Mass and Thermal Accommodation during Gas-Liquid Condensation of Water

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In this Letter we report, for the first time, direct and simultaneous determinations of mass and thermal accommodation coefficients for water vapor condensation in air, based on the observation of droplet growth kinetics in an expansion cloud chamber. Our experiments exclude values below 0.85 for the thermal and below 0.4 for the mass accommodation coefficients at temperatures ranging from 250 to 290 K. Both coefficients are likely to be 1 for all studied conditions. Previously available experimental data on the mass accommodation coefficient for water span about 3 orders of magnitude. Our results provide new and firm insight to cloud microphysics and consequently to the global radiative balance.

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Gas-liquid phase transitions and heterogeneous chemical reactions are important phenomena in cloud microphysics and chemistry as well as in materials science, fluid physics, aerosol physics, atmospheric chemistry, and other areas. The stability of clouds and their ability to produce precipitation are strongly influenced by the number density and size distribution of their constituent water droplets [1]. The activation of aerosol particles (cloud condensation nuclei) and their subsequent growth into cloud droplets are clearly related to the transfer of water vapor molecules into liquid droplets.

Two parameters that fundamentally influence the interaction of vapor molecules with liquid surfaces are the mass accommodation (or condensation) coefficient (α_m), i.e., the probability that a vapor molecule striking a liquid surface enters into the bulk liquid phase, and the thermal accommodation coefficient (α_t), i.e., the fraction of molecular collisions that result in equilibration of the kinetic and vibrational or rotational energies of the impinging gas molecule with the mean energy of the liquid surface molecules. A proper description of formation and growth of cloud droplets requires detailed knowledge of vapor, particularly water vapor transport as well as heat transport in the vicinity of atmospheric aerosol particles and cloud droplets. The mass fluxes and the resulting heat transfers are coupled [2]. For droplet sizes in the continuum regime gas phase diffusion and thermal conductivity are the controlling phenomena for mass and heat fluxes. However, in the kinetic as well as in the transition regime these fluxes are at least partly under gas kinetic control and depend on the mass accommodation and thermal accommodation coefficients, α_m and α_t. Low values of these coefficients would result in limitations of the rate of droplet growth [3–7].

Several attempts to determine the mass accommodation coefficient of water vapor have been performed by various authors, and values between ~0.001 and 1 were reported [8]. Recent computational fluid dynamics (CFD) analyses of the droplet train technique resulted in a range 0.4 to 1 and molecular dynamic (MD) simulations in a value of unity at 273 K [9]. However, although the most important application of thermal as well as mass accommodation coefficients is related to growth or evaporation of water droplets in the atmosphere, these coefficients have so far not been determined simultaneously over a sufficient temperature range. The thermal accommodation coefficient, e.g., has been determined only at room temperature [10].

In the present study we have simultaneously determined thermal and mass accommodation coefficients for water vapor condensation in air at different temperatures and pressures from a quantitative comparison of experimental and theoretical droplet growth curves. Pseudosteady state growth of droplets in practically monodispersed droplet populations is observed at uniform ambient thermodynamical conditions. For the sizes and growth rates of the droplets considered the droplet temperature is practically uniform, and radiative and convective heat transport as well as convective mass transport in the vicinity of the droplets are negligible. Accordingly, a clear and accurate theoretical description is possible using state-of-the-art condensation models [6,11], in which the increase of droplet temperature due to latent heat of the condensing water vapor is accounted for quantitatively.

The mass flux directed away from the droplet is given by [11]

$$I = \beta_m C \frac{4\pi a M D p}{R T_\infty} \ln\left(\frac{1 - X_\infty}{1 - X_a}\right), \qquad (1)$$

where a is the droplet radius, p is the total pressure of the gas, M is the molecular weight of the vapor, D is the binary (between vapor and the inert gas) diffusion coefficient at the temperature T_∞ far from the droplet, R is the gas constant, and X_∞ is the vapor mole fraction far from the droplet. X_a is the mole fraction just above the liquid surface calculated as a ratio of the partial vapor pressure at the surface (determined by the saturation vapor pressure and accounting for the Kelvin effect due to the surface curvature) to the total pressure. C takes into account the temperature dependence of D more rigorously than the commonly used geometric mean. β_m is the transition regime correction for mass transfer [12]

$$\beta_m = \frac{1 + Kn}{1 + (\frac{4}{3\alpha_m} + 0.377)Kn + \frac{4}{3\alpha_m}Kn^2}, \qquad (2)$$

where the Knudsen number Kn is the ratio of the mean effective free path of the vapor molecules, calculated from the vapor diffusivity, to the droplet radius.

