On the dependence of a critical supersaturation on pressure of a two-component background gas in a diffusion cloud chamber

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Abstract

An analytical dependence of a critical supersaturation S_* on partial pressures P_i of a two-component (index $i = 1,2$) background gas at a constant temperature in a diffusion cloud chamber (DCC) is obtained on the basis of a theory of diffusion-controlled nucleation proposed earlier by the author (J. Aerosol Sci., submitted). Despite this theory qualitatively and even quantitatively reproduces the available experimental data of Heist [1] a new experiment is proposed in order to examine it more carefully. For this purpose we imply to use a two-component mixture of insoluble gases as a background gas when performing a traditional experiment on studying the dependence of S_* on the background gas pressure in DCC. A new model of nucleation at such conditions is developed and it is shown that a variation of the pressures of both components of the two-component background gas in an appropriate way in DCC at a constant nucleation rate and the temperature in the maximum nucleation plane can result in both the increase and the decrease of critical supersaturation S_* and even keep S_* to be constant. This conclusion is the main result of the present theory which admits a direct experimental verification. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

In the existing theories of homogeneous nucleation it is accustomed to consider that a concentration of a noncondensible (carrier) gas does not affect the rate of nucleation. Moreover, it is supposed that the higher the gas concentration, the closer the nucleation process is to the isothermal one for which classical nucleation theory (CNT) was originally built. However, in paper [1] and many others on the

basis of the experimental data on homogeneous condensation of H_2O, D_2O and some alcohols in an inert gaseous atmosphere it was discovered that the critical supersaturation linearly increases with the increase of the carrier gas pressure P_0. Besides, with the temperature decrease a slope of isotherms $S_*(P_0)$ becomes more abrupt.

That is why the aim of our recent paper was to consider in more detail the kinetic processes in DCC using some ideas specific for the kinetics of chemical reactions. In particular, as pointed out in Ref. [4] when a certain chemical reaction realizes in the nature its observed rate is determined on the one

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hand by a real chemical kinetics on the surface of the interacting particles, but on the other hand by the rate of a transport of the reacting medium to this surface due to the molecular or convective (in particular, turbulent) diffusion. As can be shown the second way becomes extremely important when the concentration of the reacting component is small (a rarefied vapor) as compared with the concentration of a carrier gas and simultaneously the rate of a chemical reaction is much more than the rate of diffusion.

In Ref. [9] a model of the nucleation process under conditions when a transport of condensing molecules to the cluster surface is determined by their diffusion through a carrier gas has been proposed. The main physical idea exploited within our approach is the following. 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 a 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 to be 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 in view 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.

In Ref. [9] we use a special mathematical formalism which is strongly based on the microscopic theory of nucleation [7] put forward by the author which allows an analytical representation of the cluster's concentrations through supersaturation, the gas temperature and, that is quite new in the case of DCC, the carrier gas pressure. It is shown that the usual conditions of experiments in diffusion cloud chambers where the concentration of the vapor is small, meet the requirements of the model validity that means this model can be adopted to explain a mechanism of the carrier gas pressure influence on the nucleation kinetics observed in experiments [1]. In particular, as follows from our analysis instead of a usual supersaturation S all expressions of the the-

ory contain a product $S\Theta$ where $\Theta \propto 1/P_0$ and depends upon the cross-section of the carrier gas and condensing molecules.

The main conclusion which can be made based on the above results is that at certain values of the temperature and, that is more important, pressure of a carrier gas a special regime of nucleation may establish. As follows from the analysis of [10] 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 wide occur in chemical kinetics [4]. However, for nucleation this effect have been considered in Ref. [9] for the first time.

From the results obtained it follows that in addition at the diffusion-limited nucleation the quasisteady concentrations of clusters as well as the rate of the evolution of the monomer's mass fraction α_1 become no longer be 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.

Based on the results obtained an analysis of the available experimental data on the dependence of S_* on P_0, T and the nature of the condensing and background gases have been developed in Ref. [10]. The typical scheme of an experiment on studying nucleation in DCC is as follows [5]. DCC usually consists of two horizontal plates — top cold and bottom hot, but an inverse scheme has also been utilized (for instance, by [11]). Over the bottom plate there is a liquid which 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 the temperature and pressure the vapor evaporating from the bottom surface moves due to diffusion through the chamber then cooling and again condensing. As a result of these processes an appropriate 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 condensed vapor is detected by some kind of light-scattering or even visually.

Since the vapor concentration in the chamber is low as compared with the concentration of the buffer gas, the processes of condensation do not practically influence the distribution of the temperature and pressure over the height of the chamber which are determined only by the boundary conditions at the walls and by the carrier gas pressure P_0. Moreover, it is possible to show that gradients of the temperature $\mathrm{d}\ln T/\mathrm{d}\xi \approx 0.1$ cm^{-1} and density realized in the chamber are small as compared with the gradients of the clusters' concentrations and in the first approximation may be neglected when describing the nucleation kinetics in DCC.

