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Regularities of Binary Condensation of Vapors When One of Them Is Undersaturated

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Abstract—Simple analytical expressions are derived for the stationary concentration of a binary solution in a markedly supercritical droplet growing isothermically in diffusion or free-molecular regimes in mixed vapors when one of condensing vapors is supersaturated and present in a small amount and another vapor is slightly undersaturated and present in a large amount. The condensation of sulfuric acid and water vapors on a droplet under the conditions of Earth atmosphere is considered as an example of practical importance. Under isothermic conditions, analytical expressions are obtained for the time of establishing a power law for variations in a droplet radius with time under the diffusion and free-molecular regimes of the droplet growth. The power laws are derived in an explicit form under these regimes, which describe the rapid establishment of a stationary concentration of a solution in a growing droplet.

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INTRODUCTION

The goal of this communication is to analytically describe the regularities of the binary isothermic condensation of a mixture of vapors on a markedly supercritical droplet when one of the condensing vapors is supersaturated and present in a small amount and another vapor is slightly undersaturated and present in a large amount. It is this specific, though, prevailing in nature, situation which we come across when considering the condensation of sulfuric acid and water vapors under the conditions of the Earth atmosphere. In this situation, the droplet growth regime may both either diffusion or free-molecular.

Previously [1–8], when investigating various problems of binary condensation and nucleation, this problem was not considered. Nevertheless, the approach that we propose is based on the results obtained in [2] for determining the stationary solution concentration that is established in a markedly supercritical droplet that grows in the diffusion regime owing to the isothermic binary condensation.

In this paper, simple analytical relations will be derived for the stationary concentration of a binary solution in an isothermally growing droplet when one of the condensing vapors is supersaturated and present in a small amount and another vapor is slightly undersaturated and present in a large amount. For this case, a small parameter will be introduced, which will play an important role throughout our study. In particular, this parameter allows us to linearize and easily solve the nonlinear equation for the stationary concentration of a binary solution in a droplet. This method appears to be much simpler than the passage from the general solution obtained in [2] for the quadratic equation of the stationary concentration of a binary solution in a droplet to the situation that we consider. The method will be applied to both the diffusion and free-molecular regimes of the droplet growth.

Using this method and the results of the kinetic theory developed in [9], we shall establish important regularities for the binary isothermic vapor condensation, which were not discussed in [1–9]. For example, the times required for establishing the power dependence of droplet radius on time will be analytically derived for the diffusion and free-molecular regimes of droplet growth. For these regimes, power relations will be also obtained in an explicit form for rapid establishing the stationary concentration of a solution inside a growing droplet.

1. DETERMINATION OF THE STATIONARY CONCENTRATION OF A BINARY SOLUTION IN A DROPLET

The following denotations will be applied: c_1 and c_2 are the mole fractions or relative concentrations of molecules of components 1 and 2, respectively, in a liquid solution inside a droplet ($0 < c_1 < 1$, $0 < c_2 < 1$, $c_1 + c_2 = 1$); n_1 and n_2 are the number densities of molecules of components 1 and 2, respectively, in a two-component mixture of vapors surrounding the droplet; and $n_{1\infty}(c_1)$ and $n_{2\infty}(c_2)$ are their equilibrium densities over a flat surface of a liquid solution with concentrations c_1 and c_2 of these components, respectively.

For the further considerations, we use the following initial conditions:

$$n_1 > n_{1\infty}(c_1), \quad n_2 > n_{2\infty}(c_2), \tag{1.1}$$

under which both components 1 and 2 are condensed in the droplet. Further, c_1 and c_2 will refer to the stationary concentrations that are inevitably established during the growth of a supercritical droplet.

