

EPA-650/2-73-012

August 1973

Environmental Protection Technology Series

**PROPERTIES OF AMMONIUM SULFATE,  
AMMONIUM BISULFATE,  
AND SULFUR DIOXIDE SOLUTIONS  
IN AMMONIA SCRUBBING PROCESSES**



Office of Research and Development  
National Environmental Research Center  
U.S. Environmental Protection Agency  
Research Triangle Park, N.C. 27711

# **PROPERTIES OF AMMONIUM SULFATE, AMMONIUM BISULFATE, AND SULFUR DIOXIDE SOLUTIONS IN AMMONIA SCRUBBING PROCESSES**

by

J.E. Boone and J.H. Turner

Research Branch  
Control Systems Laboratory  
National Environmental Research Center  
Research Triangle Park, North Carolina 27711

ROAP 21ACX, Task No. 62  
Program Element No. 1A2013

Prepared for

OFFICE OF RESEARCH AND DEVELOPMENT  
U.S. ENVIRONMENTAL PROTECTION AGENCY  
RESEARCH TRIANGLE PARK, N.C. 27711

August 1973

This report has been reviewed by the Environmental Protection Agency and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

## ABSTRACT

The report gives the results of a study that involved the collection of data that should be useful in evaluating pilot plant operation of an ammonia scrubber with an ammonium bisulfate regeneration system. The study determined: (1) the density, pH, and composition of saturated  $(\text{NH}_4)_2\text{SO}_4$  solutions at 50, 65, and 80°C; (2) the effects on density, pH, and composition of  $\text{NH}_4\text{HSO}_4$  addition to the solutions in (1); and (3) the solubility and the stripping rates of  $\text{SO}_2$  in saturated solutions of ammonium sulfate containing ammonium bisulfate at 65°C and 80°C.

The solubility of  $(\text{NH}_4)_2\text{SO}_4$  in water was determined and compared with accepted values: good agreement was found. Addition of  $\text{NH}_4\text{HSO}_4$  to the saturated solutions lowered the solubility of  $(\text{NH}_4)_2\text{SO}_4$ , decreased the pH, and increased the density. The solubility of  $\text{SO}_2$  in saturated  $(\text{NH}_4)_2\text{SO}_4$  decreased with increasing temperature and with increasing concentration of  $\text{NH}_4\text{HSO}_4$ . For the system and conditions used in this experiment,  $\text{SO}_2$  stripping rates were found to be first order with respect to concentration of  $\text{SO}_2$  except when the pH rose above 2.6. The stripping rate is dependent on temperature,  $\text{NH}_4\text{HSO}_4$  concentration, and almost certainly on sweep gas rate and agitation rate.

## CONTENTS

<u>Section</u>	<u>Page</u>
I Conclusions	1
II Recommendations	2
III Introduction	3
Background	3
Objectives	4
IV Procedure	5
Equipment	5
Materials	5
Experimental Methods	5
V Discussion	8
VI Acknowledgements	13
VII References	14
VIII Appendices	34
Appendix A - Lot Analysis of Chemicals Used	35
Appendix B - The Effects of $\text{NH}_4\text{HSO}_4$ on Density, pH, and Composition of Saturated Solutions of $(\text{NH}_4)_2\text{SO}_4$ at $80^\circ\text{C}$ , Using Procedure A	36

## FIGURES

<u>No.</u>		<u>Page</u>
1	NH <sub>3</sub> Scrubbing -- NH <sub>4</sub> HSO <sub>4</sub> Regeneration Process	15
2	Effect of NH <sub>4</sub> HSO <sub>4</sub> on Concentration of (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> in a Saturated Solution--Grams Per Liter	16
3	Effect of NH <sub>4</sub> HSO <sub>4</sub> on Concentration of (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> in a Saturated Solution--Moles Per 100 Moles H <sub>2</sub> O	17
4	Effect of NH <sub>4</sub> HSO <sub>4</sub> on pH Reading of a Saturated (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> Solution	18
5	Effect of NH <sub>4</sub> HSO <sub>4</sub> on Density of a Saturated (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> Solution	19
6	Absorption of SO <sub>2</sub> in Saturated (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> Solutions Containing NH <sub>4</sub> HSO <sub>4</sub> at 65°C	20
7	Aborsption of SO <sub>2</sub> in Saturated (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> Solutions Containing NH <sub>4</sub> HSO <sub>4</sub> at 80°C	21
8	SO <sub>2</sub> Solubility in Saturated (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> Solutions Containing NH <sub>4</sub> HSO <sub>4</sub>	22
9	Stripping Rates for SO <sub>2</sub> in Saturated (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> Solutions Containing NH <sub>4</sub> HSO <sub>4</sub> at 65°C	23
10	Stripping Rates for SO <sub>2</sub> in Saturated (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> Solutions Containing NH <sub>4</sub> HSO <sub>4</sub> at 80°C	24
11	SO <sub>2</sub> Stripping as a Function of SO <sub>2</sub> Concentration at 65°C	25
12	SO <sub>2</sub> Stripping as a Function of SO <sub>2</sub> Concentration at 80°C	26

## TABLES

<u>No.</u>		<u>Page</u>
1	Density, pH, and Composition of Saturated Ammonium Sulfate Solutions at 50, 65, and 80°C	27
2	Effects of $\text{NH}_4\text{HSO}_4$ on Density, pH, and Composition of Saturated $(\text{NH}_4)_2\text{SO}_4$ Solutions at 50, 65, and 80°C	28
3	Absorption of $\text{SO}_2$ in Saturated $(\text{NH}_4)_2\text{SO}_4$ Solutions Containing $\text{NH}_4\text{HSO}_4$ at 65°C	29
4	Absorption of $\text{SO}_2$ in Saturated $(\text{NH}_4)_2\text{SO}_4$ Solutions Containing $\text{NH}_4\text{HSO}_4$ at 80°C	30
5	Stripping Rates for $\text{SO}_2$ in a Saturated $(\text{NH}_4)_2\text{SO}_4$ Solution Containing $\text{NH}_4\text{HSO}_4$ at 65°C	31
6	Stripping Rates for $\text{SO}_2$ in a Saturated $(\text{NH}_4)_2\text{SO}_4$ Solution Containing $\text{NH}_4\text{HSO}_4$ at 80°C	32
7	Stripping Rate Constants	33

## Section I

### CONCLUSIONS

For the experimental conditions used:

1. The pH, density, and composition of saturated ammonium sulfate solutions determined at 50, 65, and 80°C are consistent with literature values.<sup>1</sup>
2. Ammonium bisulfate addition to the above solutions lowered  $(\text{NH}_4)_2\text{SO}_4$  solubility, decreased pH, increased density, and lowered  $\text{SO}_2$  solubility.
3. The stripping rate of  $\text{SO}_2$  from  $(\text{NH}_4)_2\text{SO}_4$  solutions,  $-\text{dSO}_2/\text{dt}$ , was found to be a linear function of  $\text{SO}_2$  concentration for pH values below 2.6.



## Section II

### RECOMMENDATIONS

A valuable addition to the accomplishments listed in this report would be an investigation of the effects of agitation and gas flow rate on  $\text{SO}_2$  stripping rates. It would be useful to know the effects of these variables on the first order stripping rate constant. Without these data, scale up is difficult. The usefulness of the rate data which are contained in this report is limited to qualitative work only.

Another area requiring investigation is the effect of ammonium bisulfate on the release rates from ammonium sulfite-sulfate solutions. These data would be of great benefit in studying acidifier kinetics in the ammonia scrubbing process.

### Section III

#### INTRODUCTION

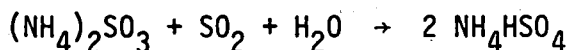
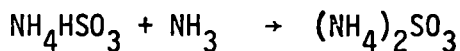
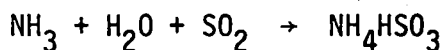
##### Background

The problem of stack gas desulfurization has received much attention in the past few years. As a result, modifications of  $\text{NH}_3$  scrubbing of  $\text{SO}_2$  with an  $\text{NH}_4\text{HSO}_4$  regeneration cycle are being investigated. The original work is described in Hixon and Miller patent No. 2,405,747. .

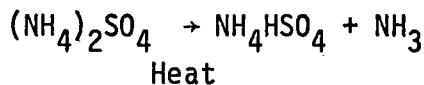
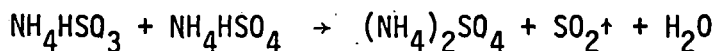
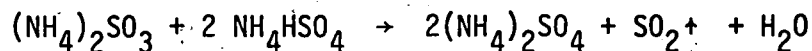
This process essentially consists of scrubbing the flue gas stream with an  $\text{NH}_3$  and  $(\text{NH}_4)\text{SO}_4$  solution. The scrubber effluent is then acidified with  $\text{NH}_4\text{HSO}_4$  to release the greater portion of  $\text{SO}_2$ , stripped of the remaining  $\text{SO}_2$  in a stripper, neutralized with  $\text{NH}_3$ , and crystallized to yield solid  $(\text{NH}_4)_2\text{SO}_4$ . The solid  $(\text{NH}_4)_2\text{SO}_4$  is thermally decomposed to yield  $\text{NH}_4\text{HSO}_4$  and  $\text{NH}_3$  which are recycled back into the process (see Figure 1).

The reactions below describe the chemistry of the system.

##### Scrubber Reactions



##### Regeneration Reactions



## Objectives

This study will be used as a basis to evaluate the results of the pilot plant operation. In particular, basic  $\text{SO}_2$  release rate data are needed to evaluate the effectiveness of the stripper and acidifier.

There were three objectives that this work was to meet in order to satisfy the need of the pilot plant project. First, measurements of the density, pH, and composition of saturated  $(\text{NH}_4)_2\text{SO}_4$  solutions were to be determined at 50, 65, and 80°C. Since the solutions throughout the process would be nearly saturated it is important to know these values. Also some of these data were available in the literature<sup>1</sup> as a check on accuracy of the measurements. Second, the effects of addition of  $\text{NH}_4\text{HSO}_4$  on density, pH, and composition of these solutions were to be studied. These effects are important in the operation of the acidifier. Finally, the solubility and the stripping rates of  $\text{SO}_2$  in saturated solutions of  $(\text{NH}_4)_2\text{SO}_4$  containing incremental amounts of  $\text{NH}_4\text{HSO}_4$  were to be studied at 65 and 80°C. These data would yield the characteristics of the release of  $\text{SO}_2$  in the acidifier and in the stripper.

## Section IV

### PROCEDURE

#### Equipment

The reaction vessels in this experiment were 500 and 1000 ml, three-necked, round-bottom flasks. Agitation was supplied by a 6.25 cm. Teflon blade on a 0.95 cm. diameter glass rod powered by a Fisher Dyna Mix. The  $\text{SO}_2$  and  $\text{N}_2$  gas flow rates were measured by Brooks Rotameters. An Instrumentation Laboratories Model 245 pH meter (with a Beckman 39183 Combination Electrode) was used to measure pH. Density was measured by weighing the sample with a Sartorius analytical balance.

