

KINETICS OF CONDENSATION ON SOLUBLE NUCLEI

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UDC 533.77:541.123

A kinetic equation is derived to describe the fluctuational overcoming of an activation barrier by drops nucleated in a supersaturated vapor on condensation nuclei that are soluble in the drops. It is shown that the activation energy in the case of heterogeneous condensation is the gradient of the heights of the potential hill and potential well of the work of drop formation, rather than the height of the potential hill of the work for the critical drop (as in the case of homogeneous condensation). It is found that the rate of heterogeneous formation of supercritical drops is steady. The subsequent growth of these drops is unconstrained. An incubation period is established for the steady-state growth. It is shown that the incubation period also determines the characteristic time scale for the development of the heterogeneous phase transformation throughout the metastable region of the vapor, where the degree of supersaturation is low. Estimates are made of characteristics of the process of condensation on soluble nuclei in the case when the substance of the nuclei is surface-inactive.

The importance of understanding the kinetics of condensation on soluble nuclei was demonstrated in [1]. Being the final link between thermodynamics and experimentation, kinetics is of course needed for the information that it can give to thermodynamics. The present article is devoted to the kinetics of condensation on soluble nuclei — a subject which has not been examined previously in the literature. We will focus on the prethreshold region of metastability of the vapor. In this region, activation energy is already substantial but remains below the level at which heterogeneous phase transformation takes place. It is in this region that the kinetics of heterogeneous condensation is of the most interest, since a greater understanding of this subject may make it possible to externally control the development of the phase transformation over time and extract the maximum amount of information from experimental data on the molecular properties of the substance condensing from the vapor.

The kinetic theory constructed below is general in the sense that it is based on fundamental thermodynamic characteristics of heterogeneous nucleation: the threshold value of the chemical potential of the vapor; the positions and half-widths of the potential well and potential hill of the work of heterogeneous drop formation; activation energy. All of these characteristics were found in [1] for the case when the substance of the nucleus is surface-inactive.

Principles of the Kinetics of Overcoming of the Activation Barrier by Near-Critical Drops. We will use the notation employed in [1]. Here ν is the number of condensate molecules in a drop (condensed from the vapor phase); ν_n is the number of molecules or ions in the condensation nucleus; T is the temperature of the drop and the vapor — as medium surrounding it; R is the radius of the drop; b_d and b are the chemical potentials of the condensate in the drop and the vapor, respectively, expressed in thermal energy units kT (k being the Boltzmann constant) and reckoned from the value corresponding to equilibrium of the vapor with the condensing liquid when their contact surface is planar; a is the dimensionless surface tension of the drop determined by Eq. (4) from [1]; a_0 subscript characterizes values corresponding to the maximum chemical potential of the condensate; subscripts e and c characterize values for equilibrium and critical drops; F is the work of heterogeneous drop formation in the vapor on the condensation nucleus, expressed in thermal energy units kT ; $\Delta\nu_e$ and $\Delta\nu_c$ are the half-widths of the potential well and potential hill of the work F .

The chemical potential of the vapor b is conveniently represented as

$$b = b_{tr} (1 - \epsilon). \quad (1)$$

([1], Eq. (16)), where b_{tr} is the threshold chemical potential of the vapor. The parameter ϵ , determining the value of b , satisfies the following estimate within the prethreshold region of metastability that we are interested in

$$\epsilon^{1/2} \sim \nu_n^{-1/2} \quad (2)$$

([1], expression (36)).

To construct the kinetic equation controlling the fluctuational surmounting of the activation barrier by near-critical nuclei, we need to know their equilibrium distribution and the rate of change over time in the variable that describes them.

Referred to a unit volume of the vapor, the equilibrium distribution of the drops with respect to the variable ν will be designated as $n^{(e)}(\nu)$. For simplicity, we will assume that all of the condensation nuclei are identical. We will use n_n to represent the number of such nuclei per unit volume of the vapor.

