

Laboratory Measurements of Heterogeneous Reactions on Sulfuric Acid Surfaces

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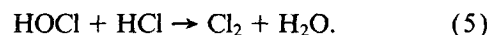
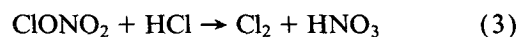
ABSTRACT

Increasing evidence from field, modeling, and laboratory studies suggests that heterogeneous reactions on stratospheric sulfate aerosol particles may contribute to global ozone depletion. Using a Knudsen cell reactor technique, the authors have studied the uptake, reactivity, and solubility of several trace atmospheric species on cold sulfuric acid surfaces representative of stratospheric aerosol particles. The results suggest that the heterogeneous conversion of N_2O_5 to HNO_3 is fast enough to significantly affect the partitioning of nitrogen species in the global stratosphere and thus contribute to global ozone depletion. The hydrolysis of $ClONO_2$ is slower and unlikely to be important under normal conditions at midlatitudes. The solubilities of HCl and HNO_3 in sulfuric acid down to 200 K were found to be quite low. For HCl , this means that little HCl is available for reaction on the surfaces of stratospheric sulfate aerosol particles. The low solubility of HNO_3 means that this product of heterogeneous reactions will enter the gas phase, and the denitrification observed in polar regions is unlikely to occur in the global stratosphere.

1. Introduction

The importance of heterogeneous processes in the chemical balance of the stratosphere has been dramatically illustrated by the annual appearance of the ozone hole during the Antarctic spring (Solomon et al. 1986; Solomon 1988). Heterogeneous reactions on particle surfaces in the polar stratospheric clouds convert chlorine reservoir molecules into easily photolyzed active chlorine species that lead to ozone destruction. In addition, heterogeneous reactions remove odd nitrogen that would normally sequester active chlorine in stable reservoir molecules. There is now increasing evidence that similar heterogeneous chemistry on the background stratospheric sulfate aerosol may be contributing to global ozone depletion (Arnold et al. 1990; Hofmann and Solomon 1989; Rodriguez et al. 1991). In this paper, we present the results of laboratory experiments aimed at measuring reaction rates of atmospherically important molecules on sulfuric acid surfaces under conditions of stratospheric composition and temperature.

The following reactions are considered to be key contributors to the Antarctic ozone hole (Solomon 1988):



In the laboratory, some of these reactions occur efficiently on water ice and nitric acid trihydrate, the materials believed to make up polar stratospheric clouds (PSCs) (Tolbert et al. 1987; Tolbert et al. 1988a; Molina et al. 1987; Hanson and Ravishankara 1991a, 1992; Leu 1988; Leu et al. 1991; Moore et al. 1990). Reactions (1), (3), and (4) convert the stable chlorine reservoir species, $ClONO_2$ and HCl , into the more easily photolyzed species, $HOCl$, Cl_2 , and $ClNO_2$. When the sunlight returns during the Antarctic spring, photolysis releases active chlorine radicals that destroy ozone via catalytic cycles. In addition, all four reactions generate nitric acid, which readily sticks to water ice to make solid hydrates. This deposition of odd nitrogen onto PSCs (denitrification) reduces the ability of the $ClONO_2$ reservoir to sequester active chlorine.

While the Antarctic ozone hole is startling and obvious, more subtle changes are occurring in the strato-

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spheric ozone layer on a global scale. Both ground-based and satellite measurements indicate that global ozone concentrations have decreased about 5% at midlatitudes over the last decade (World Meteorological Organization 1991). Moreover, model calculations including only gas phase chemistry are unable to simulate this decrease (World Meteorological Organization 1991). One possibility is that heterogeneous chemistry may play a role at midlatitudes as well as in the polar regions.

