HIGH-PRESSURE MELTING–SOLIDIFICATION OF A SUBSTANCE

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Thermodynamic properties of a liquid at a high pressure are calculated on the basis of the empirical Tate equation. Numerical studies, using the conjugate mathematical model of heat and mass transfer involving solidification–crystallization of a substance, have revealed the specific features of ice melting at a high pressure.

A design of new technologies of pressure casting and crystallization has necessitated the study of heat and mass transfer processes at the "melting–solidification" phase transition. A casting pressure can increase to 20 MPa and up [1-3], the properties of metals and alloys in this case become dependent not only on temperature but on pressure as well. The pressure effect on substance properties in a solid-state phase has been investigated [4] but thermophysical properties of melts in a wide pressure range are insufficiently studied and classified.

Mathematical modeling of the process is a matter of concern in [5, 6]. In [5], the heat conduction equation is used to treat solidification of a cylindrical casting without considering melt hydrodynamics. The high-pressure effect is taken into consideration by increasing the heat transfer coefficient of the casting surface. Liquid crystallization in a closed vessel [6] entails an increase of pressure across the liquid phase at the expense of increasing a specific volume of the solid-state phase.

In the present work, using the example of water solidification, a comparative analysis is made of the processes at atmospheric and higher external pressures with the aid of the conjugate mathematical model of heat and mass transfer in solid-state and liquid phases. Thermophysical properties of a liquid at a high pressure are calculated based on the empirical equation of state and approximation of data listed in handbooks.

Thermodynamic and thermophysical liquid properties at high pressure. A liquid is intermediate in physical properties between a solid and a gas. A physical pattern of a liquid is complicated, for this reason there is no theoretical justified equation of state for a liquid phase. Liquid properties in a wide range of pressures and temperatures are described by the empirical Tate equation [7]

$$\left(\frac{\partial v}{\partial p} \right)_T = - \frac{K}{L(T) + p},$$ (1)

where $L(T)$ is some empirical temperature function determined from experimental data. Integrating this equation along an isotherm going from some fixed pressure p_0 (e.g., atmospheric) to current p, we obtain

$$\frac{v}{v_0} - 1 = -\frac{1}{n} \ln \frac{p_0 + L(T)}{p + L(T)},$$

where the new constant $1/n \equiv K/v_0$ is introduced. Represent the latter equation in the exponential form. Expanding the exponent into a series and leaving the two first terms of expansion, we finally arrive at

$$\frac{p_0 + L(T)}{p + L(T)} = \left(\frac{v}{v_0} \right)^n.$$ (2)

TABLE 1. Specific Volume of Water as a Function of Pressure at Some Fixed Temperature

p, MPa	$v \cdot 10^3$, m^3/kg [10]	$v \cdot 10^3$ m^3/kg; calculation by (2)	p, MPa	$v \cdot 10^3$, m^3/kg [10]	$v \cdot 10^3$, m^3/kg; calculation by (2)
1	1,0117	1,0116	40	0,9953	0,9952
5	1,0099	1,0098	50	0,9914	0,9913
10	1,0077	1,0076	75	0,9820	0,9820
20	1,0034	1,0034	100	0,9733	0,9733
30	0,9993	0,9992			

Note: t = 50°C. In calculations by formula (2), p_0 = 1 atm = 0.101325 MPa, v_0 = 1.0120 × 10^{-3} m^3/kg.

Calculate thermal (more exactly thermodynamic) coefficients [8]. They are as follows: the isothermal coefficient of compressibility

$$\alpha = -\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_T = \frac{1}{n(p+L)}; \tag{3}$$

the coefficient of volumetric expansion

$$\beta = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_p = \frac{p-p_0}{n(p_0+L)(p+L)}\frac{dL}{dT}; \tag{4}$$

the thermal coefficient of pressure

$$\gamma = \frac{1}{p}\left(\frac{\partial p}{\partial T}\right)_v = \frac{p-p_0}{p(p_0+L)}\frac{dL}{dT}. \tag{5}$$

Unlike the equation of state for the Mendeleev – Clayperon ideal gas, which is derived strictly in the molecular-kinetic theory of a gas, the Tate equation is empirical and valid only at $p > p_0$. In connection with this, the limiting transition $p \to p_0$ has no sense in (4)-(5).

