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The laws of establishing stationary composition in a droplet condensing in a binary vapor–gas environment

Fedor M. Kuni, Alexandra A. Lezova, Alexander K. Shchekin*

Department of Statistical Physics, St Petersburg State University, Ulyanovskaya 1, Petrodvorets, St Petersburg, 198504, Russian Federation

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ABSTRACT

It is shown that the mole fractions of components within a droplet growing in an atmosphere of two condensing gases and a carrier gas approach their stationary values with a power-law behavior in time on a large scale and with exponential behavior on a small scale for both diffusion-controlled and free-molecular regimes of isothermal condensation. The parameters of the power and the exponential laws are specified for each regime of binary condensation and are linked to the thermodynamic and kinetic characteristics of condensing vapors and to the stationary mole fractions of the components in a growing binary droplet. The stationary composition of the solution within the droplet is shown to be established at a comparatively small relative increase of the droplet radius. A relaxation equation for the droplet composition at arbitrary initial deviations of mole fractions from their stationary values has been solved, and the limitations on the initial deviations allowing monotonic establishment of stationary composition in solution within a growing droplet have been considered.

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0. Introduction

The formation and growth of droplets in binary or multicomponent vapors is a common phenomenon, the understanding of which is very important in the physics of phase transitions and environmental sciences as well as in many branches of technological applications and chemical engineering. This paper proposes an analytical investigation of the regularities of establishment of a stationary concentration in the binary solution within a supercritical droplet growing in an atmosphere of two condensing vapors and a carrier gas. This investigation is a necessary step in establishing hierarchy of the time scales of setting the regimes of droplet growth in the binary condensation process. To study the general case of the hierarchy independently of initial conditions and specific properties of the vapor–gas system, one requires an analytical approach.

The subject of this paper has a direct relation to the problems of aerosol formation investigated earlier. It has a relevance to kinetic theory of binary nucleation, which includes thermal effects and the effects of vapor inflow and has been developed in Refs. [1,2]. It is close to the subject of Refs. [3–5], where several analytical and numerical models for the growth of a single binary supercritical droplet under isothermal and non-isothermal conditions have been proposed (the generalization of these models to droplet growth due to non-isothermal multicomponent condensation has been considered in Ref. [6]).

It was found in Refs. [3–5] that, if the vapor pressures of condensing species and the temperature far from the droplet do not change in time, the mole fractions of the species within the droplet and the droplet temperature settle to stationary values (independent of the droplet radius) after a short onset stage. When the final mole fractions of the condensing species

* Corresponding author. Tel.: +7 911 9495666; fax: +7 812 4287240.

E-mail address: akshch@list.ru (A.K. Shchekin).

within the droplet and the droplet temperature are settled, the well-known one-half power law for the diffusion-controlled growth and the linear law for the free-molecular growth may be used for the dependence of the droplet radius on time in the theory of binary condensation [7,8]. Finding the regularities and conditions for the above mentioned onset stage in both regimes of droplet growth and revealing the laws for establishing a stationary composition in the droplet are the goals of this paper. These goals have not previously been accomplished; however, the significance of this problem has recently been brought up in Refs. [9,10], where a new self-similar scaling solution of non-stationary binary condensation onto a single supercritical droplet was found. The approach developed in Refs. [9,10] assumes the presence of a constant composition of a solution in a growing droplet, and the questions arise of what are the conditions of establishing this composition and how fast it occurs.

To simplify the problem, we will assume that condensational growth of the droplet is isothermal and of non-Stefan type due to the presence of a large amount of carrier gas. Speaking about a supercritical droplet, we mean that the growth of the droplet is regular one, and the fluctuation, the capillarity (Kelvin) and adsorption effects can be neglected for markedly supercritical droplets. We will not consider here the transitional growth regime for a binary droplet, for which a simple interpolation model in the Knudsen number [3,8] can be used, because the stationary composition of the droplet in this regime depends on the droplet radius and is not a constant.

As a first step, we will find analytically the times between the moment of nucleation of a markedly supercritical droplet and the moment of reaching the power-law-in-time behavior of the droplet radius under diffusion-controlled or free-molecular regimes of isothermal binary vapor condensation. As a second step, we will derive the power laws of establishing stationary composition in the binary solution within a growing droplet under the same regimes of binary condensation on the large time scales allowing power-law growth of the droplet radius. As a third step, we consider the possibility of an exponential law for establishing the stationary concentrations under both regimes of binary condensation on the small time scales when the droplet radius is practically unchanged. It will be shown how the parameters of the power and exponential laws are specified for each regime of binary condensation and how they are linked to the thermodynamic and kinetic characteristics of the condensing components in the gas environment and to the stationary mole fractions of these components in the binary droplet. To do that, we will extend the analytical results [3] related to finding the stationary concentration of the binary solution within a supercritical growing droplet to the case of a free-molecular regime. These results are important for setting links between the parameters of the laws of establishing the stationary concentrations in a droplet in time, because the parameters themselves depend on these stationary concentrations.

1. General relations of binary condensation onto a droplet

Let n_1 and n_2 be the numbers of molecules of the first and the second components in the liquid solution within the droplet. We denote the partial molecular volumes of these components in the solution as v_1 and v_2 . The mole fractions x_1 and x_2 of the first and second components in the liquid solution can be written as

$$x_1 \equiv \frac{n_1}{n_1 + n_2}, \quad x_2 \equiv 1 - x_1 \equiv \frac{n_2}{n_1 + n_2} \quad (0 < x_1 < 1, \quad 0 < x_2 < 1). \quad (1.1)$$

Obtaining the equality $(1 - x_1)n_1 = x_1 n_2$ from Eq. (1.1) and differentiating this equality with respect to time t , we have

$$(n_1 + n_2) \frac{dx_1}{dt} = (1 - x_1) \frac{dn_1}{dt} - x_1 \frac{dn_2}{dt}. \quad (1.2)$$

This equation will be the key one for the following analysis.