Since the experimental investigations of the carrier gas effect on the nucleation rate in DCC became relatively popular it is possible to note from the literature that there is a trend to present the experimental data in coordinates $S_*(P_0)$ or $S_*(T_*)$ where S_* is the supersaturation corresponding to $J = 1$ drop/cm^3/s. In order to reproduce them in Ref. [10] we proposed a new approach which combines a proper treatment of physical processes in DCC and our new kinetic scheme of nucleation in the presence of the background gas (a diffusion-limited kinetics of nucleation). Fist we analyzed the transport processes in DCC with allowance for brownian diffusion, gravity, drag and thermophoretic forces, that values depend on the cluster size or the Knudsen number specific for droplets, nucleation and the droplet growth and revealed their role with respect to the measured number of drops in DCC. Than we analyzed what is the nucleation rate J actually determined in the experiment. Because usually experimenters represent their results (in particular, J) as a function of S_*, T_* and P_0 where subscript $*$ marks the point of the maximum supersaturation or a close point of the maximum nucleation rate, the main goal of that consideration was to express explicitly J through these parameters. However, for this purpose a certain kinetic model of nucleation should be introduced. Thus, we studied in more detail processes in the zone of active nucleation because they determine the number of droplets which then are measured in the experiment.

Finally, analytical dependencies of critical supersaturation S_* and $\partial S_*/\partial P$ on a carrier gas pressure P_0 and temperature T in DCC were derived on the basis of the above approach. These dependencies qualitatively reproduce the available experimental data of Heist and his group [1,5,6]. In addition the influence of the nature of both the carrier gas and condensing vapor on the observed phenomenon is discussed in Ref. [10]. The conclusion is made that the effect of the carrier gas in the experiments in DCC has no connection to the real rate of chemical reactions of clusterization and at other conditions (for instance, in expansion chambers) may not occur. Nevertheless an existence of the carrier gas influence on the total nucleation rate can be of great importance for the control of nucleation.

We must also mention that nowadays there exist some other attempts to explain the observed experimental facts on the influence of the background gas on the nucleation rate [12,16], however within these approaches it is difficult to restore even the qualitative picture of the discussed phenomenon (see discussion in Ref. [9]). Nevertheless in order to give an additional evidence for the diffusion mechanism of the considered effect it would be reasonable to perform some special experiments. Fortunately, a consideration of nucleation in DCC when a background gas is a mixture of two insoluble gases gives a good opportunity to make such a verification practically at similar experimental conditions. That is why the aim of this paper is utilizing this idea to develop a model of nucleation at such conditions and to propose a scheme of the experiment which could bring an essential information on the physical mechanism of the process.

2. Diffusion-controlled regime of nucleation in the environment of a two-component background gas

As pointed out in Introduction 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, but 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 in Ref. [9] the second way becomes extremely

important when the concentration of the reacting component is small as compared with the concentration of a carrier gas and simultaneously the rate of a chemical reaction is much more than the rate of diffusion, and the typical conditions in DCC meet these requirements.

Below we analyze how this special regime affects the form of the respective kinetic equations and their solutions.

2.1. Diffusion-controlled kinetics of nucleation

We start from a usual expression of the nucleation theory for the flux I_j in a space of cluster sizes for clusters consist of j molecules

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

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

$$K_j^+ = \alpha_c K j^{2/3} \tag{2}$$

where $K = K_1 (3m_v / 4\pi \rho_l)^{2/3}$, $K_1 = (k_B T / 2\pi m_v)^{1/2}$, i.e. $K_1 n_1$ is a free molecular flux per surface of a unit sphere, m_v is the vapor molecular mass, ρ_l is the liquid density, k_B is the Boltzmann constant, α_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 found from the principle of the microscopic reversibility for the reaction $A_{j-1} + A_1 \leftrightarrow A_j$ 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 a 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 to be 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 in view 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. Further we study this problem in more detail.

Let us consider an isolated cluster surrounded by a mixture of the condensible vapor and a two-component background gas. We will use subscripts 1 and 2 to denote the components of the background gas and assume that these components are insoluble. In accordance with the design of DCC the total numerical density of the background gas $n_0 = n_{01} + n_{02}$ is few orders more that the numerical density of the vapor n_1. Therefore, the mean free path of the vapor molecule in the own vapor λ_v is about two orders more in length than the mean free path of this molecule in the carrier gases λ_{v1} and λ_{v2}. Hence, the structure of the Knudsen layer around the droplet can be presented as shown in Fig. 1. Here we assume that $\lambda_{v2} > \lambda_{v1}$ but it is not essential for the future. We also 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 then the collision occurs when this molecule reaches the surface of the
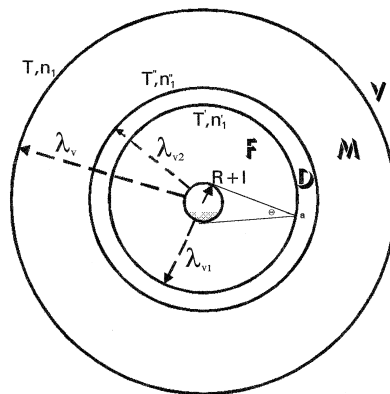

Fig. 1. Areas around a cluster, R is the radius of the cluster, l is the radius of the condensing molecule, λ_v, λ_{v1}, λ_{v2} are mean free paths of vapor molecules in the vapor and in the first and second carrier gases, T, T', T'', T_k and n_1, n_1', n_1'', n_k are temperatures and numerical densities 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 first carrier gas, M is an area of diffusion of the vapor through the mixture of the carrier gases, V a fluid dynamic area.

