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DISTRIBUTION OF DISSOLVED GAS IN WATER AND BUBBLES IN ICE UPON MOVEMENT OF A CRYSTALLIZATION FRONT

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The distribution of dissolved gas in water upon increase in a crystallization front is considered. Optimal conditions are derived for water crystallization, under which the gas-bubble distribution in the ice formed will be the most homogeneous.

As is well known [1], the solubility of air in water is at least an order higher than its solubility in ice. Thus, upon crystallization of water at the phase boundary the dissolved air is liberated and diffuses into the water volume and partially into the ice. Thus, in both the water and the ice the air solution becomes supersaturated. Usually, the water contains a number of particles of a different substance, which may become centers of gas-bubble formation at relatively low supersaturations. Gas bubbles are formed ahead of the crystallization front on these centers. With increase in supersaturation, the number of active bubble-formation centers increases. Therefore, the structure of the ice formed by crystallization of water will be determined by the degree of supersaturation of the solution ahead of the crystallization front, which, in turn, is dependent on the gas-liberation rate at the crystallization front. With increase in crystallization-front displacement

velocity, there occurs a significant increase in the number of bubbles forming ahead of the front, while the dimensions of these bubbles decrease simultaneously. If external conditions are such that the bubbles cannot ascend to the water surface, then in the crystallization process these bubbles will pass through the phase boundary and be included in the ice volume. Thus, there is a direct relationship between the crystallization-front displacement velocity and the concentration and size of gas bubbles in the ice. In particular, the character of bubble distribution within the volume of a freezing droplet will be determined by the droplet crystallization velocity and, consequently, by the temperature of the medium. In [2] broad experimental studies were performed of the dependence of ice structure on air temperature in freezing droplets. These studies permit use of the character of bubble distribution in the freezing droplets to derive conclusions as to the temperature of the medium at which the crystallization process took place.

If the crystallizing water is supercooled, then the increase in water temperature at the crystallization front will cause additional supersaturation, since with increase in temperature, gas solubility in water decreases. The degree of this supersaturation may be determined from the known water-temperature distribution ahead of the crystallization front.

Determination of supersaturation of air solutions in water ahead of a crystallization front with consideration of the kinetics of bubble formation is beset with many difficulties. In part, these difficulties are connected with the fact that the number of active bubble-formation centers and the dependence of the activity of these centers on the degree of supersaturation of the gas solution are not known beforehand. Therefore, the simplest possible case will be considered here, in which the crystallizing water is so well purified of foreign impurities that bubble formation does not occur ahead of the crystallization front.

To analyze the process of gas liberation from the crystallization front, we initially consider the case of crystallization of a homogeneous liquid occupying the volume $x > 0$ at the initial moment of time. Let T_0 be the initial liquid temperature; c_0 is the initial gas concentration in the liquid. At the moment $t = 0$ the temperature in the plane $x = 0$ decreases to T and remains constant during the liquid crystallization process. As is well known [3], the problem of solidification of a liquid in such a formulation allows an analytic solution. The phase division boundary then moves in the direction of positive x according to the law

$$\xi(t) = 2\alpha \sqrt{\varkappa_1 t}, \tag{1}$$

where $\varkappa_1$ is the coefficient of thermal diffusivity of ice; t is time. The parameter α is determined by the transcendental equation

$$\frac{\exp(-\alpha^2)}{\Phi(\alpha)} - \frac{\lambda \sqrt{\varkappa_1} T \exp\left(-\dfrac{\varkappa_1 \alpha^2}{\varkappa}\right)}{\lambda_1 \sqrt{\varkappa} \, \Phi^*\left(\alpha \sqrt{\dfrac{\varkappa_1}{\varkappa}}\right)} = \frac{\alpha L \sqrt{\pi} \rho}{c_i}. \tag{2}$$

Here λ, $\varkappa$ are the coefficients of thermal conductivity and diffusivity of water; λ_1, $\varkappa_1$ are corresponding values for ice; ρ is the density of water; c_i is the heat capacity of ice; L is the heat of fusion of water; $\Phi(x)$ is the error function; and $\Phi^*(x) = 1 - \Phi(x)$.

