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ARTICLE *in* THE JOURNAL OF PHYSICAL CHEMISTRY · SEPTEMBER 1996

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## Solubility of Nitrous Acid (HONO) in Sulfuric Acid Solutions

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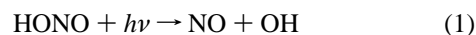
Received: April 18, 1996; In Final Form: June 24, 1996<sup>©</sup>

The Henry's law solubility of nitrous acid (HONO) has been studied in sulfuric acid solutions as a function of acid concentration in the range 0.3–73.6 wt % and temperature between 248 and 298 K by measuring the distribution of HONO between the gas and liquid phases using a bubbler-type gas–liquid reactor. Gas phase concentrations have been measured by highly sensitive tunable diode laser spectrometry, whereas the liquid phase has been analyzed by ion chromatography. At 298 K the Henry's law constant of HONO in sulfuric acid is well described for H<sub>2</sub>SO<sub>4</sub> concentrations < 53 wt % by  $K_H = (47.2 \pm 2.8) \exp[(-0.044 \pm 0.002) c_{\text{H}_2\text{SO}_4}] \text{ mol kg}^{-1} \text{ bar}^{-1}$ , with  $c_{\text{H}_2\text{SO}_4}$  in wt %. The exponential dependence of  $K_H$  on  $c_{\text{H}_2\text{SO}_4}$  that has been observed with increasing H<sub>2</sub>SO<sub>4</sub> concentration is explained by the Setschenow equation. The values of  $\Delta H_{\text{sol}}$  and  $\Delta S_{\text{sol}}$  for the dissolution of HONO have been determined as a function of sulfuric acid concentration. The results were fitted to a four-parameter equation that allows the calculation of the effective solubility of HONO in the temperature and concentration ranges studied. In addition, the equilibrium between HONO and NO<sup>+</sup> is discussed.

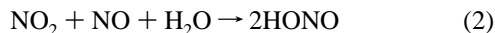
### Introduction

The chemical transformation and removal of atmospheric trace gases by heterogeneous processes is of great importance in atmospheric chemistry, since it is known that these processes can lead, for example, to significant changes in gas phase photochemistry. For the removal of atmospheric nitrogen compounds heterogeneous reactions leading to the final end-product HNO<sub>3</sub> are of special interest. However, these reactions may also lead to the formation of other nitrogen species such as nitrous acid (HONO).

Nitrous acid has recently attracted considerable attention, because the photolysis of HONO significantly enhances photooxidation processes early in the morning due to the rapid production of OH radicals:



The mechanisms by which HONO is formed in the atmosphere are not understood at present. Two gas phase reactions have been suggested:



However, the above reactions are much too slow to explain the observed nighttime HONO production rates.<sup>1</sup> Evidence of heterogeneous HONO production by the surface reaction of NO<sub>x</sub> (NO<sub>x</sub> = NO + NO<sub>2</sub>) with water vapor has been found in smog chamber studies.<sup>2–5</sup> In addition, heterogeneous production of HONO has also been proposed in order to explain the high HONO concentrations that have been measured in the troposphere.<sup>1,6–9</sup>

Since one of the potentially important routes for the formation of HONO is the heterogeneous reaction of NO<sub>x</sub> with liquid water, e.g., on the surface of a sulfuric acid aerosol followed by the liberation of this compound from the aqueous solution to the gas phase,<sup>10</sup> it is necessary to determine the aqueous phase

solubility of HONO, which has presently only been determined for pure water.<sup>11,12</sup> Also, because the liquid phase of the aerosol possibly exists as a highly concentrated acid solution such as has been observed in the polar sunrise experiment where the composition of the aerosol was found to be a sulfuric acid solution of ~70 wt %, <sup>13</sup> the Henry's law solubility of HONO has to be known not only for pure water but also for strong acids as a function of acid concentration and, additionally, as a function of temperature. Recently, the heterogeneous chemistry of HONO on liquid sulfuric acid has been investigated under conditions that prevail in the stratosphere by Zhang and co-workers.<sup>14</sup> The authors concluded from their experimental findings that the reaction of HCl with HONO on sulfate aerosols could provide a mechanism for chlorine activation and, subsequently, affect the stratospheric ozone balance. However, estimated Henry's law constants were used for these calculations, and therefore, the values are probably associated with a large degree of uncertainty.

In addition, the knowledge of the Henry's law solubility of HONO in sulfuric acid solutions is of importance since a recent study from our laboratory<sup>15</sup> showed that NO<sub>2</sub> is heterogeneously converted on acid surfaces into HONO and consecutively into N<sub>2</sub>O. Accordingly, the Henry's law solubility of HONO in strong acids is an important parameter to estimate the potential N<sub>2</sub>O source strength by this reaction sequence.

In the present study the Henry's law solubility of nitrous acid in sulfuric acid solutions has been studied as a function of acid concentration and temperature by measuring gas and liquid phase concentrations of HONO by highly sensitive tunable diode laser spectrometry (TDL) and ion chromatography, respectively.

### Experimental Section

The Henry's law solubility of nitrous acid in sulfuric acid solutions was studied under atmospheric pressure in a 11-L Pyrex glass reactor that was connected with a temperature-controlled bubbler. A schematic diagram of the experimental setup is shown in Figure 1. The Henry's law constant was determined by measuring the distribution of HONO between the gas and liquid phases. Gas phase concentrations of HONO,

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<sup>©</sup> Abstract published in *Advance ACS Abstracts*, August 15, 1996.

