

EXACT SOLUTION TO THE PROBLEMS OF  
MASSIVE FREEZING IN A SOLUTION

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The problem of massive freezing in a hypoeutectic solution is analyzed under various boundary conditions at the free surface.

In [1] the authors have considered the first boundary-value problem of massive freezing ( $0 \leq x \leq \infty$ ) in a hypoeutectic solution with the free surface ( $x = 0$ ) held at a rather low constant temperature  $T_1(0, t) = \theta_0$ . Such a situation may arise, for instance, when the solution comes into contact with strongly ("ideally") stirred convective air.

In that article we have solved the first boundary-value problem for the other (extreme) case, namely where the solution ( $0 \leq x \leq \infty$ ) is in contact with still air ( $-\infty \leq x \leq \infty$ ) and the temperature of the latter is held constant at a low enough level to allow the solution to freeze. Also the second and the third boundary-value problem of massive freezing have been solved for the case of constant respective boundary conditions at the free surface ( $x = 0$ ). For a pure solvent, these solutions become those arrived at in [2].

1. We will now consider the freezing of a solution in contact with still air. Let the air occupy the region ( $-\infty \leq x \leq 0$ ) and let the solution initially occupy the region ( $0 \leq x \leq \infty$ ). Let  $\theta(x, t)$ ,  $T_1(x, t)$ , and  $T_2(x, t)$  denote the temperatures of the air, of the freezing solvent, and of the solution respectively, while  $c(x, t)$  denotes the solute concentration.

These quantities must satisfy the following equations:

$$\begin{aligned} \frac{\partial \theta}{\partial t} = \kappa_* \frac{\partial^2 \theta}{\partial x^2}, \quad -\infty \leq x \leq 0, \quad \frac{\partial T_1}{\partial t} = \kappa_1 \frac{\partial^2 T_1}{\partial x^2}, \quad 0 \leq x \leq l(t), \\ \frac{\partial T_2}{\partial t} = \kappa_2 \frac{\partial^2 T_2}{\partial x^2}, \quad \frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}, \quad l(t) \leq x \leq \infty, \end{aligned} \quad (1)$$

with the boundary conditions at infinity and the initial conditions

$$\theta(-\infty, t) = \theta_0, \quad T_2(x, 0) = T_2(\infty, t) = T_0, \quad c(x, 0) = c(\infty, t) = c_0, \quad (2)$$

as well as the boundary conditions at  $x = 0$  and at the interphase boundary  $x = l(t)$ :

$$\begin{aligned} \theta(0, t) = T_1(0, t), \quad \lambda_* \frac{\partial \theta}{\partial x} \Big|_{x=0} = \lambda_1 \frac{\partial T_1}{\partial x} \Big|_{x=0}, \\ \rho L \frac{dl}{dt} = \lambda_1 \frac{\partial T_1}{\partial x} \Big|_{x=l} - \lambda_2 \frac{\partial T_2}{\partial x} \Big|_{x=l}, \quad T_1(l, t) = T_2(l, t) = T_* [1 - kc(l, t)], \\ \frac{dl}{dt} = - \frac{D}{[c(l, t) - c_*]} \cdot \frac{\partial c}{\partial x} \Big|_{x=l}. \end{aligned} \quad (3)$$

Here  $k = (RT_*/L) \cdot (M'/\rho M)$ .

We will seek the solution to the problem in the form:

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$$\begin{aligned}\theta(x, t) &= E_* + F_* \operatorname{erfc} \left( -\frac{x}{2\sqrt{\kappa_* t}} \right), \\ c(x, t) &= A + B \operatorname{erfc} \left( \frac{x}{2\sqrt{Dt}} \right), \quad l(t) = 2\sqrt{\alpha t}, \\ T_i &= E_i + F_i \operatorname{erfc} \left( \frac{x}{2\sqrt{\kappa_i t}} \right) \quad (i = 1, 2).\end{aligned}$$

