Experimental determination of the thermal accommodation and condensation coefficients of water
Raymond A. Shaw and Dennis Lamb

Citation: The Journal of Chemical Physics 111, 10659 (1999); doi: 10.1063/1.480419
View online: http://dx.doi.org/10.1063/1.480419
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/111/23?ver=pdfcov
Published by the AIP Publishing

Articles you may be interested in
Measurement of thermal accommodation coefficients using a simplified system in a concentric sphere shells configuration
J. Vac. Sci. Technol. A 32, 061602 (2014); 10.1116/1.4901011

Molecular dynamics studies to understand the mechanism of heat accommodation in homogeneous condensing flow of carbon dioxide

Slow evaporation and condensation on a spherical droplet in the presence of a noncondensable gas
Phys. Fluids 22, 067101 (2010); 10.1063/1.3432130

Evaporation and condensation Knudsen layers for nonunity condensation coefficient
Phys. Fluids 15, 1348 (2003); 10.1063/1.1564097

Molecular dynamics studies of evaporation and condensation coefficients in nucleation theory
Experimental determination of the thermal accommodation and condensation coefficients of water

Raymond A. Shaw
National Center for Atmospheric Research, Boulder, Colorado 80307-3000

Dennis Lamb
Department of Meteorology, Penn State University, University Park, Pennsylvania 16802

(Received 3 June 1999; accepted 20 September 1999)

The condensation coefficient of water vapor on liquid water and the thermal accommodation coefficient of air on liquid water are poorly known despite their importance in many applications, such as cloud physics. We have developed a new technique for determining the condensation and thermal accommodation coefficients experimentally. The technique consists of simultaneously measuring the homogeneous nucleation rate of ice and the evaporation rate of liquid water droplets as a function of pressure (droplet Knudsen number). As the Knudsen number increases, surface kinetic processes limit mass and energy fluxes and, as a result, the equilibrium temperature of an evaporating droplet is a function of the condensation and thermal accommodation coefficients. The homogeneous freezing nucleation rate is used as a sensitive measure of the droplet temperature. The nucleation and evaporation rates are determined by observing the scattered light from evaporating water droplets suspended in an electrodynamic levitation system housed within a controlled environment. The observed rates are consistent with a condensation coefficient between 0.04 and 0.1, with 0.06 being most probable, and a thermal accommodation coefficient between 0.1 and 1, with 0.7 being most probable. © 1999 American Institute of Physics. [S0021-9606(99)00147-6]

I. INTRODUCTION

The processes of condensation and evaporation are inherently linked to the transfer of mass and energy across the liquid–vapor interface. Energy transfer is especially significant for an associating liquid like water that is characterized by a large enthalpy (latent heat) of vaporization. The equilibrium vapor pressure of water is thus strongly dependent on the surface temperature, implying that energy exchange may not be ignored in experimental or computational studies except at relatively low temperatures. Therefore, if energy fluxes to or from the surface are impeded for any reason, mass fluxes will tend to decrease as well. The net flux of water molecules away from an evaporating cloud droplet, for instance, results in cooling of the surface and a decreased vapor flux. As the droplet cools relative to its environment, gradients of temperature establish a net flux of thermal energy into the droplet. The end result is that the combined processes of mass and energy transfer determine the net evaporation rate of the droplet. For a droplet large compared to the mean free path of the surrounding gas, the problem may be treated using continuum theories of heat and mass transfer. For smaller droplets, however, surface processes can limit the transport fluxes.

The kinetics of mass and energy exchange with a liquid surface are characterized by the condensation coefficient and the thermal accommodation coefficient, respectively. The condensation coefficient \( \alpha_c \), the probability that a molecule from the vapor phase impinging on a surface will stick to that surface, is usually assumed to be equal to the evaporation coefficient. The accommodation coefficient is defined by \( \alpha_a = (\epsilon_2 - \epsilon_1) / (\epsilon_s - \epsilon_1) \), where \( \epsilon_1 \) and \( \epsilon_2 \) are the energies of a molecule before and after a collision with a surface, respectively, and \( \epsilon_s \) is the energy of a surface molecule. The accommodation coefficient varies with the particular gas in contact with the surface, whereas the condensation coefficient applies only to the vapor.

The surface properties of water, as described by the condensation and thermal accommodation coefficients, have been the subject of scientific investigation for many decades. At present there is no consensus as to their magnitudes;\(^1\) this is in spite of their importance in many fields of study, including aqueous surface chemistry and the evolution of aerosol and cloud particles in the atmosphere. Considerable attention has been given to studying the condensation coefficient of water molecules on liquid water surfaces, but relatively few studies have concentrated on the accommodation coefficient of water vapor or other gas-phase species on liquid water.

