Rate of reaction of nitric oxide and oxygen by metal sulfides
by Kent Moroni Hodgson

A thesis submitted in partial fulfillment of the requirements for the degree of MASTER OF SCIENCE in Chemical Engineering
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Abstract:
Nitric oxide has received a great deal of attention as- one of the major air pollutants- with which environmentalists are concerned. Nitric, oxide is emitted into the atmosphere -where it can then Be oxidized to NO2 in the presence of sunlight and oxidizing agents. No. commerically acceptable method for removing NO from exhaust and flue gas has been developed yet.

This research is concerned with the rate of two reactions.

MeS + 4N0 → MeSO4 + 2N2 MeS + 202 -> MeSO4 The rates of reaction at 300°C, 4000C, 500°C for these two reactions were determined for ten metal sulfides, The rates of reaction were studied using a Cahn R-100 continuous recording electrobalance. This device was used to measure the weight of a sample continuously as it hung suspended from one arm of the balance into the reactor. The rate of reaction was calculated, from the continuously recorded weight increase. The rate of reaction of NO with metal sulfides was determined using a gas mixture with a composition of 2.5% NO and 97.5% He. The rate of reaction of O2 with metal sulfides was determined using a gas mixture with a composition of 2.5% O2 and 97.5% He, In general, the reaction of the metal sulfide with oxygen proceeds faster for all temperatures tested. The reaction rates with NO ranged from 3.38 x 10“° grams of FeSO4 formed per minute per gram of FeS to 2.076 x 10^-4 grams of FeSOlt formed per minute per gram of FeS. The reaction rates with O2 ranged from 5.9 x 10^-6 grams of ZnSO4 formed per minute per gram of ZnS to 6.48 x 10^-4 grams of PbSO4 formed per minute per gram of > PbS8 The sulfides of Ba, Fe, Sr, Cd, Pb, Ca, Zn and sulfurated potash -reacted with both the O2 and the NO to form the sulfate.

The relative reaction rates of NO with a given amount of ZnS or SrS at 300°C and a given amount of BaS, SrS or CdS at 400°C for a given time are greater than the relative rates of reaction of O2 with the same amount of BaS, SrS or CdS at 4000 and the same amount of ZnS or SrS at 300°C for the same time.

Cupric sulfide, thallium sulfide, manganese sulfide, and molybdenum disulfide could not be used because they decompose below- 300°C.

Tungsten disulfide when reacting with NO and 02 produced a net weight lost indicating that undesirable side reactions were controlling, Sulfurated potash produced the fastest reaction rates with NO and O2. However, since the composition was unknown, rates of reaction of the solid could not be calculated.

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Date November 18, 1975

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TABLE OF CONTENTS

Page

LIST OF TABLES

LIST OF FIGURES

ABSTRACT

Nitric oxide has received a great deal of attention as one of the major air pollutants with which environmentalists are concerned. Nitric oxide is emitted into the atmosphere where it can then be oxidized to NO_2 in the presence of sunlight and oxidizing agents. No commerically acceptable method for removing NO from exhaust and flue gas has been developed yet.

This research is concerned with the rate of two reactions.

$$MeS + 4NO \rightarrow MeSO_4 + 2N_2$$
$$MeS + 2O_2 \rightarrow MeSO_4$$

The rates of reaction at 300°C, 400°C, 500°C for these two reactions were determined for ten metal sulfides.

The rates of reaction were studied using a Cahn R-100 continuous recording electrobalance. This device was used to measure the weight of a sample continuously as it hung suspended from one arm of the balance into the reactor. The rate of reaction was calculated from the continuously recorded weight increase. The rate of reaction of NO with metal sulfides was determined using a gas mixture with a composition of 2.5% NO and 97.5% He. The rate of reaction of O_2 with metal sulfides was determined using a gas mixture with a composition of 2.5% O_2 and 97.5% He.

In general, the reaction of the metal sulfide with oxygen proceeds faster for all temperatures tested. The reaction rates with NO ranged from 3.38×10^{-6} grams of $FeSO_4$ formed per minute per gram of FeS to 2.076×10^{-4} grams of $FeSO_4$ formed per minute per gram of FeS. The reaction rates with O_2 ranged from 5.9 x 10-6 grams of $ZnSO_4$ formed per minute per gram of ZnS to 6.48×10^{-4} grams of $PbSO_4$ formed per minute per gram of FbS.

The sulfides of Ba, Fe, Sr, Cd, Pb, Ca, Zn and sulfurated potash reacted with both the O_2 and the NO to form the sulfate.

The relative reaction rates of NO with a given amount of ZnS or SrS at 300°C and a given amount of BaS, SrS or CdS at 400°C for a given time are greater than the relative rates of reaction of O_2 with the same amount of BaS, SrS or CdS at 400° and the same amount of ZnS or SrS at 300°C for the same time.

