Condensation and Evaporation of H₂O on Ice Surfaces

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The condensation and evaporation coefficients for H₂O on ice surfaces were measured using optical interference techniques. The condensation coefficient, α, was determined at ice surface temperatures from 20 to 185 K. For H₂O vapor at 300 K, the condensation coefficient decreased as a function of surface temperature from α = 1.06 ± 0.10 at 20 K to α = 0.65 ± 0.08 at 185 K. The temperature dependence of the condensation coefficient could be fit by a precursor-mediated adsorption model. The evaporation coefficient, γ, was obtained at various surface temperatures using isothermal desorption measurements. The evaporation coefficient was observed to be constant at γ = 0.63 ± 0.15 for ice surface temperatures from 173 to 205 K. Over the temperature range where the condensation and evaporation coefficients could both be measured, α and γ were equivalent within the experimental error limits. This equivalence indicates that evaporation or condensation rates are dictated only by temperature and pressure and can be treated individually during net condensation, net evaporation, or steady-state desorption kinetics expected for multilayer desorption. The activation barrier for desorption was E₉ = 11.9 ± 0.2 kcal/mol with a preexponential of ν₀ = 2.8 × 10^10 ± 1.0 × 10^8 molecules/(cm² s). Quasi-equilibrium experiments also determined an enthalpy of sublimation for H₂O from ice of ΔHᵣₛₘ = 11.8 ± 0.2 kcal/mol and an entropy of sublimation of ΔSᵣₛₘ = 31.0 cal/(K mol). The equivalency of the kinetic desorption barrier and the quasi-equilibrium enthalpy of sublimation indicates that there is no barrier for H₂O adsorption on ice surfaces. The measured condensation and evaporation coefficients predict the presence of polar stratospheric clouds over the Antarctic pole at 10–20 km. These measurements also reveal that ice surfaces in the polar stratosphere are very dynamic with H₂O condensation and evaporation rates of 10–1000 ML/s (1 ML = 9.8 × 10^14 molecules/cm²) for equilibrium conditions between 180 and 210 K.

I. Introduction

The condensation and evaporation of H₂O vapor on both liquid water and solid ice has been studied for many years.1–9 Interest in this topic is motivated by its significance in understanding how processes such as cloud formation and growth occur in the atmosphere.7–9,14 A detailed knowledge of the condensation and evaporation coefficients for H₂O on ice has increased in importance since recent atmospheric studies have revealed the role of heterogeneous chemistry on ice particles.10 In particular, the ozone hole over Antarctica in the spring is intimately linked to the presence of ice particles known as polar stratospheric clouds.5–12 Modeling of heterogeneous chemistry in the stratosphere is dependent on accurate condensation and evaporation coefficients. Unfortunately, experimentally derived values of the condensation coefficient extend from approximately α = 0.013,14,15 to α = 1.0,13,19–22 This considerable range of values can be attributed to the numerous techniques, experimental parameters, and theoretical assumptions that have been employed by the various studies. The temperature of the H₂O vapor and surface may also be very important, although no studies have established the dependence of the condensation coefficient on these parameters.

The condensation coefficient, α, and the evaporation coefficient, γ, are defined as

\[ \alpha = \frac{C_{\text{exp}}}{C_{\text{max}}} \tag{1} \]

\[ \gamma = \frac{E_{\text{exp}}}{E_{\text{max}}} \tag{2} \]

In these expressions, C_{\text{exp}} and E_{\text{exp}} are the experimental rates of condensation and evaporation, respectively. Likewise, C_{\text{max}} = P (2 \pi m k Tₗ)⁻¹/₂ and E_{\text{max}} = P (2 \pi m k Tₗ)⁻¹/₂ are the maximum theoretical rates of condensation and evaporation. P is the vapor pressure at temperature Tₗ, P is the vapor pressure that would be present for a system at equilibrium at a surface temperature

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TABLE I: Known Evaporation Coefficient Measurements versus Temperature Using Evaporation and Heat Transfer Techniques

<table>
<thead>
<tr>
<th>Method</th>
<th>Temp range, K</th>
<th>Ref</th>
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</thead>
<tbody>
<tr>
<td>droplet evaporation</td>
<td>265-333</td>
<td>1, 18, 23, 24</td>
</tr>
<tr>
<td>liquid evaporation</td>
<td>273</td>
<td>28</td>
</tr>
<tr>
<td>droplet evaporation</td>
<td>293</td>
<td>30</td>
</tr>
<tr>
<td>ice evaporation</td>
<td>188-213</td>
<td>2</td>
</tr>
<tr>
<td>droplet evaporation</td>
<td>260-316</td>
<td>29</td>
</tr>
<tr>
<td>droplet evaporation</td>
<td>293-301</td>
<td>30</td>
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<tr>
<td>droplet evaporation</td>
<td>301-310</td>
<td>25</td>
</tr>
<tr>
<td>liquid evaporation</td>
<td>280</td>
<td>26</td>
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<tr>
<td>liquid evaporation</td>
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<td>heat transfer</td>
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<td>21</td>
</tr>
<tr>
<td>heat transfer</td>
<td>323</td>
<td>34</td>
</tr>
</tbody>
</table>

Optical interference techniques have also been employed recently to measure rates of chemical vapor deposition, laser-induced epitaxial crystallization, bulk lattice temperature during laser annealing, and molecular adlayer thicknesses.

