

18 Deliquescence and Efflorescence Barriers in Heterogeneous Nucleation in Undersaturated Vapor

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Doch erscheint eine Rückerinnerung an die älteren Erfahrungen, die zur Festlegung der gebräuchlichen Begriffe und zur Aufstellung oft erwähnter empirischer Regeln geführt haben, notwendig, weil sie bei der heutigen Generation grossenteils in Vergessenheit geraten sind. Von diesen umfangreichen Arbeiten der früheren Zeit . . . ist in die modernen Hand- und Lehrbücher fast nichts übergegangen – ein Zeugnis dafür, wie gering die Summe vieljähriger rein empirischer Forschung gewertet wird, der die Einfügung in das physikalisch-chemische Gesamtbild mangelt.

Max Volmer (1939)

Abstract

The well and the saddle points of the work of droplet formation on a soluble nucleus in undersaturated vapor have been analyzed in their dependence on droplet and nucleus sizes and chemical potential of vapor molecules. The direct (deliquescence) and reversal (efflorescence) activation barriers for transitions of droplets between states with partially and completely dissolved condensation nuclei have been numerically studied. It has been taken into account that the behavior of the work of droplet formation in the vicinity of its saddle point differs essentially in the cases when the vapor chemical potential is

close to its threshold value corresponding to barrierless dissolution of condensation nucleus (deliquescence threshold) and when it is noticeably below this threshold value (but far from reaching the efflorescence threshold). Coefficients of the diagonalized quadratic forms of the work of droplet formation on a soluble nucleus in undersaturated vapor in the neighborhood of the minimum and the saddle points of the work have been numerically studied. Exchange of the roles of thermodynamically stable and thermodynamically unstable variables in transitions over the deliquescence and efflorescence barriers near the deliquescence threshold and noticeably below it has been found and explained.

18.1 Introduction

Thermodynamics of thin liquid films plays the key role in understanding the specific features of the deliquescence stage in nucleation on soluble nuclei in supersaturated and undersaturated vapors [1, 2, 3, 4]. We will rely in the present work upon the basic thermodynamic relations describing the deliquescence stage in nucleation on soluble nuclei. In particular, the conditions of chemical equilibrium of the droplet with partially dissolved nucleus and the expression for the work of droplet formation on a soluble condensation nucleus are of importance [4].

Y [1-4]

It is known [1, 2, 3, 4, 5] that there are two specific values of the vapor chemical potential in nucleation on soluble nuclei which are called the deliquescence and efflorescence thresholds. Above the deliquescence threshold, the activation barrier for formation of a droplet around a soluble condensation nucleus vanishes and heterogeneous nucleation occurs intensively with complete dissolution of the nuclei in droplets (i.e. deliquescence proceeds barrierlessly). Below the efflorescence threshold, the activation barrier for crystallization of a salt nucleus within the droplet of solution becomes so small that the nuclei form in the droplets immediately (i.e. efflorescence proceeds very fast).

Y [1-5]

At the state of internal equilibrium of the droplet with incompletely dissolved condensation nucleus, the size of the residue of the nucleus is a function of the number of condensate molecules in the droplet. The deliquescence threshold value of the vapor chemical potential coincides with a maximum in the dependence of the condensate chemical potential in the heterogeneous droplet on the number of condensate molecules in the droplet. In the case of high solubility of the matter of condensation nuclei in the liquid condensate, this maximum turns to be below the equilibrium value of the condensate chemical potential ~~in the case of~~ flat interface between liquid and vapor phases of pure condensate. Thus the deliquescence threshold value of the vapor chemical potential corresponds to negative vapor supersaturations and can be well observed in undersaturated vapor [5].

Y for

Below the deliquescence threshold, the kinetic theory of heterogeneous nucleation [6, 7, 8] provides a link between thermodynamics and experimental data on nucleation rates and characteristic times. The kinetic theory requires knowledge of the direct (deliquescence) and reversal (efflorescence) activation barriers for the transition of the droplet between the states with partially and completely dissolved nucleus. If we decrease the vapor chemical potential below the deliquescence threshold, the probability of overcoming the direct activation barrier stays significant only at small deviations from the threshold.

✓ [6-8]

We will extend in this paper the description of the deliquescence stage of soluble nuclei in undersaturated vapor by investigation of the dependence of the deliquescence and efflorescence barriers on the vapor undersaturation. First we will study the behaviour of minima and saddle points of the work of droplet formation on soluble condensation nucleus as functions of the nucleus size and vapor chemical potential. As a next step, the values of the direct and reversal activation barriers will be numerically found. For a droplet formed around partially dissolved condensation nucleus, the analysis of coefficients of the quadratic forms of the work of the droplet formation in the vicinities of extrema of the work will be performed. This analysis will allow us to establish and explain the important new fact: exchange of roles of thermodynamically stable and thermodynamically unstable variables in transitions over the deliquescence and efflorescence barriers at values of the vapor chemical potential near the deliquescence threshold and noticeably below it but far from reaching the efflorescence threshold.