Thus, conditions (2)-(4) yield

$$A = c_0, \quad B = \frac{\sqrt{\pi\alpha/D} c_0 (1 - c_*/c_0)}{\exp \left( -\frac{\alpha}{D} \right) - \sqrt{\pi\alpha/D} \operatorname{erfc} \left( \sqrt{\frac{\alpha}{D}} \right)},$$

$$E_* = \theta_0, \quad E_2 = T_0, \quad F_2 = \frac{T_* (1 - kc_0) - T_0 - T_* kB \operatorname{erfc} \left( \sqrt{\frac{\alpha}{D}} \right)}{\operatorname{erfc} \sqrt{\frac{\alpha}{\kappa_2}}}, \quad (6)$$

$$F_* = -\frac{\lambda_1}{\lambda_*} \sqrt{\frac{\kappa_*}{\kappa_1}} F_1, \quad E_1 = \theta_0 - \left( 1 + \frac{\lambda_1}{\lambda_*} \sqrt{\frac{\kappa_*}{\kappa_1}} \right) F_1,$$

$$F_1 = -\frac{T_* (1 - kc_0) - \theta_0 - T_* kB \operatorname{erfc} \left( \sqrt{\frac{\alpha}{D}} \right)}{\operatorname{erf} \sqrt{\frac{\alpha}{\kappa_1}} + \frac{\lambda_1}{\lambda_*} \sqrt{\frac{\kappa_*}{\kappa_1}}}.$$

The equation for  $\alpha$  is derived from the calorimetric condition (4):

$$\begin{aligned}\frac{\rho L \kappa_2}{\lambda_2 T_*} \sqrt{\frac{\pi\alpha}{\kappa_2}} &= \frac{\left[ (1 - kc_0) - \frac{T_0}{T_*} - kB \operatorname{erfc} \left( \sqrt{\frac{\alpha}{D}} \right) \right] \exp \left( -\frac{\alpha}{\kappa_2} \right)}{\operatorname{erfc} \left( \sqrt{\frac{\alpha}{\kappa_2}} \right)} \\ &+ \frac{\lambda_1}{\lambda_2} \sqrt{\frac{\kappa_2}{\kappa_1}} \frac{\left[ (1 - kc_0) - \frac{\theta_0}{T_*} - kB \operatorname{erfc} \left( \sqrt{\frac{\alpha}{D}} \right) \right] \exp \left( -\frac{\alpha}{\kappa_1} \right)}{\operatorname{erf} \left( \sqrt{\frac{\alpha}{\kappa_1}} \right) + \frac{\lambda_1}{\lambda_*} \sqrt{\frac{\kappa_*}{\kappa_1}}}.\end{aligned} \quad (7)$$

When  $\lambda_* = \infty$ , we have  $\theta(x, t) \equiv \theta_0$  and formulas (6), (7) become those in [1].

Problem (1)-(7) and the problem analyzed in [1] describe the extreme cases of massive freezing in a solution in contact with air.

The preceding problem, as has been mentioned earlier, corresponds to the case of still air without convection (purely conductive heat transfer in the gaseous phase). The freezing rate calculated for these conditions will be the lowest possible. The problem in [1], on the other hand, can be interpreted as one of massive freezing in a solution in contact with air during convective stirring so strong ("ideal") that  $\theta(x, t) \equiv \theta_0$ . In this case the freezing rate will be the highest possible. Under actual conditions of convective air stirring, the freezing rate will be somewhere between those two extreme ones.