TABLE II: Known Condensation Coefficient Measurements versus Temperature Using Direct Condensation Techniques

<table>
<thead>
<tr>
<th>Method</th>
<th>Temp range, K</th>
<th>Ref</th>
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</thead>
<tbody>
<tr>
<td>gravimetric</td>
<td>213-233</td>
<td>3</td>
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<tr>
<td>gravimetric</td>
<td>133-158</td>
<td>5</td>
</tr>
<tr>
<td>liquid crystall radial growth</td>
<td>193-223</td>
<td>11</td>
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<td>liquid crystall radial growth</td>
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<tr>
<td>droplet radial growth</td>
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<tr>
<td>droplet radial growth</td>
<td>185-213</td>
<td>7</td>
</tr>
<tr>
<td>vapor loss</td>
<td>293</td>
<td>22</td>
</tr>
<tr>
<td>gravimetric</td>
<td>138-152</td>
<td>36</td>
</tr>
<tr>
<td>vapor loss</td>
<td>280</td>
<td>8</td>
</tr>
<tr>
<td>liquid film growth</td>
<td>293</td>
<td>37</td>
</tr>
<tr>
<td>vapor flow loss</td>
<td>200</td>
<td>9</td>
</tr>
<tr>
<td>IR absorption</td>
<td>150</td>
<td>38</td>
</tr>
</tbody>
</table>

$T_m$ is the mass of the molecule, and $k$ is Boltzmann's constant. Early examinations of liquid water and solid ice surfaces focused on the evaporation of $H_2O$ molecules and assumed that the condensation coefficient was equivalent to the evaporation coefficient. However, this assumption of equality between condensation and evaporation coefficients has often been questioned. A summary of the known evaporation experiments, results, and temperature ranges is presented in Table I.

A number of investigators have also measured the interfacial heat transfer resistance of condensing $H_2O$ vapor at a liquid water surface. All of these experiments have been performed at surface temperatures where $H_2O$ evaporation could not be neglected. Consequently, determination of the condensation coefficients again required the assumption that condensation and evaporation coefficients were equivalent. The results of the various heat transfer measurements and their corresponding temperature ranges are given in Table I.

Techniques were developed more recently to measure condensation coefficients directly. Unfortunately, values for $\alpha$ from these direct measurements vary from $\alpha = 0.026$ to $\alpha = 1.0$. A number of studies have utilized gravimetric methods to determine growth rates at an ice surface under a known $H_2O$ vapor. Additional experiments have measured photographically the growth rates of ice crystals and water droplets. Other techniques based on vapor pressure variation in a closed system, a fast flow reactor, optical interference, and Fourier transform infrared absorption spectroscopy have also been implemented to measure $\alpha$. The known investigations that have attempted to measure the $H_2O$ condensation coefficient are listed in Table II.

In this paper, the condensation and evaporation coefficients of $H_2O$ will be both measured accurately and independently with the use of an optical interference technique. In this optical interference method, reflected laser light produces interference fringes as the adlayer thickness changes on an optically flat substrate. Holmberg and Dowell originally established this method for the measurement of thin crystalline sample thicknesses. Groner et al. later suggested this technique for the measurement of sticking coefficients, as well as for determining the growth of transparent matrix materials used in matrix isolation spectroscopy. The typical condensation experiment involved raising the $Al_2O_3$ crystal to a specified temperature. A Uniphase He-Ne laser beam with a wavelength of $\lambda = 6328 \text{ Å}$ and an output power of 8 mW was incident on the $Al_2O_3(1120)$ surface at an angle of 22.5° off

II. Experimental Section

A schematic diagram of the UHV chamber and experimental setup for this study has been shown elsewhere. The UHV chamber was pumped by a 190 L/s Balzers turbomolecular pump, which was backed by another Balzers 50 L/s turbomolecular pump. After a bakeout, this tandem turbomolecular pump system yielded a base pressure of $5 \times 10^{-10}$ Torr as measured by a Bayard-Alpert ion gauge. Additionally, the chamber was equipped with a UTI quadrupole mass spectrometer with a 1–300 amu mass range and 300 A/Torr sensitivity. The mass spectrometer was used for background gas analysis and temperature-programmed desorption.

