Kinetics of Dissolution, Adsorption, and Relaxation of the Matter Comprising Condensation Nucleus to Equilibrium in a Droplet Originating on the Nucleus

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Abstract—The equations describing the dissolution and adsorption of the matter comprising the condensation nucleus in the droplet originating on this nucleus from supersaturated vapor were derived. The relaxation of the solution of the matter comprising the nucleus inside the droplet to chemical equilibrium with allowance made for its transport into the solution from the nucleus and its consumption by the adsorption surface layer of a droplet was studied. The dependences of the time of chemical relaxation of a solution on the sizes of the droplet and solid residue of the nucleus, the nucleus solubility, the rate of dissolution of the matter comprising nucleus, the coefficient of its diffusion in a solution, the adsorption, the coefficients of adsorption and desorption of this matter on the droplet surface, and the logarithmic derivative of adsorption with respect to solution concentration were revealed. The passage from the local (over the course of time) approximation where the adsorption is determined by the current value of the solution concentration at its boundary with the droplet surface layer was made for an arbitrary adsorption isotherm. Times of solution chemical relaxation under conditions typical of partial or complete dissolution of nucleus in a droplet were found in the analytical form. It was proved that the variation of droplet boundaries might be neglected at the initial (important for nucleation) stage of surmounting the activation barrier of nucleation by the droplets. It was shown that, at this stage, the state of the solution inside the droplets remains virtually constant. The hierarchy of the scale of kinetic times was disclosed, which enables us to understand the complex multistage process of overcoming the activation barrier of nucleation by the droplets. The applicability of thermodynamics to the kinetics of this process was also demonstrated.

INTRODUCTION

The kinetic theory of the initial (important for nucleation) stage where the activation barrier is surmounted by the droplets originating in supersaturated vapor on the macroscopic condensation nuclei was developed in [1]. The height of this barrier is specified by the vapor supersaturation-dependent difference of the height of the potential maximum and the depth of the potential minimum of the work of the heterogeneous droplet formation on the nucleus.

The kinetic theory was developed [1] in such a general way that it allows the coverage of both surface-inactive and surface-active condensation nuclei, which may completely or only partially dissolve in the droplets during the surmounting the activation barrier of nucleation by these droplets. Undoubtedly, the application of this kinetic theory makes it necessary to formulate basic relationships specified by the thermodynamics of the droplet formation on the macroscopic nuclei. At complete dissolution of the nucleus in a droplet, these thermodynamics were developed for the case of surface-inactive nuclei in [2] and for surface-active nuclei in [3–7]. At partial dissolution of the nucleus in a droplet, i.e., at the formation of a liquid film on the solid residue of the nucleus, these thermodynamics were developed in [8–10].

In order to make the thermodynamic results obtained in [2–10] truly applicable to the kinetic theory developed in [1], the hierarchy of the following typical kinetic times should exist (in the order of their increase), such as the adsorption relaxation time of the droplet surface layer, the chemical relaxation time of a solution inside the droplet, the time of the establishment of the steady-state droplet size distribution over the course of the surmounting of the activation barrier of nucleation, and the time of droplet size variation in this process. The aim of this work was to disclose this hierarchy.

Because thermal equilibrium in a droplet is established during very short times [11], whereas the mechanical equilibrium of the droplet is reached much faster, the hierarchy (involved in this work) of typical kinetic times should be supplemented by the condition of the smallness of the thermal relaxation time of a droplet as compared to the adsorption relaxation time of the droplet surface layer. As this inequality is obvious, it will not be mentioned further in this work.

The disclosure of the hierarchy of characteristic kinetic times (stated as the final aim of this work) at the stage corresponding to the surmounting of the activation barrier of nucleation by the droplets originating on the macroscopic nuclei requires the determination of these times per se; first of all, the relaxation time of the solution of the matter comprising nucleus inside the droplet to the chemical equilibrium should be determined (note that this time scarcely studied). It is the determination of the chemical relaxation time of a solution that is the main problem of this work. Calculations will be performed for the arbitrary adsorption isotherm by the solution of the equation of the nonstationary diffusion of the matter comprising nucleus in a solution inside the droplet with account for two complex boundary conditions: (1) transport of the matter comprising nucleus from the residue of the nucleus into the solution is governed by the rate of its dissolution; (2) consumption of the matter comprising nucleus from the solution by the droplet surface layer is determined by its adsorption ability. Generally speaking, this ability has a nonlocal (in time) character and is dependent on the solution concentration at the boundary with the droplet surface layer both at the current time and at all preceding times.

When the condensation nuclei are macroscopic, the droplet sizes in the near critical region only slightly exceed the size, at which the maximal chemical potential of the condensate is reached. Data on the width of the near critical region and on the dependence (in this region) of the droplet radius and the thickness of its liquid film (at nucleus partial dissolution) on the nucleus initial size, the droplet surface tension, and the possible effect of adsorption in the droplet surface layer are provided by the thermodynamics developed in [2–10]. When the nucleus is surface-active, the effect of adsorption on the droplet surface tension might be significant. Together with this effect, the influence of adsorption on the chemical relaxation time may also be rather noticeable.

Earlier, the issue of adsorption (governed by the adsorption and desorption in the surface layer) and diffusion-controlled (determined by the diffusion transfer in bulk solution) kinetics of the surfactant solution relaxation was treated in [12–17]. For example, three types of boundary conditions have been analyzed in the diffusion-controlled kinetics of adsorption [12–15]; the integral-differential equations of the adsorption kinetics were derived and numerically solved for various adsorption isotherms in [16, 17].

This work is unique because it is aimed at the study of the widely spread natural kinetic process of droplet nucleation in the supersaturated vapor on the macroscopic condensation nuclei, the determination of the adsorption relaxation time of the droplet surface layer for the arbitrary adsorption isotherm, and the calculation of the chemical relaxation time of the solution of the matter comprising the condensation nucleus inside the droplet with allowance made both for the transport of this matter from the nucleus into the solution and its consumption from the solution by the adsorption surface layer of the droplet.

1. DISSOLUTION KINETICS OF THE NUCLEUS

Let v_n be the number of molecules in the condensation nucleus with radius R_n present initially in the vapor–gas medium. If the matter comprising nucleus dissociates to the ions during its dissolution in the condensate, the v_n quantity specifies the number of ions, which may be formed from the initial condensation nucleus. Further, let $\tilde{v}_n$ be accordingly the number of molecules or ions in the solid residue of the condensation nucleus with radius $\tilde{R}_n$ inside the droplet at the moment when the nucleus is not yet completely dissolved. Assuming that the nucleus and its solid residue are spherical, v_n and R_n, and $\tilde{v}_n$ and $\tilde{R}_n$ are interrelated by the evident relationships:

$$v_n = 4\pi R_n^3/3 v_n, \quad \tilde{v}_n = 4\pi \tilde{R}_n^3/3 v_n, \qquad (1.1)$$

where v_n is the volume per molecule (or ion) in the condensation nucleus.

