

Kinetic Model of Effect of a Carrier Gas on Nucleation in a Diffusion Chamber

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For the first time a model of nucleation when a transport of condensing molecules to the cluster surface is determined by their diffusion through a carrier gas is proposed. The approach in use is strongly based on the microscopic theory of nucleation put forward by the author and allows an analytical representation of the cluster's concentrations through supersaturation, gas temperature, and carrier gas pressure, which is quite new. It is shown that usual conditions of experiments in diffusion cloud chambers meet the requirements of the model validity that means this model can be used to explain a mechanism of the carrier gas pressure influence on the nucleation kinetics observed in experiments.

INTRODUCTION

In the existing theories of homogeneous nucleation it is accustomed to consider that a concentration of a noncondensable (carrier) gas does not affect the rate of nucleation. For instance, classical nucleation theory (CNT) originally treats the nucleation process as an isothermal one. So from the point of view of this theory, high concentration of the carrier gas just provides such isothermal conditions while at low concentrations one should probably take care about taking into account non-isothermal effects. That is why when in Chukanov and Kuligin (1987); Heist et al. (1994) and some other works it had been discovered that critical supersaturation of the condensable vapor linearly increases with the increase of the carrier gas pressure, it stimulated a new and significant interest to this problem. A number of investigators have attempted to model these experimental results that have been published representing the effect of the background gas on nucleation with little or no success. Meanwhile, some new effects have been revealed on the basis of the experimental data on homogeneous condensation of H_2O , D_2O , and some alcohols in an inert gaseous atmosphere, in particular

that a slope of isotherms $S_{cr}(P_0)$ becomes more abrupt with the temperature decrease while this effect has not been detected for methanol. Moreover, a direct comparison of the experimentally measured and predicted by CNT rates of nucleation has shown a difference of about 8–24 orders of magnitude. The attempt of the authors (Chukanov and Kuligin 1987) to make a correction of the theoretical data was without success.

Furthermore, it is known from the experiment and has not been explained in the framework of CNT yet that there is a difference in the behavior of the maximum supercooling ΔT of water vapor and the moist air when varying the initial relative humidity ϕ . Experiments were made in the Laval nozzle (Gorbunov et al. 1984; Binnie and Woods 1938). In accordance with the results of these papers, supercooling of the moist air decreases monotonically as ϕ increases while for pure water vapor the opposite situation is observed. In addition, Gorbunov et al. (1984) have noticed a great discrepancy of the absolute ΔT values for water vapor ($\Delta T_1 = 50 - 60K$) and water vapor in the air where $\Delta T_2 = 70 - 90K$. At such ΔT_2 , the size of the critical nucleus determined by the classical theory turns out to be less than the water molecule itself that demonstrates an internal inconsistency of the theory. Also note a surprising disagreement between CNT and the data of nucleation experiments in the region near the critical point (Binder and Stauffer 1976; Itkin et al. 1984), where the critical nuclei are much larger and the concepts of CNT might be expected to work well. However, the observed supercooling by about a factor of two exceeds that predicted by CNT and even more that predicted by the Lothe and Pound theory (Binder and Stauffer 1976; Gorbunov et al. 1984).

These results drew special attention to investigation of a carrier gas influence on the condensation kinetics and a lot of experimental work has been done. We'll mention only recent experiments in high-pressure cloud chambers (Heist et al. 1994, 1995; Bertelsmann et al. 1996), diffusion cloud chambers (DCC) (Kane and El-Shall 1996; Wright et al. 1993, 1990), expansion chambers (Viisanen and Strey 1994; Strey et al. 1994; Viisanen et al. 1993; Van Remoortere et al. 1996) and nozzles (Wyslouzil et al. 1994) (see also numerous references in these papers) performed in order to reveal the main features of this effect. As a

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result a number of the experimental data for various substances is now available. Meanwhile, modest progress was achieved in the theory. In particular, within the framework of our microscopic nucleation theory (MNT) the effect of the background gas is explained by its influence on the rate of relaxation of the intracluster vibrations on the nucleation kinetics (Itkin and Kolesnichenko 1997; Itkin et al. 1991). As shown in Itkin and Kolesnichenko (1997) MNT succeeds in reproducing the difference in the nucleation rate for pure water vapor and moist air in the above mentioned experiments (Gorbunov et al. 1984; Binnie and Woods 1938). Other authors try to associate the discussed phenomenon with nonisothermal effects (Ford 1992), the influence of the background gas on the capture of vapor molecule by a drop (Novikov et al. 1997), and some others. A group of researchers associate the influence of the carrier gas with the transport processes in DCC. Apparently, the simplest and most plausible explanation was proposed in (Vitovec et al. 1989; Kane et al. 1997), where the effect of the background gas is treated as the influence of the latter on the further growth of a previously formed critical nucleus. Thus the idea of that work is that at higher carrier gas pressures the growth of droplets is retarded and particles may not grow large enough to be detected by visual methods. In other words, this effect is assumed to be not kinetic, but its treatment is only some misunderstanding of the technique of experiments.

Some criticism should be made with respect to all mentioned approaches, namely, the following.

- When treating the effects inside high-pressure and diffusion cloud chambers within the framework of the original version of MNT in our previous works we did not take into account the influence of the carrier gas on the further growth of particles but only on the nucleation kinetics. Moreover, a recent detailed study of the available experimental results revealed that under specific conditions of these experiments, MNT fails to predict the carrier gas influence in high-pressure and diffusion cloud chambers in contrast to experiments in nozzles and jets. This problem is discussed below in more detail, however, under the conditions of these devices MNT in its original version fails to predict the observed results.
- On the contrary, models which account only for the cluster growth do not take into account the direct influence of the background gas on the rate of nucleation. It can be shown (see discussion at the end of this paper) that such a model predicts the influence of the carrier gas pressure on the critical supersaturation in DCC, but the form of this dependence is far from the linear one observed in experiments.
- Another problem is concerned with the work of Novikov et al. (1997). The authors of this paper take into account details of interaction between a droplet and a vapor molecule that results, in particular, in the disturbance of the Maxwell distribution of molecules over the ve-

locity in the vicinity of the drop. However, the steady state rate of nucleation which is used to estimate the effect of this interaction on the nucleation rate could be derived from the respective kinetic equation only under the assumption made that the distribution of both clusters and monomers is Maxwellian. Otherwise, it is also possible to present the steady nucleation rate in the usual form, as in Novikov et al. (1997), but the rate constants now depend on the concentrations of monomers in a rather complex and, more importantly, implicit way. For instance, one can introduce a small correction to the Maxwell distribution, as is usually done when describing the Knudsen layer, and further try to solve analytically the corresponding kinetic equation in order to reveal an explicit form of the quasisteady equations for concentrations and the steady state rate of nucleation.

