Revised Kinetics in the Droplet-Train Apparatus Due to a Wall Loss

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An equation for analyzing the kinetic results for the droplet-train apparatus with a wall loss is derived. We show that the presence of a radial concentration gradient due to loss on the flow reactor wall significantly affects the measured uptake coefficient γ_{meas} on droplets in the center of the reactor. For an efficient wall loss, γ_{meas} can be ~60% less than that calculated without consideration of the loss on the wall. This revision of the kinetics for species with a wall loss leads to an increase in the uncertainty of the extracted gas−surface reaction probability for high water vapor pressure experimental conditions.

Introduction

The extraction of fundamental physical and chemical parameters from the results of a heterogeneous chemistry experiment can be difficult when processes other than the one that is the aim of the study dominate the kinetics. One such example is the study of gas−surface reaction probabilities where diffusion of the reactant through a bath gas is a significant, or perhaps the major, rate-limiting process.

The droplet-train apparatus (DTA) has been utilized to study heterogeneous chemistry for many years.[1,2] It is uniquely suited to study the interactions of reactant species with aqueous surfaces where a relatively high vapor pressure of water is present. This is because evaporation/condensation of the droplets is small or negligible during the short time the droplets travel through the interaction region. It also allows for the study of uptake due to solvation for short (ms) gas−liquid contact times.

However, there are a few DTA results for uptake onto liquids that have a significant vapor pressure of H_2O[8,18] that are at odds with the results of another experiment[5,16] and with molecular[19,20] and fluid dynamics[3,4] computational studies. Specifically, for uptake onto dilute sulfuric acid solutions (20−40 wt % H_2SO_4) near room temperature, the mass accommodation coefficients α for NH_3[8] and HCl[18] are reported to be near ~0.3 while the α values measured in aerosol flow reactor experiments are reported to be near unity (NH_3,[5] HCl[16]). Note that for NH_3 uptake onto very dilute acid solutions (pH > 3.7, equivalent $[H_2SO_4] \leq$ 0.001 wt %), another experimental result[21] is in accord with the DTA results[22] for this case (elsewhere[23] we have provided a critique of the model used in ref 21). Molecular dynamics simulations of the uptake of ethanol[19,20] onto water and the computational fluid dynamics simulations of a droplet train[3,4] also do not quantitatively agree with DTA results. This paper focuses on a regime of the DTA analysis that addresses the issues surrounding these discrepancies.

The analysis of the results of the DTA in the presence of several Torr of water vapor (or another bath gas) when there is an efficient uptake is complicated. The kinetics of diffusion and of the surface reaction probability (γ_t) are treated separately and comprise the measured reaction probability (γ_{meas}). Consequently, a value for γ_t can be obtained by applying a correction to γ_{meas} due to the resistance of gas-phase diffusion, *DiffCorr*

$$\frac{1}{\gamma_t} = \frac{1}{\gamma_{meas}} - DiffCorr \qquad (1)$$

Presently, the valuation of *DiffCorr* for experiments in the DTA[2] is determined by empirical results because, as stated in ref 2, "...an exact treatment of the full gas uptake process is not available..." This approach is reasonable, and the functionality of *DiffCorr* is based on sound physical arguments (see the discussion in refs 1 and 2 and references therein), and it yields a cohesive set of results for γ_t, the true uptake coefficient. The use of *DiffCorr* has been established over a wide range of experimental conditions.[2] For efficient uptake coefficients (γ_t near unity), these experiments have usually employed variable amounts of a noble gas (He, Ne, Ar, or Kr) to provide the diffusion resistance.[2,8] But there is a subset of measurements for γ_t near unity where a significant amount of water vapor was present: the uptake of deuterated species onto water droplets. The losses of CD_3COOD,[6] D−ethanol,[6] and D_2O[7] on H_2O−water are notable in this respect. The results for CD_3-COOD and D_2O have been used to affirm the applicability of *DiffCorr* to uptake measurements on water droplets where H_2O vapor provides the diffusive resistance.[2,6]

However, there may be additional uncertainty in the results for these species due to an error in the determination of γ_{meas}.

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Shi et al.[6] report that CD_3COOD (and to a lesser extent D−ethanol) was lost efficiently on the wall. It is reasonable to consider also the possibility of D_2O loss on the wall because measurements were conducted in the presence of a large excess of H_2O vapor, although wall loss for D_2O was not mentioned by Li et al.[7] The presence of a wall loss is a significant difference from the majority of the previous DTA experiments where conditions were such that no wall loss occurred. Loss on the reactor wall can lead to a significant concentration gradient across the flow reactor radius which deviates from the assumptions[1,2,9] employed in the calculation of γ_{meas}.