18.2 Two-dimensional Surface of the Work of Droplet Formation

As was shown in [4], the work $W(\nu, \nu'_n)$ of droplet formation on a partially dissolved nucleus (determined as a function of the number ν of molecules condensed in the droplet out of vapor, the number ν'_n of molecules in spherical residue of condensation nucleus, and the chemical potential μ^β of vapor molecules at absolute temperature T) has the following form in the approximation of an ideal solution within the liquid film around the residue of nucleus:

$$\begin{aligned}
 W = & -\nu (\mu^\beta - \mu_\infty) + k_B T (\nu_n - \nu'_n) \left(\ln \left(\frac{x}{x_\infty} \right) - 1 \right) + 4\pi R_n'^2 \sigma^{\gamma\alpha} + \\
 & + 4\pi R^2 \sigma^{\alpha\beta} - 4\pi R_n^2 \sigma^{\gamma\beta} + 4\pi R_n'^2 l K \exp \left[-\frac{(R - R'_n)}{l} \right],
 \end{aligned}
 \tag{18.1}$$

where μ_∞ is the equilibrium value of the condensate chemical potential in the case of flat interface between liquid and vapor phases of pure condensate, k_B is the Boltzmann constant, ν_n is the initial number of molecules within the soluble nucleus, $x = (\nu_n - \nu'_n)/\nu$ is the relative bulk solute concentration (in the solution with the same chemical potentials of the solvent and solute molecules as in the thin liquid film around the residue of the nucleus), x_∞ is the solubility of the nucleus matter at equilibrium with a flat interface between solid phase of the nucleus matter and the bulk solution. Indices α , β and γ mark the quantities referred to the liquid, vapor and solid phases, correspondingly, while the double indices $\gamma\beta$, $\gamma\alpha$ and $\alpha\beta$ mark the quantities referred to the interfaces between the solid particle and vapor, solid particle and liquid film, the film and the vapor, respectively; $\sigma^{\gamma\beta}$, $\sigma^{\gamma\alpha}$ and $\sigma^{\alpha\beta}$ are the surface tensions referred to indicated interfaces. $4\pi R_n^2$, $4\pi R'_n{}^2$ and $4\pi R^2$ are the areas of spherical surfaces with radii R_n , R'_n and R . The last term in Eq. (18.1) takes into account the effect of overlapping of the liquid film surface layers at the boundaries with the vapor and the residue of the nucleus. This overlapping is responsible for existence of the disjoining pressure in the film. It is assumed in Eq. (18.1) that the structural component Π_D of the disjoining pressure plays the main role: $\Pi_D = K \exp [-(R - R'_n)/l]$ [6, 9, 10] where $K = (\sigma^{\gamma\beta} - \sigma^{\alpha\gamma} - \sigma^{\alpha\beta})/l$ and l are the parameters of the isotherm of structural component of the disjoining pressure.

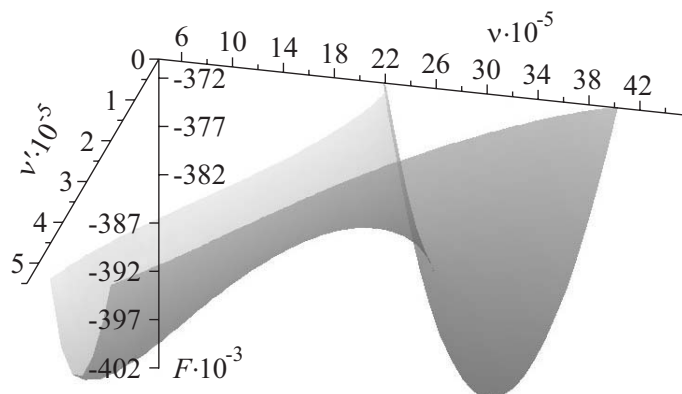


Fig. 18.1 Surface of the work $F(\nu, \nu'_n)$ of droplet formation at the vapor chemical potential $b = -0.2$.

Under the assumption of nonvolatile nucleus matter and negligible adsorption of condensate and dissolved matter of nucleus at the boundaries of the liquid film in the droplet, the number ν of condensate molecules in the droplet with partially dissolved nucleus may be related to the droplet volume $V_R = 4\pi R^3/3$, to the

volume of the nucleus residue $V_{R'_n} = 4\pi R_n'^3/3$, to the numbers $\nu_n = 4\pi R_n^3/3v_n$ and $\nu'_n = 4\pi R_n'^3/3v_n$ of molecules in the nucleus and its residue (v_n is the specific molecular volume of the nucleus matter in solid phase) by the relation

$$\nu = [V_R - V_{R'_n} - v_n^\alpha (\nu_n - \nu'_n)] / v^\alpha, \quad (18.2)$$

where v^α and v_n^α are the partial molecular volumes in bulk solution for solvent and solute, respectively.

