ЖЭТФ, 2016, том 150, вып. 1 (7), стр. 151–160

INTERACTION BETWEEN PHASES IN THE LIQUID–GAS SYSTEM

R. S. Berry [a], *B. M. Smirnov* [b*]

[a] *Department of Chemistry, University of Chicago*
Chicago, IL 60637, USA

[b] *Institute for High Temperatures, of Russian Academy of Sciences*
127412, Moscow, Russia

Received April 7, 2016

This work analyzes the equilibrium between a liquid and a gas over this liquid separated by an interface. Various gas forms exist inside the liquid: dissolved gas molecules attached to solvent molecules, free gas molecules, and gaseous bubbles. Thermodynamic equilibrium is maintained between two phases; the first phase is the liquid containing dissolved and free molecules, and the second phase is the gas over the liquid and bubbles inside it. Kinetics of gas transition between the internal and external gas proceeds through bubbles and includes the processes of bubbles floating up and bubble growth as a result of association due to the Smoluchowski mechanism. Evolution of a gas in the liquid is considered using the example of oxygen in water, and numerical parameters of this system are given. In the regime under consideration for an oxygen–water system, where transport of oxygen into the surrounding air proceeds through micron-size bubbles with lifetimes of hours. This regime is realized if the total number of oxygen molecules in water is small compared with the numbers of solvated and free molecules in the liquid.

DOI: 10.7868/S0044451016070142

1. INTRODUCTION

A disperse system, i. e., a liquid with micron-size gas bubbles, is a well-known physical object of interest for both fundamental physics and applications. Such bubbles are used in various industrial processes, such as ore flotation [1], water remediation, and waste water treatment [2, 3]. Basic applications of liquids with gaseous bubbles appear in medicine, in particular, for drug delivery to internal parts of a body [4], for anesthesia [5], for delivery of a contrast agent in ultrasonography [6, 7], for breast biopsies [8], and others. These applications are all based on the long lifetimes of bubbles in liquids and are an impetus for a deep understanding of the fundamental aspects of this problem.

In this paper, we consider the character of evolution of a gas that passes into an open reservoir filled by a liquid under conditions in which this gas forms bubbles in the liquid. A general scheme of this system is represented in Fig. 1. In a particular example, oxygen molecules form under the action of solar rays near the bottom of a reservoir as a result of photosynthesis processes in plants near the reservoir bottom. These molecules move toward the air–water boundary 3, and in the course of this motion they form bubbles, which float to the phase boundary. At low flow rates, the gas forms bubbles in the host liquid and subsequently the bubbles float to the upper liquid surface and disappear into air. These bubbles may form in natural processes, as in the case of methane produced by putrefaction processes in marsh. Photosynthesis processes in water generate oxygen, which may take the form of bubbles

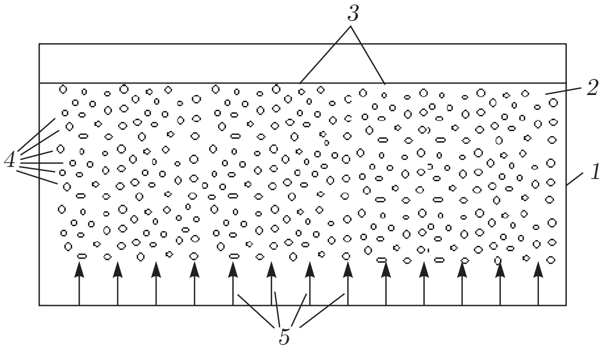

Fig. 1. Geometry of a liquid with a gas: *1* — vessel, in which a liquid (*2*) is located; *3* — boundary between liquid and gas, *4* — bubbles in the liquid, *5* — flux of gaseous molecules

---

[*] E-mail: bmsmirnov@gmail.com

and influence living organisms in the water. Along with natural processes, one may deliberately saturate a liquid with a gas, e. g., by loading an aquarium with oxygen. One property of disperse matter consisting of a liquid containing gaseous bubbles is a low electric field strength required for electric breakdown of this system compared to that of a pure liquid. This property may be used for purification of a water flow. Because the gasification process in liquids is slow, the energetics of this process are low and such processes occur fairly readily in real systems.

Formation of gas bubbles in a liquid can occur in any liquid system. For example, ageing of some liquids results from chemical reactions that are accelerated due to bubble formation. In particular, oil degradation in a power transformer occurs by oil decomposition with formation of gaseous bubbles. Consequently, bubbles are the matter through which electric breakdown is realized in power units. Another example of bubble formation proceeds in the course of solidification. If an alloy is formed in cooling a liquid, gaseous bubbles may remain within the material and determine the subsequent strength of this material. Thus, we find many situations in which gaseous bubbles form and develop in a liquid. The bubble growth may result both from attachment of individual molecules to bubbles and by coalescence of bubbles. We here consider the kinetics of bubble growth in a liquid if a gas is dissolved or is injected into the liquid.

In considering the kinetics of evolution of gases in liquids through bubble formation and their eventual floating-up, we are guided by air bubbles in water, since information about this system is available and allows us to find real parameters of this process. We therefore, consider a general situation of air dissolving in water of a stagnant basin or in flowing water of a reservoir. The air molecules first accumulate in the water in the form of separated molecules. The same occurs when oxygen is formed in water by photosynthesis. Such processes of oxygen accumulation typically proceed continuously for long times. When the amount of a dissolved gas exceeds the limit of its water solubility, the gas molecules aggregate into bubbles in the water. These bubbles grow via both coagulation and coalescence; simultaneously, they float up. In the end, we obtain a stationary picture in which new portions of molecules are injected in water as others leave the liquid as they float up to its surface.

