

Experimental Investigations of Nucleation in Helium–Oxygen Mixtures

Vladimir Baidakov,* Alexei Kaverin, and Grey Boltachev

Institute of Thermal Physics, Urals Branch of Russian Academy of Sciences, GSP-828, Ekaterinburg, 620219, Russia

Received: March 29, 2001; In Final Form: July 30, 2001

The paper presents the results of experimental investigations of nucleation in helium–oxygen gas-filled mixtures. Temperature dependences of the mean lifetime of a mixture in the metastable (superheated) state have been determined, and nucleation rates have been calculated by experiments at fixed pressures of 1.171 and 1.667 MPa and at several values of concentrations. Experimental data are compared with results of the homogeneous nucleation theory in a macroscopic (capillary) approximation and with allowance for the dependence of the properties of nuclei on the curvature of their dividing surface. The size effect of nucleation is taken into account in the framework of the van der Waals, Cahn–Hilliard method. The equation of state of the mixture has been built, and the boundary of stability of homogeneous states, the diffusion spinodal, has been determined. The paper discusses the problems of building a nucleation theory for gas-filled mixtures and states a good agreement between theory and experiment at nucleation rates $J \approx 10^7 \text{ m}^{-3} \text{ s}^{-1}$ when the size effect in nucleation is taken into account.

I. Introduction

A supersaturated solution of gas in liquid is an example of a two-component metastable system, in which nonequilibrium is caused by the excess of the concentration of a dissolved component over its value in the saturated state. The removal of supersaturation takes place as a result of separation of the gas phase in the form of numerous bubbles (“the effect of champagne”). This phenomenon manifests itself as the bends and is used for degassing liquids, foaming polymeric materials, and other technological processes.

If at a given temperature and pressure of a supersaturated mixture a pure solvent (liquid) and a dissolved substance (gas) are in the stable state, the solvent in the mixture is characterized by a low volatility and the dissolved gas by a low solubility. New-phase nuclei in such mixtures can practically fully consist of molecules of the dissolved substance. The nucleation theory of gas-filled nonvolatile liquids was suggested by Derjaguin and Prokhorov¹ and Kuni et al.²

The first experimental investigations of nucleation in non-volatile gas-filled liquids were made by Hemmingsen,³ Finkelstein and Tamir,⁴ and Bowers et al.⁵ Supersaturation was created in these works by an abrupt release of pressure on the liquid (water), which was saturated with a gas at pressures equal to several hundreds of atmospheres. The concentration of a dissolved gas x' was determined in this case by the value of the saturation pressure p_s , and the depth of penetration into the metastable region by the pressure difference $\Delta p_n(x', T) = p_s - p_n$, where $p_n(x', T)$ is the pressure of intensive gas emission.

An approach to the investigation of nucleation in gas-supersaturated water mixtures different from that used in ref 3 was suggested by Rubin and Noyes.⁶ In mixture, which was in a vessel of a fixed volume at controllable values of temperature and pressure, supersaturation was initiated by a chemical reaction. If the rate of gas production during a chemical reaction in a solvent considerably exceeds the rate of its removal through

a free interface, considerable supersaturations can be achieved in the volume of a liquid solvent. A decay of the metastable state was accompanied by abrupt (explosive) liberation. The concentration of a dissolved gas in supersaturated mixture was determined by the data for the volumes of the mixture gas and liquid phases in a measuring cell and the pressure increase in the system during the initiation of gas liberation by stirring the mixture or by sonication. In this case, the value of supersaturation is characterized by the value of $\Delta x'_n(p, T) = x'_n - x'_s$. By the data of ref 6, the concentration x'_n of nitrogen dissolved in water before the formation of bubbles was 20–40 times greater than its equilibrium concentration x'_s at atmospheric pressure.

A comparison of experimental data obtained by two different methods of creating supersaturation in a gas-filled liquid with the homogeneous nucleation theory has shown that the degrees of metastability obtained by experiment are considerably lower than their theoretical values. Thus, in the system oxygen–water, the limiting values of concentration x'_n calculated from the homogeneous nucleation theory at atmospheric pressure and a nucleation rate $J = 10^7 \text{ s}^{-1} \text{ m}^{-3}$ have proven to be 15 times greater than those achieved by experiment.⁷ In this system, in accordance with ref 7 at the limiting values of supersaturation registered in experiment, the critical bubble is characterized by radius $R_* \approx 15 \text{ nm}$, and the pressure $p''_* \approx 9.5 \text{ MPa}$. The Gibbs number $G = W_*/kT$, i.e., the relation between the work of formation of a critical nucleus and the energy of thermal motion of molecules kT , is in this case⁸ $\sim 1.56 \times 10^4$. Overcoming such a high potential barrier by means of homogeneous nucleation of the gas phase in characteristic times of experiment is an unlikely event. In the case of spontaneous nucleation of bubbles in superheated pure liquids the value of G is ~ 72 .⁹

To eliminate contradictions between theory and experiment, a number of authors have suggested models of nucleation in gas-supersaturated mixtures different from those in the classical thermodynamic model.^{8,10} It is postulated that the origination of gas bubbles in mixture proceeds in two stages. At the first stage, according to Kwak,¹⁰ the molecules of a dissolved gas

* Corresponding author. E-mail: bai@itp.uran.ru.

form a cluster, which has no distinct interface and, consequently, no surface energy. In the paper by Bowers et al.,⁸ the local region of increased gas concentration in mixture is called a “blob”. The small difference of gas concentrations in a “blob” and the surrounding liquid ensures, in the authors opinion,⁸ a small surface contribution to its excess free energy. The latter proves to be much lower than that in a bubble of the same size. Both the cluster of Kwak¹⁰ and the “blob” of Bowers et al.,⁸ after achieving a certain size exceeding the size of a critical nucleus, are transformed into a supercritical gas bubble. The models described in refs 8 and 10 make it possible, for limiting supersaturations observed by experiment,^{3,6} to decrease the height of the activation nucleation barrier to $\sim 10^2 kT$.

A different situation is observed in the region of temperatures close to the critical point of a solvent when the latter is in the metastable (superheated) state. Here one can no longer neglect the solvent volatility, and viscous, inertial forces and heat exchange at the phase boundary begin to play an important role in the dynamics of the bubble growth. The nucleation theory of such mixtures has been developed by Baidakov.¹¹ Experimental investigations of limiting superheats $\Delta T(p, x') = T_n - T_s$ of solutions of carbon dioxide and nitrogen in organic liquids have been made by Mori et al.¹² and Forest and Ward.¹³ These works used the method of floating-up drops. At nucleation rates $J = 10^{24} - 10^{26} \text{ s}^{-1} \text{ m}^{-3}$, gas-filled mixtures of high-temperature liquids were investigated by the method of pulse wire probe.¹⁴ The gas-saturation of a liquid resulted in a shift of the boundary of spontaneous nucleation of bubbles toward lower temperatures. The authors of refs 12–14 state satisfactory agreement between the homogeneous nucleation theory and experiment, at least regarding the value of the mixture limiting superheat.