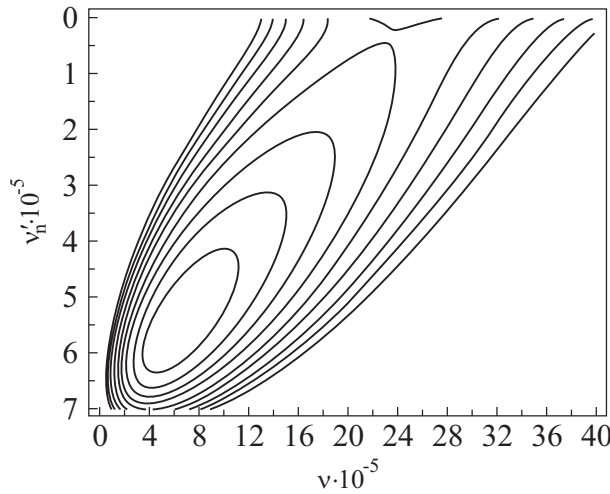


Fig. 18.2 Level lines of the work $F(\nu, \nu'_n)$ of droplet formation at the vapor chemical potential $b = -0.25$.

We will deal below with the dimensionless work of droplet formation $F \equiv W/k_B T$ and the dimensionless chemical potential of vapor $b \equiv (\mu^\beta - \mu_\infty) / k_B T$. The computed surface of the dimensionless work of droplet formation $F(\nu, \nu'_n)$ is shown in Fig. 18.1 for the value $b = -0.2$ of the vapor chemical potential. This surface of the work has been computed with Eqs. (18.1) and (18.2) and following numerical values for the parameters:

$$\begin{aligned} R_n &= 15 \cdot 10^{-7} \text{ cm}, & v_n &= 2 \cdot 10^{-23} \text{ cm}^3, \\ v^\alpha &= 3 \cdot 10^{-23} \text{ cm}^3, & v_n^\alpha &= 2.2 \cdot 10^{-23} \text{ cm}^3, \\ T &= 298 \text{ K}, & \sigma^{\alpha\gamma} &= 200 \text{ dyn/cm}, & \sigma^{\alpha\beta} &= 72 \text{ dyn/cm}, \\ x_\infty &= 0.2, & l &= 2 \cdot 10^{-7} \text{ cm}, & K &= 3 \cdot 10^9 \text{ dyn/cm}^2. \end{aligned} \quad (18.3)$$

Profile of the bottom of the surface of work $F(\nu, \nu'_n)$ of droplet formation in Fig. 18.1 corresponds to a specific (equilibrium) path of transition of the condensing droplet between the states with partially and completely dissolved nucleus that goes through the states where the residue of the nucleus stays in equilibrium with solution in the liquid film. This path is clearly visible in Fig. 18.1 as the valley-line with minimum and maximum. The similar path has no maximum in the case of droplet formation at the value $b = -0.25$ of the vapor chemical potential. So we used in Fig. 18.2 the lines of level to show the behaviour of the work $F(\nu, \nu'_n)$ of droplet formation at the value $b = -0.25$ of the vapor chemical potential. Fig. 18.1 illustrates the situation when the droplet state with completely dissolved nucleus is more stable than the droplet state with partially dissolved nucleus because the minimum of the work $F(\nu, \nu'_n)$ at the state of complete dissolution of nucleus in droplet is deeper than the minimum at the state with partially dissolved nucleus. Fig. 18.2 illustrates the opposite case when the state with partially dissolved nucleus corresponds to deeper minimum of the work $F(\nu, \nu'_n)$ than the state with completely dissolved nucleus.

Previously [4], within the framework of the one-dimensional kinetic approach associated with the equilibrium path of droplet transition from the state with partially dissolved nucleus to the state with completely dissolved nucleus, we did not consider heterogeneous nucleation at such notable undersaturations of vapor as in the case corresponding to the value of the vapor chemical potential $b = -0.25$. The one-dimensional kinetic approach is applicable in the vicinity of the deliquescence threshold. The deliquescence transition is impossible noticeably below the deliquescence threshold, but the efflorescence transition may take place if we already have a distribution of droplets with completely dissolved nuclei.

Below we will analyze the well and saddle points of the work $F(\nu, \nu'_n)$ of heterogeneous droplet formation and their two-dimensional neighborhoods in variables ν and ν'_n at any concentration of undersaturated vapor, keeping in mind not only the kinetics of direct transitions with dissolution of nucleus in droplet but also the development of kinetics of reversal transitions with crystallization of nucleus in droplet of solution.

