THEORY OF THE FREEZING PROCESS IN THICK LAYERS OF SOLUTIONS

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The geophysically important problem of the freezing of an infinitely thick liquid subjected to a constant external temperature sufficient to freeze it was formulated and solved by Stefan as long ago as 1891 [1]. In both nature and technology, however, solutions of various substances are encountered rather than pure liquids. For this reason it is of interest to consider the analogous problem for solutions.

In this study we limit ourselves to the case of binary solutions which on freezing do not form mixed crystals ("solid solutions"). To solutions of this type belong, in particular, solutions of many inorganic substances in water (for example, sodium chloride in water).

We will also assume that the concentration of the dissolved substance is less than the eutectic concentration [2]. Such relatively weak solutions are most often encountered in nature. In fact, the salt content of sea and lake waters usually does not exceed several percent by weight, while the eutectic concentration of sodium chloride in water is about 30%.

It is well known [2] that during the freezing of solutions of subeutectic composition only the solvent solidifies. Consequently, if a sufficiently low constant temperature is applied to the surface of such a solution, a zone of solvent solidification will extend from the surface into the depth of the solution. The dissolved substance must move away from this zone. If the freezing process is taken to be sufficiently slow, then it is natural to assume that the withdrawal of the substance occurs by diffusion. Thus the freezing of binary solutions at relatively low concentrations will be described by simultaneous equations of thermal conductivity and diffusion.

We present below a mathematical formulation of the problem of the freezing of such solutions, give its solution, and evaluate the effect of diffusion processes during the freezing of aqueous salt solutions.

1. Formulation of the problem. Let the solution initially occupy the lower portion of a space, and the x axis be directed down into it. We take $T_1(x, t)$, $T_2(x, t)$ as the temperatures of the frozen solvent and the solution, and $c(x, t)$ as the concentration of the substance dissolved in the solution. These quantities will satisfy the following equations:

$$\begin{gathered}\frac{\partial T_1}{\partial t} = \varkappa_1 \frac{\partial^2 T_1}{\partial x^2} \qquad (0 \leqslant x \leqslant l(t)) \qquad (l(0) = 0), \\ \frac{\partial T_2}{\partial t} = \varkappa_2 \frac{\partial^2 T_2}{\partial x^2}, \qquad \frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \qquad (l(t) \leqslant x \leqslant \infty).\end{gathered} \tag{1.1}$$

Here $l(t)$ is the coordinate of the moving boundary of the phase transition, $\varkappa_1$, $\varkappa_2$ are the thermal conductivity coefficients of the solid and liquid phases, D is the diffusion coefficient. In addition, it is necessary to fulfil the initial conditions and conditions at infinity,

$$T_2(x, 0) = T_2(\infty, t) = T_0, \qquad c(x, 0) = c(\infty, t) = c_0, \tag{1.2}$$

and also the boundary conditions for T_1 and T_2 at $x = 0$ and $x = l(t)$,

$$\begin{gathered}T_1(0t) = \theta, \qquad \rho L \frac{dl}{dt} = -\lambda_2 \frac{\partial T_2}{\partial x}\bigg|_{x=l} + \\ + \lambda_1 \frac{\partial T_1}{\partial x}\bigg|_{x=l}, \quad T_1(l, t) = T_2(l, t) = T^\circ,\end{gathered} \tag{1.3}$$

where ρ is the solvent density, λ_1, λ_2 are the thermal conductivity coefficients of the solid and liquid phases, and L is the specific heat of melting of the solvent.

There exists a relationship between the solution concentration $c(l, t)$ at the phase transition boundary and the solidification temperature of the solution, T°; it is given [2] by the equation

$$T^\circ = T_* [1 - kc(l, t)] \qquad \left(k = \frac{RT_*}{L} \frac{M'}{\rho M}\right). \tag{1.4}$$

Here T_* is the freezing temperature of the pure solvent in °K, and M', M are the molecular weights of the solvent and the solute; R is the gas constant.