This paper is the first to pose the problem of determination of the temperature, the baric, and the concentration dependence of the nucleation rate in gas-filled mixtures in the region of state variables where a two-component system is “twice” as metastable. At predetermined p , T , and x' , a mixture is supersaturated with respect to the equilibrium pressure $\Delta p(T, x') = p_s - p$, and a pure solvent in this case is superheated by the value of $\Delta T(p) = T - T_s(x'=0)$. Experiments are made with solutions of helium in liquid oxygen. Gas-filled mixtures of cryogenic liquids belong to the class of weak solutions. The solubility of helium in oxygen at pressures of 5 MPa does not exceed 2–3 mol %.¹⁵ A considerable difference between the parameters of the potential of intermolecular interaction in helium and oxygen results in essential unideality of mixtures. Helium in such systems can manifest itself as a surfactant reducing the excess free energy of the liquid–vapor boundary.¹⁶

The structure of the paper is as follows. The second section examines nucleation thermodynamics in binary mixtures. The consideration is based on the van der Waals capillary theory and the Gibbs method of dividing surfaces. The p , ρ , T , and x properties of stable and metastable helium–oxygen mixtures are described by an empirical equation of state built in the framework of a one-fluid model. The third section is devoted to the nucleation theory of gas-filled liquids and analysis of the main factors determining the dynamics of growth of a vapor-gas bubble in such systems. The fourth section gives a short description of the experimental technique and presents experimental data on the nucleation rate and limiting supersaturations of the investigated mixtures. In the fifth section, experimental data are compared with the homogeneous nucleation theory.

II. Nucleation Thermodynamics

A. Nucleus of a New Phase in a Binary Mixture. According to the van der Waals capillarity theory,¹⁷ an increment in the

great thermodynamic potential because of formation of spherical inhomogeneity in a binary isotropic system may be presented as follows:

$$\Delta\Omega\{\rho_1, \rho_2\} = 4\pi \int_0^\infty \left(\Delta\omega + \sum_{i,j=1}^2 \kappa_{ij} \frac{d\rho_i}{dr} \frac{d\rho_j}{dr} \right) r^2 dr \quad (1)$$

$$\Delta\omega = f - f' - \sum_{i=1}^2 \mu'_i (\rho_i - \rho'_i) \quad (2)$$

where f is the free-energy density of a homogeneous system, μ_i is the chemical potential of the i -th component, and κ_{ij} is the matrix of the influence parameters. One prime refers to the initial value of a parameter in the liquid phase; a parameter without primes shows the local value.

The conditions of stability of a two-phase system require

$$\kappa_{11}\kappa_{22} - \kappa_{12}^2 > 0, \quad \kappa_{11} > 0, \quad \kappa_{22} > 0 \quad (3)$$

As it is seen in ref 18, where an argon–krypton system is used as an example, the cross influence parameter in a first approximation may be presented in the following form:

$$\kappa_{12} = (\kappa_{11}\kappa_{22})^{1/2} \quad (4)$$

According to relation 3, this corresponds to the indifferent equilibrium of a system with respect to the density gradients that are opposite in sign and determines the limiting value of the parameter κ_{12} . With allowance for eq 4, expression 1 assumes a more simple form:

$$\Delta\Omega\{\rho_1, \rho_2\} = 4\pi \int_0^\infty \left[\Delta\omega + \kappa_{22} \left(\frac{d\rho_\beta}{dr} \right)^2 \right] r^2 dr \quad (5)$$

Here the value of ρ_β is determined by the relation $\rho_\beta = \rho_1(\kappa_{11}/\kappa_{22})^{1/2} + \rho_2$. The distribution of densities ρ_i ($i = \beta, 1, 2$) in a critical nucleus is found by the Euler system of equation for the functional (eq 5), which contains a single differential equation

$$\frac{d^2\rho_\beta}{dr^2} + \frac{2}{r} \frac{d\rho_\beta}{dr} = \frac{\mu_2 - \mu'_2}{2\kappa_{22}} \quad (6)$$

with boundary conditions $\rho_\beta \rightarrow \rho'_\beta$ at $r \rightarrow \infty$, $(d\rho_\beta/dr) \rightarrow 0$ at $r \rightarrow 0$ and $r \rightarrow \infty$, and a single algebraic equation

$$\mu_1 - \mu'_1 = (\kappa_{11}/\kappa_{22})^{1/2} (\mu_2 - \mu'_2) \quad (7)$$

The work of formation of a critical nucleus is

$$W_* = \min \max \Delta\Omega\{\rho_1, \rho_2\} \quad (8)$$

In the Gibbs method of dividing surfaces¹⁹

$$W_* = \frac{16}{3} \frac{\pi\sigma^3}{(p''_* - p')^2} \quad (9)$$

where σ is the nucleus surface tension and p''_* is the pressure in a nucleus determined from the condition of its real (chemical) equilibrium with the surrounding metastable phase

$$\mu_i(T, p''_*, x'_*) = \mu_i(T, p', x'), \quad i = 1, 2 \quad (10)$$

The connection between σ and the bubble tension surface radius R_* is shown by the Laplace relation

$$p_*'' - p' = \frac{2\sigma}{R_*} \quad (11)$$

Expressions 8–11 make it possible to determine the dependence $\sigma(R_*)$. To solve this problem, it is necessary to know the equation of state of a binary mixture and the influence parameters κ_{ij} . The values of κ_{ij} are temperature functions and depend only slightly on the density.²⁰ If the dependence of κ_{ij} on ρ_i is neglected, the value of κ_{22} of a pure solvent can be determined by data on the surface tension at a flat interface

$$\sigma_\infty = 2\kappa_{22}^{1/2} \int_{\rho_*}^{\rho_s} (\Delta\omega)^{1/2} d\rho \quad (12)$$

For mixtures, this formula will be written as follows:

$$\sigma_\infty = 2 \int_{-\infty}^{\infty} \Delta\omega dz = 2 \int_{-\infty}^{\infty} \sum_{i,j=1}^2 \kappa_{ij} \frac{d\rho_i}{dz} \frac{d\rho_j}{dz} dz \quad (13)$$

At known κ_{22} and condition 4, this makes it possible to calculate the helium influence parameter κ_{11} . The density distribution in a transition layer will be found from the equations

$$\kappa_{22} \left(\frac{d\rho_\beta}{dz} \right)^2 = \Delta\omega \quad (14)$$

$$\mu_1 - \mu'_{1,s} = (\kappa_{11}/\kappa_{22})^{1/2} (\mu_2 - \mu'_{2,s}) \quad (15)$$

with known boundary conditions.

Cahn and Hilliard were the first to use the van der Waals capillarity theory in the problem of nucleation.²¹ For describing properties of a new-phase nucleus and the nucleation in simple one-component liquids, it was used in refs 9, 22, and 23. A more rigorous description of heterogeneous systems is founded on the density functional method.²⁴ This method was applied to the theory of nucleation by Talanquer and Oxtoby.²⁵ Obtained from this method, properties of nuclei of a new phase correlate qualitatively with Cahn–Hilliard’s approach.²¹

B. Equation of State and Boundary of Thermodynamic Stability. To calculate properties of new-phase nuclei and determine the boundary of stability of mixture homogeneous phases with respect to continuous changes of the state variables, the spinodal, it is necessary to have an equation of state describing both stable and metastable states. Such an equation of state for a helium–oxygen system has been obtained in the framework of a one-fluid model on the basis of experimental data on thermodynamic properties of pure components and phase equilibrium in mixture. A unified oxygen equation of state²⁶ has been used as a base equation. This equation shows that the liquid and gas phases in the region of liquid–gas transition have isotherms of the van der Waals type. The saturation values can be calculated from the equation of state through the use of the Maxwell criterion. As the region of existence of the oxygen liquid phase lies considerably higher than the critical temperature of helium, helium here may be regarded as a gas close to ideal. This circumstance makes it possible to use for describing helium properties the oxygen equation of state after introducing into the latter the corrective factor φ

$$\frac{p}{\rho k T} = 1 + \varphi \sum_{ij} b_{ij} \tilde{\rho}^i \tilde{T}^{-j} \quad (16)$$