If the medium (\*) is air, then conditions (6) and (7) can be simplified. Indeed, for air we have  $\lambda_* = 5.3 \cdot 10^{-5} \text{ cal/cm} \cdot \text{sec} \cdot \text{°C}$ ,  $\kappa_* = 1.7 \cdot 10^{-1} \text{ cm}^2/\text{sec}$  and  $\kappa_1 = 1.15 \cdot 10^{-2} \text{ cm}^2/\text{sec}$ ,  $\lambda_1 = 5.3 \cdot 10^{-3} \text{ cal/cm} \cdot \text{sec} \cdot \text{°C}$  (ice). Therefore,  $\lambda_1/\lambda_* \sqrt{\kappa_*/\kappa_1} \approx 3.8 \cdot 10^2$ , i. e.,  $\lambda_1/\lambda_* \sqrt{\kappa_*/\kappa_1} \gg 1$  and  $\lambda_1/\lambda_* \sqrt{\kappa_*/\kappa_1} \gg \operatorname{erf} \sqrt{\alpha/\kappa_1}$  (since  $\operatorname{erf} \sqrt{\alpha/\kappa_1} \leq 1$ ).

Consequently,

$$E_1 \approx \theta_0 - \frac{\lambda_1}{\lambda_*} \sqrt{\frac{\kappa_*}{\kappa_1}} F_1, \quad F_1 \approx -\frac{\lambda_*}{\lambda_1} \sqrt{\frac{\kappa_1}{\kappa_*}} \left[ T_* (1 - kc_0) - \theta_0 - T_* kB \operatorname{erfc} \left( \sqrt{\frac{\alpha}{D}} \right) \right], \quad (8)$$

and Eq. (7) becomes

$$\begin{aligned}\frac{\rho L \kappa_2}{\lambda_2 T_*} \sqrt{\frac{\pi\alpha}{\kappa_2}} &= \frac{\left[ (1 - kc_0) - \frac{T_0}{T_*} - kB \operatorname{erfc} \left( \sqrt{\frac{\alpha}{D}} \right) \right] \exp \left( -\frac{\alpha}{\kappa_2} \right)}{\operatorname{erfc} \left( \sqrt{\frac{\alpha}{\kappa_2}} \right)} \\ &+ \frac{\lambda_*}{\lambda_2} \sqrt{\frac{\kappa_2}{\kappa_*}} \left[ (1 - kc_0) - \frac{\theta_0}{T_*} - kB \operatorname{erfc} \left( \sqrt{\frac{\alpha}{D}} \right) \right] \exp \left( -\frac{\alpha}{\kappa_1} \right).\end{aligned} \quad (7')$$

If  $T_0 = T^* (1 - kc_0)$ , then (7) can be rewritten as

$$\frac{\Delta\theta_0}{T^*} = \Psi_1(z) + \Psi_2(z),$$

$$\Psi_1(z) = \frac{\rho L \sqrt{\pi \kappa_* \kappa_1}}{\lambda_* T^*} z e^{z^2}, \quad \Psi_2(z) = kB(z) \operatorname{erfc} \left( \sqrt{\frac{\kappa_1}{D}} z \right)$$

$$\times \left[ 1 + \frac{\lambda_2 \sqrt{\kappa_*} \exp \left[ -z^2 \left( \frac{\kappa_1}{\kappa_2} - 1 \right) \right]}{\lambda_* \kappa_2 \operatorname{erfc} \left( \sqrt{\frac{\kappa_1}{D}} z \right)} \right], \quad (9)$$

where  $z = \sqrt{\alpha/\kappa_1}$  and  $B(z)$  is found from expression (6).

The  $\Psi_2(z)$  term characterizes the effect of diffusion on the freezing process. For a pure solvent  $\Psi_2(z) \equiv 0$ .