In ref 6, the wall loss of CD_3OOD was addressed, and it was stated that "...in principle, the depletion signal due to gas−droplet interaction should be independent of wall loss." In essence, because the wall loss was present for both measured signals that were used to determine γ_{meas}, its effect would cancel out. Here we demonstrate, however, that a wall loss can affect the kinetics in the DTA reactor and γ_{meas} can be significantly decreased when the wall loss is taken into account. If there is an error in γ_{meas}, then the *DiffCorr* might have additional uncertainty if applied to measurements where the droplets have a significant vapor pressure of water, which would lead to an increased uncertainty in the extracted value for γ_t.

Analytical Solution of the Kinetics of Uptake in DTA with Wall Loss

As was presented by Gardner et al.,[9] the kinetic equations for the DTA can be derived assuming a plug-flow velocity profile, insignificant axial diffusion, and negligible gradients due to finite rates of diffusion to the droplets (i.e., *DiffCorr* is assumed to be 0). This approach is much simpler than that of solving the appropriate convecto-reacto-diffusive (CRD) equations.[10−14] A detailed analytical solution of the plug-flow CRD that takes into account axial diffusion and models the gradients due to diffusive uptake onto the droplet train is presented in the Appendix. The results of that solution are nearly identical to those from the approach described in this section.

Sufficiently far from the inlet such that entrance effects can be neglected (i.e., the axial decay constant has settled down to the fundamental mode), a species that is lost on the wall of a flow reactor has a first-order wall-loss rate coefficient denoted by k_w (cm^{-1}), where the incremental first-order loss[10−12] in a length dz of the flow reactor is

$$\frac{d\bar{n}(z)}{\bar{n}(z)} = -k_w\, dz \tag{2}$$

where $d\bar{n}(z)$is the change (loss) in the average concentration of the species denoted by $\bar{n}(z)$. This equation in essence provides a definition for k_w and $\bar{n}(z) = \bar{n}(0)\exp(-k_w z)$, where $\bar{n}(0)$ is the cross sectional average of $n(r,0)$ at a position designated $z = 0$. $\bar{n}(0)$ is equal to $(\int n(r,0)2\pi r\, dr)/\pi R^2$, where R is the flow reactor radius. The value of k_w depends on the radial profile, the diffusion coefficient, the flow rate, and the loss rate on the wall surface. The value of k_w can also be dependent on other losses, such as uptake onto droplets, if they affect the radial profile.

With the addition of a beam of spherical particles on the central axis of the flow reactor, an additional loss $d\bar{n}(z)_{het}$ ensues

$$\frac{d\bar{n}(z)}{\bar{n}(z)} = -k_w\, dz + \frac{d\bar{n}(z)_{het}}{\bar{n}(z)} \tag{3}$$

This additional loss is given by the gas-kinetic flux times the uptake coefficient γ multiplied by the surface area of the particles contained in length dz of the flow reactor and divided by the volume flow rate of the carrier gas, V_{FR}

$$d\bar{n}(z)_{het} = -\frac{\gamma c n(0,z)}{4V_{FR}} A_d \eta\, dz \tag{4}$$

The particles in the droplet train have a radius a (a single droplet has a surface area $A_d = 4\pi a^2$) and a linear number density η (particle cm^{-1}). $n(0,z)$ is the species concentration along the flow reactor axis (radial position, $r = 0$), i.e., that which is in contact with the particles. The flux to the particles is assumed to follow $cn(0,z)/4$, where c is the mean molecular speed of the reactant. This assumption has no consequence on the conclusions of this work. Because there is no difference between γ_t and γ_{meas} in this treatment, we designate the uptake coefficient by γ.

The incremental loss becomes

$$\frac{d\bar{n}(z)}{\bar{n}(z)} = -k_w\, dz - \frac{\gamma c n(0,z) A_d \eta\, dz}{4\bar{n}(z)V_{FR}} \tag{5}$$

Integration of (5) from 0 to L yields

$$\ln\left(\frac{\bar{n}(L)}{\bar{n}(0)}\right) = -Lk_w - \frac{\gamma c A_d \eta}{4V_{FR}} \int_0^L \frac{n(0,z)}{\bar{n}(z)}\, dz \tag{6}$$

As above, if kinetic measurements are conducted far enough from the inlet, the radial profile of the species is independent of the axial distance along the flow reactor,[10−14] and the integrand is constant. We define a parameter

$$\beta = n(0,z)/\bar{n}(z) \tag{7}$$

With this simplification, eq 6 becomes

$$\ln\left(\frac{\bar{n}(L)}{\bar{n}(0)}\right) = -Lk_w - \frac{\gamma c A_d \eta}{4V_{FR}}\beta L \tag{8}$$

