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**HETEROGENEOUS CHEMISTRY AFFECTING
UPPER TROPOSPHERIC AND
STRATOSPHERIC OZONE**

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Heterogeneous Chemistry

Affecting

Upper Tropospheric and Stratospheric Ozone

Introduction This collaborative research program between Aerodyne Research, Inc. and Boston College (ARI/BC) has studied the heterogeneous gas-liquid interactions related to ozone formation and destruction processes in the atmosphere. This involves laboratory determination of gas/liquid mass transport rates using bubble column and droplet apparatuses capable of measuring both fast and slow heterogeneous processes. The research plan was to study heterogeneous chemistry of nitrogen containing species, including ammonia NH_3 and so-called 'NO' gas phase species (including NO , NO_2 , NO_3 , HNO_2 and CH_2O) on atmospherically relevant aqueous solutions (including sulfuric acid and nitrosyl sulfuric acid).

The project comprised four tasks involving laboratory measurements of gas/liquid kinetics:

- 1) Uptake of CH_2O into aqueous solution utilizing the ARI/BC bubbler apparatus. This included upgrading the bubbler to a horizontal flow design. This work was the first direct measurement of acid and base catalyzed CH_2O hydrolysis over the full range of pH (0 to 14) in aqueous solution (Swartz et al, 1997).
- 2) Uptake of CH_2O into concentrated sulfuric and nitric acid solution over the temperature range 245-275K. This work utilized the ARI/BC droplet apparatus modified for generation of acid solution. This work confirmed and quantified previous reports of enhanced CH_2O uptake in acid solution (Jayne et al, 1996)
- 3) Reaction of CH_2O with HNO_3 in concentrated sulfuric acid solution. This involved the design and construction of mixed liquid reaction vessel coupled to the mass spectrometric detection system for monitoring the evolution of product gases from solution. This work showed that the autocatalytic reaction of CH_2O with HONO (in HNO_3 mixtures) is acid catalyzed in H_2SO_4 solution. However, the rate is likely too slow to be atmospherically important.
- 4) Uptake of NH_3 into aqueous and sulfuric acid solution over the temperature range 245-290K. This work showed that the accommodation coefficient (α) of NH_3 depends on relative humidity, with $\alpha \sim 0.1$ on water increasing to $\alpha = 1$ for H_2SO_4 concentration $> 50\text{wt}\%$. Combined with re-analysis of previous aerosol neutralization studies, this work shows that NH_3 uptake coefficients under atmospheric conditions will be less than unity and thus potentially rate-limiting for atmospheric aerosol nucleation and growth (Shi et al, 1999; Swartz et al, 1999).

The results (with the exception of Task 3) have been published (or submitted for publication) and thus will only be summarized here. The abstracts of the published manuscripts are attached as appendices. Appendix D contains the entire submitted manuscript (Swartz et al, 1999) describing in detail Task 4.

Task 1 Uptake of CH₂O into aqueous solution

Because of its low physical solubility (Henry's Law constant, $H = 2.5 \text{ M atm}^{-1}$ at room temperature; Betterton and Hoffmann, 1988), the effective solubility of CH₂O(g) in aqueous solution is determined by the formation of its gem-diol, CH₂(OH)₂,

which gives an effective solubility of $H^* \sim 2300 \text{ M atm}^{-1}$. The uptake of CH₂O(g) into solution is then determined by the rate of formation of CH₂(OH)₂ via (3), according to the rate law

$$k_{\text{rxn}} = k_{\text{H}_2\text{O}} + k_{\text{H}^+} [\text{H}^+] + k_{\text{OH}^-} [\text{OH}^-] \quad (2)$$

reflecting acid and base catalysis of reaction (2) (Bell and Evans, 1966; Schecker and Schulz, 1969). In earlier work (Jayne et al. 1992), we studied the uptake behavior of formaldehyde over the pH range of 0 to 14. At high pH > 10 extremes the uptake is governed by the base catalyzed reaction to form the diol and appeared to be consistent with reported hydration rates. In the intermediate pH range (pH 3-10), where the hydration is slow, uptake was not measurable (within the sensitivity of our experiment) due to the low physical solubility (H) for CH₂O.

The experiments have utilized bubble train apparatuses, which can measure slow gas/liquid uptake rates for interaction times on the order of seconds. The horizontal bubble train apparatus is a improved version of our previously described vertical bubble column technique (Shorter et al, 1995). Extensive experiments on soluble and reactive gases served to characterize and calibrate bubble generation and transport, including convective mixing of the liquid surrounding the bubble. Formaldehyde uptake experiments were performed as a function of pH by adding NaOH and H₂SO₄ to the aqueous solution. In addition, salting out experiments were performed up to 4M NaCl solution. In these bubble train experiments, CH₂O(g) was detected via electron impact ionization and quadrupole mass spectrometric analysis (see Appendix A; Swartz et al, 1997).

This is demonstrated in Figure 1, which plots the results of CH₂O(g) uptake into the bubble train, measured over the range of pH = 0 to 10. Results are plotted as k , the hydration rate for diol formation, derived from the uptake equation

$$\gamma_{\text{rxn}} = 4\text{HRT} (D_1 k_{\text{rxn}})^{1/2} / c \quad (3)$$

where D_1 is the liquid diffusion coefficient and c the molecular speed of the gas molecules. As described for the vertical bubble column technique (Shorter et al, 1995), detailed analysis of bubble uptake observations takes into account convective mixing within the liquid surrounding the bubble, which effectively enhances D_1 (Swartz et al, 1997).

The solid line in Figure 1 reflects reported values of $k_{\text{H}_2\text{O}}$, k_{H^+} and k_{OH^-} (Bell and Evans, 1966; Schecker and Schulz, 1969). The agreement is excellent, confirming both the calibration of bubble train technique and understanding of the CH₂O aqueous kinetics. In fact, k_{OH^-} was adjusted lower by a factor of 3.2 to account for the temperature dependence of the ionization of water that was not accounted for in the Schecker and Schulz (1969) analysis.

Figure 1 Hydration rate for $\text{CH}_2\text{O}(\text{g})$ uptake into aqueous solution as a function of bubble pH (Swartz et al, 1996). Model curve from equation (2). Droplet points from Jayne et al, 1992.

Also plotted in Figure 1 are several experimental points from our droplet experiments (Jayne et al, 1992). The agreement in basic solution is excellent. The acidic droplet points (pH 1 and 2) are somewhat high due to a surface adsorption, which is only observable at short liquid exposure times as in the droplet experiment (see Appendix B; Jayne et al, 1996). Figure 1 demonstrates the complimentary capabilities of the droplet and bubble train techniques, which can together measure gas uptake rates spanning a range of six orders of magnitude.

These results are described in detail in the published manuscript, Swartz et al, 1997, whose abstract is attached as Appendix A. In summary, this work both confirmed aqueous kinetic parameters for CH_2O uptake over a wide range of pH and also demonstrated the capabilities of the new horizontal bubble apparatus.

Task 2 Uptake of CH_2O into concentrated sulfuric and nitric acid solution

This project extended CH_2O uptake kinetics to concentrated acid solutions relevant to upper atmospheric aerosols. The experiments utilized the ARI/BC fast-moving droplet apparatus, which can measure gas/liquid uptake rates on millisecond interaction times. Upgrades

were made in the data acquisition and gas handling systems in order to enhance experimental productivity and gas detection sensitivity. This apparatus is capable of producing droplets up to 80 wt% H_2SO_4 , cooled down to 230K, matching the range of conditions for upper tropospheric and lower stratospheric aerosols. Formaldehyde gas is produced by heating a glass column (60C) packed with solid paraformaldehyde. The $\text{CH}_2\text{O}(\text{g})$ was detected using a tunable diode laser (TDL) spectrometer. A CH_2O infrared absorption line at a frequency of $2916.8183 \text{ cm}^{-1}$ (with line strength of $3.6 \times 10^{-20} \text{ cm}^2 \text{ molecule}^{-1} \text{ cm}^{-1}$) yield a fractional absorbance of 5% for a gas phase densities of $\sim 5 \times 10^{12} \text{ cm}^{-3}$.

Experiments measured the uptake of $\text{CH}_2\text{O}(\text{g})$ on droplets composed of 10 to 80 wt% H_2SO_4 and on 40 wt% H_2SO_4 with added 10 to 20 wt% HNO_3 over the temperature range -30 to 0C. Figure 2 displays uptake rates measured at -10C (for 8 millisecond gas/liquid interaction times) for the acid solutions, together with our earlier results on pure aqueous solution. The results are plotted as uptake coefficients, which are derived by normalizing the observed loss rates of $\text{CH}_2\text{O}(\text{g})$ to the gas/surface collision rates, determined from the liquid surface area and exposure time. The data are plotted versus acidity as derived from a model of ternary liquid $\text{H}_2\text{SO}_4\text{:HNO}_3\text{:H}_2\text{O}$ (Carslaw et al, 1995).

Figure 2 Uptake coefficients for CH_2O into concentrated H_2SO_4 (up to 80 wt%) and HNO_3 (up to 54 wt%) solution. Uptake increase is modeled via CH_2O^+ formation (reaction 4). Taken from Jayne et al, 1997.

The new results for uptake at high acidity extend the previous measurements by using concentrated sulfuric acid droplets, which match the composition of aerosols in the upper troposphere/lower stratosphere. These new measurements show that the uptake is significantly larger than the prediction based on the rate of hydration (the dashed-dotted line in Fig. 2). This is consistent with the work of Tolbert et al. (1993). To account for the increased uptake we have added a new reaction channel for CH_2O in aqueous solution, involving direct protonation,

The model curves (solid and dashed lines) in Fig. 2 includes the acid and base catalyzed formation of the diol (reaction (3)) and the new protonation channel (4). This model takes into account change in activity of acidity, water and CH_2O itself as H_2SO_4 composition is increased. For example, the decrease in uptake due to reaction (3) alone (the dashed line at high acidity) reflects the decrease in CH_2O and H_2O activity in concentrated H_2SO_4 solution.

