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High pressure nucleation in water/nitrogen systems

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Nucleation rate measurements of water in the presence of nitrogen as a carrier gas are reported at total pressures near 10, 25, and 40 bar, and temperatures of 230 and 250 K. The results were obtained using our pulse-expansion wave tube, particularly suited for high pressure nucleation research. Enhanced fugacity of water vapor in the mixture, due to the presence of nitrogen, was quantitatively taken into account. Values of the enhancement factors as a function of pressure and temperature were correlated from accurate gravimetric measurements available in literature. The results demonstrate a strong influence of nitrogen pressure on the nucleation behavior of water, when temperature and supersaturation are kept fixed. The effect is associated with a decrease of the surface tension of water, due to the adsorption of nitrogen onto the liquid surface. A tentative model is presented that qualitatively describes this decreasing surface tension with pressure. The competition between the opposing effects of enhanced fugacity and decreasing surface tension is identified as a complicating factor in detecting pressure effects on nucleation. This conclusion is expected to hold for other vapor/carrier gas systems as well. © 1997 American Institute of Physics.

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I. INTRODUCTION

The effect of carrier gas pressure on homogeneous nucleation from the vapor phase has been a subject of discussion ever since quantitative nucleation rate measurements became possible. Systematic investigations, however, were only initiated during the past few years. At present, both theoretical and experimental work on pressure effects have been reported by several authors.1–4

It is useful to make clear at this point what we define as a carrier gas. Initially, most experimentalists considered the carrier gas merely as a latent heat reservoir, necessary to keep the nucleating vapor at isothermal conditions. However, it was soon realized that the carrier might also influence the nucleation process in other ways. We explicitly define a carrier gas here as a noncondensing constituent of a gas-vapor mixture. Note that we are not excluding the possibility for the carrier gas to influence the nucleation; the only restriction is that the carrier is not present in the interior of the liquid droplets. In this way, the systems we consider here form a kind of intermediary between unary and binary nucleation. Systems in which the—supercritical—carrier gas constitutes part of the droplet interior have been extensively discussed by Looijmans et al.5–7

The role of nonideal gas effects on nucleation in the presence of a carrier gas has been pointed out theoretically by Ford,1 Kashchiev,3 and Fisk and Katz.4 These authors describe the gas-vapor mixture using a virial equation of state. They conclude that the presence of the carrier gas may result in a change of the equilibrium vapor fugacity, thereby changing the supersaturation ratio of the vapor. An increase of equilibrium fugacity with total pressure is referred to as enhancement.8

Besides real gas effects, Fisk and Katz discuss the role of liquid compressibility. Although the latter can positively influence nucleation rates by about one order of magnitude for the nucleation conditions we will present here, it is not an effect exclusively associated with high-pressure nucleation.9 In this paper, we will concentrate on specific effects of total nucleation pressure and leave compressibility out of consideration.

Experimentally, very little information is available that considers the effects of carrier gas pressure on nucleation. Usually, total pressures are no higher than a few bars in experimental investigations. Only Heist et al.2 have reported measurements at total pressures up to 40 bar, using an upward thermal diffusion cloud chamber (TDCC). They observed an increase in critical supersaturation of n-propanol with helium pressure. Kane and El-Shall,10 also using a TDCC, recently reported the same behavior for the glycerol/helium system. In a TDCC type of setup, pressure can play a role in several ways. It may not only change the transport properties of the mixture (for which reliable correlations are not always available) but, as has been realized recently, the range of conditions at which the TDCC can be reliably operated also depends on total pressure.11 For the moment, it seems that expansion chamber techniques are at least more straightforwardly interpreted.

Unfortunately, no high pressure experiments (exceeding a few bars) from expansion chambers were available until now, except for the data by Looijmans et al.6 and recent work of Muitjens.12 In the present paper we report nucleation rate measurements in water/nitrogen systems at pressures up to 40 bar, obtained in the pulse-expansion wave tube setup developed by Looijmans et al.6,13,14. The technique is based on the creation of a well-defined pressure dip (nucleation pulse) at the end wall of the driver section of a shock tube, using the reflection of the shock wave at a local widening in the driven section. The wave tube can be operated at total...
(nucleation) pressures up to 50 bar, starting from initial pressures up to 100 bar.

The water/nitrogen system shows an increasing water fugacity with nitrogen pressure. To describe this behavior, we will not use the virial equation of state, but rather rely on (semi)empirical data of the so-called enhancement factor. The enhancement factor accounts for the increase in saturated (partial) vapor pressure due to the presence of the carrier gas.

