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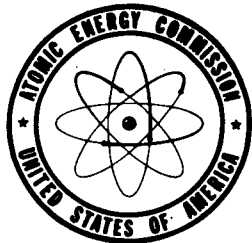
RMO-2036

## AMMONIUM SULFATE DECOMPOSITION

By
Gordon L. Dugger
J. B. Adams
Roger Bart

February 28, 1955

International Minerals and Chemical Corporation
Chicago, Illinois

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AEC, Oak Ridge, Tenn.

# AMMONIUM SULFATE DECOMPOSITION

February, 1955

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Prepared by:

*Gordon L. Dugger*

G. L. Dugger
Research Engineer

*J B Adams*

J. B. Adams
AEC Section Leader

*Roger Bart*

Roger Bart, Supervisor
Chemical Engineering Department

Approved by:

*I. Milton LeBaron*

I. Milton LeBaron
Director of Research

*Paul Manning*

Paul D. V. Manning
Vice President in
Charge of Research

RESEARCH DIVISION
INTERNATIONAL MINERALS AND CHEMICAL CORPORATION
CHICAGO, ILLINOIS

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# I. INTRODUCTION

A study of a process for the thermal decomposition of ammonium sulfate in the presence of zinc oxide for recovery of ammonia and sulfate values is covered in this report. The process was studied in both the laboratory and pilot plant. Work was based on the necessity of disposing of a large amount of by-product ammonium sulfate in a multi-product process for recovery of values from leached zone.

Work reported represents the combined efforts of the members of International Minerals & Chemical Corporation's AEC Research Section under Contract AT(49-1)-545, with the U. S. Atomic Energy Commission.

## II.   SUMMARY

A process for the recovery of ammonia and sulfate values from ammonium sulfate has been developed. It involves a two-stage reaction essentially as expressed in the following overall equations:

A.   $(NH_4)_2SO_4 + ZnO \xrightarrow[\text{Temp.}]{\text{Low}} ZnSO_4 + 2NH_3 + H_2O$

B.   $ZnSO_4 \xrightarrow[\text{Temp.}]{\text{High}} ZnO + SO_2 + 1/2\ O_2.$
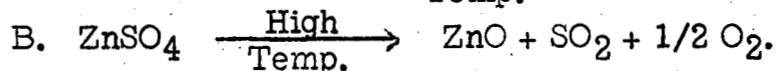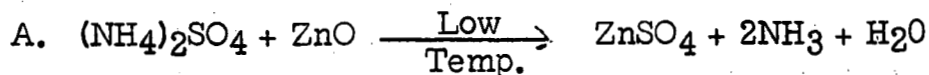
Reaction A represents the evolution of ammonia and water vapor and formation of zinc sulfate in a low temperature stage. Reaction B represents the evolution of sulfur dioxide and oxygen and formation of the zinc oxide in a high temperature stage. Zinc oxide produced is recycled for use in the low temperature stage.

Optimum conditions for these reactions, as determined in the laboratory are as follows:

1.   Intimate mixing of the solid reactants.
2.   A temperature of 400°C to 500°C in the low temperature stage.
3.   A temperature of 800°C to 1000°C in the high temperature stage.

Experimental data show that all nitrogen values are recovered as ammonia, uncontaminated by sulfur oxides, in the low temperature stage. Sulfur values given off in the high temperature stage were found to be essentially all as sulfur dioxide.

Laboratory studies of the capacity of both new and used zinc oxide-impregnated pellets, as used in the pilot plant moving bed unit, were made. New pellets showed a decrease in capacity over the first few temperature cycles, leveling off thereafter. The effect of monoammonium phosphate and ferric sulfate impurities in the ammonium sulfate on pellet capacity was not completely clarified over the seven test cycles run. Although a slight decrease may have occurred, the long range effect is not certain.

Pellets that were removed from the pilot plant moving bed unit after considerable use were found to have capacity in excess of that expected, based on zinc oxide content alone. This has not been fully explained. Though iron contamination may help in increasing the capacity, it probably has a deleterious effect on the overall process. Iron sulfate will release part of the sulfate held with it into the ammonia gases from the low temperature reaction zone of the pilot plant unit thus fouling the ammonia product and lowering sulfur dioxide recovery.

The moving bed method was chosen to carry out the solid-solid reaction between ammonium sulfate and zinc oxide on a pilot plant scale. Porous 1/4-inch alundum pellets were used as the zinc oxide carrier. A 10-inch by 30-foot reaction tower was built, the upper half serving as the ammonium sulfate decomposition zone and the lower half serving as the zinc sulfate decomposition (catalyst regeneration) zone. Regenerated catalyst was returned to the top of the tower by an air lift. Ammonia and sulfur dioxide were absorbed in spray scrubbers.

The equipment was not operated for sufficiently long periods to permit controlled studies of effects of variables under equilibrium conditions. For the few short periods in July and August, 1953, when fairly complete data were obtained, the indicated ammonia recoveries average only 45 percent. Some data from one of the better runs are presented showing the considerable time variation of feed rate, ammonia recovery, and temperature.

In spite of the many operating problems encountered, most of which were mechanical in nature, it is possible that the moving bed pilot plant could be made to work satisfactorily with further experience and a few changes. However, with the operating information now available, a reevaluation of the economics of the moving bed process against other types of equipment would probably indicate no such advantage for the moving bed as was originally visualized.

# III. EXPERIMENTAL

## A. Laboratory

### 1. General

A laboratory investigation was made of methods of decomposing ammonium sulfate for recovery of nitrogen and sulfur values separately as ammonia and sulfur dioxide. It was found that a two-stage solid-solid reaction between ammonium sulfate and zinc oxide appeared to yield the desired results. The primary reactions taking place are believed to be as follows:

(a) $ZnO + (NH_4)_2SO_4 \xrightarrow{\text{Low Temp.}} ZnSO_4 + 2NH_3 + H_2O$

(b) $ZnSO_4 \xrightarrow{\text{High Temp.}} ZnO + SO_2 + 1.2 O_2.$
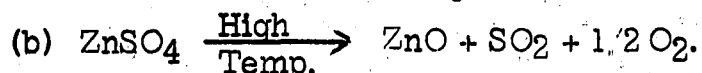
In the low temperature reaction step, zinc oxide acts on a basic acceptor for the acid sulfate radical in the thermal decomposition of ammonium sulfate, allowing the complete evolution of ammonia values as gases. Thermal decomposition of ammonium sulfate alone results in many other side reactions with loss of ammonia values as nitrogen and production of undesirable compounds. In the high temperature step, decomposition of zinc sulfate yields sulfurous oxides and zinc oxide for recycle use. Thus, the process involves cyclic use of zinc oxide to decompose ammonium sulfate into ammonia and into sulfur dioxide for manufacture of sulfuric acid.

Reactions involved in this process were investigated by the following methods:

(a) Direct roasting of mixtures of zinc oxide and ammonium sulfate for determination of time-temperature-recovery curves; material balances, for nitrogen and sulfur values by analysis of solid residues and by collection of off gases in suitable absorbents for chemical analysis.

(b) Tests of reaction mixtures by use of Chevenard thermobalance which gives a continuous curve of sample weight versus time when heated in a furnace at a constant rate of temperature rise.

(c) Tests of reaction mixtures by use of differential thermal analysis equipment which gives a continuous curve of the temperature difference between a sample and an inert standard versus the temperature of the inert standard when both are heated in a furnace at a constant rate of temperature rise.

(d) Tests of sulfur oxides evolved to determine if present as $SO_2$ or as $SO_3$.

(e) Examination of thermal data from the literature to estimate heats of reaction, free energies and equilibrium constants for various reactions. Reaction mixtures were prepared by screening, blending and ball-milling the reactants. Laboratory reagents were used for most tests. Furnace tests were ran by placing the finely powdered sample in a thin layer in a silica dish of a size appropriate for the laboratory furnaces used.

Zinc oxide was chosen as most applicable to this process from a number of other metal oxides that were tested. Iron oxides, cupric oxide, aluminum oxide, calcium oxide, and magnesium oxide were tested. Oxides of nickel, manganese, titanium, and cobalt were also considered. All were less satisfactory than zinc oxide. Calcium oxide is too basic and forms a stable sulfate. The other oxides were apparently not basic enough, allowing ammonia gases to be contaminated with sulfur gases given off in the same temperature range. Other side reactions also occurred, including sublimation of a compound thought to be ammonium sulfamate.

## 2. Ammonia Recovery

Samples of ammonium sulfate - 10 percent excess zinc oxide were fired in a muffle furnace at temperatures of 300°C, 350°C, 400°C, and 500°C for periods of 10 minutes to 90 minutes. The percent ammonia volatilization was determined by difference from the residue analysis. Results are summarized in Figure 1. Essentially complete volatilization of ammonia has occurred in 45 minutes at a furnace temperature of 400°C.

A test was run with the same mixture heated to 400°C in a tube furnace. The off gases were scrubbed with acid to recover ammonia and analysis showed that 100 percent of the nitrogen values in the original sample were recovered in the scrubber liquor as ammonia.

To show that in the temperature range where ammonia is evolved, no sulfur dioxide is given off, the residue from a number of test runs in the 300°C to 500°C range were analyzed for percent ZnO and percent $SO_4$. As shown in Figure 2, the ratio of percent $SO_4$ to percent ZnO was found to be approximately constant and equal to the same ratio in the original prepared reaction mixture. In addition, in tube furnace tests at 400°C, where off gases were scrubbed with phosphoric acid, no trace of sulfur values could be found in the scrubber liquor.