18.3 Well and Saddle Points of the Work of Droplet Formation at Partial Dissolution of the Nucleus

The equations for extreme points of the work $W(\nu, \nu'_n)$ of droplet formation at partial dissolution of the nucleus serve as conditions of chemical equilibrium within the droplet with respect to the solvent and solute. These conditions lead to

the Gibbs-Kelvin-Kohler and Ostwald-Freudlich equations [4], respectively:

$$\mu^\beta - \mu_\infty = k_B T \frac{\nu_n - \nu'_n(\nu)}{\nu} - \frac{2\sigma^{\alpha\beta} v^\alpha}{R} + \frac{R_n'^2}{R^2} K v^\alpha \exp\left[-\frac{(R - R'_n)}{l}\right], \quad (18.4)$$

$$k_B T \ln\left(\frac{\nu_n - \nu'_n(\nu)}{\nu x_\infty}\right) = \frac{2v_n}{R'_n(\nu)} \left[\sigma^{\alpha\gamma} + lK \exp\left(-\frac{R - R'_n(\nu)}{l}\right) \right] \quad (18.5)$$

$$- \frac{2\sigma^{\alpha\beta} (v_n^\alpha - v_n)}{R} + K \exp\left(-\frac{R - R'_n(\nu)}{l}\right) \left[v_n - \frac{R_n'^2(\nu)}{R^2} (v_n - v_n^\alpha) \right].$$

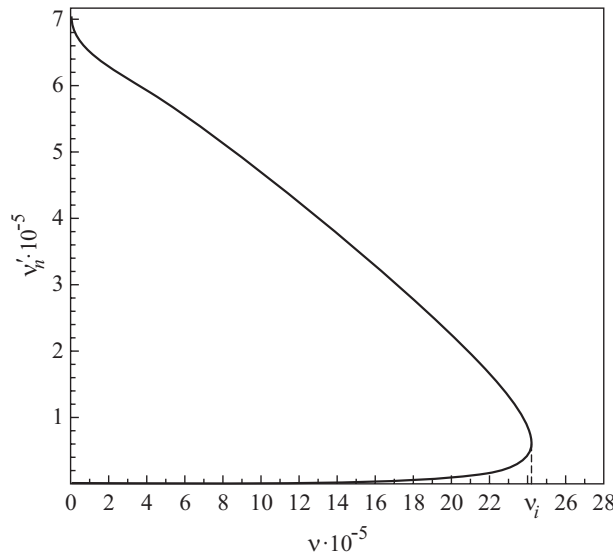


Fig. 18.3 Dependence of equilibrium values of ν'_n on ν .

The numerical solution of the equation Eq. (18.4) with the help of Eqs. (18.2) and (18.3) allows us to determine an equilibrium path $\nu'_n(\nu)$ which is depicted in Fig. 18.3. We see that the path $\nu'_n(\nu)$ has a turning point at $\nu = \nu_i$. The solution in a droplet cannot be in equilibrium with the residue of nucleus at $\nu > \nu_i$. It means that the nucleus should be completely dissolved in the droplet in equilibrium state at $\nu > \nu_i$. Let us notice that ν_i depends on the initial number ν_n of molecules in the nucleus as the external parameter of the task.

If a value of the number ν of condensate molecules in a droplet is not arbitrary but satisfies Eq. (18.4) at a specified value of dimensionless vapor chemical potential

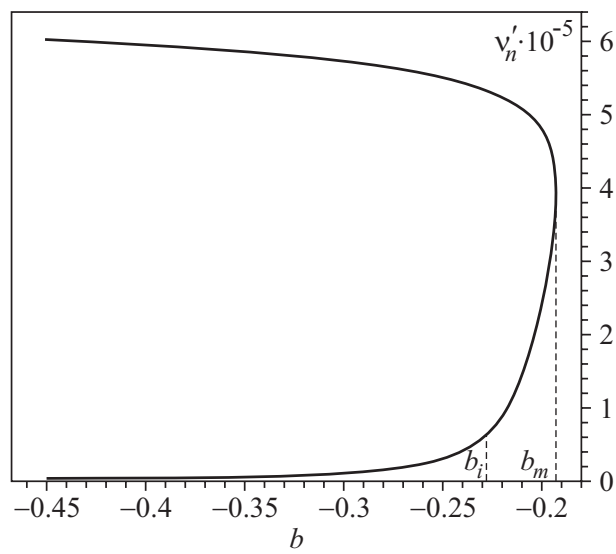


Fig. 18.4 Dependence of equilibrium values of ν'_n on dimensionless vapor chemical potential b .

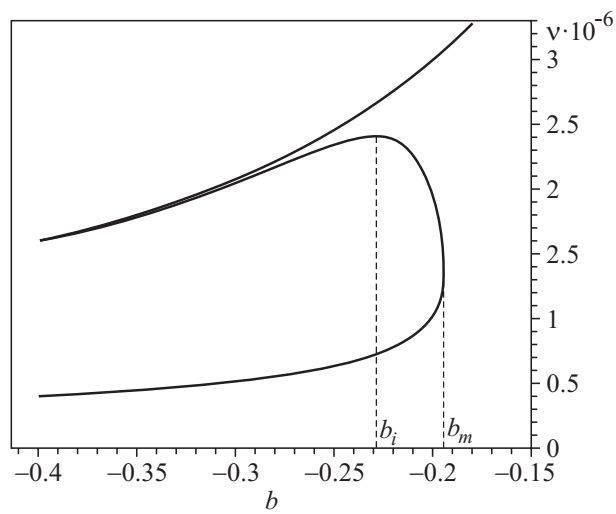


Fig. 18.5 Dependence of equilibrium values of ν on dimensionless vapor chemical potential b .

