

Stationary Concentration of a Binary Solution in a Growing Drop and the Time of Its Establishment

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In the general case, the problem of describing the growth of a drop of a binary solution in a mixture of vapors of its constituent substances and a passive gas is quite difficult to solve. To solve this problem, even in the relatively simple case of diffusion-controlled drop growth, it is usually assumed [1, 2] that the solution concentration in the drop rapidly reaches a stationary value. To confirm this assumption, the time dependence of the concentration of an ideal binary solution in drops at various initial compositions was numerically calculated [2]. However, these numerical calculation results [2] show that the stationary solution concentration in a drop may be reached over quite a long time. It has recently been studied [3] how the stationary concentration of an ideal binary solution in a drop growing under diffusion control is reached, but neither has the value of this stationary solution concentration been found nor has the law under which the stationary concentration is reached with time been explicitly determined.

In this work, we will study the case where the number density of molecules of each component in a two-component mixture of vapors that have condensed to form a drop noticeably exceeds the number density of molecules of each component in a two-component mixture of vapors being in equilibrium with this drop. In this interesting case, each of the two components of the vapor mixture intensely condenses to the drop. For diffusion-controlled drop growth, we will obtain expressions for the time dependence of the drop radius and the numbers of molecules of the substances that have condensed to the drop from the vapor mixture. We will find the time in which these expressions and the diffusion-controlled mode of drop growth become valid after drop nucleation. We will find the stationary solution concentration in the drop growing under diffusion control and also will derive the power law under which the stationary solution concentration is reached with time. We will show that the stationary solution concentration

in the growing drop is reached with time rather rapidly in comparison with the relatively slow drop growth. Unlike recent works [1–3], we will need no assumption of ideality of the solution in the drop.

Let us consider a drop of a binary solution that has nucleated in an initially uniform vapor–gas medium of a passive gas and a two-component mixture of vapors of the same substances as in the drop. After nucleation, the drop grows because of the condensation of each of the two components of the vapor mixture. The amount of the passive gas in the vapor–gas mixture is assumed to be much larger than the amount of the vapors. The drop grows under diffusion control when the drop radius R noticeably exceeds the free path length λ of molecules of the vapors in the passive gas, i.e., when $R \geq R_0$, where

$$R_0 \cong (3-4)\lambda \quad (1)$$

is the drop radius above which the drop grows under diffusion control. The large relative amount of the passive gas in the vapor–gas medium ensures isothermal conditions of condensation and also allows one to ignore the Stefan flow of the vapor–gas medium and the effect of the diffusion flows of molecules of the vapors on each other.

Let x_i , $i = 1, 2$, be the number of molecules of component i in the drop at a current moment of time and v_i , $i = 1, 2$, be the partial volume occupied by a molecule of component i in the solution within the drop. As Grinin and Lezova [3], for simplicity, we assume the volumes v_1 and v_2 to be constant. It was shown [3] that the solution within the drop is uniform. Obviously,

$$c = \frac{x_1}{x_1 + x_2} \quad (2)$$

is the concentration of component 1 in the drop, $0 < c < 1$. Then, the concentration of component 2 in the drop is $\frac{x_2}{x_1 + x_2}$. Let n_i , $i = 1, 2$, be the number density of molecules of component i in the initially uniform two-com-

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ponent mixture of the vapors that have condensed to the drop.

Evidently,

$$(1-c)x_1 = cx_2, \quad (3)$$

$$x_1v_1 + x_2v_2 = \frac{4\pi R^3}{3} \quad (4)$$

(expression (3) is only another form of expression (2)). In quasi-stationary theory in the diffusion-controlled drop growth mode, we have [4]

$$\frac{dx_i}{dt} = 4\pi D_i [n_i - n_{i\infty}(c)]R, \quad i = 1, 2, \quad (5)$$

where t is time counted from the time of drop nucleation ($t = 0$), D_i is the diffusion coefficient of molecules of component i of the vapor mixture in the passive gas, and $n_{i\infty}(c)$ is the number density of molecules of component i of the mixture of the vapors being in equilibrium with the drop of radius R (the dependence of $n_{i\infty}(c)$ on R can be ignored at sufficiently large drop radii, where the drop grows under diffusion control).