The heat flux directed away from the droplet, which for the conditions considered in this study is mainly carried by the molecules of the inert gas (air), is given by [11]

$$E = 2\pi a\beta_t(k_a + k_\infty)(T_a - T_\infty) + H_v I, \qquad (3)$$

where k_a and k_∞ correspond to the thermal conductivities of the inert gas at the droplet temperature (T_a) and the gas temperature far from the droplet, respectively. H_v is the specific enthalpy of vapor, and β_t is the transitional regime correction for heat transfer,

$$\beta_t = \frac{1 + Kn_t}{1 + (\frac{4}{3\alpha_t} + 0.377)Kn_t + \frac{4}{3\alpha_t}Kn_t^2}. \qquad (4)$$

The Knudsen number Kn_t for heat transfer is defined analogously to Kn by replacing the mean free path of vapor by a length scale for heat transfer, which is provided by the mean effective free path of the carrier gas molecules calculated from the heat conductivity of the inert gas [2]. Clearly in this study α_m refers to water vapor molecules, while α_t refers (mainly) to inert air molecules.

The transition regime corrections used in the present study in conjunction with the proper definitions of the Knudsen numbers [12] have been found to provide good approximations for molecular mass ratios ranging from values $\ll 1$ (light vapors) up to values exceeding 10 [13].

The equations for mass and heat fluxes are coupled, and knowledge of the droplet temperature is required in order to calculate the mass flux. For the conditions considered in the present study an analytical expression based on a pseudo-steady-state heat balance results in droplet temperatures very close to the non-steady-state values, allowing one to calculate the mass flux to a single droplet. In numerical calculations of simultaneous condensational growth in a monodispersed droplet population, we accounted for the depletion of vapor as well as the production of latent heat. While the ambient gas temperature generally increases during condensation, the droplet temperature was shown to remain nearly constant during the entire droplet growth process observed.

We studied liquid droplets nucleated on Ag particles and growing due to condensation of supersaturated water vapor using the experimental system shown schematically in Fig. 1. The apparatus includes a source of monodispersed particles and a vapor saturation unit. Vapor supersaturation is achieved by adiabatic expansion in a computer controlled thermostated expansion chamber resulting in well defined uniform thermodynamical conditions in the measuring volume. Growth of droplets is observed using the constant-angle Mie scattering (CAMS) detection method [14] providing absolute, time-resolved, and noninvasive simultaneous determination of droplet diameter and number density. Details of the experimental system are presented elsewhere [6,15].

Particles were generated by evaporation of Ag in a tube furnace at 1333 K and subsequent condensation. Using an electrostatic classifier a nearly monodispersed particle fraction was extracted. This fraction was neutralized in order to avoid the possible effect of surface charges on the outcome of the condensation experiments. The size distribution of the Ag particles obtained was monitored by an electrical mobility spectrometer, a mean particle diameter of 9.0 nm and a geometric standard deviation of 1.06 were found.

Water vapor was subsequently added to the system by evaporation from a thermostated cylindrical liquid film inside the vapor saturation unit. During a computer controlled measurement cycle, the saturated binary vapor-air mixture together with the Ag particles was passed into a thermostated expansion chamber. In order to achieve the desired vapor supersaturation, adiabatic expansion was

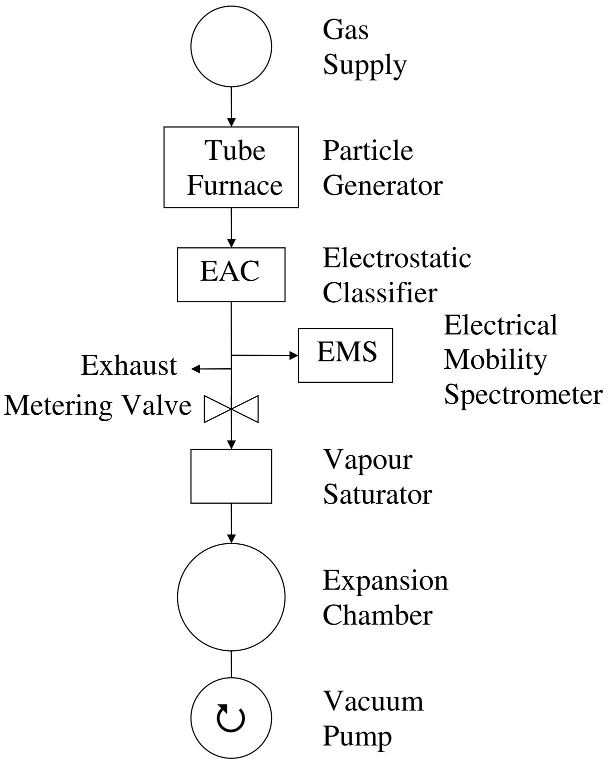

FIG. 1. Experimental setup. See text for additional details.

