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The Critical Supersaturations Predicted by Nucleation Theory

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A general set of equations is derived for calculating the supersaturation required to obtain a given rate of nucleation. This set is general enough to encompass all the present theories, the classical theory, the Lothe–Pound theory, the Reiss–Katz–Cohen theory, a recent theory by H. Reiss, and any other theory which includes a size-dependent correction to the classical theory. Comparison of these predictions is made for various substances.

KEY WORDS: nucleation; condensation; supersaturation; fluids.

The classical theory of the homogeneous nucleation of a liquid from its supersaturated vapor was developed from 1925–1942 by Volmer, Becker, and Doering,(1) and Zeldovich(2) and can most briefly be summarized as follows. Using detailed balancing, one obtains the following result for the rate of nucleation, thus reducing the rate problem to one of determining the "equilibrium" concentration, n_i, of clusters containing i molecules:

$$J = \beta \Big/ \sum_{i=1}^{\infty} [s_i n_i]^{-1} \tag{1}$$

where

$$\beta = \alpha P/(2\pi mkT)^{1/2}, \qquad s_i = (36\pi v^2)^{1/3}\, i^{2/3}$$

where J is the number of nuclei formed per unit time per unit volume, β is the rate at which ideal-gas molecules impinge on a unit surface, and s_i is the surface area of a cluster containing i molecules; and where P is pressure, T is temperature, m is mass per molecule, k is Boltzmann's constant, v is the volume per molecule in the

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liquid phase, and α is the mass accommodation coefficient ($\alpha \leqslant 1$). The classical theory assumes that the free energy of a cluster containing i molecules is equal to that of i molecules in the liquid phase plus a surface free energy. Using this assumption one can easily show$^{(3)}$ that

$$n_i = N \exp[i \ln S - \gamma i^{2/3}] \tag{2}$$

where

$$\gamma = (36\pi v^2)^{1/3}\, \sigma/kT \tag{3}$$

σ is the surface free energy, $S \equiv P/P_e$ is the supersaturation, P_e is the equilibrium vapor pressure, and N is the total number of clusters of all sizes per unit volume. It is important to realize that N, assuming the supersaturated gas to be at a sufficiently low pressure to be ideal, is to be obtained from the relation $N = P/kT$.$^{(3)}$

Various authors$^{(4-7)}$ have criticized and offered corrections to Eq. (2). These corrections are usually given in terms of a size-dependent multiplicative factor, f_i. It is convenient to put the various corrections into the exponential of Eq. (2) which thus becomes

$$n_i = N \exp[g_i + i \ln S - \gamma i^{2/3}] \equiv N \exp[U_i] \tag{4}$$

where $g_i = \ln f_i$ and, by definition, $U_i \equiv g_i + i \ln S - \gamma i^{2/3}$.

The rate of nucleation has traditionally been evaluated$^{(2)}$ by converting the summation in Eq. (1) to an integration, expanding the logarithm of n_i in a Taylor series about its minimum value and extending the lower limit of integration to $-\infty$. In the immediately following paper, E. R. Cohen$^{(8)}$ critically discusses these approximations, providing both estimates and bounds to the errors due to them. For all substances, and for all nucleation rates for which the theory can be justified physically, he finds that the mathematical approximations introduce an error of less than 1%.

Converting the summation to an integration, Eq. (1) is replaced by

$$J = \beta \Big/ \int_1^\infty [s(x)\, n(x)]^{-1}\, dx \tag{1$'$}$$

where the continuous variable x now replaces the discrete variable i. Substituting Eq. (4) and the definitions of β and s into Eq. (1′), one obtains

$$J = \frac{\alpha N P (36\pi v^2)^{1/3}}{(2\pi m k T)^{1/2}} \Big/ \int_1^\infty x^{-2/3} \exp[-U(x)]\, dx. \tag{5}$$

