulfide when only carbon monoxide was used. When water was used with the carbon monoxide reducing gas, the final concentration of calcium sulfide was lowered, indicating that the calcium sulfate was reduced to something other than calcium sulfide.

Figure 5 is a graph of the per cent conversion of calcium sulfate versus the initial weight per cent of ferric oxide present. This data was recorded for a reaction temperature of 720°C and a processing time of 45 minutes. Carbon monoxide was used as the reducing gas. As can be seen, the optimum concentration of ferric oxide catalyst was approximately 9 per cent. At concentrations below 7 per cent the conversion dropped off sharply. At concentrations above 10 per cent the conversion slowly decreased.

Figure 6 summarized the effect of increased carbon monoxide flow rate on conversion. The graph relates per cent conversion of calcium sulfate and time for various flow rates. The reaction temperature was 660°C, and the initial ferric oxide concentration was 12.5 weight per cent. The open circles represent runs made at various reaction times for a carbon monoxide flow rate of 0.022 gram moles per minute. The solid markings represent runs made at various times for increased carbon monoxide flow rates. The results of

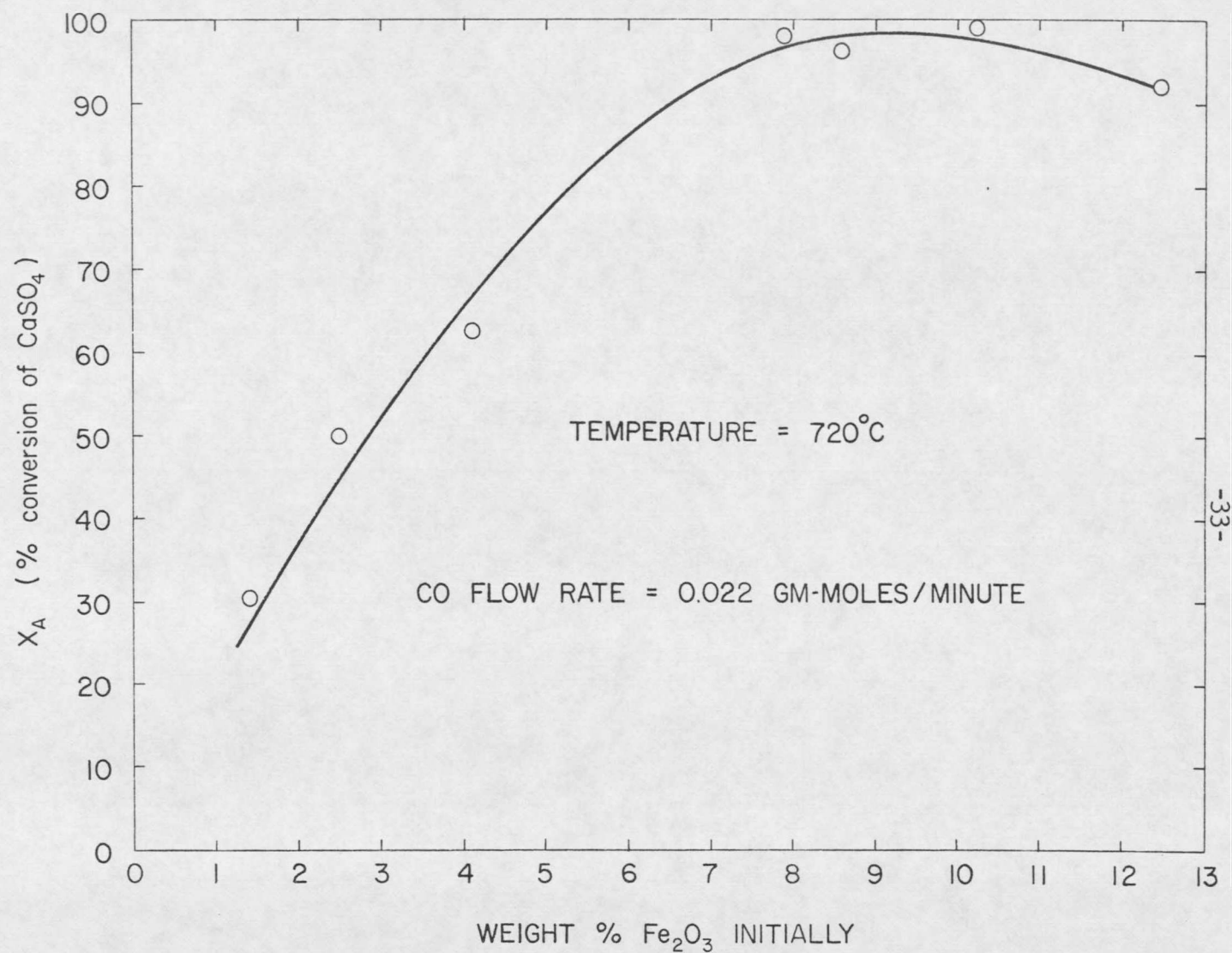


Figure 5. Per Cent Conversion of Calcium Sulfate vs the Initial Weight Per Cent Ferric Oxide for a Reaction Temperature of 720°C .

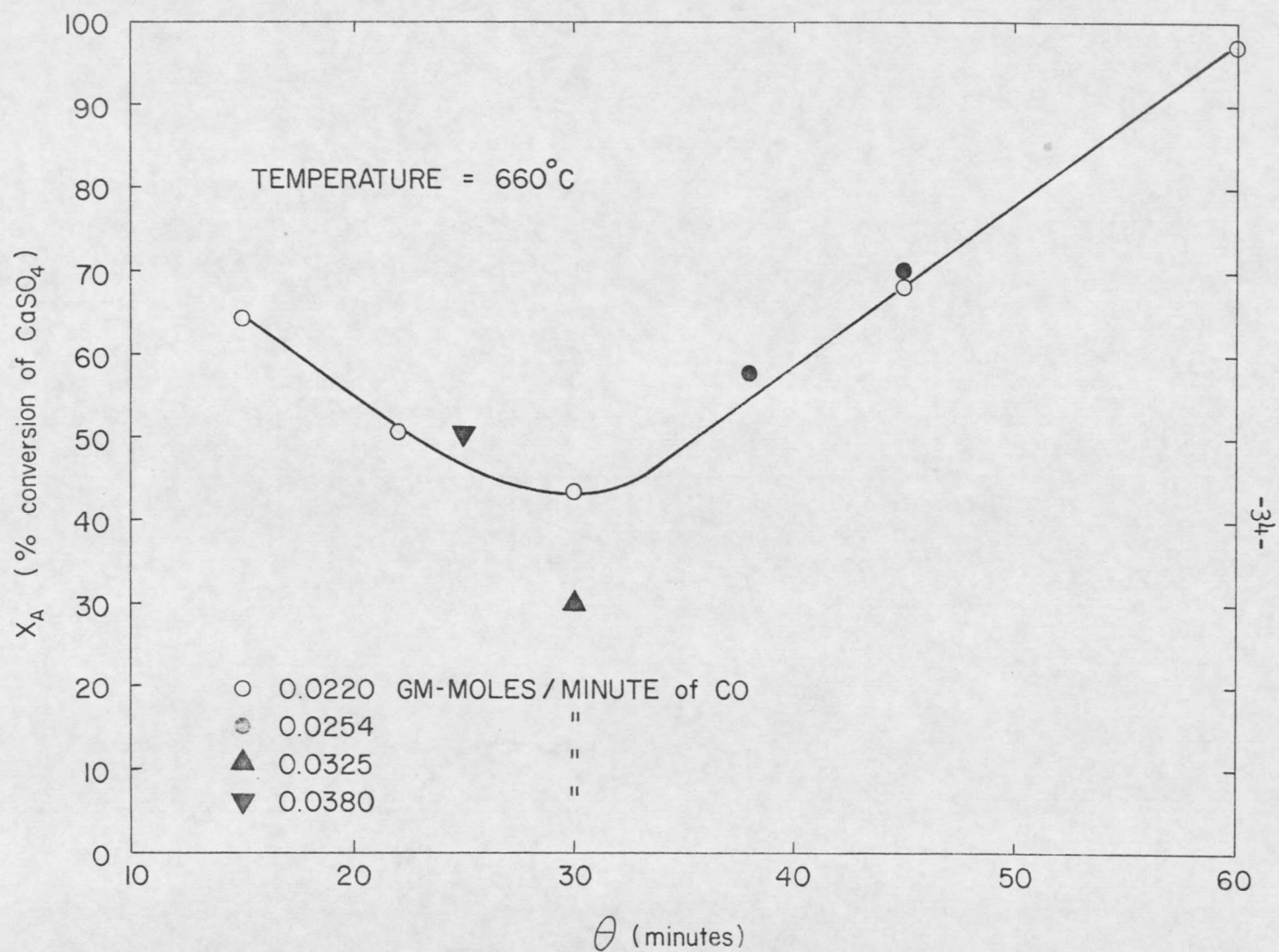


Figure 6. Per Cent Conversion of Calcium Sulfate vs Time for Various Carbon Monoxide Flow Rates. The Reaction Temperature was 660°C.

these runs indicated that the carbon monoxide flow rate exhibited little effect on the conversion of calcium sulfate.