Shown in Figure 3 are Chevenard thermobalance curves for zinc sulfate and for a mixture of ammonium sulfate - 10 percent excess zinc oxide. Both curves give the characteristic two-step evolution of sulfur dioxide between 700°C and 1000°C. The reactions involved are:

(a) $3ZnSO_4 \longrightarrow ZnO \cdot 2ZnSO_4 + SO_2 + 1/2\,O_2$

(b) $ZnO \cdot 2ZnSO_4 \longrightarrow 3ZnO + 2SO_2 + O_2$

FIG. 1

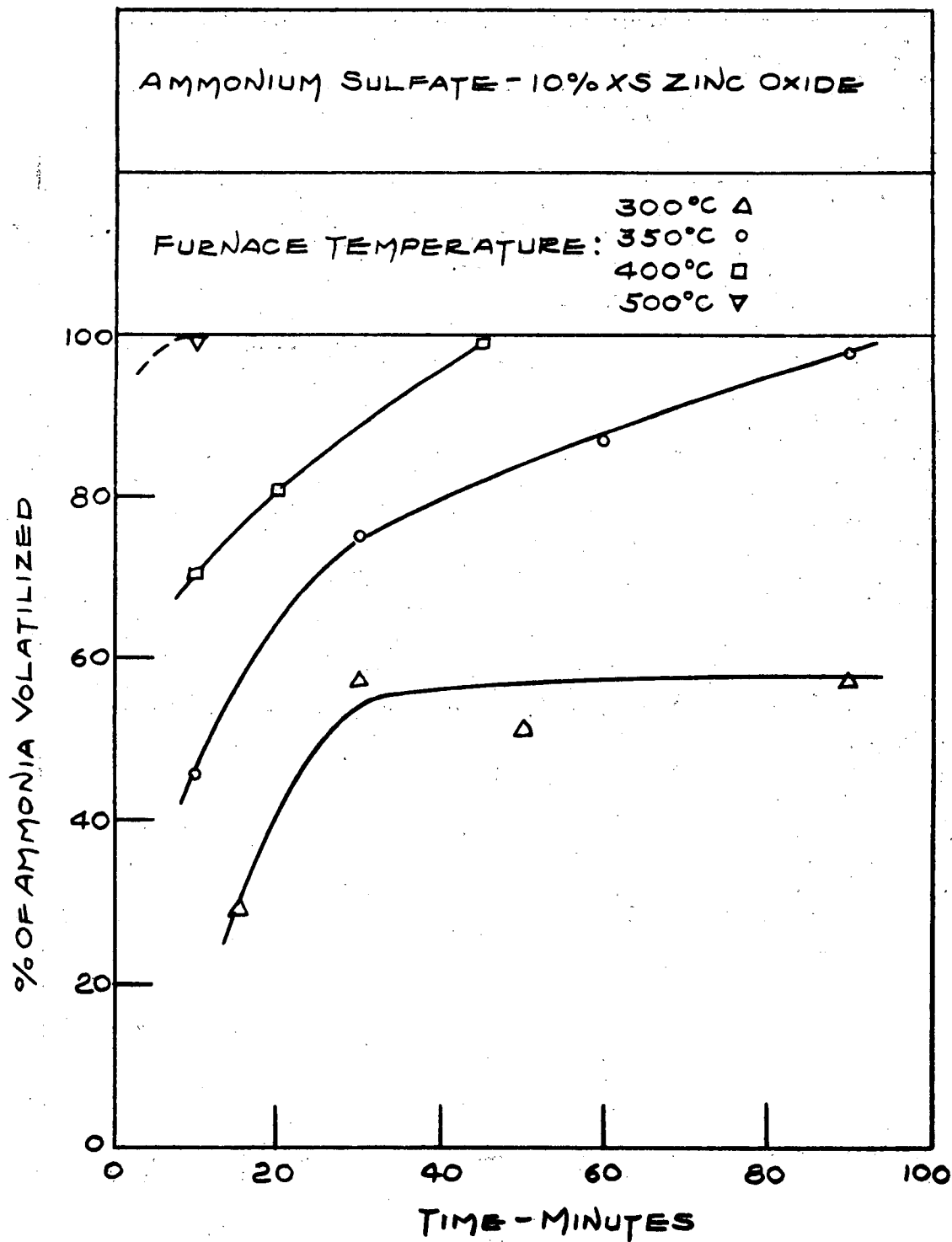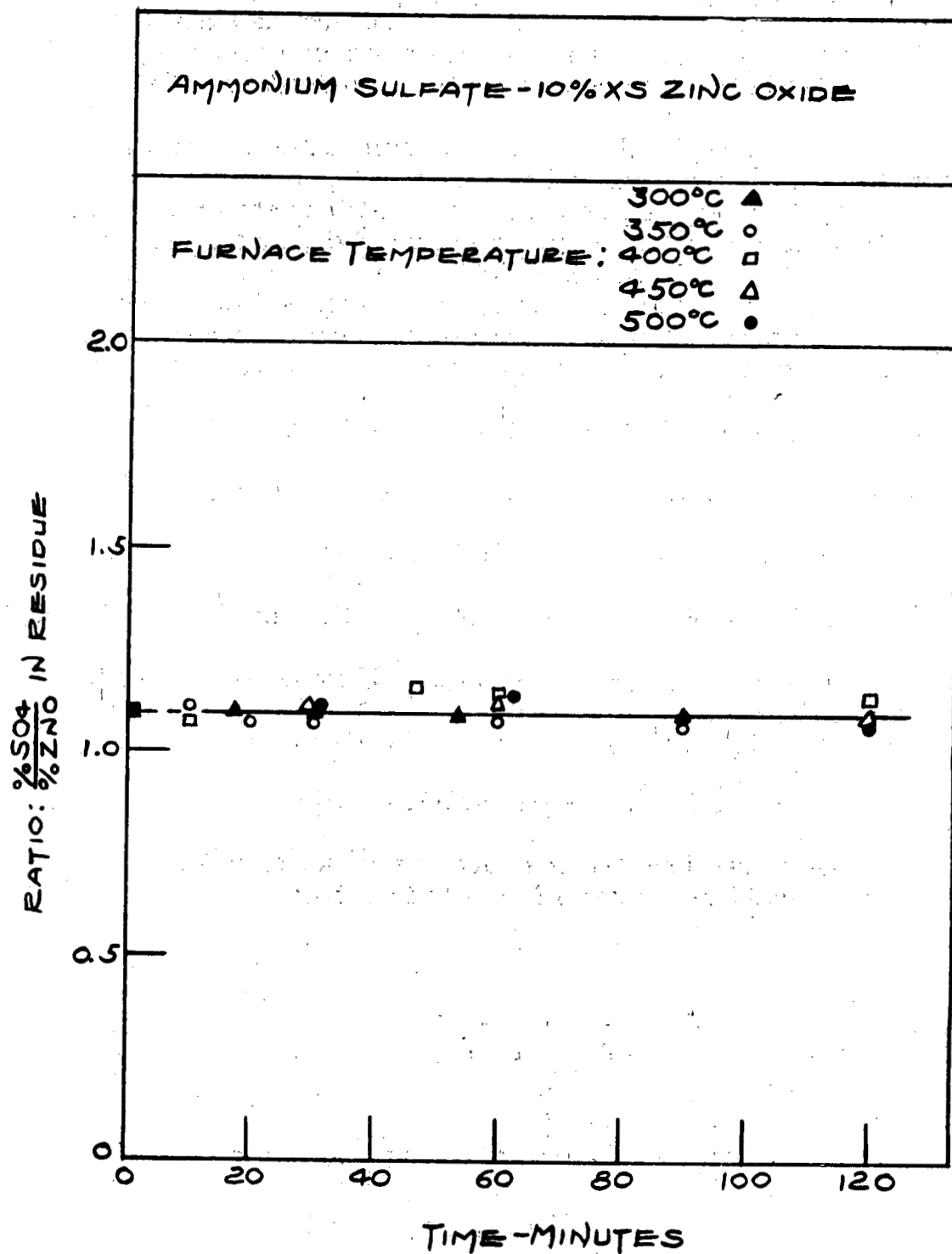VOLATILIZATION OF AMMONIA FROM AN AMMONIUM
SULFATE ZINC OXIDE REACTION MIXTURE

FIG.2

RATIO $\frac{\%\ SO_4}{\%\ ZnO}$ IN REACTION RESIDUE

AMMONIUM SULFATE - 10% XS ZINC OXIDE

FURNACE TEMPERATURE:
300°C ▲
350°C ○
400°C □
450°C △
500°C ●

RATIO: $\frac{\%\ SO_4}{\%\ ZnO}$ IN RESIDUE
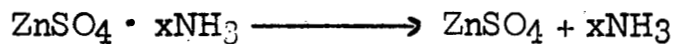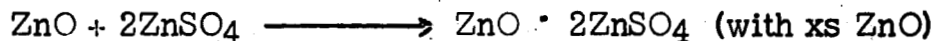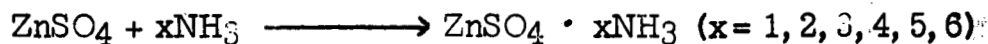
TIME-MINUTES

13

Reaction (a) indicates the formation of a basic zinc sulfate with evolution of one-third of the sulfur values; reaction (b) shows the decomposition of basic zinc sulfate. Weight loss in curve No. 2 up to 450°C represents the evolution of combined ammonia and water. The wide temperature range, 250°C, between completion of ammonia evolution and the start of sulfur dioxide evolution, where no loss in weight occurs, makes separation of the two gaseous products relatively simple.

Shown in Figure 4 and 5 are the differential thermal analysis curves for an ammonium sulfate – 10 percent excess zinc oxide mixture and for zinc sulfate. Reactions shown in both graphs above 600°C are characteristic of the decomposition of zinc sulfate. Those below 600°C are, in Figure 4, for evolution of ammonia and water, and in Figure 5 are for evolution of water. Though the overall reaction of ammonium sulfate and zinc oxide for evolution of ammonia and water is:

$$(NH_4)_2SO_4 + ZnO \longrightarrow ZnSO_4 + 2NH_3 + H_2O$$
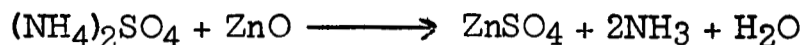
Other intermediate reactions are probably occurring, such as:

$$(NH_4)_2SO_4 \longrightarrow NH_4HSO_4 + NH_3$$

$$ZnSO_4 + xNH_3 \longrightarrow ZnSO_4 \cdot xNH_3 \quad (x = 1, 2, 3, 4, 5, 6)$$

$$ZnO + 2ZnSO_4 \longrightarrow ZnO \cdot 2ZnSO_4 \quad (with\ xs\ ZnO)$$

$$NH_4HSO_4 + ZnO \longrightarrow ZnSO_4 + NH_3 + H_2O$$

$$ZnSO_4 \cdot xNH_3 \longrightarrow ZnSO_4 + xNH_3$$

These reactions and possibly others, make differential thermal analyses curves difficult to interpret.