$\bar{x}$, the value of x at the minimum of $n(x)$, and S, the critical supersaturation, are related by the equation

$$\ln S = 2\gamma/(3\bar{x}^{1/3}) - g'(\bar{x}) \tag{6}$$

which immediately follows upon applying the definition of $\bar{x}$, i.e., $n'(\bar{x}) = 0$, to Eq. (4). The integral can be readily approximated, with the result that

$$J = \left(\frac{2\sigma}{\pi m}\right)^{1/2} \frac{\alpha N P v}{kT} \left[1 + \frac{9\bar{x}^{4/3}}{2\gamma} g''(\bar{x})\right]^{1/2} \exp\left[g(\bar{x}) - \bar{x} g'(\bar{x}) - \frac{\gamma}{3} \bar{x}^{2/3}\right] \tag{7}$$

where γ has been defined in Eq. (3), and where Eq. (6) has been used. From Eq. (7) we see that a size-dependent correction factor not only affects the rate of nucleation for a given value of S explicitly (the $g(\bar{x})$ term) but also implicitly through Eq. (6) which defines the value of $\bar{x}$ and, to a minor extent, through its second derivative. Note that Eq. (6) is not the Kelvin equation! Only in the case of the classical theory, where $g'(\bar{x}) = 0$, does it reduce to the Kelvin equation. With the inclusion of a size-dependent correction, the cluster of critical size (i.e., a cluster in unstable equilibrium with its surrounding gas) does not contain the same number of molecules as a droplet in equilibrium with its surrounding gas.

The introduction of an $\bar{x}$-dependent correction makes it necessary to treat $\bar{x}$ instead of S as the central variable. Equation (7) can be readily solved using Newton–Raphson iteration, noting that almost all the dependence on $\bar{x}$ is in the exponent. Equation (7) depends on P and thus on the supersaturation $S = P/P_e$; in performing the iteration both Eqs. (6) and (7) must be used. Expressing Eqs. (6) and (7) in directly measurable variables one obtains for the $(n + 1)$th estimate of $\bar{x}$,

$$\bar{x}_{n+1} = \bar{x}_n - [U(\bar{x}_n) + A(\bar{x}_n) + B]/U'(\bar{x}_n) \tag{8}$$

where

$$U(\bar{x}_n) = g(\bar{x}_n) - \bar{x}_n g'(\bar{x}_n) - \gamma \bar{x}_n^{2/3}/3$$

$$A(\bar{x}_n) = 2 \ln S_n + \tfrac{1}{2} \ln[1 + 4.5\bar{x}_n^{4/3} g''(\bar{x}_n)/\gamma]$$

$$B = \ln \left[\frac{\alpha}{J} \left(\frac{P_e}{RT}\right)^2 \left(\frac{2\sigma M}{\pi}\right)^{1/2} \frac{N_0^{3/2}}{d}\right]$$

$$\ln S_n = 2\gamma/\bar{x}_n^{1/3} - g'(\bar{x}_n), \qquad \gamma = \left(\frac{36\pi N_0 M^2}{d^2}\right)^{1/3} \frac{\sigma}{RT}$$

and where N_0 is Avogadro's number, d is the density of the liquid, M is the molecular weight, and R is the gas constant.

The critical supersaturation, i.e., the supersaturation at a rate of nucleation of one nucleus cm^{-3} sec^{-1}, can be obtained from the general solution given by Eqs. (8) once one specifies $g(\bar{x})$ and its derivatives. The classical theory has no correction factor; thus, trivially, g and its derivatives are:

$$g_{\text{classical}} = 0, \qquad g'_{\text{classical}} = 0, \qquad g''_{\text{classical}} = 0. \tag{9}$$

Lothe and Pound$^{(4)}$ have argued that the free energy of a cluster should be increased by a translational and rotational free energy and decreased by the loss of six vibrational degrees of freedom whose value they approximately estimated as $-kT \ln 10^3$. Thus

$$g(\bar{x})_{LP} = \ln \left\{ \left(\frac{2\pi \bar{x} mkT}{h^2}\right)^{3/2} v_g \cdot \pi^{1/2} \left(\frac{8\pi^2 kT}{h^2} \cdot \tfrac{2}{5}\bar{x}m\right)^{3/2} \frac{3\bar{x}v}{4\pi} \cdot 10^{-3} \right\} \tag{10}$$

where h is Planck's constant and $v_g = kT/P$ is the volume per molecule in the gas phase. Combining the variables and constants and converting to the directly measurable variables used in Eq. (8), one obtains

$$g(\bar{x})_{LP} = \ln\left\{1.183\,\frac{(MRT)^4}{N_0{}^8h^6dP_e}\right\} - \ln S + 4\ln\bar{x},$$

$$g'(\bar{x})_{LP} = 4/\bar{x}, \qquad g''(\bar{x})_{LP} = -4/\bar{x}^2 \tag{11}$$

Note that instead of P, the identity $P \equiv P_eS$ was used to emphasize that in the iterative solution of Eqs. (8) and (10) it is necessary to use the current value of S.