Figure 7 shows the conversion of calcium sulfate as a function of time for two reaction temperatures. As can be seen, the results obtained at 660°C gave an oscillating curve. Since the data was checked and found to be accurate to within plus or minus two per cent, the oscillation was not the result of poor experimental procedure. At 680°C the oscillating curve was not observed.

Since there were only two phases present, gas and solid, it was hypothesized that the chemical mechanism must involve some type of gas-solid contacting. In order to test this proposition, a run was made in which the ferric oxide catalyst was physically separated from the calcium sulfate bed. This separation was effected by devising a small cylindrical chamber with porous stainless steel ends into which the ferric oxide could be placed. This chamber was positioned just below the fluidized bed. Using this system, 12.55 per cent reduction of the calcium sulfate was obtained. The reaction temperature was 720°C, and the reaction time was 45 minutes. At these same conditions a 4.0 per cent conversion was obtained without a catalyst. When a catalyst was mixed with the calcium sulfate, a 92.1 per cent conversion resulted at similar reactor conditions. It is difficult to make a definite statement based on these results.

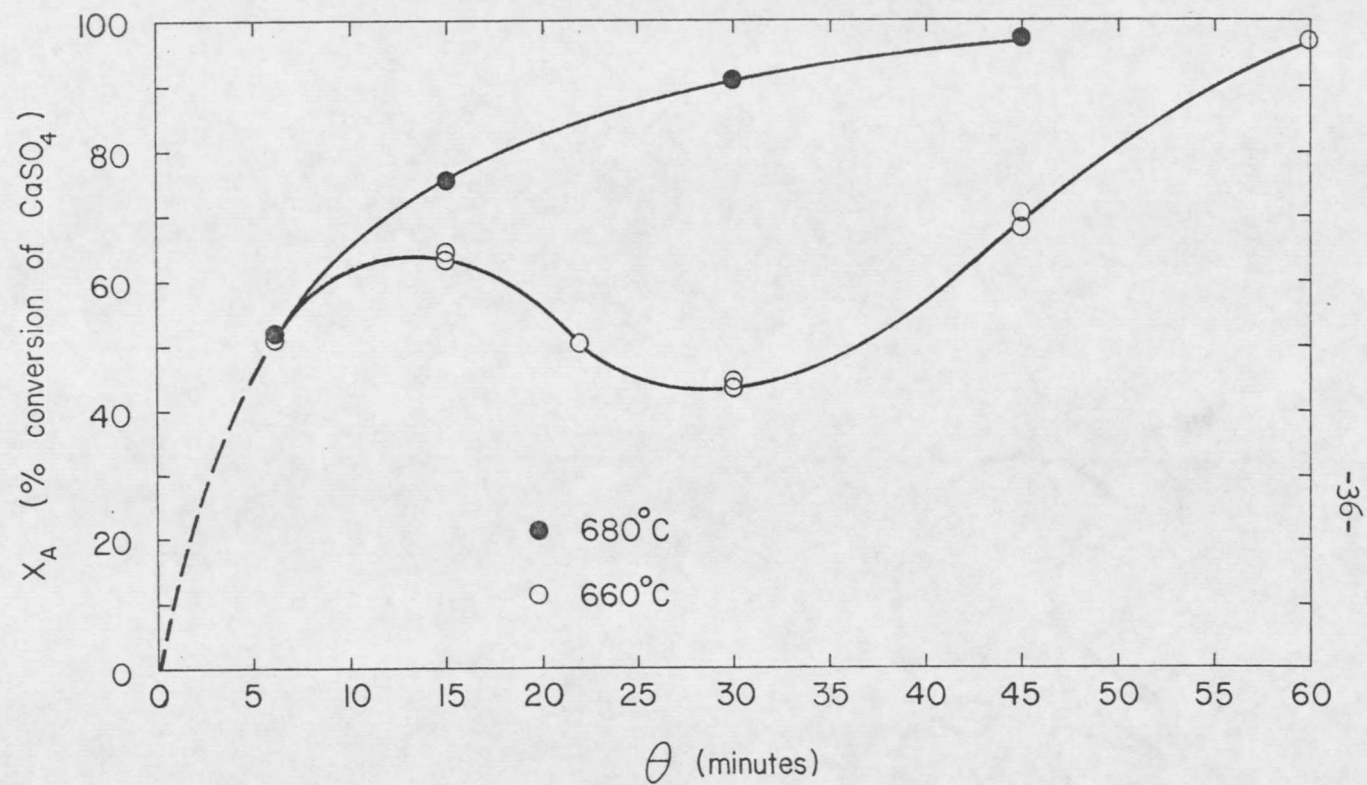


Figure 7. Per Cent Conversion of Calcium Sulfate vs Time for Reaction Temperatures of 660 and 680°C.

The separated catalyst run was slightly higher in conversion than the run made without a catalyst. It was much lower than the conversion effected with a mixed reactant. If some of the ferric oxide leaked up into the fluidized bed, a slightly higher conversion would result. However, tests for ferric oxide in the analytical procedure were negative for this run. Hence, an activated gas might be being formed, but this cannot be proven at this time.

Table III in the Appendix summarizes all of the experimental data reported in this paper.

DISCUSSION OF RESULTS

By definition, a catalyst is a material which can increase the rate of a chemical reaction without itself being consumed.²⁰ Though a catalyst may speed up a reaction, it never determines the equilibrium or end point of a reaction. This is governed by the thermodynamics alone. Therefore, a catalyst will only facilitate the approach to equilibrium.

An important characteristic of a catalyst is its selectivity. It will affect the rates of certain sequential reactions leaving the others unaffected. Since the catalytic mechanism is not known in all cases, very few generalities can be made. The scientific selection of a catalyst to promote a specific reaction is not very well understood. For this reason, extensive trial and error are needed to produce a satisfactory catalyst.

In some instances, duplication of the chemical constitution of a good catalyst is no guarantee that the material produced will have any catalytic activity. Often, heating a catalyst above a certain critical temperature will cause the catalyst to lose its activity. Therefore, the physical or crystalline structure of a compound may impart catalytic activity to the material.

In terms of transition state theory the catalyst reduces the potential energy barrier over which the reactants must pass to form

products. If the rate constant can be calculated according to the Arrhenius' Law, then for a given chemical rate equation the decrease in potential energy should be reflected by a corresponding decrease in the activation energy for the reaction. This, in turn, increases the rate of the reaction. The lowering of the energy barrier is shown schematically in Figure 8.

Ferric oxide has exhibited a definite catalytic activity on the reduction of calcium sulfate. One might also conclude from these results that calcium sulfide autocatalytically enhances its own rate of formation. In order to calculate the drop in activation energy which resulted from this catalytic activity, one would have to know the actual chemical rate expression for this process. The determination of this expression was beyond the scope of this study. Although the actual decrease in potential energy or a corresponding decrease in activation energy cannot be calculated from these results, the catalytic effect of these materials has been clearly demonstrated.

The presence of water in the reducing gas was found to have an adverse effect on the conversion. The reason for this might be explained by the autocatalytic activity of calcium sulfide and the effect of water on its formation. When water is introduced into the system, it might react with the calcium sulfide according to the reaction:¹⁸

