NASA TECHNICAL TRANSLATION NASA TT F-17088

ABSORPTION OF NITROGEN OXIDE BY SULFURIC ACID SOLUTIONS

A. V. Baranov, E. A. Liberzon and T. I. Popova

Translation of "Pogloshcheniye Dvuokisi Azota Rastvorami Sernoy Kisloty," Trudy Sibirskogo Tekhnologicheskogo Instituta," Vol. 38, 1966, pp. 77-86.

(NASA-TT-F-17088) ABSORPTION OF NITROGEN OXIDE BY SULFURIC ACID SOLUTIONS (Kanner (Leo) Associates, Annapolis, Md.) 12 p HC $3.50 CSCL 07D
N76-27388
Unclas
G3/25 44592

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON, D. C. 20546 MAY 1976

STANDARD TITLE PAGE

1. Report No.	2. Government Accession No.	3. Recipient's Catalog No.
NASA TT F-17088		

4. Title and Subtitle	5. Report Date
ABSORPTION OF NITROGEN OXIDE BY SULFURIC ACID SOLUTIONS	May 1976
	6. Performing Organization Code
7. Author(s) A. V. Baranov, E. A. Liberzon, T. I. Popova	8. Performing Organization Report No.
	10. Work Unit No.
9. Performing Organization Name and Address Leo Kanner Associates Annapolis, Maryland 21401	11. Contract or Grant No. NASw-2790
	13. Type of Report and Period Covered Translation
12. Sponsoring Agency Name and Address NASA, Code KSI Washington, D. C. 20546	14. Sponsoring Agency Code

15. Supplementary Notes Translation of "Pogloshcheniye Dvuokisi Azota Rastvorami Sernoy Kisloty," Trudy Sibirskogo Tekhnologicheskogo Instituta," Vol. 38, 1966, pp. 77-86.

16. Abstract A study is made of the composition of the liquid phase formed upon absorption of nitrogen dioxide by sulfuric acid as a function of the concentration of oxides in the gas, temperature and concentration of sulfuric acid. It is found that in the process of absorption of NO_2, mixtures consisting of $HNO_3 + HNOSO_4 + H_2SO_4 + H_2O$ are formed, containing quite definite maximum concentrations of $HNOSO_4$, dependent on temperature, NO_2 concentration in the gas and concentration of absorbing sulfuric acid. This dependence is established. An equation is produced for determination of the maximum concentration of $HNOSO_4$. The possibility is shown of producing mixtures with high HNO_3 content by absorption of nitrogen oxides.

17. Key Words (Selected by Author(s))	18. Distribution Statement
	Unclassified. Unlimited

19. Security Classif. (of this report)	20. Security Classif. (of this page)	21. No. of Pages	22. Price
Unclassified	Unclassified		

NASA-HQ

ABSORPTION OF NITROGEN OXIDE BY SULFURIC ACID SOLUTIONS[1]

A. V. Baranov, E. A. Liberzon and T. I. Popova

Concentrated nitric acid is presently produced primarily by concentration of weak nitric acid in the presence of sulfuric acid. One significant shortcoming of this process is the need to concentrate large quantities of treated sulfuric acid, involving significant capital expenditures and operating costs. /77*

Trinary mixtures of the necessary composition can be produced by absorption of nitrogen oxides by aqueous solutions of sulfuric acid which, when distilled, produce concentrated nitric acid. The treated sulfuric acid, it is suggested, can be sent without preliminary concentration to an ordinary absorption installation to produce the trinary mixtures. The cumbersome and expensive process of concentration of the spent sulfuric acid is thus eliminated. Based on the literature data [1-4], we know that gaseous nitrogen dioxide is absorbed by sulfuric acid at a rather high rate with the formation of nitrosyl sulfate and nitric acid.

The kinetics of absorption of oxides of nitrogen by solutions of sulfuric acid have formed the subject of a number of investigations [5-10]. Particular attention has been given to the explanation of the relative rate of absorption of oxides of nitrogen of various compositions by sulfuric acid. When nitrogen dioxide interacts with sulfuric acid, the following reaction occurs:

$$2NO_2 + H_2SO_4 \rightleftarrows HNOSO_4 + HNO_3, \qquad (1)$$

Equivalent quantities of nitrosyl sulfate and nitric acid are formed only by absorption of nitrogen dioxide commercial

[1]Reported at a conference of workers of nitric acid plants in Dneprodzerzhinsk, 1953.