#### Materials

$(\text{NH}_4)_2\text{SO}_4$  was obtained from two suppliers: Matheson, Coleman, and Bell and Fisher Scientific. The latter was used for all  $\text{SO}_2$  absorption and stripping rates; the former was used for the 50 and 65°C solubility data only. A comparison made between the salts failed to show a difference. The comparison results can be seen in Figures 2 through 5. The 65°C data in these figures were determined using each salt. Material from Matheson, Coleman, and Bell was used in procedure A and from Fisher Scientific in procedure B.  $\text{NH}_4\text{HSO}_4$  was purchased from Fisher Scientific.  $\text{N}_2$  and pure anhydrous  $\text{SO}_2$  were supplied by Matheson Gas Products. Appendix A is a lot analysis of the solid chemicals used in these experiments.

#### Experimental Methods

The properties of  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{NH}_4\text{HSO}_4$  solutions at 50 and 65°C were determined by a different method than the one used for the 80°C data. The change in procedure resulted from several factors, the most important of which was the inadequacy of the sampling technique used in the original method for temperatures above 65°C. A change in the determination of solution composition was made to increase the accuracy of readings at lower bisulfate concentrations. The change in suppliers of  $(\text{NH}_4)_2\text{SO}_4$  was due to a greater than anticipated usage of the chemical.

For simplicity, procedure A for the 50 and 65°C data will be described in detail; changes made for the 80°C data, procedure B, will follow.

For procedure A (used for 50 and 65°C data), saturated  $(\text{NH}_4)_2\text{SO}_4$  solutions were prepared by placing 400 g of the reagent grade crystals and 320 ml of deoxygenated, deionized water into a three-necked flask. The solution was heated for 2 hours at 95°C and cooled to the desired temperature by adding ice to the bath as needed. After 20 minutes a sample of the solution was withdrawn with a standard 5 ml transfer pipet and drained into a tared vessel. The sample was weighed to determine density and analyzed by a barium perchlorate titration<sup>2</sup> for  $\text{SO}_4^{2-}$  and the Kjeldal analysis<sup>3</sup> for  $\text{NH}_4$ . The pH was recorded at the time the sample was taken. The measurements made above were repeated on  $(\text{NH}_4)_2\text{SO}_4$  saturated solutions containing  $\text{NH}_4\text{HSO}_4$  which had been added incrementally. Twenty minutes was allowed for each portion of bisulfate to dissolve, and complete solution was verified by a non-changing pH response.

For procedure B (used for the 80°C data), an insulated and heated automatic pipet replaced the standard pipet. An NaOH titration using formaldehyde to tie up  $\text{NH}_4^+$  ions was used for the  $(\text{NH}_4)_2\text{SO}_4$  determination.<sup>4</sup>

Solubility of  $\text{SO}_2$  and the  $\text{SO}_2$  stripping rates were determined in procedure B by preparing 1 liter of saturated  $(\text{NH}_4)_2\text{SO}_4$  in the same manner as for procedure A. Pure  $\text{SO}_2$  was bubbled into the flask at a rate of 600  $\text{cm}^3/\text{min}$  through a fritted glass impinger immersed in the solution. Agitation was constant at 200 rpm. In order to take a liquid sample, agitation had to be stopped to allow settling of excess  $(\text{NH}_4)_2\text{SO}_4$  crystals. Thus, for this period gas flow was stopped, and the sample period was not included in the time measurement. Initially, and at each sample period, the pH, composition, and density were measured. The saturated  $\text{SO}_2$  solution produced above was then stripped with  $\text{N}_2$  gas at 1000  $\text{cm}^3/\text{min}$  and 200 rpm agitation. Samples were taken and analyzed using procedure B, and  $\text{SO}_2$  concentrations were determined iodimetrically.<sup>5</sup>

The effects of  $\text{NH}_4\text{HSO}_4$  on stripping and solubility of  $\text{SO}_2$  were determined by making the same measurements on saturated sulfate solutions containing incremental amounts of  $\text{NH}_4\text{HSO}_4$ .

A discussion of measurement accuracy follows. First the reading on the pH meter was accurate to  $\pm 0.01$  pH unit when tested against known standards. Density measurements were found to be within 0.005 g/ml of the correct value. This deviation was the maximum error found in several determinations of the density of distilled water. The accuracy of the analytical methods for composition was for the most part good. Both of the methods for sulfate and sulfite analysis were found to be within 1% accuracy. The bisulfate analyses were accurate to within 1% except when  $\text{SO}_2$  analyses were also performed. In these cases the tests were only accurate to within 10 g/l. This effect is explained in the discussion.

## Section V

### DISCUSSION

Table 1 contains the properties of saturated  $(\text{NH}_4)_2\text{SO}_4$  solutions. The composition of the solutions agrees to within 1% of the values listed in the literature. Linke and Seidell<sup>1</sup> list the solubility of  $(\text{NH}_4)_2\text{SO}_4$  in weight percent rather than grams per liter. Thus, to compare the Table 1 values with Linke and Seidell values, both the density and the concentration in Table 1 must be used. This situation indicates that the experimental values of both concentration and density are reliable. There is a question, however, as to the reliability of the pH reading. It should be pointed out that all pH's reported are instrument readings: no corrections were made for electrode processes as the correction factor was assumed negligible for the present work. For saturated solutions the pH drifted with time to lower values. Raising the temperature of the solution accelerated the pH drop. Information available from the lot analysis of the chemical indicated that the pH of a 5% solution would be in the range of 5.0 to 6.0 pH units. Freshly made saturated and 5% solutions fell into this pH range, but in both cases pH drifted to lower values according to the time-temperature history of the solution. It is thought that this drop in pH was due to thermal decomposition of  $(\text{NH}_4)_2\text{SO}_4$  to  $\text{NH}_4\text{HSO}_4$ . However, this has not been confirmed because the analysis for  $\text{NH}_4\text{HSO}_4$  is not sensitive to such low concentrations.

The effects of  $\text{NH}_4\text{HSO}_4$  addition can be noted from Table 2 and Figures 2-5. Figures 2 and 3 show that the addition of  $\text{NH}_4\text{HSO}_4$  to saturated  $(\text{NH}_4)_2\text{SO}_4$  solutions lowers the solubility of the latter salt in that solution. Figure 3 shows the data on a constant water basis. The major source of error in these data is the determination of low  $\text{NH}_4\text{HSO}_4$  concentrations. In the 50 and 65°C data, this error resulted from taking a small difference between two large titrations. The 80°C readings using procedure B should be somewhat more reliable because they were determined by direct titration. The work for 50 and 65°C had already been completed when the analysis in procedure B was initiated.

A second effect, the pH lowering due to the acid nature of  $\text{NH}_4\text{HSO}_4$ , is shown in Figure 4. The pH lowering is independent of temperature. There are no data in the available literature with which a comparison can be made. The pH reading did not suffer from the same drift as noted above in the pure saturated solutions.

A third effect of  $\text{NH}_4\text{HSO}_4$  on  $(\text{NH}_4)_2\text{SO}_4$  solutions is the increase in density of the solution with the increase of  $\text{NH}_4\text{HSO}_4$ . It appears from Figure 5 that the density of the saturated solutions is independent of temperature. One explanation of this is that the increase of salt concentration offsets the increase in volume.

Absorption rates for  $\text{SO}_2$  in  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{NH}_4\text{HSO}_4$  solutions were measured to indicate when the solutions were reaching saturation. Thus, the end points of the curves in Figures 6 and 7 show solutions which are approximately saturated in  $\text{SO}_2$ . Figure 8 shows the decrease of the solubility of  $\text{SO}_2$  in solution as the concentration of  $\text{NH}_4\text{HSO}_4$  increases. Tables 3 through 6 show that the density measurements were unaffected by the concentration of  $\text{SO}_2$ . Although there is scatter in the data, these tables indicate that concentration of  $\text{SO}_2$  has no effect on the concentration of  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{NH}_4\text{HSO}_4$ . The scatter was produced by an analytical method which required taking differences among large numbers when  $\text{SO}_2$  was present in the sample. For solutions having no  $\text{SO}_2$  (those at zero time in Tables 3 through 6), the  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{NH}_4\text{HSO}_4$  values were found from direct titrations and are more accurate. Stopping agitation and sweep gas apparently had no effect on the results. The pH did not change during the delay period, indicating no  $\text{SO}_2$  evolution, and the experimental stripping curves matched derived, first-order curves closely enough to indicate absences of  $\text{SO}_2$  evolution.

The stripping curves in Figures 9 and 10 were analyzed in greater detail than the absorption curves. The instantaneous rate was found at various points on the curves and plotted against the concentration of  $\text{SO}_2$



as shown in Figures 11 and 12. The plots, which appear linear except at low concentrations of  $\text{SO}_2$  and  $\text{NH}_4\text{HSO}_4$  (pH values above 2.6), indicate that the first order differential equation below applies:

$$\frac{-dC}{dt} = kC \quad (1)$$

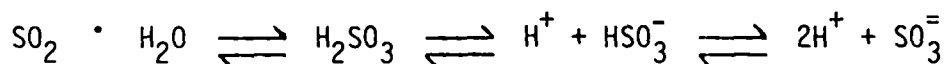
Where C is concentration of  $\text{SO}_2$ , g/l; k is the proportionality constant,  $\text{min}^{-1}$ ; and t is time, min. This equation can be integrated to find the concentration at any time which is given by

$$C = C_0 e^{-kt} \quad (2)$$

where  $C_0$  is the initial concentration of  $\text{SO}_2$ , g/l; and e is the natural logarithm base. The rate constant k, which is the slope of the lines in Figures 11 and 12, is listed in Table 7 for various concentrations of  $\text{NH}_4\text{HSO}_4$  and temperatures. Using equation 2 and obtaining the constants from Figure 8 and Table 7, curves of concentration versus time can be generated and compared with curves in Figures 9 and 10. The agreement is good for all portions of the curve where equation 1 was valid or for portions below a pH of 2.6.

Equation 2 cannot be used in the general case because the dependency of k on temperature,  $\text{NH}_4\text{HSO}_4$  concentration, sweep gas rate, and agitation is not known.

The deviation in first order behavior above a 2.6 pH is not fully understood. One possible explanation of this phenomenon is that the dissolved  $\text{SO}_2$  exists in several forms as described by the following:



According to this hypothesis the mass transfer of  $\text{SO}_2$  from the liquid phase to the gas phase is proportional to the concentration of  $\text{SO}_2 + \text{H}_2\text{O}$ , the driving force. At low pH readings: the  $\text{H}^+$  concentration is high,

the equilibrium is shifted to the left, and the  $\text{SO}_2$  present is almost exclusively in the hydrated form. Accordingly, the concentration of total  $\text{SO}_2$  which is determined analytically is an accurate measure of the true driving force. However, at higher pH values: the  $\text{H}^+$  concentration is lower, the equilibrium is shifted to the right, and the  $\text{SO}_2$  present is distributed among the several forms. In this case the total  $\text{SO}_2$  which is measured analytically is larger than the true driving force, the  $\text{SO}_2 \cdot \text{H}_2\text{O}$ . It is postulated that if only the  $\text{SO}_2 \cdot \text{H}_2\text{O}$  were measured at any time the first order behavior would be observed over the whole pH range.