In addition to the relations (1.3) and (1.4), one more condition must be fulfilled at the phase transition boundary. Let us consider the mass balance for the solute (in units of area) included between the cross sections $x = x_0$ and $x = l(t)$, where $x_0 > l(t)$. On the one hand, we can write

$$\frac{dm}{dt} = D \frac{\partial c}{\partial x}\bigg|_{x=x_0}. \tag{1.5}$$

On the other hand, using the diffusion equation, we find

$$\begin{gathered}\frac{dm}{dt} = \frac{d}{dt} \int\limits_{l(t)}^{x_0} c\, dx = \int\limits_{l(t)}^{x_0} \frac{\partial c}{\partial t} dx - c(l, t) \frac{dl}{dt} = \\ = D \frac{\partial c}{\partial x}\bigg|_{x=x_0} - D \frac{\partial c}{\partial x}\bigg|_{x=l} - c(l, t) \frac{dl}{dt}.\end{gathered} \tag{1.6}$$

Equating (1.5) and (1.6) we obtain

$$\frac{dl}{dt} = -\frac{D}{c(l, t)} \frac{\partial C}{\partial x}\bigg|_{x=l(t)}. \tag{1.7}$$

Thus the problem of the freezing of a weak solution (subeutectic) is completely described by Eqs. (1.1) and the conditions (1.2)-(1.4), (1.7).

2. The general solution. Carrying out a dimensional analysis of the controlling parameters of the problem, using the method described in [3], we conclude that it is self-similar. The solution takes the form

$$\begin{gathered}c(x, t) = c_0 \left(A + B \operatorname{erfc} \frac{x}{2\sqrt{Dt}}\right), \\ T_i(x, t) = E_i + F_i \operatorname{erfc}\left(\frac{x}{2\sqrt{\varkappa_i t}}\right) \quad (i = 1, 2), \\ l(t) = 2\sqrt{\alpha t} \qquad \left(\operatorname{erfc} \xi = 1 - \operatorname{erf} \xi, \quad \operatorname{erf} \xi = \frac{2}{\sqrt{\pi}} \int\limits_0^\xi e^{-\sigma^2} d\sigma\right).\end{gathered} \tag{2.1}$$

Using the conditions (1.2), (1.4), (1.7) and also the first and third conditions of (1.3), we obtain

$$\begin{gathered}A = 1, \qquad B = \frac{\sqrt{\pi\alpha/D}}{e^{-\alpha/D} - \sqrt{\pi\alpha/D} \operatorname{erfc} \sqrt{\alpha/D}}, \\ E_1 = \\ = \frac{T_* [1 - kc_0 - (\theta / T_*) \operatorname{erfc} \sqrt{\alpha / \varkappa_1} - kc_0 B \operatorname{erfc} \sqrt{\alpha / D}]}{\operatorname{erf} \sqrt{\alpha / \varkappa_1}}, \quad E_2 = T_0, \\ F_1 = -\frac{T_* (1 - kc_0 - \theta / T_* - kc_0 B \operatorname{erfc} \sqrt{\alpha / D})}{\operatorname{erf} \sqrt{\alpha / \varkappa_1}}, \\ F_2 = \frac{T_* [1 - kc_0 - T_0 / T_* - kc_0 B \operatorname{erfc} (\sqrt{\alpha / D})]}{\operatorname{erfc} \sqrt{\alpha / \varkappa_2}}.\end{gathered} \tag{2.2}$$

From the first equation of (2.1) it is seen that at the phase transition boundary the solute concentration $c(l, t)$ is constant, where $c(l, t) > c_0$. It therefore follows from (1.4) that the temperature T° is also constant and $T^\circ < T_*(1 - kc_0)$.

We obtain the equation for determining α from the second condition (1.3),

$$\frac{\rho L\varkappa_2}{\lambda_2 T_*}\left(\frac{\pi\alpha}{\varkappa_2}\right)^{1/2} =$$

$$= \frac{\Delta\theta \exp(-\alpha/\varkappa_2)}{T^* \operatorname{erfc}(\sqrt{\alpha/\varkappa_2})}\left[1 - \frac{(T_0 - \theta)}{\Delta\theta} - \frac{kc_0 T_*}{\Delta\theta} B \operatorname{erfc}\left(\frac{\alpha}{D}\right)^{1/2}\right] +$$

$$+ \frac{\lambda_1}{\lambda_2}\left(\frac{\varkappa_2}{\varkappa_1}\right)^{1/2} \frac{\Delta\theta \exp(-\alpha/\varkappa_1)}{T_* \operatorname{erf}(\sqrt{\alpha/\varkappa_1})}\left[1 - \frac{kc_0 T_*}{\Delta\theta} B \operatorname{erfc}\left(\frac{\alpha}{D}\right)^{1/2}\right],$$

$$\Delta\theta = T_*(1 - kc_0) - \theta. \qquad (2.3)$$

It is seen from Eq. (2.3) that $\alpha = 0$ for $\theta = T_*(1 - kc_0)$.