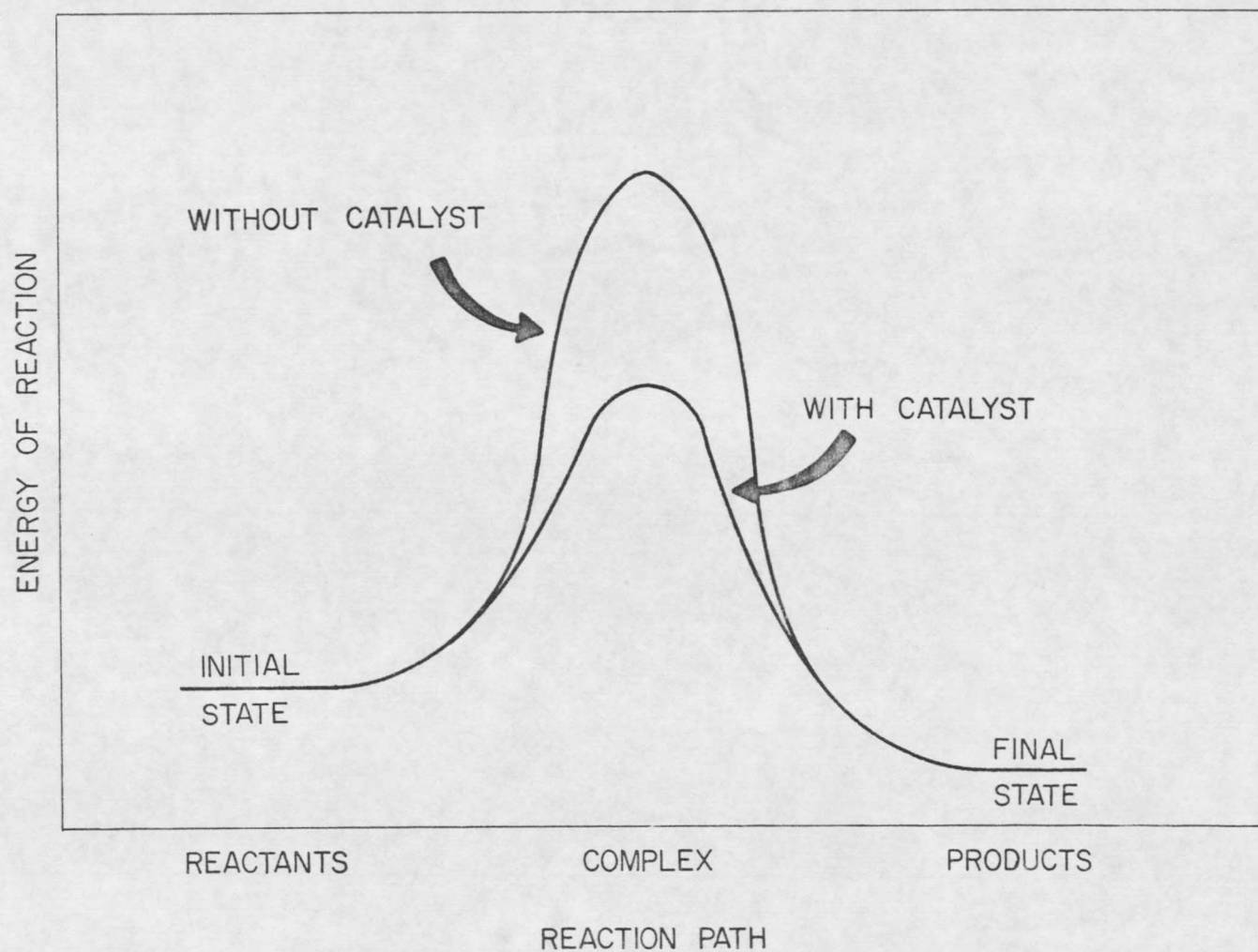
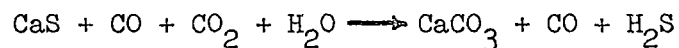


Figure 8. Energy of Reaction vs Reaction Path for Reactions With and Without a Catalyst.



In this reduction atmosphere it is quite possible that all of these reactant gases are present. When water is introduced in an attempt to form nascent hydrogen, it probably reacts with the calcium sulfide to form calcium carbonate. Since this decreased the concentration of calcium sulfide, the catalytic activity must also be decreased. This resulted in a relatively slower rate of reaction.

The results of the iodimetric analysis for iodine support this theory. For runs of nearly the same per cent conversion of calcium sulfate, there was a much lower percentage of sulfide ion present when water was included as a reducing agent. The calculations indicated that all of the calcium sulfate was being reduced to calcium sulfide when only carbon monoxide was used. Therefore, the presence of water in the reaction had indeed lowered the final concentration of sulfide ion in the products. This might explain the reported adverse effect of water.

The optimum weight percentage of ferric oxide catalyst was found to be approximately 9 per cent. Several studies have been made concerning the catalytic reduction of sodium sulfate. C. J. Nyman and T. D. O'Brien¹⁶ reported a maximum conversion of sodium sulfate using reactants which were 1.5 weight per cent iron. In

this study, hydrogen was used as a reducing gas. V. R. Puttagunta¹⁷ studied the catalytic reduction of sodium sulfate using several reducing gases in a fluidized bed reactor. He reported the most effective catalyst to be iron at a concentration of 1.0 per cent by weight. The iron was added as either a sulfate or an oxide. These concentrations give a reactant which was 1.15 to 1.82 weight per cent ferric oxide. This is much lower than the 9 weight per cent ferric oxide which was found to be the optimum concentration for a calcium sulfate reduction process.

In developing a continuous-reaction model for a solid catalyzed gas phase reaction, various processes may cause resistance to reaction. When film diffusion from the main body of the fluid to the exterior surface of the catalyst limits the rate of reaction, an expression incorporating the mass transfer coefficient between the gas and solid must be developed. If the reaction is controlled by the rate of diffusion through the pores of the catalyst, an expression incorporating a constant for pore diffusion must be developed. If the rate of reaction is controlled by some surface resistance (assuming that the gas is actually adsorbed to the surface of the catalyst), then an expression must be developed which accounts for this particular phenomenon.

It was necessary to determine whether or not film resistance was the controlling mechanism. According to Levenspiel²⁰ this can be done in a variety of ways. If experimental rate data are available, the mean first order rate constant for these runs can be compared with the predicted mass transfer coefficient for this type of a flow system. In all cases we should find that the mass transfer coefficient is the upper limit to the reaction rate, or

$$K V_p \leq k_g S_{EX}$$

where K is the reaction rate constant, V_p is the volume of the solid particles, k_g is the gas phase mass transfer coefficient, and S_{EX} is the exterior surface area of the particles. If the two terms in this equation are of the same order of magnitude, one might reasonably suspect that the gas film is playing a role in determining the reaction rate.

By experiment one can determine whether film diffusion plays a role by using varying flow rates of identical feed. Where gas film resistance is important, conversion will vary significantly with changing gas flow rate. Where gas film resistance does not influence the rate of reaction, conversion should remain approximately the same for various flow rates.

The results of Figure 6 indicated that the carbon monoxide flow rate exhibited little effect on the conversion of calcium sulfate. In general, the conversions were reasonably close to those recorded at the lowest flow rate. Therefore, film diffusion can be eliminated as a controlling mechanism.

The effect of pore diffusion was not studied. In order to investigate the effect of pore diffusion on this reaction, particles of various known sizes are required. This would mean that the reactants would have to be screened. The reactants used in this study were finely ground reagent grade particles and were not suitable for sizing. Since pore diffusion did not affect the reaction rate in other studies, and since none of the results of this study indicated that pore resistance might be important, an experimental study of the pore resistance was not included in this work.

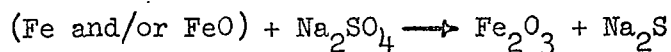
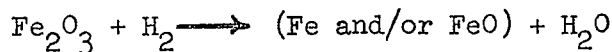
Since pore diffusion was arbitrarily eliminated as a controlling mechanism, and since film diffusion was found not to be controlling, one of the surface phenomena must control the reaction. Kinetic equations based on active site theory are extremely complex. To explore these would require an extensive research program. Therefore, no attempt was made to find an actual mechanism. However, some interesting and potentially enlightening observations were made.

What actually happens at the catalytic surface is not known. It is thought that reactant molecules are somehow changed, energized, or affected to form intermediates in the region close to the catalytic surface. In one theory the intermediate is viewed as an association of a reactant molecule with a region of a surface; that is, the molecules are activated while attached to the surface. In another theory, molecules are activated in an atmosphere close to the surface and under the influence of the surface. In this theory the molecules are mobile but are nevertheless modified by the surface forces. In still a third theory it is felt that an active complex is formed at the surface of the catalyst. This complex then moves back into the main gas stream, triggering a chain of reactions with molecules before being dissipated. This theory views the catalytic surface as a source or generator of activated complexes which then react in the main body of gas far from the surface.

Recalling the results of the separated catalyst experiment, one can further discuss these theories. In the first theory, an activated intermediate would form and react on the catalytic surface. For this particular process this theory would imply a solid-solid mechanism, and this is not acceptable. The presence of an activated atmosphere close to the catalytic surface would not contradict the experimental results. This would imply that the calcium sulfate

would have to be close to the catalytic surface in order to be reacted by the activated gas. This would explain the percentage conversion of the separated-catalyst run. In the third theory, an activated gas is formed at the surface of the catalyst and this activated complex moves into the gas stream to further react with the calcium sulfate. If the free radical was activated for a relatively short time, this might also agree with the results of the separated-catalyst run. Therefore, assuming a gas-solid mechanism, either of the last two theories were supported by the results of this run.

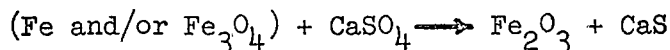
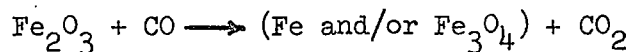
In studying the catalytic reduction of sodium sulfate, V. R. Puttagonta¹⁷ proposed the following mechanism as the most likely reaction scheme:



He goes on to state that since the product of reaction was found to be magnetic, the iron oxides resulting from the reaction must include magnetite (Fe_3O_4). These reactions would continue successively in a chain reaction until the sodium sulfate was used up or no longer accessible to the catalyst. Since sodium sulfate is in the liquid phase at the reaction temperatures, this mechanism in-

volves solid-liquid contacting. The mobility of the liquid phase is probably important in bringing the sulfate into contact with the catalyst. The result of a test at 593°C, below the temperature at which fusion begins, showed that the reaction was very slow without the presence of a liquid phase. However, at this lower temperature the chemical rate constant might be considerably smaller. The decreased activity cannot conclusively be attributed to the absence of a liquid phase. For this reaction it was proposed that chemical rather than physical steps are rate controlling.

