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Conference paper

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Concentration profiles around and chemical composition within growing multicomponent bubble in presence of curvature and viscous effects

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Abstract: The regularities of changing chemical composition and size of a ultra-small multicomponent gas bubble growing in a viscous solution have been analyzed. The full-scale effects of solution viscosity and bubble curvature at non-stationary diffusion of arbitrary number of dissolved gases with any value of gas supersaturations and solubilities in the surrounding liquid solution have been taken into account. The non-uniform concentration profiles of gas species in supersaturated solution around the growing bubble with changing composition have been found as a function of time and distance from the bubble center. Equations describing transition to stationary concentrations of gases in the bubble with increasing radius have been obtained. Analytic asymptotic solutions of these equations for a ternary system have been presented.

Keywords: bubble chemical composition; bubble growth; curvature effect; degassing; diffusion; Mendeleev-21; multicomponent solution; viscous effects.

Introduction

There are two general approaches to theory of first-order phase transitions in a closed system with a limited availability of the nucleating species: the approach with the mean-field supersaturation and the approach with the excluded volume. The first approach implies that nucleation and growth of new-phase particles is governed by stationary diffusion of molecules and accompanied by a synchronous and uniform decrease in the mean supersaturation of the metastable phase [1–5]. The excluded volume approach is based on a self-similar solution for non-stationary diffusion onto the growing supercritical particles and takes into account that nucleation of new particles is strongly suppressed around growing ones [3–10]. Only the theory of excluded volume describes strong swelling of liquid solutions with dissolved gas at fast decompressing [3, 5, 6].

In the case of liquid solution with several dissolved gases, both approaches assume stationary concentrations of gases in the bubbles growing with steady rate [3, 5]. However, strong influence of the Laplace pressure in a submicron gas bubble and viscosity of liquid solution on the growth rate of the bubble is able to postpone significantly establishing the stationary chemical composition in the bubble and its steady growth rate. As a result, application of the self-similar concentration profiles around the bubble in the theory of bubble nucleation is under the question. "Equations for bubble pressure and gas concentration profile around the bubble" of this paper answers how the dynamics of a multicomponent bubble growth in supersaturated

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solution with several dissolved gases should be reformulated to include the full-scale viscosity and capillarity (the Laplace pressure or curvature) effects, non-stationary diffusion of gas components at any value of their supersaturations and solubilities in the surrounding liquid solution and changing the bubble chemical composition. Equations describing transition to stationary concentrations of gases in the bubble with increasing radius are considered in “Joint evolution of the radius and chemical composition of a growing bubble”. Analytical asymptotic solutions of these equations for a ternary system are presented in “Asymptotics of reaching steady-state and self-similar diffusion growth regime”.

Equations for bubble pressure and gas concentration profile around the bubble

Let us consider a growing gas bubble in viscous liquid solution with arbitrary number k of dissolved gases. The dependence of total gas pressure P_g in a free supercritical spherical bubble growing in the liquid solution with supersaturated dissolved gases on the bubble radius R (and its derivatives R' and R'' with respect to time) is described by the Rayleigh–Plesset equation [11, 12]

$$\rho\left(RR''+\frac{3}{2}R'^2\right)=P_g-P-\frac{2\sigma}{R}-4\eta\frac{R'}{R} \tag{1}$$

where P is the pressure in the liquid solution, σ is the bubble surface tension, ρ and η are the liquid solution density and viscosity, respectively. We can neglect in most cases the contribution from inertial effects [given by the left-hand side of eq. (1)] [10] and to reduce eq. (1) to the form

$$P_g=P+\frac{2\sigma}{R}+4\eta\frac{R'}{R}. \tag{2}$$

Under assumption that all gases in the bubble are uniformly distributed and ideal, we have the following relation for the total gas concentration $n(R)=\sum_{i=1}^{k}n_i$ as a function of the bubble radius R with the full-scale account of the Laplace pressure $2\sigma/R$ and viscosity η:

$$n(R)=\frac{P_g}{k_BT}=\bar{n}\left[1+\frac{R_*}{R}\left(1+\frac{2\eta R'}{\sigma}\right)\right] \tag{3}$$

where $\bar{n}\equiv P/k_BT$, $R_*\equiv 2\sigma/P$. If the bubble radius is larger ten nanometers, we can neglect adsorption of gas components at the bubble surface, then the total number N of gas molecules in the bubble equals

$$N=\frac{4\pi}{3}n(R)R^3=\frac{4\pi}{3}\bar{n}R^3\left[1+\frac{R_*}{R}\left(1+\frac{2\eta R'}{\sigma}\right)\right]. \tag{4}$$