On the basis of this brief consideration the aim of this work is to consider in more detail the kinetic processes in DCC and HPCC using some ideas specific for the kinetics of chemical reactions (Fuchs 1995; Frank-Kamenetskii 1947). We also use the MNT approach because this way allows one to get an explicit representation for concentrations of clusters of an arbitrary size through supersaturation, the gas temperature, and the carrier gas pressure, which is quite new. In particular, for the first time a model of the nucleation processes under conditions when a transport of condensing molecules to a cluster's surface is determined by their diffusion through a carrier gas is proposed. It is shown that the usual conditions of experiments in diffusion cloud chambers meet the requirements of the model validity, which means this model can be adopted to explain a mechanism of the carrier gas pressure influence on the nucleation kinetics observed in the experiments. In the second part of this work the results obtained are used to explain the available experimental data in HPCC and DCC. We also discuss what the carrier gas really does influence, the nucleation kinetics or the transport processes in DCC, and why this effect differs for nozzles and jets on the one hand and for DCC and HPCC on the other hand.

DIFFUSION-LIMITED REGIME OF NUCLEATION

As pointed out in Frank-Kamenetskii (1947), when a certain chemical reaction realizes in nature its observed rate is determined on the one hand by a real chemical kinetics on the surface of the interacting particles, and on the other hand by the rate of transport of the reacting medium to this surface due to the molecular or convective (in particular, turbulent) diffusion. As shown below, the second way becomes extremely important when the concentration of the reacting component is small as compared to the concentration of the carrier gas and simultaneously the rate of the chemical reaction is much more than the rate of diffusion. In what follows, we intend to show that the typical conditions in DCC just meet these requirements and hence this is the case when nucleation kinetics in DCC is a diffusion-limited one.

We start from a usual expression of the nucleation theory for the flux I_j in a space of the available cluster's sizes

$$I_j = K_j^+ n_{j-1} n_1 - K_j^- n_j. \quad [1]$$

Here K_j^+ is the rate constant of the formation of j cluster, which consists of j molecules, from the $j - 1$ one by attaching a monomer, K_j^- is the dissociation rate constant of j cluster, and n_j is the concentration of j clusters. For the rate of growth of j clusters K_j^+ the following expression is commonly used:

$$K_j^+ = \gamma_c K j^{2/3}, \quad [2]$$

where $K = K_1(3m_1/4\pi\rho_l)^{2/3}$, $K_1 = (k_B T/2\pi m_1)^{1/2}$ is a free molecular flux per surface of a unit sphere, m_1 is the vapor molecular mass, ρ_l is the liquid density, k_B is the Boltzmann constant, and γ_c is the condensation coefficient characterizing the ratio of the number of molecules sticking to the cluster (the number of the "efficient" collisions) and the total number of monomers' collisions with the cluster. The rate of the unimolecular decay K_j^- is usually determined from the principle of the microscopic reversibility for the reaction $\Omega_{j-1} + \Omega_1 \leftrightarrow \Omega_j$ that yields $K_j^- = K_j^+ n_{j-1} e^{n_{1e}/n_{je}}$ with n_{je} being the equilibrium concentration of j clusters.

Thus if a certain cluster transits to another sort by attaching a monomer, the rate of this process in the usual nucleation theory is proportional to the free-molecular flux of monomers on the surface of this cluster, and this flux is determined by the volume concentration of monomers.

Under the conditions of DCC this assumption stops being valid because the real concentration of monomers at the external boundary of the Knudsen layer over the cluster surface differs from the concentration n_1 determined far from the cluster because of the presence of a carrier gas. It is caused by the existence of a concentration jump in the vicinity of the cluster surface, and the value of this jump becomes considerable when the mean free path of the condensing molecules in the carrier gas is of order of the cluster radius. We study this problem in more detail.

Let us consider an isolated cluster surrounded by a mixture of the condensable vapor and background gas. In accordance with the design of DCC, the number density of the background gas n_0 is a few orders more than the number density of the vapor n_1 . Therefore the mean free path of the vapor molecule in the vapor λ_v is about two orders more in length than the mean free path of this molecule in the carrier gas λ_{vg} . Hence the structure of the Knudsen layer around the droplet can be presented as shown in Figure 1. We assume that two vapor molecules collide when the distance between their centers is $2l$, with l being the effective radius of the molecule. However, it is more convenient to consider the molecule flying at the cluster being pointwise and if so the collision occurs when this molecule reaches the surface of the absorbing sphere of the radius $R + l$, R is the cluster radius. In Figure 1, T_k and n_k are the temperature and

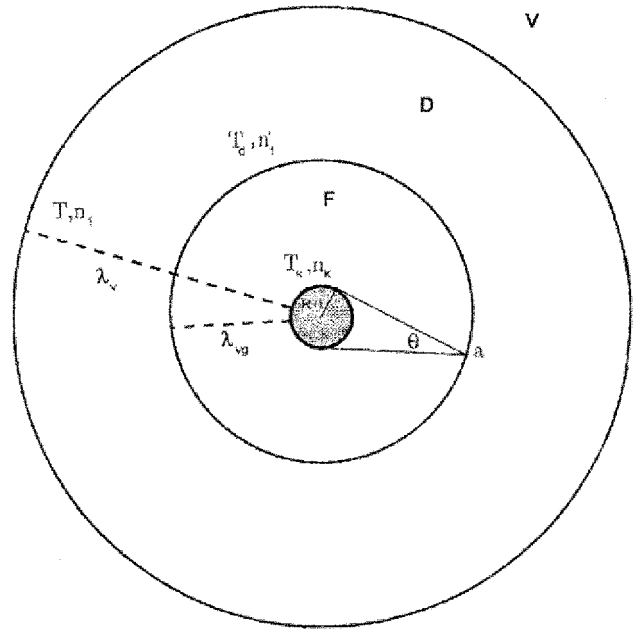


Figure 1. Areas around a cluster, R is the radius of the cluster, l is the radius of the condensing molecule, λ_v and λ_{vg} are mean free paths of vapor molecules in the vapor and in the carrier gas, T , T_d , T_k and n_1 , n'_1 , n_k are temperatures and numerical densities of the vapor in the respective areas, F is an area of a free-molecular flow, D is an area of diffusion of the vapor through the carrier gas, and V is a fluid dynamic area.

concentration of the incident molecules at the surface of the droplet, T_d and n'_1 are the corresponding parameters at the internal interface, which is located approximately at the distance λ_{vg} from the surface of the absorbing sphere, and T and n_1 are the corresponding parameters at the external interface, which is located approximately at the distance of λ_v from the surface of the sphere.