The rate $\overset{\star}{\tilde{v}}_n$ of the variation in the number $\tilde{v}_n$ with time is defined by the equation

$$\overset{\star}{\tilde{v}}_n = 4\pi \tilde{R}_n^2 k_n (\tilde{c}|_{r=\tilde{R}_n} - \tilde{c}_n). \qquad (1.2)$$

Here, r is the radial coordinate in the spherical system with the origin in the nucleus center; k_n is the coefficient of the dissolution of the matter comprising the nucleus in the condensate [18, 19]; $\tilde{c}$ is the concentration of molecules (or ions) of the matter comprising the nucleus per unit of the droplet volume at the current time moment t; and $\tilde{c}_n$ is the concentration of molecules (or ions) of the matter comprising nucleus per unit of the droplet volume when the solution and the residue of the nucleus with specified radius $\tilde{R}_n$ are in equilibrium.

The k_n coefficient is almost independent of the solution concentration in the droplet and can be represented as

$$k_n = A_n \exp(-E_n/kT), \qquad (1.3)$$

where k is the Boltzmann constant, T is the absolute temperature, and parameter A_n has the dimensionality of the rate and may be estimated by the value of the average Maxwell velocity of the molecules of the matter comprising nucleus at the solution temperature. The E_n parameter in (1.3) has the meaning of the activation energy of the nucleus dissolution. The experimental data on the values of parameters A_n and E_n are available

for various solid–solvent systems, first of all, for inorganic salts in water [18]. Information on the dependence of these parameters on the size of dissolving solid particle is lacking.

Equilibrium solution concentration $\tilde{c}_n$ (solubility of nucleus residue in condensate) entering into equation (1.2) is dependent on the $\tilde{R}_n$ radius of the nucleus residue. According to the Ostwald–Freundlich equation, we obtain

$$\tilde{c}_n = c_n \exp(2\gamma_n v_n / kT\tilde{R}_n), \qquad (1.4)$$

where c_n is the equilibrium volume concentration of the matter comprising nucleus in a solution (solubility of the matter comprising nucleus in a condensate) at the flat solution–solid interface, and γ_n is the surface tension of the nucleus residue which was determined mechanically. Unlike the surface tension of solids determined thermodynamically, the information on the γ_n values is insufficient at present. Note that at macroscopic dimensions of the nucleus residue, both $\tilde{c}_n$ and c_n, as well as A_n and E_n, are slightly different from their values for the flat surface of nucleus.

2. KINETICS OF ADSORPTION

Passing to the description of the adsorption kinetics of the dissolved matter comprising nucleus at the droplet surface, we deal with the most interesting case when the nucleus contains a soluble surfactant capable of forming an adsorption monolayer. Let $\tilde{\Gamma}$ be the adsorption of the matter comprising nucleus at the current time moment at the droplet surface with radius R, i.e., the number of adsorbed molecules (or ions) per unit area of the monolayer at the droplet surface. Let us write the equation for the rate of the adsorption $d\tilde{\Gamma}/dt$ variation with time t in the following form:

$$d\tilde{\Gamma}/dt = \alpha(\tilde{\Gamma})\tilde{c}|_{r=R}(1 - \tilde{\Gamma}/\Gamma_\infty) - \beta(\tilde{\Gamma})\tilde{\Gamma}, \qquad (2.1)$$

where $\alpha(\tilde{\Gamma})$ and $\beta(\tilde{\Gamma})$ are the coefficients of adsorption and desorption, respectively; and Γ_∞ is the adsorption capacity of the monolayer, i.e., the limiting value of adsorption corresponding to the complete coverage of a monolayer.

The first term in the right-hand part of equation (2.1), which is proportional to the free surface area, describes the flux of surfactant molecules adsorbing from the solution. This flux is linearly dependent on the concentration and is generally determined [via $\alpha(\tilde{\Gamma})$] by the state of the monolayer. The second term in the right-hand part of (2.1), which is proportional to the monolayer area covered with surfactant molecules, describes the flux of surfactant molecules desorbing from the monolayer into the solution. As is seen from the definition, this flux is independent of the state of the

solution (of the solution concentration) and is determined [via $\beta(\tilde{\Gamma})$] only by the monolayer properties.

In general, the dependence of the $\alpha(\tilde{\Gamma})$ and $\beta(\tilde{\Gamma})$ coefficients on adsorption $\tilde{\Gamma}$ can be rather complex. For the ratio of these coefficients under the equilibrium of the adsorption monolayer with solution; i.e., at $d\tilde{\Gamma}/dt = 0$, we find from (2.1) that

$$\beta(\Gamma)/\alpha(\Gamma) = (c/\Gamma)(1 - \Gamma/\Gamma_\infty). \qquad (2.2)$$

Here, Γ and c are the equilibrium values of adsorption and the volume concentration of the solution, respectively. Using the known theoretical or experimental adsorption isotherms, we determine c and derive [by means of (2.2)] the expression for the dependence of the $\beta(\Gamma)/\alpha(\Gamma)$ ratio on the equilibrium value Γ. Because the $\beta(\Gamma)/\alpha(\Gamma)$ ratio is independent of the state of solution, we extend the expression thus obtained to the case of nonequilibrium $\tilde{\Gamma}$ values.

Dealing further with the monolayer relaxation to the equilibrium state, we consider the relative deviations of adsorption $\tilde{\Gamma}$ and concentration $\tilde{c}$

$$\delta\Gamma \equiv (\tilde{\Gamma} - \Gamma)/\Gamma, \qquad \delta c \equiv (\tilde{c} - c)/c \qquad (2.3)$$

from their equilibrium values small

$$|\delta\Gamma| \ll 1, \qquad |\delta c| \ll 1. \qquad (2.4)$$

The linearization of equation (2.1) with the account for (2.2)–(2.4) yields

$$d\delta\Gamma/dt = \beta(\Gamma)[\delta c|_{r=R} - (d\ln c/d\ln\Gamma)\delta\Gamma]. \qquad (2.5)$$