Here, $\tilde{\rho} = \rho/\rho_{c,i}$, and $\tilde{T} = T/T_{c,i}$; $\rho_{c,i}$ and $T_{c,i}$ are the density and the temperature at the critical point of substance ($i = 1$ for helium, $i = 2$ for oxygen), and the coefficients b_{ij} have been determined by experimental data on the thermodynamic parameters of oxygen and presented in ref 26. In pure oxygen, $\varphi = 1$; at $\varphi = 0.431$, the equation of state 16 with coefficients b_{ij} of oxygen describes the p , ρ , and T properties of helium in the most optimal way in the range of reduced densities $0 < \tilde{\rho} < 1$ and temperatures $0.6 < \tilde{T} < 1$.

The equation of state 16 is used for describing the p , ρ , T , and x properties of a helium–oxygen system in the range of temperatures 90–150 K and pressures up to 7 MPa. Three individual parameters of the equation T_c , $\rho_c = 1/v_c$, φ are regarded in this case as concentration functions

$$T_c(x) = T_{c,1}x^2 + 2\alpha_T T_{c,12}x(1-x) + T_{c,2}(1-x)^2 \quad (17)$$

$$v_c(x) = v_{c,1}x^2 + 2\alpha_v v_{c,12}x(1-x) + v_{c,2}(1-x)^2 \quad (18)$$

$$\varphi(x) = \varphi_1x^2 + 2\alpha_\varphi \varphi_{12}x(1-x) + (1-x)^2 \quad (19)$$

where the cross coefficients $T_{c,12}$, $v_{c,12}$, φ_{12} are given by the relations

$$T_{c,12} = (T_{c,1}T_{c,2})^{1/2} \quad (20)$$

$$v_{c,12} = (v_{c,1}^{1/3} + v_{c,2}^{1/3})^3/8 \quad (21)$$

$$\varphi_{12} = (1 + \varphi_1)/2 \quad (22)$$

The free parameters of the equation α_T , α_v , and α_φ may be determined by the pressure of saturated vapor and the composition of the liquid and the vapor phase of the mixture. However, the available data¹⁵ on p_s , x' , and x'' have proven to be insufficient for a reliable representation of the phase diagram in the range of temperatures adjoining the solvent critical point. In the absence of information about the p , ρ , T , and x properties of a helium–oxygen system, we used as additional information data on the surface tension.¹⁶ Including into consideration an information about the properties of a liquid–vapor interface made it possible not only to increase the reliability of description of the mixture p , ρ , T , and x properties by the equation of state 16, but also to determine the influence parameter of pure helium, κ_{11} . Calculations were made by eqs 16–22 and 13–15. The solvent influence parameter was determined from eq 12 by data on the surface tension of pure oxygen.²⁷ The results of such calculation are given in the following form: where $\epsilon = 1 -$

$$\begin{aligned} \kappa_{22}\rho_{c,2}^{8/3}/p_{c,2} &= 0.5552 + 12.6638\epsilon - 187.164\epsilon^2 + \\ &1468.46\epsilon^3 - 6583.0\epsilon^4 + 16993\epsilon^5 - 23465\epsilon^6 + 13500\epsilon^7 \end{aligned} \quad (23)$$

$T/T_{c,2}$. The temperature dependences of the free coefficients in eqs 17–19 and also the parameter κ_{11} have been approximated by the following expressions:

$$\alpha_T = 3, \quad \alpha_v = 2.88 - 16.8\epsilon + 54.0\epsilon^2 - 50.0\epsilon^3$$

$$\alpha_\varphi = -0.238 + 14.95\epsilon - 61.1\epsilon^2 + 103.0\epsilon^3 - 61.0\epsilon^4 \quad (24)$$

$$\begin{aligned} \kappa_{11}\rho_{c,2}^{8/3}/p_{c,2} &= 7.93 - 176.5\epsilon + 1530\epsilon^2 - 6248\epsilon^3 + \\ &12100\epsilon^4 - 8900\epsilon^5 \end{aligned} \quad (25)$$

The parameter κ_{12} was found according to eq 4.

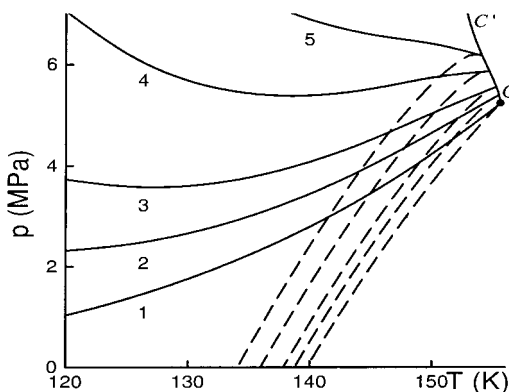


Figure 1. P , T projection of the phase diagram of He–O₂ mixture. Solid lines show the curves of phase equilibrium, dashed lines the diffusion spinodals. $x' = 0$ (line 1), 0.5 (line 2), 1 (line 3), 2 (line 4), and 3 (line 5) mol %. CC' is the critical line.

The phase diagram of a helium–oxygen system calculated by the equation of state 16 is given in Figure 1. The lines of phase equilibrium separate the regions of stable and metastable phases on the thermodynamic surface of homogeneous states. The metastable phase of a two-component system retains the restoring reaction to infinitesimal changes of state variables to the diffusion spinodal determined by the condition

$$\left(\frac{\partial \Delta \mu}{\partial x}\right)_{p,T} = 0 \quad (26)$$

where $\Delta \mu = \mu_1 - \mu_2$. In a one-component system, stability of the metastable phase is disturbed if

$$\left(\frac{\partial p}{\partial v}\right)_T = 0 \quad (27)$$

In pure oxygen at a temperature $T = 140$ K a stretch of the liquid phase $\Delta p_{sp}(T) = p_s - p_{sp} = 2.65$ MPa corresponds to the spinodal. Dissolution in oxygen of 1 mol % of helium results in a rise of the limiting value of the tensile stress up to $\Delta p_{sp}(T, x) = p_s - p_{sp} \approx 3.17$ MPa. Thus, with increasing concentration of a dissolved gas, the width of the metastable region increases. It should be mentioned that at high gas fillings ($x' > 3$ mol %), penetration into the metastable region at a fixed external pressure is already connected with decreasing rather than increasing temperature (see Figure 1).

C. Work of Formation and Surface Tension of Critical Nuclei. Distributions of densities of the mixture components in a critical bubble obtained by numerical integration of the system of eqs 6 and 7 are presented in Figure 2. As distinct from Ar–Kr type mixtures with complete solubility of components, the density of the first (gas) component in a bubble exceeds that in a solvent. The presence of a weak maximum on the density profile on the side of the gas phase is indicative of the excess adsorption of the first component in the surface layer of a nucleus.