As the total volume of the solution in the droplet is the first order homogeneous function with respect to n_1 and n_2 and the partial volumes v_1 and v_2 are zero order homogeneous functions with respect to n_1 and n_2 , then

$$v_1 n_1 + v_2 n_2 = 4\pi R^3/3 \quad (1.3)$$

where R is the droplet radius. As follows from Eqs. (1.1) and (1.3),

$$n_1 + n_2 = \frac{4\pi R^3}{3} \frac{1}{x_1 v_1 + (1 - x_1) v_2}. \quad (1.4)$$

Let ρ_1 and ρ_2 be the number densities of molecules of the first and the second components in the vapor–gas environment far away from the droplet. We denote as $\rho_{1\infty}(x_1)$ and $\rho_{2\infty}(x_2)$ the equilibrium (saturated over liquid solution with mole fractions x_1 and x_2) values of these densities near the droplet surface.

We consider the vapor mixture to be metastable with respect to each component. That means

$$\rho_1 > \rho_{1\infty}(x_1), \quad \rho_2 > \rho_{2\infty}(x_2). \quad (1.5)$$

To provide condensation of both vapor components onto droplet, both conditions (1.5) are required.

According to the equations of an ideal solution,

$$\rho_{1\infty}(x_1) = \tilde{\rho}_{1\infty} x_1, \quad \rho_{2\infty}(x_2) = \tilde{\rho}_{2\infty} x_2 \quad (1.6)$$

where $\tilde{\rho}_{1\infty}$ and $\tilde{\rho}_{2\infty}$ are the number densities of molecules of saturated vapors over pure liquids of the first and the second components. For non-ideal solutions, the right-hand sides of relations in Eq. (1.6) can be represented as the following series in the mole fractions

$$\rho_{1\infty}(x_1) = \tilde{\rho}_{1\infty}x_1 + \sum_{k=2} \alpha_k^{(1)}x_1^k, \quad \rho_{2\infty}(x_2) = \tilde{\rho}_{2\infty}x_2 + \sum_{k=2} \alpha_k^{(2)}x_2^k \quad (1.7)$$

where the first terms correspond to the ideal approximation, $\alpha_k^{(1)}$ and $\alpha_k^{(2)}$ ($k = 2, 3, \dots$) are the coefficients of the series for the first and second components, respectively.

2. Diffusion-controlled regime of droplet growth

Let us first consider binary condensation in the continuum diffusion-controlled regime. The amounts of condensing vapors are assumed to be much smaller than the amount of carrier gas. In this case one can consider droplet growth as an isothermal process. Furthermore, the diffusion of condensing components may be regarded as binary diffusion through the carrier gas, uncoupled from vapor–vapor interactions. The Stefan flow is also negligible under this assumption [7]. The isothermal droplet growth runs in the diffusion-controlled regime if the strong inequality $R/\lambda \gg 1$ is valid, where λ is the free path length of vapor molecules in the carrier gas. The corresponding Maxwell equations for numbers n_1 and n_2 of molecules of the condensing components in a droplet have the form [7] (even in the case of a self-similar scaling solution of the binary condensation [9,10])

$$\frac{dn_1}{dt} = 4\pi D_1 [\rho_1 - \rho_{1\infty}(x_1)] R, \quad \frac{dn_2}{dt} = 4\pi D_2 [\rho_2 - \rho_{2\infty}(x_2)] R \quad (2.1)$$

where D_1 and D_2 are the diffusion coefficients for molecules of vapors in the carrier gas.

Let x_{1s} be the stationary mole fraction of the first component in the solution within a growing droplet. Taking into account that $dx_{1s}/dt = 0$ and using Eqs. (1.2) and (2.1), we find

$$\frac{D_1 [\rho_1 - \rho_{1\infty}(x_{1s})]}{D_2 [\rho_2 - \rho_{2\infty}(1 - x_{1s})]} = \frac{x_{1s}}{1 - x_{1s}}. \quad (2.2)$$

According to the thermodynamic stability conditions of solutions [11] one has $\partial \rho_{1\infty}(x_{1s}) / \partial x_{1s} > 0$ and $\partial \rho_{2\infty}(1 - x_{1s}) / \partial x_{1s} < 0$. Then, in view of the conditions (1.5), Eq. (2.2) unambiguously determines x_{1s} (because the left- and the right-hand sides of Eq. (2.2) vary in opposite directions on changing x_{1s}) and provides $0 < x_{1s} < 1$. Eq. (2.2) was first derived in Ref. [3].

Let us differentiate both sides of Eq. (1.3) with respect to time t at $x_1 = x_{1s}$ and fixed v_1 and v_2 . Using Eqs. (2.1) at $x_1 = x_{1s}$, we find

$$dR^2/dt = \beta^2 \quad (2.3)$$

where

$$\beta^2 \equiv 2D_1 v_1 [\rho_1 - \rho_{1\infty}(x_{1s})] + 2D_2 v_2 [\rho_2 - \rho_{2\infty}(1 - x_{1s})]. \quad (2.4)$$

Evidently, the positivity of parameter β^2 , that follows from Eqs. (2.4) and (1.5), corresponds to the droplet growth.

We will count off time t from the moment $t = 0$ of nucleation of the markedly supercritical droplet. Let t_D and R_D be the values of time t and droplet radius R , starting from which Eq. (2.3) practically holds. To provide this, one can take $R_D \sim (3-4)\lambda$. Let us next introduce t_0 as a value of time which satisfies the strong inequality $t_0 \gg t_D$. Integrating Eq. (2.3) over time t from t_D to t_0 , we obtain $R_0^2 - R_D^2 = \beta^2(t_0 - t_D)$ where $R_0 \equiv R|_{t=t_0}$. In view of $t_0 \gg t_D$, we have $R_0 \gg R_D$ and can write $R_0^2 = \beta^2 t_0$. Because $R_D \sim (3-4)\lambda$, it is sufficient to take $R_0 \sim (10-20)\lambda$. Then the condition $R/\lambda \gg 1$ of the continuum regime will be valid long before the moment of time t_0 , and, by integrating Eq. (2.3) with respect to time, we find with a good accuracy that droplet radius satisfies the one-half power law growth in time,

$$R = \beta t^{1/2} \quad (t \geq t_0). \quad (2.5)$$

The accuracy of Eq. (2.5) grows with increasing time t over t_0 .