FIG. 3

THERMAL BALANCE CURVES

CURVE No1 ZNSO4
    100°C - 225°C EVOLUTION OF MOISTURE
    760°C - 980°C EVOLUTION OF SULFUR DIOXIDE

CURVE No.2 (NH4)2 SO4 - 10% XS ZNO
    100°C - 450°C EVOLUTION OF H2O & NH3
    710°C - 980°C EVOLUTION OF SULFUR DIOX.

CURVE No.1

CURVE No.2

WEIGHT LOSS

TEMPERATURE, °C

15

# FIG. 4

## DIFFERENTIAL THERMAL ANALYSIS CURVE



SAMPLE: $(NH_4)_2 SO_4$ -10% XS ZNO

PEAKS:
270°C, 450°C — EVOLUTION OF $NH_3$ AND $H_2O$
740°C — TRANSITION POINT FOR $ZNSO_4$
ABOVE 740°C — EVOLUTION OF SULFUR DIOXIDE

TEMPERATURE DIFFERENCE
ENDOTHERMIC ⟵ ⟶ EXOTHERMIC

FURNACE TEMPERATURE - °C

16

FIG. 5

DIFFERENTIAL THERMAL ANALYSIS CURVE

SAMPLE: ZNSO4·X H2O

PEAKS
BELOW 500°C - EVOLUTION OF HYDRATED H2O
740°C - TRANSITION POINT FOR ZNSO4
ABOVE 740°C - EVOLUTION OF SULFUR DIOXIDE

TEMPERATURE DIFFERENCE
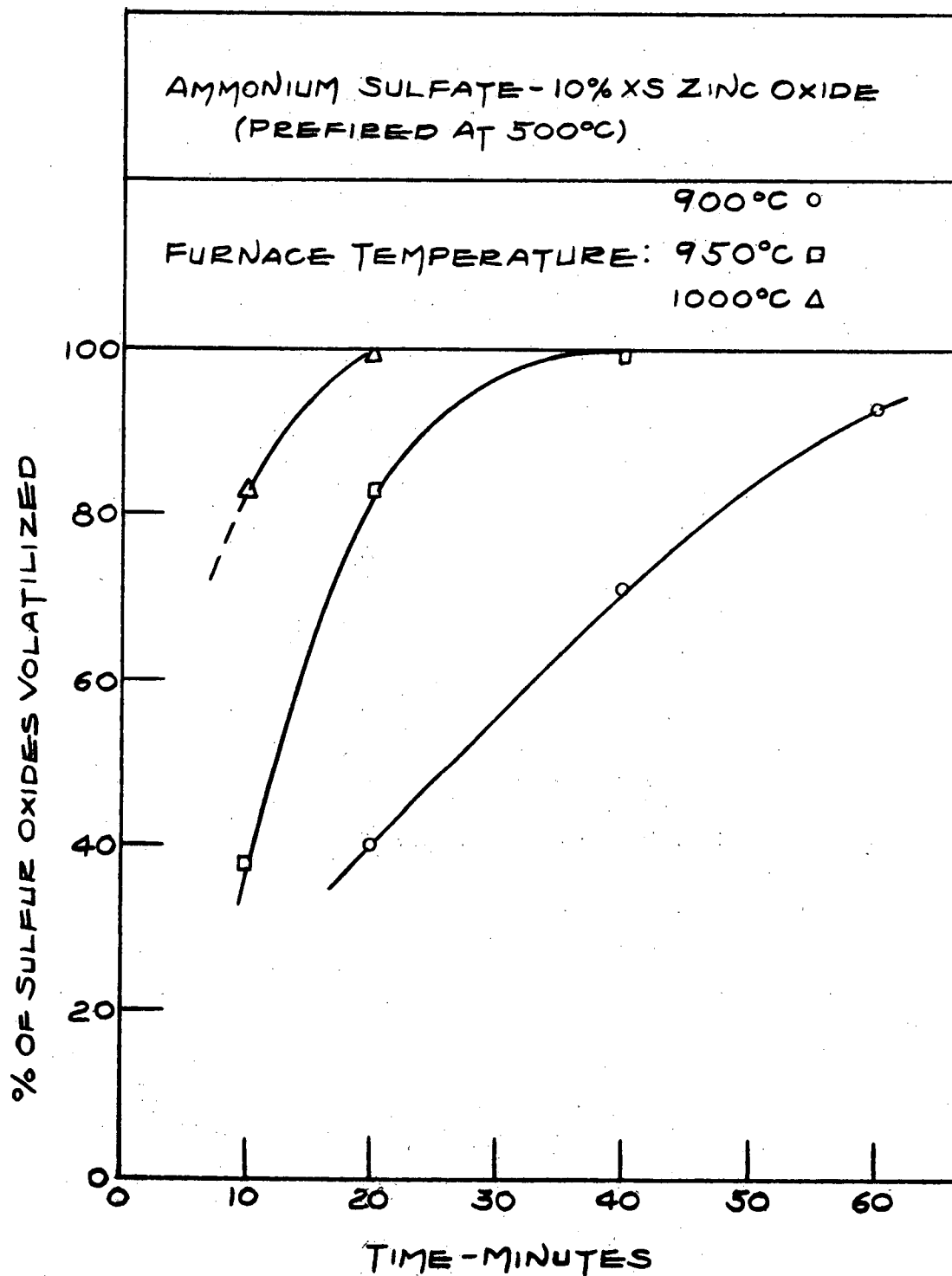EXOTHERMIC
ENDOTHERMIC

FURNACE TEMPERATURE, °C

17

### 3. Recovery of Sulfur Oxides.

A sample of ammonium sulfate - 10 percent excess zinc oxide was fired at 500°C to remove all traces of ammonia. Samples of this mixture were fired in a muffle furnace at 900°C, 950°C, and 1000°C for periods of from 10 minutes to 60 minutes. The percent of sulfate volatilized was determined by difference from analyses of the residues. Results are summarized in Figure 6. Under static conditions, 20 minutes at 1000°C or 40 minutes at 950°C, are sufficient to decompose zinc sulfate. Reaction time includes heating of sample from room temperature to furnace temperature.

A tube furnace test was run to determine at what temperature evolution of oxides of sulfur start and what species are formed. A small current of air was blown over the sample to remove gases as formed. Acidified barium chloride solution was used for detection of sulfur trioxide as barium sulfate. Acidified potassium iodate solution with starch as an indicator was used for detection of sulfur dioxide. First traces of sulfur oxides were detected near 800°C, all of which was as sulfur dioxide. No sulfur trioxide was detected at this temperature or higher temperatures.

FIG.6

VOLATILIZATION OF SULFUR DIOXIDE

AMMONIUM SULFATE - 10% XS ZINC OXIDE
(PREFIRED AT 500°C)

FURNACE TEMPERATURE: 
900°C o
950°C □
1000°C △

% OF SULFUR OXIDES VOLATILIZED

TIME - MINUTES

19

4. Capacity Tests on Catalyst Pellets.

The pilot plant unit was designed by Catalytic Construction Company as a moving bed operation. The zinc oxide reactant was impregnated on alundum catalyst pellets and was circulated in a tower through two heating zones to accomplish the two-stage reaction. When the impregnated pellets became available, capacity tests were run to check their efficiency. Both unused pellets and pellets that had been used in the pilot plant were tested.