When normalizing our data by theoretical predictions of the classical nucleation theory, taking into account the enhancement effect, a clear pressure trend is observed: nucleation rates tend to increase with pressure. This important observation is explained in terms of a decrease of the water surface tension by adsorption of nitrogen onto the droplet surface. A tentative model will be presented that qualitatively describes this phenomenon.

Finally, an explanation is proposed accounting for the difficulty of detecting pressure effects on nucleation. The competition between enhanced water fugacity and decreased surface tension will turn out to play a key role. Since both effects are caused by intermolecular interactions, this explanation might serve as well for other vapor/carrier mixtures.

**II. HIGH PRESSURE NUCLEATION**

Consider a mixture of a condensable component $i$ in the presence of one or more carrier gases. The system has a total pressure $p$, a temperature $T$, and a molar fraction of the vapor component $y_i$, not necessarily equal to the equilibrium fraction $y_i^{eq}$. The equilibrium condition, expressing the equality of chemical potentials of component $i$ in the vapor and the liquid phase, reads

$$RT \ln \left( \phi_i^{eq} y_i^{eq} p \right) = RT \ln \left( \phi_i^s p_i^s \right) + \int_{p_i^s}^{p} v_i'(p') dp' + RT \ln \left( y_i^{eq} x_i^{eq} \right).$$

(1)

In this expression, $\phi_i^{eq}$ and $\phi_i^s$ are fugacity coefficients of component $i$ in the mixture at equilibrium and in the pure component saturated state (with vapor pressure $p_i^s$). The integral, in which $v_i'$ is the partial molar volume of $i$ in the liquid, represents the shift in liquid chemical potential due to the carrier gas pressure, often referred to as the Poynting effect. Finally, the mole fraction in the liquid $x_i^{eq}$ accounts for the possible dissolution of the carrier gas into the liquid (for the sake of generality not yet excluded here), and the activity coefficient $y_i^{eq}$ expresses the nonideality of the resulting liquid mixture.

The enhancement factor $f_{i(j)}$ is defined as the multiplication factor between the saturated vapor pressure $p_i^s$ and the (enhanced) partial vapor pressure $p_i^{eq}(p,T)$ in the above equilibrium state. Since the partial pressure is defined as the product of mole fraction and total pressure, we have

$$f = \frac{p_i^{eq}(p,T)}{p_i^s(T)} = \frac{y_i^{eq}(p,T)p}{p_i^s(T)},$$

(2)

or, upon substitution of Eq. (1),

$$f = \frac{\phi_i^s}{\phi_i^{eq}} y_i^{eq} x_i^{eq} \exp \left[ \frac{1}{RT} \int_{p_i^s}^{p} v_i'(p') dp' \right].$$

(3)

As the system moves into a supersaturated state, there is no longer a macroscopic equilibrium. Yet, an equilibrium does exist between the vapor phase and a metastable droplet, known as the critical nucleus in the classical (capillary) droplet model. For this particular cluster size, the increase of chemical potential due to the internal (Laplace) pressure exactly balances the increased fugacity of the vapor with respect to the equilibrium state. The condition for this metastable equilibrium is (note the upper limit of the integration interval)

$$RT \ln (\Phi_{i,y_i,p}) = RT \ln (\phi_i^s p_i^s) + \int_{p_i^s}^{p + \frac{2\sigma_i}{r}} v_i'(p') dp'$$

$$+ RT \ln (\gamma_i x_i).$$

(4)

We now define the supersaturation of the vapor component $i$ as the ratio of its actual fugacity to that in the equilibrium state:

$$S = \frac{\phi_i y_i p}{\phi_i^{eq} x_i^{eq} p_i^s} = \frac{y_i p}{f \frac{p_i^s(T)}{p(T)}} \frac{1}{x_i^{eq}} \Phi_i \gamma_i.$$  

(5)

The fugacity coefficients $\Phi_i$ and $\Phi_i^{eq}$, accounting for the intermolecular force that a water molecule experiences from its surroundings, are generally not equal to unity for our high pressure systems. However, since vapor fractions in both the actual (supersaturated) and equilibrium states are very small, $\Phi_i$ and $\Phi_i^{eq}$ are equal to one another to a very high degree of approximation (nearly all neighbors are nitrogen molecules). Hence, from Eq. (5) we obtain

$$S = \frac{y_i}{y_i^{eq}} = \frac{\gamma_i x_i}{f \frac{p(T)}{p_i^s(T)}},$$

(6)

the expression that is used for our forthcoming calculations. It expresses the supersaturation in experimentally measurable quantities ($y_i$ and $p$), the familiar pure component saturated vapor pressure $p_i^s(T)$, and the enhancement factor $f$. The supersaturation as defined above is easily interpreted: being the ratio of actual fraction to equilibrium fraction, it is simply a measure of the “overpopulation” of the vapor phase. For low pressures, the enhancement factor $f$ is unity and the commonly used definition of $S$ as the ratio of actual vapor pressure to saturated vapor pressure is retrieved.

