Condensation of supersaturated water vapor on submicrometer particles of SiO$_2$ and TiO$_2$

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(Received 27 May 1999; accepted 25 January 2000)

Condensation of supersaturated water vapor on monodisperse submicrometer SiO$_2$ and TiO$_2$ particles is investigated in a flow cloud chamber (FCC). The dependence of the critical supersaturation $S_{cr}$ on particle size in the range of 15 to 120 nm and on temperature in the range of 10 to 50 °C are determined experimentally. The results show that the experimental $S_{cr}$ decreases with increasing particle size, at a rate in reasonable agreement with that predicted by Fletcher’s version of Volmer’s theory of heterogeneous nucleation, but decreases with increasing temperature at a rate higher than that predicted by Fletcher’s theory. The experimental $S_{cr}$ is smaller than the theoretical prediction even with the line tension and surface diffusion taken into account; the particles induce heterogeneous nucleation better than theory predicts even for perfectly wetted particles. The discrepancy cannot be fully accounted for by the effects of line tension, surface diffusion, or the curvature dependence of the physical properties. The condensation of supersaturated vapor on singly-positively-charged particles with diameters of 30, 60, and 90 nm is also examined. No obvious effect of charge on $S_{cr}$ is observed, in agreement with the theoretical prediction. The law of corresponding states was extended to heterogeneous nucleation, and a simple correlation was obtained. © 2000 American Institute of Physics. [S0021-9606(00)71015-4]

I. INTRODUCTION

Fine aerosols are an important component of natural and anthropogenic aerosols. On entering the atmosphere, aerosol particles reach the Boltzmann equilibrium charge distribution in about 100 min by interacting with ions formed continuously in the atmosphere due to cosmic radiation and radioactive gases emanating from the soil. Over land, about 10 ion pairs per cm$^2$ per second are formed. These ions combine with each other to yield small ions (molecular clusters) with an equilibrium concentration of 100–5000 cm$^{-3}$ and these ions attach to aerosol particles. Fine aerosols are important because they pose potential health hazards, and these ions attach to aerosol particles. Fine aerosols are important because they pose potential health hazards.

Condensation of supersaturated vapor on neutral particles is influenced by the surface properties and size of the particles. However, the dependency is not well known, and observations are reported which are both consistent and inconsistent with theory. Measurements of heterogeneous nucleation of water vapor on submicrometer AgI and wax particles$^3$ and DOP (dioctyl phthalate) particles$^5$ show that these particles behave like pure water droplets. Nucleation of water vapor on ultrafine Ag aerosol$^5$ shows that the experimental critical supersaturation is in satisfactory quantitative agreement with calculations based on the macroscopic theory of heterogeneous nucleation. However, in a study of the effect of surface properties of ultrafine particles on the condensation of water and $n$-butanol,$^6,7$ the critical supersaturation for the condensation of $n$-butanol vapor on NaCl and Ag particles is smaller than that for perfectly wetted particles. In our earlier studies of water and $n$-butanol vapor nucleation on fine aerosols of SiC, naphthalene, SiO$_2$, Al$_2$O$_3$, TiO$_2$, and carbon black, all of the aerosols except naphthalene induced heterogeneous nucleation better than perfectly wetted particles.$^8$–$^{10}$

Condensation of a vapor onto charged particles is influenced by the sign and the amount of charge and the dipole moment of the vapor molecules. The sign preference$^{11,12}$ depends on the permanent dipole moment, the dipole moment orientation relative to the electric field created by the charge on a particle, and the surface molecular structure of the condensing vapor. No sign preference, negative sign preference, and positive sign preference are observed. Experimentally, as the dipole moment of the vapor molecule increases, the critical supersaturation required for nucleation to occur decreases.$^{13}$

Since Wilson’s pioneering observations of ion-induced nucleation in a system free of aerosol particles,$^{14}$ many experimental and theoretical studies have been performed. Various nucleation theories have been developed,$^{15–19}$ the effects of ions on the nucleation were measured,$^{11,13,20–22}$ and intercomparison among theories or experimental observations were made.$^{18,19,21,23,24}$ Ions are believed to interact with the condensing vapor and change the energy barrier for nucleation.$^{25}$ The change depends on the properties of the condensing vapor (e.g., dipole moment, size, etc.) and of the ions (e.g., the sign of charge, size, etc.).

So far, the size of the ions tested ranges from single

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atoms or small molecules consisting of a few atoms\textsuperscript{13,20,21} to macromolecules containing hundreds of atoms.\textsuperscript{22} For small ions with diameters less than 1 nm, there is no reported dependence of the nucleation rate on the size and the chemical makeup.\textsuperscript{20} but for macromolecules with diameters of about 1 nm, a decrease in the critical supersaturation with ion size is observed.\textsuperscript{22} However, only scant data are available for the condensation of vapor onto charged particles with diameters in the range of tens of nanometers.