Since the work F_e is negative and — in the prethreshold region of metastability of the vapor — has a high absolute value (i.e., compared to the thermal energy), nearly each of the nuclei captures the number of vapor molecules at which the resulting drop turns out to be at the bottom of the potential well of work F . As a result, we also obtain an equilibrium distribution of heterogeneously formed drops.

Considering that the equilibrium distribution has the form of a Gibbs distribution, we find that

$$n^{(e)}(\nu) = (n_n / \pi^{1/2} \Delta\nu_e) \exp [-(F - F_e)] \quad (3)$$

To check the correctness of the normalization factor in this distribution, we integrated over the near-equilibrium neighborhood $|\nu - \nu_e| \lesssim \Delta\nu_e$ in which it is concentrated. Using the equation

$$F = F_e + [(\nu - \nu_e)/\Delta\nu_e]^2 \quad (|\nu - \nu_e| \lesssim \Delta\nu_e) \quad (4)$$

([1], Eq. (29)), we conclude that the integral is equal to n_n — as it should be.

The idea expressed by Eqs. (3) and (4) — that heterogeneously formed stable-phase nuclei accumulate at the bottom of the potential well of nucleus formation work before their fluctuational surmounting of the activation barrier — was used in [2] in a theory explaining the nucleation of drops on ions in metastable vapor.

In the important (for kinetics) near-critical neighborhood $|\nu - \nu_c| \lesssim \Delta\nu_c$ the following is valid

$$F = F_c - [(\nu - \nu_c)/\Delta\nu_c]^2 \quad (|\nu - \nu_c| \lesssim \Delta\nu_c) \quad (5)$$

([1], Eq. (30)). Using (3) and allowing for (5), we obtain the following in this neighborhood (in which the equilibrium distribution gives a relatively small number of drops and is of purely formal significance):

$$n^{(e)}(\nu) = \frac{n_n}{\pi^{1/2} \Delta\nu_e} \exp(-\Delta F) \exp \left[\left(\frac{\nu - \nu_c}{\Delta\nu_c} \right)^2 \right] \quad (|\nu - \nu_c| \lesssim \Delta\nu_c) \quad (6)$$

where, in accordance with definition (27) from [1], we put

$$\Delta F = F_c - F_e \quad (7)$$

the fact that F_e and F_c enter into (6) in the form of the difference $F_c - F_e$ at once shows why a differential expression is sufficient in the heterogeneous theory, rather than the finite-difference relation

$$\partial F / \partial \nu = b_\nu - b \quad (8)$$

([1], Eq. (22)). In the present case, the work F is determined only to within the constant term.

Let us now find the time rate of change $\dot{\nu}$ in the variable ν in a near-critical nucleus. We will use ρ and ρ_ν to represent the density of the number of molecules of vapor actually present and the same for a hypothetical vapor in which the temperature T is the same as in the real vapor but in which a drop with the number ν of molecules of condensed liquid is critical. Assuming the real and hypothetical vapors to be ideal, we have

$$\rho = \rho_\infty \exp(b), \quad \rho_\nu = \rho_\infty \exp(b_\nu) \quad (9)$$

where ρ_∞ is the density of the number of molecules of vapor in equilibrium with the condensing liquid in the case of a plane contact surface.

Using the Knudsen formula

$$\dot{\nu} = W(1 - \rho_\nu/\rho) \quad (10)$$

where

$$W = \pi \alpha v_T \rho R^2 \quad (11)$$

Here, α is the condensation coefficient of the vapor molecules and v_T is the mean thermal velocity of these molecules. The quantity R has an upper bound [3] due to the assumption made in connection with (10) that free-molecular mass exchange occurs between the drop and the vapor. However, as will be shown somewhat later, this restriction is so slight that it is almost always observed at the stage of supercritical-drop formation even despite the fact that it is in opposition to the restriction on the macroscopic nature of the nucleus

$$\nu_n^{-1/3} \gg 1 \quad (12)$$

([1], restriction (37)).

