

PRINCIPLES OF THE THERMODYNAMICS OF CONDENSATION ON SOLUBLE NUCLEI WITH ALLOWANCE FOR ADSORPTION OF THE SUBSTANCE OF THE NUCLEUS

A. I. Rusanov, F. M. Kuni,
and A. K. Shchekin

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Allowance is made for the adsorption of the substance of the nucleus on the surface of the drop in the material balance equation for a condensation nucleus dissolved in a drop. The thermodynamics of nucleation is studied for the case of a high degree of adsorption undersaturation. A condition is established in thermodynamic form to determine the extremum of the chemical potential of the condensate in the drop in the general case of an arbitrary degree of adsorption saturation. With allowance for adsorption of the substance of the nucleus, a closed system of equations is constructed to link the thermodynamic characteristics of a drop in which the condensate has a chemical potential with an extremum.

The study [1] and earlier publications [2-4] on the thermodynamics of condensation on nuclei that are soluble in newly formed drops did not consider adsorption of the substance of the nucleus on the surface of the drop. Under the conditions of practical interest, condensation on soluble nuclei occurs with a low level of vapor supersaturation, and drops with a low concentration of the substance of the nucleus in the solution inside the drop play the determining role in the thermodynamics of condensation [1]. As a result, the assumption made in [4] that the absolute value of adsorption is small is quite acceptable for inorganic electrolytes (frequently with negative adsorption). Their particles are always present in the winter atmosphere, and their possible role as condensation nuclei has been discussed repeatedly in the literature (see [4], for example). As regards surfactants — whose adsorption is appreciable even for very low solution concentrations — this assumption is almost never valid. We will concern ourselves with soluble surfactant nuclei in this article.

Depending on the concentration of the solution inside the drop, adsorption in turn affects concentration. At the same time, adsorption also affects the surface tension of the drop, causing it to be dependent on concentration. The nonlinear relationships which arise in this case greatly complicate the behavior of the chemical potential of the condensate (condensed in the drop from the vapor of the substance). In the case when the substance of the nucleus is surface-active, these relationships may lead to the existence of more than one extremum and even more than one maximum of condensate chemical potential.

Finding the threshold chemical potential of the vapor — which is determined by the maximum of the chemical potential of the condensate or the largest maximum of same (if there is more than one maximum) — is the central problem in the thermodynamics of condensation on soluble nuclei. Approaching the solution of this problem with allowance for adsorption of the substance of the nucleus, we first study the simplest case of a high degree of adsorption undersaturation. By studying this case, we will also be able to explain how adsorption could have been ignored in [1-4]. Then considering the general case of an arbitrary degree of adsorption saturation, we formulate the principles of thermodynamics on soluble nuclei and construct a closed system of equations linking the thermodynamic characteristics of a drop in which the chemical potential of the condensate has an extremum. In conclusion, we will examine the transition to the limiting situation of complete adsorption saturation.

The system of equations that we construct will be studied further in subsequent articles.

Effect of Adsorption of the Substance of the Condensation Nucleus on the Surface of a Drop. We will use c to denote the concentration of the condensate inside the bulk phase of the drop — the number of molecules of the condensate per

unit volume. The notation c_n will be used to represent the concentration of the substance of the nucleus dissolved inside the bulk phase — the number of molecules or ions of this substance per unit volume. When $c \gg c_n$, the radius of the equimolecular (in regard to the condensate) interface nearly coincides with the radius of the drop R determined by Eq. (2) from [1]:

$$R = (3v_l \nu / 4\pi)^{1/3} \equiv \lambda \nu^{1/3} \quad (1)$$

where v_l is the molecular volume of the condensing liquid; λ is a linear parameter (the radius of an equivalent sphere); ν is the total number of condensate molecules in the drop.

