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# KNOWLEDGE OF THE SYSTEM $H_2O$-$SO_3$-$N_2O_3$ REPORT I. THE SYSTEM $H_2SO_4$-$H_2O$-$N_2O_3$

K. Stoppe‡ka, F. Kilz

Translation of Zur Kenntnis des Systems $H_2O$-$SO_3$-$N_2O_3$ I, "Ueber das System $H_2SO_4$-$H_2O$-$N_2O_3$". Zeitschrift für anorganische und allgemeine Chemie. Vol. 348, 1966, pp. 58-70.



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16. Abstract

The amount of $N_2O_3$ being absorbed in 50-100% $H_2SO_4$ at 19, 60, and 95°C is directly proportional to the acid concentration and inversely proportional to the temperature. $NO^+$ formation according to the above-formulated equation occurs only at $H_2SO_4$ concentrations greater than 52%. Absorption in highly concentrated sulfuric acid results in the formation of crystalline $NOHSO_4$ (powder data being communicated.).

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# KNOWLEDGE OF THE SYSTEM $H_2O$-$SO_3$-$N_2O_3$. REPORT I.
# THE SYSTEM $H_2SO_4$-$H_2O$-$N_2O_3$

K. Stopperka, F. Kilz

SUMMARY /58*

The amount of $N_2O_3$ being absorbed in 50-100% $H_2SO_4$ at 10, 60, and 95°C is directly proportional to the acid concentration and inversely proportional to the temperature. $NO^+$ formation, according to the above-formulated equation occurs only at $H_2SO_4$ concentrations greater than 52%. Absorption in highly concentrated sulfuric acid results in the formation of crystalline $NOHSO_4$ (powder data being communicated).

## 1. INTRODUCTION

$N_2O_3$ in the gas phase is not available in pure form under standard pressure and temperature, but rather the following equilibrium results from an equal mole-mixture of NO and $NO_2$ for the constituents NO, $NO_2$, $N_2O_3$ and $N_2O_4$ [1, 2]:

$$NO + NO_2 = N_2O_3 \quad (I)$$
$$NO_2 + NO_2 = N_2O_4 \quad (II)$$
$$2NO + N_2O_4 = 2N_2O_3 \quad (III)$$

According to Abel and Proisl [1], at 25°C and 760 torr, only 10% /59 of an equimolar mixture of NO and $NO_2$ is present as undissociated $N_2O_3$. Thus, it would be possible that competing reactions occur during the absorption between $N_2O_3$, $NO_2$, $N_2O_4$ and NO on the one hand, and sulfuric acid on the other. Studies by other authors [3-8] and our own observations lead to the conclusion that in this gas mixture the main mass of the $N_2O_3$ in this equilibrium reacts with the sulfuric acid. The momentary adjustment of the $N_2O_3$ - equilibriums (I and III) proceeds very fast and the $N_2O_3$ taken from the equilibrium system by the absorption is instantly replenished.

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* Numbers in margin indicate pagination in original foreign text.

It was recognized very early that $N_2O_3$ reacts with sulfuric acid to form $NOHSO_4$ [9-14]. However, these qualitative studies were mostly aimed at clarifying the reaction mechanisms in the lead chamber process [15] and resulted in most contradictory statements.

Millen [16] was the first to state that the following reaction occurred:

$$N_2O_3 + 3\,H_2SO_4 \rightleftharpoons 2\,NO^+ + 3\,HSO_4^- + H_3O^+. \qquad \text{(IV)}$$

He arrived at this conclusion after an evaluation of Raman spectrographs run on the reaction products of the replacement reaction between concentrated sulfuric acid and liquid $N_2O_3$.

Chanukvadze and colleagues [17] believe to have established a compound $H_2SO_4 \cdot N_2O_3$ (m.p. 56°C) in the $H_2SO_4 - H_2O - N_2O_3$ system which decomposes when heated to 70-80°C. In addition, they examined the solubility of $N_2O_3$ in 72.2, 48.45 and 26.68% sulfuric acid and determined that the solubility of $N_2O_3$ decreases with decreasing acid concentration.