Single crystals of $Al_2O_3(1120)$ were purchased from Saphikon. The $Al_2O_3$ crystal was mounted on a cold finger that was at the end of a double-vacuum-jacketed Dewar capable of holding liquid helium or liquid nitrogen. The $Al_2O_3(1120)$ surface was cleaned by heating to approximately 400 K with simultaneous exposure to an oxygen plasma discharge lasting at least 45 s. This plasma process has been shown to produce clean $Al_2O_3$ surfaces. A schematic diagram of the $Al_2O_3(1120)$ sample mounting technique has been previously shown.

A film of tantalum with a thickness of 6000 Å was evaporated onto the back side of the $Al_2O_3(1120)$ sample. A clear window with a diameter of 0.25 in. remained at the center of the crystal. This arrangement allowed the crystal to be resistively heated by passing current through the tantalum film. Accurate crystal temperature measurement could be achieved with a chromel alumel thermocouple that was attached directly to the crystal with Ceramabond 569 high-temperature adhesive. The temperature was maintained by a temperature controller that could maintain temperatures to within ±0.5 K. Using liquid helium cooling, a temperature range from 20 to 700 K was obtainable.

Distilled and deionized water was obtained and placed in a cold finger attached to a gas handling line. Further purification of the water was implemented with several freeze–pump–thaw cycles. Specific backfill pressures of water vapor varying from $1.0 \times 10^{-4}$ to $1.0 \times 10^{-3}$ Torr could be introduced into the UHV chamber by employing a variable leak valve. The water vapor pressure was measured by the Bayard-Alpert ion gauge. Because ion gauge pressure readings are known to drift with time and their absolute sensitivities may be in error by as much as ±50%, the ion gauge pressure was calibrated with an absolute MKS Barytron at pressures between $1.0 \times 10^{-3}$ and $1.0 \times 10^{-2}$ Torr. This calibration was linear and was subsequently extrapolated to calibrate the lower $H_2O$ pressures employed in this investigation.

The typical condensation experiment involved raising the $Al_2O_3$ crystal to a specified temperature. A Uniphase He-Ne laser beam with a wavelength of $\lambda = 6328 \text{ Å}$ and an output power of 8 mW was incident on the $Al_2O_3(1120)$ surface at an angle of 22.5° off
temperature changed, the gas temperature remained constant at
signals all begin at their first minimum. Because of the favorable
A1203,
and the reflected interference signal was held at a constant value.
desorbed and the ice multilayer decreased in thickness, the re-
conditions, the condensation and desorption rates were equivalent
deposition because only one reflection originates at the vacu-
coefficients and the kinetic parameters for H2O desorption from
ice surface temperatures during condensation. The interference
signal was monitored
from the vacuum/H2O and
the interference technique
the surface normal. The laser beam was reflected from both the
ice/vacuum interface and the ice/crystal interface as shown in
Figure 1. These two reflections combined to form an interference
signal. As the H2O vapor deposited on the surface, the interference
signal sinusoidally oscillated as the H2O adlayer grew on the
Al2O3(1120) surface.

The interference signal was attenuated with a Schott
neutral density filter, measured by an EG & G FOD-100 photo-
diode, and digitized with a Stanford Research Systems Model 245
digitizer. The interference signal was at a maximum before H2O
deposition because only one reflection originates at the vacuum/
Al2O3(1120) interface. To study the condensation of H2O on
ice surfaces, the initial portion of the interference signal was
ignored until the first minimum was attained. This first minimum
 corresponds to an H2O multilayer with a thickness of approxi-
 mately 1250 Å.

Isothermal experiments were used to determine the evaporation
coefficients and the kinetic parameters for H2O desorption from
ice surfaces. In these studies, the substrate temperature was raised
to a constant desorption temperature and the reflected interfer-
ence signal was monitored as a function of time. As the H2O
molecules desorbed and the ice multilayer decreased in thickness, the
reflection signal displayed a sinusoidally oscillating interference
signal that was similar to the signals observed during condensation.

Quasi-equilibrium experiments were also performed by raising
the Al2O3 substrate temperature and H2O pressure simultaneously
to maintain a constant H2O multilayer thickness. Under these
conditions, the condensation and desorption rates were equivalent
and the reflected interference signal was held at a constant value.
These are quasi-equilibrium conditions because as the substrate
temperature changed, the gas temperature remained constant at
Tg = 300 K.

III. Results

Figure 2 displays the interference signals versus time for three
ice surface temperatures during condensation. The interference
signals all begin at their first minimum. Because of the favorable
change in the refractive index between vacuum, H2O-ice, and
Al2O3, the modulation depth was typically 90–95% of the peak of
the reflected signal intensity. The traces were obtained by
monitoring the He–Ne reflection from the vacuum/H2O and
H2O/Al2O3(1120) interfaces during H2O adsorption. These
experiments were performed at 5 K increments for surface tem-
peratures from 20 to 185 K. The background H2O pressures were
P0 = 3.3 × 10^{-6} Torr for surface temperature between 20 and 165
K. In order to overcome H2O desorption rates, the H2O pressures
were increased to P0 = 8.2 × 10^{-6} Torr at 170 K and to P0 = 6.6
× 10^{-5} Torr at 185 K. The faster oscillation frequency at lower
surface temperatures displayed in Figure 2 indicates a more rapid
H2O multilayer growth rate and a higher condensation coefficient.