To gain more insight into the heterogeneous nucleation process, we used the flow cloud chamber\textsuperscript{8} (FCC) to examine the effects of charge as well as surface properties, particle size, and condensable vapor on the nucleation process. A charge effect may provide us with useful information about the vapor molecules’ orientation in the droplet and their interaction with the particle surface. The FCC creates the continuous supply of supersaturated vapor required for condensation, efficient nuclei growth, and particle precipitation from the gas stream, and it provides a steady-state profile of supersaturation whose degree of supersaturation can be easily controlled. As the aerosol passes through the FCC, some particles are removed from the gas stream because they diffuse to a surface due to Brownian motion and mass sweeping diffusion. Other particles undergo heterogeneous nucleation, grow, and are dragged down due to gravity. During sedimentation, nucleated particles travel with the gas stream and are trapped in the FCC if they reach the bottom surface. The efficiency with which particles are removed from the gas stream depends on the vapor supersaturation, the size and wetting properties of the particles, the flow rate of the gas stream, and the geometry of the FCC. Our experiments were carried out under conditions where nucleation dominates the particle removal process. The onset of heterogeneous nucleation is then investigated by measuring the efficiency of particle removal as a function of supersaturation.

In the present study, SiO\textsubscript{2} and TiO\textsubscript{2} aerosols were examined. The contact angles of SiO\textsubscript{2} and TiO\textsubscript{2} with water were measured using the sessile drop technique. The critical supersaturation required to induce heterogeneous nucleation was measured for particles with diameters in the range of 15 to 120 nm, and the temperature dependence of the critical supersaturation was measured for 40 nm TiO\textsubscript{2} aerosols. The condensation of water vapor onto monodisperse particles, each carrying a single positive charge, was examined for particles with diameters of 30, 60, and 90 nm. The law of corresponding states\textsuperscript{26} was extended to heterogeneous nucleation, and the critical supersaturation was correlated as a function of the reduced temperature.

\section*{II. Experiment}
\subsection*{A. Experimental setup}

The experimental apparatus is illustrated in Fig. 1. Argon gas carries the reactant vapor out of the reactant flask. The Ar-reactant stream is mixed with a second gas stream (argon for SiO\textsubscript{2} and oxygen for TiO\textsubscript{2}) and enters the oven. The polydisperse aerosol generated in the oven passes through an electrostatic classifier (Model 3071A, TSI) to produce a singly-positively-charged monodisperse aerosol. The charged monodisperse particles enter an aerosol neutralizer (Model 3077, TSI) to reach a charge equilibrium. The charged particles are removed by an electrostatic collector. The uncharged monodisperse aerosol is diluted with clean air, and then flows through the FCC. The removal efficiency is obtained by comparing particle concentrations at the inlet and the outlet of the FCC. The particle concentration is measured using an ultrafine condensation particle counter (Model 3025A, TSI). In experiments that measure the charge effect, the aerosol neutralizer and the electrostatic collector are not used. The charged particles from the classifier are diluted with clean air and enter the FCC directly as indicated by the dashed line.

The equipment and instruments mentioned above have been described in detail elsewhere.\textsuperscript{8–10} Only a brief description of the equipment specific or important to the current study is given here.

\subsection*{1. Flow cloud chamber (FCC)}

The FCC consists of two plates (length 1.5 m, thickness 0.03 m, width 0.3 m), separated on both sides by two glass strips (length 1.5 m, height 0.05 m, thickness 0.01 m) and two stainless steel funnels at both ends (as shown in Fig. 2, Ref. 8). Each plate is attached to a separate manifold through which fluid circulates, maintaining the top plate at a higher temperature than the bottom. A sheet of glass wool was used to create a thin layer of water at the lower surface of the top plate by capillary action. Water evaporates from the upper surface, diffuses downward through the gas stream, and condenses on the bottom plate to form a pool which is maintained at a 2 mm depth.

\subsection*{2. Aerosol generators}

Two aerosols, SiO\textsubscript{2} and TiO\textsubscript{2}, were generated by the chemical vapor decomposition of Si(O\textsubscript{2}C\textsubscript{2}H\textsubscript{2})\textsubscript{4}, silicon tetraethoxide (STE), and Ti(OCH(CH\textsubscript{3})\textsubscript{2})\textsubscript{4}, titanium tetraisopropoxide (TTIP), respectively. The aerosol generator consists of an 80 cm long, 5 cm OD quartz tube and a 30 cm long tubular oven.\textsuperscript{10}

During SiO\textsubscript{2} aerosol generation, 0.03 to 0.1 lpm of Ar flows through a flask containing STE that is kept in an ice bath at ice temperature. The STE vapor-laden Ar enters the quartz tube where it is diluted by a second argon stream to produce a 0.5 lpm flow of reaction gas. As the reaction gas
stream flows through the heating zone at 800 °C, STE vapor thermally decomposes to form SiO₂ aerosol via the reaction Ti(OCC₂H₅)₄(g) → SiO₂(g) + 4C₂H₄(g) + 2H₂O(g).

To generate TiO₂ aerosol, 0.4 to 0.8 lpm of Ar flows through a flask containing TTIP that is kept in a thermostat at room temperature (298 K). The TTIP-Ar stream enters the quartz tube and is mixed with 0.8 lpm O₂ to form the reaction gas. As the reaction gas stream flows through the heating zone at 900 °C, TTIP vapor reacts with O₂ to form TiO₂ aerosol via the reaction Ti(OC₂H₅)₄ + 18 O₂ → TiO₂ + 12 CO₂ + 14 H₂O.

At the exit of the quartz tube, the aerosol is diluted with an air stream of more than 0.5 lpm. Aerosol with different particle size distributions and number concentration are obtained by adjusting the flow rates of the carrier gas and dilution streams. The morphology of the particles, analyzed by x-ray diffraction (XRD), shows the SiO₂ is amorphous and the TiO₂ is crystalline (anatase-type).