It is follows from eq. (4) that the rate N' of changing the total number N in time equals

$$N'=N(R)\frac{3}{R}R'\left(1+\frac{R}{3}\frac{d\ln n(R)}{dR}\right) \tag{5}$$

where

$$1+\frac{R}{3}\frac{d\ln n(R)}{dR}=\left[1+\frac{R_*}{R}\left(1+\frac{2\eta R'}{\sigma R}\right)\right]^{-1}\left[1+\frac{2R_*}{3R}\left(1+\frac{2\eta R'}{\sigma}+\frac{\eta R}{\sigma}\frac{dR'}{dR}\right)\right]. \tag{6}$$

As seen from eqs. (4) and (5), the number N_i and the rate N_i' of changing molecules of ith gas component in the bubble can be related to its volume concentrations n_i in the similar to eq. (5) way

$$N_i' = N_i(R)\frac{3}{R}R'\left(1+\frac{R}{3}\frac{d\ln n_i(R)}{dR}\right). \tag{7}$$

Because the surface of the growing bubble with radius R shifts at every point with the velocity of an incompressible liquid solvent, so we have for the rate N_i' of ith gas component and the total rate N' the following balance equations

$$N_i' = 4\pi R^2 D_i \left.\frac{\partial c_i(r,t)}{\partial r}\right|_{r=R} \quad (i=1,2,\ldots,k), \tag{8}$$

$$N' = 4\pi R^2 \sum_{i=1}^{k} D_i \left.\frac{\partial c_i(r,t)}{\partial r}\right|_{r=R} \tag{9}$$

where D_i is the diffusivity of molecules of ith gas component ($i=1, 2, \ldots, k$) in a solvent and $c_i(r, t)$ is the volume concentration of molecules of this component at time t in solution at distance r from the center of the bubble. The concentration $c_i(r, t)$ satisfies in the most general case the non-stationary diffusion equation [3, 5]

$$\frac{\partial c_i(r,t)}{\partial t} = \frac{D_i}{r^2}\frac{\partial}{\partial r}\left[r^2\frac{\partial c_i(r,t)}{\partial r}\right] - \frac{R^2(t)R'(t)}{r^2}\frac{\partial c_i(r,t)}{\partial r} \quad (i=1,2,\ldots,k) \tag{10}$$

with boundary conditions

$$c_i(r\to\infty, t) = c_{i0}, \quad c_i(r=R(t),t) = c_i(R). \tag{11}$$

Here $c_i(R)$ is the equilibrium concentration of ith gas component at the bubble surface. According to the Henry law, $c_i(R)=s_i n_i(R)$ where s_i is the solubility of the same component in the liquid solvent.

A self-similar solution of eq. (10) has been considered in [3, 5, 6, 9, 13] in the case of one dissolved gas in absence of the viscosity and the Laplace pressure effects and been extended in [3, 5] to the case of several dissolved gases. To include the viscous effects on bubble growth in the solution with one dissolved gas under conditions of nonstationary diffusion, it was recently proposed [14, 15] to use an approximate expression for the gas concentration profile around the bubble which is similar to that for the self-similar solution without viscosity. In this paper, we make a next step and propose an approximate anzatz for the concentration profile at nonstationary diffusion of ith ($i=1, 2, \ldots, k$) gas component dissolved in multicomponent liquid solution in the most general case when the rates N' and N_i' of changing the number of molecules in the bubble is determined by eqs. (5)–(7). In this way, we will take into account the full-scale viscosity and capillarity effects.

In accordance with the previous results [3, 5, 13–15], the concentration profile around the growing multicomponent bubble can be approximately written in the form

$$c_i(\rho,R) = c_{i0} - (c_{i0}-c_i(R))\frac{\int_\rho^\infty \frac{dz}{z^2}\exp\left[-\frac{RR'}{2D_i}h_i(R)\left(z^2+\frac{2}{z}-3\right)\right]}{\int_1^\infty \frac{dz}{z^2}\exp\left[-\frac{RR'}{2D_i}h_i(R)\left(z^2+\frac{2}{z}-3\right)\right]} (i=1,2,\ldots,k), \quad \rho=\frac{r}{R(t)}. \tag{12}$$