2. OXYGEN IN WATER

In considering the behavior of a gas in a liquid, including formation of gaseous bubbles within the liquid, we are guided by properties of oxygen in water that allow us to represent and parameterize the character of this behavior. We first consider oxygen solubility in water under conditions in which oxygen is at atmospheric pressure over the gas–liquid interface separating the two phases (see Fig. 1). Molecules of the oxygen solute appear in a bound state with knots — local structures offering potential minima — of the liquid, such that if the liquid transforms into the solid state, the dissolved molecules are located in knots of the crystal lattice. Therefore, in considering equilibrium of a liquid and a soluble gas, we assume the existence of a certain number of potential wells within the liquid, i. e., local minima, where gas molecules may be in locally bound states.

Under these conditions, we can consider solution of a gas in a liquid based on the classical model (see, e. g., [9]) in which a certain number of identical particles (balls) are distributed over a certain number of boxes. Potential wells inside the liquid, where bound molecules are located, fulfill the role of these boxes. Because only one molecule can be bonded within a given well, the dissolved molecules form a Fermi–Dirac distribution, which passes into the Boltzmann distribution in the limit of high temperatures. In this limit, the equilibrium under consideration is described by the equation

$$M + U \leftrightarrow MU, \tag{2.1}$$

where M is the gas molecule, U is the potential well, and MU is the bound state of the gas molecule in a local potential miminum of the liquid. The relation between the number density of free molecules [M], the number density of bound molecules [MU], and the number density of potential wells [U] in the liquid is described by the Saha relation [10, 11]

$$\frac{[M][U]}{[MU]} = C \exp\left(-\frac{\Delta\varepsilon}{T}\right), \tag{2.2}$$

where the temperature T is expressed in energy units, the constant C is independent of the densities of the components, and $\Delta\varepsilon$ is the binding energy of a molecule located in a state bound in the potential well. The number density of bound molecules decreases with increasing temperature in accordance with usual equilibrium between bound and free states of molecules in matter. It is convenient to represent this formula in the form [14]

$$c_s = c_0 p \exp\left(\frac{\Delta\varepsilon}{T}\right), \tag{2.3}$$

where c_s is the concentration of dissolved molecules in the liquid, c_0 is the characteristic total concentration

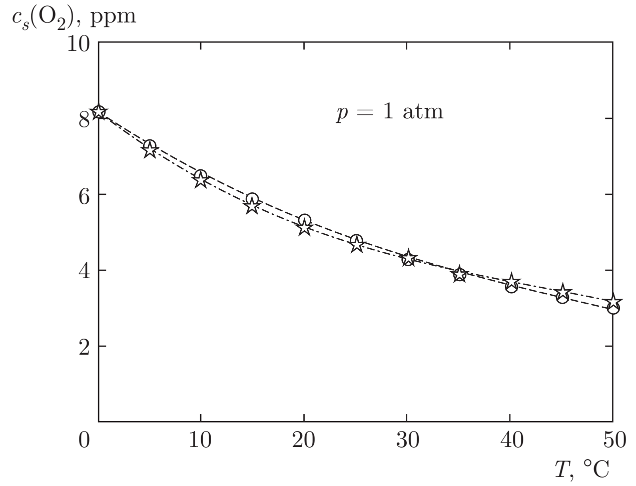

Fig. 2. Temperature dependence of the oxygen solubility in water at atmospheric pressure; the maximum concentration c_s of dissolved oxygen at a given temperature T. Stars correspond to measurements [12], and open circles are from calculations using the formula $c_s = 0.013\exp(1760/T)$, where T is given in K

of molecules, and p is the gas partial pressure over the liquid. We express this pressure in atm. Figure 2 shows the temperature dependence of the oxygen concentration dissolved in water. We see that formula (2.3) describes the experimental data well, and that $c_s \approx 5$ ppm at room temperature.

We now consider an equilibrium of a gas bubble in a liquid, with the bubble separated from the liquid by a spherical film. The relation between an external gas pressure p and the pressure p_s inside the liquid is given by the Laplace equation [13]

$$p = p_s + p_{ef}, \quad p_{ef} = \frac{2\alpha}{r}, \qquad (2.4)$$

where α is the surface tension and r is the bubble radius. Here, we assume water to have many internal potential wells in which air molecules, oxygen or nitrogen, can be captured. We next assume the water temperature $T = 298$ K, close to room temperature. The surface tension for water at this temperature is $\alpha = 72$ dyn/cm [15], and hence compression of oxygen bubbles by water creates an additional pressure inside a micron-size bubble. This additional pressure $p_{ef} = 2\alpha/r$ for a bubble of a radius r located in water at room temperatures is

$$p_{ef} = \frac{C}{r}, \quad C = 1.44 \text{ atm} \cdot \mu\text{m}. \qquad (2.5)$$

Figure 3*a* represents the dependence of the pressure inside a bubble in water, with the bubble radius r and atmospheric pressure outside the water.