The tests were run by weighing a number of pellets in a tared silica boat, covering them with enough ammonium sulfate to insure a large excess. The tray was fired two hours at 500°C to remove all ammonia and uncombined sulfate. Weights were obtained and a sample of pellets removed for chemical analysis. The tray and remaining pellets were then fired for two hours at 800°C to remove sulfate combined with zinc oxide on the pellets. Weights were obtained and a sample of pellets removed for chemical analysis. The tray and remaining pellets were then fired for two hours at 800°C to remove sulfate combined with zinc oxide on the pellets. Weights were obtained and a sample of pellets removed for chemical analysis. Cyclic use of the pellets in this manner was continued as required for the test. Tests of this type, with a large excess of ammonium sulfate, were run to estimate the maximum loading capacity and effect of impurities on the physical properties and chemical activity of the pellets. However, the maximum loading estimated by this method would not be reached in plant operations where an excess of pellets would be used to insure high recovery of ammonia and sulfur dioxide.
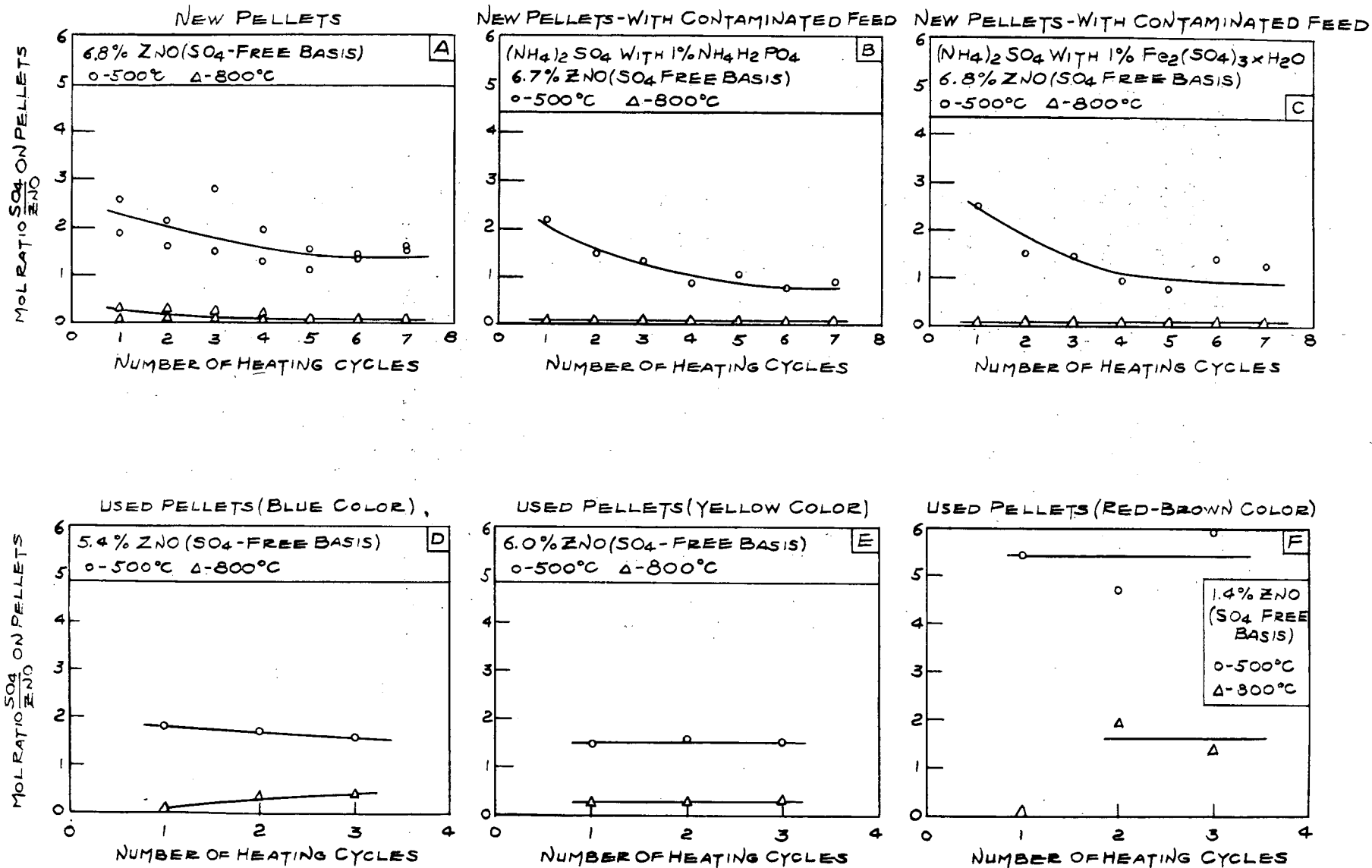
Results of cyclic loading tests on various types of pellets are shown in Figure 7. Data shown in Figures 7A, 7B, and 7C were run using unused pellets over seven test cycles. Pellets as received from Catalytic Construction Company analyzed 2.33% $SO_4$ and 8.23% ZnO, equivalent to 8.40% ZnO on an $SO_4$-free basis. During the first three cycles, some of the zinc oxide on the surface apparently dusted off since the pellet analysis averaged 6.8% ZnO on a $SO_4$-free basis over the last four cycles without any further change. On a theoretical basis, it might be expected that the maximum loading should be at a mol ratio of $SO_4$ to ZnO of one. With fresh pellets the loading appears to approach and level out close to this limit. Figure 7A shows the $SO_4$ to ZnO mol ratio on the pellets over seven heating cycles at 500°C and 800°C when using CP ammonium sulfate. This test was run in duplicate to check the reproducibility of the method. Data shown in Figures 7B and 7C were for similar tests excepting that ammonium sulfate containing one percent of either mono-ammonium phosphate or ferric sulfate was used. These impurities are the ones most likely to be encountered in actual operations. Over this limited number of cycles, a slight decrease in capacity appears to have occurred with either impurity present. This decrease is, however, probably within the error of the method. More data would be needed to clarify the effect of impurities on the process. Sulfate unloading curves at 800°C, showed relatively complete sulfate removal.

After one period of continued operation, the pilot plant unit was shut down and pellets emptied out. The pellets were examined and found to be of three general color-types, blue, yellow and red-brown. A sample of each type was hand picked and a three-cycle loading test run in the laboratory. Results are shown in Figures 7D, 7E and 7F. Blue and yellow pellets showed sulfate loadings slightly in excess of that to be expected based on their zinc oxide content, which was still adequate, at 5.4% and 6.0% ZnO. The color of both blue and yellow pellets returned to the original white during the test. Analysis of the red-brown pellets showed them to contain only 1.4% ZnO and

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the dark color indicated considerable iron contamination. The loading curve was erratic showing highly excessive loading based on zinc oxide content. Excess capacity is probably due to formation of iron sulfate. This capacity is not of value in the actual pilot plant unit since iron sulfate has been found to release part of its sulfate in the same temperature range as ammonia is evolved, thus fouling the ammonia product stream and lowering sulfur dioxide recovery. It was also observed that the red-brown pellets had somewhat less physical strength than other samples tested. It is apparent that iron contamination, both in the ammonium sulfate feed and from corrosion in the reactor equipment, should be held to a minimum to allow proper operation of the unit.

FIG. 7

CAPACITY & DEGRADATION OF ZINC OXIDE-IMPREGNATED PELLETS

New Pellets

$6.8\%$ ZNO($SO_4$-FREE BASIS)
$o-500°C$   $\triangle-800°C$   A

New Pellets-With Contaminated Feed

$(NH_4)_2 SO_4$ WITH $1\%$ $NH_4 H_2 PO_4$
$6.7\%$ ZNO($SO_4$ FREE BASIS)
$o-500°C$   $\triangle-800°C$   B

New Pellets-With Contaminated Feed

$(NH_4)_2 SO_4$ WITH $1\%$ $Fe_2(SO_4)_3 \times H_2O$
$6.8\%$ ZNO($SO_4$ FREE BASIS)
$o-500°C$   $\triangle-800°C$   C

Mol Ratio $\frac{SO_4 \text{ ON PELLETS}}{ZNO}$

NUMBER OF HEATING CYCLES

Used Pellets (Blue Color)

$5.4\%$ ZNO ($SO_4$-FREE BASIS)
$o-500°C$   $\triangle-800°C$   D

Used Pellets (Yellow Color)

$6.0\%$ ZNO($SO_4$-FREE BASIS)
$o-500°C$   $\triangle-800°C$   E

Used Pellets (Red-Brown Color)

$1.4\%$ ZNO
($SO_4$ FREE BASIS)

$o-500°C$
$\triangle-800°C$   F

Mol Ratio $\frac{SO_4 \text{ ON PELLETS}}{ZNO}$

NUMBER OF HEATING CYCLES

## B. Pilot Plant

The moving bed technique was believed to be a good way to carry out the solid-solid reaction between ammonium sulfate and zinc oxide on a pilot plant scale. It was estimated that investment and operating costs would be less with moving bed equipment than with mechanical hearth equipment, and it appeared that the moving bed method offered advantages over a fluidized bed operation. A 10-inch inside-diameter continuous reaction tower was designed for this purpose by the Catalytic Construction Company. The zinc oxide was supported on porous alundum pellets, 1/4-inch in diameter, which made up the moving solids bed. The ZnO-impregnated pellets were developed and produced by the Catalyst Manufacturing Plant of the Houdry Process Corporation at Paulsboro, New Jersey.

In the moving bed technique, granular solids move downward by gravity, remaining more or less in contact and thus forming a continuous bed moving through a reaction zone. In the present application, solid ammonium sulfate is fed into the bed as it enters the reaction zone. The ammonia and water vapor which are released at 500°C pass out of the reaction zone, and the zinc oxide on the pellets is converted to zinc sulfate. As the pellets move downward through a hotter zone (850-1000°C), the zinc sulfate is decomposed, releasing $SO_2$ and oxygen.

### 1. Equipment Description

The flow sheet for ammonium sulfate decomposition is presented in Figure 8 following. For brevity, the ZnO-impregnated alundum pellets will hereinafter be called the catalyst.

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Solid ammonium sulfate was fed into the catalyst stream as it entered the top of the tower. The best feeding arrangement found was a screw feeder, feeding directly to a short vertical line into the catalyst return leg. Air was blown past the end of the screw to partially cool it and blow the ammonium sulfate into the catalyst.

The tower was 10 inches in inside diameter and thirty feet high, fabricated in six sections. It was made of 24-inch carbon steel pipe, lined with 2-1/2 inches of insulation and 4-1/2 inches of refractory. The refractory was fabricated with circumferential grooves, notched upward at the various take-off and entry points to provide annular zones between refractory and catalyst bed for distribution of gases entering or leaving the tower. Heat was supplied by two propane burners mounted on refractory-lined 16-inch pipe. The fuel-air ratio and the gas temperature within the bed were controlled automatically. Tempering air was added to the short combustion chamber below each burner as required.

Heat for the ammonium sulfate decomposition was supplied by the catalyst, which entered the tower at 550° to 600°C. Ammonia (and water vapor) was drawn off through either of two taps near the top of the tower. The ammonia was absorbed by water in a simple spray scrubber (not packed). Most of the flue gas from the upper burner was drawn off through the next lower tap in the tower. As the pellets moved past the lower burner, they were heated to 850° to 1000°C. The $SO_2$ and oxygen evolved (and some flue gas) were drawn off through the two taps in the lower part of the tower and passed through a scrubber. The spray liquid for this scrubber was the weak ammonia solution from the ammonia scrubber. (No use was made of the ammonia and sulfur dioxide produced by the pilot plant.)

The regenerated catalyst flowed down a refractory-lined seal leg into the engager of the catalyst lift system. The engager was made from a 9-foot length of 30-inch carbon steel pipe lined with six inches of refractory. Hot compressed air entered the engager through a jet tube that was centered about 3/4 inch below the lift pipe. The catalyst was lifted to the disengager by the hot air through a 50-foot length of insulated 2-inch pipe.