The value of the stationary concentrations is revealed by an equation that relates them to one another. In the diffusion regime of droplet growth, where we begin our analysis, this equation has the following form:

$$\frac{D_1[n_1 - n_{1\infty}(c_1)]}{D_2[n_2 - n_{2\infty}(c_2)]} = \frac{c_1}{1 - c_1}, \quad (1.2)$$

where D_1 and D_2 are the diffusion coefficients of molecules of components 1 and 2 of mixed vapors in a passive gas. The presence of passive gas in a considerable amount is necessary to ensure the diffusion regime of droplet growth and the isothermic mode of the condensation. According to Eq. (1.2), the ratio between the diffusion fluxes of components 1 and 2 of the mixed vapors to a droplet is equal to the stationary concentration ratio of the components in the droplet. Hence, at stationary concentrations c_1 and c_2 and constant number densities n_1 and n_2, there is a balance between the numbers of molecules removed from the mixed vapors due to diffusion and added to the growing droplets, which remains preserved for an infinite time period. This circumstance reveals the meaning of stationary concentrations c_1 and c_2. Note that, at stationary concentrations, if even one of the conditions in (1.1) is satisfied, then, as follows from Eq. (1.2), the other condition will be satisfied as well.

Let us take advantage of the following relations, which are valid for ideal solutions:

$$n_{1\infty}(c_1) = c_1\tilde{n}_{1\infty}, \quad n_{2\infty}(c_2) = c_2\tilde{n}_{2\infty}, \quad (1.3)$$

where $\tilde{n}_{1\infty}$ and $\tilde{n}_{2\infty}$ are the number densities of molecules in saturated vapors of pure liquid components 1 and 2. Hereafter, without additional stipulations, we employ dependences (1.3) and relations $0 < c_1 < 1$, $0 < c_2 < 1$, and $c_1 + c_2 = 1$.

Now we consider the situation that we are interested in, i.e., when one of the condensing vapors is supersaturated and present in a small amount and another is slightly undersaturated and present in a large amount. Let

$$n_1 > \tilde{n}_{1\infty}, \quad (1.4)$$

thus ensuring the first of the inequalities (1.1) to be valid at any concentration c_1. It is obvious that inequality (1.4) implies that component 1 of the mixed vapors is supersaturated over its pure liquid phase.

Then, let

$$\tilde{n}_{2\infty} \gg \tilde{n}_{2\infty} - n_2 > 0, \quad (1.5)$$

thus ensuring the validity of the second of conditions (1.1) at

$$c_1 > \frac{\tilde{n}_{2\infty} - n_2}{\tilde{n}_{2\infty}}. \quad (1.6)$$

The necessity of satisfying inequality (1.6) is clearly seen from the following relation, which is easy to derive:

$$n_1 - n_{2\infty}(c_2) = \tilde{n}_{2\infty}\left(c_1 - \frac{\tilde{n}_{2\infty} - n_2}{\tilde{n}_{2\infty}}\right). \quad (1.7)$$

Inequality (1.5) is evident to imply a slight undersaturation of component 2 of the mixed vapors over its pure liquid phase. Together, inequalities (1.4) and (1.5) correspond to the situation under consideration.

Suppose that, despite constraint (1.6), the following inequality is valid:

$$c_1 \ll 1, \quad (1.8)$$

which implies that the droplet mainly consists of component 2. Now, let us assume that inequality (1.8) is really fulfilled, while the conditions of its fulfillment will be clarified somewhat below.

Relations (1.4) and (1.8) yield the following with a high accuracy:

$$n_1 - n_{1\infty}(c_1) = n_1. \quad (1.9)$$

Using eq. (1.7)-(1.9), we reduce Eq. (1.2) to the following expression:

$$D_2\tilde{n}_{2\infty}c_1\left(c_1 - \frac{\tilde{n}_{2\infty} - n_2}{\tilde{n}_{2\infty}}\right) = D_1n_1. \quad (1.10)$$

We shall solve Eq. (1.10) in the form of

$$c_1 = \frac{\tilde{n}_{2\infty} - n_2}{\tilde{n}_{2\infty}}(1 + \varepsilon), \quad 0 < \varepsilon \ll 1. \quad (1.11)$$