The substrate for heterogeneous chemistry in the global stratosphere is the surface of particles in the existing aerosol layer. These particles are believed to consist of supercooled concentrated sulfuric acid solutions (Steele et al. 1983). The composition depends on the temperature and the partial pressure of water vapor. Steele and Hamill (1981) calculated equilibrium compositions ranging between 60 and 80 wt% sulfuric acid for typical stratospheric conditions of temperature (210–240 K) and water vapor (5 parts per million by volume, or ppmv). The particles become less concentrated as the temperature decreases or the water vapor increases. The background sulfate aerosol particles range in size from 0.01 to 0.5 μm and provide a surface area of roughly $1 \mu\text{m}^2 \text{cm}^{-3}$ of atmosphere (World Meteorological Organization 1991). After a large volcanic eruption, the sulfate surface area can increase by up to two orders of magnitude.

Reactions (1)–(5) have been studied on sulfuric acid surfaces by several different groups (Tolbert et al. 1988b; Manion et al. 1994, personal communication; Hanson and Ravishankara 1991b; Mozurkewich and Calvert 1988; Van Doren et al. 1991). The results from our laboratory are discussed in more detail below. In summary, it appears that reaction (1) is too slow on sulfuric acid at stratospheric compositions and temperatures to have much impact on global ozone depletion, at least at midlatitudes. Reaction (2) is significantly faster and may affect the partitioning of NO_x in the stratosphere. This in turn affects the partitioning of chlorine between active and inactive species through the formation of ClONO_2 . Reaction (2) has recently been included in models of stratospheric chemistry and has been shown to impact the calculated ozone depletion (Brasseur et al. 1990; Rodriguez et al. 1991).

The solubility of trace species like HNO_3 and HCl in sulfuric acid is an important issue. Reactions (1)–(4) generate HNO_3 and its solubility determines whether the product dissolves or is released into the gas phase. The measured solubility of HNO_3 in sulfuric acid is small enough that most of the stratospheric nitric acid will be in the gas phase (Reihs et al. 1990; Zhang et al. 1993). Thus the denitrification that contributes to polar ozone depletion will not occur on the global sulfate aerosol. The solubility of HCl in sulfuric acid will determine the efficiency of reactions (3), (4), and (5). HCl solubilities have been measured recently and are several orders of magnitude smaller than HNO_3

solubilities (Williams and Golden 1993; Zhang et al. 1993; Worsnop 1992, personal communication). This implies that very little HCl is present in the midlatitude sulfate aerosol, and that reactions (3) and (4) are probably not fast enough at midlatitudes to contribute significantly to ozone depletion.

2. Experimental technique

Heterogeneous reaction rates and solubilities of trace species were measured using a Knudsen cell reactor shown schematically in Fig. 1 (Golden et al. 1973). Each half of the experimental apparatus consists of two chambers separated by a valve. The material of interest, in this case sulfuric acid, is placed in the bottom chamber, which can be cooled down to stratospheric temperatures using thermoelectric coolers. The gas-phase species is introduced into the top chamber, which has a small escape aperture leading to a differentially pumped mass spectrometer detection system. The concentration in the top chamber is kept low enough that molecular flow applies, so the residence time in the top chamber is determined by the size of the escape aperture. When the valve between the two chambers is opened, loss of the gas-phase species to the surface competes with escape through the aperture and is observed as a decrease in the mass spectrometer signal. Loss of molecules to the surface can be due to reaction on the surface, or uptake by the surface followed by diffusion into the bulk.

The experimentally measured quantity is the net uptake coefficient γ defined as

$$\gamma = \frac{\text{number of molecules lost to the surface}}{\text{number of gas-surface collisions}} \quad (6)$$

The number of molecules lost to the surface is measured by the change in flow through the escape aperture upon exposing the surface, and the number of gas-surface collisions is derived from gas kinetic theory as $\bar{c}n/4V$ where \bar{c} is the average velocity, n is the number of gas molecules, and V is the volume of the reactor. In terms of the experimental parameters of the Knudsen cell reactor, γ is expressed as