Alternatively, Eqs. (4) and (1) may be subtracted to yield

$$S = \frac{\gamma_i x_i}{y_i^{eq} x_i^{eq}} \exp \left[ \frac{1}{RT} \int_{p_i^s}^{p + \frac{2\sigma_i}{r}} v_i'(p') dp' \right].$$

(7)

We now apply the above result to the kind of mixture we are dealing with, i.e., small mole fractions of the condensing vapor in the gas state and negligible dissolution of the carrier gas into the liquid. In this case, all $x_i$’s and $y_i$’s equal unity. Moreover, we use the incompressible approximation for the liquid, so that the integration becomes trivial. Under these assumptions, Eq. (7) transforms into the familiar Kelvin relation,
In view of this unchanged Kelvin relation at high pressures, the expression for the nucleation rate according to the classical nucleation theory retains its commonly used form:\textsuperscript{19}

\[ J_{\text{CNT}} = \frac{2\sigma M (y_i p) \rho_i k_B T^2}{\pi N_A \rho_i \rho_w k_B T^2 S} \exp \left( -\frac{16\pi M^2 \sigma^3}{3N_A \rho_i \rho_w k_B T^3 \ln^2 S} \right), \]

where the factor $1/S$ has been included in the prefactor. This has recently been regarded as more consistent than omitting it, although there is still an ongoing discussion about this.\textsuperscript{20,21}

The partial vapor pressure in the prefactor has been written in the form $y_i p$.

**III. THE ENHANCEMENT FACTOR**

The description of the mixture using the concept of enhancement factors has the advantage that these factors can be obtained from experimentally observable quantities. Wylike and Fisher determined $f$ over a wide range of pressures and temperatures for the systems water/air\textsuperscript{15} and water/oxygen.\textsuperscript{16} They gravimetrically measured the water content of these mixtures, and calculated $f_w$ (enhancement factor of water) according to definition (2). These values were then interpolated using the virial equation of state, up to the third (interaction) virial coefficients. Much earlier, Hyland and Wexler\textsuperscript{17,18} followed the same procedure—up to the second virial coefficient—to obtain $f_w$ values of water/air even for temperatures below 0 °C. They tabulated values of $f_w$ and $f_{\text{ice}}$ (reliable for temperatures down to −50 °C), which are consistent with the Wylike and Fisher data for the higher temperatures.

Although the above authors used the results to find the second and third interaction virial coefficients, we need not make this detour: we can simply correlate the enhancement factors as a function of pressure and temperature. The only problem to overcome is that we need enhancement factors below the freezing point of water.

According to the assumptions in the preceding section and Eq. (3), the enhancement factor can be expressed as

\[ \ln f = \ln \left( \frac{\phi_i^{\text{eq}}}{\phi_i^{\text{vir}}} \right) + \frac{v_i (p - p_i^{\text{eq}})}{RT}. \]

For a fixed pressure, the experimental values of $f$ for water/air show a slight jump at 0 °C (see Fig. 1). This can only be caused by somewhat different Poynting factors due to the difference in molar volume between water and ice, since the gas contribution—the first term in Eq. (10)—is not affected by the water being frozen.

Since molar volumes for supercooled water are available,\textsuperscript{22} we were able to deduce the required enhancement factors for supercooled water according to

\[ \ln f_w(p, T) = \ln f_{\text{ice}}(p, T) + \frac{v_w - v_{\text{ice}}}{RT} (p - p_w^{\text{eq}}(T)). \]

![FIG. 1. Enhancement factor of water/air for a fixed pressure of 50 bar. Below 0 °C, ice values predicted by Hyland;\textsuperscript{18} above zero, values according to Wylike and Fisher.\textsuperscript{15} Note the slight jump at the freezing point.](image1)