In area V a behavior of both the vapor and the carrier gas is described by usual fluid dynamic models. In area D vapor molecules collide only with the carrier gas, while in area F vapor molecules move as in vacuums without collisions with the velocity u' . Therefore the actual flux of the vapor molecules per unit time on j cluster in the simplest approximation could be written in the form

$$K_j = 4\pi\gamma_c(R + l)^2(u'n'_1 - \Psi_o), \quad [3]$$

where Ψ_o is the flux of outgoing molecules (evaporating and reflecting from the cluster surface), and n'_1 should be found from the solution of the Knudsen layer problem with boundary conditions established at the external interface and at the surface of the absorbing sphere. However, it is an extremely labor-consuming task to find an exact solution to such a problem which is not solved yet, therefore we further use some more rough estimations.

Let us find the concentration of vapor molecules in zone D by solving a corresponding one-dimensional steady equation of diffusion. At given concentrations at the external and internal interfaces it yields

$$n_v(z) = \frac{n_1 - n'_1}{\lambda_v - \lambda_{vg}} (R + l + \lambda_{vg}) \left(1 - \frac{R + l + \lambda_v}{z} \right) + n_1, \quad [4]$$

where z is a radial coordinate measured from the center of the absorbing sphere. From the outside through the internal interface the following number of molecules diffuse per unit time:

$$\begin{aligned} \Psi &= 4\pi(R + l + \lambda_{vg})^2 D_1 \frac{dn_v}{dz} \Big|_{z=R+l+\lambda_{vg}} \\ &= 4\pi D_1 \frac{(R + l + \lambda_{vg})^2}{\lambda_v - \lambda_{vg}} \frac{R + l + \lambda_v}{R + l + \lambda_{vg}} (n_1 - n'_1). \end{aligned} \quad [5]$$

Here D_1 is a coefficient of binary diffusion of vapor through the carrier gas. Just the same number of molecules at a steady regime of diffusion penetrates to the absorbing sphere and the number of these molecules per unit time K_j^\dagger is given by Equation (3).

In what follows, let us assume that $\gamma_c \approx 1$. We discuss this assumption later.

What is u' ? In view of the essential difference between the molecular mass of the carrier gas and vapor molecules, the momentum and energy of the vapor molecule change slightly after the collision with the gas molecule. For instance, the velocity of the vapor molecule in one collision is altered proportionally to $m_0/m_1 \ll 1$, where m_0 is the molecular mass of the carrier gas. On the other hand, under diffusion through zone D with allowance for the velocity persistence, the vapor molecule collides about $\lambda_v/\lambda_{vg} \gg 1$ times. Numerical estimations show that under typical conditions of experiments in DCC (Bertelsmann et al. 1996) the product $m_1\lambda_{vg}/m_0\lambda_v$ is of order of unity that means the vapor molecule attains the mean velocity of the carrier gas. Thus we assume that u' is equal to the free-stream velocity of the carrier gas at the internal interface, i.e.,

$$u' = \left(\frac{8k_B T_d}{\pi m_0} \right)^{1/2}. \quad [6]$$

Another remark should be made regarding the total number of the vapor molecules colliding with the cluster. As follows from Figure 1, only a certain fraction of the vapor molecules having diffused to point "a" from the external interface can collide with the cluster, namely, those that have the direction of the velocity within the angle θ . On the other hand, in point "a" all directions of the velocity are equiprobable and hence as follows from Figure 1 the fraction of the collided molecules is $\Delta_j = \arcsin[(R + l)/(R + l + \lambda_{vg})]/\pi$. Strictly speaking, to estimate this fraction more precisely one has to consider a multidimensional diffusion equation, but for a qualitative estimation our consideration is sufficient. This problem has been explored in more detail in Sampson and Springer (1969).

In order to determine the flux Ψ_o , note that the number of molecules evaporating from the cluster surface is proportional to the activation energy, i.e., in a crude approximation $n_k \propto \exp(-L/k_B T_k) \propto n_{1e}(T_k)$, where L is the latent heat of condensation. Thus it is possible to assume $n_k = n_{1e}(T_k)$. As far as the velocity of outgoing molecules is concerned it has to be found by solving the full Knudsen layer problem while it is rather difficult to introduce a certain reasonable assumption on its value. Therefore we use the simplest approximation and based on the physical consideration note that in equilibrium $u'n'_1 = \Psi_o$. At $T = T_d$ this yields $u_k \approx u'$.

Further substituting Equation (6) in Equation (3), assuming $T_k \approx T_d \approx T$ and equating K_j and $\Delta_j \Psi$, we obtain

$$n'_1 = \frac{n_1 + n_{1e} a_j}{1 + a_j}, \quad a_j = \frac{u'(R + l)^2 \lambda_v}{D_1 (R + l + \lambda_{vg})(R + l + \lambda_v) \Delta_j}, \quad R = R(j), \quad [7]$$

and hence

$$K_j^\dagger = 4\pi(R + l)^2 u' n_1 \frac{S + a_j}{S(1 + a_j)}, \quad [8]$$

where $S = n_1/n_{1e}$ is supersaturation. If $a_j \ll 1$, i.e., if the diffusion rate is much more as compared with the rate of the chemical reaction, this formula gives a commonly used expression of the rate constant of the cluster formation. On the contrary, if $a_j \gg 1$, the rate of the cluster formation is determined by the transfer of the reacting molecules to the surface of the cluster.