The disengager was made from a 9-foot length of 48-inch carbon steel pipe lined with six inches of re-fractory. A baffle plate near the top of the disengager prevented any pellets from leaving with the air. The catalyst flowed out of the lift at relatively low velocities, dropped to the bottom of the disengager, and flowed into the tower through a carbon steel seal leg.

FIG. 8

FLOW SHEET FOR AMMONIUM SULFATE DECOMPOSITION

27
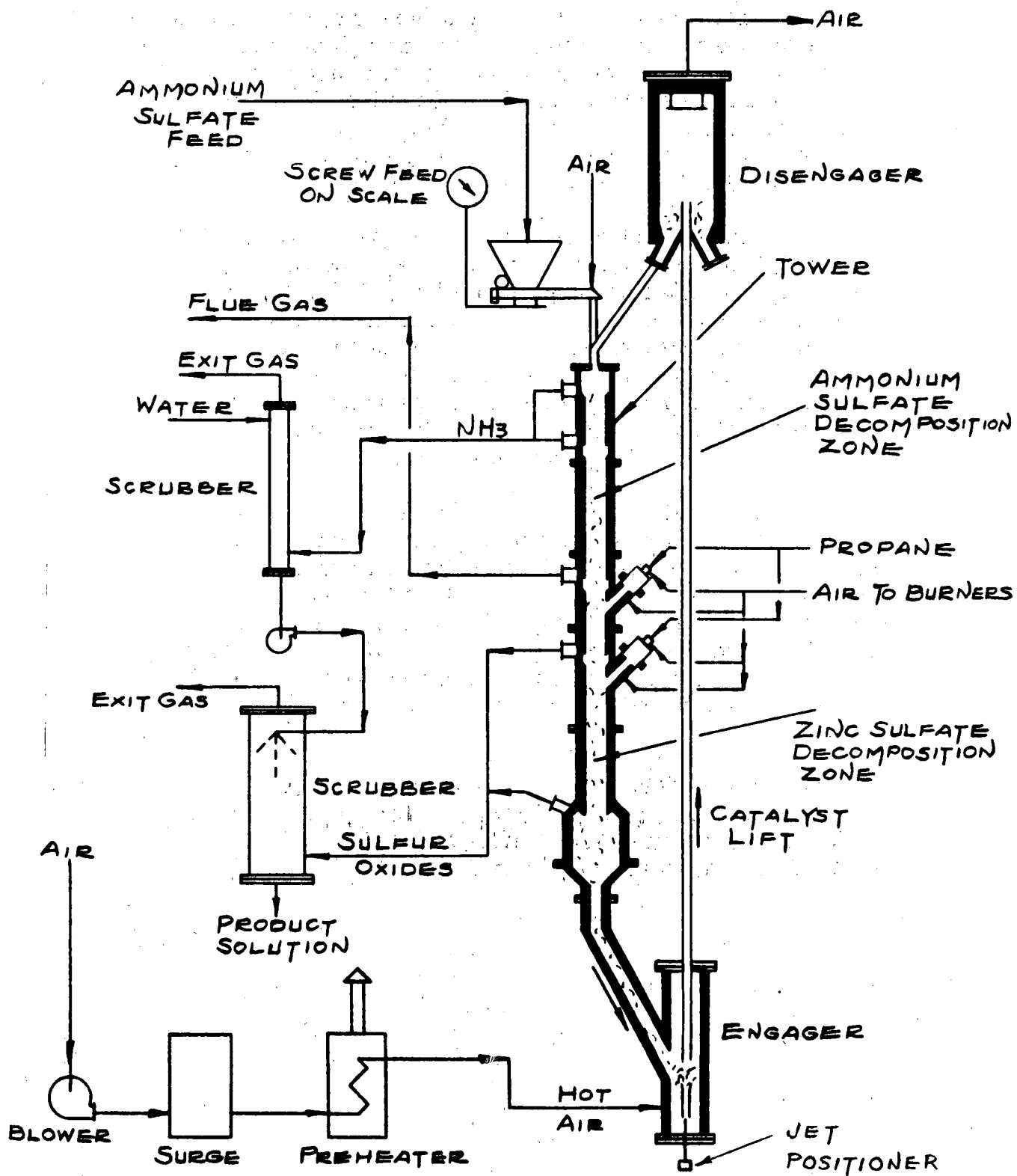
## 2. Results

The pilot plant was operated with only partial success for a few short periods before funds were cut off. Continuous operation was not maintained for long enough periods to permit studies of the effects of operating variables after equilibrium conditions were obtained. (Operating difficulties are discussed hereinafter.) The data which were obtained, particularly with regard to recoveries, were quite sketchy and unreliable.

Of the runs which were made, the most complete data were obtained for a few short runs in July and August, 1953. Instrument readings were taken hourly and ammonia recoveries were determined by measuring the absorber water rate and analyzing the resultant weak ammonia solution. For a total of 75 readings, both the arithmetic mean and the median ammonia recoveries were 45 percent. Only four of these readings showed recoveries higher than 70 percent, and they were probably erroneously high.

Ammonia and sulfur dioxide recoveries determined by laboratory personnel by sampling gases directly from the ammonia and $SO_2$ lines leaving the tower were even lower. The ammonia samples were pulled through a 40-foot sampling line and flowmeter into dilute sulfuric acid. Ammonia recoveries from these samples average 7.5%. Sulfur dioxide samples were metered through a six-foot sample line into dilute sodium hydroxide; calculated recoveries averaged 8.6 percent.

Some of the data from a 28-hour run on August 13 and 14, 1953, are presented in Figures 9 through 12. The time variation of the ammonium sulfate feed rate and the calculated ammonia recovery are shown in Figure 9. Figure 10 shows

the time variation of temperature for one thermocouple position each in the upper tower (ammonium sulfate decomposition) and lower tower (zinc sulfate decomposition). The upper tower temperature was much the steadier of the two, as might be expected.

The temperature distribution down the length of the tower is shown in Figure 11. The curve is drawn through the arithmetic mean temperatures for the 28-hour period. The vertical lines represent the data spread for each thermocouple. The curve indicates that temperature control was satisfactory in the ammonium sulfate decomposition zone (upper ten feet), but that the necessary temperatures for good zinc sulfate decomposition were not maintained continuously in the lower section. The mean temperature exceeded 800°C only in the bottom cone of the tower. It is not surprising, therefore, that $SO_2$ recoveries were low (as indicated by the sampling procedure of the laboratory group).

Figure 12 shows temperature versus pressure in the lower tower. There is some indication that the highest temperatures were obtained when the pressures dropped. However, no reason for this behavior can be advanced, because there was no apparent correlation between high temperature (11 to 17 hours after start of run) and feed rate, ammonia recovery, lift air rate, or burner input rates.