*Numbers in the margin indicate pagination in the foreign text.

sulfuric acid. /78

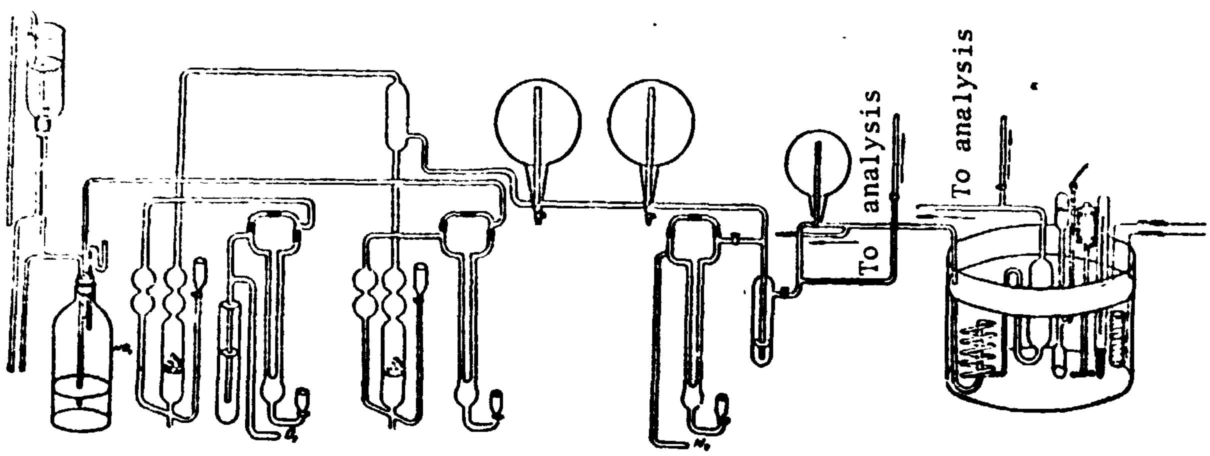

Figure 1. Diagram of Experimental Installation

In aqueous solutions of sulfuric acid, nitrosyl sulfate is hydrolyzed, and the nitric acid formed is decomposed, forming nitric acid and nitric oxide /79

$$HNOSO_4 + H_2O \rightleftarrows HNO_2 + H_2SO_4, \quad (2)$$

$$3HNO_2 \rightleftarrows HNO_3 + 2NO + H_2O. \quad (3)$$

Only when these reactions continue to completion can they be represented by the overall equation:

$$3NO_2 + H_2O \rightleftarrows 2HNO_3 + NO. \quad (4)$$

Nitrosyl sulfate is fully hydrolyzed only in dilute aqueous solutions of sulfuric acid (about 57%). In more concentrated sulfuric acid, the degree of hydrolysis of $HNOSO_4$ depends on a number of factors. The data available do not allow us to determine the composition of the mixtures produced upon absorption of nitrogen dioxide by sulfuric acid.

In the present work, we studied the composition of the liquid phase formed upon absorption of nitrogen dioxide by sulfuric acid as a function of the concentration of oxides in the gas, temperature and concentration of sulfuric acid. The studies were performed on the installation shown in Figure 1. The nitric oxide from the gas meter was sent through a dryer and rheometer to a mixer. Here oxygen was sent from a cylinder, after also passing through a dryer and rheometer. After the mixer, the mixture of gasses passes through the oxidizing volume, where NO is practically completely oxidized to NO_2. The nitrogen dioxide formed is liquefied at 10-12 C. By thermostating the vessel with liquid oxides of nitrogen and passing an inert gas (nitrogen) or oxygen through it, we produce a mixture of gasses of the required composition. A gas of the predetermined composition is sent through a coil in a thermostat to an absorbing vessel.

