PRESSURE GROWTH DYNAMICS DURING FREEZING
OF A CLOSED VOLUME OF WATER WITH DISSOLVED GASES

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A model for the freezing of a closed volume of water with dissolved gases is proposed and studied numerically. It is shown that gas release during ice formation leads to a considerable time delay in the time of a sudden pressure increase. In the freezing process, the pressure depends not only on the volume of ice formed but also on the freezing rate, which is determined by the cooling rate and the geometry and dimensions of the freezing volume.

Key words: *freezing, dissolved gas, diffusion, gas release, numerical modeling.*

Introduction. The freezing of water media in the pore space of soils, water handlings, and in and near wells in permafrost rock occurs in closed volumes and gives rise to high pressures resulting in unfavorable consequences, such as soil foaming [1], deformation, rupture, and collapse of well and pipeline casings [2]. In the unfrozen region, the pressure increases with increasing volume fraction of ice because the density of ice is lower than that of water. Usually, the pressure variation is estimated taking into account only the compressibility of water and ice [2, 3]. In this case, the pressure in the unfrozen region is uniquely determined by the volume fraction of ice formed and does not depend on other factors influencing the freezing rate.

In practice, water contains dissolved air even under atmospheric conditions. At a temperature $T = 0°C$ its volume fraction is about 3.6%; under different conditions, the concentration of dissolved gases can be higher. During ice formation, gas molecules are almost completely forced into water. In this case, the dissolved-gas flow that arises at the freezing boundary exceeds the gas-diffusion flows in water. As a result, the gas concentration near the ice surface increases and conditions for its passage from the solution into the free phase are produced. Similar processes are involved in melt crystallization [4].

The occurrence of even small amounts of free gas in the volume can have a strong effect on the compressibility of the system and the pressure rise rate. In the present paper, we propose and numerically study a mathematical model for the freezing of water with dissolved gas in a closed volume including the classical formulation of the Stefan problem with a moving phase-transition boundary taking into account the displacement of the gas dissolved in water at the interface, diffusion transfer with possible passage of the gas into the free phase, pressure variation in the system with a variable amount of free gas, and a pressure dependence of the freezing temperature.

Calculating the kinetics of formation and growth of gas bubbles in a supersaturated solution (including their amount and size distribution) is a separate complex challenge. Therefore, in the model considered, the structure of the free gas phase is ignored as a first approximation and its compressibility is assumed to depend only on its total volume in the unfrozen medium. The dependence of the rate of gas release into the free phase on the gas concentration in the supersaturated solution is taken to be a linear function, By specifying the proportionality coefficient in this function, it is possible to model the delay in the time of consolidation of molecules into bubbles, which increase the compressibility of the medium. The possibility of entraining the bubbles in ice crystals due to microperturbations of the freezing boundary is also ignored in the model.

In spite of a number of simplifying assumptions, the formulation of the problem provides a more complete description of freezing processes in closed volumes. An important feature that distinguishes this model from the case where the presence of dissolved gas is ignored is the dependence of rate of pressure rise on the conditions determining the rate of ice formation.

The problem of heat transfer and diffusion with a moving boundary is solved numerically using the finite-element method with moving coupled meshes proposed in [5] for nonlinear heat-conduction problems and tested in [6] for the heat- and mass-transfer equations in the problem of freezing of a salt solution. Calculation of fields using moving coupled meshes reduces to an analysis of displacements of points with specified nodal values of the solution. This approach allows one to determine the phase-transition boundary with minimum computational costs and to calculate the simultaneous heat-transfer and diffusion processes, whose characteristic rates differ by three orders of magnitude. In particular, a coupled mesh automatically arranges nodes inside a thin diffusion layer that moves together with the interface.

Formulation of the Problem. We consider a water volume V_0 which has the shape of a flat layer of thickness R with a heat insulated surface $r = 0$ or the shape of a cylindrical or spherical region of radius R. In the initial state, the water temperature is T_0 and its pressure is P_0. The water contains a dissolved gas in homogeneous equilibrium volume concentration C_0. Cooling from the surface $r = R$ occurs by heat convection or by maintenance of the specified temperature on the surface. Subsequently, we assume that the initial temperature T_0 is equal to the freezing temperature of the medium at the specified initial pressure and a cooling temperature $T_b < T_0$, so that for any forms of cooling, freezing begins at the initial time.