Having all the enhancement factors available, we correlated them as a function of temperature and pressure. This is merely a matter of computational convenience, since such a correlation simply summarizes the available data in the tables of Refs. 15–18 and the values derived by us for supercooled water. For a fixed temperature, the logarithm of $f_w$ is approximately linear in the deviation from the pure saturated vapor pressure $(p - p_w^{\text{eq}})$. This comes as no surprise, since the departure of $f_w$ from unity is caused by the presence of the carrier gas. Expressing the correlation for each tabulated temperature as

\[ \ln f_w = b(T) \times [p - p_w^{\text{eq}}(T)], \]

the function $b(T)$ can be described by a third-order polynomial,

\[ b(T) = c_0 + c_1 T + c_2 T^2 + c_3 T^3, \]

without any disturbance visible at 0 °C, as is shown for water/air in Fig. 2. Values of the polynomial coefficients

![FIG. 2. Correlation coefficients from enhancement data of water, ice, and supercooled water in air (see text).](image2)
TABLE I. Values of polynomial coefficients of \( b(T) \) for several carrier gases. \( b(T) \) is obtained in units of \((\text{bar})^{-1}\).

<table>
<thead>
<tr>
<th>Carrier gas</th>
<th>( c_0 ) (\text{bar}^{-1})</th>
<th>( c_1 ) (\text{bar}^{-1} \text{K}^{-1})</th>
<th>( c_2 ) (\text{bar}^{-1} \text{K}^{-2})</th>
<th>( c_3 ) (\text{bar}^{-1} \text{K}^{-3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>( 4.186 \times 10^{-2} )</td>
<td>(-2.87 \times 10^{-4} )</td>
<td>(6.91 \times 10^{-7} )</td>
<td>(-5.63 \times 10^{-10} )</td>
</tr>
<tr>
<td>Oxygen</td>
<td>( 3.354 \times 10^{-2} )</td>
<td>(-2.30 \times 10^{-4} )</td>
<td>(5.50 \times 10^{-7} )</td>
<td>(-4.40 \times 10^{-10} )</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>( 4.420 \times 10^{-2} )</td>
<td>(-3.03 \times 10^{-4} )</td>
<td>(7.31 \times 10^{-7} )</td>
<td>(-5.98 \times 10^{-10} )</td>
</tr>
</tbody>
</table>

involved can be found in Table I.

As a last step, the enhancement factors for water/air and water/oxygen are linearly combined to water/nitrogen values, using the composition of dry air.\(^\text{23}\) This is a justified procedure, since the contributions to \( \ln(f_w) \) of the several constituents of air are additive. Air consists of 78.08% nitrogen, 20.95% oxygen, and about 1% of other gases, mainly argon. These other constituents are lumped with the oxygen, resulting in a 21.92% “lumped oxygen” content. The values of \( b(T) \) are accordingly obtained from

\[
b_{\text{N}_2} = \frac{b_{\text{air}} - 0.219 \times b_{\text{O}_2}}{0.781},
\]

resulting in the values for nitrogen given in Table I.

IV. NUCLEATION EXPERIMENTS

We performed the nucleation experiments in our pulse-expansion wave tube setup, described in detail elsewhere.\(^\text{6,7,13}\) A schematic picture is shown in Fig. 3. The device essentially consists of a shock tube, modified through a local widening in the low pressure section, just beyond the diaphragm. When the tube is operated—by rupture of the diaphragm—an expansion wave travels into the high pressure section (HPS). The shock wave, propagating in the reverse direction, is partly reflected at the widening as another small expansion, followed by a slight recompression as it reaches the constriction. This wave pattern travels back into the HPS, and effectively creates a short period of lowest pressure (the so-called “nucleation pulse”) at the HPS end wall. The pulse is then followed by a period of nearly constant pressure, allowing the droplets to grow to macroscopic sizes. Constant angle Mie scattering under 90° is used to determine the time-resolved droplet radius during the growth period. The combination of the growth pattern obtained in this way with the attenuation of the transmitted laser beam—using time-resolved extinction efficiencies—yields the droplet concentration. Finally, the nucleation rate \( J_{\text{exp}} \) is obtained by dividing the droplet concentration by the time duration of the pressure dip. The accuracy of the value obtained for \( J_{\text{exp}} \) is estimated to be better than 20%.

Apart from the nucleation rate, the thermodynamic state at which it occurs must be measured in order to compare the results to any theoretical model. The pressure history is monitored by a Kistler 603B dynamic pressure transducer, combined with a Druck PDCR200 sensor for the initial static pressure. The total nucleation pressure \( p_{\text{exp}} \) is obtained from averaging the pressure over the nucleation pulse (during which the pressure may vary by about 1%).