Substituting relation (1.11) into Eq. (1.10) and ignoring the term, which is quadratic with respect to the introduced small parameter ε, we easily find the following equation:

$$\varepsilon = \frac{D_1n_1\tilde{n}_{2\infty}}{D_2(\tilde{n}_{2\infty} - n_2)^2}. \quad (1.12)$$

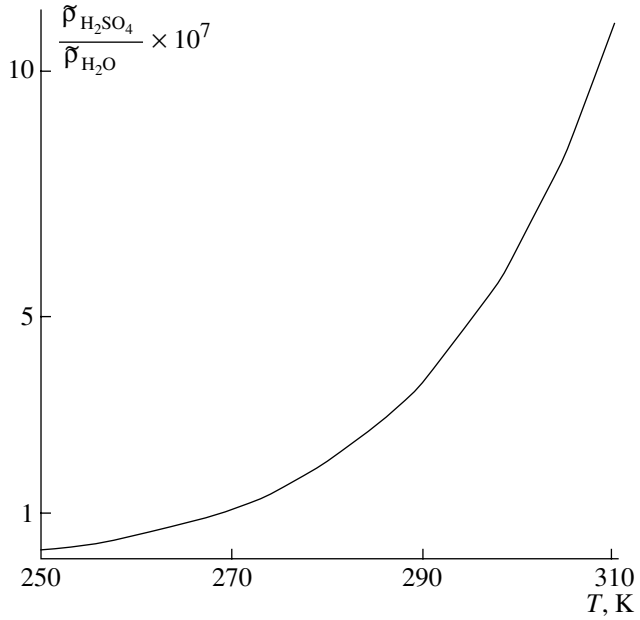
As can be seen from Eq. (1.12), for satisfying the inequality $0 < \varepsilon \ll 1$, the following constraint is required:

$$D_1n_1 \ll \frac{D_2(\tilde{n}_{2\infty} - n_2)^2}{\tilde{n}_{2\infty}}. \quad (1.13)$$

When inequality (1.13) is satisfied, relations (1.11) and (1.12) yield the equation

$$c_1 = \frac{\tilde{n}_{2\infty} - n_2}{\tilde{n}_{2\infty}}\left[1 + \frac{D_1n_1\tilde{n}_{2\infty}}{D_2(\tilde{n}_{2\infty} - n_2)^2}\right]. \quad (1.14)$$

The solution of Eq. (1.14) suggests that the conditions for fulfilling strong inequality (1.8) (the condi-



Ratio $\tilde{p}_{H_2SO_4}/\tilde{p}_{H_2O}$ between the saturation vapor pressures of sulfuric acid and water over their pure liquid phases as a function of temperature T.

tions of a low stationary concentration of component 1 in the droplet) are inequalities (1.5) and (1.13). The solution of Eq. (1.14) ensures the fulfillment of constraint (1.6). The corrective role of the n_1-containing term in expression (1.14), enabled us to replace $(1 - c_1)D_1n_1$ by D_1n_1 in Eq. (1.10) at $c_1 \ll 1$.

Combining inequalities (1.13) and (1.5), we arrive at

$$D_1n_1 \ll \frac{D_2(\tilde{n}_{2\infty} - n_2)^2}{\tilde{n}_{2\infty}} \ll D_2\tilde{n}_{2\infty}. \qquad (1.15)$$

The positivity of the $\tilde{n}_{2\infty} - n_2$ value (the undersaturation of component 2 of the mixed vapors over its pure liquid phase), which is required for inequality (1.5), is not seen in inequalities (1.15), because inequality (1.5) is present in them, but as a squared value. However, inequality $\tilde{n}_{2\infty} - n_2 > 0$ must be satisfied for the existence of the solution for Eq. (1.14). As can be seen from relation (1.4), two-sided inequality (1.15) may be consistent only at

$$\frac{D_1\tilde{n}_{1\infty}}{D_2\tilde{n}_{2\infty}} \ll 1. \qquad (1.16)$$

This inequality conditions the applicability of the theory. If inequality (1.16) is satisfied with a great excess, two-sided inequality (1.15) admits n_1 values well above $\tilde{n}_{1\infty}$. However, as, according to relation (1.5), $n_2 \simeq \tilde{n}_{2\infty}$, two-sided inequality (1.15) still implies that $D_1n_1 \ll D_2n_2$ (a small amount of the supersaturated vapor and a large amount of the slightly undersaturated one). As a result, we may conclude that inequalities (1.4), (1.5), and (1.13), as well as two-sided inequality (1.15), which follows from them, precisely correspond to the situation in question.