Reiss and Katz,⁽⁵⁾ and Reiss, Katz, and Cohen⁽⁶⁾ argued that it is necessary to start from the partition function of the entire system and in a consistent fashion make all microscopic corrections (rotation, translation) before making the thermodynamic identification with the drop. Reiss and Katz assumed that the center of mass of a droplet with fixed boundaries fluctuates over the entire droplet. To be more realistic, Reiss, Katz, and Cohen (to be referred to as RKC) made a model calculation for the actual fluctuation of the center of mass. The RKC correction lies between the following limits:

$$g(\bar{x})_{\mathrm{RKC1}} = \tfrac{3}{2}\ln(6\bar{x}/\pi) \quad \text{and} \quad g(\bar{x})_{\mathrm{RKC2}} = \ln\left\{\left(\frac{12}{\pi}\right)^{3/2}\frac{v_g}{v}\,\bar{x}^{1/2}\right\} \tag{12}$$

When converted to directly measurable variables they become

$$g(\bar{x})_{\mathrm{RKC1}} = 0.970 + 3/2\ln\bar{x},$$

$$g'(\bar{x})_{\mathrm{RKC1}} = 3/(2\bar{x}), \qquad g''(\bar{x})_{\mathrm{RKC1}} = -3/(2\bar{x}^2) \tag{13}$$

and

$$g(\bar{x})_{\mathrm{RKC2}} = \ln[7.465RTd/MP_e] - \ln S + \tfrac{1}{2}\ln\bar{x}$$

$$g'(\bar{x})_{\mathrm{RKC2}} = 1/(2\bar{x}), \qquad g''(\bar{x})_{\mathrm{RKC2}} = -1/(2\bar{x}^2) \tag{14}$$

Reiss⁽⁷⁾ has recently evaluated the correction to nucleation theory using the same basic philosophy, but dividing up phase space in such a manner that the answer was obtained directly in terms of the free energy of a drop. This probably more accurate approach leads to the following correction,

$$g(\bar{x})_R = \ln(P_xV/NkT) \tag{15}$$

where P_x is the pressure of the gas phase in unstable equilibrium with a drop containing $\bar{x}$ molecules and is obtained from Kelvin equation

$$\ln S_x = \ln(P_x/P_e) = 2\gamma/(3\bar{x}^{1/3}) \tag{16}$$

Note the difference between Eqs. (6) and (16). This is because Eq. (6) applies to a cluster and Eq. (16) to a drop. Reiss⁽⁷⁾ discusses the source of this correction, pointing out that it arises only because one calculates the properties of a cluster by placing it in equilibrium with the surrounding gas. In reality it is only the critical cluster,