The radius of the tension surface R_* and the value of the surface tension σ of a critical bubble are determined by the system of eqs 8–11. For radii of equimolecular dividing surfaces of components $R_{e,i}$, we have

$$R_{e,i} = \left(\frac{3N_i}{4\pi\Delta\rho_i}\right)^{1/3}$$

$$N_i = 4\pi \int_0^\infty (\rho'_i - \rho_i) r^2 dr, \quad \Delta\rho_i = \rho'_i - \rho''_i \quad (28)$$

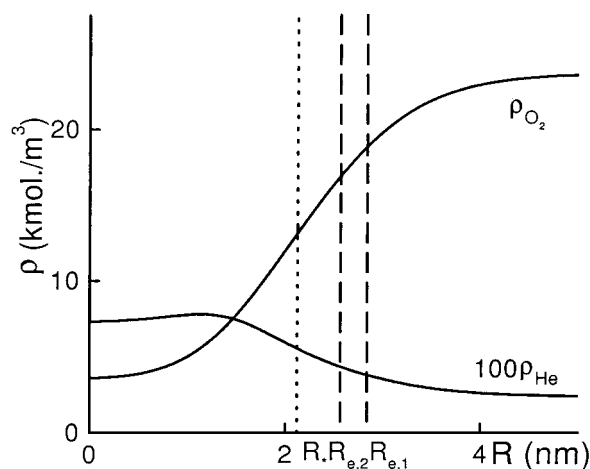


Figure 2. Density distributions of the mixture components in a critical bubble, $T = 140$ K, $x' = 0.1$ mol %, $p' = 1.0$ MPa.

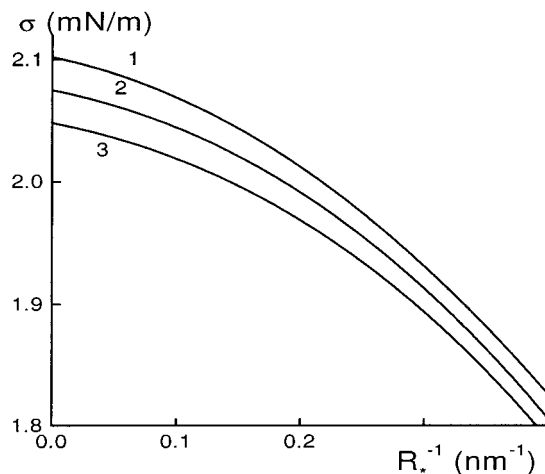


Figure 3. Surface tension of the mixture critical bubbles on line $x' = \text{const}$ at $T = 140$ K: $x' = 0$ (line 1), 0.1 (line 2), and 0.2 (line 3) mol %.

The Tolman's length of the components of a binary mixture ($\delta_i = R_{e,i} - R_*$, $i = 1, 2$) behaves in the same manner as the Tolman's length δ of pure substances: they both increase monotonically with increasing curvature of the interface. In the region of large curvature radii (in the region of weak metastability), the dependence $\delta_i(1/R_*)$ is linear. At small radii of the bubble tension surface, the Tolman's length increases as $R_*^{-1/3}$. As distinct from δ_1 and δ_2 , the value of $\delta_{1(2)} = \delta_1 - \delta_2 = R_{e,1} - R_{e,2}$ shows a weak dependence both on the curvature of the dividing surface and on the concentration.

Figure 3 presents the dependence of the surface tension of critical bubbles on the curvature of the tension surface at a constant temperature for several compositions of the external phase. Small additions of helium to liquid oxygen do not change the character of the size dependence of the surface tension monotonically decreasing it.

At a small curvature of the dividing surface, σ may be presented in the form of a series in $1/R_*$, in which the first expansion term is the surface tension at a flat interface.²⁸ The linear dependence $\delta_i(1/R_*)$ at large values of R_* signifies that in expanding σ in $1/R_*$, one can restrict oneself in a first approximation only to a term square-low in $1/R_*$

$$\sigma = \sigma_0 + \sigma_1/R_* + \sigma_2/R_*^2 \quad (29)$$

As is shown in refs 18 and 28, such an approach makes it possible to describe the dependence $\sigma(R_*)$ of vapor bubbles up to sizes characteristic of the boundary of mixture spontaneous nucleation. Taking into account the dependence $\sigma(R_*)$ in the work of formation of a critical nucleus leads to a decrease in the height of the activation barrier from $G = W_*/kT = 85$ to 70 and facilitates the nucleation in gas-filled mixture.

III. Nucleation Kinetics

The problem of boiling-up of gas-supersaturated mixture is a multiparameter problem of the nucleation theory. The state of a nucleus in mixture is characterized by several chosen variables, and the dynamics of its growth is determined by the totality of the processes of heat and mass transfer at the bubble–mixture interface: the volatility of components, the diffusion supply of a substance to a growing bubble, viscous and inertial forces, and the thermal growth regime. In ref 11, Baidakov considered a nucleation theory of gas-filled liquids which took into account the volatility of the mixture components, the diffusion supply of a dissolved gas to a bubble, and the liquid viscosity. In accordance with the scheme of Zeldovich–Kramers,²⁹ the fluctuation growth of near-critical bubbles is presented as a diffusion process in the field of thermodynamic forces in the space of variables: the bubble volume v and partial pressures of the mixture components p_1'' and p_2'' in it. For a stationary nucleation rate, a classical expression has been obtained

$$J = C_v B \exp(-W_*/kT) \quad (30)$$

$$B = |\lambda_0| \frac{R_*^2}{v_*} \left(\frac{kT}{\sigma} \right)^{1/2} \quad (31)$$

where C_v is the normalizing constant of the equilibrium distribution function of the nuclei on their volumes, B is the kinetic factor, λ_0 is the decrement of increase of an unstable variable (nucleus volume), and v_* is the volume of a critical bubble. The dynamics of the bubble growth is mainly taken into account by the parameter λ_0 , for which a cubic equation has been obtained¹¹

$$\begin{aligned} \tilde{\lambda}^3 - \tilde{\lambda}^2 \left[\frac{3-b}{3b} + \frac{1}{b_1} \left(\frac{1}{\gamma_1} + \frac{1}{\omega_1} \right) + \frac{1}{b_2} \left(\frac{1}{\gamma_2} + \frac{1}{\omega_2} \right) \right] + \\ \frac{\tilde{\lambda}}{b_1 b_2} \left(\frac{3-b_2}{3\omega_1} + \frac{3-b_1}{3\omega_2} + \frac{1}{\omega_1 \omega_2} + \frac{1}{\omega_1 \gamma_2} + \frac{1}{\omega_2 \gamma_1} \right) + \\ \frac{1}{3b_1 b_2 \omega_1 \omega_2} = 0 \quad (32) \end{aligned}$$

Here

$$\begin{aligned} \tilde{\lambda} = \lambda \frac{3bp''}{4\eta}, \quad b = \frac{2\sigma}{p_* R_*}, \quad \omega_i = \frac{p_i'' R_*}{\beta_i v_{ii} \eta} \\ \gamma_1 = \frac{4D_g p_*' \rho' (1-x_*')}{\beta_1 v_{i1} d_1 R_* \rho'' x_*'}, \quad \gamma_2 = \frac{4D_g \rho' p_*''}{\beta_2 v_{i2} d_2 R_* \rho''} \quad (33) \end{aligned}$$

η is the mixture viscosity, β_i is the condensation coefficient, $v_{ii} = (8kT/\pi m_i)^{1/2}$ presents the average thermal velocities of motion of the mixture components molecules, m_i is the molecule mass, D_g is the diffusion coefficient of gas in liquid, and $d_i = (dp_i''/dx)$. Expression 32 suggests that gas molecules move in solvent to a bubble and from it in a diffusion way; however,

the exchange of molecules between the mixture and the bubble always proceeds in the free-molecular regime.