We shall consider only a conductive heat-transfer mechanism. The heat-transfer process with simultaneous freezing is described by the one-dimensional system of equations in the appropriate coordinate system:

$$\frac{\partial T_w}{\partial t} = a_w \Delta T_w, \qquad 0 < r < r_m(t),$$

$$\frac{\partial T_i}{\partial t} = a_i \Delta T_i, \qquad r_m(t) < r < R, \qquad \Delta T = \frac{1}{r^s}\frac{\partial}{\partial r}\left(r^s \frac{\partial T}{\partial r}\right),$$

$$T_w = T_i = T_m(P), \qquad \lambda_i \frac{\partial T_i}{\partial r} - \lambda_w \frac{\partial T_w}{\partial r} = -\rho_i L \frac{dr_m}{dt}, \qquad r = r_m(t),$$

$$\lambda_i \frac{\partial T_i}{\partial r} = h(T_b - T_i) \quad \text{or} \quad T_i = T_b, \qquad r = R,$$

$$r^s \frac{\partial T_w}{\partial r} = 0, \qquad r \to 0,$$

$$T_w = T_0, \qquad r_m = R, \qquad t = 0.$$

Here T is the temperature, λ and a are the thermal conductivity and temperature diffusivity, respectively; the superscripts $s = 0$, 1, and 2 refer to flat, cylindrical, and spherical geometries, respectively; $T_m(P)$, L, and $r_m(t)$ are the temperature, specific heat, and coordinate of the boundary of the water–ice phase transition, P is the pressure, ρ is the density, and h is the heat-transfer coefficient. The subscripts w and i refer to water and ice, respectively.

The freezing temperature depends on pressure according to the Clausius–Clapeyron law

$$\frac{dT_m}{dP} = \left(\frac{1}{\rho_w} - \frac{1}{\rho_i}\right)\frac{T_m + 273.2}{L},$$

where the variations in the densities of water and ice with increasing pressure can be ignored.

The expulsion of the dissolved gas during water freezing, the redistribution of the gas concentration due to diffusion, and possible gas passage into the free phase are described by the equations

$$\frac{\partial C}{\partial t} = D\Delta C - f(C), \qquad 0 < r < r_m(t),$$

$$D\frac{\partial C}{\partial r} = -C\frac{dr_m}{dt}, \qquad r = r_m(t),$$

$$r^s \frac{\partial C}{\partial r} = 0, \qquad r \to 0,$$

$$C = C_0, \qquad t = 0,$$

where D is the gas diffusion coefficient in water, $f(C)$ is a function that defines the rate of gas release from the solution when the gas concentration exceeds the value corresponding to the equilibrium pressure. The pressure dependence of the gas concentration is described by the linear Henry law

$$C_{\text{eq}} = C_0 + \Gamma(P - P_0),$$

where Γ is the solubility constant. The water cooling due to the release of dissolved gas is ignored (because of its small volume fraction).

During water freezing, the excess volume of ice is compensated by the corresponding decrease in the volumes of water, ice, and free gas due to their compressibility. Thus, when the volume of ice increases by dV_i, the following equality should be satisfied:

$$\left(1 - \frac{\rho_i}{\rho_w}\right) dV_i = -(\delta V_i + \delta V_w + \delta V_a). \tag{1}$$

Here δV is the volume change of the corresponding media due to their compressibility; the subscript a corresponds to the gas in the free state.

Taking into account the compressibility only due to pressure rise, for ice and water we obtain the relations

$$\delta V_i = -\beta_i V_i \, dP, \qquad \delta V_w = -\beta_w V_w \, dP, \tag{2}$$

and for the gas,

$$V_a = \frac{(V_a)_0 P_0}{P}, \qquad \delta V_a = -\frac{(V_a)_0 P_0}{P^2} \, dP. \tag{3}$$

Here β is the compression ratio and $(V_a)_0$ is the free-gas volume V_a referred to the initial pressure P_0. The free-gas accumulation in the system is calculated by integrating the source function $f(C(r, t))$ in the diffusion equation over the region $0 < r < r_m(t)$ for the entire period of time. The rate of gas release into the free phase is described by the linear relation

$$f(C) = k_c H(C - C_{\text{eq}})(C - C_{\text{eq}}),$$

where $H(C)$ is a Heaviside function, k_c is a coefficient that simulates the delay due to the consolidation of molecules into bubbles, which increase the compressibility of the medium.

