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Reply to "Comment on 'The NH_3 Mass Accommodation Coefficient for Uptake onto Sulfuric Acid Solutions'"

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The Comment by Worsnop, Davidovits, and co-workers (BC/A collaborators) on our manuscript[1] includes the claim that they have previously addressed each of the issues we raised. However, we think that some of the empirical arguments posed by BC/A are subject to interpretation. We present our point of view on each of the points raised in their Comment. Finally, we rebut their speculation that our method of generating sulfuric acid particles could lead to impurities that affect their chemistry.

(1) NH_3 Flux. We stated that a very distinct difference in the gas−surface conditions between the two experiments was the flux of ammonia: in the droplet train apparatus (DTA)[2] the initial [NH_3] and thus the impinging flux of ammonia was typically 1000 times that in our aerosol laminar flow reactor.[1] In HK[1] we acknowledged that BC/A had considered this in another paper;[3] however, we believed, and still do, that the difference in gas−surface conditions is noteworthy. For example, Swartz et al.[2] claim that ammonia uptake onto the sulfuric acid solutions occurs via a surface reaction. Thus uptake could be impeded if a significant NH_3 or NH_4^+ concentration were to build up on the surface. To reiterate, we agree with BC/A that a high flux is not likely to be an issue, but this concern has not been completely alleviated, as the dependence of the results upon initial NH_3 density was not explored for uptake onto 20-to-70 wt. % H_2SO_4 droplets.

(2) Empirical Diffusion Correction. We stipulate that BC/A has arrived at an empirical description of the kinetics of uptake coupled with the impedance of the rate of diffusion to the droplets in a DTA. However, it has been suspected for some time (D. Hanson, private communication to D. Worsnop, 1990) that the BC/A description does not represent a well-defined and proper accounting of diffusion to a droplet train. A recent series of papers by Morita et al.,[4−6] who used computational fluid dynamics to simulate the DTA, have calculated these rates of diffusion. Their picture of diffusion to the surface of the droplets in a DTA is not in accord with that routinely used by BC/A. The BC/A empirical correlation[7,8] suggests that the diffusion rate can be up to 30% higher than the maximum found by Morita et al. Why is this so? We believe it is because the kinetics of the DTA, i.e., how the quantity of interest γ_{meas} is related to the measured losses, does not follow the plug-flow approximation which is an inherent assumption of BC/A. It is clear that the flow in a droplet train is not plug[4−6,9] and, when diffusion impedes transport to the particles, there is a concentration gradient. These conditions taken together are a clear violation of the plug-flow approximation,[10] thus, BC/A could be reporting a value for γ_{meas} that does not represent a clear physical process. This error in the value of γ_{meas} occurs only when diffusion is a significant impediment and is consequently included in their empirical diffusion correction. Their empirical diffusion correction is really a kinetics and diffusion correction term. This is important for understanding the uptake rate onto the droplets in a DTA, and we intend to explore this in detail [Hanson and Morita, manuscript in preparation]. It is not clear to us that it is always applicable to such a high degree of accuracy as BC/A proposes it is under a variety of experimental conditions, especially aqueous solutions exhibiting high water vapor pressures. Confidence in the BC/A results will be gained upon further comparison with the results of independent experimental results.

(3) H_2O Evaporation. Our concern is that a source of heat to the droplet surface results in a net flux of water vapor from the surface that impedes the rate of diffusion of absorbate toward the surface. We presented a rough calculation that suggested this effect could be on the order of 10 percent of the uptake rate. BC/A state that they observe no dependence of γ_{meas} on temperature for the uptake of D-ethanol on water droplets at 283 K as the temperature of the gas was changed from 303 to 371 K. However, the γ_{meas} do show a 4% decrease at the higher temperature in accord with an evaporation effect. We would also like to point out that the most relevant quantity is the change in the actual uptake coefficient γ_0 (corrected for diffusion and kinetic effects) upon warming. The effective diffusion coefficient at each temperature is to be evaluated at the temperature of the gas that is one mean free path (∼6 μm) from the droplet surface.[7] For wall temperatures of 303 and 371 K, these are temperatures of 285 and 291 K, respectively. This leads to about a 4% higher Γ_d to apply to the γ_{meas} at the higher temperature. Using the BC/A kinetic and diffusion correction, γ_0 is in fact about 10% lower when the flux of heat to the droplets is increased. Note that if diffusion plays a larger role than BC/A believes, the difference in the final uptake coefficients would be larger than 10%. Note also that there are other sources of heat that the droplet surfaces might experience (see the appendix in ref 7.) Although a 10 percent effect is not enough to explain the differences between our results[1] and the Swartz et al.[2] data, this effect should be kept in mind when considering the details of the BC/A experiment.