Also shown in Fig. 2 are CH_2O uptake coefficients with added HNO_3 . Based on the Carslaw et al (1995) model of ternary $\text{H}_2\text{SO}_4\text{:HNO}_3\text{:H}_2\text{O}$ solutions, added HNO_3 increases uptake of CH_2O as predicted for reaction (4) at increased acidity. This indicates that any extra reaction of HNO_3 with CH_2O is not rate limiting for CH_2O uptake under these conditions.

As described in Jayne et al, 1996, the detailed model accounts for temperature and composition dependencies of chemical activities, gas solubility, liquid diffusion, mass accommodation, and aqueous reaction in a phenomenologically self-consistent manner. Also included was a surface adsorption channel for CH_2O uptake in acidic solution, which accounts for inversely time dependent uptake observed between pH = 0 and 2 (see Appendix B; Jayne et al, 1996). This modeling approach is directly applicable to estimating CH_2O dissolution into aerosols in atmospheric photochemical models.

Task 3 Reaction of CH_2O with HNO_3 in concentrated sulfuric acid solution

The above results indicate that reaction of HNO_3 with CH_2O is not rate limiting for CH_2O uptake, even in concentrated acid solution. However, the results do not preclude the possibility of a secondary $\text{CH}_2\text{O} + \text{HNO}_3$ reaction channel (as in reaction (1) or (2)). In order to further investigate that possibility, bulk solution experiments on mixtures of CH_2O with H_2SO_4 and HNO_3 acid solutions were carried out. Using both visible and infrared spectrometers, gas evolution of NO , NO_2 and CO_2 was observed in concentrated mixed solutions

This work is motivated by modeling of upper tropospheric ozone photochemistry which indicates there is a "missing source of NO_x " (Fan et al, 1993). The heterogeneous reaction of the diol form of CH_2O with HNO_3 to form methanediol nitrates (Walker, 1964),

The laboratory work was inspired by the observation of enhanced uptake of CH_2O in sulfuric acid solution (Tolbert et al, 1993), which has now been confirmed (Jayne et al, 1996).

The goal of this task the elucidation of the heterogeneous kinetics underlying reactions (5) and (6) under atmospheric conditions. A new apparatus was constructed, consisting of a continuously stirred 200 cm³ reaction vessel coupled to a differentially pumped mass spectrometer. A flow of Helium 3scc/sec was used to sweep the gaseous species into the flow tube of the mass spectrometer. The reaction vessel was maintained at 50 Torr total pressure and continuously stirred at 293 K. 50 cm³ of a known formaldehyde concentration in aqueous H₂SO₄ was placed in the 200cm³ vessel and stirred continuously. A solution of aqueous HNO₃ was placed in a 50 cm³ burette and connected to the reaction vessel. The volatile components of the CH₂O/H₂SO₄ mixture were monitored for time periods up to 30 minutes. Approximately 10 cm³ of HNO₃ was subsequently added to this mixture and monitoring was continued until reaction went almost to completion.

During the experiment, the mass spectrometer monitored up to eight mass peaks continuously (28, 29, 30, 44, 45,46,47,63 amu) in order to time resolve the evolution of gases from the mixed solution. Figure 3 shows the typical time evolution sequence. Initially the peak at mass 29 monitored gaseous CH₂O as shown in Figure 2. After equilibration for 30 minutes a known volume of HNO₃ was added rapidly from the burette, resulting in an immediate increase in the signal at mass 63 and a smaller increase at mass 47 due to HONO formation (note that most of the mass spectrometer single for HNO₃ appears at fragment ions at masses 30 and 46, not shown in Figure 3). After a period of 2 to 30 minutes (depending on the experimental conditions) a rapid burst in new signals were observed. The HONO signal at mass 47 was observed to grow in first followed by a CO₂ single signal at mass 44. At the same time, the HNO₃ and CH₂O signals decrease. This signal burst was accompanied by a rapid rise in both the

Figure 3 Gas evolution from CH₂O/H₂SO₄ solution. A HNO₃ aliquot was added at t=1800 sec. Sudden evolution of HONO (mass 47) and CO₂ (mass 44) at ~4500 sec is consistent with autocatalytic reaction of CH₂O and HONO described in equations 7 to 10.

solution temperature and the flask partial pressure. During this period vigorous bubbling of the flask contents due to evolution of low soluble gases also occurred. The characteristic brown color due to NO_2 was observed. The reaction subsequently subsided but evolution of gaseous products was observed for an extended period (hours) and the temperature and pressure recovered to their original levels.

This reactive behavior is consistent with autocatalytic oxidation of CH_2O by HNO_3 as originally reported by Horváth et al. (1988) via the mechanism

which corresponds to the net reaction

Detailed analysis of the time sequence in Figure 3 thus shows a slow rise in HONO (mass 47) as HONO gradually builds up via reaction (8). After a delay of ~40 minutes, the HONO reaches a critical 'autocatalytic' level, shifting the equilibrium of (7) toward N_2O_4 . This leads to even more rapid production of HONO that is now observable at masses 30 and 46, (not shown in Fig. 3), as well as mass 47. Finally, CO_2 production (mass 44) is observed, indicative of reaction (9). The observed gas evolution is clearly consistent with the net reaction described by reaction (10).

The overall rate of HONO production can be expressed as the rate law,

$$d/dt[\text{HONO}] \sim k [\text{H}^+] [\text{NO}_3^-] [\text{HONO}] [\text{CH}_2\text{O}] \quad (11)$$

and indeed the variation in observed induction periods is consistent with this expression. Specifically, we have resolved the acid component by varying the H_2SO_4 concentration in solution. Overall, these results confirm the mechanism for autocatalytic HONO production via HNO_3 and CH_2O reaction (Horváth et al, 1988).

However, in view of the slow reaction times (minutes or longer) observed in these experiments (for relatively high CH_2O and HNO_3 concentrations) it is unlikely that this reaction will be important in the atmosphere. While the rate will be enhanced in the presence of H_2SO_4 solution, at atmospheric aerosol levels evaporation of HONO will preclude build-up of HONO within the condensed phase. However, more work is required to quantify expected steady state reaction rates at realistic atmospheric HNO_3 , HONO and aerosol levels.

Task 4. Uptake of NH_3 into aqueous and sulfuric acid solution

In the final year of the project work shifted to the kinetics of uptake of ammonia (NH_3) vapor into aqueous and H_2SO_4 acid solution. This is a critical atmospheric system since in the troposphere the uptake of NH_3 largely controls the acidity of newly nucleated $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ aerosols. And more recent studies suggest that ternary nucleation of NH_3 , H_2SO_4 and H_2O may be typical of new particle nucleation under many atmospheric conditions (Weber et al, 1996). Under these conditions, accurate uptake coefficients for NH_3 are critical to microphysical modeling of the competition between new particle formation and condensation on pre-existing aerosols. This work is described in detail in the Shi et al (1999) and Swartz et al (1999) manuscripts (submitted to the Journal of Physical Chemistry) that are attached as Appendices C and D. (Note the entire Swartz et al manuscript, describing NH_3 uptake into H_2SO_4 solution, is attached). We only briefly describe the results here.

Figure 4 summarizes the atmospheric implications of the work. The solid line plots the observed NH_3 uptake coefficient (γ) as a function of relative humidity over $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ solution. The magnitude of γ varies between one at low humidity RH (RH <30%, H_2SO_4 >50wt%) to ~0.1 on pure water (RH=100%). The value on water has a negative temperature dependence indicative of the mass accommodation coefficient measured for a number of species on water. In contrast, the unity uptake coefficient on concentrated acid is interpreted as a fast surface reaction with H^+ to directly form NH_4^+ in the acid solution (see Appendix D; Swartz et al, 1999).

Figure 4. Uptake coefficients for NH_3 into H_2SO_4 solution derived from this work (solid line; see Appendix D, Swartz et al, 1999) and aerosol neutralization experiments as labeled. Concentrations of H_2SO_4 on the top axis correspond to relative humidities plotted on the bottom axis.

Also plotted in Figure 4 are results (shown as bars) derived from aerosol neutralization experiments that report NH_3 uptake coefficients less than unity on H_2SO_4 solutions neutralized to $\sim\text{NH}_4/\text{SO}_4$ ratios of about 1. Actually, the bars for Huntzicker et al (1980) have been re-analyzed since their measured uptake at low neutralization levels (i.e. on binary $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$) solution appear to be gas diffusion limited, consistent with our observation of near unity uptake coefficient on 40-40wt% H_2SO_4 solution. In summary, the implication of all the results taken together is that NH_3 uptake rates will be typically be less than unity at typical tropospheric relative humidities and NH_3 vapor levels. A key question is how these vapor condensation rates are related to ternary nucleation kinetics for $\text{NH}_3/\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ vapors (see discussion in Appendix D; Swartz et al, 1999).

Conclusions / Plans Results from first three tasks have delineated much of the heterogeneous atmospheric chemistry of CH_2O in aqueous and acid solution. Task 1 quantitatively confirmed the hydrolysis kinetics of CH_2O in aqueous solution while Task 2 measured the enhanced up take of CH_2O in sulfuric and nitric acid solutions. Task 4 identified new heterogeneous channel for CH_2O uptake via reaction with HNO_3 in upper tropospheric / lower stratospheric aerosols. Further work is required to provide a detailed kinetic model for application to models under atmospheric conditions. Future work will utilize chemical ionization mass spectrometry in order to detect low levels of HONO production under better controlled conditions in the horizontal bubbler.

