Mass accommodation coefficient of water vapor on liquid water

P. Davidovits,[1] D. R. Worsnop,[2] J. T. Jayne,[2] C. E. Kolb,[2] P. Winkler,[3] A. Vrtala,[3] P. E. Wagner,[3] M. Kulmala,[4] K. E. J. Lehtinen,[4,5] T. Vesala,[4] and M. Mozurkewich[6]

[1] Clouds play a critical role in both the Earth's radiation budget and hydrologic cycle. The activation of aerosol particles and subsequent growth of these particles into cloud droplets are often controlled by the transfer of water vapor molecules into liquid droplets. Two parameters that fundamentally influence the interaction of water vapor or any other gaseous molecule with a liquid surface are: the mass accommodation (or condensation) coefficient and the thermal accommodation coefficient. The mass accommodation coefficient is the probability that a gaseous molecule striking a liquid surface enters into the bulk liquid phase. The thermal accommodation coefficient is the fraction of collisions that result in the energy of the impinging gas molecule equilibrating with the mean energy of the liquid surface molecules. Here we discuss mass accommodation coefficient data for water vapor obtained using two unique experimental methods: the droplet train/fast flow reactor and the expansion cloud chamber system. Both methods show that mass accommodation coefficient for atmospherically relevant temperatures is always greater than 0.1; the latter method yields values very near 1.0. These studies show that for lower atmospheric clouds the growth of cloud droplets in clean air will be controlled by diffusion of water vapor to and heat from the droplets' surface without any significant limitation due to accommodation probabilities.

[2] The growth of cloud droplets and aqueous atmospheric aerosol particles is controlled by both heat and mass transfer. Water vapor fluxes and the resulting heat transfer are particularly important. These mass and heat transfers are coupled [see, e.g., Wagner, 1982]. In the continuum regime gas phase diffusion and thermal conductivity are the controlling phenomena. In the kinetic regime these fluxes are under gas kinetic control and the mass accommodation

and thermal accommodation coefficients, α and α_T, may limit the rate of growth for smaller droplets [Yum et al., 1998; Nenes et al., 2001; Kulmala and Wagner, 2001; Kulmala et al., 1996; Rudolf et al., 2001, and references therein]. However, if α and α_T are large enough, diffusion of water vapor and heat will control the rate of aqueous droplet growth. Cloud activation simulations [Kulmala et al., 1996; Rudolf et al., 2001] show that for most atmospheric conditions relevant to cloud formation, if the mass accommodation coefficient of water vapor is below 0.1, water vapor saturation in nascent clouds will increase so much that a much larger fraction of aerosol particles will activate as cloud droplets. This will lead to more stable clouds with a higher number density of smaller droplets, that is, clouds that are less likely to form precipitation. On the other hand, the above mentioned cloud activation simulations show that cloud droplet nucleation and growth rates are relatively insensitive to variations in α above 0.1.

[3] Because of its importance, the mass accommodation coefficient of water vapor has been the subject of at least 40 published experimental studies over the past 75 years. These studies obtained results that range over three orders of magnitude. The first measurement of this parameter [Rideal, 1925] yielded a value $\alpha = 0.003$. Prior to 1985, experiments yielded values of α ranging between ~0.001 and 1 (see the two most recent reviews: Mozurkewich [1986] and Marek and Straub [2001]). More recent measurements of α, published between 1987 and 2000, still span two orders of magnitude, between 0.01 and 1. Specific values from the more recent works (with temperature stated where provided) include: $\alpha = 0.01$ [Garnier et al., 1987]; $\alpha = 0.30$ at T = 258 K [Beloded et al., 1989]; $0.01 \leq \alpha \leq 1$ at T = 282 K to 293 K [Hagen et al., 1989]; $\alpha = 0.1$ at T = 298K [Maerefat et al., 1990]; $0.04 \leq \alpha \leq 0.1$ at T = 238 K [Shaw and Lamb, 1999]; $0.01 \leq \alpha \leq 0.1$ [Zagaynov et al., 2000]. The temperature dependence of α was not established in any of these studies.

[4] Fewer determinations of the thermal accommodation coefficient (α_T) for $H_2O(g)$ on water are found in the literature. Alty and Mackay [1935] reported a value of $\alpha_T = 1$. More recently values of α_T were measured in the range $0.1 \leq \alpha_T \leq 1$ with most likely values quoted at $\alpha_T = 1$ [Sageev et al., 1986] and $\alpha_T = 0.6$ [Shaw and Lamb, 1999]. The values of α (as well as α_T, when measured) quoted above were generally obtained either from measurements of evaporation or condensation rates from/on bulk water surfaces, or from measurements of droplet (aerosol) growth rates in supersaturated environments. Possible experimental and modeling uncertainties that may in part account for the wide range of quoted α values are discussed in the cited reviews. Marek and Straub [2001] suggest that values of $\alpha < 0.1$ are likely due to contamination of the water surface.

