THERMODYNAMICS OF CONDENSATION ON SOLUBLE
NUCLEI OF SURFACE-INACTIVE SUBSTANCES

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Substantiation is provided for the possibility of barrier-less nucleation of a drop in supersaturated vapor on nuclei of surface-inactive substances soluble in the drop. For the conditions of practical interests — when heterogeneous phase transformation occurs with low levels of supersaturation of the vapor — a determination is made of all of the thermodynamic characteristics of heterogeneous nucleation that are needed for kinetics and are manifest in experiments: the threshold chemical potential of the vapor at which barrier-less heterogeneous nucleation becomes possible; the position and half-width of the potential well and potential hill of the work of heterogeneous drop formation; the activation energy for heterogeneous condensation, determined by the gradient of the heights of the potential hill and potential well of the work of drop formation.

Realization of the homogeneous mechanism of phase transformation requires levels of supersaturation of the metastable phase high enough so that such transformations actually rarely occur. More likely is the heterogeneous mechanism of phase transformation, whereby foreign particles that are almost always present in the metastable phase (albeit in small amounts) serve as nucleation centers for the stable phase. Common examples of such particles are the salt granules and drops of acid present (abundant, even) in the winter atmosphere. Such grains and drops are typically highly soluble in condensing moisture.

The present article examines the thermodynamics of nucleation of drops of stable liquid in vapor supersaturated with this liquid. Here, nucleation takes place on nuclei that are soluble in the drop but essentially not adsorbed on its surface. The key to the study will be the fact, established below, that the main role in heterogeneous condensation occurring with a low level of vapor supersaturation is played by drops in which the number of molecules of the condensing substance is many times greater than the number of molecules or ions of the substance present in the vapor from the condensation nuclei. Thus, the drops consist of weak solutions of the substances but have a much higher concentration of the condensate. Not only do these circumstances greatly simplify the entire investigation, they also make it unnecessary to assume that the nucleus is completely soluble in the drop.

Although the substance which is present in the solution inside the drop from the nucleus is relatively small, it nonetheless reduces the chemical potential of the condensate — the substance condensing into the drop from the vapor. It is for this reason that heterogeneous condensation is energetically possible before homogeneous condensation. It is also the reason that the activation energy in heterogeneous condensation may completely vanish.

The quantity which is of decisive importance for predicting whether or not heterogeneous phase transformation is energetically possible with a low level of vapor supersaturation is the predicted (by thermodynamics) threshold chemical potential of the vapor. Beginning with this potential, heterogeneous nucleation occurs without the overcoming of an activation barrier (it occurs in the absence of an activation energy).

However, the kinetics of the phase transformation is still important in practical terms. A metastable vapor is not usually formed instantaneously under natural or artificial conditions (even in laboratory experiments, such as in a Wilson chamber or a diffusion chamber). However, as was shown in [1, 2], effective heterogeneous formation of supercritical (viable) drops which can continue to grow unrestrainedly ends long before the moment at which the chemical potential of the vapor

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would reach its threshold value in the absence of vapor absorption by the drops. This in turn means that, in practice, heterogeneous phase transformation occurs by a barrier-less method. Gradual (controlled over time) creation of metastability in the parent phase in which heterogeneous phase transformation occurs by the barrier method is useful in engineering applications because it allows control of the development of the phase transition over time.

It should be noted especially that in a lab experiment which permits instantaneous creation of any initial value of vapor supersaturation, the level of supersaturation may turn out to be in the "prethreshold" region. In this region, activation energy is already substantial but is still not great enough to realize heterogeneous phase transformation. It is in this region of vapor metastability that the greatest amount of information can be obtained on the inverse problem — determination of the molecular properties of the condensing substance from data obtained in a laboratory experiment.

Kinetic description of the process by which drops overcome an activation barrier requires that thermodynamics provide knowledge not only of the threshold chemical potential of the vapor, but also specific information on the work of heterogeneous drop formation: the position and half-widths of the potential well and potential hill of the work; the activation energy, determined by the gradient of the heights of the potential hill and potential well. All of this information is obtained in the present article for the prethreshold region of vapor metastability.