## Section VI

### ACKNOWLEDGEMENTS

Assistance is gratefully acknowledge to L. I. Griffin for the original concept of this work, to J. H. Abbott for providing much helpful criticism and analysis, and to R. Grote for assistance with laboratory requirements.

## Section VII

### REFERENCES

1. Linke, William F. and A. Seidell. Solubilities of Inorganic and Metal-Organic Compounds, Volume II. Washington, D. C., American Chemical Society, 1965.
2. Fritz, J. S. and S. S. Yamamura. Rapid Microtitration of Sulfate. Anal. Chem. 27, 9:1461-1464, September 1955.
3. Van Peursem, R. L. and H. C. Imes. Elementary Quantitative Analysis. New York, McGraw Hill, 1953. p. 267-269.
4. Official and Tentative Methods of Analysis of the Association of Official Agricultural Chemists, 8th edition. AOAC, 1955. p. 13.
5. Laitinen, H. A. Chemical Analysis. New York, McGraw Hill, 1960. p. 394, 395, 400, 401 and 410.

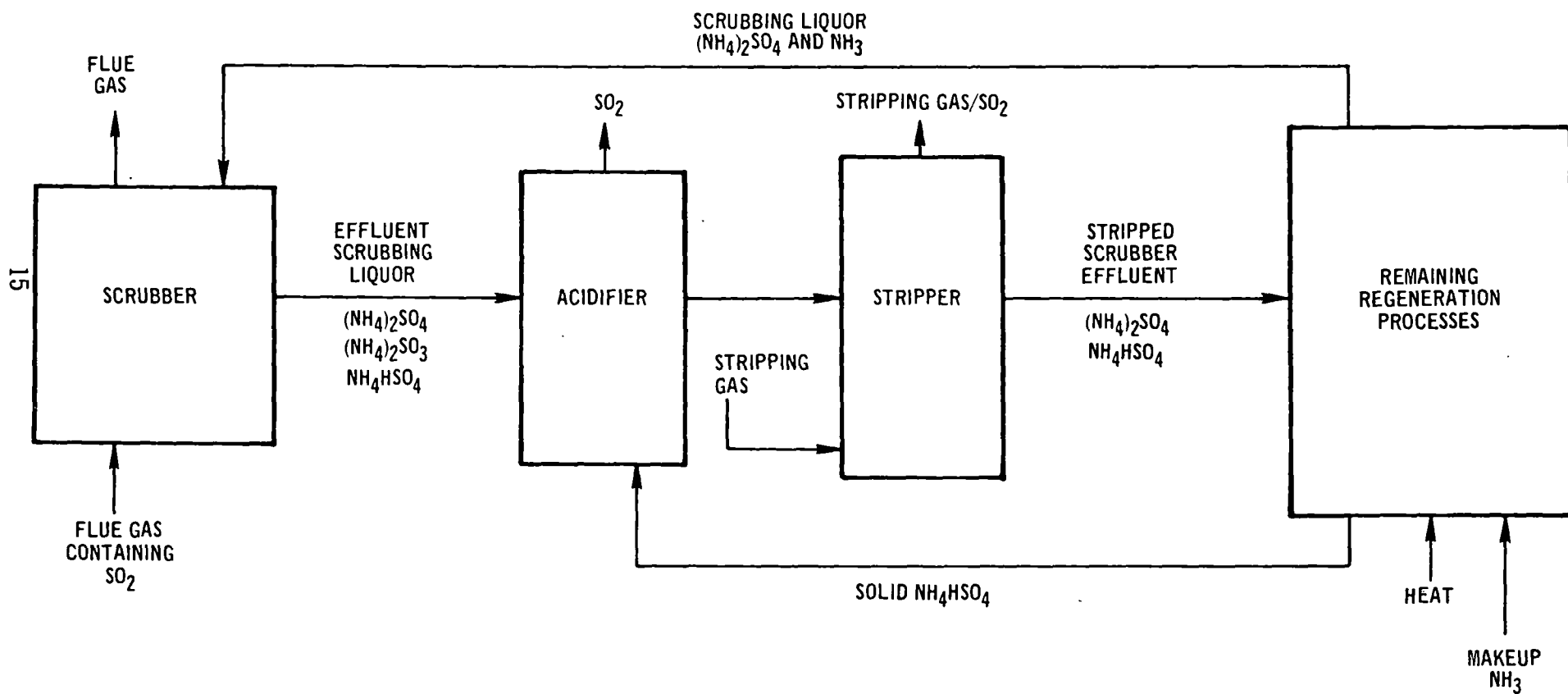


Figure 1. Ammonia scrubbing--ammonia bisulfate regeneration process.

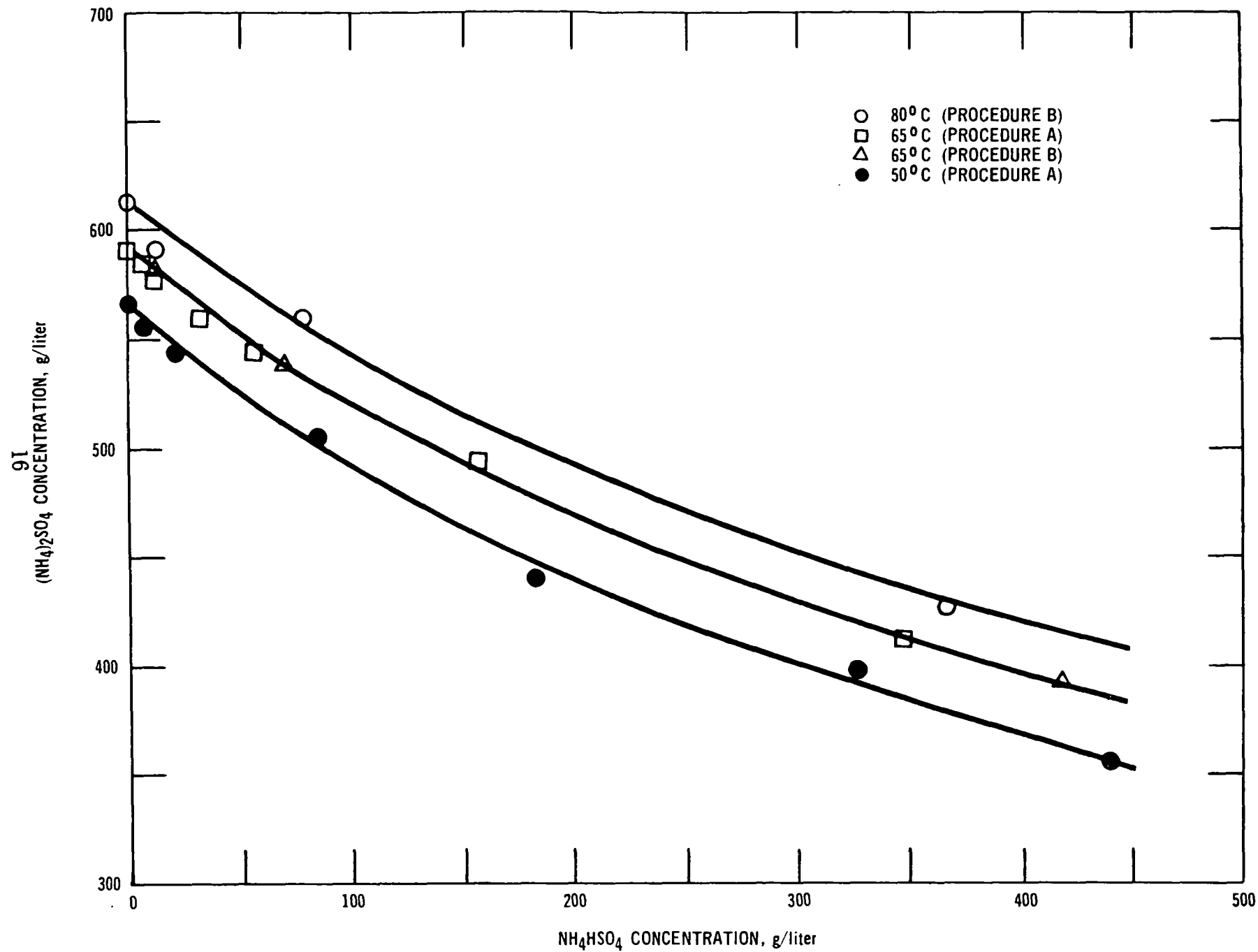


Figure 2. Effect of  $\text{NH}_4\text{HSO}_4$  on concentration of  $(\text{NH}_4)_2\text{SO}_4$  in a saturated solution.

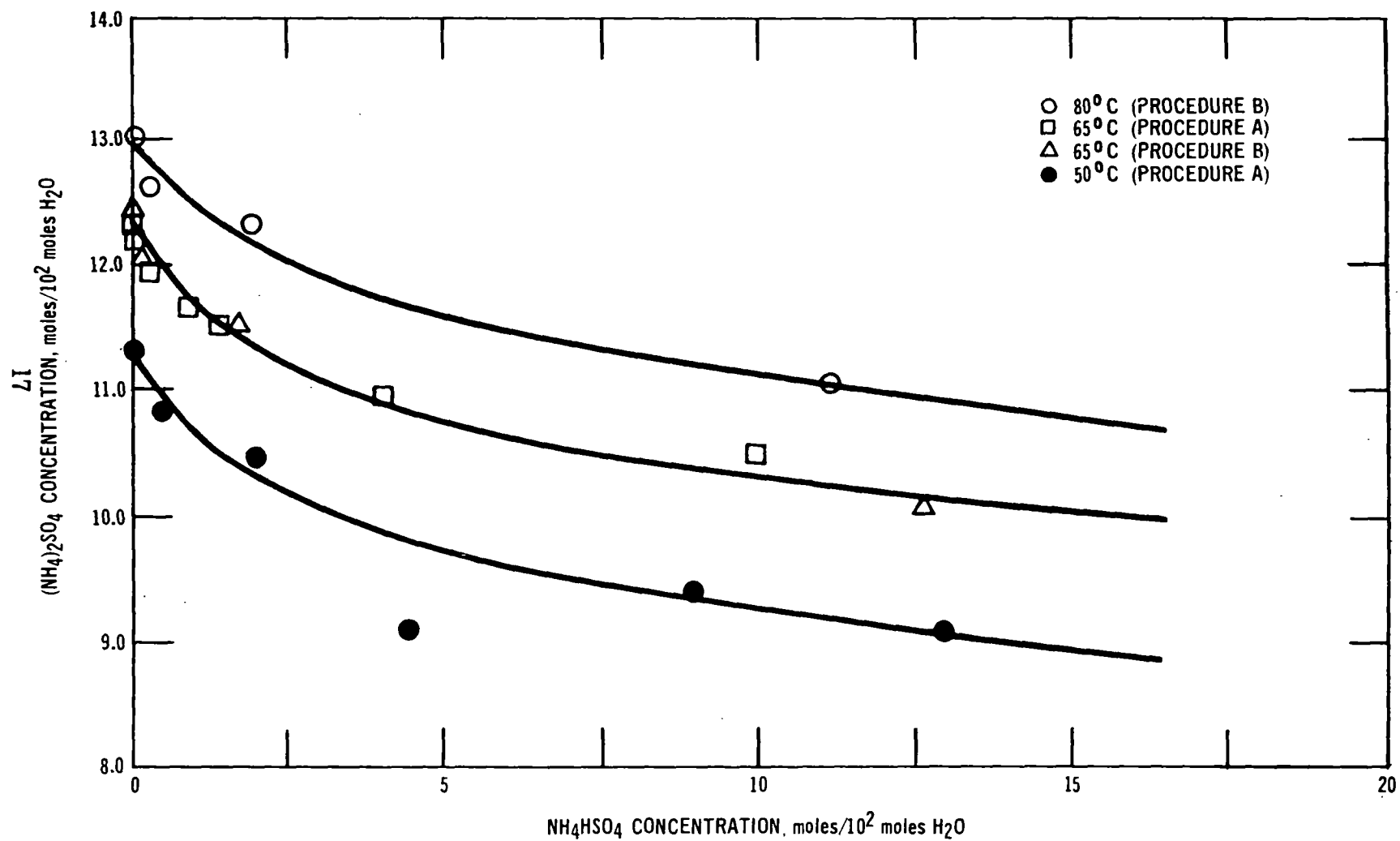


Figure 3. Effect of NH<sub>4</sub>HSO<sub>4</sub> on concentration of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> in a saturated solution.

