Kinetics and Catalysis, Vol. 41, No. 1, 2000, pp. 1–11. Translated from Kinetika i Kataliz, Vol. 41, No. 1, 2000, pp. 5–16.

A Kinetic Model for Nonisothermic Homogeneous Nucleation

V. N. Smirnov

Semenov Institute of Chemical Physics, Russian Academy of Sciences, Moscow, Russia

Received April 1, 1998

Abstract—A model for isothermal homogeneous nucleation is proposed that improves the classical model. A quasiequilibrium distribution of clusters was calculated on a basis of the Frenkel'–Lothe–Pound theory. The dependence of the free energy of clusters on their size was represented by an interpolation formula relating the free energy of dimers and large clusters to which a notion of macroscopic surface tension is applicable. The nucleation rate and the dependence of the cluster temperature on their size were calculated by balance equations describing the heating of from a cluster due to the condensation of monomers and its cooling due to collisions with an ambient gas. It is shown that the nucleation rate in excess buffer gas is higher than for the pure condensing gas by approximately two orders of magnitude. The model adequately describes the experimental data for the nucleation of methanol supersaturated vapor.

INTRODUCTION

Starting from early fundamental studies described in [1–4], building an adequate cluster model for the calculation of the equilibrium size distribution of clusters remains the mainstream research in nucleation theory. This distribution is needed for the calculation of the nucleation rate.

In the classical nucleation model, clusters are viewed as macroscopic drops; the stability of the drops depends on their size and the free energy of molecules (atoms) in the bulk and on the surface. Note that, despite its simplicity, the drop model in many cases gives results close to experimental data. However, for many systems, the difference between the nucleation rate predicted by classical theory and its experimental value reaches several orders of magnitude. Therefore, researchers turned to the dependence of the specific free energy on the cluster radius [5–9].

Lothe and Pound [10, 11] substantially advanced nucleation theory when they pointed out that a drop in the gas phase must have translational and rotational degrees of freedom. The drop loses six degrees of freedom characteristic of an imaginary drop in the bulk of the condensed phase. Lothe and Pound's findings formed the ground for the development of the molecular approach to the nucleation problem [12–18]. However, it should be mentioned that Frenkel' [4, p. 348] was the first to propose an expression for the quasiequilibrium concentration of clusters that takes into account translational and rotational degrees of freedom, but he did not use this expression for the calculation of the nucleation rate [4].

Another important problem in homogeneous nucleation theory is the energy exchange between clusters and ambient gas. In the classical model, the temperatures of clusters and ambient gas are considered the same. However, some experimental data and theoretical findings (see [7, 19] and references therein) show that this is not the case. The process should be considered nonisothermic.

In our opinion, the nonisothermicity of homogeneous nucleation was analyzed in most detail in [19], where nonisothermicity was taken into account by solving a system of kinetic equations of the mass and energy balance for water clusters consisting of less than 200 molecules. This approach enables the calculation of the changes in the concentration and temperature of clusters of each size with time and, consequently, the flux (or the rate) of nucleation. However, the solution to this problem involves much calculation and is not illustrative. In this work, we derived an expression for the rate of nonisothermic homogeneous nucleation, which is a simple modification of the classical expression [7] and automatically transforms to it when the temperatures of clusters and the ambient medium are the same.

Predictive power of the model was illustrated by the example of the methanol vapor nucleation. This compound was chosen for the following reasons. One is that comprehensive experimental data on the nucleation rate over a wide ranges of temperatures and degrees of supersaturation are available for this compound [20–22]. Furthermore, some thermodynamic parameters of clusters containing from 2 to 256 molecules were theoretically obtained in [23–25], the accommodation coefficient for the addition of a methanol molecule to the bulk of liquid methanol at room temperature was calculated in [26], and the concentrations of dimers and larger clusters in methanol vapor were measured in [27, 28].

0023-1584/00/4101-0001$25.00 © 2000 MAIK "Nauka/Interperiodica"

THERMOCHEMICAL PARAMETERS OF CLUSTERS

As already mentioned, the classical nucleation theory is based on the drop model of clusters. In this model, the basic parameter is the free energy of surface tension. However, the applicability of this parameter to small clusters, in which all or the most part of monomers are on the surface, is problematic [7, 14]. (Hereafter, by a monomer is meant a single atom or molecule comprising a cluster.)

Therefore, many researchers considered corrections for the dependence of the specific free energy on the cluster (drop) size [7, 8, 29–31]. Others attempted avoiding the use of the free energy of surface tension [14, 15, 17]. In these models, clusters are treated as large molecules whose thermodynamic parameters can be calculated by the methods of statistical mechanics. This approach sounds most reasonable, although it is difficult to put into practice: it is necessary to calculate the frequencies, dissociation energy, and geometry of clusters containing up to several thousands of atoms. This can be done with molecular dynamics methods (see [25] and references therein) but requires much calculation.

An alternative approach is to construct interpolations describing the free energy of clusters as a continuous function of their size [8, 13, 14, 30]. The main idea of this approach is the expansion of the free energy (the chemical potential) of clusters in terms of their radii or $i^{1/3}$ (i is the number of atoms in the cluster). At $i = 1$ and $i = 2$, this expansion should give the free energy of monomers and dimers and transform into the expression for the free energy in the classical drop model when $i \longrightarrow \infty$. However, as mentioned in [32], the requirement to the interpolation formula to give the free energy of monomers is physically unjustified because monomers are not clusters. This is evident when monomers are represented by atoms, which, unlike clusters, have neither rotational nor vibrational degrees of freedom. Therefore, we used the idea of the approach developed in [8, 30] but abandoned the extension of the free energy interpolation formula to monomers.

In the description of thermodynamic parameters of clusters, their translational, rotational, and vibrational degrees of freedom and the partition function of substitution were explicitly taken into account.

According to the mass action law, the equilibrium concentration of clusters with a size of i can be calculated by the expression

$$c_i = q_i(c_1/q_{1,g})^i, \quad (1)$$

where q_i is the partition function for the cluster containing i monomers, and $q_{1,g}$ is the partition function for a monomer in the gas phase. In expression (1), the monomer concentration c_1 is determined by the experimental conditions, and $q_{1,g}$ is calculated by the standard procedure [33]. An expression for q_i can be derived within the framework of a somewhat modified Frenkel'–Lothe–Pound method [4, 10, 11]. Let us represent a cluster as a piece of the condensed phase having surface and external rotational and translational degrees of freedom. For this cluster, we can write [6]:

$$q_i = \frac{q_{i,\text{trans}}q_{i,\text{rot}}}{q_{\text{rep}}}\left(\frac{q_{1,g}}{c_{1,\text{sat}}}\right)\varphi_{i,s}, \quad (2)$$

where $\varphi_{i,s}$ is a factor that accounts for the contribution of the surface, $c_{1,\text{sat}}$ is the concentration of monomer saturated vapor, and q_{rep} is the partition function of replacement. The partition functions for the cluster over its external translational, $q_{i,\text{trans}}$, and rotational, $q_{i,\text{rot}}$, degrees of freedom have the form [6]:

$$q_{i,\text{trans}} = (2\pi i m_1 kT/h^2)^{1.5}, \quad (3)$$

$$q_{i,\text{rot}} = (8\pi I_i kT/h^2)^{1.5}\pi^{0.5}, \quad (4)$$

where I_i is the inertia momentum of a spherical cluster with a size of i:

$$I_i = (2/5)i^{5/3}m_1 v_1^{2/3}(3/4\pi)^{2/3}. \quad (5)$$

Here, m_1 and v_1 are the weight and the volume of the monomer in the condensed phase. The partition function of substitution is introduced to account for the loss of six internal degrees of freedom by the cluster transferred from the condensed phase into the gas phase [4, 10, 11], in which these degrees transform to three translational and three rotational degrees (see below).