b , then the points of the path $\nu'_n(\nu)$ in Fig. 18.3 correspond to different values of b . In particular, the point $\nu'_n(\nu_i)$ at $\nu = \nu_i$ corresponds to the value $b = b_i$. The dependences of equilibrium values of ν'_n and ν on b , obtained as a result of

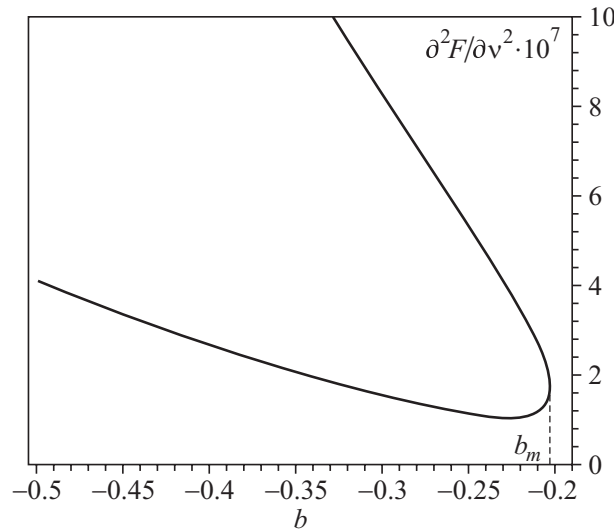


Fig. 18.6 Dependence of the second-order derivative ($\partial^2 F / \partial \nu^2$) on dimensionless vapor chemical potential b for equilibrium $\nu'_n = \nu'_n(b)$ and $\nu = \nu(b)$.

simultaneous numerical solution of Eqs. (18.4) and (18.5) with use of Eqs. (18.2) and (18.3), are shown in Figs. 18.4 and 18.5. The upper curve for $\nu(b)$ in Fig. 18.5 corresponds to the droplet state with completely dissolved nucleus and the lower curve (with turning points $b = b_i$ and $b = b_m$) corresponds to the state with partially dissolved nucleus.

As can be seen from Fig. 18.4 and Fig. 18.5, there are no stable equilibrium values of ν'_n and ν in the state with partially dissolved nucleus at $b > b_m$, but there are stable values of ν at the state of full dissolution of the nucleus. Obviously, the value b_m coincides with the deliquescence threshold value of vapor chemical potential for transition of droplet from the states with partially dissolved nucleus to states with completely dissolved nucleus.

Let us now separate the equilibrium values of $\nu'_n(b)$ and $\nu(b)$ in Figs. 18.4 and 18.5 with respect to minimum and saddle points of the work of droplet formation in the state at incomplete dissolved nucleus in the droplet. We will mark quantities taken at the minimum and saddle points with the lower indices e and c , respectively.

As is known, the criteria of a minimum of the work $F(\nu, \nu'_n)$ as a function of two variables can be written as

$$\left. \frac{\partial F}{\partial \nu} \right|_{\nu_e, \nu'_n(\nu_e)} = 0, \quad \left. \frac{\partial F}{\partial \nu'_n} \right|_{\nu_e, \nu'_n(\nu_e)} = 0, \quad (18.6)$$

$$\left. \frac{\partial^2 F}{\partial \nu^2} \right|_{\nu_e, \nu'_n(\nu_e)} > 0, \quad D|_{\nu_e, \nu'_n(\nu_e)} > 0, \quad (18.7)$$

where

$$D \equiv \left(\frac{\partial^2 F}{\partial \nu^2} \right) \left(\frac{\partial^2 F}{\partial \nu'^2_n} \right) - \left(\frac{\partial^2 F}{\partial \nu \partial \nu'_n} \right)^2. \quad (18.8)$$

The corresponding criteria of a saddle point of the work $F(\nu, \nu'_n)$ have the form

$$\left. \frac{\partial F}{\partial \nu} \right|_{\nu_c, \nu'_n(\nu_c)} = 0, \quad \left. \frac{\partial F}{\partial \nu'_n} \right|_{\nu_c, \nu'_n(\nu_c)} = 0, \quad D|_{\nu_c, \nu'_n(\nu_c)} < 0. \quad (18.9)$$

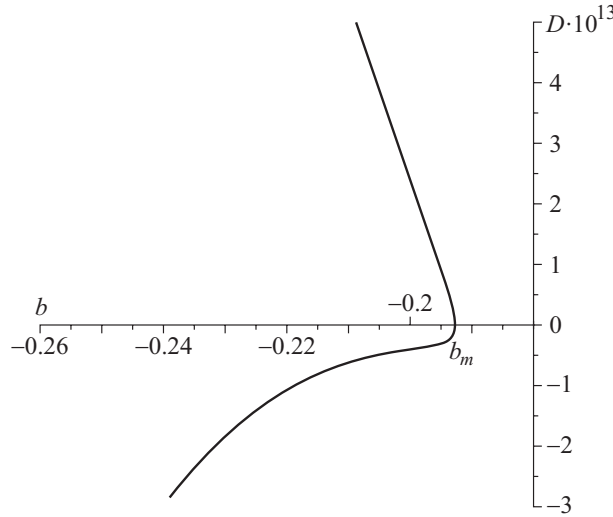


Fig. 18.7 Dependence of D on dimensionless vapor chemical potential b .