As follows from Eq. (2.5) at $t = t_0$,

$$t_0 = R_0^2 / \beta^2. \quad (2.6)$$

The value t_0 is the time after nucleation of the markedly supercritical droplet, after which the power law (2.5) of droplet radius growth comes into force. With the help of Eq. (2.6) we can rewrite Eq. (2.5) as

$$R/R_0 = (t/t_0)^{1/2} \quad (t \geq t_0). \quad (2.7)$$

Now we consider establishing the stationary mole fractions x_{1s} and x_{2s} in the droplet. With the help of Eq. (1.2), we can formulate an iteration method to find the deviation of fraction x_1 from the stationary fraction x_{1s} within the droplet at an arbitrary moment of time t . We will discuss first large time scales $t \geq t_0$.

As follows from Eqs. (2.5) and (2.4) with account of Eq. (2.2) (which allows us to express $D_2 [\rho_2 - \rho_{2\infty} (1 - x_{1s})]$ through $D_1 [\rho_1 - \rho_{1\infty} (x_{1s})]$), we can rewrite Eq. (1.4) at $t \geq t_0$ as

$$n_1 + n_2 = \frac{8\pi}{3} R t \frac{D_1}{x_{1s}} [\rho_1 - \rho_{1\infty} (x_{1s})] \frac{x_{1s} v_1 + (1 - x_{1s}) v_2}{x_1 v_1 + (1 - x_1) v_2}. \quad (2.8)$$

Using Eqs. (2.1) and taking into account Eq. (2.2), (1.6), (1.7), and equality $x_2 - x_{2s} = -(x_1 - x_{1s})$, one can find

$$(1 - x_1) \frac{dn_1}{dt} - x_1 \frac{dn_2}{dt} = -4\pi (x_1 - x_{1s}) R \frac{D_1}{x_{1s}} [\rho_1 - \rho_{1\infty} (x_{1s})] - 4\pi (x_1 - x_{1s}) R [(1 - x_1) D_1 (\tilde{\rho}_{1\infty} + f_1(x_1)) + x_1 D_2 (\tilde{\rho}_{2\infty} + f_2(x_1))] \quad (2.9)$$

where

$$f_1(x_1) \equiv \frac{\rho_{1\infty}(x_1) - \rho_{1\infty}(x_{1s})}{x_1 - x_{1s}} - \tilde{\rho}_{1\infty} = \sum_{k=2} \alpha_k^{(1)} \frac{x_1^k - x_{1s}^k}{x_1 - x_{1s}}, \quad (2.10)$$

$$f_2(x_1) \equiv \frac{\rho_{2\infty}(x_2) - \rho_{2\infty}(x_{2s})}{x_2 - x_{2s}} - \tilde{\rho}_{2\infty} = \sum_{k=2} \alpha_k^{(2)} \frac{x_2^k - x_{2s}^k}{x_2 - x_{2s}} \quad (2.11)$$

are the non-ideal contributions to the ratios $\frac{\rho_{1\infty}(x_1) - \rho_{1\infty}(x_{1s})}{x_1 - x_{1s}}$ and $\frac{\rho_{2\infty}(x_2) - \rho_{2\infty}(x_{2s})}{x_2 - x_{2s}}$.

Substituting Eqs. (2.8) and (2.9) in Eq. (1.2) and canceling common factors from both sides leads to the following relaxation differential equation for the mole fraction $x_1(t)$ in the solution within a growing binary droplet in the diffusion-controlled regime

$$\frac{dx_1}{dt} = -\frac{3(x_1 - x_{1s})}{2t} \left\{ 1 + \frac{(1 - x_1) x_{1s} D_1 (\tilde{\rho}_{1\infty} + f_1(x_1)) + x_1 x_{1s} D_2 (\tilde{\rho}_{2\infty} + f_2(x_1))}{D_1 [\rho_1 - \rho_{1\infty} (x_{1s})]} \right\} \frac{x_1 v_1 + (1 - x_1) v_2}{x_{1s} v_1 + (1 - x_{1s}) v_2}. \quad (2.12)$$

The fact that Eq. (2.12) contains the factor $x_1 - x_{1s}$, is the principal one for the iteration method of solution of Eq. (1.2) with respect to deviation $x_1 - x_{1s}$. Indeed, the smallness of derivative dx_1/dt when x_1 is close to x_{1s} allowed us to use Eq. (2.5) at $x_1 = x_{1s}$ in the sum $n_1 + n_2$ on the left-hand side of Eq. (1.2). Along with that, Eq. (2.5) does not needed to specify the right-hand side of Eq. (1.2). The right-hand side of Eq. (1.2) has been found in Eq. (2.9) rigorously.