We then have the material balance equation

$$\nu = cV, \quad \nu_n = c_n V + 4\pi R^2 \Gamma_n \quad (2)$$

where ν_n is the total number of molecules or ions of the condensation nucleus; $V = 4\pi R^3/3$ is the volume of the drop; Γ_n is the adsorption of the dissolved substance (the excess number of molecules — for the electrolyte, it is the sum of the excess number of all ions per unit area of the surface). Introducing the relative concentration

$$x \equiv c_n/c \quad (3)$$

and the dimensionless adsorption

$$s \equiv 4\pi \lambda^2 \Gamma_n \quad (4)$$

and excluding the volume V from Eqs. (2), after using (1) we find that

$$x = \nu_n \nu^{-1} - s \nu^{-1/3} \quad (5)$$

Henceforth, we will refer to x and s simply as concentration and adsorption.

Differentiating (5) with respect to ν and applying to s the rule on differentiation of quantities dependent on x

$$\partial/\partial \nu = (\partial x/\partial \nu) \partial/\partial x \quad (6)$$

we obtain an equation for $\partial x/\partial \nu$. Solving it, we have

$$\partial x/\partial \nu = -(\nu_n - \frac{1}{3} s \nu^{2/3})/\nu^2 (1 + \nu^{-1/3} \partial s/\partial x) \quad (7)$$

(ν_n is assumed to be fixed).

As (5) shows, in physical terms we will have $\nu_n - s \nu^{2/3} > 0$ and, all the more, $\nu_n - (1/3) s \nu^{2/3} > 0$. We see that $\partial s/\partial x > 0$ for soluble surfactants. Thus, it follows from (7) that

$$\partial x/\partial \nu < 0 \quad (8)$$

In accordance with (8), there is a one-to-one correspondence between the concentration x and the number of condensate molecules ν , and the former decreases monotonically with the latter.

Using the same reasoning as in [1] to find the chemical potential of the condensate inside the bulk phase of the drop, we have

$$b_\nu = -x + (2/3) a \nu^{-1/3} \quad (9)$$

As in [1], the chemical potential b_ν is expressed in thermal energy units and is reckoned from the value corresponding to equilibrium of the vapor with the condensing liquid when their contact surface is planar. The dimensionless surface tension of the drop a is determined by Eq. (4) from [1].

In contrast to the analogous formula (3) from [1], in formula (9) the concentration x does not coincide with the ν_n/ν and is determined by Eq. (5). Inserting (5) into (9), we obtain

$$b_\nu = -\nu_n \nu^{-1} + (2/3) (a + 3s/2) \nu^{-1/3} \quad (10)$$

We should note that the weakness of the solution of the substance of the nucleus always (if the substance of the nucleus is an electrolyte) guarantees small values of electrical corrections to (9) and (10) for the chemical potential of the condensate relative to the nonelectrical contributions in (9) and (10).

Besides the already-established effect on the concentration of the solution inside the drop, another important effect of adsorption is its influence on the surface tension of the drop. As a result of this, drop surface tension becomes a function of solution concentration inside the drop.

The dependence of surface tension on concentration is given by the Gibbs adsorption equation. In the dimensionless variables a , x , and s introduced by definition (4) from [1] and definitions (3-4) above, this equation takes the form

$$\partial a / \partial x = -s/x \quad (11)$$

The fact that Eq. (10) contains quantities a and s which depend on solution concentration x — which is in turn a function of ν — greatly complicates the thermodynamics of heterogeneous condensation. In this case, finding the thermodynamic characteristics of a drop in which the chemical potential of the condensate has a maximum requires the solution of a complex nonlinear problem.

We will be concerned with this below. First we study the simplest case, in which the effect of adsorption of the substance of the condensation nucleus on the drop surface remains weak. In particular, this allows us to find a condition which validates the decision made in [1-4] to ignore the effect of adsorption in the thermodynamics of condensation on soluble nuclei.

Thermodynamics of Nucleation in the Case of a High Degree of Undersaturation of the Vapor. We will study the case in which

$$s/s_\infty \ll 1 \quad (12)$$

where s_∞ is adsorption in the case of complete saturation. This case corresponds to a high degree of adsorption undersaturation.

In the above expression, s is proportional to x :

$$s = (s_\infty/x_\alpha) x \quad (13)$$

where the proportionality factor is also the definition of characteristic concentration x_α . In accordance with (13), inequality (12) is equivalent to

$$x/x_\alpha \ll 1 \quad (14)$$

Usually the ratio s_∞/a is considerably less than unity. Thus, the following inequality is observed in addition to (12)

$$s/a \ll 1 \quad (15)$$

this inequality appreciably facilitating the rest of our investigation.

