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Trapping of impurity molecules in condensation from mixtures of gases

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Abstract

The problems of trapping of impurity molecules in deposition of substance from a mixture of gases are investigated. Both internal and external problems are considered. The influence of the condensation rate of basic substance on the concentration of impurity molecules in a condensed phase is analyzed. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Condensation of a substance from a mixture of gases plays an important part in many areas of modern technology [1]. These areas involve both processes in which it is necessary to maintain a definite composition of a gas phase, while transition of particles into a condensed phase is a factor which allows one to control the concentration of components in the gas phase (here a cryotrapping phenomenon can be an example [2]), and the processes where the concentration of components in a condensed phase is of principal interest (e.g., in vacuum deposition of thin films of definite composition for the elements of microelectronics). In studying the process of condensation from a mixture of gases a number of problems occur related both to mass and energy transfer in a gas and a condensed phase, and to the conditions of conjugation of the phases mentioned. In the present work, some problems of the influence of the nonequilibrium of condensation conditions (condensation rate) on the transition of molecules from a gas to a condensed phase are considered.

In calculation of the process of deposition from a mixture of gases it is often assumed that the molecules of the component, which is non-condensing under given thermodynamic conditions, do not enter into a condensate. On the other hand, just the entrance of a non-condensing component into the condensate in deposition of an easily condensing component enables one to create cryopumps operating on the principle of cryotrapping [2]. Note that, in principle, the phenomenon analogous to cryotrapping can be realized also under ordinary conditions and not only at very low (cryogenic) temperatures.

The problems mentioned above arise also in problems related to the growth of aerosol particles in deposition of substance from a mixture of gases. They involve both the problems of obtaining nano-particles by chemical deposition [3–5], when the composition of particles (their purity in a number of cases) plays a

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Nomenclature

C	concentration of molecules in condensate
G	trapping coefficient of impurity molecules
h	Planck constant
I	resultant flux of molecules into condensate
J	density of radiation flux
k	Boltzmann constant
l	dimensionless length of a channel, $l = L/R_c$
L	length of a channel
m	mass of a molecule
n	number density of molecules in a gas phase
n_s	total number density of molecules in condensate
N	density of the flux of molecules incident on a surface
Q	energy of evaporation of a molecule from condensate
r	radial coordinate
R	radius of an aerosol particle
R_c	radius of a channel
S	area of a surface
T	temperature of a surface
T_g	gas temperature
v	mean thermal velocity of molecules
V	volume
x	dimensionless coordinate, $x = X/L$

Greek symbols

α	coefficient of sticking of molecules to a surface
γ	fraction of excited molecules
ν	radiation frequency
σ	cross-section of radiative transitions of molecules
τ	relaxation time

Subscripts

g	gas
i	i-component of a mixture
s	condensed phase
ν	excited molecules
1	basic condensing component
2	impurity component
∞	gas parameters at an infinite distance from an aerosol particle

very important part, and the problems connected with the physics of the atmosphere (trapping of impurity in condensational growth of drops in the atmosphere) [6].

The problem of purification of different volumes of impurity molecules, including non-condensing ones (the problem of pure rooms in the technology of microelectronics, the cleaning of the atmosphere from injurious, in particular, radioactive, impurities and so on) is very important for many fields of chemical technology. The phenomenon of trapping of impurity molecules by growing layer of condensate (or by growing aerosol particles) can also be used for these purposes. Here the following methods of purification can be applied: trapping (immuring) of impurity molecules on a panel where condensation of an easily condensing component occurs; use of channels (porous bodies) for pumping a mixture of gases with condensation of one of the components on the walls of the channel (pores) and trapping of an impurity component; creation of conditions for the production and growth of aerosol particles in a purified volume. The particles with trapped impurity molecules can further be taken out from the purified volume.

Usually, in determining the concentration of components in a forming condensate either thermodynamic relations are used, which are valid only for the conditions of equilibrium (when the number of evaporating molecules is equal to the number of condensing ones), or the other limiting case, when the evaporation of molecules of the impurity component from a condensate is not taken into account whatsoever. But real conditions of condensation can lie between these limiting cases.

All of the above shows the necessity for investigating the process of substance deposition from mixtures of gases on the basis of a molecular–kinetic approach.