The DTA experimental result for γ is deduced from the change in the signal upon a change in the droplet surface area. Thus, for a constant exposure length L, the quantity $A_d\eta L = A_i$ is varied ($A_i = A_2 - A_1 = L\{A_{d2}\eta_2 - A_{d1}\eta_1\}$). We specifically allow for k_w to depend on the amount of loss on the droplets and denote these $k_{w,1}$ and $k_{w,2}$ for wall loss in the presence of droplets of surface area A_1 and A_2, respectively. Subtracting eq 8 for A_1 from that for A_2 results in

$$\ln\left(\frac{\bar{n}_{A_2}(L)}{\bar{n}_{A_1}(L)}\right) = -\frac{\gamma c \Delta A}{4V_{FR}}\beta - L(k_{w,2} - k_{w,1}) \tag{9}$$

Here it is assumed, as it is for the previous derivations of the kinetics of the DTA,[2,6,9] that $\bar{n}(0)$ is unaffected by the change in the size and spacing of the droplets. With a change in notation, $V_{FR} = F_g$, $\bar{n}_{A_2}(L) = n_g'$, and $\bar{n}_{A_1}(L) = n_g$, eq 9 can be rearranged to yield

$$\gamma = \frac{4F_g}{c\Delta A}\frac{1}{\beta}\left(\ln\frac{n_g}{n_g'} - L(k_{w,2} - k_{w,1})\right) \tag{10}$$

This equation is different from eq 17 of Shi et al., and the changes are due to the consideration of a wall loss. Specifically, the kinetic equation is altered through the factor β in the

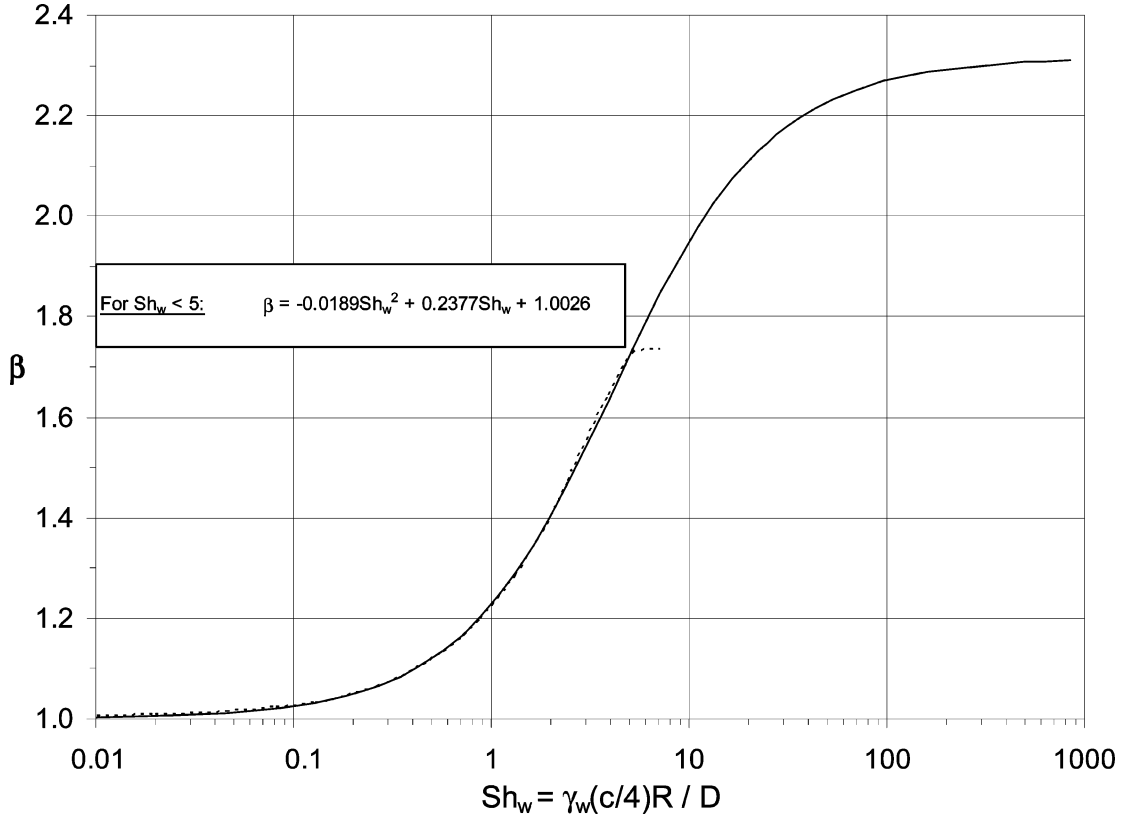

Figure 1. The divisor β (from eq 12) to be applied to the measured uptake coefficient plotted vs the Sherwood number for loss on the wall. The dashed line is a polynomial fit to the data for $Sh_w \leq 5$ giving β to within ~1% of eq 12. These results are for the plug-flow approximation with negligible axial diffusion; see the Appendix for an alternate calculation of β.