The NH_3 uptake experiments have provided much of the fundamental gas/liquid kinetics required for modeling NH_3 neutralization of acid aerosols in the atmosphere. Further work is required for complete parameterization of NH_3 uptake rates as a function of NH_3 neutralization and its applicability to aerosol growth and nucleation microphysics. Further droplet and aerosol experiments are planned for the future.

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Appendix A

Uptake of Gas-Phase Formaldehyde by Aqueous Acid Surfaces

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Journal of Physical Chemistry, 100 8015-8022 (1996).

Abstract The uptake of gas-phase formaldehyde, CH_2O , by aqueous sulfuric and nitric acid droplets has been measured as a function of temperature, acid concentration and gas-droplet contact time. The results are interpreted in terms of the mass accommodation coefficient for formaldehyde on aqueous surfaces, the Henry's law constant for formaldehyde in aqueous acid solutions and the liquid-phase formation kinetics of methylene diol, $\text{CH}_2(\text{OH})_2$, and protonated formaldehyde, CH_3O^+ . Time dependant uptake studies under mildly acid solutions where $\text{CH}_2(\text{OH})_2$ and CH_3O^+ formation is slow reveal the existence of a chemisorbed surface complex for CH_2O at the gas-liquid interface. Uptake studies on nitric acid and mixed sulfuric acid/nitric acid solutions show slightly enhanced uptake relative to sulfuric acid only solutions. This observation has been attributed to variation of formaldehyde solubility (expressed as Setchenow coefficients) and CH_3O^+ equilibrium constant in nitric and sulfuric acid solutions. The implications of these measurements for the aqueous acid chemistry of formaldehyde and its role in atmospheric chemistry are discussed.

Appendix B

Uptake of Gas-Phase Formaldehyde by Aqueous Acid Surfaces

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The uptake of gas-phase formaldehyde, CH_2O , by aqueous sulfuric and nitric acid droplets has been measured as a function of temperature, acid concentration and gas-droplet contact time. The results are interpreted in terms of the mass accommodation coefficient for formaldehyde on aqueous surfaces, the Henry's law constant for formaldehyde in aqueous acid solutions and the liquid-phase formation kinetics of methylene diol, $\text{CH}_2(\text{OH})_2$, and protonated formaldehyde, CH_3O^+ . Time dependant uptake studies under mildly acid solutions where $\text{CH}_2(\text{OH})_2$ and CH_3O^+ formation is slow reveal the existence of a chemisorbed surface complex for CH_2O at the gas-liquid interface. Uptake studies on nitric acid and mixed sulfuric acid/nitric acid solutions show slightly enhanced uptake relative to sulfuric acid only solutions. This observation has been attributed to variation of formaldehyde solubility (expressed as Setchenow coefficients) and CH_3O^+ equilibrium constant in nitric and sulfuric acid solutions. The implications of these measurements for the aqueous acid chemistry of formaldehyde and its role in atmospheric chemistry are discussed

Appendix C

Uptake of Gas-Phase Ammonia 1: Uptake by Aqueous Surfaces as a Function of pH

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Journal of Physical Chemistry, submitted (1999)

Abstract

The uptake of gas phase ammonia by aqueous surfaces was measured as a function of temperature, gas liquid interaction time and pH in the range 0 to 13. Uptake measurements at low pH yielded values of the mass accommodation coefficient (α) as a function of temperature. The mass accommodation coefficient increases as the temperature decreases, from 0.08 at 290 K to 0.35 at 260 K. Time dependence of the uptake yielded values for the Henry's law constant. Uptake measurements at high pH indicate that an ammonia surface complex is formed at the interface. Co-deposition studies in which an aqueous surface, initially at pH = 4, was simultaneously exposed to both gas phase ammonia and SO₂ were also performed. In such a co-deposition experiment, the species entering the liquid neutralize each other and as a result the uptake of each species is enhanced. Modeling calculations indicate that the uptake of each species is in accord with bulk liquid phase kinetics.

Appendix D

Uptake of Gas-Phase Ammonia 2: Uptake by Sulfuric Acid Surfaces

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Journal of Physical Chemistry, submitted (1999)

Abstract

The uptake of gas phase ammonia by sulfuric acid surfaces was measured as a function of temperature (248 - 288 K), gas-liquid interaction time (2 - 15 ms), and acid concentration (20 - 70 wt% H_2SO_4) using a droplet train apparatus. The uptake coefficient increases as a function of acid concentration and reaches unity at about 55 wt% H_2SO_4 . The increased NH_3 uptake in acid solution is apparently due to reaction between NH_3 and H^+ at the gas-liquid interface. The results yielded parameters required to model the reaction of NH_3 with H^+ at the gas-liquid interface. These uptake experiments were expanded to include a detailed study of gas transport to a moving train of droplets. An analysis of previous sulfuric acid aerosol neutralization experiments, shows that the uptake of ammonia by ternary $\text{NH}_3/\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ solutions is significantly lower than by fresh binary $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ solutions. At typical tropospheric water and ammonia vapor concentrations, NH_3 uptake coefficients need to be included in detailed microphysical models of sulfuric acid aerosols.

Introduction

Aerosols play an important role in the atmospheric chemistry of both the stratosphere and the troposphere. Aerosols also affect the earth's climate by directly scattering radiation, and indirectly, by serving as cloud condensation nuclei (CCN). The number of cloud droplets formed is directly proportional the number density of cloud condensation nuclei. The size, density and composition of these cloud droplets in turn determine the effect of clouds on the Earth's albedo.¹

Ammonium (NH_4^+) and sulfate (SO_4^{2-}) are two of the primary ionic components in cloud condensation nuclei. Ammonia (NH_3) in the atmosphere originates primarily from surface sources, including decaying organic matter and chemical fertilizers. Sources of sulfur in the atmosphere include biogenic species such as CH_3SCH_3 , H_2S , OCS , anthropogenic sources (mostly SO_2), and volcanic emissions (principally SO_2). These emitted species are in the S(IV) oxidation state and are further oxidized in the atmosphere to form S(VI), principally H_2SO_4 , which in turn plays a key role in the formation of aerosols.

Current models for tropospheric aerosol growth depend on the condensation rates of gaseous ammonia, sulfuric acid, and water vapor.² Because atmospheric water vapor levels are high, aerosol growth rates are largely governed by the uptake of H_2SO_4 and NH_3 vapors. Recent measurements have shown that the uptake coefficient for H_2SO_4 vapor is near unity (essentially collision limited).^{3, 4} Well determined values for the uptake coefficient for $\text{NH}_3(\text{g})$ by acidic aerosols are required for quantitative modeling of atmospheric aerosol growth rates.

Knowledge of the ammonia uptake rate is also important in view of a recent suggestion^{5, 6} that ternary nucleation of $\text{NH}_3\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ vapors is a likely explanation of fast new particle formation rates inferred from field measurements of ultrafine particles.^{5, 7-8} Modeling of such particle formation rates in the atmosphere depends critically on the competition between condensation on pre-existing particles and new particle nucleation. New particle formation is favored by slow gas uptake rates on pre-existing particles, which increase steady state vapor levels.⁹

Previous studies of $\text{NH}_3(\text{g})$ interactions with H_2SO_4 liquid surfaces include a molecular beam scattering study¹⁰⁻¹³ and several flow reactor aerosol neutralization experiments¹⁴⁻¹⁷. In the scattering study the absence of detectable inelastic scattering was interpreted as evidence for a unity uptake coefficient on concentrated H_2SO_4 solution (98.8wt%). In the aerosol studies, ammonia-aerosol interaction times are mostly on the order of seconds. Based on composition changes observed in collected aerosols, $\text{NH}_3(\text{g})$ uptake coefficients ranging from 0.1 to 0.5 were deduced. In all these studies, the concentration of $\text{NH}_3(\text{g})$ was such that the composition of the aerosol was changing significantly during the experiment, making it difficult to extract kinetic parameters for binary sulfuric acid solutions.

In the present work we study the interaction of $\text{NH}_3(\text{g})$ with $\text{H}_2\text{SO}_4 / \text{H}_2\text{O}$ surfaces, using the droplet train apparatus. The gas phase NH_3 density was low ($5 \times 10^{12} \text{ cm}^{-3}$) and the gas-liquid interaction time was on the order of milliseconds. The low gas phase concentration of $\text{NH}_3(\text{g})$ and the short gas-liquid interaction time minimize droplet composition changes. The uptake of gas phase ammonia by aqueous sulfuric acid was measured as a function gas-liquid interaction time (2 - 15 ms), acid concentration (20 - 70 wt% H_2SO_4) and temperature (248 - 288 K). The results yielded parameters required to model the reaction of NH_3 with H^+ at the gas-liquid interface.

A proper understanding of gas phase diffusive transport of the trace gas to the droplet train is central to an accurate analysis of our uptake data. In our previous gas uptake experiments with aqueous droplets, the flow tube pressure was relatively high set by the equilibrium water vapor pressure (4 - 20 Torr). This limited the range of pressures over which we could test our understanding of gas phase diffusion. By contrast, in the present studies with sulfuric acid droplets, the partial pressure of H_2O vapor is relatively low. For example, for a 70 wt% H_2SO_4 solution at 250 K, the equilibrium water vapor pressure is only 0.02 Torr. The overall pressure in the flow tube is then determined principally by the inert carrier gas. Under these conditions, it is

possible to significantly expand our previous studies of trace gas uptake by a moving train of droplets and place our understanding of gas phase diffusive transport on a firmer footing.

The apparatus, basic experimental procedure, data analysis and modeling used in this study are described in the preceding companion article.¹⁸ Here, we will present only those aspects of the experiment, which are specific to the NH_3 -sulfuric acid studies.