### B. Removal efficiency measurements

Blank runs were first carried out for each aerosol stream to serve as a base line for comparison with experiments where heterogeneous nucleation was important. The experimental procedure has been described in detail elsewhere. Only modifications to the experiments and the operating conditions are given.

To minimize the uncertainty in determining the critical supersaturation, a 7 mW He–Ne laser (beam diameter of 0.8 mm) was used to illuminate the FCC at a few millimeters above the bottom surface to detect light scattered by the falling droplet produced by nucleation. The location (distance from the entrance) where nucleation occurred and the number of droplets were recorded. These observations, together with the rapid change in particle removal efficiency with supersaturation, let us determine the supersaturation at which nucleation occurs.

For the blank runs, the top and the bottom plates of the FCC were kept wet and set to the temperature that the bottom plate had during the actual experiment (283 to 303 K). In the removal runs, the bottom plate was set to the desired temperature (283 to 303 K), and the temperature of the top plate was set at temperature from 2 to 22 K higher. Most of the runs were carried out at a bottom plate temperature of 303 K, and the bottom plate was set to other temperatures only for the runs measuring the temperature dependence of Sₚ. The maximum value of the supersaturation profile studied, Sₚ, and the corresponding temperature, Tₛ, at the position where peak supersaturation occurs are listed in Table I.

### C. Contact angle measurements

The contact angle of the particles with water was measured employing the sessile drop technique. Because water quickly penetrates into compressed tablets of the SiO₂ and TiO₂ powders, measurements of the contact angle of a sessile drop were made with a face contact anglemeter (Model CA-A, Kyowa Kaimenkagaku Co.) on films formed by chemical vapor deposition on a silicon substrate. The deposited film was prepared by placing the silicon substrate in the

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**Table I.** The values of the temperatures at plate surfaces, Tₛ, for each removal run. The values of Sₚ, the maximum values from the supersaturation profiles calculated from the plate surface temperatures [using Eqs. (1) and (2) in Ref. 9]. The value Tₛ is the temperature at which the peak supersaturation occurs.

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reaction gas near the exit of the oven. A copper plate cooled by a cooling coil was attached to the back of the substrate to enhance deposition by thermophoresis. A white colored film was formed.

III. REMOVAL EFFICIENCY CALCULATION

Certain particles in the gas stream passing through the FCC nuclei in the supersaturated vapor grow rapidly, and settle out with appreciable velocity. Before the particles are trapped on the surface of the liquid pool, they travel with the gas stream. Particles that travel less than the length of the FCC are removed. Particles may also be trapped on surfaces if they move to them by Brownian motion and mass sweeping diffusion. The removal efficiency of particles has been evaluated theoretically by first solving the mass and energy transfer equations to obtain profiles for temperature, vapor pressure, and supersaturation. These profiles, in conjunction with heterogeneous nucleation theory and fluid mechanics, were then used to calculate the particle nucleation rate, the falling time, and the distance traveled. Finally, the particle concentration was evaluated from a transfer equation describing the loss of particles due to nucleation, Brownian motion, and sweeping diffusion.

The removal efficiency calculations have been explained in more detail in our earlier studies.8–10 Presented here is a brief description of features important or specific to the study.

A. The profiles of temperature, vapor pressure, and supersaturation in FCC

Gas entering the FCC absorbs heat and vapor from the top plate, transfers them to the bottom plate, and sets up temperature (T), partial pressure (P), and supersaturation (S) profiles in the process. Since the main component of the gas stream is air, the transfer of water vapor is reduced to a transfer in a binary system (i.e., water vapor through air). The profiles can be simultaneously found from solving a set of mass and energy transfer equations9,27 using the parameters and physical properties corresponding to the water–air system.

B. The onset of nucleation

The onset of condensation of a supersaturated vapor on particles is controlled by the nucleation rate. The higher the nucleation rate, the better the removal efficiency. In the present study, we used Fletcher’s theory28 to calculate the nucleation rate initiated by neutral particles.9,29 For charged particles, the ion interacts with the condensing vapor and lowers the energy barrier to nucleation.25 If a charged particle is treated as a perfectly wetted ion of a radius \(R_0\), then the change in the Gibbs free energy required to form a critical embryo, \(\Delta G^*\), is written as

\[
\Delta G^* = -\frac{4\pi\rho_e RT}{3M} \ln(S) + 4\pi\gamma(i_r^3 - i_r^1) + \frac{q^2}{2} (\kappa_0 - \kappa^{-1}) \left( \frac{1}{i_r^3} - \frac{1}{i_r^1} \right).
\]

Here \(\gamma\) is the surface tension of water, \(\kappa_0\) and \(\kappa\) are the dielectric constant of air and liquid, \(q\) is the electronic charge in Gaussian units, \(i_r\) is the radius that the charged particle has when it is in stable equilibrium with the vapor, and \(i_r^1\) and \(i_r^3\) are the largest and the next smaller roots of \(\partial \Delta G/\partial r = 0\):

\[
\frac{\rho_e RT}{M} \ln S - \frac{2\gamma}{r} \left( \frac{r^2 - r^1}{r^3} \right) \frac{\partial G}{\partial r} + \frac{q^2}{8\pi r^4} (\kappa_0 - 1) = 0.
\]

To evaluate \(\Delta G^*\), \(i_r\) is set to \(R_0\) if \(i_r < R_0\) and it is set to \(r_a\) if \(r_a > R_0\). For a given vapor pressure, a cluster of radius \(r_a\) is in stable equilibrium with the vapor, and any ion or charged particle with a radius \(R_0\) smaller than \(r_a\) will spontaneously grow up to \(r_a\).