If this type of a mechanism were suggested for the reduction of calcium sulfate, the reactions would be:



For these reactions the formation of FeO was not thermodynamically feasible. The second step in this mechanism would involve solid-solid contacting, and this does not seem reasonable since the probability of obtaining sufficient contacting to result in high conversions would appear low. With this type of mechanism one would have to assume that the reaction occurs only at the surface of the solids, and the results do not support this assumption. Therefore, this type of chemical mechanism is not likely for the reduction of

calcium sulfate. The reaction products were magnetic, and this supports the formation of magnetite. However, ferric oxide in the presence of carbon monoxide will react to form some magnetite at these reaction temperatures. This does not imply any subsequent reaction of the magnetite with the calcium sulfate, nor does it necessarily imply that ferric oxide is reacted to another form as the calcium sulfide is reduced. It is possible that ferric oxide is a true catalyst, and that the presence of magnetite is due only to the reduction of ferric oxide with carbon monoxide.

Continuing with this discussion of possible chemical mechanisms, one might possibly explain the occurrence of the oscillating curve reported in Figure 7. In 1910, A. J. Lotka wrote a paper²¹ entitled "Contribution to the Theory of Periodic Reactions." The basic concepts of this work are summarized in the Appendix. In this article, he described how an autocatalytic reaction of a certain mechanism could result in a damped, oscillating curve when concentration is plotted versus time.

If one assumes that an activated gas contacts the calcium sulfate, and if one couples to this assumption other experimental facts, the following steps are likely to occur. First, the reaction of carbon monoxide in the presence of a ferric oxide catalyst results in the formation of some activated form of gas. For this

process the concentration of carbon monoxide is relatively high and constant since it is continuously fed into the reactor. Second, the calcium sulfate reacts with the energized gas to form calcium sulfide. And finally, it is known from experimentation that the calcium sulfide somehow oxidizes to form calcium sulfate. Since calcium sulfate and carbon monoxide are present in higher concentrations, the activated gas and the calcium sulfide might be considered limiting reagents. For simplicity, assume that the kinetic equations for these steps depend only on the concentration of these limiting substances. If these three steps occur irreversibly, and assuming the simplest kinetic law applies to these expressions, one can write:

$$\frac{dC_A}{d\theta} = H - k_1 C_A \quad (1)$$

$$\frac{dC_B}{d\theta} = k_1 C_A - k_2 C_B \quad (2)$$

In these equations " C_A " represents the concentration of activated gas, " C_B " is the concentration of calcium sulfide, and H , k_1 , and k_2 are constants.

Now, we have previously established through experimentation that calcium sulfide autocatalytically affected its own rate of

formation. If one assumes that this influence follows the simplest possible law, k_1 can be defined in the following manner:

$$k_1 = kC_B \quad (3)$$

Then, the rate expressions become

$$\frac{dC_A}{d\theta} = H - kC_A C_B \quad (4)$$

$$\frac{dC_B}{d\theta} = kC_A C_B - k_2 C_B \quad (5)$$

These equations are identical to those reported by Lotka. Their solution leads to the second order differential equations of the damped vibration type. This solution is summarized in the Appendix. The reaction is periodic provided that:

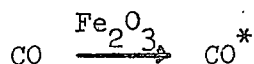
$$L < 4k$$

where L is the equilibrium concentration of calcium sulfide and k is the ratio of the rate constants k_2/k .

This mechanism and the subsequent rate expressions were developed to satisfy the experimental results reported in this work. Certain physical similarities between this reduction process and that of Lotka are apparent. For certain values of the constants,

this solution will yield curves similar to those obtained from the experimental data. Figure 9 is a plot of the weight fraction of calcium sulfide versus time. At 660°C the experimental results indicate that this curve oscillates. At 680°C the curve is exponential. Since the rate constant is a function of temperature, one might expect different values for the constants and possibly an exponential function at higher temperatures. Figure 10 presents Lotka's solution for selected values of the constants. Both concentration and time are plotted in arbitrary units. Although these curves are not identical to those in Figure 9, they do duplicate the general trends.

What the exact chemical mechanism is cannot be proven at this time. However, one can suggest a possible mechanism which might explain the occurrences previously discussed. Assume that the reduction of calcium sulfate resulted from the following reactions:



The first step of these reactions results in the formation of an activated complex denoted CO^* . For this process the concentration

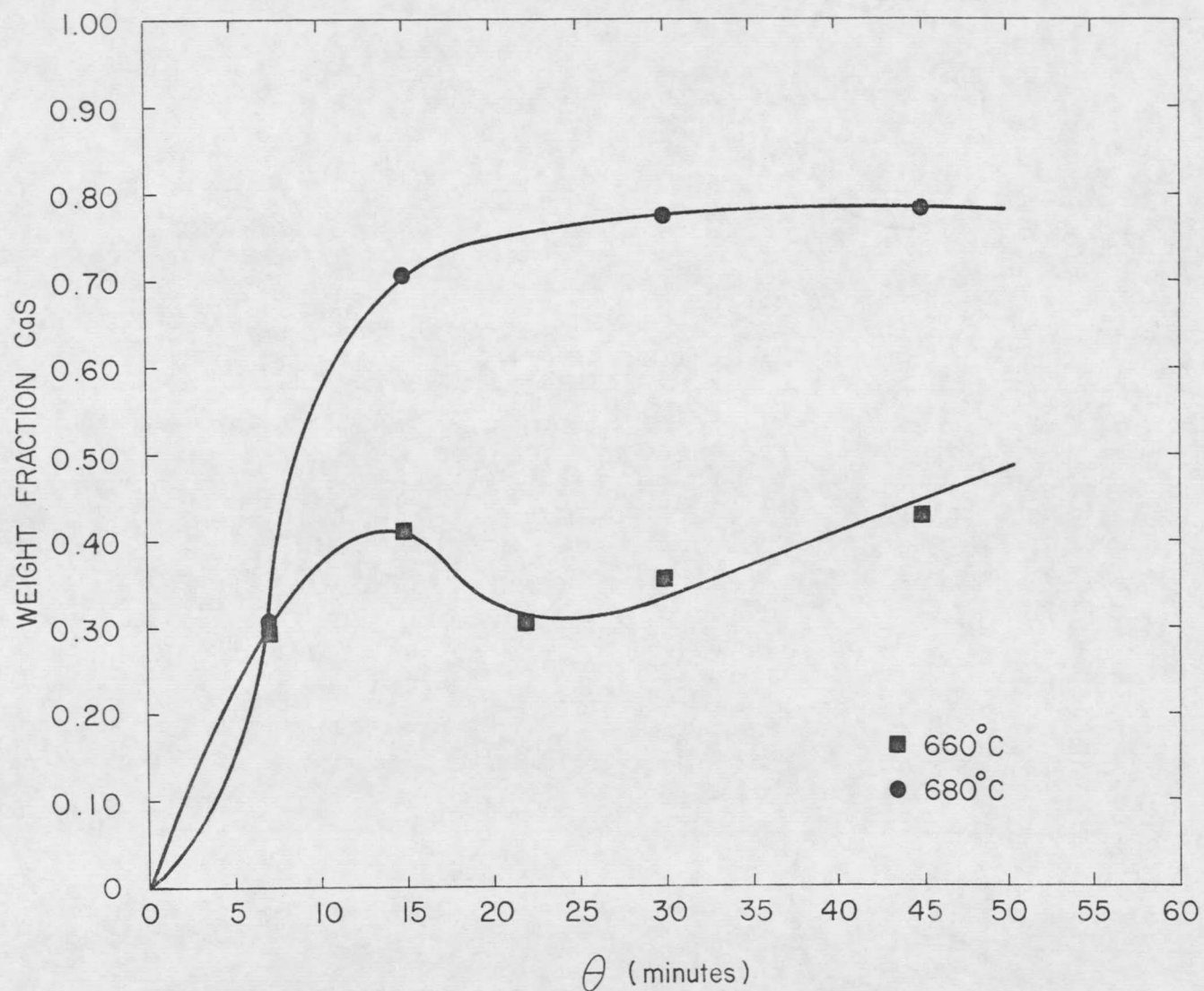


Figure 9. Weight Fraction Calcium Sulfide vs Time for Reaction Temperatures of 660 and 680°C.

