

Thermodynamic Principles of Condensation Kinetics on the Soluble Nuclei of a Surfactant

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Abstract – Strict relationships have been established between the experimentally measurable thermodynamic parameters that are necessary in order to describe the effects of the condensation kinetics of a supersaturated vapor on the soluble nuclei of a surfactant. These expressions are not restricted to a particular form of adsorption isotherm for the matter comprising a nucleus on the surface of a nucleating droplet. Using the relationships obtained, an algorithm is formulated for the calculation of the thermodynamic characteristics of the condensation kinetics as functions of the external parameters involved in the condensation problem. This algorithm is employed for the construction of asymptotic thermodynamic characteristics in two limiting cases: (i) very low coverage of the surface of a droplet by adsorbed matter comprising nuclei and (ii) virtually complete adsorption of all the matter comprising the nuclei on the surface of a droplet. It is shown that both limiting cases can be encountered in practice.

INTRODUCTION

The kinetic theory serves as a final link between theoretical and experimental investigations of phase transformations. Naturally, the development of the kinetic theory is based on data provided by the thermodynamic theory of phase transformation.

A characteristic feature of the heterogeneous nucleation of droplets from a supersaturated vapor on the condensation nuclei (which can be either soluble or insoluble in the droplets) is the presence of a maximum on the curve of the chemical potential of the condensate (i.e., of the substance formed from the vapor) versus the droplet size [1, 2]. This maximum determines the threshold value of the chemical potential of the vapor and, hence, the threshold value for supersaturation of the vapor. Above this value, the work of the droplet formation on the nucleus monotonically decreases with increasing droplet size and, therefore, the vapor condenses on the nuclei without surmounting the activation barrier. Below the threshold value of the chemical potential of vapor, the work of the droplet formation does not monotonically decrease with an increase in the droplet size, but rather exhibits a potential minimum and a potential maximum. In this case, the condensation of vapor on the nuclei requires an activation energy determined by the potential drop between the maximum and the minimum, which is essentially the work of the droplet formation on the nucleus. For the macroscopic dimensions of the condensation nuclei (which are of practical significance and will be dealt with further), the activation energy grows rapidly as the chemical potential of vapor decreases below the threshold value.

This circumstance allows us to establish [1, 3] an extremely narrow subthreshold range of values of the

chemical potential of the vapor (lying slightly below the threshold) in which the activation barrier for condensation is significant, yet can be surmounted. In this range, the barrier mechanism of heterogeneous condensation is of real importance, and (as was shown in [1, 3]) the kinetic theory of heterogeneous condensation is of principal interest.

This theory was developed earlier in a general form [3], independent of the magnitude (and sign) of the effect of adsorption of the matter comprising a nucleus on the droplet surface. Within the framework of this theory, the thermodynamics must provide, in addition to the threshold chemical potential of the vapor, data on the work of heterogeneous droplet formation, that is, on the position and halfwidth of the potential minimum and maximum, and the activation energy (i.e., the potential drop between maximum and minimum).

The present work is devoted to establishing the key thermodynamic characteristics of the condensation kinetics in the complicated case of surfactant nuclei soluble in the droplets. Once these characteristics are known, one may readily determine all the other experimentally measurable thermodynamic parameters that are necessary for the description of the condensation kinetics of a supersaturated vapor in the subthreshold range of the chemical potential of the vapor.

The investigation will not be restricted to a particular form of adsorption isotherm of the matter comprising a nucleus on the surface of a droplet. Nor will we consider a particular form of the two-dimensional equation of the state of the adlayer of this substance on the droplet surface, which is related to the isotherm by the Gibbs adsorption equation. The approach used in this work is based on the concepts formulated in [4].

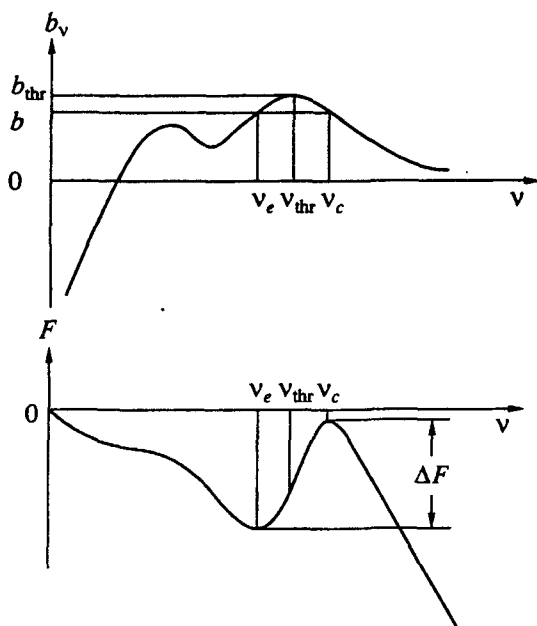
In the case of surface-inactive substances, a similar exhaustive (i.e., complete from the standpoint of the condensation kinetics) treatment was made in [1]. As for the surface-active nuclei, earlier [5 - 7] thermodynamic results referred to a single, albeit principal, thermodynamic characteristic of the condensation kinetics, i.e., the threshold value of the chemical potential of vapor. Earlier results were additionally restricted by assuming a constant value of adsorption [6], or the applicability of the Langmuir adsorption isotherm [7].

SUBTHRESHOLD REGION OF VAPOR METASTABILITY

It was shown earlier [6 - 9] that the chemical potential of condensate in a droplet, as a function of the size of that droplet that nucleates on the soluble nucleus of the surfactant, may exhibit several maxima rather than a single one. The nature of these maxima is related to the properties of the surfactant monolayer on the droplet surface, the micelle formation in the bulk of the droplet, or the effect of the surface forces of the nucleus when it is incompletely dissolved in the droplet. The threshold value of the chemical potential of vapor is determined by the greatest maximum.