Using (9) and (8) in (10), we find that

$$\dot{\nu} = W [1 - \exp(\partial F/\partial \nu)] \quad (13)$$

In the near-critical neighborhood $|\nu - \nu_c| \lesssim \Delta \nu_c$, in accordance with (5) and $\Delta \nu_c \gg 1$ ([1], the second of inequalities (40)) the condition $|\partial F/\partial \nu| \ll 1$ is observed. In the same neighborhood, in accordance with the formula $R_c = R_0 [1 + (2\epsilon/3)^{1/2}]$ ([1], the second of formulas (21)) and the inequality $\epsilon^{1/2} \ll 1$ (which follows from (2) and (12) in the prethreshold region of metastability of the vapor) $R = R_0$ with a high degree of accuracy. Here, by virtue of the relation

$$\nu_0 = (9\nu_n/2a)^{1/2} \quad (14)$$

([1], Eq. (6)), R_0 is given by the expression

$$R_0 = 3\lambda (\nu_n/2a)^{1/2} \quad (15)$$

in which $\lambda \equiv (3v_l/4\pi)^{1/2}$ (v_l is the molecular volume of the condensing liquid). Using (5) and (11), we find from (13) that

$$\dot{\nu} = 2W_0 (\nu - \nu_c) / (\Delta \nu_c)^2 \quad (|\nu - \nu_c| \lesssim \Delta \nu_c) \quad (16)$$

where

$$W_0 = 9\pi \alpha v_T \rho \lambda^2 (\nu_n/2a) \quad (17)$$

Kinetic Equation for Overcoming of the Activation Barrier by Near-Critical Drops. The kinetic equation controlling the fluctuational overcoming of the activation barrier by near-critical nuclei is the Fokker—Planck equation linearized in the neighborhood of a critical nucleus [4-6].

It has the form of the continuity equation

$$\partial_t n(\nu, t) = -\partial_\nu j \quad (18)$$

Here, t is time; $n(\nu, t)$ is the distribution of the nuclei with respect to the variable ν describing them; j is the flux of nuclei. We have adopted the abbreviated notation $\partial_t \equiv \partial/\partial t$ and $\partial_\nu \equiv \partial/\partial \nu$ as the operators for differentiation with respect to t and ν . We assume below that $n(\nu, t)$ — as the equilibrium distribution $n^{(e)}(\nu)$ — is referred to a unit volume of the vapor.

In accordance with general principles of physical kinetics, we have

$$\dot{\gamma} = (\dot{\nu} + \beta \partial_\nu) \cdot n(\nu, t) \quad (19)$$

The term with the operator ∂_ν describes the fluctuational growth of the nuclei. This growth blurs obscures the regular growth of an individual nucleus described by the term with $\dot{\nu}$. The unknown coefficient β in the term with the operator ∂_ν is determined from the condition of vanishing of the flux of nuclei for their equilibrium distribution.

Taking into account (6) and (16) in (19), we then obtain

$$j = -W_0 \{ \partial_\nu - 2(\nu - \nu_c)/(\Delta\nu_c)^2 \} n(\nu, t) \quad (20)$$

Inserting (20) into (18), we finally obtain

$$\partial_t n(\nu, t) = W_0 \partial_\nu \{ \partial_\nu - 2(\nu - \nu_c)/(\Delta\nu_c)^2 \} n(\nu, t) \quad (21)$$

(the operator ∂_ν acts on all of the factors to the right of it). Kinetic equation (21) is written in the same form as in the classical theory of homogeneous condensation [5]. However, the parameters ν_c , $\Delta\nu_c$, and W_0 in this equation turn out to be quite different.

The following natural (for the kinetics of phase transformations) boundary conditions [5, 6] are written for the distribution $n(\nu, t)$

$$\begin{aligned} n(\nu, t)/n^{(e)}(\nu) &\simeq 1 & (\nu \simeq \nu_c - \Delta\nu_c) \\ n(\nu, t)/n^{(e)}(\nu) &\simeq 0 & (\nu = \nu_c + \Delta\nu_c) \end{aligned} \quad (22)$$

The equilibrium distribution $n^{(e)}(\nu)$ under these conditions, determined by Eq. (6), also differs significantly from the distribution that would be obtained in the classical theory of homogeneous condensation.