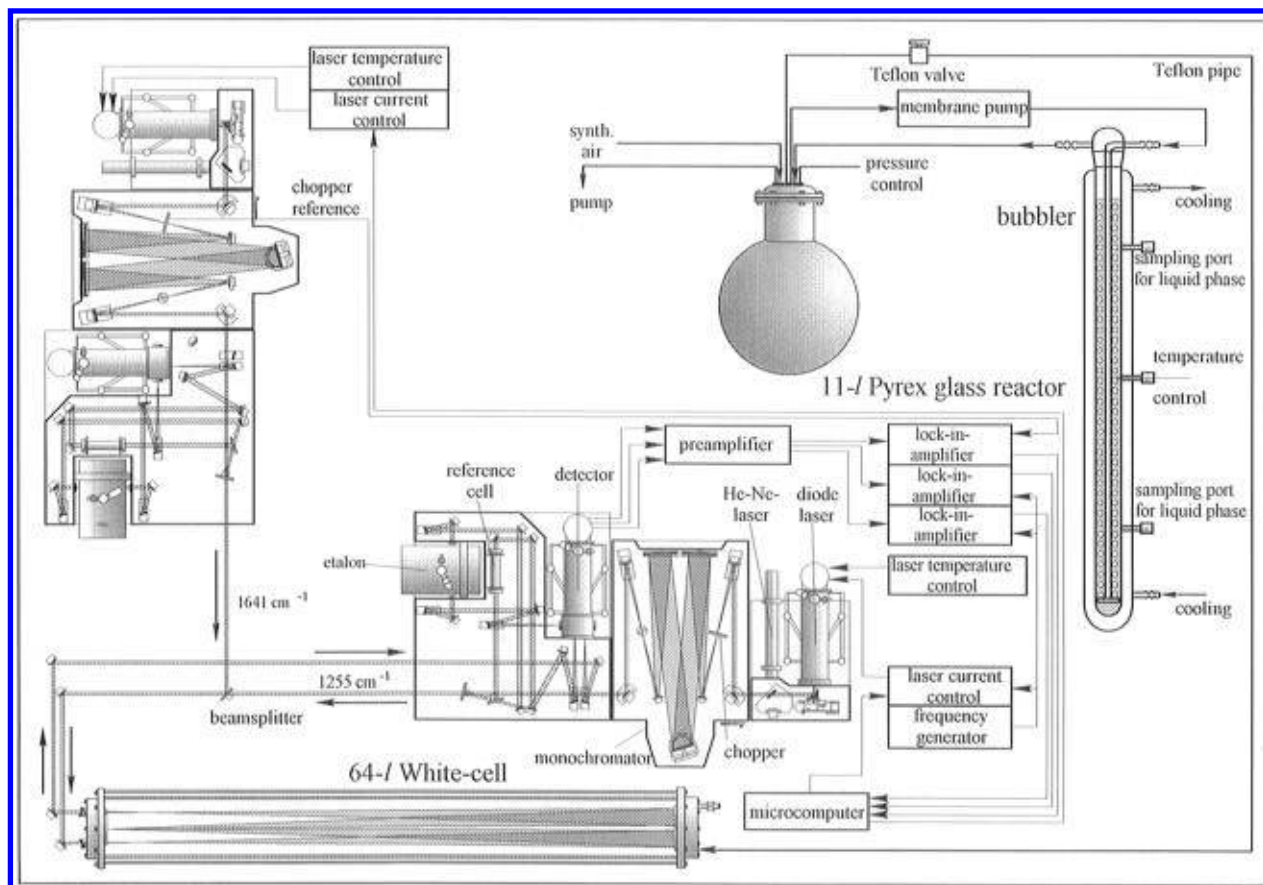


Figure 1. Schematic diagram of the experimental setup.

$\text{NO}_2$ , and  $\text{N}_2\text{O}$  were measured by time-resolved highly sensitive tunable diode laser spectrometry, whereas in the liquid phase HONO and  $\text{HNO}_3$  were analyzed by ion chromatography.

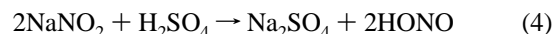
TDL transmission spectra were obtained by expanding a proportion of the gas mixture from the 11-L reactor through a Teflon pipe into a long path absorption cell that was equipped with a White mirror system. The optical path length used was 136 m. To exclude the influence of pressure broadening of the absorption lines, the total pressure in the White cell, which was measured by a calibrated capacity manometer (MKS Baratron), was always kept between 1 and 7 Torr. The absolute concentrations of HONO and  $\text{NO}_2$  were calculated from the transmission spectra using tabulated line strengths of single rotational vibrational lines.<sup>16,17</sup> The  $\text{N}_2\text{O}$  concentration was determined relative to the absorption signal of gas mixtures containing known concentrations of  $\text{N}_2\text{O}$ . The details of the diode laser spectrometer and the long path absorption cell have been described previously.<sup>18</sup>

The liquid phase concentrations of HONO and  $\text{HNO}_3$  were determined using a Shimadzu HIC-6A ion chromatograph. A Hamilton PRP-X 100 column was used for anion separation using a 0.1 mol/L phosphoric acid eluent at pH 6.7 and a flow rate of 1.5 mL/min. Samples of the liquid phase were taken with a syringe from the bubbler and were injected immediately into a solution of NaOH, resulting in a slightly alkaline solution in which the formed nitrite and nitrate ions were found to be stable for several days. It was shown that under the experimental conditions of the present study nitrite and nitrate concentrations down to 0.02 mg/L could be analyzed by UV absorption (Shimadzu SPD-6A) at 209 nm in the presence of sulfate concentrations up to 150 g/L. The calibration of the nitrite concentration was carried out by redox titration with  $\text{KMnO}_4$ . The sulfuric acid concentration was determined by standard titration with NaOH. For the conversion of the  $\text{H}_2\text{SO}_4$

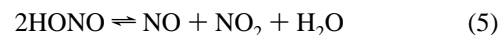
concentration from mol/L to mol/kg or to wt % a density function reported by Carslaw and co-workers<sup>19</sup> was used. The error in the sulfuric acid concentration was estimated to be  $\leq 0.5\%$ . Taking into account the uncertainties caused by the sampling method and the analyses of both gas and liquid phase, the systematic error in the Henry's law constant was estimated to be  $\leq 15\%$ .