TABLE 1: Values for β as a Function of $Sh_w = \gamma_w(c/4)R/D$ and the Axial Flow Velocity Profile[a]

Sh_w	γ_w [b]	β, laminar flow	β, plug flow	$\beta_{w,2}$ [c]	$\beta_{w,1}$ [c]
0.126	0.0001	1.05	1.031	1.049	1.029
0.379	0.0003	1.15	1.093	1.053	1.031
1.26	0.001	1.42	1.28	1.064	1.038
3.79	0.003	1.83	1.62	1.082	1.048
12.6	0.01	2.24	2.01	1.094	1.055
1260	1	2.54	2.31	1.098	1.057

[a] See the Appendix for a detailed explanation of the parameter $\beta_{w,i}$, which was calculated for plug flow. [b] Values for γ_w are for $D = 5$ cm^2/s, $c/4 = 8425$, and $R = 0.75$ cm. [c] Wall-loss enhancement factors for plug flow. Subscript 1 indicates values for the loss representative of a typical far-apart droplet geometry, and subscript 2 indicates that for a typical closely spaced droplet geometry.

denominator and through the last term in brackets that is due to a dependency of the wall loss rate coefficient on droplet surface area.

Discussion

To begin the discussion of the magnitude of the wall-loss effect, we evaluate the factor β with the assumption that the loss on the wall determines the radial profile of the trace gas. This assumption also has the effect of making the last term in eq 10 equal to zero. Within the plug flow approximation, the fundamental mode of the solutions to the CRD equation[13,14] for a species that is lost only on the wall yields a radial profile for [reactant], $n(r)$, that is given by the zero-order Bessel function: $n(r) = c_1 J_0(x)$, where c_1 is an arbitrary constant and $x = r(k_w u/D)^{0.5}$, where u is the linear flow velocity and D is the diffusion coefficient. The boundary condition at the wall determines a value for $x = \lambda = R(k_w u/D)^{0.5}$ from the solution to

$$\gamma_w(c/4)J_0(\lambda) = -D\left.\frac{dJ_0(x)}{dr}\right|_R = -D\frac{dJ_0(x)}{dx}\left.\frac{dx}{dr}\right|_{x=\lambda} = DJ_1(\lambda)\frac{\lambda}{R} \quad (11)$$

γ_w is the reaction probability on the wall, and J_1 is the first-order Bessel's function. The quantity β is given by

$$\beta = \frac{n(r=0)}{\bar{n}} = \frac{J_0(0)}{\int_0^R J_0(x)2\pi r\, dr}\pi R^2 = \lambda/2J_1(\lambda) \quad (12)$$

where the integral is from Wheelon.[17] For an efficient wall loss and $D \leq 10$ cm^2/s, which is typical for the DTA at high water vapor pressure conditions, $\gamma_w(c/4)$ is much greater than $D\lambda/R$, and λ takes a value near the first root of J_0, which is ~2.4. $J_1(2.4)$ is ~0.52; thus a value of ~2.3 for β is obtained for these conditions. A few values for β are shown in the fourth column of Table 1 for a range of γ_w for $D = 5$ cm^2/s. The wall loss has a very large effect on the kinetics measured within a DTA if γ_w/D is ≥ 0.002 s/cm^2 ($\beta \geq 2$). Shown in Figure 1 is the quantity β as a function of $Sh_w = \gamma_w(c/4)R/D$, which is the Sherwood number for loss on the wall.

In this context, the effect of a wall loss in the DTA can be given a physical interpretation. The droplets at the center of the reactor experience a higher than average reactant concentration resulting in a higher than average loss rate. The loss is then averaged via diffusion in the radial direction, which obscures the relationship between the experimentally determined quantities (e.g., n_g, n_g', and the droplet surface area density) and the desired result, γ. The inclusion of the factor $1/\beta$ in eq 10 can thus be thought of as the need for proper accounting within the flow reactor.

