Reply to "Comment on 'Gas-Phase Flow and Diffusion Analysis of the Droplet-Train/Flow-Reactor Technique for the Mass Accommodation Processes'"

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The preceding Comment by Worsnop et al.[1] shows quantitative discrepancy in uptake coefficients between our computational fluid dynamics (CFD) simulation and the droplet-train/flow-reactor experiments performed by the authors and their co-workers, posing some questions about the validity of the CFD calculations. As possible explanations, they raised four problems (1−4) in our computational modeling. In this Reply, first we briefly answer the four problems, demonstrating that these problems do not elucidate the discrepancy, and provide future perspectives to solve the discrepancy.

Suggested Problems (1−4). The items (1) and (2) in their Comment essentially deal with two different definitions of the uptake coefficient γ. In our previous papers,[2,3] we have calculated γ from the amount of uptake into droplets, whereas the droplet-train apparatus (DTA) experiments usually derive γ from the concentration decay in the gas-phase flow. To distinguish the two definitions, we call the former "local γ" and the latter "slope γ".[4] The two descriptions are proved to be equivalent under the plug assumption of gas flow, on which most of the experimental analyses are based. However, as the Comment pointed out, the two may not be rigorously identical when the gas flow is not plug. This difference could complicate both the experimental and numerical analyses, and should be quantitatively addressed.

In our previous papers, we have employed the droplet-fixed coordinate to model the DTA, where the droplet-train is fixed and the wall is moving, whereas the DTA experiments are usually analyzed in the wall-fixed coordinate. While the two coordinates obviously differ by an offset of a constant axial velocity, it was technically difficult to calculate the slope γ in the droplet-fixed coordinate. Therefore, we revised the CFD calculations in the wall-fixed coordinate to directly compare the two definitions on the same footing. As described in more detail elsewhere,[4] the new CFD calculations have confirmed that the deviation in our previous treatment is fairly insignificant, within ∼10%. (According to the notations in the Comment, $\bar{v}_{cg}$ is actually not very different from $\bar{v}_{tg}$.) This minor deviation is understood from the fact that the strongly perturbed region of the gas flow by the moving droplets is limited to the vicinity of the tube axis, as illustrated in Figure 2 (a) in ref 3, and thus occupies a relatively small fraction of the radial cross section. More extensive discussion will be given in a forthcoming paper.[4]

In item (2), the Comment insists that the gas liquid interaction time is much shorter in the droplet-fixed coordinate. This effect is already discussed in ref 3, concluding that the calculated uptake coefficient should be therefore regarded as an upper bound. Consequently, it is not able to resolve the descrepancy. We also note that this problem does not hold any more for the revised CFD calculations.[4]

Item (3) points out possible consequences caused by the side gas inlet, which is not taken into account in our previous CFD calculations. Therefore, we have carried out CFD simulation in the wall-fixed coordinate, equipped with the side inlet according to the experimental apparatus,[4] and found that the transient anomaly caused by the side inlet decays within a few cm and that the downstream region is well described by the steady laminar flow in addition to the perturbation by the moving droplets. The side inlet is demonstrated to be of minor significance in the gas-flow modeling and the overall uptake.

Item (4) deals with the momentum transfer between the fast moving droplets and the gas flow, which causes a slight deceleration of the droplet motion. First we should make sure that the CFD simulation also incorporates the momentum transfer via the shear force and the gas viscosity, which is evident in the gas flow profile perturbed by the droplet motion (e.g., Figure 2(a)[3]). In our simulation, the counter perturbation of the gas flow on the three droplets is neglected, whereas the droplet motion perturbs the gas flow. This treatment is quite well justified to describe the gaseous resistance by the CFD results in ref 3 and its Appendix A, that change in the droplet velocity by 4% has negligible influence on the uptake coefficient, and the overall uptake kinetics is well described by integrating the uptake at each axial segment of the flow tube.

Future Perspectives. Figure 1 of the Comment exhibits discrepancy between the DTA experiment and the CFD simulation on the plot between their effective Knudsen number and the observed uptake coefficient. We have argued above that the discrepancy is not attributed to the above problems (1−4), but it remains to be elucidated at present. We think that Figure 1 involves number of uncertainties that hamper direct comparison.