Cupric sulfide, thallium sulfide, manganese sulfide, and molybdenum disulfide could not be used because they decompose below 300°C.

Tungsten disulfide when reacting with NO and O_2 produced a net weight lost indicating that undesirable side reactions were controlling.

Sulfurated potash produced the fastest reaction rates with NO and O_2. However, since the composition was unknown, rates of reaction of the solid could not be calculated.

INTRODUCTION

The elimination of NO_x as an air pollutant has been a major concern of environmentalists since it was established in 1952 that NO_x participates in smog reactions (Bartok et al., 1971). NO_x represents the two oxides of nitrogen, NO(nitric oxide) and NO_2(nitrogen dioxide). The average U.S. urban concentration of nitrogen oxides in air is 20-25 times the natural atmospheric condition (Hopper and Yaws, 1974). On a nationwide basis about half the NO_x comes from stationary sources and about half from mobile sources (Science News, 1972).

Most of these oxides are released in the form of NO. The conditions for the formation of these two oxides are quite different. In high temperature combustion processes NO is almost exclusively formed (Bartok et al., 1971). However, at the ambient temperature of the atmosphere, the equilibrium between NO_2, O_2 and NO highly favors NO_2.

PREVIOUS WORK

There has been a great deal of work done concerning oxides of nitrogen. The author does not intend to give a comprehensive summary of all the work done. This is only a summary of some of the work that seems to offer promise of being significant in the control of NO_x.

Shaw (1973) in studying the reduction of nitrogen oxide emissions from a gas turbine combustor by fuel modification found that soluble organo metallic additives which became heterogeneous reduction or decomposition catalysts would reduce the NO_x emmission by 30%. A number of other additives were experimented with; however, the organo metallic additives produced the best results. The major drawback of these additives is that it seems to be a case of trading one pollutant for another.

The Bell Laboratory has developed a manganese, rare earths, lead on a ceramic support catalyst. This is mainly for use in automobiles. Good results have been obtained, however, a small amount of NH_3 is produced. In experimenting with this catalyst their experience showed that when CO and hydrocarbon emissions were controlled effectively the NO yield increased. And when the NO was controlled effectively the CO and hydrocarbon yield increased (Scientific American, 1973).

A dual bed catalyst system for the simultaneous reduction of SO_2 and NO has been developed by Sood and Kittrell (1974). The reactions:

$$CO + NO \rightarrow CO_2 + 1/2\ N_2$$

$$2CO + SO_2 \rightarrow 2CO_2 + 1/2\ S_2$$

$$CO + 1/2\ S_2 \rightarrow COS$$

$$2COS + SO_2 \rightarrow 3/2\ S_2 + 2CO_2$$

are considered to take place in this system. To get 90% removal stoichiometric quantities are necessary and the catalyst bed temperature must be controlled very carefully.

The reduction of nitric oxide with various hydrocarbons as studied by Ault and Ayen (1971) has shown that in general, an increase in carbon number in the hydrocarbon studied resulted in a decrease in the required temperature for a given nitric oxide conversion. For a given carbon number the required temperature for a given nitric oxide conversion decreased with degree of saturation. The catalyst used was a barium promoted copper chromite catalyst.

Good results were obtained by reducing nitric oxide using a copper nickel catalyst. The results indicated that the catalyst activity was dependent on the copper-nickel ratio. In general, activity increases with increasing copper content. Activation of the catalyst in CO at 500°C led to the opposite trend in activity; that is activity increased with an increase in nickel content.(Bauerle et al., March, 1974).

Ammonia has been the only reductant purported to show true selectivity for the heterogeneous reduction of nitric oxide to nitrogen in the presence of excess oxygen. A study by Bauerle et al.(December, 1974) indicates that the catalytic reduction of NO with NH_3 on Pt in a simulated plant exhaust is not strictly selective in the sense that the NH_3-O reaction has little appreciable effect on NO reduction. Nitrous oxide (N_2O) is a major reaction product and is produced by the reduction of both NO and O_2 with NH_3.

Regenerative sorption of nitric oxide has been found to work good for small concentrations of NO (Gidaspow and Onischak, 1973). The NO is sorbed with $FeSO_4$.

$$FeSO_4 + NO \rightarrow FeSO_4 \cdot NO$$

This reaction can be reversed with heat. The main drawback is that the flue gas and exhaust gases must be cooled below 100°C.

A fluidized bed of catalyst to catalytically reduce nitric oxide has been studied. Using a platium silica alumnia catalyst a conversion efficiency of over 99% was obtained. This was using a stream of pure NO (Dieteven et al., 1973).

REDUCTION WITH METAL SULFIDES

It was shown by White (1973) initially that metal sulfides will reduce nitric oxide. Complete reduction was attained over a temperature range of 400°C to 800°C. White also successfully lowered the temperature for the reduction of nitric oxide by the addition of various chemicals, the temperature range was from 400°C to 550°C. It was also shown that NO would be reduced in the presence of O_2 and that the presence of water vapor did not appear to deter the reduction of NO. White also determined that in the reduction of NO with calcium sulfide the solid product was 80 weight per cent calcium sulfate.

