Comment on “The NH_3 Mass Accommodation Coefficient for Uptake onto Sulfuric Acid Solution”

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Introduction. A recent article by Hanson and Kosciuch (HK)[1] describes measurements of the mass accommodation coefficient (α) for ammonia on aqueous solutions of H_2SO_4 as a function of wt. % acid, using small particles (∼100 nm) in a laminar flow tube. There is a clear difference between the Boston College − Aerodyne Research Inc. (BC/ARI) measurements of α_{NH3} using a droplet apparatus, and the measurements of HK. For wt. % H_2SO_4 less than about 40% the BC/ARI values fall off from unity, reaching about 0.1 for pure water at 290 K.[2,3] The HK values stay constant at $\alpha = 1$ down to their lowest acidity of about 15 wt. % H_2SO_4. Based on this discrepancy, HK question several aspects of the BC/ARI experiments. They suggest that: (1) The density of NH_3(g) in the BC/ARI studies may be too high. (2) The treatment of the diffusive gas transport may be incorrect. (3) The evaporative water vapor flux may impede gas uptake. (4) The magnitude and temperature dependence of α for many molecules may be artifacts of measurement. They conclude: “The truth of this speculation awaits further independent study of the chemical systems that BCA has reported on.”

We have previously considered and addressed every one of the issues raised in the HK manuscript. Their speculations are contradicted by a wide range of published studies from the BC/ARI laboratories and the laboratories of other groups. Because of space limitations, here we will discuss the issues only in outline. A more detailed discussion is found in the cited literature and in the Supporting Information. A complete understanding of the issues requires of the reader to examine the arguments and evidence included therein.

Discussion of Issues. *1. Density of NH_3.* Hanson and Kosciuch suggest that the higher density of NH_3(g) in the BC/ARI studies ($10^3\times$ higher than in the HK experiments) may affect the α-measurements. Published analysis shows[2] that under the conditions of the BC/ARI experiments, the NH_3 molecules entering the liquid do not affect the uptake measurements. This was confirmed experimentally by measuring uptake with NH_3(g) density increased by more than an order of magnitude. For more detail see ref 2 and the Supporting Information.

2. Gas-Phase Diffusive Transport to a Train of Moving Droplets. HK suggest that our treatment of the diffusive gas transport is incorrect. They also question our ability to correctly treat gas phase transport in the presence of relatively high water vapor pressures. They cite the results of a simulation of the droplet apparatus by Morita et al.[5] to support these assertions. A discussion validating our treatment of gas-phase diffusive transport to a train of moving droplets is presented in the preceding Comment on the Morita et al. publication. In addition, we have gathered a considerable body of data showing that our treatment of gas phase transport in the presence of high water vapor partial pressures is correct. Under the same conditions of relatively high water vapor, we have measured uptake coefficients over a large range from ∼0.02 to unity, demonstrating that water vapor does not limit our ability to measure uptake coefficients. Discussion of specific experiments related to this issue is presented in the Supporting Information.

3. Effect of H_2O(g) Evaporative Flux. HK suggest that in the droplet apparatus, a net flux of water away from the droplets due to a slight positive temperature difference between the interior and the surface of the droplets may impede diffusion of trace gas to the droplets. The temperature difference is set up because the temperature of the gas in the flow tube is higher than that set by the water vapor pressure. We considered this effect early in our work[6] and we conducted experiments to test its magnitude. For a given set of conditions, we heated the flow tube walls over a range of temperature from 30 °C to about 100 °C, raising the temperature of the droplet-surrounding gas. The measured uptake coefficient did not change significantly.

Further, we have measured a wide range of uptake coefficients for different trace gases on water droplets under the same conditions. The uptake coefficients ranged (at 273 K) from 0.026 for $CH_3CH_2CH_2OH$[7] to $\gamma_o = 1$ for D_2O.[8] We could not be measuring uptake coefficients over such a wide range, up to unity, if evaporation of water were to significantly impede gas uptake. More detail about these and other studies related to this issue are found in the Supporting Information.

4. Magnitude and Temperature Dependence of α. Our measured uptake coefficients as a function of Kn and temperature are in accord with our treatment of gas-phase diffusion, at all temperatures studied, and for a range of α-values from 0.1 to 1.[9] Our demonstration that we account correctly for gas-phase diffusion refutes the suggestion that the small α-values and the temperature dependence of α reported in our work may be an artifact of incorrect diffusive transport calculations. Specific examples from our published work posted in the Supporting Information provide further evidence that the measured temperature dependence of α is real.