The behaviour of the quantities $\partial^2 F / \partial \nu^2$ and D in their dependences on the vapor chemical potential is shown in Figs. 18.6 and 18.7, respectively. These quantities have been calculated for a droplet with partially dissolved nucleus of condensation with Eqs. (18.1)–(18.3) at equilibrium values of $\nu'_n = \nu'_n(b)$ and $\nu = \nu(b)$ (which correspond to the curves in Figs. 18.4 and 18.5) at different values of vapor chemical potential. As follows from Eqs. (18.6) and (18.9), the points $\nu'_n = \nu'_n(b)$ and $\nu_c = \nu(b)$ at values b for which the curve D in Fig. 18.7 lies below zero, coincide with the saddle points of the work of droplet formation. We have at this $0 < \nu'_n(\nu_c) < \nu'_n(b_m)$ and $\nu(b_m) < \nu_c < \nu(b_i)$. The points $\nu'_n = \nu'_n(b)$

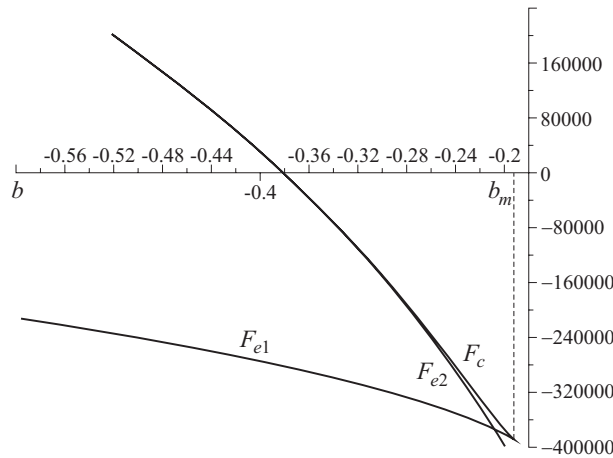


Fig. 18.8 Dependence of minima and saddle point of the work F of droplet formation on dimensionless vapor chemical potential b .

and $\nu_e = \nu(b)$ at values b for which the curve D in Fig. 18.7 lies above zero, coincide with the minimum points of the work of droplet formation. We have at this $\nu'_n(b_m) < \nu'_n(\nu_e) < \nu_n$ and $0 < \nu_e < \nu(b_m)$.

The results obtained, together with Eqs. (18.1)–(18.3), allow us to study the behaviour of the values F_{e1} , F_{e2} of the work of droplet formation in the minima points at partial and complete dissolution of nucleus and the behavior of the values F_c of the work of droplet formation in the saddle points. The corresponding dependences of F_{e1} , F_{e2} and F_c on the vapor chemical potential are presented in Fig. 18.8. As we can see from Fig. 18.8, the curves of F_{e1} and F_c converge at the deliquescence threshold value $b = b_m$ of vapor chemical potential. The curves of F_{e1} and F_{e2} can intersect at some value of the chemical potential. This means that the values of direct $\Delta F_1 \equiv F_c - F_{e1}$ and reversal $\Delta F_2 \equiv F_c - F_{e2}$ activation barriers for transition of droplet between states with partially and completely dissolved nucleus become equal at this value.

For clarity sake, the dependences of deliquescence and efflorescence barriers on the vapor chemical potential are shown in Fig. 18.9. It should be noted that transitions between the states of the droplet with partially and completely dissolved nucleus are possible in a real situation only at $\Delta F_{1,2} \ll 100$. As follows from Fig. 18.9, the activation barrier ΔF_1 is small at those values of undersaturated vapor chemical potential, at which the activation barrier ΔF_2 is always very high, and on the contrary, the activation barrier ΔF_2 is small at those values of vapor chemical potential, at which the activation barrier ΔF_1 appears to be high. As

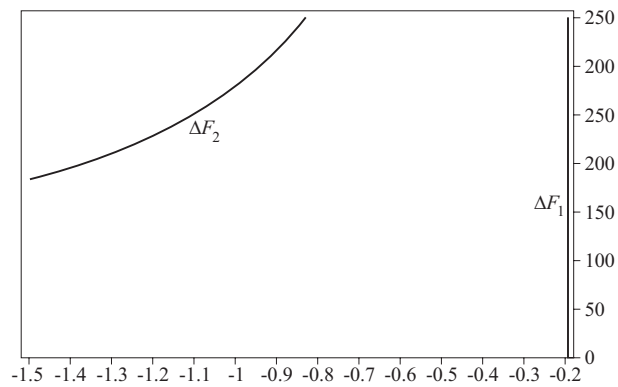


Fig. 18.9 Dependence of values of direct ΔF_1 and reversal ΔF_2 activation barriers on dimensionless vapor chemical potential b .

