8542 *J. Phys. Chem. A* **2004,** *108,* 8542−8543

COMMENTS

Comment on “Gas-Phase Flow and Diffusion Analysis of the Droplet-Train/Flow-Reactor Technique for the Mass Accommodation Process”†

D. R. Worsnop,* L. R. Williams, and C. E. Kolb
Center for Aerosol and Cloud Chemistry, Aerodyne Research, Inc., Billerica, Massachusetts 01821-3976

M. Mozurkewich
Chemistry Department, York University, Toronto, Ontario M3J 1P3, Canada

M. Gershenzon† and P. Davidovits
Chemistry Department, Merkert Chemistry Center, Boston College, Chestnut Hill, Massachusetts 02167-3809

Received: August 24, 2003; In Final Form: April 21, 2004

A recent article by Morita, Sugiyama, and Koda (MSK)[1] describes modeling transport of trace gas-phase species to a train of moving droplets used to measure gas uptake by liquids in an apparatus developed at Boston College and Aerodyne Research Inc. (BC/ARI). The authors conclude that our treatment of diffusive gas transport under conditions of high water vapor partial pressure is inaccurate and therefore so are the mass accommodation (α) values quoted in the BC/ARI publications. Their conclusions imply that the α values are higher than those obtained in the BC/ARI studies.

The fluid dynamics simulation of MSK is an important addition to the literature of droplet train gas interactions. Their results confirm most of our key experimental findings about the nature of diffusive gas transport to a train of moving droplets. However, as will be discussed, the quantitative results of their model calculations are not fully in accord with the measurements, and their implication that the true values of α are higher than quoted in our publications is incorrect.

From the very beginning it was clear that gas-phase diffusive transport in the droplet train apparatus would have to be characterized experimentally because of the complexity of the process. Consequently, extensive uptake studies were performed over a wide range of Knudsen numbers (Kn: 0.05 to 4.5), gas mixtures, and uptake coefficients ($\gamma_o = 0.01$ to 1). Experiments were done with droplet forming orifices of diameters in the range 22 to 70 μm, producing droplets in the size range from ∼70 to 300 μm in diameter. As has been documented in the BC/ARI publications, diffusive transport to a stream of fast moving droplets has the same functional dependence on Kn as the Fuchs−Sutugin expression for transport to a stationary droplet, except that the droplet diameter in the expression for Kn must be replaced by an effective diameter d_f that we determined to be 2.0 (±0.1) times the diameter of the droplet-generating orifice. (This work is summarized in ref 2.)

The MSK fluid dynamics simulations confirm our key experimental findings. Namely, for droplets of differing diameters produced by changing the vibration frequency of a given droplet-generating orifice, the diffusion transport resistance does not depend on the droplet diameter. Rather, as we have shown experimentally, the diffusion transport resistance is characterized by the diameter of the droplet-forming orifice. Both our experimental results and the calculations of MSK conclude that the effect of gas-phase diffusion can be accounted for by using the Fuchs−Sutugin equation with an effective diameter, d_f, that is related to the droplet generating orifice diameter, d_o, by $d_f = C \times d_o$, where C is a constant. Further, the calculations of MSK show that the diffusion transport resistance is only moderately dependent on the droplet velocity, and this dependence tends to zero as Kn increases. This again is in accord with our experiments that show diffusive transport to be unaffected by variations in droplet velocity over a relatively wide range.

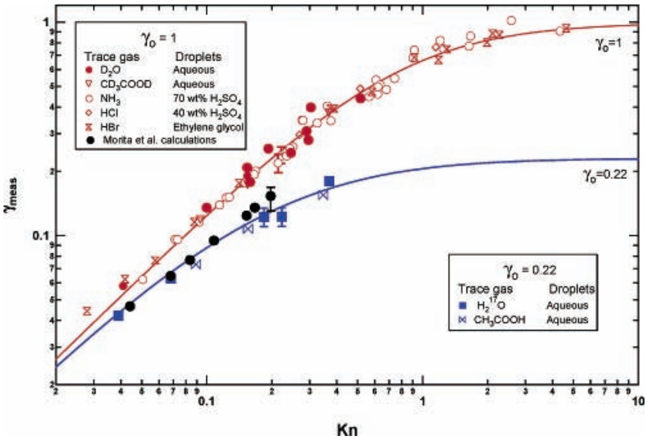

Figure 1. Plot of measured uptake coefficient γ_{meas} as a function of Kn. The asymptote at large Kn is the uptake coefficient without gas-phase diffusion limitation (γ_o). In the absence of surface reactions, $\gamma_o = \alpha$. The figure shows BC/ARI experimental data for $\gamma_o = 1$ and 0.22 together with the MSK model calculation for $\gamma_o = 1$ (taken from their work). The solid lines are Fuchs−Sutugin plots with the BC/ARI multiplicative factor of C = 2.0. The measured uptake coefficients (γ_{meas}) in the figure were obtained from the following uptake studies: D_2O, H_2O from ref 4; CD_3COOD, CH_3COOH from ref 5; NH_3 from ref 3; HCl, from ref 6; HBr from ref 7. The standard deviation of the experimental γ_{meas} data on the $\gamma_o = 1$ line is ± 0.05 and on the $\gamma_o = 0.22$ is ± 0.01. A typical error bar for each of the three sets of data is also shown (i.e., for BC/ARI $\gamma_o = 1$, $\gamma_o = 0.22$, and for the MSK model calculation with $\gamma_o = 1$).