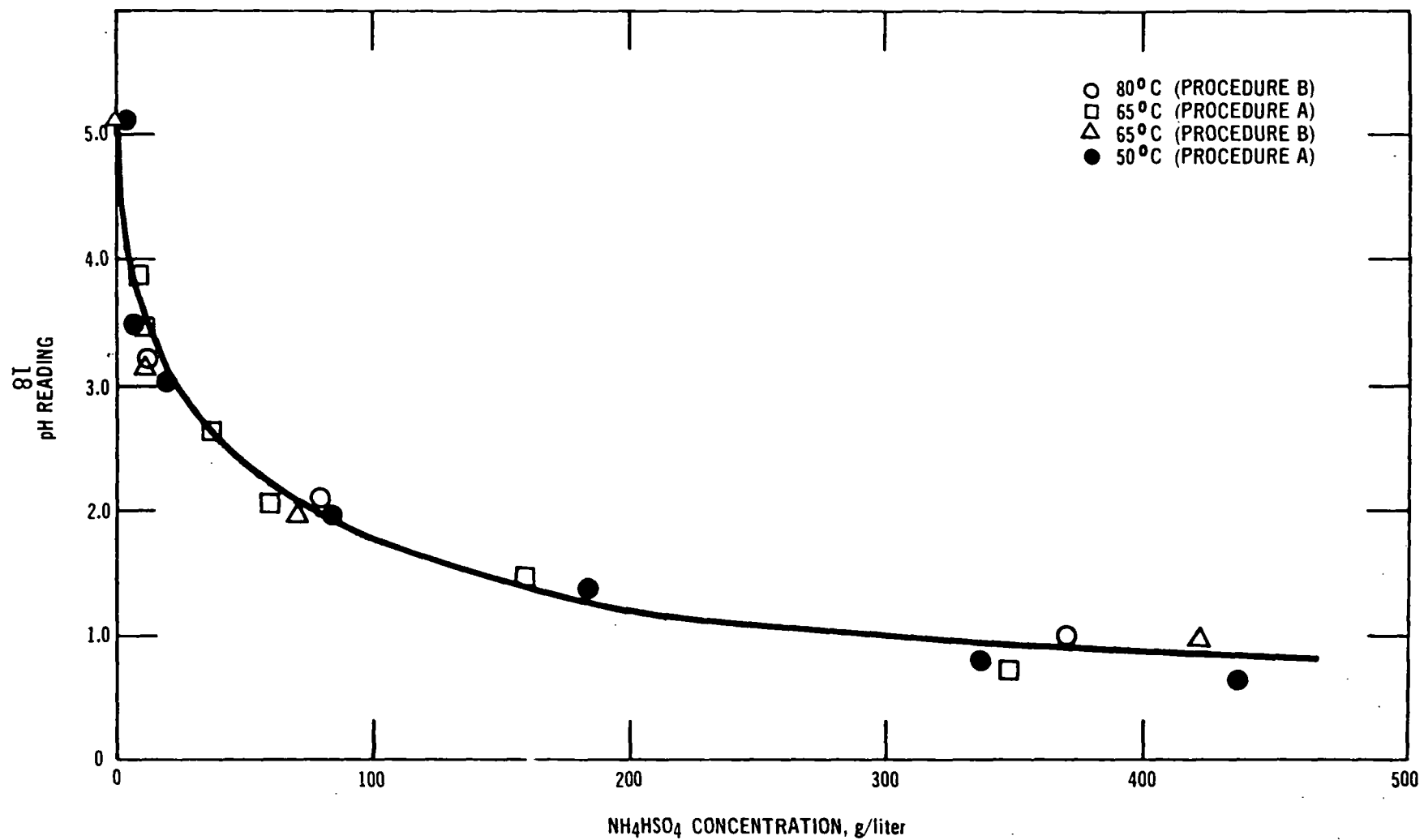


Figure 4. Effect of  $\text{NH}_4\text{HSO}_4$  on pH reading of a saturated  $(\text{NH}_4)_2\text{SO}_4$  solution.



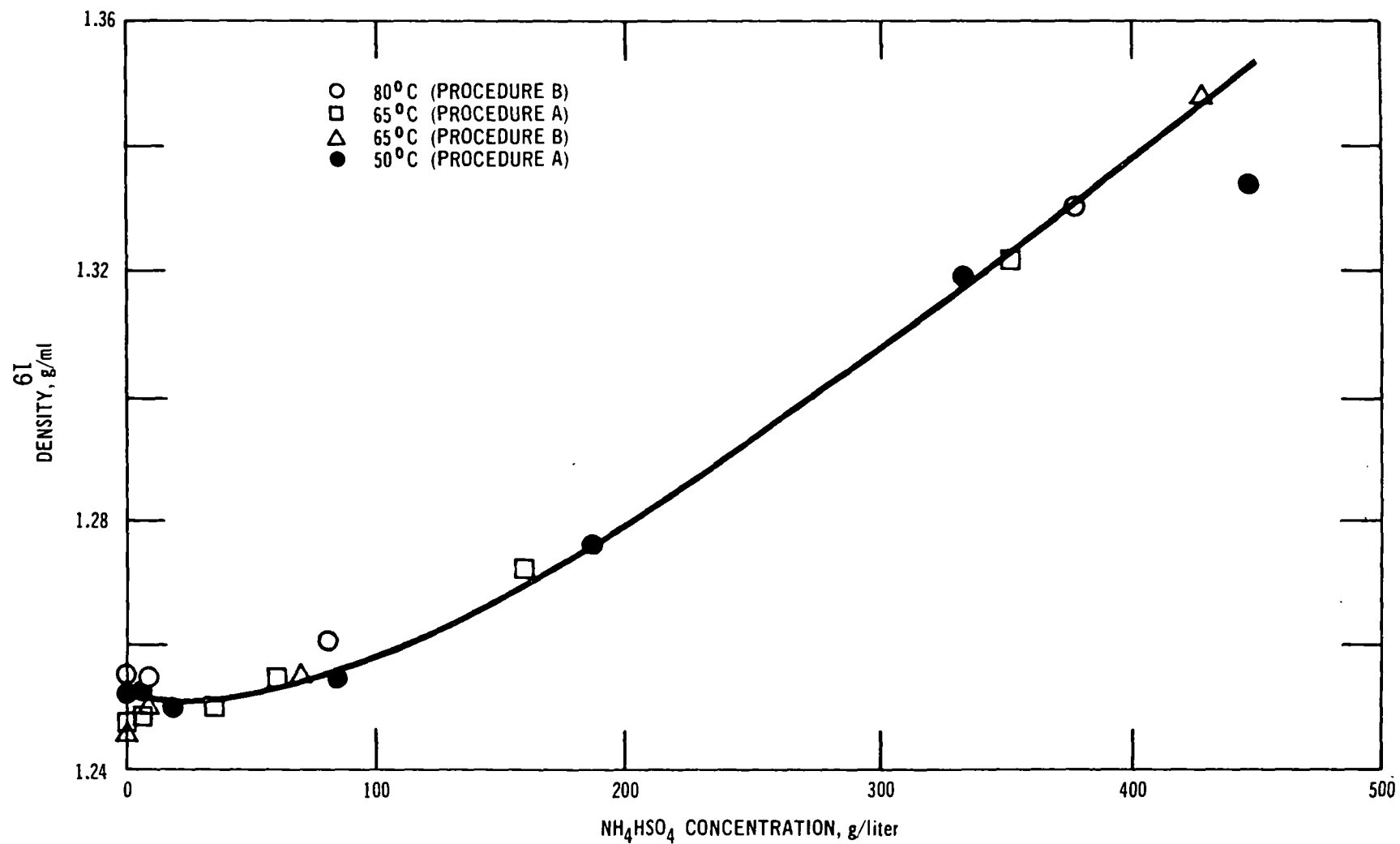


Figure 5. Effect of  $\text{NH}_4\text{HSO}_4$  on the density of a saturated  $(\text{NH}_4)_2\text{SO}_4$  solution.