2. Kinetics of the deposition of a substance from a gas mixture

In formulation of problems of molecular-kinetic theory for mixtures of gases in the case of deposition of components on surfaces, it is necessary to have expressions for resultant fluxes of components onto a surface. Consider a single-stage model of substance deposition in which the molecules of a gas are assumed to enter directly in the condensate layer already available on the surface (the processes of the formation of a condensate on a pure surface, as well as the processes related to the surface structure and transport of impurity molecules over the surface and in the condensate volume are not considered, the concentrations of the components on the surface of the condensate and in its volume are assumed to be equal). Note that in a more detailed description of the process of trapping one should use a model which takes account of the possibility for the presence of a different number of bonds of an impurity molecule with the molecules of the basic component (similarly to the model used to describe a layered growth of crystals which considers the migration of particles over the surface and their imbedding into the steps and terraces existing on the surface [7]).

Let us express the concentrations of components in a condensate via the values of the densities of resultant molecular fluxes I_i similarly to [8,9]

$$C_i = \frac{I_i}{\sum_k I_k}, \tag{1}$$

where the quantities I_i are expressed as

$$I_i = \alpha_i N_i - \frac{I_i}{\sum_k I_k} F_i. \tag{2}$$

Here, α_i is the coefficient of the sticking of the molecules of the component i to the condensate surface, N_i is the flux density of the molecules of the component i incident on the surface; this flux should be found from a joint solution of Eq. (2) and the external problem for a gas phase. Under the assumption of the Maxwell velocity distribution function we have: $N_i = n_i v_i/4$, where n_i and v_i are the density in a gas phase and mean thermal velocity of the molecules of the component i, respectively. We have the following expression for the quantity F_i characterizing the re-evaporation of molecules from the condensate [10]

$$F_i = A_i \exp\left\{-\frac{Q_i}{kT}\right\}, \tag{3}$$

where $A_i = n_s (kT/2\pi m_i)^{1/2}$, n_s is the density of molecules in a condensed phase (assumed to be constant), Q_i is the heat of evaporation of a molecule of the component i from the condensate, which, in general, depends on the concentration of components in the condensate (and, respectively, on I_i in accordance with Eq. (1)). The flux density of evaporating molecules can also be expressed via the saturated vapour pressure of the given component.

In Refs. [8,9,11–18], correlations (1)–(3) were used for investigation of both external problems related to trapping of impurity molecules in deposition of substance from a mixture of gases on a substrate or to the growth of aerosol particles and the problems of deposition of substance on the internal surface of a cylindrical channel. An approach connected with the expression of concentration in a droplet in terms of the resultant fluxes of components into the droplet (expression (1)) is also used in Refs. [19,20], with investigation of the problem of the growth of a droplet from a mixture.

Note that the quantity α_i in Eq. (2) is the mean value of the coefficient of sticking of the molecules of the component i to the condensate surface. The difference in the sticking coefficients of different molecules can be caused both by the possible occurrence of molecules in different states in a gas phase (e.g., in excitation of a part of molecules by resonance laser radiation) and by the probability for molecules to enter into the surface regions occupied by molecules of different components. In the first case, the quantity i can be presented as

$$\alpha_i = \gamma_i \alpha_{iv} + (1 - \gamma_i)\alpha_{i0} = \alpha_{i0} + \gamma_i(\alpha_{iv} - \alpha_{i0}). \tag{4}$$

Here, it is assumed that the part γ_i of the molecules of the component i can be in excited state being characterized by the sticking coefficient α_{iv}, different from the sticking coefficient of nonexcited molecules α_{i0} (a double-level model for transitions of molecules from one state to another is considered for simplicity). The quantity γ_i is defined as $\gamma_i = n_{iv}/(n_i + n_{iv})$, where n_i, n_{iv} are the densities of nonexcited and excited molecules of the component i, respectively, in a gas phase, which are determined from the system of equations [21]

$$\frac{dn_{iv}}{dt} = \frac{J\sigma_i}{h\nu}(n_i - n_{iv}) - \frac{n_{iv}}{\tau_i}, \tag{5}$$

$$\frac{dn_i}{dt} = \frac{J\sigma_i}{h\nu}(n_{iv} - n_i) + \frac{n_{iv}}{\tau_i}, \tag{6}$$

where J is the intensity of radiation, σ_i is the cross-section of radiative transitions of the molecules of the component i from one state to another, τ_i is the relaxation time of molecules of the component i.