For following approximate formulas apply to  $\Psi_1(z)$  and  $\Psi_2(z)$ :

$$\Psi_1(z) \approx \frac{\rho L \sqrt{\pi \kappa_1 \kappa_*}}{\lambda_* T^*} z \quad \text{for } z \ll 1,$$

$$kB \operatorname{erfc} \left( \sqrt{\frac{\kappa_1}{D}} z \right) \approx kc_0 \sqrt{\frac{\pi \kappa_1}{D}} z \quad \text{for } \sqrt{\frac{\kappa_1}{D}} z \ll 1$$

$$\text{и } \Psi_2(z) \approx kc_0 \sqrt{\frac{\pi \kappa_1}{D}} \left[ 1 + \frac{\lambda_2}{\lambda_*} \sqrt{\frac{\kappa_2}{\kappa_*}} \right] z \quad \text{for } \sqrt{\frac{\kappa_1}{D}} z \ll 1, \quad (10)$$

$$kB(z) \operatorname{erfc} \left( \sqrt{\frac{\kappa_1}{D}} z \right) \approx kc_0 \left[ \frac{2\kappa_1}{D} z^2 - 1 \right] \quad \text{for } \sqrt{\frac{\kappa_1}{D}} z \gg 1.$$

The last formula in (10) can be derived by an asymptotic expansion of  $\operatorname{erfc}(z)$  for large  $z$ .

Values of  $z = f(\Delta\theta_0/T^*)$  calculated according to formula (9) are listed in Table 1 for a pure solvent ( $\Psi_2 \equiv 0$ ) and for a solution. These values are based on  $\lambda_* = 5.3 \cdot 10^{-5}$  cal/cm · sec · °C,  $\lambda_1 = 5.3 \cdot 10^{-3}$  cal/cm · sec · °C,  $\lambda_2 = 1.44 \cdot 10^{-3}$  cal/cm · sec · °C,  $\kappa_* = 1.7 \cdot 10^{-1}$  cm<sup>2</sup>/sec,  $\kappa_1 = 1.15 \cdot 10^{-2}$  cm<sup>2</sup>/sec,  $\kappa_2 = 1.44 \cdot 10^{-3}$  cm<sup>2</sup>/sec,  $L = 79.7$  cal/g,  $D = 10^{-5}$  cm<sup>2</sup>/sec,  $c_0 \approx 5\%$ ,  $k = 2.2 \cdot 10^{-3}$ ,  $kc_0 \approx 1.1 \cdot 10^{-2}$ , and  $c^* = 0$ .

The relation  $z = f(\Delta\theta_0/T^*)$  for the other case  $\theta(x, t) = \theta_0$  was calculated in [1] with the same values of the parameters.

2. We now consider the second and the third boundary-value problem of massive freezing in a hypoeutectic solution ( $0 \leq x \leq \infty$ ) under constant boundary conditions at the surface  $x = 0$  and with a constant initial temperature distribution. For this case, the original equations can be written as

$$\frac{\partial T_1}{\partial t} = \kappa_1 \frac{\partial^2 T_1}{\partial x^2}, \quad 0 \leq x \leq l(t), \quad (11)$$

$$\frac{\partial T_2}{\partial t} = \kappa_2 \frac{\partial^2 T_2}{\partial x^2}, \quad \frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}, \quad l(t) \leq x \leq \infty.$$

The initial conditions (2) for  $T_2$  and  $c$  as well as the boundary conditions (4) at the interphase boundary are retained, while the boundary conditions at the free surface  $x = 0$  are written as follows:

$$\frac{\partial T_1}{\partial x} \Big|_{x=0} = b \quad (\text{second boundary-value problem}), \quad (12)$$

$$T_1(x, 0) + j \frac{\partial T_1}{\partial x} \Big|_{x=0} = b \quad (\text{third boundary-value problem}), \quad (13)$$

where  $b$  and  $j$  are assumed constant.

Let us solve the second boundary-value problem. For the concentration  $c(x, t)$  and for  $l(t)$  we seek the solution in the form

$$c(x, t) = A + B \operatorname{erfc} \left( \frac{x}{2 \sqrt{Dt}} \right), \quad l(t) = 2 \sqrt{\alpha t}. \quad (14)$$

TABLE 1. Argument  $z$  in Expression (9), as a Function of the Variable  $\Delta\theta_0/T_*$ , for a Pure Solvent and for a Solution