Figure 3 shows the interference signals during the isothermal
desorption of H2O from ice multilayers at three surface
 temperatures. For these results, an H2O multilayer was initially
adsorbed on the Al2O3(1120) surface. The temperature was then
increased and the reflection was monitored when the sample
reached the desired desorption temperature. These isothermal
desorption experiments were performed at 2 K increments for
surface temperatures from 173 to 203 K. The faster oscillation
frequency at higher temperatures indicates a higher rate of H2O
desorption.

Figure 4 displays the steady-state relationship between the
surface temperature and the corresponding H2O vapor pressure
required to keep the H2O multilayer thickness at a constant
coverage, i.e., an isosteric experiment. This quasi-equilibrium data
were obtained by adjusting the substrate temperature synchron-
ously with the background H2O vapor pressure. Steady state
was achieved when the reflected interference signal maintained
a constant value.

IV. Discussion

A. Condensation Coefficient. The optical interference technique
provides a convenient method to measure the H2O multilayer
thickness. Simple geometry yields the thickness of the H2O
multilayer corresponding to adjacent minima of the interference
signal:

\[ x = \lambda / 2n(T) \cos \phi \]  

In this expression, \( x \) is the H2O multilayer thickness required for
one full period of the interference signal and \( \lambda = 6328 \, \text{Å} \) is the
wavelength of the HeNe laser beam. Likewise, \( n(T) \) is the tem-
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Condesnation and Evaporation of H\textsubscript{2}O on ice as a function of ice surface temperature.

As shown in Figure 1, \( \theta \) is the laser angle of incidence relative to the Al\textsubscript{2}O\textsubscript{3} surface normal. This angle is determined according to Snell’s Law, \( \sin \theta = n_i(T) \sin \phi \), where \( \theta = 22.5^\circ \) is the angle of incidence relative to the ice surface. The temperature-dependent refraction index for ice increases from \( n_i = 1.32 \) at 20 K to \( n_i = 1.31 \) at 185 K. \(^{21}\) With these \( n_i(T) \) values, \( \phi \) changed from 16.9\(^\circ\) to 16.7\(^\circ\) and \( \varphi \) varied from 2505 to 2521 Å.

The multilayer growth rate of the H\textsubscript{2}O film is

\[ \frac{dx}{dt} = \alpha P_r / \rho(T)(2\pi mkT_y)^{1/2} \]

where \( \alpha \) is the condensation coefficient. As defined in eq 1, the condensation coefficient is the probability that an H\textsubscript{2}O molecule colliding with the ice surface will be incorporated into the bulk. In addition, \( P_r \) is the H\textsubscript{2}O vapor pressure, \( \rho(T) \) is the temperature-dependent density of crystalline ice \( n(T) \) and \( T_y \) is the impinging gas temperature. The temperature-dependent density of crystalline ice decreases from \( \rho = 0.937 \) g/cm\textsuperscript{3} at 20 K to \( \rho = 0.928 \) g/cm\textsuperscript{3} at 185 K. \(^{21}\)

The multilayer growth rate, \( dx/dt \), may be obtained from the interference signal versus time by employing eq 3. Subsequently, this multilayer growth rate can be equated with eq 4 and used to determine the condensation coefficient. At temperatures above 160 K, where desorption can be competitive with condensation, values for \( \alpha \) were determined by using a modification of eq 4 that accounts for a finite evaporation rate:

\[ \frac{dx}{dt} = \alpha P_r / \rho(T)(2\pi mkT_y)^{1/2} - v_\theta / \rho(T) e^{-E_d/RT_y} \]

In this relationship, \( v_\theta \) is the zero-order desorption preexponential, \( E_d \) is the desorption activation energy, and \( T_y \) is the ice surface temperature.

The condensation coefficients obtained from temperature-dependent interference experiments such as those shown in Figure 2 are displayed in Figure 5. The condensation coefficient decreased linearly as a function of ice surface temperature from \( k_\alpha - 1 \) at 20 K to \( k_\alpha = 0.65 \pm 0.08 \) at 185 K. The error bars represent a propagation-of-errors analysis using the uncertainties in the measurements that are given below.

Condensation coefficients of \( \alpha > 1 \) are not physically possible. We believe that \( \alpha = 1 \) at 20 K and attribute our slightly larger \( \alpha \) values to a number of possible experimental errors. These experimental errors and their approximate uncertainties are as follows: time base during interference measurements (±1%); visual fit of sinusoidal interference signals limited by analog/digital resolution (±2–3%); absolute Barytron pressure magnitude (±0.1%); calibration of the ionization gauge using the absolute Barytron and subsequent extrapolation to lower pressures (±2%); and the angle of incidence of the laser (±2%).