In the dimensionless variables

$$\xi = \frac{r}{R}, \quad \eta = \frac{r_m}{R}, \quad \tau = \frac{a_i t}{R^2}, \quad \theta = \frac{T_0 - T}{T_0 - T_b}, \quad \sigma = \frac{C}{C_0}, \quad \varphi = \frac{P}{P_0},$$

the problem reduces to the following system of equations:

$$\alpha \frac{\partial \theta_w}{\partial \tau} = \Delta \theta_w,$$

$$\delta \frac{\partial \sigma}{\partial \tau} = \Delta \sigma - k_\sigma H(\sigma - \sigma_{\text{eq}})(\sigma - \sigma_{\text{eq}}), \qquad 0 < \xi < \eta(\tau),$$

$$\frac{\partial \theta_i}{\partial \tau} = \Delta \theta_i, \qquad \eta(\tau) < \xi < 1,$$

$$\theta_w = \theta_i = \theta_m(\varphi), \qquad -\frac{\partial \theta_i}{\partial \xi} + \varepsilon_m \frac{\partial \theta_w}{\partial \xi} = \frac{1}{\text{St}} \frac{d\eta}{d\tau},$$

$$\frac{\partial \sigma}{\partial \xi} = -\delta \sigma \frac{d\eta}{d\tau}, \qquad \xi = \eta(\tau), \tag{4}$$

$$\frac{\partial \theta_i}{\partial \xi} = \text{Bi} \, (1 - \theta_i) \quad \text{or} \quad \theta_i = 1, \qquad \xi = 1,$$

$$\xi^s \frac{\partial \theta_w}{\partial \xi} = 0, \qquad \xi^s \frac{\partial \sigma}{\partial \xi} = 0, \qquad \xi \to 0,$$

$$\theta_w = 0, \qquad \sigma = 1, \qquad \eta = 1, \qquad \tau = 0.$$

Here $\alpha = a_i/a_w$, $\varepsilon_m = \lambda_w/\lambda_i$, $\delta = a_i/D$, $k_\sigma = k_c R^2/D$, $\text{St} = \lambda_i(T_0 - T_b)/(a_i \rho_i L)$ is the Stefan number, and $\text{Bi} = h\lambda_i/R$ is the Biot number.
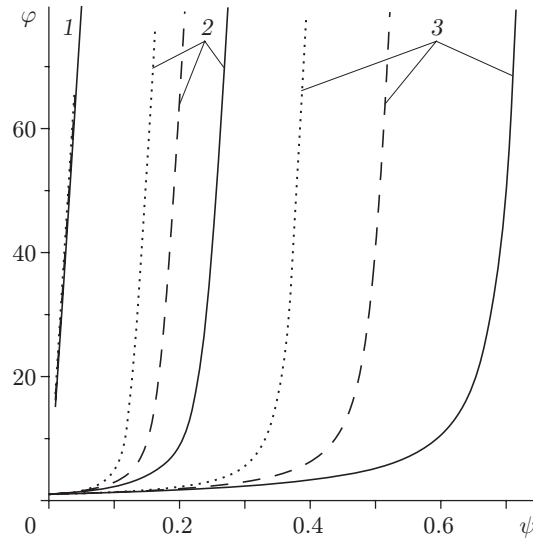
Fig. 1. Limiting estimates of the pressure rise during ice formation for $C_0 = 0.1$ (solid curves), 0.05 (dashed curves), and 0 (dotted curves) and $\nu_0 = 0$ (1), 0.01 (2), and 0.03 (3).