## Results and Discussion

At the beginning of an experiment the reactor was filled with nitrogen, which was pumped continuously with a flow rate of 2.5 L/min through the bubbler containing a fixed volume of sulfuric acid, which was normally 500 mL. After approximately 15 min a slightly basic solution of  $\text{NaNO}_2$  was injected with a syringe into the acid, which caused rapid formation of HONO due to reaction 4:

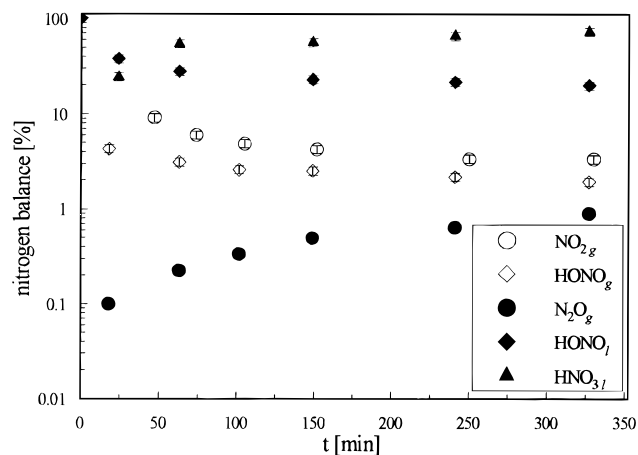


In addition to HONO, the formation of  $\text{NO}_2$  was observed according to reaction 5:



Furthermore, the formation of  $\text{HNO}_3$  and  $\text{N}_2\text{O}$  was observed, the latter of which was strongly dependent on the sulfuric acid concentration. The mechanism by which  $\text{N}_2\text{O}$  and  $\text{HNO}_3$  are formed in the reaction system is discussed in detail elsewhere.<sup>15</sup>

Figure 2 displays the temporal evolution of  $[\text{NO}_2]_g$ ,  $[\text{HONO}]_g$ ,  $[\text{N}_2\text{O}]_g$ ,  $[\text{HONO}]_l$ , and  $[\text{HNO}_3]_l$  at room temperature. Two hours after the injection of  $\text{NaNO}_2$  the establishment of an equilibrium between  $\text{HONO}_g$  and  $\text{HONO}_l$  was observed. After this time period the ratio  $[\text{HONO}]_l/[\text{HONO}]_g$  remained constant within experimental error for several hours. Therefore, one can assume



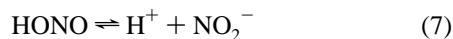
**Figure 2.** Semilogarithmic plot of the temporal evolution of  $\text{NO}_{2g}$ ,  $\text{HONO}_g$ ,  $\text{N}_2\text{O}_g$ ,  $\text{HONO}_l$ , and  $\text{HNO}_{3l}$  given as nitrogen balance [%] in the reaction of  $\text{NaNO}_2$  with sulfuric acid.

that the establishment of the equilibrium between gas and liquid phases was much faster than the slight decay in the  $\text{HONO}$  concentration that is caused by the formation of  $\text{N}_2\text{O}$  and  $\text{HNO}_3$ , which is discussed in detail elsewhere.<sup>15</sup> This is an important assumption for the calculation of the Henry's law constant  $K_H$ , which for a gas–liquid equilibrium is given by the ratio of the concentration of the dissolved species in the liquid and its partial pressure in the gas phase:

$$K_H = c_l / p \quad (6)$$

with  $c_l$  in  $\text{mol kg}^{-1}$  and  $p$  in bar.

$\text{HONO}$  rapidly establishes an equilibrium with nitrite and  $\text{H}^+$  according to equilibrium 7:



Therefore, a correction of the measured Henry's law constant  $K_H^*$  according to eq 8 had to be taken into account:

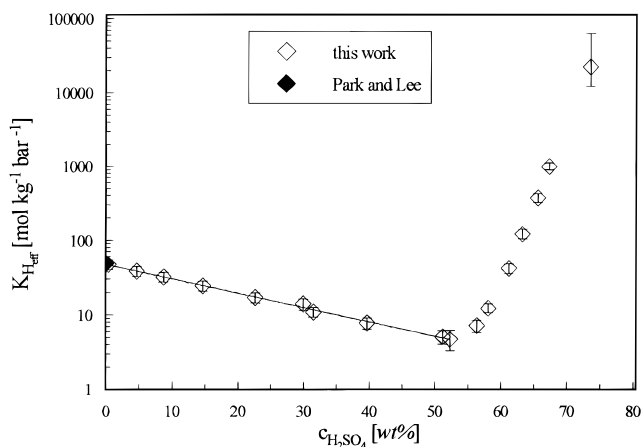
$$K_H = \frac{K_H^*}{1 + K_a/[\text{H}^+]} \quad (8)$$

$K_a$  is the dissociation constant for  $\text{HONO}$ , for which a value of  $5.3 \times 10^{-4} \text{ mol/L}$  reported by Park and Lee<sup>12</sup> was used. However, with the exception of the lowest  $\text{H}_2\text{SO}_4$  concentration it was shown that the correction could be neglected for all other sulfuric acid concentrations investigated since at higher sulfuric acid concentrations the equilibrium of the dissociation is completely shifted to the left side of equilibrium 7.