Erickson (1974) determined that the best support material for CaS was Harshaw 1602 . 1/8 inch pellets. He also tested Nalco 2910-B 1/8 inch, Alcoa T-71 1/4 inch and Linde TM-0-1114 pellets. The Harshaw 1602 gave good reduction of NO without forming any H_2S or SO_2.

In testing NiS as a reducing agent Erickson found that SO_2 was produced along with the reduction of NO. In working with contaminants in the NO gas stream it was found by Erickson that H_2O produced small amounts of H_2S and decreased the reduction of NO. The presence of H_2 seemed to increase the reductions of NO by CaS but caused the formation of H_2S. Natural gas also produced H_2S but did not seem to effect the reduction of CaS. He also found that O_2 and CO_2 did not effect the reduction of CaS.

McIntyre (1974) in studying the reaction

$$CaS(s) + 4NO(g) \rightarrow CaSO_4(s) + 2N_2(g)$$

found that the global rates for the reduction of CaS on high alumina Harshaw pellets increased from .25 x 10^{-4} at 390°C to .45 x 10^{-4} moles of $CaSO_4$ formed per hour per gram of pellet at 493°C. Linde molecular sieves gave greater average rates. Rates varied between .32 x 10^{-4} and .64 x 10^{-4} moles $CaSO_4$ formed per hour per gram of pellet for three temperatures between 392° and 438°C. McIntyre also determined that at 440°C and with a flow rate ranging from .12 std. cm^3 per second to 3.8 std. cm^3 per second external film diffusion was not important for the reaction using Harshaw pellets. It was also shown by McIntyre that the rate of reaction of CaS with O_2 is greater than the rate of reaction of CaS with NO.

This work is closely related to the work of White and McIntyre. The general reactions to be studied are:

$$MeS(s) + 4NO(g) \rightarrow MeSO_4(s) + 2N_2(g)$$

$$MeS(s) + 2O_2(g) \rightarrow MeSO_4(s)$$

As can be seen for every mole of $MeSO_4$ formed the solid will increase in weight by 64 grams. Therefore, by continually weighing the solid, the rate of reaction with time can be determined.

White has summarized in Table I the enthalpy and free energy of reactions for these various sulfides with NO. McIntyre has also shown that at least one sulfide (CaS) reacts very rapidly with oxygen. Since O_2 and NO are commonly found together it is desirable to know the rates of reactions of these two compounds with the various sulfides. This will help determine if a metal sulfide can be profitably used to remove NO from flue and exhaust gases.

Table I Free Energy Changes and Heats of Reaction for the Reduction of NO employing Metal Sulfides (White, 1973)

General Reaction: $MeS + 4NO \longrightarrow MeSO_4 + 2N_2$

Metal Sulfide	Free Energy Change (Kcal/mole) 298°K	500°K	1000°K	1500°K	Heat of Reaction (Kcal/mole) 298°K
Calcium sulfide	-284.4	-264.6	-215.7	-166.8	-313.5
Cadmium sulfide	-245.3	-226.3	-179.3	-132.3	-273.3
Cobalt sulfide	-229.4	-209.5	-160.2	-110.9	-258.8
Cupric sulfide	-220.5	-199.6	-147.7	-95.8	-251.4
Cuprous sulfide	-254.7	-235.2	-187.0	-138.8	-283.4
Lead sulfide	-261.5	-241.0	-190.1	-139.2	-291.8
Molybdenum sulfide	-208.7	-190.2	-144.5	-98.8	-235.9
Mercuric sulfide	-209.9	-190.9	-143.9	-96.9	-237.9
Silver sulfide	-220.5	-200.9	-152.5	-104.1	-249.3
Tin sulfide	-220.7	-201.0	-152.0	-103.0	-249.9
Zinc sulfide	-243.8	-224.9	-178.0	-131.1	-271.8

OBJECTIVES

The objective of this research is to determine and compare the reaction rates of the formation of metal sulfates from NO and O_2 with various metal sulfides.

APPARATUS

Figure 1 is a schematic diagram of the apparatus used to study the reactions. The balance mechanism is a Cahn R-100 continuous recording electrobalance. This device is used to measure the weight of a sample continuously as it hangs suspended from one arm of the balance in the reactor. The R-100 electrobalance has a 100 gram capacity for sample weight and container. Tare capacity is 100 grams mechanically and 50 milligram with the coarse zero. The electrobalance has three electrical weight suppression ranges capable of electronically taring as little as 10 micrograms or as much as 10 grams.