[1]Merkert Chemistry Center, Boston College, Chestnut Hill, Massachusetts, USA.
[2]Aerodyne Research, Inc., Billerica, Massachusetts, USA.
[3]Institute für Experimental Physik, Universität Wien, Vienna, Austria.
[4]Department of Physical Sciences, University of Helsinki, Helsinki, Finland.
[5]Now at Department of Applied Physics, University of Kuopio, Kuopio, Finland.
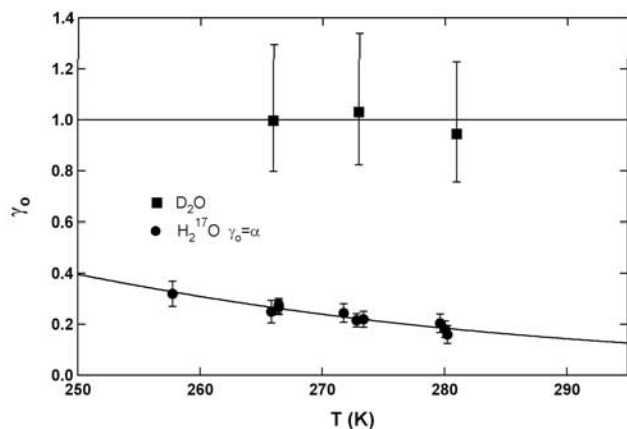[6]Chemistry Department, York University, Toronto, Ontario, Canada.

Figure 1. Uptake coefficient γ_o for $H_2O(g)$ and $D_2O(g)$ as a function of temperature obtained by the BC/ARI group. For $H_2O(g)$ γ_o is the mass accommodation coefficient α. For $D_2O(g)$ γ_o is the surface accommodation coefficient S. Reproduced from *Li et al.* [2001] by permission. The indicated error bars are based on experimental evaluation only.

[5] Recently our two research collaborations, (1) Boston College/Aerodyne Research Inc. (BC/ARI) and (2) University of Vienna/University of Helsinki (UV/UH) re-measured the mass accommodation coefficients of gas phase H_2O on liquid water employing two quite different experimental methods. In addition the UV/UH group measured α_T for air (oxygen and nitrogen molecules) on water and the BC/ARI group determined the D-H isotope exchange probability for $D_2O(g)$ interacting with the water surface. The isotope exchange probability yields a value for the surface accommodation (or adsorption) coefficient S that is the probability that a molecule striking the liquid surface becomes part of the surface (that is, in some way bonded to the surface). One can reason that a measurement of S yields the lower limit to α_T for $H_2O(g)$ on water (that is, $\alpha_T \geq S$).

[6] The BC/ARI group employed a droplet train apparatus where a fast-moving monodisperse, spatially collimated train of droplets interacts with the gas-phase species (in this case $H_2^{17}O(g)$ or $D_2O(g)$) in trace quantities [*Li et al.*, 2001]. The liquid water itself is in equilibrium with its vapor, and the uptake of the trace isotopic species (which is of course out-of-equilibrium) does not significantly perturb the bulk phase or the surface of the liquid. Mass accommodation coefficients are obtained from the uptake (condensation) of gas phase $H_2^{17}O$ isotope in trace amounts $\sim 10^{14}$ cm^{-3}, perturbing the gas liquid equilibrium only by about 10^{-3}. The surface accommodation coefficient (S) for $H_2O(g)$ is inferred from measurements of the D-H isotope exchange probability for $D_2O(g)$ interacting with the water surface. By selecting the gas inlet port and the droplet velocity, the gas-droplet interaction time can be varied between about 2 and 15 ms.

[7] In the UV/UH method, a well-defined mixture of water vapor and silver particles in air at near atmospheric pressure, is introduced into an expansion chamber. Fast adiabatic expansion of the water vapor – air mixture in the chamber produces controlled vapor supersaturation (saturation ratio 1.3 to 1.45). Subsequent condensation on the pre-existing nm-scale particles leads to simultaneous growth of monodisperse liquid droplets [*Winkler et al.*, 2004]. Of course in these, as well as in other droplet growth or evaporation experiments, the initial water vapor partial pressure and temperature are not in thermal equilibrium with the liquid water surface. However, the gas phase concentration and temperature profiles are near steady state. As the droplets are newly forming in the course of a near steady-state growth process, the composition of the droplets remains uniform throughout the entire growth process. In the UV/UH experiments droplet growth is monitored on a time scale of 6 to 200 ms by laser light scattering. The mass and thermal accommodation coefficients are obtained by fitting the measured droplet growth rates to numerical solutions of the differential equations describing the coupled mass and heat fluxes in the vicinity of the droplets [see, e.g., *Vesala et al.*, 1997].