**Concentration Dependence at  $T = 298 \text{ K}$ .** In a first set of experiments the dependence of  $K_H$  on the sulfuric acid concentration was investigated at room temperature. The result of these experiments is shown in Figure 3 and is summarized in Table 1. For  $c_{\text{H}_2\text{SO}_4} < 53 \text{ wt } \%$  it was observed that the Henry's law constant decreases exponentially with increasing acid concentration. This behavior is quantitatively described by the following equation:

$$K_H = (47.2 \pm 2.8) \exp[(-0.044 \pm 0.002)c_{\text{H}_2\text{SO}_4}] \text{ mol kg}^{-1} \text{ bar}^{-1} \quad (9)$$

with  $c_{\text{H}_2\text{SO}_4}$  in wt %. The given error limits represent  $2\sigma$  and reflect the statistical precision only. For  $c_{\text{H}_2\text{SO}_4} > 53 \text{ wt } \%$  a significant increase of the Henry's law constant was observed with increasing  $\text{H}_2\text{SO}_4$  concentration caused by the formation



**Figure 3.** Semilogarithmic plot of the effective Henry's law constant of  $\text{HONO}$  in water ( $\blacklozenge$ ) given by Park and Lee<sup>12</sup> and in sulfuric acid ( $\diamond$ , this work) as a function of acid concentration ( $T = 298 \text{ K}$ ). The solid line is the result of a linear least squares fit to the experimental data for  $c_{\text{H}_2\text{SO}_4} \leq 53 \text{ wt } \%$ .

**TABLE 1: Effective Henry's Law Constants for the Dissolution of  $\text{HONO}$  in  $\text{H}_2\text{SO}_4$  at  $298 \text{ K}$**

$c_{\text{H}_2\text{SO}_4} [\text{wt } \%]$	$K_{H,\text{eff}} [\text{mol kg}^{-1} \text{ bar}^{-1}]$
0.3	$47.2 \pm 6.9$
4.6	$38.3 \pm 5.7$
8.7	$32.1 \pm 4.7$
14.6	$24.5 \pm 3.6$
22.6	$17.0 \pm 2.6$
30.0	$14.0 \pm 2.4$
31.5	$10.9 \pm 1.6$
39.7	$7.8 \pm 1.4$
51.2	$5.1 \pm 0.7$
52.3	$4.7 \pm 1.4$
56.4	$7.1 \pm 1.4$
58.1	$12.3 \pm 1.7$
61.2	$41.6 \pm 6.5$
63.3	$120 \pm 16$
65.6	$366 \pm 51$
67.3	$986 \pm 100$
73.6	$22290^{+40000}_{-10000}$

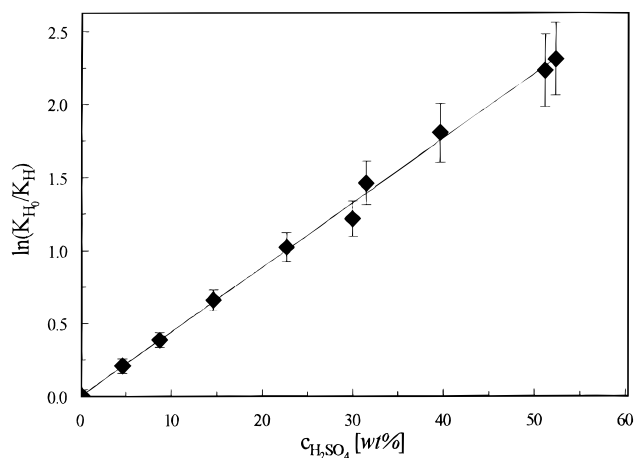
<sup>a</sup>Estimated error limits.

of nitrosylsulfuric acid ( $\text{NOHSO}_4$ ), as discussed in detail below. Therefore, the  $K_H$  values that were obtained for  $c_{\text{H}_2\text{SO}_4} > 53 \text{ wt } \%$  should be considered only as effective Henry's law constants,  $K_{H,\text{eff}}$ . For the dissolution of  $\text{HONO}$  in pure water a Henry's law constant of  $47.2 \pm 2.8 \text{ mol kg}^{-1} \text{ bar}^{-1}$  has been extrapolated from the experimental data of the present study, which is in excellent agreement with the literature value of  $48.5 \pm 3 \text{ mol kg}^{-1} \text{ bar}^{-1}$  reported by Park and Lee.<sup>12</sup>

The exponential dependence of  $K_H$  with increasing  $c_{\text{H}_2\text{SO}_4}$  is explained by the salt effect, which describes the solubility of a nonelectrolyte in an aqueous solution as given by the Setschenow equation:<sup>20</sup>

$$\ln\left(\frac{K_{H_0}}{K_H}\right) = k_s c \quad (10)$$

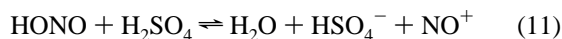
$K_{H_0}$  and  $K_H$  are Henry's law constants for the dissolution of the nonelectrolyte in pure water and in the electrolyte, in this case sulfuric acid, respectively;  $k_s$  is the salting coefficient and  $c$  is the concentration of the electrolyte. Figure 4 shows the excellent linearity obtained between  $\ln(K_{H_0}/K_H)$  and  $c_{\text{H}_2\text{SO}_4}$  for acid concentrations  $< 53 \text{ wt } \%$  at  $T = 298 \text{ K}$ . From the slope of a straight line a salting coefficient of  $0.044 \pm 0.002 \text{ wt } \%^{-1}$  was obtained. According to the electrostatic theory of the salt



**Figure 4.** Semilogarithmic plot of the ratio ( $K_{H_0}/K_H$ ) at  $T = 298$  K as a function of the sulfuric acid concentration according to the Setschenow equation. The solid line is the result of a linear least squares fit to the experimental data.

effect, HONO lowers the dielectric constant of water; that is, HONO is salted out by the electrolyte sulfuric acid.<sup>21</sup>

As already mentioned above, for sulfuric acid concentrations  $> 53$  wt % a rapid increase of the effective Henry's law constant was observed (see Figure 3), which is a result of the formation of nitrosylsulfuric acid via reaction 11:



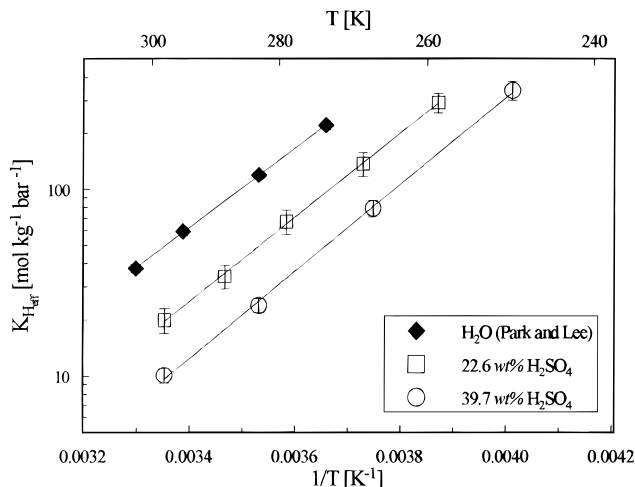
It has been previously shown that the equilibrium of  $\text{N}^{\text{III}}$  species in highly concentrated sulfuric acid involves several complex reactions between different nitrogen species and sulfuric acid.<sup>22</sup> The equilibrium between HONO and  $\text{NO}^+$  in  $\text{H}_2\text{SO}_4$  was studied in detail by Seel and Winkler at room temperature using UV spectroscopy.<sup>23</sup> The authors found the concentrations of  $\text{NO}^+$  and HONO to be equal in 55 wt %  $\text{H}_2\text{SO}_4$ . According to the equilibrium 11, the amount of soluble  $\text{N}^{\text{III}}$  species, i.e.  $\text{NO}^+$  and HONO, is increasing with increasing sulfuric acid concentration and, consequently, causes an increase of the effective Henry's law constant. The equilibrium 11 will be discussed in more detail below.

It should be pointed out that during the experiments HONO was detectable in the gas phase only for  $\text{H}_2\text{SO}_4$  concentrations  $\leq 74$  wt %. Accordingly,  $K_{H_{\text{eff}}}$  was measureable only for  $c_{\text{H}_2\text{SO}_4} \leq 74$  wt %.

**Temperature Dependence.** The temperature dependence of the effective Henry's law constant of HONO was investigated for different sulfuric acid concentrations in the range 248–298 K. Examples of the  $T$ -dependence of  $K_{H_{\text{eff}}}$  for three different sulfuric acid concentrations are shown in Figure 5. In Table 2 the effective Henry's law constants are summarized as a function of both temperature and sulfuric acid concentration. From plots of the data according to the following van't Hoff equation:

$$\ln K_H = -\Delta H_{\text{sol}}/RT + \Delta S_{\text{sol}}/R \quad (12)$$

values of  $\Delta H_{\text{sol}}$  and  $\Delta S_{\text{sol}}$  were obtained from the slopes and intercepts of the resulting straight lines, respectively. The thermodynamic data obtained from these plots are summarized in Table 3 for different  $\text{H}_2\text{SO}_4$  concentrations. For  $c_{\text{H}_2\text{SO}_4} < 53$  wt % the absolute values of  $\Delta H_{\text{sol}}$  and  $\Delta S_{\text{sol}}$  increase continuously with increasing acid concentration. However, for  $c_{\text{H}_2\text{SO}_4} > 53$  wt % eq 12 cannot be applied since the influence of nitrosylsulfuric acid formation and, consequently, the  $T$ -dependence of equilibrium 11 becomes more important. This is confirmed by the fact that the values of  $\Delta H_{\text{sol}}$  and  $\Delta S_{\text{sol}}$



**Figure 5.** Van't Hoff plot of the effective Henry's law constant of HONO for three different sulfuric acid concentrations. The solid lines are the result of linear least squares fits to the experimental data.

determined for  $c_{\text{H}_2\text{SO}_4} > 53$  wt % did not show a uniform trend with increasing acid concentration (see Table 3), and therefore, should be considered only as parameters describing the temperature dependence of  $K_{H_{\text{eff}}}$  and not the physical solubility.

To describe the effective Henry's law constant  $K_{H_{\text{eff}}}$  as a function of both temperature and  $\text{H}_2\text{SO}_4$  concentration, the solubility of HONO was calculated from the temperature dependences for different acid concentrations from Table 3. The result of the calculations is shown in Figure 6 for three different temperatures. Note that also for lower temperatures the shape of the curves is similar to that of the curve observed at room temperature. The curves can be described by the sum of two different exponential functions. Parametrization as a function of temperature yielded an equation from which the effective Henry's law constants can be calculated as a function of both temperature and  $\text{H}_2\text{SO}_4$  concentration:

$$K_{H_{\text{eff}}} = A_{(T)} \exp[B_{(T)} c_{\text{H}_2\text{SO}_4}] + D_{(T)} \exp[E_{(T)} c_{\text{H}_2\text{SO}_4}] \text{ mol kg}^{-1} \text{ bar}^{-1} \quad (13)$$

with  $c_{\text{H}_2\text{SO}_4}$  in wt %. The temperature dependence of the parameters  $A_{(T)}$ ,  $B_{(T)}$ ,  $D_{(T)}$ , and  $E_{(T)}$  is well described by the following equations:

$$A_{(T)} = 3.910 \times 10^{-6} \exp(4873/T) \text{ mol kg}^{-1} \text{ bar}^{-1}$$

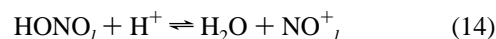
$$B_{(T)} = 12.86/T - 0.09146 \text{ wt \%}^{-1}$$

$$D_{(T)} = 1.771 \times 10^{-24} \exp(7902/T) \text{ mol kg}^{-1} \text{ bar}^{-1}$$

$$E_{(T)} = -35.69/T + 0.6398 \text{ wt \%}^{-1}$$

Equation 13 allows an excellent description of the experimental data that is shown by the solid lines in Figure 6 for three different temperatures. Only for low temperatures is a small difference between calculated and experimental data observed in the  $\text{H}_2\text{SO}_4$  concentration range where the minimum of the effective Henry's law constant occurs.