The above-noted inequality $\Delta\nu_c \gg 1$ justifies the fact that, in kinetic equation (21), we ignore the third and higher derivatives of $n(\nu, t)$ with respect to ν , i.e., this inequality justifies use of the Fokker—Planck approximation in this equation. In fact, it shows that the change in ν in an individual act of absorption or emission of a vapor molecule by a drop — equal to 1 or -1 — is small compared to the width $\Delta\nu_c$ of the potential hill of the work F (which gives the scale of the change in the distribution $n(\nu, t)$ with a change in ν).

Kinetic equation (21) is linearized in the neighborhood of the critical nucleus due to the application of quadratic approximation (5) for the work of formation of a near-critical nucleus.

Steady State of Near-Critical Drops. Let us study the steady state of near-critical drops. We will denote this state by the subscript s .

In the steady state, the quantities are independent of t , while the flux j (by virtue of (18)) is also independent of ν . In accordance with (20), (22), and (6), we then have

$$n^{(s)}(\nu) = \frac{n_n \exp(-\Delta F)}{\pi \Delta\nu_c \Delta\nu_c} \exp \left[\left(\frac{\nu - \nu_c}{\Delta\nu_c} \right)^2 \right] \int_\nu^\infty \exp \left[- \left(\frac{\nu' - \nu_c}{\Delta\nu_c} \right)^2 \right] d\nu' \quad (23)$$

Then inserting (23) into (20), we obtain

$$j^{(s)} = n_n (W_0 / \pi \Delta \nu_e \Delta \nu_c) \exp(-\Delta F) \quad (24)$$

which determines a quantity important for kinetics — the steady-state rate of heterogeneous formation of supercritical drops which subsequently grow without constraints. The factor $W_0 / \pi \Delta \nu_e \Delta \nu_c$ in (24) is the heterogeneous analog of the "Zel'dovich factor."

As can be seen from (7), the work of heterogeneous drop formation is represented in the exponent in (24) as the difference $F_c - F_e$. This shows that the activation energy in the case of heterogeneous condensation is the gradient of the heights of the potential hill and potential well of the drop-formation work, rather than the height of the potential hill of the work for the critical drop (as in homogeneous condensation).

Using results obtained in [7, 8] from study of an equation of the form (21) with boundary conditions (22), we might be able to analytically describe the process by which near-critical drops reach a steady state over time. In particular, we find that

$$t_s = (\Delta \nu_c)^2 / 2W_0 \quad (25)$$

for the time t_s of establishment of this state and, thus, the time of establishment of a steady rate of heterogeneous formation of supercritical drops.

The time t_s is observed experimentally. It is called the incubation period (or the lag time). When this period ends, supercritical nuclei of a stable phase begin to appear in the metastable phase with a regular frequency — in the amount $j^{(s)}$ per unit time in a unit volume of the metastable phase.

With allowance for $\Delta \nu_e = \Delta \nu_c$ (which, in accordance with [1], is satisfied with a high degree of accuracy in the prethreshold region of metastability of the vapor), we find from (24-25) that the number of supercritical drops forming in the steady-state regime during the time t_s in a unit volume of the vapor is a fraction $(1/\pi)\exp(-\Delta F)$ of the number n_n of condensation nuclei in the same volume. This fraction is very small in the prethreshold region — in which the activation energy ΔF is already substantial. It can be concluded that the time t_s gives the scale of the characteristic time for the development of heterogeneous phase transformation in the prethreshold region of vapor metastability. The work F of drop formation is represented in Eq. (25) for the time t_s by the width $\Delta \nu_c$ of its potential hill.

If t_s is small compared to the time during which the steady-state rate $j^{(s)}$ changes significantly when the quantities b , n_n , and T change over time (and within the volume occupied by the vapor and the gas), then the steady state of the near-critical drops will be sustained as a quasi-steady state — corresponding to instantaneous values of all of these quantities.