In this work, consideration is restricted to the case when the greatest maximum falls within the range of a completely dissolved nucleus, which leads to the formation of molecular (rather than micellar) surfactant solution inside the droplet. Note that even in this case the chemical potential of condensate may exhibit more than one maximum.

In the following, b_v will denote the chemical potential of condensate in the droplet (considered as a function of the number v of condensate molecules), and b ,



Chemical potential of condensate b_v and the work of droplet formation F versus the number of condensate molecules v .

the chemical potential of vapor. The chemical potentials b_v and b are expressed in thermal energy units kT (where k is the Boltzmann constant and T is the temperature of vapor and droplet) and are measured from a level corresponding to the equilibrium between the vapor and the condensed liquid, provided that a flat contact surface is present.

The threshold value b_{thr} of the chemical potential of vapor b is

$$b_{thr} = \max(b_v)_0, \quad (1)$$

where the subscript 0 indicates the extrema of the chemical potential of condensate, and the symbol max indicates the greatest extremum (naturally, the maximum). In the following, the quantities referring to the greatest extremum are indicated by the subscript thr. The inclusion of minima as well as maxima in the class of extrema allows the thermodynamic pattern of heterogeneous condensation to be described completely.

We will consider, as in [1, 3], only an extremely narrow range of the chemical potential of vapor (lying slightly below the b_{thr} level):

$$b = b_{thr}(1 - \epsilon), \quad (2)$$

where $\epsilon > 0$ and $\epsilon \ll 1$. For simplicity, we assume that this domain (called the subthreshold region of vapor metastability) lies above all the other extrema (except b_{thr}) of the chemical potential of condensate b_v . In cases where ϵ is sufficiently small, this assumption is not rigid.

According to the general thermodynamic relationship [10], for the work F of droplet formation (expressed, like b_v and b , in thermal units kT),

$$\partial F / \partial v = b_v - b. \quad (3)$$

The above assumption implies that the subthreshold region of vapor metastability contains a single minimum and a single maximum on the F versus v plot. Indeed, the equation

$$b_v = b, \quad (4)$$

which, according to (3), determines the extrema of the work F , has only two roots in the subthreshold region. These roots, v_e and v_c , correspond to the minimum and maximum of the work F , respectively. The point of inflection for the function F occurs between the points of extrema. According to equation (3) and the condition $(\partial b_v / \partial v)_{thr} = 0$, the inflection point coincides with $v = v_{thr}$ corresponding to the maximum b_v of the chemical potential of condensate. Apparently, the v_{thr} value is independent (like b_v and unlike v_e and v_c) of the chemical potential of the vapor b .

The plot of b_v on v and the related dependence of F on v [following from the thermodynamic relation (3)] for the subthreshold region of vapor metastability are depicted in the figure. The plots refer to the complicated case where b_v has more than one extremum (specifically, two maxima separated by a minimum). The difference ΔF between the maximum and mini-

imum work F at the points $v = v_c$ and $v = v_e$ determines the activation energy for condensation ΔF .

In the subthreshold region of vapor metastability, the activation energy for condensation can be determined as a function of ε . To this end, similar to the method employed in [1], we will consider a parabolic approximation for b_v in the vicinity of the point $v = v_{thr}$:

$$b_v = b_{tr} + \frac{1}{2} \left(\frac{\partial^2 b_v}{\partial v^2} \right)_{thr} (v - v_{thr})^2, \quad (5)$$

which is valid provided that

$$\frac{1}{3} \left| (v - v_{thr}) \left(\frac{\partial^3 b_v}{\partial v^3} \right)_{thr} / \left(\frac{\partial^2 b_v}{\partial v^2} \right)_{thr} \right| \ll 1. \quad (6)$$

Substituting formulas (2) and (5) into (4), solving this equation, and taking into account that $(\partial^2 b_v / \partial v^2)_{thr} < 0$, we obtain

$$\begin{aligned} v_e &= v_{thr} - (2\varepsilon b_{thr} / |\partial^2 b_v / \partial v^2|_{thr})^{1/2}, \\ v_c &= v_{thr} + (2\varepsilon b_{thr} / |\partial^2 b_v / \partial v^2|_{thr})^{1/2}. \end{aligned} \quad (7)$$

By the same token, substituting (2) and (5) into (3), integrating the resulting equation with respect to v from $v = v_e$ to $v = v_c$, and using formulas (7), we arrive at the final expression for the activation energy ΔF :

$$\Delta F = \frac{4}{3} \varepsilon^{3/2} b_{thr}^{3/2} [2 / |\partial^2 b_v / \partial v^2|_{thr}]^{1/2}. \quad (8)$$

On substituting the explicit expressions for b_{thr} and $(\partial^2 b_v / \partial v^2)_{thr}$ for the case of soluble nuclei of surface-inactive substances, expressions (7) and (8) are transformed into equations (17) and (28) of [1].

The condition that implies the activation barrier for condensation is significant but can still be practically surmounted appears as

$$3 \leq \Delta F \leq 30. \quad (9)$$

The double inequality (9) with ΔF , given by equation (8), determines, according to equation (2), the subthreshold region of vapor metastability. In this region, the barrier mechanism of heterogeneous condensation is of real importance.