Differential equations of thermodynamics allow determination of calorific properties as a function of pressure, provided the thermal equation of state is known [8]. Using (2), calculate the change in calorific properties by increasing the pressure from p_0 to p.

A change in entropy is

$$\Delta s \equiv s(p,\ T) - s(p_0,\ T) = -\int_{p_0}^{p}\left(\frac{\partial v}{\partial T}\right)_p dp =$$

$$= \frac{dL}{dT}\left[\frac{n}{n-1}(v_0-v) - \frac{v(p-p_0)}{(n-1)(p_0+L)}\right];$$

a change in enthalpy:

$$\Delta i \equiv i(p,\ T) - i(p_0,\ T) = \int_{p_0}^{p}\left[v - T\left(\frac{\partial v}{\partial T}\right)_p\right]dp =$$

$$= \frac{1}{n-1}\left[\left(\frac{p+L}{p_0+L}\right)v - v_0\right]\left[n(p_0+L) - T\frac{dL}{dT}\right] + T\frac{dL}{dT}(v_0-v);$$

and a change in specific heat at constant pressure:

$$\Delta c_p \equiv c_p(p,\ T) - c_p(p_0,\ T) = -T\int_{p_0}^{p}\left(\frac{\partial^2 v}{\partial T^2}\right)_p dp = \tag{6}$$

$$= T\frac{d^2L}{dT^2}\left[\frac{n}{n-1}(v_0-v) - \frac{v(p-p_0)}{(n-1)(p_0+L)}\right] + T\left(\frac{dL}{dT}\right)^2\frac{v(p-p_0)^2}{n(p_0+L)^2(p+L)}.$$
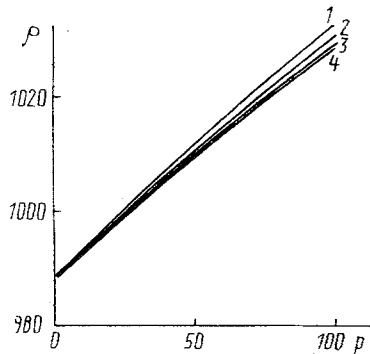
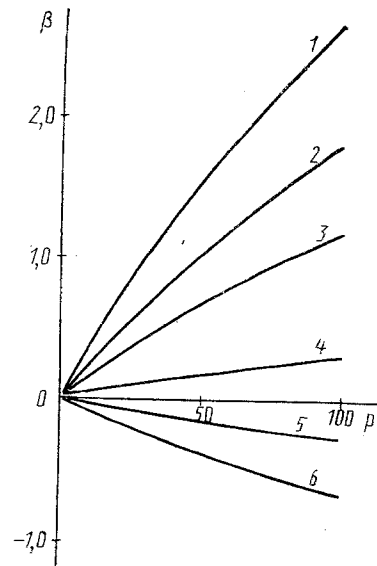Fig. 1   Fig. 2

Fig. 1. Water density ρ, kg/m^3, as a function of pressure p, MPa, at different temperatures, °C. 1) 0; 2) 10; 3) 20; 4) 80.

Fig. 2. Influence of external pressure and temperature [1) 0; 2) 10; 3) 20; 4) 40; 5) 60; 6) 80°C] on the volumetric expansion coefficient of water, 10^{-4} K^{-1}.

The differential equations of thermodynamics permit calculation of calorific characteristics as a function of a specific volume by the known equation of state [8] and as a function of pressure in terms of the equation of state.