Below we intend to show that under conditions of DCC, a_j is of order of unity for monomers and increases as j increases. This gives rise to a new expression of the rate constant of the cluster formation, which has never been utilized in the theory of nucleation. We start from a general expression of the coefficient of binary diffusion of monoatomic gases given by kinetic theory (Ferziger and Kaper 1972; Bretsznajder 1966) based on the following assumptions made: i) molecules interact like hard spheres with the Maxwellian distribution of velocities, ii) the concentration of the carrier gas is much more than the concentration of the vapor, iii) the attractive part of the potential describing the interaction between vapor molecules is taken into account by introducing the Sutherland correction. It yields

$$D_1 = \frac{3}{2n_0\sigma_{vg}^2} \left(\frac{k_B T}{\pi m_r} \right)^{1/2} \frac{1}{1 + C/T}, \quad [9]$$

where n_0 is the number density of the carrier gas, $m_r \approx 2m_0$ is the reduced mass of components, and $\pi\sigma_{vg}^2/4$ is a collision cross section of the vapor and gas molecules. Under conditions of DCC, σ_{vg} is approximately a sum of effective diameters of the vapor and gas molecules and C is the Sutherland constant. For λ_{vg} we use the following expression (Shilling 1972):

$$\lambda_{vg} = 4 \left[\pi n_0 \sigma_{vg}^2 \sqrt{1 + \frac{m_1}{m_0} \left(1 + \frac{C}{T} \right)} \right]^{-1}, \quad [10]$$

whence

$$D_1 = \frac{3\pi}{32} u' \lambda_{vg} \sqrt{1 + \frac{m_1}{m_0}}.$$

Combining all of the above expressions we find

$$a_j = \frac{(R+l)^2}{(R+l+\lambda_{vg})(R+l+\lambda_v)} \frac{32\lambda_v}{3\lambda_{vg}} \times \left[\sqrt{1 + \frac{m_1}{m_0}} \arcsin\left(\frac{R+l}{R+l+\lambda_{vg}}\right) \right]^{-1}. \quad [11]$$

In particular, at $R < \lambda_v$, with allowance for the fact that $\Delta_j \approx (R+l)/\pi(R+l+\lambda_{vg})$ at $R < \lambda_{vg}$, it yields

$$a_j \approx \frac{32(R+l)}{3\lambda_{vg} \sqrt{1 + \frac{m_1}{m_0}}}, \quad [12]$$

while at $R > \lambda_v$, one has

$$a_j \approx \frac{32\lambda_v}{3\lambda_{vg} \sqrt{1 + \frac{m_1}{m_0}}}. \quad [13]$$

Let us consider a typical experiment on nucleation of n-butanol in hydrogen (Bertelsmann et al. 1996). Numerical calculations show that at $T = 362$ K, $P_0 = 10$ bar, $l = 2.26$ Å, and $C = 60$ K (Reid et al. 1977), one has $\lambda_{vg} = 15$ Å while even for monomers we obtain $R+l = 4.5$ Å and $a_1 \approx 0.63$. Thus even for collisions of monomers the rate of diffusion determines to a considerable degree the resulting rate of this chemical reaction. For collisions of dimers and monomers when estimating σ_{vg} , one has to take into account i) a probable linear structure of the dimer and ii) the length of the hydrogen bond that yields $a_2 \sim 1$. As R further increases, a_j also increases and inequality $a_j > 1$ reinforces. That is why we introduce here the main assumption of our theory that $a_j > 1$ for all $j \geq 1$. Actually, we should choose the certain number j_1 and put $a_j > 1$ at $j \geq j_1 > 1$, but as shown later the assumption made that $j_1 = 1$ does not practically influence the final results. Thus we finally obtain

$$\begin{aligned} K_j^+ &= \mathcal{K}_j^+ \frac{S\Theta_j + 1}{S(1 + \Theta_j)} \approx \mathcal{K}_j^+ \frac{S\Theta_j + 1}{S}, \quad \Theta_j \ll 1, \\ \Theta_j &= \frac{(R+l+\lambda_{vg})(R+l+\lambda_v)}{(R+l)^2} \frac{3\lambda_{vg}}{32\lambda_v} \sqrt{1 + \frac{m_1}{m_0}} \arcsin \\ &\times \left(\frac{R+l}{R+l+\lambda_{vg}} \right) = \frac{3}{2\pi^2(1+C/T)} \frac{k_B T}{(R+l)P_0\sigma_{vg}^2} \\ &\equiv \Theta \frac{1}{(j^{1/3} + 1)} \approx \Theta j^{-1/3} \quad \text{at } R \leq \lambda_v \\ \Theta &= \frac{3}{2\pi^2(1+C/T)} \frac{k_B T}{P_0\sigma_{vg}^2} \left(\frac{4\pi\rho_l}{3m_1} \right)^{1/3}, \end{aligned} \quad [14]$$

where we introduced the notation \mathcal{K}_j^+ for the traditional (kinetic) rate constant¹ and Θ_j is our correction for the case of the

¹It is proportional to R^2 while K_j^+ in Equation (3) is proportional to $(R+l)^2$, but here we neglect this correction.

diffusion-limited kinetics. As follows from the previous analysis, $\Theta_j < 1$ and is inversely proportional to P_0 —the pressure of the carrier gas. For the sake of convenience, in what follows we will use the old notation K_j^+ for the traditional rate constant but instead in our equations the product $K_j^+(S\Theta_j + 1)/S$ appears.

As far as for the rate constant of the inverse process K_j^- is concerned it does not depend on the external environment of the cluster and is determined only by intracluster processes. A convenient approximation of K_j^- derived using the approach of the RRKM theory has been obtained in Itkin (1995) and Itkin and Kolesnichenko (1997).

Transport Processes in DCC Under Nucleation

Diffusion cloud chambers have frequently been utilized when investigating homogeneous nucleation. This section aims to reformulate theoretical representations of MNT for DCC. Preliminary results of this research have been published in part in Itkin et al. (1991) and Itkin and Kolesnichenko (1997).

The typical scheme of an experiment on studying nucleation in DCC is as follows (Heist et al. 1994). DCC consists of two horizontal plates—top cold and bottom hot. Over the bottom plate there is a liquid and the vapor condensation is a subject of the research. The space between plates is usually filled in with a background gas. By virtue of the existing distribution of temperature and pressure, the vapor evaporating from the bottom surface diffuses through the chamber that results in its cooling and then condensing. As a result of these processes, a certain steady-state distribution of supersaturation S over the height of the chamber ξ (usually reckoned from the bottom plate) is established. An occurrence of drops of the condensing vapor is detected by some kind of laser on the basis of light-scattering. With the help of such a system it is possible to determine a steady-state nucleation rate (i.e., a quantity of drops of the detectable size formed in unit of volume in time unit). Other characteristics—temperature, pressure, supersaturation—are usually found solving appropriate equations of diffusion and heat conduction under boundary conditions given on the walls of the chamber. The described scheme was repeatedly applied to study homogeneous nucleation of various substances. The experimental conditions are usually so chosen such that outside of a narrow zone where S reaches its maximum value (zone N), the latter is practically equal to unity and condensation does not occur there at all.

Since the vapor concentration in the chamber is low as compared to the concentration of the background gas, the processes of condensation do not practically influence the distribution of the temperature and pressure over the height of the chamber that are determined only by the boundary conditions at the walls and by the concentration n_0 . Moreover, it is possible to show that the temperature and the density gradients in the chamber (a typical value is $d\ln T/d\xi \approx 0.1$ cm⁻¹) are small as compared to gradients of the cluster's concentrations and in the first approximation may be neglected.

