

THE HIGH TEMPERATURE REACTIONS  
BETWEEN  
SODIUM SULFATE AND CARBON MONOXIDE

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SODIUM SULFATE AND CARBON MONOXIDE

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## INTRODUCTION

The high temperature reaction between sodium sulfate and carbon or carbon monoxide to produce sodium sulfide has had considerable industrial application. There have been many patents granted for methods of producing the reaction under different conditions and using various catalysts. The actual uncatalyzed reactions between sodium sulfate and carbon monoxide have received very little study and the studies which have been reported in chemical literature exhibit several contradictions.

This is a report of an attempt to determine the actual products produced by the reactions at about 900° C. and the manner in which the amount of each product varies with time. The results obtained establish some of the reactions which must be considered in any explanation of the complicated overall reaction.

## HISTORICAL

A high temperature reaction between sodium sulfate and carbon is mentioned by Clement and Desormes (1) as early as 1801. Berzelius (2), Berthier (3), Gay Lussac (4), and Regnault (5) all made partial studies of the reaction; but Unger (6) seems to have been the first to propose an actual equation for the reaction. He concluded that the primary reaction was:

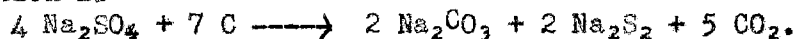


d'Heureuse (7) did further work on the reaction; and in 1858, Stromayer (8) reported finding polysulfides and carbonates among the reaction products. Mactear (9) further substantiated Stromayer's findings by stating:

When sulfate of soda is mixed with an excess of carbon and exposed to a temperature considerable above red heat, out of contact with air, the reaction is



When a temperature of dull redness, 1150-1300°F is used the reaction is

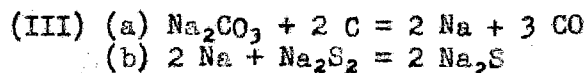
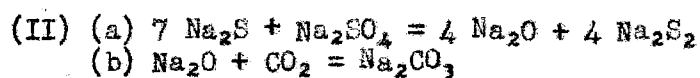


The reaction began to assume industrial importance about 1890, and Berthelot (10) made a study at 1000°C. but reported that he had trouble because the materials were reacting with the silica of the containers at that temperature.

Colson (11) ran experiments in which he mixed the sulfate with twice and four times its equivalents of carbon to determine what effect this would have upon the ratio of carbon dioxide to carbon monoxide produced. From this he hoped to establish whether the main reaction was the one with two carbon atoms to produce carbon dioxide or with four carbon atoms to produce the monoxide. He admitted that his results were inconclusive since too much depended upon the uniformity and intimacy of mixing and other factors over which he had no control. He did prove that the

reaction which takes place is dependent upon the amount of carbon present. Analysis of gas resulting from the mixture with four carbon equivalents gave twenty-five parts carbon dioxide to one hundred parts carbon monoxide and in the mixture containing two carbon equivalents the ratio was five parts carbon dioxide to one hundred of carbon monoxide. He carried out his reaction in a carbon tube inside a rifle barrel to avoid the interference of silica reported earlier by Berthelot. At 950° the reaction proved to be rapid and uniform, the above ratios being measured after the reaction had continued for twenty minutes. No analysis was reported on the solid products.

Cambi (12) studied the reactions produced by heating mixtures of sodium sulfate and carbon at 900°C in an electric furnace. In his work he used samples of sodium sulfate weighing about one hundred and seventy-five kilograms and was thus able to give his products a more complete analysis than had been possible in the earlier work. Even so, there was much as ten percent of the weight of products for which he was unable to account. He confirmed the findings of carbonates and polysulfides as reported earlier by Stromayer and by Mactear. Tables are given showing the composition of the mixture produced under different working conditions, and composition of the material taken out of the furnace at different periods of time during production. Cambi proposed that the reaction takes place chemically in three stages:

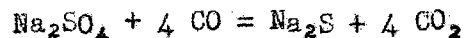


These equations correspond closely to the actual conditions which he found experimentally. As proof of the mechanism of the third stage he

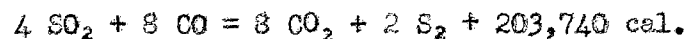
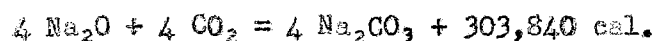


showed that there is a fairly constant ratio between the amount of polysulfide and carbonate present. His results indicated that the amount of sodium sulfide produced increased with time while the amount of carbonate and polysulfide passed through a maximum at about two and one-half hours reaction time. Although he was unable to account for the total products he was able to show that there was no loss of sodium in the reactions.

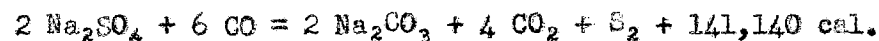
The only previous study in which the reduction of the sodium sulfate is accomplished solely by carbon monoxide was made by Okuno, Masumi, and Fukuyama (13). They used a static system with the sodium sulfate placed in a boat inside a reaction tube which was heated by an electric tube furnace. The system was arranged so they could introduce known mixtures of carbon monoxide and carbon dioxide, and measure the change in pressure as the reaction progressed. They reported the formation of quantities of sulfur dioxide even at temperatures as low as 730°C. A considerable quantity of sodium carbonate was produced in the reduced mass and free sulfur was deposited at a cold part of the reaction tube. The gas volume was also observed to decrease during the reaction. According to their results the quantity of sodium sulfide produced goes through a maximum with time, at each of the temperatures where they made studies. At 740°C. the maximum was passed through after about seventy minutes. At 800°C. the maximum was also at seventy minutes while 850°C. had a fifty minute maximum and 900°C. produced the greatest amount of product at thirty minutes reaction time. They proposed that the main reaction is:



with the secondary reaction being

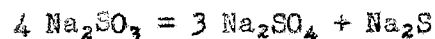


combining these four equations they got the following thermal equation:

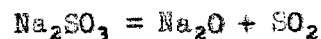


No mention is made of polysulfides being formed.