absorbing sphere with the radius $R + l$, R is the cluster radius. In Fig. 1 T_k and n_k are the temperature and concentration of the incident molecules at the surface of the droplet, T', T'' and n_1', n_1'' are the corresponding parameters at the first and second internal interfaces located approximately at the distance λ_{v1} and λ_{v2} respectively from the surface of the absorbing sphere, 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 vapor and the carrier gas is described by usual fluid dynamic models. In area M the vapor molecules collide only with the molecules of both carrier gases, in area D the vapor molecules collide only with the molecules of the carrier gas 1, while in area F they move like in vacuum 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

$$K_j = 4\pi\alpha_c(R + l)^2(u'n_1' - \Psi_0), \qquad (3)$$

where Ψ_0 is the flux of outcoming molecules (evaporating and reflecting from the cluster surface), n_1' 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 of such a problem which is not solved yet, therefore we use some more crude estimations.

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

$$n_v(z) = \frac{n_1 - n_1''}{\lambda_v - \lambda_{v2}}(R + l + \lambda_{v2})$$
$$\times\left(1 - \frac{R + l + \lambda_v}{z}\right) + n_1,$$
$$n_v(z) = \frac{n_1'' - n_1'}{\lambda_{v2} - \lambda_{v1}}(R + l + \lambda_{v1})$$
$$\times\left(1 - \frac{R + l + \lambda_2}{z}\right) + n_1'', \qquad (4)$$

where z is a radial coordinate counted from the center of the absorbing sphere, $n_v(z)$ is a respective concentration. From the outside through the internal interfaces the following number of molecules diffuse per unit time

$$\Psi_2 = 4\pi(R + l + \lambda_{v2})^2 D_{1m}\left.\frac{dn_v}{dz}\right|_{z = R + l + \lambda_{v2}}$$
$$= 4\pi D_{1m}\frac{(R + l + \lambda_{v2})(R + l + \lambda_v)}{\lambda_v - \lambda_{v2}}(n_1 - n_1''),$$
$$\Psi_1 = 4\pi(R + l + \lambda_{v1})^2 D_{v1}\left.\frac{dn_v}{dz}\right|_{z = R + l + \lambda_{v1}}$$
$$= 4\pi D_{v1}\frac{(R + l + \lambda_{v1})(R + l + \lambda_{v2})}{\lambda_{v2} - \lambda_{v1}}(n_1'' - n_1'). \qquad (5)$$

Here D_{1m} is a diffusion coefficient of the vapor through the mixture of the carrier gases, D_{v1} is a binary diffusion coefficient of the vapor through the carrier gas 1. At a steady state $\Psi_2 = \Psi_1$ and just the same flux of molecules penetrates to the absorbing sphere, and K_j^+ given by Eq. (3) is proportional to the number of these molecules per unit time.

What is u'? In view of the essential difference between the molecular masses of the carrier gas and vapor molecules the momentum and energy of the vapor molecule slightly change after the collision with the gas molecule. For instance, the velocity of the vapor molecule in one collision is altered proportionally to $m_1/m_v \ll 1$ or $m_2/m_v \ll 1$ where m_i, $i = 1,2$ are the molecular mass of the carrier gases. On the other hand, under diffusion through zone D with allowance for the velocity persistence the vapor molecule collides about $\lambda_{v2}/\lambda_{v1} \gg 1$ times. Numerical estimations show that under typical conditions of experiments in DCC [1] the product $m_v\lambda_{v1}/m_1\lambda_2$ 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 first internal interface, i.e.

$$u' = \left(\frac{8k_BT'}{\pi m_1}\right)^{1/2}. \qquad (6)$$

Another remark should be made regarding the total number of the vapor molecules colliding with the cluster. As follows from Fig. 1 only a certain fraction of the vapor molecules having diffused to point 'a' from the external interface may 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 Fig. 1 the fraction of the collided molecules is $\Delta_j = \arcsin[(R + l)/(R + l + \lambda_{v1})]/\pi$. Strictly speaking to solve this problem more rigorously one has to consider a multidimensional diffusion equation but for a qualitative estimation our consideration is sufficient. In more detail this problem is explored in Ref. [14].

In order to determine the flux Ψ_0 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 outcoming molecules is concerned it has to be found by solving the full Knudsen layer problem and it is rather difficult to introduce a certain reasonable assumption on its value. Therefore based on the physical consideration we note that in equilibrium $u'n_1' = \Psi_0$ that at $T_k = T'$ yields $u_k \approx u'$.

Further substituting Eq. (6) in Eq. (3) and assuming $T_k \approx T' \approx T'' \approx T$ with allowance for the equations $K_j = \Delta_j \Psi_1$ and $\Psi_1 = \Psi_2$ we obtain

$$n_1' = \frac{n_1 + n_{1e} a_j}{1 + a_j}, \quad a_j = \frac{u'\alpha_c (R + l)^2 (q_1 + q_2)}{q_1 q_2 \Delta_j},$$

$$R = R(j),$$

$$q_1 = D_{1m} \frac{(R + l + \lambda_{v2})(R + l + \lambda_v)}{\lambda_v - \lambda_{v2}},$$

$$q_2 = D_{v1} \frac{(R + l + \lambda_{v1})(R + l + \lambda_{v2})}{\lambda_{v2} - \lambda_{v1}}, \tag{7}$$

and hence

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

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 a 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.