Function $h_i(R)$ serves here as an important correction factor which can be determined from the requirement that the approximate solution (12) should provide a conservation of the total number of molecules of ith gas component in the bubble and solution. Note that such a correction factor has not previously been considered. Recognizing that eq. (8) for solution (12) can be rewritten as $N_i' = 4\pi R D_i \left.\partial c_i(\rho,t)/\partial\rho\right|_{\rho=1}$, we see that an acceptable approximation (12) for the concentration profile of ith dissolved gas ensures the fulfillment of this relation if

$$N_i' = 4\pi R D_i \frac{c_{i0} - c_i(R)}{\int_1^\infty \frac{dz}{z^2} \exp\left[-\frac{RR'}{2D_i} h_i(R)\left(z^2 + \frac{2}{z} - 3\right)\right]} \quad (i = 1, 2, \ldots, k). \tag{13}$$

For concentration profile (12), the decrease $\Delta N_{1i}(R)$ in the number of particles of ith gas component in the solution at time t is given by the expression

$$\Delta N_{1i}(R) = \frac{4\pi R^3 (c_{i0} - c_i(R)) \int_1^\infty d\rho \rho^2 \int_\rho^\infty \frac{dz}{z^2} \exp\left[-\frac{RR'}{2D_i} h_i(R)\left(z^2 + \frac{2}{z} - 3\right)\right]}{\int_1^\infty \frac{dz}{z^2} \exp\left[-\frac{RR'}{2D_i} h_i(R)\left(z^2 + \frac{2}{z} - 3\right)\right]} \quad (i = 1, 2, \ldots, k). \tag{14}$$

Using the identity

$$\int_1^\infty d\rho \rho^2 \int_\rho^\infty \frac{dz}{z^2} \exp\left[-\frac{b}{2}\left(z^2 + \frac{2}{z} - 3\right)\right] = \frac{1}{3b}, \tag{15}$$

which is valid for an arbitrary positive parameter b, we obtain from eq. (14)

$$\Delta N_{1i}(R) = \frac{4\pi R^3}{3} \frac{(c_{i0} - c_i(R)) D_i}{RR' h_i(R)} \left[\int_1^\infty \frac{dz}{z^2} \exp\left[-\frac{RR'}{2D_i} h_i(R)\left(z^2 + \frac{2}{z} - 3\right)\right]\right]^{-1} \quad (i = 1, 2, \ldots, k). \tag{16}$$

It follows from the condition of conservation of the number of particles of ith component of the dissolved gas in the form $\Delta N_{1i}(R) = N_i(R)$ and from eqs. (7), (13), (16) that function $h_i(R)$ equals

$$h_i(R) = 1 + \frac{R}{3} \frac{d \ln n_i(R)}{dR} \quad (i = 1, 2, \ldots, k). \tag{17}$$

Thus the gas concentration profiles around the growing multicomponent bubble are completely determined by eqs. (12) and (17) if we know a relation between radius of the bubble and its chemical composition at any moment of time.

Joint evolution of the radius and chemical composition of a growing bubble

Taking into account definition $N' = \sum_{i=1}^k N_i'$, eqs. (4), (5) and (13), we obtain the nonlinear equation for the evolution of the bubble radius in the form

$$RR' n(R)\left(1 + \frac{R}{3} \frac{d \ln n(R)}{dR}\right) = \sum_{i=1}^k D_i (c_{i0} - c_i(R)) \left(\int_1^\infty \frac{dz}{z^2} \exp\left[-\frac{RR'}{2D_i} h_i(R)\left(z^2 + \frac{2}{z} - 3\right)\right]\right)^{-1}. \tag{18}$$

In the case of one dissolved gas, in view of eqs. (6), (11) and (17), eq. (18) is sufficient for description of bubble growth. However, in the case of multicomponent solution with a number of dissolved gases, we need, in addition to evolution equation (18), to predict how the chemical composition of the bubble changes with time or with the bubble radius.

Let us introduce, together with volume concentrations n_i of ith gas component in the bubble, the mole fraction x_i of the same gas in the bubble as

$$x_i = N_i/N = n_i/n, \quad n_i = x_i n, \quad \sum_{i=1}^{k} x_i = 1. \tag{19}$$

As follows from eq. (19), the rate x_i' of changing the mole fraction of ith gas component in the bubble with time is

$$x_i' = \frac{N_i'}{N} - x_i \frac{N'}{N} \quad (i = 1, 2, \ldots, k). \tag{20}$$