In a steady state, it follows from Eqs. (5) and (6) that

$$\gamma_i = \frac{(\sigma_i J/h\nu)\tau_i}{1 + (2\sigma_i J/h\nu)\tau_i}. \tag{7}$$

Further for simplicity, the case of a binary gas mixture will be considered where the indices 1 and 2 will be related to the parameters of a basic condensing substance and an impurity gas, respectively (naturally, extension to multicomponent mixture does not involve difficulties in principle).

With a difference in the sticking coefficients of the molecules that reach the surface regions occupied by different molecules, the following expression can be written for α_i with account for Eq. (1) [12]

$$\alpha_i = \alpha_{i1}\frac{I_1}{I_1+I_2} + \alpha_{i2}\frac{I_2}{I_1+I_2}, \tag{8}$$

where α_{ij} is the coefficient of sticking of the molecules of the component i to the surface region occupied by the molecules of the component j.

Note that in the case, when $I_2/I_1 \ll 1$ and the concentration of one of the components in the condensate is much smaller than the concentration of the second (the case of an impurity component), the sticking coefficient and the heat of evaporation from the condensate can be considered as independent of concentration. They will be determined, in the main, by interaction of the molecules of the mixture components with the molecules of a basic depositing substance.

After determination of the values of I_1 and I_2 from Eqs. (1) and (2), we can find the concentration of components in the condensate. Further, we suppose for the simplicity of the analysis that $I_2/I_1 \ll 1$. Under the assumptions mentioned we obtain from Eqs. (1) and (2), neglecting the terms of the second order of smallness in I_2/I_1 [12]:

$$I_2 = \alpha_2 N_2 - \frac{I_2}{I_1}F_2, \tag{9}$$

$$I_1 = \alpha_1 N_1 - \left(1 - \frac{I_2}{I_1}\right)F_1. \tag{10}$$

An expression for the coefficient of trapping of impurity molecules G_2, defined as I_2/N_2, follows from Eq. (9)

$$G_2 = \frac{\alpha_2 I_1}{I_1+F_2}. \tag{11}$$

As seen from Eqs. (10) and (11), an increase in the flux density of a basic condensing substance leads to an increase in the coefficient of trapping of impurity molecules, and an increase in the flux density of impurity molecules, in turn, results in an increase in the flux density of a basic condensing substance (here the parameters α_i and F_i are assumed to be constant) [9,12].

Neglecting the quantity I_2/I_1 relative to unity in Eq. (10), we obtain an expression for the concentration C_2 of the impurity component in the condensate

$$C_2 = \frac{\alpha_2 N_2}{I_1+F_2}. \tag{12}$$

Note that neglecting the re-evaporation of impurity molecules ($F_2 = 0$) we can obtain from Eq. (12) the correlation for the density of impurity molecules in the condensate analogous to that presented in Ref. [22].

It is seen from Eqs. (11) and (12) that in deposition of a basic condensing component ($I_1 \neq 0$) in the case of $\alpha_2 \neq 0$, the trapping of an impurity component by the growing layer of the condensate is realized. We obtain from Eqs. (11) and (12) the following equations:

$$\frac{\mathrm{d}C_2}{\mathrm{d}I_1} = -\frac{\alpha_2 N_2}{(I_1+F_2)^2}, \tag{13}$$

$$\frac{\mathrm{d}G_2}{\mathrm{d}I_1} = \frac{\alpha_2 F_2}{(I_1+F_2)^2}. \tag{14}$$

It follows from Eqs. (13) and (14) that with an increase in the condensation rate of the basic component, with the rest parameters being constant, the value of G_2 will increase and the value of C_2 will decrease. It is connected with the fact that with an increase in the condensation rate the probability for the impurity molecules to be trapped by the growing condensate layer increases, but an ever increasing number of molecules of the basic condensing substance account for each impurity particle trapped by the condensate, which leads to a decrease in the value of C_2.

The following conclusion can be made from the foregoing. The rate of deposition (of the growth of aerosol particles) should be increased to optimize the process both in the problems of production of high-purity substances, when the entrance of impurity molecules into a condensate is undesirable, and in the problems related to purification of a certain volume of impurity molecules by means of their trapping by growing aerosol particles with subsequent removal of the particles from the volume, when a sufficiently large trapping coefficient of impurity molecules is necessary.

The influence of I_1 (and, correspondingly, of deposition rate) on the trapping of impurity molecules can be investigated by means of the described approach for both external and internal problems. First we will consider a problem which models operation of a pump on the principle of cryotrapping.