The problem reduces to determination of the gas concentration in the liquid phase, with foreknowledge of the law for crystallization-front motion — Eq. (1).

In the majority of cases the saturation density of gas in water is low. Therefore, we may neglect the effect of thermal diffusion on gas-concentration distribution in the liquid. Then the diffusion equation for concentration c will have the form

$$\frac{\partial c}{\partial t} - D \frac{\partial^2 c}{\partial x^2} = 0, \tag{3}$$

where D is the diffusion coefficient for a gas in a liquid.

The solution of Eq. (3) must satisfy the following conditions: At $t = 0$, $c = c_0$; as $x \to \infty$, $c \to c_0$.

Moreover, on the phase division boundary the balance condition must be fulfilled.

Usually, diffusion in a solid occurs several orders of magnitude more slowly than in a liquid. Thus, below we will neglect the diffusion of gas into the ice volume and assume that all gas liberated at the crystallization front will diffuse into the liquid. Then the balance condition takes on the form

$$-D\left(\frac{\partial c}{\partial x}\right) = \frac{d\xi}{dt}(c - c_1) \quad \text{for} \quad x = \xi(t), \tag{4}$$

where c_1 is the saturation gas concentration in ice at zero temperature.

We will seek a solution of Eq. (3) in the form

$$c = A + B\Phi^* \left(\frac{x}{2\sqrt{Dt}} \right),$$

(5)

where A and B are arbitrary constants. From the condition at infinity it follows that $A = c_0$. The value of B is determined from Eq. (4). The final solution has the form

$$c = c_0 + \frac{(c_0 - c_1)\alpha \sqrt{\pi \frac{\varkappa_1}{D}} \exp\left(-\frac{\alpha^2 \varkappa_1}{\varkappa}\right)}{1 - \alpha \sqrt{\pi \frac{\varkappa_1}{D}} \exp\left(\alpha^2 \frac{\varkappa_1}{D}\right) \Phi^*\left(\alpha \sqrt{\frac{\varkappa_1}{D}}\right)} \Phi^*\left(\frac{x}{2\sqrt{Dt}}\right).$$

(6)

The amount of supersaturation Δc which occurs at the phase division boundary will be equal to

$$\Delta c = c - c_0 = \frac{\alpha(c_0 - c_1)}{\sqrt{\frac{D}{\pi \varkappa_1}} \exp\left(-\frac{\alpha^2 \varkappa_1}{D}\right) \Phi\left(\alpha \sqrt{\frac{\varkappa_1}{D}}\right) - \alpha}.$$

(7)

In the case of supercooled water, to this supersaturation there will be added a supersaturation produced by increase in temperature at the crystallization front.

Estimates show that at reasonable values of α corresponding to water crystallization conditions, the value of Δc determined by Eq. (7) does not exceed the equilibrium concentration of gas in water at zero temperature. On the other hand, for spontaneous gas-bubble formation, significant supersaturation is required. Therefore, under real water-freezing conditions, homogeneous gas-bubble formation in the liquid phase is impossible.

Despite the fact that formation and growth of gas bubbles ahead of the crystallization front will significantly change the character of gas-concentration distribution in the liquid phase, a number of important conclusions follow from Eq. (6).

First of all, it should be noted that since the air dissolved in the water contains various gaseous components, differences in diffusion coefficient ahead of the crystallization front will cause stratification of these components; crystallization will be accompanied by diffusive separation of foreign impurities contained in the water. In particular, ions of varying mobility will be separated, which may lead to formation of potential differences on the phase boundary.

Another important conclusion following from Eq. (6) is the following. The self-similar solution of Eq. (2) is unique. This situation corresponds to time-independent gas concentration on the phase boundary and, consequently, the time-independent gas-bubble-formation conditions directly ahead of the crystallization front. Therefore, if the bubble-formation-center distribution in the liquid is homogeneous, then ice will be obtained with an air-bubble concentration identical throughout the volume. Under any other water crystallization regime the gas concentration at the front will vary with time; consequently, the bubble-formation conditions ahead of the crystallization front also change. Therefore, the bubble distribution in the ice will be inhomogeneous; an increase in solution bubble distribution leads to an increase in bubble concentration and size in the ice being formed. Thus, to create an ice specimen with the most homogeneous structure, it is necessary to construct the experiments in a manner such that the initial and boundary conditions formulated for the problem considered here are fulfilled.