The next article will deal specifically with description of the kinetics of condensation on soluble nuclei. It will show that the activation energy in heterogeneous condensation is equal to the gradient of the heights of the potential hill and potential well of the drop-formation work, rather than simply the height of the potential hill of the work for a critical drop (as it is in homogeneous condensation).

Later articles will study the complex effect of adsorption on heterogeneous condensation, as well as the formation of micelles by a condensation-nucleus substance which is soluble in the drops.

For now, we will discuss results obtained earlier in regard to the thermodynamics of nucleation on soluble nuclei.

Keller [3] was the first to discover the existence of a threshold for barrier-less nucleation on soluble nuclei of surface-inactive substances. This threshold corresponds to the maximum on the curve describing the dependence of the chemical potential of the condensing substance on drop size. The same study also established the following rule: The greater the radius of the soluble nucleus, the lower the possible maximum value of supersaturation of the vapor. Keller's thermodynamic analysis was subsequently generalized to the case of the dissociation of the substance of a nucleus dissolved in a drop [4, 5], while the rule formulated by Keller was experimentally substantiated in [6].

Apart from the threshold value of the chemical potential of the vapor, there has been no investigation of the thermodynamic characteristics of condensation on soluble nuclei which are necessary for an understanding of the kinetics of the process (and which are seen experimentally).

Chemical Potential of the Condensate. We will examine a drop located in vapor and consisting of a solution of the substance of a nucleus in a condensate. We will use ν to denote the number of condensate molecules in the drop. We will use ν_n to represent the total number of molecules of the nucleus dissolved in the drop or the total number of ions of this substance (if it is an electrolyte and dissociates during dissolution). We assume that the substance (if it is an electrolyte) dissociates completely. Accordingly, the quantity ν_n will always be an external parameter of the problem.

When we represent the drop as a two-component solution, we are assuming that the condensation nucleus is completely soluble in the drop. Here, the nucleus may initially be in the solid or liquid state. In the case of a nucleus composed of a surface-inactive substance, nearly all of this substance dissolves inside the drop.

We assume that the temperature of the drop is the same as the temperature T of the vapor surrounding it. The assumption that the drop is thermalized is justified by the fact that a large (compared to the vapor) amount of passive gas with little capability of exchanging molecules with the drop is almost always present outside the drop. The drop is in mechanical equilibrium with the vapor and the passive gas: Pressure in the drop is composed of the external pressure of the vapor and the passive gas and capillary pressure.

We will use R to denote the radius of the drop and b_ν to represent the chemical potential of the condensate inside the drop. We express the chemical potential b_ν in thermal energy units kT, where k is the Boltzmann constant. Chemical potential is reckoned from the value corresponding to equilibrium of the condensate with the vapor when their contact surface is planer.

As will be shown below, the following inequality is observed throughout the region of ν that is important for the theory
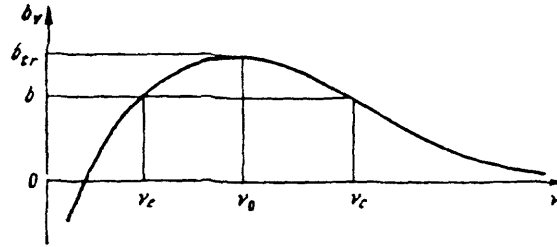
$$\nu/\nu_n \gg 1 \tag{1}$$

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Fig. 1. Dependence of the chemical potential b_ν of the condensate in a drop on the number of molecules ν of the condensate.

Here, relative to the component which is present from the nucleus, the solution in the drop will be weak: The relative concentration of the given component will be equal to the small quantity ν_n/ν. Thus, the above-assumed dissociation in the solution of the substance of the nucleus turns out to be typical (if it is an electrolyte).

In this case, we have

$$R = (3\, \upsilon_l \nu/4\, \pi)^{1/3} \equiv \lambda \nu^{1/3} \tag{2}$$

where υ_l is the molecular volume of the condensing liquid; λ is a linear parameter (the radius of an equivalent molecular sphere).