Variations of the nucleation rate with the position (the height measured from the surface of the liquid pool on the bottom plate) were evaluated for both neutral and charged particles, and trends similar to those described in earlier studies8,30 were obtained. Near the top and bottom plates, the nucleation rate is low. Moving away from the surfaces the nucleation rate increases sharply and reaches a maximum near the center of the FCC. A higher maximum rate and a wider nucleation zone were obtained with increasing supersaturation, particle size, and wettability (i.e., smaller contact angle), respectively.

C. Sweeping diffusion

In the thermal diffusion cloud chamber, diffusion plays a dominant role; water vapor evaporates from the top plate, diffuses through a flowing gas stream, and condenses on the bottom plate. There is therefore a net mass flux in the downward direction which interacts with particles, retarding their diffusion toward the top plate and enhancing their diffusion toward the bottom plate. The loss of particles has been evaluated from a transfer equation describing the transfer of particles in the FCC [i.e., Eq. (10), Ref. 9] assuming plug flow for the gas stream.

Under our operating conditions, the gas stream in the FCC flows at a Reynolds number of about 20, having an entrance zone of less than 10% of the length of the FCC.31 A laminar flow (i.e., a parabolic velocity profile) is more appropriate. To check the effect of the flow pattern on the particle concentration profile and the removal efficiency, the equation was rederived, and is given by

\[
(6z - 6z^2) \frac{\partial X}{\partial \tau} - D_m \frac{\partial^2 X}{\partial z^2} = \frac{\partial T}{\partial z} \frac{1}{T} \frac{\partial X}{\partial \tau} + D_m \frac{\partial^2 X}{\partial z^2} + \frac{\partial T}{\partial z} \frac{1}{T} \frac{\partial X}{\partial \tau} + \frac{D_m}{D_h} N_h \frac{\partial X}{\partial \tau} + \frac{D_m}{D_h} N_h \frac{\partial X}{\partial \tau} + \frac{D_m}{D_h} \frac{\partial X}{\partial \tau} = \frac{h^2}{D_h^2} X J.
\]

Here, \(X\) is the mole fraction of particles, \(J\) is the nucleation rate, and reducing parameters are \(z = z/h\), \(N_h = N_h h/(C_0 D_0 h^2)\), \(\tau = \tau h^2 / D_0 h^2\), and \(D_m = D_m / D_0 h^2\) where \(h\) is the mean distance between plates, \(C_0\) is the sum of the molar concentration of all species in the mixture, \(D_0\) is the ordinary diffusivity of particle at 290 K through 101 kPa (760 Torr) of

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air, \( D'_m = (X_h/D_h + X_c/D_c)^{-1} \), \( X_h \) is the mole fraction of vapor, \( X_c \) is the mole fraction of air, \( D_h \) is the ordinary diffusivity of particle through vapor, and \( D_c \) is the ordinary diffusivity of particle through air. Note that Eq. (3) is essentially the same as Eq. (10) in Ref. 9 except that the first term is multiplied by the factor, \( 6Z - 6Z^2 \).

The concentration profiles of particles were reevaluated as a function of position (the height measured from the liquid pool surface) for different particle diameters, supersaturations, contact angles, and residence times. Trends similar to those shown in Fig. 3 in Ref. 9 were observed. Near the top and bottom plates, particle concentrations are low because of diffusional losses to the plate surfaces. The low particle zones become wider as residence time increases. Along the center line of the FCC, there is another low concentration zone due to particle nucleation. This zone becomes wider for increasing particle size, supersaturation, and wettability (i.e., smaller contact angle).

D. Efficiency of removal

The maximum particle removal efficiency is achieved when the FCC operates under conditions where particles are removed once they initiate condensation. The maximum removal efficiency can be obtained from the particle concentration profiles and the the equation

\[
\text{Efficiency of removal} = \frac{(C_{i1} - C_{i0})}{C_{i1}}.
\]

Here \( C_{i1} \) and \( C_{i0} \) are the total particle concentrations obtained by integrating the particle concentration profile over the height at the inlet and the outlet of the FCC, respectively.

Figure 2 shows the calculated removal efficiency (solid lines) as a function of supersaturation for perfectly wetted particle with diameters ranging from 15 to 90 nm. The trend is similar to that obtained previously assuming plug flow. Two plug flow cases (dashed curves) are included for comparison. As the supersaturation increases, the efficiency increases sharply once the supersaturation passes a critical value, the critical supersaturation \( S_{cr} \), and rapidly approaches a value of 100%. Comparing the solid and dashed curves, one observes that slightly shifting the dashed curves upwards leads to both curves overlapping in the region where the sharp increase in efficiency occurs, a situation corresponding to having the same critical \( S_{cr} \). Thus, although the flow pattern effects the particle concentration profiles and removal efficiencies, it has no effect on the critical supersaturation. The variation of the critical supersaturation as a function of particle size is the same as that obtained in the earlier study.9

IV. EXPERIMENTAL RESULTS AND DISCUSSION

A. The contact angle

Using the sessile drop technique, the contact angles for SiO\(_2\) and TiO\(_2\) film, deposited on a silicon substrate, were 20°±2° and 16°±1° at 300 K, respectively. Because absorbed impurities can strongly affect the contact angle\(^{32}\) and that the microscopic contact angle might be different from the macroscopic value we measured,\(^{33,34}\) our measurements of contact angle may differ from those that the particles actually possess during removal runs in the FCC.