The readability of the electrobalance is .5 micrograms and it has six weight ranges: 10 grams, 1 gram, 100 milligrams, 1 milligram and 100 micrograms full chart scale. An automatic range expander automatically brings the chart pen back to zero up to ten times when a weight change takes the weight outside of the recorder weight range. The precision of the instrument is $\pm 10^{-3}$ of the meter and recorder range and $\pm 10^{-6}$ of load and the accuracy is $\pm 5 \times 10^{-4}$ of mass suppression range for absolute weighings. The maximum weight change is 10 grams increase or decrease.

The system shown in Figure 1 normally operates with feed gas passing through a rotometer and entering the bottom of the reactor. Exhaust gases leave just above the reactor and are vented to hood. A helium line is run into the glass bell housing the balance mechanism to keep the bell purged of exhaust gases. During startup the valve arrangement makes it possible to pass helium through the reactor as well as over

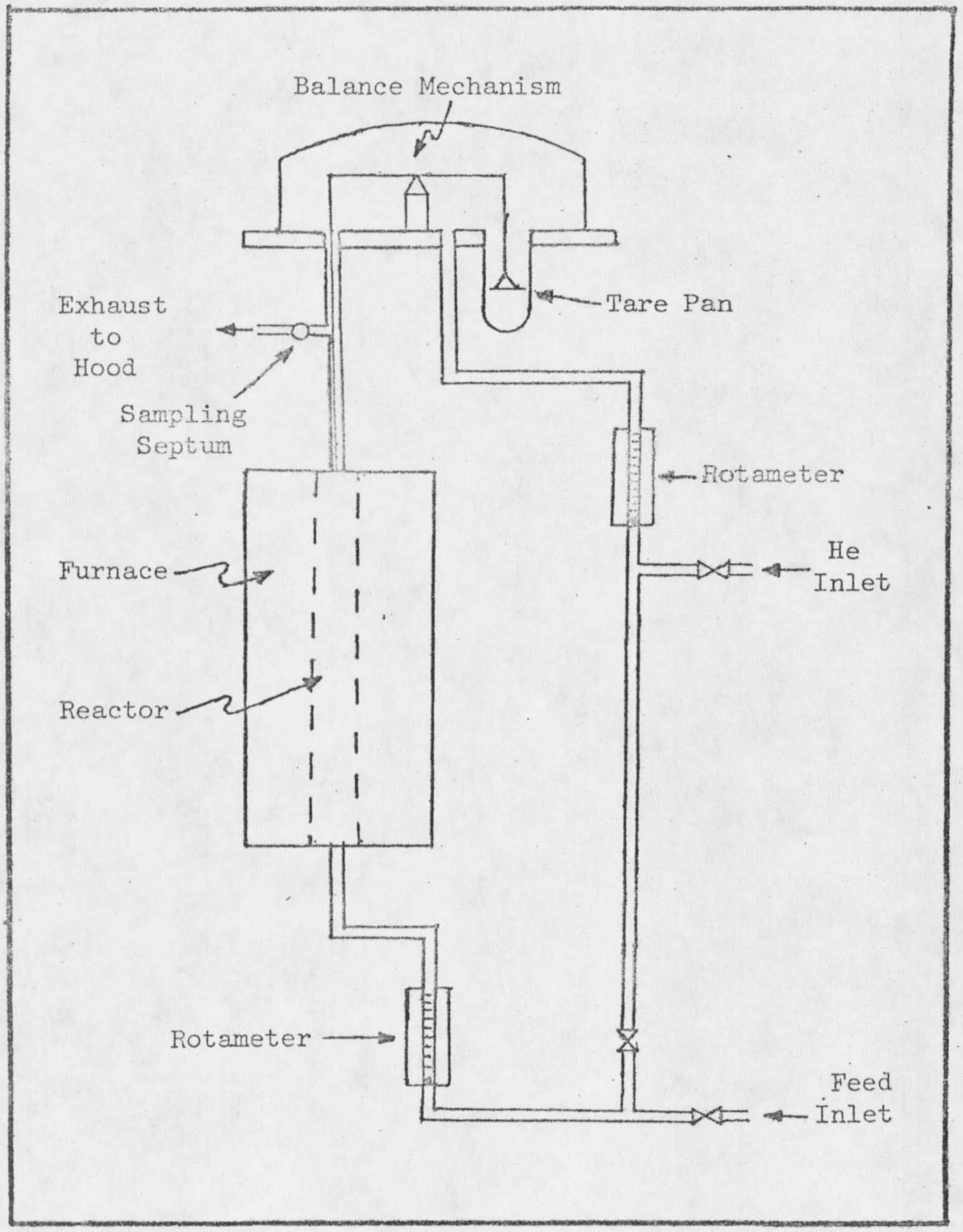

Figure 1. Flow diagram of apparatus for measuring rate of reduction of NO

the balance mechanism.

The reactor is enclosed in a Lindberg 54331 hinged tube furnace during normal operation. It can be removed to allow access to the reactor tube before and after a run. It is controlled by a Teco TC-1000 proportional temperature controller (not shown).