We will use the familiar formula from the theory of weak solutions for the chemical potential of the component whose concentration in the solution is high (this formula is also valid when the solution is ionic). Accounting for capillary pressure in the drop (which is in mechanical equilibrium with the vapor and the passive gas) and considering that this pressure is almost always many times greater than the pressure of the vapor and the passive gas when we make allowance for the low compressibility of the liquid we obtain

$$b_\nu = -\nu_n \nu^{-1} + (2/3) a \nu^{-1/3} \tag{3}$$

where

$$a = 4\, \pi\, \lambda^2 \sigma/kT \tag{4}$$

and σ is the surface tension of the drop. Since the substance of the nucleus is not surface active, expression (1) means that σ will almost always coincide with the surface tension of the pure condensing liquid. The quantity a can be regarded as dimensionless molecular surface tension (the analog of the Etvesh molar surface tension).

Having chosen ν as the variable to describe the drop, we will study the dependence of b_ν on ν. We will use the subscript 0 to denote values of quantities at the value ν_0 of the variable ν for which the following is valid

$$(\partial b_\nu/\partial \nu)_0 = 0 \tag{5}$$

Using (3), we obtain

$$\nu_0 = (9\, \nu_n/2\, a)^3 \tag{6}$$

$$(b_\nu)_0 = 4\, a/9\, \nu_0^{1/3} \tag{7}$$

$$(\partial^2 b_\nu/\partial\, \nu^2)_0 = -4\, a/27\, \nu_0^{7/3}, \quad (\partial^3 b_\nu/\partial\, \nu^3)_0 = 52\, a/81\, \nu_0^{10/3} \tag{8}$$

In accordance with (5) and (8), the chemical potential of the condensate b_ν reaches its maximum $(b_\nu)_0$ at the point $\nu = \nu_0$. Thus, the subscript 0 characterizes values of quantities at the maximum of the chemical potential of the condensate. The existence of this maximum is due to the fact that a decrease in ν is accompanied by a decrease in the chemical potential of the condensate of the substance which is formed in the solution inside the drop from the condensation nucleus.

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Figure 1 shows the dependence of b_v on v. The fact that this dependence decreases monotonically with a decrease in v in the region in which (1) is not observed and chemical potential b_v is analytically unknown is a thermodynamic consequence of the stability of the solution. Thus, the maximum of b_v at $v = v_0$ is unique. The fact that b_v approaches $-\infty$ at $v \to 0$ can be explained as follows. When $v \to 0$, i.e., when the situation which is the opposite of (1) exists, the solution inside the drop again becomes weak (and can be described analytically). However, it becomes weak only in relation to the component which comes from the vapor. In accordance with the thermodynamics of solutions, the main contribution to b_v is made by the term $\ln(v/v_n)$. This term also approaches $-\infty$ at $v \to 0$.

The equality

$$b_{tr} = \max b_v = (b_v)_0 \tag{9}$$

obviously determines the threshold value b_{tr} of the chemical potential of the vapor b expressed (as b_v) in thermal energy units kT. This potential is reckoned from the value corresponding to equilibrium of the vapor with the condensing liquid when their contact surface is planer. If $b \geq b_{tr}$, then the drop is nucleated on the condensation nucleus in the vapor without a barrier.

We can use (7) and (9) to obtain

$$b_{tr} = 4 a^{/9} v_0^{1/3} \tag{10}$$

while (6) also yields

$$b_{tr} = 2(2a)^{1/2} / 27 v_n^{1/2} \tag{11}$$

which expresses b_{tr} directly in terms of the number of molecules or ions of the condensation nucleus. Equation (11) is the Keller formula [5].

Expanding b_v into a Taylor series in the neighborhood of the point $v = v_0$ and using (5) and (7)-(8), we obtain

$$b_v = \frac{4}{9} a v_0^{1/3} - \frac{2}{27} a v_0^{-1} (v - v_0)^2 \tag{12}$$

The following is the condition of smallness of the discarded term with the third derivative of b_v with respect to v at the point $v = v_0$ relative to the retained term with the second derivative of b_v with respect to v at this point

$$13|v - v_0|/9 v_0 \ll 1 \tag{13}$$

this condition also defining the region in which approximation (12) is valid.

Equilibrium and Critical Drops. We will use the subscripts e and c to characterize quantities pertaining to the equilibrium and critical drops. These drops are in stable and unstable chemical equilibrium with the vapor, respectively.