In the free-molecular regime of the droplet growth, instead of relation (1.2), we have the following equation:

$$\frac{\alpha_1\omega_1[n_1 - n_{1\infty}(c_1)]}{\alpha_2\omega_2[n_2 - n_{2\infty}(c_2)]} = \frac{c_1}{1 - c_1}, \qquad (1.17)$$

where α_1 and α_2 ($\alpha_1 \le 1$, $\alpha_2 \le 1$) are the condensation coefficients of molecules of components 1 and 2 and ω_1 and ω_2 are their average thermal velocities, respectively. It can be clearly seen that the above analysis may be also used in this case when D_1 and D_2 are replaced by $\alpha_1\omega_1$ and $\alpha_2\omega_2$, respectively. Thus, in place of relations (1.12) and (1.14), for the free-molecular regime of the droplet growth, we have the following expressions:

$$\varepsilon = \frac{\alpha_1\omega_1n_1\tilde{n}_{2\infty}}{\alpha_2\omega_2(\tilde{n}_{2\infty} - n_2)^2} \qquad (1.18)$$

and

$$c_1 = \frac{\tilde{n}_{2\infty} - n_2}{\tilde{n}_{2\infty}}\left[1 + \frac{\alpha_1\omega_1n_1\tilde{n}_{2\infty}}{\alpha_2\omega_2(\tilde{n}_{2\infty} - n_2)^2}\right], \qquad (1.19)$$

while, instead of condition (1.16), we obtain

$$\frac{\alpha_1\omega_1}{\alpha_2\omega_2}\frac{\tilde{n}_{1\infty}}{\tilde{n}_{2\infty}} \ll 1. \qquad (1.20)$$

As the D_1/D_2 and $\alpha_1\omega_1/\alpha_2\omega_2$ are, on the order of magnitude, close to one another, conditions (1.16) and (1.20) are nearly equivalent, while expressions (1.14) and (1.19) for the stationary solution concentration, in which these ratios are only present as the components of the correlation terms, are equivalent even with a higher accuracy.

The conditions of applicability of relations (1.16) and (1.20) are fulfilled with a great excess when sulfuric acid and water play the role of components 1 and 2 in the Earth atmosphere. The figure illustrates the temperature dependence of the pressure ratio $\tilde{p}_{H_2SO_4}/\tilde{p}_{H_2O}$ plotted based on [10, 11] for sulfuric acid and water saturated vapors over their pure liquid phases within a wide range of variations in temperature under the conditions of the Earth's atmosphere. Taking into account the approximate equality $\tilde{p}_{H_2SO_4}/\tilde{p}_{H_2O} \approx \tilde{n}_{1\infty}/\tilde{n}_{2\infty}$ and the estimates $D_1/D_2 \sim 1$ and $\alpha_1\omega_1/\alpha_2\omega_2 \sim 1$, it is easy to establish that the above-considered theory is applicable for the description of the condensation of sulfuric acid and water vapors on a droplet under the conditions of the Earth atmosphere, while formulas (1.14) and (1.19) make it possible to easily find the degree of pollution of water droplets by sulfuric acid.

Note that, at a small stationary concentration of sulfuric acid in a droplet, which is ensured by inequality (1.5), formulas (1.3) derived for ideal gases are undoubtedly valid, despite the fact that they can be violated at noticeable concentrations of sulfuric acid in droplets.