When x_1 is close to x_{1s} , we can substitute with a good accuracy x_1 by x_{1s} in the factors after $x_1 - x_{1s}$ on the right-hand side of Eq. (2.12). Then, solving Eq. (2.12) with the initial condition

$$x_1|_{t=t_0} = x_{10}, \quad (2.13)$$

we obtain on large time scales

$$x_1 - x_{1s} = (x_{10} - x_{1s}) \left(\frac{t_0}{t} \right)^{3(1+\eta)/2} \quad (t \geq t_0) \quad (2.14)$$

where

$$\eta \equiv \frac{x_{1s} [(1 - x_{1s}) D_1 (\tilde{\rho}_{1\infty} + f_1(x_{1s})) + x_{1s} D_2 (\tilde{\rho}_{2\infty} + f_2(x_{1s}))]}{D_1 [\rho_1 - \rho_{1\infty} (x_{1s})]}. \quad (2.15)$$

According to Eq. (2.15), the parameter η depends not only on the thermodynamic ($\tilde{\rho}_{1\infty}$, $\tilde{\rho}_{2\infty}$) and kinetic (D_1 , D_2) characteristics of condensing vapors, but also on the stationary mole fraction x_{1s} itself and the characteristics of the solution non-ideality ($f_1(x_{1s})$, $f_2(x_{1s})$). With the help of Eq. (2.2), one can rewrite Eq. (2.15) in the form that shows the symmetry of the parameter η with respect to the first and the second condensing components. As follows from Eq. (2.15), (2.10), (2.11), and from the thermodynamic stability conditions of solutions [11] and the conditions (1.5), $\eta > 0$. The smallness of the parameter η with respect to unity is not required.

Formula (2.14) expresses the establishment of the stationary composition in the binary solution within a growing droplet with a power law in time. One can see that not only the power law (2.5) of droplet radius growth comes in force after time t_0 , but also the power law (2.14) of the stationary composition establishing in the droplet. Taking into account Eq. (2.7), we can rewrite Eq. (2.14) as

$$x_1 - x_{1s} = (x_{10} - x_{1s}) \left(\frac{R_0}{R} \right)^{3(1+\eta)} \quad (t \geq t_0). \quad (2.16)$$

Since $\eta > 0$, formula (2.16) shows that the stationary composition is established at a comparatively small relative increase of droplet radius (and at a very small relative increase of droplet radius, if inequality $\eta \geq 1$ holds).

Taking $R_0/\lambda \sim 10\text{--}20$, $\lambda \sim 3 \times 10^{-5}$ cm, $D_1 \approx D_2 \sim 2 \times 10^{-1}$ cm² s⁻¹, $v_1 \approx v_2 \sim 3 \times 10^{-23}$ cm³, $\rho_1 - \rho_{1\infty}(x_{1s}) \approx \rho_2 - \rho_{2\infty}(x_{2s}) \sim 10^{18}$ cm⁻³, we obtain with the help of Eqs. (2.6) and (2.4) an estimate for the important time t_0 in the

diffusion-controlled regime of droplet growth,

$$t_0 \sim (10^{-3} - 10^{-2}) \text{ s}. \quad (2.17)$$

Let us consider now the situation when establishment of the stationary composition is so fast that the droplet radius R has no time to grow significantly. Correspondingly, we need to replace Eq. (2.8) in the vicinity of $x_1 = x_{1s}$ by equation

$$n_1 + n_2 = \frac{8\pi}{3} R^3 \frac{D_1}{\beta^2 x_{1s}} [\rho_1 - \rho_{1\infty}(x_{1s})], \quad (2.18)$$

which follows from Eqs. (1.4) and (2.4) with account of Eq. (2.2). Consequently, Eq. (2.12) can be rewritten in the vicinity of $x_1 = x_{1s}$ with the help of Eqs. (2.15) and (2.18) as

$$\frac{dx_1}{dt} = -\frac{3(x_1 - x_{1s})\beta^2}{2R^2} (1 + \eta). \quad (2.19)$$

Integrating Eq. (2.19) with initial condition $x_1|_{t=t_D} = x_{1D}$, we obtain

$$x_1 - x_{1s} = (x_{1D} - x_{1s}) e^{-\frac{t-t_D}{t_x}} \quad (t \geq t_D) \quad (2.20)$$

where time t_x ,

$$t_x \equiv \frac{2R_D^2}{3\beta^2(1+\eta)}, \quad (2.21)$$

represents the characteristic time of exponential relaxation at fixed droplet radius. Because t_D and R_D are the values of time t and droplet radius R , starting from which Eq. (2.3) practically holds, the validity condition of the exponential law (2.20) requires, in view of Eq. (2.3), consistency of two limitations of time $t - t_D$. One of them is a limitation from below,

$$e^{-\frac{t-t_D}{t_x}} \ll 1, \quad (2.22)$$

which means that the relaxation ends for time $t - t_D$. The second is a limitation on the that time from above,

$$\frac{\beta^2(t - t_D)}{R_D^2} \ll 1, \quad (2.23)$$

which means that R^2 does not grow significantly for time $t - t_D$. Both limitations can be joined, with the help of Eq. (2.21), in the form of a double inequality

$$(1-2) < \frac{t - t_D}{t_x} \ll \frac{3}{2} (1 + \eta). \quad (2.24)$$

As one can see, condition (2.24) is fulfilled at $\eta \geq 2$.

It follows from condition (2.23), with account of inequalities $R_0 \gg R_D$, $t_0 \gg t_D$ and Eq. (2.6), that

$$t - t_D \ll t_0 - t_D. \quad (2.25)$$

Thus the exponential law (2.20) is valid on time scales which are considerably smaller than the time scales for the power law (2.14).

3. Free-molecular regime of droplet growth

Let us now consider binary condensation in a free-molecular regime of droplet growth, which is realized at $R/\lambda \ll 1$. As before, the relative amount of carrier gas in the vapor–gas environment is assumed to be sufficiently large to provide isothermal droplet growth and to fix λ as the free molecular path for vapor molecules in the carrier gas. The path λ now determines the width of the Knudsen layer around the markedly supercritical droplet, i.e., the droplet with radius R satisfying inequality $R \geq (3-4) R_c$ where R_c is the critical droplet radius, $R_c \ll \lambda$.