[8] The two groups measured similar thermal accommodation coefficients. The UV/UH group measured $\alpha_T > 0.85$ for air on water. The BC/ARI group obtained $\alpha_T = 1 \pm 0.13$ for $D_2O(g)$ on water. However, the values of the mass accommodation coefficient measured by the two groups were somewhat different. The mass accommodation coefficient of $H_2O(g)$ on water as measured by the BC/ARI group has a negative temperature dependence, with the magnitude ranging from 0.17 ± 0.03 at 280 K to 0.32 ± 0.04 at 258 K. On the other hand, the UV/UH group measured a mass accommodation coefficient that within experimental error was unity, and excluded values below 0.4 for temperature in the range 251 to 290 K [*Winkler et al.*, 2004]. The BC/ARI and UV/UH results are shown in Figures 1 and 2.
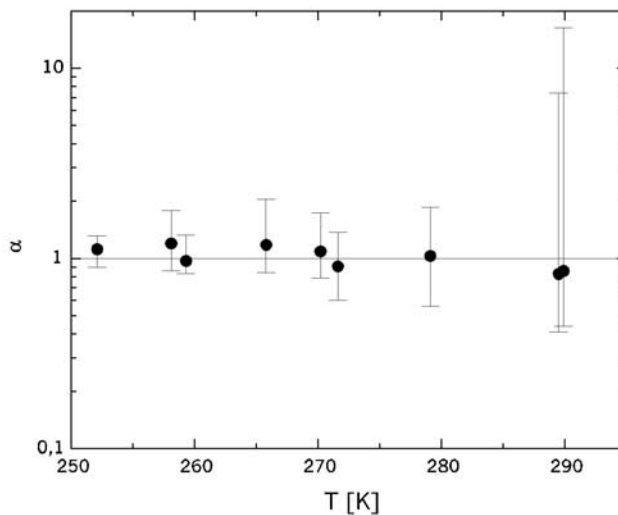

Figure 2. Mass accommodation coefficient α for $H_2O(g)$ as a function of droplet temperature obtained by the UV/UH group. Data were obtained by a two-parameter fit of theoretical droplet growth to corresponding experimental results accounting for the experimentally determined time interval for the start of droplet growth. The error bars indicate the maximum total errors resulting from combination of the uncertainties in drop growth times, system temperatures and gas pressures. (For all error considerations, see *Winkler et al.* [2004].) At increasing droplet temperatures the sensitivity of droplet growth curves with respect to α decreases resulting in increasing error. Of course, actual values of accommodation coefficients cannot exceed unity.

[9] The difference in the value of α measured by the two groups may be due to two factors. First, there may be unsuspected problems in the experimental and/or modeling procedures affecting the accuracy of the α measurements. Second, the mass accommodation process measured by these two experiments may not be the same.

[10] In connection with procedures, particular attention was paid to the treatment of gas phase diffusive transport in the droplet train apparatus. From the very beginning it was clear to the BC/ARI group that diffusive transport in the droplet train apparatus was highly complex and would have to be characterized experimentally. To this end extensive uptake studies were performed that resulted in a relatively simple formulation of gas phase diffusive transport in the droplet apparatus. These studies are summarized by *Worsnop et al.* [2001]. A fluid dynamics simulation of gas phase diffusive transport in the droplet apparatus by *Morita et al.* [2003, 2004] is under discussion [*Worsnop et al.*, 2004].

[11] As has been pointed out recently by *Hanson et al.* [2004], significant loss of trace gas at the flow tube wall can affect uptake coefficient measurements. Wall loss is routinely measured in the BC/ARI experiments, as described by *Gershenzon et al.* [2004]. In the $H_2^{17}O(g)$ and $D_2O(g)$ uptake studies, wall loss was below the detection limit and too low to significantly affect the measurements.

[12] We have examined in detail the experimental and modeling procedures employed by the two groups to obtain α. We have not found any experimental or modeling factors that would account for the difference in the α measurements. This leaves open the second issue, namely that the mass accommodation process measured by the two experiments may not be the same. To explore this possibility we first outline a formulation of the mass accommodation process.