B. Blank test

During the blank tests, particles are removed by sedimentation and adhesion onto surfaces due to diffusion or inertial impingement. As shown in Fig. 3, a low efficiency of removal (i.e., high ratio of concentration at the outlet to the inlet) was observed in all the blank tests. We have shown that when particles are smaller than 0.2 µm in diameter, particle loss by sedimentation is negligible.\(^{5,9,30}\) Particles are primarily removed by adhesion onto surfaces. The low removal efficiencies during the blank runs supports the proposition that high removal efficiencies observed in removal runs are due to heterogeneous nucleation, particle growth, and sedimentation. Note that coagulation of the particles can be neglected due to low particle concentrations. Also shown in Fig. 3 is the theoretical curve assuming that particles are removed by loss due to diffusion. Within error bars, the model curve is in good agreement with the experimental measurements. The good agreement indicates that particles are primarily removed by diffusion loss.

C. SiO\(_2\) and TiO\(_2\) aerosols

During the removal runs, more particles were removed because nucleation and particle growth induce sedimentation. Figures 4(a) and 4(b) summarize the removal efficiencies measured as a function of supersaturation for SiO\(_2\) and TiO\(_2\) aerosols for different particle sizes. The efficiency first
increases slowly with increasing supersaturation. As the supersaturation passes a critical value, the efficiency increases sharply. At even higher supersaturation, no particles were detected at the exit. The slight fluctuations of efficiency at low supersaturations may be due to the larger uncertainties indicated by the error bars (i.e., one standard deviation from the mean) which decrease from about ±13% at low efficiency, to about ±1% at high efficiency. For clarity error bars are only included for one curve. As the particle size decreases, the curves shift to higher supersaturation, qualitatively agreeing with expectations of the model shown in Fig. 2.

**D. Comparison of the experimental and theoretical critical supersaturations**

The experimental $S_{cr}$ are determined from the removal efficiency curves [Figs. 4(a) and 4(b)] together with observations of the laser light scattered by the falling droplets. The latter helps identify the probable range of $S_{cr}$ and is crucial when the removal efficiency curves are not sharp. The experimental $S_{cr}$ is identified as the supersaturation at which removal efficiency increases sharply and a few droplets per second per cm$^2$ are observed. A typical example illustrating how $S_{cr}$ is determined was published in the previous study.\textsuperscript{10} Since the number of data points and the curve fitting both affect the values of $S_{cr}$, some uncertainty is imposed on $S_{cr}$. The uncertainty was determined and is indicated by the error bar.

The theoretical $S_{cr}$ for perfectly wetted particles are determined from the critical points of curves as shown in Fig. 2. However, the $S_{cr}$ corresponding to a nucleation rate of one nucleation event per particle per second has also been evaluated using the Fletcher version of the Volmer theory of heterogeneous nucleation\textsuperscript{28} [also see Eqs. (3) and (4) in Ref. 9] and the following iteration scheme to solve for the $S_{cr}$ from the nonlinear dependence of the nucleation rate on the temperature and the supersaturation: (i) assume a temperature, $T_s$, and evaluate the $S_{cr}$; (ii) interpolate a new $T_s$ corresponding to the $S_{cr}$ from Table I; (iii) reevaluate $S_{cr}$ at the new $T_s$; and (iv) repeat above steps ii and iii until the solution converges (three iterations required). The resultant $S_{cr}$ were essentially the same as those predicted from Fig. 2, and agreed to within 0.1%.

The experimental values of $S_{cr}$ and $T_s$(K) (the temperature at the location where peak supersaturation $S_{cr}$ occurs) required to induce heterogeneous nucleation of water vapor...
TABLE II. The experimental and theoretical values of \(S_{cr}\) and \(T_s\) (the temperature at the peak supersaturation). The experimental values of \(T_s\) are interpolated from the variation of the temperature at the peak supersaturation for the top plate temperature setting given in Table I. Two sets of the theoretical values of \(S_{cr}\) and \(T_s\) are listed. One is evaluated at a \(T_s\) at the peak supersaturation, whose value changes with the peak supersaturation, and the other is evaluated assuming a constant \(T_s\) of 303.15 K.