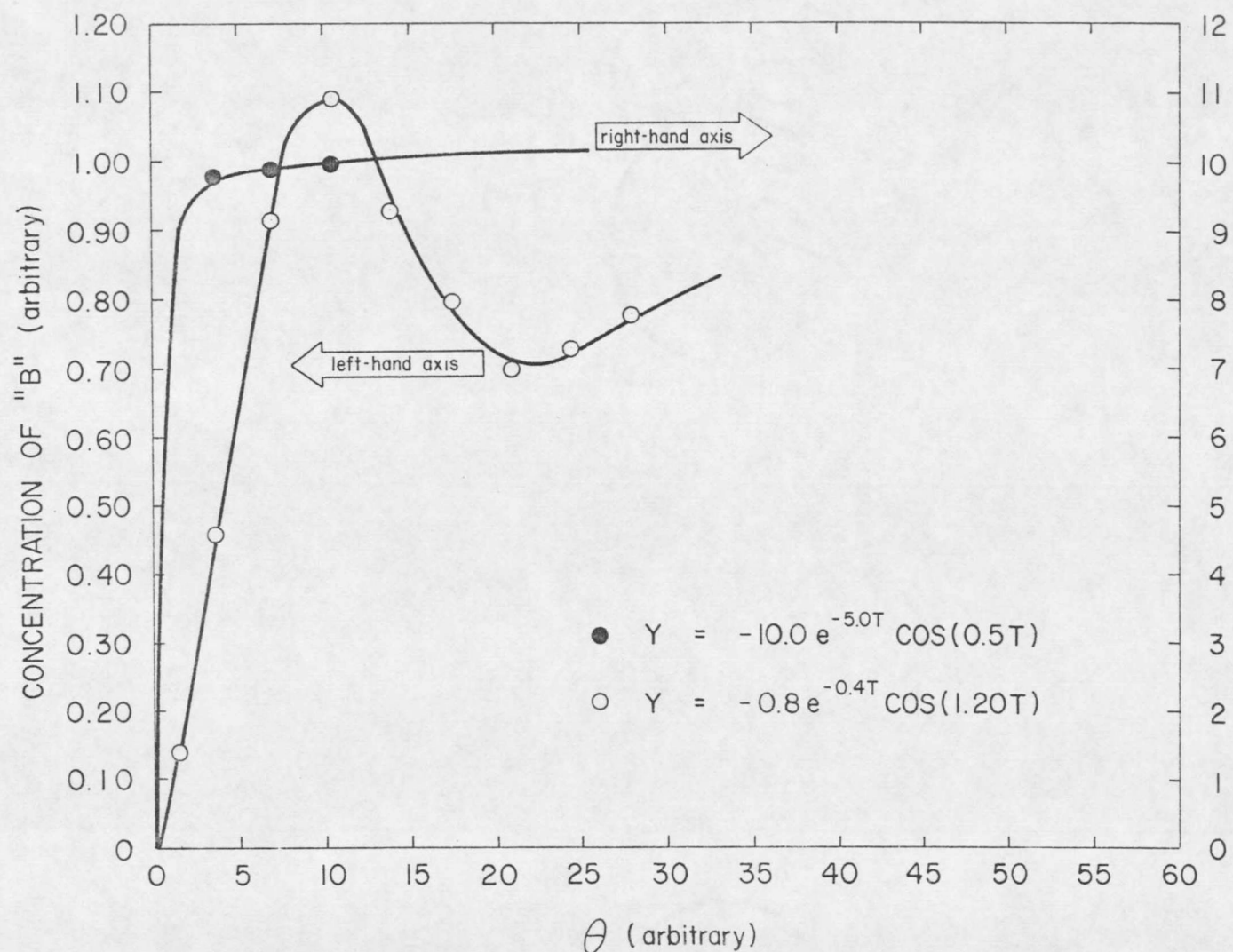


Figure 10. Concentration of "B" vs Time for Lotka's Solution and Selected Values of the Constants.

of carbon monoxide is relatively high and for practical purposes constant. The reversible reaction accounts for the reduction and subsequent formation of calcium sulfate as indicated by the experimental results. Since the activated gas and the calcium sulfide are initially present in the dilute state, they might be considered limiting reagents. Assuming the simplest kinetic law applies to the rate expressions, one can write the following equations for these limiting materials:

$$\frac{dC_A}{d\theta} = H - k_1 C_A + k_2 C_B \quad (6)$$

$$\frac{dC_B}{d\theta} = k_1 C_A - k_2 C_B \quad (7)$$

In these equations " C_A " is the concentration of activated gas, " C_B " is the concentration of calcium sulfide, and H , k_1 , and k_2 are constants.

The experimental results showed that calcium sulfide autocatalytically enhanced its own rate of formation. Assuming that this influence follows the simplest possible law, one can write:

$$k_1 = k C_B \quad (8)$$

Substituting this into the rate equations, they reduce to:

$$\frac{dC_A}{d\theta} = H - kC_A C_B + k_2 C_B \quad (9)$$

$$\frac{dC_B}{d\theta} = kC_A C_B - k_2 C_B \quad (10)$$

The complete solution of equations (9) and (10) is very complex. Assuming a very small initial concentration of calcium sulfide, the equations can be solved numerically using a second order Runge-Kutta method and the computer. For various values of the constants one can obtain an oscillating curve for this solution. However, it is difficult to damp these oscillations at higher values of time. Nevertheless, this mechanism appears to have some merit since it is based on a reasonable contacting sequence, it accounts for the oscillating curve of Figure 9, and it satisfies the kinetic restrictions of a simple order autocatalyzed reaction.

In order to postulate a mechanism for this reaction, a more sophisticated apparatus must be designed. This was not the objective of this research. A catalyst has been found to sufficiently activate this reaction so that the time and temperature might be reduced. Some work has been completed in order to optimize the reaction conditions and to determine the controlling mechanism. A probable kinetic mechanism which can account for the experimental

results has been proposed. Finally, a solid basis for future research has been presented.

CONCLUSIONS

1. Ferric oxide was found to have a relatively pronounced catalytic effect on the reaction. Although a decrease in activation energy was not calculated, a marked increase in conversion was noted when the ferric oxide catalyst was added. Reaction times and temperatures were significantly lower than those reported in the literature.
2. The optimum reaction conditions using only a ferric oxide catalyst were found to be:
 - 1) A carbon monoxide reducing gas at a flow rate above 0.015 gram moles per minute
 - 2) A reaction time of 45 minutes
 - 3) A reaction temperature of 680°C
 - 4) A reactant mixture which was 9 weight per cent ferric oxide catalyst.

Under these conditions, 97 to 99 per cent reduction of the calcium sulfate was obtained.

3. Film diffusion was not found to be the controlling rate mechanism. For this reaction, pore diffusion was not felt to be of significant resistance. It is proposed that chemical rather than physical steps are rate controlling.

4. Calcium sulfide was found to have an autocatalytic effect on the reaction. This indicates that some recycling of the reacted products would aid the reaction rate. At 720°C and a reaction time of 10 minutes, the reduction of calcium sulfate increased from 71.3 per cent to 99.4 per cent upon the addition of calcium sulfide to the reactants. These runs were made using a ferric oxide catalyst.

5. A gas-solid chemical mechanism was proposed as the controlling reaction step. This mechanism was based on the formation of an activated gas complex from the carbon monoxide in the presence of ferric oxide. The mechanism appears to have some merit since it is based on a reasonable contacting sequence, accounts for the oscillating curve of Figure 9, and satisfies the kinetic restrictions of a simple order autocatalyzed reaction. Although this mechanism does not exactly satisfy the results of Figure 7 and Figure 9, the general trends are duplicated. The mechanism was not proven in this study. However, it is brought forth as a possible explanation to these experimental results presented in this thesis. Also, it provides a sound basis for future work to be done on the reduction of calcium sulfate.

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APPENDICES

NOMENCLATURE

<u>Symbol</u>	<u>Definition and Units</u>
A_{ANN}	Cross-sectional area of the rotameter annulus, square feet
A_F	Cross-sectional area of the rotameter float, square feet
C_A	Concentration of Reactant A, moles per cubic foot
C_r	Rotameter coefficient, dimensionless
g	Acceleration of gravity, feet per second squared
k_1, k_2	Reaction rate constant, (cubic feet per mole) ¹⁻ⁿ per hour where n is the reaction order
k_g	Gas phase mass transfer coefficient, moles per hour square feet atmosphere
S_{EX}	Exterior surface area of the particles, square feet
U_{br}	Bulk velocity at the rotameter annulus, feet per second
V_p	Volume of the particles, cubic feet
V_f	Rotameter float volume, cubic feet
W	Mass flow rate, pounds per minute
ρ	Density, pounds per cubic foot
ρ_f	Density of rotameter float, pounds per cubic foot
θ	Time, minutes

CALIBRATION OF ROTAMETER

The rotameter was calibrated using a wet test meter which measured the volumetric flow rate of saturated gas in cubic feet per minute. The bulk velocity at the annulus of a rotameter can be expressed by the equation:²²

$$U_{br} = C_r \sqrt{\frac{2g\bar{V}_f(\rho_f - \rho)}{A_f \rho}}$$

The coefficient of discharge C_r is given as a function of the Reynold's number in the annulus and the type of float. This Reynold's number is based on an effective diameter for the rotameter annulus.