3. Trapping of impurity molecules by a condensate layer growing in a quasi-closed volume

Consider the process of trapping of impurity molecules in a condensate forming on a cryopanel placed in a quasi-closed volume [9]. Suppose there is the volume V which contains a cryopanel whose temperature is maintained to be low enough so that there occurs condensation of one of the components of the gas mixture entering the volume. The second component is assumed to be non-condensing under the given thermodynamic parameters. The sticking coefficients are assumed for simplicity to be equal to unity ($\alpha_1 = \alpha_2 = 1$). We can write the following balance correlations for the densities of the gas components n_i in the volume considered, assuming ideal mixing of the gas mixture:

$$V\frac{\mathrm{d}n_1}{\mathrm{d}t} = b_1\left(n_1' - n_1\right) - \left[n_1\left(\frac{kT_\mathrm{g}}{2\pi m_1}\right)^{1/2} - F_1\right]S, \tag{15}$$

$$V\frac{\mathrm{d}n_2}{\mathrm{d}t} = b_2\left(n_2' - n_2\right) - n_2\left(\frac{kT_\mathrm{g}}{2\pi m_2}\right)^{1/2} SG_2, \tag{16}$$

where T_g is the gas temperature in the volume, b_i is the quantity characterizing throughput capacity of the channel which supplies the component i to the volume, n_i' is the density of the component i in a gas phase beyond the volume, S is the surface area of the cryopanel on which gas deposition takes place.

In a steady state, we have from Eqs. (15) and (16)

$$n_2 = \frac{b_2 n_2'}{b_2 + S\left(\dfrac{kT_\mathrm{g}}{2\pi m_2}\right)^{1/2} \dfrac{I_1}{I_1 + F_2}}, \tag{17}$$

where

$$I_1 = \frac{b_1 n_1' + SF_1}{b_1 + S\left(\dfrac{kT_\mathrm{g}}{2\pi m_1}\right)^{1/2}} \left(\frac{kT_\mathrm{g}}{2\pi m_1}\right)^{1/2} - F_1. \tag{18}$$

It follows from Eq. (17) that in deposition of an easily condensing gas ($I_1 > 0$) the density of impurity molecules n_2 in the volume decreases in comparison with that which would have been present without condensation of the first component (i.e., the process of the evacuation of a non-condensing gas occurs). To create the process of intense substance condensation, it is also possible, instead of use of the cryopanel, to inject the supersaturated vapour of a basic condensing substance into the volume together with condensation centers on which vapour molecules will be deposited. Impurity molecules will be trapped by growing aerosol particles, which can thereafter be withdrawn from the volume considered.

4. Influence of the rate of deposition on the distribution of impurity in thin condensate layers

The trapping of impurity is also displayed in the problems of vacuum deposition of layers of substances from a gas phase, in particular, in production of thin films for the elements of microelectronics. It is often considered in the problems related to obtaining condensates of sufficiently high purity that the concentration of impurity in the condensate can be estimated by the correlation [23,24]

$$C_2 = \frac{N_2}{N_1}, \tag{19}$$

where N_1 and N_2 are the densities of the fluxes of condensing and impurity molecules, respectively, incident on the condensate surface. Expression (19) does not take account of the possibility for the re-evaporation of molecules, which can substantially affect the accuracy of calculation of the impurity concentration C_2. Since a very small amount of impurity can essentially change the physico-chemical properties of a condensate, the inaccuracy in the estimation of the amount of impurity or of its distribution in the condensate can lead to considerable errors in the estimate of the properties of the condensate obtained.

Some examples will be presented from the field of the production of optical coatings [24] to illustrate the influence of impurities on the properties of a condensate. Thus, for instance, in manufacturing mirrors from aluminum with a purity of 99.5%, the reflection at the wavelength of 170 nm is by about 10% worse than for the coating obtained from aluminum with a purity of 99.99%. A gold coating with the thickness of 0.14 μm deposited on a copper substrate in a vacuum of 5×10^{-9} mm Hg has a radiation stability which is 3.5 times higher than that of the coating obtained in a vacuum of 5×10^{-4} mm Hg. The part of impurities in technology of semiconductor devices is still more important.