We have

$$(b_v)_e = b, \quad (b_v)_c = b \tag{14}$$

$$(\partial b_v/\partial v)_e > 0, \quad (\partial b_v/\partial v)_c < 0 \tag{15}$$

(see Fig. 1).

In the subthreshold region $0 < b < b_{tr}$, the vapor is metastable and equilibrium and critical drops exist. When $b = b_{tr}$, these drops coincide. Above the subthreshold region, i.e., at $b > b_{tr}$, equilibrium and critical drops are generally absent. Below the subthreshold region, i.e., at $b < 0$, only equilibrium drops exist.

Since barrier-less drop nucleation occurs in the vapor at $b \geq b_{tr}$, all of the thermodynamic information important for kinetics at $b \geq b_{tr}$ is given by the value b_{tr} obtained from Eq. (10) (or (11)). Accordingly, we will subsequently be interested in the important (for kinetics) subthreshold region of vapor metastability $0 < b < b_{tr}$.

We write the chemical potential of the vapor b in the form

$$b = b_{tr}(1 - \epsilon) \tag{16}$$

where c is its relative deviation from the value b_{tr}. A program we are developing will find all of the thermodynamic characteristics needed for the kinetics of heterogeneous nucleation (and manifest in experiments) as functions of c in the subthreshold region, where $0 < c < 1$.

Using (12) and (14) and considering (10) and (16), we obtain

$$\nu_e = \nu_0 [1 - (6\epsilon)^{1/2}], \quad \nu_c = \nu_0 [1 + (6\epsilon)^{1/2}] \tag{17}$$

As is clear from (17), observance of condition (13) at $\nu = \nu_e$ and $\nu = \nu_c$ implies that

$$(13'9) \quad (6\epsilon)^{1/2} \ll 1 \tag{18}$$

In accordance with (2), we have the following in the region in which condition (13) is valid:

$$(R - R_0)/R_0 = (\nu - \nu_0)/3\nu_0 \tag{19}$$

where

$$R_0 = \lambda \nu_0^{1/3} \tag{20}$$

It follows from (17) and (19) that

$$R_e = R_0 [1 - (2\epsilon/3)^{1/2}], \quad R_c = R_0 [1 + (2\epsilon/3)^{1/2}] \tag{21}$$

Work of Drop Formation. We will use F, in energy units kT, to express the work of heterogeneous formation of a drop in vapor on a condensation nucleus. When thermal and mechanical equilibrium exist between the drop and the vapor and passive gas, we have the differential relation [7]:

$$\partial F/\partial \nu = b_\nu - b \tag{22}$$

which accounts for the fact that the number of molecules or ions of the substance formed from the nucleus remains unchanged inside the drop (here, it is also assumed that the drop is not capable of exchanging molecules with the passive gas).

Equation (22) will be used as the basis for the remainder of our investigation. This relation is valid for any value of vapor chemical potential b (both positive and negative). Equation (22) is simple because of its differential form and the use of ν as the variable to describe the drop. The differential form of (22) — in which the work F is determined only to within the constant term — not only turns out to be sufficient, but also makes it easier to obtain all of the important (for the kinetics of heterogeneous nucleation) information on nucleation work. All of the calculations would be considerably more difficult if we used the finite-difference expression for work.

Using (22) as our basis and in succession allowing for (14), (15), and (5), we obtain

$$(\partial F/\partial \nu)_e = 0, \quad (\partial F/\partial \nu)_c = 0 \tag{23}$$
$$(\partial^2 F/\partial \nu^2)_e > 0, \quad (\partial^2 F/\partial \nu^2)_c < 0 \tag{24}$$
$$(\partial^2 F/\partial \nu^2)_0 = 0 \tag{25}$$

Thus, at the points $\nu = \nu_e$, $\nu = \nu_c$, and $\nu = \nu_0$, the work has a minimum, maximum, and point of inflection, respectively, as a function of ν.