What we need is to study the processes occurring inside zone N . According to our general theory, we treat the studying mixture of gases and clusters as a mixture of ideal gases each of

which is characterized by the size of the identical clusters composing it. Usually MNT operates with a system of equations describing evolution of mass fraction of clusters which contain j molecules and have an average internal vibrational energy corresponding to a quantum state k (so, actually, $\alpha_j(k)$ is a population of this state). We assume that the cluster mass fraction changes due to processes of diffusion, condensation, and relaxation of vibrational intracuster states. However, under conditions of DCC when $n_0 \gg n_1$, relaxation of intracuster vibrations is fast as compared with the rate of nucleation limited by diffusion of the condensing molecules to each other. Thus in this case vibrational levels of clusters are in equilibrium. In other words, the main parameter of MNT, r , is equal to unity (Itkin and Kolesnichenko 1997). That is why from the very beginning we may simplify the original system of equations given in Itkin et al. (1991) and Itkin and Kolesnichenko (1997) expressing equilibrium populations $\alpha_j(k)$ through mass fractions α_j according to the Boltzmann equilibrium distribution. If so, the following continuity and diffusion equations for the mixture components obtained in the Navier–Stokes approximation may be considered

$$\begin{aligned} \partial(\rho\alpha_i)/\partial t + \nabla(\rho\mathbf{v}\alpha_i) &= \rho\Phi_i - \nabla(\rho\alpha_i\mathbf{V}_i), \\ \nabla X_i &= \sum_j^N \left(\frac{X_i X_j}{D_{ij}} \right) (\mathbf{V}_j - \mathbf{V}_i) + (\alpha_i - X_i) \frac{\nabla P}{p} + \frac{\rho\alpha_i}{p} \\ &\times \left(\mathbf{f}_i - \sum_{j=0}^N \alpha_j \mathbf{f}_j \right) + \frac{\nabla T}{T} \sum_{j=0}^N \frac{X_i X_j}{\rho D_{ij}} \left(\frac{D_{T,j}}{\alpha_j} - \frac{D_{T,i}}{\alpha_i} \right) \\ i &= 0, \dots, N, \quad \alpha_i = n_i m_1 / \rho. \quad [15] \end{aligned}$$

Here ρ , P , T are the mass density, pressure, and temperature of the mixture, t is time, \mathbf{v} is the mass-average velocity vector, α_i and \mathbf{V}_i are the mass fraction and diffusion velocity vector of i clusters, X_i is their mole fraction, \mathbf{f}_i is the mass force acting on these clusters, D_{ij} is the coefficient of binary diffusion of the gas composed of i clusters through the gas composed of j clusters, $D_{T,i}$ is the thermal diffusion coefficient, n_i are the corresponding numerical densities (concentrations), index $i = 1, \dots, N$ represents the cluster gases, and $i = 0$ —the neutral gas, Φ_i —is the kinetic source term associated with condensation. In accordance with Itkin and Kolesnichenko (1990), Itkin et al. (1991), and Itkin and Kolesnichenko (1997) at $r = 1$, Φ_i can be written as follows:

$$\begin{aligned} \Phi_j &= I_j - \frac{j}{j+1} I_{j+1} (1 - \delta_{jN}), \quad j > 1, \\ \Phi_1 &= - \sum_{j=2}^N \frac{1}{j} I_j (1 + \delta_{j2}), \quad \Phi_0 = 0, \\ I_j &= K_j^+ \theta_{j-1} \alpha_{j-1} \alpha_1 \frac{\rho j}{m_1(j-1)} - K_j^- \alpha_j, \quad \theta_j \equiv \frac{S\Theta_j + 1}{S(1 + \Theta_j)}, \end{aligned} \quad [16]$$

however, here in contrast to usual kinetic equations of nucleation a new term θ_j is presented in the definition of the flux I_j because

as described above under our conditions the nucleation kinetics is diffusion limited. In Equation (16) δ_{ij} is Kronecker's symbol.

When deriving Equation (16) the processes of formation (dissociation) of the cluster by attaching (detaching) dimer, trimer, etc. as well as triple collisions were neglected. But the law of conservation of the total number of molecules in the system has already been taken into account, because Equation (16) holds the relationship $\sum_j \alpha_j = 1$.

For further progress, a few assumptions should be made (Itkin et al. 1991; Bogdanov et al. 1991; and Itkin and Kolesnichenko 1997).

1. Usually, at DCC conditions, only steady processes with $\partial\alpha_i/\partial t = 0$ and $|\mathbf{v}| \ll |\mathbf{V}_i|$ are important.
2. Only the distribution of concentrations of various clusters over ξ is of practical interest. In these circumstances it is perfectly permissible to use a one-dimensional approximation, having chosen as the axis ξ a perpendicular drawn from the bottom plate to the top one (two-dimensional effects are discussed in Bertelsmann and Heist (1996).
3. By virtue of reasons mentioned at the beginning of this paragraph, we neglect the terms containing $\nabla P = 0$ and ∇T as well as mass forces and thermal diffusion.
4. Usually, because of the design features of DCC, $\alpha_0 \gg \alpha_i$, $i = 1, \dots, N$, and $\mu_0 \ll \mu_i$ (He or H₂ are usually used as the carrier gas). We need this assumption to be valid at least in zone N .

As shown in Itkin et al. (1991), Bogdanov et al. (1991), and Itkin and Kolesnichenko (1997) under these assumptions, Equation (15) can be reduced to the following:

$$\frac{d}{d\xi} \left[\rho D_{i0} \frac{d}{d\xi} \left(\frac{\alpha_i}{\alpha_0} \right) \right] = -\rho\Phi_i. \quad [17]$$

As $\alpha_0 \approx 1$ while $d\alpha_0/d\xi$ and $d \ln \rho/d\xi$ are quantities of the same order as $d \ln T/d\xi$ by which we neglect according to the assumption made, we finally obtain

$$\frac{d}{d\xi} \left[D_{i0} \frac{d\alpha_i}{d\xi} \right] = -\Phi_i, \quad i = 1, \dots, N. \quad [18]$$

The boundary conditions for Equation (18) can be formulated if one takes into account that at the top and bottom plates the vapor is in equilibrium, i.e., $S = 1$. It yields

$$\begin{aligned} \alpha_i|_{\xi=h} &= im_1 n_{ie} / \rho|_{\xi=h}, \\ \alpha_i|_{\xi=0} &= im_1 n_{ie} / \rho|_{\xi=0}. \end{aligned} \quad [19]$$

Thus we have managed to split the system of Equations (15), (16) into the independent equations describing diffusion of i clusters through the carrier gas with allowance for simultaneously occurring nucleation. Equation (18) obeys the additional

conditions

$$\sum_{j=1}^N D_{j0} \frac{d\alpha_j}{d\xi} = const, \quad [20]$$

$$\sum_{j=0}^N \alpha_j = 1,$$

which express the conservation of the total mass of the gas mixture.