2. APPENDICES TO THE KINETICS OF THE BINARY CONDENSATION OF VAPORS

Let us apply the results obtained in section 1 to the kinetic theory of the binary condensation [9] (note that the situation in question, which is characteristic of sulfuric acid and water vapors in the Earth atmosphere, was not considered in [9]). Similar to [9], we count time t from the moment of droplet nucleation in a vapor–gas medium.

Initially, assume that the droplet grows in the diffusion regime. In the presence of a relatively large amount of a passive gas in a mixture of vapors, this circumstance will take place when the inequality $R/\lambda \gg 1$ is satisfied, where λ is the free path of vapor molecules in the passive gas.

Let t_0 and R_0 be the t and R values beginning from which we may believe that a droplet grows for sure in the diffusion regime, so that $R_0/\lambda \sim 10$–20. Then, the condition $R/\lambda \gg 1$, which ensures the diffusion growth regime, will be fulfilled long before the t_0 time moment and, according to [9], with a high accuracy, we have

$$R = \beta t^{1/2} \ (t \geq t_0), \tag{2.1}$$

$$\beta^2 \equiv 2D_1 v_1[n_1 - n_{1\infty}(c_1)] + 2D_2 v_2[n_2 - n_{2\infty}(c_2)] \tag{2.2}$$

([9], expression (10) and definition (9)), where v_1 and v_2 are the partial volumes of molecules of components 1 and 2 in the liquid solution of the droplet. In relation (2.2), c_1 and c_2 refer to the stationary concentrations determined in section 1. The positivity of parameter β^2, which follows from relations (2.2) and (1.1), corresponds to the droplet growth.

Taking advantage of expression (1.2), we identically transform relation (2.2) into the following form:

$$\beta^2 \equiv 2D_2 \frac{c_1 v_1 + c_2 v_2}{c_2}[n_2 - n_{2\infty}(c_2)]. \tag{2.3}$$

With regard to relation (1.8), Eq. (2.3) yields

$$\beta^2 = 2D_2 v_2[n_2 - n_{2\infty}(c_2)]. \tag{2.4}$$

Applying relations (1.7) and (1.11), from Eq. (2.4), we arrive at

$$\beta^2 = 2D_2 v_2(\tilde{n}_{2\infty} - n_2)\varepsilon. \tag{2.5}$$

Using equality (1.11) once more, with a high accuracy, we determine the difference $\tilde{n}_{2\infty} - n_2$ at $0 < \varepsilon \ll 1$. As a result, Eq. (2.5) is reduced to the following form:

$$\beta^2 = 2D_2 v_2 \tilde{n}_{2\infty} c_1 \varepsilon. \tag{2.6}$$

From expression (2.1) at $t = t_0$ and from equality (2.6), we obtain

$$t_0 = \frac{R_0^2}{2D_2 v_2 \tilde{n}_{2\infty} c_1 \varepsilon}. \tag{2.7}$$

The t_0 value characterizes the time period after which the power law (2.1) of the droplet growth comes into force.

Now, let us consider the regularities of establishing the stationary concentration of a solution in a growing droplet. Denote the deviation of the true concentration of component 1 in the solution from its stationary value c_1 (determined by formula (1.14)) as Δc_1. According to [9], we have

$$\Delta c_1 = (\Delta c_1|_{t = t_0})\left(\frac{t_0}{t}\right)^{3(1+\eta)/2} \quad (t \geq t_0), \tag{2.8}$$

$$\eta \equiv \frac{c_1[(1 - c_1)D_1\tilde{n}_{1\infty} + c_1 D_2 \tilde{n}_{2\infty}]}{D_1[n_1 - n_{1\infty}(c_1)]} \tag{2.9}$$

([9], relation (14) and definition (15)). Equations (2.9) and (1.1) yield inequality $\eta > 0$. Formula (2.8) describes the power law of establishing the stationary concentration of a binary solution in a growing droplet in the course of time. It can be seen that, when time t_0 is elapsed after the droplet is nucleated, both the power law (2.1) of the droplet growth and the power law (2.8) of establishing the stationary concentration of the solution in the droplet come into force. As $\eta > 0$, the exponent at $1/t$ in Eq. (2.8) is by a factor of $3(1 + \eta)$ larger than the exponent at t in Eq. (2.1). It is easy to derive the relation $\Delta c_1 = (\Delta c_1|_{t = t_0})(R_0/R)^{3(1+\eta)}$, which indicates that the stationary concentration is established in the course of time even faster than the droplet radius grows. Let us find now how faster it is.