The reactor cross-section is shown in Figure 2. The powdered sulfide rests on a 39mm diameter circular stainless steel pan suspended by a .1mm nickel wire from the balance arm. The reactor is a 57mm diameter, 840mm long Flothru Vycor, S_j75/50, tube with a ground glass joint at the bottom and a ground glass ball joint at the top.

Attached to the bottom joint of the reactor is a glass connector, and in this connector is mounted a porous glass plate. Two thermocouples are cemented with epoxy into a hole in the side of the glass connector and extend up the Vycor tube to a point just below the support pan. One thermocouple wire is attached to a proportional controller and the other is attached to a temperature recorder. The tube is filled with 40 mesh Ottawa sand to preheat the feed gas. The gas is fed into the bottom of the reactor, passes over the powdered sulfide and is exhausted out the top.

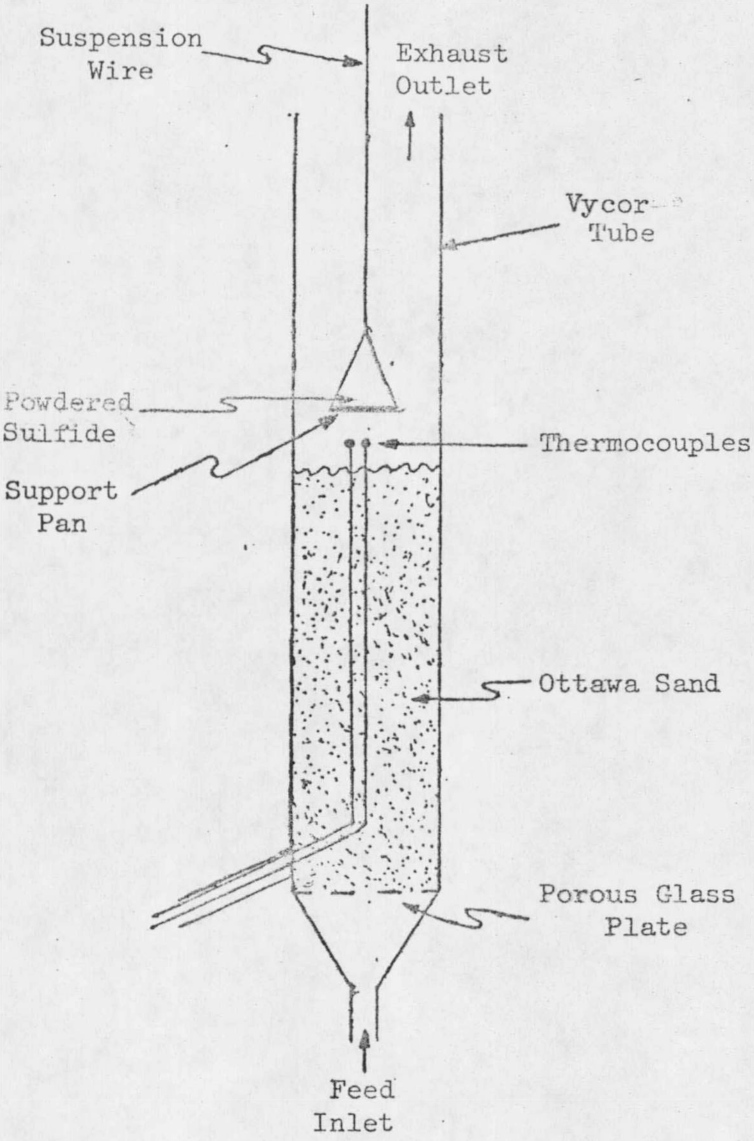

Figure 2. Reactor cross-section

PROCEDURE

For measuring the rate of reaction for a particular sulfide, the powdered sulfide was placed on the weighing pan of the Cahn electrobalance. Eight tenths of a gram of the powdered sulfide was used for each run and the powdered sulfide was evenly distributed over the weighing pan. After the weighing pan had been placed in the reactor, the reactor was heated to the operating temperature. A stream of pure helium was passed through the purge line in the bell and another stream of pure helium was passed through the reactor while heating the reactor and until no further weight change was recorded.

Next, in measuring the rate of reaction with NO, a 2.5% NO, 97.5% He mixture was fed into the reactor at an approximate rate of .2125 std. cm^3 per second. The upstream pressure was 15 psig. The reaction was then allowed to proceed for at least one hour or until it was possible to determine the rate of reaction from the recorded weight increase. This procedure was used for runs at 300°, 400° and 500°C. In determining the rate of reaction of the sulfide with oxygen, a 2.5% O_2, 97.5% He mixture was fed at a rate of approximately .2125 std. cm^3 per second into the reactor. The upstream pressure was 15 psig. This procedure was also repeated for temperatures of 300°, 400° and 500°C.