A change of internal energy is

$$\Delta u \equiv u\,(v,\ T) - u\,(v_0,\ T) = \int\limits_{v_0}^{v} \left[T\left(\frac{\partial p}{\partial T} \right)_v - p \right] dv =$$

$$= -\frac{1}{1-n}\left[T\,\frac{dL}{dT} - (p_0 + L) \right]\left[\left(\frac{v_0}{v} \right)^n v - v_0 \right] + (v_0 - v)\left(T\,\frac{dL}{dT} - L \right);$$

a change of specific heat at a constant volume is

$$\Delta c_v \equiv c_v\,(v,\ T) - c_v\,(v_0,\ T) = T\int\limits_{v_0}^{v} \left(\frac{\partial^2 p}{\partial T^2} \right)_v dv =$$

$$= T\,\frac{d^2L}{dT^2}\left\{ v\left[\frac{1}{1-n}\left(\frac{v_0}{v} \right)^n - 1 \right] + v_0\,\frac{n}{n-1} \right\}.$$

The remaining calorific properties of a liquid at a high pressure are evaluated in terms of the determined quantities.

As an example, determine the constant n and the form of the function L(T) in the Tate equation of state (2) for the most extensively studied matter, i.e., water. In [9], the table of mean coefficient values of water compressibility $\alpha(p, t)$ is given. As far as the pressure increases, α decreases (this is confirmed by the obtained expression (3)). With increasing temperature, the compressibility of liquids increases in the general case, with the exception of water — its compressibility α is at minimum approximately at 50°C. Processing these data with the help of (3) by the method of least squares and performing temperature averaging, we obtain n = 6.4. The pressure-averaged L(t) values have been approximated by the method of least squares as a polynomial in the third power

$$L\,(t) = a_0 + a_1 t + a_2 t^2 + a_3 t^3, \quad 0 \leqslant t \leqslant 80\,°C, \tag{7}$$
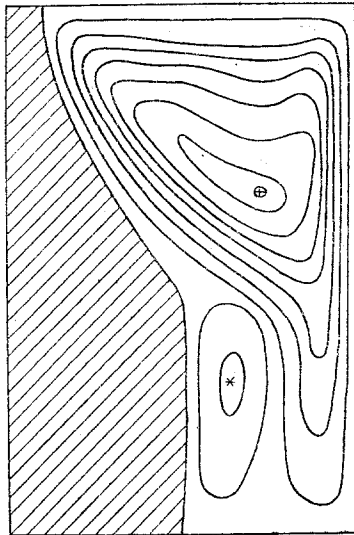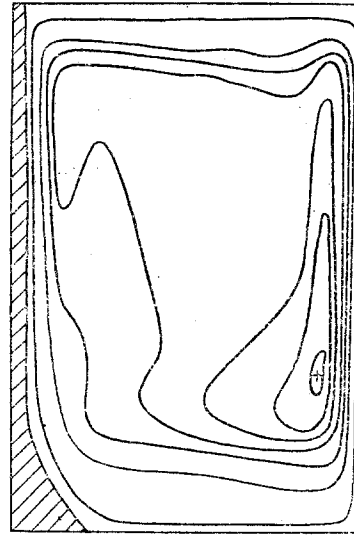
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Fig. 3

Fig. 4

Fig. 3. Isolines of the stream function of water circulation at atmospheric pressure. The hatched region is ice. Maximum values (with respect to an absolute value) of the stream function: (+) 6.7; (*) −2.

Fig. 4. Isolines of the stream function of water circulation at the increased pressure 50 MPa. Maximum stream function is (+) 9.8.

where $a_0 = 3.0504 \cdot 10^8$; $a_1 = 2.1140 \cdot 10^6$; $a_2 = -2.770 \cdot 10^{-4}$; $a_3 = 87.166$; t, °C; L, Pa.

To verify the obtained results, compare the data on $v = v(p)$ given in [10] and calculated by the Tate formula (2) for water. All the results are listed in Table 1 and illustrate good agreement.