From the initial temperature \( T_0 \) and the pressures \( p_0 \) and \( p_{\text{exp}} \), the nucleation temperature \( T_{\text{exp}} \) is calculated using the principle of adiabaticity. Since we are dealing with moderately high pressures, Joule–Thomson cooling has to be taken into account. For an adiabatic process, we have from basic thermodynamics,

\[
c_p dT - T \frac{\partial V}{\partial T} dp = 0,
\]

where \( V \) is the molar volume of the mixture and \( c_p \) is the molar heat capacity. Using the definition of compressibility, \( Z = pV/RT \), the above expression can be transformed into

\[
dT = \frac{R}{c_p} \left[ 1 + T \frac{\partial Z}{\partial T} \right] \frac{dp}{p},
\]

Since \( Z \) and \( c_p \) are only weak functions of \( T \), we can approximate the solution for small pressure steps as

\[
\frac{T}{T_0} = \left( \frac{p}{p_0} \right)^\alpha,
\]

with

\[
\alpha = \frac{R}{c_p} \left[ 1 + T \frac{\partial Z}{\partial T} \right].
\]

We computed \( T_{\text{exp}} \) from \( p_0 \) and \( p_{\text{exp}} \) in 100 pressure steps, for each of which \( c_p \) and \( Z \) and its derivative \( (\partial Z/\partial T)_p \) are evaluated and substituted into Eq. (18). For the calculation of \( Z(p,T) \) and \( c_p(p,T) \), we used the most comprehensive correlation of PVT data currently available for nitrogen, involving 73 parameters.\(^\text{24}\) In these calculations, the influence of water can be neglected, since the vapor fractions are very small.\(^\text{25}\) The uncertainty in \( T_{\text{exp}} \), mainly caused by the relative error of 0.5% in the dynamic pressure measurement, is estimated to be 0.7 K.

The mole fraction of water vapor in the mixture was determined using a Vaisala Humicap 124B humidity transducer. The best accuracy achievable is 1% RH (relative humidity) at atmospheric conditions, according to the manufacturer. Although it was designed for use at high pressures, it must be used with some precaution: the device has to be

![DIagram](image-url)
calibrated with both the relative humidity and the pressure as parameters. The overall accuracy of the vapor fraction measurement is expected to be better than 5% at high pressures. A separate calibration setup is currently being used to improve the accuracy in future measurements.

The maximum uncertainty in the supersaturation \( S \) due to the errors in \( y_w \) and \( T_{\text{exp}} \) amounts to up to 10% of \( S \).

V. RESULTS AND DISCUSSION

In Table II, the results of our nucleation experiments in high pressure water/nitrogen mixtures are presented. In this table, we also give values for the supersaturation ratio \( S \), calculated according to Eq. (6).

In Fig. 4, the experimental nucleation rates are shown as a function of \( S \). At each constant temperature, we see the effect of total pressure: the \( J(S) \) curves belonging to different pressures are separately visible, the effect being more pronounced for the lowest temperature.

To demonstrate the pressure effect more clearly, we normalized the experimental nucleation rates by predictions of classical nucleation theory, according to Eq. (9). Figures 5 and 6 show the ratio of experimental to theoretical rates as a function of nucleation pressure and temperature, respectively. Again we see the data clouds of different pressures being separated, with the larger pressure trend at 230 K. Measurements at total pressures lower than 1 bar, obtained by Looijmans\(^7\) using the same setup, are included as a reference in Fig. 6. The new high pressure results appear to be consistent with these low pressure data.

Obviously, there exists a mechanism that facilitates the nucleation process of water at higher nitrogen pressures. This might bring about the conclusion that classical theory is lacking some feature that accounts for high-pressure behavior. However, the observed effect can—at least qualitatively—be explained within the scope of the classical nucleation picture: the surface tension of water decreases under moderately high pressures of many ambient gases.

This is illustrated in Fig. 7, taken from a paper by Masoudi and King,\(^26\) who measured the surface tension of water in the presence of several low molecular weight gases at 25 °C. The observed decay of \( s \) with \( p \) at 25 °C roughly explains half of the pressure trend in Fig. 5. However, since