The dimensionless relations for the freezing temperature and the equilibrium gas concentrations become

$$\theta_m(\varphi) = \theta_* + ((\theta_m)_0 - \theta_*)\,e^{-k_\theta(\varphi-1)}, \qquad \sigma_{\text{eq}} = 1 + \gamma(\varphi - 1), \tag{5}$$

where $\theta_* = (T_0 + 273.2)/(T_b - T_0)$, $(\theta_m)_0$ is the dimensionless initial equilibrium freezing temperature, $k_\theta = \chi P_0/(\rho_i L)$, $\gamma = \Gamma P_0/C_0$, and $\chi = 1 - \rho_i/\rho_w$.

For the calculation of the pressure in the unfrozen region by relations (1)–(3) ignoring the variation in the density of water and ice on the left side of Eq. (1), we obtain the differential equation with the initial condition

$$\frac{d\varphi}{d\psi} = \frac{\chi\varphi^2}{(b_1 - b_2\psi)\varphi^2 + (1 - b_1\varphi)\nu}, \qquad \varphi(0) = 1, \tag{6}$$

where $\psi = V_i/V_0 = 1 - \eta(\tau)^{s+1}$ is the volume fraction of ice formed, $\nu = (V_a)_0/V_0$ is the volume fraction of free gas (referred to the initial pressure), $b_1 = \beta_w P_0$, and $b_2 = (\beta_w - \beta_i)P_0$.

The amount of accumulated free gas is calculated by the relation

$$\nu(\tau) = \nu_0 + C_0(s+1)k_\sigma \int\limits_0^\tau \int\limits_0^{\eta(\tau)} H(\sigma - \sigma_{\text{eq}})(\sigma - \sigma_{\text{eq}})\xi^s \, d\xi \, d\tau, \tag{7}$$

where ν_0 is the initial volume fraction of free gas.

We note that solution of Eq. (6) yields preliminary limiting estimates of the pressure rise $\varphi(\psi)$ for the freezing of a closed volume for the two limiting idealized cases of the absence of dissolved gas [for $\nu(\psi) = \nu_0$] and the release of the entire dissolved gas from the freezing water into the free phase [for $\nu(\psi) = \nu_0 + C_0\psi$]. A comparison of the solutions for these cases presented in Fig. 1 shows that they differ significantly even for small values of ν_0 and C_0 [except for the case of the absence of gas in the free state at the initial time $(\nu_0 = 0)$]. For $\nu_0 = 0$, gas release does not lead to an increase in the compressibility of the medium due to an instantaneous pressure rise in the initial period of freezing. In practice, a freezing medium always has a certain initial reserve of compressibility, which can be modeled by nonzero value of ν_0 in the model considered. From Fig. 1 it follows that an increase in ν_0 can lead to an enhancement of the effect of dissolved gas on the delay in pressure rise.