Understanding of the gas transport in the DTA experiment is still in a primitive stage, essentially because it involves many conditions (both geometrical and ambient) that might affect the uptake kinetics. The experimental analysis has often condensed those conditions into an empirical parameter of the effective Knudsen number based on the orifice diameter rather than the droplet diameter.[5] Consequently, the principal purpose of our previous CFD simulation was to shed light on the most essential factors, particularly fluid-dynamical interference among the droplet train, flow effect, and velocity and orifice dependences of the uptake rate. Although our CFD simulation has qualitatively elucidated some of the empirical assumptions in the experimental analysis, it has also suggested that their quantitative accuracy should be further examined.

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We think that quantitative comparison between experiment and simulation is the next step. The Comment properly states that "the detailed gas transport properties likely depend on the specific conditions in our droplet apparatus that are not fully matched in the MSK simulation". We agree with this statement; certainly the droplet geometry and ambient conditions in our CFD simulation do not match the experimental conditions. Figure 1 of the Comment refers to our data in Figure 6 of ref 3, which were calculated by the CFD simulation assuming some typical experimental conditions as an example. Therefore, it is difficult to draw any meaningful conclusion from Figure 1 of the Comment. To remove many ambiguities involved in Figure 1, quantitative comparison should be performed on the basis of a common specific system and well-defined conditions. Such work is in progress.[4]

Finally, we would like to state our position in the CFD simulation study. There is no doubt that the mass accommodation coefficient is a very useful phenomenological quantity to describe the heterogeneous uptake kinetics. However, there remain some inconsistencies to be elucidated between the DTA and other experiments or simulation.[6−10] If one interprets this quantity squarely in a microscopic sense, in terms of the sticking probability at liquid−vapor interface, we believe that caution should be necessary to establish the relation between the kinetic definition and the microscopic definition. (The latter can in principle be measured by molecular-beam scattering experiment or molecular dynamics simulation.) The relation is particularly challenging when extrapolation to the low-pressure limit is hampered by substantial vapor pressure. The main purpose of our CFD simulation is to establish the relation in such situations.

Erratum: A. Morita, M. Sugiyama, S. Koda, *J. Phys. Chem. A* **2003**, *107*, 1749−1759.

In page 1754, right column, four and five lines below eq 13, Fuchs−Sutugin formula of eq 1 → Fuchs Sutugin formula of eq 6, (right-hand side) of eq 1→ (right-hand side) of eq 6.

We appreciate the anonymous reviewer to point this out.

References and Notes

(1) Worsnop, D. R.; Williams, L. R.; Kolb, C. E.; Mozurkewich, M.; Gershenzon, M.; Davidovits, P. J. Phys. Chem. A, **2004**, *108*, 8542.

(2) Sugiyama, M.; Koda, S.; Morita, A. *Chem. Phys. Lett.* **2002**, *362*, 56−62.

(3) Morita, A.; Sugiyama, M.; Koda, S. *J. Phys. Chem. A* **2003**, *107*, 1749−1759.

(4) Morita, A.; Sugiyama, M.; Kameda, H.; Koda, S.; Hanson, D. R. *J. Phys. Chem. B* **2004**, *108*, 9111−9120.

(5) Worsnop, D. R.; Shi, Q.; Jayne, J. T.; Kolb, C. E.; Swartz, E.; Davidovits, P. *J. Aerosol Sci.* **2001**, *32*, 877−891.

(6) Wilson, M. A.; Pohorille, A. *J. Phys. Chem. B* **1997**, *101*, 3130−3135.

(7) Taylor, R. S.; Garrett, B. C. *J. Phys. Chem. B* **1999**, *103*, 844−851.

(8) Morita, A. *Chem. Phys. Lett.* **2003**, *375*, 1−8.

(9) Hanson, D. R.; Lovejoy, E. R. *J. Phys. Chem.* **1996**, *100*, 6397−6405.

(10) Hanson, D.; Kosciuch, E. *J. Phys. Chem. A* **2003**, *107*, 2199−2208.