Instead of the diffusion equations (2.1), we now have the free-molecular equations [7] of droplet growth,

$$\frac{dn_1}{dt} = \pi \alpha_1 w_1 [\rho_1 - \rho_{1\infty}(x_1)] R^2, \quad \frac{dn_2}{dt} = \pi \alpha_2 w_2 [\rho_2 - \rho_{2\infty}(x_2)] R^2 \quad (3.1)$$

where α_1 and α_2 ($\alpha_1 \leq 1$, $\alpha_2 \leq 1$) are the accommodation coefficients for molecules of the first and second components of the vapor mixture and w_1 and w_2 are the average thermal velocities of these molecules. As follows from the Gibbs–Kelvin equation, the dependence of saturation vapor concentrations $\rho_{1\infty}(x_1)$ and $\rho_{2\infty}(x_2)$ in Eqs. (3.1) on R can be neglected starting from $R \geq (3-4) R_c$. Notice, that the Gibbs–Kelvin equation also justifies neglecting the dependence of $\rho_{1\infty}(x_1)$ and $\rho_{2\infty}(x_2)$ on R in Eqs. (2.1) for the diffusion-controlled regime of droplet growth.

As follows from Eqs. (3.1) and (1.2), the stationary mole fraction x_{1s} now satisfies the equation

$$\frac{\alpha_1 w_1 [\rho_1 - \rho_{1\infty}(x_{1s})]}{\alpha_2 w_2 [\rho_2 - \rho_{2\infty}(1 - x_{1s})]} = \frac{x_{1s}}{1 - x_{1s}}. \quad (3.2)$$

Differentiating both sides of Eq. (1.3) with respect to time t at $x_1 = x_{1s}$ and fixed v_1 and v_2 , using Eqs. (3.1) and integrating with respect to time, we obtain instead of Eq. (2.5) a linear-in-time law of the droplet radius growth,

$$R = \gamma t \quad (\tau_0 \leq t \leq 4\tau_0) \quad (3.3)$$

where

$$\gamma \equiv \frac{1}{4} \alpha_1 w_1 v_1 [\rho_1 - \rho_{1\infty}(x_{1s})] + \frac{1}{4} \alpha_2 w_2 v_2 [\rho_2 - \rho_{2\infty}(1 - x_{1s})], \quad (3.4)$$

and we set with a good accuracy

$$\tau_0 \equiv 15R_c/\gamma. \quad (3.5)$$

Usually, $R_c \sim 10^{-7}$ cm and $\lambda \sim 3 \times 10^{-5}$ cm. In this case, the linear law (3.3) is valid with a high accuracy at $\tau_0 \leq t \leq 4\tau_0$. Indeed, according to Eqs. (3.3) and (3.5), we have $15R_c \leq R \leq 60R_c$, where the lower limit is approximately five times larger than the initial radius of markedly supercritical droplets and the upper limit stays approximately five times smaller than λ . Thus the droplet is markedly supercritical long before establishing the linear law (3.3) (this explains the lower limitation $t \geq \tau_0$ for t), and the condition $R/\lambda \ll 1$ of a free-molecular regime of growth is still fulfilled after establishing the linear law (this explains the upper limitation $t \leq 4\tau_0$ for t). The positivity of the parameter γ , which follows from Eqs. (3.4) and (1.5), corresponds to the droplet growth. Evidently one can rewrite Eq. (3.3) also as

$$R/R_0 = t/\tau_0 \quad (\tau_0 \leq t \leq 4\tau_0) \quad (3.6)$$

where

$$R_0 \equiv R|_{t=\tau_0} \quad (3.7)$$

(in the previous section radius R_0 was interpreted according to the condition $R_0 \equiv R|_{t=\tau_0}$).

Let us formulate with the help of Eq. (1.2) an iterative method for finding how the mole fraction x_1 within the growing droplet depends on time t at the free-molecular regime of droplet growth. As in the previous section, we will discuss first large time scales $\tau_0 \leq t \leq 4\tau_0$.

As follows from Eqs. (3.3) and (3.4) with account of Eq. (3.2) (which allows us to express $\alpha_2 w_2 [\rho_2 - \rho_{2\infty}(1 - x_{1s})]$ through $\alpha_1 w_1 [\rho_1 - \rho_{1\infty}(x_{1s})]$), we can rewrite Eq. (1.4) at $\tau_0 \leq t \leq 4\tau_0$ as

$$n_1 + n_2 = \frac{\pi}{3} R^2 t \frac{\alpha_1 w_1}{x_{1s}} [\rho_1 - \rho_{1\infty}(x_{1s})] \frac{x_{1s} v_1 + (1 - x_{1s}) v_2}{x_1 v_1 + (1 - x_1) v_2}. \quad (3.8)$$

Using Eqs. (3.1) and taking into account Eq. (3.2), (1.6), (1.7), and equality $x_2 - x_{2s} = -(x_1 - x_{1s})$, one can find

$$(1 - x_1) \frac{dn_1}{dt} - x_1 \frac{dn_2}{dt} = -\pi (x_1 - x_{1s}) R^2 \frac{\alpha_1 w_1}{x_{1s}} [\rho_1 - \rho_{1\infty}(x_{1s})] - \pi (x_1 - x_{1s}) R^2 \times [(1 - x_1) \alpha_1 w_1 (\tilde{\rho}_{1\infty} + f_1(x_1)) + x_1 \alpha_2 w_2 (\tilde{\rho}_{2\infty} + f_2(x_1))] \quad (3.9)$$

where f_1 and f_2 are determined by Eq. (2.10) and (2.11).