Let us also define the supersaturation ζ_i of ith gas component in the solution as

$$\zeta_i \equiv \frac{c_{i0} - c_{i\infty}}{c_{i\infty}} \quad (i = 1, 2, \ldots, k) \tag{21}$$

where $c_{i\infty}$ is the volume concentration of ith gas component at equilibrium with the bulk binary solution with the same solvent at presure P. Using eqs. (4), (11), (13), (19), equalities $c_i(R) = s_i n_i(R)$ and $c_{i\infty} = s_i \bar{n}$, eqs. (21) and (3) in eq. (20), we find

$$x_i' = \frac{3}{R^2}\left(\frac{D_i s_i \left((\zeta_i + 1)\Big/\left[1 + \frac{R_*}{R}\left(1 + \frac{2\eta R'}{\sigma}\right)\right] - x_i \right)}{\int_1^\infty \frac{dz}{z^2} \exp\left[-\frac{RR'}{2D_i} h_i(R) \left(z^2 + \frac{2}{z} - 3 \right) \right]} - x_i \sum_{j=1}^{k} \frac{D_j s_j \left((\zeta_j + 1)\Big/\left[1 + \frac{R_*}{R}\left(1 + \frac{2\eta R'}{\sigma}\right)\right] - x_j \right)}{\int_1^\infty \frac{dz}{z^2} \exp\left[-\frac{RR'}{2D_j} h_j(R) \left(z^2 + \frac{2}{z} - 3 \right) \right]} \right) \quad (i = 1, 2, \ldots, k). \tag{22}$$

With the help of eq. (19), eq. (17) for function $h_i(R)$ can be rewritten as

$$h_i(R) = 1 + \frac{R}{3}\left(\frac{d \ln n}{dR} + \frac{1}{x_i}\frac{dx_i}{dR} \right). \tag{23}$$

Substituting eq. (6) into the right-hand side of eq. (23) gives

$$h_i(R) = \left[1 + \frac{R_*}{R}\left(1 + \frac{2\eta R'}{\sigma} \right) \right]^{-1} \left[1 + \frac{2R_*}{3R}\left(1 + \frac{2\eta R'}{\sigma} + \frac{\eta R}{\sigma}\frac{dR'}{dR} \right) \right] + \frac{R}{3x_i}\frac{dx_i}{dR} \quad (i = 1, 2, \ldots, k). \tag{24}$$

Using eqs. (3), (6), (11), (19) and (21) in eq. (18), we obtain

$$RR'\left(1 + \frac{2R_*}{3R}\left(1 + \frac{2\eta R'}{\sigma} + \frac{\eta R}{\sigma}\frac{dR'}{dR} \right) \right) = \sum_{i=1}^{k} \frac{D_i s_i \left(\zeta_i + 1 - x_i \left(1 + \frac{R_*}{R}\left(1 + \frac{2\eta R'}{\sigma} \right) \right) \right)}{\int_1^\infty \frac{dz}{z^2} \exp\left[-\frac{RR'}{2D_i} h_i(R) \left(z^2 + \frac{2}{z} - 3 \right) \right]}. \tag{25}$$

The expression for $dx_i/dR = x_i'/R'$ follows from eqs. (22):

$$\frac{dx_i}{dR} = \frac{3}{R^2 R'}\left(\frac{D_i s_i \left((\zeta_i + 1)\Big/\left[1 + \frac{R_*}{R}\left(1 + \frac{2\eta R'}{\sigma}\right)\right] - x_i \right)}{\int_1^\infty \frac{dz}{z^2} \exp\left[-\frac{RR'}{2D_i} h_i(R) \left(z^2 + \frac{2}{z} - 3 \right) \right]} - x_i \sum_{j=1}^{k} \frac{D_j s_j \left((\zeta_j + 1)\Big/\left[1 + \frac{R_*}{R}\left(1 + \frac{2\eta R'}{\sigma}\right)\right] - x_j \right)}{\int_1^\infty \frac{dz}{z^2} \exp\left[-\frac{RR'}{2D_j} h_j(R) \left(z^2 + \frac{2}{z} - 3 \right) \right]} \right) \quad (i = 1, 2, \ldots, k). \tag{26}$$

It is obvious under the imposed conditions that the concentrations of all components of the solution are considered constant far away from the bubble, the requirement to preserve the total number of particles of each component in the solution together with the bubble is satisfied. However, the proposed approximate solution (12) [as well as the exact solution of the non-stationary diffusion equation (10)] provides the diffusion fluxes for each component consistent with the balance of these components at the bubble boundary precisely due to the factors h_i. As can be seen from eqs. (25) and (26), the presence of these factors directly affects the dynamics of the size and chemical composition of the bubble with time.

Expressions (22), (24)–(26) make a set of equations describing the joint evolution of the radius of multicomponent bubble and its chemical composition $\{x\}=(x_1, x_2,\dots, x_k)$. They allow one to find radius of the bubble R and all molar fractions x_i $(i=1, 2, \dots, k)$ of gases in the bubble as a function of time or the bubble radius.