We have employed the tabular data to verify the validity of the approximation $\exp\{v/v_0 - 1\} \approx v/v_0$ used to derive (2). Estimates show that with an increase of pressure from atmospheric to 100 MPa, the error of the approximation does not exceed 0.075%.

Having determined n and L(t) for water, we may calculate the density $\rho(p, t) = 1/v(\rho, t)$ from Eq. (2). Figure 1 represents $\rho = \rho(p)$ at different temperatures with an increase of the pressure, the density is seen to vary insignificantly with temperature. The estimate at t = 20°C shows that as far as the pressure increases from 1 to 100 MPa, i.e., by 99 MPa, the density increases by 40.4 kg/m³ or by 4% of its initial value.

From the approximation (7) it follows that water has some critical temperature $t^* = t \approx 50°C$, at which L(t) attains its maximal value $L_{max} = 353$ MPa, while dL/dt = 0. Consequently, the thermal coefficients β (4) and γ (5) reverse sign when going through t^*. At $t < t^*$, $\beta > 0$ and $\gamma > 0$; at $t > t^*$ $\beta < 0$ and $\gamma < 0$. Figure 2 displays $\beta = \beta(p)$ calculated by Eq. (4) at different temperatures. Here an appreciable pressure effect on β is observed, especially at low temperatures and, vice versa, after inversion at $t > t^*$ | β (t = 80°C) > | β (t = 60°C)| .

Calculations of specific heat variation at constant pressure Δc_p by formula (6), with the pressure increasing from p_0 to p, have shown that $\Delta c_p \ll c_p(p_0, t)$.

Melting temperature variation caused by an increase in pressure may be evaluated by the known Clayperon—Clausius equation [8]. Thus water at 50 MPa is transformed into ice at $t_{ph} \approx -4°C$, in this case the heat of melting—solidification, corresponding to the phase transition temperature t_{ph}, decreases by 21 kJ/kg and becomes equal to $Q_{ph} = 313$ kJ/kg.

In [11], the table of water thermal conductivities $\lambda(p, t)$ and in [12] the values of dynamic viscosity coefficient η (p, t) at different pressures and temperatures are presented. The dependence $\lambda(p, t)$ with a relative error not exceeding 0.6% is approximated by the expression

$$\lambda/\lambda_0 = [1 + (21,865 - 0,42745t + 7,4163 \cdot 10^{-3} t^2 - $$
$$- 3,5804 \cdot 10^{-5}t^3) \cdot 10^{-4}p]^{1/2};$$
$$0^\circ \, C \leqslant t \leqslant 90^\circ \, C; \quad 0,1 \leqslant p \leqslant 50 \text{ MPa.} \tag{8}$$

The dependence $\eta \, (p, t)$ is approximated with a relative error of no more than 0.1% by the expression

$$\eta/\eta_0 = 1 + (0,10257t - 3,2653) \cdot 10^{-4}p; \tag{9}$$

$$0^\circ \, C \leqslant t \leqslant 90^\circ \, C; \quad 0,1 \leqslant p \leqslant 80 \text{ MPa.}$$

In (8) and (9) λ_0 and η_0 are the values of coefficients at p = 0.1 MPa.

The conjugate mathematical heat and mass transfer model at liquid solidification. The process of water freezing in a rectangular cavity is used to investigate a high pressure effect on the process.

Consider a two-dimensional viscous fluid flow initiated by thermal convection in a rectangular region with dimensions $a \times b$ (horizontal x and vertical y coordinates, respectively). The region boundaries are impermeable, the origin of coordinates is at the left-hand bottom corner. The vertical surfaces are at x = 0; at x = a they are isothermal with temperatures T_1, T_2 ($T_1 < T_2$), the horizontal surfaces are at y = 0; at y = b they are adiabatic.