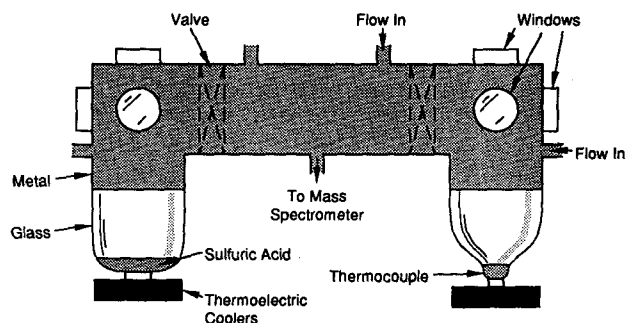
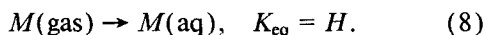


FIG. 1. Schematic of the Knudsen cell reactor.

$$\gamma = \frac{A_h F_0 - F}{A_s F}, \quad (7)$$

where A_h is the area of the escape aperture, A_s is the area of the sulfuric acid surface, F is the mass spectrometer signal when the surface is exposed, and F_0 is the signal without the surface (Golden et al. 1973; Tolbert et al. 1988b). For reactive loss on the surface, the uptake coefficient represents the reaction efficiency. For reactions with gas-phase products, the reaction can also be monitored by measuring the rise in mass spectrometer signal due to the product.

Solubilities are measured by observing the time dependence of the uptake coefficient (Reihs et al. 1990). Initially, the uptake coefficient on a clean sulfuric acid surface could be quite large. If the amount of gas-phase species that can go into solution is limited by the solubility, then as the surface layer of the solution saturates, the uptake coefficient will decrease with time. The solubility is given by Henry's law constant H , which is the equilibrium constant for the reaction



If the molecule reacts or dissociates in solution, this has the effect of increasing the observed solubility and the experiment yields an effective Henry's law constant H^* . The time dependence of the uptake coefficient is described by Eq. (9) (Schwartz 1986; Watson et al. 1990):

$$\frac{1}{\gamma} = A + \frac{\pi^{1/2} \bar{c}}{4RTH^* D^{1/2}} t^{1/2}, \quad (9)$$

where \bar{c} is the average molecular velocity in the gas phase, t is time, R is the gas constant, T is the temperature of the gas, H^* is the effective Henry's law solubility, D is the liquid phase diffusion constant of the molecule in sulfuric acid at the temperature of the liquid, and A is a constant. Equation (9) is different by $\pi^{1/2}$ from the corresponding equation in Watson et al. (1990) and Reihs et al. (1990) because of an error in the original derivation.

The slope of $1/\gamma$ versus $t^{1/2}$ is proportional to $H^* D^{1/2}$. Liquid phase diffusion constants have not been measured in sulfuric acid, and we must therefore estimate D in order to determine H^* . We used diffusion constants for HCl and HNO₃ in water at 298 K [$\sim 3.3 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ (Longworth 1963)] and corrected for the difference in viscosity between water and sulfuric acid. The diffusion constant was then extrapolated to low temperatures using the equation $D = CT/\eta$, where C is a constant and η is the viscosity. In previous work, the viscosity was extrapolated to low temperatures using an exponential temperature dependence (Watson et al. 1990; Reihs et al. 1990). We measured the viscosity of 60 wt% sulfuric acid down to 225 K and found a much steeper temperature dependence as described by the four-parameter, empirical equation given in Luo et al. (1994).

The sulfuric acid solutions were made by diluting commercially available 96 wt% H₂SO₄ with distilled water. The final concentration was determined by titration. Ten to 40 mL of solution were placed in the lower chamber and cooled to the desired temperature. All of the solutions were liquid over the temperature range of the experiments. Gas-phase concentrations were typically 10^{10} – 10^{12} molecules per cubic centimeter and were generally higher than found in the stratosphere for a particular species.