Combining (1) and (2), we obtain

$$c_i = c_{1,\text{sat}}\left\{\frac{q_{i,\text{trans}}q_{i,\text{rot}}}{c_{1,\text{sat}}q_{\text{rep}}}\right\}\left(\frac{c_1}{c_{1,\text{sat}}}\right)^i\varphi_{i,s}. \quad (6)$$

The expression for c_i is written in the form that is convenient for comparison with the classical formula. Indeed, by setting the term in braces to unity and $\varphi_{i,s} = \exp[-(36\pi)^{1/3}v_1^{2/3}\sigma i^{2/3}/kT]$, where σ is the free energy of surface tension, we obtain the classical formula for the quasiequilibrium concentration of clusters [34]. The correction to the partition functions for the surface effects can be represented as [4]

$$\varphi_{i,s} = \exp\left(-\frac{G_{i,s}}{kT}\right), \quad (7)$$

where

$$G_{i,s} = E_{i,s}(0) - T\Phi_{i,s}, \quad (8)$$

$$\Phi_{i,s} = S_{i,s} - [E_{i,s}(T) - E_{i,s}(0)]/T. \quad (9)$$

We postulate that, when $i \longrightarrow \infty$, $G_{i,s} = G_1 i_s$, $E_{i,s}(0) = E_1 i_s$, and $\Phi_{i,s} = \Phi_1 i_s$. Here, i_s is the number of surface molecules; and G_1, E_1, and Φ_1 are the changes of the free energy, internal energy, and reduced thermodynamic potential corresponding to the transfer of a molecule from the bulk of the macroscopic condensed phase to

its surface. For methanol, whose vapor nucleation is taken as an example to illustrate predicting capabilities of the model, we obtained (from the data [35])

$$E_1 = 5.96 \times 10^{-21} \text{ J/molecule}, \quad (10)$$

$$\Phi_1 = (2.31 \times 10^{-17} + 1.84 \times 10^{-19} T) \text{ J/molecule}^{-1} \text{ K}^{-1}. \quad (11)$$

For dimers, the $E_{2,s}(0)$ and $\Phi_{2,s}$ values can be determined from the experimental data [27, 28] or calculated by statistical mechanics methods from the results of quantum-mechanical calculations [23, 24].

We used the dissociation energy of dimers $E_2 = 4.0 \times 10^{-20}$ J/molecule; this value was obtained by quantum-chemical calculations in [24]. The frequencies and geometry of dimers can also be calculated by quantum-chemical methods; however, we have not found such data in the literature. Therefore, we calculated the partition functions for dimers as follows. First, we calculated the frequency of the stretching vibrations of hydrogen bonds between monomers (CH_3OH molecules) on the assumption that the intermolecular potential is described by the Lennard-Jones formula:

$$\nu = \left(\frac{18D_0}{\pi^2 d_0^2 C^2 m_{\text{eff}}}\right)^{0.5}, \quad (12)$$

where D_0 is the dissociation energy of a hydrogen bond, and m_{eff} is the reduced mass, d_0 is the intermolecular distance in the dimer, and C is the speed of light. We obtained $\nu = 145$ cm^{-1}. Then, we constructed three models of dimers: rigid, normal (moderately rigid), and loose. In the first case, all frequencies (except the internal frequencies of monomers) were taken equal to the frequency of stretching vibration of hydrogen bonds. In the second model (by analogy with known molecules consisting of two identical groups, e.g., ethane molecules), the frequencies of rocking and torsional vibrations were respectively taken about two and four times lower than the frequency of stretching vibrations of hydrogen bonds. The distance between the centers of molecules in dimers was taken equal to that for the condensed phase. The minimum inertia momentum was taken equal to the double minimum inertia momentum of methanol molecules. In the third model, each of two monomers was considered freely rotating around its axis; the spacing between the molecules was identical to that used in two other models. By equating the partition functions obtained for these three models of dimers to expression (5) at $i = 2$, we obtained three equations for $\Phi_{2,s}$. In the temperature range considered here, these equations can be approximated by the following expressions (in J molecule^{-1} K^{-1}):

$$\Phi_{2,s} = -(5.72 + 0.0144T) \times 10^{-23}, \quad (13)$$

$$\Phi_{2,s} = -(1.52 + 0.0118T) \times 10^{-23}, \quad (14)$$

$$\Phi_{2,s} = (11.6 + 0.0237T) \times 10^{-23}. \quad (15)$$

As can be seen, these expressions give different numerical values but show similar temperature dependences. With the use of the above value of the dissociation energy of clusters, the best agreement between the calculated and experimental [27] values of the concentration of dimers in methanol vapor was reached with the model of moderately rigid dimers (the maximum deviation was at most a factor of two, and, at room temperatures, close agreement was obtained). Therefore, in the calculation of the nucleation rate, we used expression (13) without further fitting.

Note that a change in the thermodynamic potential corresponding to the transfer of a monomer from the macroscopic phase onto the "surface" of a dimer is negative. The problem is that, in the case of dimers, the model of spherical clusters within our unified approach yields substantially overestimates the value of the rotational partition function. Because expression (14) was obtained from the comparison with the "diatomic" model of dimers, it takes into account this difference of the rotational partition functions and the difference of the frequencies in the macroscopic phase and in dimers. To construct an interpolation function, we can use the expansion in terms of cluster radii or else in the cubic root of the number of monomers in clusters, $i^{1/3}$, retaining two first terms. The expansion is identical in its form to the Tolman formula [5, 6]. Similar expressions for the correction coefficient to the macroscopic energy of surface tension were used in [29–31]. However, physically, it seems more correct to express the dissociation energy not as a function of the number of monomers i but in terms of the number of additions $i - 1$ required for cluster formation [13]. Thus, we have

$$E_{i,s}(0) = a + b(i-1)^{2/3} + c(i-1)^{1/3} \quad (16)$$

$$\Phi_{i,s} = d(i-1)^{2/3} + e(i-1)^{1/3}. \quad (17)$$

The coefficients $a - e$ are chosen for the following reasons. For large clusters ($i \longrightarrow \infty$), the excess free energy should asymptotically approach the energy of surface tension that is proportional to the number of surface atoms. The coefficients at $(i-1)^{1/3}$ in (16) and (17) are chosen so that, at $i = 2$, the formation energy of clusters from the condensed phase is equal to the formation energy of dimers at 0 K: $E_{2,s} = 2E_{\infty,1}(0) - E_2$ at $\Phi_{i,s} = \Phi_{2,s}$. Thus, we obtain

$$E_{i,s}(0) = E_{\infty,1}(0) + (36\pi)^{1/3} E_1 (i-1)^{2/3} + [E_{\infty,1}(0) - (36\pi)^{1/3} E_1 - E_2](i-1)^{1/3}, \quad (18)$$

$$\Phi_{i,s} = (36\pi)^{1/3} \Phi_1 (i-1)^{2/3} - [(36\pi)^{1/3} \Phi_1 - \Phi_{2,s}](i-1)^{1/3}, \quad (19)$$

where $E_{\infty,1}(0)$ is the energy for the monomer abstraction from the condensed phase at 0 K, and E_2 is the dis-

sociation energy of dimers at 0 K. The first term in expression (18) is due to the fact that the first step in the formation of clusters from the condensed phase is the vaporization of the first monomer to which other monomers are further added.