It follows from (11) and (13) that

$$a = \bar{a} - s \quad (16)$$

where the superimposed bar denotes the value of surface tension in the absence of adsorption. Inserting (16) into (10), we obtain

$$b_\nu = -\nu_n \nu^{-1} + (2/3)(\bar{a} + s/2)\nu^{-1/3} \quad (17)$$

We will show that when inequality (15) is observed, adsorption of the substance of the nucleus results in only a small correction to the theory [1-4] in the absence of adsorption.

We will use the results of this theory for the zeroth approximation. In accordance with Eq. (6) from [1], we then have

$$\nu_0 \approx (9\nu_n/2a)^{3/2} \quad (18)$$

where the zero subscript characterizes values of quantities at the maximum of the chemical potential of the condensate. The sign of the approximate equality corresponds to the zeroth approximation. Taking (18) into account, we have

$$s\nu_0^{2/3} \approx 9\nu_n s/2a \quad (19)$$

It is evident from (15) and (19) that the following is valid for a drop in which the chemical potential of the condensate is near its maximum

$$s\nu^{2/3}/\nu_n \ll 1 \quad (20)$$

This shows the smallness of the contribution of adsorption to Eq. (5), which accordingly reduces to

$$x \approx \nu_n/\nu \quad (21)$$

Thus, most of the substance of the condensation nucleus is in the solution inside the drop, rather than on its surface.

When inequality (15) is observed, adsorption also produces a small correction in (16) and (17).

It is clear from (17) that for the effect of adsorption to also be manifest in the expression for $\partial b_\nu/\partial \nu$ — which, in accordance with the equation

$$(\partial b_\nu/\partial \nu)_0 = 0 \quad (22)$$

([1], Eq. (5)) identifies the drop in which the chemical potential of the condensate is maximal (this being the most important drop in terms of the thermodynamics of condensation on soluble nuclei) — it is necessary that the following inequality be satisfied

$$|\partial s/\partial \nu| \ll \bar{a}/\nu \quad (23)$$

Using (6), (13), and (21), we obtain

$$\partial s/\partial \nu \approx -s/\nu \quad (24)$$

It is evident from (15-16) and (24) that inequality (23) actually exists.

Having demonstrated the smallness of the effect of adsorption of the substance of the condensation nucleus on the surface of the drop when inequality (15) is observed, we conclude that formula (18), obtained in the absence of adsorption, ensures a very high degree of accuracy in the zeroth approximation of ν_0 . This approximation has already been used in (19).

In accordance with (18) and (21), we thus have

$$\nu_0 \approx (9\nu_n/2\bar{a})^{3/2} \quad (25)$$

$$x_0 \approx (2\bar{a}/9)^{3/2}/\nu_n^{1/2} \quad (26)$$

where, within the range of accuracy of the zeroth approximation, we have replaced the quantity a by \bar{a} . Here, the sign of approximate equality denotes that we are ignoring corrections on the order of the small quantity $s\sqrt{a}$ — which, by virtue of (15) and (16), nearly coincides with the small quantity s/a .

As is clear from (26), satisfaction of inequality (14) for the most important drop implies satisfaction of the condition

$$\nu_n^{1/2} \gg (2\bar{a}/9)^{3/2}/x_\alpha \quad (27)$$

This condition places a lower limit on $\nu_n^{1/2}$.

We should note that (12-17), (20-21), and (23-24) and the ensuing conclusions regarding the smallness of the effect of adsorption will be even more valid in the region of ν in which $\nu/\nu_0 > 1$. However, this region is not important for the theory.

Despite this, the present study permits the following statement to be made. In the limit $\nu \rightarrow \infty$, all of the material of the condensation nucleus dissolved in the drop will be in the volume of the drop. Meanwhile, the concentration of the substance will be infinitesimal in this case.