If we put $c_0 = 0$ in (2.2) and (2.3), we obtain the formulas for the problem of the freezing of a pure solvent [1, 4]. Disregarding the finite diffusion time in the solution (i. e., for $D = \infty$ and $c = c_0$), Eq. (2.3) for the determination of α takes the form

$$\frac{\rho L\varkappa_2}{\lambda_2 T_*}\left(\frac{\pi\alpha}{\varkappa_2}\right)^{1/2} = \frac{\Delta\theta \exp(-\alpha/\varkappa_2)}{T^* \operatorname{erfc}(\sqrt{\alpha/\varkappa_2})}\left(1 - \frac{T_0 - \theta}{\Delta\theta}\right) +$$

$$+ \frac{\lambda_1}{\lambda_2}\left(\frac{\varkappa_2}{\varkappa_1}\right)^{1/2} \frac{\Delta\theta \exp(-\alpha/\varkappa_1)}{T_* \operatorname{erf}\sqrt{\alpha/\varkappa_1}}. \qquad (2.4)$$

3. The effect of solute diffusion on the velocity of the phase transition boundary. As already noted, as a result of solute diffusion from the phase transition boundary into the body of the solution, its concentration at the boundary is maintained above the equilibrium concentration.

This leads to an additional depression of the solution freezing temperature. Since the diffusion constants of solutes in liquids are small, it is expected that this effect will be significant. To evaluate this effect quantitatively it is necessary to make use of Eq. (2.3).

Let us consider, for simplicity, the case when the initial temperature $T_0 = T_*(1 - kc_0)$. Then $1 - (T_0 - \theta)/\Delta\theta = 0$ and Eq. (2.3) can be rewritten in the following form:

$$\frac{\Delta\theta}{T_*} = \Phi_1(z) + \Phi_2(z),$$

$$z = \sqrt{\alpha/\varkappa_1}, \qquad \Phi_1(z) = \frac{\sqrt{\pi}\rho L\varkappa_1}{\lambda_1 T_*} z \exp(z^2) \operatorname{erf} z,$$

$$\Phi_2(z) = kc_0 B(z) \operatorname{erfc}\left[\left(\frac{\varkappa_1}{D}\right)^{1/2} z\right]\Big(1 +$$

$$+ \frac{\lambda_2}{\lambda_1} \frac{\sqrt{\varkappa_1/\varkappa_2} \operatorname{erf} z \exp[z^2(1 - \varkappa_1/\varkappa_2)]}{\operatorname{erfc}\sqrt{\varkappa_1/\varkappa_2}\, z}\Big). \qquad (3.1)$$

Here $B(z)$ is given by Eq. (2,2). From physical considerations it is clear that the quantity $T_*^{-1}\Delta\theta$ must be a monotonically increasing function of z, giving the single-valued inverse relation $z = f(T_*^{-1}\Delta\theta)$.

For $z \ll 1$

$$\Phi_1(z) \approx \frac{2\rho L\varkappa_1}{\lambda_1 T_*} z^2,$$

$$\Phi_2(z) \approx kc_0 B(z) \operatorname{erfc}\left[\left(\frac{\varkappa_1}{D}\right)^{1/2} z\right]\left(1 + \frac{2\lambda_2}{\sqrt{\pi}\lambda_1}\left(\frac{\varkappa_1}{\varkappa_2}\right)^{1/2} z\right). \quad (3.2)$$

If the condition $\sqrt{\varkappa_1/D}z \ll 1$ is also fulfilled, then

$$B(z) \operatorname{erfc}\left[\left(\frac{\varkappa_1}{D}\right)^{1/2} z\right] \approx \sqrt{\pi\varkappa_1/D}\, z, \qquad \Phi_2(z) \approx kc_0\left(\frac{\pi\varkappa_1}{D}\right)^{1/2} z. \quad (3.3)$$

Equation (3.1) shows what the relative difference should be between the initial and boundary temperatures for the given law of boundary movement (z = const). The term $\Phi_2(z)$ in this equation characterizes the diffusion effect.