The first step in the reduction of sodium sulfate would undoubtedly be the formation of sodium sulfite. Forster and Kubel (14) observed that the thermal decomposition of sodium sulfite at 600°C. may be represented:



but above 900°C. the reaction



disturbs the equilibrium. The equilibrium is not completed in two hours at 1200°C. The rate of decomposition increases rapidly between 600°C. and 700°C., but only slowly between 700° and 800°C. M. Picon (15) found that anhydrous sodium sulfite, in vacuo, at 700°C., is rapidly converted into sulfate and sulfide.

## EXPERIMENTAL

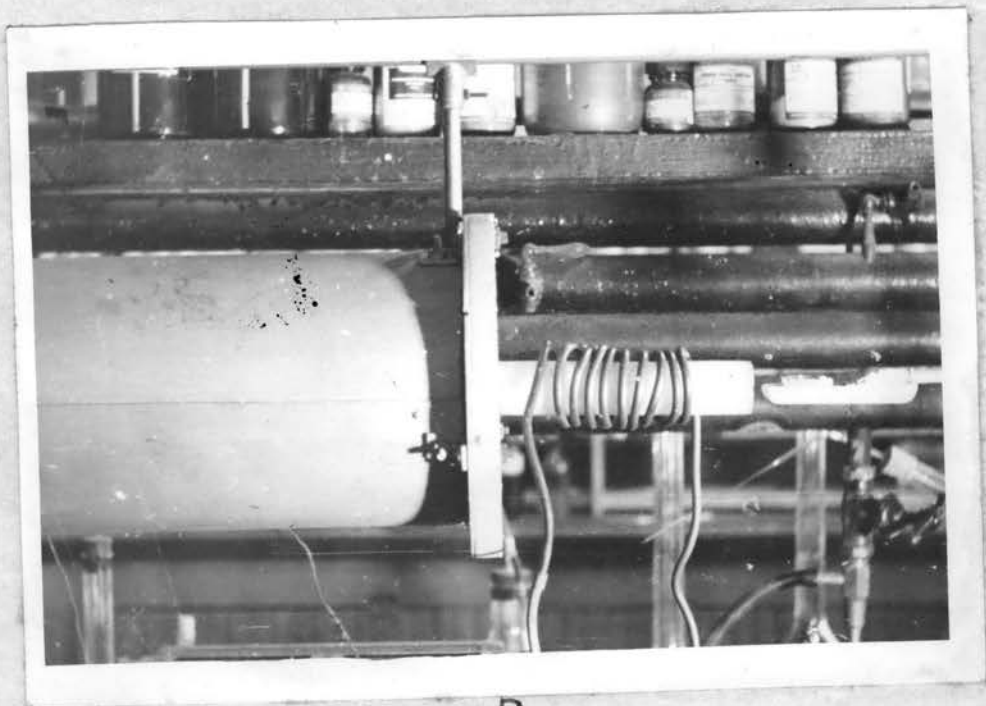
## Apparatus

The apparatus used in this research can be divided into four sections. The sections being a reaction chamber; a furnace for heating the chamber with suitable methods of measuring and controlling the temperature; a system for measuring the pressure in the reaction chamber with connections for evacuating the reaction chamber and filling it with carbon monoxide; and a system for generating, purifying, and storing the carbon monoxide.

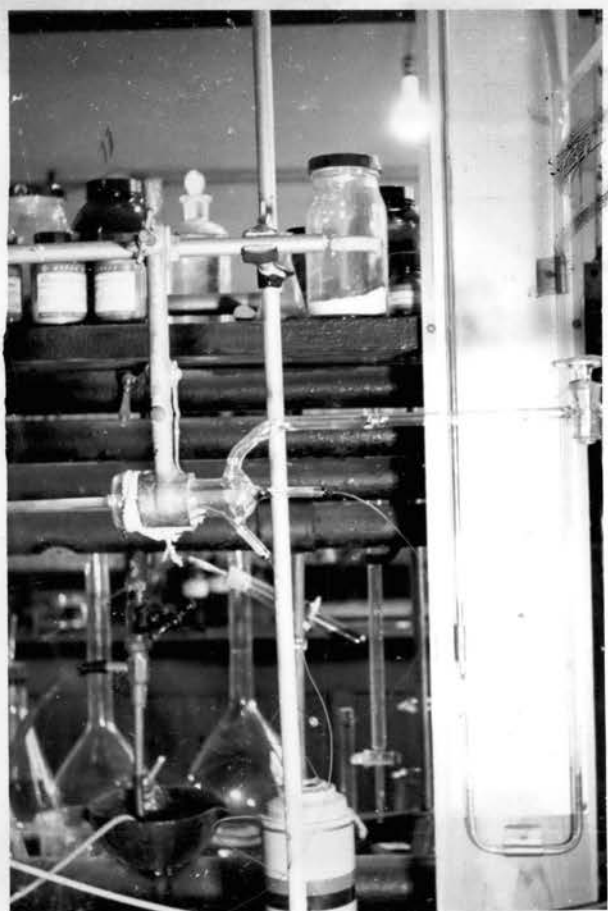
The reaction chamber is a fused silica tube (1" x 12"). One end of the tube is sealed and the other is ground to fit a standard taper ground glass joint (#29/42). The female portion of the ground glass joint has a connection to the gas handling system and outlets for the thermocouple lead wires. These outlets are made vacuum-tight by making the glass to metal seal with lead glass and coating the seal with picein. The reaction is carried out in a gold boat (1/4" x 1/4" x 3/4"). The boat is placed on a support fastened to the ends of two small fused silica tubes. These tubes also serve to protect and separate the thermocouple wires. The small silica tubes are supported by a short piece of pyrex tubing fastened to the back of the ground glass joint by a ring seal. The ground glass joint is protected from excessive heat by a copper cooling coil. Picture (A) shows a close up view of the gold boat with its support. Picture (B) shows part of the furnace, the reaction tube and the cooling coil with the boat in position to be placed in the reaction tube. Picture (C) shows the ground glass joint with the thermocouple leads and the connection to the gas handling system. The ground glass joint is also shown enlarged at F in figure I with G pointing out the thermocouple leads.