If two components of the absorption–emission interaction of a bubble with mixture, i.e., the diffusion supply of molecules from mixture to a bubble and the free-molecular exchange of molecules at the bubble–mixture boundary, are regarded as independent processes proceeding in parallel, then the rate of change of the number of molecules of the mixture components will be determined by the expressions

$$\dot{N}_1 = (\dot{N}_{1m}^{-1} + \dot{N}_D^{-1})^{-1}, \quad \dot{N}_2 = \dot{N}_{2m} \quad (34)$$

where

$$\dot{N}_{im} = \frac{\pi \beta_i v_{ii} R^2}{kT} (p_{i*}'' - p_i'') \quad (35)$$

is the rate of molecular exchange

$$\dot{N}_D = 4\pi R \rho' D_g H (p_{1*}'' - p_1'') \quad (36)$$

is the rate of the diffusion supply, and H is the Henry's constant.

One can show that in such consideration of the processes of bubble–mixture interaction the tensor of diffusion of nuclei in the space of their essential variables, as distinct from ref 11, is symmetrical, and the decrement of increase of an unsteady variable is determined by solving the equation

$$\begin{aligned} \tilde{\lambda}^3 - \tilde{\lambda}^2 \left(\frac{3-b}{3b} + \frac{v}{b_1 v \omega_1 + 1} + \frac{1}{b_2 \omega_2} \right) + \\ \frac{\tilde{\lambda}}{b_1 b_2} \left(\frac{b_1 v}{b_1 v \omega_1 + 1} + \frac{1}{\omega_2} + \frac{3-b_1}{3\omega_2} + \frac{3-b_2}{3} \frac{b_1 v}{b_1 v \omega_1 + 1} \right) + \\ \frac{1}{3b_2 \omega_2} \frac{v}{b_1 v \omega_1 + 1} = 0 \quad (37) \end{aligned}$$

where

$$v = \frac{2D_g H \rho' \eta kT}{\sigma R_*} \quad (38)$$

The diffusion supply of a substance to a bubble may be neglected if the characteristic time of diffusion is much smaller than the other time scales connected with the pressure change in a bubble. According to eqs 33 and 38, this will take place if $\gamma_i \rightarrow \infty$ and $v \rightarrow \infty$. In this case from eqs 32 and 37 follows an eq 32 of ref 11 for determining λ_0 in a viscous, volatile mixture, in which the concentration is homogeneous up to the bubble surface. If in addition to the condition $\gamma_i \rightarrow \infty$ and $v \rightarrow \infty$ one requires $p_{2*}'' \rightarrow 0$, $\beta_2 \rightarrow 0$, $x' \neq 0$, then from eqs 30, 31, 32, and 37, an expression follows for the nucleation rate in a nonvolatile gas-filled liquid, in which the molecular exchange of a gas bubble with mixture proceeds in the free molecular regime. This expression coincides with the expression from work by Derjaguin and Prokhorov.¹ If $p_{2*}'' \rightarrow 0$, $\beta_2 \rightarrow 0$, $\beta_1 \rightarrow 0$, and $x' \neq 0$, then eq 37 changes to the equation from work by Kuni et al.² and determines together with eqs 30 and 31 the nucleation rate in a nonvolatile gas-filled liquid in the diffusion regime, at which molecules of a dissolved gas move in a solvent to a bubble or from it in a diffusion way.

Figure 4 illustrates the concentration dependence of the kinetic factor B in helium–oxygen mixtures for several limiting cases of nucleation. In all approximations, the value of B depends very weakly on the temperature, pressure, and concentration as compared with the exponential factor in eq 30. To a first

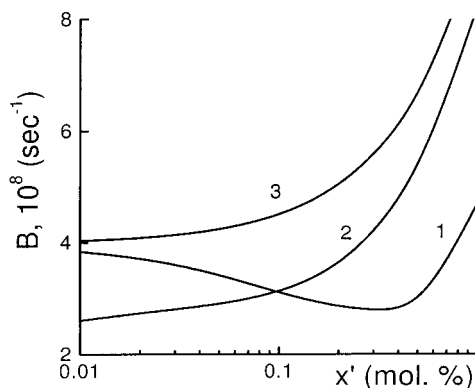


Figure 4. Concentration dependence of the kinetic factor, $T = 140$ K and $p = 1.0$ MPa: line 1, eq 32; 2, eq 37; 3, diffusionless approximation, eq 32 in ref 11.

approximation, in the region of experimentally attainable superheats, the kinetic factor may be considered constant.

Neglect of the volatility of a solvent and its viscosity results in increasing B as compared with its value calculated by the general formula 32. Ignoring the diffusion regime of supply of a substance to a bubble also increases the value of the kinetic factor.

IV. Experiment

A method of measuring the lifetime of a metastable liquid has been used to study the nucleation in supersaturated solutions of helium in liquid oxygen.^{9,30} The experimental setup is described in ref 18. A gas mixture of a given concentration was condensed into a measuring cell, which was a glass capillary soldered at one end and connected with metal bellows. The capillary was thermostated at a temperature T , and the bellows temperature was maintained close to the temperature of normal oxygen boiling. Supersaturation of the mixture in the capillary ($V = 70$ mm³) was created by pressure release to a given value p . The concentration of the gas component in the mixture was determined by data on phase equilibrium¹⁵ by the method described in ref 18. The time from the moment of changing the mixture into the metastable state to its boiling-up τ was measured in experiments at fixed T , p , and x' . After the boiling-up of the mixture, the pressure in it was increased to the value $p_B > p_s$. The mixture was "held" at a given pressure for some time, and measurements were repeated. The average time of expectation of boiling-up $\bar{\tau} = \sum_i \tau_i / N$ was found from $N = 20$ –100 measurements. The error of determining the superheat temperature was ± 0.05 K, pressure ± 0.005 MPa, and concentration ± 0.02 mol %.

The time τ registered in experiments is determined by the time of expectation of the first critical nucleus τ_w and the time of its subsequent growth τ_g to macroscopic sizes ($\tau = \tau_w + \tau_g$). In the investigated interval of the state variables of helium–oxygen mixtures, τ_g is equal to $\sim 10^{-3}$ sec. The characteristic time of an experiment is no less than 0.1 s. The condition $\tau \gg \tau_g$ makes it possible to take $\tau \approx \tau_w$ and calculate the nucleation rate as $J = 1/(\bar{\tau}V)$, where V is the superheated volume of a liquid.

Experiments have been made at two values of pressure $p = 1.171$ and 1.667 MPa and several values of helium concentration in mixture. The purity of the substances under investigation is 99.99 vol % (He) and 99.92 vol % (O₂). The interval of the measured values of the average lifetime of a metastable mixture is $0.1 \div 1000$ s, which corresponds to the nucleation rate change from 10^4 to 10^8 sec⁻¹ m⁻³.

