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THERMODYNAMIC PROPERTIES AND THERMAL EQUATIONS OF THE STATE OF
HIGH-PRESSURE ICE PHASES

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UDC 536.424

Water is characterized by a surprising number of phases compared to other materials [1, 2]. Of the solid phases (ices), the hexagonal ice I is thermodynamically stable under natural conditions on earth, while the others are high-pressure phases. Thermodynamic conditions for the existence of the high-pressure ices occur on several planets of the solar system and their satellites [3, 4]. The formation of various ice modifications has been observed in studying explosive impact loading of ice I. In this case a very complex wave picture is observed, which is related to phase transitions between the various ice modifications, and also to melting behind the compression wave front at relatively low pressure (on the order of 10^2-10^3 MPa) [5, 6].

Within the frame work of the mechanics of continuous media, a theoretical description of the processes of quasi-static and dynamic deformation of ice is based on studying the thermodynamic properties of various ice modifications, water, and their mixtures [7-9]. Here we continue the investigation, started in [10] on ice I to pressures of 210 MPa. Based on a critical analysis of experimental data [2, 11-19], a corresponding theoretical study was made of the thermodynamic properties of ices I, III, V, and VI; thermal equations of state were constructed, which are applicable for temperatures of 233-293 K and pressures of 0-10^3 MPa.

1. H_2O Phase Diagram. In studying the thermodynamic properties of ices, we choose as independent variables the temperature T and the pressure p and the limits of their variation: $233 \leqslant T \leqslant 293$ K and $0 \leqslant p \leqslant 10^3$ MPa. The corresponding set of points on the p−T phase diagram we denote by Ω. The set Ω includes 1) the thermodynamically stable states of ices I,
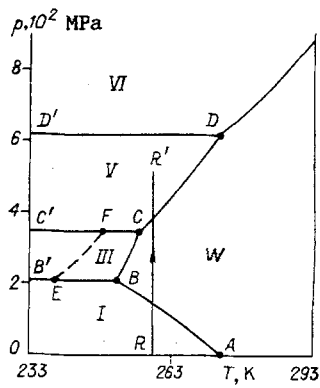
Fig. 1

TABLE 1

Melt curve MPa	T_0, K	p_0, MPa	a	c
{1w}	273,16	0	—395,2	9,0
{3w}	251,15	207	62,0	60,0
{5w}	256.15	346	410,0	8.1
{6w}	273,31	625	707,0	4,46

TABLE 2

Curve	f_0	f_1	f_2
{13}	186,1	$-1.335 \cdot 10^0$	$-1,628 \cdot 10^{-1}$
{35}	344,3	$-2,750 \cdot 10^{-1}$	$-1,099 \cdot 10^{-2}$
{56}	625,9	$6,086 \cdot 10^{-2}$	$-8,571 \cdot 10^{-4}$

III, V, and VI and liquid water, 2) the phase transition curves, and 3) six triple points (A, B, C, D, E, and F) (Fig. 1).

We introduce the following notation. The symbols w and 1, 3, 5, and 6 denote liquid water and ices I, III, V, and VI. The region of thermodynamic stability of phases i (i = 1, 3, 5, 6, and w) is denoted by Ω_i. We note that the region of the metastable states of liquid water is a significantly broader than the region Ω_w and includes a large part of Ω_1 [20]. The metastability region of ice III extends deep into the stability region of ice II, which makes it difficult to establish EF, which separates ices II and III [13].

The phase transition curves are denoted by a pair of indices in braces {ij}. For example, the curve AB for melting ice I (Fig. 1) is the curve {1w}, and the curve DD' for the phase transition from ice V to ice VI is the curve {56}. An empirical equation of the form [19]

$$p = p_0 + a[(T/T_0)^c - 1],\qquad(1.1)$$

can be used to describe the melting curves {iw} (i = 1, 3, 5, and 6), where the parameters p_0, T_0, a, and c depend on the ice modification. The values of these parameters are shown in Table 1. Data relative to the phase transition curves {13}, {35}, and {56} are given in [11, 12]. Below we will use equations we obtained in processing data [11] by the method of least squares:

$$p = f_0 + f_1 T_* + f_2 T_*^2 ,\qquad(1.2)$$

where $T_* = T - 273.15$ is the temperature in degrees centigrade. The values of the coefficients f_0, f_1, and f_2 for these three curves are shown in Table 2.

Triple points will be denoted by three indices {ijk}. Six triple points fall within the region Ω (Fig. 1): {13w} is point B; {35w} is point C; {56w} is point D; the triple point for ice I, water, and water vapor is point A; {123} is point E; and {235} is point F. The temperatures and pressures at points {ijk} from data [17] are shown in Table 3.