During the last 70 years numerous experimental studies have yielded values of the condensation coefficient of water ranging from 0.01 to 1. Comprehensive reviews of work through the 1970’s and into the mid-1980’s are available in the literature.\(^1\) Since that time, only a few experimental studies of the condensation coefficient of water have been reported.\(^2,3\) The values for the condensation coefficient found in these recent studies also vary from 0.01 to 1, thereby illustrating that large variations are reported even in the recent literature.

Perhaps more surprising than the lack of consensus re-
The diffuse of water vapor to and from the surface of a spherical droplet of a given size depends on the Knudsen number $Kn = \lambda/r$, where $\lambda$ is the mean free path of the surrounding gas and $r$ is the droplet radius. $Kn \ll 1$ corresponds to the continuum-transport regime, $Kn \gg 1$ to the kinetic-transport regime, and $Kn \sim 1$ to what is often referred to as the transition regime. The mass flux as described by continuum theory is, ignoring thermal diffusion and the effect of temperature gradients on number density, 

$$
\Phi_{M,c} = \frac{DM_{w}}{r} (n_r - n_w),
$$

(1)

where $r$ is the droplet radius, $D$ is the diffusion coefficient of water vapor in air, and $M_w$ is the mass of a water molecule. $n_r$ and $n_w$ are the number concentration of water molecules at the surface of the droplet and in the surrounding air, respectively, and are given by $n_r = \rho_r / kT$, where $k$ is the Boltzmann constant and $\rho_r$ and $T$ must be taken as the vapor pressure and temperature, respectively, of the droplet surface or of the surrounding gas. In the kinetic-transport regime, the flux takes the form

$$
\Phi_{M,k} = \frac{\alpha_c m_w}{4} (n_r - n_w),
$$

(2)

where $\alpha_c$ is the condensation coefficient, $m_w$ is the mean molecular mass of the gas molecules, given by $(8kT/\pi M_w)^{1/2}$. The ratio of the continuum flux to the kinetic flux is, therefore,

$$
\varphi_m = \frac{\Phi_{M,c}}{\Phi_{M,k}} = \frac{D}{\alpha_c'} \left( \frac{2 \pi m_w}{kT} \right)^{1/2}.
$$

(3)

As the droplet radius decreases this ratio becomes large, implying that kinetic fluxes at the surface of the droplet become the limiting process. The fundamental importance of the Knudsen number is clarified by recalling that simple gas-kinetic theory predicts $D \propto \lambda c^2$, leaving $\varphi_m \propto Kn$, as expected. Because no analytical theory exists for mass flux in the transition regime, it has been approximated in various ways. Here, we will use the method described by Fukuta and Walter because of its relative simplicity and common utility. The approach was pioneered by Langmuir, and others have advanced similar approximations as well. Because the two fluxes can be matched by multiplying the continuum flux by a factor $(1 + \varphi_m)^{-1}$, when $\varphi_m$ is small (larger droplets, all else being equal), one is left with the continuum flux, whereas when the ratio is large (smaller droplets), one is left with the kinetic flux.

A similar analysis may be applied to the energy flux into or out of the droplet. Here, the equation for the continuum flux is

$$
\Phi_{T,c} = \frac{KT}{r} (T_r - T_\infty),
$$

(4)

where $K$ is the thermal conductivity of the surrounding gas, and $T_r$ and $T_\infty$ are the temperature of the droplet and the surrounding gas, respectively. Equation (4) is thus multiplied by the factor $(1 + \varphi_r)^{-1}$, where

$$
\varphi_r = \frac{\Phi_{T,c}}{\Phi_{T,k}} = \frac{K}{\alpha_r \rho_p} \left( \frac{2 \pi m_w kT}{c_v + 0.5k} \right)
$$

(5)

in which $\Phi_{T,k}$ is the kinetic energy flux, $\alpha_r$ is the thermal accommodation coefficient, $m_w$ is the weighted mean mass per molecule of the surrounding gas, and $c_v$ is the constant volume specific heat per molecule. If multiple types of gases are present, the thermal accommodation coefficient is a measure of the combined effect (weighted mean) of all gases. Both $\varphi_m$ and $\varphi_r$ are inversely proportional to both droplet radius and pressure (the pressure dependence in $\varphi_m$ is a result of the inverse pressure dependence of $D$). Hence, the importance of the kinetic terms may be increased by reducing $r$ or $p$, or both.