Let us express parameter η from Eq. (2.9). Taking account of relations (1.8) and (1.9), equality (2.9) is transformed into the form

$$\eta = c_1 \frac{\tilde{n}_{1\infty}}{n_1} + c_1^2 \frac{D_2 \tilde{n}_{2\infty}}{D_1 n_1}. \tag{2.10}$$

From relations (1.4) and (1.8), we derive

$$c_1 \tilde{n}_{1\infty}/n_1 \ll 1, \tag{2.11}$$

and, from equality (1.11) at $0 < \varepsilon \ll 1$, with a high accuracy, we obtain the following:

$$c_1^2 \frac{D_2 \tilde{n}_{2\infty}}{D_1 n_1} = \frac{D_2(\tilde{n}_{2\infty} - n_2)^2}{D_1 n_1 \tilde{n}_{2\infty}}. \tag{2.12}$$

Then, with regard to expression (1.12), we arrive at

$$c_1^2 \frac{D_2 \tilde{n}_{2\infty}}{D_1 n_1} = \frac{1}{\varepsilon}. \tag{2.13}$$

Taking advantage of relations (2.10), (2.11), and (2.13), at $0 < \varepsilon \ll 1$, we derive the equation

$$\eta = 1/\varepsilon, \tag{2.14}$$

which is fulfilled with a high accuracy.

Let us again consider sulfuric acid and water in the Earth's atmosphere as components 1 and 2. Considering c_1 and ε as small parameters, assume that

$$c_1 \sim 10^{-2}, \quad \varepsilon \sim 2 \times 10^{-1}. \tag{2.15}$$

At concentration c_1 estimated in this way, the pollution of a water droplet by sulfuric acid is already rather low and, at the performed estimation of parameter ε, relations (2.6), (2.12), and (2.14) at $0 < \varepsilon \ll 1$ are already quite accurate.

At 0°C and a pressure of the vapor–gas mixture (actually, the pressure of the passive gas) equal to 1 atm, we apply the following estimates:

$$\begin{gathered}\lambda \sim 3 \times 10^{-5}\text{cm}, \quad D_2 \sim 10^{-1}\text{cm}^2\text{s}^{-1}, \\ v_2 \sim 3 \times 10^{-23}\text{cm}^3, \quad \tilde{n}_{2\infty} \sim 1.6 \times 10^{17}\text{cm}^{-3}.\end{gathered} \tag{2.16}$$

Assuming that $R_0/\lambda \sim 10$–20 (as was specified above) and taking into account the values of the parameters given in (2.15) and (2.16), through the formulas (2.7) and (2.14), we obtain the following estimates: $t_0 \sim 50$–200 s and $\eta \sim 5$.

Let us discuss these values. We begin with the explanation of the large time value t_0. At a slight pollution of a water droplet by sulfuric acid, the droplet radius grows in the course of time almost entirely due to water vapor condensation on the droplet. However, this condensation proceeds quite slowly because water vapor is slightly undersaturated over the pure liquid water phase. Further, at $\eta \sim 5$, we have $3(1 + \eta) \sim 18$; thus, the exponent at $1/t$ in Eq. (2.8) is nearly 18-fold larger than the exponent at t in relation (2.1). Hence, during the time period required to establish a stationary solution concentration in the droplet, its radius does not increase significantly. This result is of great importance. As can be seen from Eq. (2.14), this change in the droplet radius would be even smaller, provided that parameter ε was taken to be smaller than in relation (2.15). As can be seen from relation (1.12), this decrease in ε is possible at a not-too-high supersaturation of sulfuric acid vapor over its pure liquid phase, since inequality (1.16) is very strong for sulfuric acid and water vapors.