Differentiation of expression (3) with respect to time t gives the expression

$$(x_1 + x_2)\frac{dc}{dt} = (1-c)\frac{dx_1}{dt} - c\frac{dx_2}{dt}, \quad (6)$$

which is important for further considerations. Differentiating expression (4) with respect to time t , taking into account the constancy of v_1 and v_2 , and using expression (5), we obtain the relation

$$\frac{dR^2}{dt} = 2D_1v_1[n_1 - n_{1\infty}(c)] + 2D_2v_2[n_2 - n_{2\infty}(c)]. \quad (7)$$

According to the stated purpose of this work, we will study the case where

$$n_i \geq (4-5)n_{i\infty}(c), \quad i = 1, 2. \quad (8)$$

If relation (8) is valid, then, from expressions (5) and (7), we can obtain, with rather high accuracy,

$$\frac{dx_i}{dt} = 4\pi D_i n_i R, \quad i = 1, 2, \quad (9)$$

and

$$\frac{dR^2}{dt} = \beta^2, \quad (10)$$

where we take

$$\beta^2 \equiv 2D_1v_1n_1 + 2D_2v_2n_2. \quad (11)$$

Let us introduce the characteristic time

$$t_0 \equiv \frac{R_0^2}{\beta^2}, \quad (12)$$

where R_0 is given by equality (1). Solving Eq. (10) under the initial condition $R|_{t=t_0} = R_0$ using expression (12) produces

$$R^2 = \beta^2 t, \quad t \geq t_0, \quad (13)$$

which, together with relation (11), expresses the dependence of the drop radius R on time t . In accordance with relations (12) and (13), at times $t \geq t_0$, we have $R \geq R_0$; therefore, according to the R_0 value, the drop grows under diffusion control. Equalities (1), (11), and (12) enable one to readily find the time t_0 in which, after drop nucleation, the diffusion-controlled mode of drop growth is reached and expression (13) becomes valid. Note that R_0 and t_0 are on the order of 10^{-6} m and 10^{-3} s, respectively. It is at times $t \geq t_0$ that kinetic equations (5), (7), (9), and (10) are valid. Integration of expression (9) with respect to time t using relation (13) gives

$$x_i = \frac{8\pi}{3} D_i n_i R t, \quad t \geq t_0, \quad i = 1, 2, \quad (14)$$

which, together with relation (13), expresses the dependence of the numbers x_i of molecules of components $i = 1, 2$ in the drop on time t . Note that expression (14) is consistent with relation (4) in view of expressions (11) and (13).

Further, from expressions (6) and (9), we have

$$(x_1 + x_2)\frac{dc}{dt} = 4\pi(1-c)D_1n_1R - 4\pi cD_2n_2R. \quad (15)$$

Using relations (14) and (15), we find

$$\frac{dc}{dt} = -\frac{3c}{2t} + \frac{3D_1n_1}{2t(D_1n_1 + D_2n_2)}, \quad t \geq t_0. \quad (16)$$

Let us represent relation (16) in the form

$$\frac{dc}{dt} = -\frac{3(c - c_s)}{2t}, \quad t \geq t_0, \quad (17)$$

where

$$c_s \equiv \frac{D_1n_1}{D_1n_1 + D_2n_2} \quad (18)$$

is the stationary (limiting) solution concentration to which the concentration c tends with time t . As one might expect, c_s determined by relation (18) meets the condition $0 < c_s < 1$.