The measured condensation coefficients correspond well with some values given in Table II determined from direct condensation studies. However, other \( \alpha \) values are significantly below the values obtained in this study. These lower condensation values may be attributed to competitive evaporation, because these measurements were typically performed at temperatures above 170 K, where ice multilayer desorption rates are appreciable.

Our condensation measurements were dependent on the assumption that the temperature-dependent H\textsubscript{2}O multilayer density is equal to the density of crystalline ice \( I \). However, ice has several structures that are dependent on the adsorption temperature. Vitreous ice forms below 113 K, ice \( I \) forms above 113 K and below 133–153 K, and ice I forms above 133–153 K and below 143–203 K. \(^{21}\) The H\textsubscript{2}O multilayer density is probably somewhere between the density of crystalline ice I and supercooled water. Supercooled water densities have been measured down only to 239 K. \(^{3,9,54}\) The density for supercooled water decreases with decreasing temperature and the value at 239 K is \( \rho = 0.978 \) g/cm\textsuperscript{3}. In contrast, the density of crystalline ice I increases with decreasing temperature and is \( \rho = 0.922 \) g/cm\textsuperscript{3} at 239 K. \(^{52}\) Consequently, the densities of crystalline ice I and supercooled water are converging at temperatures less than 239 K and their differences are estimated to be ±6%.

Condensation coefficients that decrease with increasing temperature have been observed for reactive sticking on single-crystal surfaces. \(^{5,56}\) A decrease in the condensation rate with increasing surface temperature is consistent with a precursor-mediated desorption mechanism. \(^{57–59}\) In a precursor mechanism, initial adsorption occurs when an incident molecule is trapped on the surface in a weakly physisorbed state determined by van der Waals dispersion interactions. The incident physisorbed molecule can then either desorb back into the gas phase or incorporate itself into the surface.

The precursor-mediated adsorption model for the condensation of water vapor at an ice surface can be represented by the following equation:

\[ H_2O(g) \xrightarrow{k_d} H_2O(ad) \xrightarrow{k_a} H_2O(s) \]

In these equations, \( H_2O(g) \) is the gas-phase water molecule, \( H_2O(ad) \) is the precursor adsorbed species, and \( H_2O(s) \) represents the H\textsubscript{2}O molecule that has been incorporated into the ice surface. \( k_d \) and \( k_a \) are the adsorption and desorption rate constants. \( k_d \) and \( k_a \) are the rate constants for the reaction of the H\textsubscript{2}O precursor into and out of the ice surface.

The overall rate of adsorption into the precursor state can be defined by the equation \( k_d[H_2O(g)] = \phi \). In this equation, \( \phi \) is the trapping coefficient, which represents the probability that an H\textsubscript{2}O molecule colliding with the ice surface will be trapped into the physisorbed precursor state. Likewise, \( \phi \) represents the H\textsubscript{2}O collision rate at the ice surface. After introducing the steady-state approximation, \( d[H_2O(ad)]/dt \) is zero, the condensation coefficient can be defined according to the equation

\[ \alpha = \frac{\sigma}{1 + (k_d/k_a) \exp[-(E_d - E_a)/RT]} \]

where \( k_d \) and \( k_a \) are represented in Arrhenius form where \( k_d = k_0d \exp[-E_d/RT] \) and \( k_a = k_0a \exp[-E_a/RT] \). Equation 7 indicates that the condensation coefficient is dependent upon the kinetics of the two competing mechanisms which deplete the precursor state. Equation 7 can be used to fit the experimental condensation coefficient. Figure 6 displays the best fit to the experimental data that was obtained with \( \sigma = 1.06, k_0d/k_0a = 1.0, \) and \( E_d - E_a = 0.23 \) kcal/mol. The uncertainty in these values was \( k_0d/k_0a = 1.0 \pm 0.1 \) and \( E_d - E_a = 0.23 \pm 0.03 \) kcal/mol. These best-fit parameters suggest that the kinetics for desorption and reaction from the physisorbed precursor state of H\textsubscript{2}O on ice are nearly equivalent to one another. The equivalence of the preexponential factors also indicates that the transition states for desorption and reaction are similar. Assuming that reaction represents the diffusion of H\textsubscript{2}O on the ice surface, this equality suggests that the similar transition states for desorption and diffusion may be a two-dimensional gas.

The existence of an H\textsubscript{2}O precursor may also be consistent with the suggestion by Faraday\(^{60}\) that a "liquidlike" layer exists on ice surfaces. Although the presence of such a liquidlike layer on ice...
coefficients versus temperature are displayed in Figure 7.