Experimental Section

Uptake measurements of $\text{NH}_3(\text{g})$ on sulfuric acid were performed using a droplet train apparatus similar to the one shown in Figure 2 of the preceding article.¹⁸ The apparatus was modified to allow work with cold concentrated acid droplets as described by Robinson et al.¹⁹. Gas uptake was measured by passing a fast-moving (1500-3000 cm/s) and monodisperse (50 to 350 μm in diameter) collimated train of aqueous acid droplets through a 30 cm long longitudinal low pressure flow tube which contained trace amounts of NH_3 entrained in a flowing mixture of carrier (rare gas) and water vapor. Carrier gases are introduced at the entrance of the reactor. Trace gases (diluted in rare gas) are introduced through one of three loop injectors located along the flow tube. By selecting the injector and the droplet velocity, the gas-droplet interaction time can be varied between 2 and 15 ms.

Sulfuric acid solutions were prepared by diluting known volumes of reagent grade sulfuric acid (95 - 98 wt%) with known volumes of distilled water. The concentrations were determined from the densities of the solutions which were measured by weighing 10 ml aliquots.

²⁰ The accuracy of these concentration measurements is about ± 0.5 wt %.

The droplet stream was produced by forcing the acid solution through a platinum electron microscope aperture surrounded by a donut shaped piezoelectric ceramic. Before flowing through the nozzle aperture, the acid solution was precooled using an external temperature controlled circulating bath. A chromel-alumel thermocouple in a stainless steel sheath was fixed in place just above the aperture and provided a continuous measure of the droplet stream

temperature. As the droplets traverse the flow tube, they equilibrate with the ambient water vapor. In order to minimize evaporation, which would change droplet surface temperature and concentration, a flow of H₂O in helium matched to the water vapor pressure over the acid droplet was introduced into the droplet generation region of the flow tube. In previous experiments with this apparatus, direct measurements of water vapor densities demonstrated that droplet surface acid concentrations in the gas/droplet interaction region are within 0.5 wt % of their initial value and that the droplet temperature is known to within $\sim \pm 2^\circ\text{C}$.²¹

Gas uptake is determined by measuring the trace gas concentration (n_g) downstream of the flow tube as the surface area of the droplets is changed in a stepwise fashion, by varying the driving frequency of the piezoelectric ceramic. A measured decrease in the trace gas signal (Δn_g) resulting from an increase in the exposed droplet surface area corresponds to an uptake of the gas by the droplet surface. The uptake coefficient (γ_{meas}), as defined in Shi et al.¹⁸, was obtained from the measured change in trace gas signal via Eq. (1):

$$\gamma_{\text{meas}} = \frac{4 F_g}{\bar{c} \Delta A} \ln \frac{n_g}{n_g'} \quad (1)$$

The parameters are defined as in Shi et al.,¹⁸ F_g is the carrier-gas volume rate of flow ($\text{cm}^3 \text{s}^{-1}$) through the system, $\Delta A = A_1 - A_2$ is the change in the total droplet surface area in contact with the trace gas, and n_g and n_g' are the trace gas densities at the outlet of the flow tube after exposure to trains of droplets of area A_2 and A_1 respectively ($n_g = n_g' + \Delta n_g$).

The gases exiting the reaction zone flow through a multi-pass absorption cell (White cell) with an effective path length of about 750 cm. The NH₃ vapor is detected via tunable infrared diode laser differential absorption. The NH₃ absorption line used in these experiments is at a frequency of 965.3538 cm^{-1} , with a line strength of $4.32 \times 10^{-19} \text{ cm}^2 \text{ molecule}^{-1} \text{ cm}^{-1}$.²² Initial trace gas densities of $\sim 5 \times 10^{12} \text{ cm}^{-3}$ (typical in these experiments) yield a fractional absorbance of $\sim 10\%$.

Pressure differences between the flow tube and the droplet collection chamber were monitored and balanced. In other recent experiments^{19, 23} the pressure balance was checked further by monitoring the concentration of an inert reference gas, typically methane, which is added to the flow. The change in the density of the inert gas monitors the effect of the sweep-out and/or pressure unbalance as droplet frequency is changed. In the present ammonia study, absorption lines for an appropriate reference gas were not available with the diode laser. However, changes in methane concentration due to sweep-out or pressure unbalance observed in previous studies were less than 0.5%, whereas NH₃ concentration changes due to uptake were in the range of 7% - 70%, depending on the droplet composition and temperature.

Modeling NH₃(g) Gas-liquid Interactions

In our droplet train experiments, a gas phase species, in this case NH₃(g), interacts with liquid droplets and the disappearance of that species from the gas phase is monitored. The disappearance of the species is expressed in terms of a measured uptake coefficient, γ_{meas} , which is related to the experimentally observed flux (J) into a surface as:

$$J = \frac{n_g \bar{c} \gamma_{\text{meas}}}{4} \quad (2)$$

As is discussed in the companion paper,¹⁸ gas uptake is a function of several inter-related processes which may include gas phase and liquid phase diffusion, mass accommodation, Henry's law solubility, bulk phase and surface reactivity. Therefore, the parameter γ_{meas} represents a convolution of these processes, and the experimental challenge is to separate the contributions of these processes to the overall gas uptake.^{21, 23, 24} Following the discussion in the previous paper and references therein, it is convenient to express the overall uptake process in terms of a resistance formulation,

$$\frac{1}{\gamma_{\text{meas}}} = \frac{1}{\Gamma_{\text{diff}}} + \frac{1}{S} + \frac{1}{\Gamma_s + \frac{1}{\frac{S-\alpha}{S\alpha} + \frac{1}{\Gamma_b}}} \quad (3)$$

where Γ_{diff} represents the rate of gas diffusion; S is the surface adsorption coefficient, defined as the fraction of collisions that results in thermal accommodation of the trace gas onto the surface; Γ_s represents the effect on the uptake of surface processes; α is the mass accommodation coefficient (the probability that a molecule enters the bulk liquid phase upon collision with the surface); and Γ_b represents the rate of dissolution and reaction (if any) of species within the bulk liquid. This formulation aids the deconvolution of the various processes that control the overall gas uptake rate. In what follows, we will briefly discuss the bulk phase terms (where Γ_{diff} and Γ_b) and then we will focus on the interfacial model that accounts for mass accommodation (α) and surface reactivity (Γ_s). In particular, the formulation of surface reactivity within the gas liquid interface will serve as a key to understanding how NH_3 uptake in acid solutions. Surface reactions may cause the uptake coefficient to exceed the limitation normally set by the mass accommodation coefficient.

Gas Phase Diffusion. As discussed in the companion paper and references therein¹⁸, gas phase diffusive transport of a trace gas to droplets does not lend itself to a straightforward analytical solution. However, an empirical formulation of diffusive transport to a stationary droplet developed by Fuchs and Sutugin²⁵ has been shown to be in good agreement with measurements (See Widmann and Davis²⁶). Using the Fuchs-Sutugin formulation, *Hanson et al.*²⁷ extracted an expression for Γ_{diff} as:

$$\frac{1}{\Gamma_{\text{diff}}} = \frac{0.75 + 0.283K_n}{K_n(1 + K_n)} \quad (4)$$

Here, Kn is Knudsen numbers defined as $2\lambda/d_r$, where λ is mean free path and $\lambda = 3D_g / \bar{c}$; d_r is the effective diameter of droplets for the diffusive process. In our early experiments, it was shown that diffusive transport to the train of moving droplets, closely spaced (2 to 12 droplet diameters), is independent of droplet diameter but depends rather on the diameter of the droplet-forming orifice (d). (See Worsnop et al.²⁴.) Worsnop et al.²⁴ experimentally established the relationship between d_r and d as $d_r = (1.9 \pm 0.1)d$.

It is possible to formulate plausibility arguments suggesting why diffusive transport to a train of moving droplets depends on the diameter of the droplet-forming orifice, rather than on the diameter of the droplets. However, a convincing analytical formulation explaining this observation has so far not been obtained. Work towards this goal is continuing.

As was stated earlier, because of the low H_2O vapor pressure of the sulfuric acid droplets, the $NH_3(g)$ uptake measurements facilitated the study of diffusive transport over a wide range of Knudsen numbers ($Kn = 0.05$ to 4.5) with uptake coefficients ranging from 0.06 to 1 . These studies are described in the Appendix to this paper. The results confirmed the earlier findings that diffusive transport to the train of moving droplets is independent of droplet diameter, yielding a value of $d_r = (2.0 \pm 0.1)d$ where d is the orifice diameter. The studies showed that over the full range of Knudsen numbers, gas phase diffusive transport is in accord with the formulation of Fuchs and Sutugin²⁵ as expressed by Eq. 4.

Based on these results, we define γ_o as the uptake coefficient in the limit of "zero pressure", i.e. in the absence of gas diffusion limitations,

$$\frac{1}{\gamma_{\text{meas}}} = \frac{1}{\Gamma_{\text{diff}}} + \frac{1}{\gamma_o} \quad (5)$$

Solubility and Reactivity in the Bulk Liquid. In this section we discuss the effect of Henry's law solubility and chemical reactions of the NH_3 in the acid solution. The principal equilibrium processes governing NH_3 solubility in acid solutions are:

K_b' is the equilibrium constant for reaction 7, $K_b' = k_f'/k_r'$. The overall solubility of $\text{NH}_3(\text{g})$ can be expressed as an effective Henry's law coefficient H^* (M atm^{-1}) given by the sum of physically dissolved $\text{NH}_3(\text{aq})$ and protonated $\text{NH}_4^+(\text{aq})$.

$$\{[\text{NH}_3(\text{aq})] + [\text{NH}_4^+(\text{aq})]\} = H^* p_{\text{NH}_3} = [\text{NH}_3(\text{g})] R T H^* = [\text{NH}_3(\text{g})] H (1 + K_b' [\text{H}^+]) \quad (8)$$

Here p_{NH_3} is the partial pressure of ammonia (atm), R is the gas constant ($\text{atm M}^{-1} \text{K}^{-1}$).