The fluxes of mass and energy are coupled by conservation of energy; for an evaporating droplet, energy lost due to the net vaporization is balanced by energy transfer to the droplet by collisions with the surrounding gas. Multiplying both fluxes by droplet surface area and the mass flux by the latent heat of vaporization and equating them results in an expression that can be solved for the droplet temperature:

$$
\varphi_m \Phi_{M,c} = \varphi_r \Phi_{T,c} = \frac{\rho_p c_v}{\rho_w c_w} \Phi_{M,c}.
$$

(6)
The exceedingly strong temperature dependence of the homogeneous nucleation rate \( J \) is generally confirmed by experimental studies of ice nucleation.\(^\text{11,12} \) As a result, the temperature of an evaporating droplet, as given by Eq. (6), may be related to a nucleation rate using laboratory data for \( J(T) \). The relative nucleation rate as a function of various combinations of \( \alpha_c \) and \( \alpha_t \) for an evaporating water droplet is shown by the curves in Fig. 1. The figure confirms the following intuitive picture: for a small thermal accommodation coefficient and a relatively large condensation coefficient, energy transfer from the surrounding gas to the droplet, which is cooling because of evaporation, is inhibited, thereby resulting in a low steady-state droplet temperature and a large nucleation rate. The calculations correspond to \( r = 20 \mu m, T = 238.3 \text{ K}, p = 200 \text{ hPa}, \) and \( p_v = 0 \) (Kn=0.02).

\[
T_r = \frac{L_c Dm_w (1 + \varphi_i)}{K (1 + \varphi_m)} (n_w - n_r) + T_\infty. \tag{6}
\]

Here, \( n_r \) and \( T_r \) are unknown but are related by \( n_r = p_r(T_r)/kT_r \), where \( p_r(T) \) is the saturation vapor pressure, obtained by integrating the Clausius–Clapeyron equation. In the kinetic limit the droplet temperature has the form

\[
T_r = \frac{\alpha_c L_m \Gamma_{m/2} \Gamma_{a/2} (n_w - n_r)}{\alpha_t (c + 0.5k)} n_w + T_\infty, \tag{7}
\]

so for \( \alpha_t < \alpha_c \), \( |T_r - T_\infty| \) becomes very large. This implies that for droplets evaporating or growing in the transition regime, where surface effects begin to be noticeable, a measurement of droplet temperature can provide information about the relative magnitudes of \( \alpha_c \) and \( \alpha_t \). The influence of the condensation and thermal accommodation coefficients on droplet temperature has been explored theoretically by other researchers,\(^\text{10} \) but there appears to be no experimental investigation reported in the literature.

### III. EXPERIMENT: TECHNIQUE AND RESULTS

The experiment consists of measuring the evaporation rate and liquid–solid homogeneous nucleation rate of water droplets using light scattering techniques. Droplet growth and evaporation rate measurements have been the basis for much of the previous work on \( \alpha_t \) and \( \alpha_c \) for liquid water. As pointed out earlier, however, these measurements alone are often ambiguous regarding the exact values of \( \alpha_t \) and \( \alpha_c \). When combined with nucleation measurements this ambiguity is significantly reduced, thereby making assumptions about the thermal accommodation coefficient unnecessary.

#### A. Droplet temperature and ice nucleation rate

The nucleation technique presented here is based on two factors: (i) For droplets evaporating in the transition regime the droplet temperature will be lower than the ambient temperature and this temperature difference depends on the relative magnitudes of \( \alpha_c \) and \( \alpha_t \); (ii) The homogeneous nucleation rate of ice in liquid water is a sensitive function of the temperature of the liquid. In effect, the homogeneous nucleation rate is used as a sensitive measure of droplet temperature, thereby providing information about the magnitudes of the thermal accommodation and condensation coefficients of water.

The temperature and nucleation rates are related through an exponential curve fit to the data compiled in Table I of Pruppacher.\(^\text{11} \) The most striking feature in Fig. 1 is the enormous range of variation of nucleation rate, especially for small values of the thermal accommodation coefficient. If the homogeneous nucleation rate of evaporating droplets can be measured with sufficient precision for varying droplet Knudsen numbers, the accommodation and condensation coefficients can be determined.

#### B. Nucleation measurements

We have measured the homogeneous freezing rate of evaporating water droplets as a function of pressure in order to gain information about the thermal accommodation coefficient of air on liquid water and the condensation coefficient of water vapor on liquid water. The experiment consisted of injecting individual water droplets into a known, subsaturated environment and observing the droplet size and the time for a droplet to freeze. By comparing measurements and theory we are able to determine the homogeneous freezing rate for the specific temperature and pressure corresponding to the experiment. The nucleation process is stochastic in nature and therefore one must consider the cumulative probability of freezing, \( P(t) \), which is found by integrating the product of the homogeneous nucleation rate and the droplet volume \( V \),

\[
\ln(1 - P) = - \int_0^t J V dt'.
\]

For a droplet with constant volume and temperature, the cumulative probability has the simple form \( P = 1 - \exp(-J V t) \). Thus, if the droplet volume and the time...
elapsed before freezing are known, $J$ can be estimated. Previous experiments using this laboratory technique have confirmed the ability to observe homogeneous (as opposed to heterogeneous) nucleation of ice in liquid water and to relate the measurements to a nucleation rate.\textsuperscript{13}