It follows from the linearized equation (2.5) that at $\delta c|_{r=R} = \text{const}$, the characteristic time t_A of adsorption relaxation is generally determined by the logarithmic derivative of adsorption with respect to the solution concentration

$$t_A \equiv \beta(\Gamma)^{-1}\frac{d\ln\Gamma}{d\ln c}. \qquad (2.6)$$

It is seen that with allowance made for (2.6) differential equation (2.5) is equivalent to the integral interrelation

$$\delta\Gamma(t) = \exp(-t/t_A)\delta\Gamma(0)$$

$$+ \beta(\Gamma)\int_0^t d\tau \exp[(\tau - t)/t_A]\delta c(\tau)|_{r=R}, \qquad (2.7)$$

where $\delta\Gamma(0)$ is the initial value of the relative deviation of adsorption from its equilibrium value. Dealing further with the relaxation of the monolayer and the matter comprising nucleus dissolved in the droplet to the chemical equilibrium, we assume that $\delta\Gamma(0)$ and the initial value of the relative deviation $\delta c(0)|_{r=R}$ of the solution concentration at the boundary with the monolayer are equal to zero (the nonequilibrium state of a

solution arises from the dissolution of the condensation nucleus and disturbances of solution concentration). Taking these facts into account, we differentiate first the left- and right-hand sides of (2.7) with respect to t and then integrate the right-hand side by parts; as a result, after simple transformations, we arrive at the following relationship for $d\delta\Gamma/dt$:

$$d\delta\Gamma/dt = \beta(\Gamma)\int_0^t d\tau \exp[(\tau - t)/t_A]\partial\delta c/\partial\tau\big|_{r=R}. \quad (2.8)$$

We will employ this relationship further for the formulation of the boundary condition at the droplet surface for the diffusion equation.

3. KINETICS OF ADSORPTION FOR THE MONOLAYER WITH LATERAL INTERACTIONS

Let us consider the Frumkin model as an example of the monolayer with lateral interactions [20, 21]. Let us assume that the adsorption coefficient $\alpha(\tilde{\Gamma})$ is independent of the coverage of monolayer $\tilde{\Gamma}/\Gamma_\infty$; i.e., let us assume that

$$\alpha(\tilde{\Gamma}) = \alpha = \text{const}(\tilde{\Gamma}). \quad (3.1)$$

For the equilibrium Frumkin adsorption isotherm, we obtain [20, 21]

$$c = c_\alpha \frac{\Gamma/\Gamma_\infty}{1 - \Gamma/\Gamma_\infty} \exp(-2\kappa\Gamma/\Gamma_\infty), \quad (3.2)$$

where c_α is the isotherm parameter taken so that the Γ_∞/c_α quantity has the meaning of the Henry constant for the surfactant in question, and κ is the parameter of the lateral interactions of the surfactant molecules in a monolayer.

Using (2.2) with the allowance made for (3.1) and (3.2), we find the following expression for the dependence of the desorption coefficient $\beta(\Gamma)$ on Γ

$$\beta(\Gamma) = \alpha(c_\alpha/\Gamma_\infty)\exp(-2\kappa\Gamma/\Gamma_\infty). \quad (3.3)$$

The characteristic time t_A of the adsorption relaxation with account for (3.3), (3.1), and (2.6) may be defined as

$$t_A \equiv \frac{\Gamma_\infty(1 - \Gamma/\Gamma_\infty)}{\alpha c_\alpha[1 - 2\kappa\Gamma/\Gamma_\infty + 2\kappa(\Gamma/\Gamma_\infty)^2]} \quad (3.4)$$

$$\times \exp(2\kappa\Gamma/\Gamma_\infty).$$

It is easy to note that the t_A time is positive at any degree of monolayer coverage Γ/Γ_∞ within the range of admissible values ($0 \leq \Gamma/\Gamma_\infty \leq 1$) at $\kappa < 2$. As is known, at $\kappa \geq 2$, there are the ranges of the coverage degrees Γ/Γ_∞ where the monolayer is unstable. In these ranges of the Γ/Γ_∞ values, time t_A becomes negative. It is clear

that such situations are omitted from further consideration.

When the parameter of lateral interactions vanishes, time t_A reduces to the well-known time of adsorption relaxation of the Langmuir monolayer:

$$t_A = (\Gamma_\infty/\alpha c_\alpha)(1 - \Gamma/\Gamma_\infty) \quad (3.5)$$

or, with account for (3.2), to

$$t_A = (\Gamma_\infty/\alpha)(c + c_\alpha)^{-1}. \quad (3.6)$$

4. DIFFUSION OF THE MATTER COMPRISING NUCLEUS IN THE BULK PORTION OF A DROPLET

Let us assume that the characteristic time of the exchange of the droplet by the condensate molecules with the surrounding vapor–gas medium is much longer than the internal relaxation time of the droplet to chemical equilibrium with respect to the dissolved matter comprising the nucleus. Accordingly, we ignore the motion of the droplet surface; i.e., we assume that droplet radius R is independent of time. The assumption made will be rigorously substantiated for the near critical range of the droplet dimensions in Section 8.

The equation of the molecular diffusion of the dissolved matter comprising nucleus in the bulk portion of a droplet has the following form:

$$\partial\tilde{c}/\partial t = (D_n/r)\partial^2(r\tilde{c})/\partial r^2, \quad (4.1)$$

where D_n is the diffusion coefficient of molecules (or ions) of the matter comprising nucleus in a solution. At the surface of the nucleus residue at $r = \tilde{R}_n$, the boundary condition is determined by the law of its dissolution. According to (1.2), we obtain

$$D_n\partial\tilde{c}/\partial r\big|_{r=\tilde{R}_n} = k_n(\tilde{c}\big|_{r=\tilde{R}_n} - \tilde{c}_n). \quad (4.2)$$

The flux in the left-hand side is directed toward the nucleus surface. At $r = R$, the boundary condition is determined by the variation (with time) of the amount of the matter comprising nucleus that is adsorbed on the droplet surface. As a result, the second boundary condition for equation (4.1) is

$$D_n\partial\tilde{c}/\partial r\big|_{r=R} = -d\tilde{\Gamma}/dt. \quad (4.3)$$

The flux in the left-hand side is directed away from the monolayer surface.

Under the chemical equilibrium inside the droplet, the solution concentration c coincides with the solubility $\tilde{c}_n$ of the nucleus residue with radius $\tilde{R}_n$. Taking this fact into account and linearizing equation (4.1), together with the boundary conditions (4.2) and (4.3) with allowance made for (2.3), (2.4), and (2.8), we obtain

$$\partial\delta c/\partial t = (D_n/r)\partial^2(r\delta c)/\partial r^2, \quad (4.4)$$

$$D_n \partial \delta c / \partial r \big|_{r = \tilde{R}_n} = k_n \delta c \big|_{r = \tilde{R}_n}, \qquad (4.5)$$

$$D_n \partial \delta c / \partial r \big|_{r = R} = -[\beta(\Gamma)\Gamma/c]$$

$$\times \int_0^t d\tau \exp[(\tau - t)/t_A] \partial \delta c / \partial \tau \big|_{r = R}. \qquad (4.6)$$

We remind the reader that the value of adsorption $\beta(\Gamma)$ entering into condition (4.6) both directly and via desorption coefficient Γ and time t_A is not an arbitrary quantity but is related to the adsorption isotherm by the equilibrium concentration c. As was already noted, at a partially dissolved nucleus, $c = \tilde{c}_n$; hence, according to (1.4), the value of adsorption Γ is given by the radius $\tilde{R}_n$ of the nucleus residue.