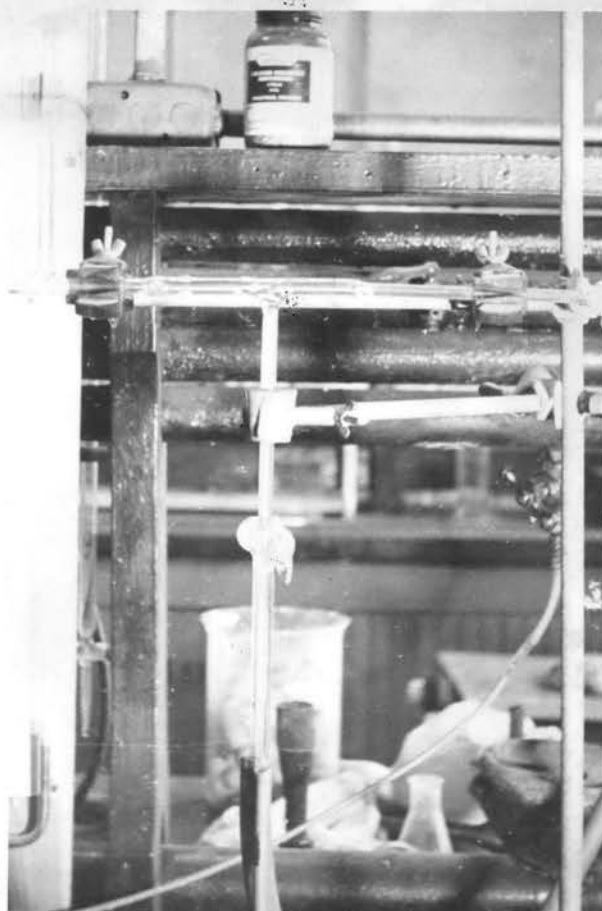
A



B

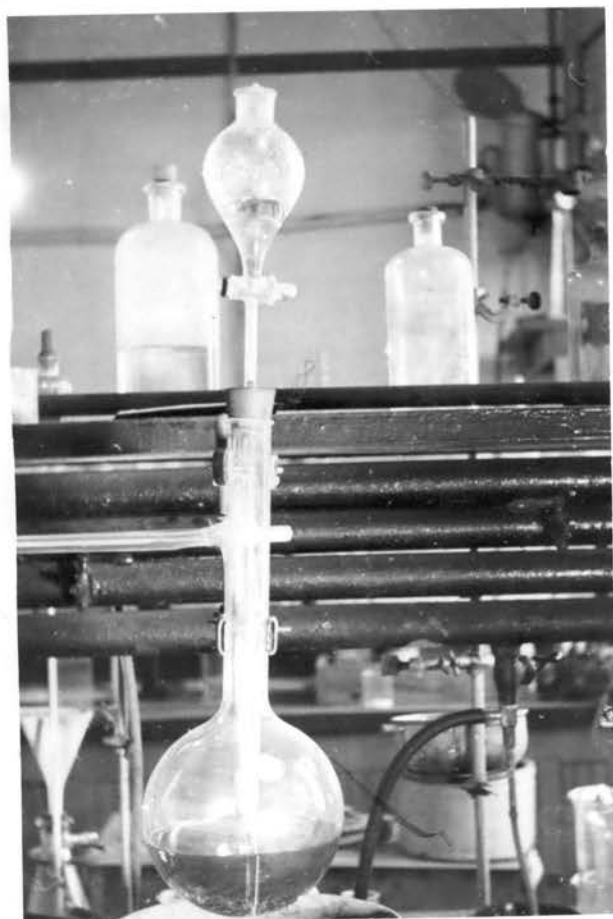


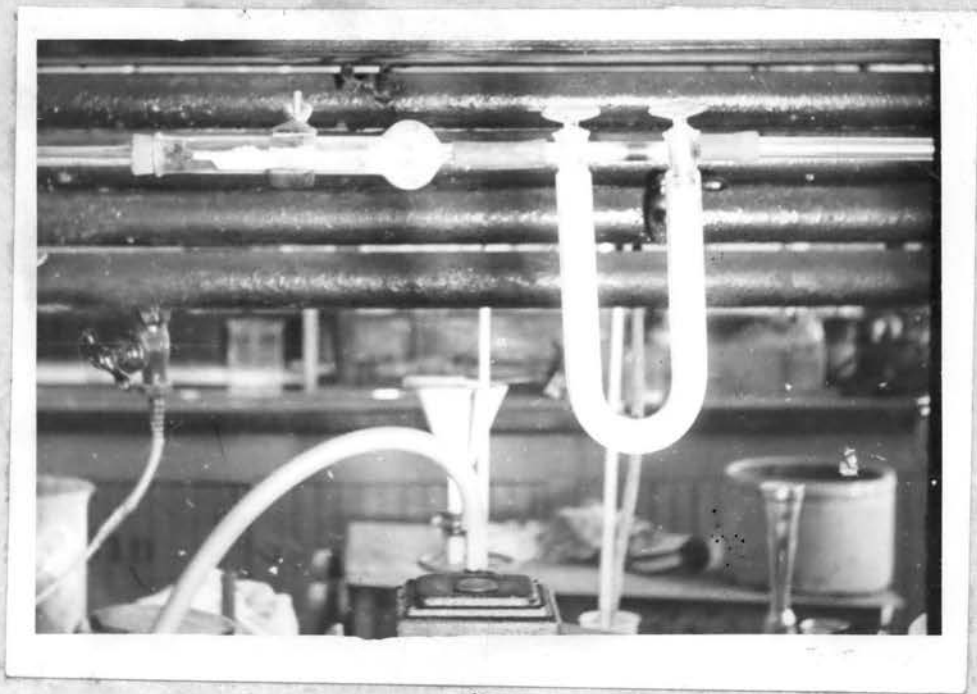
C



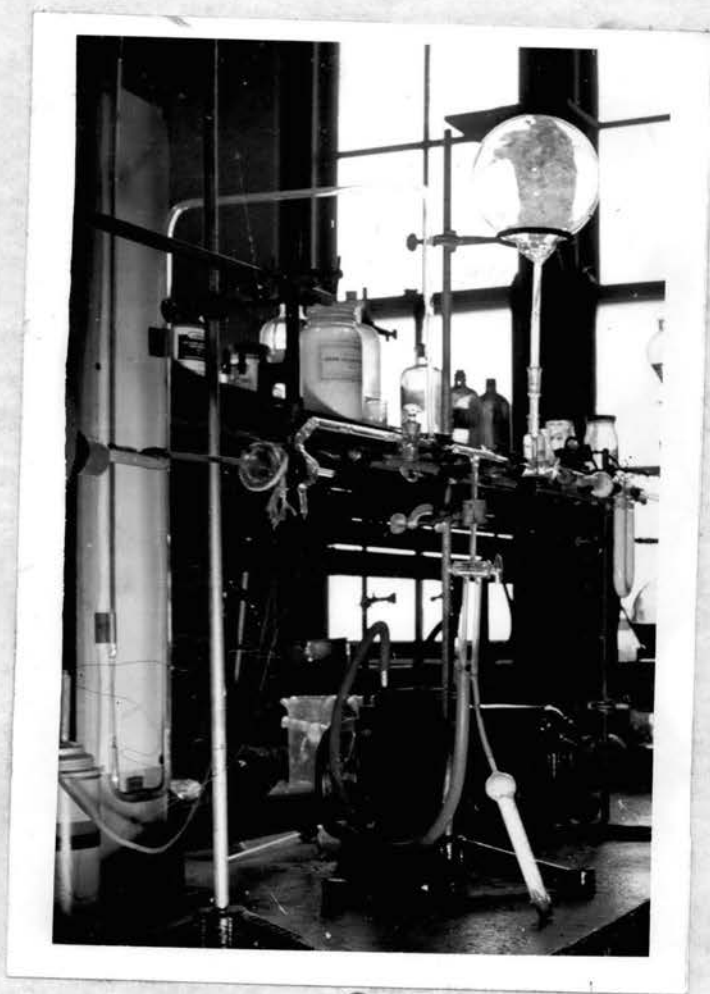
D

E





F



G



H



I

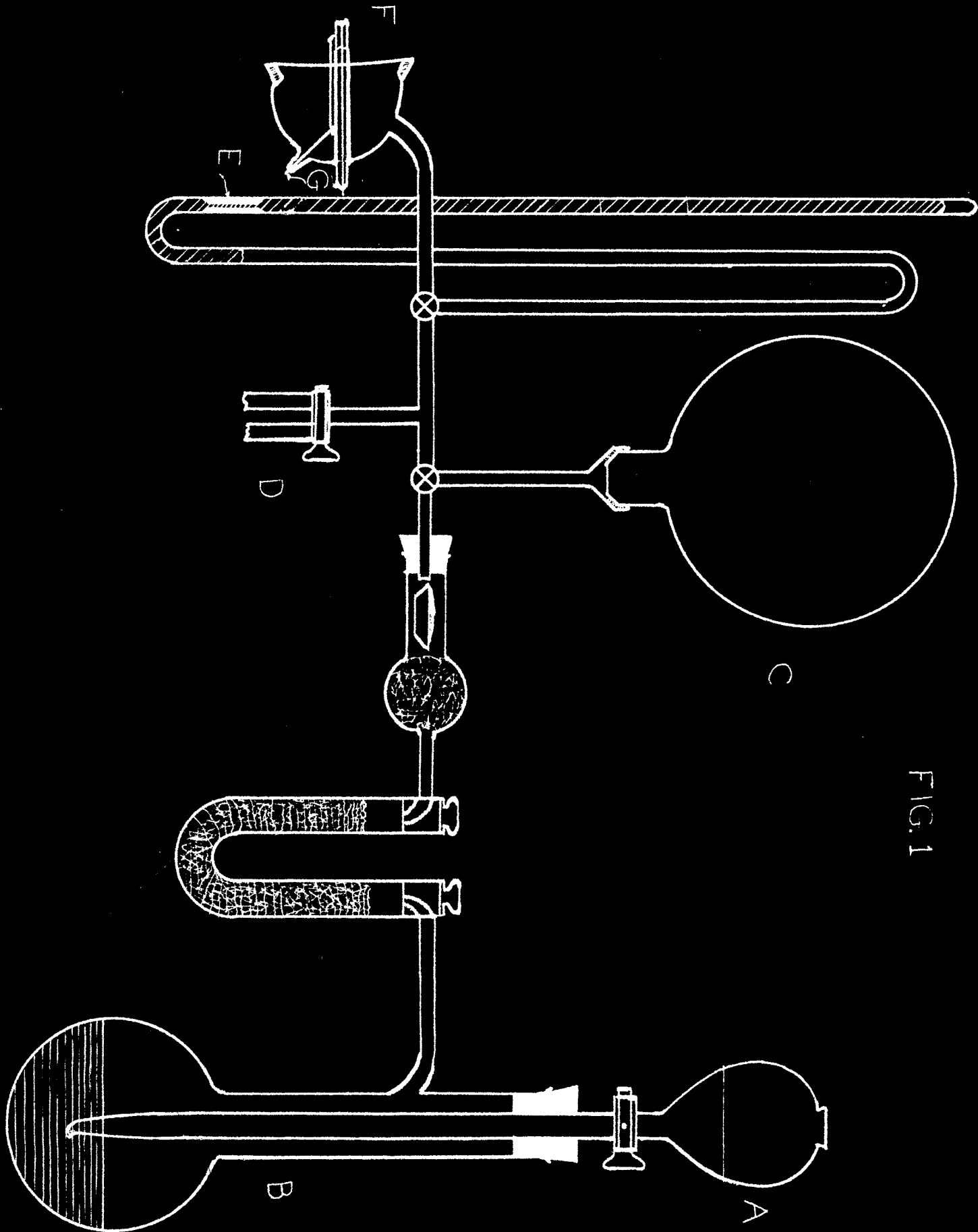


FIG. 1



The furnace is of the tube type having an internally wound nichrome heating unit. The heating unit draws about 590 watts when operated on 220 volts. The heating unit is supported by fire clay disks in an iron cylinder the annular space being filled with powdered asbestos. The furnace will reach a temperature of 900°C. in about twenty five minutes. The heating current is controlled using two fixed resistors (about 20 ohms each) and a 7.8 ohm variable resistor. The fixed resistors can be put in or removed from the circuit by conveniently mounted switches.