Figure 2 shows the dependence of F on ν as follows from (22) and Fig. 1 (and is consistent with (23)-(25). We considered the fact that $F|_{\nu=0} = 0$: The condensation nucleus is initially present in the vapor, so that no work is required for its formation. As a result, $F_e < 0$. In accordance with (17), an increase in c (a decrease in supersaturation) is accompanied by further separation of the points $\nu = \nu_e$ and $\nu = \nu_c$ to the left and right of the point $\nu = \nu_0$ (which is independent of c). Here, the minimum F_e and maximum F_c of the work F increase. From this moment on, the inequality $F_c < 0$ is invalid (it was assumed valid in Fig. 2). The inequality $F_e < 0$ is always valid
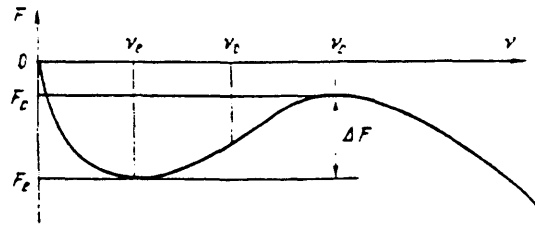
Fig. 2. Dependence of the work of drop formation F on the number of condensate molecules ν.

With allowance for (10) and (16), we find from (12) and (22) that

$$\frac{\partial F}{\partial \nu} = \frac{4a}{9\nu_c} \left[\epsilon - \frac{1}{6\nu_c^2}(\nu - \nu_0)^2 \right]$$ (26)

throughout the region in which (13) is satisfied. The interval $\nu_e \lesssim \nu \lesssim \nu_c$ falls within this region when restriction (18) is satisfied.

A quantity which is important in kinetics is the activation energy

$$\Delta F = F_c - F_e$$ (27)

— the gradient of the heights of the potential hill and potential well of the work F (see Fig. 2). Integrating Eq. (26) over ν from ν_e to ν_c and allowing for (17) and (6), we obtain

$$\Delta F = (16 \, \omega^3) \nu_n \epsilon^{3/2}$$ (28)

Taking into account (23)-(24), we have the approximations

$$F \approx F_e + |(\nu - \nu_e) \Delta \nu_e|^2 \quad (\nu - \nu_e \lesssim \Delta \nu_e)$$ (29)

$$F = F_c - |(\nu - \nu_c) \Delta \nu_c|^2 \quad (\nu - \nu_c \lesssim \Delta \nu_c)$$ (30)

where

$$\Delta \nu_e = |2 (\partial^2 F/\partial \nu^2)_e|^{1/2}, \quad \Delta \nu_c = |2 (\partial^2 F/\partial \nu^2)_c|^{1/2}$$ (31)

The quantities $\Delta \nu_e$ and $\Delta \nu_c$ determine the "half-widths" of the potential well and potential hill of F. We will use the term "near-equilibrium" and "near-critical" in describing drops for which the variable ν lies within the neighborhoods $| \nu - \nu_e | \lesssim \Delta \nu_e$ and $| \nu - \nu_c | \lesssim \Delta \nu_c$ of the points $\nu = \nu_e$ and $\nu = \nu_c$.

As is clear from (26), the below inequalities serve as the condition of smallness of the discarded (in (29) and (30)) terms with the third derivative of F with respect to ν at $\nu = \nu_e$ and $\nu = \nu_c$ relative to the retained (in the same equations) terms with the second derivative of F with respect to ν at the same two points

$$\Delta \nu_e \cdot 3 (\nu_0 - \nu_e) \ll 1, \quad \Delta \nu_c \cdot 3 (\nu_c - \nu_0) \ll 1$$ (32)

These inequalities also express the condition that heterogeneous phase transformation occurs by the barrier method (they express complete manifestation of the potential well and potential hill of the work F). Inequalities (32) and the validity of Eq. (26) itself at $\nu_e - \Delta \nu_e \lesssim \nu \lesssim \nu_c + \Delta \nu_c$ (rather than just at $\nu_e \lesssim \nu \lesssim \nu_c$) will be substantiated in the next section.