Note that equation (4.4), together with boundary conditions (4.5) and (4.6), also describes the case of the complete dissolution of the nucleus in a droplet. In this case, we should assume in condition (4.5) that $\tilde{R}_n = 0$ and $k_n = 0$. The procedure of the determination of the final (for the kinetic theory) equilibrium concentration c was demonstrated elsewhere [3–7].

We have no need for the explicit form of the initial condition for equations (4.1) and (4.4). We will deal further with the relaxation in the droplet at the times $t \gg t_A$ when the possible difference between the initial values of $\delta\Gamma(0)$ and $\delta c(0)|_{r=R}$ and the zero values [which were required for the derivation of relationship (2.8) for $d\delta\Gamma/dt$] becomes insignificant.

At times $t \gg t_A$, we seek the approximate solution of the linearized equation (4.4) with boundary conditions (4.5) and (4.6) using the standard procedure of the separation of variables.

$$\delta c \sim \sum_k \exp(-\lambda_k^2 D_n t) N_k(r). \qquad (4.7)$$

Functions $N_k(r)$ and values λ_k ($k = 1, 2, \dots$) entering into (4.7) satisfy the equations

$$d^2[rN_k(r)]/dr^2 + \lambda_k^2 r N_k(r) = 0 \qquad (4.8)$$

with boundary conditions

$$dN_k(r)/dr \big|_{r = \tilde{R}_n} = (k_n/D_n)N_k(r)\big|_{r = \tilde{R}_n} \qquad (4.9)$$

and

$$dN_k(r)/dr \big|_{r = R}$$

$$= \frac{\alpha(\Gamma)(1 - \Gamma/\Gamma_\infty)t_A\lambda_k^2}{1 - \lambda_k^2 D_n t_A} N_k(r)\big|_{r = R}. \qquad (4.10)$$

Condition (4.9) follows from (4.5), whereas condition (4.10) is obtained approximately from (4.6) using equality (2.2) with allowance made for the fact that at

$t \gg t_A$ only the series members with $\lambda_k^2 D_n \leq t_A^{-1}$ are significant because in this case $\exp[-(t_A^{-1} - \lambda_k^2 D_n)t] \ll 1$.

Solutions to equation (4.8) corresponding to the zero value of λ_k have a form $N_k(r) = B_k + C_k/r$, where both integration constants B_k and C_k are identically equal to zero in view of boundary conditions (4.9) and (4.10). At non-zero values of λ_k ($k = 1, 2, \dots$), which are of interest to us, solutions to equations (4.8) acquire the form

$$N_k(r) = (B_k/r)\sin(\lambda_k r) + (C_k/r)\cos(\lambda_k r), \qquad (4.11)$$

where coefficients B_k and C_k are determined from the initial and boundary conditions for equation (4.8). Linear homogeneous equations for B_k and C_k obtained by the substitution of (4.11) into (4.9) and (4.10) have the non-zero solutions, provided that λ_k satisfies the transcendental equation

$$\tan[\lambda_k(R - \tilde{R}_n)]$$

$$= \{\lambda_k[1/\tilde{R}_n - 1/R - \alpha(\Gamma)(1 - \Gamma/\Gamma_\infty)t_A$$

$$\times \lambda_k^2/(1 - \lambda_k^2 D_n t_A) + k_n/D_n]\}/\{\lambda_k^2 \qquad (4.12)$$

$$+ [1/R + \alpha(\Gamma)(1 - \Gamma/\Gamma_\infty)$$

$$\times t_A\lambda_k^2/(1 - \lambda_k^2 D_n t_A)](1/\tilde{R}_n + k_n/D_n)\}.$$

5. TIME OF INTERNAL RELAXATION OF A DROPLET AT THE DIFFUSION-CONTROLLED KINETICS OF ADSORPTION

As is apparent from (4.7), the least of positive values $\lambda_k^2 D_n$ ($k = 1, 2, \dots$) is responsible for the internal relaxation time for a droplet to chemical equilibrium with respect to the dissolved matter comprising condensation nucleus. The corresponding value of λ_k coincides with the least of the positive roots of transcendental equation (4.12). Let us denote the least of roots λ_k ($k = 1, 2, \dots$) of equation (4.12) by subscript 1. Then, the desired internal relaxation time of a droplet may be represented as

$$t_1 = \lambda_1^{-2} D_n^{-1}. \qquad (5.1)$$

In general, equation (4.12) makes it possible to disclose the dependence of time t_1 of internal relaxation of a droplet on the radii of the droplet and the solid nucleus residue, the nucleus solubility, the rate of solubility of the matter comprising nucleus, its diffusion coefficient in the solution inside the droplet, the adsorption, and the coefficients of adsorption and desorption at the droplet surface at the arbitrary adsorption isotherm. Time t_1 also depends on the logarithmic derivative of adsorption with respect to the solution concentration via the characteristic time t_A of adsorption relaxation.

As was already noted in the introduction of this work, the droplet radius and the thickness of the liquid film on a droplet and, hence, the radius of the solid nucleus residue in the near critical range as a function of the initial nucleus size, the droplet surface tension, and the adsorption of the matter comprising nucleus on the droplet surface layer are defined by the thermodynamics developed in [2–10].

As a whole, the dependence of time t_1 on the external characteristics of a problem seems to be rather complex; however, during its derivation, we may take advantage of a number of additional simplifying assumptions.

Hereafter, we consider that strong inequality

$$t_1 \gg t_A \tag{5.2}$$

is valid. In view of (5.1), this means that $\lambda_1^2 D_n \ll t_A^{-1}$. In this case, times $t \sim t_1$ typical of droplet internal relaxation to chemical equilibrium (with respect to the dissolved matter comprising nucleus) will fit the range $t \gg t_A$. As is seen, the first term and the time retardation in the second term in the right-hand side of (2.7) may be ignored, i.e., we may assume that $\delta c(\tau)|_{r=R} = \delta c(t)|_{r=R}$. Calculating the remaining integral with respect to τ and with allowance made for (2.6) and inequality $\exp(t/t_A) \gg 1$, equation (2.7) will be reduced to equality

$$\delta\Gamma(t) = (d\ln\Gamma/d\ln c)\delta c(t)|_{r=R}. \tag{5.3}$$

Differentiating (5.3) with respect to time, we obtain

$$d\delta\Gamma(t)/dt = (d\ln\Gamma/d\ln c)d\delta c(t)/dt|_{r=R}. \tag{5.4}$$

In this case, instead of (4.6), we have

$$D_n \partial\delta c/\partial r|_{r=R} = -(d\Gamma/dc)d\delta c/dt|_{r=R}. \tag{5.5}$$

Possible derivation of relationship (5.4) also directly from (2.8) confirms that assumptions $\delta\Gamma(0) = 0$ and $\delta c(0)|_{r=R} = 0$ made during the passage from (2.7) to (2.8) are insignificant.