For this calibration, air was used as the fluid since working with carbon monoxide in a wet test meter could pose problems. Since the bulk velocity at the annulus is proportional to $\sqrt{\frac{(\rho_f - \rho)}{\rho}}$ for a fluid, the calibration can be corrected to another fluid by the equation:

$$\frac{U_{br_2}}{U_{br_1}} = \sqrt{\frac{\rho_1 (\rho_f - \rho_2)}{\rho_2 (\rho_f - \rho_1)}}$$

where U_{br_1} is the velocity for fluid 1 which was used to calibrate the meter, and U_{br_2} is the corrected velocity for another fluid.

If the density of the float is much greater than the density of the fluids, this equation will reduce to:

$$\frac{U_{br_2}}{U_{br_1}} = \sqrt{\frac{\rho_1}{\rho_2}}$$

The bulk velocity can be converted to a mass flow rate since

$$W = \rho A_{ANN} \cdot U_{br}$$

Then, to correct the calibration from fluid 1 to fluid 2, one merely uses the expression:

$$\frac{W_2}{W_1} = \frac{\rho_2 A_{ANN} \cdot U_{br_2}}{\rho_1 A_{ANN} \cdot U_{br_1}} = \sqrt{\frac{\rho_2}{\rho_1}}$$

Using a wet test meter, the volumetric flow rate can be measured for saturated air. Using the correct stoichiometric ratios, this can be converted to a mass flow rate for dry air. The necessary data to make this calculation were taken from Perry.²³ Then, using the developed correction, the rotameter is calibrated for a mass flow rate of dry carbon monoxide. Finally, using the proper stoichiometric ratio, the rotameter was calibrated to measure gram moles per minute. Figure 11 shows this calibration.

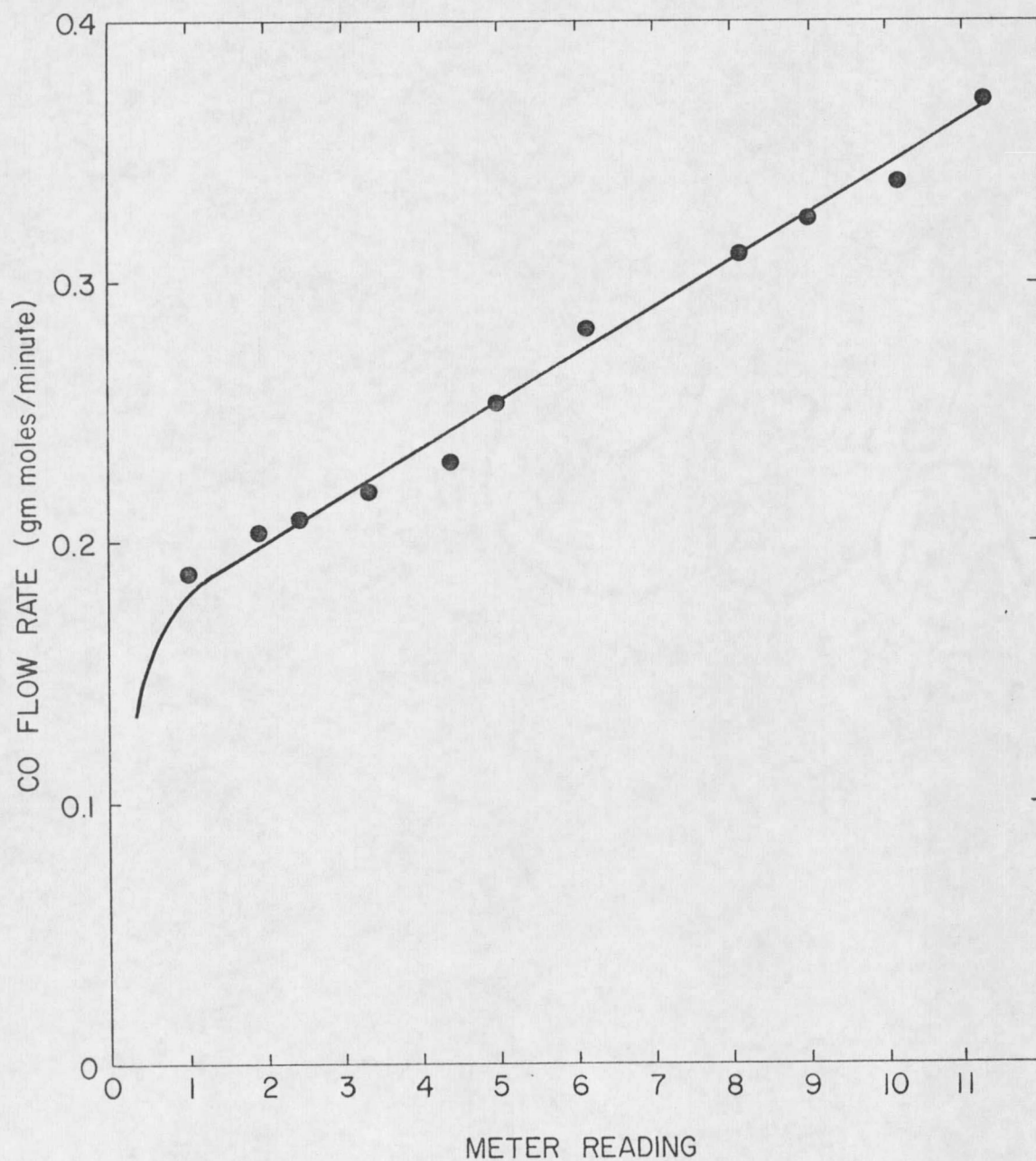


Figure 11. Calibration of the Rotameter for Various Carbon Monoxide Flow Rates.

ANALYSIS FOR SULFATE

The product was analyzed for calcium sulfate by using the barium sulfate precipitation technique. The procedure is simple and sufficiently accurate when using a careful analytical procedure. The scheme was tested with several samples of a known concentration of sulfate ion, and after becoming familiar with the technique, samples could be analyzed to within plus or minus two percent error without great difficulty. For all runs which were made, two samples were analyzed. If these were relatively close in agreement, their average was used as the final weight percentage of sulfate ion. If they did not agree, a third sample was analyzed, and based on this result a weighted average was taken as the final concentration. Knowing the initial and final concentrations of sulfate ion, the percentage conversion was calculated by the equation:

$$\text{Percentage Conversion} = \frac{\text{Wt \% initial} - \text{Wt \% final}}{\text{Wt \% initial}}$$

To begin the procedure, weigh a 1/2-gram sample into a 250-ml beaker. All samples were weighed on a Mettler Analytical Balance which could be read to 0.0001 g with little difficulty. Next, add 150 ml of distilled water and 10 ml of concentrated hydrochloric acid to the beaker. Heat the solution to boiling, and boil the solution gently for one hour to eliminate all the sulfide present in the sample as hydrogen sulfide. When this is completed, remove the

beaker from the heat and let it cool. If there is no ferric oxide present in the sample, filter the cooled solution through a retentive paper into a 400-ml beaker. Wash the insoluble residue and filter paper with distilled water, then discard it.

If Fe_2O_3 has been added to the reagents as a catalyst, it must be removed before the barium sulfate precipitate is formed. This must be done to prevent the coprecipitation of the iron ions in solution. According to Walton,²⁴ the inclusion of an impurity with a precipitate at the time that the precipitate is formed is called 'coprecipitation'. Coprecipitation can cause negative as well as positive errors in the analytical scheme. These coprecipitation effects are usually not large, but they can ruin the accuracy of a sulfate determination. In order to avoid these errors due to coprecipitation, one must try to eliminate the impurity ahead of time. In this case, add a sufficient amount of 6 N ammonium hydroxide to precipitate the iron out of solution as Fe_2O_3 . In order to get good separation, add a few extra drops of 6 N ammonium hydroxide after the ferric oxide begins to precipitate. Then filter the solution into a 400-ml beaker. Thoroughly wash the residue and paper before discarding it.

Add a few drops of methyl orange indicator to the filtrate. If the solution is not already neutralized to a yellow color, add

enough 6 N ammonium hydroxide to do so. Titrate back with concentrated hydrochloric acid to a red color, then add 12 drops in excess. Precipitate barium sulfate by slowly adding about 15 ml of 10 per cent barium chloride solution.

The barium sulfate precipitate is a finely formed particle, almost invisible to the naked eye. To give these a chance to grow larger, one must digest the precipitate by heating the solution to near boiling temperatures for about one hour. At the end of digestion, the solution above the precipitate should be quite clear. Test for complete precipitation by adding a few drops of 10 per cent barium chloride. If the precipitate is stirred up, it should settle again in a minute or so if the solution is completely digested.