Since an accurate knowledge of the $H_2SO_4 - H_2O - N_2O_3$ system is of basic importance to the tower sulfuric acid industry, it seemed desirable to take up the studies of the $SO_3 - H_2O - N_2O_3$ system again. /60

## 2. TEST RESULTS AND DISCUSSION

### 2.1 Absorption of $N_2O_3$ in sulfuric acid

The measurements of absorption were performed with the apparatus illustrated in Figure 1.

A graphic illustration of the absorption process is shown in Figure 2.

In general, it was determined that the absorbed quantity of $N_2O_3$ increases with decreasing temperature and increasing acid concentration. Up to a sulfuric acid concentration of 80%, the curves derived from the test data at 19, 60, and 95°C have similar courses. Only above the named concentration does a difference appear. The slope change of the curve at 19°C and about 80% $H_2SO_4$ - which leads to an intersection with the curve at 60°C in the direction of greater sulfuric acid concentrations - is /61

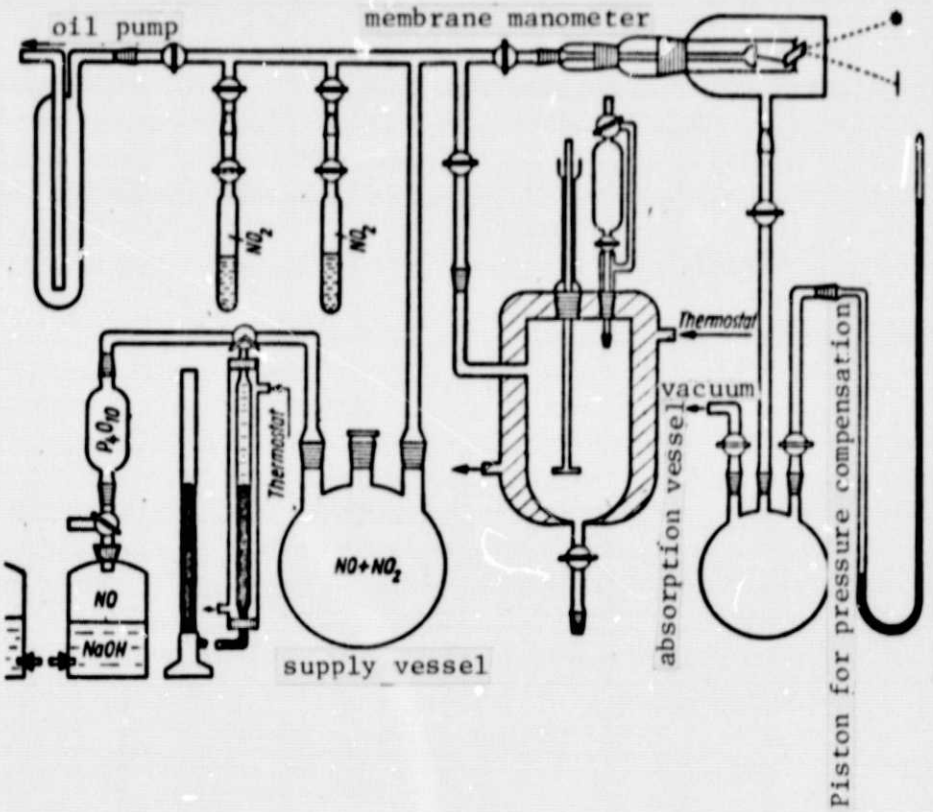


Figure 1: Measurement apparatus.



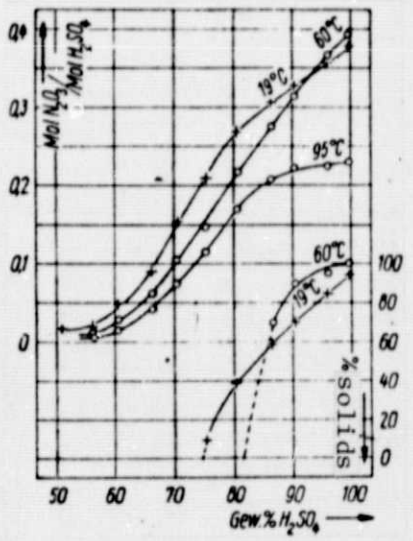


Figure 2: Course of absorption.

understandable if we remember the amount of solids precipitating during the absorption process [18] (bottom curves in Figure 2).