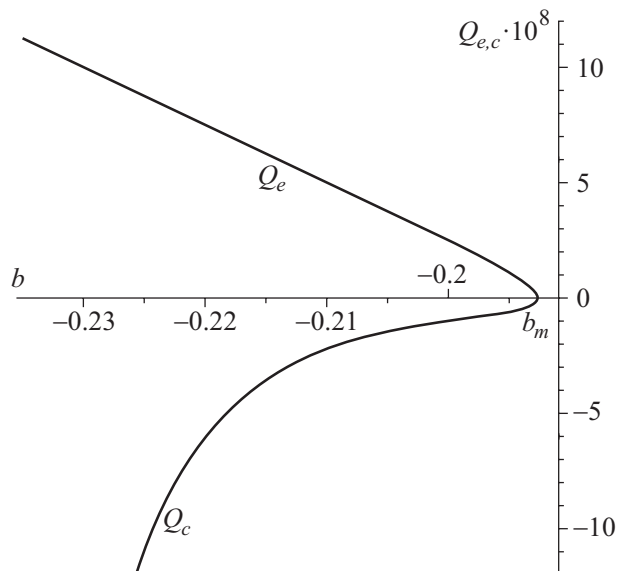


Fig. 18.10 Dependence of coefficients Q_e and Q_c on dimensionless vapor chemical potential b .

can be seen from Fig. 18.9, the range of values of the vapor chemical potential, which is of importance for deliquescence transition, lies in the very narrow vicinity of the deliquescence threshold below $b = b_m = -0.193$. The range of values of

the vapor chemical potential, which is of importance for efflorescence transition, lies in the vicinity of the efflorescence threshold at $b = b_{eff} < -1.5$.

18.4 Stable and Unstable Variables of the Droplet State

In order to describe the overcoming the activation barrier in kinetics of nucleation, one needs to know the behaviour of the work of droplet formation only in rather small neighborhoods of extreme points of the work. In these neighborhoods, the work $F(\nu, \nu'_n)$ can be approximated by the quadratic form in deviations $\nu - \nu_{e,c}$ and $\nu'_n - \nu'_{n_{e,c}}$:

$$F = F_{e,c} + \frac{1}{2} \left(\frac{\partial^2 F}{\partial \nu^2} \right)_{e,c} (\nu - \nu_{e,c})^2 + \left(\frac{\partial^2 F}{\partial \nu \partial \nu'_n} \right)_{e,c} (\nu - \nu_{e,c})(\nu'_n - \nu'_{n_{e,c}}) + \frac{1}{2} \left(\frac{\partial^2 F}{\partial \nu'^2_n} \right)_{e,c} (\nu'_n - \nu'_{n_{e,c}})^2. \quad (18.10)$$

As was already noticed, the bottom indices e and c mark the values referring to the minimum and saddle point of the work at incomplete dissolution of the nucleus, respectively. Thus the quadratic form in Eq. (18.10) refers to both the well and saddle neighborhoods.

The quadratic form in Eq. (18.10) can be reduced to a diagonal form in new variables $y^{(e,c)}$ and $z^{(e,c)}$ with the help of linear transformations [11, 12, 13]:

$$F = F_{e,c} + Q_{e,c} \left(y^{(e,c)} \right)^2 + P_{e,c} \left(z^{(e,c)} \right)^2, \quad (18.11)$$

$$y^{(e,c)} = (\nu - \nu_{e,c}) \cos \varphi_{e,c} + (\nu'_n - \nu'_{n_{e,c}}) \sin \varphi_{e,c}, \quad (18.12)$$

$$z^{(e,c)} = -(\nu - \nu_{e,c}) \sin \varphi_{e,c} + (\nu'_n - \nu'_{n_{e,c}}) \cos \varphi_{e,c}. \quad (18.13)$$

The coefficients $Q_{e,c}$ and $P_{e,c}$ in Eq. (18.11) and the parameter $\varphi_{e,c}$ of the transformations in Eqs. (18.12) and (18.13) are determined with the help of second derivatives of the work $F(\nu, \nu'_n)$ by [7]:

$$Q_{e,c} = \frac{1}{2} \left[\left(\frac{\partial^2 F}{\partial \nu^2} \right)_{e,c} \cos^2 \varphi_{e,c} + \left(\frac{\partial^2 F}{\partial \nu \partial \nu'_n} \right)_{e,c} \sin 2\varphi_{e,c} + \left(\frac{\partial^2 F}{\partial \nu'^2_n} \right)_{e,c} \sin^2 \varphi_{e,c} \right],$$

$$P_{e,c} = \frac{1}{2} \left[\left(\frac{\partial^2 F}{\partial \nu^2} \right)_{e,c} \sin^2 \varphi_{e,c} - \left(\frac{\partial^2 F}{\partial \nu \partial \nu'_n} \right)_{e,c} \sin 2\varphi_{e,c} + \left(\frac{\partial^2 F}{\partial \nu_n'^2} \right)_{e,c} \cos^2 \varphi_{e,c} \right],$$

$$\operatorname{tg} 2\varphi_{e,c} = \frac{2 \left(\frac{\partial^2 F}{\partial \nu \partial \nu'_n} \right)_{e,c}}{\left(\frac{\partial^2 F}{\partial \nu^2} \right)_{e,c} - \left(\frac{\partial^2 F}{\partial \nu_n'^2} \right)_{e,c}}. \quad (18.14)$$