\begin{table}
\centering
\begin{tabular}{cccccccc}
\hline
Run & \( p_0 \) (bar) & \( T_0 \) (K) & \( p_{\text{exp}} \) (bar) & \( T_{\text{exp}} \) (K) & \( y_w \times \times 10^3 \) & \( S \) & \( J_{\text{exp}} \) (cm\(^3\) s\(^{-1}\)) \\
\hline
89 & 23.37 & 293.25 & 10.19 & 230.5 & 2.41 & 16.2 & 2 \times 10^6 \\
90 & 23.47 & 293.75 & 10.02 & 229.5 & 2.36 & 17.3 & 2 \times 10^6 \\
91 & 23.47 & 293.95 & 10.08 & 230.0 & 2.55 & 17.8 & 1 \times 10^7 \\
77 & 57.96 & 291.95 & 25.81 & 230.0 & 0.88 & 14.3 & 5 \times 10^7 \\
79 & 57.46 & 292.95 & 25.33 & 230.2 & 1.03 & 16.2 & 1 \times 10^7 \\
80 & 57.46 & 292.85 & 25.10 & 229.5 & 1.07 & 18.0 & 8 \times 10^6 \\
83 & 90.23 & 291.65 & 41.21 & 231.1 & 0.58 & 12.3 & 4 \times 10^6 \\
84 & 90.54 & 291.85 & 41.33 & 231.2 & 0.59 & 12.5 & 9 \times 10^6 \\
85 & 90.03 & 291.35 & 41.69 & 231.8 & 0.61 & 12.2 & 4 \times 10^6 \\
86 & 90.43 & 292.05 & 40.80 & 230.6 & 0.63 & 13.9 & 8 \times 10^6 \\
87 & 90.29 & 292.65 & 41.21 & 231.8 & 0.63 & 12.5 & 8 \times 10^6 \\
94 & 17.56 & 294.75 & 9.83 & 249.3 & 9.39 & 9.8 & 3 \times 10^7 \\
95 & 17.96 & 295.25 & 9.88 & 248.4 & 9.40 & 10.7 & 2 \times 10^7 \\
96 & 17.81 & 295.45 & 9.96 & 249.8 & 9.48 & 9.6 & 3 \times 10^7 \\
97 & 17.76 & 295.25 & 10.22 & 251.6 & 9.56 & 8.3 & 5 \times 10^7 \\
98 & 18.06 & 295.45 & 9.96 & 248.7 & 9.37 & 10.5 & 2 \times 10^7 \\
99 & 17.96 & 295.45 & 10.05 & 249.8 & 9.31 & 9.5 & 8 \times 10^7 \\
72 & 42.96 & 291.55 & 24.73 & 248.0 & 3.65 & 10.1 & 2 \times 10^7 \\
73 & 43.02 & 291.85 & 25.01 & 249.0 & 3.70 & 9.4 & 2 \times 10^6 \\
74 & 42.42 & 291.45 & 25.52 & 251.1 & 3.63 & 7.8 & 1 \times 10^8 \\
75 & 42.62 & 292.05 & 25.27 & 250.6 & 3.82 & 8.5 & 3 \times 10^8 \\
58 & 69.48 & 292.95 & 39.78 & 248.4 & 2.08 & 8.3 & 1 \times 10^8 \\
61 & 69.78 & 293.35 & 40.23 & 249.3 & 2.36 & 8.7 & 6 \times 10^9 \\
62 & 69.68 & 291.35 & 40.52 & 248.2 & 2.11 & 8.7 & 9 \times 10^9 \\
63 & 68.58 & 292.15 & 40.12 & 249.3 & 2.29 & 8.5 & 2 \times 10^9 \\
\hline
\end{tabular}
\caption{Experimental values of nucleation rates and thermodynamic states \((p_0,T_0,y_w,S)\) of occurrence.}
\end{table}
the effect is ascribed to gas adsorption onto the liquid surface, it is expected to be more severe at lower temperatures. For the present case, this means that the surface tension lowering at 230 and 250 K might very well explain the full pressure influence observed in our measurements. We return to this problem in the next section.

Finally, one might wonder why pressure effects were not demonstrated earlier. An indication for this is Fig. 8, in which the experimental nucleation rates are plotted as a function of the commonly used “pure component value” of the supersaturation. This value is defined as the ratio of the partial water vapor pressure to the pure water saturation pressure, or \( \frac{y_w p_{\text{exp}}}{p_w^S} \). Equivalently, it is the value of \( S \) that is obtained upon putting \( f_w = 1 \) in Eq. (6). For each temperature, the points belonging to different total pressures practically overlap. Only for 230 K, we see the 40 bar \( J(S) \) curve slightly separated from the lower pressure curves. We are dealing here with quite a coincidence: the enhanced fugacity of water, tending to lower the supersaturation and thereby the nucleation rate, turns out to be practically compensated by the effect of decreasing surface tension. Since both effects have to do with molecular interactions of the condensing vapor and the carrier gas, such a partial compensation is expected to occur more generally, irrespective of the vapor/carry gas mixture. If no real gas effects are taken into account in the supersaturation, and the pure vapor surface tension is used, it is very well possible that pressure effects are not observed, despite their occurrence.