In this discussion, we have assumed that the loss on the wall determines the radial profile of the species in arriving at eqs 11 and 12. This assumption is useful for understanding the effect under consideration and to deduce its magnitude. A detailed treatment that takes into consideration the loss on the droplets is presented in the Appendix. The simple treatment presented above is within 3% of that presented in the Appendix providing justification for treating the kinetics of wall loss separately from the *DiffCorr* term.

Dependency of k_w upon the Loss Rate on the Droplets. There is a finding in the Appendix that is noteworthy: the loss at the center of the reactor results in a small increase in k_w. In principle, therefore, the latter term in eq 10 should not be assumed to be zero. The incorporation of this dependence in eq 10 leads to further changes in the flow reactor kinetics. In the Appendix are the details of the variation of k_w with the loss on the droplets. Also presented there is a method for evaluating the last term in eq 10.

Laminar and Other Flows. While plug-flow is a useful approximation for the kinetics of the DTA,[1,2,9] it is not representative of the actual flow. In the absence of particles, it is closely approximated as a fully developed laminar flow, while in the presence of rapidly moving particles, the flow can be substantially distorted from laminar especially near the droplets.[3,4,15] This latter flow profile cannot be treated with the current methods; however, β can be calculated for laminar flow using eq 7 and the radial profiles obtained from the solutions to the CRD equation for laminar flow.[10−13] Again for $D = 5$ cm^2/s and for $\gamma_w = 0.001$ to 1, β ranges from 1.4 to 2.5. These are also shown in Table 1 and are slightly larger than those for plug-flow. The evaluation of the last term in eq 10 for a laminar flow profile is not feasible using the methods in the Appendix. The methods presented by Dang[13] could in principle be useful for this endeavor.

The fundamental mode for the kinetics within a flow reactor can be described by eq 8 irrespective of the velocity profile. The details of the axial velocity profile enter via the dependence of k_w and β on parameters such as γ_w and D. This is strictly true only for a steady-flow profile and for low loss rates in the center of the reactor. The latter condition can be relaxed for plug flow conditions as detailed in the Appendix, and we suspect it can be relaxed for arbitrary flow profiles as long as they are steady. The value for β using steady flow profiles other than plug-flow will be addressed using numerical techniques in a forthcoming paper [Sugiyama, Hanson, Morita, manuscript in preparation.] The examination of nonsteady-flow profiles, such as those that exist very near the droplets in a DTA, will be addressed with computational fluid dynamics calculations [Morita et al., in preparation].

Application to DTA Results. It is difficult to make firm conclusions regarding the value of β for a particular experimental result without a detailed knowledge of the experimental conditions. In ref 6, a value of 0.05 cm^{-1} is quoted for k_w for CD_3COOD but neither the flow velocity nor the pressure for the experiment where this value was determined are provided. These are essential for making a proper evaluation of β. Assuming that this value for k_w applies for the typical flow rates and partial pressures in the D−acetic acid uptake experiments[6] ($F_g = 610$ cm^3/s, Ar partial pressure = 5.2 Torr, and H_2O partial pressure = 1.44 Torr, P. Davidovits, private communication, 2003), β takes a value of ∼1.14 in the plug-flow approximation. The effect on γ_{meas} of the last term in eq 10 can also be estimated as discussed in the Appendix (see A22 and the following discussion). For typical droplet geometries and a $k_w = 0.05$ cm^{-1}, the last term in eq 10 results in a 16% effect on the reported γ_{meas}. The overall correction to the reported γ_{meas} is then −25%. This is a significant correction to the reported γ_{meas}[6] as it leads to γ_t values using eq 1 that range from 0.35 to 0.6. The uncertainty in the γ_t for D−acetic acid, reported in ref 6 to be 0.96 ± 0.21, should be increased; the rough estimate of the wall-loss effect presented here suggests that the negative error bar could be increased to ∼0.5.

Note that the value of k_w that is appropriate for these experimental conditions is uncertain. The wall loss for CD_3COOD was reported to be so large that He could not be used as the carrier gas.[6] This implies that the Ar carrier gas provided sufficient gas-phase diffusion resistance to make the measurement possible. Yet, a value of 0.05 cm^{-1} for k_w for these flow rates and Ar pressures indicates that diffusion was not a major impediment to the transport to the walls (0.05 cm^{-1} is only ∼25% of the diffusion-limited wall-loss rate coefficient for laminar flow[14] given by $3.6D/R^2/u = 0.2$ cm^{-1} where u is the average linear flow velocity). However, precise knowledge of the radial flow velocity profile and the method used to determine k_w may shed light on this uncertainty.