For condition (6) to be valid in the entire interval $v_e \leq v \leq v_c$ (where the activation energy ΔF is determined), it is necessary, according to equation (7), that

$$\frac{1}{3} (2\varepsilon b_{thr})^{1/2} \left| \frac{\partial^3 b_{thr}}{\partial v^3} \right|_{thr} / \left| \frac{\partial^2 b_v}{\partial v^2} \right|_{thr}^{3/2} \ll 1. \quad (10)$$

In addition to (10), another important condition is

$$\varepsilon < [b_{thr} - (b_v)_0] / b_{thr} \quad [(b_v)_0 < b_{thr}]. \quad (11)$$

This inequality ensures the validity of the assumption that the subthreshold region of vapor metastability lies above all other extrema (except for the greatest, b_{thr})

of the chemical potential of condensate b_v . This assumption is required for the applicability of formula (8).

Inequality (9) determines [taking into account equation (8)] the lower and upper limits of variation of the quantity ε in the subthreshold region of vapor metastability. For the macroscopic dimensions of the condensation nuclei which are of practical importance, the upper limit is small enough to be compatible with the conditions (10) and $\varepsilon \ll 1$. According to (11), only an extremely narrow range of the external parameters of the condensation problem has to be excluded from consideration, in which another extremum b_v of the chemical potential is very close to the greatest maximum. The condition $\varepsilon \ll 1$ is indicative of an extremely small width of the subthreshold region of vapor metastability. For the macroscopic dimensions of the condensation nuclei, the lower limit of variation of the quantity ε in the subthreshold region of vapor metastability is comparable, by order of magnitude, with the upper limit. This circumstance shows that the subthreshold region lies only slightly below b_{thr} .

CHEMICAL POTENTIAL OF CONDENSATE

Now we will obtain expressions for the chemical potential of condensate b_v and the first and second derivatives of b_v with respect to v (the number of condensate molecules).

The chemical potential of the condensate in a droplet comprising a solution of v molecules of condensate and v_n molecules or ions of the surfactant nucleus (initially present in the vapor phase and eventually completely dissolved in the droplet) [1, 5] can be written in the form

$$b_v = -x + (2/3)a v^{-1/3}, \quad (12)$$

where x is the relative surfactant concentration (i.e., the surfactant : solvent molar ratio) in the bulk phase of the droplet, $a \equiv (36\pi v_l^2)^{1/3} \sigma / kT$ is the dimensionless surface tension of the solution (depending on the concentration x), σ is the surface tension of the solution, and v_l is the molar volume of the condensate. The first term in equation (12) represents the contribution of osmotic pressure (the same as that for a solution with a flat surface) to the chemical potential of the condensate. The second term accounts for the capillary pressure of the curved droplet surface.

The concentration x entering into equation (12) can be determined from the balance equation for the matter comprising the nucleus dissolved in the droplet:

$$x = v_n v^{-1} - s v^{-1/3}, \quad (13)$$

where $s \equiv (36\pi v_l^2)^{1/3} \Gamma_n$ is the dimensionless value of adsorption and Γ_n is the relative adsorption of the dissolved matter comprising the nucleus on the droplet surface. The quantity $s v^{2/3}$ represents the total number

of molecules or ions of the nucleus adsorbed on the droplet surface. Equation (12) is valid under the condition of a dilute solution, $x \ll 1$, which always holds for the macroscopic dimensions of the condensation nuclei.

The possibility of two-dimensional phase transitions in the adsorption layers of soluble surfactants has been reliably established [11]. Taking this fact into account, we may ascertain that, in general, the adsorption s is not a single-valued function of the concentration x . At the same time, the concentration x is a function of the adsorption s that always has a single value. Therefore, we select adsorption, rather than concentration, as a variable describing the state of the droplet.

At a fixed temperature and small concentration x , the Gibbs adsorption equation yields

$$\partial a / \partial s = -\partial \ln x / \partial \ln s. \quad (14)$$

This equation determines a as a single-valued function of s for the given $x(s)$ or, vice versa, determines x as a single-valued function of s for the given $a(s)$.

Upon differentiating (12) with respect to v , using equations (14), and taking into account that

$$\begin{aligned} \partial x / \partial v &= (\partial x / \partial s) \partial s / \partial v, \\ \partial a / \partial v &= (\partial a / \partial s) \partial s / \partial v, \end{aligned} \quad (15)$$

we obtain

$$\frac{\partial b_v}{\partial v} = \frac{\partial a}{\partial s} \frac{\partial s}{\partial v} \left(\frac{2}{3} v^{-1/3} + \frac{x}{s} \right) - \frac{2}{9} a v^{-4/3}. \quad (16)$$

Differentiating (13) with respect to v and using formulas (14) and (15), we have

$$\frac{\partial s}{\partial v} = \frac{v_n v^{-2} - (1/3) s v^{-4/3}}{v^{-1/3} - (x/s) \partial a / \partial s}. \quad (17)$$

Equations (16) and (17) determine the first derivative of b_v with respect to v .

In order to obtain the second derivative of b_v , we use equations (14) and (15) and differentiate expression (16) with respect to v :

$$\begin{aligned} \frac{\partial^2 b_v}{\partial v^2} &= \left(\frac{2}{3} v^{-1/3} + \frac{x}{s} \right) \left[\frac{\partial^2 a}{\partial s^2} \left(\frac{\partial s}{\partial v} \right)^2 + \frac{\partial a}{\partial s} \frac{\partial^2 s}{\partial v^2} \right] \\ &\quad - \frac{\partial a}{\partial s} \frac{\partial s}{\partial v} \left[\frac{4}{9} v^{-4/3} + \frac{x}{s^2} \left(1 + \frac{\partial a}{\partial s} \right) \frac{\partial s}{\partial v} \right] + \frac{8}{27} a v^{-7/3}. \end{aligned} \quad (18)$$

Then, we differentiate equation (17) with respect to v :

$$\begin{aligned} \frac{\partial^2 s}{\partial v^2} &= \frac{1}{v^{-1/3} - (x/s) \partial a / \partial s} \left\{ \frac{2}{3} v_n v^{-3} \right. \\ &\quad \left. - \frac{2}{3} v^{-4/3} \left(1 - 2 \frac{x}{s} \frac{\partial a}{\partial s} v^{1/3} \right) \frac{\partial s}{\partial v} \right. \\ &\quad \left. + \frac{x}{s} \left[\frac{\partial^2 a}{\partial s^2} - \frac{1}{s} \left(1 + \frac{\partial a}{\partial s} \right) \frac{\partial a}{\partial s} \right] \left(\frac{\partial s}{\partial v} \right)^2 \right\}. \end{aligned} \quad (19)$$

Equation (18), together with expressions (17) and (19), determines the second derivative of b_v with respect to v .