$z = \sqrt{\frac{\alpha}{\kappa_1}}$	$\Delta\theta_0 T_*^{-1}$	
	pure solvent	solution
$1 \cdot 10^{-3}$	$4 \cdot 3 \cdot 10^{-2}$	$4 \cdot 53 \cdot 10^{-2}$
$5 \cdot 10^{-3}$	$2 \cdot 15 \cdot 10^{-1}$	$2 \cdot 27 \cdot 10^{-1}$
$3 \cdot 10^{-2}$	1.29	1.45
$5 \cdot 10^{-2}$	2.14	2.59
$7 \cdot 10^{-2}$	3.01	3.49
$1 \cdot 10^{-1}$	4.3	5.72

The formulas for temperatures  $T_1$  and  $T_2$  will be written in analogy to those in [2], as

$$T_1(x, t) = E_1 + F_1 \sqrt{t} \operatorname{ierfc} \frac{x}{2 \sqrt{\kappa_1 t}} + G_1 x, \quad (15)$$

$$T_2(x, t) = E_2 + F_2 \sqrt{t} \operatorname{ierfc} \frac{x}{2 \sqrt{\kappa_2 t}} + H_2 \operatorname{erfc} \frac{x}{2 \sqrt{\kappa_2 t}} + k_2 x \Gamma \left( -\frac{1}{2}, \frac{x^2}{4 \kappa_2 t} \right),$$

where

$$\operatorname{ierfc} z = \int_z^\infty \operatorname{erfc} \tau d\tau, \quad \operatorname{erfc} z = 1 - \operatorname{erf} z, \quad \operatorname{erf} z = \frac{2}{\sqrt{\pi}} \int_0^z e^{-\tau^2} d\tau;$$

and

$$\Gamma_{(v, z)} = \int_z^\infty e^{-\tau} \tau^{v-1} d\tau \text{ is an incomplete gamma-function.}$$

Using conditions (2) and (4), we obtain

$$A = c_0, \quad B = \frac{\sqrt{\pi \alpha / D} c_0 \left( 1 - \frac{c_*}{c_0} \right)}{\exp \left( -\frac{\alpha}{D} \right) - \sqrt{\pi \alpha / D} \operatorname{erfc} \left( \sqrt{\frac{\alpha}{D}} \right)}. \quad (16)$$

It is easy to see that the expressions for the coefficients of  $T_1$  and  $T_2$  in our problem must be analogous to the expressions for the corresponding coefficients in the solution to the second boundary-value problem for a pure solvent [2], if  $T_*[1 - kc_0 - kB \operatorname{erfc}(\sqrt{\alpha/D})]$  is now regarded in lieu of  $T_1^* = T_2^*$ .

Indeed, condition (4) for  $T_1(l, t)$  and condition (12) yield for the constants  $E_1$ ,  $F_1$ , and  $G_1$

$$E_1 = T_* \left[ 1 - kc_0 - kB \operatorname{erfc} \left( \sqrt{\frac{\alpha}{D}} \right) \right], \quad F_1 = -\frac{2 \sqrt{\alpha} b}{\sqrt{\frac{\alpha}{\kappa_1}} + \operatorname{ierfc} \left( \sqrt{\frac{\alpha}{\kappa_1}} \right)}, \quad (17)$$

$$G_1 = \frac{b \operatorname{ierfc} \left( \sqrt{\frac{\alpha}{\kappa_1}} \right)}{\sqrt{\frac{\alpha}{\kappa_1}} + \operatorname{ierfc} \left( \sqrt{\frac{\alpha}{\kappa_1}} \right)}.$$