It is known that foreign impurities contained in the water are expelled from the crystallizing mass into the liquid volume — self-purification of the ice occurs in water crystallization. Solution (6) describes the distribution of the concentrations of these impurities in the liquid phase.

We will now consider the case where the crystallization front moves with constant velocity u. We assume that at the initial moment the homogeneous liquid fills the space $x > 0$ and that the initial gas concentration c_0 is constant. At the moment $t = 0$ the crystallization front begins to move to the right along the positive x axis at constant velocity.

It is required to find the distribution of concentration c in the liquid volume.

In the present case it will be more convenient to write the diffusion equation in a coordinate system moving from the right toward the left at velocity u. In such a coordinate system the phase boundary will always be located at the origin x = 0.

The equation describing gas-concentration distribution in the liquid may then be written in the form

$$\frac{\partial c}{\partial t} - D\frac{\partial^2 c}{\partial x^2} - u\frac{\partial c}{\partial x} = u(c - c_1)\,\delta(x), \tag{8}$$

where $\delta(x)$ is the Dirac delta function. The right side of Eq. (8) represents a source of power $u(c - c_1)$, located on the phase boundary at the origin.

For convenience in solving Eq. (8), we introduce the new function $\bar{c} = c - c_0$. Omitting the bar, we will have

$$\frac{\partial c}{\partial t} - D\frac{\partial^2 c}{\partial x^2} - u\frac{\partial c}{\partial x} = u(c + \Delta c)\,\delta(x), \tag{9}$$

where $\Delta c = c_0 - c_1$.

The desired solution of Eq. (9) must satisfy the following initial and boundary conditions: $c = 0$ at $t = 0$ and $c \to 0$ as $x \to \infty$. Moreover, the balance condition must be fulfilled at the phase boundary.

We apply the Laplace transform to Eq. (9). Then the equation in transform variables appears as

$$\frac{d^2\bar{c}}{dx^2} + \frac{u}{D}\cdot\frac{d\bar{c}}{dx} - \frac{p}{D}\bar{c} = -\frac{u}{D}\left(\frac{\Delta c}{p} + \bar{c}\right)\delta(x). \tag{10}$$

To find conditions on the phase boundary we integrate both sides of Eq. (10) from $-\varepsilon$ to $+\varepsilon$. We obtain

$$\frac{d\bar{c}}{dx}\Big|_{-\varepsilon}^{+\varepsilon} + \frac{u}{D}\bar{c}\Big|_{-\varepsilon}^{+\varepsilon} - \frac{p}{D}\int_{-\varepsilon}^{+\varepsilon}\bar{c}\,dx = -\frac{u}{D}\left(\frac{\Delta c}{p} + \bar{c}\right). \tag{11}$$

As ε tends to zero, in the limit the integral on the left side tends to zero. Thus

$$D\frac{d\bar{c}}{dx}\Big|_{x=0} = -u\left(2c + \frac{\Delta c}{p}\right)_{x=0}. \tag{12}$$

In the region $x > 0$ Eq. (10) has the form

$$\frac{d^2\bar{c}}{dx^2} + \frac{u}{D}\cdot\frac{d\bar{c}}{dx} - \frac{p}{D}\bar{c} = 0. \tag{13}$$

In the region $x < 0$ $\bar{c} \equiv 0$. On the boundary $x = 0$ the condition of Eq. (12) is fulfilled, and $c \to 0$ as $x \to \infty$.