The sensitivity of the quantity b_ν to ν in the neighborhood of the point $\nu = \nu_0$ turns out to be exaggerated, due to (22). When we use the general thermodynamic formula

$$b_{tr} = \max b_\nu = (b_\nu)_0 \quad (28)$$

([1], Eq. (9)) to find the threshold value b_{tr} of vapor chemical potential with a first-order correction for the small (due to (15) and (16)) quantities s/a , we only need to use approximate expression (25) for b_ν in (17) (the corrections for the small quantity s/\bar{a} were omitted in (25)). In accordance with (28), (17), and (25), we have

$$b_{tr} = \frac{2(2\bar{a})^{3/2}}{27\nu_n^{1/2}} \left(1 + \frac{3s}{4\bar{a}} \right) \quad (29)$$

where the size s of the correction factor is given by (13) and (21) with ν equal to the value ν_0 determined by means of (25). When $s = 0$, Eq. (29) becomes formula (11) from [1] — a formula that was first obtained by Keller [2-4]. The threshold value b_{tr} of the chemical potential of the vapor is expressed in thermal energy units in (28) and (29) and is reckoned from the value corresponding to equilibrium between the vapor and condensing liquid when their contact surface is planar.

It is clear from (29) that in the case of a high degree of adsorption undersaturation, the act of adsorption may either slightly increase or slightly decrease the chemical potential of the vapor. Whether an increase or a decrease occurs depends on whether $s > 0$ or $s < 0$, respectively.

Expression (29) shows that condition (27), ensuring satisfaction of inequalities (14) and (15), corresponds to the situation that is energetically the most favorable for heterogeneous condensation, i.e., the situation in which the threshold chemical potential of the vapor may be minimal.

At the same time, it is also clear that when condition (27) is observed, it is valid to (as was done in [1-4]) ignore the effect of adsorption in the thermodynamics of condensation on soluble nuclei.

The greater the surface activity of the substance of the condensation nucleus, the smaller the concentration x_α . Thus, the stronger the lower limit imposed on $\nu_n^{1/2}$ by condition (27). As a result, the situation in which there is a high degree of undersaturation of adsorption almost never occurs for drops containing a very low concentration x_α of soluble surfactants.

System of Equations of the Thermodynamics of Nucleation with an Arbitrary Degree of Adsorption Saturation.

Let us now proceed to a general investigation of the thermodynamics of condensation on soluble nuclei, with allowance for adsorption of the substance of the nucleus on the surface of the drop. Differentiating (10) with respect to ν and using (5-7) and (11), we find

$$\begin{aligned} \frac{\partial b_\nu}{\partial \nu} &= \nu_n \nu^{-2} - \frac{2}{9} \left(a + \frac{3}{2} s \right) \nu^{-4/3} + \\ &+ \frac{2}{3} s \nu^{-4/3} \frac{1 - \frac{3}{2} \frac{\partial \ln s / \partial \ln x}{1 + \nu^{-1/3} \frac{\partial s / \partial x}}{\nu_n - \frac{1}{3} s \nu^{2/3}} \end{aligned} \quad (30)$$

Inserting (30) into (22), we obtain

$$\begin{aligned} \nu_n \nu_0^{-2/3} - \frac{2}{9} \left(a + \frac{3}{2} s \right) + \\ + \frac{2}{3} s \frac{1 - \frac{3}{2} \frac{\partial \ln s / \partial \ln x}{1 + \nu_0^{-1/3} \partial s / \partial x}}{\nu_n - s \nu_0^{2/3}} = 0 \end{aligned} \quad (31)$$

For the sake of simplification, we will not indicate that the quantities x , a , s , $\partial s / \partial x$, and $\partial \ln s / \partial \ln x$ pertain to the value $\nu = \nu_0$.

The root ν_0 of Eq. (31), expanding Eq. (22), corresponds to the extremum of chemical potential b_ν . As will be seen from the below discussion, the root ν_0 may not be unique. Accordingly, chemical potential b_ν may have more than one extremum and even more than one maximum. The zero subscript then characterizes the values of quantities at the extremum of the chemical potential of the condensate — but not necessarily at its maximum. Naturally, the largest of the maxima must be used in Eq. (28) for the threshold value b_{tr} of the chemical potential of the vapor.