Remember that, according to (2.3), $\delta\Gamma$ and δc are relative (but not absolute) deviations of the $\tilde{\Gamma}$ and $\tilde{c}$ quantities from their equilibrium values; therefore, relationships (5.3)–(5.5) correspond to the approximation of the diffusion-controlled adsorption kinetics when equilibrium in a monolayer corresponding to the current solution concentration $\tilde{c}(t)|_{r=R}$ at the monolayer–solution interface is established.

In this approximation, which we confine ourselves to, equation (4.12) with allowance made for (2.2) and

(2.6) is reduced to equation

$$\tan[\lambda_k(R - \tilde{R}_n)]$$
$$= \frac{\lambda_k(1/\tilde{R}_n - 1/R - \lambda_k^2 d\Gamma/dc + k_n/D_n)}{\lambda_k^2 + (1/R + \lambda_k^2 d\Gamma/dc)(1/\tilde{R}_n + k_n/D_n)}. \tag{5.6}$$

Equation (5.6) presumes that the strong inequality $\lambda_k^2 D_n \ll t_A^{-1}$ is fulfilled at all $k = 1, 2, ...$; nevertheless, it is apparent that one should keep in mind that this inequality as well as equation (5.6) are actually required only at $k = 1$, i.e., for the least of all positive values $\lambda_k^2 D_n$. Note that the $\alpha(\Gamma)$ and $\beta(\Gamma)$ coefficients of adsorption and desorption do not enter into relationships (5.3) and (5.6). Also note that the passage to the approximation of the diffusion-controlled kinetics of adsorption was performed for the arbitrary adsorption isotherm. Earlier [12], this passage was treated for the Langmuir adsorption isotherm.

Below, we will study the dependence of the λ_1 value and, correspondingly, time t_1 on the problem parameters for two typical extreme cases of the droplet relaxation: at the initial stage of the nucleus dissolution and at its complete dissolution.

6. DROPLET RELAXATION AT THE INITIAL STAGE OF NUCLEUS DISSOLUTION

As was demonstrated in [9], the region of incomplete nucleus dissolution in a droplet at the macroscopicity of the condensation nuclei may be significant for the thermodynamics of droplet nucleation only at the initial stage of dissolution when the thickness of the liquid film of a solution is small compared to the droplet radius, i.e., when the film is actually flat. It is this approximation that we confine ourselves to during the consideration of the region of incomplete nucleus dissolution.

From (5.6) in the flat film approximation at $\tilde{R}_n \longrightarrow \infty$ and $R \longrightarrow \infty$ follows the equality

$$\tan(\lambda_k h) = \frac{k_n/D_n - \lambda_k^2 d\Gamma/dc}{\lambda_k[1 + k_n(d\Gamma/dc)/D_n]}, \tag{6.1}$$

where

$$h \equiv R - \tilde{R}_n \tag{6.2}$$

is the thickness of a droplet liquid film. While deriving (6.1), we assumed additionally that at a fairly large R the inequalities

$$k_n R/D_n \gg 1, \tag{6.3}$$

$$\lambda_k^2 R d\Gamma/dc \gg 1 \tag{6.4}$$

are valid.

Note that in the approximation under consideration the equilibrium concentration of the matter comprising

nucleus in a droplet is equal to the solubility c_n. Hence, the $d\Gamma/dc$ derivative in (6.1) and (6.4) is determined by the c_n value and is independent of the size of the nucleus residue.

The film thickness h in the near critical range of the droplet sizes is determined by its dependence [9, 10] on the initial nucleus radius, the droplet surface tension, the correlation length in a film, and the spreading coefficient of condensing liquid at the surface of condensation nucleus.

For the majority of surfactants, the Γ value at the solution concentration equal to the solubility of the matter comprising nucleus is close to the limiting value of Γ_∞ corresponding to complete monolayer coverage. It is well known that the dependence of adsorption Γ on concentration c reaches the plateau when the monolayer approaches its saturation. Therefore, it may be expected that, regardless of the ratio between the k_n and D_n values, the effect of adsorption on the internal relaxation time of a droplet will be a kind of correction at the partial nucleus dissolution. Hence, we assume that inequalities

$$\lambda_k^2 D_n (d\Gamma/dc)/k_n \ll 1 \qquad (6.5)$$

and

$$k_n (d\Gamma/dc)/D_n \ll 1 \qquad (6.6)$$

are taking place.

Then, equation (6.1) is reduced to

$$\tan(\lambda_k h) = k_n/\lambda_k D_n. \qquad (6.7)$$

Let us first consider the case when strong inequality

$$k_n h/D_n \gg 1 \qquad (6.8)$$

is valid. By its physical meaning, this case corresponds to a fairly large rate of nucleus dissolution. As is apparent from (6.7), the λ_1 root is a little bit smaller than $\pi/2h$; then, from (5.1), we obtain

$$t_1 \simeq 4h^2/\pi^2 D_n. \qquad (6.9)$$

As is seen from (6.9), the t_1 time determined for the fulfillment of condition (6.8) is independent of coefficient k_n of the rate of nucleus dissolution. Therefore, condition (6.8) implies that at given parameters h, k_n, and D_n the layer with equilibrium concentration c_n may be formed near the surface of the nucleus residue over the course of time much shorter than time t_1. In this case, the boundary condition (4.5) transforms to condition $\delta c|_{r=\tilde{R}_n} = 0$. Note that, in view of (6.8) and relation $\lambda_1 \simeq \pi/2h$, the inequality (6.5) is deliberately valid, provided that condition (6.6) is fulfilled. As is apparent from (6.9), the fulfillment of condition (5.2) requires that the inequality

$$h^2 \gg (\pi^2/4)D_n t_A \qquad (6.10)$$

should also be fulfilled.