Note that, unlike the first term, whose physical meaning is evident, the last term has ambiguous physical interpretation. Therefore, the last term in expressions (18) and (19) can be represented in a more general form by changing the power 1/3 for the fitting parameter γ ($0 < \gamma < 2/3$), which can be determined by the correlation to experimental data or calculated by the molecular dynamics method.

$E_{\infty,1}(0)$ is determined from the condition that, at equilibrium, the chemical potentials of the condensed phase and the vapor are identical [33]:

$$\mu_{1,1} = -kT\ln[q_{1,g}/c_{1,sat}] \quad (20)$$

or, in the expanded form,

$$\mu_{1,1} = -kT\ln[q_{1,trans}q_{1,rot}q_{1,vib} \times \exp(-E_{\infty,1}(0)/kT)/c_{1,sat}], \quad (21)$$

where $\mu_{1,1}$ is the chemical potential of monomers in the condensed phase; $q_{1,trans}$, $q_{1,rot}$, and $q_{1,vib}$ are the translational, rotational, and vibrational partition functions for monomers in the gas phase; and other designations are standard or identical to those used above. Because the energy is measured from the state of the condensed phase at 0 K, $\mu_{1,1}$ can be represented as [33]

$$\mu_{1,1} = \int_0^T C_{1,p}dT - T\int_0^T (C_{1,p}/T)dT, \quad (22)$$

where $C_{1,p}$ is the heat capacity of condensed methanol. For methanol, the data on $C_{1,p}$ at low temperatures (down to 20 K) are available from [35]. However, for other compounds, these data can be unavailable. Therefore, we used a simplified method for the determination of $C_{1,p}$. Taking into account that, at absolute zero, $C_{1,p} = 0$, the temperature dependence of $C_{1,p}$ can be represented as

$$C_{1,p} = AT + BT^2. \quad (23)$$

The coefficients A and B were determined from tabulated $C_{1,p}$ values and the entropy $S^0 = \int_0^T C_{1,p}/T)dT$ for the liquid phase at 298 K. The $C_{1,p}$ value determined from the temperature dependence thus obtained for methanol were close to the tabulated data [35]. Moreover, the $E_{\infty,1}(0)$ values determined by expression (21) over a wide temperature range (220–290 K) were virtually identical ($E_{\infty,1}(0) = 7.17 \times 10^{-20}$ J/molecule), which indirectly supports the correctness of the method.

The partition function of replacement was calculated according to Frenkel' [4, p. 347] on the basis of the chemical potential taken over six vibrational degrees of freedom for the condensed phase. In clusters, as in the liquid, each molecule is characterized by the internal (vibrational) degrees of freedom the hindered rotational degrees of freedom (torsional vibrations), and Debye-type vibrations. In atomic liquids, the first two types of degrees of freedom are absent. It is clear that the number of vibrational and rotational degrees of freedom in clusters is identical to that for the condensed phase with the same number of molecules. Thus, the transfer of a cluster from the condensed to gas phase results in the disappearance of the Debye-type vibrations. However, calculation by the equation [4]

$$\mu_{1,1}/n = -kT\ln\left[1 - \exp\left(\frac{h\bar{\nu}}{kT}\right)\right]^{-1}, \quad (24)$$

(here, n = 3, 5, and 6 for atoms, linear, and nonlinear molecules, respectively; the formula takes into account that the energy is measured from the state of the condensed phases at 0 K) shows that the average frequency is close to the Debye frequency (e.g., for methanol, the difference varies within 20–30% depending on the temperature). The Debye frequency was calculated by the standard procedure [33]; the velocity of transverse waves was taken equal to half the velocity of longitudinal waves. Note that $\bar{\nu}$ characterizes the average frequency of the Debye and hindered rotational vibrations of monomers in the condensed phase because, at the temperatures characteristic of the nucleation study, internal rotational degrees of freedom of monomers are virtually hindered. Thus,

$$q_{rep} = \left[1 - \exp\left(\frac{h\bar{\nu}}{kT}\right)\right]^{-6} = \exp[-6\mu_{1,1}/(nkT)], \quad (25)$$

where $\mu_{1,1}$ can be calculated as described above or taken from published data.

KINETIC NUCLEATION MODEL

In classical nucleation theory, the growth of clusters is represented as a set of consecutive steps of addition and vaporization of molecules. The growth due to collisions between clusters is not considered, which is evidently true when the concentration of clusters is much lower than the concentration of monomers. This problem was recently considered in [36], and I will briefly discuss it at the end of this article.

According to [4],

$$df_i/dt = J_{i-1} - J_i, \quad (26)$$

where J_{i-1} is the flux of clusters at the point i, i.e., the number of clusters in unit volume transferred along the size axis from the point $i - 1$ to the point i per unit time:

$$J_{i-1} = k_i^+ n_1 n_{i-1} - k_i^-(T_i)n_i. \quad (27)$$

Here, n_1, n_{i-1}, and n_i are the concentrations of monomers and clusters; and k_i^+ and k_i^- are the rate constants of the formation and vaporization of clusters with a size i. In classical nucleation theory, the process is considered steady-state. For this purpose, it is assumed that sufficiently large clusters $G + 1$ (with a much larger size than the critical) are instantaneously removed, and $G + 1$ monomers come into the system instead of each of the removed clusters. Thus, the concentrations of monomers and clusters are time-independent; mathematically, this corresponds to the condition $df_i/dt = 0$ ($i = 2, 3, 4, \ldots, G$) or

$$J_2 = J_3 = J_4 = \ldots = J_i = \ldots = J_G = J. \quad (28)$$

Because nucleation releases heat, it is evident that the temperature of clusters will be higher than the temperature of the ambient gas. Let us assume that the temperature of clusters varies with their size and is identical for all clusters of the same size [19]. Let us also assume as usual [7] that the accommodation coefficient ε for the addition of a monomer to a cluster does not depend on the cluster temperature. In this case, the vaporization rate V_i for the cluster with the temperature T_i can be represented as

$$k_i^-(T_i) = k_i^-(T)V_i(T, T_i), \quad (29)$$

$$V_i(T, T_i) = \exp[(E_{a,i}(1/T - 1/T_i)/k], \quad (30)$$

where $k_i^-(T)$ is the vaporization rate constant for the cluster at the ambient gas temperature, $E_{a,i}$ is the effective activation energy, k is the Boltzmann constant, and T_i is the temperature of clusters with a size of i.