Equation (25) justifies the above assumption that, in the course of overcoming the activation barrier, near-critical drops remain in a state of internal equilibrium. This assumption implies satisfaction of the inequality

$$t_r / t_s \ll 1 \quad (26)$$

where t_r is the time of internal relaxation of a near-critical drop. Evaluating t_r by means of $t_r \sim R_0^2 / D$ (where D is the coefficient of diffusion of molecules or ions in solution inside the drop), using (15), (25), and considering (17) and

$$\Delta \nu_e = \Delta \nu_c \simeq 27 \left(\frac{3}{2}\right)^{1/4} (2a)^{-1/2} \nu_n^{7/6} \quad (27)$$

([1], Eq. (39)), we have

$$t_r / t_s \sim \alpha \nu_T D^{-1} \rho \lambda^4 a \nu_n^{-1/3} \quad (28)$$

It is evident from (28) that given the conditions characteristic of vapor condensation, inequality (26) is satisfied with a margin of error even larger than for strong inequality (12).

Let us state the condition, adopted in (10), which corresponds to the assumption of free molecular mass exchange between the drop and the vapor. This condition reduces [3] to the form

$$R_0 \ll l/\alpha \quad (29)$$

where l is the mean free path of molecules of the vapor-gas medium surrounding the drop. Evaluating l by means of $l \sim l/(\rho + \rho_g)\lambda^2$ (where ρ_g is the density of the number of molecules of the passive gas), considering (15), and writing (29) in the form of a limitation on $\nu_n^{1/3}$, we obtain

$$\nu_n^{1/3} \ll (2a)^{1/3} [3\alpha(\rho + \rho_g)\lambda^3]^{-2/3}. \quad (30)$$

Inequality (30) is the opposite of inequality (12). However, the quantity in the right side of (30) is very large — appreciably greater than 10^2 . Thus, restriction (30) is weak: It is compatible with limitation (12) with a large margin of error.

The above-developed kinetic theory of heterogeneous condensation is universal and includes fundamental thermodynamic characteristics of heterogeneous nucleation. The restriction to cases involving nuclei composed of surface-inactive substances is required only in Eq. (27), and this equation was used only to obtain approximate relation (28).

Theory and Experiment. Equations (24) and (25) incorporate the main results of the above kinetic study. In the case of nuclei composed of surface-inactive substances, the quantities ΔF , $\Delta\nu_e$, $\Delta\nu_c$, and W_0 in these formulas are expressed through the initial parameters of the problem ν_n , a , ε , α , v_T , ρ , λ by means of the equality

$$\Delta F = (16/6^{3/2}) \nu_n \varepsilon^{1/2} \quad (31)$$

([1], Eq. (28)) and Eqs. (27) and (17). The quantity ν_n is also an initial parameter of the problem. The parameter ν_n consists of the multiplier in Eq. (24). Assuming that the substance of the condensation nucleus is not surface-active, we find that the only characteristic important for its determination is the number ν_n of molecules or ions in the nucleus.

In regard to predicting the energy capacity for heterogeneous phase transformation with a low degree of supersaturation of the vapor, the most important formula is that for the threshold value b_{tr} of the chemical potential of the vapor. This quantity was first determined by Keller [9] in the case of surface-inactive substances. Expanded in the initial parameters of the problem, this formula has the form:

$$b_{tr} = 2(2a)^{1/2} 27 \nu_n^{1/2} \quad (32)$$

([1], Eq. (11)).

However, it should be noted that Eqs. (24) and (25) also turn out to be important in experiments. In fact, under natural and process conditions (and even in laboratory experiments), the transformation to a metastable vapor is not usually instantaneous. However, as was shown in [10, 11], effective heterogeneous formation of supercritical drops is completed long before the moment when the chemical potential of the vapor would reach its threshold value in the absence of absorption of vapor by the drops. Thus, heterogeneous nucleation occurs most often by the barrier method. This method of heterogeneous nucleation is also described by Eqs. (24) and (25).

We should also note that in laboratory experiments — which make it possible to instantaneously establish an initial level of vapor supersaturation lying to the left of the prethreshold region of vapor supersaturation — Eqs. (24) and (25) will also prove more useful than Eq. (32) for using the resulting empirical data to obtain information on the molecular properties of the condensing substance.