Data from Other Research Groups. The independent study called for by HK is in fact available. Bongartz et al.[10] measured α for NH_3 on acidified aqueous solutions (pH = 3). HK incorrectly state that Bongartz et al. used a droplet train apparatus to perform their measurements. In fact Bongartz et al. used a coaxial liquid jet on the order of one millimeter in length and about 100 μm in diameter. Because the liquid jet is a cylinder and the relative velocity between the liquid and the gas in that apparatus is set to be zero, the diffusive gas transport to the liquid is very different than in the droplet train apparatus, and is straightforward to model. In the Bongartz et al. experiments, measured uptake is fit with the mass accommodation coefficient as the only variable parameter.

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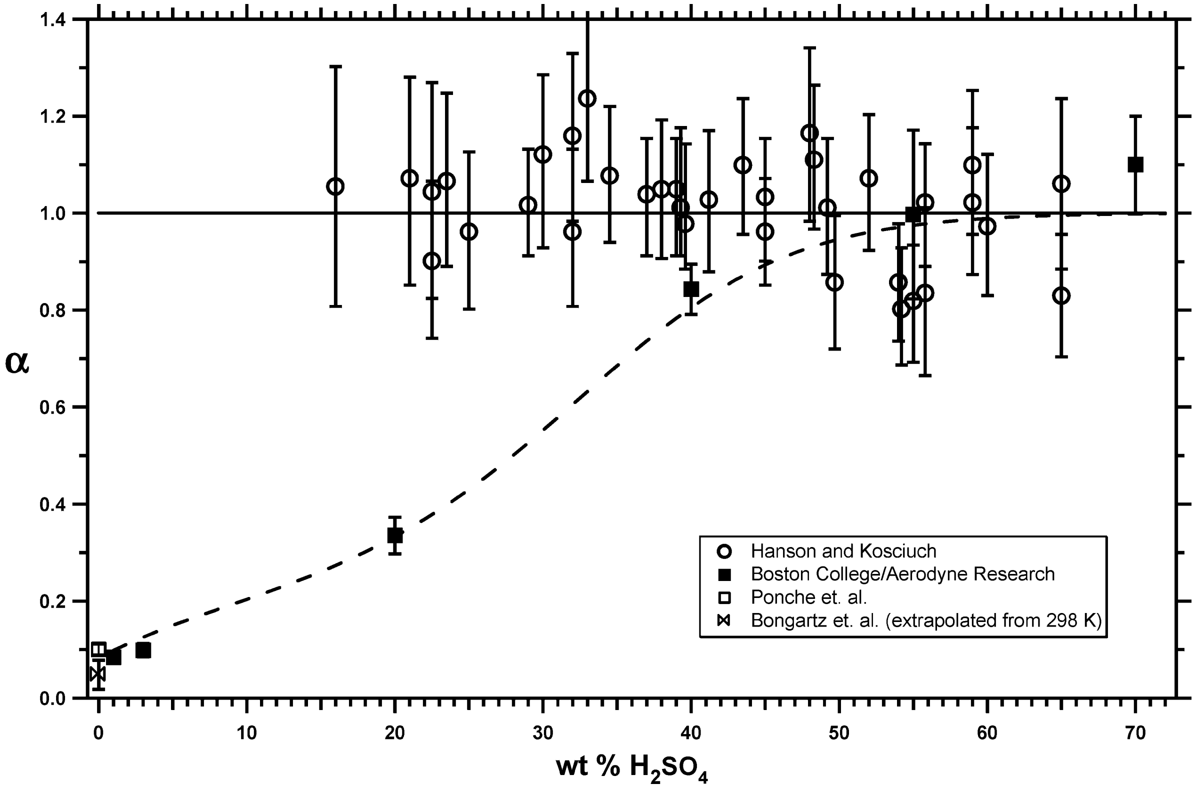

Figure 1. Mass accommodation coefficient α for NH_3(g) as a function of wt. % H_2SO_4. The figure shows results from research groups as identified. Data reported in the following studies: Hanson and Kosciuch, ref 1; Boston College−Aerodyne Research Inc., refs 2, 3; Ponche et al., ref 12; Bongartz et al., ref 10.