To calculate the steady-state nonisothermic nucleation rate, let us use the set of algebraic equations

$$\begin{aligned} J &= k_2^+ n_1 n_1 - k_2^- V_2 n_2, \\ &\ldots\ldots\ldots\ldots \\ J &= k_i^+ n_1 n_{i-1} - k_i^- V_i n_i, \\ &\ldots\ldots\ldots\ldots \\ J &= k_{G+1}^+ n_1 n_G. \end{aligned} \quad (31)$$

The last equation involves a single term because, according to the formulation of the problem, the clusters of the size $G + 1$ are instantaneously removed, and their concentration is equal to zero. Using the designation $U_i = n_i/c_i$, where c_i is the equilibrium concentration of clusters of the size i at the concentration of monomers $n_1 = c_1$, and the condition for thermodynamic equilibrium

$$k_i^+ c_1 c_{i-1} = k_i^- c_i, \quad (32)$$

we arrive at

$$\begin{aligned} J/(k_2^+ c_1 c_1) &= U_1 - U_2 V_2, \\ &\ldots\ldots\ldots\ldots \\ J/(k_i^+ c_1 c_{i-1}) &= U_{i-1} - U_i V_i, \\ &\ldots\ldots\ldots\ldots \\ J/(k_{G+1}^+ c_1 c_G) &= U_G. \end{aligned} \quad (33)$$

At $i = 2$, $U_{i-1} = n_1/c_1 = 1$ by definition. Upon multiplying the first, second, third, and last equations by $V_1 = 1$ (it is assumed that the temperature of monomers is equal to the temperature of the gas), V_1V_2, $V_1V_2V_3$, and $\prod_{j=1}^{G} V_j$, respectively, and summing the left-hand and right-hand sides of equations (33), we have

$$J\sum_{i=1}^{G}\left[\left(\prod_{j=1}^{i} V_j\right)/(k_{i+1}^+ c_1 c_i)\right] = 1 \quad (34)$$

or

$$J = \left\{\sum_{i=1}^{G}\left[\left(\prod_{j=1}^{i} V_j\right)/(k_{i+1}^+ c_1 c_i)\right]\right\}^{-1}. \quad (35)$$

At the constant temperature of clusters equal to the temperature of ambient medium, $V_i \equiv 1$ at $i = 2, 3, 4, \ldots, G$, and expression (35) transforms into the classical formula for the nucleation rate. Under nonisothermic conditions, $V_i > 1$, and, as is easily seen from (35), the nucleation rate is lower than for isothermal conditions. This is reasonable because, for overheated clusters, the rate of the reverse process of their vaporization is increased.

To use formula (35), the k_{i+1}^+, c_i, and V_i parameters should be known. The parameter k_{i+1}^+ can be represented as a product of the collision-frequency factor of the cluster (the monomer at $i = 1$) with monomer molecules by the accommodation coefficient ε; we used $\varepsilon = 0.8$ [26]. Thus,

$$k_i^+(T) = \varepsilon Z_1(300)(T/300)^{1/2} i^{2/3}. \quad (36)$$

The collision frequency factor at 300 K, $Z_1(300)$, was calculated by the standard procedure [37]. The equilibrium concentrations were calculated by formula (6) from the preceding section.

To calculate V_i, it is necessary to know the effective activation energy of vaporization of the clusters, $E_{a,i}$, and their temperature T_i (it is assumed that the temperature of the ambient gas is given). We calculated the effective activation energy by the equation [38]

$$E_{a,i} = RT^2[d(\ln k_i^-(T))/dT], \quad (37)$$

where

$$k_i^-(T) = k_i^+(T)c_1 c_{i-1} c_i^{-1}, \quad (38)$$

and c_1, c_{i-1}, and c_i are the given concentration of monomers and the respective equilibrium concentrations of the clusters.

To calculate the temperatures of clusters of each size T_i, material balance equations (31) should be supplemented by energy balance equations. In the general case, these equations are similar in their form to the equation used in [19]. However, in this work, I explicitly took into account the fact that the temperature of vaporizing monomers is equal to the temperature of clusters, i.e., higher than the temperature of ambient medium. We also used a different method for the calculation of the heat transfer rate from clusters to molecules of a buffer (noncondensable) gas (the method is based on the stepwise activation model, which is often used in the theory of monomolecular reactions).

The temperature of clusters can be calculated by two methods: either as in [19] (see Appendix) or in a simpler way as described below. Let us consider a representative cluster moving along the size axis. The time it resides in the group of clusters of size i is

$$\tau_i = n_i/J, \tag{39}$$

where n_i is the concentration of clusters of size i, and J is the nucleation flux. During this time, the representative cluster takes part in a certain number of decomposition acts to form a cluster of size $i-1$ and the same number of the formation acts (not counting the act, in which this cluster was originally formed). Because the temperature of the cluster is higher than the temperature of the ambient gas, each pair of the decomposition–addition acts will take away some portion of the energy from the cluster:

$$\Delta Q = C_{p,g}(T_i - T). \tag{40}$$

Thus, the heat removed from the cluster via this mechanism for the time τ_i is

$$Q_{vap,i}(T, T_i) = [C_{p,g}(T_i - T)k_i^- V_i]n_i/J. \tag{41}$$

The cluster can also lose heat via collisions with molecules of the buffer (noncondensable) gas; the energy thus removed for the same time is

$$Q_{buf,i}(T, T_i) = \left\{Z_i[\mathrm{M}]\frac{2}{3}\Delta E\frac{\exp(\Delta E/k(1/T - 1/T_i)) - 1}{\exp(\Delta E/k(1/T - 1/T_i)) + 1}\right\}n_i/J, \tag{42}$$

where Z_i is the factor for the frequency of binary collisions, [M] is the concentration of the buffer gas, and ΔE is the energy removed at each step of the energy transfer within the framework of the step-ladder model. The term in braces was obtained in the framework of a modified step-ladder model [18] used in the theory of chemical and photoactivation [39].

Because the energy removed during a single nucleation act (the advance of the cluster by one step on the size scale) under quasistationary conditions must be equivalent to the heat evolved, the balance equation can be written as

$$J = F_i n_i, \tag{43}$$

where

$$F_i = \frac{C_{p,g}(T_i - T)k_i^- V_i}{L_i} + Z_i[\mathrm{M}]\frac{2\Delta E}{3L_i}\frac{\exp(\Delta E/k(1/T - 1/T_i)) - 1}{\exp(\Delta E/k(1/T - 1/T_i)) + 1}. \tag{44}$$

The evolved heat is $L_i = E_i - h_{1,1}(T) + h_{1,g}(T)$, where E_i is the energy of the monomer abstraction from a cluster of size i at 0 K, and $h_{1,1}(T)$ and $h_{1,g}(T)$ are the enthalpies per molecule in the liquid and gas phases, respectively.

Using (31), (32), and (43), we obtain the recurrent formula for F_i:

$$F_{i-1} = k_i^+ c_1\left(1 + \frac{k_i^+ V_i c_1 c_{i-1}}{F_i c_i}\right)^{-1}. \tag{45}$$

The clusters of the largest size (G) are not formed by the decomposition of clusters of size $G + 1$ because these clusters, according to the problem formulation, are instantaneously removed, and their concentration is equal to zero. Hence,

$$J = k_{G+1}^+ n_1 n_G \tag{46}$$

and, with the allowance for (43), we obtain

$$F_G = k_{G+1}^+ n_1. \tag{47}$$

The temperature of clusters of each size was calculated as described below. By equating (44) to (47) at $i = G$ and solving the respective transcendental equation, we determined the temperature T_G. Then, we find F_{G-1} using recurrent formula (45) by equating it to (44) at $G-1$, and determine T_{G-1}. The recurrent procedure was repeated until the size of dimers ($i = 2$) was reached. The V_i values are calculated in parallel. The summation in (35) was performed in the reverse order, from $i = G$ to $i = 2$. Therefore, to calculate the dependence of the temperature on the cluster size and the nucleation rate in one calculation, we transformed (35) into the form

$$J = \left[\left(\prod_{j=1}^{G} V_j\right)\sum_{i=G}^{1}\left(k_{i+1}^+ c_1 c_i \prod_{j=1+1}^{G+1} V_j\right)^{-1}\right]^{-1}. \tag{48}$$

For the sake of retention of the structure of addition terms, we formally set $V_{G+1} = 1$. It is clear that this will not affect the product under the summation sign, as well as the fact that the product is taken from $j = 2$ instead of $j = 1$ because $V_1 = 1$ (see above).