When inequality (6.8) is not fulfilled, the equilibrium is established at the same film thickness over the longer time specified by relationship (6.9). Then, the t_1 time will be dependent on the k_n values. In the limiting case, when the reverse [to (6.8)] inequality

$$k_n h/D_n \ll 1 \qquad (6.11)$$

is valid, the $\lambda_1 h$ value lies at the beginning of the first quadrant. Then, from (6.7) and (5.1), we obtain

$$\lambda_1 \simeq (k_n/h D_n)^{1/2} \qquad (6.12)$$

and

$$t_1 \simeq h/k_n. \qquad (6.13)$$

Note that, in view of (6.11) and (6.12), inequality (6.6) is deliberately fulfilled, provided that inequality (6.5) is valid. As is seen from (6.13), the fulfillment of condition (5.2) requires the fulfillment of inequality

$$h \gg k_n t_A. \qquad (6.14)$$

The smaller $d\Gamma/dc$, the shorter time t_A [see (2.6)], and the inequalities (6.10) and (6.14) [hence, condition (5.2)] are better fulfilled.

In both cases in question, the presence of summands in the numerator and the denominator of the right-hand side of (6.1) describing the effect of adsorption results in a decrease in λ_1 and, correspondingly, in an increase in t_1.

As was shown in [9], in the situation described above, when the film can actually be considered flat, the relationship $\tilde{R}_n \simeq R_n$ is valid with a high accuracy. This indicates that $\tilde{R}_n$ is virtually independent of time, thereby removing at once the problem of the possible motion of the nucleus boundary.

7. DROP RELAXATION AT COMPLETE NUCLEUS DISSOLUTION

Let us now find out what will happen when the nucleus is completely dissolved and the radius of the condensation nucleus residue $\tilde{R}_n$ and coefficient k_n vanish. At $\tilde{R}_n \longrightarrow 0$ and $k_n \longrightarrow 0$, we obtain from (5.6)

$$\tan(\lambda_k R) = \frac{\lambda_k R}{1 + \lambda_k^2 R d\Gamma/dc}. \qquad (7.1)$$

The dependence of the droplet radius R in the near critical range of its sizes on the initial nucleus radius and droplet surface tension (determined by strong adsorption) was demonstrated in [3–7]. This dependence was revealed in [2] under the insignificant role of adsorption.

When the nucleus is completely dissolved in a droplet, the value of adsorption Γ can be arbitrary small, the

equilibrium concentration c can also become arbitrarily small as the droplet radius R increases at fixed initial nucleus radius. As the adsorption Γ decreases, the value of $d\Gamma/dc$ derivative either monotonically increases, as is the case for the Langmuir adsorption isotherm and the Frumkin adsorption isotherm at low coefficients of the lateral interactions κ, or reaches its maximal value in some intermediate point of the $0 < \Gamma/\Gamma_\infty < 1$ range, as in the case of the Frumkin isotherm for larger values of κ. Let us consider as an example the limiting situation where $\Gamma/\Gamma_\infty \ll 1$. Considering that at the fulfillment of strong inequality $\Gamma/\Gamma_\infty \ll 1$ the Henry adsorption law is valid, we obtain

$$d\Gamma/dc = \Gamma_\infty/c_\alpha, \qquad (7.2)$$

where Γ_∞/c_α is the Henry constant.

As follows from (7.1), (7.2), and (5.1), for the droplets whose radii satisfy strong inequality

$$R \gg \pi^2\Gamma_\infty/c_\alpha, \qquad (7.3)$$

the internal relaxation time t_1 is represented by the expression

$$t_1 \simeq R^2/(1.43\pi)^2 D_n. \qquad (7.4)$$

According to (7.1) and (7.2), as the Γ_∞/c_α ratio increases at fixed droplet radius R, the λ_1 value decreases. When the reverse [with respect to (7.3)] inequality

$$R \ll \pi^2\Gamma_\infty/c_\alpha \qquad (7.5)$$

is reached, the λ_1 value becomes equal to π/R. In this case, in view of (5.1), time t_1 becomes as large as the following value

$$t_1 \simeq R^2/\pi^2 D_n. \qquad (7.6)$$

Times t_1 given by relationships (7.4) and (7.6) and time t_A specified by relationship (3.5) satisfy the condition (5.2) because the inequality

$$R^2 \gg \pi^2\Gamma_\infty D_n/\alpha(\Gamma)c_\alpha \qquad (7.7)$$

is valid for macroscopic droplets.

Inequality (7.7) is compatible with the reverse inequality (7.5) because the relationship $\pi^2\alpha(\Gamma)\Gamma_\infty/c_\alpha D_n \gg 1$ is usually readily true.

8. CHARACTERISTIC TIME OF THE MOTION OF THE DROPLET BOUNDARY IN THE NEAR CRITICAL RANGE OF ITS SIZES

Let us substantiate the assumption made in Section 4 that the droplet motion in the near critical range of its sizes may be ignored. Denote the characteristic time required for the external droplet boundary to be substantially displaced due to the absorption and evaporation of the molecules by a droplet by t_R. Evidently, the

desired substantiation is reduced to the demonstration that strong inequality

$$t_1/t_R \ll 1 \qquad (8.1)$$

is valid.

To begin with, let us consider the case when the near critical range of the droplet sizes corresponds to the complete dissolution of the condensation nucleus in a droplet. At time t_R, we have

$$t_R = R/|\dot{R}|, \qquad (8.2)$$

where $\dot{R}$ is the rate of the variation of the droplet radius R with time. As was shown in [1], in the near critical range, the exchange of molecules between the droplet and the vapor occurs almost always in the free-molecule regime. Then, according to formulas (11) and (16) from [1], in this range we have

$$\dot{R} = \alpha_c v_T(n_V/n_L)(\nu - \nu_c)/2(\Delta\nu_c)^2, \qquad (8.3)$$

where α_c is the condensation coefficient for the droplet surface; v_T is the thermal velocity of the vapor molecules; n_V is the number of vapor molecules per unit volume of the vapor-gas medium; n_L is the number of the condensate molecules per unit volume of a solution in a droplet; ν is the number of the condensate molecules in a droplet; ν_c is the number of the condensate molecules in a critical droplet; and $\Delta\nu_c$ is the halfwidth of the near critical range of the droplet dimensions at the ν-axis.