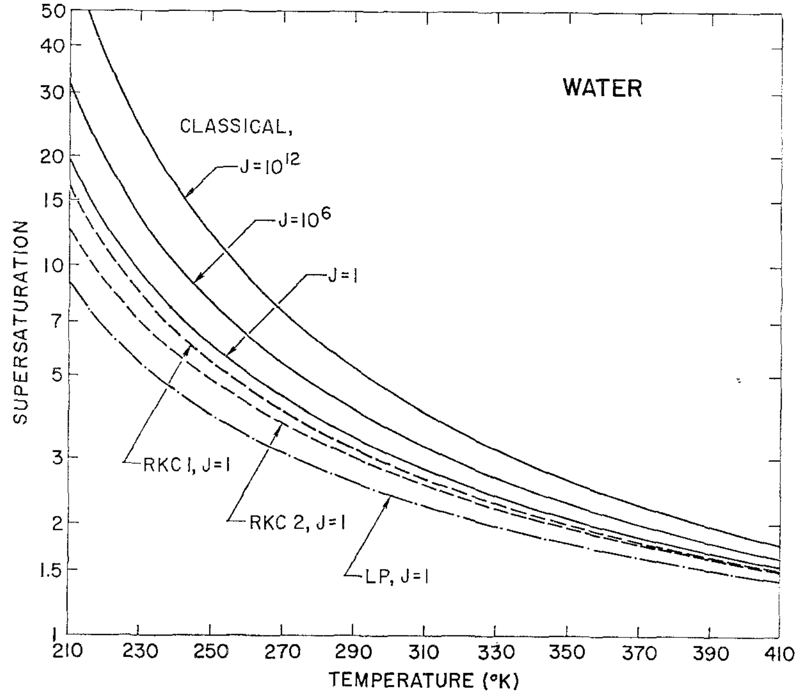

Fig. 1. The predicted critical supersaturation required for the homogeneous nucleation of liquid water from its supersaturated vapor for various theories and rates of nucleation.

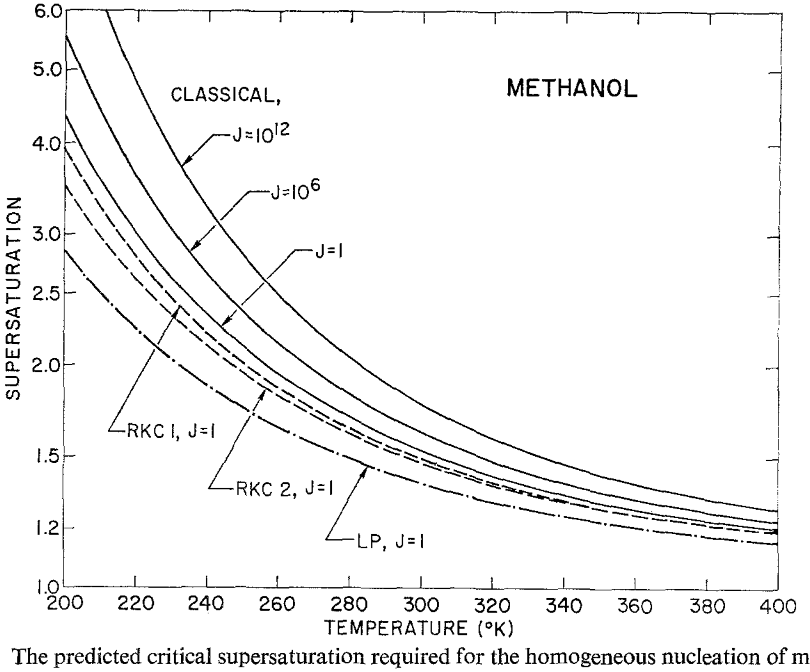

Fig. 2. The predicted critical supersaturation required for the homogeneous nucleation of methanol from its supersaturated vapor for various theories and rates of nucleation.

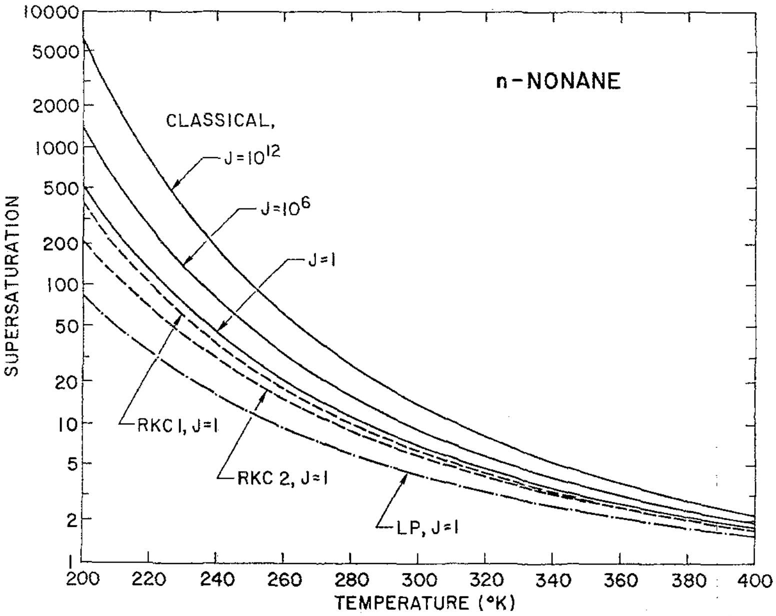

Fig. 3. The predicted critical supersaturation required for the homogeneous nucleation of *n*-nonane from its supersaturated vapor for various theories and rates of nucleation.