This portion of solids is 40% in the sulfuric acid concentration mentioned above, and is already so great that the mixing of the crystal slurry by the agitator is insufficient, i.e., the sulfuric acid clinging to the crystals is removed from the reaction with $N_2O_3$. For the 60°C and 95°C test series, this effect did not

occur. In this temperature range, no solids precipitate during the absorption. Only after cooling off to room temperature does the precipitation begin in the $N_2O_3$-saturated sulfuric acid solutions treated at 60°C and 86% $H_2SO_4$. The absorption solutions of the 95°C test series, however, remain clear even at room temperature and do not precipitate after standing.

The relatively low $N_2O_3$-uptake of the more highly-concentrated sulfuric acids in the 95°C test series is apparently due to the fact that pure $NOHSO_4$ melts and decomposes at 73.5°C and this tendency to decompose acts against the formation of a higher $NO^+$-ion concentration.

The measurements permit us to draw the conclusion that the absorbed $N_2O_3$ quantity will continue to fall for additional increases in temperature of the absorbant solution.

The absorbant temperature, the rate of agitation and the degree of $N_2O_3$ saturation of the absorption solutions are of particular influence on the rate of absorption. As a result of supersaturation a clear reduction in the rate of absorption occurs shortly before the precipitation; however, this reduction ceases immediately after the onset of crystallization.

If we observe the concentration range in Figure 2, in which the sulfuric acid solutions react with $N_2O_3$ to form nitrosyl ions, then the question of the reaction mechanism assumes a greater interest. On the basis of the IR-spectrographic studies of the $H_2SO_4$ - $H_2O$ system, it was recently demonstrated [19] that the region of existence for molecular sulfuric acid in the $H_2SO_4$ - $H_2O$ system lies between 75% and 100% $H_2SO_4$. In this range, the concentration of molecular sulfuric acid increases to the extent that the $HSO_4^-$ ion concentration falls. This concentration has the value of zero when the $H_2SO_4$ reaches 100% concentration. However, from the previous studies it is quite clear that even in the concentration range of 52% - 75% $H_2SO_4$ definite reactions with $N_2O_3$ occur. The reaction mechanism suggested by Millen [16] and by Gillespie and colleagues [20] in accordance with equation (IV) cannot be correct. Rather, if we regard the region of existence for $H_2O$ and $H_3O^+$, demonstrated by the studies on the $H_2SO_4$ - $H_2O$

/62

system [19], then it is clear that a noticeable reaction occurs between the aqueous sulfuric acid and the $N_2O_3$, even at concentrations at which the concentration ratio of $H_3O^+$ to $H_2O$ is shifted far toward the formation of $H_3O^+$; and that in addition, only small amounts of molecular water are detected. It thus appears more correct to us to formulate the reaction mechanism according to the following equation (V):

$$2\,H_3O^+ + N_2O_3 \rightleftharpoons 2\,NO^+ + 3\,H_2O. \qquad (V)$$

The erroneous assumption of earlier authors that only molecular sulfuric acid was capable of reacting with $N_2O_3$, according to equation (IV) to form $NO^+$ ions is attributable to the fact that they considered the molecular sulfuric acid to be the reaction partner with $N_2O_3$ rather than the agent which pulled water from the equilibrium (V) to hydrate its dissociation products and thus shifted this equilibrium to the right. If the necessary water were not drawn from the equilibrium according to equation (V) by subsequent reactions, then the $NO^+$ ion would not be able to stabilize. These phenomena were particularly evident when the experiment to absorb $N_2O_3$ in aqueous sulfuric acid (less than 50% $H_2SO_4$) was performed with the apparatus described in Figure 1. Whereas no reaction with formation of $NO^+$ ions was observed in the concentration range from 0 - 45% $H_2SO_4$ - except for a low physical dissolving [21] of the $N_2O_3$, at concentrations between 45% and 52% $H_2SO_4$ a low level of reaction must be occurring because of the slightly blue coloration of the absorption solution. According to Seel [22], the sometimes very intense colorations appearing at higher sulfuric acid concentrations can be attributed to the formation of nitric oxide nitrosyl ions according to equation (VI). This coloration passes from blue to green, and finally yellow. /63

$$NO^+ + NO \rightleftharpoons N_2O_2^+. \qquad (VI)$$

2.2 IR-Spectra of the Absorption Solutions.

The IR-spectra of the absorption solutions taken between silicon discs are shown in Figure 3.