RESULTS AND DISCUSSION

In the calculation of the nucleation rate of methanol supersaturated vapor in the framework of the above-described model, we used the following parameters:

Density (g/cm^3), $d_{Me} = 0.81015 - 1.0041 \times 10^{-3}x - 1.802 \times 10^{-6}x^2 - 16.57 \times 10^{-9}x^3$, where $x = T - 273.15$ [31].

Pressure of saturated vapor (bar), $P_{sat} = \exp(58.434 - 6341.267/T - 5.61\ln T)$ [31].

Surface tension (mJ/m^2), $\sigma = 36.59 - 1.417 \times 10^{-2}T - 1.32 \times 10^{-4}T^2$ (the interpolation of the data [35]).

Enthalpy and the heat capacity of liquid methanol at 298.15 K (both in J mol^{-1} K^{-1}), $S^0 = 126.7$ and $C_p = 81.6$ [40].

Accommodation coefficient, $\varepsilon = 0.8$ [26].

Energy of the monomer abstraction from the methanol macroscopic phase at 0 K, $E_{\infty,1}(0) = 43.16$ kJ/mol.

The energy step in the step-ladder model of the energy transfer by collisions of a cluster with argon atoms, $\Delta E = RT$.

The only fitting parameter in the model is γ, which characterizes the degree of the deviation of the free energy of a cluster from that used in the drop model. We could take $\gamma = 1/3$ as in (18) and (19); however, in this case, the free energy of dimers would not agree with the experimental data. Moreover, as noted above, there is no physical reason to set $\gamma = 1/3$. We fitted the model to the results of a single experiment (no. 3 in the table) and obtained $\gamma = 0.41$. It will be of interest to see further whether this value is correct for other systems. The J values calculated with $\gamma = 1/3$ are on the average higher by two orders of magnitude.

Figure 1 compares the dependence used here for the reduced dissociation energy of clusters calculated per molecule versus the cluster size and the results of theoretical calculations. As can be seen, the scatter of values obtained by different methods is rather high. Note that dependence (18) used in this work represents some averaged trend.

The calculated values of the nucleation rate for methanol supersaturated vapor are correlated to the experimental data [20] in the table. The measured and calculated values are in good agreement, especially taking into account that the experimental data and the predictions of classical nucleation theory are different. At first sight, the situation seems paradoxical: classical theory does not take into account external degrees of freedom of clusters; therefore, it should give a lower concentration of critical clusters and, consequently, a lower nucleation rate in comparison with those obtained in the framework of our model. However, as is seen from Fig. 2, the dependence for the free energy in (7) calculated in the framework of our model is far above that for the classic model; this explains the apparent difference.

The developed model also adequately describes the experimental data on the dependence of the critical degree of supersaturation (s) on temperature (Fig. 3) obtained in a diffusion chamber ($J \sim 1$ cm^{-3} s^{-1}). The observed difference between the experimental data and the predictions of our model is possibly explained by the fact that, under conditions of slow nucleation, the system is highly sensitive to the presence of foreign condensation nuclei [7].

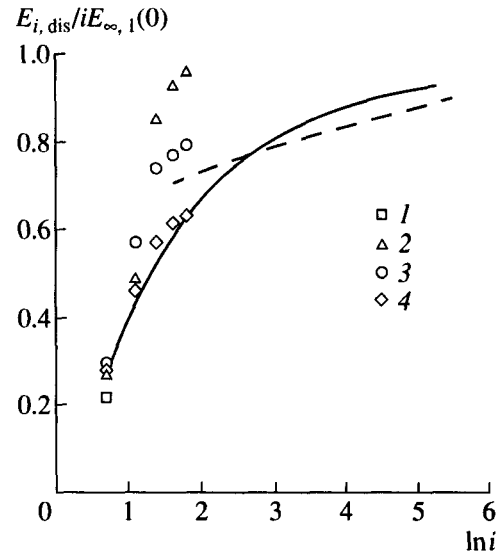

Fig. 1. Effect of the cluster size on the dissociation energy of methanol clusters calculated per monomer and divided by the vaporization energy per molecule for the bulk of methanol. The solid line represents the results of calculation by expression (18) (this work); the dashed line corresponds to Monte-Carlo calculation [25]. The data of quantum-chemical calculation (*1*) [23] and (*2–4*) [24] were used.

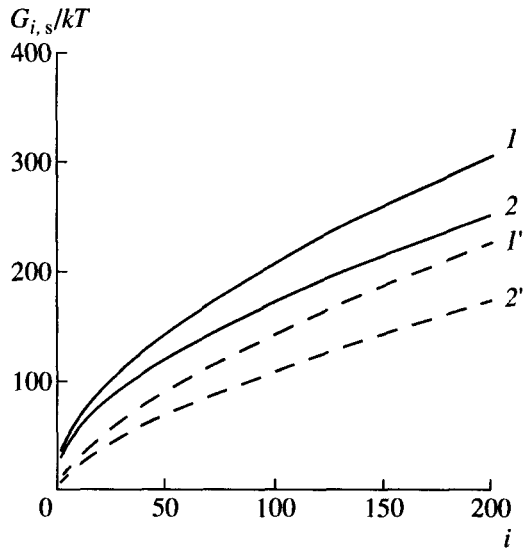

Fig. 2. Effect of the cluster size on the free energy of methanol clusters at (*1*, *1'*) 229.31 and (*2*, *2'*) 274.63 K. Solid lines represent the results of calculation by the model proposed in this work; dashed lines correspond to the drop model.

The curves for the quasiequilibrium (c_i) and quasistationary (n_i) concentrations of clusters and overheating $\Delta T_i = T_i - T$ as functions of the cluster size are presented in Fig. 4 for the two limiting cases: high supersaturation at a low temperature and low supersaturation at a high temperature (see the table, experiments 12

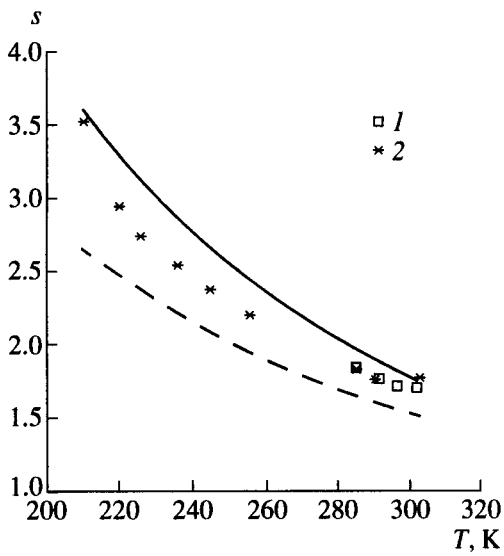

Fig. 3. Critical degree of supersaturation for the condensation of methanol in a diffusion chamber vs. temperature. The experimental data from (*1*) [21] and (*2*) [22] are shown by different points. The solid line represents the results of calculation by the model developed in this work; the dashed line corresponds to classical model [21].