First, we will consider the distribution of impurity in the condensate layer forming on a plane isothermal substrate when the source of the substance deposited can be assumed to be a point one; it is also assumed that the impurity molecules are supplied from the same source as the basic deposited substance. Taking account of Eqs. (1) and (2), the following expression can be written for the concentration of impurity in the condensate [15]

$$C_2 = \frac{\alpha_2 g_2}{\alpha_1 g_1 - \left[A_1 \exp\left\{-\dfrac{Q_1}{kT}\right\} - A_2 \exp\left\{-\dfrac{Q_2}{kT}\right\}\right]\phi^{-1}}. \tag{20}$$

Here g_i is the number of the molecules of the component i leaving the source per time unit, and the function ϕ has the form

$$\phi = \frac{z}{4\pi(z^2 + d^2)^{3/2}}. \tag{21}$$

where z is the minimum distance between the source and the substrate, d is the distance between the projection of the source onto the substrate and the considered point on the substrate. It is seen from Eq. (20) that if the expression in the square brackets is negative, the concentration of impurity will be maximum at the center of the layer deposited (i.e., with $d = 0$). If this expression is positive, the impurity concentration will increase from the center to the periphery of the layer. In Ref. [15], the case is also discussed when the molecules of impurity fall on the condensate surface from the environment (i.e., when the flux density of impurity molecules is uniformly distributed over the condensate surface).

In the case of deposition of a condensate layer of uniform thickness on the substrate, when $I_1 = \text{const} = D$ (this can be realized by creating specific temperature distribution on the substrate [15]), we obtain the following expression for the concentration of impurity in the condensate neglecting the temperature dependence of the quantities A_i:

$$C_2 = \frac{\alpha_2 g_2 \phi}{D + A_2\left[A_1^{-1}(\alpha_1 g_1 \phi - D)\right]^{Q_2/Q_1}}. \tag{22}$$

When impurity molecules are incident from the environment, the quantity $\alpha_2 N_2$ will be written in the numerator of Eq. (22).

5. Internal problems of the deposition of substance from a mixture of gases

The problem of uniform deposition of a substance layer on the inner surface of channels of different configurations is urgent in the technology of the manufacture of microelectronics elements [25]. It is connected with the fact that otherwise cavities can be formed in a filler during the occupation of channels by a substance by means of deposition from a gas phase, which leads to the worsening of the quality of the items produced. The number and distribution of impurity molecules in a forming condensate also affect the quality of microelectronics products. Note that the process of deposition is often realized in a free molecular regime of gas flow in a channel. The problem of uniform deposition of substance on the inner surface of a cylindrical channel in this regime was investigated in Ref. [26]. It is shown that to obtain uniformity, it is necessary for the temperature to change along the channel wall by a definite law. But the change in the temperature on the phase transition surface affects, in turn, the distribution of impurity molecules in the condensate. With account for Eqs. (1) and (2), we can write the following expressions for the densities of the resultant fluxes of molecules into the condensate forming on the inner surface of a cylindrical channel of length L and radius R_c in quasi-stationary approximation (the thickness of the condensate layer is assumed to be much smaller than the radius of the channel) [15]

$$I_i = \alpha_i \left\{ \int_0^1 \left[\frac{I_i(x')}{\sum_k I_k(x')} F_i(x') + B_i(x') \right] \times K_1\left(|x - x'|\right) \mathrm{d}x' + N_i(0)K(x) + N_i(1) \times K(1 - x) \right\} - \frac{I_i(x)}{\sum_k I_k(x)} F_i(x), \tag{23}$$

$$B_i = (1 - \alpha_i) \left\{ \int_0^1 \left[\frac{I_i(x')}{\sum_k I_k(x')} F_i(x') + B_i(x') \right] \times K_1\left(|x - x'|\right) \mathrm{d}x' + N_i(0)K(x) + N_i(1) \times K(1 - x) \right\}, \tag{24}$$

where x is the dimensionless coordinate directed along the channel, K_1, K are the functions characterizing the probability of molecule incidence from one element of the surface on another [27,28], B_i is the flux density of elastically scattered molecules, the quantity in the square brackets characterizes the flux density of the molecules of the component i incident on an element of the lateral surface of the channel in the vicinity of the point x.

For a binary gas mixture with the condition $I_2/I_1 \ll 1$ being satisfied taking account of Eqs. (23) and (24) in exponential approximation of the functions K, K_1 [27], we can find an expression for the temperature distribution $T(x)$ along the channel, which is required for a uniform deposition of substance on the channel wall [26].