For better assurance of contact of the gas mixture with the liquid, we used the bubbling method. The gas mixture entered the absorbing vessel from the bottom through a porous glass plate in the form of tiny bubbles, forming a small foam layer above the liquid. To determine the concentration of nitrogen oxides in the incoming and outgoing gas, we used the method of absorption by alkali. The gas was drawn through the absorption battery by an aspirator. In the liquid phase, we determined the content of nitric acid, nitrosyl sulfate and sulfuric acid. In one specimen, by the method of back titration, we determined the total acidity of the mixture. In another specimen we determined the quantity of nitrosyl sulfate by the method of Beskov and Slizkovskaya [11]. This method was used because the ordinary /80 permanganate titration method yields unsatisfactory results. In a separate specimen, using a Lunge titrometer, we determined the sum of nitric acid and nitrosyl sulfate. With all data in gram equivalents per unit of weight of the mixture, it is easy to determine its composition in %. The content of nitrosyl sulfate in the mixture was converted to nitric acid.

The influence of contact time on the composition of the mixture formed by absorption of nitrogen dioxide with sulfuric acid was studied at sulfuric acid concentrations of about 70%. The concentration of nitrogen dioxide in the gas was maintained at 41%. The gas flow rate was 40 cm^3/min. The volume of absorbing sulfuric acid was 100 cm^3. The temperature was varied between 20 and 60 C. The results produced are presented graphically in Figures 2 and 3.

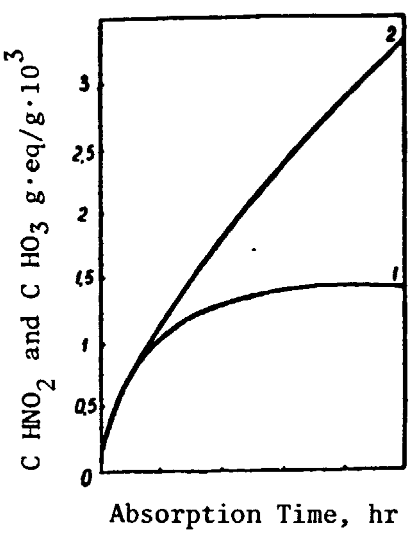

Figure 2. Composition of Mixtures Produced at 20 C

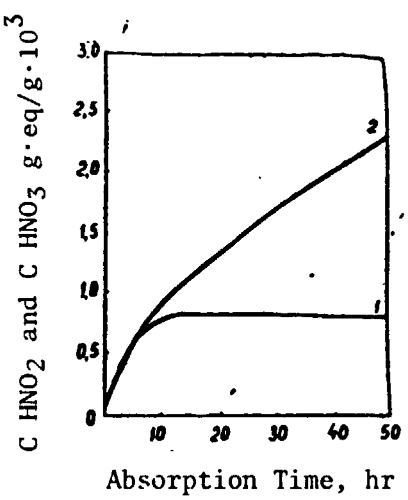

Figure 3. Composition of Mixtures Produced at 40 C

During the initial period of absorption of oxides of nitrogen by sulfuric acid, equivalent quantities of nitrosyl sulfate are formed, corresponding to the equation of reaction (1). After a certain quantity of nitrosyl sulfate is accumulated in the solution, the reaction of equation (2) begins to occur. With further absorption of the dioxide, more nitric and less nitrous acid begins to form, according to reactions (2) and (3).

When a certain concentration of /81
$HNOSO_4$ is achieved in the mixture -- we will call it the "limiting" concentration -- further absorption of NO_2 leads to an increase only in the content of nitric acid. The content of $HNOSO_4$ remains constant, regardless of the time of passage of oxides of nitrogen, though the concentration of HNO_3 in the mixture continues to increase.

The rate of the process of interaction of NO_2 and H_2SO_4 according to formula (1) decreases as nitric acid is formed. At the same time, the increase in the content of HNO_3 leads to a decrease in the quantity of water in the mixture, which decreases the rate of hydrolysis of $HNSO_4$ according to equation (2).

As a result, the rates of the reactions according to equations (1), (2) and (3) become identical. The rate of formation of $HNOSO_4$ according to equation (1) becomes equal to the rate of its decomposition according to equations (2) and (3).

The limiting concentration of $HNOSO_4$ in the mixture depends on the temperature, concentration of initial sulfuric acid and concentration of nitrogen dioxide.