Using (26) and (31) with allowance for (6) and (17), we obtain

$$\Delta \nu_e = \Delta \nu_c = 2^{7/6}(3/2)^{1/2} (2a)^{-1} \nu_n \epsilon^{-1/4}$$ (33)

$$\Delta \nu_e (\nu_0 - \nu_e) = \Delta \nu_c (\nu_c - \nu_0) = 2/(3 \Delta F)^{1/2}$$ (34)

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Prethreshold Region of Vapor Metastability. As will be shown in the next article, the rate of heterogeneous nucleation of supercritical drops which subsequently grow without restraint depends on ΔF as $\exp(-\Delta F)$. Regardless of the concentration of condensation nuclei in the vapor, we will be interested only in the part of the pre-threshold region of vapor metastability in which

$$3 \lesssim \Delta F \lesssim 30 \tag{35}$$

In fact, to the right of this region, i.e., at $\Delta F \gtrsim 30$, the exponent $\exp(-\Delta F)$ is so small that heterogeneous nucleation almost never occurs. To the left of this region, i.e., at $\Delta F \lesssim 3$, inequality (32) is violated (as is clear from (34)) and the exponent $\exp(-\Delta F)$ is already quite substantial. Heterogeneous nucleation then takes place almost without a barrier, which simplifies the kinetics of heterogeneous phase transformation to the extent that only the value of b_{tr} given by (10) (or (11)) is needed out of all of the thermodynamic information obtained above (the same was true of the region $b \geq b_{tr}$).

In accordance with (28) and (35), we have

$$\epsilon^{1/2} \sim \nu_n^{-1/3} \tag{36}$$

where we have taken into account that the range of $(\Delta F)^{1/3}$ is considerably narrower than the range of ΔF. Accordingly, we have put $(6^{1/2}\Delta F/16)^{1/3} \sim 1$.

As has already been noted, the heterogeneous mechanism of phase transformation merits special study in that it opens up the possibility of phase transformation at a low level of supersaturation of the parent phase. Focusing on this possibility and noting, in accordance with (11), that it arises when the condensation nuclei are sufficiently large, we will henceforth assume that

$$\nu_n^{1/3} \gg 1 \tag{37}$$

We will refer to the region of metastable vapor in which (35) is observed and, thus, in which $\epsilon^{1/2}$ satisfies (36), as the "prethreshold" region. By virtue of (36) and (37), the following is valid in this region

$$\epsilon^{1/2} \ll 1 \tag{38}$$

It can be seen from (36)-(38) that the prethreshold region occupies only a very narrow zone within the subthreshold region $0 < \epsilon < 1$. The width of this zone is on the order of the distance of the zone from the upper boundary of the subthreshold region. The prethreshold region will be the focus of our next investigation.

We will show that in this region — specifically, under condition (37) — all of the assumptions used above in the analytical theory are still valid.

It follows from (38) that restriction (18) must be observed. Further, a requirement that inequalities (32) be observed follows from (34)-(35). Then, it is clear from (17) and (38) that the inequalities $\Delta\nu_e/\nu_e \ll 1$, $\Delta\nu_c/\nu_c \ll 1$, are satisfied with larger domain than inequalities (32). This justifies use of (26) not only at $\nu_e \lesssim \nu \lesssim \nu_c$, but also at $\nu_e - \Delta\nu_e \lesssim \nu \lesssim \nu_c + \Delta\nu_c$. Thus, the near-equilibrium and near-critical neighborhoods $|\nu-\nu_e| \lesssim \Delta\nu_e$ and $|\nu-\nu_c| \lesssim \Delta\nu_c$ of the points $\nu = \nu_e$ and $\nu = \nu_c$ do not overlap but do lie near the point $\nu = \nu_0$.

The foregoing, when considered together with (6) and (37), shows that inequality (1) is observed with a large margin of error throughout the region of ν that is of importance for the theory $\nu_e - \Delta\nu_e \lesssim \nu \lesssim \nu_c + \Delta\nu_c$

Taking this into account, after (36) we see that extraction of the square root from the latter yields not just an estimate, but the approximate equality $\epsilon^{1/4} = \nu_n^{-1/6}$ (we ignore the factor $(6^{1/2}\Delta F/16)^{1/6}$ in the right side of this expression, since it is nearly equal to unity by virtue of (35)). It follows from (33) and $\epsilon^{1/6} = \nu_n^{-1/4}$ that

$$\Delta\nu_e = \Delta\nu_c \simeq 27(3/2)^{1/4}(2a)^{-1/2}\nu_n^{3/4} \tag{39}$$

in which c is generally omitted.

In accordance with (37) and (39), we have

In particular, the value of inequalities (40) lies in the fact that they permit [8] a continuum treatment of the variable ν (which is in essence discrete) within the limits of the potential well and potential hill of the work F.