Modeling Results. The problem (4)–(7) was solved numerically using an implicit finite-element scheme with moving coupled meshes [5, 6]. In this case, the phase-transition boundary and the adjoining layer with a perturbed concentration of dissolved gas is selected automatically. Calculations showed that in using this scheme to solve heat-conduction equations and the equations describing the diffusion and release of dissolved gas, 21 nodes for each case are sufficient. For control, we examined the balance of the volumes of the gas forced out during water
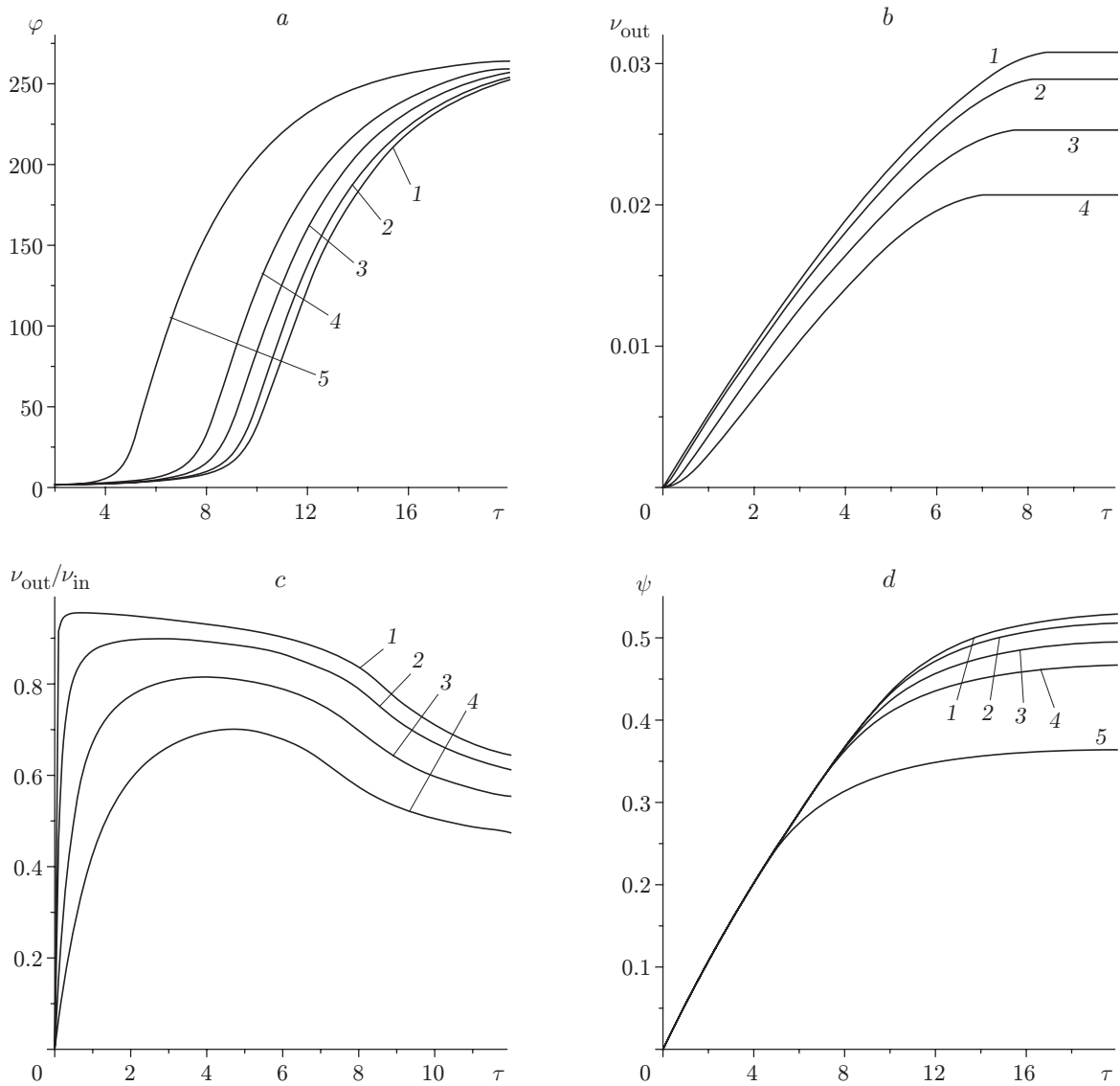
Fig. 2. Time dependences of the pressure (a), the total volume of the released gas (b), the ratio $\nu_{\text{out}}/\nu_{\text{in}}$ (c), and the volume fraction of ice formed (d) for various values of the dimensionless coefficient of the gas-release rate: $k_\sigma = 10^5$ (1), 10^4 (2), $2.5 \cdot 10^3$ (3), 10^3 (4), and 0 (5); $\nu_0 = 0.02$, $C_0 = 0.1$, $T_b = -2°$C, and Bi = 5.

freezing, the gas dissolved in it, and the gas released into the free phase. The difference between the calculation results did not exceed 0.25% of the relative value of the parameter.

In the calculations, the following initial data were used: $\lambda_w = 0.567$ W/(m·K), $\lambda_i = 2.22$ W/(m·K), $a_w = 1.35 \cdot 10^{-7}$ m²/sec, $a_i = 1.14 \cdot 10^{-6}$ m²/sec, $\rho_w = 1000$ kg/m³, $\rho_i = 917$ kg/m³, $L = 332 \cdot 10^3$ J/kg, $\beta_w = 5.1 \cdot 10^{-10}$ Pa^{-1}, $\beta_i = 1.1 \cdot 10^{-10}$ Pa^{-1}, $D = 1.6 \cdot 10^{-9}$ m²/sec, $\Gamma = 1.35 \cdot 10^{-7}$ nm³/(m³·Pa), $T_0 = 0°$C, and $P_0 = 10^5$ Pa. During the numerical experiments, we varied the parameters describing the cooling rate (T_b and Bi), the parameters determining the compressibility of the medium due to the presence of dissolved and free gas (C_0 and ν_0), and the coefficient of the rate of gas release into the free phase k_σ; the solutions for different geometries of the freezing volume were compared.