As is seen from equations (16) - (19), the particular values of the first and second derivatives of b_v with respect to v depend on the two-dimensional equation of the state of the adsorption layer, $a = a(s)$. The thermodynamic formulas (12) - (14) and (16) - (19) provide an exhaustive solution of the problem formulated in the beginning of this section.

In order to obtain the threshold value b_{thr} of the chemical potential of the vapor and the activation energy for condensation ΔF from equation (8), we must know the values of b_v and $\partial^2 b_v / \partial v^2$ at $v = v_{thr}$. The quantity v_{thr} is a root of the equation $\partial b_v / \partial v = 0$. Unfortunately, this equation is very complicated, as can be seen from expressions (16) and (17). Thus, for an arbitrary parameter v_n of the nucleus and an arbitrary adsorption isotherm, it is impossible to obtain analytical expressions for v_{thr} as a function of v_n or for the functional of the adsorption isotherm $x = x(s)$.

On the basis of strict thermodynamic results obtained above, we can formulate an algorithm for the calculation of the thermodynamic characteristics b_{thr} , v_{thr} , $(\partial^2 b_v / \partial v^2)_{thr}$, and ΔF as functions of the external parameters of the condensation problem. These characteristics are the key values for the entire condensation kinetics. The derivative $(\partial^2 b_v / \partial v^2)_{thr}$ is included in the set of characteristics not only because it enters into formula (8) for ΔF . Once this derivative is known, we can readily find from equation (7) the coordinates v_e and v_c for the positions of the minimum and maximum of the work F on the v axis. Then, we can use equations (3) and (5) to calculate the derivatives $(\partial^2 F / \partial v^2) |_{v=v_e}$ and $(\partial^2 F / \partial v^2) |_{v=v_c}$, which determine (see formulas (31) in [1]) the halfwidths Δv_e and Δv_c of the potential well and the potential maximum, respectively, for the work F plotted against v . Note that the conditions of applicability of this method for the determination of Δv_e and Δv_c (see equation (32) in [1]) and the corresponding restriction from below for ΔF (see equation (34) in [1]) are still valid. Therefore, these conditions are satisfied in the subthreshold region of vapor metastability, whose definition in [1] coincides with inequality (9).

Below we will formulate the algorithm for the calculation of the thermodynamic characteristics b_{thr} , v_{thr} , $(\partial^2 b_v / \partial v^2)_{\text{thr}}$, and ΔF of the condensation kinetics. The algorithm is not restricted to a particular form of adsorption isotherm.

ALGORITHM FOR THE CALCULATION OF THERMODYNAMIC CHARACTERISTICS OF THE CONDENSATION KINETICS

First, we will derive a number of strict thermodynamic relations. In what follows, we consider the state of the droplet corresponding to an extremum of the chemical potential of condensate, that is, at $v = v_0 = 0$. Now we introduce the quantity

$$z \equiv s v_0^{2/3} / v_n \quad (0 \leq z \leq 1), \quad (20)$$

which represents the adsorbed fraction of the matter comprising the nucleus at the point of extremum of the chemical potential of condensate. For simplicity, we will omit the subscript 0, which indicates that the adsorption s (and the quantities used below, such as the surface tension a , its derivative with respect to s , and the concentration x) refers to the extremum of the chemical potential of condensate.

Using the expressions (13), (16), (17), and (20), the equation $(\partial b_v / \partial v)_0 = 0$, which determines the extrema of the chemical potential of condensate, can be written in the form:

$$[2(a/s)z(1-z) - (3-z)^2] \partial a / \partial s = 2(a/s)z^2. \quad (21)$$

Note that, taking (14) into account, this relation is equivalent to equation (40) from [5].

Equations (12), (13), and (20) give

$$(b_v)_0 = \left(\frac{s}{z}\right)^{3/2} v_n^{-1/2} \left(\frac{2az}{3s} + z - 1\right), \quad (22)$$

$$v_n^{1/2} = (s^{3/2}/x) (1-z)/z^{3/2}. \quad (23)$$

Expressing the derivative $\partial a / \partial s$ through z by using formula (21), taking into account (13) and (20), and substituting these expressions into (17) and (19), we obtain:

$$\left(\frac{\partial s}{\partial v}\right)_0 = \left(\frac{s}{z}\right)^{5/2} v_n^{-3/2} \frac{2(a/s)z(1-z) - (3-z)^2}{3(3-z)}, \quad (24)$$

$$\begin{aligned} \left(\frac{\partial^2 s}{\partial v^2}\right)_0 &= -\left(\frac{s}{z}\right)^4 v_n^{-3} \frac{2(a/s)z(1-z) - (3-z)^2}{9(3-z)^2} \\ &\times \left\{ 2(6-z) + 2\frac{a(1-z)(3+z)}{s(3-z)} - 4\frac{a^2(1-z)z}{s^2(3-z)^2} \right. \\ &\left. + \frac{1-z}{z^2} \left[\frac{2(a/s)(1-z)z - (3-z)^2}{3-z} \right]^2 \frac{\partial^2 a}{\partial s^2} \right\}. \quad (25) \end{aligned}$$