Discussion of the Thermodynamic Laws of Heterogeneous Condensation. In accordance with (3), the chemical potential b_ν of the condensate in a drop formed on a condensation nucleus that is fully soluble in it has two components. The first, always negative, accounts for the effect of the substance of the condensation nucleus on the drop. The second component, always positive, describes the effect of capillary pressure on the drop. This component increases relatively slowly with a decrease in ν. The second component is dominant for sufficiently large values of the variable ν, while the first component is more important for relatively small values of this variable. The competition between these two contributions to condensate chemical potential also explains the existence of the maximum of potential b_ν in a heterogeneously formed drop.

In accordance with (22) and the condition F $|_{\nu=0} = 0$, the greater the chemical potential of the vapor b, the lower the work F of heterogeneous drop formation for each value of ν.

If $b \geq b_{tr}$ (with b_{tr} being equal to the maximum for b_ν), then, by virtue of (22) and the condition F $|_{\nu=0} = 0$, F decreases monotonically with an increase in ν throughout the physical region $\nu > 0$ from 0 at the point $\nu = 0$. This shows that heterogeneous phase transformation definitely occurs without a barrier at $b \geq b_{tr}$ as well (this result is unaffected by the fact that the derivative $\partial F / \partial \nu$ vanishes at the individual point $\nu = \nu_0$ of the maximum of b_ν when $b = b_{tr}$).

Thermodynamic relation (22) and the condition F $|_{\nu=0} = 0$ of course also remain valid in the case of homogeneous drop formation. However, in this case the chemical potential of the condensate b_ν (which coincides with the chemical potential of the drop) is on the whole determined only by the contribution which describes the effect of capillary pressure on the drop.

Using a superimposed tilde to denote quantities for the homogeneous case, we see that the inequalities F $|_{\nu=0} = 0$ are valid for any value of the variable ν describing the drop. The second of these inequalities is invariant to the value of vapor chemical potential b, although it is negative (b_ν and $\tilde{b}_\nu$ are independent of b). The inequality $b_\nu < \tilde{b}_\nu$ is weakened with an increase in ν. It becomes very weak at $\nu \gtrsim \nu_0$ and for practical purposes is transformed into the approximate equality $b_\nu = \tilde{b}_\nu$. The latter is more accurate, the greater ν is compared to ν_0. Here, the difference F $-$ F is always negative, becomes nearly independent of ν, and reaches its limiting value. This value, unimportant in practice, was linked in [9] with the hoped-for energy benefit from heterogeneous phase transformation compared to the homogeneous mechanism.

The fact that the maximum of b_ν turns out to be very small for sufficiently large condensation nuclei also explains why the heterogeneous condensation process can take place in the region of very low degrees of vapor supersaturation.

The fact that the chemical potential of the stable-phase nuclei has a component which has a sign opposite that of the contribution from capillary pressure and which increases relatively rapidly in absolute value with a decrease in nucleus size is also an important characteristic of heterogeneous phase transformation and its energy advantage over homogeneous phase transformation.

Here, the work done in creating the metastable phase of the nucleus in the course of heterogeneous nucleation of the stable phase is unimportant. In fact, having been ignored in the above study, this quantity is relevant only to whether or not nuclei can exist in the metastable phase. If such nuclei do exist for one or more reasons — a question which is the starting point in the analysis of heterogeneous phase transformation in the volume of the metastable phase (as opposed to its external boundaries) — then the entire subsequent development of heterogeneous phase transformation will be completely determined by the work that must be done, during the formation of a nucleus of the stable phase, to attach molecules of the metastable phase to a nucleus already present in it. In sum, the total amount of work done should be reckoned beginning with the work done in creating a nucleus of the stable phase (which is consistent with the condition F $|_{\nu=0} = 0$ cited above). The stipulation that the heterogeneous phase transformation occur in the volume of the metastable phase precludes consideration of the "boundary" mechanism of this transformation [4] on the external boundaries of the metastable phase. The latter mechanism does not play any significant role under artificial conditions, when the volume of the metastable phase is large and, even more so, under natural conditions in the winter atmosphere.