If we compare these spectra with those of blank sulfuric acids of the same concentrations [19], then the dilution expected from

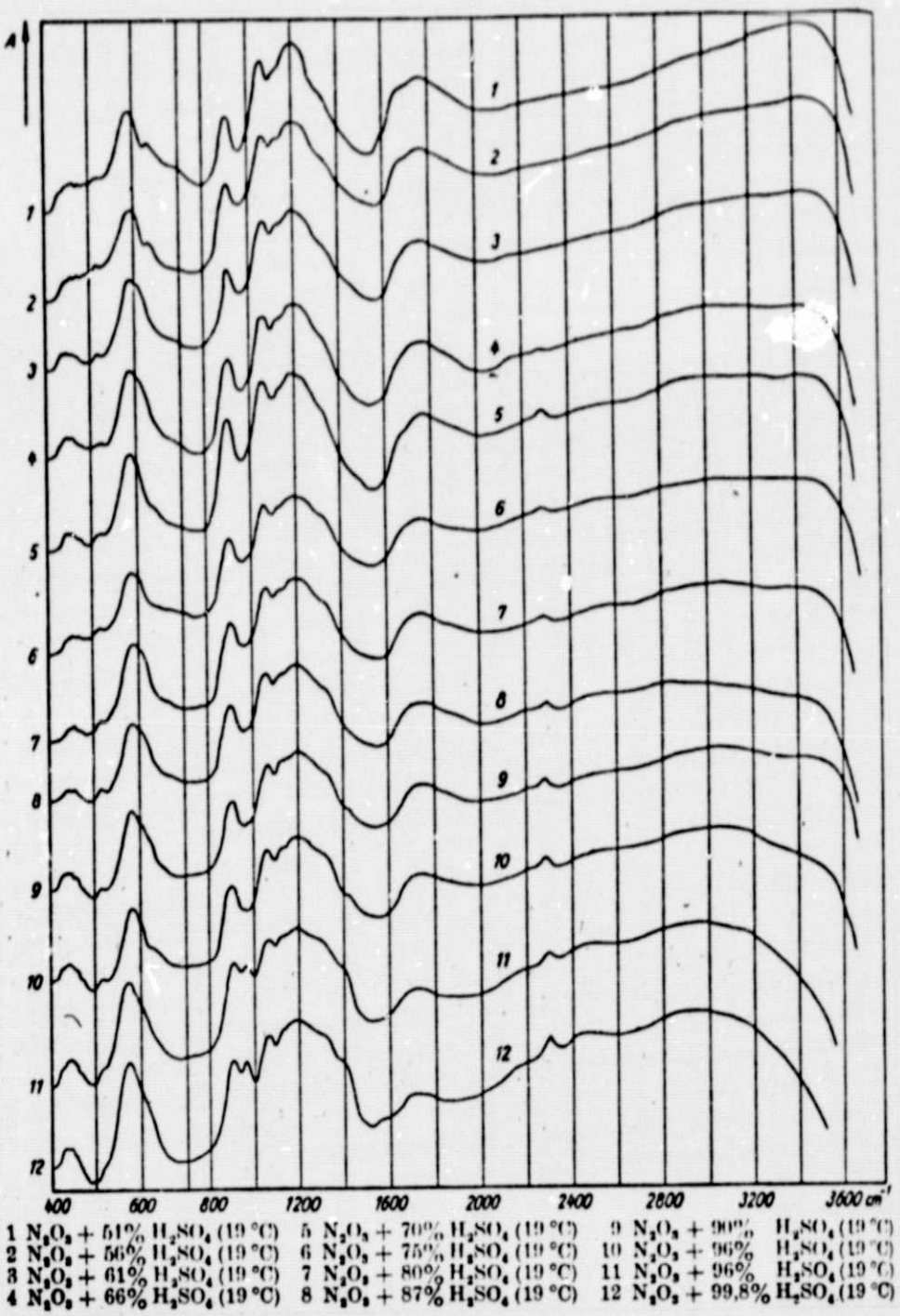


Figure 3: IR-spectra of the $N_2O_3$-saturated absorption solutions.

from equation (V) can be found, especially at the higher concentrations (at which more $N_2O_3$ was absorbed).