The data presented here were collected with a laboratory system specifically designed for studying individual cloud particles under upper-tropospheric conditions.\textsuperscript{14} The system consists of an electrodynamic levitation cell (quadrupole trap) for suspending individual particles, housed within an environmental control chamber where variables such as temperature, pressure, and relative humidity are controlled and monitored. Data on the size and phase of trapped particles are obtained from light-scattering measurements. For example, the radius of a liquid droplet is obtained by comparing measured scattered light with Mie theory.\textsuperscript{15} The transition of a liquid droplet to the solid phase is easily identified by an abrupt change from regular interference fringes to a distorted, irregular pattern. The two key variables measured are the droplet radius as a function of time and the elapsed time before a freezing event occurs.

Information about the thermal accommodation coefficient and the condensation coefficient is obtained by observing the variation of homogeneous nucleation rate with droplet Knudsen number. This allows for a relative measurement of nucleation rate in the continuum evaporation regime (where theory is well established) and nucleation rate in the transition regime (where surface kinetics are significant). The Knudsen number can be varied by changing the droplet radius or the ambient pressure [also see Eqs. (3) and (5)]. With the levitation system used for this study it is relatively simple to vary the pressure by about an order-of-magnitude, so pressure was chosen for varying Kn. To allow the experiments to be conducted without changing the pressure, a low-pressure droplet injector and a feedback-controlled pressure control system were designed. In the experiments reported here, the minimum pressure was 200 hPa, being limited primarily by the onset of electrical breakdown in the vicinity of the high voltage electrodes in the electrodynamic levitation cell. For the droplet sizes suspended in the trap ($r \sim 20 \text{ \mu m}$) and a pressure range of 200–1000 hPa, the corresponding Knudsen number range is roughly 0.02–0.004, implying that the droplets are just entering the transition regime at the lowest pressure.

The resulting data are displayed in Fig. 1, along with theoretical curves calculated from Eq. (6). Data were obtained at pressures of 1000, 400, and 200 hPa, the surrounding atmosphere consisting of dry air (frost point less than $-65^\circ \text{C}$, or $p_v/p_s<0.02$) at $T = -34.9 \pm 0.2^\circ \text{C}$. The error bars associated with the measured nucleation rates are large due to the limited number of data points obtained. The range of $\alpha_c$ and $\alpha_r$ that are consistent with the data are shown in Fig. 2 in the shaded region on the left. This shaded area corresponds to the full range of plausible nucleation rates based on their error bars, and the black curve in the middle of the shaded area corresponds to the most probable value of $J$. The measurements of nucleation rate alone, while not constraining the accommodation coefficient much, suggest that the condensation coefficient of water is less than 0.1.

The overlap of possible values of $\alpha_c$ and $\alpha_r$ from the nucleation and evaporation measurements is indicated by dark shading in Fig. 2. The advantages of combining the two data sets are clear in that the total range of possible combinations of $\alpha_c$ and $\alpha_r$ is greatly reduced. More importantly, the combination of evaporation data with homogeneous nucleation data eliminates the ambiguity pointed out in the preceding paragraph, suggesting that droplet mass fluxes are limited primarily by a small condensation coefficient.

\section*{IV. CONCLUSIONS}

This new technique for experimentally determining the thermal accommodation and condensation coefficients of liq-
uid water, which consists of simultaneously measuring the homogeneous nucleation rate of ice and the evaporation rate of liquid water droplets over a range of pressures, provides a value for $\alpha_c$ that is not based on assumptions about the value of $\alpha_i$. The underlying physics of the nucleation technique is essentially that the temperature of an evaporating droplet is a function of the thermal accommodation and condensation coefficients of water and that the homogeneous nucleation rate is extremely sensitive to the droplet temperature. This combination of techniques has lead to what appears to be the first experimental determination of the thermal accommodation coefficient of air on liquid water.

The most probable magnitudes of the condensation and thermal accommodation coefficients as determined by the measured nucleation and evaporation rates are $\alpha_c = 0.06$ and $\alpha_i = 0.7$. These values are determined by the intersection of the two curves in Fig. 2. The possible ranges of values consistent with the uncertainties in the data are $0.04 < \alpha_c < 0.1$ and $0.1 < \alpha_i < 1$.

ACKNOWLEDGMENTS

We thank W. A. Cooper, W. Hall, and D. Hanson for helpful comments and R. Ziegler for his assistance in making the measurements. This research was supported in various parts by the NCAR Advanced Study Program, NASA/JPL (Contract No. 960019), and NSF (Grant No. ATM-9528255). The National Center for Atmospheric Research is sponsored by the National Science Foundation.

15. C. F. Bohren and D. R. Huffman, Absorption and Scattering of Light by Small Particles (Wiley, New York, 1983), Chap. 4.