In acid solutions ($\text{pH} < 2$), the H^+ concentration is so large that the protonation step in the equilibrium is shifted far toward NH_4^+ , making H^* sufficiently large ($> 10^9 \text{ M/atm}$) so that on the millisecond time scale of the droplet train experiment reaction (Eq. 7) is irreversible. In other words, in the droplet train experiments under highly acidic conditions, re-evaporation of dissolved NH_3 can be neglected. Under those conditions, Γ_b is determined by the forward reaction rate in Eq. 7, which is expressed by the term Γ_{rxn} .²⁸

$$\Gamma_b = \Gamma_{\text{rxn}} = \frac{4HRT}{\bar{c}} \sqrt{D_1 k_1} \quad (9)$$

Here k_1 is the pseudo first order reaction rate for the formation of NH_4^+ in Eq. 7, given by

$$k_1 = k_f' [\text{H}^+] \quad (10)$$

The rate constant k_r' in Eq. 10 is $4.3 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ at 293 K.²⁹ With this value of k_r' , Γ_b is larger than 8 for $\text{pH} < 2$. The $1/\Gamma_b$ term is negligible compared to $1/\alpha$ and therefore, Γ_b is not rate limiting for $\text{NH}_3(\text{g})$ uptake into acid solutions for $\text{pH} < 2$.

Interfacial Processes. Processes occurring at the gas-liquid interface can be taken into account via the kinetic model described in the preceding article. (Eq. 5 in Shi et al.¹⁸; also see Nathanson et al.³⁰, and Hanson³¹):

Here the subscripts g, s and l represent the gas, surface and liquid state of the species. In Eq. 11, the reverse processes going from the bulk to the interface (i.e. reverse rates parallel to k_{sol} and k_{rxn}) are accounted for by Γ_b and, as was noted, can be neglected for NH_3 uptake into acid solutions. Interfacial processes are then formulated in terms of mass accommodation (depending on k_{sol} and k_{des}) and surface reaction (depending on k_{surf}). As was stated in the preceding paper,

$$1/\alpha = 1/S + k_{\text{des}} / S k_{\text{sol}} \quad (12)$$

As in Shi et al.¹⁸, here also, the adsorption coefficient S is expected to be close to unity.³⁰
³² For simplicity, here we will assume $S = 1$. Thus, the mass accommodation coefficient α depends on the ratio $k_{\text{sol}}/k_{\text{des}}$, constrained to a maximum probability of unity by the adsorption collision rate.

Further, if we assume that $\Gamma_b = \Gamma_{\text{rxn}} \gg 1$, as is the case for NH_3 uptake into acid solution

$$1/\gamma_o = 1 + 1/(\Gamma_s + k_{\text{sol}}/k_{\text{des}}) \quad (13)$$

Here, as before Γ_s represents the effect on the uptake of surface processes.

The mass accommodation coefficient is expressible as,^{33, 30}

$$\alpha / (1-\alpha) = k_{\text{sol}}/k_{\text{des}} = \exp(-\Delta H_{\text{obs}} / RT + \Delta S_{\text{obs}} / R) \quad (14)$$

In the companion paper¹⁸, it was shown that in aqueous solutions, in the pH range 0 to 4, the $\text{NH}_3(\text{g})$ uptake was limited by mass accommodation, and with reference to Eq. 14, α for $\text{NH}_3(\text{g})$ is characterized by $\Delta H_{\text{obs}} = -9.02 \pm 0.8$ kcal/mol and $\Delta S_{\text{obs}} = -35.9 \pm 2.9$ cal/(mol K). This corresponds to a negative temperature dependence of α , with α varying from 0.35 to 0.08 between 260 and 290 K.

Surface Reactivity. In aqueous solution ($\text{pH} > 0$), $\text{NH}_3(\text{g})$ uptake is described by mass accommodation as in Eqs. 13 and 14, with no evidence of surface reaction.^{18, 34} In contrast, as will be shown in the next section, the rate of $\text{NH}_3(\text{g})$ uptake into sulfuric acid solutions (H_2SO_4 concentration $> 20\text{wt}\%$) increases sharply with acidity and the measured uptake coefficient is larger than the mass accommodation coefficient (α) for aqueous solutions. This increase is most consistently explained by a surface reaction as characterized by Γ_s in Eq. 13. (See Discussion section.) This surface reaction is most likely an acid catalyzed formation of NH_4^+ analogous to the bulk phase reaction in Eq. 7. That is,

where the protonation of NH_3 occurs within the interface without species uptake into the bulk solution.

Surface reaction channels within the gas-liquid interface have been observed for a number of aqueous and acid systems. These include the reaction of ClONO_2 with HCl in $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ solution^{35, 36}, reactions of halogen molecules with aqueous halide ions (e.g. Cl_2 , Br_2 + Br^- , I^-)³⁷, ClONO_2 + I^- reaction in aqueous solution³⁸, and, most recently, acid and base catalyzed D/H isotope exchange for deuterated ethanol on aqueous solutions³⁹. The distinguishing feature of these studies is the observation that uptake rates are linearly proportional to reactant

concentration, as opposed to the square root dependence for liquid diffusion limited bulk reactivity (Eq. 9). In all these cases it was possible to distinguish between surface and bulk liquid reaction channels by performing a detailed analysis of uptake kinetics.

The effect of surface reactions on trace gas uptake is formulated in terms of n_s and k_{surf} in Eq. 11 and as derived in Shi et al.¹⁸ (their Eq. 12), the surface uptake coefficient Γ_s is:

$$\Gamma_s^{\text{rxn}} = 4 (n_s/n_g) k_{\text{surf}} \quad (16)$$

Formally, n_g (cm^{-3}) and n_s (cm^{-2}) are the gas phase and surface concentrations of ammonia and k_{surf} is the pseudo first order rate constant for the reaction of the interfacial ammonia with the H^+ ion.

A quantitative calculation of Γ_s requires knowledge of the magnitudes of these interfacial parameters. However, since these parameters are not known, they have to be estimated. We will assume that the interfacial parameters are linearly proportional to their bulk phase counterparts. In this approximation, we take the vapor-liquid interface to be a sharp but finite transition, few molecular diameters thick, within which the molecular density increases from the gas to the liquid. We will assume that the thickness δ of the interface is 10^{-7} cm ($10 \text{ \AA}$).

The bulk liquid phase concentration n_l of ammonia can be expressed in terms of the gas phase concentration, Henry's law coefficient (H) for ammonia and f_{NH_3} , the activity coefficient of NH_3 in acidic solutions. In accord with our assumption that the interfacial parameters are linearly proportional to their bulk phase counterparts, the ratio (n_s/n_g) can be expressed:

$$n_s/n_g = c_1 f_{\text{NH}_3} H R T \delta \quad (17)$$

where c_1 is an assumed constant of proportionality between the interfacial and bulk-liquid phase ammonia concentrations.

In terms of the bulk phase parameters the rate constant k_{surf} is:

$$k_{\text{surf}} = c_2 a_{\text{H}^+} k_f' \quad (18)$$

Here a_{H^+} is the bulk concentration (or activity) of H^+ , c_2 is the constant of proportionality between the interfacial and bulk H^+ concentrations and k_f' is the rate for the $NH_3(aq)$ reaction with H^+ in the bulk phase. (See Eq. 7.)

The activity coefficient of NH_3 in acidic solutions is not known. Therefore, we will approximate it with the activity of water, a_{H_2O} . (See Hanson³⁶.) The activity of water is a dimensionless parameter, defined as unity in pure water, which decreases with increased acidity.^{40, 41} With these assumptions, the surface uptake coefficient $\Gamma_s = \Gamma_s^{rxn}$ for ammonia is expressed as:

$$\Gamma_s^{rxn} = 4 c_1 a_{H_2O} HRT [c_2 a_{H^+}] k_f' \delta / \bar{c} \quad (19)$$

The Henry's law coefficient is obtained from the fitted values obtained in Shi et al.¹⁸. Convenient representations of a_{H_2O} and a_{H^+} can be obtained from Tabazadeh et al.⁴² and Michelsen⁴³, respectively. These in turn provide analytical expressions for the exact formulation of Carslaw et al.⁴¹ The rate coefficient k_f' is a diffusion limited rate (see Eq. 10) and therefore its temperature dependence will be inferred from the temperature dependence of the diffusion coefficient.²⁹

Note that in the formulation of Eq. 19, the dependence of Γ_s on reactant concentration (or activity, a_{H^+}) is linear. By contrast the bulk phase reactive uptake coefficient (Γ_{rxn} , in Eq. 9) depends on the square root of reactant concentration. With the assumptions stated above, the surface kinetics in Eq. 19 is characterized by the constants of proportionality c_1 and c_2 . The experimental uptake data will provide the product $c_1 c_2$.

Results and Analysis

Uptake Measurements. As an example of NH_3 uptake data, we show in Figure 1a and b plots of $\ln(n_g/n_g')$ as a function of $\bar{c} \Delta A / 4F_g$ at 250 K and 70 wt% H_2SO_4 . Here $\bar{c} \Delta A / 4F_g$ was varied by changing the gas flow rate and the effective droplet surface area (ΔA). Each point in the figure is the average of at least ten area change cycles with the error bars representing one standard

deviation from the mean in the experimental $\Delta n_g/n_g$ value. In this experiment, the water pressure was set to 0.02 Torr, corresponding to the equilibrium H_2O vapor pressure of a 70 wt% H_2SO_4 solution at 250 K. The measurements shown in Figures 1a and 1b were performed under the same conditions except for the carrier gas pressure. The pressures in the experiments of Figure 1a and b were 4 Torr of He ($Kn=1$) and 23 Torr Kr ($Kn=0.05$) respectively. (Note the abscissa scale differs in the two figures.) The higher pressure experiments were part of the gas phase diffusive transport studies. The slopes of the lines in the Figures 1a and b yield values for γ_{meas} of 0.74 ± 0.02 and 0.060 ± 0.001 , respectively.