Although the $\nu_{as}S(OH)_2$ of molecular sulfuric acid is weak at 975 $cm^{-1}$ in the IR-spectrum of a pure sulfuric acid sample of 90% $H_2SO_4$, and becomes strong for 90% $H_2SO_4$, this characteristic band for molecular $H_2SO_4$ was not observed, even in the IR-spectrum of an absorption solution of 96% $H_2SO_4$ treated at 19°C. However, if the absorption of $N_2O_3$ in 96% sulfuric acid is performed at 95°C, then the decreased $N_2O_3$-absorption seen in Figure 2 results in a lower level of dilution according to equation (V) which can be clearly seen by the appearance of the $\nu_{as}S(OH)_2$ of $H_2SO_4$ at 975 $cm^{-1}$.

The characteristic absorption frequency [16, 23-25] for the $NO^+$ ion around 2300 $cm^{-1}$ which corresponds to the $\nu NO^+$ appears weak in spectrum 4 of Figure 3, but becomes more pronounced in the more highly concentrated absorption solutions.

Absorption bands which could be attributed to the oscillations of the nitryl ion [26-28] were not observed. Thus, the condition necessary for an unequivocal absorption process - that only $N_2O_3$ reacts with the sulfuric acid according to equation (V), is confirmed. If a competing or secondary reaction proceeded between $NO_2$ or $N_2O_4$ and the absorption solution, then nitryl ions would /65 be detectable according to equation (VII):

$$N_2O_4 + 2\,H_3O^+ \rightleftharpoons NO^+ + NO_2^+ + 3\,H_2O. \qquad \text{(VII)}$$

But since no absorption bands of nitrate ions are found in spectra 1 and 2 of Figure 3 - the latter could have resulted from the reaction of the $NO_2$ or $N_2O_4$, according to equation (VIII):

$$3\,NO_2 + 3\,H_2O \rightleftharpoons NO + 2\,H_3O^+ + 2\,NO_3^- \qquad \text{(VIII)}$$

and since noticeable $N_2O_2^+$ ion concentrations are detected on the basis of the pale blue coloring, it can be explained by an $NO_3^-$ concentration which is less than the detection limit, or it is explained by Milligas [4] according to equation(IX):

$$2\,NO + 4\,H_3O^+ + NO_3^- \rightleftharpoons 3\,NO^+ + 6\,H_2O. \qquad \text{(IX)}$$

## 3. EXPERIMENTAL SECTION

### 3.1 Apparatus and Empirical Methods

The apparatus used is shown in Figure 1. It can be coarsely

divided into three parts: the gas dosage unit, the absorption vessel and the device for regulating pressure.

The absorption vessel was provided with a thermostat, an agitator and a dropping funnel. The absorption solutions could be drained off by a stopcock for further examination.

It was difficult to find a method which made possible an accurate gas dosage. The simplest way, namely that of a volumetric dosage of a gas mixture prepared by mixing equal volumes of NO and $NO_2$ (or $N_2O_4$) cannot be considered if we remember the equilibrium from equation (II) since there is no blocking liquid which satisfies the requirements. Addition of the appropriate quantity of oxygen to a given quantity of NO,so that half of the NO reacts to form $NO_2$ in the desired final ratio of 1:1 for both components, fails because the NO dried for the absorption measurement over phosphorus (V)-oxide, will not react, or will react only incompletely - with oxygen [29-31].

Liquid $N_2O_3$ can be vaporized and the decrease in weight in the supply vessel could be used as a measure of the quantity of $N_2O_3$ absorbed; however, this will also not meet the requirements since $N_2O_3$ distills incongruously. Consequently, a preset quantity of liquid $N_2O_3$ must be quantitatively converted to the gaseous state to get an actual equimolar gas mixture. Difficulties are encountered here with regard to the 760-Torr pressure which is supposed to exist in the apparatus at the end of the absorption. Moreover, it must always be possible to quickly supplement the $N_2O_3$ consumed by the absorption, in the proper ratio.