The substitution of (24) and (25) into (18) yields

$$\begin{aligned} \left(\frac{\partial^2 b_v}{\partial v^2}\right)_0 &= \left(\frac{s}{z}\right)^{9/2} \frac{v_n^{-7/2}}{27(3-z)^3} \left\{ 8\left(\frac{a}{s}\right)^3 z^2(1-z) \right. \\ &- 4\left(\frac{a}{s}\right)^2 z(1-z)(3-z)(6+z) \\ &- 6\frac{a}{s}(3-z)^2(z^2+4z-3) \\ &\left. - \left[2\frac{a}{s}z(1-z) - (3-z)^2 \right]^3 \frac{s}{z^2} \frac{\partial^2 a}{\partial s^2} \right\}. \quad (26) \end{aligned}$$

The algorithm for the calculation of the thermodynamic characteristics b_{thr} , v_{thr} , $(\partial^2 b_v / \partial v^2)_{\text{thr}}$, and ΔF as functions of the external parameters of the condensation problem [the parameter of the nucleus v_n and either the form of the adsorption isotherm $x = x(s)$ or the equation of the state of the adsorption layer $a = a(s)$] is as follows.

First, by integrating the Gibbs adsorption equation (14) with the given function $x(s)$ [or $a(s)$], we obtain the unknown function $a(s)$ [or $x(s)$]. The resulting function $a(s)$ is substituted into equation (21), which determines the extrema of the chemical potential of condensate. The expression is considered as a square equation with respect to z , and the function $z(s)$ is determined (in general terms, rather than uniquely). Then, the functions $x(s)$ and $z(s)$ are substituted into equation (23), which describes the balance of the matter comprising the nucleus that is dissolved in the droplet, and a relation between v_n and s is obtained. This equation is solved with respect to s , which yields (also in general terms) the function $s(v_n)$. Finally, the functions $a(s)$, $z(s)$, and $s(v_n)$ are substituted into the strict thermodynamic relations (22), (20), (26), and (8). Each time, the maximum $(b_v)_0$ value is determined, yielding, according to (1), the threshold value b_{thr} of the chemical potential of the vapor. Assuming that the subscripts 0 and thr are identical, we can determine all the thermodynamic characteristics of the condensation kinetics as functions of the external parameters of the condensation problem.

The realization of the algorithm in the general case involving an arbitrary parameter of the nucleus v_n and an arbitrary adsorption isotherm (or an arbitrary equation of the state of the adsorption layer) would obviously require numerical calculations. Nevertheless, this is a more efficient procedure as compared to direct numerical calculation of the chemical potential of condensate b_v in the entire variation range of the parameter v , containing all the potential extrema. The main disadvantage of direct calculation consists in the inability of this method to reveal a relatively complicated pattern of the effects of all the external parameters of the condensation problem upon the thermodynamic characteristics of the condensation kinetics.

The results of numerical calculation of the thermodynamic characteristics of the condensation kinetics on soluble nuclei of a surfactant will be reported in the next article.

THERMODYNAMICS OF CONDENSATION, UNDER CONDITIONS OF VERY LOW COVERAGE OF THE DROPLET SURFACE BY THE ADSORBED MATTER COMPRISING THE NUCLEUS

The next two sections are devoted to the analysis of two limiting cases of the condensation on soluble nuclei of a surfactant, in which the thermodynamics of condensation can be significantly simplified by asymptotic constructions. As will be shown below, both situations (especially the latter) may be encountered in practice.

The first limiting case corresponds to a very low coverage of the droplet surface by adsorbed matter comprising the nucleus. This condition is expressed by the inequality

$$s/s_{\infty} \ll 1, \quad (27)$$

where s_{∞} is the adsorption capacity of the surfactant monolayer. The algorithm proposed above will be strictly followed in calculating the thermodynamic characteristics of the condensation kinetics, until the entire calculation has been completed.

If inequality (27) is satisfied, then, according to the Henry adsorption law,

$$x = x_{\alpha} s / s_{\infty}, \quad (28)$$

where x_{α} is the characteristic concentration of the solution such that the ratio x_{α}/s_{∞} equals the Henry constant. Equation (14) also implies

$$\partial a / \partial s = -1. \quad (29)$$

As a rule, the ratio s_{∞}/\bar{a} (where \bar{a} is the dimensionless surface tension of the pure condensate) is well below unity. Therefore, condition (27) is supplemented with inequality

$$s/\bar{a} \ll 1. \quad (30)$$

Integrating equation (29) yields, to within a first-order correction with respect to the small parameter s/\bar{a} in the left-hand part of inequality (30),

$$a = \bar{a}(1 - s/\bar{a}). \quad (31)$$

On substituting formulas (29) and (31) into equation (21), taking into account the conditions given by inequalities (30), and

$$z \ll 1 \quad (32)$$

[as shown below, the latter inequality follows from (30)], and solving the resulting equation using the perturbation technique with respect to z , we obtain

$$z = (9s/2\bar{a})(1 - 2s/\bar{a}). \quad (33)$$

Note that this result is valid with an accuracy as high as that in (31). According to (33), z is of the same small

order of magnitude as the parameter s/\bar{a} in the left-hand part of equation (30). This shows evidence that inequality (32) holds with the same strength as (30).