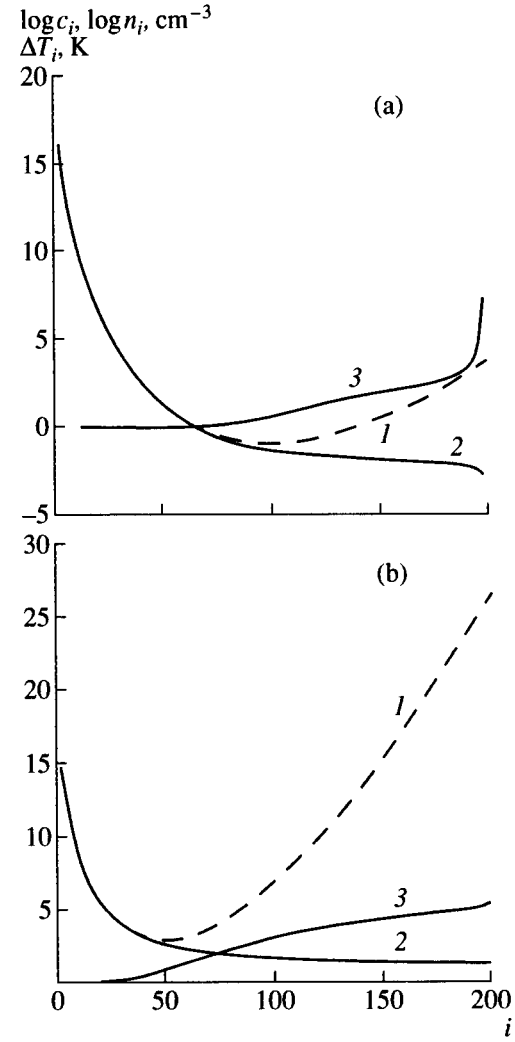

Fig. 4. Curves for the (*1*) quasiequilibrium (c_i), (*2*) quasistationary (n_i) concentrations, and (*3*) the overheat ΔT_i of methanol clusters relative to the ambient gas as functions of the cluster size at (a) T = 274.63 K and s = 2.39 and (b) T = 229.31 K and s = 4.07 (table, experiments nos. 8 and 12).

and 8). As seen from Fig. 4, the deviation of the temperature of clusters from the temperature of the ambient gas becomes noticeable in the region of critical sizes and increases with increasing the number of atoms in clusters. A deviation of n_i from c_i is observed in the same region. Physically, this means that, in this region, due to low cluster concentrations, there is a noticeable resistance to the nucleation flux. In the undercritical region characterized by a high concentration of clusters, the forward and back processes are virtually in equilibrium; therefore, n_i and c_i coincide very closely.

Figure 5 demonstrates the effect of the concentration of the buffer (noncondensable) gas on the nucleation rate for the same limiting conditions (table, experiments 12 and 8); these conditions were used in [20] in the measurement of the nucleation rate. (In Fig. 5, the nucleation rate is related to the respective value obtained for the isothermal model of the process.) The effect is of two orders of magnitude. At high concentrations of the buffer gas, the temperature of the clusters is equal to the temperature of the ambient gas. As the buffer gas concentration is decreased, the situation changes and, in the limiting case, only the molecules of condensing gas (monomers) are responsible for cooling. Figure 6 presents temperature profiles as functions of the cluster size at different degrees of dilution. It is seen that, even at a methanol concentration of about 10^{-1}–10^{-2}%, the temperature of clusters differs from the temperature of the ambient gas; as a consequence, the nucleation rate decreases.

It is of interest that, in the vicinity of the limiting size G, especially at $i = G$, the temperature of clusters sharply increases. This is due to the fact that, in this region, the concentration of clusters decreases with the size more sharply than far from G (see Fig. 4) because of the removal of clusters of size $G + 1$. Therefore, the rate of back processes decreases, and clusters are highly overheated. A change in the G value is accompanied by a respective shift of the region of the increased overheat. Note that, in the region $G > 2i^*$, where i^* is the critical size, the changes in G virtually have no effect on the nucleation rate under both isothermic and nonisothermic conditions.

The calculation shows that the effect of the overheat only slightly depends on the degree of supersaturation (Fig. 7). This is probably because the nucleation rate is proportional to the concentration of clusters in the critical region [4, 7]. In this case, the heat loading of a cluster virtually remains unchanged.

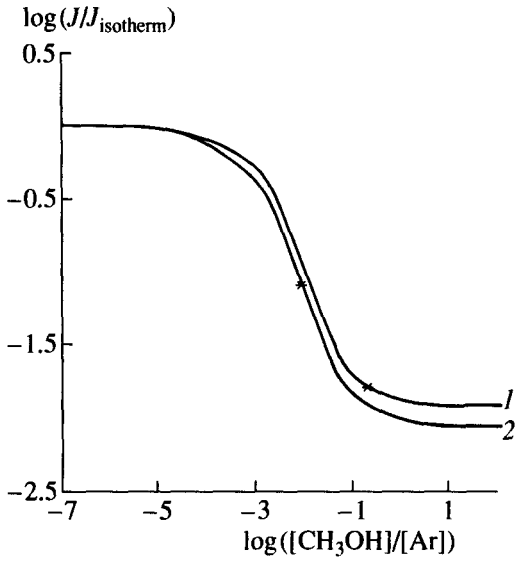

Fig. 5. The effect of the dilution (with argon) on the nucleation rate of methanol vapor at two limiting temperatures and degrees of supersaturation: (*1*) $T = 274.63$ K, $s = 2.39$, and (*2*) $T = 229.31$ K, $s = 4.07$. The points in the curves correspond to experiments 8 and 12 from the table.

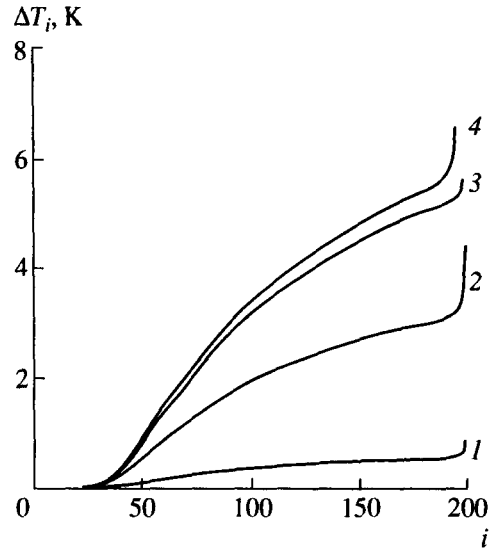

Fig. 6. The effect of the dilution (with argon) on the profile of the overheat (ΔT_i) of methanol cluster against the cluster size: $[CH_3OH]/[Ar]$ is equal to (*1*) 10^{-4}, (*2*) 10^{-3}, (*3*) 10^{-2}, and (*4*) ∞.

To estimate the contribution from the collisions between clusters into the total nucleation flux, I calculated all collisions between clusters that lead to the formation of overcritical clusters. The maximum contribution of these collisions is equal to ~20% of the flux that is due to the consecutive addition of monomers. However, this value is substantially overestimated because it does not take into account the backward flux from the overcritical region, especially when we consider that the basic contribution into the additional flux is due to the addition of dimers to the precritical clusters of size $i^* - 1$. For water, the contribution of cluster–cluster collisions is 10% [36].