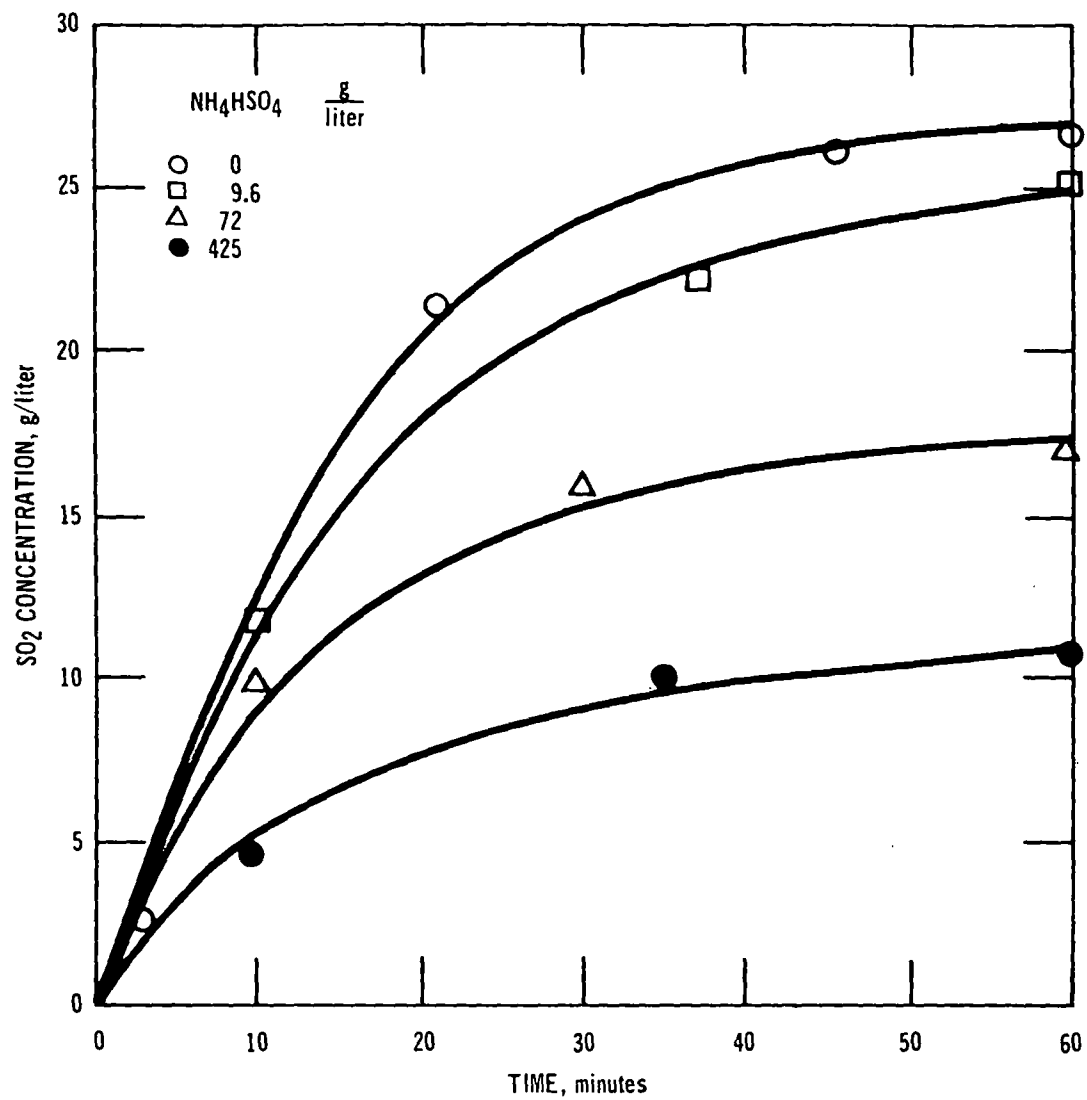


Figure 6. Absorption of  $\text{SO}_2$  in saturated  $(\text{NH}_4)_2\text{SO}_4$  solutions containing  $\text{NH}_4\text{HSO}_4$  at  $65^\circ \text{C}$ .

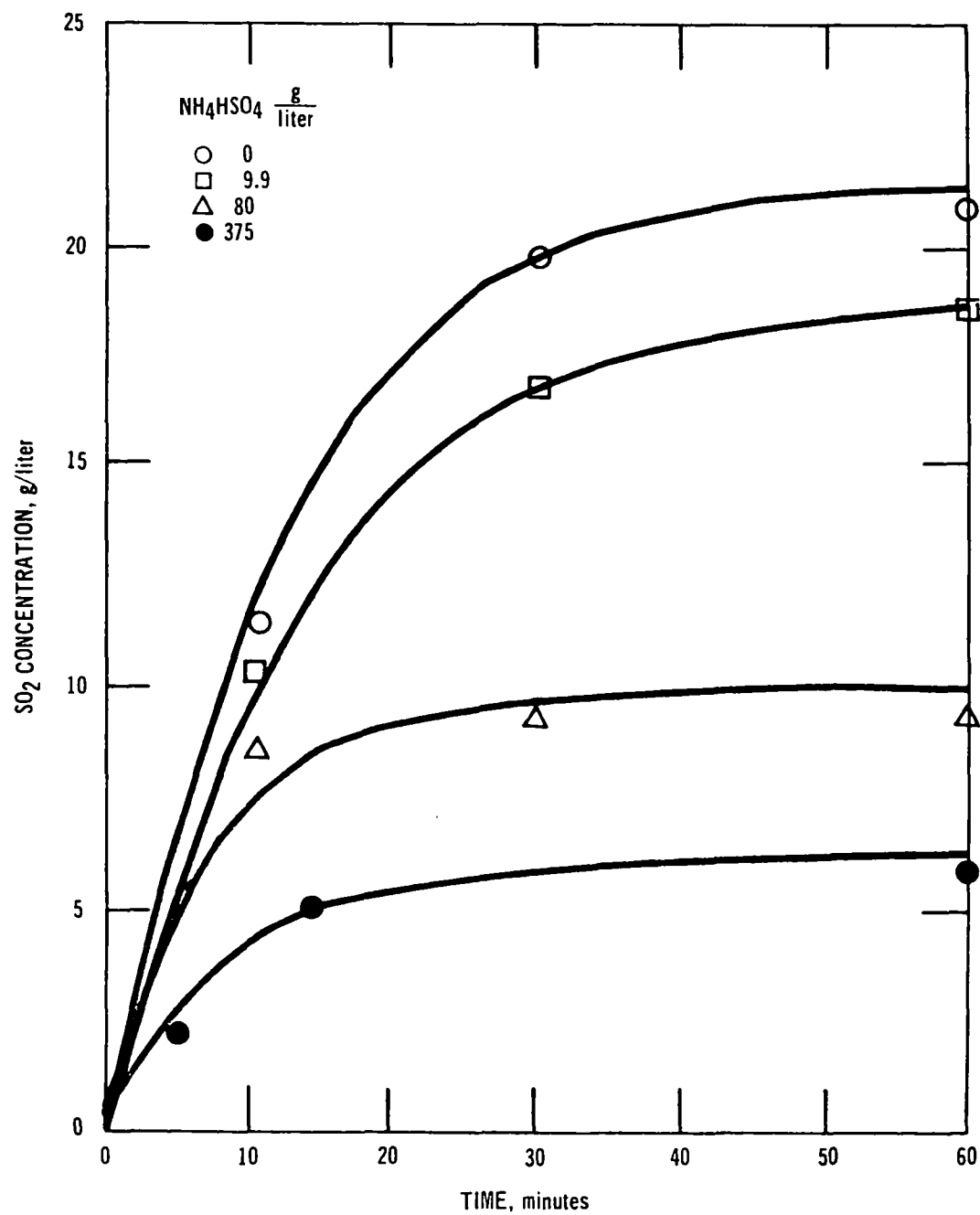


Figure 7. Absorption of  $\text{SO}_2$  in saturated  $(\text{NH}_4)_2\text{SO}_4$  solutions containing  $\text{NH}_4\text{HSO}_4$  at  $80^\circ\text{C}$ .

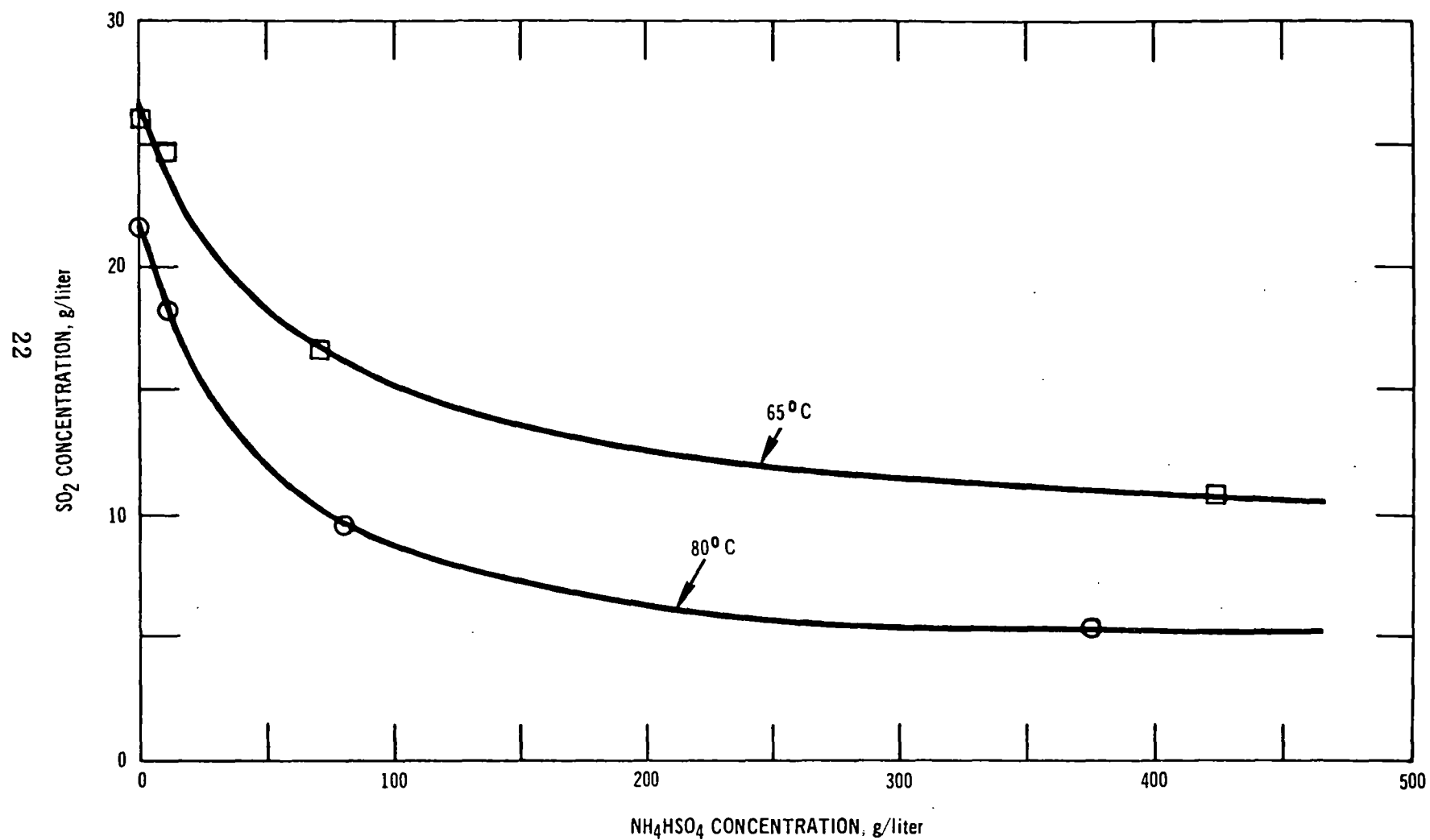


Figure 8. SO<sub>2</sub> solubility in saturated (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> solutions containing NH<sub>4</sub>HSO<sub>4</sub>.