Now, let us assume that the droplet grows in the free-molecular regime. This situation takes place at $R/\lambda \ll 1$. We suppose the droplet is noticeably supercritical, i.e., $R \geq (3\text{–}4)R_c$, where R_c is the critical droplet radius satisfying the strong inequality $R_c \ll \lambda$. According to [9], with a high accuracy, we have that

$$R = \gamma t \ (\tau_0 \leq t \leq 3\tau_0), \tag{2.17}$$

$$\begin{aligned}\gamma \equiv \frac{1}{4}\alpha_1\omega_1 v_1[n_1 - n_{2\infty}(c_1)] \ + \\ + \frac{1}{4}\alpha_2\omega_2 v_2[n_2 - n_{2\infty}(c_2)]\end{aligned} \tag{2.18}$$

([9], relation (18) and definition (19)), where

$$\tau_0 = 30R_c/\gamma, \tag{2.19}$$

and c_1 and c_2 are the stationary concentrations found in section 1. Commonly, $R_c \sim 10^{-7}$ cm and $\lambda \sim 3 \times 10^{-5}$ cm. In this case, the law of the growth (2.17), which is linear with respect to time, will be valid at $\tau_0 \leq t \leq 3\tau_0$. Indeed, under these constraints, from expressions (2.17) and (2.19), we find that $30R_c \leq R \leq 90R_c$, and the droplet is for sure supercritical within this time interval (inequality $t \geq \tau_0$ limits t from below); however, its radius still satisfies the condition $R/\lambda \ll 1$ of the free-molecular growth regime (inequality $t \leq 3\tau_0$ limits t from above). Note that the positive values of parameter γ, which follow from relations (2.18) and (1.1), correspond to the particle growth.

Using inequality (1.17), relation (2.18) is transformed into the following form:

$$\gamma = \frac{1}{4}\alpha_2\omega_2\frac{c_1 v_1 + c_2 v_2}{c_2}[n_2 - n_{2\infty}(c_2)]. \tag{2.20}$$

In the same way as we passed from relation (2.3) to expression (2.6), let us pass from Eq. (2.20) to the following formula:

$$\gamma = \frac{1}{4}\alpha_2\omega_2 v_2\tilde{n}_{2\infty}c_1\varepsilon, \tag{2.21}$$

in which parameter ε is specified by formula (1.18).

For the deviation Δc_1 of the true concentration of component 1 in the droplet from its stationary value c_1 (which is specified by formula (1.19)), we have the following equation:

$$\Delta c_1 = (\Delta c_1|_{t = t_0})\left(\frac{\tau_0}{t}\right)^{3(1+\chi)} \quad (\tau_0 \leq t \leq 3\tau_0) \tag{2.22}$$

([9], relation (20)), where parameter χ is determined by equality (2.9), in which D_1 and D_2 are replaced by $\alpha_1\omega_1$ and $\alpha_2\omega_2$, respectively; i.e.,

$$\chi \equiv \frac{c[(1 - c_1)\alpha_1\omega_1\tilde{n}_{1\infty} + c_1\alpha_2\omega_2\tilde{n}_{2\infty}]}{\alpha_1\omega_1[n_1 - n_{1\infty}(c_1)]}. \tag{2.23}$$

As follows from relations (2.23) and (1.1), $\chi > 0$. It can be seen that the power law for the droplet radius growth (2.17) and the power law for establishing the stationary solution concentration in the droplet are valid within the same period $\tau_0 \leq t \leq 3\tau_0$ of time t. As $\chi > 0$, the exponent at $1/t$ in Eq. (2.22) is $3(1 + \chi)$ times larger that the exponent at t in Eq.(2.17). It is easy to show that $\Delta c_1 = (\Delta c_1|_{t = \tau_0})(R_0/R)^{3(1+\chi)}$, where $R_0 \equiv R|_{t = \tau_0}$. Thus, the stationary solution concentration in the droplet is established in the course of time faster than the

droplet radius grows. Let us determine now how faster it is.