FIG. 9

TIME VARIATION OF FEED RATE
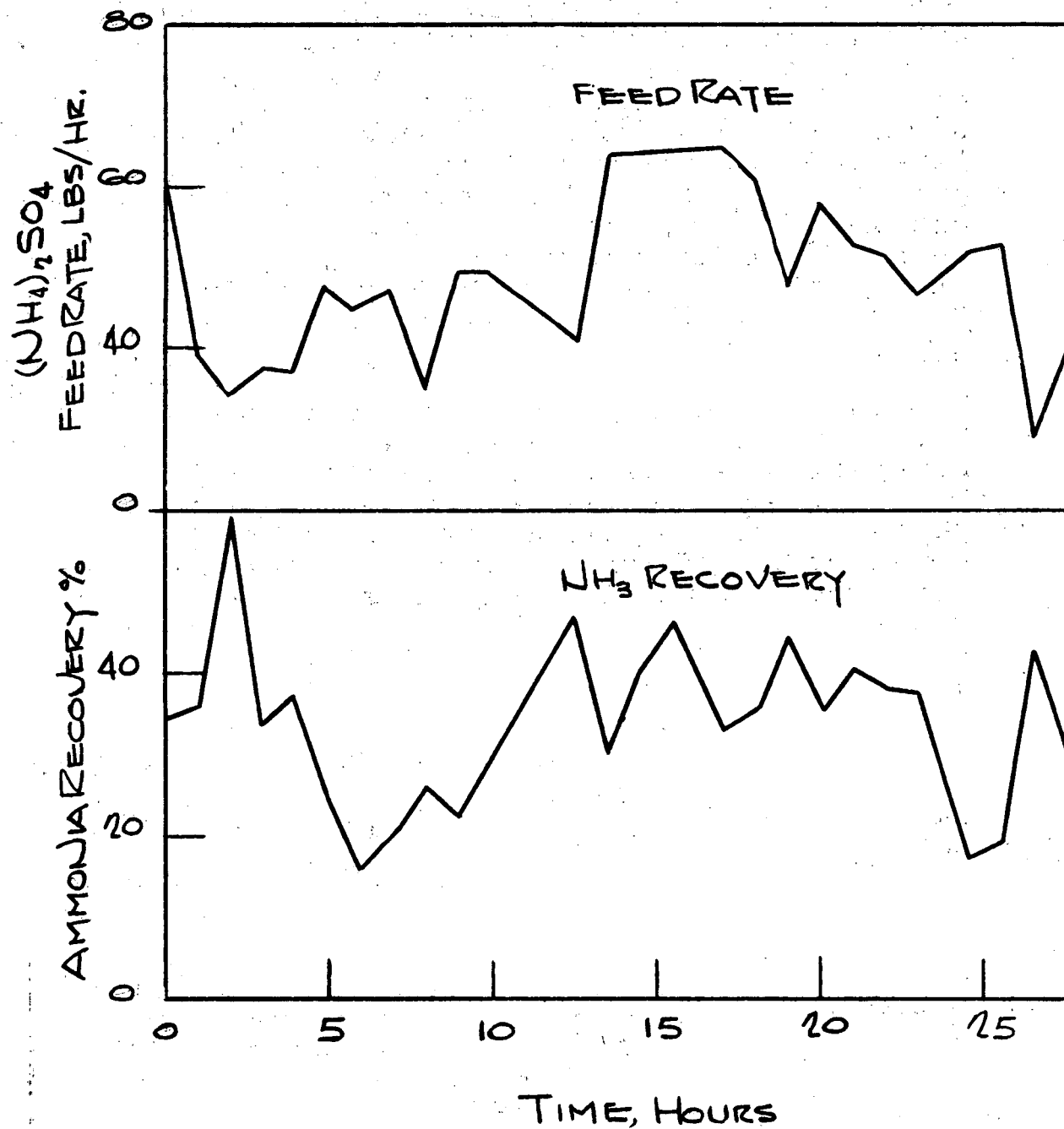AND AMMONIA RECOVERY
AUGUST 13-14, 1953

TIME, HOURS

30

# Fig. 10

## Time Variation of Tower Temperatures
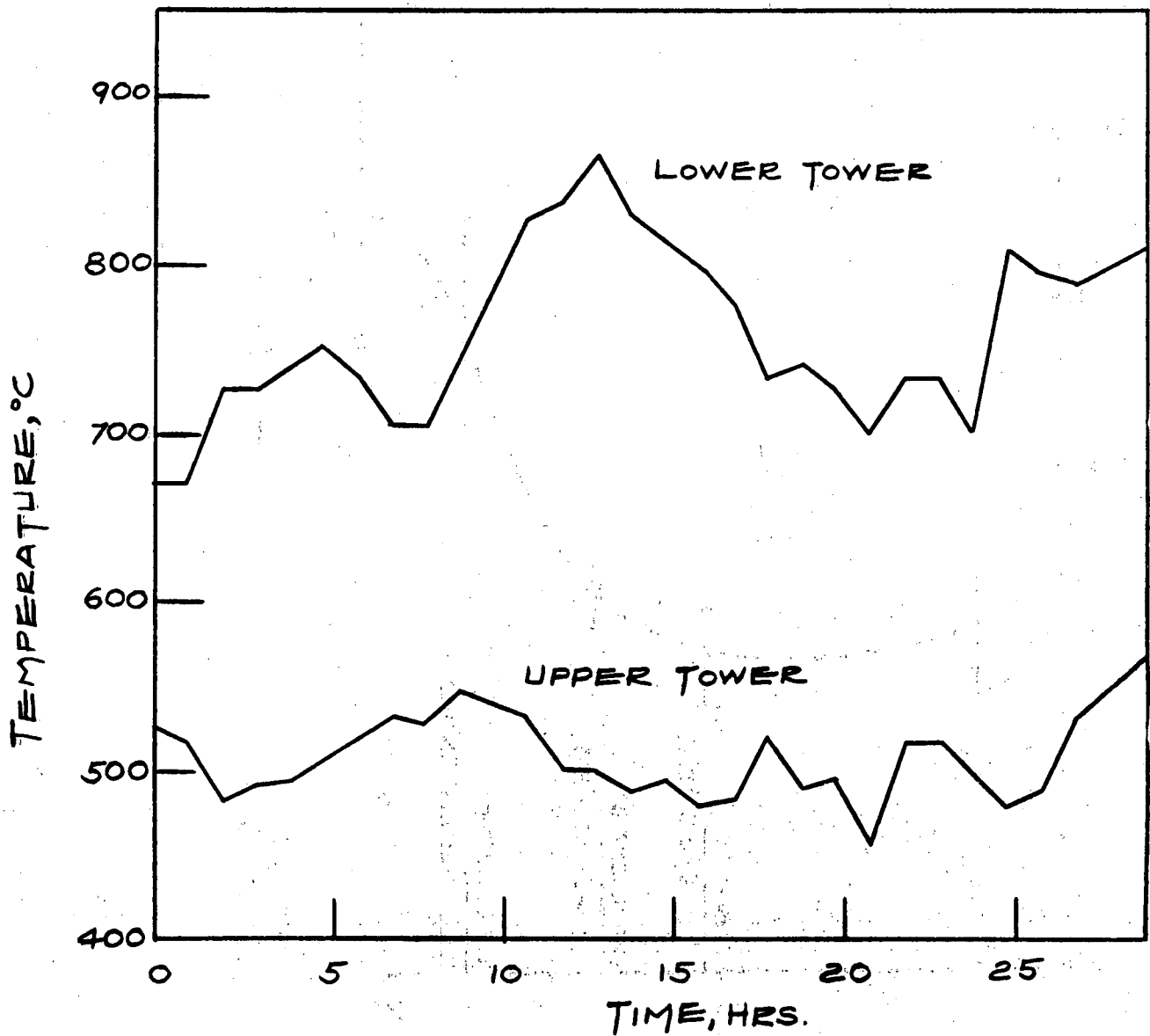
### August 13-14, 1953



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FIG. 11

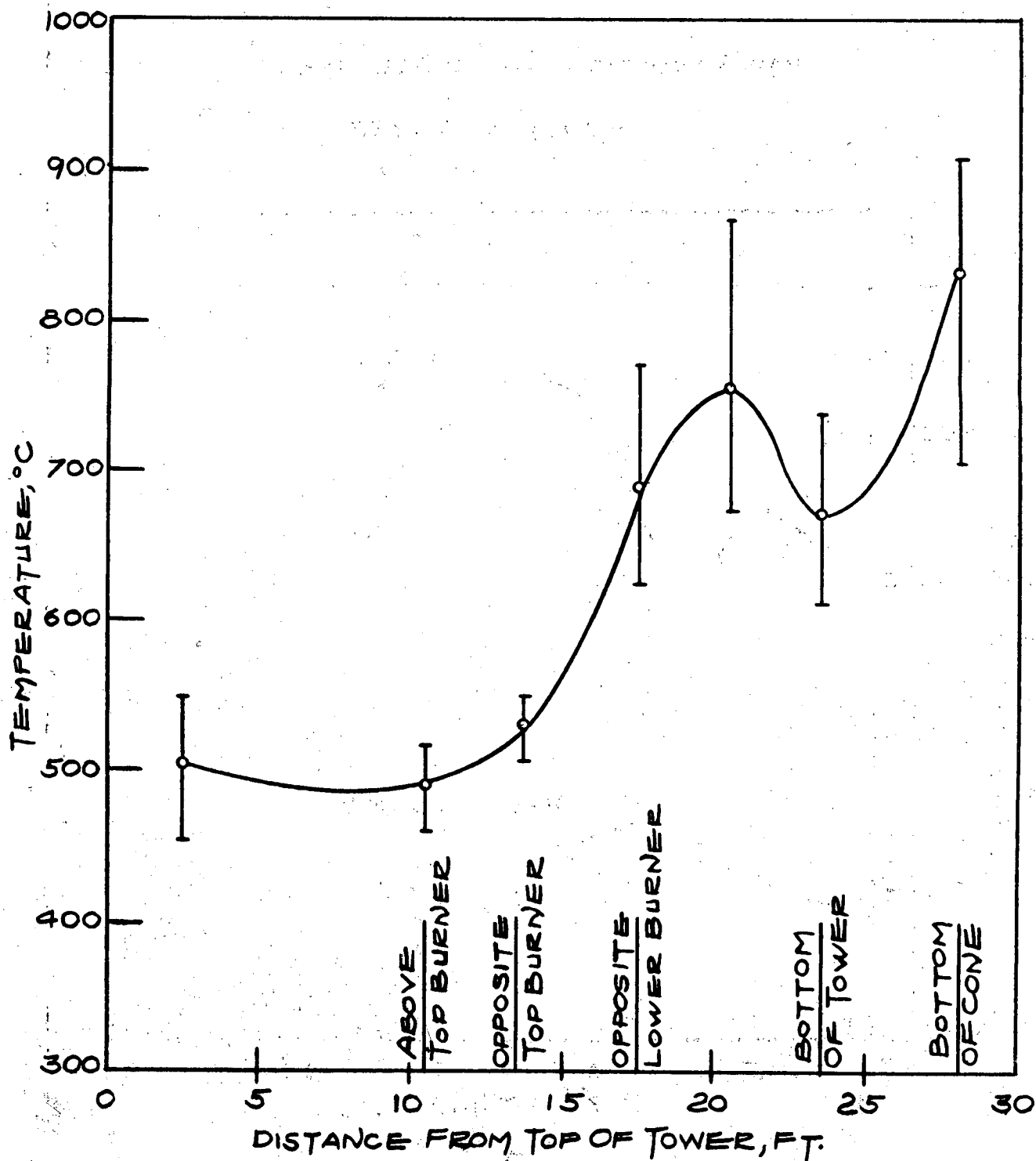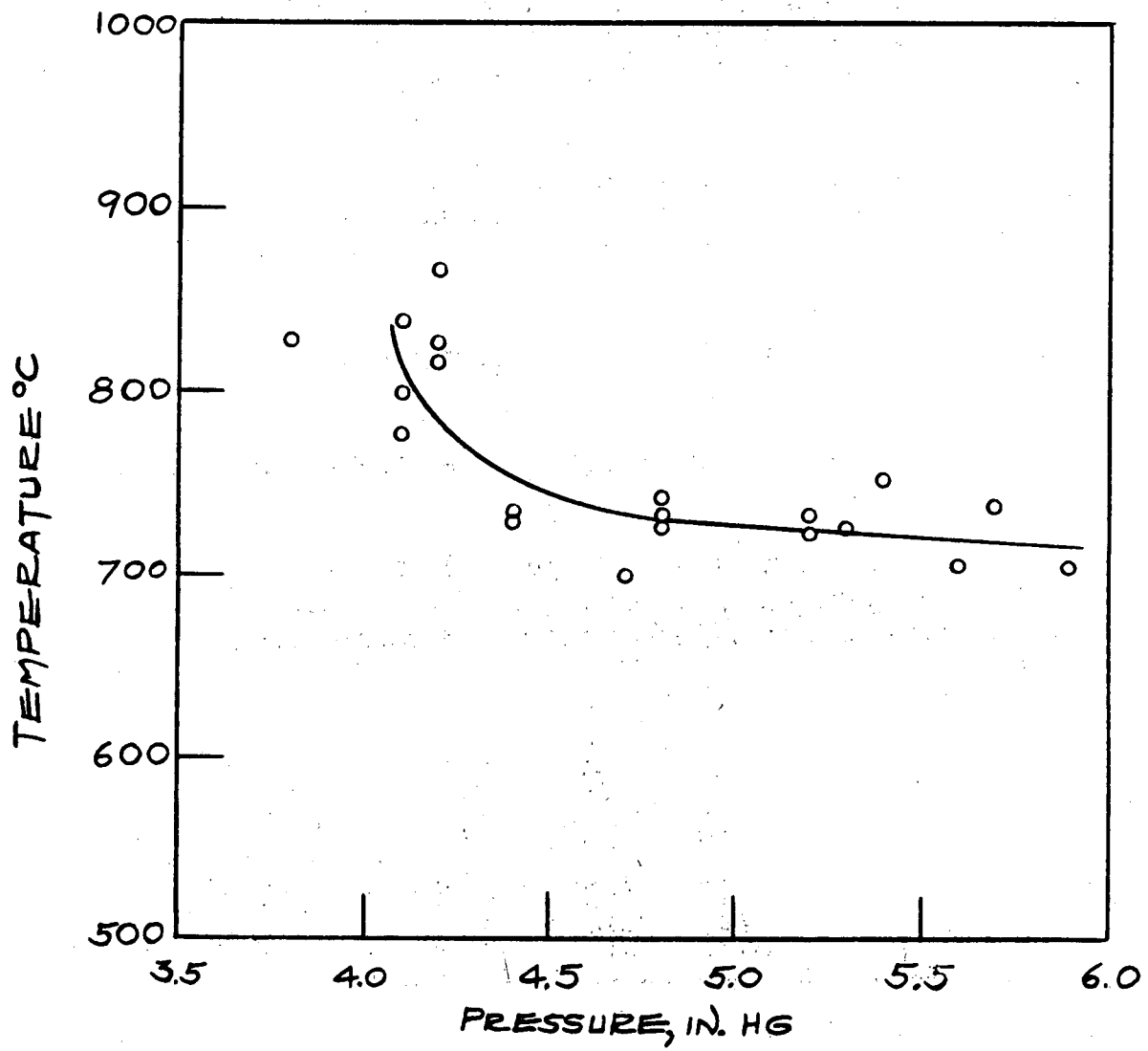TEMPERATURE DISTRIBUTION
DOWN TOWER
AUGUST 13-14, 1953