Wall loss due to H−D exchange for other deuterated species (D−ethanol on H_2O and ethanol on D_2O, ref 6, and D_2O)[7] that have been studied in a DTA might be large enough to significantly affect the reported uptake coefficient. In ref 6, the k_w for D−ethanol was described in detail and the determination of its value was corroborated in mass balance experiments where the relative abundances of CD_3CD_2OD and CD_3CD_2OH were monitored in the absence of droplets. k_w was reported to range from 0.01 to 0.05 cm^{-1} for D−ethanol, dependent upon conditions, and the data reported in the paper were taken under the low wall loss conditions. Nonetheless, β and the second term in eq 10 should be calculated to provide values for γ_{meas} for ethanol that are as accurate as possible. Wall loss for D_2O was not reported in ref 7, yet a non-negligible wall loss might have occurred for this species. It is reasonable to postulate this because keeping track of the relative signals between injection points is not necessary to obtain values for γ_{meas}. Thus a small but possibly nonnegligible wall loss can go undetected if not looked for specifically. To provide a point of reference, assuming similar experimental conditions as those quoted above for D−acetic acid, a value for $k_w \leq 0.02$ cm^{-1} would lead to a correction to γ_{meas} of ≤10%.

Conclusions

We have shown that the loss of a species on the reactor wall should be taken into account when analyzing the kinetic results of the DTA. Because of the form of the diffusion correction in eq 1, a reliable value for γ_t depends critically in assessing accurate values for γ_{meas} and *DiffCorr*. The measured uptake coefficient γ_{meas} can be decreased by 60% (i.e., it is divided by $\beta = 2.5$), assuming laminar flow and neglecting the last term in eq 10. We showed that even a small revision of −25% in the γ_{meas} for D−acetic acid can lead to a large increase in the uncertainty of the extracted surface reaction probability, γ_t. The use of the results for CD_3COOD to affirm the applicability of *DiffCorr* to uptake measurements on water droplets where H_2O vapor provides the diffusive resistance should be re-evaluated.[2,6]

Finally, one should keep in mind that the *DiffCorr* term in eq 1 where the value for γ_t is determined is a correction in the opposite direction of these corrections to γ_{meas}. The consideration of wall loss in the DTA presented here allows for the possible revision of the applicable γ_{meas}. This is important for considering alternative values for *DiffCorr* such as that of Morita, Sugiyama,

and co-workers.[3,4] Even though the effect of a wall loss may be relatively small, it is important to consider it to fully evaluate all the kinetic processes within the DTA.

The consideration of wall-loss effects, along with diffusion treatments such as those from the fluid dynamics simulation, will allow for a better understanding of the kinetic measurements within a DTA. Contrary to the considerable body of empirical evidence that affirms the present DTA analysis,[2] we believe these considerations will provide part of the basis for re-evaluating the uncertainties of the extracted mass accommodation coefficients from measurements at high water vapor pressures. This could lead to a better agreement of some of the DTA results with the results of other investigations.

Appendix

Plug-Flow Kinetics in a Model DTA for Significant Loss on the Droplets. We represent the droplet train as a liquid rod of radius a centered within the flow reactor of radius R. We consider the steady-state solution to the CRD equation

$$\frac{\partial n}{\partial t} = 0 = D\nabla^2 n - u\frac{\partial n}{\partial z} \tag{A1}$$

with a wall loss that occurs with an efficiency γ_w at $r = R$ and the loss to the particles is taken into account by a collisional loss efficiency γ_t at the surface of the rod. Sufficiently far from the reactant inlet, we assume that the axial decay of $n(z,r)$ can be separated into two functions $f(z)g(r)$, where $f(z)$ is an exponential function with a first-order decay constant k_m. The radial profile $g(r)$ obeys

$$Dg'' + Dg'/r + (Dk_m^2 + k_m u)g = 0 \tag{A2}$$

Upon the transformation

$$x = r(A)^{1/2} \qquad A = k_m^2 + k_m u/D \tag{A3}$$

the dimensionless radial profile $g(x)$ is a solution to a Bessel's equation

$$g'' + g'/x + g = 0 \tag{A4}$$

which is a linear combination of Bessel's functions of the first and second kinds of zeroth order

$$g(x) = c_1 J_0(x) + c_2 Y_0(x) \tag{A5}$$

The constant A and the ratio c_2/c_1 are determined by the boundary conditions (c_1 can be set to an arbitrary value.) At the surface of the rod, the boundary condition

$$D\nabla g = D\left.\frac{\mathrm{d}g}{\mathrm{d}r}\right|_a = \gamma_t \frac{c}{4} g(a) \tag{A6}$$