**Equilibrium  $\text{HONO} \rightleftharpoons \text{NO}^+$ .** As shown by Seel and Winkler,<sup>23</sup> HONO behaves like a triphenylcarbinol base. Accordingly, in solutions with high acidity the establishment of equilibrium 14 occurs:



**TABLE 2: Effective Henry's Law Constants for the Dissolution of HONO in H<sub>2</sub>SO<sub>4</sub> at Different Temperatures<sup>a</sup>**

$c_{\text{H}_2\text{SO}_4}$ [wt %]	$T$ [K]	$K_{\text{Heff}}$ [mol kg <sup>-1</sup> bar <sup>-1</sup> ]	$K_{\text{Heff}}$ (Fit) [mol kg <sup>-1</sup> bar <sup>-1</sup> ]	$K_{\text{Heff}}/K_{\text{Heff}}$ (Fit)
0.0	273	220 ± 11	216	1.02
	283	119.5 ± 5.9	116	1.03
	295	59.4 ± 3.0	57.8	1.03
	303	37.7 ± 2	37.4	1.01
	269	180 ± 23	191	0.94
8.7	278	108.5 ± 18.6	109	0.99
	285	67.8 ± 9.3	69.8	0.97
	291	46.5 ± 7.5	49.5	0.94
	298	32.1 ± 4.7	32.2	0.99
	258	246 ± 29	239	1.03
22.6	268	115 ± 17	114	1.01
	279	56.7 ± 8.4	53.8	1.05
	288	28.9 ± 4.2	29.4	0.98
	298	17.0 ± 2.6	16.3	1.04
	250	330 ± 40	322	1.02
31.5	267	87.2 ± 11.9	85.4	1.02
	283	24.4 ± 3.2	27.7	0.88
	298	10.9 ± 1.4	10.7	1.02
	249	253 ± 33	249	1.01
	267	59.1 ± 7.5	60.2	0.98
39.7	283	18.0 ± 3.0	18.8	0.96
	298	7.8 ± 1.4	7.17	1.07
	249	211 ± 27	167	1.27
	267	44.0 ± 5.5	38.3	1.15
	283	11.8 ± 1.4	11.7	1.00
51.2	298	5.1 ± 0.7	4.34	1.17
	246	226 ± 26	370	0.61
	259	92.1 ± 13.2	122	0.76
	272	38.0 ± 5.3	41.3	0.92
	286	12.9 ± 2.0	14.6	0.89
56.4	298	7.1 ± 1.4	6.3	1.13
	251	440 ± 65	409	1.08
	266	97.1 ± 13.1	112	0.86
	283	27.0 ± 4.0	29.8	0.91
	298	12.3 ± 1.7	10.6	1.16
61.2	250	2720 ± 320	1610	1.69
	268	398 ± 51	342	1.16
	283	112 ± 16	112	1.00
	298	41.6 ± 6.5	40.7	1.02
	250	5300 ± 3150	4220	1.25
63.3	265	1155 ± 180	1180	0.98
	283	283 ± 38	312	0.91
	298	120 ± 16	113	1.06
	254	9350 ± 3700	9840	0.95
	268	3190 ± 620	3130	1.02
65.6	283	897 ± 126	1030	0.87
	298	366 ± 51	376	0.97
	251	26600 ± 15300	28100	0.95
	268	7500 ± 3080	7380	1.02
	283	2520 ± 621	2420	1.04
67.3	298	986 ± 100	912	1.08

<sup>a</sup>Values for  $c_{\text{H}_2\text{SO}_4} = 0$  were taken from Park and Lee;<sup>12</sup>  $K_{\text{Heff}}$ , effective Henry's law constants obtained experimentally;  $K_{\text{Heff}}$  (Fit), effective Henry's law constants calculated using eq 13.

The corresponding equilibrium constant  $K$  is defined by

$$K = \frac{[\text{NO}^+][\text{H}_2\text{O}]}{[\text{HONO}][\text{H}^+]} \quad (15)$$

and can be calculated from the intercept of the straight line obtained from a plot of the logarithm of  $[\text{HONO}]/[\text{NO}^+]$  versus  $H_R$  according to eq 16:

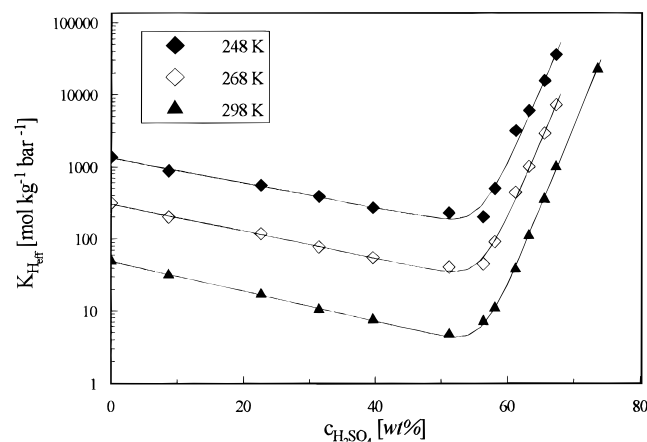
$$\log\left(\frac{[\text{HONO}]}{[\text{NO}^+]}\right) = H_R - \log(K) \quad (16)$$

$H_R$  is the experimental acidity function, which has to be used

**TABLE 3:  $\Delta H_{\text{sol}}$  and  $\Delta S_{\text{sol}}$  for Different Acid Concentrations from the Present Study<sup>a</sup>**