QUASISTEADY-STATE METHOD

A special method based on the ideas of MNT as applied to Equation (18) has been proposed in Itkin et al. (1991). Below we shortly formulate its main features. First of all, we transform Equation (18) to the form

$$\begin{aligned} d\alpha_j/d\xi &= -\eta_j/D_{j0}, \\ d\eta_j/d\xi &= \Phi_j, \quad j = 1, \dots, N, \end{aligned} \quad [21]$$

introducing new variables η_j . Further, instead of variables η_j we substitute first new variables $g_j = \eta_j/\alpha_j$ and then variables G_j in accordance with the relations

$$\begin{aligned} G_0 &= \frac{g_1}{D_{10}}, \\ G_j &= \frac{(g_{j+1} - g_j)}{(\alpha_{1e} D_{j0})}, \end{aligned}$$

where α_{je} is the equilibrium mass fraction of j clusters (Bogdanov et al. 1992; Itkin and Kolesnichenko 1997). Finally, the fourth and major step is that we take advantage of the MNT idea (Itkin and Kolesnichenko 1990) of a nonlinear substitution of variables $\alpha_j, j = 1, \dots, N \rightarrow f_1, \dots, f_{N-1}$, where

$$\begin{aligned} f_j &= \frac{\bar{n}_{j+1}}{\theta_j S \bar{n}_j}, \quad j = 1, \dots, N-1, \\ \bar{n}_j &= \frac{n_j}{n_{je}}, \quad S = \frac{n_1}{n_{1e}}, \quad n_j = \frac{\alpha_j \rho}{j m_1}. \end{aligned} \quad [22]$$

The variables f_j have a lot of advantages over the initial variables α_j . For instance, they are dimensionless and turn to unity at the equilibrium. However, their main advantage is that it is possible to split them into two groups—the slow and fast ones (see Itkin and Kolesnichenko (1997) and Itkin (1998)) that can never be done for concentrations. It is caused by the circumstance that in Equation (16) Φ_j is defined as the difference between two fluxes (for instance, $I_j - I_{j+1}$) that can be small at the equilibrium and large far from it. Therefore it is hard to estimate the order of the magnitude of Φ_j if they are written through variables α_j .

Let us formulate briefly the essence of our method.

1. We show that with new variables the initial system of the coupled nonlinear equations for the cluster concentrations

(or mass fractions) could be decomposed in such a way that each equation of this new system could be solved independently from each other (factorization). Three important assumptions are made to do that.

- For the large clusters the following relationship is valid $K_j^+, K_j^- \propto j^k, k \leq 1$.
- The equilibrium concentrations follow the relationship $n_{je}/n_{1e} \ll 1$.
- Variables f_j smoothly depend upon j so that

$$1 - \frac{f_j}{f_{j-1}} \simeq \varepsilon \ll 1.$$

In Itkin and Kolesnichenko (1993), Itkin (1995), and Itkin and Kolesnichenko (1997), the model expressions of the cluster formation and decay rate constant were obtained with the help of the statistical theory of chemical reactions. As shown in these works, for such constants there is a reliable evidence of these assumptions.

- It turns out that among all new variables only α_1 and $f_j, j > (2/3\varepsilon)^3, \varepsilon \ll 1$ are the slow ones in contrast to the other fast f_j . It can be shown that the slow f_j make a weak contribution to the variation of α_1 as against the fast f_j . It enables the equation for α_1 to be independent of the others and one can solve it separately. The other α_j could be found by means of the analytical expressions derived by us in Itkin et al. (1991) with α_1 and T determined before.

In particular, in Itkin and Kolesnichenko (1997, 1990) the following expressions for the equilibrium concentrations of the cluster have been obtained: $n_{je} = A(T) \exp(-bj^{2/3}), b = (4\pi\sigma/k_B T)(3m_1/4\pi\rho_l)^{2/3}$, where σ is the surface tension, A is a certain coefficient given in Itkin and Kolesnichenko (1997).

As applied to the case of diffusion-limited kinetics this method is described in more detail in Itkin et al. (1991). Based on that consideration we arrive at the following final solutions

$$\begin{aligned} G_j &= 0, \quad f_j = 1, \quad j \leq y, \\ G_j &= 0, \quad f_j = C_j/A_j, \quad j > y, \end{aligned} \quad [23]$$

where y is the root of the equation $C_y/A_y = 1$ and A_j and C_j are determined in Itkin et al. (1991) as

$$A_j = [K_{j+1}^+(1 - \delta_{jN}) - K_j^+]S, \quad C_j = [K_{j+1}^- - K_j^-(1 - \delta_{j1})]/n_{1e}.$$

Note that the solutions obtained for f_j coincide with that obtained in Itkin and Kolesnichenko (1990) for spatially uniform systems. Therefore, taking argumentation of that paper into account one further gets the following equations for the slow variables $\alpha_1, G_0, f_j, G_j, j = \bar{j} + 1, \dots, N - 1$ (see the definition

of \bar{j} in Itkin et al. (1991):

$$\begin{aligned} \frac{d \ln \alpha_1}{d \xi} &= -G_0 \alpha_{1e}, \\ \frac{d G_0}{d \xi} &= G_0^2 \alpha_{1e} - n_{y+1,e} S^y K_{y+2}^- \frac{2b}{9y^{7/3} \alpha_1 \alpha_{1e} D_1} \prod_{i=1}^y \theta_i, \\ \frac{d f_j}{d \xi} &= f_j (G_0 - G_j) \alpha_{1e}, \\ \frac{d G_j}{d \xi} &= -\frac{\phi_j}{f_j} \bar{R}(f_j) + G_j \alpha_{1e} \\ &\quad \times \left[G_j + 2G_0 \frac{D_1}{D_j} + 2 \sum_{i=1}^{j-1} G_i \frac{D_i}{D_j} (1 - \delta_{j, \bar{j}+1}) \right], \\ j &= \bar{j} + 1, \dots, N - 1. \end{aligned} \quad [24]$$

From the first two equations of (24) a closed equation for α_1 follows:

$$\frac{d}{d \xi} \left(D_1 \frac{d \alpha_1}{d \xi} \right) = n_{y+1,e} S^{y+1} K_{y+2}^- \frac{2b}{9y^{7/3}} \prod_{i=1}^y \theta_i. \quad [25]$$

Solving this equation one can get α_1 . The boundary conditions for Equation (25) are quite natural because at the top and bottom of the chamber $S \approx 1$, hence $\alpha_1 = \alpha_{1e}(T)$.