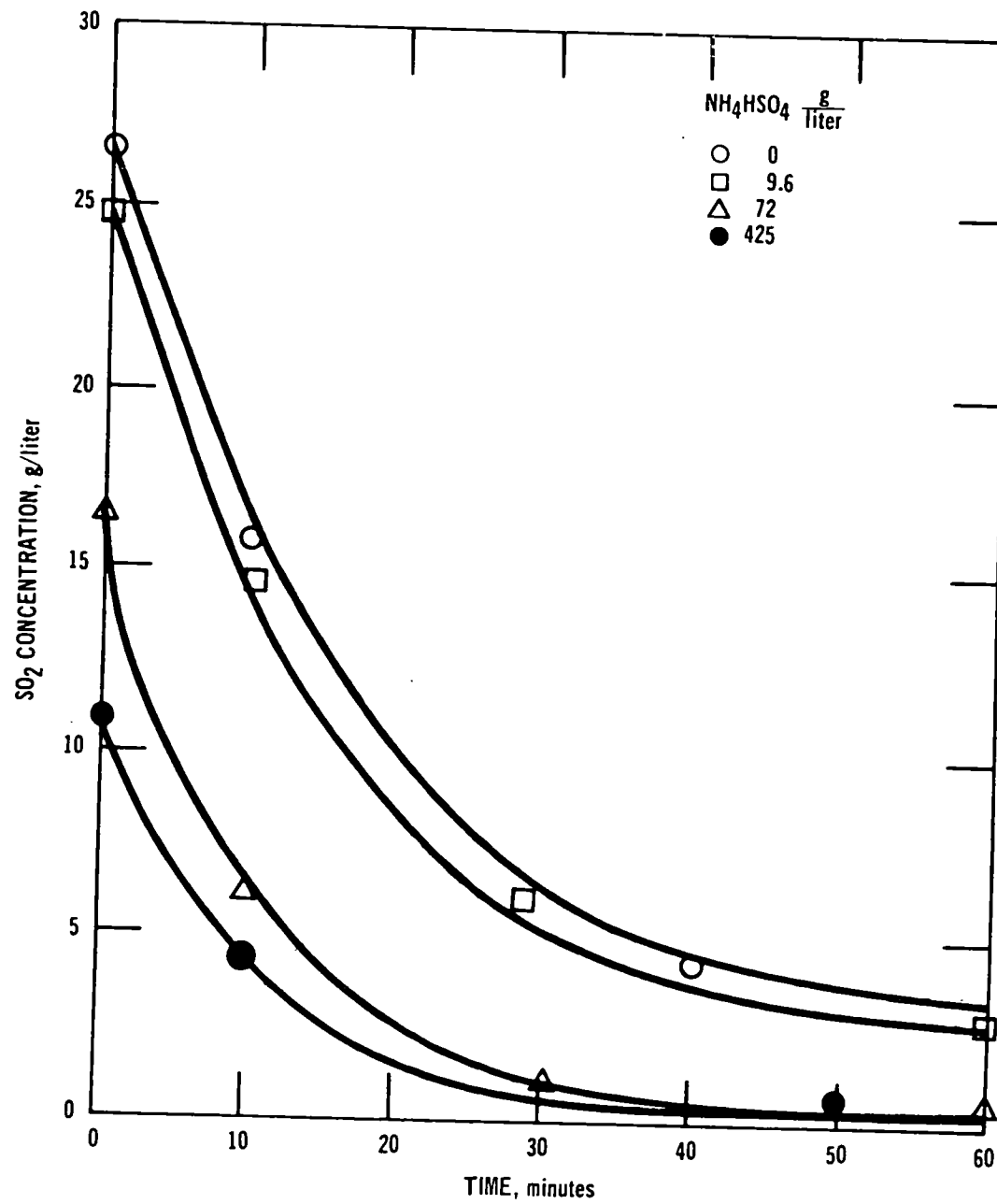


Figure 9. Stripping rates for  $\text{SO}_2$  in saturated  $(\text{NH}_4)_2\text{SO}_4$  solutions containing  $\text{NH}_4\text{HSO}_4$  at  $65^\circ \text{C}$ .

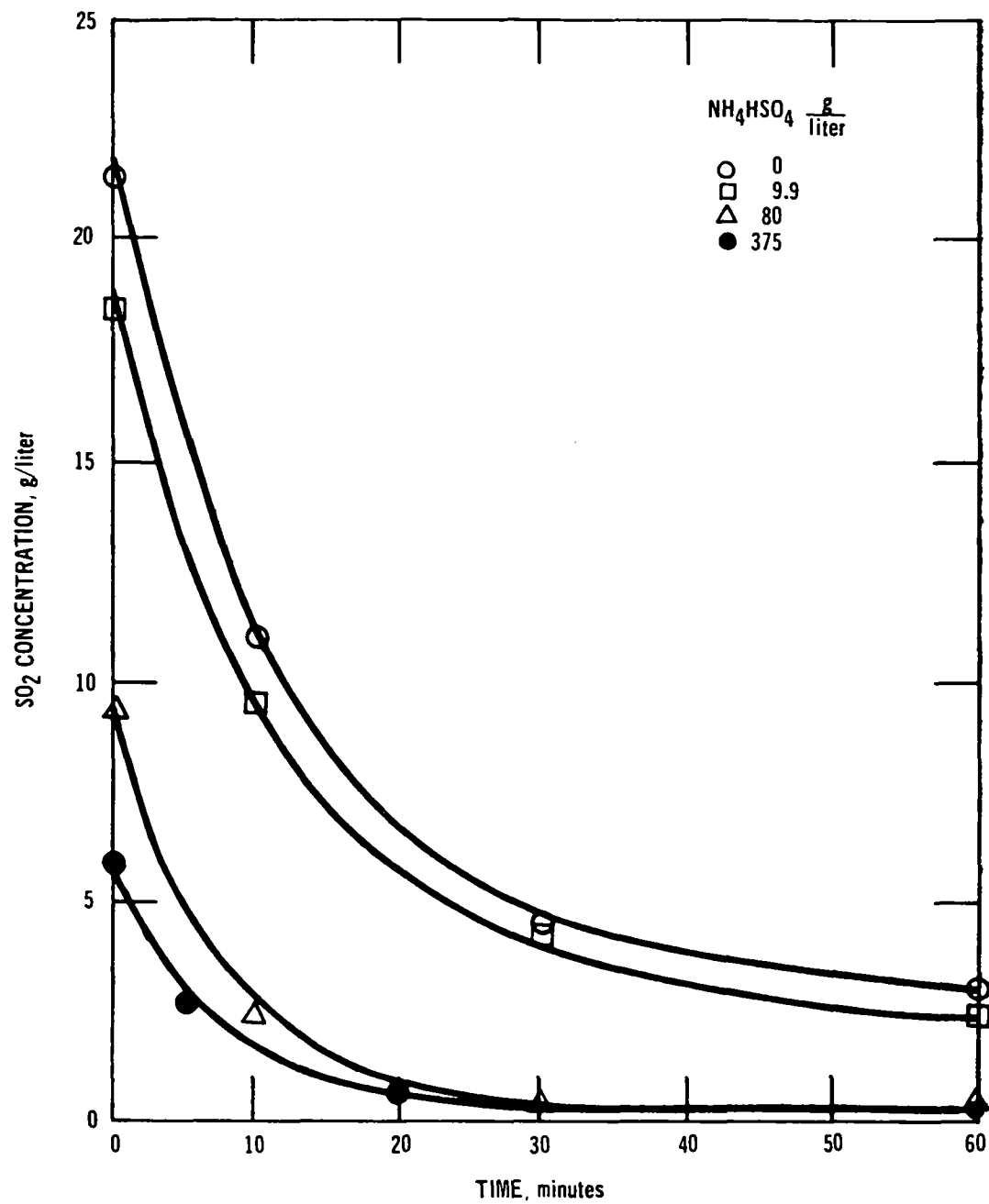


Figure 10. Stripping rates for SO<sub>2</sub> in saturated (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> solutions containing NH<sub>4</sub>HSO<sub>4</sub> at 80° C.

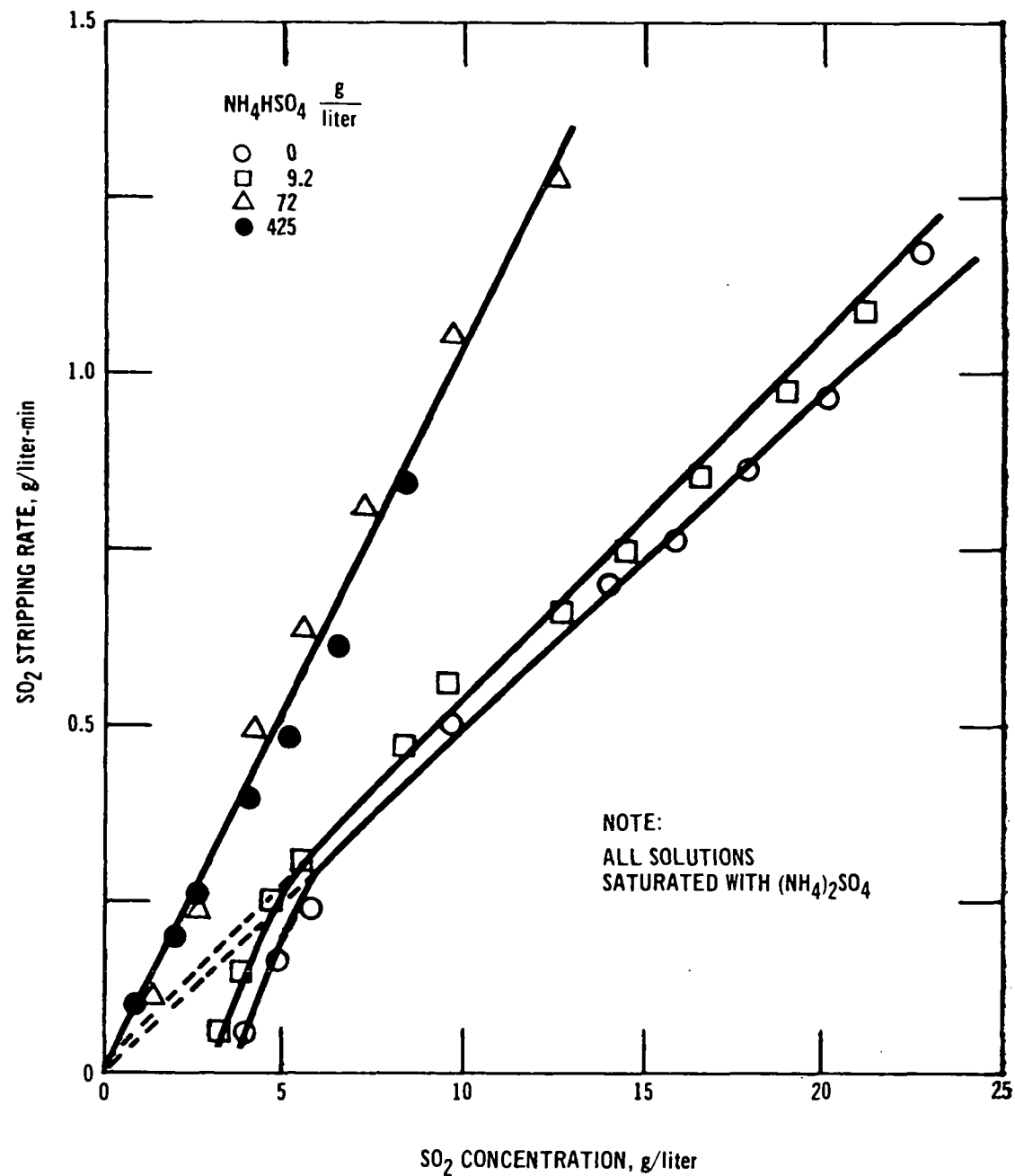


Figure 11.  $\text{SO}_2$  stripping as a function of  $\text{SO}_2$  concentration at  $65^\circ\text{C}$ .