3. Results

a. Uptake of ClONO₂ and N₂O₅ by sulfuric acid

Figure 2 shows the uptake coefficient for ClONO₂ on sulfuric acid as a function of concentration at a temperature of 223 K (shaded squares) (Manion et al. 1994, personal communication). The open circles are results from Hanson and Ravishankara (1991b) using a wetted-wall flow tube technique. The two different techniques are in excellent agreement. The data points from both groups are fit to within $\pm 5\%$ by the equation $\gamma = 1.87 - 0.074 (\text{wt\% H}_2\text{SO}_4)$, shown with a solid line in Fig. 2. This expression is applicable only over the range 40–75 wt% H₂SO₄ at temperatures near 220 K. The shaded region represents the concentrations expected for stratospheric aerosol particles at most latitudes. The uptake coefficient is small over this range and reaction (1) is unlikely to be important for background conditions of stratospheric aerosol over most of the globe. Because of the strong dependence on sulfuric acid concentration, reaction (1) will be more important at high latitudes where colder temperatures lead to more dilute aerosol particles.

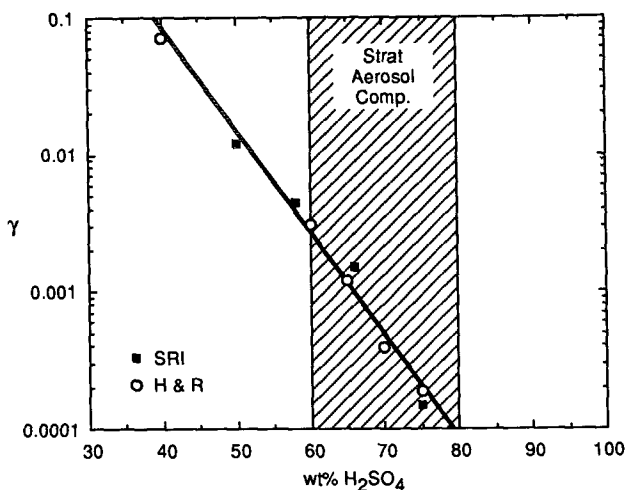


FIG. 2. Uptake coefficient for ClONO₂ as a function of weight percent H₂SO₄ (filled squares) and comparison with previous results (open circles) (Hanson and Ravishankara 1991b). The shaded regions show the approximate range of stratospheric interest.

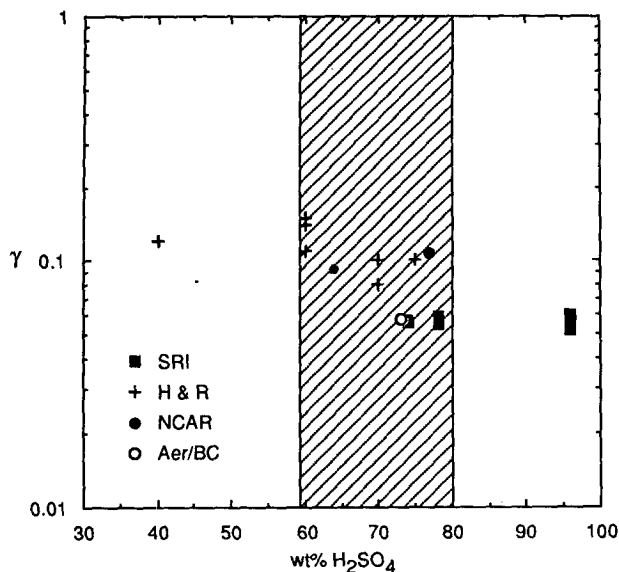


FIG. 3. Uptake coefficient for N_2O_5 on sulfuric acid from the present work (solid squares) and other laboratories. The open circle is data obtained on $100\text{-}\mu\text{m}$ -radii droplets at 283 K (Van Doren et al. 1991), the solid circles are results obtained on $0.07\text{-}\mu\text{m}$ -radii droplets at 274 and 293 K (Mozurkewich and Calvert 1988), and the crosses are from wetted-wall flow tube experiments of Hanson and Ravishankara (1991b).