translates into the equation

$$g'(\epsilon) = N_{sh} g(\epsilon) \tag{A7}$$

where $\epsilon = a(A)^{1/2}$ and $N_{sh} = \gamma_t c/4D(A)^{1/2}$ is the Sherwood number for loss on the rod divided by ϵ. This leads to a relation for c_2/c_1

$$\frac{c_2}{c_1} = -\frac{J_1(\epsilon) + N_{sh}J_0(\epsilon)}{Y_1(\epsilon) + N_{sh}Y_0(\epsilon)} \tag{A8}$$

using the identities[17] $J_0'(x) = -J_1(x)$ and $Y_0'(x) = -Y_1(x)$. For loss on the flow reactor wall with a collision efficiency of γ_w, the boundary condition at $x = \lambda = R(A)^{1/2}$ is

$$g'(\lambda) = -N_{shw} g(\lambda) \tag{A9}$$

where N_{shw} is equal to $\gamma_w c/4D(A)^{1/2}$ (the Sherwood number for loss on the wall divided by λ). This leads to another relation for c_2/c_1

$$\frac{c_2}{c_1} = -\frac{J_1(\lambda) - N_{shw}J_0(\lambda)}{Y_1(\lambda) - N_{shw}Y_0(\lambda)} \tag{A10}$$

Subtracting A10 from A8, a value for A is obtained by determining the root of

$$0 = -\frac{J_1(\epsilon) + N_{sh}J_0(\epsilon)}{Y_1(\epsilon) + N_{sh}Y_0(\epsilon)} + \frac{J_1(\lambda) - N_{shw}J_0(\lambda)}{Y_1(\lambda) - N_{shw}Y_0(\lambda)} \tag{A11}$$

whereupon the solution is fully determined.

Diffusion to the droplets in a DTA may be slow enough that significant concentration gradients develop near the droplets. In this case, the parameter β is not given by the simple relation in eq 7. Since the parameter β describes the enhancement in the loss on the droplet train (here a rod of radius a) due to the loss on the flow reactor wall at $r = R$, we can provide a more rigorous definition: β is the ratio of the loss rates on the rod when a wall loss is present to that in the absence of a wall loss. The number of molecules s^{-1} lost on a length of the rod z is the area of the rod times the gas kinetic flux

$$\text{molecule/s} = 2\pi a z \gamma_t \frac{c}{4} n(a) \tag{A12}$$

The first-order loss rate coefficient for the reactor k_{rod}^I (cm^{-1}) is obtained by dividing by the number of molecules in a length z of the flow reactor and by u

$$k_{rod}^I = \frac{\text{molecule/s}}{\bar{n}\pi(R^2 - a^2)zu} = 2a\gamma_t \frac{c}{4} n(a)/\bar{n}(R^2 - a^2)u \tag{A13}$$

Finally, we arrive at an expression for β

$$\beta = \frac{k_{rod}^I}{k_{rod,0}^I} = \frac{n(a)/\bar{n}}{n_0(a)/\bar{n}_0} = \frac{g(\epsilon)/\bar{g}}{g_0(\epsilon_0)/\bar{g}_0} \tag{A14}$$

where the zero subscript indicates that they are evaluated in the absence of a wall loss.

The average of $g(x)$ along a cross section of the flow reactor is given by

$$\bar{g} = \frac{\int_\epsilon^\lambda g(x)2\pi x\,\mathrm{d}x}{\int_\epsilon^\lambda 2\pi x\,\mathrm{d}x} = \frac{\epsilon g'(\epsilon) - \lambda g'(\lambda)}{(\lambda^2 - \epsilon^2)/2} \tag{A15}$$

using the integrals from Wheelon.[17] With eqs A7 and A9, it can be shown

$$\frac{g(\epsilon)}{\bar{g}} = \frac{\lambda^2 - \epsilon^2}{2N_{sh}\epsilon}\frac{1}{1 + \dfrac{R\gamma_w g(\lambda)}{a\gamma_t g(\epsilon)}} = \frac{A}{1 + \dfrac{R\gamma_w g(\lambda)}{a\gamma_t g(\epsilon)}}\frac{2D(R^2 - a^2)}{\gamma_t c a} \tag{A16}$$

Finally, β is given by

$$\beta = \frac{A}{A_0}\frac{1}{1+\dfrac{R\gamma_w g(\lambda)}{a\gamma_t g(\epsilon)}} \tag{A17}$$