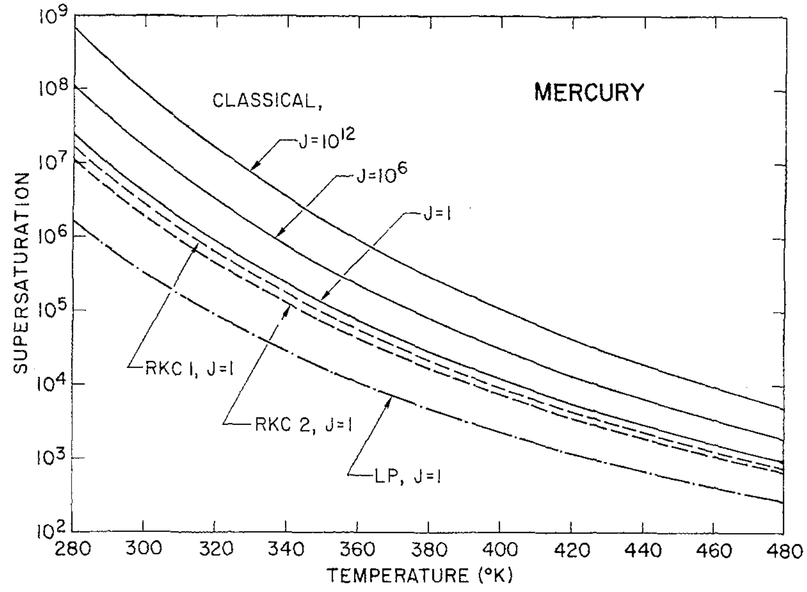

Fig. 4. The predicted critical supersaturation required for the homogeneous nucleation of mercury from its supersatured vapor for various theories and rates of nucleation.

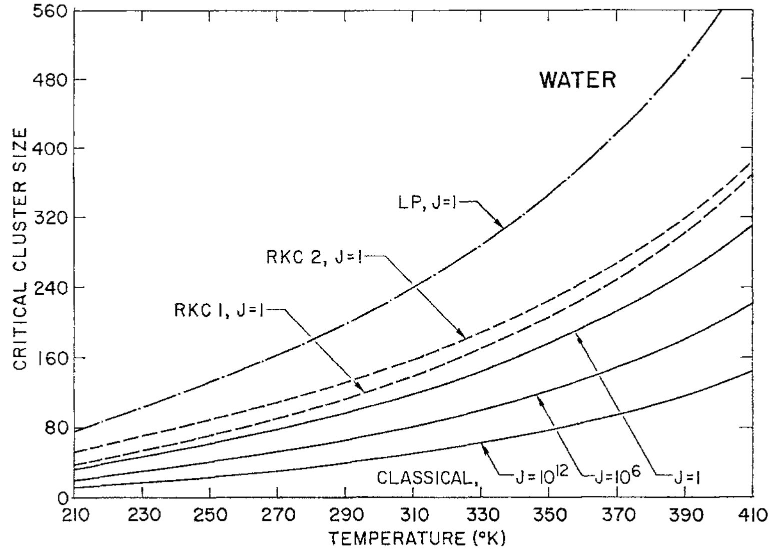

Fig. 5. The predicted size of the critical-size cluster of water at the supersaturations given in Fig. 1.