After the solution has cooled, filter it. Wash the precipitate carefully. Again check the filtrate for complete precipitation. Carefully lift each paper with its precipitate from the filtering apparatus, and press it gently into a weighed crucible. Set the crucible on a clay triangle and tilt it at about a 45-degree angle. Heat it with a very small flame so as to dry the paper smoothly without spurting. Char the paper without having it burn with a flame. Have a crucible cover and tongs handy so that if a flame starts in the crucible it can be stopped by covering the crucible for a moment. When the paper is all carbonized, turn the burner on full and heat

the crucible to redness. Keep the crucible tilted to give adequate circulation of air in it. Gradually the carbon will burn off, glowing red as it does. When all the carbon is gone, heat the crucible an additional 10 minutes. Cool the crucible in a desiccator. Weigh it after it has cooled. The weight per cent of the sulfate ion is given by:

$$\frac{\text{Wt Ba} \cdot \text{SO}_4 \times 0.41158}{\text{Wt of Sample}} \times 100 = \text{Wt } \% \text{SO}_4 =$$

ANALYSIS FOR SULFIDE

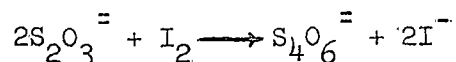
In order to analyze the product for the weight per cent sulfide which was present, an iodimetric analysis technique²⁵ was used. It was desirable to analyze for the presence of sulfide to determine to what the calcium sulfate was being reduced. The technique involves preparing several solutions of oxidizing and reducing agents. These solutions must be standardized to determine the exact concentration of the oxidizing or reducing agent present. The solutions can change concentration upon exposure to light, so they must be re-standardized with fresh solutions weekly. This involved a great deal of time. As a result, only certain runs were analyzed for the sulfide ion.

This technique involves preparing several solutions. The first of these is a .1 normal iodine solution. It is very difficult to obtain pure iodine which is dry. Therefore, an approximately .1 normal solution was made using the following technique. Place 12.7 grams of reagent grade iodine in a 250-ml beaker; add 40 g of iodate-free potassium iodide and 25 ml of water. Stir at intervals to hasten solution of the iodine, and when it has all dissolved, dilute the solution to one liter. Keep the solution in a glass-stoppered bottle. Store the solution in a cool place and protect the solution from the light as much as possible.

The iodine solution can be standardized by titrating against a standard .1 normal arsenious oxide solution. Pure arsenious oxide can be obtained from various manufacturers. If necessary, the substance may be further purified by recrystallization from hot 20 per cent hydrochloric acid. The powder is thus obtained and dried in a desiccator over sulfuric acid. Then weigh out 2.4725 g of pure dry arsenious oxide and dissolve it in 20 ml of 1 normal sodium hydroxide solution. Add 1 normal hydrochloric acid to the solution until the reaction is neutral or only slightly acid to litmus paper. Transfer the solution to a 500-ml volumetric flask and dilute it to the mark. Pipette 25 ml into a 250-ml Erlenmeyer flask, add 25 to 50 ml of water, 1 g of sodium bicarbonate, and a few milliliters of starch solution. Titrate with the iodine solution to the first blue color.

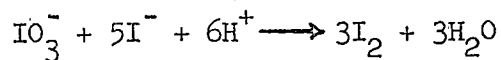
The starch solution used as an indicator is easily made up. Triturate 2 g of soluble starch and 10 mg of mercuric iodide (preservative) with a little water. Add the suspension slowly to a liter of water. Continue to boil the solution until it is clear. Then cool the solution and transfer it to a glass-stoppered bottle. Use 5 ml of this starch solution for every 100 ml of solution to be titrated. In the titration of iodine, starch should not be added until just before the end point is reached because the fading color of the iodine is a good indication of the approach of the endpoint.

The most important reaction applied in iodimetric titrations is the oxidation of thiosulfate to tetrathionate by iodine:



To prepare a standard .1 normal sodium thiosulfate solution, dissolve 25 g of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ in one liter of freshly boiled, cooled water. Add .1 g of sodium bicarbonate to the solution. Allow it to stand for a day before standardizing. The solution must be standardized since it is not possible to prepare sodium thiosulfate solutions of definite concentrations. The amount of water hydrated in the crystal is hard to determine since it effloresces very easily.

To standardize the .1 normal thiosulfate solution, various standard substances are available. For this scheme, potassium iodate was used. Potassium iodate is obtainable in a pure state by recrystallization from water and drying at 180°C . With only a slight excess of hydrogen ions, the reaction rapidly goes to completion as follows:



Therefore, weigh out .14 to .15 g of pure potassium iodate. Dissolve this in 25 ml of water and add 2 g of potassium iodide (iodate-free) and 10 ml of 1 normal hydrochloric acid. Titrate with standard thio-

sulfate solution with constant stirring. Add a few milliliters of starch solution when the color of the liquid has become a pale yellow, and continue the titration until the color changes from blue to colorless.

With these solutions made up and standardized, the weight per cent sulfide present could be determined using the following scheme. Pour 75 ml of 10 per cent acetic acid into a clean 250-ml Erlenmeyer flask. Add, from a burette, an amount of standard .1 normal iodine solution so that more than enough iodine is present to oxidize all the sulfide in the weight of sample used. One milliliter of exactly .1 normal iodine solution will oxidize .0016 g of sulfide. Depending on the estimated sulfide content, weigh .1 to .5 g of a sample into the flask. Immediately stopper the flask and let it stand for one hour. Periodically shake the flask to permit all the sulfide present to be oxidized. Then remove the stopper and add 3 ml of concentrated hydrochloric acid to guarantee that sufficient acid is present to assure complete oxidation of sulfide. Now titrate excess iodine with the standardized .1 normal sodium thiosulfate solution using starch as an indicator. Assuming that the iodine and thiosulfate solutions are exactly .1 normal, the calculation would be:

$$\text{Wt \% Sulfide} = \frac{(\text{ml I}_2 - \text{ml Na}_2\text{S}_2\text{O}_3) \times (0.0016) \times (100)}{\text{Wt of Sample}}$$

ANALYSIS AND THE CATALYST

The presence of the ferric oxide catalyst affects the analysis procedure in two ways. The first of these was previously mentioned in the discussion of the barium sulfate precipitation technique.

When barium sulfate first precipitates, its crystals are very fine and feathery. They are far too fine to be seen by the naked eye. From the moment they form, these crystals absorb impurities on their surfaces. The polar forces of the barium ion and sulfate ion attract other charged particles from the solution. Some of these impurities are sloughed off as the crystal grows, others are actually imprisoned within the precipitate. This inclusion of an impurity with a precipitate at the time the precipitate is formed is called coprecipitation. This phenomenon can cause both positive and negative errors, depending on whether the impurity is in excess or actually replaces ions of the barium sulfate lattice.

Coprecipitation effects are not usually large, but they can ruin the accuracy of the determination if special care is not taken. So, in order to avoid the errors due to coprecipitation, the impurities must be removed from solution before the barium ion is added. In some instances this can be done using an ion exchange technique. The ferric oxide was removed by adding ammonium hydroxide to the dissolved sample to precipitate the ferric oxide out of solution.

The second problem in the analysis due to the addition of the catalyst occurred in the calculation of a reaction conversion. Since some of the ferric oxide was being reduced to either magnetite or elemental iron, the basis for comparing initial and final sulfate concentrations was changing. Although this error is probably small since it appeared that only part of the ferric oxide was reduced, the author felt that it should be brought to the reader's attention.

For a reactant which is initially 12.5 weight per cent ferric oxide and 87.5 weight per cent calcium sulfate, the error is very small if all the ferric oxide is reduced to magnetite. If none of the ferric oxide is reduced to magnetite, the product would be 21.3 weight per cent ferric oxide and 78.7 weight per cent calcium sulfide. If all of the ferric oxide is reduced to magnetite, the product would be 21.0 weight per cent magnetite and 79.0 weight per cent calcium sulfide.

For the reduction of ferric oxide to elemental iron the error is somewhat larger. If all of the ferric oxide is reduced to iron, the product would be 16.2 weight per cent iron and 83.8 weight per cent calcium sulfide.

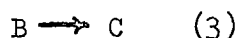
It does not appear that all of the ferric oxide is reduced. A very small percentage of the product is magnetic. To analyze each run for the weight per cent ferric oxide, iron, and magnetite would

be very time consuming. Since the error is small, and since this error results in lower calculated conversions than are actually present, no attempt was made to analyze for ferric oxide or its reduced products.

CONTRIBUTION TO THE THEORY OF PERIODIC REACTIONS

In 1910, A. J. Lotka wrote an article describing how an autocatalytic reaction of a certain mechanism could result in a damped, oscillating curve when concentration is graphed versus time.

Consider the following series of consecutive reactions, each of which is supposed to be practically irreversible:



It is understood that the capitals refer to substances in the state of "dilute" gas or solution. It is further assumed that "a" is present in an approximately constant concentration; for example, as the saturated vapor in contact with its condensed phase. In this example the conversion of "a" to "A" is assumed slow as compared to the establishment of equilibrium between the condensed phase and its vapor. Assume that diffusion effects may be left out of consideration.