We decided to introduce NO and $NO_2$ in equal quantities into a supply chamber as follows: Nitrogen monoxide was measured volumetrically by using Hg as the barrier liquid. Nitrogen dioxide was vaporized into the apparatus from a supply vessel and determined by weighing. In order to be able to control the dosage of both gases before and during the absorption as well as the pressure ratios in the apparatus, a manometer was needed. The indirect pressure measurement by means of a glass-membrane manometer [32-36] in balancing circuit design proved to be the simplest and /66
most suitable for our purposes. The membrane had reproducible sensitivity to pressure differences of 1.5 Torr. In our apparatus

with a capacity of about 2 liters, that meant that 4 $cm^3$ of gas had to be admitted before any reading of the pressure change would occur by the glass-membrane manometer. If two gases were present, which did not react with each other and which did not associate or dissociate, then one could admit a volume of each component which corresponded to a pressure change of 380 Torr and thereby arrive at a total pressure of 760 Torr. But since the components $NO_2$, $N_2O_4$, NO and $N_2O_3$ are present in the gas mixture, the corresponding equilibria (equations I-III) must be remembered.

For a mathematical formulation of the total system with its equilibria, in the first step, the partial pressure [37] of $N_2O_3$ is neglected - this is only permissible at normal pressure for temperatures above 150°C [1]. For $P_{ges}$**, we have the following equation

$$p_{ges.} = p_{NO} + p_{NO_2} + p_{N_2O_4}. \tag{1}$$

we need

$$p_{NO} = 2\,p_{N_2O_4} + p_{NO_2}. \tag{2}$$

From (1) and (2) we have

$$3\,p_{N_2O_4} + 2\,p_{NO_2} = p_{ges.}. \tag{3}$$

In addition, for the equilibrium from equation (II), when $p_o$ is the pressure of $N_2O_4$ before dissociation:

$$p_{NO_2} = 2\alpha\,p_o \tag{4}$$

$$p_{N_2O_4} = (1-\alpha)\,p_o. \tag{5}$$

From (4) and (5), we have

$$p_{N_2O_4} = \frac{p_{NO_2}}{2\alpha}(1-\alpha) \tag{6}$$

or

$$p_{NO_2} = \frac{2\alpha}{(1-\alpha)} \cdot p_{N_2O_4}. \tag{7}$$

For $p_{N_2O_4}$, we then have from (3) and (4),

$$p_{N_2O_4} = \frac{p_{ges.}}{3+\alpha^*}(1-\alpha^*). \tag{8}$$

From the requirement that $p_{ges}$ = 760 Torr and the calculated $p_{N_2O_4}$ from (8) by means of an assumed $\alpha^*$-value, $p_{NO_2}$ can be determined from (3). Now, all quantities are known so that finally, the value of $p_{NO}$ can be calculated from (1).

**translator's note - ges = total.

Experimentally, we proceeded so that NO was admitted into the apparatus illustrated in Figure 1 (supply and absorption vessels) through a burette until the calculated value for $p_{NO}$ had been reached. From the $NO_2$-supply vessel, gas was added slowly until a total pressure of 760 Torr was reached for the gas mixture of $N_2O_4$ and $NO_2$ in the apparatus according to the equilibrium (II). By determining the weight differences, the $NO_2$-mass was converted to a $NO_2$-volume and compared to the NO-volume read from the burette. If the requirement $v_{NO} = v_{NO_2}$ was not met, then the given $\alpha^*$-value was corrected again. The $\alpha^*$-value was varied until the $NO_2$-volume corresponded to the NO volume. At a temperature of 19°C, the $\alpha^*$-value determined by approximation equalled 0.10. /67

The simplification needed for mathematical formulation - namely, the initial neglect of $p_{N_2O_3}$ - was then corrected by a pre-given $\alpha^*$ which had been checked for accuracy against the criterion that $v_{NO_2} = v_{NO}$, since this includes the equilibria (I) and (III).

When admitting the sulfuric acid solution into the absorption vessel, the total pressure falls in the apparatus as a result of the absorption of the $N_2O_3$-portion at equilibrium, and NO and $NO_2$ must be supplemented to maintain the 760 Torr pressure. If the calculation of $p_{NO}$ as described above is to succeed, then $\alpha^*$ must be independent of pressure or be a linear function of the pressure.