The number density N of molecules inside a bubble and the number of bubble molecules n are given by

$$N = N_0\left(1 + \frac{r_0}{r}\right), \quad n = \frac{4\pi N_0 r^2 (r + r_0)}{3}, \qquad (2.6)$$

with the parameters

$$N_0 = 2.46 \cdot 10^{19} \text{ cm}^{-3}, \quad r_0 = 0.83 \text{ Å}.$$

Figures 3*b* and *c* show the dependences $N(r)$ and $n(r)$. In particular, for the bubble radius $r = 1$ μm, we have $N = 6.0 \cdot 10^{19}$ cm^{-3} and $n = 1.5 \cdot 10^8$. The bubble surface energy ε_{sur} per molecule is

$$\varepsilon_{sur} = \frac{4\pi r^2 \alpha}{n} = \frac{\varepsilon_{max}}{1 + r/r_0}, \qquad (2.7)$$

where

$$\varepsilon_{max} = \frac{3\alpha}{N_0 r_0} = 610 \text{ K}, \qquad (2.8)$$

and at the bubble radius $r = 1$ μm, formula (2.7) gives $\varepsilon_{sur} = 360$ K. Figure 3*d* gives the dependence of the surface energy ε_{sur} on the bubble radius r.

3. EQUILIBRIUM IN A DISPERSE SYSTEM

We can see that for micron-size bubbles, the surface energy per bubble molecule is small compared to the binding energy of dissolved oxygen molecules in water. This allows us to separate components of a disperse system into two phases. The first spatially uniform phase includes the liquid and dissolved and free molecules inside it. The second phase involves the gas located over the liquid and inside bubbles. Under these conditions, the thermodynamic equilibrium between these phases results from transitions of gas molecules between the different phases via the free state of gas molecules in the liquid. Returning to the example of a disperse system consisting of water and oxygen, we consider a regime where equilibrium is reached via attachment of oxygen molecules to oxygen bubbles and the subsequent evaporation of oxygen bubbles from water. We now give the criterion that the equilibrium in a disperse system be established through bubbles. The rate of molecule attachment to a bubble of a radius r is given by the Smoluchowski formula [16]

$$\nu_{at} = 4\pi D r N_b, \qquad (3.1)$$

where D is the diffusion coefficient for molecules in a liquid and N_b is the number density of gas molecules in bubbles. In particular, the diffusion coefficient of oxygen molecules in water at room temperature is

$$D(O_2) = 2.4 \cdot 10^{-5} \text{ cm}^2/\text{s},$$

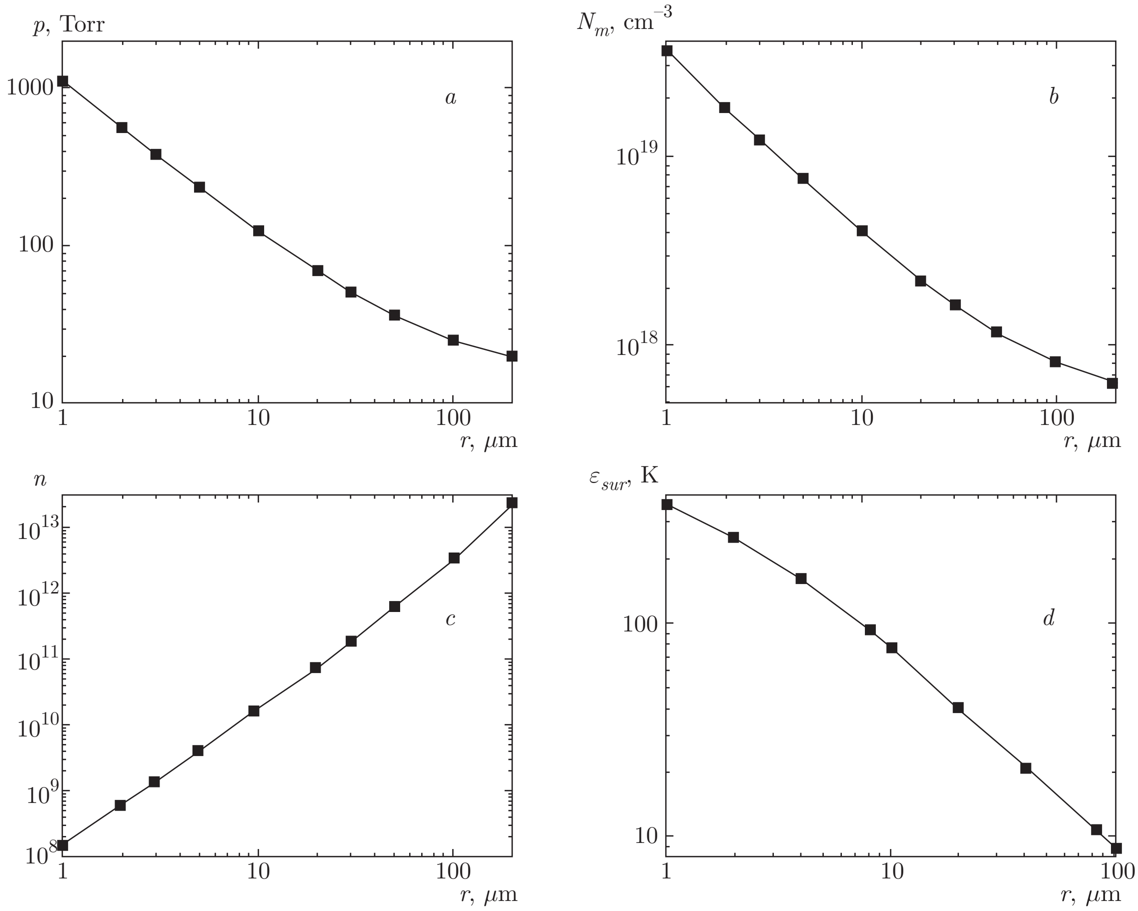

Fig. 3. Some parameters of an oxygen bubble in water as a function of the bubble radius: a — air pressure p inside the bubble, b — the number density of air molecules in the bubble, c — the number of air molecules in the bubble, d — the surface energy ε_{sur} per molecule. $T = 298$ K, $p = 1$ atm