Figure 2 shows the results of solution of the problem for a cylindrical volume obtained for various values of the coefficient k_σ. The value of k_σ is determined by the ratio of the rate of consolidation of gas molecules into the free phase to the rate of their diffusion in the solution, and by the dimensions of the freezing volume. In the lack of
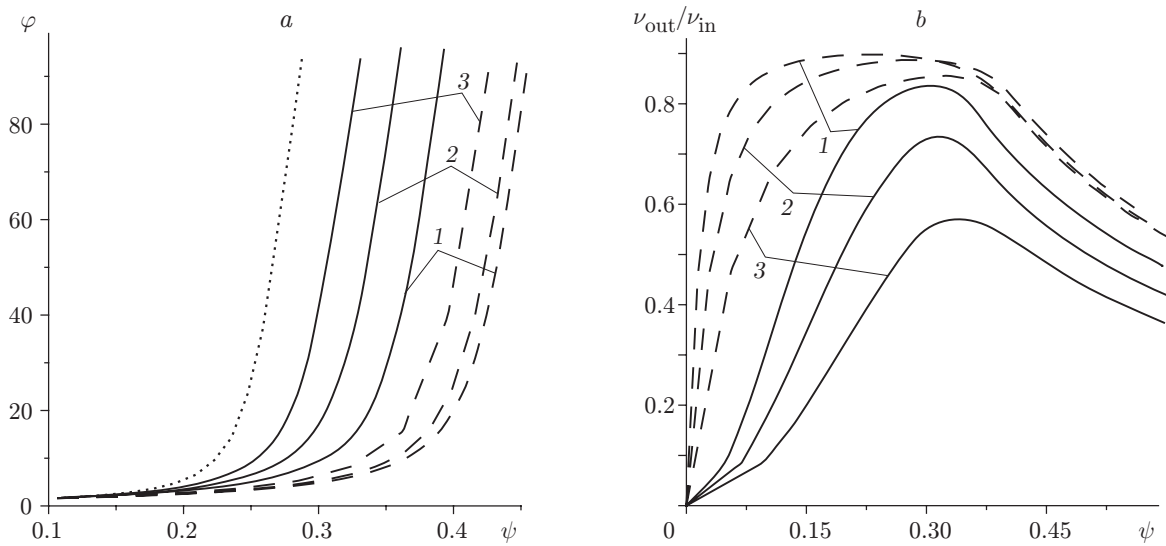
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Fig. 3. Pressure in the unfrozen volume (a) and the ratio $\nu_{\text{out}}/\nu_{\text{in}}$ (b) versus the volume fraction of ice formed at temperatures $T_b = -5$ (1), -10 (2), and $-20°$C (3) and different cooling conditions ($\nu_0 = 0.02$, $C_0 = 0.1$, and $k_\sigma = 10^4$): the solid curves refer to a fixed temperature on the cooling surface and the dashed curves to convective cooling for Bi $= 5$; the dotted curve refers to the calculation ignoring the effect of dissolved gas.

experimental data, the values of this coefficient were varied over a broad range; the value of $k_\sigma = 10^5$ corresponds to almost instantaneous gas release into the free phase.

The nature of the curves presented in Fig. 2a indicates the period preceding the sharp pressure rise increases with increasing coefficient k_σ. For comparison, Fig. 2a shows the curve obtained by solving the problem ignoring dissolved-gas release ($k_\sigma = 0$). In this case, the pressure rise in the volume begins much earlier. The delay in the pressure rise depends on the volume fraction of free gas accumulated by the moment of the sharp pressure rise and the termination of gas release; the volume fraction, in turn, depends on the coefficient k_σ. The time dependences of the volume of the gas released into the free phase ($\nu_{\text{out}} = \nu - \nu_0$) and its fraction in the total amount of the gas forced out from the freezing water (ν_{in}) are presented in Fig. 2b and c. An increase in the compressibility of the medium due to gas release leads to a change in the freezing dynamics and an increase in the maximum volume of ice formed by the moment the freezing and cooling temperatures become equal (Fig. 2d). For rapid gas release ($k_\sigma = 10^4$–10^5) the volume of ice formed by the moment of attainment of thermodynamic equilibrium is 1.5 times larger than that in the case of ignoring dissolved-gas release.