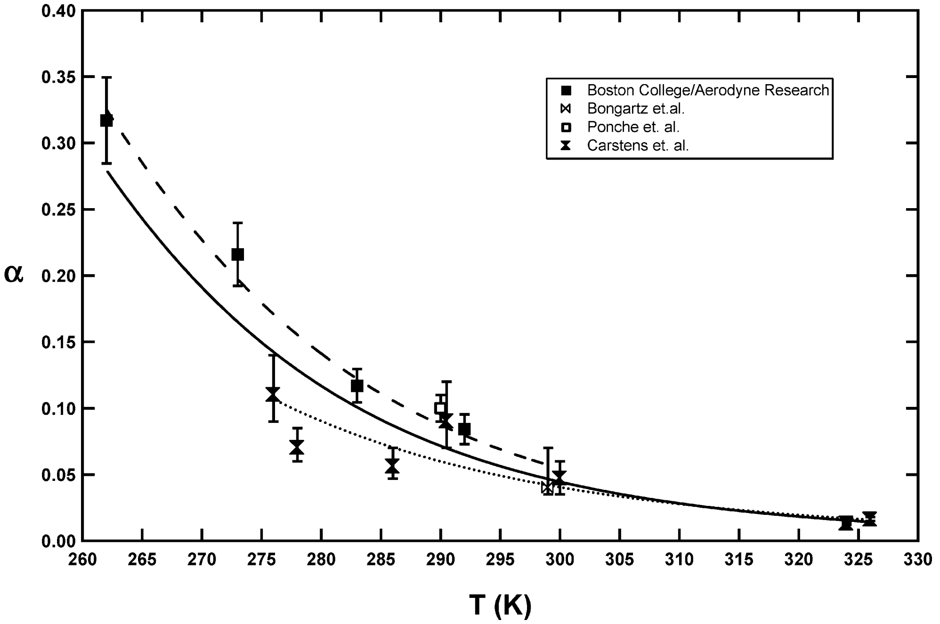

Figure 2. Mass accommodation coefficient α for NH_3(g) on water as a function of temperature. The figure shows results from research groups as identified. Data reported in the following studies: Boston College−Aerodyne Research Inc., ref 2; Ponche et al., ref 12; Bongartz et al., ref 10; Carstens et al., ref 13. In re-plotting the data of Carstens et al., we combined and averaged experimental points taken near the same temperature. Solid line in the figure is the fit to all of the points. Dashed line is the fit to the BC/ARI data only, and dotted line is the fit to the Carstens et al. data only.

The results of Bongartz et al. over a range of jet lengths, jet speeds, and gas diffusion conditions yielded α_{NH3} at 298 K = 0.04 (+0.030/−0.005). To test the effect of gas-phase diffusion conditions, Bongartz et al. measured the uptake with air as well as He carrier gases at the same pressure. The diffusion coefficient of NH_3 in He is more than three times higher than in air (for air, $D_g = 0.234$ cm^2 s^{-1}; for He, $D_g = 0.747$ cm^2 s^{-1}, both at 1 atm). Their measured mass accommodation coefficient remained the same within experimental error (0.035 in air; 0.04 in He). This value is in good agreement with our value of $\alpha_{NH3} = 0.05$ extrapolated to 298 K from measurements at 290 K. In a similar study the Schurath group[11] measured α for formic and acetic acids on water at 298 K. Here again their values are in good agreement with our measurements.[7]

In Figure 1, which is a plot of α_{NH3} as a function of wt. % H_2SO_4, we bring together the results of HK, our results, the measurement of Bongartz et al., and also Ponche et al.[12] Ponche et al. used a droplet train apparatus. While the HK experiments do not extend to H_2SO_4 concentrations lower than 15 wt. %, the authors indicate in the text and in their Figure 3 the expectation that $\alpha_{NH3} = 1$ all the way to pure water. Figure 1 shows that the measurements of the Schurath group are in agreement with our results and that α on pure water is clearly not unity.

In addition, Carsten et al.[13] used the coaxial jet method to measure the temperature dependence of α_{NH3} in the region 275−326 K. We have plotted in Figure 2 their results together with our measurements[2,3] and the measurement of Ponche et al.[12] The dashed lines are nonlinear least-squares fits to the individual data sets with an exponential function (see ref 2 eq 31). The solid line in the figure is the fit to all points. The negative temperature dependence is evident in each data set, and the results of the two data sets are in reasonable agreement.

At this point we do not know the source of discrepancy between the HK NH_3 uptake results and ours at lower H_2SO_4 acid concentrations. The key to explaining the difference may lie in the two major differences between the experiments of the BC/ARI group and the HK experiments. They are the gas-particle interaction times (100 milliseconds in the former, 10 s of seconds in the latter[14]) and the method of generating particles. In the BC/ARI experiments the droplets are generated from sulfuric acid aqueous solutions. In the HK experiments the aerosols are generated via nucleation starting with H_2SO_4 vapor at pressures on the order of 0.1 to 1 Torr. Shorter trace gas droplet interaction times mitigate against secondary heterogeneous chemistry or aerosol microphysics processes that may be difficult to recognize or quantify. Direct introduction of liquid droplets of known composition avoids the necessity of assuming that complex nucleation and condensation processes produce droplets of known composition.

Supporting Information Available: Detailed discussion of the issues raised in the HK manuscript. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

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(14) Here we have defined the gas-droplet interaction time as the time of gas exposure to the droplets, which is determined by the gas flow velocity. This is distinguished from the time of droplet exposure to the gas, which is determined by the droplet velocity. The gas-droplet interaction time is on the order of 100 ms; the droplet exposure time is on the order of ms.