As shown in Ref. [9] under conditions of DCC a_j is of order of unity even for monomers and increases as j increases that gives rise to a new expression of the rate constant of the cluster formation which has been never utilized yet in the theory of nucleation. But here in contrast to [9] these parameters depend on the properties of two background gases — 1 and 2. In order to reveal an explicit form of this dependence we start from an expression of the diffusion coefficient of a certain gas through the mixture of other gases known as the Wilce formula [13]

$$D_{1m} = \left(\frac{y_1}{D_{v1}} + \frac{1 - y_1}{D_{v2}} \right)^{-1} \tag{9}$$

where y_i is the mole fraction of the i-th carrier gas in the mixture and it is taken into account that $y_1 + y_2 \approx 1$.

In what follows instead of a_j we introduce $\Theta_j = 1/a_j$ and with allowance for Eq. (9) and Eq. (7) represent Θ_j in the form

$$\Theta_j = \frac{(R + l + \lambda_{v2})}{\pi(R + l)}$$

$$\times \frac{dD_{v1}}{[R + l + \lambda_{v1} + d(\lambda_{v2} - \lambda_{v1})]u'\alpha_c},$$

$$R + l \leq \lambda_{v1},$$

$$d = \frac{D_{v2}}{D_{v2} y_1 + D_{v1}(1 - y_1)}. \tag{10}$$

For further progress let us use a general expression of the coefficient of binary diffusion of monoatomic gases given by the kinetic theory [3,2] under the following assumptions made: (i) molecules interact like hard spheres with the Maxwellian distribution over 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 the vapor molecules is taken into account by introducing the Satherland correction. It yields

$$D_{vi} = \frac{3}{2 n_{0i} \sigma_{vi}^2} \left(\frac{k_B T}{\pi m_{ri}} \right)^{1/2} \frac{1}{1 + C_i/T} \tag{11}$$

where n_{0i} is the numerical density of the i-th carrier gas, $m_{ri} \approx 2m_i$ is the reduced mass of components, $\pi \sigma_{vi}^2/4$ is a collision cross-section of the vapor and gas molecules, therefore σ_{vi} under conditions of DCC is approximately a sum of effective diameters of the vapor and the i-th gas molecules, C_i is the Satherland constant. For λ_{vi} we use the following expression [15]

$$\lambda_{vg} = 4 \left[\pi n_{0i} \sigma_{vi}^2 \sqrt{1 + \frac{m_v}{m_i}} \left(1 + \frac{C_i}{T} \right) \right]^{-1} \qquad (12)$$

whence

$$D_{vi} = \frac{3\pi}{32} u' \lambda_{vi} \sqrt{1 + \frac{m_v}{m_i}}$$

Combining all the above expressions we find

$$\Theta_j = \frac{3}{32\,\alpha_c} \frac{R + l + \lambda_{v2}}{R + l} \sqrt{1 + \frac{m_v}{m_1}}$$

$$\times \frac{d\lambda_{v1}}{(R + l + \lambda_{v1} + d(\lambda_{v2} - \lambda_{v1})}$$

$$\approx \Theta j^{-1/3} \text{ at } \lambda_{v1} \geq R \gg l,$$

$$\Theta = \frac{3}{32\,\alpha_c} \frac{R + l + \lambda_{v2}}{\eta} \sqrt{1 + \frac{m_v}{m_1}}$$

$$\times \frac{d\lambda_{v1}}{R + l + \lambda_{v1} + d(\lambda_{v2} - \lambda_{v1})} , \qquad (13)$$

where $\eta = (3m_v/4\pi\rho_l)^{1/3}$, and Θ weakly depends on R, i.e. on j.

Let us consider following [9] a typical experiment on nucleation of n-butanol in hydrogen [1]. Numerical calculations show that at $T = 362$ K, $P_0 = 10$ bar, $l = 2.26$ Å and $C = 60$ K [13] one has $\lambda_{v1} = 15$ Å while even for monomers we obtain $R + l = 4.5$ Å and thus at $\alpha_c = 1$ we arrive at $\Theta_1 \approx 1.4$. Thus, even for collisions of monomers the rate of diffusion determines in a considerable degree a resulting rate of this chemical reaction. For collisions of dimers and monomers when estimating σ_{v1} one has to take into account i) a probable linear structure of the dimer and ii) the length of the hydrogen bond that yields $\Theta_2 \approx 1$. As R further increases Θ_j decreases and inequality $\Theta_j < 1$ reinforces. That is why here we introduce the main assumption of our theory that

$\Theta_j \leq 1$ for all $j \geq 1$. Actually, we should choose the certain number j_1 and put $\Theta_j < 1$ at $j \geq j_1 > 1$ but as shown in Refs. [9,10] the assumption made that $j_1 = 1$ does not practically influence the final results.