At $T_1 < T_{ph}$ (T_{ph} is independent of pressure), a solid-state phase (ice), with constant thickness ε in the no-convection approximation, is formed at the left vertical boundary of the region, while a solidification boundary represents a vertical line. Free convection causes energy redistribution in the liquid phase and distortion of the solidification boundary. Here the thickness of the solid phase ε becomes a variable quantity.

In order to write the heat and mass transfer equations in a dimensionless form, we have chosen the characteristic linear dimension $l = b$, temperature difference $\delta T = T_2 - T_{ph}$, velocity $u_0 = (g\beta\delta Tl)^{1/2}$, and time $\tau_0 = l/u_0$ as scales. These parameters form the dimensionless Grashof Gr = $g\beta\delta Tl/\nu_0^2$, Reynolds Re = $u_0 l/\nu_0$, and Peclet Pe = $u_0 l/a_3$ numbers. The specific heat of a phase transition Q_{ph} is taken into account in the effective thermal diffusivity a_{eff} abruptly changing at the solidification boundary. In the Boussinesq approximation, the solidification accompanied by liquid phase circulation, is described in terms of the variables "vorticity—current function $(\omega - \psi)$" by the conjugate system of equations [13] for energy transfer, vorticity, and the Poisson equation:

$$\frac{\partial T}{\partial \tau} + \frac{\partial}{\partial x}(uT) + \frac{\partial}{\partial y}(vT) = \frac{1}{\text{Pe}} \nabla \left(\frac{\lambda}{\lambda_0} \nabla T \right); \tag{10}$$

$$\frac{\partial \omega}{\partial \tau} + \frac{\partial}{\partial x}(u\omega) + \frac{\partial}{\partial y}(v\omega) = \tag{11}$$

$$= \frac{1}{\text{Re}} \nabla \left(\frac{\nu}{\nu_0} \nabla \omega \right) + \frac{\text{Gr}}{\text{Re}^2} \frac{\partial T}{\partial x}; \tag{12}$$

$$- \omega = \nabla^2 \psi,$$

where $u = \partial\psi/\partial y$, $v = -\partial\psi/\partial x$ are the velocity components; $\nabla^2 = \partial^2/\partial x^2 + \partial^2/\partial y^2$ is the Laplacian.
At the initial moment of time

$$T(0, x, y) = T_2; \quad \omega(0, x, y) = \psi(0, x, y) = 0. \tag{13}$$

The set of equations (10)-(12) is closed by the boundary conditions for a temperature

$$T(\tau, 0, y) = T_1; \quad T(\tau, a, y) = T_2; \quad \left. \frac{\partial T}{\partial y} \right|_{y=0} = \left. \frac{\partial T}{\partial y} \right|_{y=b} = 0 \tag{14}$$

and the stream function

$$\psi(\tau, 0, y) = \psi(\tau, a - \varepsilon, y) = \psi(\tau, x, 0) = \psi(\tau, x, b) = 0. \tag{15}$$

The boundary values of vorticity on solid surfaces, confining a liquid phase, and on the movable solidification boundary, are determined from the Poisson equation (12).

The formulated problem has been solved by the time-dependent technique. For quantization of the equations, we used the implicit scheme of alternating directions. The two-dimensional equations were reduced by the separation method to a convergent sequence of one-dimensional equations which were then solved by the longitudinal-transverse elimination technique using the straight-through counting scheme without evident separation of a phase boundary. A movable solidification boundary was determined by the position of the isotherm $T = T_{ph}$. We used a regular network; when the curvilinear solidification boundary did not coincide with the network points, use was made of differences with variable steps along the stream function and vorticity coordinates. The vorticity of a liquid phase at solid boundaries was calculated with the aid of a two-contour scheme [14] allowing the boundary conditions of "adhesion" to be satisfied with the required accuracy.

Convection terms in transfer equations (10)-(11) were approximated with the help of a conservative scheme with donor cells [15]. This scheme is distinguished with the transport property, and velocity averaging preserves a partial second order of accuracy in it, which is typical for the schemes with central differences. In [16] it is shown that this scheme of quantization of convective terms requires less computation time compared to other schemes.