(see [15]). A typical time τ_D for a gas molecule to reach the liquid–gas interface is estimated as

$$\tau_D \approx 2L^2/D, \qquad (3.2)$$

where L is the vertical size of the liquid reservoir. Evidently, the regime we consider here, under which free gas molecules first attach to a bubble and then leave the liquid in this bubble, requires the criterion $\nu_{at}\tau_D \gg 1$ or

$$X = \nu_{at}\tau_D = \frac{\tau_D}{\tau_{at}} = 2\pi L^2 r N_b \gg 1. \qquad (3.3)$$

In particular, for a typical bubble size $r = 1$ μm and for the number density of bubbles $N_b = N_s/n$, where $N_s = 1.6\cdot10^{17}$ cm^{-3} is the number density of dissolved water molecules in water at room temperature, this criterion gives $L \gg 20$ μm. Thus, in reality, bubbles partake in establishment of equilibrium under laboratory conditions ($L \sim 1$ cm) at a low number density of bubble molecules.

The loss of gas bubbles in a liquid under the regime we consider results from bubbles floating up. A typical time τ_{fl} for this process is given by

$$\tau_{fl} = \int\limits_0^L \frac{dz}{v_{fl}}, \qquad (3.4)$$

where z is the vertical coordinate and L is the distance from the interface to a point of bubble formation. The velocity of the bubble floating up, v_{fl}, follows from the equality of the gravitation force on a bubble in a liquid to the resistance force. In determining the resistance force via the Stokes formula [17,18], we find the velocity of a small bubble of radius r

$$v_{fl} = \frac{2\rho g r^2}{9\eta}, \qquad (3.5)$$

where $g = 980$ cm^2/s is the free fall acceleration, ρ is the density difference of a liquid containing gas bubbles and the pure liquid density, and η is the liquid viscosity coefficient. A more careful analysis shows that the Stokes formula [17,18] corresponds to motion of a solid particle in gaseous or liquid matter, but if a gaseous or liquid particle is moving in a liquid with higher density, the Stokes force must be multiplied by the factor 2/3 [19]. This gives the floating-up velocity of a gaseous particle in a liquid as

$$v_{fl} = \frac{4\rho g r^2}{27\eta}. \tag{3.6}$$

In particular, for an oxygen bubble that moves in water at room temperature ($\rho = 1$ g/cm^3, $\eta = 8.9 \times \times 10^{-3}$ g/(cm $\cdot$ s)), this formula takes the form

$$v_{fl} = Cr^2, \quad C = 1.6 \cdot 10^4 \text{ cm}^{-1} \cdot \text{s}^{-1}. \tag{3.7}$$

For typical parameters of the process under consideration $r \sim 1$ μm and $L \sim 1$ cm, we find that the lifetime of oxygen bubbles in water τ_{fl} is measured in hours.

We thus have determined that the disperse system under consideration can be constructed from two phases, the first phase being a liquid with bound and free dissolved molecules, and a gas over the gas–liquid interface, and the second phase is gaseous bubbles in the liquid. The second phase is in a metastable state because bubbles grow steadily within the liquid and join with the gas over the interface when they reach that interface by floating up. Our task is to analyze evolution of bubbles in the liquid while accounting for the indicated processes. We consider the regime of bubble evolution under which free molecules in the liquid reach a bubble interface. This corresponds to the criterion that gas molecules attain the liquid–gas interface primarily in the form of bubbles. The rate of free molecules reaching the interface is N_f/τ_D, where N_f is the number density of free gaseous molecules inside the liquid and τ_D is a characteristic time for those free molecules to reach the interface in accordance with formula (3.2). The rate at which gaseous molecules attain the interface as bubbles is N_m/τ_{fl}, where N_m is the total number density of molecules inside bubbles and $\tau_{fl} \approx L/v_{fl}$ is the floating-up time of bubbles. The regime under consideration in which gaseous molecules leave the liquid in the form of bubbles requires meeting the criterion

$$\frac{N_m}{\tau_{fl}} \gg \frac{N_f}{\tau_D}, \tag{3.8}$$

which can be represented as

$$\frac{N_m}{N_f} \gg Y, \quad Y = \frac{\tau_{fl}}{\tau_D}. \tag{3.9}$$

In the case of oxygen in liquid water, the left-hand side of this criterion has the form $Y \approx Lr^2$, where L is expressed in cm, and the bubble radius r is given in μm. Being guided by $L > 1$ cm and $r > 1$ μm, we find that criterion (3.9) is fulfilled.