Thus, we finally obtain

$$K_j^+ = \mathscr{K}_j^+ \frac{S\Theta_j + 1}{S(1 + \Theta_j)} , \qquad (14)$$

where we introduced the notation $\mathscr{K}_j^+$ for the traditional (kinetic) rate constant [2] and Θ_j is our correction for the case of the diffusion-limited kinetics. As follows from the previous analysis $\Theta_j \leq 1$ and is inversely proportional to P_1 — the pressure of the first 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 $K_j^+(S\Theta_j + 1)/S(1 + \Theta_j)$ 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 an approach of the RRKM theory has been obtained in Refs. [8,7].

At the end of this paragraph let us transform a little the expressions for parameters d and y. The definition of the mole fraction yields

$$y_1 = \left(1 + \frac{P_2}{P_1} \right)^{-1} , \qquad (15)$$

where P_i, $i = 1,2$ is the partial pressure of the respective component of the background gas. For d using Eq. (11) it is easy to find

$$d = [\, y_1 + (1 - y_1)\gamma\,]^{-1},$$

$$\gamma = \frac{P_2 \sigma_{v2}^2 (C_2 + T)}{P_1 \sigma_{v1}^2 (C_1 + T)} \sqrt{\frac{m_2}{m_1}} . \qquad (16)$$

2.2. Solutions of the kinetic equations

As mentioned in Introduction a new model of a diffusion-controlled nucleation have been developed

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[2] It is proportional to R^2 while K_j^+ in Eq. (14) is proportional to $(R + l)^2$ but here we neglect this correction.

in Refs. [9,10] which results in the following expression of the measured nucleation rate in DCC

$$J \approx A(T)\left[\exp\left(-by^{2/3}\right)\prod_{j=1}^{y}\frac{S\Theta+j^{1/3}}{\Theta+j^{1/3}}\right]^2$$

$$\times qj_d^{2/3}S^2 K_{y+2}^{-}\frac{2b}{9y^{7/3}},\tag{17}$$

where all variables in Eq. (17) are related to zone N and

$$j_d = \left[y^{4/3}+4\eta^{4/3}\frac{D_1*}{\rho_{l*}}\frac{P_s(T_*)S_*}{k_B T_*/m_v}\frac{9\mu_*}{2\rho_{l*}g}\right.$$

$$\left.\times f(h_d)\right]^{3/4} \approx \eta\left[4\frac{D_{1m}*}{\rho_{l*}}\frac{P_s(T_*)S_*}{k_B T_*/m_v}\right.$$

$$\left.\times\frac{9\mu_*}{2\rho_{l*}g}f(h_d)\right]^{3/4}.\tag{18}$$

Here y is the root of the equation

$$\frac{2b}{3y^{1/3}}-\ln S\theta_y=0,\tag{19}$$

S is supersaturation, parameter b appears from the equilibrium concentration of j-cluster $n_{je}=A(T)\exp(-bj^{2/3})$ [7] and $b=4\pi\sigma\eta^2/k_B T$, σ is the surface tension of the condensing medium. The definition of θ_j is the following

$$\theta_j = \frac{S\Theta_j+1}{1+\Theta_j}.$$

Other notation is as follows: μ is the viscosity of the background gas, g is the gravity acceleration, P_s is the saturation pressure, $qj_d^{2/3}$ is the surface of the registered droplets. Note that this product appears in Eq. (17) if experimenters can not detect directly the number of droplets and for this purpose first use light-scattering and then the Mie theory, so the intensity of a scattered light is proportional to the square of the droplet. In particular, a minimum detectable size j_d of droplets is that which radius is approximately equal to a half of the wavelength of the detecting laser $\lambda_w/2$. But, for instance, for experiments of Heist et al. [1,5,6] where the falling droplets were registered visually by a telescope Eq. (17) has to be modified a little because in this case the term

$qj_d^{2/3}$ should be removed from this equation. Function $f(h_d)$ is presented in Ref. [10] with h_d being a coordinate of a zone where falling drops are detected and h_d is counted from the maximum nucleation plane.

It is easy to check that in the case of a two-component background gas the expression for the nucleation rate J could be derived in a similar way like in Ref. [10] and coincides with Eq. (17) but now we have to use Θ given by Eq. (13). Respectively one may use Eq. (19) to determine the parameter y if again Θ is given by Eq. (13).

We already mentioned that experimeters often present the experimental data in coordinates $S_*(P_0)$ or $S_*(T_*)$ where S_* is the maximum supersaturation in the chamber corresponding to the detected flux of droplets $J=1$ drop/cm^3/s. In order to reduce the expressions of our theory to such a form we should put this value of J into Eq. (17) and take the logarithm of both sides of this equation. It yields

$$0 \approx -by^{2/3}+\ln\prod_{j=1}^{y}\frac{S\Theta+j^{1/3}}{\Theta+j^{1/3}}+\tfrac{1}{2}\ln f(T_*)$$

$$+\ln S-\tfrac{5}{6}\ln y+\tfrac{1}{2}\ln qj_d^{2/3}\approx -by^{2/3}$$

$$+\int_1^y\ln S\theta_j\,dj+\ln S+\tfrac{1}{2}\ln f(T_*),$$

$$f(T_*)=\tfrac{2}{9}A(T_*)W_d(T)\exp(-E_a/k_B T)b.\tag{20}$$

Here we took into account that $K_y^{-}\approx W_d(T)y^{2/3}\exp(-E_a/k_B T)$ [7] where E_a is an activation energy of the molecule capable to dissociate from the cluster, $W_d(T)$ is a certain coefficient determined in Ref. [7]. We also neglected the term proportional to $\ln y$ as compared with $by^{2/3}$ because at usual experimental conditions y is of the order of a classical critical size $j_{*,cl}$, i.e. about 200–700. In addition term qj_d weakly depends on P_0 (see Eq. (18)) or even should be removed at all (see comments of the previous paragraph).