At 20 C, the limiting concentration of $HNOSO_4$ as HNO_2 is 1.45 g·eq, or 6.8% (Figure 2). The reaction according to equations (2) and (3) begins to occur with an $HNOSO_4$ concentration in the mixture of about 0.95 g·eq, or 4.46% HNO_2. The rate gradually increases until it reaches a value equal to the rate of the reaction according to equation (1). The accumulation of HNO_3 in the mixture occurs as a result of reactions according to equations (1) and (3).

As the temperatures increase to 40 C, the limiting concentration of $HNOSO_4$ reaches approximately 4% HNO_2, with an initial /82 concentration of sulfuric acid of about 70% (Figure 3). At 60 C, the limiting concentration of $HNOSO_4$ is 2.8% HNO_2. Naturally, there is a limiting concentration of HNO_3 in the mixture, corresponding to equilibrium between the gas and liquid phases.

The dependence of limiting $HNOSO_4$ concentration on temperature is shown in Figure 4. The nature of the curves in coordinates $\log C^{lim}_{HNO_2} - \frac{1}{T}$ leads to an equation of the following form:

$$C^{lim}_{HNO_2} = A \cdot \ell^{1800/T}$$

The apparent energy
The apparent energy = 3,600.

If we represent the data presented in coordinates of $\log C^{lim}_{HNO_2}$ vs. log t, the nature of the curves can be represented by the equation

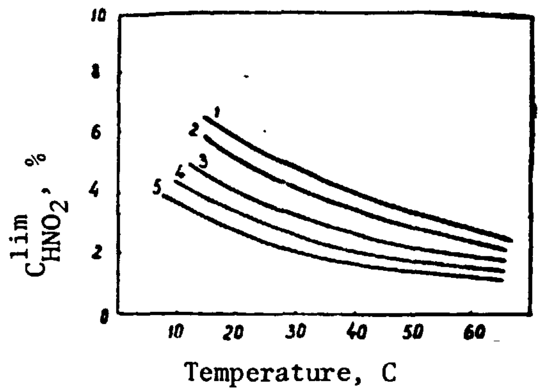

Figure 4. Limiting Concentration of $HNOSO_4$ as a Function of Temperature. Content of NO_2, %: 1, 40; 2, 30; 3, 20; 4, 15; 5, 10

$$C^{lim}_{HNO_2} = A_1 \cdot t^{-0.7}$$

The influence of concentration of nitrogen dioxide in the gas on composition of the mixture produced was studied with an NO_2 content in the gas of 41%, 20.8% and 10.8%. The temperature was maintained equal to 25, 30, 40, 50 and 60 C. The gas flow rate was 40 cm^3/min. The concentration of the initial H_2SO_4 was 70%. The results of these studies are presented in Figure 5 in the forms of isotherms of limiting $HNOSO_4$ concentrations in the mixture as a function of NO_2 concentration in the gas.

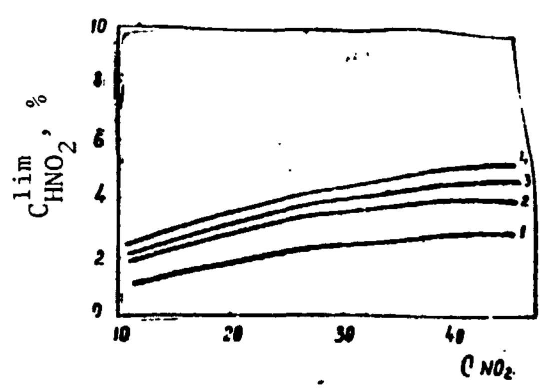

Figure 5. Limiging Concentration of $HNOSO_4$ as a Function of Nitrogen Dioxide Content in the Gas at Temperature, C: 1, 60; 2, 40; 3, 30; 4, 25

As the content of NO_2 in gas decreases, the limiting concentration of $HNOSO_4$ in the mixture decreases according to the equation /83

$$C^{lim}_{HNO_2} = A_2 \cdot C^{0.57}_{NO_2} .$$

The limiting concentration of $HNOSO_4$ in the mixture changes in proportion to the concentration of NO_2 in the gas with an exponent of 0.57.