As was shown in [2], under the condition of the macroscopicity of the condensation nuclei in the near critical range R may be replaced by R_0 where the zero subscript indicates the values in the point of maximum of the condensate chemical potential. Also taking into account that, according to (8.3), the $|\dot{R}|$ value in the near critical range is maximal at the boundaries of this range (where $\nu = \nu_c \pm \Delta\nu_c$) from (8.2) and (8.3), we obtain the inequality

$$t_R > 2(n_L/n_V)R_0\Delta\nu_c/\alpha_c v_T. \qquad (8.4)$$

In the considered case of the complete dissolution of nucleus in a droplet, if we employ the largest [of all values given by relationships (7.4) and (7.6)] time t_1, we arrive at the approximate inequality

$$\frac{t_1}{t_R} \lesssim \frac{\alpha_c v_T(n_V/n_L)R_0}{2\pi^2 D_n\Delta\nu_c}. \qquad (8.5)$$

The dependence of the R_0 and $\Delta\nu_c$ values on the initial number ν_n of molecules (or ions) in a droplet and on the droplet surface tension (determined by strong adsorption) was established for the case of complete dissolution of a nucleus in [3-7]. If we may neglect the

effect of adsorption, then for R_0 and Δv_c we obtain simple formulas [1, formulas (15) and (27)]

$$R_0 = 3(3/4\pi n_L)^{1/3}(v_n/2a)^{1/2} \qquad (8.6)$$

and

$$\Delta v_c \simeq 27(3/2)^{1/4}(2a)^{-3/2}v_n^{7/6}, \qquad (8.7)$$

where $a = 4\pi(3/4\pi n_L)^{2/3}\sigma/kT$, and σ is the droplet surface tension.

Using (8.6) and (8.7) and assuming that $a \simeq 10$, $v_T \simeq 10^2$ m s^{-1}, $n_L \simeq 3 \times 10^{28}$ m^{-3}, $n_V \simeq 10^{23}$ m^{-3} (typical values for the condensation of the water vapor), and $D_n \simeq 10^{-9}$ m^2 s^{-1}, we obtain

$$\frac{\alpha_c v_T(n_V/n_L)R_0}{2\pi^2 D_n \Delta v_c} \simeq 6.8 \times 10^{-5}\alpha_c v_n^{-2/3}. \qquad (8.8)$$

As is seen from (8.5) and (8.8), the inequality (8.1) is rather readily true at any v_n and $\alpha_c \leq 1$.

Let us now pass to the case where the near critical range of the droplet sizes corresponds to the partial dissolution of the condensation nucleus in a droplet. As was mentioned in Section 6, this case may be significant for the thermodynamics of the droplet nucleation only when the thickness of the solution liquid film is small in comparison with the droplet radius, i.e., when the film is almost flat. We confine ourselves to the flat film approximation, discussed in Section 6. In this approximation, the relationship $\tilde{R}_n \simeq R_n$ [9] is valid with a rather high accuracy (at low solution concentration, the film thickness and, correspondingly, the droplet radius are mainly determined by the supply of the matter from the vapor rather than from the condensation nucleus). As was already mentioned in Section 6, in this case, the displacement of the nucleus boundary is negligible.

For the characteristic time t_R, which is required for the external boundary of a droplet to be significantly displaced due to absorption and evaporation of the molecules by the droplet (the film thickness is also significantly varied), instead of (8.2) we now obtain

$$t_R = h/|\dot{R}|. \qquad (8.9)$$

Since the rate $\dot{R}$ of the variation of the droplet radius R with time in the near critical range of droplet size is, evidently, determined by the same expression (8.3), then, similarly to (8.4), we obtain the inequality

$$t_R > 2(n_L/n_V)h_0\Delta v_c/\alpha_c v_T. \qquad (8.10)$$

Using for time t_1 in the flat film approximation the relationships (6.9) and (6.13) derived under the adherence to inequality (6.8) and reverse inequality (6.11), respectively, we arrive at the following approximate

inequalities:

$$\frac{t_1}{t_R} \lesssim \frac{2\alpha_c v_T(n_V/n_L)h_0}{\pi^2 D_n \Delta v_c} \quad (k_n h_0/D_n \gg 1) \qquad (8.11)$$

and

$$\frac{t_1}{t_R} \lesssim \frac{\alpha_c v_T n_V/n_L}{2k_n\Delta v_c} \quad (k_n h_0/D_n \ll 1). \qquad (8.12)$$

In the case of the partial dissolution of a nucleus, expression (8.7) for the halfwidth Δv_c of the near critical range of the droplet sizes is already not applicable at the v-axis. In this case, according to estimate (6.26) from [10], for Δv_c, we have

$$\Delta v_c \sim a^{-1/3}(4\pi n_L l^3/3)^{1/9}\tilde{v}_0^{-2/3}, \qquad (8.13)$$

where l is the correlation length in a film. Hence, this value is added to the set of the initial parameters of the theory. The $\tilde{v}_0$ value is defined by the equality

$$\tilde{v}_0 = 4\pi n_L R_0^3/3; \qquad (8.14)$$

i.e., it has the meaning of the number of the condensate molecules in a droplet (at maximal chemical potential of the condensate), which would occur in the absence of the condensation nucleus in a droplet. For the flat film, in view of approximate equality $R \simeq \tilde{R}_n$ and the aforementioned rather accurate relationship $\tilde{R}_n \simeq R_n$, it follows from (8.14) and (1.1) that $\tilde{v}_0 \simeq n_L v_n v_n$ (v_n is the volume per molecule or ion in a nucleus). Then, the estimate (8.13) is written as

$$\Delta v_c \sim a^{-1/3}(4\pi n_L l^3/3)^{1/9}(n_L v_n)^{2/3}v_n^{2/3}. \qquad (8.15)$$

Using (8.15) and letting $n_L v_n \simeq 1$ and $l \simeq 2 \times 10^{-9}$ m (as for the film of pure water on quartz [22]) and taking for other parameters the same values as for the considered case of the complete dissolution of a nucleus, we obtain

$$\frac{2\alpha_c v_T(n_V/n_L)h_0}{\pi^2 D_n \Delta v_c} \sim 1.4 \times 10^{-4}\alpha_c(h_0/l)v_n^{-2/3}, \qquad (8.16)$$

and

$$\frac{\alpha_c v_T n_V/n_L}{2k_n\Delta v_c} \sim 3.3 \times 10^{-4}\alpha_c(D_n/k_n l)v_n^{-2/3}, \qquad (8.17)$$

where on the right-hand sides we deliberately showed multipliers h_0/l and $D_n/k_n l$ in order to avoid explicit estimates of the h_0 and k_n values (the analytical expression for the dependence of film thickness h_0 on the initial nucleus radius, the correlation length in a film, and the spreading coefficient of the condensing liquid at the surface of the condensation nucleus was reported in [9, 10]).

It was shown in [9, 10] that the film plays an important role in the thermodynamics of the droplet nucle-

ation when its thickness h_0 does not exceed the correlation length l by more than the order of magnitude. Therefore, even if no explicit estimate of h_0 is made, it is apparent from (8.11) and (8.16) that inequality (8.1) is readily valid at $k_n h_0/D_n \gg 1$. Further, it is seen from (8.12) and (8.17) that inequality (8.1) is also true at $k_n h_0/D_n \ll 1$; however, the stronger condition $k_n h_0/D_n \ll 1$ becomes, the worse it is fulfilled.