In the same way in which we passed from equality (2.9) to relation (2.14), we pass from Eq. (2.23) to the following expression:

$$\chi = 1/\varepsilon \qquad (2.24)$$

(ε is specified by formula (1.18)). Assuming that $R_c \sim 10^{-7}$ cm, $\omega_2 \sim 5 \times 10^4$ cm s^{-1}, and $\alpha_2 = 1$ and involving estimates (2.15) and (2.16), from formulas (2.19), (2.21), and (2.24), we obtain the following values of the parameters: $\tau_0 \sim 2.5 \times 10^{-2}$ s and $\chi \sim 5$.

Let us compare these values with the estimates $t_0 \sim$ 50–200 s and $\eta \sim 5$ obtained for the diffusion regime of the droplet growth. Although the time τ_0 required for establishing power laws (2.17) and (2.22) in the free-molecular regime of the droplet growth is much shorter than time t_0, it is, nevertheless, rather long. As before, the reason for this is that water vapor is slightly undersaturated over the pure liquid phase. Further, at $\chi \sim 5$, we have $3(1 + \eta) \sim 18$; hence, exponent at $1/t$ in relation (2.22) is approximately 18-fold larger than the exponent at t in Eq. (2.17). Thus, the stationary solution concentration in the droplet is established over a time during which the droplet radius changes insignificantly. Again, as can seen from Eq. (2.24), this change in the droplet radius would be even smaller if parameter ε is taken to be smaller than that in (2.15). As can be seen from Eq. (1.18), this reduction in ε is possible at a not-too-high supersaturation of sulfuric acid vapor over its pure liquid phase because inequality (1.20) is very strong for sulfuric acid and water vapors.

Note that, as the droplet size increases, the droplet growth may consecutively pass from the free-molecular to the diffusion regime. As was mentioned above, expressions (1.14) and (1.19) derived for the stationary solution concentrations in the diffusion and free-molecular regimes of the droplet growth, respectively, are nearly equivalent to each other. When the D_1/D_2 and $\alpha_1\omega_1/\alpha_2\omega_2$ ratios are close to one another as usual, laws (2.8) and (2.22) for establishing the stationary concentrations in the diffusion and free-molecular growth regimes are nearly equivalent.

CONCLUSIONS

In the above study, a key role was played by the inequality $\tilde{n}_{1\infty}/\tilde{n}_{2\infty} \ll 1$, which is fulfilled for sulfuric acid and water vapors with a great excess. This inequality, in combination with inequalities (1.4) and (1.5), determines the situation under consideration in which one component of condensing mixed vapors is supersaturated and another one is slightly undersaturated, which ensures the condition for the applicability of the entire above-described theory.

Inequality $\tilde{n}_{1\infty}/\tilde{n}_{2\infty} \ll 1$ enabled us to introduce parameter ε determined by formulas (1.12) and (1.18), with this parameter being small despite the existence of constraint (1.5). In turn, the smallness of parameter ε made it possible to easily derive simple expressions (1.14) and (1.19) for the stationary solution concentration in a growing droplet.

In addition, inequality $\tilde{n}_{1\infty}/\tilde{n}_{2\infty} \ll 1$ led us to draw the following important conclusion: the stationary solution concentration is established in a droplet over a time during which its radius increases insignificantly. The stronger the inequality $\tilde{n}_{1\infty}/\tilde{n}_{2\infty} \ll 1$ and, accordingly, the inequality $\varepsilon \ll 1$, the slower, according to relations (2.6) and (2.21) and dependences (2.1) and (2.17), a rise in the droplet radius, however, according to formulas (2.14) and (2.24) and dependences (2.8) and (2.22), the faster the establishment of the stationary solution concentration in the droplet. Thus, in both diffusion and free-molecular regimes, most of time, a droplet grows under the condition of stationary solution concentration when simple dependences (2.1) and (2.17) are valid for the droplet radius growth in the course of time.

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