In contrast to $ClONO_2$, N_2O_5 exhibits a large uptake coefficient that is independent of sulfuric acid concentration. The uptake coefficient for N_2O_5 on sulfuric acid is shown in Fig. 3 for sulfuric acid concentrations between 40 and 95 wt% and a temperature range of 215–293 K. In these experiments, the solutions were stirred gently to keep the product HNO_3 in solution. Otherwise HNO_3 interferes with the mass spectrometer signal at mass 46 for N_2O_5 and decreases the apparent γ . The results from the Knudsen cell experiment (Manion et al. 1994, personal communication) are in fairly good agreement with the results of other experimental techniques (Hanson and Ravishankara 1991b; Van Doren et al. 1991; Mozurkewich and Calvert 1988). The uptake coefficient does not vary significantly with temperature or sulfuric acid concentration in our experiments.

The large uptake coefficient for N_2O_5 suggests that reaction (2) will occur readily on stratospheric aerosol particles over a wide range of temperatures and compositions. Modeling calculations show that uptake coefficients of this magnitude could significantly affect both the NO_2 – HNO_3 balance and the ozone concentration. For example, calculations by Hofmann and Solomon (1989) have shown that reaction (2) occurring with an efficiency of 0.06 could change the NO_2 – HNO_3 balance after the eruption of El Chichón. Measurements by Arnold et al. (1990) of increased nitric acid levels in the El Chichón volcanic cloud were attributed to heterogeneous conversion of reactive nitro-

gen to nitric acid. They inferred a reaction efficiency of greater than or equal to 0.02, in agreement with values measured in the laboratory. The indirect effect of reaction (2) on the ozone concentration through the coupling of the nitrogen and chlorine families is demonstrated in calculations by Brasseur et al. (1990) and by Rodriguez et al. (1991). When reaction (2) is included in models of the global stratosphere, the amount of ozone depletion approximately doubles from 1% or 2% to 4% or 5% and is much closer to observed trends.

b. Solubility of HCl and HNO_3 in sulfuric acid

One of the factors limiting the rate of heterogeneous reactions such as (3), (4), and (5) is the availability of the second reactant at the surface. For a trace species like HCl , this may be determined by the solubility of the species in sulfuric acid. Figure 4 shows recent measurements of the effective Henry's law constant for HCl in sulfuric acid solutions between 50 and 60 wt% (Williams and Golden 1993). Because the solubility is low, the range of temperatures and compositions over which the Knudsen cell experiment could be performed is limited. However, extrapolation to the room temperature measurements of Watson et al. (1990) looks reasonable, and the agreement with results of other groups is good (Zhang et al. 1993; Worsnop 1992, personal communication).

The solubility increases with decreasing temperature and increases with decreasing sulfuric acid concentration. These trends combine to make HCl most soluble in the coldest regions of the stratosphere where the

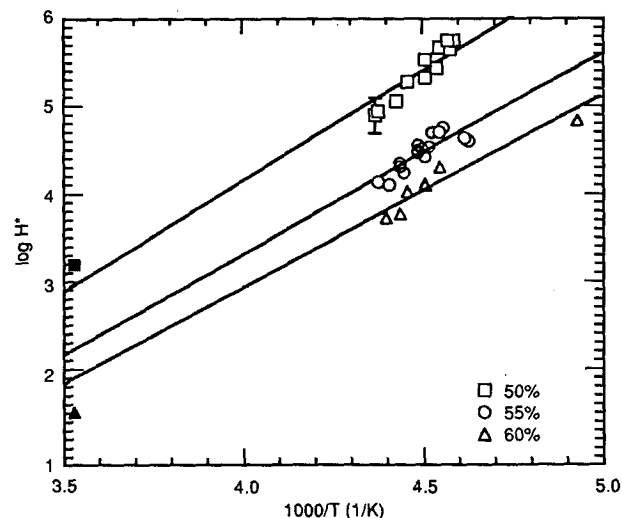


FIG. 4. Temperature dependence of the effective Henry's law constant for HCl in 50 (open squares), 55 (solid circles), and 60 wt% (open triangles) sulfuric acid solutions. The solid square for 50 wt% and the solid triangle for 60 wt% at 283 K are from Watson et al. (1990). The lines are fits to the data assuming an intercept of $-30\text{ cal (mol K)}^{-1}$.