Let us change over from ν_0 to the quantity

$$z \equiv s \nu_0^{2/3} / \nu_n \quad (0 \leq z \leq 1) \quad (32)$$

which represents the fraction of the adsorbed substance of the condensation nucleus from the total amount at the extremum of the chemical potential of the condensate. This fraction will obviously be within the range from 0 to 1, as indicated in definition (32). We can now write (32) in the form

$$\nu_0 = (\nu_n / s)^{3/2} z^{3/2} \quad (33)$$

In accordance with (5) and (32), we have

$$\nu_n^{1/2} = \frac{s^{3/2}}{x} \frac{1-z}{z^{3/2}} \quad (34)$$

$$\nu_0^{1/3} \leq \frac{s}{x} \frac{1-z}{z} \quad (35)$$

Having put

$$u \equiv a/s$$

$$q \equiv 1 - \frac{1 - \frac{3}{2} \frac{\partial \ln s / \partial \ln x}{1 + \nu_0^{-1/3} \partial s / \partial x}}{1 + \nu_0^{-1/3} \partial s / \partial x} \quad (36)$$

$$q \equiv 1 - \frac{1 - \frac{3}{2} \frac{\partial \ln s / \partial \ln x}{1 + \nu_0^{-1/3} \partial s / \partial x}}{1 + \nu_0^{-1/3} \partial s / \partial x} \quad (37)$$

and then using (33), we reduce Eq. (31) to the form

$$2qz^2 + 2uz^2 + z^2 - 6qz - 2uz - 6z + 9 = 0 \quad (38)$$

Solving Eq. (38) for q , we find

$$q = \frac{(3-z)^2 - 2uz(1-z)}{2z(3-z)} \quad (39)$$

We equate the right sides of Eqs. (37) and (39) for the same value of q , here accounting for (35) in (37). The resulting equality is then reduced to a common denominator. After multiplying the entire equation by the factor $1 - z$, we obtain

$$(1 + 2u - 2u \partial \ln s / \partial \ln x) z^2 - 2(u + 3)z + 9 = 0 \quad (40)$$

which does not contain q and is quadratic in terms of the variable z . Equations (40) and (36) take the condition for the extremality of condensate chemical potential, expressed by (22), and expand it into thermodynamic form.

Proceeding on the basis of (9) and (35-36), we obtain the following general thermodynamic expression for the extreme value $(b_\nu)_0$ of the chemical potential of the condensate

$$(b_\nu)_0 = x \left[\frac{2zu}{3(1-z)} - 1 \right] \quad (41)$$

The main goal of the thermodynamics of nucleation in the case of adsorption of the substance of the condensation nucleus is determination of the pattern of behavior of the thermodynamic characteristics of a drop in which the chemical potential of the condensate has an extremum. Of particular interest here are drops in which the chemical potential of the condensate is maximal. It is convenient to construct this pattern as a function of z rather than ν_n (which is an external parameter of the problem). In this case, ν_n will be a function of z . The transition in the final formulas from the independent variable z to the independent variable ν_n is made without difficulty.

We therefore choose z as the independent variable to describe a drop in which the chemical potential of the condensate has an extremum. Relation (36) and Eq. (40), together with the formulas in the theory of surface solutions which determine the dependence of adsorption s and surface tension a on solution concentration x , form a closed system of equations connecting the variables z and x . While the formulas from the theory of surfactant solutions needed to close (36) and (40) determine the dependence of solution concentration x and surface tension a on adsorption s , the closed system of equations links the variables z and s .

Dependence of Adsorption and Surface Tension on the Concentration of the Surfactant Solution. We will restrict ourselves to the study of monolayer adsorption. Then the dependence of adsorption and surface tension on the concentration of the surfactant solution is described well by the Langmuir and Shishkovskii formulas [5, 6]:

$$s = s_\infty x / (x + x_\alpha) \quad (42)$$

$$a = \bar{a} - s_\infty \ln[(x + x_\alpha)/x_\alpha] \quad (43)$$

These formulas satisfy the Gibbs adsorption equation (11) and, when inequality (14) is observed, agree with (13) and (16).