MSK simulated values of γ_{meas} for different values of Kn assuming $\alpha = 1$. They then fit their simulated points using our Fuchs−Sutugin formulation (eq 13 in MSK), with the mass accommodation coefficient, which they call α_{eff}, and d_{eff} as fitting parameters. The best fit is obtained with $\alpha_{eff} = 0.35$ and $d_{eff} = 137$ μm. In other words, the fitting of the MSK simulation yields a multiplicative factor close to ours that is 2.3 instead of 2. However, the best-fit via our Fuchs−Sutugin formulation to the MSK simulation yields $\alpha < 1$, specifically $\alpha_{eff} = 0.35$, while the MSK simulation used $\alpha = 1$. Based on this, they conclude that our way of accounting for gas-phase diffusion is not accurate enough and therefore likewise the mass accommodation coefficient we obtain is not accurate. This conclusion is incorrect as is demonstrated in Figure 1.

Figure 1 shows a plot of the measured uptake coefficient, γ_{meas}, as a function of Kn from the continuum (Kn < 0.1) to

---

* Corresponding author. E-mail: Worsnop@aerodyne.com.

† Current address: Sandia National Laboratories, Livermore, CA 94551.

10.1021/jp036517p CCC: $27.50

the near free molecular (Kn > 1) regime. Also shown in the figure are the simulation results of MSK. The asymptote at large Kn is the uptake coefficient (γ_o) without gas-phase diffusion limitation.

The BC/ARI experimental data in Figure 1 were obtained as follows. For a given trace gas and droplet composition, the uptake was measured with the maximum attainable Kn. The Knudsen number was then varied, (i.e., decreased) by changing the orifice diameter and/or the type of carrier gas and its pressure. The solid lines are Fuchs−Sutugin plots with our value of $C = 2.0$ and with γ_o set at 1 and 0.22. In the absence of surface reactions, $\gamma_o = \alpha$. The figure shows our experimental data for several species with $\gamma_o = 1$ and for species with $\gamma_o = 0.22$ ($\sim \pm 15\%$), together with the MSK simulation results for $\gamma_o = 1$ (taken from Figure 6 of their work). The plotted measured uptake coefficients (γ_{meas}) were obtained from several uptake studies[3−7] as identified in the figure. The figure includes results from uptake studies with D_2O[4] and CD_3COOD[5] that undergo facile isotopic exchange surface reactions. Our formulation of the gas-phase transport matches the measurements over the full range from the continuum (Kn < 0.1) to the near-free molecular regime (Kn > 1). Similar agreement was obtained for other values of α and other chemical systems.

In drawing their conclusions about the BC/ARI data in relation to their calculations, MSK focus on the relatively narrow region of their continuum regime modeling. Because their simulation results with an assumed value of $\alpha = 1$ overlap in part of this region with our Fuchs−Sutugin formulation with $\alpha = 0.35$ or, as shown in the figure, at low Kn even with the measurement of $\alpha \sim 0.22$, they assert that we have miscalculated diffusion and that our α here is really 1. This is an incorrect conclusion. Their continuum-regime calculation yields a linear relationship between the uptake coefficient and Kn. The inevitable curvature toward the asymptotic value of the diffusion-free uptake coefficient at higher Kn cannot be simulated in a valid way by their continuum-regime calculations. The BC/ARI measurements follow the uptake coefficient over the range of Kn to a point where the curvature toward the diffusion-free asymptote is evident, showing that our value of $\gamma_o = 1$ is indeed just that, and the value we determined to be $\alpha = 0.22$ is *not* unity but is in fact 0.22 within the experimental accuracy of ±15%. (See Figure 1.) Data sets for some of the other γ_o values likewise show that the asymptote is almost reached, confirming the validity of the BC/ARI uptake formulation.[2]

MSK ignore this asymptotic approach of our measurements toward the diffusion free uptake coefficient. They also ignore the fact that for various species we have indeed measured a $\gamma_o = 1$, again all the way to the asymptotic diffusion-free value, and that their calculations do not match these measurements. Our uptake coefficients on the line corresponding to $\gamma_o = 1$ represent the maximum measured uptake for a given Kn. These measured values are *larger* than the MSK calculations predict to be possible. (That is, the MSK points in the figure are the maximum γ_{meas} according to their simulation.)