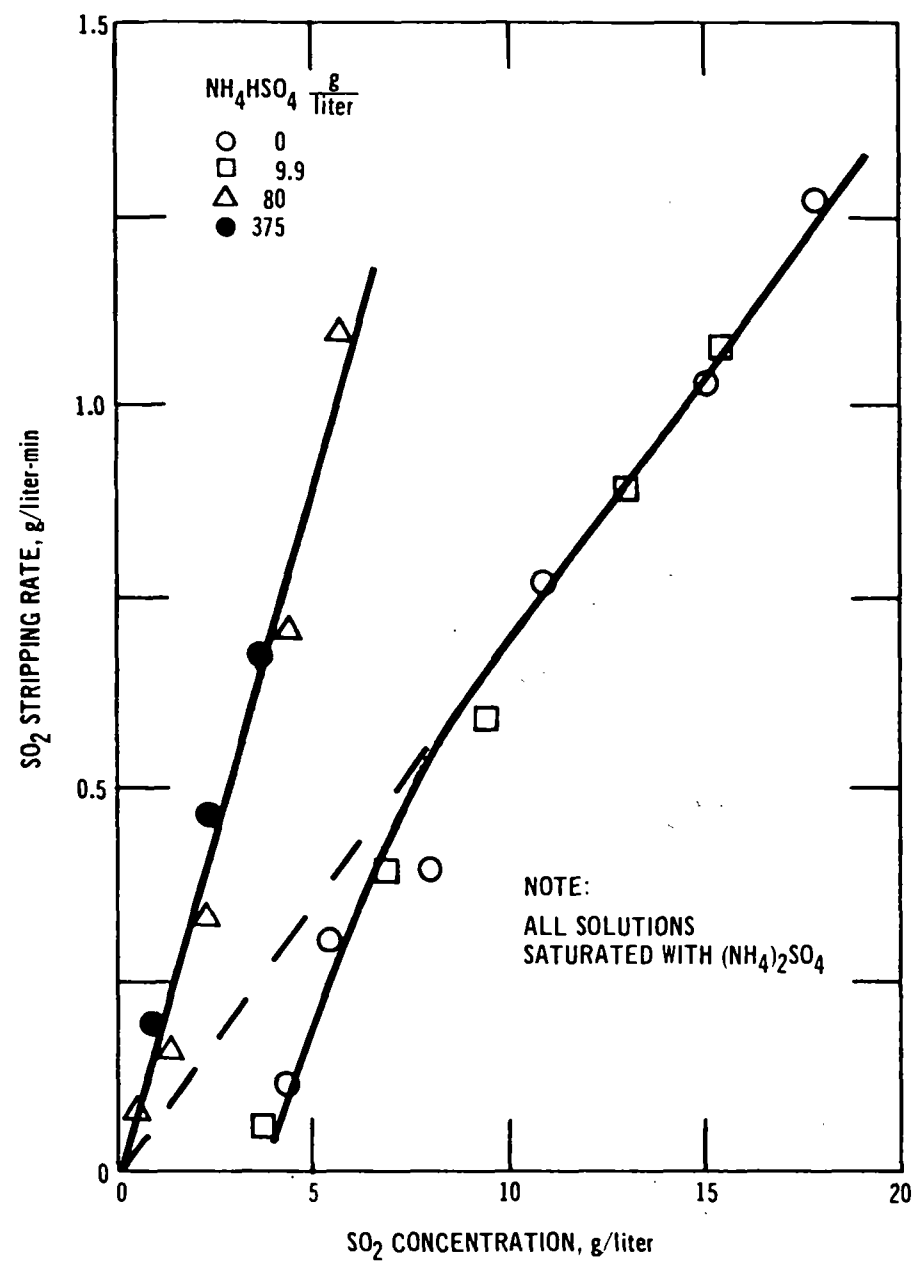


Figure 12.  $\text{SO}_2$  stripping as a function of  $\text{SO}_2$  concentration at  $80^\circ\text{C}$ .



Table 1. DENSITY, pH, AND COMPOSITION OF SATURATED  
 $(\text{NH}_4)_2\text{SO}_4$  SOLUTIONS AT 50, 65, AND 80°C

Temperature °C	Conc $(\text{NH}_4)_2\text{SO}_4$		Density $\text{g/cm}^3$	pH Reading
	g/l	moles/100 moles $\text{H}_2\text{O}$		
50	570	11.4	1.254	5.18
65	596	12.4	1.251	5.10
80	616	13.1	1.256	5.17

Table 2. EFFECTS OF  $\text{NH}_4\text{HSO}_4$  ON DENSITY, pH, AND COMPOSITION  
OF SATURATED  $(\text{NH}_4)_2\text{SO}_4$  SOLUTIONS AT 50, 65, and 80°C

Conc $(\text{NH}_4)_2\text{SO}_4$		Conc $\text{NH}_4\text{HSO}_4$		pH Reading	Density $\frac{\text{grams}}{\text{cm}^3}$
$\frac{\text{grams}}{\text{liter}}$	$\frac{\text{moles}}{100 \text{ moles } \text{H}_2\text{O}}$	$\frac{\text{grams}}{\text{liter}}$	$\frac{\text{moles}}{100 \text{ moles } \text{H}_2\text{O}}$		

Results at 50°C (Procedure A)

570	11.4	0	0	5.18	1.254
561	11.1	6	0.14	3.51	1.255
547	10.9	20	0.46	3.05	1.250
509	10.5	85	2.01	2.00	1.255
442	9.2	185	4.37	1.39	1.276
402	9.4	332	8.87	0.82	1.320
358	9.1	441	12.9	0.64	1.334

Results at 65°C (Procedure A)

596	12.4	0	0	5.10	1.251
590	12.3	5	0.12	3.85	1.248
579	12.0	10	0.24	3.50	1.247
562	11.7	35	0.84	2.66	1.250
548	11.6	60	1.45	2.09	1.255
498	11.0	160	4.07	1.50	1.273
414	10.5	352	9.91	0.74	1.322

Results at 65°C (Procedure B)

596	12.5	0	0	5.18	1.245
584	12.1	9.6	0.23	3.11	1.251
544	11.6	72.0	1.76	2.00	1.251
394	10.1	425.0	12.55	0.98	1.349

Results at 80°C (Procedure B)

616	13.1	0	0	5.17	1.255
597	12.7	9.9	0.25	3.11	1.254
565	12.4	80.0	2.0	2.13	1.261
430	11.1	375.0	11.1	1.05	1.331

Table 3. ABSORPTION OF  $\text{SO}_2$  IN SATURATED  $(\text{NH}_4)_2\text{SO}_4$   
SOLUTIONS CONTAINING  $\text{NH}_4\text{HSO}_4$  AT  $65^\circ\text{C}$

Time min	pH Reading	Density $\text{g/cm}^3$	$\text{SO}_2$ $\text{g/l}$	$(\text{NH}_4)_2\text{SO}_4$ $\text{g/l}$	$\text{NH}_4\text{HSO}_4$ $\text{g/l}$
Concentration $\text{NH}_4\text{HSO}_4 = 0$ grams/liter					
0	5.18	1.245	0	586	0
3	3.25	1.246	2.5	580	0
21	2.62	1.244	21.2	586	0
45	2.53	1.247	26.0	590	0
60	2.52	1.250	26.4	583	0
Concentration $\text{NH}_4\text{HSO}_4 = 9.6$ grams/liter					
0	3.11	1.251	0	584	9.6
19	2.64	1.250	12.1	582	5.7
35	2.37	1.256	22.6	593	4.5
60	2.31	1.255	24.8	586	3.5
Concentration $\text{NH}_4\text{HSO}_4 = 72$ grams/liter					
0	2.00	1.256	0	544	72.0
10	1.91	1.257	10.2	543	70.0
30	1.87	1.257	15.7	547	63.0
60	1.87	1.260	16.5	554	61.0
Concentration $\text{NH}_4\text{HSO}_4 = 425$ grams/liter					
0	0.98	1.349	0	394	425.0
10	0.95	1.350	4.6	394	418.0
35	0.94	1.352	9.6	391	405.0
60	0.93	1.351	10.9	396	415.0

Table 4. ABSORPTION OF  $\text{SO}_2$  IN SATURATED  $(\text{NH}_4)_2\text{SO}_4$  SOLUTIONS  
CONTAINING  $\text{NH}_4\text{HSO}_4$  at  $80^\circ\text{C}$

Time min	pH Reading	Density $\text{g/cm}^3$	$\text{SO}_2$ g/l	$(\text{NH}_4)_2\text{SO}_4$ g/l	$\text{NH}_4\text{HSO}_4$ g/l
Concentration $\text{NH}_4\text{HSO}_4 = 0$ grams/liter					
0	5.17	1.255	0	616	0
10	2.91	1.256	11.4	608	0
30	2.68	1.259	19.7	611	0
60	2.66	1.258	21.3	610	0
Concentration $\text{NH}_4\text{HSO}_4 = 9.9$ grams/liter					
0	3.11	1.254	0	585	9.9
10	2.66	1.260	10.3	582	3.7
30	2.54	1.258	16.8	609	11.5
60	2.50	1.259	18.4	598	8.1
Concentration $\text{NH}_4\text{HSO}_4 = 80$ grams/liter					
0	2.13	1.261	0	565	80.0
15	2.10	1.267	8.6	562	76.0
35	2.09	1.266	9.4	564	84.0
55	2.08	1.270	9.4	566	80.0
Concentration $\text{NH}_4\text{HSO}_4 = 375$ grams/liter					
0	1.05	1.331	0	430	375.0
5	1.06	1.329	2.2	436	372.0
15	1.05	1.335	5.0	440	364.0
60	1.04	1.333	5.9	435	382.0

Table 5. STRIPPING RATES FOR  $\text{SO}_2$  IN A SATURATED  $(\text{NH}_4)_2\text{SO}_4$  SOLUTION  
CONTAINING  $\text{NH}_4\text{HSO}_4$  AT  $65^\circ\text{C}$

Time min	pH Reading	Density $\text{g/cm}^3$	$\text{SO}_2$ $\text{g/l}$	$(\text{NH}_4)_2\text{SO}_4$ $\text{g/l}$	$\text{NH}_4\text{HSO}_4$ $\text{g/l}$
Concentration $\text{NH}_4\text{HSO}_4 = 0$ grams/liter					
0	2.52	1.250	26.4	583	0
10	2.70	1.274	15.8	586	0
40	3.10	1.244	4.2	580	0
Concentration $\text{NH}_4\text{HSO}_4 = 9.6$ grams/liter					
0	2.31	1.255	24.8	586	3.5
10	2.54	1.253	14.6	582	5.7
28	2.76	1.253	5.8	586	5.7
52	2.94	1.251	3.0	587	3.5
Concentration $\text{NH}_4\text{HSO}_4 = 72$ grams/liter					
0	1.87	1.260	16.5	554	61.0
10	1.93	1.258	5.9	547	73.0
30	1.95	1.255	0.9	548	75.0
60	1.97	1.256	0.5	548	70.0
Concentration $\text{NH}_4\text{HSO}_4 = 425$ grams/liter					
0	0.93	1.348	10.9	396	415
10	0.95	1.350	4.5	394	420
50	0.96	1.347	0.5	396	430