Substituting Eqs. (3.8) and (3.9) in Eq. (1.2) and canceling common factors from both sides lead to the relaxation differential equation for mole fraction $x_1(t)$ in the solution within a growing droplet in the free-molecular regime

$$\frac{dx_1}{dt} = -\frac{3(x_1 - x_{1s})}{t} \times \left\{ 1 + \frac{(1 - x_1) x_{1s} \alpha_1 w_1 (\tilde{\rho}_{1\infty} + f_1(x_1)) + x_1 x_{1s} \alpha_2 w_2 (\tilde{\rho}_{2\infty} + f_2(x_1))}{\alpha_1 w_1 [\rho_1 - \rho_{1\infty}(x_{1s})]} \right\} \frac{x_1 v_1 + (1 - x_1) v_2}{x_{1s} v_1 + (1 - x_{1s}) v_2}. \quad (3.10)$$

This equation is an analog of Eq. (2.12). The factor $x_1 - x_{1s}$ on the right-hand side of Eq. (3.10) allowed us to apply the iteration method of solution of Eq. (1.2) with respect to the deviation $x_1 - x_{1s}$.

When x_1 is close to x_{1s} , we can substitute with a good accuracy x_1 by x_{1s} in the factors after $x_1 - x_{1s}$ on the right-hand side of Eq. (3.10). Then, solving Eq. (3.10) with the initial condition

$$x_1|_{t=\tau_0} = x_{10}, \quad (3.11)$$

we obtain a power law for establishing the stationary droplet composition in time on large time scales in the free-molecular regime of droplet growth

$$x_1 - x_{1s} = (x_{10} - x_{1s}) \left(\frac{\tau_0}{t} \right)^{3(1+\chi)} \quad (\tau_0 \leq t \leq 4\tau_0). \quad (3.12)$$

The parameter χ is determined here by the right-hand side of Eq. (2.15) with substitution of D_1 and D_2 by $\alpha_1 w_1$ and $\alpha_2 w_2$, i.e.

$$\chi \equiv \frac{x_{1s} [(1 - x_{1s}) \alpha_1 w_1 (\tilde{\rho}_{1\infty} + f_1(x_{1s})) + x_{1s} \alpha_2 w_2 (\tilde{\rho}_{2\infty} + f_2(x_{1s}))]}{\alpha_1 w_1 [\rho_1 - \rho_{1\infty}(x_{1s})]}. \quad (3.13)$$

According to (3.13), the parameter χ depends not only on thermodynamic ($\tilde{\rho}_{1\infty}, \tilde{\rho}_{2\infty}$) and kinetic ($\alpha_1 w_1, \alpha_2 w_2$) characteristics of condensing vapors but also on the stationary mole fraction x_{1s} itself and the characteristics of the solution non-ideality ($f_1(x_{1s}), f_2(x_{1s})$) at the stationary composition. As follows from Eqs. (2.10), (2.11) and (3.13), and from the thermodynamic stability conditions of solutions [11] and the conditions (1.5), $\chi > 0$. The smallness of the parameter χ with respect to unity is not required.

It is clear that the power law (3.3) of droplet radius growth and the power law (3.12) for establishing stationary composition in the solution within the droplet are valid in the same range $\tau_0 \leq t \leq 4\tau_0$ of times t (counted off from the moment of nucleation of a markedly supercritical droplet in a vapor–gas environment). Taking into account Eq. (3.6), we can rewrite Eq. (3.12) as

$$x_1 - x_{1s} = (x_{10} - x_{1s}) \left(\frac{R_0}{R} \right)^{3(1+\chi)} \quad (\tau_0 \leq t \leq 4\tau_0). \quad (3.14)$$

Since $\chi > 0$, formula (3.14) shows that the stationary concentration of the solution within the droplet is established at comparatively small relative increase of droplet radius (and even at very small relative increase of droplet radius, if inequality $\chi \geq 1$ takes place).

Let us estimate the important time τ_0 with the help of Eqs. (3.4) and (3.5). Taking $R_c \sim 10^{-7}$ cm, $\alpha_1 \approx \alpha_2 \sim 1$, $w_1 \approx w_2 \sim 5 \times 10^4$ cm s⁻¹, $v_1 \approx v_2 \sim 3 \times 10^{-23}$ cm³, $\rho_1 - \rho_{1\infty}(x_{1s}) \approx \rho_2 - \rho_{2\infty}(x_{2s}) \sim 10^{18}$ cm⁻³, we obtain

$$\tau_0 \sim 10^{-5} \text{ s}. \quad (3.15)$$

Comparing the estimate (3.15) with the estimate (2.17), we conclude that $\tau_0 \ll t_0$.

Let us now consider the situation when establishing the stationary composition is so fast that the droplet radius R has no time to grow significantly in the free-molecular regime. Correspondingly, we need to replace Eq. (3.8) in the vicinity of $x_1 = x_{1s}$ by equation

$$n_1 + n_2 = \frac{\pi}{3} R^3 \frac{\alpha_1 w_1}{\gamma x_{1s}} [\rho_1 - \rho_{1\infty}(x_{1s})], \quad (3.16)$$

which follows from Eq. (1.4) and (3.4) with account of Eq. (3.2). Consequently, Eq. (3.10) can be rewritten in the vicinity of $x_1 = x_{1s}$ with the help of Eqs. (3.13) and (3.16) as

$$\frac{dx_1}{dt} = - \frac{3(x_1 - x_{1s})\gamma}{R} (1 + \chi). \quad (3.17)$$

Integrating Eq. (3.17) with initial condition $x_1|_{t=\tau_\lambda} = x_{1\lambda}$ where the time τ_λ is determined by the condition $R|_{t=\tau_\lambda} = 3R_c$, we obtain

$$x_1 - x_{1s} = (x_{1\lambda} - x_{1s}) e^{-\frac{t-\tau_\lambda}{\tau_x}} \quad (t \geq \tau_\lambda). \quad (3.18)$$

The characteristic time τ_x of exponential relaxation at fixed droplet radius for the free-molecular regime is determined here as

$$\tau_x \equiv \frac{R_c}{\gamma(1+\chi)}. \quad (3.19)$$

Because τ_λ and $3R_c$ are the values of time t and droplet radius R , starting from which equation $dR/dt = \gamma$ practically holds, the validity condition of the exponential law (3.18) requires, in view of equation $dR/dt = \gamma$, consistency of two limitations of time $t - \tau_\lambda$. One of them is a limitation from below,

$$e^{-\frac{t-\tau_\lambda}{\tau_x}} \ll 1, \quad (3.20)$$

which means that the relaxation ends to the moment for time $t - \tau_\lambda$. The second is a limitation on the that time from above,

$$\frac{\gamma(t - \tau_\lambda)}{3R_c} \ll 1, \quad (3.21)$$

which means that radius R does not significantly grow for time $t - \tau_\lambda$. Both limitations can be joined, with the help of Eq. (3.19), in the form of a double inequality

$$(1-2) < \frac{t - \tau_\lambda}{\tau_x} \ll 3(1 + \chi). \quad (3.22)$$

As one can see, condition (3.22) is fulfilled at $\chi \geq 1$.