In all the situations considered in this section, a decrease in α_c and an increase in v_n make the inequality (8.1) stronger.

9. HIERARCHY OF CHARACTERISTIC TIME SCALES OF THE KINETICS OF DROPLET NUCLEATION ON THE MACROSCOPIC NUCLEI

Together with times t_A, t_1, and t_R, there is yet one characteristic time scale of the nucleation process, namely, time t_s of the establishment of the steady-state droplet distribution in the near critical range of their sizes [1]. Unlike times t_A, t_1, and t_R for a single droplet, this time scale is of statistic origin. It is determined by the width of the potential maximum of the droplet formation work at the given vapor supersaturation.

When formulating the kinetic theory of the heterogeneous nucleation, it was assumed [1] that, in the near critical range of the sizes, the droplets remain under the internal equilibrium during the fluctuation surmounting the activation barrier of nucleation. Evidently, this process requires the adherence to strong inequality

$$t_1/t_s \ll 1. \tag{9.1}$$

In general, time t_s is given by the relationship

$$t_s = (\Delta v_c)^2/2\pi\alpha_c v_T n_V R_0^2. \tag{9.2}$$

This relationship is defined by formulas (11) and (25) from [1]. Let us find out when the inequality (9.1) is valid.

As in Section 8, we begin with the case when the dissolution of the nucleus in a droplet is complete. Using the largest [of all times given by relationships (7.4) and (7.6)] time t_1, we arrive at the approximate inequality

$$\frac{t_1}{t_s} \le \frac{2\alpha_c v_T n_V R_0^4}{\pi D_n(\Delta v_c)^2}. \tag{9.3}$$

Further, using (8.6) and (8.7) and taking the same values of the initial parameters as in Section 8, we obtain

$$\frac{2\alpha_c v_T n_V R_0^4}{\pi D_n(\Delta v_c)^2} \simeq 10^{-4}\alpha_c v_n^{-1/3}. \tag{9.4}$$

It is apparent from (9.3) and (9.4) that inequality (9.1) is readily true. This conclusion was made earlier in [1].

Let us pass now to the case when the dissolution of the nucleus in a droplet is incomplete, to be more exact,

when almost flat liquid film is formed around the nucleus residue that had no time to be dissolved (it is this case that is of interest for the thermodynamics of the droplet nucleation).

Using for time t_1 in the flat film approximation relationships (6.9) and (6.13) derived for the adherence of inequality (6.8) and reverse inequality (6.11), respectively, we arrive at the approximate equalities

$$\frac{t_1}{t_s} \simeq \frac{8\alpha_c v_T n_V h_0^2 R_0^2}{\pi D_n(\Delta v_c)^2} \quad (k_n h_0/D_n \gg 1) \tag{9.5}$$

and

$$\frac{t_1}{t_s} \simeq \frac{2\pi\alpha_c v_T n_V h_0 R_0^2}{k_n(\Delta v_c)^2} \quad (k_n h_0/D_n \ll 1). \tag{9.6}$$

Then, using in the flat film approximation estimate (8.15) and relationship $R_0 \simeq R_n$, taking into account (1.1), and assuming the same values of the initial parameters as in Section 8, we obtain

$$\frac{8\alpha_c v_T n_V h_0^2 R_0^2}{\pi D_n(\Delta v_c)^2} \sim 4 \times 10^{-3}\alpha_c(h_0/l)^2 v_n^{-2/3} \tag{9.7}$$

and

$$\frac{2\pi\alpha_c v_T n_V h_0 R_0^2}{k_n(\Delta v_c)^2} \sim 10^{-2}\alpha_c(D_n/k_n l)(h_0/l)v_n^{-2/3}, \tag{9.8}$$

where on the right-hand sides we deliberately showed the multipliers $(h_0/l)^2$ and $(D_n/k_n l)(h_0/l)$ in order to avoid explicit estimates of the h_0 and k_n values.

As was noted in Section 8, the film thickness h_0 does not exceed the correlation length l by more than the order of magnitude; therefore, it is seen from (9.5) and (9.7) that inequality (9.1) is true at $k_n h_0/D_n \gg 1$. As is seen from (9.6) and (9.8), the adherence to inequality (9.1) at $k_n h_0/D_n \ll 1$ for nuclei with a slow dissolution rate may require the establishment of the lower boundary for all nucleus sizes that are permissible by the theory.

In all the situations considered in this and previous sections, a decrease in α_c and an increase in v_n makes inequality (9.1) stronger.

The estimates of the ratios of characteristic times t_1/t_R and t_1/t_s obtained in this and preceding sections enable us to reveal the domain of the values of the initial parameters of a problem where conditions (8.1) and (9.1) that are necessary for the construction of thermodynamics and kinetics of the droplet nucleation are valid.

It is apparent already from the comparison of relationships (8.8), (8.16), and (8.17) with (9.4), (9.7), and (9.8), respectively, that condition (9.1) is more rigorous than (8.1); i.e., the time t_R is longer than time t_s. Let us

verify this conclusion by the direct comparison of the t_R and t_s times.

At the complete dissolution of the condensation nucleus in a droplet, from (8.4) and (9.2), we have the inequality

$$t_R/t_s > 3v_0/\Delta v_c, \qquad (9.9)$$

where $v_0 = 4\pi n_L R_0^3/3$ is the number of the condensate molecules in the droplet with radius R_0. According to strong inequalities (32) from [2], the relationship $v_0/\Delta v_c \gg 1$ is readily true. Then, the fulfillment of strong inequality

$$t_R/t_s \gg 1 \qquad (9.10)$$

readily follows from (9.9).

When the condensation nucleus is partially dissolved in a droplet (to be more exact, when the flat film is formed around the undissolved nucleus residue), from (8.10), (8.13), (8.14), and (9.2), we obtain the inequality

$$t_R/t_s > 3^{7/9}(4\pi n_L)^{2/9}a^{1/3}h_0/l^{1/3}. \qquad (9.11)$$

Taking into account that $h_0/l \sim 10$ and $n_L^{1/3} l \sim 10$, we prove again that strong inequality (9.10) is true.

It is evident from (5.2), (9.1), and (9.10) that the hierarchy of the characteristic times of the kinetics of the droplet nucleation on the macroscopic condensation nuclei ranges as follows:

$$t_A \ll t_1 \ll t_s \ll t_R. \qquad (9.12)$$

This hierarchy enables us to understand the complex, multistage process of the surmounting the activation barrier of nucleation by the droplets and to demonstrate the applicability of the thermodynamics of this process developed in [2–10] to its kinetics elaborated in [1].

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