Similar dependences are obtained in calculations of freezing with a specified surface temperature maintained on the surface. In this case, however, for the same initial data, the curves corresponding to intermediate values of k_σ are distributed more uniformly, which indicates that the process is influenced by cooling conditions.

If dissolved-gas release is taken into account, the pressure depends not only on the volume fraction of ice formed but also on the freezing rate. With decreasing cooling rate, which is determined by the cooling temperature and the heat-transfer coefficient, the pressure increases much more slowly with increasing volume of ice, which is confirmed by the calculation results presented in Fig. 3a. This is due to the fact that in the case of slower ice formation, a larger amount of dissolved gas is released into the free phase. On the other hand, a high rate of freezing leads to a rapid pressure rise and an increase in the equilibrium gas concentration in the solution, resulting in a decrease in the gas-release rate and the amount of free gas in the volume. This conclusion is confirmed by the nature of the time dependence of the ratio $\nu_{\text{out}}/\nu_{\text{in}}$ with increasing volume fraction of ice: as the cooling rate increases, the fraction of the gas released into the free phase decreases compared to the fraction of the gas remaining in the dissolved state (Fig. 3b). If the presence of dissolved gas is ignored, then, by virtue of Eq. (6), the pressure is uniquely determined only by the volume fraction of ice irrespective of the cooling conditions (the dotted curve in Fig. 3a).

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In the numerical experiments, similar results were obtained for freezing regions of different geometries. Under the same conditions, freezing proceeds faster in a spherical volume than in a cylindrical or a flat region. Accordingly, for the same volume of ice, the pressure increases faster in a spherical cavity.

Conclusions Water freezing in closed volumes leads to a pressure rise in the unfrozen region. A rapid pressure rise occurs as the compressibility reserve of the medium is exhausted. As shown by the numerical experiments using the proposed mathematical model, the presence of gas dissolved in water leads to an increase in the period preceding the rapid pressure rise. The effect of dissolved gas is more pronounced the lower the freezing rate, which depends on the cooling conditions and the geometry and dimensions of the freezing region. The effect of dissolved gas becomes more significant as the gas concentration in the solution and the initial compressibility of the medium increase. The indicated factors also influence the results of calculations of the ice formation dynamics. In particular, the larger maximum possible volume of ice is formed by the moment of attainment of thermodynamic equilibrium.

In conclusion, we note that in all cases considered, up to the attainment of equilibrium values of the pressure and the fraction of ice formed, the boundary of the diffusion layer did not reach the center of the solidifying volume, which is due to the low initial gas concentration in water. Thus, the possibility of the formation of a solid region with free gas in the volume under the conditions considered was ruled out.

REFERENCES

1. É. D. Ershov, *General Geocriology* [in Russian], Nedra, Moscow (1990).
2. R. I. Medvedskii, *Construction and Operation of Oil and Gas Wells in Permafrost Rock* [in Russian], Nedra, Moscow (1987).
3. M. Sugawara, N. Seki, and K. Kimoto, "Freezing limit of water in a closed circular tube," *Wärme- und Stoffübertrag*, No. 17, 187–192 (1983).
4. A. I. Fedorchenko and A. A. Chernov, "Analytical solutions of the problem of displacement of a gas dissolved in a melt by flat and spherical crystallization fronts," *J. Appl. Mech. Tech. Phys.*, **44**, No. 1, 109–113 (2003).
5. R. I. Medvedskiii and Yu. A. Sigunov, "On the solution of one-dimensional nonlinear heat-conduction problems on an isothermal mesh," *Zh. Vychisl. Mat. Mat, Fiz.*, **29**, No. 11, 1742–1746 (1989).
6. Yu. A. Sigunov, "Method of isopotential meshes for heat- and mass transfer problems in phase transitions," in: *Collected Papers of Surgut State University* [in Russian], No. 4 (1998), pp. 54–61.