In order to produce the curves presented in Figure 5, we first found the limiting concentration of $HNOSO_4$ during absorption for various temperatures and concentrations of NO_2 in the gas.

For a temperature of 25 C, these results were as shown in Figure 6.

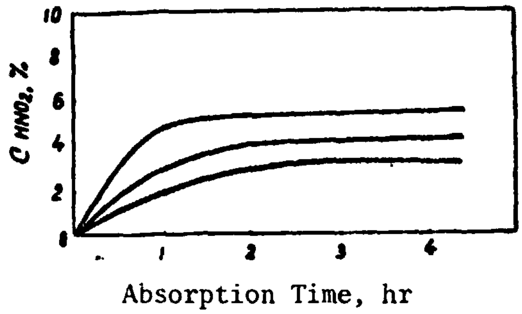

Figure 6. Concentration of $HNOSO_4$ as a Function of Absorption Time (Temperature 25 C, Initial H_2SO_4 Concentration 70%, v = 40 cm^3/min). Concentration of NO_2 in %: 1, 14.8; 2, 25; 3, 40 (Bottom to Top)

In the mixture studied, an exceptionally great role was played by the process of hydrolysis of nitrosyl sulfate, the occurrence of which depends on the quantity of water in the solution or the concentration of sulfuric acid. The literature /84 presents data on the hydrolysis of dilute solutions of nitrosyl sulfate, but no data for solutions containing nitric acid. The influence of concentration of initial sulfuric acid on the composition of the mixtures formed has been studied upon absorption of nitrogen dioxide by solutions of sulfuric acid with concentrations of 61, 69, 83.9 and 94.1%. In all experiments, the concentration of nitrogen dioxide in the gas was about 40%. The temperature was maintained at 20 C. The results produced are presented in Figures 7 and 8.

As the concentration of initial sulfuric acid increases, /85
the content of nitric acid in the mixture decreases (Figure 7), since in dilute acids HNO_3 is converted due to the reactions of equations (1) and (3), while in concentrated acids it primarily follows the reaction of equation (1). The content of nitrosyl sulfate in the mixture increases with increasing concentration of the initial sulfuric acid. When NO_2 is absorbed by 61% sulfuric acid, the limiting concentration of $HNOSO_4$ is 2.6% HNO_2. In the case of 69.1% sulfuric acid, the limiting concentration of $HNOSO_4$ is 5.6% HNO_2. In acid containing 83.9% H_2SO_4 it is 12.8% HNO_2. For 94.1% sulfuric acid, the limiting concentration of nitrosyl sulfate is 18% HNO_2.

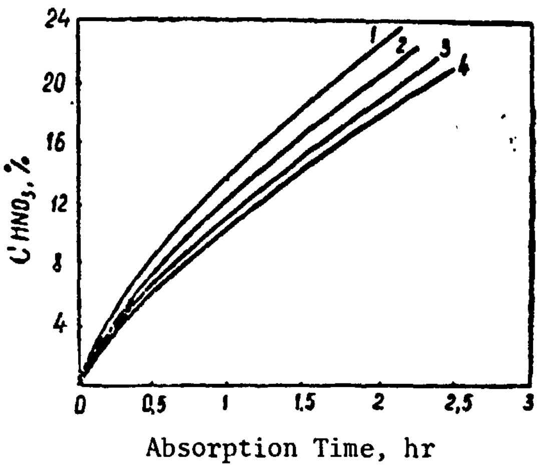

Figure 7. Change in Content of Nitric Acid During Absorption by Various Concentrations of Sulfuric Acid. H_2SO_4 Concentration in %: 1, 61; 2, 69; 3, 83.9; 4, 94

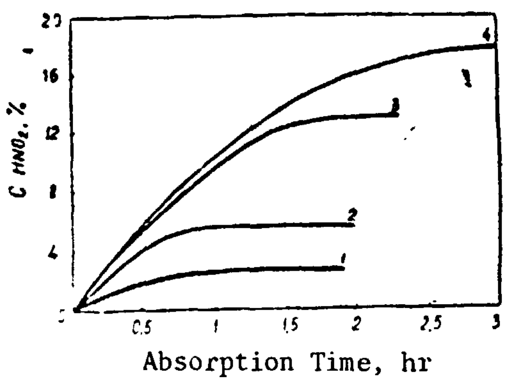

Figure 8. Change in Content of $HNOSO_4$ During Absorption with Various Concentrations of Initial Sulfuric Acid. H_2SO_4 Concentration in %: 1, 61; 2, 69; 3, 83.9; 4, 94