<table>
<thead>
<tr>
<th>Particle diameter (nm)</th>
<th>Experimental values</th>
<th>Theoretical values</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(S_{cr})</td>
<td>(T_s) (K)</td>
</tr>
<tr>
<td>SiO(_2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15 1.130±0.008</td>
<td>311.2</td>
<td>...</td>
</tr>
<tr>
<td>20 1.085±0.005</td>
<td>309.9</td>
<td>...</td>
</tr>
<tr>
<td>25 1.070±0.003</td>
<td>309.3</td>
<td>1.052±0.003</td>
</tr>
<tr>
<td>30 1.052±0.003</td>
<td>308.5</td>
<td>1.040±0.003</td>
</tr>
<tr>
<td>40 1.040±0.003</td>
<td>308.0</td>
<td>1.031±0.003</td>
</tr>
<tr>
<td>50 1.032±0.003</td>
<td>307.5</td>
<td>1.022±0.002</td>
</tr>
<tr>
<td>60 1.022±0.003</td>
<td>306.8</td>
<td>1.019±0.002</td>
</tr>
<tr>
<td>70  ...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>80  ...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>90 1.017±0.002</td>
<td>306.4</td>
<td>1.014±0.002</td>
</tr>
<tr>
<td>100 ...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>110 ...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>120 1.013±0.002</td>
<td>306.0</td>
<td>1.010±0.002</td>
</tr>
</tbody>
</table>

on SiO\(_2\) and TiO\(_2\) aerosols is summarized in Table II and are compared to theoretical predictions in Fig. 5. Curve ...○... indicates the experimental values of \(S_{cr}\) and \(T_s\) for SiO\(_2\) aerosols with diameters from 15 to 120 nm, and curve ...●... for TiO\(_2\) with diameters from 25 to 120 nm.

The top solid curve indicates the theoretical \(S_{cr}\) and \(T_s\) (K) for perfectly wetted particles as a function of diameter. From the second to bottom, each solid line corresponds to the theoretical \(S_{cr}\) evaluated at a reduced value of the surface tension generated by replacing 75.64 with 60, 50, 

...or 20 dyne/cm in the expression \(\gamma = 75.64 - 0.1411 T - 0.000275 T^2\), \(T\) in °C, respectively.

Also shown in Fig. 5 is a dashed curve for the theoretical \(S_{cr}\), whose values are listed in Table II, evaluated at the bulk surface tension and a constant \(T_s\) of 303.15 K, for perfectly wetted particles. The slight difference between the dashed and the top solid curve shows that under our experimental conditions changing \(T_s\) by this small amount only leads to a negligible change in \(S_{cr}\). Thus, it is reasonable to neglect the change in \(T_s\) and to treat all variations of \(S_{cr}\) with particle diameter in Fig. 5 as at a constant temperature of 303.15 K.

For both SiO\(_2\) and TiO\(_2\) aerosols, the experimental values of \(S_{cr}\) are lower than those predicted by assuming a contact angle of 0°. Within the framework of a macroscopic theory of heterogeneous nucleation, the results suggest that both SiO\(_2\) and TiO\(_2\) aerosols induce heterogeneous nucleation with an efficiency better than perfectly wetted particles. The experimental values of \(S_{cr}\) for TiO\(_2\) aerosols are smaller than those for SiO\(_2\) aerosols, consistent with theoretical expectations based on an observed contact angle of 16°±1° for TiO\(_2\) and 20°±2° for SiO\(_2\), i.e., larger contact angles require higher supersaturations.

The increase of the experimental \(S_{cr}\) with decreasing particle size shown in Fig. 5 agrees reasonably with the theoretical prediction. This is shown by comparing the increase of the \(S_{cr}\) for SiO\(_2\) (TiO\(_2\)) by 12.6% (4.2%) to the theoretically predicted 11.3% (6.2%) on decreasing particle size from 120 (120) nm to 15 (25) nm.

In summary, the results in Fig. 5 show that the nucleation ability of SiO\(_2\) and TiO\(_2\) aerosols is qualitatively consistent with the theoretical prediction; and that, quantitatively, the experimental \(S_{cr}\) is smaller than the value predicted by the Fletcher’s theory for perfectly wetted particles.

Our observation of a smaller \(S_{cr}\) than the prediction is consistent with our previous observations\(^8\)–\(^10\) and those of
Koutsy et al.\textsuperscript{35} It is also interesting to note the homogeneous nucleation results observed by Heist and Reiss,\textsuperscript{36} Miller et al.,\textsuperscript{37,38} and Schmitt,\textsuperscript{39} where they observe that the values of the critical supersaturation of water lie above those predicted by the Becker–Doering–Zeldovich theory of homogeneous nucleation over the temperature range 230 to 320 K. Since both the heterogeneous and the homogeneous nucleation theory mentioned above base their application on macroscopic concepts like surface free energy to small embryo, the inconsistent deviation of the experimental $S_{cr}$ from the theoretical prediction suggests that the interaction between water and particle surface plays a very important role in enhancing the heterogeneous nucleation rate.

Note that, for the 30 and 40 nm diameter SiO$_2$ aerosol, the experimental $S_{cr}$ observed in the present study is slightly higher than that observed in the earlier study.\textsuperscript{9} This discrepancy may be due to changes in the surface properties of the SiO$_2$ aerosol, caused by altering the generation process, i.e., we now use thermal decomposition of Si(OCH$_3$)$_2$ instead of oxidation of SiCl$_4$.

E. Particle coagulation

As the aerosol flows through the system, the particle size distribution could change\textsuperscript{1} as particles coagulate. Under our operating condition, it has been shown theoretically that the size distribution of the monodisperse aerosol at the inlet of the FCC is “frozen” at the size distribution at the exit of the classifier.\textsuperscript{10,40} Essentially the same critical supersaturation was obtained experimentally even when the residence time from the classifier to the FCC was tripled.\textsuperscript{10} Thus, the deviation between the theory and the experiments cannot be attributed to coagulation effects.