The assumption made that $\Theta_j\le 1$ allows one to rewrite Eq. (20) in the form

$$0 \approx -by^{2/3}+\int_1^y\ln\left(1+\frac{S\Theta}{j^{1/3}}\right)\,dj$$

$$+\tfrac{1}{2}\ln f(T_*)+\ln S.\tag{21}$$

Here y depends on T_*, P_0 and S_* and is determined by Eq. (19). Thus, generally speaking solutions of Eq. (20) lie on a surface in a foure-dimensional space S_*, T_*, P_1 and P_2. Therefore, any dependence like $S_*(P_0)$ or $S_*(T_*)$ is a certain cross-section of this surface. In Ref. [10] we considered in more detail an explicit form of such dependencies and it turned out that they allow a qualitative and even quantitative interpretation of the available experimental data.

For instance by analogy with the case of a one-component background gas let us consider the dependence of S_* upon P_i, $i = 1,2$.

Differentiating Eq. (21) with respect to P_i with allowance for Eq. (19) we obtain

$$\left[-\frac{2b}{3y^{1/3}} + \ln\left(1 + \frac{S\Theta}{y^{1/3}}\right) \right] \frac{\partial y}{\partial P_i} + 3\frac{\partial S\Theta}{\partial P_i} \times \left\{ \tfrac{1}{2}y^{2/3} \right.$$
$$- S\Theta y^{1/3} + (S\Theta)^2 \ln\left(\frac{y^{1/3} + S\Theta}{1 + S\Theta} \right) - 3\frac{\partial \Theta}{\partial P_i}$$
$$\times \left\{ \tfrac{1}{2}y^{2/3} - \Theta y^{1/3} + (\Theta)^2 \ln\left(\frac{y^{1/3} + \Theta}{1 + \Theta} \right) \right\}$$
$$+ \frac{\partial \ln S}{\partial P_i} = 0. \tag{22}$$

Here the term in square brackets vanishes due to the definition of y in Eq. (19) and the last term in the L.H.S. is small as compared with the previous one because $y \gg 1$ and $\Theta \propto O(1)$. Just for the same reason the leading term in braces is $y^{2/3}/2$. Thus, the solution of Eq. (22) is $\Theta(S-1) = $ const or

$$S_* - \bar{S}_*(T) = c_1(T)\left[\frac{1}{\Theta(T, P_i)} - \frac{1}{\Theta(T, \bar{P}_{0i})} \right], \tag{23}$$

where $\bar{S}_*$ and $\bar{P}_{0i}$ are certain initial values of S_* and P_i at $T_* = $ const.

3. Discussion

The first idea that comes to mind when analyzing Eq. (23) is to check whether it is possible to increase simultaneously the pressures of both components (or at least, one of them) in a certain way that the critical

supersaturation S_* remains constant. In order to get a reply on this questions we consider in more detail the expression of Θ in Eq. (13).

First of all let us show that at certain experimental conditions $R + l \gg \lambda_{v1}$ and $R + l \gg \lambda_{v2}$. In doing so we consider nucleation of n-butanol in hydrogen and directly find y by numerical solving of Eq. (19) where Θ now is determined like in Ref. [9], i.e. for a one-component background gas. Thermophysical properties of the condensing vapor are taken from [1,5,6,13]. In particular for butanol we used $\rho_l = 0.936331 - 8.775192 \times 10^{-5}t - 1.16705 \times 10^{-6}t^2$, $m_v = 74.123$. To determine the other parameters we used some correlations from [2,13] built on the basis of critical parameters of the vapor. For butanol the temperature, pressure in the critical point and the normal boiling temperature (at $P = 1$ atm) are respectively $P_c = 43.6$ atm, $T_c = 562.9$ K, $T_b = 390.9$ K. Then coefficients determining the dependence $\sigma_* = \sigma_1 - \sigma_2 T_*$ of the surface tension on T_* are obtained as follows: $\sigma_1 = P_c^{2/3}T_c^{1/3}[0.1207(1 + T_{br}\ln P_c)/(1 - T_{br}) - 0.281]$, $\sigma_2 = \sigma_1/T_c$, where $T_{br} = T_b/T_c$. The Satherland constant C is determined according to the formula [2] $C = 1.47\sqrt{T_{bv}T_{b0}}$ with T_{bv} and T_{b0} being the normal boiling temperatures of the vapor and the background gas, respectively. We also put the condensation coefficient to be equal to unity and since did not vary it.