It follows from condition (3.21) with account of Eq. (3.7) and inequalities $R_0 \gg 3R_c$, $\tau_0 \gg \tau_\lambda$ and Eq. (3.3) that

$$t - \tau_\lambda \ll \tau_0 - \tau_\lambda. \quad (3.23)$$

Thus the exponential law (3.18) is valid on time scales which are considerably smaller than the time scales for the power law (3.12).

4. Total time dependence of mole fractions within a growing droplet of ideal solution

Whether the establishment of a stationary composition in solution within a growing droplet would be possible at any initial mole fraction x_{10} in the initial conditions (2.13) or (3.11) on the large time scales $t \geq t_0$ or $t \geq \tau_0$ and at any values of the thermodynamic and kinetic characteristics of condensing components, and would occur for a sufficiently short time allowing us to consider the droplet growth to be stationary, is an interesting question. An answer to this question cannot be obtained within the frameworks of the theory considered in Sections 3 and 4 where the relaxation equations have been solved under a priori assumption that the value of the fraction x_1 is close to x_{1s} . However, solving the general relaxation equations (2.12) and (3.10) without the assumption of smallness of the deviation of x_1 from x_{1s} , we may find the limitations on the initial molar fraction x_{10} in the initial conditions (2.13) and (3.11) and the limitations on the values of thermodynamic and kinetic characteristics of condensing components, at which the conclusions made in Sections 2 and 3 are confirmed or violated. In this way we will find an answer to the question posed above.

General relaxation equations (2.12) and (3.10) may be strictly rewritten at ideality of solution (when Eq. (1.6) holds) at $t \geq t_0$ or $t \geq \tau_0$ in the form

$$\frac{d\delta x_1}{dt} = -\frac{\gamma}{t} \delta x_1 (1 + a\delta x_1) (1 + b\delta x_1) \quad (4.1)$$

where

$$\delta x_1 \equiv x_1 - x_{1s}, \quad \delta x_{10} \equiv x_{10} - x_{1s}, \quad (4.2)$$

$$\gamma \equiv \begin{cases} \frac{3}{2} (1 + \eta) & \text{(diffusion-controlled regime),} \\ 3 (1 + \chi) & \text{(free-molecular regime),} \end{cases} \quad \gamma > 0, \quad (4.3)$$

$$a \equiv \begin{cases} -\frac{x_{1s}}{1 + \eta} \frac{D_1 \tilde{\rho}_{1\infty} - D_2 \tilde{\rho}_{2\infty}}{D_1 [\rho_1 - \rho_{1\infty}(x_{1s})]} & \text{(diffusion-controlled regime),} \\ -\frac{x_{1s}}{1 + \chi} \frac{\alpha_1 w_1 \tilde{\rho}_{1\infty} - \alpha_2 w_2 \tilde{\rho}_{2\infty}}{\alpha_1 w_1 [\rho_1 - \rho_{1\infty}(x_{1s})]} & \text{(free-molecular regime),} \end{cases} \quad (4.4)$$

$$b \equiv \frac{v_1 - v_2}{x_{1s} v_1 + (1 - x_{1s}) v_2}. \quad (4.5)$$

The values of δx_1 and coefficients a and b can be of any sign.

An analytical solution of Eq. (4.1) with initial conditions (2.13) and (3.11) can be found by separating variables and decomposition in partial fractions. This solution has the form

$$\gamma \ln \left(\frac{t}{t_i} \right) = -\ln \left(\frac{\delta x_1(t)}{\delta x_{10}} \right) + \frac{a}{a-b} \ln \left(\frac{1 + a\delta x_1(t)}{1 + a\delta x_{10}} \right) - \frac{b}{a-b} \ln \left(\frac{1 + b\delta x_1(t)}{1 + b\delta x_{10}} \right) \quad (4.6)$$

where we denoted for brevity t_0 and τ_0 as a single time t_i . The solution exists (within the real-valued domain) only when the following conditions are fulfilled

$$\frac{\delta x_1}{\delta x_{10}} > 0, \quad \frac{1 + a\delta x_1}{1 + a\delta x_{10}} > 0, \quad \frac{1 + b\delta x_1}{1 + b\delta x_{10}} > 0. \quad (4.7)$$

The solution (4.6) can be rewritten equivalently with account of Eq. (4.3) as

$$\begin{aligned} & \frac{x_1 - x_{1s}}{x_{10} - x_{1s}} \left[\frac{1 + a(x_{10} - x_{1s})}{1 + a(x_1 - x_{1s})} \right]^{\frac{a}{a-b}} \left[\frac{1 + b(x_1 - x_{1s})}{1 + b(x_{10} - x_{1s})} \right]^{\frac{b}{a-b}} \\ &= \begin{cases} \left(\frac{t_0}{t} \right)^{3(1+\eta)/2} & (t \geq t_0, \text{ diffusion-controlled regime}), \\ \left(\frac{\tau_0}{t} \right)^{3(1+\chi)} & (t \geq \tau_0, \text{ free-molecular regime}). \end{cases} \end{aligned} \quad (4.8)$$