The solution of Eq. (13) satisfying these conditions has the form

$$\bar{c} = \frac{2\Delta c}{p\sqrt{1 + \dfrac{4pD}{u^2}} - 3}\cdot\exp\left[-\frac{u}{2D}\left(1 + \sqrt{1 + \frac{4pD}{u^2}}\right)x\right]. \tag{14}$$

Transforming to the original, we obtain

$$c = \frac{\Delta c\exp\left(-\dfrac{ux}{2D}\right)}{\pi i}\int_{a-i\infty}^{a+i\infty}\frac{e^{pt}\exp\left(-\dfrac{u}{2D}\sqrt{1 + \dfrac{4pD}{u^2}}\right)}{p\left(\sqrt{1 + \dfrac{4pD}{u^2}} - 3\right)}\,dp.$$

Using, in turn, the displacement theorem and the theorem of integration of the original [4], we finally obtain

$$c = \frac{\Delta cu}{\sqrt{\pi D}}\exp\left(-\frac{ux}{2D}\right)\int_0^t\frac{\exp\left(-\dfrac{u^2\tau}{4D} - \dfrac{x^2}{4D\tau}\right)}{\sqrt{\tau}}\,d\tau + \frac{3\Delta cu^2}{2D}\exp\left(-\frac{2ux}{D}\right)\int_0^t\Phi^*\left(\frac{x}{2\sqrt{D\tau}} - \frac{3u\sqrt{\tau}}{2\sqrt{D}}\right)d\tau. \tag{15}$$

Integrating the second integral by parts, the solution of Eq. (15) may be written as

$$c = \frac{\Delta cu}{\sqrt{\pi D}}\exp\left(-\frac{ux}{2D}\right)\int_0^t\frac{\exp\left(-\dfrac{u^2\tau}{4D} - \dfrac{x^2}{4D\tau}\right)}{\sqrt{\tau}}\,d\tau$$

$$+ \frac{3\Delta cu^2}{2D}\exp\left(-\frac{2ux}{D}\right)\left[t\Phi^*\left(\frac{x}{2\sqrt{Dt}} - \frac{3u\sqrt{t}}{2\sqrt{D}}\right) - \int_0^t\frac{x + 3u\tau}{4\sqrt{D\tau}}\exp\left(\frac{(x - 3u\tau)^2}{4D\tau}\right)d\tau\right]. \tag{16}$$

On the boundary, from Eq. (16) we have

$$c(0, t) = \frac{4\Delta c}{\sqrt{\pi}} \, \Phi\left(\frac{u\sqrt{t}}{2D}\right) + \frac{\Delta c u \sqrt{t}}{2\sqrt{D}} \exp\left(-\frac{9u^2 t}{4D}\right) - \frac{\Delta c}{3} \, \Phi\left(\frac{3u\sqrt{t}}{2\sqrt{D}}\right) + \frac{3u^2\Delta c t}{2D}\left[1 + \Phi\left(\frac{3u\sqrt{t}}{2\sqrt{D}}\right)\right].$$

From this it is simple to see that as $t \to \infty$ the quantity

$$c(0, t) \to \frac{3u^2\Delta c}{D}\, t.$$

Thus, the gas concentration on the phase boundary for constant velocity of crystallization-front motion grows proportionally to time t and to the square of this velocity. Thus, in principle, after a certain period of time homogeneous gas-bubble formation should begin.

In the case considered here the effect of diffusion separation of gas components ahead of the crystallization front will appear to a still higher degree.

In conclusion, we note that solutions of problems analogous to those considered above but with other crystallization-front displacement velocities are obviously quite difficult to achieve. The solutions obtained above offer definite descriptions of the character of ice-structure formation in the water-crystallization process.

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EFFECT OF ULTRASOUND ON THE PROCESS OF
MASS TRANSFER IN CEMENT MORTAR
AND CONCRETE

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We present new results in the investigation of the depth and rate of impregnation of cement mortar and concrete. We show the effect of ultrasound on the process of mass transfer in concrete. We establish the possibility of using ultrasound for accelerating the impregnation of concrete and also of other capillary-porous materials.

The most important materials for the industrial production of structural elements of buildings and industrial installations are concrete and cement−sand mortar. Both of these materials belong to the category of capillary-porous substances, whose distinguishing feature is their capacity for actively absorbing moisture and gases from the surrounding medium. This phenomenon is due to the chemical properties of the cement stone and its micropore structure.

The absorptive and capillary intake by the concrete or the mortar of substances which are harmful to the cement stone leads to a reduction of strength, an increase in deformability, and a change in the heat-engineering characteristics of structural elements. These phenomena are more often observable at chemical-industry enterprises [1-4], where there is always a high concentration of aggressive reagents in the surrounding medium.