With the knowledge of $T(x)$, we obtain the following expression for C_2 under the symmetric conditions $N_1(0) = N_1(1) = N_1$, $N_2(0) = N_2(1) = N_2$ and with the satisfaction of the condition $F_2/I_1 \gg 1$ [15]

$$C_2 = \frac{\alpha_2 N_2}{A_2 \left\{ \dfrac{\alpha_1 I_1}{A_1} \left[\dfrac{N_1}{I_1} - \dfrac{l}{2} - \dfrac{l^2}{2} x(1 - x) \right] - \dfrac{I_1}{A_1} \right\}^{Q_2/Q_1}}, \tag{25}$$

where $l = L/R_c$.

It is seen from Eq. (25) that the maximum value of C_2 is realized at the channel center ($x = 1/2$). The inverse situation can also occur. For example, under the symmetric conditions for $N_i(0)$, $N_i(1)$ in the case, when the reflection of impurity molecules from the condensate surface and the re-evaporation of the molecules from the condensate can be neglected, the concentration of impurity will be minimum at the channel center [15].

Also of interest is the problem of the passage through a cylindrical channel of the molecules of the component, which is non-condensing under the given values of thermodynamic parameters with condensation of an easily condensing component on the channel walls [9]. Here, the molecules of the non-condensing component can enter the layer of the condensate growing on the walls of the channel and remain there (be immured into the condensate). This lowers the probability for the molecules of the non-condensing component to pass through the channel. This phenomenon can be used in separation of gas mixtures, as well as in the problems of purification of a gas phase of the molecules of a poorly condensing component. For simplicity, the coefficients of sticking of molecules of both components to the condensate are assumed to be equal to unity and the temperature of the phase transition surface is assumed to be a constant quantity. Considering that $N_1(0) = N_1(1) = N$, $I_1/1_2 \gg 1$, with exponential approximation for K, K_1 we have from Eqs. (23) and (24) for the probability of the passage of molecule through the channel, being determined in accordance with [28], the following expression in the first approximation with respect to the parameter $\varepsilon = (N_1 - F_1)/F_2$ which is assumed to be small in comparison with unity [9]:

$$W = \frac{2}{2+l}\left[1 - \varepsilon\frac{2l + \exp\{-l\} - 1}{2+l}\right]. \tag{26}$$

The second term in Eq. (26) characterizes a decrease in the probability for a molecule of the non-condensing component to pass through the channel due to trapping of the molecule by the growing layer of the condensate. After calculation of the resultant flux of the molecules of the impurity component into the condensate, we can find the total number of impurity molecules trapped per unit time over the entire length of the channel:

$$M = 2\pi R_c L \int_0^1 I_2(x)\,\mathrm{d}x. \tag{27}$$

6. Trapping of impurity molecules by growing aerosol particles

The problem of the trapping of impurity molecules by growing aerosol particles will be considered using the production of nano-size aerosol particles as an example. This problem is topical for a number of the areas of modern technology related to the manufacture of highly efficient catalysts, as well as to the production of new, in particular, superconductor materials. Here, the method of laser chemical deposition of substance from a gas phase is effective [5]. Since in chemical deposition of substance there are molecules of a basic condensing component in a gas phase, as well as impurity molecules, including those non-condensing for the given values of thermodynamic parameters, a question arises concerning the incidence of these molecules into the aerosol particles (trapping of impurity molecules by growing particles). Further we will neglect, for simplicity, the trapping of the molecules of an inert gas, which serves as a gas carrier in the processes of laser chemical deposition, considering the coefficient of sticking of inert gas molecules to the particle surface to be sufficiently small. Impurity molecules can enter a reactor, where laser chemical deposition of substance occurs, from the atmosphere, as well as appear there as a result of the chemical reaction used for the production of the molecules of a condensing component. As an example of such a reaction, the decomposition of the vapours of $Si(OC_2H_5)_4$ (tetraethylorthosilicate) into the molecules of SiO_2 can be considered during the subsequent condensation of which aerosol particles are produced [3]. Besides, the molecules of C_2H_4 and H_2O appear in this reaction.