Data plots similar to these shown in Figure 1 were obtained for the full range of uptake studies. In these studies the uptake signal $\Delta n_g/n_g$ typically varied from 7% to 70%. The linearity of these plots over an order of magnitude validates the measurement procedure, indicating that the uptake is well described by a single value of γ_{meas} , as in Eq. 1. The difference in uptake rates for the two plots in Figure 1 is due to the effect of gas phase diffusion, (Γ_{diff}) which is much slower in 23 Torr of Kr than in 4 Torr He. In fact, using Eqs. 4 and 5, it is evident that the γ_{meas} values in both Figures 1a and 1b correspond to $\gamma_0 = 1$ for $NH_3(g)$ uptake into 70 wt% H_2SO_4 . (See Appendix.)

Uptake as a Function of Gas-Liquid Interaction Time. In Figure 2 we show the measured uptake coefficient γ_{meas} as a function of gas-liquid contact time for 20, 40 and 70 wt% H_2SO_4 at 285 K. As is evident, no time dependence is observed in this data set. This is in accord with expectations since for sulfuric acid concentrations > 20 wt%, the effective solubility is large ($H^* = 1.8 \times 10^{11} \text{ M atm}^{-1}$ for 20 wt% H_2SO_4) and therefore $\Gamma_b \gg 1$. On the millisecond time scale of our experiments the uptake is limited by α and Γ_s as described by Eq. 13.

In the sections that follow, uptake will be expressed in terms of γ_0 after correcting γ_{meas} for gas phase diffusion via Eqs. 4 and 5. For the results in Figure 2, γ_{meas} values of 0.24, 0.50 and 0.77 for 20, 40 and 70 wt% H_2SO_4 correspond to γ_0 values of 0.34, 0.82 and 1.01, respectively.

Uptake as a Function of Acidity. In Figure 3, γ_o is plotted as a function of acidity. This is a specific set of data obtained at 285 K (closed diamonds). The solid line is a plot of Eq. 13 with $\alpha = 0.11$ as determined by Shi et al. (see eq. 14).¹⁸ In calculating Γ_s (Eq. 19), the value of $c_1 c_2$ is $(5.4 \pm 2.0) \times 10^{-4}$ obtained via a global fit to uptake data at all temperatures studied. (See next section.) For completeness, the plot includes experimental results on aqueous droplets obtained by Shi et al. at a slightly higher temperature of 291 K (open symbols) and at a gas-liquid contact time of 5 ms.¹⁸ Acidity is defined as $-\log[a_{H^+}]$, where a_{H^+} is the activity of H^+ . For aqueous solutions, $[a_{H^+}] = [H^+]$ and acidity is equivalent to pH. In sulfuric acid solutions, the activity of H^+ is calculated using the multi-component mole-fraction-based thermodynamic model of Carslaw et al..⁴¹

As discussed in Shi et al, the decrease in the uptake rate for $pH > 4$ is due to limitation imposed by NH_3 physical solubility (Eq. 6).¹⁸ In this pH range the formation rate of NH_4^+ is reduced due to low H^+ concentration (Eq. 7). The plateau in the NH_3 uptake rate approached at $pH < 4$ in aqueous solution, is due to limitation imposed by the mass accommodation coefficient. In this region Γ_b is much larger than α , Γ_s is negligible and therefore here $\gamma_o = \alpha$ (Eq. 3 and 5). As will be shown the increase in γ_o beyond α in concentrated H_2SO_4 solution, can be explained by a surface reactivity.

Uptake as a Function of Temperature. In Figure 4, we show a plot of the uptake coefficients, γ_o , as a function of temperature for 20, 40, 55, and 70 wt% sulfuric acid. The figure, which is on a logarithmic scale, also shows the mass accommodation coefficients for NH_3 on aqueous solution at $pH = 1$ measured by Shi et al. as open circles.¹⁸ (See Figure 6 in Shi et al.¹⁸). The negative temperature dependence of α is consistent with previous results.^{18, 33} It is important to note that with increasing H_2SO_4 concentration the magnitude of γ_o increases and the temperature dependence of γ_o decreases. The uptake coefficient γ_o reaches the limit of 1 for $H_2SO_4 > 50\text{wt}\%$, at which point γ_o is independent of temperature.

The lines in Figures 3 and 4 connecting the experimental points are plots of Eq. 13 including the value of α measured by Shi et al.¹⁸ and the surface NH_3 and H^+ reaction channel calculated via Eq. 19. The best fit to the data is obtained with the value of the product $c_1 c_2$ in Eq. 19 equal to $(5.4 \pm 2.0) \times 10^{-4}$ (see Eqs. 17 and 18). This single value of $c_1 c_2$ was used to fit the data at all temperatures.

Discussion

Interactions at the Gas-Liquid Interface. Figures 3 and 4 contain the principal findings of this study. In Figure 3, ammonia uptake is presented as a function of acid concentration from 70 wt% sulfuric acid to pH 13 ($-\log[a_{\text{H}^+}] = -4.0$ to 13, respectively). The present work together with that of Shi et al.¹⁸ is the first presentation of the $\text{NH}_3(\text{g})$ uptake over a range of 17 orders of magnitude in H^+ activity.

As was noted in the preceding paper, the uptake coefficient above pH 10 is limited by the physical solubility of NH_3 .¹⁸ With increasing acidity the solubility increases, and the uptake coefficient rises toward a plateau at about pH 2, where $\gamma_0 = \alpha$, as discussed in Shi et al.¹⁸. Perhaps the most notable feature in Figure 3 is the further rise of γ_0 at higher acid concentrations, with γ_0 reaching unity at ~50 wt% H_2SO_4 .

One might guess that the increase in γ_0 for higher acid concentrations (> 10 wt% H_2SO_4) is due to an increase in the mass accommodation coefficient. However, two observations argue against this explanation. First, the uptake coefficient (γ_0) exhibits a plateau between pH = 0 and 3, suggesting that the increase below pH = 0 signals the onset of a new process. Second, in the uptake experiments with $\text{HCl}(\text{g})$ on sulfuric acid¹⁹, where no such increase in uptake with acidity was observed, the mass accommodation coefficient was shown to be independent of sulfuric acid concentration. We suggest that the increase in NH_3 uptake with acidity for pH < 0 is indicative of

a separate process, most likely a surface specific reaction of NH_3 with H^+ ions near the gas-liquid interface.

The hypotheses of a surface specific reaction is supported by the observation that, in the region of increasing uptake (pH 0 to 55 wt% H_2SO_4), the rising part of the uptake coefficient γ_0 is best fitted by a function Γ_s linear in a_{H^+} as formulated in Eq. 19. This is illustrated in Figure 5. Here we have extracted Γ_s values from experimental data via Eq. 13, and rearranged those values via Eq. 19 so that data obtained at different temperatures could be displayed on the same plot.⁴⁴ This entailed dividing Γ_s by the factor $f(T) = 4 a_{\text{H}_2\text{O}} \text{HRT } k_f' \delta/\bar{c}$, and plotting the resulting expression as a function of a_{H^+} in logarithm space. Data are shown for the five temperatures studied. Error bars are calculated from uncertainties in Figure 4 using Eq. 13. The straight line is the best fit to the function $\Gamma_s = f(T)c_1c_2(a_{\text{H}^+})^n$. This procedure yields $n = 0.98 \pm 0.16$ and $c_1c_2 = (5.6 \pm 2.0) \times 10^{-4}$, which is in near exact agreement with the previously determined value $c_1c_2 = (5.4 \pm 2.0) \times 10^{-4}$. A dependence proportional to the square root of activity ($a_{\text{H}^+}^{1/2}$) consistent with bulk phase reaction does not fit the data. Clearly, the plot confirms the linear dependence of Γ_s on a_{H^+} , in accord with the hypotheses of a $\text{NH}_3\text{-H}^+$ surface reaction.

The factors c_1 and c_2 relate surface to bulk liquid values for solvated ammonia and H^+ (Eqs. 17 and 18). The small magnitude of c_1c_2 , of order 5×10^{-4} , is not surprising. The interfacial density of H^+ is expected to be much lower than that in the bulk. Both calculations and experiments show that there is a substantial barrier for ions to approach the surface of an aqueous medium. In an experiment using laser induced second harmonic generation, Eisenthal estimated that an H^+ ion density at the surface is about two orders magnitude lower than in the bulk.⁴⁵ We do not have a reliable guide for estimating the surface density of ammonia. However, if c_2 were on the order 0.01 as suggested by the work of Eisenthal⁴⁵, then c_1 (the ratio of surface to bulk concentration of ammonia) would be about 0.056. This value obviously depends on several assumptions used in the formulation of Eq. 19, among them for example, assumption that the

physical solubility of NH_3 in acid solutions can be approximated by the activity of water, that is, by $f_{\text{NH}_3} \cong a_{\text{H}_2\text{O}}$.

Two conclusions can be drawn from Figure 5. First, the linear dependence on acid activity rather than on $a_{\text{H}^+}^{1/2}$ dependence provides the best fit to the experimental results. Second, the formulation of uptake that includes α and Γ_s as described in Eqs. 3, 15, and 19 accounts for the experimental observations including the plateau of $\gamma_0 \sim 0.1$ in the pH region between 0 and 6.