RESULTS AND DISCUSSION

Figure 3 shows an example of a typical run. The section marked "a" represents the time during which the furnace is heated and pure He is fed through the reactor. This was continued until the equipment settled down and a horizontal line was recorded. Then the reaction mixture was fed through the reactor. This is section "b" in Figure 3. This weight increase represents the formation of the metal sulfate. The reaction would eventually slow and stop. This is section "c". The time for this was different for the different sulfides and was not investigated. The rate of reaction that was calculated was from section "b" and was the initial rate of reaction. This was determined by the weight change in the first hour of reaction or sooner if possible.

The sulfides used either came in a powdered form or were powdered before using. No attempt was made to make the particle size of the different sulfides the same. The primary concern of this investigation was not to compare the reaction rates of the different sulfides, but to compare the relative rates of each sulfide with nitric oxide and O_2.

Table II is a summary of the reaction rates determined in this research. In this table the units are mg of metal sulfate formed per minute per mg of metal sulfide initially on the weighing pan. The negative signs denote competing reactions which are proceeding faster than the desired oxidation resulting in a loss of weight instead of a gain in weight. This indicates that some unknown reaction is taking place. The "d" represents temperatures at which the metal sulfide

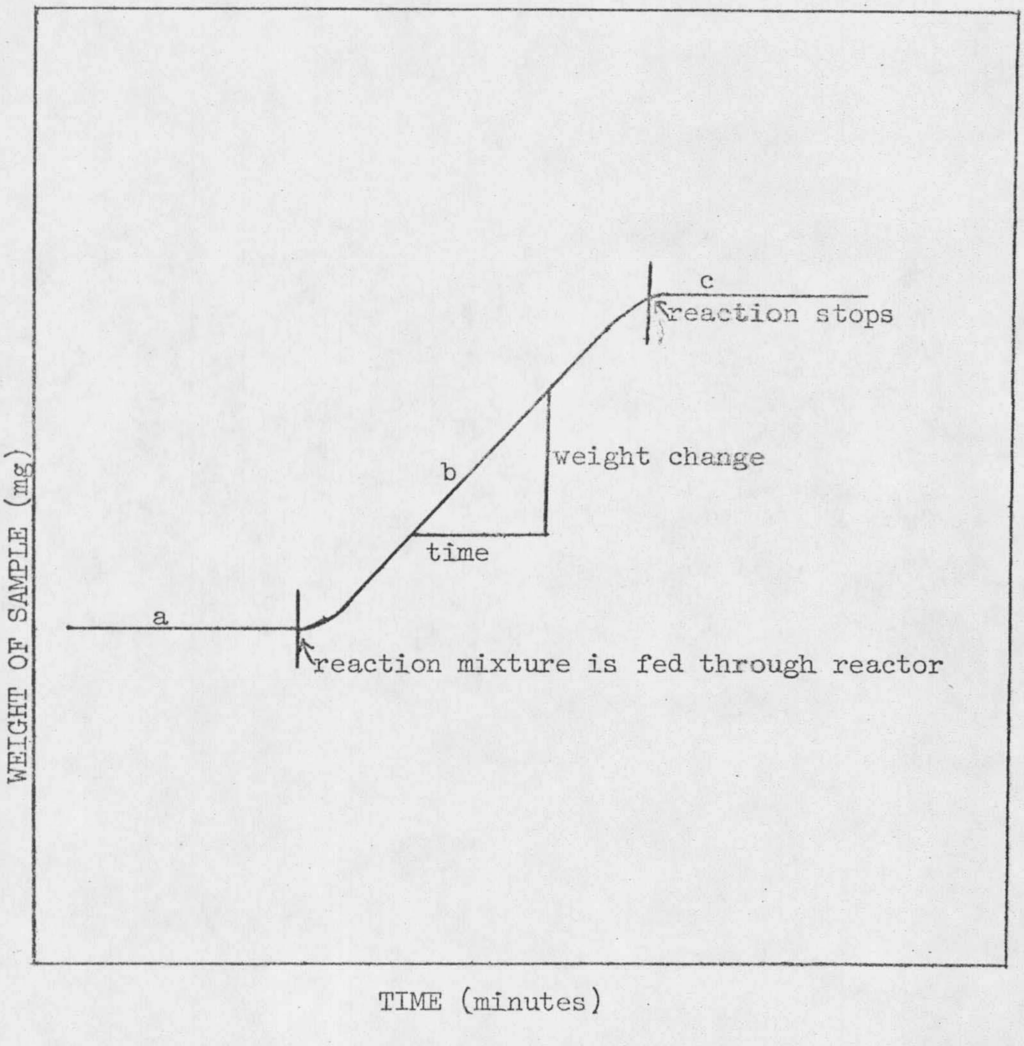

FIGURE 3. A sample recording from the Cahn R-100 continuously recording electrobalance