initiated by opening a valve connecting the expansion chamber to a low pressure buffer tank. The pressure drop inside the expansion chamber was monitored by a fast precision pressure transducer. Expansion times around 5 ms were typically observed. Temperature and vapor phase activity (saturation ratio) at the end of expansion were determined using Poisson's law. The particle generator, the classifier, and the spectrometer are continuously operated at atmospheric pressure; however, appropriate setting of a precision metering valve at the inlet of the vapor saturation unit (see Fig. 1) allows condensation experiments to be performed at initial total gas pressures before expansion ranging from about 1000 hPa down to 100 hPa.

Those Ag particles causing heterogeneous nucleation at the vapor supersaturations considered lead to formation and growth of liquid droplets. Growth rates and number densities of the condensing droplets were measured using the CAMS detection method [14]. As described below, comparison of experimental and theoretical droplet growth curves yields quantitative information on mass accommodation coefficients α_m and thermal accommodation coefficients α_t. We have performed a numerical sensitivity analysis showing that at initial total gas pressures around 1000 hPa the theoretical droplet growth rates are about equally sensitive with respect to changes of α_m and α_t. As seen from Fig. 2, however, at a reduced initial total gas pressure of about 200 hPa growth is found to be far more sensitive with respect to α_t as compared to α_m. This allows the thermal accommodation coefficient α_t to be determined practically independent of α_m. Subsequently, at known α_t a comparison of experimental and theoretical droplet growth curves at an initial total gas pressure around 1000 hPa allows a unique determination of the mass accommodation coefficient α_m.

We have performed experiments covering a range of droplet temperatures from about 252 to 290 K. Water vapor phase activities (saturation ratios) S_0 at the end of expansion were chosen ranging from 1.3 to 1.5 just sufficient to nucleate droplets with number densities between about 3 and 4×10^3 cm^{-3} as required for quantitative light scattering evaluations. In separate experiments we determined the minimum vapor saturation ratio S_{low}, below which no significant heterogeneous nucleation by the Ag particles is observed. A detailed analysis of the pressure as a function of time during the adiabatic expansion accounting for the value of S_{low} allows determination of the time interval Δt at the end of the expansion process, within which the start of droplet growth occurs. Typical experimental droplet growth data are shown in Fig. 2 together with the experimental time interval Δt mentioned above. The error bars refer to the experimental uncertainties of the droplet growth times as obtained by means of the CAMS detection method.

In order to obtain the accommodation coefficients α (α_t or α_m), the experimental droplet growth data corresponding to a vapor saturation ratio S_0 at the end of expansion were compared to theoretical droplet growth curves. In the calculations starting time for droplet growth as well as α were varied in a two parameter fit procedure, and the uncertainties of the CAMS data were accounted for. The fit generally indicates a start of the growth process within the above-mentioned experimental time interval Δt. Accordingly, the *position* of the experimental time interval Δt is found to be consistent with the fit to the droplet growth data and therefore does not influence the fit value of α. On the other hand, by considering theoretical growth curves, which are assumed to pass through the left or right limit of the experimental time interval Δt, lower or upper limits of the accommodation coefficient α were obtained, respectively, in a one parameter fit procedure. Accordingly, the *length* of Δt allows the determination of the maximum error range of α corresponding to uncertainties in the starting time for droplet growth at one fixed value of S_0. The vapor saturation ratio S_0 is determined by the temperatures of the humidifier and the expansion chamber, the initial total gas pressure before expansion, and the total pressure drop during expansion. The uncertainties of these quantities result in an uncertainty in S_0 of 0.01 and 0.03 at initial total gas pressures of 1000 and 200 hPa, respectively. Combination of the maximum error corresponding to uncertainties in the starting time for droplet growth with the error caused by the uncertainty of the saturation ratio S_0 results in the maximum total error of the accommodation coefficient α.