4. KINETICS OF BUBBLE GROWTH IN LIQUID

We now consider the kinetics of bubble growth and bubble transport in a liquid. We assume the regime of bubble growth to be the one resulting from molecules contacting and joining bubbles, as well as from bubble coagulation according to the scheme

$$M_{n-m} + M_m \to M_n, \tag{4.1}$$

where M is an air molecule. We introduce the size distribution f_n of bubbles such that $f_n dn$ is the number of bubbles per unite volume with the number of molecules between n and $n+dn$. If bubble growth takes place in a uniform matter, this distribution function satisfies the Smoluchowski equation [20]

$$\frac{\partial f_n}{\partial t} = -f_n \int k(n,m) f_m dm + \\ + \int k(n-m,m) f_{n-m} f_m dm \,, \tag{4.2}$$

where $k(n-m,m)$ is the rate constant of process (4.2), and the distribution function is normalized as

$$\int f_n dn = N_b,$$

where N_b is the number density of bubbles.

Along with the number density of bubbles in a liquid, we introduce the total number density of molecules as

$$N_m = \int_0^\infty n f_n dn.$$

We obtain an equation for N_m by multiplying Eq. (4.2) by n and integrating over dn, which gives

$$\frac{dN_m}{dt} = -\int n k(n,m) f_n dn f_m dm + \\ + \int n k(n-m,m) f_{n-m} f_m dn dm, \tag{4.3}$$

with $n > m$ in the second integral. Replacing $n - m$ by n in the right-hand side of this relation, we obtain the terms that mutually cancel, and $dN_m/dt = 0$, i. e., within the framework of the Smoluchowski equation, the total number density N_m of molecules in bubbles N_m is conserved in the course of the growth process. In addition, we can introduce the average bubble size $\overline{n}$, i. e., the average number of molecules per bubble, as

$$\overline{n} = \frac{N_m}{N_b}. \qquad (4.4)$$

We can also introduce the average number of molecules per bubble $\overline{n}$ in the form

$$\overline{n} = \frac{\displaystyle\int n dN_m}{N_b} = \frac{\displaystyle\int_0^\infty n^2 f_n dn}{\displaystyle\int_0^\infty n f_n dn}. \qquad (4.5)$$

Association process (4.1) results from diffusive motion of bubbles in a liquid, and in the limit where the mean free path of a bubble is small compared to the mean bubble size, the rate is determined by the liquid viscosity coefficient η and is (see, e. g., [21, 22])

$$k(n,m) \equiv k_{as} = \frac{8T}{3\eta}, \qquad (4.6)$$

where T is the liquid temperature expressed in energy units, and we use the analogy of the process (4.1) of association of liquid clusters in a gas in this regime. In particular, for bubbles in water at room temperature, the association rate constant is [23]

$$k_{as} = 6.1 \cdot 10^{-11}\ \mathrm{cm}^3/\mathrm{s}.$$

Assuming the association rate constant to be independent of the bubble size, we can reduce the Smoluchowski equation to the form

$$\frac{\partial f_n}{\partial t} = -k_{as} f_n \int_0^\infty f_m dm + k_{as} \int_0^n f_{n-m} f_m dm. \qquad (4.7)$$

We now operate with average bubble parameters and their variation in time. Then we use integral relations from the Smoluchowski equation. We replace the integration sequence for any function of bubble size, to obtain the symmetry relation

$$\int_0^\infty dn \int_0^n F(n,m) dm = \int_0^\infty dm \int_m^\infty F(n,m)\, dn.$$

Multiplying Smoluchowski equation (4.7) by n and integrating over dn, we can obtain [21, 22]

$$\frac{d}{dt} \int_0^\infty n f_n dn \equiv \frac{dN_m}{dt} = 0, \qquad (4.8)$$

where N_m is the total number density of molecules in bubbles. This means that in the course of bubble association in a motionless liquid, the total number of molecules in bubbles is conserved. We now multiply Smoluchowski equation (4.7) by n^2 and integrate over dn. Defining the average number of molecules in bubbles as

$$\overline{n} = \frac{\displaystyle\int_0^\infty n^2 f_n dn}{\displaystyle\int_0^\infty n f_n dn}, \qquad (4.9)$$

we can reduce the integral relation for a yield to the form

$$\frac{d}{dt}(\overline{n} N_m) = k_{as} N_m^2. \qquad (4.10)$$

In the foregoing, we ignored transport phenomena that describe the flowing-up of bubbles. To address this, we assume the auto-model character of the size distribution function, as is usually done in processes of nucleation (see, e. g., [18, 24, 25]). Then the size distribution function has the form

$$f_n \equiv F(n/\overline{n}). \qquad (4.11)$$

This allows us to separate processes of bubble growth and transport in the vertical direction. For the flux of molecules inside bubbles, we have

$$j = \int v_{fl}(n) n f_n dn = C\langle r^2 \rangle N_m, \qquad (4.12)$$

where the average is taken with the size distribution function, and we use formula (3.7) for the floating-up velocity. This flux is independent of a vertical height z due to the continuity equation, which allows expressing the total number density of molecules at a given height as

$$N_m = \frac{j}{C\langle r^2 \rangle}. \qquad (4.13)$$

If we use expression (2.6) for the number of bubble atoms, then Eq. (4.10) and the equation of motion

$$\frac{dz}{dt} = C\langle r^2 \rangle$$

give

$$j dz = A(\langle r^2 \rangle)^3 d\left[\frac{\langle r^2 (r + r_0)\rangle}{\langle r^2 \rangle}\right], \qquad A = \frac{4\pi N_0 C^2}{3k_{as}}, \qquad (4.14)$$

with $A = 4.3 \cdot 10^{38}$ cm$^{-8} \cdot$ s^{-1} in the case of oxygen bubbles in water. This formula testifies to a weak dependence of the final sizes of bubbles on the initial flux of molecules.