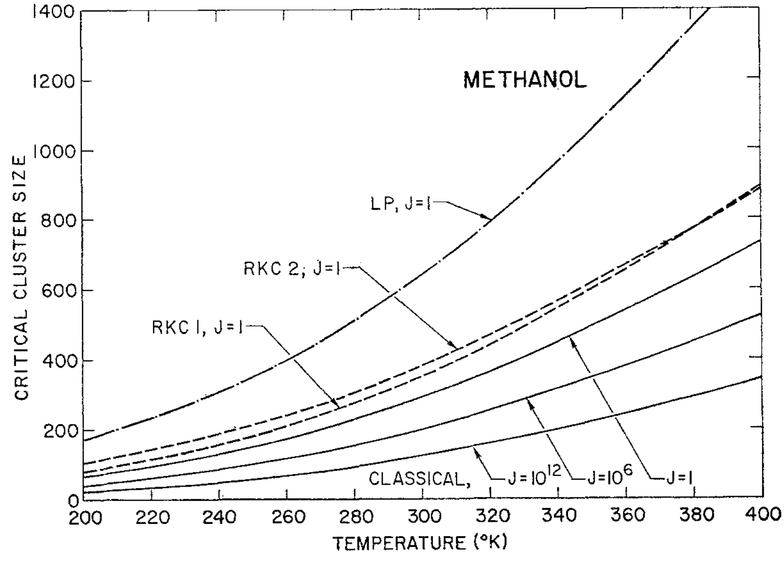

Fig. 6. The predicted size of the critical-size cluster of methanol at the supersaturations given in Fig. 2.

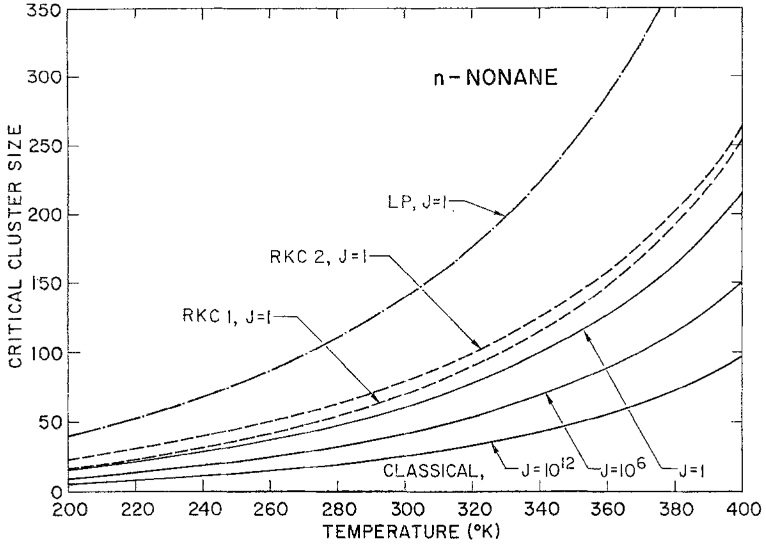

Fig. 7. The predicted size of the critical-size cluster of *n*-nonane at the supersaturations given in Fig. 3.

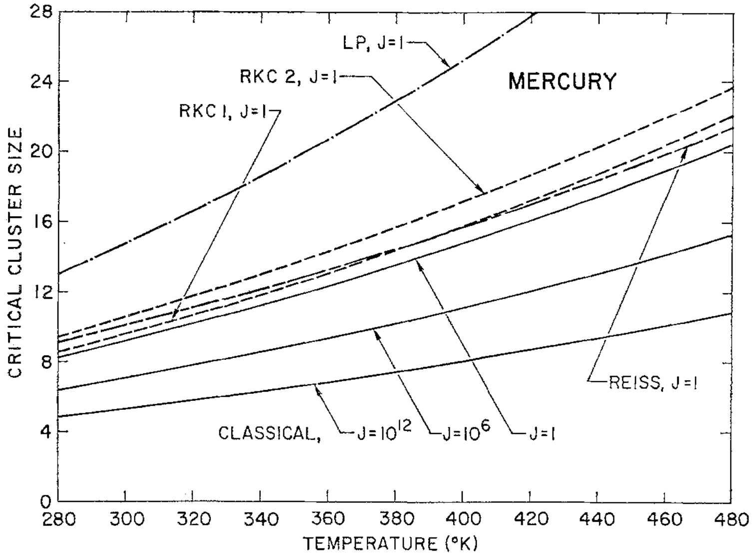

Fig. 8. The predicted size of the critical-size cluster of mercury at the supersaturations given in Fig. 4. Since the Reiss theory *is* distinguishable from the classical theory on the scale of this plot, it has been included for a rate of nucleation $J = 1$ nucleus cm^{-3} sec^{-1}. In general the Reiss theory predicts a critical cluster size approximately 1 molecule larger than does the classical theory.