We must also mention that the time t_s determined by Eq. (25) gives the scale of the characteristic time for the development of heterogeneous phase transformation not only in the prethreshold region of vapor metastability, but also in the lower part of the superthreshold region $b > b_{tr}$. In accordance with (1), $\varepsilon < 0$, $|\varepsilon|^{1/2} \ll 1$ in this region.

Let us prove this. Formula (8) and, with it, the approximation

$$\frac{\partial F}{\partial \nu} = \frac{4a}{9\nu_0^{1/3}} \left[\varepsilon - \frac{1}{6\nu_0^2} (\nu - \nu_0)^2 \right] \quad (33)$$

([1], approximation (26)) are not limited by the fact that $b < b_{tr}$, i.e., $\varepsilon > 0$. It is apparent from (33) and (13) that $\dot{\nu} > 0$ when $\varepsilon < 0$. The fact that the rate $\dot{\nu}$ at which the variable ν changes regularly over time at $\varepsilon < 0$ is positive makes it possible to ignore the contribution of fluctuations in heterogeneous drop growth and regard it approximately as a completely determinate

(as opposed to random) process occurring at the rate $\dot{\nu}$. At $\varepsilon < 0$ and $|\varepsilon|^{1/2} \ll 1$, it follows from approximation (33) in the neighborhood of the point $\nu = \nu_0$ (where this approximation is valid — [1], condition (13)) that $|\partial F/\partial \nu| \ll 1$. We also find that, with a high degree of accuracy, $W = W_0$ in the same neighborhood. Proceeding on the basis of (33) and (13), we then obtain

$$\dot{\nu} = \frac{4aW_0}{9\nu_0^{1/3}} \left[|\varepsilon| + \frac{1}{6\nu_0^2} (\nu - \nu_0)^2 \right] \quad (34)$$

In accordance with (34), the rate $\dot{\nu}$ reaches its minimum (positive) at the point $\nu = \nu_0$ and increases with an increase in $|\nu - \nu_0|$. This increase is more rapid, the smaller $|\varepsilon|$. As a result, we can evaluate the characteristic time τ of development of heterogeneous phase transformation by means of

$$\tau \sim \int_{-\infty}^{\infty} \frac{d\nu}{\dot{\nu}} \quad (35)$$

Of course, the limits of integration in (35) are of purely formal significance. It is important only that the main contribution to the integral comes from the neighborhood $|\nu - \nu_0| \lesssim 6^{1/2}\nu_0 |\varepsilon|^{1/2}$ of the point $\nu = \nu_0$ at which the condition for the validity of (33) and (34) still holds when $|\varepsilon|^{1/2} \ll 1$. Inserting (34) into (35), calculating the integral, and using Eq. (14), we obtain

$$\tau \sim (3^7/6^{3/2}) \pi (2a)^{-3} \nu_n^2 |\varepsilon|^{-1/2} W_0^{-1} \quad (36)$$

Let us compare the time τ with the time t_s , assuming that the negative quantity ε in (36) has the same absolute value as the positive quantity ε in (25) and thus (in accordance with (2), (12)) satisfies the condition $|\varepsilon|^{1/2} \sim \nu_n^{-1/3} \ll 1$. With allowance for (27) and $|\varepsilon|^{1/2} \sim \nu_n^{-1/3}$, we find from (25) and (36) that

$$\tau/t_s \sim 1 \quad (37)$$

Although estimate (36) somewhat overstates the actual time of development of heterogeneous phase transformation in the superthreshold region $b > b_{tr}$ of vapor metastability (the above-ignored fluctuations accelerate this process), relation (37) nevertheless shows that the time t_s gives the characteristic time scale for the development of heterogeneous phase transformation even in the lower part of the superthreshold region of vapor metastability. The region above this part is no longer of interest in regard to the occurrence of such transformation with a low level of supersaturation of the vapor.