Comparison with Previous Surface Studies. The results of three types of experiments can be usefully compared to the current work: gas uptake studies, beam studies, and aerosol neutralization studies.

Gas uptake studies. As was previously mentioned, a surface reaction channel at the gas-liquid interface was observed in several previous gas uptake studies.³⁵⁻³⁹ In all these studies including the current one, two main factors identify surface reactions: 1. Enhancement of uptake over values that would be observed based on bulk phase processes and 2. A linear dependence of the enhancement on reactant concentration in the region of enhanced uptake. There is however, one notable difference between the previous and present surface reactivity studies. In the halogen/halide³⁷, $\text{ClNO}_2 + \text{I}^-$ ³⁸ and $\text{CH}_3\text{CH}_2\text{OD}$ isotope exchange³⁹ studies, the uptake coefficient initially increased (linearly) as a function of reactant concentration and then reached a plateau at a value of the uptake coefficient (γ_0) less than unity. In those studies the plateau value of $\gamma_0 < 1$ most likely reflects interfacial barriers between surface adsorbed species and solvated ions, similar to the free energy barrier inferred from negative temperature dependent α observations (see discussion in Shi et al.³⁹). By contrast, in the present $\text{NH}_3(\text{g})$ uptake study, $\gamma_0 = 1$ at high acidities. This implies, that, even though the concentration of the H^+ ion at the interface is greatly reduced, the protonation of NH_3 is so highly favored (and the mobility of H^+ within the interface so large) that at high acidities, every ammonia molecule that strikes the surface irreversibly reacts to form NH_4^+ . In this case there is no interfacial barrier to limit surface reactivity.

We note that uptake coefficients approaching unity have been observed in several other uptake studies on H_2SO_4 solutions both with and without indication of surface reactions. In the uptake of $\text{ClONO}_2 + \text{HCl}$ on sulfuric acid, enhanced uptake due to surface reactivity was observed.³⁶ However the experiment was done at low temperature (203K), where α approaches unity, precluding separation of mass accommodation and surface reaction. Poschl et al. observed near unity uptake coefficients for gas phase H_2SO_4 on liquid sulfuric acid, but this is most likely due to nearly unit mass accommodation probability.⁴

The uptake of HCl on H_2SO_4 solution is governed by the mass accommodation coefficient α , as indicated by a negative temperature dependence, with $\gamma_0 < 1$ for $T > 240\text{K}$, independent of sulfuric acid concentration.¹⁹ There was no sign of surface reactivity. Even in concentrated acid solutions (40-50wt%) HCl uptake is limited by mass accommodation (α), analogous to NH_3 (and $\text{CH}_3\text{CH}_2\text{OH}$) in aqueous solution.^{18, 39} It is evident that in both aqueous and acid solution, the uptake of HCl requires dissolution of the species, involving dissociation into H^+ and Cl^- ions. In contrast to ammonia that forms NH_4^+ at the interface, the dissociation of HCl , requiring solvation of both H^+ and Cl^- , does not occur at the interfacial region.

Beam studies. The research group of Nathanson¹¹⁻¹³ conducted molecular beam scattering experiments of gases, including NH_3 ¹⁰, from films of highly concentrated $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ solution (98.8 wt%). In those studies, inelastic scattering yields information on the degree of desorption of thermally adsorbed ("trapped") molecules. Uptake coefficients can be inferred from the degree of inelastic scattering. For concentrated acid films, only species with high acid/base reactivity had uptake coefficients approaching unity as indicated by the absence of inelastic scattering. This includes NH_3 uptake results on 98.8% H_2SO_4 , which is in agreement with results from our present NH_3 studies for $\text{H}_2\text{SO}_4 > 55$ wt%. While the scattering experiments cannot directly distinguish surface and bulk reactivity, Fiehrer and Nathanson¹³ suggest that the absence of inelastic scattering is likely due to fast reactions within the interface, much as inferred here for NH_3 uptake in concentrated acid solution. Unit collision efficiency was also observed for isotope

exchange of deuterated water and formic acid on H_2SO_4 surfaces, indicative of fast proton exchange. The inference of $\gamma_0 \sim 1$ for ethanol (as well as ammonia) uptake into concentrated acid is of particular interest. The uptake behavior of $\text{CH}_3\text{CH}_2\text{OH}$ is analogous to that of NH_3 in which both have an uptake coefficient $\gamma_0 < 1$ on aqueous solutions.^{46, 39} Fiehrer and Nathanson¹³ interpreted the $\gamma_0 \sim 1$ for $\text{CH}_3\text{CH}_2\text{OH}$ on H_2SO_4 in terms of its basicity in the highly concentrated acid solution, analogous to NH_3 (Eq. 15). Smaller γ_0 values for other species correlate inversely with basicity. The uptake behaviour of HCl observed by Robinson et al. can be understood from this perspective. The acidic nature of HCl impedes dissociation in a highly acidic medium and prevents surface reaction. In contrast, the basicity of NH_3 is so large that $\gamma_0 \sim 1$ via protonation, is observed even at H_2SO_4 concentrations as low as 55wt%.

Aerosol neutralization studies. To our knowledge, the only previous studies to have investigated $\text{NH}_3(\text{g})$ uptake into concentrated sulfuric acid solutions were experiments where the neutralization of acidic aerosols was measured.^{14-17, 47} These aerosol experiments differ from the current droplet studies in that the entire volume of the sub-micron aerosol equilibrates with the gas phase during the uptake experiment. Since the magnitude of NH_3 uptake is measured by the degree of neutralization of the collected aerosol, the very nature of the experiment is such that the composition of the sulfuric acid aerosol changes during the experiment. In most cases the $\text{NH}_4^+/\text{SO}_4^{2-}$ ratio increases up to about 1. This is in contrast to the droplet experiments where the $\text{NH}_4^+/\text{SO}_4^{2-}$ ratios remains < 0.01 , because of the short gas-liquid exposure time and the relatively low $\text{NH}_3(\text{g})$ concentration ($5 \times 10^{12} \text{ cm}^{-3}$). Thus, the range of uptake coefficients measured in the aerosol experiments, (0.1 - 0.5) is most likely due to the changing aerosol composition as the H_2SO_4 solution is neutralized.

The aerosol experiments of Huntzicker et al.¹⁵ utilized an atmospheric pressure aerosol flow tube coupled to a sulfate analyzer, with a movable aerosol injector that permitted variable aerosol exposure times. This experiment included NH_3 uptake measurements at relatively low H_2SO_4 neutralization. They reported uptake coefficients in the range of 0.1 - 0.4, based on a

kinetic model that assumed a constant uptake coefficient, independent of exposure time and composition. Our re-analysis of their data indicates that the uptake rate changed with time. The rate decreased as the aerosol was neutralized. In fact, for the shortest exposure time (0.5 sec), corresponding to small composition changes ($\text{NH}_4^+/\text{SO}_4^{2-} < 0.05$), the observed uptake rate matched the gas diffusion limit at one atmosphere. That is, the measured uptake rate is consistent with $\gamma_0 = 1$. For the experiments where detailed time dependent results were reported, re-analysis of the results indicates that $\gamma_0 \leq 0.1$ as the $\text{NH}_4^+/\text{SO}_4^{2-}$ ratio approaches 1.

The aerosol neutralization studies make it evident that the NH_3 content of the aerosol affects the $\text{NH}_3(\text{g})$ uptake rate. We attempted to model NH_3 uptake into $\text{NH}_3\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ ternary solution via Eqs. 13 and 19 using chemical activities (e.g. a_{H^+}) parameterized for the ternary solution by Clegg et al.⁴⁸. In order to fit the aerosol neutralization data, the product $c_1 c_2$ in Eq. 19 has to be 5-10 times lower for NH_3 uptake into $\text{NH}_3\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ ternary solutions than derived for the binary $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ solution. This might reflect differences in NH_3 activity (i.e. physical solubility, represented by c_1) or the surface acidity (represented by c_2) in the binary and ternary solutions. Such differences might be expected since the added NH_3 , forming ammonium sulfate, is likely to change the nature of the liquid, both bulk and surface.

Atmospheric Implications

As has been stated earlier, the concentration of H_2O vapor in the atmosphere far exceeds the concentrations of both NH_3 and H_2SO_4 , therefore aerosol growth rates are relatively insensitive to the H_2O uptake coefficient and are governed primarily by the uptake coefficient of NH_3 and H_2SO_4 . In Figure 6, we show the ammonia uptake coefficient (γ_0) at 290K as a function of relative humidity (RH) obtained from Figures 3 and 4. These NH_3 uptake results, combined with recent measurements of H_2SO_4 accommodation coefficients⁴, indicate that on concentrated H_2SO_4 solution (RH < 30%) the uptake coefficients of both NH_3 and H_2SO_4 approach unity. Therefore, growth of concentrated H_2SO_4 aerosol is collision limited. However, the present

results show that NH_3 uptake coefficients will be less than unity in the troposphere, where relative humidity is typically >30-40%, corresponding to H_2SO_4 compositions < 40-50 wt%.

The aerosol neutralization studies indicate that for the $\text{NH}_4^+/\text{SO}_4^{2-}$ ratios larger than ~0.1, $\text{NH}_3(\text{g})$ uptake coefficients are likely to be less than unity even at low relative humidity (RH). Taken together, the dependence of the uptake coefficient on relative humidity presented here for binary $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ solutions and the re-analysis of NH_3 neutralization results imply that under tropospheric conditions, with either high RH ($\geq 40\text{-}60\%$) or high NH_3 content ($\text{NH}_4^+/\text{SO}_4^{2-} \geq 0.1$ to 2), NH_3 uptake coefficients will be less than unity, often as low as 0.1.