On substituting formulas (28) and (33) into (23), we arrive at an equation relating v_n and s . Solving this equation with respect to s , using the perturbation technique, yields in the principal order [provided that inequalities (30) and (32) are valid], with respect to the small parameter in the left-hand side of (30),

$$s = (2\bar{a}/9)^{3/2} s_{\infty} / x_{\alpha} v_n^{1/2}. \quad (34)$$

Using equation (34), we can readily pass from the asymptotics in adsorption s to the asymptotics with respect to the number v_n of molecules or ions of the nucleus. Inequality (27) can be written in the form of the restriction below for v_n :

$$v_n^{1/2} \gg (2\bar{a}/9)^{3/2} / x_{\alpha}. \quad (35)$$

The solutions (33) and (34) to equations (21) and (23) are unique. According to (22), this implies the uniqueness of the extremum value $(b_v)_0$ of the chemical potential b_v , which is evidently the maximum value. Then condition (11) can be omitted and the subscript 0 can be replaced by thr. Equation (26) can be written as

$$\begin{aligned} \left(\frac{\partial^2 b_v}{\partial v^2} \right)_0 &= -\frac{4}{27} \left(\frac{s}{z} \right)^{7/2} \frac{a v_n^{-7/2}}{(3-z)^2} \left\{ (3-z)(3+2z) \right. \\ &\quad - 2 \frac{a}{s} z^2 - 2 \left(\frac{a}{s} \right)^2 \frac{z^3}{(3-z)} \frac{1}{(\partial a / \partial s)^2} \left(1 + \frac{\partial a}{\partial s} \right) \\ &\quad \left. + 2 \left(\frac{a}{s} \right)^2 \frac{z^3 s}{(3-z) (\partial a / \partial s)^3} \frac{\partial^2 a}{\partial s^2} \right\}. \quad (36) \end{aligned}$$

On substituting (31) - (34) into (22), (20), (36), and (8), and taking into account that $(b_v)_{\text{thr}} \equiv b_{\text{thr}}$ we eventually obtain:

$$b_{\text{thr}} = 2 \left(\frac{2\bar{a}}{9} \right)^{3/2} \frac{1}{v_n^{1/2}} \left[1 + \frac{1}{6} \left(\frac{2\bar{a}}{9} \right)^{1/2} \frac{s_{\infty}}{x_{\alpha} v_n^{1/2}} \right], \quad (37)$$

$$v_{\text{thr}} = \left(\frac{9}{2\bar{a}} \right)^{3/2} v_n^{3/2} \left[1 - \frac{2}{3} \left(\frac{2\bar{a}}{9} \right)^{1/2} \frac{s_{\infty}}{x_{\alpha} v_n^{1/2}} \right], \quad (38)$$

$$\left(\frac{\partial^2 b_v}{\partial v^2} \right)_{\text{thr}} = -\frac{2}{3} \left(\frac{2\bar{a}}{9} \right)^{9/2} \frac{1}{v_n^{7/2}} \left[1 + \frac{4}{3} \left(\frac{2\bar{a}}{9} \right)^{1/2} \frac{s_{\infty}}{x_{\alpha} v_n^{1/2}} \right], \quad (39)$$

$$\Delta F = \frac{16\epsilon^{3/2} v_n}{6^{1/2}} \left[1 - \frac{5}{12} \left(\frac{2\bar{a}}{9} \right)^{1/2} \frac{s_{\infty}}{x_{\alpha} v_n^{1/2}} \right]. \quad (40)$$

Expressions (37) - (40) give the thermodynamic characteristics of the condensation kinetics as functions of the external parameters involved in the condensation problem. According to (34), these expressions are asymptotic with respect to the small parameter s/\bar{a} entering into the left-hand part of (30). Note that these asymptotics are strict, despite the fact that formula (34) was obtained in the principal order with respect to the small parameter s/\bar{a} . This circumstance is explained by the fact that the quantities s and z appear in equation (20) and in the principal terms of (22), (23), (33), and (36) only as the ratio s/z .

The domain of applicability of asymptotics (37) - (40) is restricted by condition (35), which is equivalent to inequality (27), determining the validity of the Henry adsorption law expressed by (28). The corrections to the Henry law, which are of the order of the small parameter s/s_∞ , are missing from asymptotics (37) - (40). When the adsorption is completely neglected, asymptotics (37) - (40) transform into expressions derived in [1].

For condition (10) to be valid within the entire sub-threshold region of vapor metastability, as determined by the double inequality (9), it is necessary (according to (37), (39), (40), and an expression for $(\partial^3 b_v / \partial v^3)_{\text{thr}}$ obtained in [1]) that $v_n^{1/3} \gg 1$, which implies macroscopic dimensions of the condensation nuclei. For the values of x_α which are much smaller than unity (which is typical of surfactants), this inequality is ensured with considerable reliability by condition (35).

Now we will assess the degree of validity of inequality (35), which is responsible for the asymptotics (37) - (40). The radius of the nuclei of surfactants encountered in practice (e.g., those occurring in the ambient atmosphere) is of the order 10^{-7} - 10^{-3} cm, which corresponds to the parameter v_n varying within a very wide range: $10 \leq v_n \leq 10^{13}$. For the typical values $\bar{a} = 15$ and $x_\alpha = 10^{-5}$, condition (35) can be written in the form of an approximate (rather than strong) inequality: $v_n \geq 4 \times 10^{13}$. Thus, for the external parameters selected, asymptotics (37) - (40) correspond to the ultimately large practical dimensions of surfactant nuclei. However, restriction (35) is highly sensitive to the parameter x_α . Because the value of this parameter in various surfactants varies within wide limits (10^{-5} - 10^{-3}), the domain of applicability of asymptotics (37) - (40) may also significantly vary (from $v_n \geq 10^{13}$ to $v_n \geq 10^9$). The value $v_n \geq 10^9$ includes a considerable part of the range $10 \leq v_n \leq 10^{13}$, where surfactant nuclei are known to be encountered in practice.