[13] Results of trace gas uptake studies for more than 30 gas phase species can be explained by representing mass accommodation as a two step process [see *Kolb et al.*, 2002, and references therein]. First, the gas molecule strikes the surface and is adsorbed as surface species n_s. Adsorption involves surface accommodation. In the absence of surface reactions, the surface species then either enters the liquid or desorbs from the surface. The process can be represented as:

$$n_g \underset{k_{des}}{\overset{k_{ads}}{\rightleftharpoons}} n_s \overset{k_{sol}}{\longrightarrow} n_l \qquad (1)$$
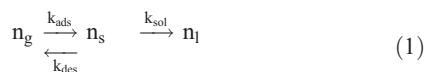
Here the subscripts g, s and l represent the gas, surface and liquid state of the species. In this representation the reverse arrow from n_l to n_s is omitted because here only the mass accommodation process is represented. Desorption from the bulk liquid is accounted for separately. The adsorption rate constant (or deposition velocity) is $k_{ads} = S\bar{c}/4$, where $\bar{c}$ is the average thermal speed, and S is the trace gas surface accommodation coefficient. (It can be argued convincingly that thermal and surface accommodation are essentially the same process, i.e., $S = \alpha_T$.)

[14] By mass conservation and with $S = \alpha_T = 1$, we obtain,

$$\alpha n_g \bar{c}/4 = n_g \bar{c}/4 - n_s k_{des} = n_s k_{sol} \qquad (2)$$

and

$$\frac{\alpha}{1 - \alpha} = \frac{k_{sol}}{k_{des}} \qquad (3)$$

Note that the formulation in equation (3) precludes the value of α to be exactly one, because $\alpha = 1$ implies that $k_{sol}/k_{des} = \infty$. Of course, α can approach 1.

[15] At present, no ab initio theory exists to predict the mass accommodation of gaseous species on liquid surfaces. However, the patterns observed in the measured values of α for a wide range of molecules, (more than 30 in number), led the BC/ARI group to formulate a surface nucleation model for the uptake of gas phase species by liquid water that provides an explanation for the observed uptake results, including the temperature dependence of α. [*Kolb et al.*, 2002; *Davidovits et al.*, 1991, and references therein.].

[16] The two-step mechanism for mass accommodation noted above is a possible description of the uptake of a gas molecule into the bulk liquid under equilibrium water vapor conditions. However, the growth of droplets at saturation ratios of 1.3 to 1.5, as in the UV/UH experiments, may be effectively a single step process, governed by the surface accommodation coefficient S of $H_2O(g)$ on liquid water. Under fast droplet growth conditions surface accommodation of water vapor molecules might be followed by very efficient mass accommodation as the newly arriving flux promotes their incorporation into the bulk liquid. The higher uptake rates observed in the UV/UH experiment might be related to the newly arriving flux of water vapor molecules to the liquid surface, characteristic of the supersaturated vapor/droplet growth measurements leading to higher values of k_{sol} and accordingly α. A simple estimate using a Langmuir-Hinshelwood type mechanism suggests that somewhat higher values of the uptake rates are feasible. The Langmuir-Hinshelwood mechanism could also explain the larger values of the mass accommodation coefficient measured by the UV/UH group for nitric acid [*Rudolf et al.*, 2001]. However, the quantitative parameters such as surface diffusion rates and the binding energy of a surface accommodated molecule required for a reliable calculation are not presently available.

[17] Model calculations of ambient aerosol activation to cloud droplets show that the computed fraction of aerosol particles activated is very sensitive to assumed values of α below 0.1, but this fraction is relatively insensitive to larger values [*Yum et al.*, 1998; *Nenes et al.*, 2001; *Kulmala et al.*, 1996; *Rudolf et al.*, 2001 and relevant references therein]. Even though the values of α measured by the two groups are different, both methods show that mass accommodation coefficient for atmospherically relevant temperatures is always greater than 0.1, consistent with the review of Marek and Straub and the field measurements of *Leaitch et al.* [1986] and *Hudson et al.* [2000]. Therefore, for typical temperatures characterizing tropospheric clouds, activation of cloud droplets in clean air by normal inorganic aqueous aerosol particles will be controlled by diffusion of water vapor and heat to the droplets' surface without any significant limitation due to accommodation probabilities. However, in polluted atmospheres the droplet surfaces may become contaminated, reducing α to a point where mass accommodation may limit droplet growth.

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P. Davidovits, Merkert Chemistry Center, Boston College, Chestnut Hill, MA 02467–3809, USA. (paul.davidovits@bc.edu)

J. T. Jayne, C. E. Kolb, and D. R. Worsnop, Aerodyne Research, Inc., Billerica, MA 01821–3976, USA.

M. Kulmala and T. Vesala, Department of Physical Sciences, University of Helsinki, FIN-00014 Helsinki, Finland.

K. E. J. Lehtinen, Department of Applied Physics, University of Kuopio, Kuopio, FIN-70211 Finland.

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

A. Vrtala, P. E. Wagner, and P. Winkler, Institute für Experimental Physik, Universität Wien, A-1090 Vienna, Austria.