For $c/4 = 8500$ cm/s, $D = 5$ cm^2/s, $u = 200$ cm/s, $\gamma_t = 1$, $R = 0.745$ cm, and $a = 0.002$ cm, β takes values of 1.27, 2.04, and 2.37 for $\gamma_w = 0.001$, 0.01, and 1, respectively. These are within a few percent of the values determined using the simpler approach in the main body of the paper. A rod of radius 20 μm was chosen because it has the same surface area per axial distance as is typical for the droplets in a DTA. For a point of reference, the loss on the rod in the absence of a wall loss, $k^I_{rod,0}$, is 0.016 cm^{-1}. The value of β is not significantly dependent on the value of a or γ_t. This is because $g(\epsilon)/g(\lambda)$ varies to compensate for variations in a and γ_t for these conditions so that the quantity $a\gamma_t g(\epsilon)/g(\lambda)$ is nearly constant.

There is an increase in the wall loss due to the presence of the loss on the rod. This is because the value of k_w must reflect the changes in the radial profile of the reactant when loss on the rod is important. Similar to eq A17, an enhancement factor β_w for the wall loss rate coefficient can be derived

$$\beta_{w,i} = \frac{A}{A_0}\frac{1}{1+\dfrac{a\gamma_{t,i} g_i(\epsilon)}{R\gamma_w g_i(\lambda)}} = \frac{k_{w,i}}{k_{w,0}} \tag{A18}$$

where the zero subscript now indicates that they are evaluated in the absence of a loss on the rod. Because β_w depends on the loss rate at the center of the reactor, we designate it with subscript i ($i = 1$ or 2.) For the conditions listed in the preceding paragraph and $\gamma_{t,2} = 1$, $\beta_{w,2}$ takes values of 1.06 and 1.10 for $\gamma_w = 0.001$ and 1, respectively. For $\gamma_{t,1} = 0.075$ (to give a lower loss rate that simulates a far apart droplet geometry, i.e., $k^I_{rod,0} = 0.010$ cm^{-1}), $\beta_{w,1}$ ranges from 1.04 to 1.06 as γ_w goes from 0.001 to 1. Listed in the last two columns of Table 1 are representative values for $\beta_{w,i}$.

The overall first-order loss rate coefficient is equal to

$$\frac{d\bar{n}(z)}{dz}\frac{1}{\bar{n}(z)} = -(k_{w,i} + k^I_{rod,i}) = -(\beta_{w,i}k_{w,0} + \beta k^I_{rod,0}) \tag{A19}$$

The loss on the rod couples to the loss on the wall to make an overall effect on the loss rate coefficient that could make the value for β appear to be even larger than that given by A17. This coupling should be considered when evaluating the overall effect of a wall loss on the kinetics in a droplet train apparatus.

The Second Term on the Right-Hand Side of Equation 10. Equation 10 can be rearranged to give

$$\gamma = \gamma_m \frac{1}{\beta}\left(1 - \frac{L(k_{w,2} - k_{w,1})}{\ln(n_g/n_g')}\right)$$

where

$$\gamma_m = \frac{4F_g}{c\Delta A}\ln\left(\frac{n_g}{n_g'}\right) \tag{A20}$$

is the measured, uncorrected uptake coefficient. The correction for wall loss is separated into the $1/\beta$ term and the last term in brackets. The last term can be transcribed by integrating A19, taking the difference between two droplet configurations, and obtaining for the measured quantity $\ln(n_g/n_g')$

$$\ln(n_g/n_g') = L(k^I_{rod2} - k^I_{rod1} + k_{w,2} - k_{w,1}) = L\beta(k^I_{rod2,0} - k^I_{rod1,0}) - Lk_{w,0}(\beta_{w,2} - \beta_{w,1}) \tag{A21}$$

With this, the last term in eq A20 becomes

$$\left(1 - \frac{L(k_{w2} - k_{w1})}{\ln(n_g/n_g')}\right) = \left(1 + \frac{k_{w,0}(\beta_{w,2} - \beta_{w,1})}{\beta(k^I_{rod2,0} - k^I_{rod1,0})}\right)^{-1} \tag{A22}$$

As shown in Table 1, the quantity $\beta_{w,2} - \beta_{w,1}$ ranges from 0.02 to 0.04 depending upon the Sherwood number for loss on wall. β also depends on the Sherwood number, and it varies such that the quantity $(\beta_{w,2} - \beta_{w,1})/\beta \approx 0.02$ is nearly independent of Sh_w. A typical value for the quantity $k^I_{rod2,0} - k^I_{rod1,0}$ is 0.006 cm^{-1}, and thus eq A22 is given approximately by $1/(1 + 3.3k_{w,0})$.

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References and Notes

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