Note that asymptotics (37) - (40) are also valid in the case of soluble nuclei representing a surface-inactive substance. Although in that case the s_∞ value cannot be treated as an independent parameter in the theory, the ratio x_α/s_∞ (i.e., the only form in which the quantity s_∞ enters into the asymptotics) still retains the meaning of

the Henry constant. The sign of this constant for a solution of a surface-inactive substance is negative. For example, a water-soluble NaCl nucleus is characterized by $x_\alpha/s_\infty = -0.092$ [12]. Estimation of the relative corrections for adsorption in asymptotics (37) - (40) at the lower applicability limit (i.e., at $v_n^{1/2} = 35$) yields values not exceeding 7.5 and 19% for b_{thr} and ΔF , respectively.

THERMODYNAMICS OF CONDENSATION UNDER CONDITIONS OF NEARLY COMPLETE ADSORPTION OF THE MATTER COMPRISING THE NUCLEUS ON THE DROPLET SURFACE

Now we will study the second limiting case of condensation on soluble nuclei of a surfactant, when the condensation thermodynamics are also considerably simplified at the expense of the asymptotic construction. In this situation, the quantity z defined by equation (20) (representing the adsorbed fraction of the matter comprising the nucleus at the point of extremum of the chemical potential of condensate) falls within the immediate vicinity of its upper limit, equal to unity.

Thus, the case under consideration corresponds to $z \rightarrow 1$, or

$$1 - z \ll 1. \quad (41)$$

The following consideration is not restricted to a particular form of adsorption isotherm. The procedure strictly follows the algorithm proposed above for the calculation of the thermodynamic characteristics of the condensation kinetics. However, certain deviations from the algorithm will be adopted that allow it to be simplified. As is seen from the comparison of inequalities (32) and (41), and from the fact that $0 \leq z \leq 1$, the situation studied in this section, like that considered above, actually represents the extremal case.

First, equation (14) is integrated for the given function $x(s)$ (specified adsorption isotherm) or $a(s)$ (specified equation of the state of the adsorption layer) to find the function $a(s)$ [or $x(s)$]. Then, the function $a(s)$ is substituted into equation (21). In this case, equation (21) is used to determine the derivative $\partial a / \partial s$ at $z = 1$, rather than to find the z value [which is known from condition (41) to almost coincide with unity]. Thus, we have

$$(\partial a / \partial s)_1 = -a_1 / 2s_1, \quad (42)$$

where the subscript 1 refers to the values corresponding to $z = 1$. For the known function $a(s)$, equation (42) determines (even uniquely, by virtue of the inequality $\partial a / \partial s < 0$, typical of surfactants in the range of monolayer coverages) the quantities s_1 and a_1 . For the known function $x(s)$, the quantity x_1 is also uniquely determined.

According to the algorithm for the calculation of the thermodynamic characteristics of the condensation

kinetics, this is followed by determination of the function $s(v_n)$ through equation (23). However, this procedure can be omitted because, with high precision, $s = s_1$, where s_1 is the value determined above. Then, equation (23) with $s = s_1$ and $x = x_1$ (the latter value was also determined above), with high precision [by virtue of (41)], reduces to

$$v_n^{1/2} = (s_1^{3/2}/x_1) (1 - z). \quad (43)$$

This relation allows condition (41) to be written in the form of the restriction from above for v_n :

$$v_n^{1/2} \ll s_1^{3/2}/x_1. \quad (44)$$

The fact that the value of v_n is restricted from above rather than from below, as in (35), confirms that the situation studied in this section, like that considered above, actually represents the extremal case.

By virtue of (41), the quantities z and s are uniquely determined (being virtually equal to 1 and s_1 , respectively). According to (22), this implies the uniqueness of the extremum value $(b_v)_0$ of the chemical potential b_v , which is evidently the maximum value (similar to the case studied in the previous section). Then, condition (11) can be omitted and the subscript 0 can be replaced by thr. For the principal order with respect to the small parameter given by inequality (41) (i.e., for $z = 1$, $s = s_1$ and $a = a_1$), from (11), (20), (26), (8) for $(b_v)_{thr} \equiv b_{thr}$ we eventually obtain:

$$b_{thr} = 2s_1^{1/2} a_1 / 3v_n^{1/2}, \quad (45)$$

$$v_{thr} = (v_n/s_1)^{3/2}, \quad (46)$$

$$\left(\frac{\partial^2 b_v}{\partial v^2}\right)_{thr} = -\frac{2s_1^{7/2} a_1}{9v_n^{7/2}} \left[1 - \frac{4s_1^2}{3a_1} \left(\frac{\partial^2 a}{\partial s^2}\right)_1\right], \quad (47)$$

$$\Delta F = \frac{16a_1 \varepsilon^{3/2} v_n}{6^{1/2} \times 3s_1} \left[1 - \frac{4s_1^2}{3a_1} \left(\frac{\partial^2 a}{\partial s^2}\right)_1\right]^{-1/2}. \quad (48)$$

Once the function $a(s)$ is determined (or specified) and s_1 is found, the second derivative $(\partial^2 a/\partial s^2)_1$ can be considered known. Equations (45) - (48), representing the principal terms of asymptotics with respect to the small parameter $1 - z$ from the left-hand part of inequality (41), give the thermodynamic characteristics of the condensation kinetics as functions of the external parameters involved in the condensation problem. As a rule, in the range of coverage of the surfactant monolayer, $\partial^2 a/\partial s^2 < 0$ (which implies that the curve of the surface tension versus the adsorption is convex). Therefore, equations (47) and (48) ensure the inequalities $(\partial^2 b_v/\partial v^2)_{thr} < 0$ and $\Delta F > 0$ (which are natural conditions for the maximum chemical potential of condensate and the activation energy, respectively).