TABLE 1. Temperature dependence of effective Henry's law constant for HCl in H₂SO₄. A standard state correction was used to convert $\Delta S = -30 \text{ cal (mol K)}^{-1}$ to an intercept. Assuming a standard state of 1 atm, the intercept is equal to $(\Delta S/4.58 + \log[\text{solvent}])$, where [solvent] is the molarity of the sulfuric acid.

H ₂ SO ₄ (wt%)	ΔH (kcal mol ⁻¹)
50	-11.5
55	-10.5
60	-10.0

sulfate aerosol is most dilute. The temperature dependence of the Henry's law constant is described by

$$\ln H = \frac{-\Delta H_{\text{sol}}}{RT} + \frac{\Delta S_{\text{sol}}}{R}, \quad (10)$$

where ΔH_{sol} (kcal mol⁻¹) is the heat of solvation of HCl, ΔS_{sol} [cal (mol K)⁻¹] is the change in entropy upon solvation, and R is the gas constant (Wilhelm 1977); H in Eq. (10) is expressed as the mole fraction of the solute in the solvent assuming a standard state of 1 atm for the partial pressure of the gas-phase solute molecules. For a log plot of H^* in our units (M atm⁻¹), the intercept is equal to $(\Delta S/4.58 + \log[\text{solvent}])$ where [solvent] is the molarity of the sulfuric acid. The temperature dependence of the effective Henry's law constant measured here yields a ΔH and ΔS that reflect both solvation and dissociation. The temperature range of the data is not large enough to justify a least-squares fit to determine both ΔH and ΔS . We use the ΔS for HCl in the gas phase going to H⁺ and Cl⁻ ions in aqueous solution [$-30 \text{ cal (mol K)}^{-1}$] (Bell 1973) to fix the intercept of the fit. The solid lines in Fig. 4 show the fit to the data with ΔS fixed at $-30 \text{ cal (mol K)}^{-1}$. The resultant ΔH 's are given in Table 1 and are similar to ΔH 's determined from the temperature dependence of H^* measured by other groups (Worsnop 1992, personal communication; Zhang et al. 1993).

For the 60–80 wt% H₂SO₄ concentrations representative of stratospheric aerosol particles, the solubility of HCl is quite low—a typical aerosol particle will contain only a few HCl molecules. The extremely small amount of HCl available in solution means that reactions (3), (4), and (5) are likely to be unimportant on the sulfate aerosol in the midlatitude global stratosphere. This is consistent with model calculations that show that most of the discrepancy between measured and calculated ozone at midlatitudes can be accounted for by including only heterogeneous reaction (2) in the model calculations (Arnold et al. 1990; Rodriguez et al. 1991). In the laboratory, reactions (3) and (5) have been observed to occur, although under conditions of very high HCl concentration (Tolbert et al. 1988b; Hanson and Ravishankara 1991). In extremely cold parts of the stratosphere where the sulfate aerosol con-

tains more water and the HCl solubility is correspondingly higher, these reactions could start to become important.