The temperature inside the reaction chamber is measured with a chromel-alumel thermocouple made of number twenty two wire. It is usually necessary to make a new thermocouple after each run as the metal wires are rapidly corroded at 900°C. in the reducing atmosphere. The electromotive force of the thermocouple is measured with a potentiometer using a galvanometer having a resistivity of 102 megohms as a null point indicator. By manually operating the fixed and variable resistors it is possible to hold the temperature of the furnace constant to within five degrees at 900°C. An electromotive force of  $36.00 \pm 0.10$  millivolts corresponds to  $896 \pm 5^\circ\text{C}$ . with the thermocouples used. The electromotive force-temperature relation of the wire used in making the couples was determined by calibrating a couple at several fixed points.

The closed end manometer (shown in picture C) is used to measure the pressure in the system. This manometer has a capillary tube constriction (E in figure I) to slow the mercury column so it will not break the end of the manometer if the pressure in the system increases rapidly. The manometer has been reduced in scale on figure I so all of it could be shown. The reaction chamber and the remainder of the system can be evacuated using a Cenco Hyvac pump connected to one of the outlet tubes of

stopcock D (figure I, and picture D). Air can be admitted to the system through a calcium chloride tube with the other opening of D. The stopcocks are so arranged that each part of the system can be separately evacuated.

The carbon monoxide is generated by adding formic acid from a dropping funnel to hot ( $120^{\circ}$ - $150^{\circ}$ C) concentrated sulfuric acid in a previously evacuated system. (Shown in picture E and represented by A and B in figure I.) The carbon monoxide is then purified by passing it through soda lime to remove carbon dioxide and acid spray and then through calcium chloride and over phosphorus pentoxide to remove water (picture F). After purification the carbon monoxide is stored in a two liter flask (C in figure I) at about one atmosphere pressure. The stopcock connecting the storage flask to the rest of the system is a three way T stopcock so the storage flask may be connected to both the generation and reaction systems at the same time or to each system separately.

Picture G shows an overall view of the apparatus. The author and sponsor are shown in picture H and I respectively.

## EXPERIMENTAL

## Procedure

In the actual making of a run the gold boat is filled with a weighed sample (four tenths to five tenths of a gram) of anhydrous reagent grade sodium sulfate. The gold boat is then placed on a piece of gold foil to retain the molten sodium sulfate which creeps out through the folded ends of the boat due to its high surface tension. The molten material must not be allowed to contact either silica or ceramic ware since it rapidly reacts with such materials. The gold boat and foil are then placed on its support and the silica tube placed around it and fitted into the ground joint. The furnace is then placed in position and the reaction tube is heated to  $896^{\circ} \pm 5^{\circ}\text{C}$ . The tube is held at this temperature for about five minutes and then evacuated and filled with carbon monoxide to a pressure of 550 to 600 mm. The reactants are kept at the indicated temperature for the desired period of time. The reaction is stopped by removing the furnace, pumping out the gaseous products and flushing the reaction tube twice with dry air.

## EXPERIMENTAL

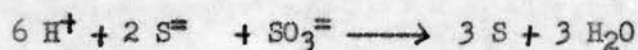
## Analytical

The solid products of the reaction are quantitatively analyzed for sulfate, sulfite, sulfide, and carbonate. No attempt is made to analyze the gaseous products.

The solid products are dissolved in water and diluted to one hundred milliliters. The analyses are made on a aliquots of this solution.

The sulfate analysis is made on a twenty-five milliliter aliquot by the standard barium sulfate gravimetric method taking care to keep the acidity low. The aliquot is made just acid to litmus and then one milliliter of one tenth normal hydrochloric acid added. The sulfate analysis has an overall error of about  $\pm 2\%$ .

The total equivalents of sulfite and sulfide are determined in a five milliliter sample of the basic reaction solution by titration with one thousandth normal iodine in potassium iodide solution. A second five milliliter aliquot is acidified and allowed to stand for about two hours during which time following reaction takes place:



After this reaction has gone to completion, the excess sulfide or sulfite is titrated with one thousandth normal iodine solution. In the cases where it is doubtful as to whether the sulfide or sulfite is present in excess a qualitative test is made by treating the acidified solution with p-aminodimethylaniline as outlined by Lindsay (16). A small trace of sulfide will react with the p-aminodimethylaniline to give the characteristic color of methylene blue. Sulfite exhibits no visible reaction with this organic compound. It is necessary to run blanks on all of the iodine titrations when using such dilute solutions. The end point in the iodine

titrations is hard to see because the solution turns brownish-orange as the iodine is added. An example of the method used to calculate the sulfide and sulfite present is given below:

A five milliliter aliquot requires thirty milliliters of one thousandth normal iodine solution after the amount of the blank has been subtracted.

Another five milliliter aliquot, when acidified and allowed to stand for two hours, requires ten milliliters of one thousandth normal iodine solution after correction for the blank has been made.

Sulfide is found to be in excess.

$$S^{2-} + SO_3^{2-} = 30.00 \times 0.001$$

for five milliliters of solution or

$$S^{2-} + SO_3^{2-} = 30.00 \times 0.001 \times 20$$

for the entire sample. Since it requires two equivalents of sulfide for each equivalent of sulfite for the reaction in acid we have the following equation:

$$S^{2-} - 2 SO_3^{2-} = 10 \times 0.001 \times 20$$

Combining our equations we have

$$3 SO_3^{2-} = 0.400$$

$$SO_3^{2-} = 0.133 \text{ milliequivalents}$$

$$S^{2-} = 0.600 - 0.133 = 0.465 \text{ milliequivalents}$$

Therefore we have 18.14 milligrams of sodium sulfide present and 8.38 milligrams of sodium sulfite.

The overall error on the sulfide determination is about -17% and about -40% on the sulfite determinations.

The carbonate determination involved the liberation of carbon dioxide from the sample, absorption of the evolved carbon dioxide in a

solution of sodium carbonate, and determining the amount of carbon dioxide absorbed by the change in pH of the carbonate solution.