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FIG.12

TEMPERATURE VS. PRESSURE IN LOWER TOWER
AUGUST 13-14, 1953

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## 3. Discussion

The very low indicated recoveries for ammonia and sulfur dioxide may have resulted from some combination of the following:

(1) Incomplete ammonium sulfate decomposition. In the few short runs made, no studies on the effects of catalyst/feed ratio and retention time in the decomposition section were possible. If feed-catalyst contact was poor, ammonium sulfate may have been thermally decomposed, releasing nitrogen rather than ammonia.

(2) Inaccurate and irregular feed rates. Feed rates were determined by a small weight difference (25-65 lb.) in a large total weight (r 1000 lb.). Feed rates varied continually.

(3) Loss of products in the flue gas. A few samples taken by the laboratory personnel indicated that 1 to 4 percent of the ammonia was lost in the flue gas, but $SO_2$ loss was less than one percent.

(4) Low scrubbing efficiency. The scrubbers were simple, unpacked spray towers.

(5) Loss of gases or undecomposed feed through the vent of the disengager.

(6) Sampling errors in the samples collected by the laboratory personnel: (a) faulty gas flow measurements, or (b) condensation and absorption in sampling lines.

Operating problems and changes from original design fabrication and operating conditions were many and varied. A comparison of some of the design flow rates with actual rates in the July-August operations are given below.

| | Design flow rate February, 1953 | Operating flow rate July-August, 1953 |
|---|---|---|
| $(NH_4)_2SO_4$ feed | 84 lb./hr. | 25-65 lb./hr. |
| Catalyst circulation | 240 lb./hr. | 1300-1600 lb./hr. |
| $NH_3$ produced | 21.6 lb./hr. | 1-6 lb./hr. in scrubber discharge |
| $SO_2$ produced | 40.7 lb./hr. | 1-3 lb./hr. in $SO_2$ line (lab. sampling) |
| Total gas to $NH_3$ scrubber | 44 SCFM | 30-50 SCFM |
| Total gas to $SO_2$ scrubber | 97 SCFM | 150-280 SCFM |
| Flue gas | 32 SCFM | 15-50 SCFM |
| Upper burner input | 200,000 BTU/hr. | 200,000-500,000 BTU/hr. |
| Lower burner input | 400,000 BTU/hr. | 200,000-500,000 BTU/hr. |
| Lift air | 103 SCFM | 75-95 SCFM (delivered at 550°C) |

Aside from the low product recoveries, the striking points
are that the average feed rate was approximately one-half the
design rate and the catalyst circulation was six times the design
rate. The latter was largely due to the fact that when the tower
was designed, it was believed that smaller pellets (1/8 inch) with
a higher zinc oxide content would be used. The change to the
1/4 inch alundum pellets led to a greater heat requirement, part
of which was supplied by preheating the lift air. Preheating the
lift air also eliminated a thermal shock problem which resulted
when cold air was first used to lift the hot pellets.

Control of the ammonium sulfate feed rate was a problem
which was still not satisfactorily solved at the close of operations.
Early attempts to feed ammonium sulfate from ground level to the
top of the tower with an air lift failed, because this hygroscopic
solid rapidly plugged the lines. The screw feeder - actually an
Iron Fireman Coal feeder-arrangement described heretofore,
was still not satisfactory because feed rates were erratic and
the line to the tower often became plugged with melted and re-
solidified ammonium sulfate.

Another major source of difficulties was the relatively soft
and low-melting silica-alumina refractory used to line the moving
bed equipment. This refractory was eroded rapidly under the
forces of the moving bed. Moreover, when the tower discharge
became plugged, the burners caused local overheating of the
catalyst and refractory, and the catalyst pellets fused with the
refractory. Chunks of this fused mass, which resembled peanut
brittle, were later torn away by the moving bed. Accumulation
of these solids in the tower discharge would eventually cause
another stoppage. A subway grating was installed at the base of
the tower to collect fused solids, but it was burned out in a few
hours. Another grate was successfully installed in the engager to
prevent fused solids from plugging the lift. Use of high-melting
alumina refractory would eliminate these problems.

There was also some trouble caused by solids being blown into the gas take-off lines. The gas velocities required in operation were greater than anticipated, the design size for the take-offs was too small. Stainless steel screens were placed over the take-off openings to prevent solids entrainment.

In conclusion, it is believed that most of the problems met in the operation of the moving bed pilot plant were mechanical in nature and could be solved with further experience and a few changes.

# IV. APPENDIX - Thermal Calculations

Data available from the literature, as compiled by K. K. Kelley of the U.S. Bureau of Mines in Bulletin No. 476[*], was used to make thermodynamic calculations for various reactions.

(a) Evolution of Ammonia

Reaction: $(NH_4)_2SO_4 + ZnO \longrightarrow ZnSO_4 + 2NH_{3(g)} + H_2O(g)$
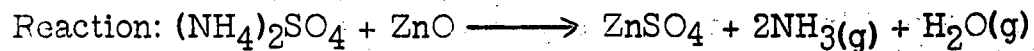
Molecular Wt. : 132. 15   81. 38      161. 45   2(17. 032)   18. 016

Heats of
 Formation:    -281. 46   -83. 5      -233. 4   2(-11. 00)   -57. 801
 (kcal/mol)25°

Heat of Reaction:      $\Delta H_R^{25°C} = +51. 759$ kcal. /mol

Entropy:
(cal/°C/mol)25°C  52. 6   10. 43      30. 6   2(45. 98)   45. 13

Entropy Change      $\Delta S^{25°C} = + 104. 66$ cal/mol./°C


[*] "Contributions to The Data on Theoretical Metallurgy:
  X. High-Temperature Heat-Content, Heat Capacity,
     and Entropy Data for Inorganic Compounds."

## Heat Capacity of Products (T in °K)

$ZnSO_4 - Cp = 17.07 + 20.80 \times 10^{-3}T$

$2NH_3(g) - Cp = 14.22 + 12.00 \times 10^{-3}T - 0.7210^5T^{-2}$

$H_2O(g) - Cp = 7.17 + 2.56 \times 10^{-3}T + 0.0810^5T^{-2}$

$\Sigma Cp$ Products $= 38.46 + 35.36 \times 10^{-3}T - 0.6610^5T^{-2}$

## Heat Capacity of Reactants (T in °K)

$(NH_4)_2SO_4 - Cp = 24.77 + 67.20 \times 10^{-3}T$

$ZnO - Cp = 11.71 + 1.22 \times 10^{-3}T - 2.18 \times 10^5T^{-2}$

$\Sigma Cp$ Reactants $= 36.48 + 68.42 \times 10^{-3}T - 2.18 \times 10^5T^{-2}$

$\Delta Cp = (\Sigma Cp$ Products $- \Sigma Cp$ Reactants$)$

$\Delta Cp = 1.98 - 33.06 \times 10^{-3}T + 1.52 \times 10^5T^{-2}$

## Heat of Reaction as a Function of Temperature

$$\Delta H = \int \Delta Cp \, dT$$

$$\Delta H = \int \left(1.98 - .03306T + \frac{152000}{T^2}\right) dT$$

$$\Delta H = 1.98T - \frac{.03306}{2}T^2 - \frac{152000}{T} + I_H$$

Where $I_H$ is a constant of integration and can be
evaluated by insertion of known values at 298.16°K(25°C).