The solubility of HNO₃ in sulfuric acid will determine whether the products of reactions (1)–(4) remain in solution or enter the gas phase. Figure 5 shows the effective Henry's law constant H^* for HNO₃ in sulfuric acid as a function of temperature for solutions between 58 and 87 wt% (Reihs et al. 1990). The data in Reihs et al. (1990) has been reanalyzed with the corrected version of Eq. (9), and with the steeper dependence of the viscosity on decreasing temperature. As a result, the H^* 's in Fig. 5 increase more rapidly with decreasing temperature than shown in Reihs et al. (1990). Fits to the data yield ΔS 's for greater than 66 wt% sulfuric acid that are between -23 and $-25 \text{ cal (mol K)}^{-1}$ in reasonable agreement with what one would estimate using Trouton's rule [$\sim -21 \text{ cal (mol K)}^{-1}$]. We expect Trouton's rule to be a reasonable estimate because less than 1% of the HNO₃ dissociates in solution over this concentration range of sulfuric acid. The solid lines in Fig. 5 are fits to the data with the intercept determined by $\Delta S = -21 \text{ cal (mol K)}^{-1}$. The resultant ΔH 's are given in Table 2. Reanalysis of the Reihs et al. (1990) data brings the H^* 's into much better agreement with the results of Zhang et al. (1993).

The solubility of HNO₃ is low enough that reactions (1)–(4) will produce predominantly gas-phase HNO₃. These heterogeneous reactions convert odd nitrogen to the more stable species nitric acid but will not remove nitrogen completely from circulation as is observed during Antarctic ozone hole formation when denitrification by polar stratospheric clouds occurs.

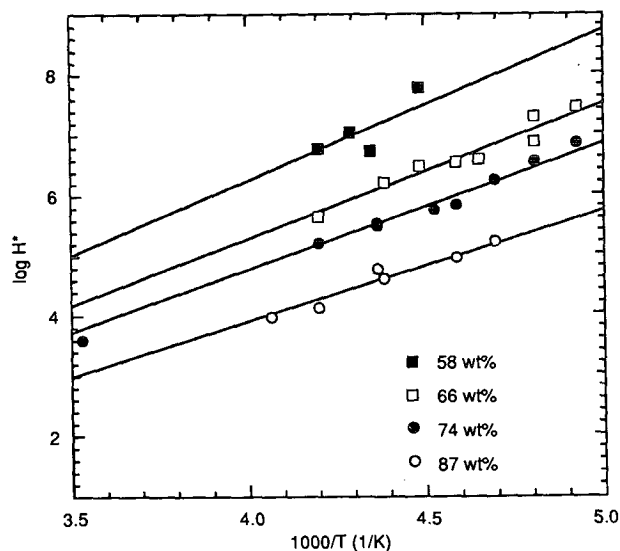


FIG. 5. Temperature dependence of the effective Henry's law constant for nitric acid in 58 (solid squares), 66 (open squares), 74 (solid circles), and 87 wt% (open circles) sulfuric acid solutions. The value at 283 K is from Van Doren et al. (1991). The lines are fits to the data, assuming a Trouton's rule intercept of $-21 \text{ cal (mol K)}^{-1}$.

TABLE 2. Temperature dependence of effective Henry's law constant for HNO_3 in H_2SO_4 . Intercept determined as for Table 1 with $\Delta S = -21 \text{ cal (mol K)}^{-1}$.

H_2SO_4 (wt%)	ΔH (kcal mol ⁻¹)
58	-11.3
66	-10.1
74	-9.5
87	-8.3

4. Conclusions

Recent laboratory results on the rates of heterogeneous reactions on sulfuric acid surfaces have increased our understanding of global stratospheric chemistry. Of the reactions implicated in the Antarctic ozone hole, only reaction (2) appears to be fast enough on 60–80 wt% sulfuric acid to affect the partitioning of nitrogen species and thus the ozone concentration in the mid-latitude global stratosphere. In the high-latitude stratosphere, temperatures are colder and the sulfate aerosol becomes more dilute. Under these conditions, reaction (1) may be fast enough to become important. In addition, the solubilities of both HCl and HNO_3 are greatly increased for colder, more dilute sulfuric acid. This may affect the heterogeneous chemistry, as well as the nucleation of polar stratospheric cloud particles.

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