Vapor pressures were determined directly by the steady-state technique for the parallel velocity component. At elevated surface temperatures, the adsorption kinetic model also provides a physical picture that illustrates the effect of surface temperature. Under the appropriate conditions, less momentum transfer and a lower sticking coefficient are predicted at higher surface temperatures.

Recent theoretical modeling for Ar on Pt(111) also provides a picture that illustrates the effect of surface temperature. The calculations show rapid equilibration for the normal component of argon's velocity on Pt(111) and much slower equilibration for the parallel velocity component. At elevated surface temperatures, the Ar residence time is decreased and desorption occurs before the parallel component can equilibrate with the surface. Consequently, there is decreased adsorption at higher surface temperatures in agreement with the precursor-mediated adsorption kinetic model.

**B. Evaporation Coefficient.** Equation 2 defines the evaporation coefficient, \( \gamma \), as the experimental rate of evaporation, \( E_{\text{exp}} \), divided by the maximum theoretical rate of evaporation, \( E_{\text{max}} \). The vapor pressure, \( P_v \), must be defined to obtain the maximum theoretical rates of evaporation versus temperature. The standard procedure is to assume that \( P_v \) is equivalent to the equilibrium vapor pressure of ice at the given surface temperature, \( T_s \). These equilibrium vapor pressures were determined directly by the steady-state experimental results for the surface temperature and vapor pressure displayed in Figure 4.

The experimental rates of evaporation, \( dx/dt \), versus temperature were obtained from temperature-dependent interference measurements such as those shown in Figure 3. In the case of evaporation

\[
\frac{dx}{dt} = -\gamma P_v / \left[ \rho(T)(2\pi mkT)^{1/2} \right]
\]

where \( \gamma \) denotes the evaporation coefficient and all other symbols have been defined previously. Equation 7 can be rearranged to solve for \( \gamma \) in terms of \( dx/dt, P_v, \rho(T), \) and \( T \). The evaporation coefficients versus temperature are displayed in Figure 7.

The evaporation coefficients were essentially constant over the measured temperature range with an average value of \( \gamma = 0.63 \pm 0.15 \). There is a large disparity between this value and the majority of the evaporation coefficients shown in Table I, which are an order of magnitude lower. However, most of the evaporation studies displayed in Table I represent evaporation from liquid water. The single measurement of the evaporation coefficient for ice was from a very early previous investigation that obtained a slightly larger value of \( \gamma = 0.94 \pm 0.06 \) between 188 and 213 K.

**C. Comparison of Condensation and Evaporation Coefficients.** This investigation is the first study in which condensation and evaporation coefficients of H2O on ice surfaces have been measured by the same technique. Figure 8 displays the comparison between the condensation coefficients from Figure 5 and the evaporation coefficients from Figure 7. Figure 8 reveals that the previously assumed equivalency between condensation and evaporation coefficients is correct within the error limits of these experiments. One previous study has obtained both evaporation and condensation coefficients of H2O on liquid water surfaces. This earlier study determined that the evaporation and condensation coefficients of H2O on liquid water surfaces are nearly equivalent and \( \alpha \approx \gamma \approx 1.0 \).

The equivalence of the condensation and evaporation coefficients indicates that condensation and evaporation can be considered separately during net condensation, net evaporation, or steady-state equilibrium. The incoming H2O vapor flux does not interfere with desorbing H2O molecules up to H2O vapor pressures of at least 1 x 10^-6 Torr. The equivalency also suggests that evaporative cooling and condensative heating of the ice surface are negligible. Evaporation does not reduce desorption rates by the cooling of the ice surface. Likewise, impinging H2O molecules do not induce the evaporation of surface H2O molecules through a surface heating mechanism.

The observed equivalence of the condensation and evaporation coefficients also indicates that the condensation of the incoming H2O vapor phase is probably independent of vapor temperature up to 300 K. This proposed temperature independence may be
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attributed to the efficient dissipation of the kinetic energy of the vapor by the ice crystal lattice. The equivalence also suggests that the ice surface structure does not influence condensation and evaporation. Vitreous ice and ice I are both formed at their respective temperatures over the 20–185 K temperature range of the condensation coefficient experiments. The condensation coefficients shown in Figure 5 do not display any discontinuities that may be associated with different surface structures. Likewise, Figure 7 does not manifest any evidence of reconstructions of the ice surface that may occur as a result of evaporation in the temperature range from 173 to 205 K.

D. Isothermal Desorption Kinetics. The sinusoidally varying interference signals observed in Figure 3 indicate a constant desorption rate at each temperature. This behavior provides evidence for zero-order desorption kinetics. Zero-order kinetics are expected in multilayer desorption. For zero-order kinetics, the isothermal desorption rate is

\[ \frac{d\theta}{dt} = v_0 e^{-E_d/RT} \]  

where \( \theta \) is the coverage in units of molecules per centimeter squared. All other symbols have been previously defined.