In Fig. 2 these results are presented as a dependence of $R = \eta y^{1/3}$ upon the pressure of hydrogen P at four different temperatures and $S = 2.5$. The dependencies of the mean free path of the condens-
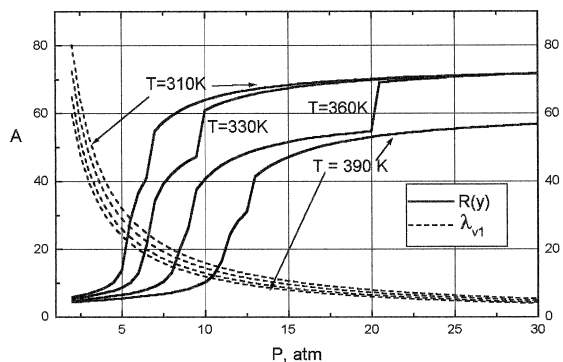

Fig. 2. Dependence of $R = \eta y^{1/3}$ for n-butanol on the pressure of hydrogen P and the mean free path of the n-butanol molecules through hydrogen λ_{v1} at four different temperatures and $S = 2.5$
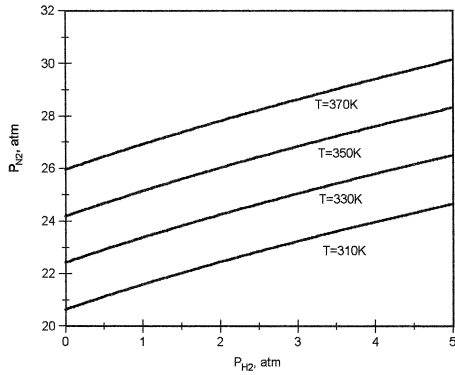
Fig. 3. Dependence of P_1 (P_2) or in other words P_{N2} (P_{H2}) which provides the equality $\Theta = \Theta_0 = 1$ and respectively $S_* =$ const at $T =$ const. Points of the plot lie on the ellipse with the centers in $\Theta_0 P_1 = \lambda/2\xi_1$ and $\Theta_0 P_2 = \lambda/2\xi_1\xi_2$.

ing molecules through the background gas λ_{v1} are also presented in this plot. It is seen that for instance at $P = 10$ atm and $T < 390$ K the data well meet the inequality $R + l \gg \lambda_{v1}$.

Let us also assume that the value of d is of order of unity. For instance, it is the case if as the background gas we choose a mixture of N2 (gas 1) and H2 (gas 2) with the pressures of components being not far from each other. Then with allowance for the previous inequality that in this case gives $R + l \gg \lambda_{v1}$ and $R + l \gg \lambda_{v2}$ the expression of Θ in Eq. (13) can be rewritten in the form

$$\Theta = \frac{3\pi d \lambda_{v1}}{64 \eta \alpha_c} \sqrt{1 + \frac{m_v}{m_1}} , \qquad (24)$$

where we also took into account that at $R + l \gg \lambda_{v1}$ one has $\Delta_j \approx 1/2$.

Using Eq. (24) it is possible to find at what pressures of the components of the background gas Θ remains to be constant which we denote as Θ_0. For this purpose we utilize the definitions of d, λ_{v1} and y_1 given in Eqs. (16), (12) and (15) and arrive to the following equation

$$\left(\Theta_0 P_1 - \frac{\lambda}{2\xi_1} \right)^2 + \xi_2 \left(\Theta_0 P_2 - \frac{\lambda}{2\xi_1\xi_2} \right)^2$$

$$= \left(\frac{\lambda}{2\xi_1} \right)^2 + \xi_2 \left(\frac{\lambda}{2\xi_1\xi_2} \right)^2 ,$$

$$\xi_2 = \frac{\sigma_{v2}^2(C_2 + T)}{\sigma_{v1}^2(C_1 + T)} \sqrt{\frac{m_2}{m_1}} ,$$

$$\xi_1 = \frac{64 \eta \alpha_c}{3\pi \sqrt{1 + m_v/m_1}} , \qquad (25)$$

where $\lambda(T) = \lambda_{v1} P_1$. Thus, the pressures $\Theta_0 P_1$ and $\Theta_0 P_2$ that provide the equality $\Theta = \Theta_0 = $ const and respectively $S_* = $ const at $T = $ const lie on the ellipse with the centers in $\Theta_0 P_1 = \lambda/2\xi_1 \equiv P_y$ and $\Theta_0 P_2 = \lambda/2\xi_1\xi_2 \equiv P_x$ (see Fig. 3). The large semiaxis of the ellipse is $a = \sqrt{(\lambda/2\xi_1)^2 + (\lambda/2\xi_1\xi_2)^2}$, the small one is $b = a/\sqrt{\xi_2}$.

A segment of each this ellipse is presented in Fig. 3 at four different temperatures and in Table 1 parameters of these ellipses are given. As it is seen from Fig. 3 it is possible simultaneously to increase the pressures of N2 and H2 in a special way that despite the increase of these pressures as well as the total pressure of the two-component background gas the critical supersaturation does not change in contrast to the experiments with a one-component background gas. However, as follows from the above this contradiction is only apparent because such a behavior in both cases of one- and two-component background gas is determined by a common mechanism of the diffusion-limited nucleation.