The distribution function (4.11) of bubble radii has a maximum because small bubbles remain below and may float up only after they undergo association. We consider the limit case where this maximum is narrow and the distribution function

$$f_n \sim \delta[r - r_a(z)].$$

Here, r is a current bubble radius and $r_a(z)$ is the average bubble radius for a given cross section. Then the solution of Eq. (4.14) at a given height z gives

$$jz = \frac{Ar_a^7}{7}. \tag{4.15}$$

We note the peculiarities of the process under consideration. At the beginning, free gas molecules are formed near the bottom of the reservoir of liquid. These molecules form bubbles, and during this process, the paths of free molecules are relatively short. The principal transport of the gas in the liquid proceeds via bubbles floating up, after the molecules have aggregated into bubbles. This regime is governed by criteria (3.3) and (3.8); the fulfilment of these criteria does not necessarily mean that the majority of the gas molecules are in bubbles. Nevertheless, near the gas–liquid interface, most of the gas molecules are in bubbles and go into the surrounding atmosphere in this form. We connect the flux of molecules j reaching the gas–liquid interface with the energy flux J consumed on formation of these molecules according to formula

$$J = \delta\varepsilon j, \tag{4.16}$$

where $\delta\varepsilon$ is the energy consumed per formation of one gaseous molecule. Considering the photosynthesis process as

$$\hbar\omega + \mathrm{CO_2} \to \mathrm{C} + \mathrm{O_2}, \tag{4.17}$$

we find that the energy for formation of one oxygen molecule is 11.4 eV if the carbon atom is formed in the gaseous phase. In reality, this value is less, and for definiteness in our discussion below, we take $\delta\varepsilon = 10$ eV. It is convenient to take the unit of the energy flux as the solar irradiance $J_0 = 1365$ W/m^2.

Some results of solving Eq. (4.15) at the interface are given in Fig. 4. Specifically, Fig. 4*a* contains the dependence of the average bubble radius $r_a(L)$ at the interface on the reduced energy flux of the absorbed energy, which is based on the equation

$$J(L) = \frac{A\delta\varepsilon \cdot r_a^7(L)}{7L}. \tag{4.18}$$

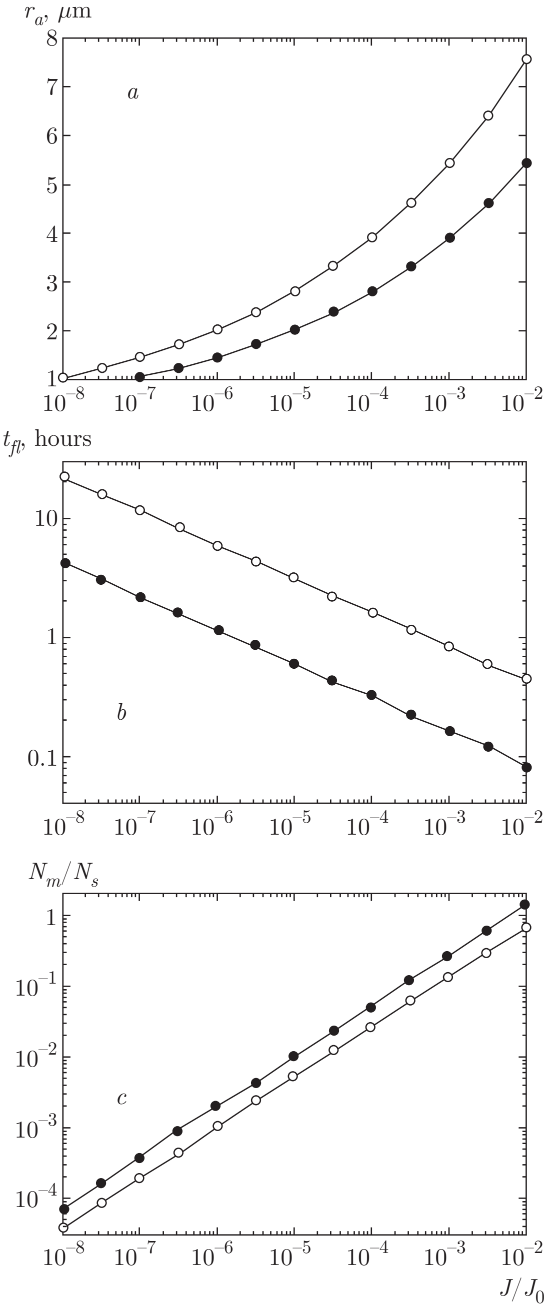

Fig. 4. Some parameters of oxygen bubbles in water as functions of the relative rate of molecule generation in water: a — average bubble radius, b — time of floating-up of bubbles, c — the total number density of oxygen molecules in bubbles. $L = 1$ cm (dark circles) and 10 cm (open circles)

Figure 4*b* represents the dependence on the reduced absorbed energy flux for the bubble lifetime τ, which starts from bubble's origin and is given by

$$\tau_{fl} = \int \frac{dz}{v_{fl}(z)} = \frac{1.4L}{v_{fl}(L)}. \tag{4.19}$$

Next, Fig. 4*c* represents the reduced total number density $N_m(L)$ of oxygen molecules in bubbles at the interface. As a unit of the molecule number density, N_s we take given in Fig. 2, the number density of dissolved oxygen molecules. The results in Fig. 4 correspond to atmospheric pressure and room temperature.