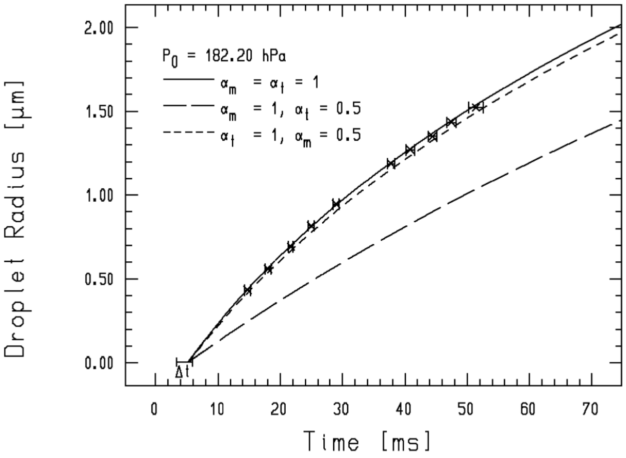

FIG. 2. Droplet radius vs time during condensation of water vapor. Vapor saturation ratio at the end of expansion $S_0 = 1.49$, gas temperature at the end of expansion $T_0 = 282.1$ K, and total gas pressure after expansion $P_0 = 182.20$ hPa. Curves were calculated assuming different values of the accommodation coefficients α_m and α_t. Corresponding experimental data are shown for comparison.

The independently obtained experimental accommodation coefficients α_t (for air) and α_m (for water) are shown as functions of the droplet temperature in Fig. 3. The maximum total errors are indicated. The error ranges for α_m show a tendency to increase with increasing droplet temperature. This is related to a decrease of the sensi-

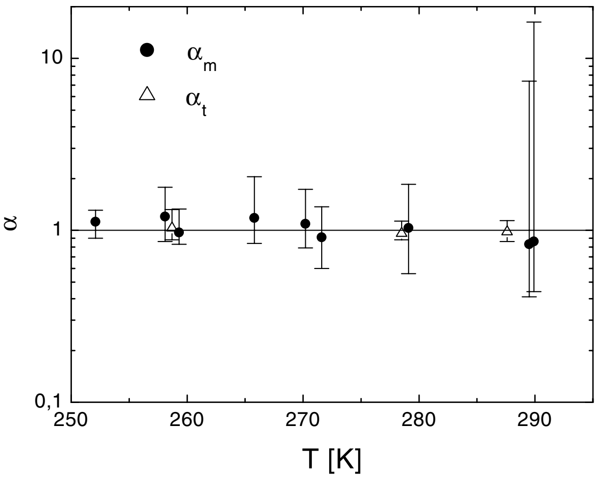

FIG. 3. Mass and thermal accommodation coefficients, α_m and α_t, for condensation of water vapor in air measured as a function of the temperature T of the liquid surface.

tivity of droplet growth rates with respect to α_m with increasing droplet temperature. Particularly the large error ranges at about 290 K are notable. Of course, the actual values of accommodation probabilities cannot exceed unity.

The experimental data presented in this Letter result in definitive lower limits of both mass and thermal accommodation coefficients for condensation of water vapor in air over a considerable temperature range. We can state that values of $\alpha_t < 0.85$ are excluded over the whole temperature range considered. For temperatures from 250 to 270 K values of $\alpha_m < 0.8$ are excluded, and for higher temperatures up to 290 K we can exclude values of $\alpha_m < 0.4$. All our data are consistent with α_m and α_t equal to 1. This result resolves long-standing open questions on these values and is supported by recent CFD and MD simulation results [9]. It is worth noting that the results of this study are obtained from absolute, noninvasive measurements of droplet growth at well defined thermodynamical conditions. Furthermore, a clear and accurate state-of-the-art condensation model allows a direct interpretation of the experimental data. Conditions facilitating a unique determination of accommodation coefficients are fulfilled to a good approximation in this study [5], particularly the thermodynamical conditions at the gas-liquid interface are well defined.

The physical importance of the results is clear: No empirical factors are required to describe heat and mass fluxes to or from a water droplet. Also the atmospheric relevance is evident: Simulations [6,7] on cloud droplet formation and growth assuming the mass accommodation coefficient of water vapor to be below 0.1 show that water vapor saturation in nascent clouds would typically increase so much that a considerably larger fraction of aerosol particles would activate as cloud droplets. This would lead to more stable clouds with a higher number density of smaller droplets, i.e., 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_m above 0.5. The values of the accommodation coefficients presented in this Letter enable accurate predictions of the formation and growth of cloud droplets required in order to correctly parametrize cloud light scattering or absorption and precipitation properties in meteorological and climate models.

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