The sulfide, sulfite, and other reducing ions in a ten milliliter aliquot are oxidized by adding potassium permanganate to the alkaline solution and boiling. The oxidized solution is placed in a test tube so connected that carbon-dioxide-free air can be bubbled through the solution. Dilute sulfuric acid is added from a dropping funnel and the evolved carbon dioxide is swept into a measured amount of standard sodium carbonate solution. If the air is passed through the acidified solution for about fifteen minutes all of the liberated carbon dioxide is swept into the sodium carbonate solution. The change in pH of the sodium carbonate solution is measured using a glass electrode. A calibration curve, in which change in pH is plotted against milligrams of sodium carbonate, has been prepared using known samples of carbonate. The overall error in the carbonate determinations is about  $\pm 10\%$ .

Slight traces of what may be free sulfur appear on dissolving products when the reaction is continued for sixty minutes or longer.

The color produced when the iodine solution is added and the fact that the ignited barium sulfate is purple in color are considered strong evidence that gold is present in the products when the reaction is continued longer than thirty minutes. Gold was proved to be present in the products of the two-hour experiment by the "Purple of Cassius" test in which an acid solution of the gold is reduced by stannous chloride to give a characteristic purple color due to colloidal gold.

## RESULTS AND CONCLUSIONS

This research has proved that the reaction between sodium sulfate and carbon monoxide at 900°C. is not a simple one but consists of several consecutive and possibly some simultaneous reactions producing a variety of products.

No entirely satisfactory material for constructing the reaction vessel was found. A few trials were made with boats of ceramic materials. These boats were soon discarded because of the formation of quantities of sulfur dioxide and some free sulfur when the reaction was continued for even fifteen minutes. The results obtained with the ceramic boats indicate that Okuno, Massumi, and Fukuyama (13) may have used this type of boat, for they reported the formation of sulfur dioxide and free sulfur in their research.

A series of experiments was made using platinum boats. These boats were unsatisfactory because the platinum rapidly reacted with the sodium sulfide formed. This removed the sulfide from the reaction and thereby interfered with any reactions depending upon the sulfide. It was also difficult to determine the platinum sulfide quantitatively. Sulfite was shown to be present in the reaction products by the liberation of sulfur dioxide when the products were acidified. The formation of sodium sulfite has not been mentioned by the other workers who have studied this problem. The data of two typical thirty-minute runs in which platinum boats were used is presented below.

Milligrams  $\text{Na}_2\text{SO}_4$  reacted

Milligrams PtS produced

56.5

15.8

63.4

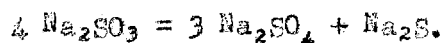
10.5

The results of the experiments using gold boats are shown in table I and graphs I and II. These results show wide variation due to errors in analysis and inability to reproduce experimental conditions. Despite the variations we can follow the general trend of the reactions.

The quantity of sodium sulfite produced increases rapidly with time until the reaction has continued for sixty minutes; then the quantity of sulfite seems to remain almost constant for the further time intervals studied. The probable reaction for the formation of sulfite is:



The amount of sodium sulfide in the products increases very rapidly from fifteen to sixty minutes and only slowly from sixty to one hundred and twenty minutes. Okuno, Masumi, and Fukuyama (13) reported that the amount of sodium sulfide produced passed through a maximum at about thirty minutes when the reaction at 900°C. was studied. There is no evidence of a maximum at thirty minutes in graph I. The sodium sulfide is believed to be formed by thermal decomposition of the sodium sulfite according to the reaction of Forster and Kubel (14)



This is undoubtedly a several-step reaction with the formation of several sodium sulfoxy compounds as intermediates. No attempt was made to analyze for these intermediate compounds.

A considerable quantity of sodium carbonate is produced when the reaction is continued only fifteen minutes. The quantity of carbonate increases almost linearly with time after fifteen minutes. There is no experimental evidence in this research to suggest a reaction mechanism for formation of carbonate.



TABLE I\*

Temperature  $896 \pm 50^\circ\text{C}$ . All weights in grams. CO pressure 550-600 mm.

Duration of Exp.	15 min.	30 min.	60 min. 1	60 min. 2
Wt. $\text{Na}_2\text{SO}_4$ sample	0.5188	0.5869	0.5191	0.4056
Apparent wt. product	0.5164	0.5796	0.4938	0.3839
Wt. $\text{Na}_2\text{SO}_4$ not reacted	0.4713	0.5344	0.4461	0.3338
Wt. $\text{Na}_2\text{SO}_4$ reacted	0.0475	0.0525	0.0730	0.0718
Wt. $\text{Na}_2\text{SO}_3$ found	0.0008	0.0022	0.0079	0.0061
$\text{Na}_2\text{SO}_4$ equi. of $\text{Na}_2\text{SO}_3$	0.0009	0.0025	0.0089	0.0069
Wt. $\text{Na}_2\text{S}$ found	0.0000	0.0035	0.0168	0.0208
$\text{Na}_2\text{SO}_4$ equi. of $\text{Na}_2\text{S}$	0.0000	0.0063	0.0306	0.0378
Wt. $\text{Na}_2\text{CO}_3$ found	0.0025	0.0043	0.0043	0.0057
$\text{Na}_2\text{SO}_4$ equi. of $\text{Na}_2\text{CO}_3$	0.0034	0.0058	0.0058	0.0076
$\text{Na}_2\text{SO}_4$ accounted for	0.4756	0.5490	0.4904	0.3861
$\text{Na}_2\text{SO}_4$ not accounted for	0.0432	0.0379	0.0287	0.0195