Below we will suppose that $\delta x_{10} > 0$, and, in view of Eq. (4.7), also $\delta x_1 > 0$. In the case when $\delta x_1 < 0$, we have from Eq. (4.1) an equation for $|\delta x_1| \equiv -\delta x_1$, which differs from Eq. (4.1) only in replacement of δx_1 , $1 + a\delta x_1$, and $1 + b\delta x_1$ by $|\delta x_1|$, $1 - a|\delta x_1|$, and $1 - b|\delta x_1|$, respectively, i.e. it is equivalent to the replacement of the values of coefficients a and b by values $-a$ and $-b$. As is clearly seen, solution (4.8) transforms into solutions (2.14) and (3.12) when x_{10} and, in view of Eq. (4.1), x_1 are close to x_{1s} or when $|a| \ll 1$ and $|b| \ll 1$. Moreover, we may ascertain from Eqs. (4.7) and (4.8) with the help of Eq. (4.1) that the positive ratio $(x_1 - x_{1s}) / (x_{10} - x_{1s})$ decreases monotonically to zero with increasing t at $|a| < 1$, $|b| < 1$, and at any value of initial concentration $x_{1s} < x_{10} < 1$. The same behavior will be at any positive values of coefficients a and b . Thus we have in both the latter cases positive answer to the question posed at the beginning of this section.

However, it follows from Eq. (4.1) that there is no monotonic decrease to zero for solution (4.8) with increasing time t at $a > 0$, $b < 0$, $|b| > 1$, if the initial concentration satisfies inequality $x_{1s} + 1/|b| < x_{10} < 1$. Note, at this $d\delta x_1/dt|_{t=t_i} > 0$.

Such an initial concentration may be realized in practice only when $0 < x_{1s} \ll 1$ or $|b| \gg 1$. It also follows from Eq. (4.1) that a monotonic decrease to zero for solution (4.8) with increasing time t is impossible at $a < 0$, $b < 0$, $|a| < 1$, and $|b| > 1$, as well as at $a < 0$, $b < 0$, $|a| > 1$, $|b| > 1$, and $|b| < |a|$, if the initial concentration satisfies the previous inequality $x_{1s} + 1/|b| < x_{10} < 1$. Note here that the first situation corresponds to $d\delta x_1/dt|_{t=t_i} > 0$, while the second situation corresponds to $d\delta x_1/dt|_{t=t_i} < 0$ with $\delta x_1 \rightarrow 1/|b|$ as $t \rightarrow \infty$. All that was said above in this paragraph is true if we exchange the values of parameters a and b .

Thus we see that some initial values x_{10} should be excluded at negative values of coefficients a and b . In this way, we give a full answer to the question posed at the beginning of this section.

5. Discussion and conclusions

We have considered establishing the power-law-in-time growth of the droplet radius and the stationary composition in a binary solution on large time scales within a growing droplet at two characteristic regimes of isothermal binary condensation in a vapor–gas environment. In fact, the regimes of droplet growth can gradually change from free-molecular to diffusion-controlled with an increase in droplet size. Evidently, the transition from Eq. (2.2) for the stationary mole fraction x_1 in the solution in a droplet under the diffusion-controlled growth regime to Eq. (3.2) for a stationary mole fraction x_1 in the solution in a droplet under the free-molecular growth regime formally requires a replacement of the ratio D_1/D_2 by the ratio $\alpha_1 w_1/\alpha_2 w_2$. At a typical proximity of the order of magnitude of the ratios D_1/D_2 and $\alpha_1 w_1/\alpha_2 w_2$, Eqs. (2.2) and (3.2) are almost equivalent. Hence, the stationary mole fractions in the two considered regimes should be of the same magnitude also.

Similarly, the transition from Eq. (2.15) for the parameter η in the case of the diffusion-controlled regime to Eq. (3.13) for the parameter χ in the case of the free-molecular regime requires formally a replacement of the ratio D_1/D_2 by the ratio $\alpha_1 w_1/\alpha_2 w_2$. At a typical proximity of the order of magnitude of the relations D_1/D_2 and $\alpha_1 w_1/\alpha_2 w_2$, the parameters η and χ in the two considered regimes would be then approximately of the same magnitude.

As the droplet grows in the diffusion-controlled regime, the condition $R/\lambda \gg 1$ of this regime holds better and better. Vice versa, as the droplet grows in the free-molecular regime, the condition $R/\lambda \ll 1$ of that regime holds worse and worse. This fact results in a large difference in the time intervals available for the theory in both cases considered.

The number densities $\tilde{\rho}_{1\infty}$ and $\tilde{\rho}_{2\infty}$ of the molecules of saturated vapors of pure liquids can strongly differ (for instance, this is true for the vapors of water and sulfuric acid). The analytical formula obtained in [3] for the binary solution stationary concentration can give very different particular values of the stationary mole fraction x_{1s} . Since the parameters η and χ depend, according to Eqs. (2.15) and (3.13), on both densities $\tilde{\rho}_{1\infty}$ and $\tilde{\rho}_{2\infty}$ and on the stationary fraction x_{1s} , then the values of the positive parameters η and χ can lie in a very wide range. In particular, if the relations $\eta \geq 2$ and $\chi \geq 1$ hold, then, according to Eqs. (2.16), (2.20) and (3.14), (3.18), the stationary composition of the droplet solution will be established at very small relative increase of the droplet radius. This means that the droplet would grow in the diffusion-controlled and free-molecular regimes at stationary composition of the droplet solution for a major part of time. Then the simple formulae (2.5) and (3.3) are valid for the time dependence of droplet radius.

The results obtained in Section 4 at arbitrary deviation of x_1 from x_{1s} confirm the results of Sections 2 and 3 concerned with the monotonic establishment of the stationary composition in a droplet on large time scales which have been found by solving relaxation equations (2.12) and (3.10) with a priori assumption of proximity of the droplet composition to the stationary composition.

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