Constants  $E_2$ ,  $F_2$ , and  $G_2$  are determined from the initial condition (2) for  $T_2$ , from the relation for  $T_2(l, t)$ , and from the calorimetric condition (4), namely:

$$E_2 = T_0, \quad H_2 = \frac{T_* (1 - kc_0) - T_0 - T_* kB \operatorname{erfc} \left( \sqrt{\frac{\alpha}{D}} \right)}{\operatorname{erfc} \left( \sqrt{\frac{\alpha}{\kappa_2}} \right)},$$

$$F_2 = \frac{2 \lambda_1 \sqrt{\frac{\alpha}{\kappa_1}} \sqrt{\kappa_1} \Gamma \left( -\frac{1}{2}, \frac{\alpha}{\kappa_1} \right) G_1 - \lambda_1 \sqrt{\frac{\alpha}{\kappa_1}} \operatorname{erfc} \left( \sqrt{\frac{\alpha}{\kappa_1}} \right) F_1}{\lambda_2 \operatorname{erfc} \left( \sqrt{\frac{\alpha}{\kappa_2}} \right) \left[ 2 \lambda_2 \sqrt{\kappa_2} \exp \left( -\frac{\alpha}{\kappa_2} \right) - \Gamma \left( -\frac{1}{2}, \frac{\alpha}{\kappa_2} \right) \right]}, \quad (18)$$

$$k_2 = -\frac{F_2 \operatorname{erfc} \left( \sqrt{\frac{\alpha}{\kappa_2}} \right)}{2 \sqrt{\alpha} \Gamma \left( -\frac{1}{2}, \frac{\alpha}{\kappa_2} \right)}.$$

From the calorimetric condition (4) follows also an equation for  $\alpha$ :

$$\frac{\rho L \kappa_2}{\lambda_2} \sqrt{\frac{\pi \alpha}{\kappa_2}} \exp \left( \frac{\alpha}{\kappa_2} \right) = H_2(\alpha). \quad (19)$$

Using this expression for  $H_2$ , we can rewrite (19) as follows:

$$\sqrt{\frac{\pi\alpha}{\kappa_2}} \left\{ \frac{\rho L \kappa_2}{\lambda_2} \exp\left(\frac{\alpha}{\kappa_2}\right) \operatorname{erfc}\left(\sqrt{\frac{\alpha}{\kappa_2}}\right) + \frac{T_* k \sqrt{\frac{\kappa_2}{D}} (c_0 - c_*) \operatorname{erfc}\left(\sqrt{\frac{\alpha}{D}}\right)}{\exp\left(-\frac{\alpha}{D}\right) - \sqrt{\frac{\pi\alpha}{D}} \operatorname{erfc}\left(\sqrt{\frac{\alpha}{D}}\right)} \right\} = T_* (1 - kc_0) - T_0. \quad (19')$$

It is quite evident, according to (19), that in this case a solution can freeze only when  $T_0 < T_*(1 - kc_0)$ , i. e., after initial subcooling within the entire half-space  $x \geq 0$ . It also follows from (19) that the freezing rate is here independent of  $b$ . Physical considerations require only that  $b$  be positive (this requirement becomes obvious when one considers, for example, the expression for  $T_1(x, t)$ ). However, the temperature profile depends on  $b$ .

If the temperature difference  $[T_*(1 - kc_0) - T_0]$  is small, then expression (19) can be approximated as follows:

$$\sqrt{\frac{\pi\alpha}{\kappa_2}} = \frac{T_* (1 - kc_0) - T_0}{T_* \left[ \frac{\rho L \kappa_2}{\lambda_2 T_*} + k \sqrt{\frac{\kappa_2}{D}} (c_0 - c_*) \right]}. \quad (20)$$

Let us now consider the third boundary-value problem. It is quite evident that the solution for this case must be sought in the form

$$\begin{aligned} c(x, t) &= A + B \operatorname{erfc}\left(\frac{x}{2 \sqrt{Dt}}\right), \\ T_1(x, t) &= E_1 + F_1 \sqrt{t} \operatorname{erfc}\left(\frac{x}{2 \sqrt{\kappa_1 t}}\right) + G_1 x + H_1 \varphi(t, x), \\ T_2(x, t) &= E_2 + F_2 \sqrt{t} \operatorname{erfc}\left(\frac{x}{2 \sqrt{\kappa_1 t}}\right) \\ &+ H_2 \operatorname{erfc}\left(\frac{x}{2 \sqrt{\kappa_2 t}}\right) + k_2 x \Gamma\left(-\frac{1}{2}, \frac{x^2}{4\kappa_2 t}\right), \end{aligned} \quad (21)$$