MSK correctly note that the diffusive gas-transport properties in the droplet train are surprising and not intuitively obvious. The detailed gas transport properties likely depend on the specific conditions in our droplet apparatus that are not fully matched in the MSK simulation. Some of the ways in which the experiment differs from the simulations are outlined below and discussed in greater detail in the Supporting Information posted on the web site of this journal. (1) In our experiments the velocity used to convert distance to time for the calculation of the uptake coefficient is, of necessity, the average carrier gas flow velocity, $\bar{v}_{\mathrm{cg}}$. In the MSK simulation, the gas-droplet interaction time is expressed in terms of the concentration-weighted average trace gas flow velocity $\bar{v}_{\mathrm{tg}}$, (a quantity not directly accessible to measurement). At low Kn the two gas flow velocities are not the same; specifically, $\bar{v}_{\mathrm{cg}} > \bar{v}_{\mathrm{tg}}$. As a result, γ_{meas} in the Morita et al. simulation is not the same as the γ_{meas} measured in our experiments. Further, γ_{meas} in the Morita et al. simulation is not measurable in the droplet train apparatus and is not readily comparable to γ_{meas} obtained in our experiments. (2) In the actual experiment the droplets move with speed (v_{d}) and the gas flows at a speed $\bar{v}_{\mathrm{g}}$ that is about 1/10 of the droplet speed. It is the gas speed $\bar{v}_{\mathrm{g}}$ that determines the trace gas-droplet interaction time. In the MSK simulation the gas is moving at the speed ($v_{\mathrm{d}} - \bar{v}_{\mathrm{g}}$) while the droplets are stationary. This makes the gas liquid interaction time in their simulation shorter by about a factor of 10, compared to the actual experimental interaction time and of the same order as the characteristic radial diffusion time. As a result, the simulated trace gas radial distribution does not properly model the experimental conditions.[8] (3) The MSK simulation does not take into account the effect of the gas flow carrying the trace gas that is injected at high speed radially into the main flow through inlet loops. (4) The droplets decelerate about 4% in their travel down the length of the flow tube. The effect of the momentum transfer on gas transport may be significant. While this effect is discussed in the MSK article, it is not included in the simulation.

The listed differences 1, 3, and 4 are expected to reduce diffusion limitation. The effect of 2 is not clear. Thus, it is not likely that the simplified simulation used by MSK can provide an adequate representation of the complex trace gas to droplet transport processes. We hold that in the face of these complex gas transport conditions, thorough experiments are the only reliable way to characterize the system.

To summarize, we have shown that diffusive transport to a stream of fast moving droplets has the same functional dependence on Kn as the Fuchs−Sutugin expression for transport to a stationary droplet, except that the droplet diameter in the expression for Kn must be replaced an effective diameter $d_{\mathrm{f}} = C \times d_{\mathrm{o}}$, where d_{o} is the diameter of the droplet-generating orifice and C is a constant determined to be 2.0 (±0.1). The parameter C is an experimentally determined instrument constant for our specific setup. It empirically corrects for deviations from the Fuchs−Sutugin formulation, which include physical effects that are not accounted for by the MSK simulation (such as the four issues discussed above).

Supporting Information Available: Extended discussion of the ways in which the experiment differs from the simulations. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Morita, A.; Sugiyama, M.; Koda, S. *J. Phys. Chem.* A, **2003**, 107, 1749. Preliminary results of this work were first published in *Chem. Phys. Lett.* **2002**, *362*, 56.

(2) Worsnop, D. R.; Shi, Q.; Jayne, J. T.; Kolb, C. E.; Swartz, E.; Davidovits, P. *J. Aerosol Sci.* **2001**, *32*, 877.

(3) Swartz, E.; Shi, Q.; Davidovits, P.; Jayne, J. T.; Worsnop, D. R.; Kolb, C. E. *J. Phys. Chem.* A, **1999**, *103*, 8824.

(4) Li, Y. Q.; Davidovits, P.; Shi, Q.; Jayne, J. T.; Kolb, C. E.; Worsnop, D. R. *J. Phys. Chem.* A, **2001**, *105*, 10627.

(5) Shi, Q.; Li, Y. Q.; Davidovits, P.; Jayne, J. T.; Worsnop, D. R.; Mozurkewich M.; Kolb, C. E., *J. Phys. Chem. B* **1999**, *103*, 2417.

(6) Robinson, G. N.; Worsnop, D. R.; Jayne, J. T.; Kolb, C. E.; Swartz, E.; Davidovits, P. *J. Geophys. Res.* **1998**, *103*, 25371.

(7) Li, Y. Q.; Zhang, H. Z.; Davidovits, P.; Jayne, J. T.; Kolb, C. E.; Worsnop D. R. *J. Phys. Chem. A* **2001**, *106*, 7, 1220.

(8) Discussions of this issue with D. R. Hanson are appreciated.