The dependence of limiting $HNOSO_4$ concentration on initial H_2SO_4 concentration in the solution is presented in Figure 9. Mathematical processing of these curves has shown that the limiting concentration of nitrosyl sulfate in the mixture changes in proportion to the concentration of sulfuric acid with an exponent of 4.25. The equation of this dependence is:

$$C^{lim}_{HNO_2} = A_3 \cdot C^{4.25}_{H_2OS_4}.$$

The equation for determination of the limiting concentration in a mixture as a function of the temperature, concentration of initial sulfuric acid and concentration of NO_2 in the gas is as follows:

$$C^{lim}_{HNO_2} = 0.1218 \cdot 10^{10} \cdot$$ /86

$$\cdot e^{1800/T} \cdot C^{0.57}_{NO_2} \cdot C^{4.25}_{N_2SO_4}.$$

Conclusions

1. The composition of mixtures formed upon abosrption of nitrogen dioxide by sulfuric acid is studied as a function of

temperature, H_2SO_4 concentration and concentration of NO_2 in the gas.

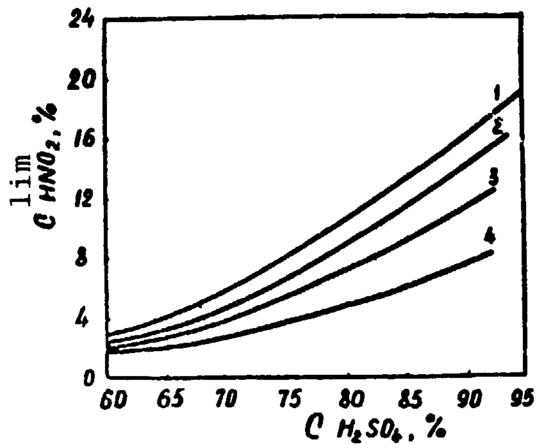

Figure 9. Limiting Concentration of $HNOSO_4$ as a Function of Initial Concentrat.. ›n of Sulfuric Acid in Solution. Content of NO_2: 1, 40; 2, 30; 3, 20; 4, 10

2. It is found th.. in the process of absorption of NO_2, mixtures consisting of HNO_3 + $HNOSO_4$ + H_2SO_4 + H_2O are formed, containing quite definite "limiting" concentrations of $HNOSO_4$, dependent on the temperature, NO_2 concentration in the gas and concentration of the absorbing sulfuric acid.

3. The dependence of the limiting concentration of $HNOSO_4$ on temperature, NO_2 concentration in the gas and H_2SO_4 concentration is established.

4. An equation is produced for determination of the limiting concentration of $HNOSO_4$ in the mixture and its dependence on various factors.

5. The possibility is shown of producing mixtures of $HNOSO_4$ + HNO_3 + H_2SO_4 + H_2O with high HNO_3 content by absorption of nitrogen oxides.

REFERENCES

1. Lunge, G., Berl E Zt. angew. Chem., 19, 807, 1906.
2. Lunge, G., Berl E Zt. angew. Chem., 20, 1713, 1907.
3. Raschig, F., Zt. andew. Chem., 20, 1907.
4. Canforche, A and L. Rondier, Bl. Soc. Chim., 43, 1923.
5. Foerster, F., Blich i Zt. angew. Chem., 2017, 1910.
6. Gerbert-Geybovich, Kabanov, Krivosheyev, Ukr. Khim. Zh., 2.
7. Szego, L. and A. Malaguli, Uspekhi Khim. Prom. 2, 54, 1933.
8. Kuz'minikh, I. N., Khim. Prom., 11, 38, 1934.
9. Anakhov, I. N., Khim. Prom., 9, 7950.
10. Ganz, S. N., Khim. Prom., 7, 1956.
11. Beskov, Slizkovskaya, Khim. Prom., 1, 1935.