The number of parameters in the developed model is greater than for its predecessors. In particular, it additionally includes thermochemical parameters of

The experimental [20] and calculated values of the nucleation rate J for methanol vapor (J_{cl} and J_{tw} are the results of calculations by classical theory [20] and the model proposed in this work, respectively)

Experiment	s^*	T, K	J_{exp}	J_{tw}	J_{cl}	Experiment	s^*	T, K	J_{exp}	J_{tw}	J_{cl}
			$cm^{-3}\ s^{-1}$						$cm^{-3}\ s^{-1}$		
1	2.61	272.02	8.0×10^7	1.0×10^8	1.5×10^{17}	14	3.34	231.86	2.4×10^5	2.5×10^4	3.5×10^{10}
2	2.66	271.49	2.3×10^8	3.2×10^8	2.7×10^{17}	15	3.73	238.32	4.7×10^8	1.5×10^9	5.0×10^{14}
3	2.71	270.86	8.4×10^8	8.4×10^8	4.9×10^{17}	16	3.82	237.98	1.8×10^9	3.9×10^9	7.7×10^{14}
4	2.58	272.32	3.9×10^7	4.8×10^7	1.0×10^{17}	17	3.62	238.75	2.4×10^8	3.9×10^8	2.0×10^{14}
5	2.54	272.86	1.1×10^7	1.8×10^7	6.3×10^{16}	18	3.34	239.98	6.7×10^6	7.3×10^6	1.6×10^{13}
6	2.48	273.46	3.0×10^6	3.3×10^6	2.6×10^{16}	19	3.22	240.51	1.2×10^6	9.1×10^5	4.4×10^{12}
7	2.44	274.02	9.4×10^5	1.1×10^6	1.5×10^{16}	20	3.07	241.22	1.3×10^5	4.6×10^4	6.9×10^{11}
8	2.39	274.63	1.9×10^5	2.2×10^5	6.3×10^{15}	21	3.21	255.47	7.5×10^8	7.4×10^9	6.6×10^{16}
9	3.65	230.72	2.3×10^7	3.7×10^6	1.1×10^{12}	22	3.14	255.91	3.6×10^8	2.6×10^9	3.7×10^{16}
10	3.79	230.25	7.4×10^7	2.4×10^7	4.0×10^{12}	23	3.00	256.81	2.7×10^7	2.5×10^8	9.4×10^{15}
11	3.90	229.87	4.5×10^8	8.8×10^7	1.1×10^{13}	24	2.92	257.34	5.3×10^6	5.4×10^7	3.8×10^{15}
12	4.07	229.31	1.9×10^9	5.3×10^8	3.7×10^{13}	25	2.82	258.00	7.5×10^5	3.6×10^6	1.2×10^{15}
13	3.49	231.29	2.8×10^6	3.4×10^5	1.6×10^{11}						

* s is the degree of supersaturation.

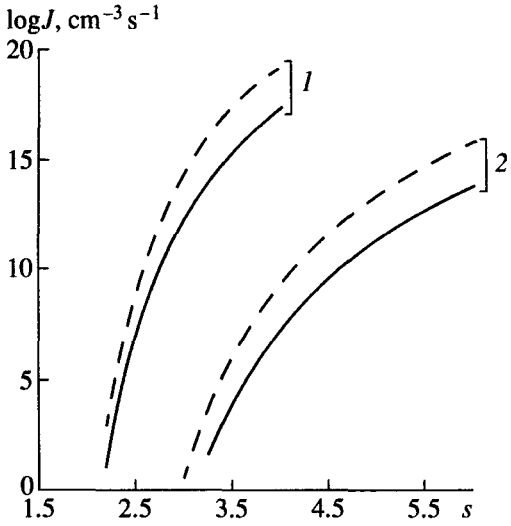

Fig. 7. The nucleation rate vs. supersaturation for the infinitely dilute mixture (the solid lines) and pure methanol vapor (the dashed lines) at (*1*) 274.63 and (*2*) 229.31 K.

dimers. However, because of widespread use of quantum-chemical calculation methods and due to the improvement of experimental methods for the investigation of small clusters, we may expect that these data will become readily available in the future. Purposeful experiments on the effect of the nature and the pressure of buffer gases on the nucleation rate are of great interest for further model testing. I plan to use this model for the description of nucleation in vapors of substances of different types.

APPENDIX

As seen from the above, the nucleation rate was determined on the assumption that the heat liberated at the elementary step of passing from the size $i-1$ to i is removed from only the cluster with a size of i. This means that the heat flux between clusters, whose sizes differ by unity, was ignored. A more rigorous consideration can be performed with the use of the enthalpy balance equations similar to those used in [19]:

$$\begin{aligned} &\mathrm{d}[n_i h_i(T_i)]/\mathrm{d}t \\ &= \beta_{i-1} n_{i-1}[E_i + h_{i-1}(T_{i-1}) + h_{1,\mathrm{g}}(T)] \\ &- \alpha_i n_i[E_i + h_{i-1}(T_i) + h_{1,\mathrm{g}}(T_i)] - \beta_i n_i[h_i(T_i)] \\ &+ \alpha_{i+1} n_{i+1}[h_i(T_{i+1})] - Q_{\mathrm{buf},i}(T, T_i) n_i = 0, \end{aligned} \tag{49}$$

where $\beta_{i-1} = k_i^+ n_1$, $\beta_i = k_{i+1}^+ n_1$, $\alpha_i = k_i^- V_i$, $\alpha_{i+1} = k_{i+1}^- V_{i+1}$; $h_{i-1}(T_{i-1})$, $h_{i-1}(T_i)$, $h_i(T_i)$, and $h_i(T_{i+1})$ are the enthalpies of the clusters with sizes $i-1$ and i at respective temperatures (at the points $i-1$, i, and $i+1$); and E_i is the energy of monomer abstraction from a cluster with the size i. $Q_{\mathrm{buf},i}(T, T_i)$ is given by the expression

$$\begin{aligned} &Q_{\mathrm{buf},i}(T, T_i) \\ &= Z_i[\mathrm{M}] \frac{2\Delta E}{3L_i} \frac{\exp(\Delta E/k(1/T - 1/T_i)) - 1}{\exp(\Delta E/k(1/T - 1/T_i)) + 1}, \end{aligned} \tag{50}$$

where $L_i = E_i - h_{1,\mathrm{l}}(T) + h_{1,\mathrm{g}}(T)$. Equation (49) was derived on the assumption that, in the decomposition of a cluster, the temperatures of the monomer and a smaller cluster are equal to the temperature of the initial cluster. This assumption is based on the model of homogeneous energy distribution used in the theory of unimolecular reactions [41].

Finally, we arrive at

$$\begin{aligned} &J[E_i - h_{1,\mathrm{l}}(T) + h_{1,\mathrm{g}}(T)] \\ &- \alpha_i n_i[C_{1,\mathrm{g}}(T_i - T)] - Q_{\mathrm{buf},i}(T, T_i) n_i \\ &+ \{\beta_i n_i C_{1,\mathrm{l}} i(T_{i+1} - T_i) \\ &- \alpha_i n_i C_{1,\mathrm{l}}(i-1)(T_i - T_{i-1})\} = 0. \end{aligned} \tag{51}$$

In equation (51), the expression in square brackets does not take into account the difference between the enthalpies of the monomers at the temperatures of the cluster and ambient gas. The heat capacity of the cluster was represented as a product of the number of monomers in the cluster and the heat capacity of monomers in the condensed phase $C_{1,\mathrm{l}}$ [19]; as shown by Monte-Carlo calculation [25], this is a rather good approximation.