VI. HIGH PRESSURE SURFACE TENSION

Numerous publications exist in which the decrease of surface tension with pressure is addressed. As early as the beginning of the 1960s some papers appeared on the subject, treating it either theoretically or experimentally. For
water with low molecular weight gases, surface tensions have been reported by Masterton et al. and Massoudi and King. A serious problem in applying their results to the present nucleation data is the temperature. Practically all surface tension data have been measured at room temperature or higher, whereas we need values at lower temperatures, even for supercooled water. Since the decrease of surface tension is generally ascribed to adsorption of the inert component, the effect will be more pronounced at these lower temperatures. Clearly, no measurements of equilibrium surface tensions are possible at these conditions. Therefore, we have to refer to some physically based extrapolation. In the following, we will present a tentative model.

Consider a flat liquid surface with a nondissolving pressurizing gas above it. The derivative of surface tension with total pressure follows from the fundamental thermodynamic relation,

$$\frac{d\sigma}{dp}_{A,T} = \frac{\partial V}{\partial A}_{p,T}.$$  \hspace{1cm} (19)

This equation expresses the derivative in terms of the volume change accompanying an increase of surface area. Such an increase can happen in two ways: either by migration of a liquid molecule (species 1) from the bulk to the surface, or by adsorption of a gas molecule (species 2) onto the surface. The first event brings about a slight increase in system volume, since a molecule at the surface occupies a somewhat larger volume than in the bulk liquid. Adsorption of a gas molecule, restricting it to the surface layer, causes a considerable decrease in volume.

Mathematically, the derivative can be written as

$$\frac{d\sigma}{dp} = c_1'(v_1'-v_1) + c_2'(v_2'-v_2).$$  \hspace{1cm} (20)

where surface concentrations $c_1'$ and molecular volumes $v_1'$ in the gas, liquid, and surface have been defined. The difference of molecular volumes in the first term is small and nearly always negligible. For water/helium it is the only remaining term, resulting in a very slight increase of $\sigma$ with $p$. For water/nitrogen, all terms can be shown to be negligible compared to the last one, $-c_2'v_2'$. In this case, we have

$$\frac{d\sigma}{dp} = -c_2'v_2',$$  \hspace{1cm} (21)

which is the relation that is generally used to determine the amount of gas adsorption on a liquid surface. In view of the impossibility of measuring liquid surface tensions below the freezing point, we have to go the opposite way: we must derive surface tensions from extrapolated values of the surface adsorption.

For the nitrogen surface concentration we write $c_2' = n_0 \theta$, where $n_0$ is the number of adsorption sites per unit area and $\theta$ is the surface coverage. According to the simple Langmuir adsorption model, valid up to coverages of about 30% it can be expressed as

$$\theta = \frac{p}{p+p_L},$$  \hspace{1cm} (22)

where $p_L$ is the Langmuir reference pressure. The latter can be derived from a simple statistical mechanical model to give

$$p_L = \left[\frac{mk_BT}{2\pi \hbar^2}\right] k_BT \exp\left(-\frac{E_a}{k_BT}\right).$$  \hspace{1cm} (23)

where $m$ is the molecular mass of the adsorbing gas and $E_a$ is the adsorption energy per molecule. Finally, for the molecular volume in the gas phase we use the ideal value $v_2^2 = k_BT/p$.

Substituting the above assumptions into Eq. (21) we obtain

$$\frac{d\sigma}{dp} = -n_0 \frac{p}{p+p_L} k_BT = -\frac{n_0 k_BT}{p+p_L}.$$  \hspace{1cm} (24)

This expression can be straightforwardly integrated to

$$\sigma(p) = \sigma(0) - n_0 k_BT \ln\left(\frac{p+p_L}{p_L}\right).$$  \hspace{1cm} (25)

The form of the $\sigma(p)$ dependence observed in experiments (a decaying surface tension with pressure, with a positive second derivative) is very well reproduced by this relation. Although Massoudi and King represent $\sigma$ as a quadratic function of $p$, their data could as well be cast in a fit of the above form, without any loss of accuracy.

We are left with the problem of determining $n_0$ and $p_L$. The number of adsorption sites can easily be estimated to be approximately $6 \times 10^{18}$ m$^{-2}$. Using this value, the Langmuir pressure $p_L$ can be obtained from a fit to the $\sigma(p)$ data at room temperature. For the data in Fig. 7, a value of 326 bar is found. It is clear that the surface coverages are sufficiently low at this temperature for the Langmuir model to be valid. From $p_L$, the molecular adsorption energy $E_a$ is calculated using Eq. (23) to be 4.04 $\times 10^{-20}$ J, or 24.3 kJ per mole. If we assume $E_a$ to be independent of temperature and pressure, we can now calculate $p_L$ at the nucleation temperatures of interest: $p_L(250 \text{ K}) = 32 \text{ bar}$ and $p_L(230 \text{ K}) = 9.3 \text{ bar}$.