$$I_H = \Delta H - 1.98T + 0.01653T^2 + \frac{152000}{T}$$

$$= 51759 - (1.98)(298.2) + (.01653)(298.2)^2 + \frac{152000}{298.16}$$

$$= 53149 - 590 + 1470 + 510$$

$$I_H = 53149$$

$$\Delta H = 53149 + 1.98T - 0.01653T^2 - \frac{152000}{T}$$

## Entropy Change as a Function of Temperature

$$\Delta S = \int \Delta Cp \, \frac{dT}{T}$$

$$\Delta S = \int \left(\frac{1.98}{T} - .03306 + \frac{152000}{T^3}\right) dT$$

$$\Delta S = 1.98 \ln T - 0.03306T - \frac{152000}{2T^2} + I_S$$

Where $I_S$ is a constant of integration and can be evaluated by insertion of known values at 298.16°K (25°C)

$$I_S = \Delta S - 1.98 \ln T + 0.03306T + \frac{152000}{2T^2}$$

$$I_S = 104.66 - 1.98 \ln(298.16) + (.03306)(298.16) + \frac{152000}{2(298.16)^2}$$

$$I_S = 104.66 - 11.28 \qquad + 9.86 \qquad + 0.85$$

$$I_S = 104.09$$

$$S = 104.09 + 1.98 \ln T - 0.03306T - \frac{152000}{2T^2}$$

## Free Energy Change as a Function of Temperature

$$\Delta F = \Delta H - T \Delta S$$

$$\frac{\Delta F}{T} = \frac{\Delta H}{T} - \Delta S$$

$$\frac{\Delta F}{T} = \frac{53149}{T} + 1.98 - 0.01653T - \frac{152000}{T^2}$$

$$- 104.09 + 0.03306T + \frac{152000}{2T^2} - 1.98 \ln T$$

$$\frac{\Delta F}{T} = \frac{53149}{T} - 102.11 + 0.01653T - \frac{152000}{2T^2} - 1.98 \ln T$$

Since $\Delta F° = -RT \, /nK$  (R = 1.99 cal/°C/mol)

$$/nK = - \frac{\Delta F}{RT}$$

$$K = e^{-\Delta F/RT}$$

| T°C | T°K | $\Delta F/T$ | $\Delta F$ | $-\Delta F/RT$ | K | Partial Pressure of $NH_3$ - Atm. |
|-----|-----|--------------|------------|----------------|---|-----------------------------------|
| 127 | 400 | +25.03 | 10012 | -12.58 | --- | --- |
| 177 | 450 | +10.96 | 4932 | - 5.51 | $4.04 \times 10^{-3}$ | 0.21 |
| 227 | 500 | - 0.15 | -75 | + 0.075 | 1.08 | 1.34 |
| 277 | 550 | - 9.13 | -5022 | + 4.59 | 98.5 | --- |

If K for this reaction is assumed to have the form

$$K = P_{NH_3}^{2} \cdot P_{H_2O}$$

which is approximately true at low pressure where partial pressures can be taken as equal to the activity of gases, then

$$2 \ln P_{NH_3} + \ln P_{H_2O} = -\frac{\Delta F}{RT}$$

For this reaction, approximately

$$P_{NH_3} \cong 2 P_{H_2O}$$

and $2 \ln 2P_{H_2O} + \ln P_{H_2O} = -\dfrac{\Delta F}{RT}$

or $2 \ln 2 + 2 \ln P_{H_2O} + \ln P_{H_2O} = -\Delta F/RT$

$$\ln P_{H_2O} = \frac{-\Delta F/RT - 2\ln 2}{3}$$

At 500°K

$$P_{H_2O} = e^{\left(\frac{-\Delta F/RT - 2\ln 2}{3}\right)} = e^{\left(\frac{0.075 - 1.29}{3}\right)} = e^{-0.40} = 0.67$$

$$P_{NH_3} = 2(0.67) = 1.34 \text{ atm}$$

At 450°K

$$P_{H_2O} = e^{\frac{-5.51 - 1.29}{3}} = e^{-2.27} = 0.103$$
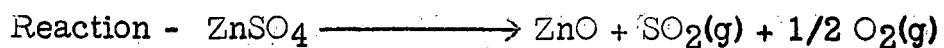
$$P_{NH_3} = 2(.103) = 0.206 \text{ atm}$$

The heat of reaction at 500°K (227°C) is calculated as

$$\Delta H = 53149 + 1.98T - .01653T^2 - \frac{152000}{T}$$

$$= 53149 + 1.98(500) - (.01653)(500)^2 - \frac{152000}{500}$$

$$= 53149 + 990 - 4133 - 304$$

$$\Delta H = 49702 \text{ cal/mol.}$$

This is equivalent to 1.35 million BTU per ton of ammonium sulfate processed

### (b) Evolution of Sulfur Dioxide

Reaction - $ZnSO_4 \longrightarrow ZnO + SO_2(g) + 1/2\ O_2(g)$

M. Wt. - 161.45          81.38   64.06    1/2(32)

$\Delta H_F^{25°C}$ - 233.4        -83.5   -70.92      --

$\Delta H_R^{25°C}$ -        $\Delta H_R^{25} = +78980$ cal/mol

$S^{25°C}$ - 30.6          10.43   59.24    1/2(49.01)

$\Delta S_R^{25°C}$ -        $\Delta S_R^{25°C} = 63.58$ cal/°C/mol

#### Heat Capacity of Products (T in °K)

ZnO -    $11.71 + 1.22 \times 10^{-3}T - 2.18 \times 10^5 T^{-2}$

$SO_2$ -    $10.38 + 2.54 \times 10^{-3}T - 1.42 \times 10^5 T^{-2}$

$1/2(O_2)$ - $3.58 + 0.50 \times 10^{-3}T - 0.20 \times 10^5 T^{-2}$

$\Sigma$ Cp Products $= 25.67 + 4.26 \times 10^{-3}T - 3.80 \times 10^5 T^{-2}$

#### Heat Capacity of Reactants (T in °K)

$ZnSO_4$ - $17.07 + 20.80 \times 10^{-3}T$

$\Delta Cp = 8.60 - 16.54 \times 10^{-3}T - 3.80 \times 10^5 T^{-2}$

#### Heat of Reaction as a Function of Temperature

$$\Delta H = \int \Delta Cp\, dT$$

$$= \int \left( \frac{8.60}{T} - .01654 - \frac{380000}{T^3} \right) dT$$

$$\Delta H = 8.60T - .00827 \, T^2 + \frac{380000}{T} + I_H$$

$$I_H = \Delta H - 8.60 \, T + .00827 \, T^2 - \frac{380000}{T}$$

$$I_H = 78980 - 8.60(298.16) + (.00827)(298.16)^2 - \frac{380000}{298.16}$$

$$I_H = 78980 - 2564 + 735 - 1274$$

$$I_H = 75877$$

$$\Delta H = 75877 + 8.60 \, T - .00827 \, T^2 + \frac{380000}{T}$$

## Entropy Change as a Function of Temperature

$$\Delta S = \int \Delta Cp \; \frac{dT}{T}$$

$$= \int \left( \frac{8.60}{T} - .01654 - \frac{380000}{T^3} \right) \, dT$$

$$\Delta S = 8.60 \ln T - .01654 T + \frac{380000}{2T^2} + I_s$$

$$I_s = \Delta S - 8.60 \ln T + .01654 T - \frac{380000}{2T^2}$$

$$I_s = 63.58 - 8.60(5.698) + (.01654)(298.16) - \frac{380000}{2(298.16)^2}$$

$$I_s = 63.58 - 49.00 + 4.93 - 2.14 = 17.37$$

$$\Delta S = 17.37 + 8.60 \ln T - 0.01654 T + \frac{380000}{2T^2}$$

## Free Energy Change as a Function of Temperature

$$\Delta F = \Delta H - T \Delta S$$

$$\frac{\Delta F}{T} = \frac{\Delta H}{T} - \Delta S$$

$$= \frac{75877}{T} + 8.60 - 0.00827T + \frac{380000}{T^2}$$
$$- 17.37 + 0.01654T - \frac{380000}{2T^2} - 8.60 \ln T$$

$$\frac{\Delta F}{T} = \frac{75877}{T} - 8.77 + .00827T + \frac{380000}{2T^2} - 8.60 \ln T$$

$$K = e^{-\Delta F/RT}$$

| T°C | T°K | $\Delta F/T$ | $\Delta F$ | $-\Delta F/RT$ | K | Partial Pressure of $SO_2$ - Atm |
|-----|-----|--------|--------|--------|---|-----------------------|
| 727 | 1000 | 16.11 | 16110 | -8.10 | $3.04 \times 10^{-4}$ | 0.0056 |
| 827 | 1100 | 9.25 | 10175 | -4.65 | $9.56 \times 10^{-3}$ | 0.057 |
| 927 | 1200 | 3.54 | 4248 | -1.78 | 0.169 | 0.38 |
| 1027 | 1300 | -1.20 | -1560 | +0.603 | 1.83 | 1.99 |

$$K \cong p_{SO_2} \cdot p_{O_2}^{1/2}$$

$$\ln p_{SO_2} + 1/2 \ln p_{O_2} = -\frac{\Delta F}{RT}$$

$$p_{SO_2} \cong 2p_{O_2}$$

$$\ln 2 + \ln p_{O_2} + 1/2 \ln p_{O_2} = -\frac{\Delta F}{RT}$$

$$\ln p_{O_2} \cong \frac{-\frac{\Delta F}{RT} - \ln 2}{1.5}$$

$$p_{O_2} \cong e^{\frac{-\frac{\Delta F}{RT} - 0.693}{1.5}}$$

The estimated heat of reaction at 1000°K (727°C) is calculated as

$$\Delta H = 75877 + 8.60T - .00827\,T^2 + \frac{380000}{T}$$

$$= 75877 + 8.60(1000) - (.00827)(1000)^2 + \frac{380000}{1000}$$

$$= 75877 + 8600 - 8270 + 380$$

$$\Delta H = 76587 \text{ cal./mol}$$

This is equivalent to 2.09 million BTU per ton of ammonium sulfate processed.