Expression (51) can be rewritten as

$$J = (F_i + \Delta F_i) n_i, \tag{52}$$

where F_i is determined by expression (44), and

$$\begin{aligned} \Delta F_i = \{&\alpha_i n_i C_{1,\mathrm{l}}(i-1)(T_i - T_{i-1}) \\ &- \beta_i n_i C_{1,\mathrm{l}} i(T_{i+1} - T_i)\}/L_i. \end{aligned} \tag{53}$$

As can be seen, expression (52) differs from simplified expression (43) by the additional term ΔF_i. Expression (43) was derived on the assumption that the energy released by clusters of a given size is entirely removed into the ambient gas, but it is not transferred to clusters of nearest sizes. The additional term accounts for the energy transfer that occurs along the size scale.

To estimate this effect, I first calculated the dependence of the overheat $(T_i - T)$ on the size i by simplified formula (43) and approximated the $(T_i - T)$ vs. i dependence by the expression

$$(T_i - T) = a' \exp(-b' i^{-c'}). \tag{54}$$

This expression provides us with a rather close approximation for the $(T_i - T)$ vs. i dependence. We substituted the dependence obtained into (53) and used (52) instead of (43) to calculate the nucleation rate and the dependence of $(T_i - T)$ on i. For all experiments presented in the table, the effect of the term in braces in

(53) on the nucleation rate is within 30%, which is insignificant in comparison to the discrepancy between experimental and theoretical results.

REFERENCES

1. Volmer, M. and Weber, A., *Z. Phys. Chem.*, 1926, vol. 119, p. 277.
2. Becker, R. and Döring, W., *Ann. Phys.*, 1935, vol. 21, p. 719.
3. Zel'dovich, Ya.B., *Zh. Eksp. Teoret. Fiz.*, 1942, vol. 12, p. 545.
4. Frenkel', Ya.I., *Kineticheskaya teoriya zhidkosti* (Kinetic Theory of Liquids), Moscow: Akad. Nauk SSSR, 1946.
5. Tolman, R.C., *J. Chem. Phys.*, 1949, vol. 17, no. 2, p. 333.
6. Wegener, P.P. and Parlange, J.Y., *Naturwissenschaft*, 1970, vol. 57, no. 11, p. 525.
7. Lushnikov, A.A. and Sutugin, A.G., *Usp. Khim.*, 1976, vol. 45, no. 3, p. 385.
8. Zhukhovitskii, D.I., *J. Chem. Phys.*, 1994, vol. 101, no. 6, p. 5076.
9. Giessen, J.A.E., Blokhuis, E.M., and Bukman, D.J., *J. Chem. Phys.*, 1997, vol. 108, no. 3, p. 1148.
10. Lothe, J. and Pound, G.M., *J. Chem. Phys.*, 1968, vol. 48, no. 4, p. 1849.
11. Lothe, J. and Pound, G.M., *J. Chem. Phys.*, 1962, vol. 36, no. 8, p. 2080.
12. Konyukhov, V.K. and Faizulaev, V.N., *Prikl. Mat. Teor. Fiz.*, 1977, no. 3, p. 41.
13. Gordiets, V.F., Shelepin, L.A., and Shmotkin, Yu.M., *Khim. Fiz.*, 1982, vol. 2, no. 10, p. 1391.
14. Frurip, D.J. and Bauer, S.H., *J. Phys. Chem.*, 1977, vol. 81, no. 10, p. 1001.
15. Vlasov, P.A., Zaslonko, I.S., Karasevich, Yu.K., and Smirnov, V.N., *Khim. Fiz.*, 1988, vol. 7, no. 3, p. 370.
16. Pal, P. and Hoare, M.R., *J. Phys. Chem.*, 1987, vol. 91, no. 10, p. 2474.
17. Wilcox, C.F. and Bauer, S.H., *J. Chem. Phys.*, 1991, vol. 94, no. 12, p. 8302.
18. Vlasov, P.A., Karasevich, Yu.K., and Smirnov, V.N., *Teplofiz. Vys. Temp.*, 1996, vol. 34, no. 5, p. 676.
19. Wyslouzil, B.E. and Steifeld, J.H., *J. Chem. Phys.*, 1992, vol. 97, no. 4, p. 2661.
20. Strey, R., Wagner, P.E., and Schmeling, T., *J. Chem. Phys.*, 1986, vol. 84, no. 12, p. 2325.
21. Flageollet, C., Cao, M., and Mirabel, P., *J. Chem. Phys.*, 1980, vol. 72, no. 1, p. 544.
22. Garnier, J.P., Mirabel, P., and Rabeony, H., *J. Chem. Phys.*, 1983, vol. 79, no. 4, p. 2097.
23. Anwander, E.H.S., Probst, M.M., and Rode, B.M., *Chem. Phys.*, 1992, vol. 166, no. 3, p. 341.
24. Buck, U. and Schmidt, B., *J. Chem. Phys.*, 1993, vol. 96, no. 12, p. 9410.
25. Wright, D. and El-Shell, M.S., *J. Chem. Phys.*, 1996, vol. 105, no. 24, p. 11199.
26. Matsumoto, M. and Kataoka, Y., *Phys. Rev. Lett.*, 1992, vol. 69, no. 26, p. 3782.
27. Frurip, D.A., Curtiss, L.A., and Blander, M., *Int. J. Thermophys.*, 1981, vol. 2, no. 2, p. 115.
28. Curtiss, L.A., Frurip, D.A., and Blander, M., *J. Chem. Phys.*, 1981, vol. 75, no. 12, p. 5900.
29. Ford, I.J., *J. Chem. Phys.*, 1997, vol. 106, no. 23, p. 9734.
30. Ford, I.J., Barrett, J.C., and Lazaridis, M., *J. Aerosol. Sci.*, 1993, vol. 24, no. 5, p. 581.
31. Dillmann, A. and Meier, G.E.A., *J. Chem. Phys.*, 1991, vol. 94, no. 5, p. 3872.
32. Wilemski, G., *J. Chem. Phys.*, 1995, vol. 103, no. 3, p. 1119.
33. Levich, V.G., *Vvedenie v statisticheskuyu fiziku* (Introduction to Statistical Physics), Moscow: Gosudarstvennoe Izdatel'stvo Tekhniko-Teoreticheskoi Literatury, 1954.
34. Courtney, W.G., *J. Chem. Phys.*, 1961, vol. 35, no. 8, p. 2249.
35. *Fizicheskie velichiny: Spravochnik* (Physical Values: A Handbook), Grigor'ev, I.S. and Meilikhov, E.Z., Eds., Moscow: Energoatomizdat, 1991.
36. Arstila, H., *J. Chem. Phys.*, 1997, vol. 107, no. 8, p. 3196.
37. Hirschfelder, J.O., Curtiss, C.F., and Bird, R.B., *Molecular Theory of Gases and Liquids*, London: Wiley, 1963.
38. Benson, S., *Thermochemical Kinetics*, New York: Wiley, 1976.
39. Forst, W., *Theory of Unimolecular Reactions*, London: Academic, 1973.
40. Baron, N.M., Kvyat, E.I., Podgornaya, E.A., *et al.*, *Kratkii spravochnik fiziko-khimicheskikh velichin* (An Abridged Handbook of Physical and Chemical Values), Mishchenko, K.P. and Ravdelya, A.A., Eds., Leningrad: Khimiya, 1967.
41. Kuznetsov, N.M., *Kinetika monomolekulyarnykh reaktsii* (Kinetics of Unimolecular Reactions), Moscow: Nauka, 1982.