F. Sweeping diffusion and flow patterns

Including the effect of sweeping diffusion in the model shifts the predicted removal efficiency-supersaturation curve up and leads to qualitative agreement with the experimental curve. The critical supersaturation derived from the model curves, however, remains unchanged. Thus, sweeping diffusion does not affect the predicted $S_{cr}$. As previously illustrated in Fig. 2, the removal efficiency curves have been evaluated both for laminar flow (solid curves) and plug flow (dashed curves). A slight shift upward of the dashed curves makes them overlap the solid curves in the region where the sharp increase in efficiency occurs; in other words, both flow patterns lead to the same $S_{cr}$. Thus, neither sweeping diffusion nor the flow pattern can explain the differences that exist between the experimental and the predicted $S_{cr}$ curves.

G. Physical properties—contact angle and surface tension

In the macroscopic theory of nucleation the nucleation rate is very sensitive to physical properties, especially surface tension and contact angle, and a change of a few percent in the surface tension may lead to a change of several orders-of-magnitude in the nucleation rate. In general, the bulk physical properties are used in the theoretical calculation. Any difference in the values of the physical properties between the bulk and the microscopic systems leads to a significant change in the predicted rate. It is interesting to estimate the difference required to make the predicted removal efficiency agree the experimental values.

We recalculated $S_{cr}$ as a function of particle diameter using different values of the surface tension of water at 0 °C but maintaining the same temperature dependence. As the surface tension is decreased the critical supersaturation curves are shifted down. As illustrated in Fig. 5 for TiO$_2$, the predicted curve agreed well with the experimental curve for a surface tension (at 0 °C) of 50 dyne/cm. This value is much smaller than the bulk surface tension of 75.64 dyne/cm. A lower surface tension was also required for SiO$_2$, suggesting that if the macroscopic theory of nucleation is valid then the physical properties in the microsystems must be different from those in the bulk system.

During the last few decades, the curvature-dependence of the surface tension and density have been extensively examined and discussed using either thermodynamics\textsuperscript{41–45} or molecular dynamics.\textsuperscript{46} The effect of incorporating a curvature-dependent surface tension into the nucleation process has also been theoretically examined. Schmelzer et al.\textsuperscript{47} showed that accounting for the curvature-dependence of surface tension does significantly change the energy of formation of the critical cluster, but does not lead to qualitative changes in the nucleation process. Based on the molecular dynamics study of Thompson et al.\textsuperscript{46} and the thermodynamic study of Schmelzer,\textsuperscript{45} one must conclude that the curvature-dependence of the surface tension is negligible for droplets with radii greater than 15σ, where σ is a parameter in the Lennard-Jones equation (i.e., the distance between molecules at which the potential is zero, σ=0.2641 nm for water).\textsuperscript{48} Thus, the curvature-dependence of the surface tension may be neglected for a water droplet with a radius larger than 4 nm. Since the radii implied by the experimental values of $S_{cr}$ are 8.1 to 78 nm for perfectly wetted particles of 15 to 120 nm diameter, the discrepancy in $S_{cr}$ shown in Fig. 5 cannot be explained by the curvature-dependent physical properties.

H. Effect of line tension and surface diffusion

In our calculation of the nucleation rate, the growth of the embryo is assumed to occur only through direct impingement of vapor molecules. In addition to the direct impingement on the embryo surface, vapor molecules can also adsorb on the particle surface and diffuse over the surface to join the embryo.\textsuperscript{49,50} Including surface diffusion can greatly enhance the rate of nucleation.\textsuperscript{51,52} Furthermore, the concept of line tension has been investigated,\textsuperscript{53–55} and negative values of the line tension lead to higher nucleation rates.\textsuperscript{56} In our earlier study\textsuperscript{9} both surface diffusion and line tension were included in the description of the nucleation process, and the enhancements in the nucleation rate and the removal efficiency were examined.

Both a higher nucleation rate and a wider nucleation zone were observed when a negative line tension and the surface diffusion were included. Enhancing the nucleation rate led to a slightly higher removal efficiency and a lower supersaturation to achieve a given removal efficiency. As shown in Fig. 6, however, including a negative line tension...
and surface diffusion for partially wetted particles with a contact angle of 8° only shift the theoretical curves slightly toward the theoretical curve for perfectly wetted particles, which represents the highest efficiency possible. Comparing the experimental curves with the theoretical curves, a gap still remains. Therefore, the effects of line tension and surface diffusion cannot account for the discrepancy between the experimental and the theoretical removal efficiencies.

I. Temperature dependence of the critical supersaturation

Figure 7 illustrates the temperature dependence of the experimental and theoretical $S_{cr}$ values required to induce heterogeneous nucleation on 40 nm TiO$_2$ particles. As the temperature increases, both the experimental and the theoretical values of $S_{cr}$ decrease. The experimental $S_{cr}$, however, decreases at a higher rate than the theory predicts. Comparing the theoretical curves corresponding to particle diameters of 30, 40, 60, and 90 nm, one finds that the decreasing rate reduces as the particle becomes larger.

J. Charge effect on the critical supersaturation

Figure 8 illustrates the experimental $S_{cr}$ for particles of SiO$_2$ and TiO$_2$ with diameters of 30, 60, and 90 nm, each carrying a single positive charge. The experimental values of $S_{cr}$ for neutral particles are also shown. The charged particles seem to have lower values of $S_{cr}$, but the differences are so small, almost within experimental uncertainty, that there is no obvious effect of charge on $S_{cr}$. This observation agrees with the predictions of the classical ion-nucleation theory as shown in Fig. 9. For radii less than 0.6 nm, the critical supersaturation required to induce a nucleation rate of one embryo per particle per second for perfectly wetted charged particles, as shown by curve 1, is constant. As the particle size increases, the $S_{cr}$ decreases and approaches the $S_{cr}$ for neutral particles indicated by curve 2, i.e., there is no effect of charge on $S_{cr}$ for large particles.