Then the equations expressing the rate of change of the concentrations of A and B are:

$$\frac{dC_A}{d\theta} = H - k_1 C_A$$

$$\frac{dC_B}{d\theta} = k_1 C_A - k_2 C_B$$

where H , k_1 , and k_2 are constants, and C_A and C_B are the concentrations of the respective compounds.

Now, let the substance B influence autocatalytically its own rate of formation. Assuming that this influence follows the simplest possible law, one can write:

$$k_1 = kC_B \quad (3)$$

Substituting this into the rate equations, they reduce to:

$$\frac{dC_A}{d\theta} = H - kC_A C_B \quad (4)$$

$$\frac{dC_B}{d\theta} = kC_A C_B - k_2 C_B \quad (5)$$

The complete solution of (4) and (5), giving the entire course of the reaction, would present difficulties. Of the final stages of the process, one can easily obtain an expression.

First, one must simplify equations (4) and (5) by changing the scale of time and combining some constants. One might substitute these relations:

$$T = k\theta \quad (6)$$

$$h = H/k \quad (7)$$

$$K = k_2/k \quad (8)$$

making these substitutions into equations (4) and (5), one has:

$$\frac{dC_A}{dT} = h - C_A C_B \quad (9)$$

$$\frac{dC_B}{dT} = (C_A - K)C_B \quad (10)$$

A further transformation is suggested by the reflection that the system will ultimately settle down to steady state when:

$$\frac{dC_A}{dT} = h - C_A C_B = 0 \quad (11)$$

$$\frac{dC_B}{dT} = (C_A - K)C_B = 0 \quad (12)$$

Therefore, at steady state the following equalities will hold:

$$C_A = K \quad (13)$$

$$C_A C_B = K C_B = h \quad (14)$$

$$C_B = h/K = L \quad (15)$$

Now, if we change variables and deal with the excess of existing concentrations over those at equilibrium, the following equations will hold:

$$X = C_A - K \quad (16)$$

$$Y = C_B - L \quad (17)$$

Introducing these equations into (9) and (10) and rearranging, one will obtain

$$\frac{-dX}{dT} = X \cdot Y + K \cdot Y + L \cdot X \quad (18)$$

$$\frac{dY}{dT} = X \cdot Y + L \cdot X \quad (19)$$

Up to this point no restrictions have been introduced. However, in the final stages of the process when steady state is nearly reached, X and Y are both very small. Therefore, we can neglect the product X·Y. By eliminating X·Y and rearranging (18) and (19) the second order, linear differential equations result:

$$\frac{d^2X}{dT^2} + L \frac{dX}{dT} + KLX = 0 \quad (20)$$

$$\frac{d^2Y}{dT^2} + L \frac{dY}{dT} + KLY = 0 \quad (21)$$

These equations are recognized as the wellknown damped vibration type. The reactions are periodic provided that:

$$L < 4K$$

The solution of (20) and (21) in that case, written in the simplest form, is:

$$Y = Y_0 \cdot e^{-pT} \cos qT \quad (23)$$

$$X = 1/L \cdot \frac{dY}{dT} = -ZY_0 e^{-pT} \sin (\phi + qT)$$

$$X = me^{-pT} \sin (\phi + qT) \quad (24)$$

where

$$p = L/2 \quad (25)$$

$$q = \frac{\sqrt{4KL - L^2}}{2} \quad (26)$$

$$L \cdot Z = \sqrt{p^2 + q^2} \quad (27)$$

$$\sin \phi = \frac{p}{\sqrt{p^2 + q^2}} \quad (28)$$

$$\cos \phi = \frac{q}{\sqrt{p^2 + q^2}} \quad (29)$$

The origin of time is arbitrarily chosen so that equation (23) contains no sine term. The constant Y_0 is the value of Y at the time $T = 0$. Therefore, using these equations to describe a system of consecutive reactions which occur in the presence of an autocatalytic decomposition product, the requisite condition for a damped periodic process are established.

Table III. A Summary of the Experimental Results Reported in this Study.

Run Units	Time Min	Temp °C	Catalyst	Wt g	CO Flow g mole min	H ₂ O Flow g mole min	Wt CaSO ₄ grams	Conversion percentage
1	45	700	Na ₂ CO ₃	0.5	0.022	0.045	3.5	6.5
2	45	700	Cr ₂ O ₃	0.5	0.022	0.045	3.5	6.0
3	45	700	Fe ₂ O ₃	0.5	0.022	0.045	3.5	45.4
4	45	680	Fe ₂ O ₃	0.5	0.022	0.045	3.5	26.7
5	45	720	Fe ₂ O ₃	0.5	0.022	0.045	3.5	81.9
6	45	740	Fe ₂ O ₃	0.5	0.022	0.045	3.5	98.0
7	45	760	Fe ₂ O ₃	0.5	0.022	0.045	3.5	99.9
8	45	740	Fe ₂ O ₃	0.5	0.022	None	3.5	99.8
9	45	700	Fe ₂ O ₃	0.3	0.022	0.045	3.5	31.0
			NiO	0.2				
10	45	700	Fe ₂ O ₃	0.3	0.022	0.045	3.5	32.8
			Cr ₂ O ₃	0.2				
11	30	660	Fe ₂ O ₃	0.5	0.022	None	3.5	43.6

Table III (continued)

Run Units	Time Min	Temp °C	Catalyst	Wt g	CO Flow g mole min	H ₂ O Flow g mole min	Wt CaSO ₄ grams	Conversion percentage
12	45	660	Fe ₂ O ₃	0.5	0.022	None	3.5	68.2
13	15	660	Fe ₂ O ₃	0.5	0.022	None	3.5	64.4
14	7	660	Fe ₂ O ₃	0.5	0.022	None	3.5	51.9
15	30	660	Fe ₂ O ₃	0.5	0.022	None	3.5	44.5
16	15	660	Fe ₂ O ₃	0.5	0.022	None	3.5	63.6
17	7	660	Fe ₂ O ₃	0.5	0.022	None	3.5	51.0
18	22	660	Fe ₂ O ₃	0.5	0.022	None	3.5	50.8
19	60	660	Fe ₂ O ₃	0.5	0.022	None	3.5	97.2
20	15	680	Fe ₂ O ₃	0.5	0.022	None	3.5	75.6
21	30	680	Fe ₂ O ₃	0.5	0.022	None	3.5	90.8
22	7	680	Fe ₂ O ₃	0.5	0.022	None	3.5	50.2
23	45	700	Fe ₂ O ₃	0.5	0.022	None	3.5	95.4
24	45	680	Fe ₂ O ₃	0.5	0.022	None	3.5	97.1
25	45	660	Fe ₂ O ₃	0.5	0.0254	None	3.5	70.4

Table III (continued)

Run Units	Time Min	Temp °C	Catalyst	Wt g	CO Flow g mole min	H ₂ O Flow g mole min	Wt CaSO ₄ grams	Conversion percentage
26	45	640	Fe ₂ O ₃	0.5	0.022	None	3.50	45.9
27	38	660	Fe ₂ O ₃	0.5	0.0254	None	3.50	58.7
28	30	660	Fe ₂ O ₃	0.5	0.0325	None	3.50	31.5
29	25	660	Fe ₂ O ₃	0.5	0.038	None	3.50	50.6
30	45	720	Fe ₂ O ₃	0.05	0.022	None	3.50	30.5
31	45	720	Fe ₂ O ₃	0.09	0.022	None	3.50	50.0
32	45	720	Fe ₂ O ₃	0.328	0.022	None	3.50	96.2
33	45	720	Fe ₂ O ₃	0.30	0.022	None	3.50	98.0
34	45	720	Fe ₂ O ₃	0.40	0.022	None	3.50	99.3
35	45	720	Fe ₂ O ₃	0.50	0.022	None	3.50	92.1
36	45	720	Fe ₂ O ₃	0.04	0.022	None	3.50	47.2
			CaS	0.46				
37	10	720	Fe ₂ O ₃	0.3	0.022	None	3.50	71.3

Table III (continued)

Run Units	Time Min	Temp °C	Catalyst	Wt g	CO Flow g mole min	H ₂ O Flow g ² mole min	Wt CaSO ₄ grams	Conversion percentage
38	10	720	Fe ₂ O ₃	0.30	0.022	None	3.50	99.4
			CaS	0.20				
39	10	720	Fe ₂ O ₃	sep.	0.022	None	3.50	12.5
40	10	720	CaS lum.	0.2	0.022	None	3.50	5.9
41	10	720	Fe ₂ O ₃	0.30	0.022	None	3.50	48.9
			CaS lum.	0.20				
42	45	620	Fe ₂ O ₃	0.50	0.022	None	3.50	19.0
43	45	660	Fe ₂ O ₃	0.15	0.022	None	3.50	62.8
44	45	600	Fe ₂ O ₃	0.50	0.022	None	3.50	10.7
45	120	750	None		0.022	0.045	4.0	14.2

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