and not all clusters, which are in equilibrium. Assuming the gas phase to be ideal, i.e., $V/NkT = 1/P$, Eq. (15) becomes

$$g(\bar{x})_R = \ln(P_x/P) \tag{17}$$

Combining Eqs. (16) and (17), g and its derivatives for the Reiss theory are:

$$\begin{gathered} g(\bar{x})_R = 2\gamma/(3\bar{x}^{1/3}) - \ln S, \\ g'(\bar{x})_R = 2\gamma/(9\bar{x}^{4/3}), \qquad g''(\bar{x})_R = 8\gamma/(27\bar{x}^{7/3}). \end{gathered} \tag{18}$$

Equations (8–18) thus provide the formulas needed to evaluate the critical supersaturation of a substance for the various theories. One finds that for all substances the Reiss theory predicts a critical supersaturation which differs from the classical theory by at most 0.01%. In Figs. 1 through 4 are presented the predicted supersaturations for the Reiss or classical theory, for the Lothe–Pound theory, and for the upper and lower limits of the Reiss–Katz–Cohen theory for a representative set of substances (water, methanol, *n*-nonane and mercury) over a 200°K temperature range for a rate of nucleation of 1 nucleus $\text{cm}^{-3}\,\text{sec}^{-1}$ and a condensation coefficient α equal to unity.[3] To show the variation of supersaturation with rate of nucleation, the classical or Reiss values in Figs. 1–4 (indistinguishable on the scale of these plots) have been plotted for rates of nucleation of 10^6 and 10^{12} nuclei $\text{cm}^{-3}\,\text{sec}^{-1}$, with $\alpha = 1$. In Figs. 5–8 are plotted the predictions of the various theories of the size of critical cluster, $\bar{x}$, over the same temperature range, rates of nucleation, and substances as in Figs. 1–4.

Although the Reiss theory predicts a critical supersaturation which differs negligibly from that of the classical theory, it predicts that the critical nucleus will contain one molecule more than is predicted by the classical theory. Such a difference may be important for substances like mercury whose predicted critical nucleus size for a rate of nucleation of 1 nucleus $\text{cm}^{-3}\,\text{sec}^{-1}$ is either 9 or 10 molecules at 300°K depending on which theory one uses. It is also important for most of the experiments done with supersonic nozzles where, since the rates of nucleation are typically 10^{12}–10^{18} nuclei $\text{cm}^{-3}\,\text{sec}^{-1}$, the critical sizes are much smaller. For example, at $J = 10^{12}$ nuclei $\text{cm}^{-3}\,\text{sec}^{-1}$, at 220°K, the classical theory predicts a critical size cluster of nonane containing 8 and of water containing 14 molecules while the Reiss theory predicts 9 and 15 molecules respectively.

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[3] Equation (8) is very simple and can be readily solved on a desk calculator, given the vapor pressure, surface free energy, density of the liquid, and molecular weight of the substance at the temperature of interest. However, it is very tedious to perform such a calculation for several theories, and many different substances, and over a range of temperatures, and this is best done on an electronic computer. A Fortran IV program has been written which will perform such a calculation and plot the results, for the following substances: methanol, ethanol, *n*-propanol, *n*-butanol, *n*-pentane, *n*-hexane, *n*-heptane, *n*-octane, *n*-nonane, *n*-decane, water, mercury, and 2-phenylpentane, and can be easily modified for any other substance. A copy of this program and of the computer output for all of the above substances is available by ordering document NAPS-01058, from ASIS–National Auxiliary Publications Service, c/o CCM Information Corporation, 909 Third Avenue, New York, New York, 10022, remitting $2.00 for each microfiche or $7.90 for each photocopy.

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