For a sufficiently large bubble, for which the influence of the curvature and viscosity becomes inessential, the self-similar regime of bubble growth is realized as an exact solution of nonstationary eq. (10). In this case we have [3, 5] $x_i=x_{is}=const$, $h_i(R)=1$ $(i=1, 2, \dots, k)$,

$$c_i(\rho)=c_{i0}-(c_{i0}-x_{is}c_{i\infty})\frac{\int_\rho^\infty \frac{dz}{z^2}\exp\left[-\frac{(RR')_s}{2D_i}\left(z^2+\frac{2}{z}-3\right)\right]}{\int_1^\infty \frac{dz}{z^2}\exp\left[-\frac{(RR')_s}{2D_i}\left(z^2+\frac{2}{z}-3\right)\right]}\ (i=1, 2, \dots, k), \tag{27}$$

$$RR'=(RR')_s=\frac{D_i s_i(\zeta_i+1-x_{is})}{x_{is}\int_1^\infty \frac{dz}{z^2}\exp\left[-\frac{(RR')_s}{2D_i}\left(z^2+\frac{2}{z}-3\right)\right]}=\sum_{i=1}^k \frac{D_i s_i(\zeta_i+1-x_{is})}{\int_1^\infty \frac{dz}{z^2}\exp\left[-\frac{(RR')_s}{2D_i}\left(z^2+\frac{2}{z}-3\right)\right]}. \tag{28}$$

The corresponding equations for stationary bubble composition $\{x_s\}$ and steady rate $(RR')_s$ in the regime of self-similar growth look as

$$x_{is}=\frac{D_i s_i(\zeta_i+1)}{(RR')_s\int_1^\infty \frac{dz}{z^2}\exp\left[-\frac{(RR')_s}{2D_i}\left(z^2+\frac{2}{z}-3\right)\right]+D_i s_i}\ (i=1, 2, \dots, k), \tag{29}$$

$$\sum_{i=1}^k \frac{D_i s_i(\zeta_i+1)}{(RR')_s\int_1^\infty \frac{dz}{z^2}\exp\left[-\frac{(RR')_s}{2D_i}\left(z^2+\frac{2}{z}-3\right)\right]+D_i s_i}=1. \tag{30}$$

In the limit of slow bubble growth at $(RR')_s/D_i\ll 1$, one can find that

$$\int_1^\infty \frac{dz}{z^2}\exp\left[-\frac{(RR')_s}{2D_i}\left(z^2+\frac{2}{z}-3\right)\right]\approx 1. \tag{31}$$

As a result, a steady-state diffusion of gases to the bubble is established, and eqs. (28)–(30) transform to

$$(RR')_s=D_i s_i\left(\frac{\zeta_i+1}{x_{is}}-1\right)=\sum_{i=1}^k D_i s_i(\zeta_i+1-x_{is}), \tag{32}$$

$$x_{is}=\frac{D_i s_i(\zeta_i+1)}{(RR')_s+D_i s_i}\ (i=1, 2, \dots, k), \tag{33}$$

$$\sum_{i=1}^{k}\frac{D_i s_i(\zeta_i+1)}{(RR')_s+D_i s_i}=1. \tag{34}$$

Another limit is reached for fast bubble growth at $(RR')_s/D_i \gg 1$ ($i=1, 2, \ldots, k$). In this case,

$$\int_1^{\infty}\frac{dz}{z^2}\exp\left[-\frac{(RR')_s}{2D_i}\left(z^2+\frac{2}{z}-3\right)\right]\approx\left(\frac{\pi D_i}{6(RR')_s}\right)^{1/2}, \tag{35}$$

and eqs. (28)–(30) transform as

$$(RR')_s^{1/2}=\left(\frac{6D_i}{\pi}\right)^{1/2}s_i\left(\frac{\zeta_i+1}{x_{is}}-1\right)=\left(\frac{6}{\pi}\right)^{1/2}\sum_{i=1}^{k}D_i^{1/2}s_i(\zeta_i+1-x_{is}). \tag{36}$$

$$x_{is}=\frac{s_i(\zeta_i+1)}{(\pi(RR')_s/6D_i)^{1/2}+s_i}\quad (i=1, 2, \ldots, k), \tag{37}$$

$$\sum_{i=1}^{k}\frac{s_i(\zeta_i+1)}{(\pi(RR')_s/6D_i)^{1/2}+s_i}=1. \tag{38}$$

Let us note that in the case of a two-component bubble, the self-similar growth regime at stationary chemical composition of bubble was considered earlier in [16]. In particular, the differences in the stationary molar fractions of gases in the bubble for the Henry and Sieverts laws of gas dissolution have been analyzed.