The magnitude of the gas uptake coefficient can indirectly affect aerosol nucleation in the atmosphere.^{9, 49} Nucleation of new aerosol particles is favored by slower uptake rates, since nucleation competes with condensation growth of pre-existing aerosols. Slower uptake on pre-existing particles results in higher steady state levels of condensable vapor. This in turn increases the nucleation rate, which is a steep function concentration of condensable species concentration.

If, as suggested by Weber et al.⁵, $\text{NH}_3/\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ ternary nucleation is important in the atmosphere, then the relative humidity dependence of $\text{NH}_3(\text{g})$ uptake rates measured here and neutralization dependence as suggested by the aerosol experiments will be critical to microphysical modeling of steady state levels of $\text{NH}_3(\text{g})$ in the atmosphere. Detailed modeling of atmospheric aerosol microphysics will require extension of the current $\text{NH}_3(\text{g})$ uptake study on binary $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ liquid solution to the ternary $\text{NH}_3/\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ systems.

Finally, the question must be raised about the applicability of uptake coefficients obtained on macroscopic surfaces to uptake on ultra-fine aerosol particles. The latter are defined as particles of diameter < 100 nm, for which the surface tension and the equilibrium vapor pressure are significantly increased. It is not known how these perturbations affect the uptake rates. Specifically, uptake rates onto critical clusters, containing on the order of tens of molecules, might be significantly different, affecting new particle nucleation rates. Full

understanding of gas/surface kinetics underlying aerosol microphysics, including aerosol nucleation and growth, will require extension of the gas uptake measurements to ultra-fine aerosol particles.

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Appendix

Gas phase Diffusive Transport. As noted in the text, and discussed in the companion paper,¹⁸, gas phase transport to a train of moving closely spaced droplets is well described by the Fuchs and Sutugin formulation (Eq. 4). However, as stated in the text, the transport rate does not depend on the droplet diameter but rather depends on the diameter of the droplet forming orifice.²⁴

In the present uptake experiments on concentrated H₂SO₄ solutions the H₂O vapor pressure is low and therefore gas phase diffusion rates are determined principally by the pressure of the inert carrier gas. As a result, gas phase diffusive transport to the droplet train can be studied over a wide range of Knudsen numbers. In order to confirm and better quantify our understanding of gas diffusive transport, experiments were performed with several inert carrier gases (He, Ne, Ar, Kr) over a range of Kn from 0.05 to 4.5.

The gas transport coefficient in Eq. 4 is formulated in terms of the Knudsen number, Kn = 2λ / d_f, where d_f is the effective droplet diameter and λ is the mean free path, defined as λ = 3 D_g / $\bar{c}$. The gas phase diffusion coefficient D_g for NH₃(g) in a mixed carrier gas is calculated by:

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$$\frac{1}{D_g} = \frac{P_{H_2O}}{D_{NH_3-H_2O}} + \frac{P_X}{D_{NH_3-X}} \quad (A-1)$$

Here, P_{H₂O} and P_X are the partial pressures (atm) of the water vapor and an inert carrier gas (X) in the flow tube, and D_{NH₃-H₂O} and D_{NH₃-X} are the binary diffusion coefficients for NH₃(g) with water vapor and the inert gas respectively. The values for binary gas phase diffusion coefficients used in Eq. A-1 were calculated using CHEMKIN.⁵⁰ The program uses the following input parameters for NH₃(g): Lennard-Jones potential well depths (ε/k_B = 481.0 K), Lennard-Jones

collision diameters ($\sigma = 2.920 \text{ \AA}$), dipole moments ($\mu = 1.470 \text{ Debye}$), and rotational relaxation collision numbers ($Z_{\text{rot}} = 10.00$).

In units of $\text{atm cm}^2 \text{ s}^{-1}$, at 298 K, the calculated binary diffusion coefficients are: $D_{\text{NH}_3\text{-H}_2\text{O}} = 0.215$; $D_{\text{NH}_3\text{-He}} = 0.901$; $D_{\text{NH}_3\text{-Ne}} = 0.417$; $D_{\text{NH}_3\text{-Ar}} = 0.233$; $D_{\text{NH}_3\text{-Kr}} = 0.184$. The diffusion coefficients with rare gases vary approximately as $T^{1.7}$, while $D_{\text{NH}_3\text{-H}_2\text{O}}$ varies as $T^{2.0}$.

Figures 1a and b illustrate the nature of gas phase diffusion studies. Here the $\text{NH}_3(\text{g})$ uptake, in the form $\ln(n_g/n_g')$ is plotted as a function of $\bar{c} \Delta A / 4F_g$, 70 wt% H_2SO_4 at 250 K. The results shown in Figures 1a and b were obtained with carrier gases 4 Torr He and 23 Torr Kr respectively. The other conditions of the experiment were identical. The slopes of the solid lines in the figure yield measured uptake coefficients $\gamma_{\text{meas}} = 0.74$ at 4 Torr He, and $\gamma_{\text{meas}} = 0.06$ at 23 Torr of Kr. Both values extrapolate, via Eq. 4, to $\gamma_0 = 1$.

In Figure A-1 we plot uptake coefficients, γ_{meas} , as function of Knudsen number, for $\text{NH}_3(\text{g})$ obtained on 70 wt% H_2SO_4 at 250, 263, 284 K. Each point on the curve was derived from plots such as shown in Fig. 1. The Knudsen number was varied by changing the carrier gas (He, Ne, Ar, Kr) and its pressure in the range 3 - 24 Torr. The Knudsen number range was further extended by varying the orifice diameter. Orifices of several diameters were used. For simplicity of display, we will group them into two categories: 22 to 30 μm (open symbols) and 57 to 70 μm (closed symbols). In a given experiment, the diameter of the orifice was determined from liquid flow rate and droplet velocity measurements.⁵¹ The solid line in Figure A-1 is the best fit to the Fuchs and Sutugin²⁵ equation (Eqs. 4 and 5) yielding $\gamma_0 = 1.02 \pm 0.04$. The diffusive process is independent of droplet diameter with the best fit obtained at $d_f = 2.0(\pm 0.1) d_0$ where d_0 is the orifice diameter. This is in good agreement with the earlier result of Worsnop et al.²⁴ Such Fuchs and Sutugin plots (γ_{meas} vs. Kn) were obtained for all the temperatures and sulfuric acid concentrations studied, confirming our treatment of gas phase diffusion for γ_0 in the range 0.3 to 1. Previous studies demonstrated the validity of our gas

transport calculation at lower values of γ_o . As noted in the text, uptake rates were then reported as γ_o values obtained from γ_{meas} values via Eqs. 4 and 5.

Figure A-1 demonstrates the applicability of the Fuchs and Sutugin formulation to the droplet train for a wide range on Knudsen numbers, gas mixtures, and uptake coefficients up to $\gamma_o = 1$. The data confirm that gas phase diffusive transport to a stream of fast moving droplets can be formulated in terms of an effective diameter which depends not on the diameter of the droplet but rather on the diameter of the droplet-generating orifice.

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Figures

Figure 1. Plot of $\ln(n_g/n_g')$ versus $\bar{c} \Delta A / 4F_g$ for $\text{NH}_3(\text{g})$ on 70 wt% H_2SO_4 ; $T = 250 \text{ K}$, water vapor pressure = 0.02 Torr .

(a) Carrier gas of 4 Torr He ($\text{Kn} = 1$), $\gamma_{\text{meas}} = 0.74 \pm 0.02$.

(b) Carrier gas of 23 Torr Kr ($\text{Kn} = 0.05$), $\gamma_{\text{meas}} = 0.06 \pm 0.001$.

Both measurements correspond to $\gamma_o \sim 1$, after accounting for gas diffusion via Eq. 5.

Figure 2. Uptake coefficient γ_{meas} as a function of gas-liquid contact time for $\text{NH}_3(\text{g})$ on 70 wt% H_2SO_4 (upper curve), 40 wt% H_2SO_4 (middle curve), and 20 wt% H_2SO_4 (lower curve) at $T = 285 \text{ K}$.

Figure 3. The uptake coefficient γ_o for NH_3 as a function of $-\log[\text{aH}^+]$. The solid line is the plot of Eq. 13 with parameters as given in the text. Uptake results of Shi et al. (ref 18) on aqueous solution are shown as open symbols.

Figure 4. The uptake coefficient γ_o for NH_3 as a function of temperature. Solid points are from this study. Lines are the plots of Eq. 13 with α obtained by Shi et al. (ref 18). Best fit to the data yields $c_1 c_2 = (5.4 \pm 2.0) \times 10^{-4}$ (see Eq. 19). Mass accommodation coefficients for NH_3 on aqueous solution at $\text{pH} = 1$, measured by Shi et al. (ref 18), are also shown (open circles).

Figure 5. Dependence of Γ_s on a_{H^+} . Values of Γ_s derived from γ_o via Eq. 13 are adjusted as shown to facilitate display of data at all temperatures studied. The straight line is the best fit to the function $\Gamma_s = f(T) c_1 c_2 (\text{a}_{\text{H}^+})^n$; $f(T) = 4 \text{a}_{\text{H}_2\text{O}} \text{RT} k_f' \delta / \bar{c}$. Solid line gives best-fit $c_1 c_2$ and a_{H^+} power law as labeled.

Figure 6. NH_3 uptake coefficient, γ_o , as a function of relative humidity at 290K. Points are calculations obtained via Eqs. 13 and 19.

Figure A-1. Plot of γ_{meas} as function of Knudsen number (Kn) for $\text{NH}_3(\text{g})$ uptake on 70 wt% H_2SO_4 droplets at 250, 263, 284 K. Knudsen number is varied by changing the diameter of the droplet-forming orifice and by varying the carrier gas composition and pressure. (See insert.) Solid line is best fit to Eq. 3 with $\gamma_o = 1.02 \pm 0.04$.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure A-1