Finally, solving Eq. (17) under the initial condition $c|_{t=t_0} = c_0$, where c_0 is an arbitrary initial concentration taking values between 0 and 1, we obtain

$$c - c_s = (c_0 - c_s) \left(\frac{t_0}{t} \right)^{3/2}, \quad t \geq t_0. \quad (19)$$

At $c_0 > c_s$, relation (19) implies $c > c_s$, and at $c_0 < c_s$, it implies $c < c_s$. Since both c_0 and c_s are between 0 and 1, we have $|c_0 - c_s| < 1$. No constraint on the smallness of the initial deviation $c_0 - c_s$ in relation (19) is neces-

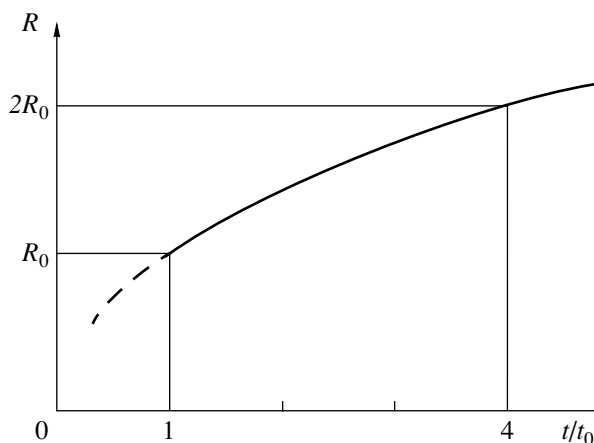


Fig. 1. Time dependence of the radius of a growing drop.

sary. The stationary value c_s of the concentration c as determined by expression (18) is the only possible one.

Writing expression (13) under the condition $R|_{t=t_0} = R_0$ in the form

$$R = R_0 \left(\frac{t}{t_0} \right)^{1/2}, \quad t \geq t_0, \quad (20)$$

and comparing the result with expression (19), we draw the following conclusion. The exponent in power law (19) of damping of the deviation $c - c_s$ with time is three times larger than the exponent in power law (20) of increase in the drop radius R with time. Thus, the stationary (limiting) solution concentration in the growing drop is reached with time rather rapidly in comparison with the relatively slow drop growth. This is illustrated by Figs. 1 and 2, which present the graphs of expressions (20) and (19) for the dependence of the drop radius R and the deviation $c - c_s$ of the solution concentration c from its stationary value c_s on dimensionless

time $\frac{t}{t_0}$. These graphs are valid at $\frac{t}{t_0} \geq 1$, when the drop grows under diffusion control. For definiteness, we assume that $c_0 - c_s > 0$. Time t is counted from the time of drop nucleation ($t = 0$).

In a more general case, where relation (8) may be invalid, it is sufficient to have $n_i > n_{i\infty}(c)$, $i = 1, 2$; then, the following equation for the stationary solution con-

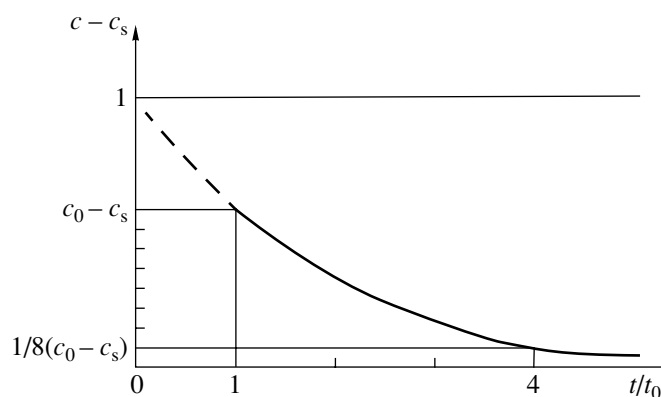


Fig. 2. Time dependence of the deviation of the solution concentration in a drop from its stationary value.

centration c_s follows directly from relations (5) and (6) under the stationarity condition $\frac{dc}{dt} = 0$:

$$\frac{c_s}{1 - c_s} = \frac{D_1[n_1 - n_{1\infty}(c_s)]}{D_2[n_2 - n_{2\infty}(c_s)]}. \quad (21)$$

If the solution in the drop is ideal, this equation appears as Eq. (12) from Kulmala et al. [2].

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