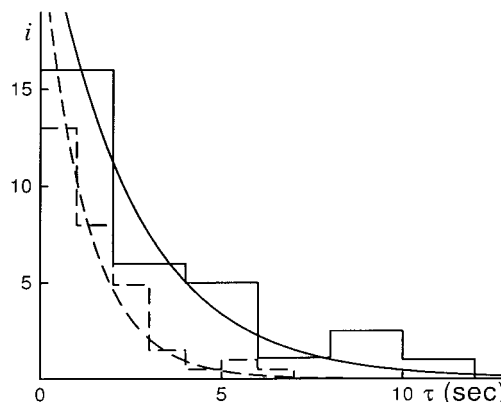


Figure 5. Distributions of the number of boiling-up i that fall within the interval $\tau, \tau + \Delta\tau$: $x' = 0.14$ mol %; $p = 1.171$ MPa; $T = 166.66$ K; $N = 31$. Solid lines, $\bar{\tau} = 2.66$ s at a "holding" time of 40 min; dashed lines, $\bar{\tau} = 1.34$ s at a "holding" time of 3 min.

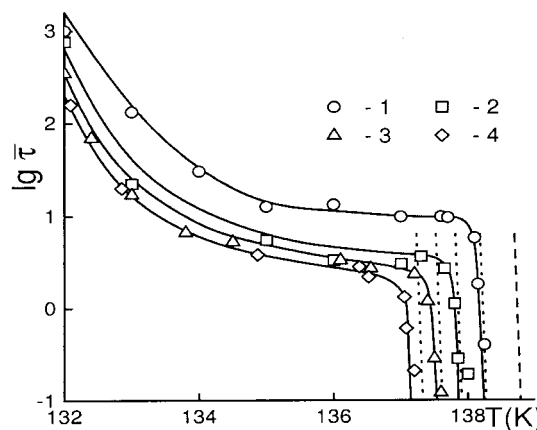


Figure 6. Temperature dependence of the mean lifetime of a metastable mixture at a pressure $p = 1.171$ MPa and concentration: $x' = 0$ (line 1), 0.08 (line 2), 0.14 (line 3), and 0.20 (line 4) mol %. A dashed line shows calculation of a one-component system by the homogeneous nucleation theory with $\sigma = \sigma_\infty$; a dotted line shows calculation by the homogeneous nucleation theory with $\sigma = \sigma(R_*)$.

Under fixed external conditions (T , p , $x' = \text{const}$), the appearance of the first viable nucleus in a metastable liquid is an event of the Poisson type. This has been confirmed by experiments on one-component liquids.⁹ The time of "holding" the liquid under pressure was in these experiments ~ 3 min, and it was sufficient for complete decompression of the vapor phase and relaxation of thermal inhomogeneities in the measuring system. In experiments with gas-filled liquids, it has been discovered that at "holding" times ~ 3 min, one can often observe boiling-up with expectation times that are "anomalously" small for the given T , p , and x' . "Anomalously" small values of τ may appear and disappear in the course of the experiment or may be retained during the whole period of measurements. Such a behavior of a gas-filled system is analogous to that of a one-component system when in the latter there are easily activated nucleation centers.³¹ The law of distribution of "anomalously" low times of boiling-up expectation is also close to the Poisson one (Figure 5, dashed smoothly curve). With increasing "holding" time between measurements up to 30–40 min (i.e., by 1 order of magnitude!), premature liquid boiling-up did not reveal itself. In processing experimental data, "anomalously" low values of τ were excluded from consideration.

In Figures 6 and 7 on a semilogarithmic scale, one can see the results of determining the average lifetime and the nucleation

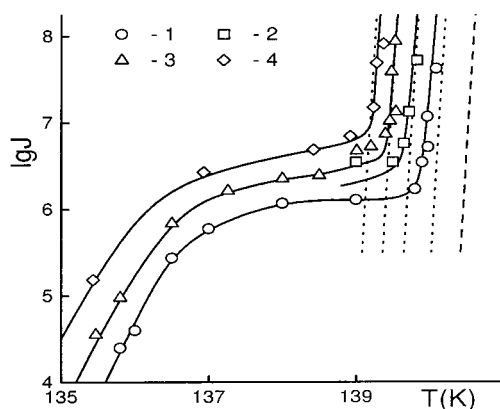


Figure 7. Temperature dependence of the nucleation rate at a pressure $p = 1.667$ MPa and concentration: $x' = 0$ (line 1), 0.08 (line 2), 0.14 (line 3), and 0.20 (line 4). For the dashed and the dotted line, see Figure 6.

rate in helium–oxygen mixtures at two pressure values. As in the case of one-component liquids, on the curves $\bar{\tau}(T)$ and $J(T)$, two sections with different temperature dependences may be distinguished. At low superheats, experimental isobars have characteristic, gently sloping sections, which with increasing temperature are replaced by sections with an abrupt change of the time of expectation of the mixture boiling-up. The first section is connected with initiated and the second with spontaneous nucleation. Dissolution of 0.1 mol % helium in liquid oxygen reduced the limiting superheat $\Delta T = T_n - T_s$ in the region of spontaneous liquid boiling-up by approximately 10%. In the region of initiated nucleation, the mixture average lifetime decreases in this case by a factor of 3 or 4. It is essential that most greatly gas filling manifests itself here at very small helium concentrations.

High-energy particles generated by cosmic radiation and the radiation background are regarded as the main factor initiating liquid boiling-up and leading to a bend of isobars.³⁰ However, in the framework of this model, it is difficult to explain such a strong effect of gas-filling on the decrease of stability of a metastable mixture in the region of initiated nucleation. As has been mentioned in ref 31, at low superheats, the action of ionizing radiation is not the only reason for an abrupt decrease in the time of expectation of boiling-up of a superheated liquid.

In sections of an abrupt decrease of τ (increase of J) the value of the derivative $(d \ln J)/dT$ within the limits of experimental error does not depend on the concentration. At a pressure of 1.171 MPa, it is 18; at $p = 1.667$ MPa, it is 21. This corresponds to an increase of the nucleation rate by approximately 8 or 9 orders with increasing temperature by 1 K.

V. Correlation between Theory and Experiment

In this section, experimental data on the boiling-up kinetics of helium–oxygen mixtures are analyzed in the framework of the stationary homogeneous nucleation theory. Evaluation of the time of establishment of a stationary flow of nuclei in mixtures τ_1 is given in ref 32. In the range of state variables where the experiments have been made, the time τ_1 does not exceed 10^{-8} sec, which justifies the neglect of nonstationarity.

In the expression 30 for the nucleation rate, the exponential term is dominant. As indicated in section II, the value of the kinetic factor B depends weakly on the temperature, pressure, and concentration. A very strong dependence of the nucleation rate on the exponent index makes differences in evaluations of the factor B immaterial. Thus, the uncertainty of the value of B

TABLE 1: Temperature of Attainable Superheat of Helium–Oxygen Mixtures, $J = 10^7 \text{ s}^{-1} \text{ m}^{-3}$

x' (mol %)	T_s (K)	p_s (MPa)	T_n (K)		
			exp.	theory ^a	theory ^b
$p = 1.171$ MPa					
0	122.40	2.570	138.17	138.73	138.22
0.08	118.96	2.640	137.79	138.38	137.85
0.14	114.55	2.686	137.43	138.11	137.56
0.20	—	2.732	137.06	137.85	137.27
$p = 1.667$ MPa					
0	129.05	2.786	140.00	140.53	140.13
0.08	127.12	2.860	139.72	140.18	139.76
0.14	125.34	2.910	139.46	139.91	139.47
0.20	123.04	2.963	139.23	139.64	139.19

^a $\sigma = \sigma_\infty$; σ_∞ from ref 16. ^b $\sigma = \sigma(R_*)$; results of this work.

of 1–2 orders results in an uncertainty in the temperature of the liquid attainable superheat equal to 0.1–0.2 K, which does not exceed the error of determination of this value in experiment.