(4a) We speculated on the need to revise data from the BC/A collaboration that had not been called into question by the results of other experiments. We suggested that the cause of the acknowledged disagreement in the experimental results for two molecules on dilute acid solutions (i.e., for NH_3, the results of HK[1] and Swartz et al.[2] and for HCl, the results of Hanson and Lovejoy[11] and Robertson et al.[12]) might pertain also to the multitude of BC/A results on pure water. Concomitantly, we believe that α is not a strongly varying function of composition for H_2SO_4 content ≤ 15 wt. % (mole fraction H_2SO_4 ≤ 0.03).

BC/A point out that for ammonia uptake onto water, the results from the liquid jet technique[13] yield a mass accommodation coefficient of ∼0.04, which is consistent with the DTA value for pure water.[3] We note, however, that this value relies on comparison of the measurements to a complex numerical model that is subject to many assumptions. For example, axial diffusion and convection were not considered in the uptake calculations. However, gradients in the axial velocity of the carrier gas near the liquid surface are large in the first 100 μs of exposure. This time period is for a jet exposure length of ∼0.2 mm using t_s from eq 3.8 of ref 13 and Figure 13 of Kirchner et al.[14] (note that the gas in contact with the liquid surface and the liquid surface are assumed to travel at the same speed.) Furthermore, concurrent with the small axial velocities are large axial gradients in gas-phase [absorbate] (Figure 4 of

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ref 14). Because transport via axial diffusion is most important when axial velocities are small, it should not be assumed that axial diffusion can be neglected in this region. In addition to affecting [absorbate] in this region, these neglected transport issues can affect [absorbate] at zero time. Thus, the model's boundary condition that [absorbate] has a constant radial profile at time zero should be examined. Because the calculated uptake of NH_3 is most sensitive to the value of α during the first 100 μs of exposure (Figure 10 of ref 13), consideration of these transport issues may be particularly important. Another transport effect that was not included in the model is net evaporation of water from the liquid jet (section 3.2 in ref 13) through which the absorbate must diffuse (see 3 above and Appendix B in ref 1.)

Moreover, the calculated concentrations at large α require a high degree of accuracy for a number of parameters, as discussed in ref 13. For example, if the diffusion coefficient is varied by as little as 5%, the liquid jet measurements conducted in air would be consistent with $\alpha = 1$. This can be seen by consulting Fig. 6 in ref 13, in which the measured [NH_3] are within 5 and 7% of the calculated [NH_3] for unit α at $t = 600$ and 200 μs, respectively, and Figure 10a, which shows gas-phase diffusion is exhibiting ~90% control of the uptake. Similarly, the measured [NH_3] in the liquid are within 11% of [NH_3] calculated under the assumption that $\alpha = 1$ ($t = 500$ μs in Fig. 7 of ref 13) for the measurements with He as carrier gas. Note that axial diffusion effects for measurements in He could affect overall transport to the liquid jet more than those for measurements in air. Also, there is no mention of multicomponent diffusion involving water vapor in ref 13 or 14, and it is possible that the presence of ~2.8% H_2O vapor in the carrier gas was not taken into account. The overall diffusion coefficient of NH_3 in a mixture comprising 738 Torr He and 22 Torr H_2O is about 7% less than that for NH_3 in He at 760 Torr (using the NH_3-H_2O and NH_3-He diffusion coefficients in ref 3.)

(4b) Our questioning of the accuracy of the BC/A values for α led us to question the widespread applicability of their general theory for α, and its temperature dependency. In support of this temperature dependency, BC/A present arguments that lead to the conclusion that gas-phase diffusion cannot be solely responsible for a potential artifact in those results. There are many temperature-dependent processes that affect the uptake in a DTA and, if they are not properly accounted for, can lead to an artifact temperature dependency for α. For example, the effect of an evaporating flux of water would decrease with temperature (see (3) above.) Also, the Henry's law solubility of a given species increases as temperature decreases; thus an incorrect accounting of how solubility and liquid-phase diffusion affect the uptake could contribute to the temperature dependencies that BC/A claims for α. To investigate this latter issue, we present our concerns with some of the BC/A experimental results for (i) ethanol, (ii) HCl, and (iii) ammonia, where solubility and liquid phase diffusion can significantly affect the measured uptake.