where

$$\varphi(t, x) = \frac{\partial}{\partial x} \left[ x^2 \int_z^\infty \operatorname{erfc} \tau \frac{d\tau}{\tau^3} \right]; \quad z = \frac{x}{2 \sqrt{\kappa_1 t}} \quad (\text{see [2]}).$$

The coefficients in (21) are easily determined from conditions (2), (4), and (13).

We will not write out these expressions here. We will only note that those for  $A$  and  $B$  remain the same, namely (16), and the coefficients of  $T_1$  and  $T_2$  are analogous to the respective coefficients in [2] for a pure solvent with  $T_1^* = T_2^*$  replaced by  $T_*[1 - kc_0 - kB \operatorname{erfc}(\sqrt{\alpha/D})]$ . The formal solution to the second or the third boundary-value problem is easily obtained, even when the initial solvent temperature varies linearly. One more term, namely a  $G_2(x)$  term, must then be added to the expression for  $T_2$  [2].

We note, in conclusion, that this analysis of the freezing (crystallization) of binary solutions applies to systems which can form simple eutectic mixtures and whose initial concentration is below the eutectic level  $c_e$  [1]. This calls for an additional restriction in the problem here, a consequence of the physical aspects [1, 3]:

$$c(l, t) < c_e. \quad (22)$$

The problem cannot have a solution when  $c(l, t) > c_e$ . For this reason, one must always verify inequality (22) before calculations are made.

For the first boundary-value problem, (22), (5), and (7) yield the following additional limitation to supplement (5)-(7):

$$1 + \frac{\sqrt{\pi\alpha/D}(1 - c_*/c_0) \operatorname{erfc}(\sqrt{\alpha/D})}{\exp(-\alpha/D) - \sqrt{\pi\alpha/D} \operatorname{erfc}(\sqrt{\alpha/D})} < \frac{c_e}{c_0}. \quad (23)$$

For the second boundary-value problem, we formally obtain the same inequality from (22), (14), and (16), but the equation for  $\alpha$  will obviously be different (see (19)).

A limiting inequality can also be obtained for the third boundary-value problem.

#### NOTATION

$T_1$	is the temperature of the freezing solvent;
$T_2$	is the temperature of the solution;
$T_*$	is the freezing point of the pure solvent;
$\theta$	is the temperature of the air;
$c$	is the concentration of the dissolved substance;
$c_*$	is the concentration of the dissolved substance in the solid phase;
$D$	is the diffusivity of the dissolved substance;
$M'$	is the molecular weight of the solvent;
$M$	is the molecular weight of the solute;
$R$	is the gas constant;
$L$	is the heat of melting of the solvent;
$x$	is the longitudinal coordinate;
$t$	is the instantaneous time;
$l$	is the coordinate of the interphase boundary;
$\lambda_*, \kappa_*$	are the thermal conductivity and the thermal diffusivity of the gaseous phase;
$\lambda_1, \kappa_1$	are the thermal conductivity and the thermal diffusivity of the solid phase;
$\lambda_2, \kappa_2$	are the thermal conductivity and the thermal diffusivity of the liquid phase;
$\rho$	is the density of the solvent.

#### LITERATURE CITED

1. P. P. Zolotarev, *Prikl. Mekhan. i Tekh. Fiz.*, No. 3 (1966).
2. Yu. A. Buevich, *Izv. Akad. Nauk SSSR, Ser. Geofiz. Nauk*, No. 1 (1964).
3. L. L. Rubinstein, *The Stefan Problem* (Mathematical Monographs, Vol. 27) Am. Math. Soc., Providence, R. I. (1969).