Obviously, these low values of $p_L$ lead to high values of the surface coverage $\theta$ (as large as 81% for 230 K and 40 bar), which violates the assumptions underlying the Langmuir model. We must therefore conclude that it is not useful to apply the present model to our nucleation conditions. However, our description gives some useful qualitative insights, which might be used as guidelines in developing more sophisticated models for the present range of temperatures and pressures.

VII. CONCLUSIONS

We have reported the first experimental data on high pressure nucleation in water with nitrogen as a carrier gas. Nucleation rates were measured at temperatures near 230 and 250 K, and nucleation pressures of 10, 25, and 40 bar. The results were obtained using our nucleation pulse-expansion wave tube, which is shown to be a very valuable tool in
studying high pressure nucleation and droplet growth phenomena. In evaluating our experimental results, real gas effects were taken into account in several ways.

Nucleation temperatures were obtained from the pressure drop in each experiment, using real gas thermodynamics to describe the adiabatic expansion and a comprehensive correlation of PVT data for nitrogen by Sychev et al.\textsuperscript{24} Supersaturation ratios were calculated taking into account the enhanced fugacity of water vapor in the presence of nitrogen gas. Quantitative values of the enhancement factors were correlated from gravimetric measurements by Wylie and Fisher\textsuperscript{15,16} and Hyland and Wexler.\textsuperscript{17,18}

Our results show a strong dependence of nucleation rates on total pressure: nucleation rates tend to increase with pressure when temperature and supersaturation are kept fixed. This observation is ascribed to the decrease of water surface tension with increasing nitrogen pressure. A qualitative model is presented to account for this effect; however, it is not ready for use at the nucleation conditions (low temperatures and high pressures) under consideration.

When nucleation rates are plotted as a function of the commonly used value of supersaturation (the partial vapor pressure over the pure component saturated vapor pressure) practically no pressure effect is visible. This can be explained by the compensating mechanism of enhanced vapor fugacity (hampering the nucleation process) and decreasing surface tension (facilitating nucleation). Since both are caused by molecular interactions, such a partial compensation is expected for other gas/vapor mixtures as well. This might explain the present ambiguity of observations concerning (the existence of) pressure effects on nucleation.

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APPENDIX: PHYSICAL PROPERTIES OF PURE WATER

Molar mass:

\[ M = 0.018016 \text{ (kg mole}^{-1} \text{)}. \]  

(A1)

Saturated vapor pressure:

\[
p_v^s(T) = 610.8 \times \exp \left[ -5.1421 \ln \left( \frac{T}{273.15} \right) - 6828.77 \left( \frac{1}{T} - \frac{1}{273.15} \right) \right] \text{ (Pa)}. \]  

(A2)

Liquid density:

\[ \rho_l = 999.84 + 0.086(T - 273.15) - 0.0108(T - 273.15)^2 \text{ (kg m}^{-3} \text{).} \]  

(A3)

Surface tension:

\[ \sigma = 0.111773(1 - T/647.3)^{0.712012} \text{ (N m}^{-1} \text{).} \]  

(A4)


\textsuperscript{9} Compressibility effects are mainly caused by the very high internal pressure in the classical picture of the critical nucleus. This Laplace pressure, equal to \(2\sigma/r\), can be as large as a few thousand bars. Compared with this pressure, the total nucleation pressure is insignificant.


\textsuperscript{14} K. N. H. Looijmans and M. E. H. van Dongen, Exp. Fluids (to be published).


\textsuperscript{24} V. V. Sychev, A. A. Vasserman, A. D. Kozlov, G. A. Spiridonov, and V. A. Tsymarny, \textit{Thermodynamic Properties of Nitrogen} (Springer Verlag, Berlin, 1987).

\textsuperscript{25} The use of different “equations of state” to describe the PVT behavior here and the enhancement effect in Sec. III is only an apparent inconsistency: it is justified by the simple argument that both properties are best described by the respective correlations mentioned.


\textsuperscript{32} Although Massoudi and King (Ref. 26) report no pressure dependence at all for the water/helium surface tension, other authors (Refs. 30 and 27) claim to observe a slight increase with pressure.