Another crucial moment connected with the use of formula 30 is the value of the normalization constant of the equilibrium function of nucleus volume distribution C_v . Usually, it is assumed that if a nucleus may form on any molecule of a system, then $C_v = \rho' = \rho'_1 + \rho'_2$, where ρ'_1 and ρ'_2 are the numerical densities of the solvent and the dissolved substance in the liquid phase. Another approach to the determination of C_v has been given by Derjaguin.³³ According to ref 33 $C_v = v_* \rho'^2$. Going from the normalization constant $C_v = \rho'$ to $C_v = v_* \rho'^2$ decreases the temperature of attainable superheat of helium–oxygen mixture by approximately 0.2–0.3 K. When correlating theory and experiment, we use the normalization constant for the distribution function $C_v = \rho'$.

Table 1 presents data on the temperature of attainable superheat of helium–oxygen mixture corresponding to the nucleation rate $J = 10^7 \text{ sec}^{-1} \text{ m}^{-3}$. The results of experiments are compared with calculations of T_n by the homogeneous nucleation theory in a macroscopic approximation ($\sigma = \sigma_\infty$) and with allowance for the dependence of the bubble surface tension on the curvature of its dividing surface ($\sigma = \sigma(R_*)$). The kinetic factor B has been determined by the formula 32. Values of saturated temperature T_s for given pressure p and values of saturated pressure p_s corresponding with experimental temperature of attainable superheat T_n are presented in the Table 1 too. Figures 6 and 7 present temperature dependences of $\bar{\tau}$ and J according to formula 30 with allowance for the dependence $\sigma(R_*)$ and also the results of calculating the functions $\bar{\tau}(T)$ and $J(T)$ for pure oxygen in a macroscopic approximation. The data from Table 1 and Figures 6 and 7 show good agreement between experiment and the classical homogeneous nucleation theory when the latter takes into account the dependence of the properties of critical nuclei on their sizes. The discrepancy between theoretical and experimental values of attainable-superheat temperatures is within the limits of experimental error and accuracy of determination of thermophysical parameters in eqs 30 and 31.

The characteristic parameters of critical bubbles according to the Gibbs number $G = 70$ (W_* is determined by eq 8) are given in the Table 2. Calculating W_* by eq 9 with macroscopic approximation ($\sigma(R_*) = \sigma_\infty$) increases the magnitude of G for same nuclei up to 85. From the table, it follows that at a temperature $T = 138.149$ K and pressure $p = 1.171$ MPa, the radius of a critical bubble in superheated pure oxygen R_* is equal 3.732 nm, and the number of molecules in it n'_* is approximately equal 457. Dissolution in oxygen of 0.2 mol % helium decreases the critical-bubble size under condition of

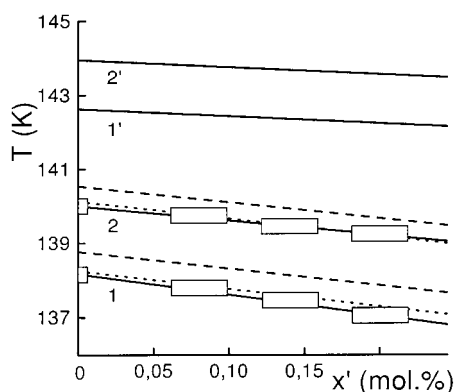


Figure 8. Temperature of attainable superheat (1, 2; $J = 10^7 \text{ sec}^{-1} \text{ m}^{-3}$) and spinodal (1', 2') at pressures $p = 1.171$ (1, 1') and 1.667 MPa (2, 2'). A dashed line shows calculation by the homogeneous nucleation theory in a macroscopic approximation $\sigma = \sigma_\infty$; a dotted line, with allowance for the dependence $\sigma(R_*)$.

TABLE 2: Characteristic Parameters of Critical Bubbles of Pure Oxygen and Helium–Oxygen Mixtures at the Pressure $p = 1.171$ MPa and the Gibbs Number $G = 70$

parameter	x' , mol %		
	0	0.1	0.2
T (K)	138.149	137.650	137.150
p , (MPa)	2.567	2.665	2.754
B , 10^8 sec^{-1}	1.969	0.855	0.556
$\log J$, eqs 30 and 32	6.09	5.72	5.60
σ_∞ (mN/m)	2.44	2.51	2.58
$\delta_{\infty,1}$ (nm)	--	0.301	0.297
$\delta_{\infty,2}$ (nm)	0.0363	0.0367	0.0371
R_* (nm)	3.732	3.673	3.615
$\sigma(R_*)$ (mN/m)	2.288	2.354	2.422
n''_*	457	442	428
n'_*	—	16	31
δ_1 (nm)	—	0.463	0.458
δ_2 (nm)	0.215	0.213	0.210
x''_* (mol. %)	0	3.03	6.02
n'_1	0	5	9
n'_2	3894	3731	3575

constancy of G and p up to $R_* \approx 3.615$ nm. It is balanced with by increasing $\sigma(R_*)$ from 2.288 to 2.422 mN/m. The concentration of helium in a bubble in this case is $x''_* \approx 6$ mol %, the number of molecules is $n''_* \approx 428$, and the bubble is practically free of helium atoms ($n'_1 \approx 31$). Before the formation of the bubble, its volume was occupied by $n'_2 \approx 3575$ molecules of oxygen and $n'_1 \approx 9$ atoms of helium. The supply of ~ 22 helium atoms to a growing bubble evidently does not require a diffusion process and may take place as a result of molecular exchange. Thus, the process of nucleation in a gas-filled mixture at temperatures close to the solvent temperature of attainable superheat is little different from the process of nucleation in a superheated pure liquid. A decrease in the liquid superheat temperature with dissolution in it of a gas component is first of all connected with a shift of the line of equilibrium coexistence of phases and, to a lesser degree, with the change of the surface tension. All this differentiates a gas-filled mixture in the vicinity of a solvent critical point from a gas-filled liquid at low temperatures.

Figure 8 shows the line of attainable superheat and the spinodal at two investigated pressures. Helium dissolution in oxygen decreases both the superheat temperature and the temperature of the loss of the system restoring reaction to infinitesimal concentration perturbations. At a helium concentration in oxygen of 0.3 mol %, the temperature of spontaneous boiling-up of a mixture is approximately 1.2–1.5 K lower than

that of oxygen. At a concentration of 0.1 mol % and a pressure of 1.171 MPa the superheat is $\Delta T \approx 20$ K, and the loss of stability of the mixture homogeneous state takes place at $\Delta T_{sp} \approx 25$ K.