Figure 9 shows the Arrhenius plot of the isothermal desorption rates obtained from the isothermal desorption experiments. The slope of a linear fit to this plot yielded a desorption activation barrier of \( E_d = 11.9 \pm 0.2 \) kcal/mol. The intercept produced a zero-order preexponential of \( v_0 = 2.8 \times 10^{10} \pm 1.0 \times 10^{10} \) molecules/(cm² s). The magnitude of this preexponential is characteristic of zero-order multilayer desorption. The desorption activation barrier is also in agreement with previous temperature-programmed desorption studies of ice multilayers on metal surfaces, which have measured \( E_d = 11.5 \) kcal/mol.

E. Quasi-Equilibrium Measurements. The term quasi-equilibrium indicates that the isotherm experiments are performed under steady-state conditions but not true equilibrium conditions. Under true equilibrium conditions, the gas temperature, \( T_g \), and the surface temperature, \( T_s \), are equal. However, the difference between true equilibrium and quasi-equilibrium conditions has previously been shown to be negligible. Consequently, the analysis of quasi-equilibrium measurements generally proceeds as if the measurements were performed at true equilibrium.

For the equilibrium between a gas and its solid, the equilibrium at any temperature is characterized by the vapor pressure:

\[ K_{eq} = P = \exp\left[-\frac{\Delta G_{sub}}{RT}\right] \]  

In this expression, \( K_{eq} \) is the equilibrium constant, \( \Delta G_{sub} \) is the free energy of sublimation, and \( \Delta G_{sub} = \Delta H_{sub} - T \Delta S_{sub} \) where \( \Delta H_{sub} \) is the enthalpy of sublimation and \( \Delta S_{sub} \) is the entropy of sublimation. Rearrangement of this relationship yields the slope-intercept form of the Clausius-Clapyron equation:

\[ \ln(P_s) = -\frac{\Delta H_{sub}}{RT} + \frac{\Delta S_{sub}}{R} \]  

The enthalpy of sublimation, \( \Delta H_{sub} \), and the entropy of sublimation, \( \Delta S_{sub} \), may be obtained by fitting eq 11 to the data in Figure 4. The resultant \( \ln(P_s) \) vs \( 1/T \) plot is shown in Figure 10 with \( P_s \) in atmospheres. This plot yields a slope corresponding to \( \Delta H_{sub} = 11.8 \pm 0.2 \) kcal/mol and a y-intercept giving \( \Delta S_{sub} = 31.0 \) cal/(K mol).

The value determined for the heat of sublimation is in agreement with the measured value of \( \Delta H_{sub} = 12.2 \) kcal/mol determined previously by Davy and Somorjai for crystalline ice and \( \Delta H_{sub} = 12.2 \) kcal/mol for amorphous ice. Similarly, the measured value for the entropy of sublimation is in good agreement to that expected for the addition of the entropy of fusion \( \Delta S_{sub} = 5.3 \) cal/(K mol) and the entropy of vaporization \( \Delta S_{vap} = 26.0 \) cal/(K mol). Within experimental error, the measured value for the enthalpy of sublimation, \( \Delta H_{sub} = 11.8 \pm 0.2 \) kcal/mol, is also equivalent to the desorption activation energy of \( E_d = 11.9 \pm 0.2 \) kcal/mol that was determined by the isothermal desorption experiments. This equivalency between the equilibrium and kinetic values indicates that there is no apparent kinetic barrier for H₂O adsorption on H₂O multilayers.

An approximation for the average hydrogen bond energy in crystalline ice can be derived if the intermolecular binding energy of the H₂O lattice is attributed to hydrogen bonding. Because each H₂O molecule in the crystal lattice participates in two hydrogen bonds, the strength of each hydrogen bond may be determined by dividing the enthalpy of sublimation by two:

\[ E_{H-bond} = \frac{\Delta H_{sub}}{2} \]  

Applying this definition and using \( \Delta H_{sub} = 11.8 \) kcal/mol, we derive an average hydrogen bond energy of \( E_{H-bond} = 5.4 \) kcal/mol for temperatures between 164 and 190 K. This hydrogen bond energy compares favorably with \( E_{H-bond} = 5.66 \) kcal/mol obtained from relevant thermodynamic data for ice I at 0 K. F. Relevance to Heterogeneous Atmospheric Chemistry. Polar stratospheric clouds (PSCs) are ice particles in the polar stratosphere at altitudes of 10–20 km. Heterogeneous chemistry on PSCs has recently been suggested as a mechanistic step in the catalytic destruction of ozone over Antarctica. Although the presence of these ice particles over the polar regions is well documented, modeling of PSC growth and stability is contingent upon accurate values for the condensation and evaporation rates for H₂O on ice. In this study, the rates of condensation and evaporation have been accurately determined as a function of temperature. Under the assumption that particle nucleation will
or in the ice bulk is not known. However, the ice surface
the ice surfaces of polar stratospheric clouds. The possible in-
the heterogeneous reaction kinetics raises important questions in
performances for heterogeneous atmospheric chemistry.15 For ex-
conclusions for heterogeneous atmospheric chemistry. Understanding the nature
of these heterogeneous reactions is a fascinating frontier in ice
surface chemistry and will be pursued in future studies.