Undoubtedly it would be of interest to perform a corresponding experimental test in order to verify this prediction of our theory. In particular, working mediums and parameters of the background gases presented in Fig. 3 correspond to the experiments of [1,5,6] and therefore it seems such an experiment

Table 1
Parameters of ellipses $\Theta_0 P_{N2}(\Theta_0 P_{H2})$ which provides the equality $\Theta = \Theta_0 = 1$ and respectively $S_* = $ const at $T = $ const, P_x and P_y are the centers of ellipses, a,b are the large and small semiaxes (all parameters are given in atm).

T	P_y	P_x	a	b
310.00	10.329	61.093	27.161	66.056
330.00	11.225	65.763	29.397	71.155
350.00	12.117	70.364	31.613	76.182
370.00	13.000	74.880	33.801	81.121

could be implemented at the same experimental devices. In doing so we should first measure the critical supersaturation at certain temperature and pressures P_{1*} and P_{2*}, then using these values of parameters calculate Θ_0 based on the relationship

$$\Theta_0 = \frac{\lambda}{\xi_1} \frac{P_{1*} + P_{2*}}{P_{1*}^2 + P_{2*}^2} \qquad (26)$$

and finally vary P_1 and P_2 in an appropriate way that products $\Theta_0 P_1$ and $\Theta_0 P_2$ would obey Eq. (25) measuring the corresponding values of critical supersaturation S_*. As it is possible to expect based on this theory these S_* should be identical.

In Fig. 4 the ratio $\lambda_{v,H2}/\lambda_{v,N2}$ is presented as a function of P_{H2} at four different temperatures. The pressure $P_{N2}(P_{H2})$ is determined according to Fig. 3, i.e. from the condition $\Theta = \text{const}$ and belong to the respective ellipse. We choose $\Theta_0 = 1$ at each temperature i.e. the initial value of the hydrogen pressure was small ($P_{H2*} \approx 0.1$ atm while $P_{N2*} = 21$ atm at $T = 310$ K, $P_{N2*} = 22.4$ atm at $T = 330$ K, $P_{N2*} = 24.2$ atm at $T = 350$ K, $P_{N2*} = 26$ atm at $T = 310$ K. It is seen that as the pressure increases the external interface (the mean free path of the condensing n-butanol molecules through hydrogen) approaches the internal interface (the mean free path of the condensing n-butanol molecules through nitrogen) however never cross it. Thus, in this case there is an evidence for all assumptions made under formulation of the model.
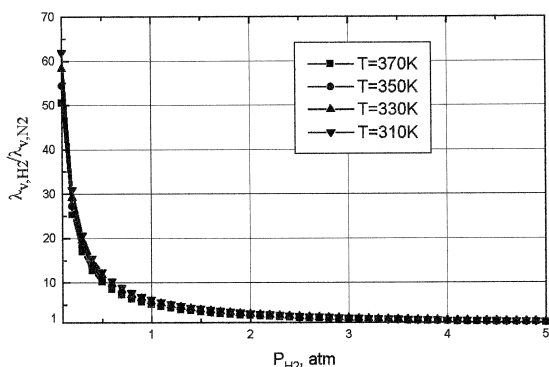
One more interesting fact can be revealed if we analyze the sign of partial derivatives $\partial\Theta/\partial P_i$, $i = 1,2$. Using Eq. (24) we find

$$\left.\frac{\partial\Theta}{\partial P_1}\right|_{P_2 = \text{const}} = \frac{-P_1^2 - 2P_1 P_2 + \xi_2 P_2^2}{(P_1 + P_2)(P_1^2 + \xi_2 P_2^2)},$$

$$\left.\frac{\partial\Theta}{\partial P_2}\right|_{P_1 = \text{const}} = \frac{P_1^2 - 2\xi_2 P_1 P_2 - \xi_2 P_2^2}{(P_1 + P_2)(P_1^2 + \xi_2 P_2^2)}. \qquad (27)$$

Let us return to the mixture of the condensing n-butanol vapor with nitrogen (gas 1) and hydrogen (gas 2) which have been considered above. Substituting the values of P_{N2} and P_{H2} that belong to an ellipse in Fig. 3 in Eq. (27) one obtains

$$\left.\frac{\partial\Theta}{\partial P_1}\right|_{P_2 = \text{const}} < 0, \qquad \left.\frac{\partial\Theta}{\partial P_2}\right|_{P_1 = \text{const}} > 0. \qquad (28)$$

It means that in the area of pressures that in Fig. 3 lie below the corresponding ellipse the increase of both pressures P_{N2} and P_{H2} results in the increase of Θ and correspondingly in the decrease of S_*. On the contrary in the area of pressures that in Fig. 3 lie above the corresponding ellipse the increase of the pressures P_{N2} and P_{H2} results in the decrease of Θ and in the increase of S_*. Thus, a variation of the pressures of both components of the two-component background gas in an appropriate way in DCC at a constant nucleation rate and the temperature in the maximum nucleation plane can result in both the increase and the decrease of critical supersaturation S_* and even keep S_* to be constant. This conclusion is the main result of the present theory which admits a direct experimental verification.

Acknowledgements

Fig. 4. Ratio $\lambda_{v,H2}/\lambda_{v,N2}$ as a function of P_{H2} at four different temperatures and $\Theta_0 = 1$.

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