(i) The latest BC/A measurements of α for ethanol[15] are 30, 110, 220, and 300% greater than their previous results[16] at $T = 263$, 273, 283, and 291 K, respectively. These discrepancies were not explained. However, to explain a difference of 25% in α for acetic acid at 258 K (reported in refs 15 and 16), the BC/A investigators state[15] that a likely reason is that they are now better able to determine gas flow rates. Also, the solubility and diffusivity of ethanol was reported[16] to be much less dependent on temperature than expected. A demonstration of the sensitivity of the value of α upon experimental conditions such as total flow rate, injector flow rate, and injector geometry should be presented; there may be nonlinear effects for uptake measurements that can be affected by desorption (such as ethanol.)

(ii) The BC/A group (Li et al.[27]) report values for α for HCl on liquid water that are 35 and 55% greater than their previous work.[28,12] Further, the solubility and diffusivity of HCl for the 49 wt. % acid data in ref 12 are more disparate with literature values the higher the temperature. These discrepancies suggest a sensitivity of the results to experimental conditions that may influence the value of α.

(iii) The measured uptake of ammonia on water at pH ≥ 9 (ref 3) led to values for the solubility of ammonia that are inconsistent with a number of previous measurements. This disagreement was due to the inclusion of a surface complex in their model that was needed to explain the time behavior of the measured uptake. The BC/A investigators have since acknowledged[17] that their previously reported values for the Henry's law coefficient of NH_3 are incorrect and that more work is needed to ascertain the existence of the surface complex of NH_3. For the BC/A model to explain the measurements and to be congruent with the accepted values of the NH_3 solubility, an augmented amount of NH_3 must reside at the surface. Yet there are inconsistencies with surface tension measurements (e.g., Donaldson[29]) when high NH_3 surface concentrations are postulated (BC/A has acknowledged[3] these difficulties.) Alternatively, the BC/A model used to interpret the measurements could overestimate the abundance of the surface complex. This could arise from an inadequacy in how the BC/A uptake model incorporates liquid-phase solubility and diffusion and how these affect desorption. A deficiency in the BC/A model can also have implications for the uptake issues in (i) and (ii).

This topic warrants a very detailed examination that we are not prepared to present at this time. Yet we can point out an important issue with the theory the BC/A investigators have employed in their model. Their equation to describe time-dependent uptake into the solution (e.g., eq A1-1 of ref 3) has the boundary condition of a gas-phase concentration that is invariant with time (along with the surface resistance condition, eq 2.3 of ref 18 and eq 3−4 of ref 19). The gas-phase region is assumed to be so large that the amount of absorbate that goes into solution does not affect the gas-phase [absorbate]. Equivalent to the Danckwerts[18,19] formulations, Carslaw and Jaeger[20] present solutions of heat transfer problems for a slab in contact with a well stirred, infinitely thick fluid.[21] In the droplet train flow reactor, however, the gaseous reservoir from which to draw absorbate molecules should not be approximated as infinitely thick because gas-phase [absorbate] in the flow reactor decreases with axial distance. Thus the droplets experience a decreasing gas-phase concentration as they travel along the axis of the flow reactor. It is precisely the uptake onto the droplets that causes the decrease in [absorbate] in the gas-phase. A more appropriate treatment is that presented by Jaeger[22] (specifically section 4) who discussed heat conduction within a slab in contact with a well-stirred fluid of finite thickness. The amount of uptake (i.e., $\gamma_{\rm meas}$) given by this theory can have a dependency on flow rate that is not linear. This is because the size of the gas-phase reservoir available to a droplet depends on the gas flow rate.

The effect can perhaps be understood with this simplified picture: as gas-phase [absorbate] decreases along the length of the flow reactor, the gross flux of absorbate molecules onto a droplet also decreases as it travels the length of the flow reactor. Yet, the instantaneous gross flux of molecules desorbing from a droplet at a given axial position is influenced by its previous exposure at shorter axial positions where gas-phase [absorbate] was higher. Thus the net flux of molecules into the droplet at times (i.e., axial positions) when the gas-phase [absorbate] has decreased will be less in principle than that given by the current theory of the BC/A investigators.

Finally, BC/A imply that our method of generating sulfuric acid particles could lead to a composition that differs from that of a bulk solution at the same temperature and water partial pressure. The uptake of a number of species (N_2O_5, $ClONO_2$, HCl, HOCl, and $BrONO_2$) onto sulfuric acid aerosol particles that were generated in the same manner as in ref 1 have been compared to the uptake measured on bulk solutions. The results[11,23−26,30] are in excellent agreement over a wide range of values for the reaction probability (0.002 to 1). These results suggest that the composition of a sulfuric acid particle (> 50 nm diameter) generated in this manner does not differ from that of the corresponding bulk solution.

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