Parameter y and Quasisteady Concentrations

As mentioned y is the root of the equation $C_y/A_y = 1$. To express C_j and A_j in an explicit form we need to know quasisteady concentrations of the clusters. In turn, for $j \geq 2$ they could be found using the definition of f_j given in Equation (22). Inverting the dependence of f_j on n_j and S we find

$$\bar{n}_j = S^j \prod_{i=1}^{j-1} f_i \theta_i. \quad [26]$$

As shown in Itkin et al. (1991) at $j < y$ the quasisteady solution in f variables is $f_j = 1$, hence

$$n_j = n_{je} S^j \prod_{i=1}^{j-1} \theta_i, \quad j \leq y. \quad [27]$$

At $j > y$ one has $f_j = C_j/A_j$. According to the definition of C_j and A_j given in Itkin et al. (1991),

$$\begin{aligned} \frac{C_j}{A_j} &= \frac{K_{j+1}^+ \frac{n_{je} n_{1e}}{n_{j+1,e}} - K_{j+1}^+ \frac{n_{j-1,e} n_{1e}}{n_{je}}}{[K_{j+2}^+ \theta_{j+1} (1 - \delta_{j, N-1}) - K_{j+1}^+ \theta_j] n_1} \\ &\approx \frac{1}{S} \frac{\partial (K_{j+1}^+ \frac{n_{je}}{n_{j+1,e}})}{\partial j} \left[\frac{\partial (K_{j+1}^+ \theta_j)}{\partial j} \right]^{-1} \\ &= \frac{1}{S \theta_j} \frac{n_{je}}{n_{j+1,e}} \frac{1 + \delta_j}{1 + \delta_j (3j^{1/3}/2b)}, \\ \delta_j &= \frac{\partial \ln n_{je}/n_{j+1,e}}{\partial j} \left[\frac{\partial \ln K_{j+1}^+}{\partial j} \right]^{-1}. \end{aligned} \quad [28]$$

As shown in Itkin and Kolesnichenko (1997) for the rate constants obtained in Itkin and Kolesnichenko (1993) and Itkin (1995) $\delta_j \ll 1$ if S exceeds 2–3 as it usually does in zone N in experiments in DCC. At $1 < S < 2$ we need to take the value of δ_j into account, but actually this correction is small enough. Therefore from Equation (28) we find approximately

$$\frac{C_j}{A_j} = \frac{1}{S \theta_j} \frac{n_{je}}{n_{j+1,e}}. \quad [29]$$

Thus with allowance of the expression of n_{je} given above, y is a root of the equation

$$\frac{2b}{3y^{1/3}} - \ln S \theta_y = 0, \quad [30]$$

where θ_j is determined in the previous sections. Generally, this equation has to be solved numerically. In addition, from Equations (26) and (28) we obtain

$$n_j = n_{ye} S^y \prod_{i=1}^{y-1} \theta_i \prod_{k=y}^{j-1} \frac{\frac{\partial \ln K_{k+1}^+}{\partial j} + \frac{\partial \ln n_{je}/n_{j+1,e}}{\partial j}}{\frac{\partial \ln K_{k+1}^+}{\partial j} + \frac{\partial \ln \theta_k}{\partial j}}, \quad j > y. \quad [31]$$

These formulae can be used for any arbitrary relation between the rates of diffusion and chemical reactions because the term θ_j yields $S \theta_j + 1$ at small $\Theta_j \ll 1$ (diffusion-limited nucleation), while at high Θ_j (usual nucleation) it yields 1. It is interesting that at high Θ_j and intermediate S Equation (30) yields $y \approx j_{*,cl}$, where $j_{*,cl}$ is the critical size—a parameter inherent to all nucleation theories. From the physics standpoint it is easy to see that an individual droplet with size y is in equilibrium with the surrounding vapor at the diffusion-limited kinetics and, hence, y is an analog of $j_{*,cl}$ in this case. But at arbitrary S and θ_j the value of y differs from $j_{*,cl}$.

ANALYSIS OF THE MODEL ASSUMPTIONS

The main conclusion that can be made based on the above results is that at certain values of the temperature and, more important, pressure of the carrier gas a special regime of nucleation is established where the rate of the cluster formation is determined mainly by the rate of diffusion of the vapor molecules to the surface of the cluster. This situation occurs if the rate of a chemical reaction itself—a capture of the monomer attaching the cluster—is much more than the rate of diffusion. As follows from Equation (14) this case is realized at high pressures of the carrier gas, a large effective diameter (or cross section) of the condensing molecules, comparatively low temperatures. We call this regime “diffusion-limited nucleation,” but such processes are well known and even rather widely occur in chemical kinetics (Frank-Kamenetskii 1947; Fuchs 1955). However, for nucleation this effect here is considered for the first time.

When developing a theory of the diffusion-limited nucleation on the basis of our microscopic nucleation theory we made few

assumptions which have a clear physical sense. The only point that should be discussed is the value of the condensation coefficient γ_c . In the above we considered the case $\gamma_c = 1$, while strictly speaking there is no reliable data on the condensation coefficient in the literature. Various authors based on the macroscopic experiments estimate this value to range from 1 and to 0.001 (Mason 1971; Andreev et al. 1972), while the theoretical prediction made in our work (Itkin and Kolesnichenko 1993, 1997) on the base of the RRKM theory gives the values of γ_c of order of $10^{-2} - 10^{-4}$. It is clear that accounting for γ_c modifies, for instance, Equation (12) as follows

$$a_j \approx 32\gamma_c(R+l) \left(3\lambda_{vg} \sqrt{1 + \frac{m_1}{m_0}} \right)^{-1}. \quad [32]$$

Thus at small γ_c the value of a_j is small for small clusters and hence for them the usual kinetics of nucleation takes place. As the size of the cluster increases, a_j also increases and beginning from the certain number j_1 the value of a_j will be more than unity. However, at small γ_c the number j_1 could be large enough and such clusters slightly contribute to the observable rate of nucleation. Thus for small γ_c it is reasonable to expect that the carrier gas does not considerably affect nucleation. On the other hand, an existence of the effect of the carrier gas on the observed nucleation rate permits one to expect that this is just the case when γ_c is of order of unity.