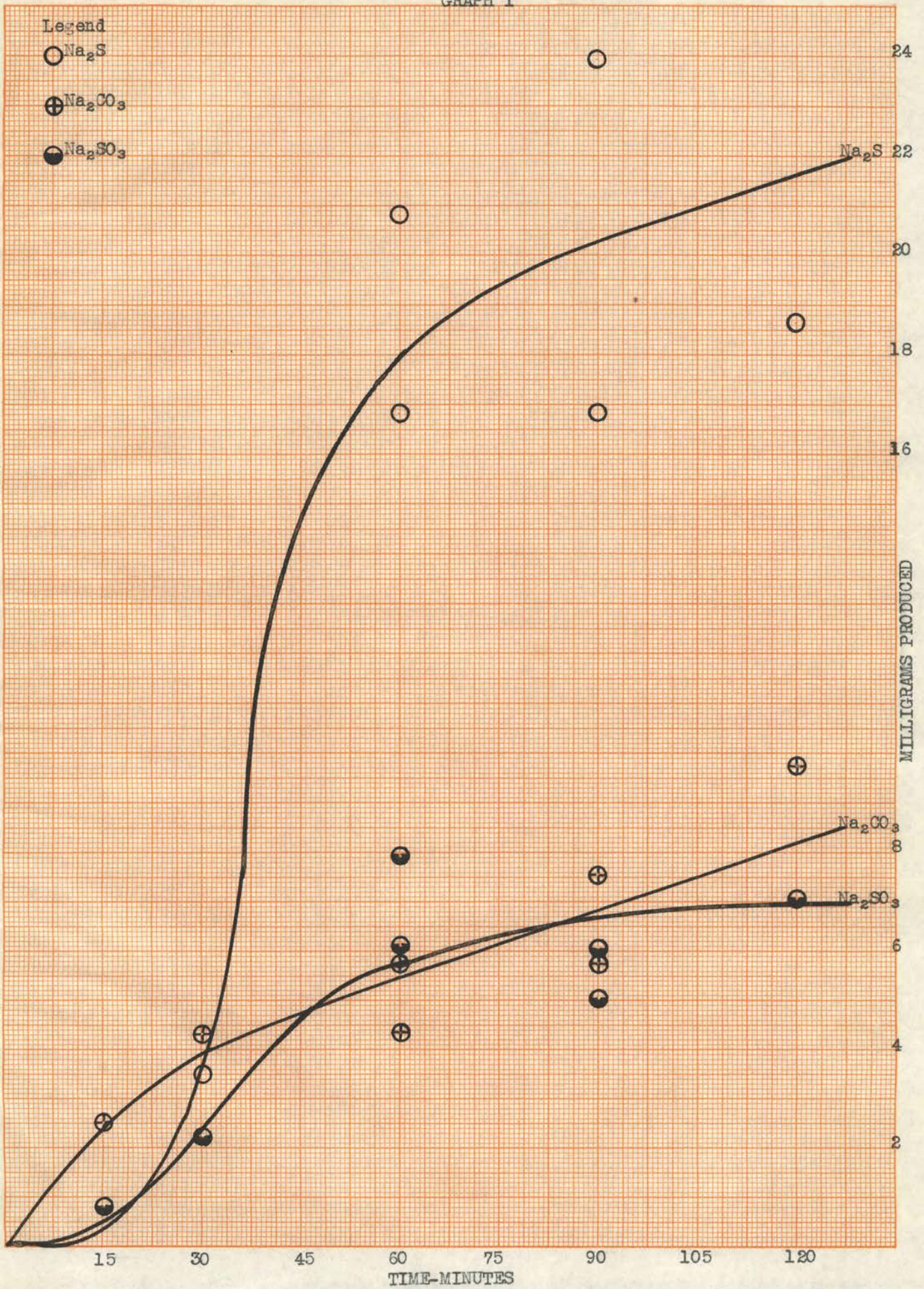
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\* Analytical results when gold boats were used.

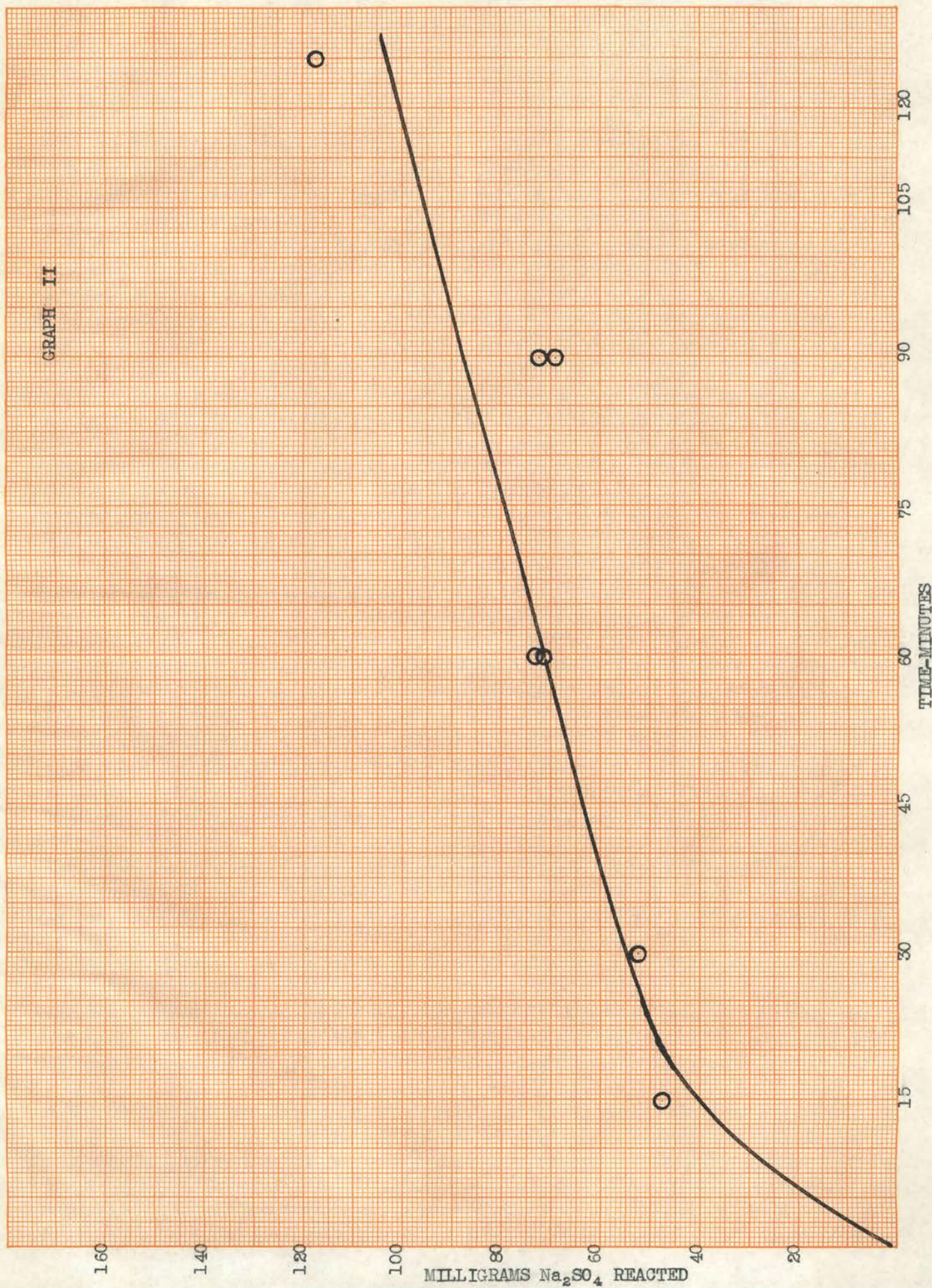
TABLE I  
(continued)