It is interesting to investigate the dependence of the coefficients $Q_{e,c}$ and $P_{e,c}$ on the vapor chemical potential b . The behaviour of the coefficients $Q_{e,c}$ and $P_{e,c}$ near the threshold value $b = b_m$ of the vapor chemical potential is shown in Figs. 18.10 and 18.11. The curves of Q_e and Q_c , as well as curves P_e and P_c , merge at the threshold value $b = b_m$ of the vapor chemical potential.

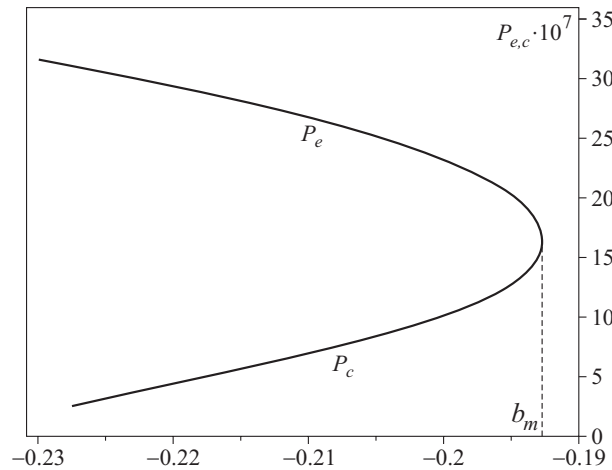


Fig. 18.11 Dependence of coefficients P_e and P_c on dimensionless vapor chemical potential b .

As follows from Fig. 18.10, $Q_c < 0$ and $Q_e > 0$. As follows from Fig. 18.11, $P_e > 0$ at any $b \leq b_m$, whereas P_c remains positive only at $b_i < b \leq b_m$. It was noticed in [11, 12, 13], that the positive coefficient before a squared variable in the diagonalized form in Eq. (18.11) means, that this variable is stable during phase transformation, i.e. the droplet tends to return to an equilibrium state after deviation of this variable from its equilibrium value. Negative coefficient before a squared variable in the diagonalized form in Eq. (18.11) means, that this variable is unstable during the phase transformation, i.e. the phase transformation occurs with changing this variable. Thus the variable $y^{(c)}$ is unstable while the variable

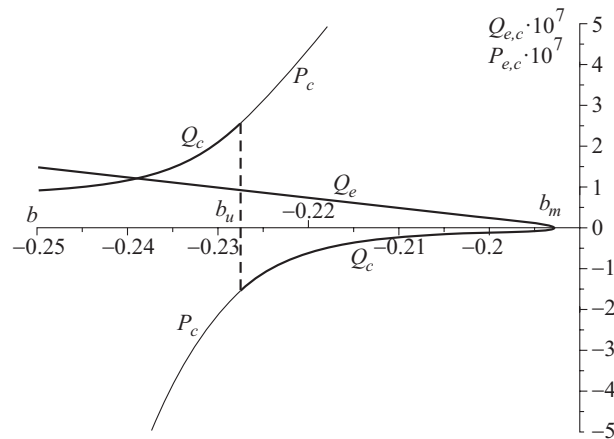


Fig. 18.12 Switching of coefficients Q_c and P_c in the neighborhood of the value $b = b_i$.

$z^{(c)}$ is stable in transitions over direct and reversal activation barriers slightly below the deliquescence threshold.

Let us see the behaviour of coefficients Q_c and P_c in the range of values of vapor chemical potential $b \leq b_i$ which is noticeably below the deliquescence threshold but can be well above the efflorescence threshold. As follows from Fig. 18.12, there is a jump of coefficients Q_c and P_c at the point $b = b_u$, $b_i \lesssim b_u$. Both coefficients change their signs with passing $b = b_u$, the coefficient Q_c becomes positive at $b < b_u$ whereas it was negative at $b > b_u$, and the coefficient P_c becomes negative at $b < b_u$ whereas it was positive at $b > b_u$. Therefore we can say that the variables $y^{(c)}$ and $z^{(c)}$ interchange their roles with passing $b = b_u$. The variable $y^{(c)}$ becomes thermodynamically stable and the variable $z^{(c)}$ turns to be thermodynamically unstable in transitions over the deliquescence and efflorescence activation barriers below $b = b_u$. This interchange of the roles of variables corresponds to switching (with decreasing the vapor chemical potential) from the heterogeneous nucleation of droplets on condensation nuclei in the vapor (with slow dissolution of the nucleus in the droplet and fast increasing the droplet size) to fast homogeneous crystallization of nuclei in the existing droplets consisted of supersaturated solution (with slow decreasing the droplet size).

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