The importance of kinetic study of condensation on soluble nuclei also stems from the following. We find from (32) that b_{tr} is proportional to $a^{3/2}/\nu_n^{1/2}$ (and is independent of α), while it follows from (25), (27), and (17) that t_s is proportional to $\nu_n^{4/3}/\alpha a^2$. Using the symbol \propto to denote that the quantities are proportional to one another (as opposed to being of the same order, denoted by the symbol \sim), we then have

$$b_{tr} \propto a^{3/2}/\nu_n^{1/2} \quad (38)$$

$$t_s \propto \nu_n^{4/3}/\alpha a^2 \quad (39)$$

In accordance with (38) and (39), an increase in ν_n and a decrease in a are accompanied by a decrease in b_{tr} and an increase in t_s . A decrease in the condensation coefficient α has no effect on b_{tr} but does increase t_s .

Thus, our kinetic investigation leads to the following practically important conclusion: Although an unlimited increase in the size of the nuclei dissolved in the drops may make a heterogeneous phase transformation energetically feasible regardless of the level of vapor supersaturation, this would inevitably entail an increase in the incubation period — the period which must elapse before supercritical drops can begin to systematically form in the vapor. Formulas (38) and (39) show the proportional relationship between the dependence of the threshold chemical potential of the vapor and the incubation period on the size of the condensation nucleus. This proportionality is more fully reflected by formulas (32), (25), (27), and (17).

On the whole, Eqs. (32), (24), and (25) permit the following to be stated without exaggeration. In cases in which the theory combining thermodynamics and kinetics can predict the possibility of heterogeneous phase transformation with a low degree of supersaturation of the parent phase, the same theory can also analytically describe this transformation.

When discussing the kinetics of heterogeneous condensation above, we always had in mind only the first stage of condensation — the stage during which supercritical drops are efficiently formed. The studies [10, 11] provided a general description of how the subsequent stages proceed in relation to the first-stage laws discussed in the present article. The same studies also examined later stages in relation to the external conditions responsible for the formation of a metastable vapor and changes in the concentration of condensation nuclei in this phase over time.

In practice, the radius R_n of a condensation nucleus is a more convenient parameter than ν_n . The radius of the nucleus is connected with ν_n by the obvious relation

$$R_n = (3\nu_n \nu_n / 4\pi)^{1/3} \quad (40)$$

where ν_n is the volume occupied by one molecule in the nucleus or the mean volume per ion in the nucleus (if the substance of the nucleus is an electrolyte).

By virtue of (9), the supersaturation of the vapor $\zeta \equiv \rho\rho$ is connected with the chemical potential b by the equality $\zeta = \exp(b) - 1$. At the low levels of supersaturation of interest to us — when $b \ll 1$ — we have $\zeta \approx b$. This allows us to assume that ζ and b are nearly identical. In this case, the parameter ε in (1) can be regarded as the relative deviation of supersaturation ζ downward from its threshold value ζ_{tr} .

Estimates of Characteristics of Condensation on Soluble Nuclei. To better understand the predictions of the theory developed in [1] and in this article, we will use it to estimate the thermodynamic and kinetic characteristics of heterogeneous condensation.

We put $\nu_n^{1/3} \approx 50$, i.e., $\nu_n \sim 1.2 \cdot 10^5$. This satisfies both limitations (12) and (30) with a large margin of error. We then put $a \sim 10$, $v_l \approx 3 \cdot 10^{-23} \text{ cm}^3$, $v_t \approx 10^4 \text{ cm} \cdot \text{sec}^{-1}$, $\rho \approx 10^{17} \text{ cm}^{-3}$, which is characteristic of condensing substances — especially water. We also put $n_n \approx 10^3 \text{ cm}^{-3}$. For the chosen value of v_l , we will have $\lambda \approx 2 \cdot 10^{-8} \text{ cm}$.

The parameter ε — in accordance with (1) giving the chemical potential of the vapor b or, equivalently, its supersaturation ζ — is left as a free parameter, since it has a relatively large effect on ΔF (according to (31)) and greatly influences $\exp(-\Delta F)$. We recall that ε changes only within the range in which estimate (2) is valid. In addition, we do not fix the value of the parameter α — the condensation coefficient of the vapor molecules — since we know relatively little about it.