Duration of Exp.	90 min. 1	90 min. 2	120 min.
Wt. $\text{Na}_2\text{SO}_4$ sample	0.3988	0.3207	0.3154
Apparent wt. product	0.3646	0.3031	0.2468
Wt. $\text{Na}_2\text{SO}_4$ not reacted	0.3264	0.2517	0.1981
Wt. $\text{Na}_2\text{SO}_4$ reacted	0.0724	0.0690	0.1173
Wt. $\text{Na}_2\text{SO}_3$ found	0.0060	0.0050	0.0070
$\text{Na}_2\text{SO}_4$ equi. of $\text{Na}_2\text{SO}_3$	0.0068	0.0056	0.0079
Wt. $\text{Na}_2\text{S}$ found	0.0239	0.0168	0.0186
$\text{Na}_2\text{SO}_4$ equi. of $\text{Na}_2\text{S}$	0.0435	0.0306	0.0340
Wt. $\text{Na}_2\text{CO}_3$ found	0.0075	0.0057	0.0097
$\text{Na}_2\text{SO}_4$ equi. of $\text{Na}_2\text{CO}_3$	0.0100	0.0076	0.0130
$\text{Na}_2\text{SO}_4$ accounted for	0.3864	0.2955	0.2530
$\text{Na}_2\text{SO}_4$ not accounted for	0.0121	0.0252	0.0624

GRAPH I

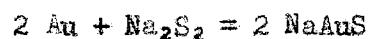
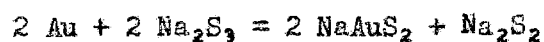


GRAPH II



As was mentioned in the analytical section, traces of what appeared to be free sulfur were produced when the reaction was continued longer than thirty minutes. The presence of free sulfur would suggest polythionates and polysulfides in the reaction mixture.

Since gold is known not to react directly with sodium sulfate, free sulfur, or sodium monosulfide, the gold compounds found in the reaction products may have been sodium thioaurate and/or sodium thioaurite, which can be formed by the following reactions:



Thus the presence of gold in the reaction products is an indication, but not a proof, of the presence of polysulfides.

The following are proposed as suggestions for further work:

1. Formulation of a system of analysis which will give more accurate results and which will determine the products present that were merely indicated by this research. Specifically, determine sulfate, sulfite, sulfide, polysulfides, and polythionates each in presence of all the others, also analysis of the gaseous products.
2. Search for a container material which has a high melting point and does not react with any of the products.
3. The design and construction of a thermocouple or thermometer which will not deteriorate in an atmosphere of carbon monoxide at 900°C., or else a method of protecting the chromel-alumel

thermocouple from the carbon monoxide.

4. Construction of a flow system rather than a static system.
5. Actual studies of effect of catalysts upon the reaction.
6. Studies of the high temperature reactions between carbon monoxide and the sulfates of other alkali and alkaline earth metals.

## SUMMARY

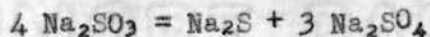
Studies of the uncatalyzed reactions between sodium sulfate and carbon or carbon monoxide began as early as 1801. Since then there have been many patents granted for variations of the basic process, particularly for catalysts, but few detailed studies have been made.

The apparatus consisted of (a) a reaction chamber, (b) apparatus for heating and controlling the temperature of the reaction chamber, (c) a system for admitting carbon monoxide to the reaction chamber, measuring the pressure of the gases in the reaction chamber, and flushing the reaction gases from the chamber with air, and (d) a system for generating, purifying, and storing the carbon monoxide.

Experiments were made with sodium sulfate samples of about 0.5 gram, carbon monoxide pressure being 550-600 millimeters, and the temperature  $896 \pm 5^\circ\text{C}$ . Ceramic and platinum containers for the reacting sodium sulfate proved very unsatisfactory and gold boats were only partially satisfactory.

Analysis of the solid products proved that sodium sulfite, sodium sulfide, and sodium carbonate are formed. The analysis indicated that polythionates, polysulfides, and other compounds are also produced.

The reactions



are proposed for the formation of the sulfite and sulfide.

The manner in which the amounts of sulfite, sulfide, and carbonate vary with reaction time was determined, and presented in tables and graphs.

Several suggestions are made for further studies.

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## BIOGRAPHY

Wf Roberts was born in Oklahoma City, Oklahoma, on October 13, 1924. He attended Willard grade school in Oklahoma City, and had his junior high and high school training in the Putnam City school system, graduating from Putnam City High School in May, 1942. He entered Oklahoma Agricultural and Mechanical College in September, 1942 and graduated with the Bachelor of Science Degree in August, 1945. He did graduate study at Northwestern University, Evanston, Illinois, from September, 1945, until April, 1946. In April, 1946, he reentered Oklahoma Agricultural and Mechanical College to complete the requirements for his degree of Master of Science.

He was employed by the Department of Chemistry during the entire period of his undergraduate study. For the first semester he worked in the storeroom. From February, 1943, until June, 1945, he was lecture demonstration assistant, and, during June and July of 1945, he was a laboratory research assistant on work being done for the Barnsdall Oil Company. He taught as a graduate assistant while attending Northwestern University and as a graduate fellow while completing his work at Oklahoma Agricultural and Mechanical College.

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