$c_{\text{H}_2\text{SO}_4}$ [wt %]	$\Delta H_{\text{sol}}$ [kJ mol <sup>-1</sup> ]	$\Delta S_{\text{sol}}$ [J mol <sup>-1</sup> K <sup>-1</sup> ]
0.0 <sup>b</sup>	-40.7 ± 0.6	-104.2 ± 2
8.7	-40.9 ± 1.8	-108.6 ± 6.4
22.6	-43.0 ± 1.3	-120.7 ± 4.5
31.5	-44.6 ± 1.3	-130.1 ± 13.6
39.7	-44.3 ± 1.9	-131.9 ± 7.0
51.2	-47.8 ± 3.3	-147.6 ± 12.0
56.4	-41.3 ± 2.4	-122.4 ± 8.8
58.1	-47.2 ± 5.8	-138.4 ± 21.0
61.2	-54.3 ± 4.0	-151.9 ± 14.4
63.3	-49.3 ± 4.8	-126.5 ± 17.5
65.6	-46.6 ± 3.1	-107.7 ± 11.2
67.3	-44.0 ± 0.5	-90.4 ± 1.6

<sup>a</sup> The given error limits represent  $2\sigma$  and reflect the statistical precision only. For  $c_{\text{H}_2\text{SO}_4} > 53$  wt % see text. <sup>b</sup>Values reported by Park and Lee.<sup>12</sup>



**Figure 6.** Effective Henry's law constant  $K_{\text{Heff}}$  as a function of the sulfuric acid concentration for three different temperatures. The values were calculated using the temperature dependences of the solubility of HONO in sulfuric acid given in Table 3. The solid lines are the result of calculations of the effective Henry's law constant using eq 13.

instead of the pH scale since acid solutions of high concentration have to be treated as nonideal.

However, to calculate the equilibrium constant 15 from the experimental data, two assumptions were made.

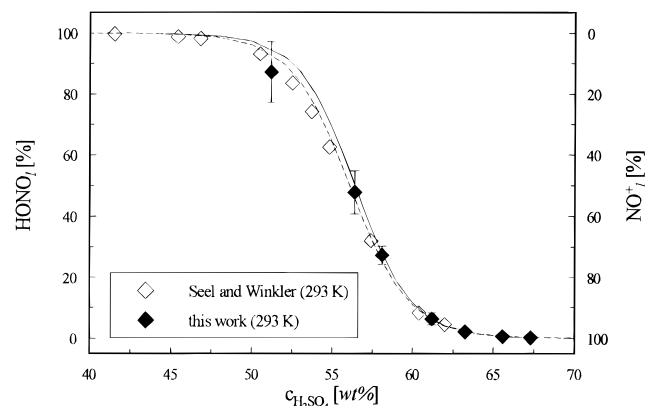
(1) The true Henry's law constant  $K_H$ , which is defined as the ratio of HONO dissolved and HONO in the gas phase, continues to decrease with increasing acid concentration even for  $c_{\text{H}_2\text{SO}_4} > 53$  wt %, and  $K_H$  can thus be obtained by extrapolation for  $c_{\text{H}_2\text{SO}_4} > 53$  wt % from the experimental data obtained in the concentration range 0–40 wt %.

(2) The increase of the effective Henry's law constant  $K_{\text{Heff}}$  for  $c_{\text{H}_2\text{SO}_4} > 53$  wt % results only from equilibrium 14.

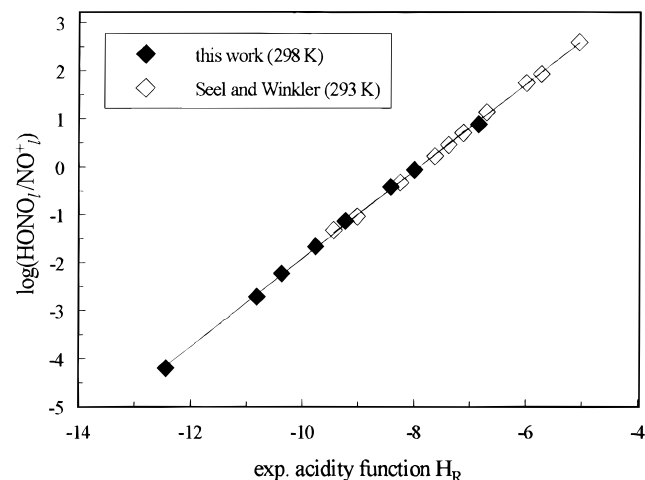
From Figure 6 it becomes obvious that these assumptions are reasonable for the temperature range investigated. On the basis of the assumptions made above the ratio  $[\text{HONO}]/[\text{NO}^+]$  can be calculated as a function of  $c_{\text{H}_2\text{SO}_4}$  from eq 17 using the corresponding effective Henry's law constant  $K_{\text{Heff}}$  and the true Henry's law constant  $K_H$ :

$$\frac{[\text{HONO}]}{[\text{NO}^+]} = \left(\frac{K_{\text{Heff}}}{K_H} - 1\right)^{-1} \quad (17)$$

This ratio can be converted into the amount of dissolved HONO in percent by:



**Figure 7.** Concentration of  $\text{HONO}_l$  and  $\text{NO}_l^+$  as a function of  $c_{\text{H}_2\text{SO}_4}$  for  $T = 293 \text{ K}$  compared with the data of Seel and Winkler,<sup>23</sup> (—) calculation for  $T = 293 \text{ K}$ ; (---) calculation for  $T = 248 \text{ K}$  using eqs 13 and 17.



**Figure 8.** Plot of  $\log(\text{HONO}_l/\text{NO}_l^+)$  determined in the present study versus the experimental acidity function  $H_R$  compared with the data of Seel and Winkler.<sup>23</sup>

$$[\text{HONO}_l] = 100 \left( 1 + \frac{[\text{NO}_l^+]}{[\text{HONO}_l]} \right)^{-1} \quad (18)$$

In Figure 7 the result of these calculations is shown for  $T = 293 \text{ K}$  and compared with the data of Seel and Winkler.<sup>23</sup> The result from the present study is in very good agreement with the data of Seel and Winkler,<sup>23</sup> who measured the concentrations of both HONO and  $\text{NO}^+$  directly. The concentrations of  $\text{NO}^+$  and HONO were found to be equal in 56 wt %  $\text{H}_2\text{SO}_4$ , which is in excellent agreement with the value of 55 wt % reported by Seel and Winkler.<sup>23</sup> This demonstrates again that the assumptions made above are reasonable.