If, in fact, diffusion were to occur instantaneously ($D = \infty$, $c = c_0$), then

$$\frac{\Delta\theta}{T_*} = \Phi_1(z), \qquad \Phi_2(z) = 0. \qquad (3.4)$$

In evaluating the quantities $\Phi_1(z)$ and $\Phi_2(z)$ we will consider the important practical case of a solution of sodium chloride in water. If the sodium chloride concentration is expressed in weight percent, then for such a solution $k = 2.2 \cdot 10^{-3}$ (see [4]) and $D = 10^{-5}$ cm^2/sec.

z	$\Phi_1(z)$	$\Phi_2(z)$
$3.5 \cdot 10^{-4}$	$1.6 \cdot 10^{-7}$	$2.12 \cdot 10^{-4}$
$3.5 \cdot 10^{-3}$	$1.6 \cdot 10^{-5}$	$1.9 \cdot 10^{-3}$
$3.5 \cdot 10^{-2}$	$1.6 \cdot 10^{-3}$	$4.9 \cdot 10^{-2}$

In addition, we will take $c_0 \approx 5\%$ and λ_1, $\varkappa_1$, L, $\varkappa_2$, λ_2 will be understood as the corresponding quantities for pure ice and water. Thus,

$$\lambda_1 = 5.3 \cdot 10^{-3} \text{ cal/cm} \cdot \text{sec} \cdot \text{deg}, \ \varkappa_1 = 1.15 \cdot 10^{-2} \text{ cm}^2\text{/sec},$$
$$L = 79.7 \text{ cal/g}, \ \lambda_2 = 1.44 \cdot 10^{-3} \text{ cal/cm} \cdot \text{sec} \cdot \text{deg},$$
$$\varkappa_2 = 1.44 \cdot 10^{-3} \text{ cm}^2\text{/sec}.$$

Putting these numerical values of the parameters into equation (3.1) we obtain the values of $\Phi_1(z)$ and $\Phi_2(z)$ given in the table. The range of values of z in this table correspond to an adequately wide variation in $\Delta\theta$ (from $\approx 6 \cdot 10^{-2}$ ° C to 14° C, $c(c, t) < 30\%$).

It is seen from the table that

$$\Phi_2(z) \gg \Phi_1(z),$$

throughout the chosen range of values of z, and

$$\Delta\theta / T_* \approx \Phi_2(z). \qquad (3.5)$$

The values obtained are also applicable to weak solutions of many other mineral salts in water, since k for them does not differ greatly from the analogous constant for sodium chloride. Thus, for calcium chloride, in the same units, $k \approx 1.8 \cdot 10^{-3}$ [4].

Thus diffusion phenomena have an important effect on the freezing process in aqueous salt solutions.

4. Generalization of the problem for the case of partial freeze-in of solute in ice. It was previously assumed that all the solute moves away from the solidifying solvent. In fact, in many cases some portion of it remains in the solid phase. Thus, for example, in the freezing of sea water, cells (capillaries containing strong brine) are formed between crystals of pure ice and cannot freeze at the given temperature. The entrapment of a drop of brine by the solid phase occurs because the solidification front is not absolutely plane and possesses a "rough" structure. The "roughness" of the front, and consequently the number of entrapped brine bubbles, is the greater, the lower the temperature at which the freezing process occurs [6].

In order to take account of this phenomenon, the model considered earlier must be generalized. This can be done in the following way.

We will assume that part of the solute remains in the solid phase, the content of solute per unit volume of this phase c_* remaining constant ($c_* < c_0$).

The latter assumption is justified if the spacial uniformity and isotropicity of the process are taken into account.

With these assumptions, instead of condition (1.5) we will obviously have

$$[c(l, t) - c_*]\frac{dl}{dt} = -D \left.\frac{\partial c}{\partial x}\right|_{x=l}. \qquad (4.1)$$

The remaining initial and boundary conditions stay as before, and therefore the expressions for A, E_i, and F_i retain their previous form (2.2). The equation for determining α, as before, will be written in the form of (2.3). However, the expression for the constant B will be somewhat different.

In the case under consideration this parameter is given by

$$B' = \left(1 - \frac{c_*}{c_0}\right) B, \tag{4.2}$$

where B is given by the second equation of (2.2). Therefore in Eq. (3.1) the function $\Phi_1(z)$ stays the same, but $\Phi_2(z)$ takes the form

$$\Phi_2'(z) = \left(1 - \frac{c_*}{c_0}\right) \Phi_2(z). \tag{4.3}$$

Thus the freezing of a proportion c_*/c_0 of the solute into the ice decreases the quantity $\Phi_2(z)$ in Eq. (3.1) by the factor $(1 - c_*/c_0)$.

According to results given in [7], c_*/c_0 can reach 0.5 in freshly formed sea ice.

However, in this case, as seen from the table and from equation (4.3), the inequality $\Phi_2'(z) \gg \Phi_1(z)$ is satisfactorily fulfilled in the range of variation of z considered.

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