To solve the difference analog of the Poisson equation (12), we have applied the method of successive linear upper relaxation with optimization of the relaxation parameter. A solution algorithm of the problem is discussed in detail in [17].

Computation results. A process of water freezing in a rectangular cell was computated: a) for solidification at an atmospheric pressure; b) at a high external pressure p = 50 MPa. The computation network consisted of 40 × 60 nodes.

Thermophysical characteristics of water at 50 MPa were calculated in accordance with the above information. Ice density was calculated by the formula [18]

$$\rho = 916{,}8\,[1 + 0{,}94 \cdot 10^{-6}\,(p - 1)]\,(1 - 1{,}53 \cdot 10^{-4}\,t),\quad kg/m^3.$$

where t, °C; p, MPa.

Thermophysical characteristics of water at an atmospheric pressure are given in [13]. Heat capacity and thermal conductivity depend on temperature and change in a stepwise manner with a transition through a solidification boundary:

$$c \;\; (kJ/kg) = \begin{cases} 2{,}090 + 0{,}0052t, & t < t_{\phi}; \\ 4{,}212 - 0{,}0011t, & t \geqslant t_{\phi}, \end{cases}$$

$$\lambda \;\; (W/(m \cdot K)) = \begin{cases} 2{,}210 - 0{,}0115t, & t < t_{\phi}; \\ 0{,}569 + 0{,}0016t, & t \geqslant t_{\phi}. \end{cases}$$

A specific feature in water behavior at atmospheric pressure near a solidification temperature is the density inversion. To describe this phenomenon, a temperature-dependent coefficient of volumetric expansion was introduced:

$$\beta\,(T) = \frac{a + 2bT + 3cT^2 + 4dT^3}{1 + aT + bT^2 + cT^3 + dT^4},$$

where $a = -6.789645 \times 10^{-5}$; $b = 9.072943 \times 10^{-6}$; $c = -9.645681 \times 10^{-8}$; $d = 8.737030 \times 10^{-10}$; T, K.

Density was assumed to be constant both for water and ice, with the exception of the phase boundary where it becomes discontinuous:

$$\rho \;\; (kg/m^3) = \begin{cases} 999{,}841, & t \geqslant t_{\phi}; \\ 917{,}345, & t < t_{\phi}. \end{cases}$$

Kinematic viscosity of water was assumed to be equal to

$$v = 1{,}429 \cdot 10^{-6} \;\; m^2/sec.$$

In both calculation variants (p = 0.1 and 50 MPa), the temperature of the left-hand boundary was taken as $t_1 = -6.7°C$, of the right boundary $t_2 = 14.5°C$, the height of the working cavity was $a = 0.073$ m, and the width was b = 0.045

m. Such parameters were not chosen arbitrarily. In [13], quantitative comparison of calculations according to the given procedure with a physical experiment at atmospheric pressure showed satisfactory agreement of results.

Figure 3 exhibits an ice crust profile and water circulation lines at an atmospheric pressure. A convection effect manifests itself in thinning of the ice crust in the upper section of the region. A liquid phase circulates to form two stable stratified vortices. Here in the upper section of the region near a solidification boundary, water flows downward, while in the upper part — upward. The maximum flow velocity is 2.27×10^{-3} m/sec.

The ice crust profile and the stream function isolines essentially differ in the case of increased pressure (Fig. 4). A liquid circulates in one stratified vortex and rotates counterclockwise. A maximum flow velocity is 5.29×10^{-3} m/sec.

Conclusions. A conjugate mathematical model of heat and mass transfer at the melting–solidification transition is developed with inhomogeneous substance properties taken into consideration.

Expressions are obtained for thermodynamic properties of the liquid phase at an increased pressure based on the empirical Tate equation of state. As an example, water properties are calculated at 50 MPa.