The equilibrium constant  $K$  was determined for  $T = 298 \text{ K}$  according to eq 16 by plotting  $\log([\text{HONO}_l]/[\text{NO}_l^+])$  as a function of  $H_R$ , which was taken from Deno et al.<sup>24</sup> The plot shown in Figure 8 exhibits good linearity, with a slope of  $0.92 \pm 0.03$  compared with the value of 1.0, which is expected theoretically. From the intercept of the straight line in Figure 8 an equilibrium constant of  $(1.2_{-0.5}^{+1.0}) \times 10^{-8}$  was derived, which agrees well with the value of  $1.4 \times 10^{-8}$  reported by Seel and Winkler.<sup>23</sup>

To determine the temperature dependence of the equilibrium constant, the  $T$ -dependence of the experimental acidity function  $H_R$  has to be taken into account. The temperature dependence of  $H_R$  was studied by Arnett et al.<sup>25</sup> in the range 273–318 K and by Cook et al.<sup>26</sup> in the range 298–363 K, respectively.

However, since the data of these studies are not consistent with one another, an extrapolation of  $H_R$  to the lower temperatures employed in the present study would be very speculative.

However, it should be pointed out that it is also possible to determine the ratio  $[\text{HONO}_l]/[\text{NO}_l^+]$  as a function of temperature and sulfuric acid concentration using eq 13. As discussed already above, this equation gives an excellent description of  $K_{\text{H,eff}}$  in the investigated temperature and  $\text{H}_2\text{SO}_4$  concentration ranges. Since the first term of eq 13 with the  $T$ -dependent parameters  $A_{(T)}$  and  $B_{(T)}$  yields the concentration and temperature dependence of the real Henry's law constant  $K_H$ , the ratio of  $[\text{HONO}_l]/[\text{NO}_l^+]$  can be calculated according to eq 17. In Figure 7 the result of these calculations is shown by the solid and dashed curves for two different temperatures. It can be seen that the shape of the two different curves is quite similar for 293 and 248 K, respectively. From this it can be concluded that the sulfuric acid concentration for which the concentrations of HONO and  $\text{NO}^+$  in the solution are equal does not depend on temperature.

### Atmospheric Implications

For  $\text{H}_2\text{SO}_4$  concentrations < 53 wt % HONO is less soluble in sulfuric acid than in water. Accordingly, in tropospheric aerosols most HONO will be found in the gas phase if the acidity is lower than compared with a sulfuric acid concentration of 53 wt %. However, under circumstances such as low temperature or low relative humidity the aerosol can exist as a highly concentrated  $\text{H}_2\text{SO}_4$  solution in which HONO reacts with  $\text{H}_2\text{SO}_4$  forming nitrosylsulfuric acid. This reaction causes an effective solubility that can be orders of magnitude larger than in water. In the polar sunrise experiment, for example, the aerosol was found to be 70 wt %  $\text{H}_2\text{SO}_4$ .<sup>13</sup> In the stratosphere the sulfuric acid concentration is in the range 50–80 wt %;<sup>27,28</sup> therefore, also in this case the equilibrium between HONO and  $\text{NO}^+$  needs to be taken into account for the calculation of the solubility of HONO. Furthermore, previous studies in aerosols<sup>10,29</sup> in which a nonequilibrium between  $\text{HONO}_g$  and  $\text{HONO}_l$  was reported should be reinvestigated since in these studies the Henry constant of HONO in water was used.

### Conclusion

In the present study the Henry's law constant of HONO in sulfuric acid solutions has been determined as a function of the  $\text{H}_2\text{SO}_4$  concentration and temperature for the first time. It has been shown that for  $c_{\text{H}_2\text{SO}_4} < 53 \text{ wt } \%$   $\text{H}_2\text{SO}_4$  the Henry's law constant  $K_H$  decreases exponentially with increasing acid concentration for the temperature range investigated. This effect has been explained by the salt effect. For  $\text{H}_2\text{SO}_4$  concentrations > 53 wt % the effective solubility of HONO increases because HONO reacts with sulfuric acid, forming nitrosylsulfuric acid. It has been found that the Henry's law constant increases with decreasing temperature. The values of  $\Delta H_{\text{sol}}$  and  $\Delta S_{\text{sol}}$  for the physical dissolution of HONO have been determined as a function of the sulfuric acid concentration. Extrapolation of the experimental results to pure water as solvent leads to excellent agreement with literature data. A mathematical relation has been derived from which the effective Henry's law constant can be calculated as a function of both temperature and  $\text{H}_2\text{SO}_4$  concentration. The equilibrium between HONO and the nitrosyl cation, which has been investigated from the increase of the effective Henry's law constant for  $\text{H}_2\text{SO}_4$  concentrations > 53 wt %, has been described at 298 K using the acidity function  $H_R$ . It has been observed that the concentration of sulfuric acid for which equal concentrations of HONO and  $\text{NO}^+$  were determined in the solutions is independent of temperature.

The results from the present work imply that previous studies on HONO in sulfuric acid should be reinvestigated since in these studies the Henry constant of HONO in pure water was used.

**Acknowledgment.** The financial support by the “Deutsche Forschungsgemeinschaft (DFG)” within the DFG-Priority Programme “Basics of the Impact of Air and Space Transportation on the Atmosphere” and the “Bundesministerium für Bildung, Wissenschaft, Forschung und Technologie (BMBF)” within the BMBF-Priority Programme “Klimaschwerpunkt-Spurenstoffkreisläufe” is gratefully acknowledged.

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JP961140R