TABLE II. Reaction Rates of NO and O_2

with Various Metal Sulfides

$$\text{Rate} \times 10^6 \quad \frac{\text{grams of MeSO}_4\text{ formed}}{\text{minutes initial grams of MeS}}$$

	300°C		400°C		500°C	
Sulfides	NO	O_2	NO	O_2	NO	O_2
BaS	–	0.00	18.60	24.00	32.60	874.00
FeS	–	–	3.38	85.00	207.60	428.00
ZnS	4.80	5.90	0.00	14.00	0.00	25.10
SrS	7.92	7.65	9.81	18.70	13.20	27.70
CuS	d	d	d	d	d	d
CdS	3.98	15.50	14.70	22.80	9.79	116.00
Cu_2S					0.00	37.00
PbS	14.80	50.30	20.50	191.00	9.18	648.00
WS_2	0.00	–	–	–	–	–
MoS_2	0.00	–	d	d	d	d
Sulfurated Potash	+	+	+	+	d	d
Thallium Sulfide	d	d	d	d	d	d
CaS	–	0.00	5.58	17.40	10.90	86.50
MnS	d	d	d	d	d	d

decomposes, therefore, no reaction rate was determined. The positive (+) sign in Table II represents the fact that there was a weight gain. However, the exact composition of the sulfide was unknown and the rate of reaction could not be determined. Table II shows that the metal sulfides reacted faster with oxygen in every case except one. At 300°C strontium sulfide reacted slightly faster with nitric oxide than with oxygen. From the data presented in Table II, it can be seen that BaS, FeS, SrS, CdS, PbS, CaS and sulfurated potash all react both with oxygen and nitric oxide. The SrS rates for oxygen and nitric oxide are nearly the same for the various temperatures at which data was taken. The rates of reaction listed in Table II also increase with temperature with few exceptions. At 300°C most of the rates are fairly small, but at 400°C and 500°C they increase significantly.

MnS, thallium sulfide, CuS and MoS_2 decomposed at temperatures such that no rates of reaction could be determined. The fact that they were decomposing was indicated by the electrobalance. The electrobalance would continuously show a loss of weight when the reactor and the bell were being purged by a pure stream of helium.

For cuprous sulfide rates of reaction with nitric oxide and oxygen were not determined at 300°C and 400°C due to the lack of a sufficient amounts of the chemical. At 500°C cuprous sulfide does not react with NO, but it does react with oxygen. Zinc sulfide also does not react with NO at 400°C and 500°C, but does react with O_2.

It should be noted that the rate of reaction to form $PbSO_4$ from PbS and NO is slower at 500°C than at 400°C. This may be caused by a competing side reaction. A competing side reaction may also be the reason that at 300°C the reaction of FeS with O_2 and NO showed a weight loss where at temperatures greater than 400°C the sulfate producing reaction seemed to increase to such a point that a fairly rapid weight gain was recorded.

Negative weight gains or no weight gains are seen for several of the sulfides at 300°C. This seems to be the temperature at which side reactions dominate or at which no reaction takes place.

In the case of sulfurated potash the reaction was very fast as indicated by a very rapid weight gain. The exact chemical composition of the sulfurated potash is not known so it was impossible to calculate rates of reaction. Table III gives a summary of the weight gained or lost per unit time for all the sulfides tested. Table III shows that the greatest increase in weight with time was recorded for the sulfurated potash and O_2 at 300°C. The run reacting sulfurated potash with NO at 500°C was not repeated with oxygen because after the run with NO at 500°C a loss is the weight of the weighing pan of about .3 grams led to the conclusion that some type of reaction with the stainless steel pan was taking place.

The fact that in general metal sulfides react faster with oxygen than with nitric oxide may be slightly misleading. Since the objective

TABLE III. A Summary of the Weight Gained or Lost for the Various Sulfides Reacting with NO and O_2

$\text{RATE} \times 10^3 \ \frac{\text{grams of weight changed}}{\text{minute}}$

	300°C		400°C		500°C	
Sulfides	NO	O_2	NO	O_2	NO	O_2
BaS	-2.08	0	4.09	5.3	7.22	182.00
FeS	-2.27	-20.80	1.172	27.58	70.9	144.00
ZnS	1.50	1.77	0	4.53	0	7.97
SrS	2.22	2.15	2.73	5.29	3.68	7.81
CuS	d	d	d	d	d	d
CdS	.98	3.80	3.62	5.50	2.43	27.6
Cu_2S					0	8.07
PbS	2.53	8.26	3.52	31.70	1.59	108.00
WS_2	0	-3.08	-8.33	-22.90	-6.54	-25.20
MoS_2	0		d		d	
Sulfurated Potash	38.8	185.00	79.8	88.70	127.00	
Thallium Sulfide	d		d		d	
CaS	-.49	0	2.08	6.50	3.85	32.40
MnS	d		d		d	

of studying these reactions is to remove the NO from the atmosphere. If we look at the amount of NO removed compared to the amount of oxygen removed we find that for every mole of $MeSO_4$ formed from MeS and NO four moles of NO are required. When O_2 reacts only two moles are required. This says that even though the oxygen may react faster more nitric oxide maybe consumed inspite of its rate of reaction with the solid being slower.