But both requirements are not quite correct; rather, from

$$Kp_{NO_2/N_2O_4} = \frac{4\alpha^2}{1-\alpha^2} p_{ges.} \quad \text{we have} \quad \alpha_{N_2O_4} = \sqrt{\frac{Kp}{4p_{ges.} + Kp}}$$

or from

$$Kp_{NO,\,NO_2/N_2O_3} = \frac{\alpha^2}{1-\alpha^2} p_{ges.} \quad \text{we have} \quad \alpha_{N_2O_3} = \sqrt{\frac{Kp}{p_{ges.} + Kp}}.$$

However, from our studies it turned out that a sufficiently accurate calculation of the partial pressure is possible nevertheless. This fact is understandable if we examine the pressure dependence of the $\alpha$-values for the equilibria (I) and (II) more closely.

In Figure 5, the degree of dissociation is plotted as a function of the pressure for equilibrium (II) at 20°C according to

Natanson [38].

Figure 4 shows the same dependence for equilibrium (I) according to Abel and Proisl [1] at 25°C.

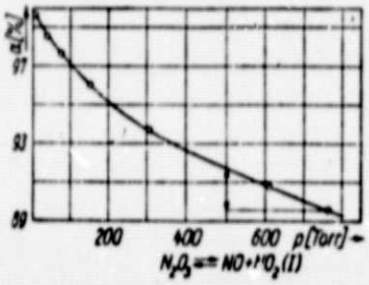


Figure 4: Pressure dependence of the degree of dissociation α for equilibrium (II)

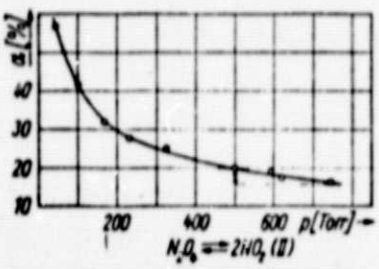


Figure 5: Pressure dependence of the degree of dissociation α for equilibrium (II)

From the course of the curves, we can see that the influence of pressure on the degree of dissociation is relatively low in the region of importance to the measurements (about 500-760 Torr). The maximal deviations for equilibrium (II) are 4% of the α-value; for equilibrium (I), 2% of the α-value. As the experimental results confirm, these changes have no noticeable influence and lie within the limits of error of the measurement method. /68

In the following tables, the measured values for the absorption of $N_2O_3$ in sulfuric acid are summarized:

The volume data relate to standard conditions of temperature and pressure.

Table 1: Measured Values of the Absorption performed at 19°C.

| weight-% $H_2SO_4$ | l $N_2O_3$ / 100 g $H_2SO_4$ | Mol $N_2O_3$ / Mol $H_2SO_4$ | color of solution | % prec | °C m.p. | % N | % S |
|---|---|---|---|---|---|---|---|
| 50,7 | 0,21 | 0,018 | black blue | | | | |
| 56,3 | 0,27 | 0,021 | blue | | | | |
| 60 5 | 0,50 | 0,050 | green | | | | |
| 66,3 | 1,38 | 0,091 | yellowgreen | | | | |
| 70,2 | 2,47 | 0,154 | " | | | | |
| 75,2 | 3,60 | 0,209 | " | 10 | 73 | 10,8 | 25,0 |
| 80,4 | 4,97 | 0,271 | " | 40 | 71 | | |
| 86,8 | 6,10 | 0,308 | yellow | 60 | 71 | 10,9 | 25,2 |
| 90,1 | 6,78 | 0,329 | " | 70 | 72 | | |
| 96,1 | 7,88 | 0,358 | " | 85 | 71 | 10,8 | 25,1 |
| 99,8 | 8,68 | 0,381 | " | 95 | 72 | 10,9 | 25,1 |

Table 2: Measured values of the Absorption performed at 60°C.

| weight-% $H_2SO_4$ | $\frac{l\ N_2O_3}{100\ g\ H_2SO_4}$ | Mol $N_2O_3$ / Mol $H_2SO_4$ | color of solution | % prec | °C m.p. | % N | % S |
|---|---|---|---|---|---|---|---|
| 56,3 | 0,15 | 0,012 | entirely blueblack | | | | |
| 60,5 | 0,38 | 0,028 | black | | | | |
| 66,3 | 3,95 | 0,092 | bluegreen | | | | |
| 70,2 | 4,68 | 0,105 | yellowgreen | | | | |
| 75,2 | 2,53 | 0,147 | yellow | | | | |
| 80,4 | 3,93 | 0,214 | " | | | | |
| 86,5 | 5,43 | 0,275 | " | 70 | 72 | 10,9 | 25,2 |
| 90,1 | 6,50 | 0,316 | " | 90 | 71 | 11,0 | 25,1 |
| 96,1 | 8,08 | 0,368 | " | 95 | 73 | 10,9 | 25,2 |
| 99,8 | 9,01 | 0,395 | " | 100 | 72 | 10,8 | 25,0 |