Asymptotics of reaching steady-state and self-similar diffusion growth regime

As follows from the results of the previous section, if we consider bubble growth in the presence of viscosity and curvature effects, then the composition of the bubble changes while its size grows until these effects become negligible. It is important to establish the size interval for reaching the stationary composition in the bubble. In the case of ternary solution with two dissolved gases, we can describe asymptotic reaching the stationary composition $\{x_s\}$ in the growing bubble analytically.

Let us first consider the case of slow bubble growth at $(RR')_s/D_i \ll 1$ ($i=1, 2$). Denote the molar fraction of first dissolved gas in solution as $x\equiv x_1$. As follows from eqs. (25), (26) and (31) at $x_1 = x$, $x_2=1-x$,

$$RR'\left[1+\frac{2R_*}{3R}\left(1+\frac{2\eta R'}{\sigma}+\frac{\eta R}{\sigma}\frac{dR'}{dR}\right)\right]=D_1s_1\left[\zeta_1+1-x\left(1+\frac{R_*}{R}\left(1+\frac{2\eta R'}{\sigma}\right)\right)\right]+D_2s_2\left[\zeta_2+1-(1-x)\left(1+\frac{R_*}{R}\left(1+\frac{2\eta R'}{\sigma}\right)\right)\right], \tag{39}$$

$$\frac{dx}{dR}=\frac{3}{R^2R'}\left[D_1s_1(1-x)\left(\frac{\zeta_1+1}{1+\frac{R_*}{R}\left(1+\frac{2\eta R'}{\sigma}\right)}-x\right)-xD_2s_2\left(\frac{\zeta_2+1}{1+\frac{R_*}{R}\left(1+\frac{2\eta R'}{\sigma}\right)}-1+x\right)\right], \tag{40}$$

It is convenient to introduce new notation

$$u \equiv \frac{R_*}{R}\left(1+\frac{2\eta R'}{\sigma}\right),\quad v \equiv \frac{2R_*}{3R}\left(1+\frac{2\eta R'}{\sigma}+\frac{\eta R}{\sigma}\frac{dR'}{dR}\right),\quad \Delta x(R) \equiv x - x_s. \tag{41}$$

With increasing the bubble radius R and approaching stationary molar fraction x_s in the bubble, quantities u, v, $\Delta x(R)$ tend to zero and $RR' \to (RR')_s$ where the molar fraction x_s and the rate $(RR')_s$ of stationary bubble growth can be found from eqs. (33) and (34). Being interested in finding the asymptotic solutions of eqs. (39) and (40), we can set $RR' = (RR')_s$ and, correspondingly, use $R' = (RR')_s/R$ on the right-hand side of expressions for u and v:

$$u = \frac{R_*}{R}\left(1+\frac{2\eta(RR')_s}{\sigma R}\right),\qquad v = \frac{2R_*}{3R}\left(1+\frac{\eta(RR')_s}{\sigma R}\right). \tag{42}$$

Keeping the terms of the first order with respect to small u, v and $\Delta x(R)$, we obtain from eqs. (39)–(41) with the help of eq. (32)

$$RR' \approx (RR')_s(1-v) - (D_1 s_1 - D_2 s_2)\Delta x - (D_1 s_1 x_s + D_2 s_2(1-x_s))u, \tag{43}$$

$$\frac{d\Delta x}{dR} \approx -\frac{3}{R(RR')_s}\left[((RR')_s + D_1 s_1(1-x_s) + D_2 s_2 x_s)\Delta x + x_s(1-x_s)(D_1 s_1 - D_2 s_2)u\right], \tag{44}$$

With use of eq. (42), eqs. (43) and (44) can be rewritten as

$$RR' \approx (RR')_s\left[1-\frac{R_*}{R}\left(\frac{2}{3}\left(1+\frac{\eta(RR')_s}{\sigma R}\right)+\frac{D_1 s_1 x_s + D_2 s_2(1-x_s)}{(RR')_s}\left(1+\frac{2\eta(RR')_s}{\sigma R}\right)\right)\right] - (D_1 s_1 - D_2 s_2)\Delta x, \tag{45}$$

$$\frac{d\Delta x}{dR} \approx -\frac{3\lambda}{R}\Delta x - \frac{3}{(RR')_s}x_s(1-x_s)(D_1 s_1 - D_2 s_2)\frac{R_*}{R^2}\left(1+\frac{2\eta(RR')_s}{\sigma R}\right), \tag{46}$$

where

$$\lambda \equiv 1 + \frac{(1-x_s)D_1 s_1 + x_s D_2 s_2}{(RR')_s} = 1 + \frac{D_1 s_1(1-x_s) + D_2 s_2 x_s}{D_1 s_1(\zeta_1 + 1 - x_s) + D_2 s_2(\zeta_2 + x_s)} > 1. \tag{47}$$