It should be noted that the best agreement with experimental data on surface tension and adsorption is obtained from the Frumkin formulas, which account for lateral interactions of molecules or ions of surfactants in the monolayer on the surface [7]:

$$x/x_\alpha = [s/(s_\infty - s)] \exp(-2\kappa s/s_\infty) \quad (44)$$

$$a = \bar{a} + s_\infty [\ln(1 - s/s_\infty) + \kappa (s/s_\infty)^2] \quad (45)$$

where κ is a parameter characterizing the lateral interaction. However, as shown by the experiment in [8], this parameter is much less than unity. Also small [9] is the correction — not accounted for by Eqs. (44) and (45) — for Coulomb interaction in the surface layer in the case of an ionic surfactant. Also, since Eqs. (44) and (45) reduce to Eqs. (42) and (43) when $\kappa = 0$, we can use the Langmuir and Shishkovskii formulas without significant loss of accuracy.

It will be convenient to henceforth use the following notation

$$v \equiv a/s_\infty \quad (46)$$

$$w \equiv \bar{a}/s_\infty \quad (47)$$

$$\xi \equiv x/x_\alpha \quad (48)$$

For the sake of brevity, we will refer to ξ simply as concentration.

With allowance for (46-48), we find from (42-43) that

$$s = s_\infty \xi / (\xi + 1) \quad (49)$$

$$v = w - \ln(\xi + 1) \quad (50)$$

$$\partial \ln s / \partial \ln x = 1 / (\xi + 1) \quad (51)$$

For the quantity determined by (36), we use (46) and (49) to obtain:

$$u = v(\xi + 1)\xi^2 \quad (52)$$

Equation (40) and Eqs. (50-52) form a closed system of equations connecting the variables z and ξ of a drop in which the chemical potential of the condensate has an extremum. The system is valid for an arbitrary degree of saturation of monolayer adsorption. Here, the quantities ν_n and ν_0 are expressed through z and ξ by (34-35) and (48-49). The quantities s_∞ , and w play the role of initial parameters of the problem.

When the inequality $x/x_\alpha \gg 1$ (which is the opposite of inequality (14)) is observed, the Langmuir and Shishkovskii formulas (42) and (43) become

$$s = s_\infty \quad (53)$$

$$a = \bar{a} - s_\infty \ln(x/x_\alpha) \quad (54)$$

which, as (42) and (43), identically satisfy Gibbs adsorption equation (11). Equations (53) and (54) express the limiting situation of complete saturation of monolayer adsorption on the surface of the drop — when adsorption turns out to be constant.

With allowance for (46-48), we find from (53-54) that

$$v = w - \ln \xi \quad (55)$$

$$\partial \ln s / \partial \ln x = 0 \quad (56)$$

$$u = v \quad (57)$$

which is also easily obtained directly from (50-52) at $\xi \gg 1$.

For the case of complete saturation of monolayer adsorption, Eq. (40) and Eqs. (55-57) form a closed system of equations connecting the variables z and ξ of a drop in which the chemical potential of the condensate has an extremum. Here, the quantities ν_n and ν_0 are expressed through z and ξ by (34-35), (48), and (53). As before, x_α , s_∞ , and w are initial parameters of the problem.

The limiting situation described by Eqs. (53-57) when $\xi \gg 1$ corresponds to a model of a drop with constant adsorption. In general, the use of this model is not limited to the range of application of the Langmuir and Shishkovskii formulas. In fact, it follows from Gibbs adsorption equation (11) that the below is valid upon attainment of complete saturation of adsorption, i.e., when (53) is satisfied

$$a = a_\infty - s_\infty \ln(x/x_\infty) \quad (58)$$

where x_∞ is the solution concentration at which complete saturation of adsorption begins; a_∞ is the surface tension corresponding to this concentration. Formula (58) is not connected with any specific mechanism of monolayer saturation. The dependence on x in (58) is the same as in Eq. (54). Since $x_\infty \gg x_\alpha$, the ranges of application of these formulas $x/x_\infty \geq 1$ and $x/x_\alpha \gg 1$ also coincide.

Although relatively simple, the drop model with constant adsorption nonetheless makes it possible to describe laws which in general characterize the thermodynamics of condensation on soluble surfactant nuclei. We will study this model in the next article.

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