The conducted numerical investigations have shown that water crystallization at atmospheric and increased (50 MPa) pressures qualitatively differ.

The mathematical model developed here may be useful for predicting technological regimes of casting and crystallization under pressure.

NOTATION

v, specific volume of the liquid; p, pressure; T, temperature, K; K, coefficient; $L(T)$, temperature function in the Tate equation; p_0, initial pressure at integration of the Tate equation; v_0, corresponding specific volume; n, constant; α, isothermal coefficient of compressibility; β, coefficient of volumetric expansion; γ, thermal coefficient of pressure; s, specific entropy; i, specific enthalpy; c_p, c_v, specific heat capacities; u, specific internal energy; t, temperature, °C; a_0, a_1, a_2, a_3, coefficients of the polynomial; t^*, critical temperature; t_{ph}, temperature of melting–crystallization; Q_{ph}, heat of the phase transition; λ, thermal conductivity; η, coefficient of dynamic viscosity; a, b, dimensions of the rectangular cavity; T_1, T_2, temperature of vertical surfaces of the cavity; ε, thickness of ice crust; l, characteristic linear dimension; δT, temperature difference; u_0, characteristic velocity; τ_0, characteristic time; g, free fall acceleration; criteria: Gr, Re, Pe, Grashof, Reynolds, Peclet numbers; a, effective thermal diffusivity; ω, vorticity; ψ, stream function; u, v, velocity components of convective liquid flow; τ, time; ν, kinematic viscosity of a liquid.

REFERENCES

1. A. I. Batyshev, Pressure Crystallization of Metals and Alloys [in Russian], Moscow (1990).
2. G. P. Borisov, Pressure in Casting Control [in Russian], Kiev (1988).
3. M. B. Bekker, M. L. Zaslavskii, Yu. F. Ignatenko, et al., Pressure Casting [in Russian], Moscow (1990).
4. A. Ya. Shinyaev, Phase Transformations and Properties of Alloys at High Pressures [in Russian], Moscow (1973).
5. M. N. Zakharov, Izv. Vyssh. Uchebn. Zaved., Mashinostr., No. 5, 85-88 (1987).
6. N. I. Nikitenko and Yu. N. Kol'chik, Prom. Teplotekhnika, 12, No. 1, 16-22 (1990).
7. J. Girshfelder, Ch. Kertis, and R. Bird, Molecular Theory of Gases and Liquids [Russian translation], Moscow (1961).
8. E. E. Shilrine and P. M. Kesselman, Fundamental Principles of the Theory of Thermophysical Properties of Substances [Russian translation], Moscow (1977).
9. Chemist's Handbook [in Russian], Vol. 1, Moscow–Leningrad (1962).
10. S. L. Rivkin and A. A. Aleksandrov, Thermodynamic Properties of Water and Its Vapor [in Russian], Moscow (1984).
11. N. B. Vargaftik, L. P. Filippov, A. A. Tarzimanov, et al., Heat Conduction of Liquids and Gases [in Russian], Moscow (1978).
12. N. B. Vargaftik, Handbook on Thermophysical Properties of Gases and Liquids [in Russian], Moscow (1972).
13. A. I. Tsaplin, Heat and Mass Transfer Processes of a Viscous Fluid, Collected Papers of the Ural Scientific Center of the USSR Academy of Sciences, Sverdlovsk (1986).
14. V. M. Paskonov, V. I. Polezhaev, and L. A. Chudov, Numerical Simulation of Heat and Mass Transfer Processes [in Russian], Moscow (1984).

15.   P. Roch, Computational Hydrodynamics [Russian translation], Moscow (1980).

16.   A. I. Tsaplin and K. S. Galyagin, Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Tekh. Nauk, **1**, No. 3, 30-36 (1983).

17.   A. I. Tsaplin, Numerical Solution of Convective Heat Transfer Problems [in Russian], Perm (1985).

18.   E. Pownder, Ice Physics [Russian translation], Moscow (1967).