VI. Conclusion

The performed experiments and an analysis of their results in the framework of the classical homogeneous nucleation theory show a good agreement between theory and experiment. At temperatures close to those of the solvent spontaneous boiling-up the homogeneous nucleation theory not only qualitatively, but also quantitatively correctly reproduces the temperature of attainable superheat of gas-filled mixtures and, which is more significant, reproduces correctly the temperature, concentration, and baric dependence of the nucleation rate. The discrepancy between theory and experiment does not exceed the experimental error in the superheat temperature if the theory takes into account the size dependence of the surface tension of a critical vapor-gas bubble. Such an agreement is circumstantial evidence justifying the assumption of equilibrium composition of a vapor-gas mixture in a critical nucleus used in the theory. As is shown in section V, close to the temperature of spontaneous boiling-up of a pure solvent, a critical bubble of a gas-filled mixture contains a number of molecules of the dissolved substance approximately 1 order of magnitude smaller than that of the solvent. If it is assumed that the gas is evenly distributed in the solvent, then in the process of nucleation molecules of the solvent predominantly leave the volume where a critical nucleus forms. For obtaining an equilibrium composition of the dissolved gas, diffusion may not be required, as the inflow of the missing number of the gas molecules may occur at the expense of a random thermal motion of molecules.

The situation is reversed if nucleation proceeds at temperatures removed from the critical temperature of the solvent. Thus, at a temperature of 100 K and a pressure of 1.171 MPa, when the helium concentration in mixture is 3 mol % and the mixture is supersaturated so that the Gibbs number is $G \approx 80$, i.e., is close to what we had in our experiments on the boiling-up of helium–oxygen mixtures at elevated temperatures, the radius of a critical nucleus will be ~ 1.7 nm, the number of helium molecules in a bubble will be $n'_* \approx 176$, and the number of oxygen molecules will be $n''_* \approx 3$. Before the formation of a nucleus in the volume of critical size, there were ~ 12 helium molecules. To achieve equilibrium gas is bound to diffuse for a distance about 2.5 times greater than the bubble radius. The characteristic diffusion time in this case is $\tau_D = 2.5^2 R_*^2 D_g^{-1} \approx 2 \times 10^{-8}$ s, which is comparable with the time of establishment of stationary nucleus size distribution. Besides, as is shown by our investigations,³⁴ a stronger size dependence of the surface tension of critical bubbles is possible here, and the character of the dependence $\sigma(R_*)$ differs from that revealed at elevated temperatures not only quantitatively, but also qualitatively (see Figure 3). Thus, the reasons for discordance between the homogeneous nucleation theory and experiment^{3–8} at low temperatures require more detailed both theoretical and experimental investigations.

Acknowledgment. This work was supported by Russian Foundation of the Basic Researches, Grants 99-02-16377 and 00-15-96719. The authors are grateful to Professor F. M. Kuni for useful remarks on the theory of nucleation in mixtures, which are taken into account in this paper.

References and Notes

- (1) Derjaguin, B. V.; Prokhorov, A. V. *Kolloid. Zh.* **1982**, *44*, 847.

- (2) Kuni, F. M.; Ochenko, V. M.; Ganiuk, L. N.; Grechko, L. G. *Kolloid. Zh.* **1993**, 55, 28.
- (3) Hemmingsen, E. A. *Science* **1970**, 167, 1493; Gerth, W. A.; Hemmingsen, E. A. *Z. Naturforsch.* **1976**, 31a, 1711.
- (4) Finkelstein, Y.; Tamir, A. *AIChE J.* **1985**, 31, 1409.
- (5) Bowers, P. G.; Hofstetter, C.; Ngo, H. L.; Toomey, R. T. *J. Colloid Interface Sci.* **1999**, 215, 441.
- (6) Rubin, M. B.; Noyes, R. M. *J. Phys. Chem.* **1987**, 91, 4193.
- (7) Bowers, P. G.; Hofstetter, C.; Letter, C. R.; Toomey, R. T. *J. Phys. Chem.* **1995**, 99, 9632.
- (8) Bowers, P. G.; Bar-Eli, K.; Noyes, R. M. *J. Chem. Soc., Faraday Trans.* **1996**, 92, 2843.
- (9) Baidakov, V. G. *Superheat of Cryogenic Liquids*; Ural Branch of RAN: Ekaterinburg, Russia, 1995.
- (10) Kwak, H.; Panton, R. L. *J. Chem. Phys.* **1983**, 78, 5795.
- (11) Baidakov, V. G. *J. Chem. Phys.* **1999**, 110, 3955.
- (12) Mori, Y.; Hijikata, K.; Nagatani, T. *Int. J. Heat Mass. Trans.* **1976**, 19, 1153.
- (13) Forest, T. W.; Ward, C. A. *J. Chem. Phys.* **1978**, 69, 2221.
- (14) Pavlov, P. A.; Skripov, P. V. *Teplofiz. Vysok. Temp.* **1985**, 23, 70.
- (15) Herring, R. N.; Barrick, P. L. *Int. Adv. Cryogenic Eng.* **1965**, 10, 151.
- (16) Baidakov, V. G.; Sulla, I. I. *Int. J. Thermophys.* **1995**, 16, 909.
- (17) van der Waals, J. D.; Kohnstamm, Ph. *Lehrbuch der Thermodynamik*; Maas and van Suchtelen: Leipzig, 1908.
- (18) Baidakov, V. G.; Kaverin, A. M.; Boltachev, G. Sh. *J. Chem. Phys.* **1997**, 106, 5649.
- (19) Gibbs, J. W. *Collected Works*; Yale University Press: New Haven, CT, 1948. Vol. 1.
- (20) Baidakov, V. G. *Interface of Simple Classical and Quantum Liquids*; Nauka: Ekaterinburg, Russia, 1994.
- (21) Cahn, J. W.; Hilliard, J. F. *J. Chem. Phys.* **1959**, 31, 688.
- (22) Baidakov, V. G.; Kaverin, A. M. *Teplofiz. Vys. Temp.* **1981**, 19, 321.
- (23) Baidakov, V. G.; Skripov, V. P. *Zh. Fiz. Khim.* **1982**, 56, 1234.
- (24) Ebner, C.; Saam, W. F.; Stroud, D. *Phys. Rev. A* **1976**, 14, 2264.
- (25) Talanquer V.; Oxtoby D. W. Nucleation of Bubbles in Binary Fluids. *J. Chem. Phys.* **1995**, 102 (5), 2156–2164.
- (26) Sichev, V. V.; Vasserman, A. A.; Koslov, A. D.; Spiridonov, G. A.; Psimarnii, V. A. *Thermodynamical Properties of Oxygen*; Isdat. standartov: Moscow, 1981.
- (27) Baidakov, V. G.; Hvostov, K. V.; Muratov, G. N. *Zh. Fiz. Khim.* **1982**, 56, 814.
- (28) Baidakov, V. G.; Boltachev, G. Sh. *Phys. Rev. E* **1999**, 59, 469.
- (29) Zeldovich, Ya. B. *Zh. Eksp. Teor. Fiz.* **1942**, 12, 525.
- (30) Skripov, V. P. *Metastable Liquids*; Wiley: New York, 1974.
- (31) Baidakov, V. G.; Kaverin, A. M. *Teplofiz. Vys. Temp.* **1990**, 28, 90.
- (32) Baidakov, V. G. *Metastable States and Phase Transitions*; Ural Branch of RAN: Ekaterinburg, Russia, 1998; Vol. 2, p 12.
- (33) Derjaguin, B. V.; Prokhorov, A. V.; Tunitsky, N. N. *Zh. Eksp. Teor. Fis.* **1977**, 73, 1831.
- (34) Baidakov, V. G.; Boltachev, G. Sh. *Zh. Fiz. Khim.* **2001**, 75, 33.