5. REGIME OF EVOLUTION OF OXYGEN MOLECULES IN WATER WITH BUBBLE FORMATION

Analyzing the results of the above evaluations, we formulate the regime under consideration. Our system consists of four components: oxygen over the interface, bound dissolved oxygen, free oxygen molecules inside water, and bubbles of oxygen molecules. Figure 5 represents the processes that establish equilibrium among these components; we now consider this equilibrium between oxygen and water at atmospheric pressure and room temperature. The rate of establishing this equilibrium for free molecules is given by formula (3.1),

$$\nu_f = 4\pi D r_k N_k, \tag{5.1}$$

where N_k is the number density of knots where molecules are in a bound state with the liquid, and r_k is the knot radius. Because $N_k > N_s$ and r_k is of the order of an atomic value, we can estimate this time as $1/\nu_f \sim 10^{-6}$ s. It hence follows that the equilibrium between free and bound dissolved molecules is realized faster than for other channels in Fig. 5.

We let N_{sat} denote the equilibrium number density of free molecules in the water, by analogy with the equilibrium between a gas and clusters formed from the gas. Because molecules of dissolved oxygen are bonded in knots of water, we have

$$N_{sat} \ll N_s. \tag{5.2}$$

The equilibrium number density of free molecules in water N_{sat} is determined by the energy of the barrier that must be crossed for transitions from the surrounding air into water,

$$N_{sat}(r_a) = N_s \exp\left(\frac{\varepsilon_{sur}}{T}\right), \tag{5.3}$$

where ε_{sur} is the bubble surface energy per molecule given by formula (2.7).

We also compare typical times to achieve equilibrium in the oxygen–water system in Fig. 6. In particular, on the basis of formula (3.1), we have a typical time τ_{at} for molecule attachment to a bubble to establish equilibrium between free molecules in water and bubbles as

$$\tau_{at} = \frac{1}{4\pi D r_a N_b}, \tag{5.4}$$

where $D = 2.4 \cdot 10^{-5}$ cm^2/s is the diffusion coefficient of oxygen molecules in water, N_b is the number density of bubbles, and r_a is the average bubble radius. In particular, it follows from Fig. 6*a* for the regime under consideration that

$$\tau_{at} \ll \tau_{fl}, \tag{5.5}$$

i. e., equilibrium of free molecules with bubbles is established fast. Next, it follows from Fig. 6*c* that criterion (3.9) can be fulfilled even if $N_m \ll N_f$, i. e., the amount of oxygen in bubbles is small compared with that of free oxygen molecules in the water. Thus, the regime under consideration, in which transport of molecules out of the liquid proceeds through gaseous bubbles, is realized even if only a small fraction of the molecules in water is in bubbles, not only compared with the total number of dissolved molecules, as in Fig. 6*c*, but also compared with the number of only the free molecules in the water.

Indeed, near the interface, the equilibrium time range is between 10^{-5}–10^{-3} s, which is several orders of magnitude less than the lifetime of bubbles inside water (see Fig. 4*b*). From this analysis, it follows that there exists a minimal molecular flux j_{min} and a corresponding energy flux J_{min} such that the regime under consideration takes place at $J > J_{min}$. Unfortunately, we cannot determine this value, which satisfies the relation $J_{min} \ll J_0$. Nevertheless, the regime under consideration exists above small fluxes J. In this regime, there is a fixed value of the number density N_s of dissolved

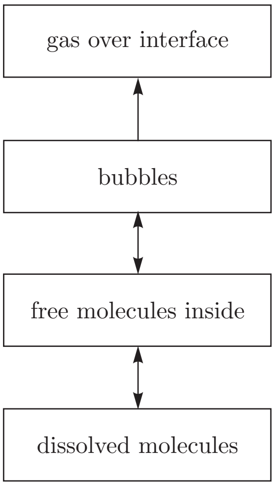

Fig. 5. Processes of transfer between oxygen components in the water and outside it