Table 3: Measured values of the Absorption performed at 95°C. /69

| weight-% $H_2SO_4$ | $\frac{l\ N_2O_3}{100\ g\ H_2SO_4}$ | Mol $N_2O_3$ / Mol $H_2SO_4$ | color of solution |
|---|---|---|---|
| 56,3 | 0,005 | 0,0076 | entirely blueblack |
| 60,5 | 0,21 | 0,015 | yellowblack |
| 66,3 | 0,65 | 0,043 | yellow |
| 70,2 | 1,22 | 0,076 | yellow |
| 75,2 | 1,97 | 0 115 | yellow |
| 80,4 | 3,10 | 0,169 | yellow |
| 86,5 | 4,12 | 0,208 | 1,01 green<br>1,51 violet<br>2,61 yellow |
| 90,1 | 4,58 | 0,223 | 1,21 green<br>2,21 violet<br>2,51 yellow |
| 96,1 | 4,92 | 0,226 | Only a brief, |
| 99,8 | 5,24 | 0,230 | weak green and violet coloration |

3.2 Solutions

The sulfuric acids needed for the absorption were prepared by dilution of concentrated $H_2SO_4$. A precise determination of concentration was performed by titration or, in the case of the 100% $H_2SO_4$, by conductivity measurement.

$NO_2$ was prepared according to the method of Meldrum [ ] from copper and nitric acid in a stream of oxygen.

Of the different methods for preparing NO, we selected that of Johnston and Glauque [40] in which semi-concentrated sulfuric acid is added by drops to a solution of $KNO_2$ and KI.

The gases were dried before the absorption measurements by phosphorus (v)-oxide.

3.3 Analysis

The sulfur determination was done gravimetrically as $BaSO_4$. For the nitrogen determination, the available $N^{3+}$ was reduced by Devard-alloy and determined according to Kjeldahl.

3.4 Spectra

The spectra were taken with the UR 10 of the People's Carl Zeiss Co., Jena. The preparation and recording techniques of Stopperka [19] were applied.

3.5 X-ray Photographs /70

The goniometer recordings were prepared with the horizontal counter tube goniometer of the People's Freiberg Precision Mechanics Co. The locations of the X-ray interferences of $NOHSO_4$ are shown as a bar graph in Figure 6.

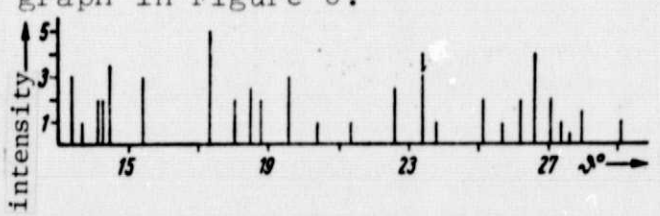


Figure 6: Powder data (debyeogram) of $NOHSO_4$.

The exact location of the interferences with the attendant intensities determined from 5 photographs can be seen in Table 4.

Photo conditions: Cu-$K_\alpha$ radiation, Ni-filter, 35 kV.

Table 4: X-ray Interference of $NOHSO_4$.

| ϑ | I | ϑ | I |
|---|---|---|---|
| 13,4 | 3 D | 23,4 | 4 D |
| 13,7 | 1 | 23,8 | 1 D |
| 14,15 | 2 | 25,15 | 2 D |
| 14,25 | 2 | 25,65 | 1 |
| 14,45 | 3–4 T | 26,2 | 2 D |
| 15,4 | 3 T | 26,6 | 4 D |
| 17,35 | 5 T | 27,05 | 2 D |
| 18,05 | 2 | 27,35 | 1 |
| 18,5 | 2–3 D | 27,6 | 0–1 |
| 18,8 | 2 | 27,95 | 1–2 D |
| 19,6 | 3 T | 29,1 | 1 |
| 20,4 | 1 | 30,1 | 2 T |
| 21,35 | 1 | 34,0 | 3 D |
| 22,6 | 2–3 D | 34,1 | 2 D |

D = doublet T = Triplet

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