The general solution to eq. (47) with the initial condition for molar fraction deviation $\Delta x(R)\big|_{R=R_0} = \Delta x_0$ at an arbitrary $R = R_0$ has the form

$$\Delta x(R) \approx \Delta x_0\left(\frac{R_0}{R}\right)^{3\lambda} + \frac{3x_s(1-x_s)(D_1 s_1 - D_2 s_2)}{(RR')_s}\frac{R_*}{R}\left[\frac{1}{3\lambda-1}\left(1-\left(\frac{R_0}{R}\right)^{3\lambda-1}\right)+\frac{2}{3\lambda-2}\frac{\eta}{\sigma R}\left(1-\left(\frac{R_0}{R}\right)^{3\lambda-2}\right)\right]. \tag{48}$$

Equations (48) and (45) give the desired asymptotic behavior in bubble radius R for molar fractions of gases in the bubble and the bubble growth rate at slow bubble growth and describe the transition to the steady-state diffusion. As we can see, the most long-lived are terms that decrease with increasing size like R^{-1} and R^{-2}.

Let us now consider case of fast bubble growth at $(RR')_s/D_i \gg 1$ $(i = 1, 2)$. In view of eq. (35) we have

$$\left(\int_1^\infty \frac{dx}{z^2}\exp\left[-\frac{RR'}{2D_i}h_i(R)\left(z^2+\frac{2}{z}-3\right)\right]\right)^{-1} \approx \left(\frac{6}{\pi}\frac{RR'}{D_i}h_i(R)\right)^{1/2}. \tag{49}$$

As well as in the case of slow diffusion, with increasing the bubble radius R and approaching stationary molar fraction x_s in the bubble, quantities u, v, $\Delta x(R)$ tend to zero and $RR' \to (RR')_s$. However the molar fraction x_s and the rate $(RR')_s$ of stationary bubble growth should be sought now from eqs. (37) and (38). Keeping the terms of the first order with respect to small u, v and $\Delta x(R)$, we obtain from eq. (25) at $x_1 = x$, $x_2 = 1 - x$ in view of eqs. (41)

$$(RR')^{1/2}(1+v) = \left(\frac{6}{\pi} D_1 h_1(R)\right)^{1/2} s_1(\zeta_1 + 1 - x_s - \Delta x - x_s u) + \left(\frac{6}{\pi} D_2 h_2(R)\right)^{1/2} s_2(\zeta_2 + x_s + \Delta x - (1-x_s)u). \tag{50}$$

Using eqs. (24) and (41), (42), we find with the same accuracy

$$h_1^{1/2}(R) \approx 1 - \frac{R_*}{6R}\left(1 + \frac{4\eta R'}{\sigma}\right) + \frac{R}{6x_s}\frac{d\Delta x}{dR}, \tag{51}$$

$$h_2^{1/2}(R) \approx 1 - \frac{R_*}{6R}\left(1 + \frac{4\eta R'}{\sigma}\right) - \frac{R}{6(1-x_s)}\frac{d\Delta x}{dR}, \tag{52}$$

Substituting $h_1^{1/2}(R)$ and $h_2^{1/2}(R)$ with the help of eqs. (51) and (52) into eq. (50) and using eqs. (36) and (42) allows us to rewrite expression for $(RR')^{1/2}$ in the form

$$(RR')^{1/2} = (RR')_s^{1/2}\left[1 - \frac{R_*}{R}\left(\frac{5}{6} + \frac{4\eta(RR')_s}{3\sigma R} + \frac{D_1^{1/2}s_1x_s + D_2^{1/2}s_2(1-x_s)}{D_1^{1/2}s_1(\zeta_1 + 1 - x_s) + D_2^{1/2}s_2(\zeta_2 + x_s)}\left(1 + \frac{2\eta(RR')_s}{\sigma R}\right)\right)\right]$$
$$- \left(\frac{6}{\pi}\right)^{1/2}(D_1^{1/2}s_1 - D_2^{1/2}s_2)\Delta x(R). \tag{53}$$

As follows from eqs. (45) and (53), the ratio between the contributions of viscous forces and Laplace forces during the evolution of the bubble substantially depends on the degree of non-stationarity of diffusion flows of gas molecules in solution. Quantitatively, this ratio can be characterized by the value of a dimensionless quantity $\eta(RR')_s/\sigma R$. Thus, with an increase in the degree of nonstationary diffusion and a corresponding increase in the magnitude $(RR')_s$, the relative role of the viscosity forces, ceteris paribus, increases monotonously.