We use (14-15) and (40) to obtain $v_0 \sim 1.3 \cdot 10^7$, $R_0 \approx 4.6 \cdot 10^{-6} \text{ cm}$, $R_n \approx 6.7 \cdot 10^{-6} \text{ cm}$, putting $\nu_n \approx v_l$ in the last of the approximate equalities for the sake of simplicity. For the relative concentration ν_n/ν_0 of the solution inside the drop, we have $\nu_n/\nu_0 \approx 9.6 \cdot 10^{-3}$.

In accordance with (32), we find $b_{tr} \approx \zeta_{tr} \approx 1.9 \cdot 10^{-2}$. This shows that heterogeneous condensation is energetically possible with very low degrees of vapor supersaturation.

We can use (31), (27), and (17) to establish $\Delta F \approx 8.2 \cdot 10^5 \varepsilon^{1/2}$, $\Delta\nu_c = \Delta\nu_e \approx 3 \cdot 10^5$, $W_0 \approx 6.6 \cdot 10^{10} \alpha \text{ sec}^{-1}$. For the heterogeneous analog of the Zel'dovich factor in (24) in this case, we have $W_0/\pi\Delta\nu_c\Delta\nu_e \approx 2.4 \cdot 10^{-1} \alpha \text{ sec}^{-1}$.

Finally, in accordance with (24-25), we obtain $j^{(s)} \approx 2.4 \cdot 10^2 \alpha \cdot \exp(-8.2 \cdot 10^5 \varepsilon^{1/2}) \text{ cm}^{-3} \text{ sec}^{-1}$ and $t_s \approx 0.7 \alpha^{-1} \text{ sec}$.

By strengthening inequality (12) without violating inequality (30) (particularly at $\alpha \ll 1$), for $\nu_n^{1/3}$ we can take a value several times greater than the chosen value of 50. Here, as can be seen from (38), there would be a decrease in the threshold value b_{tr} . However, as can be seen from (39), there would also be a sharp increase in the time t_s .

For the condensation of water vapor in a drop $\alpha \sim 10^{-1} - 10^{-2}$ [3]. In the winter atmosphere, usually $\rho + \rho_g \sim (10^{18} - 10^{20}) \text{ cm}^{-3}$. Limitation (30) then even allows $\nu_n^{1/3} \sim 10^2 - 10^3$, i.e., $R_n \sim (2 \cdot 10^{-6} - 2 \cdot 10^{-5}) \text{ cm}$. In this case, we have $b_{tr} \approx \zeta_{tr} \sim 6.6 \cdot 10^{-3} - 2 \cdot 10^{-4}$ and $t_s \sim (10^2 - 10^7) \text{ sec}$. Thus, the supersaturation of water vapor may even be very slight for its effective heterogeneous condensation. An enormous range of incubation periods (embracing five orders) is possible in the large scales of the physics of the winter atmosphere.

We could have examined a diffusional regime of mass exchange between drops and vapor, along with a regime representing a transition from free molecular exchange to diffusional exchange. This would have made it possible (without particular technical complications) to generalize the theory to the region of condensation nuclei large enough so that limitation (30) would be unnecessary. However, although the threshold value b_{tr} of the chemical potential of the vapor would be extremely small given such nucleus dimensions, the incubation period t_s would be so huge that the theory would have almost no practical application.

In this connection, it is appropriate to recall the observation made in [1] that for very large condensation nuclei and a high concentration of passive gas in a vapor-gas medium, thermodynamics itself places a restriction on the smallness of the

threshold chemical potential of the vapor: the latter has a lower bound of $v_l \rho_g$. At $v_l \cong 3 \cdot 10^{-23} \text{ cm}^3$, $\rho_g \sim 10^{19} \text{ cm}^{-3}$, we have $v_l \rho_g \sim 10^{-4}$. If $v_l^{1/3} \geq 10^3$, then the quantity $v_l \rho_g$ (which is independent of ν_n) also influences the threshold value of the chemical potential and supersaturation of the vapor. Here, the level of supersaturation will generally be as low as is permitted by thermodynamics.

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