Table 6. STRIPPING RATES FOR  $\text{SO}_2$  IN SATURATED  $(\text{NH}_4)_2\text{SO}_4$  SOLUTIONS CONTAINING  $\text{NH}_4\text{HSO}_4$  AT  $80^\circ\text{C}$

Time min	pH Reading	Density $\text{g/cm}^3$	$\text{SO}_2$ $\text{g/l}$	$(\text{NH}_4)_2\text{SO}_4$ $\text{g/l}$	$\text{NH}_4\text{HSO}_4$ $\text{g/l}$
Concentration $\text{NH}_4\text{HSO}_4 = 0$ grams/liter					
0	2.66	1.258	21.3	610	0
10	2.96	1.258	10.9	610	0
30	3.27	1.255	4.5	613	0
60	3.54	1.255	2.9	611	0
Concentration $\text{NH}_4\text{HSO}_4 = 9.9$ grams/liter					
0	2.50	1.259	18.4	598	8.1
10	2.71	1.258	9.5	580	5.3
30	2.86	1.254	4.2	607	11.3
60	2.99	1.254	2.5	600	7.5
Concentration $\text{NH}_4\text{HSO}_4 = 80$ grams/liter					
0	2.08	1.270	9.4	566	80.0
10	2.11	1.267	2.3	563	80.0
30	2.12	1.267	0.3	564	86.0
60	2.12	1.267	0.3	568	83.0
Concentration $\text{NH}_4\text{HSO}_4 = 375$ grams/liter					
0	1.04	1.351	5.9	435	382.0
5	1.05	1.355	2.6	425	386.0
20	1.06	1.360	0.7	434	372.0
60	1.08	1.359	0.4	430	372.0

Table 7. STRIPPING RATE CONSTANTS

Temperature C°	Conc $\text{NH}_4\text{HSO}_4$ g/l	Rate Constant $\text{min}^{-1}$
65	0	0.049
65	9.6	0.053
65	72	0.110
65	425	0.110
80	0	0.070
80	9.9	0.070
80	80	0.180
80	375	0.180

Section VIII  
APPENDICES

<u>Appendix</u>		<u>Page</u>
A	Lot Analysis of Chemicals Used	30
B	The Effects of $\text{NH}_4\text{HSO}_4$ on Density, pH, and Composition of Saturated Solutions of $(\text{NH}_4)_2\text{SO}_4$ at 80°C Using Procedure A	31



## Appendix A

### LOT ANALYSIS OF CHEMICALS USED

#### A. Ammonium Sulfate, $(\text{NH}_4)_2\text{SO}_4$

Manufacturer - Matheson, Coleman, and Bell

##### Maximum Impurities & Specifications

Arsenic. . . . .	.0.00002%
Chloride . . . . .	.0.0005%
Heavy metals (as Pb) . . . . .	.0.0005%
Insoluble matter . . . . .	.0.005%
Iron . . . . .	.0.0005%
Nitrate. . . . .	.0.001%
pH of a 5% solution. . . . .	.5.0 - 6.0
Phosphate. . . . .	.0.0005%
Residue after ignition . . . . .	.0.005%

#### B. Ammonium Bisulfate, $\text{NH}_4\text{HSO}_4$

Manufacturer - Fisher Scientific Company

##### Maximum Impurities

Chloride . . . . .	.0.0003%
Iron . . . . .	.0.0004%
Non-volatile matter. . . . .	.0.003%
Other heavy metals (as Pb) . . . . .	.0.001%

# Appendix B

THE EFFECTS OF  $\text{NH}_4\text{HSO}_4$  ON DENSITY, pH, AND COMPOSITION OF  
SATURATED SOLUTIONS OF  $(\text{NH}_4)_2\text{SO}_4$  AT  $80^\circ\text{C}$   
USING PROCEDURE A<sup>a</sup>

Conc $(\text{NH}_4)_2\text{SO}_4$		Conc $\text{NH}_4\text{HSO}_4$		pH	Density g/cm <sup>3</sup>
grams	moles	grams	moles		
liter	100 moles $\text{H}_2\text{O}$	liter	100 moles $\text{H}_2\text{O}$		

## Run Number 1

610	13.0	0	0	4.00	1.249
396	12.6	6	0.15	3.86	1.248
565	11.6	18	0.42	3.55	1.250
530	10.7	44	1.00	2.95	1.252
535	11.44	80	1.96	2.22	1.253
423	9.69	252	6.62	1.50	1.270

## Run Number 2

607	13.0	0	0	4.02	1.250
530	10.6	40	0.92	2.91	1.249
495	9.91	78	1.79	2.61	1.254
366	9.90	407	12.6	1.47	1.277
310	9.05	538	18.0	0.98	1.314

<sup>a</sup>These data are believed incorrect but are included for completeness.

<b>BIBLIOGRAPHIC DATA SHEET</b>		1. Report No. <b>EPA-650/2-73-012</b>	2. Recipient's Accession No.
4. Title and Subtitle <b>Properties of Ammonium Sulfate, Ammonium Bisulfate, and Sulfur Dioxide Solutions in Ammonia Scrubbing Processes</b>		5. Report Date <b>August 1973</b>	
7. Author(s) <b>J. E. Boone and J. H. Turner</b>		8. Performing Organization Rept. No.	
9. Performing Organization Name and Address <b>EPA, Office of Research and Development NERC-RTP, Control Systems Laboratory Research Triangle Park, North Carolina</b>		10. Project/Task/Work Unit No. <b>21ACX (Task 62)</b>	
		11. Contract/Grant No. <b>In-House Report</b>	
12. Sponsoring Organization Name and Address <b>NA</b>		13. Type of Report & Period Covered <b>Final</b>	
		14.	
15. Supplementary Notes			
16. Abstracts The report gives results of a study involving data that can be used to evaluate pilot-plant operation of an NH <sub>3</sub> scrubber with NH <sub>4</sub> HSO <sub>4</sub> regeneration. It determined the density, pH, and composition of saturated (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> solutions at 50, 65, and 80°C; effects on density, pH, and composition of adding NH <sub>4</sub> HSO <sub>4</sub> to the above solutions; and the solubility and stripping rates of SO <sub>2</sub> in saturated solutions of (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> containing NH <sub>4</sub> HSO <sub>4</sub> at 65 and 80°C. (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> solubility in water compared favorably with accepted values. Adding NH <sub>4</sub> HSO <sub>4</sub> to the saturated solutions lowered (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> solubility, decreased pH, and increased density. SO <sub>2</sub> solubility in saturated (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> decreased with both increasing temperature and increasing NH <sub>4</sub> HSO <sub>4</sub> concentration. SO <sub>2</sub> stripping rates were found to be first order with respect to SO <sub>2</sub> concentration except when the pH rose above 2.6. Stripping rate depends on temperature, NH <sub>4</sub> HSO <sub>4</sub> concentration, and almost certainly on sweep gas and agitation rates.			
17. Key Words and Document Analysis. 17a. Descriptors <b>Air Pollution</b> <b>Liquid Saturation</b> <b>Washing</b> <b>Desorption</b> <b>Sulfur Dioxide</b> <b>Ammonium Compounds</b> <b>Ammonia</b> <b>Flue Gases</b> <b>Solubility</b> <b>Density (Mass/Volume)</b> <b>pH</b>			
17b. Identifiers/Open-Ended Terms <b>Air Pollution Control</b> <b>Ammonia Scrubbing</b> <b>Gas Stripping</b>			
17c. COSATI Field/Group <b>7D, 7A, 13B</b>			
18. Availability Statement  <b>Unlimited</b>		19. Security Class (This Report) <b>UNCLASSIFIED</b>	21. No. of Pages <b>42</b>
		20. Security Class (This Page) <b>UNCLASSIFIED</b>	22. Price

# INSTRUCTIONS FOR COMPLETING FORM NTIS-35 (10-70) (Bibliographic Data Sheet based on COSATI)

Guidelines to Format Standards for Scientific and Technical Reports Prepared by or for the Federal Government, PB-180 600).

1. **Report Number.** Each individually bound report shall carry a unique alphanumeric designation selected by the performing organization or provided by the sponsoring organization. Use uppercase letters and Arabic numerals only. Examples FASEB-NS-87 and FAA-RD-68-09.
2. Leave blank.
3. **Recipient's Accession Number.** Reserved for use by each report recipient.
4. **Title and Subtitle.** Title should indicate clearly and briefly the subject coverage of the report, and be displayed prominently. Set subtitle, if used, in smaller type or otherwise subordinate it to main title. When a report is prepared in more than one volume, repeat the primary title, add volume number and include subtitle for the specific volume.
5. **Report Date.** Each report shall carry a date indicating at least month and year. Indicate the basis on which it was selected (e.g., date of issue, date of approval, date of preparation).
6. **Performing Organization Code.** Leave blank.
7. **Author(s).** Give name(s) in conventional order (e.g., John R. Doe, or J. Robert Doe). List author's affiliation if it differs from the performing organization.
8. **Performing Organization Report Number.** Insert if performing organization wishes to assign this number.
9. **Performing Organization Name and Address.** Give name, street, city, state, and zip code. List no more than two levels of an organizational hierarchy. Display the name of the organization exactly as it should appear in Government indexes such as USGRDR-I.
10. **Project Task Work Unit Number.** Use the project, task and work unit numbers under which the report was prepared.
11. **Contract/Grant Number.** Insert contract or grant number under which report was prepared.
12. **Sponsoring Agency Name and Address.** Include zip code.
13. **Type of Report and Period Covered.** Indicate interim, final, etc., and, if applicable, dates covered.
14. **Sponsoring Agency Code.** Leave blank.
15. **Supplementary Notes.** Enter information not included elsewhere but useful, such as: Prepared in cooperation with . . . Translation of . . . Presented at conference of . . . To be published in . . . Supersedes . . . Supplements . . .
16. **Abstract.** Include a brief (200 words or less) factual summary of the most significant information contained in the report. If the report contains a significant bibliography or literature survey, mention it here.
17. **Key Words and Document Analysis.** (a). **Descriptors.** Select from the Thesaurus of Engineering and Scientific Terms the proper authorized terms that identify the major concept of the research and are sufficiently specific and precise to be used as index entries for cataloging.  
(b). **Identifiers and Open-Ended Terms.** Use identifiers for project names, code names, equipment designators, etc. Use open-ended terms written in descriptor form for those subjects for which no descriptor exists.  
(c). **COSATI Field/Group.** Field and Group assignments are to be taken from the 1965 COSATI Subject Category List. Since the majority of documents are multidisciplinary in nature, the primary Field/Group assignment(s) will be the specific discipline, area of human endeavor, or type of physical object. The application(s) will be cross-referenced with secondary Field/Group assignments that will follow the primary posting(s).
18. **Distribution Statement.** Denote releasability to the public or limitation for reasons other than security for example "Release unlimited". Cite any availability to the public, with address and price.
- 19 & 20. **Security Classification.** Do not submit classified reports to the National Technical
21. **Number of Pages.** Insert the total number of pages, including this one and unnumbered pages, but excluding distribution list, if any.
22. **Price.** Insert the price set by the National Technical Information Service or the Government Printing Office, if known.