As follows from eqs. (26) at $x_1 = x$, $x_2 = 1 - x$ in view of eqs. (41), (49) and smallness of u, v, $RR' - (RR')_s$ and Δx,

$$\frac{d\Delta x}{dR} \approx \frac{3}{R}\left(\frac{6}{\pi}\frac{1}{(RR')_s}\right)^{1/2}\Big[(D_1h_1(R))^{1/2}s_1(1 - x_s - \Delta x)(\zeta_1 + 1 - x_s - \Delta x - x_s u)$$
$$- (x_s + \Delta x)(D_2h_2(R))^{1/2}s_2(\zeta_2 + x_s + \Delta x - (1-x_s)u)\Big]. \tag{54}$$

Substituting $h_1^{1/2}(R)$ and $h_2^{1/2}(R)$ with the help of eqs. (51) and (52) into eq. (54) and using eqs. (36) and (42) allows us to rewrite expression for Δx in the form

$$\frac{d\Delta x}{dR} \approx -\frac{6\mu}{R}\Delta x - 6\frac{D_1^{1/2}s_1 - D_2^{1/2}s_2}{D_1^{1/2}s_1(\zeta_1 + 1 - x_s) + D_2^{1/2}s_2(\zeta_2 + x_s)}x_s(1-x_s)\frac{R_*}{R^2}\left(1 + \frac{2\eta(RR')_s}{\sigma R}\right) \tag{55}$$

where

$$\mu \equiv 1 + \left(\frac{6}{\pi}\frac{1}{(RR')_s}\right)^{1/2}(D_1^{1/2}s_1(1-x_s) + D_2^{1/2}s_2x_s) = 1 + \frac{D_1^{1/2}s_1(1-x_s) + D_2^{1/2}s_2x_s}{D_1^{1/2}s_1(\zeta_1 + 1 - x_s) + D_2^{1/2}s_2(\zeta_2 + x_s)} > 1. \tag{56}$$

The solution to eq. (55) can be constructed in the same way as for eq. (43) (the equations differ only in the coefficients in terms on the right-hand side). Integration of eq. (55) with initial condition $\Delta x(R)\big|_{R=R_0}=\Delta x_0$ at an arbitrary $R=R_0$ gives

$$\Delta x(R)\approx\Delta x_0\left(\frac{R_0}{R}\right)^{6\mu}+\frac{6(D_1^{1/2}s_1-D_2^{1/2}s_2)x_s(1-x_s)}{D_1^{1/2}s_1(\zeta_1+1-x_s)+D_2^{1/2}s_2(\zeta_2+x_s)}\frac{R_*}{R}\times\left[\frac{1}{6\mu-1}\left(1-\left(\frac{R_0}{R}\right)^{6\mu-1}\right)+\frac{1}{6\mu-2}\frac{2\eta(RR')_s}{\sigma R}\left(1-\left(\frac{R_0}{R}\right)^{6\mu-2}\right)\right]. \quad (57)$$

Equations (57) and (55) give the desired asymptotic behavior in bubble radius R for molar fractions of gases in the bubble and the bubble growth rate at fast bubble growth and describe the transition to the self-similar diffusion of gas components. Finally, we see from eqs. (57) and (53) that, as in the case of slow growth, the most long-lived terms are those that decrease with increasing size as R^{-1} and R^{-2}.

Conclusions

The results of this research can be directly applied to kinetics of distribution of bubbles in radii and composition at degassing of a multicomponent decompressed solution. Using an approximate solution (12) of the non-stationary diffusion equation (10) allows one to completely take into account the capillary and viscosity effects in the evolution of the bubble distribution in time in the entire range of bubble radii above the unstable equilibrium radius. Thus, the general approach to an adequate description of the kinetics of the nucleation stage of the bubbles arises, not only under the assumption of their self-similar growth, but also in a such situation when, by the end of this stage, the self-similar growth mode and stationary composition of the bubbles have not yet been established. A significant difference between expression (12) and that proposed in [14, 15] in the case of one-component bubble growth in a viscous solution is the presence of factor h [h_i in the one-component case determined by eq. (17)], the choice of which, as shown, provides the requirement to preserve the total number of gas molecules in the system. Setting $h=1$ generally violates the condition of such a balance.

The role of the capillary effects jointly with the viscosity effects, as well as the multicomponent case with arbitrary number of dissolved gases, has not been considered previously. As said above, we were focused in this study on possible application to nucleation theory, in particular from the point of reaching the stationary growth and steady composition of supercritical bubbles at the nucleation stage. However, the obtained results should be of interest for planning experiments with single bubbles which were intensively studied in [17, 18].

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