Now we will turn to an analysis of condition (10). By differentiating equations (18) and (19) with respect to v using equations (14) and (15), passing at $v = v_0$

from v_0 to z with the aid of relation (20), and making allowance for inequality (41) while taking into account that subscript 0 can be replaced by thr under the conditions studied, for $z = 1$ we obtain:

$$\left(\frac{\partial^3 b_v}{\partial v^3}\right)_{thr} = \frac{26s_1^5 a_1}{27v_n^5} \left[1 - \frac{24}{13} \frac{s_1^2}{a_1} \left(\frac{\partial^2 a}{\partial s^2}\right)_1 - \frac{8}{39} \frac{s_1^3}{a_1} \left(\frac{\partial^3 a}{\partial s^3}\right)_1\right]. \quad (49)$$

As a rule, in the range of full coverage of the surfactant monolayer we have $\partial^2 a/\partial s^2 < 0$ and $\partial^3 a/\partial s^3 < 0$. According to (49), this yields $(\partial^3 b_v/\partial v^3)_{thr} > 0$ (thus, the sign of the third derivative of b_v with respect to v at $v = v_{thr}$ is the opposite of the sign of the second derivative at the same point). On substituting (45), (47), and (49) into (10), the latter inequality reduces to

$$\frac{13(6\varepsilon)^{1/2}}{9} [1 - (24s_1^2/13a_1) (\partial^2 a/\partial s^2)_1 - (8s_1^3/39a_1) (\partial^3 a/\partial s^3)_1] \times [1 - (4s_1^2/3a_1) (\partial^2 a/\partial s^2)_1]^{-3/2} \ll 1. \quad (50)$$

Then, using equation (48), we obtain an estimate for ε from the double inequality (9), which is valid in the entire subthreshold region of vapor metastability:

$$\varepsilon^{1/2} \sim (s_1/a_1 v_n)^{1/3} [1 - (4s_1^2/3a_1) (\partial^2 a/\partial s^2)_1]^{1/6}. \quad (51)$$

According to (51), in the entire subthreshold region of vapor metastability, it is required that

$$v_n^{1/3} \gg 3.5 [1 - (24s_1^2/13a_1) (\partial^2 a/\partial s^2)_1 - (8s_1^3/39a_1) (\partial^3 a/\partial s^3)_1] \times \left\{ [1 - (4s_1^2/3a_1) (\partial^2 a/\partial s^2)_1]^{4/3} \right\}^{-1} \quad (52)$$

in order for condition (50) (and, hence, condition [10]) to remain valid, and this implies a restriction from below for v_n .

Thus, the values of the parameter v_n , which are admitted by the asymptotic theory for the case of nearly complete adsorption of the matter comprising the nucleus on the droplet surface [i.e., for condition (41)], are restricted from above and below by inequalities (44) and (52), respectively.

Now we will estimate the domains of the parameter v_n , given by inequalities (44) and (52), for the case when the adsorption of a soluble nucleus of a surfactant on the droplet is described by the Frumkin adsorption isotherm [13]. In the notation of this work, the isotherm has the form

$$x = [x_{\alpha s}/(s_{\infty} - s)] \exp(-2\kappa s/s_{\infty}), \quad (53)$$

where κ is the parameter of lateral interactions in the monolayer. On substituting expression (53) into equation (14) and accomplishing the integration, we obtain a two-dimensional equation for the state of the adsorption layer of the surfactant:

$$a = \bar{a} + s_{\infty}[\ln(1 - s/s_{\infty}) + \kappa(s/s_{\infty})^2]. \quad (54)$$

At $\kappa = 0$, this relation is known as the van Laar equation. In the case of strong adsorption undersaturation [i.e., for condition (27)], expressions (53) and (54) transform into (28) and (31), respectively.

Let $\bar{a} = 10$ (this corresponds to water as the condensate at $T = 273$ K), $s_{\infty} = 1$, and $x_{\alpha} = 10^{-5}$ (a realistic condition). We also assume that $\kappa = 1.95$. On one hand, this value is below the level $\kappa = 2$ (where the Frumkin isotherm exhibits a phase transition in the monolayer), and on the other hand, it is sufficiently large to reveal the ultimate role of the lateral interactions. Solving equation (42) with a given by relation (54), we obtain $s_1 = 0.886$ (i.e., adsorption on the droplet surface is close to saturation) and $a_1 = 9.36$. In this case, equation (53) yields $x_1 = 2.45 \times 10^{-6}$. Then, condition (44) reduces to $v_n^{1/2} \leq 3.4 \times 10^5$. This can be written in the form of an approximate (rather than strong) inequality: $v_n^{1/3} \leq 10^3$.

Using relation (54) and substituting the s_1 and a_1 values from above into the right-hand part of inequality (52), the latter condition is reduced to $v_n^{1/3} \geq 6$, which, in effect, is valid even at $v_n^{1/3} \geq 10$.

In concluding, note that inequalities (44) and (52) are reliably compatible. Their combination determines the interval of values for the parameter v_n , in which the asymptotics (45) - (48) are valid: $10 \leq v_n^{1/3} \leq 10^3$ or $10^3 \leq v_n \leq 10^9$. This interval contains a rather wide (and important) part of the entire range ($10 \leq v_n \leq 10^{13}$) of the dimensions of surfactant nuclei encountered in practice.

Note that asymptotics (45) - (48) and the principal terms of asymptotics (37) - (40) depend in the same manner on v_n (being proportional to $v_n^{-1/2}$, $v_n^{3/2}$, $v_n^{-7/2}$, and v_n , respectively), although the two groups of asymptotics refer to the opposite extremal cases.

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