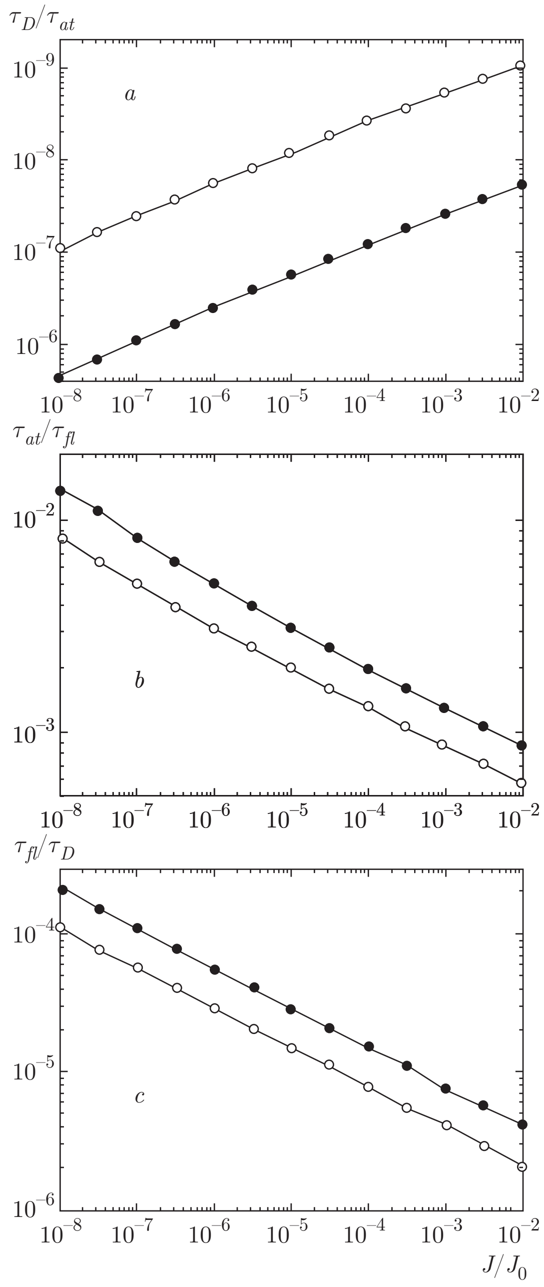

Fig. 6. Ratio of typical times in the oxygen–water system at atmospheric pressure and room temperature: a — $X = \tau_D/\tau_{fl}$, Eq. (3.3), b — τ_{at}/τ_{fl}, c — $Y = \tau_{fl}/\tau_D$, Eq. (3.8), where typical times τ_D, τ_{fl}, and τ_{at} are given by Eqs. (3.2), (3.4), and (5.4). $L = 1$ cm (dark circles) and 10 cm (open circles)

oxygen that depends on the temperature and pressure above water, and the number density of free molecules N_{sat} that depends on the average bubble size. Any excess of free molecules in the water passes into bubbles.

6. CONCLUSION

We here consider some types of equilibria for a liquid and a gas that is distributed both over the liquid and in it, in the form of bound dissolved molecules, free molecules in the liquid, and molecules in gaseous bubbles. In the regime under consideration, molecules injected into the liquid leave it in gaseous bubbles. Assuming the liquid to be simple, i. e., the interface between the liquid and bubbles to have the same structure as in the bulk of the liquid, we find that a contact of two bubbles leads to joining of these bubbles into a single bubble, similarly to two contacting drops, in accordance with the Smoluchowski mechanism. The lifetime of gas molecules in a liquid is determined by the rate of bubbles floating up, which is in turn connected with the rate of their growth as a result of association. This analysis for the oxygen–water system shows that a typical size of bubbles is of the order of microns and a typical lifetime of bubbles ranges from minutes to hours. In addition, the regime of the gas–liquid interaction considered here, in which gaseous molecules leave the liquid in bubbles, is realized at low number densities of free gas molecules in a liquid.

This work was supported by the Russian Science Foundation for the support (grant № 14-50-00124).

REFERENCES

1. G. H. Kelsall, S. Tang, S. Yurdakul, and A. L. Smith, J. Chem. Soc. Faraday Trans **92**, 3997 (1996).
2. M. Takahashi, J. Phys. Chem. B **109**, 21858 (2005).
3. M. Takahashi, K. Chiba, and P. Li, J. Phys. Chem. B **111**, 1343 (2007).
4. W. M. Saltzman, *Drug Delivery: Engineering Principles for Drug Theraphy*, Oxford Univ. Press, Oxford (2001).
5. D. R. Vanderipe, Toxicol. Mechan. Meth. **11**, 207 (2001).
6. A. L. Kibanov, Adv. Drug Deliv. Rev. **37**, 139 (1999).
7. E. Quaia, *Media in Ultrasonography*, Springer, Berlin (2005).
8. B. B. Golberg, J. S. Raichlen, and F. Forsberg, *Ultrasound Contrast Agents: Basic Principles and Clinical Applications*, Martin Dunitz, London (2011).
9. A. S. Kompaneetz, *Theoretical Physics*, GITTL, Moscow (1957).

10. M. N. Saha, Proc. Roy. Soc. A **99**, 135 (1921).

11. L. D. Landau and E. M. Lifshitz, *Statistical Physics*, Pergamon Press, Oxford (1976).

12. http://www.engineeringtoolbox.com/air-solubility-water-d-639.html.

13. P. S. Laplace, Méchanique Céleste (Suppl.), Vol. 10 (1806).

14. Ch. Kittel, *Thermal Physics*, Wiley, New York (1969).

15. *Handbook of Chemistry and Physics*, 86th edition, ed. by D. R. Lide, CRC Press, London (2003–2004).

16. M. V. Smoluchowski, Z. Phys. **17**, 585 (1916).

17. G. G. Stokes, Trans. Cambr. Philos. Soc. **9 II**, 8 (1851).

18. L. D. Landau and E. M. Lifshitz, *Fluid Dynamics*, Pergamon Press, Oxford (1986).

19. V. G. Levich, *Physical-Chemical Hydrodynamics*, Fizmatgiz, Moscow (1959) [in Russian].

20. M. V. Smoluchowski, Z. Phys. Chem. **92**, 129 (1918).

21. B. M. Smirnov, *Clusters and Small Particles in Gases and Plasmas*, Springer, New York (1999).

22. B. M. Smirnov, *Cluster Processes in Gases and Plasmas*, Wiley, Berlin (2010).

23. B. M. Smirnov and R. S. Berry, Chem. Centr. J. **9**, 48 (2015).

24. E. M. Lifshitz and L. P. Pitaevskii, *Physical Kinetics*, Pergamon Press, Oxford (1981).

25. I. Gutzow and J. Schmelzer, *The Vitreous State*, Springer, Berlin (1995).