An equation of diffusion in an inert gas can be written for each of the components of the gas mixture under the condition of smallness of the density of this component compared with the density of an inert gas, neglecting the convective constituent of mass transfer. The solution of this equation in a steady case has the form

$$n_i = a_i - \frac{b_i}{r}, \tag{28}$$

where r is the coordinate reckoned from the center of the aerosol particle of radius R, a_i and b_i are the integration constants which are found from boundary conditions. Further, we assume that $n_i|_{r=\infty} = n_{i\infty}$, from which it follows that $a_i = n_{i\infty}$. The values of $n_{i\infty}$ in the presence of chemical transformations in a gas phase due to laser radiation (for example, decomposition of $Si(OC_2H_5)_4$ according to the above-mentioned scheme) should be found from the equations describing the process of heat and mass transfer with account for chemical transformations and excitation of molecules in a radiation field. Below we will consider the question of the trapping of impurity molecules by aerosol particles growing due to condensation assuming the values of $n_{i\infty}$ to be known.

The following boundary condition can be written on the particle surface (at $r = R$)

$$D_i\frac{\mathrm{d}n_i}{\mathrm{d}r}|_{r=R} = I_i, \tag{29}$$

where D_i is the diffusion coefficient of the component i, I_i is the density of the resultant flux of molecules of the component i into a particle expressed by Eq. (2).

Assuming the density of the resultant flux of impurity molecules into an aerosol particle to be much smaller than the density of the resultant flux of the basic depositing substance, for the density of the resultant flux of impurity molecules into the particle, with account for Eqs. (2), (28) and (29) we obtain [13,29]

$$I_2 = \frac{\alpha_2 \dfrac{n_{2\infty} v_2}{4}}{1 + \dfrac{F_2}{I_1} + \alpha_2 \dfrac{v_2 R}{4D_2}}. \tag{30}$$

The value of the density of the resultant flux I_1 of the basic condensing component is obtained similarly as Eq. (30), taking account of the fact that the coefficient at F_1 in Eq. (2) written for I_1 can be assumed to be equal to unity. We have the following expression for the flux density of the molecules of the basic condensing component

$$I_1 = \frac{\alpha_1 \dfrac{n_{1\infty} v_1}{4} - A_1 \exp\left\{ - \dfrac{Q_1(R)}{kT} \right\}}{1 + \alpha_1 \dfrac{v_1 R}{4D_1}}. \tag{31}$$

As follows from Eqs. (1), (30) and (31), the concentration of impurity in the condensate will decrease with an increase in I_1 (and, correspondingly, in the rate of particle growth which in condition $I_2 \ll I_1$ can be written as $v_R = I_1/n_s$). In the case when F_2/I_1 is much higher than the first and third terms in the denominator of Eq. (30), the value of C_2 practically does not depend on I_1. The influence of different factors on the concentration of impurity in the particle (this question is actual in the manufacture of high-purity substances) can be analyzed by means of Eqs. (1), (30) and (31).

The resultant flux into a particle both of an impurity and of a basic substance can also change during the growth of the aerosol particle in connection with the change in the particle radius, which, in principle, will lead to the change in the concentration along the particle radius. In particular, this can be caused by the rise in the temperature of the aerosol particle (and, correspondingly, by the change in the value of F_i) in radiation effect.

It is also seen from Eqs. (1), (30) and (31) that the possibility appears for affecting the concentration of impurity in the particles by radiation exciting molecules, which leads to the difference in the sticking coefficients of excited and non-excited molecules, as well as to a change in the value of Q_i (and, correspondingly, of F_i) in the radiation field.

Thus, in growth of aerosol particles from a gas phase in the processes of laser chemical deposition the possibility should be taken into account for the trapping, by growing particles, of the impurity molecules arriving into a reactor from outside, as well as of the molecules forming as a result of chemical reaction. Here, particle heating by radiation, as well as resonance effects changing the character of interaction of molecules with the particle surface can influence the concentration of impurity in the particles in a radiation field.

7. Conclusion

Analysis of the problems of condensation from gas mixtures based on a simple single-stage model with the use of expressions (1) and (2) [8,9] enabled one to estimate the effects related to the nonequilibrium of a deposition process (deposition rate) and affecting impurity concentration in the condensate forming during deposition. This is important for both estimation of the purity of the condensate obtained and calculation of the efficiency of purification of gas phase in trapping of impurity molecules by a growing layer of the condensate (or by growing aerosol particles). The model considered provides also the possibility to take account of the mutual influence of components on the condensation process, in particular, to describe the effect of the trapping of molecules of the component, which is non-condensing at the given values of thermodynamic parameters, in condensation of an easily condensing gas (a phenomenon of the type of cryotrapping).

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