Another point which has to be made is that when deriving Equation (30) we assume S to be not very close to unity. In doing so we based on the typical experimental conditions in DCC but, in a general case, one may consider arbitrary supersaturations. Indeed, a general expression of MNT for the unimolecular dissociation rate constant of the j cluster is as follows (Itkin 1995; Itkin and Kolesnichenko 1993, 1997):

$$\begin{aligned} K_j^- &\approx W_d(T) j^{2/3} \exp(-E_a/k_B T), \\ W_d(T) &= \frac{8h\nu_l}{k_B T} Z_{1,2,r}^+ \left(\frac{\eta}{d_1} \right)^2 \nu_t (1 + 1/\beta_t), \\ E_a &= E_b \bar{y}_j, \quad \beta_i = \exp\left(\frac{h\nu_i}{k_B T} \right) - 1, \quad i = t, l. \end{aligned} \quad [33]$$

Here h is the Planck constant, ν_l and ν_t are the mean geometric frequencies of the translational and librational intracluster vibrations, d_1 is an effective diameter of the monomer in the cluster (at $j = 1$ one has $d_1 = \sigma_1$), $\eta = (3m_1/4\pi\rho_l)^{1/3}$, $Z_{1,2,r}^+$ is the partition function of free rotations of the activated complex (the cluster with the dissociating molecule) around the axes perpendicular to the reaction coordinate (in Itkin (1995) and Itkin and Kolesnichenko (1993, 1997) the following representation is obtained $Z_{1,2,r}^+ = 2\mu_j (r^+)^2 k_B T \pi / h^2$, where μ_j is the reduced mass of fragments ($\mu_j \approx m_1$), r^+ is about twice the bond length between the dissociating monomer and the cluster consisting of the other $j - 1$ molecules), and E_b is the average dissociation energy per one chemical bond, \bar{y}_j is the average number of bonds of the molecule which could be capable of leaving the cluster,

with the other molecules in the cluster. For instance, it is known (Kistenmacher et al. 1974) that the small water clusters can exist in two different configurations: 1) a circular one in which each molecule is bonded with its neighbors by two hydrogenous bonds (the most energetically profitable configuration for the clusters with $j > 2$); 2) a linear structure in which the neighboring molecules are connected by the only bond. In contrast to that for the large clusters containing over 100 molecules a molecule located at the cluster surface (the most probable to dissociate) has up to the maximum number of bonds. For the water clusters, this maximum number is equal to 4 (Dae et al. 1972).

Unfortunately, at present there is no available experimental and especially theoretical data on the \bar{y}_j variation under j growth. Therefore in Itkin (1995) and Itkin and Kolesnichenko (1993, 1997), the simplest approximation was used.²

$$\bar{y}_j = l_1 - \frac{l_2 m}{(j + m - 2)}, \quad [34]$$

where l_1 , l_2 , and m for each substance are constants. We choose l_1 , l_2 , and m in an indirect way, namely, we used MNT when calculating the condensation process in nozzles, jets, aerodynamic tubes, thermal diffusion chambers, etc. and compared the results of our prediction with the experimental data further fitting the above parameters. It turns out that, for instance, for water vapor one manages to reach the best agreement at $l_1 = 3.5$, $l_2 = 1.5$. The half-integer values of l_1 and l_2 are taken because the water dimer can exist in two configurations which correspond to the circular and linear structure of the dimer and we take the average value of l_1 and l_2 for these two structures. The variation of m weakly influences the final results on the condensation kinetics, however, this parameter allows one to change the rate of the \bar{y}_j variation. In our calculations we assume that the cluster containing more than 150–200 molecules is a macrocluster so the difference between \bar{y}_∞ and \bar{y}_{100} should not exceed 5%. Hence, $m \approx 16$ –20. In the limiting cases $j = 2$ and $j \rightarrow \infty$ approximation Equation (34) gives correct values of \bar{y}_j . Note that for the water molecule E_b is of order of 5–6 kcal/mol so that $E_b/k_B T \approx 2500/T \approx 8$ at $T = 300K$. Therefore K_j^- considerably decreases under j growth. That is why for the large clusters the rate of relaxation at high levels is much greater than the rate of dissociation at these levels in contrast to the small clusters for which the opposite relationship takes place.

The rate of the cluster formation K_j^+ could be expressed through the rate of the cluster unimolecular decay K_j^- using the relationship of the detailed balancing

$$K_j^+ = K_j^- n_{j+1,e} / n_{j,e} n_{1,e}. \quad [35]$$

Using the above expressions it is easy to show that at low S the root of the equation $C_y/A_y = 1$ has to be found by equating

²Generally speaking, the energy of the hydrogenous bond per molecule increases with j growth (Kistenmacher et al. 1974).

the right-hand side of the definition of C_j/A_j in Equation (28) to unity. Thus y exists for any S but it has another form at low S .

At intermediate S and low $j \sim m$ we consider the relationship

$$\begin{aligned} \delta_j &= \frac{\partial \ln\left(\frac{n_{j+1,e}}{n_{j,e}}\right)}{\partial j} \left(\frac{\partial \ln \bar{K}_j^+}{\partial j}\right)^{-1} \\ &= -\frac{b}{3j^{1/3}} \left[1 - \frac{3}{2} \frac{\hat{E}_b m l_{2j}}{(j+m)^2} H(j_k - j)\right]^{-1}, \end{aligned}$$

where $H(j_k - j)$ is the Heaviside step function and put $j_k \approx 5m$. At intermediate S and low $j \sim m$ the value of the square bracket is rather large, therefore δ_j is small enough and hence we obtain the relationship which has been used above when deriving Equation (30), namely, $\partial \ln K_{j+1}^+ / \partial j \gg \partial \ln(n_{j,e}/n_{j+1,e}) / \partial j \sim \partial \ln \Theta_j / \partial j = -1/3j$.

From the results obtained it follows that at the diffusion-limited nucleation the quasisteady concentrations of clusters as well as the rate of the evolution of α_1 or S are no longer a function of two parameters, T and S , but three because now in addition they depend on the carrier gas pressure as well as on the nature of both the carrier gas and the condensing vapor. This dependence appears through the values of the collision cross section and the mean free path of the vapor molecules through the carrier gas and it must be taken into account when treating the experimental results and comparing them with the others and with a theoretical prediction.

In conclusion note that the proposed theory allows one to develop a special investigation of the nucleation kinetics in DCC and even quantitatively compare this prediction with the available experimental data. This analysis is presented in Itkin (2000).

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