For particles smaller than 0.9 nm in radius, there is an obvious charge effect. At a radius of 0.9 nm, a $S_{cr}$ of 2.1 is required for charged particle compared with a $S_{cr}$ of 2.2 for neutral particles at a radius of 0.9 nm. The effect is negligible for particles larger than 2 nm in radius. For even larger size, the $S_{cr}$ values for the charged and the neutral particles...
approach that predicted by the Kelvin equation and the difference is less than 0.0045 at a radius of 10 nm. Thus, no charge effect will be observed for particles with diameters greater than 20 nm.

The theoretical variation of $S_{cr}$ with ion size also agrees well with the experimental observation that there is no dependence of nucleation rate on size and chemical makeup for small ions containing only a few atoms\(^2\) but there is a size dependence of $S_{cr}$ for macromolecules containing hundreds of atoms.\(^2\)

One major defect in the classical theory is that it cannot differentiate between positive and negative ions. Water has been observed to condense at lower supersaturations on negative ions and the alcohols prefer positive ions.\(^1\) The charge reversal symmetry is broken by the dipole layer which is found at the liquid–vapor interface of a system of polar molecules.\(^1\) If the ion reinforces this polarization, one might expect a lowered barrier for nucleation; if the ion must reorient the dipole, energy must be expended, and a higher nucleation barrier might be expected. Surface water molecules are believed to have the positive protons pointing toward the fluid.\(^5\) This polarization should interact unfavorably with positively charged particles and could lead to a very small charge effect we observed.

**K. A corresponding state correlation of the heterogeneous nucleation**

From thermodynamics we know that different substances follow the same equation of state when the variables are given in a suitably reduced form, i.e., the corresponding state approach. McGraw\(^2\) successfully extended this idea to metastable (supersaturated) vapor. He recast the classical Becker–Doering–Zeldovitch nucleation theory in dimensionless form based on empirical relations for the surface tension and density of a simple fluid, and used Pitzer’s acentric parameter to correlate departures from simple fluid behavior. He obtained a strong correlation of the measured critical supersaturation for homogeneous nucleation, as a function of the reduced temperature, for vapors with similar structure (i.e., similar Pitzer’s acentric parameter).

We have successively extended the law of the corresponding states to heterogeneous nucleation of vapor on particles to reveal patterns which are not easily seen on a substance-by-substance comparison between theory and experiment.\(^1\) In the extension, two more parameters, the contact angle and the particle size, are needed, and the same arguments and approaches described by McGraw\(^2\) for the homogeneous nucleation are applied to heterogeneous nucleation.

Figure 10 illustrates the variation in the theoretical ratio of $S_{cr,het}$ to $S_{cr,hom}$ as a function of reduced temperature for perfectly wetted particles of a 40 nm diameter. From top to bottom, the curve in each set corresponds to a contact angle and a diameter of 30°/40 nm, 10°/40 nm, and 0°/40 nm, using bulk physical properties. Also illustrated is a theoretical curve — obtained by setting $\gamma_0$ to 50 in the surface tension expression of water during the evaluation of $S_{cr,het}$. The data points indicate the experimental results for water obtained using TiO$_2$ aerosol with a diameter of 40 nm.
diameter using water as condensing vapor. In this dimensionless form, the data also fall along a straight line, suggesting that extending the law of corresponding states to heterogeneous nucleation of vapor on particles is reasonable.

V. SUMMARY

Condensation of water on submicrometer particles of SiO2 and TiO2 was investigated in the FCC. The onset of heterogeneous nucleation was determined by measuring the particle removal efficiency as a function of supersaturation. Our results show that heterogeneous nucleation is induced on both types of particles at lower critical supersaturations than predictions based on Fletcher’s theory and bulk physical properties. This is true even when the line tension and surface diffusion are taken into account. The experimental $S_{cr}$ decreases with increasing particle size with a rate in reasonable agreement with the predictions and agrees well with the theoretical $S_{cr}$ if a lower value of the surface tension is used. As the temperature increases the experimental $S_{cr}$ decreases with a rate higher than the theory predicts. No obvious effect on $S_{cr}$ is observed, in agreement with the theoretical predictions. The law of corresponding states was extended to heterogeneous nucleation, and a simple correlation was obtained.

Our results suggest that if the macroscopic theory of nucleation is valid then the physical properties such as the surface tension in micro-system must be significantly different from those in the bulk system. However, this is inconsistent with the known curvature dependency of the physical properties. The discrepancy between the experimental and theoretical critical supersaturation cannot yet be fully accounted for by the effects of line tension and surface diffusion and the existing theory concerning the curvature dependent physical properties. Further studies will be needed to account for the discrepancy.

ACKNOWLEDGMENT

We wish to thank Dr. Stanley L. Kaufman for his critical reading of the manuscript. The support of this research by the National Science Council of the Republic of China through Grants NSC86-2214-E006-006 and NSC87-2214-E006-001 is gratefully acknowledged.