The studies [10, 11] examined the contribution to the chemical potential of the stable-phase nucleus which is opposite in sign to the contribution from capillary pressure and which increases relatively rapidly in absolute value with a decrease in the size of the nucleus. This contribution was examined in a problem concerning heterogeneous condensation on nuclei that were not soluble in the drops of stable liquid being formed. That problem differs qualitatively from the problem examined in the present article, where the condensation nuclei are conversely assumed to be fully soluble in the drops. As was explained

in [10, 11], the "countercontribution" opposing the contribution of capillary pressure to the chemical potential of the drops is due to the disjoining pressure of the liquid film of the drop between the vapor and the insoluble (in the liquid) condensation nucleus. This countercontribution has also been shown [10, 11] to be responsible for the existence of the maximum of the chemical potential of the drop and, together with this, for the possibility of heterogeneous condensation with low degrees of vapor supersaturation. Here, the degree of supersaturation may be lower, the larger the condensation nucleus.

The laws of heterogeneous phase transformation discovered in [10, 11] and in our study show that the essence of this process can be understood by determining the above-mentioned countercontribution to the chemical potential of a heterogeneously formed stable-phase nucleus. If this contribution is found, then a thermodynamic and kinetic theory of heterogeneous phase transformation can be constructed by the method developed here. Such an undertaking is outside the scope of the present problem, concerning heterogeneous condensation on nuclei fully soluble in the drops of condensate.

Throughout the above thermodynamic theory of condensation on soluble nuclei (and in earlier studies [3-5] of this subject) the pressure of the vapor−gas medium on the drop was ignored compared to capillary pressure in the drop. Nevertheless, in the case of large drops and a high concentration of passive gas in the medium, the capillary pressure may be comparable to — or even less than — the ambient pressure that was not accounted for in Eq. (3). Taking this pressure into account, we obtain the additional contribution $v_l (\rho_g + \rho - \rho_\infty)$ to the chemical potential of the condensate b_ν, where ρ_g, ρ, and ρ_∞ are the density of the number of molecules of passive gas, vapor, and saturated vapor above the plane surface. Due to its independence relative to ν, we obtain the same contribution to the threshold value b_{tr} of the chemical potential of the vapor. As a result, b_{tr} increases by the amount $v_l \rho_g$. Here, we have taken into account that $\rho_g \gg \rho - \rho_\infty$ when there is a high concentration of passive gas in the medium. In this case, the value of $v_l \rho_g$ will be limited to the threshold value of vapor chemical potential. If inequality (37) is so strong that the quantity in the right side of (11) is much less than $v_l \rho_g$, then $v_l \rho_g$ (independent of ν_n) will also determine the threshold value b_{tr} of vapor chemical potential. It will be the lowest value allowed by thermodynamics.

We should also note that many researchers who have examined heterogeneous condensation on soluble nuclei in the winter atmosphere [12-14] have been interested in describing the growth of drops with high concentrations of the dissolved substance of the nucleus. It was shown in our study that when the condensation nuclei are macroscopic and when there is a monotonic decrease in the concentration of the dissolved substance of the nucleus with an increase in the number of condensate molecules, drops with a high concentration of the nucleus substance turn out to be subcritical for low levels of supersaturation of the vapor and thus play no role in the thermodynamics of heterogeneous phase transformation taking place by the barrier method. This is the situation that prevails for liquid condensation nuclei.

If the nucleus is solid and if, in the course of its dissolution, equilibrium can be established between the solid residue of the nucleus and the substance of the nucleus in solution inside the growing drop, then the concentration of dissolved nucleus material will increase with a decrease in the size of the nucleus as it undergoes dissolution. This might in turn lead to the appearance of an additional maximum on the curve describing the dependence of the chemical potential of the condensate on the number of condensate molecules. This maximum would be located to the left of the maximum examined in the present article and would correspond to a drop with a higher concentration of dissolved nucleus material. The threshold chemical potential of the vapor would then determine the larger of the maxima. The very existence of such an additional maximum and the role it might play in the thermodynamics of condensation on soluble nuclei have not been discussed previously. A quantitative description of this maximum cannot be given without specific representations on the enveloping of the soluble solid nucleus by the liquid condensing on it. Such a description is a separate problem and concerns condensation on solid nuclei that are not fully soluble.

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