From Table IV it can be seen that at 300°C the relative rate of reaction of NO with a given amount of ZnS or SrS in a given time is greater than the relative reaction rate of O_2. Also at 400°C the relative rate of reaction of NO with a given amount of BaS, SrS or CdS in a given time is greater than the relative rate of reaction of O_2.

To check the reproducibility of the results recorded in Tables II, III, and IV, three independent determinations of the reaction rate of CaS with oxygen were made at 500°C. These rates were determined to be .000087, .0000865, and .000081 grams $CaSO_4$ formed per minute per gram of CaS. This indicates that the results of this research are reproducible to within about 6.9%.

TABLE IV The Relative Rates at which NO and O_2 React with the Various Sulfides

$$\text{RATE} \times 10^7 \quad \frac{\text{moles of NO reacted}}{\text{minute initial grams of MeS}} \text{ or } \frac{\text{moles of } O_2 \text{ reacted}}{\text{minute initial grams of MeS}}$$

	300°C		400°C		500°C	
	NO	O_2	NO	O_2	NO	O_2
BaS	–	0	3.19	2.06	5.59	74.90
FeS	–	–	.89	11.20	54.80	56.40
ZnS	1.19	.73	0	1.73	0	3.11
SrS	1.73	.83	2.14	2.04	2.88	3.02
CdS	.76	1.49	2.82	2.19	1.88	11.10
Cu_2S					0	3.32
PbS	1.95	3.32	2.70	12.60	1.21	42.70
CaS	–	0	1.64	2.56	3.20	5.71

CONCLUSIONS

1. The reaction

$$MeS_{(s)} + 2O_{2(g)} \rightarrow MeSO_{4(s)}$$

proceeds faster than the reaction

$$MeS_{(s)} + 4NO_{(g)} \rightarrow MeSO_{4(s)} + 2N_{2(g)}$$

at 300°C, 400°C, 500°C.

2. When BaS, FeS, SrS, CdS, PbS, CaS and sulfurated potash are reacted with NO or O_2 an increase in weight is observed indicating that the sulfate is formed.

3. Strontium sulfide reacts with NO and O_2 at practically the same rate at the temperatures 300°C, 400°C, and 500°C.

4. When the rate of reaction could be determined it increased with temperature is almost every case. The exceptions being ZnS + NO, CdS + NO and PbS + NO. This indicates that side reactions were probably occuring.

5. Cupric sulfide, thallium sulfide, manganese sulfide and molybdenum disulfide should not be considered in processes which involve temperatures greater than 300°C because they decompose below 300°C.

6. Tungsten disulfide should not be considered further. When tungsten disulfide is reacted with NO or O_2 a weight loss is recorded. This indicates that competing side reactions far exceed the desired reaction.

7. Sulfurated potash reacts the fastest of all the sulfides tested with NO and O_2.

8. At 300°C the relative rate of NO reacting with a given amount of ZnS or SrS in a given time was greater than the relative reaction rate of oxygen reacting with the same amount of ZnS or SrS for the same time.

9. At 400°C the relative rate of NO reacting with a given amount of BaS, SrS, or CdS in a given time was greater than the relative reaction rate of oxygen reacting with the same amount of BaS, SrS, or CdS for the same time.

RECOMMENDATIONS

Although there has been quite a bit of work done recently concerning the reduction of nitric oxide with metal sulfides there are still some areas in which continued investigation would be benefical.

Zadick (1971) showed that $CaSO_4$ could be regenerated almost completely and quite economically to CaS. The economics and whether or not $BaSO_4$, $ZnSO_4$, $SrSO_4$ and $CdSO_4$ can be regenerated to their respective sulfides should be studied.

Sulfurated potash reacts very rapidly with NO and O_2 and should be studied more. The composition of the sulfurated potash should be determined. Unless the composition is known the rate of the reaction cannot be determined.

A detailed study should be made of the sulfides of potassium and how they react with NO and O_2.

If the regeneration of $BaSO_4$, $SrSO_4$, $ZnSO_4$ and $CdSO_4$ is economical, the use of support materials with these sulfides should be studied.

More work should be done in developing a catalyst which would increase the rate of reaction of the metal sulfides with NO, and which would reduce the rate of reaction of the metal sulfides with oxygen.

No attempt was made to determine the effect of the concentrations of the NO and O_2 in the reaction mixtures on the reaction rate. This should be studied to better understand the feasibility of using metal sulfides to eliminate nitric oxide from the atmosphere.

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Hodgson, Kent M
Rate of reaction of nitric oxide and oxygen by metal sulfides