V. Conclusion
Optical interference techniques were used to measure the
condensation coefficients for H2O on ice surfaces for surface
temperatures from 20 to 185 K. The condensation coefficients,
\(\alpha\), were observed to decrease with ice surface temperature
from an initial value of \(\alpha = 1.06 \pm 0.10\) at 20 K to \(\alpha = 0.65 \pm 0.08\)
at 185 K. This decrease with surface temperature was consistent with a precursor-mediated adsorption model.
The evaporation coefficients for H2O from H2O multilayers
were examined at surface temperatures from 173 to 205 K. These
isothermal desorption measurements also employed optical inter-
ference techniques. The evaporation coefficients were deter-
mined to be constant at \(\gamma = 0.63 \pm 0.15\) versus temperature
between 173 and 205 K. The evaporation coefficients were
equivalent to the condensation coefficients within the experimental
error limits over the temperature range where they both could be
measured. This equivalency indicates that evaporation or
condensation do not perturb or alter the ice surface. In addition,
evaporation and condensation can be considered independent of
one another during net condensation, net evaporation, or
steady-state equilibrium.
The isothermal desorption kinetics for H2O desorption from
ice surfaces were also measured using optical interference tech-
niques. An Arrhenius analysis of the isothermal desorption rates
versus temperature revealed zero-order desorption kinetics as
expected for H2O multilayer desorption. The activation barrier
for desorption was \(E_d = 11.9 \pm 0.2\) kcal/mol with a zero-order
preexponential of \(v_0 = 2.8 \times 10^8 \pm 1.0 \times 10^{953} \text{ molecules/cm}^2 \text{s}^{-1}\).

Quasi-equilibrium optical experiments also determined the
enthalpy of sublimation, \(\Delta H_{\text{sub}}\), and entropy of sublimation,
\(\Delta S_{\text{sub}}\), for H2O multilayers. The quasi-equilibrium measurements versus
temperature yielded \(\Delta H_{\text{sub}} = 11.8 \pm 0.2\) kcal/mol and \(\Delta S_{\text{sub}} =
31.0 \text{ cal/K mol.}\) The equivalency of the kinetic desorption
activation barrier, \(E_d\), and the enthalpy of sublimation, \(\Delta H_{\text{sub}}\),
displays the predicted adsorption and desorption coefficients
that there is no barrier for H2O adsorption on ice surfaces.
The enthalpy of sublimation, \(\Delta H_{\text{sub}}\), also yields an average hydro-
gen bond energy in ice of \(E_{\text{H-bond}} = 5.4\) kcal/mol.

These results for the condensation and evaporation of H2O on
ice surfaces have important implications for heterogeneous atmosphe-
pheric chemistry. Adsorption and desorption rates of 10-1000
ML/s are predicted over the stratospheric temperature range from
180-210 K under equilibrium conditions. The ice surface is
extremely dynamic and rapid solvation by impinging H2O
molecules may occur on a millisecond time scale. As a result, het-
erogeneous atmospheric reactions may occur in the ice bulk rather
than on a static ice surface.

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A Comparison of Electrochemical and Gas-Phase Decomposition of Methanol on Platinum Surfaces

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By using electrochemical and ultrahigh-vacuum (UHV) techniques, combined with an isotope substitution method, it is found that the mechanism of methanol decomposition on platinum in the electrochemical environment is different than that in the UHV. In the UHV, the first step in the decomposition process is the scission of an O-H bond to yield a methoxy intermediate, whereas in the electrochemical environment, the first step is the scission of a C-H bond. The difference in the decomposition mechanism is discussed in terms of differences in the local electric field at the surface and in terms of methanol hydrophobic/hydrophilic interactions in solution. The latter affect methanol-water near-surface surface conformation and predetermine the destiny of the individual methanolic bonds in the catalytic splitting.

Introduction
Oxidation of methanol on polycrystalline platinum electrodes has been studied extensively.1-18 Bagotzky et al.12 postulated that the rate-determining step involved the rupture of the C-H bond in a methyl group to yield a CH3OH intermediate:

$$\text{CH}_3\text{OH} \rightarrow \text{CH}_2\text{OH} + \text{H}^+ + e^- \quad (1)$$

In the gas phase, and at low temperature, methanol was found to adsorb molecularly on group VIII metals and to decompose with an increase in temperature via the mechanism shown in Figure 1.19 First, methanol undergoes O-H bond scission to yield a methoxy (CH3O) intermediate. Then, the methoxy sequentially decomposes to yield carbon monoxide and hydrogen.