TABLE 3

Triple point (Fig. 1)	T, K	p, MPa	Triple point (Fig. 1)	T, K	p, MPa
A	273,16	0	D	273,31	625
B	251,15	207	E	238,45	213
C	256,15	346	F	248,85	344

The thermal equation of state of a material connects three parameters (pressure p, temperature T, and specific volume V) and has the form

$$V = V(p, T). \qquad (1.3)$$

For isotropic solids, Eq. (1.3) is used in the case where the stresses developed in the material exceed the material yield strength τ_* (hydrostatic approximation) [21]. The yield strength and the ultimate strength of ice I is less than several megapascals under normal conditions, while the effects of melting and phase transitions of the other phases occur at pressures on the order of 10-200 MPa. This fact was used [10] to construct a thermal equation of state for ice I. Laboratory experiments [13] with polycrystalline samples of ices II, III, and V showed that the strength of ice II is comparable with that of ice I; the strength of ice V is somewhat less, and the strength of ice III is substantially less. In this regard we will use the hydrostatic approximation, will neglect shear stresses, and consider p as the only real component of the stress tensor, as we did in [10].

The thermal equation of state $V_i = V_i(p, T)$ (i = 1, 3, 5, and 6) can be constructed from experimental data on the volumetric expansion coefficient $\alpha_{Ti} = 1/V_i(\partial V_i/\partial T)_p$ and the isothermal compressibility $\beta_{Ti} = -1/V_i(\partial V_i/\partial p)_T$ by integrating the expression

$$dV_i/V_i = \alpha_{Ti} dT - \beta_{Ti} dp \qquad (1.4)$$

along some curve in region Ω. The thermal equation of state of ice I constructed in this manner has the form

$$V_1 = \frac{V_1^0(T)}{\left[1 + m_1 \beta_{T1}^0(T) p\right]^{1/m_1}}, \qquad (1.5)$$

where $V_1^0(T)$ and $\beta_{T1}^0(T)$ are known functions of temperature, and m_1 is a constant. The value $m_1 = 4.4$ is used in [10]. New experiments [14] make it possible to refine m_1: $m_1 = 5.3668$. The densities $\rho_1 = 1/V_1$, computed from (1.5), were compared with measurements [14] of ρ_1 for $T_* = -35.5°C$ and p = 0-200 MPa. The relative error does not exceed 0.1%, which indicates that Eq. (1.5) is in good agreement with the experimental results. Equations (1.1), (1.2), and (1.5) are used below to construct and investigate the thermal equations of state of various ice modifications.

2. Thermal Equations of State of Ices III, V, and VI. Now we construct the thermal equation of state of high-pressure ices. We will assume that we know the values of ΔV_{ij}, the jumps in specific volume of the ices along the curves {13}, {35}, and {36}, as well as the functional dependence of the isothermal compressibility of ices III, V, and VI on temperature and pressure. Then the thermal equations of state of high-pressure ices can be constructed sequentially using the method described below, starting from the thermal equation of state of ice III.

By using Eq. (1.5), we determine the specific volume of ice I on the curve {13}, which has the equation $p = p_{13}(T)$ [see (1.2)]. The value of the specific volume of ice III on this curve is $V_1(p_{13}(T), T) + \Delta V_{13}$, where ΔV_{13} is the jump in the specific volume during the phase transition from ice I to ice III. The thermal equation of state of ice III can now be established by integrating Eq. (1.4) along the isotherm:

$$V_3 = [V_1(p_{13}(T), T) + \Delta V_{13}] \exp\left\{-\int_{p_{13}(T)}^{p} \beta_{T3}(p, T) dp\right\}. \qquad (2.1)$$

Then we find values of $V_3(p_{35}(T), T)$ on {35} by using (2.1). By using data on the jump ΔV_{35} on this curve and the functional dependence $\beta_{T5} = \beta_{35}(p, T)$ (which are assumed to be known), we obtain the thermal equation of state for ice V similarly to (2.1):

TABLE 4

Ice	d_0	d_1	d_2	ΔV_0	a	b	A	T_{1*}	$p_0(T_*)$
III	$1,0683 \cdot 10^{-3}$	$2,9191 \cdot 10^{-7}$	$2,1658 \cdot 10^{-9}$	$-1,92 \cdot 10^{-4}$	$1,1321 \cdot 10^2$	$1,2057 \cdot 10^{-2}$	$-2,0 \cdot 10^{-3}$	$-27,2$	$p_{13}(T_*)$
V	$8,6108 \cdot 10^{-4}$	$1,3667 \cdot 10^{-7}$	$9,9961 \cdot 10^{-10}$	$-5,45 \cdot 10^{-5}$	$1,2218 \cdot 10^2$	$9,0895 \cdot 10^{-3}$	$-7,0 \cdot 10^{-4}$	$-35,5$	$p_{35}(T_*)$
VI	$7,9011 \cdot 10^{-4}$	$1,0513 \cdot 10^{-7}$	$3,7347 \cdot 10^{-10}$	$-3,8 \cdot 10^{-5}$	$1,2945 \cdot 10^2$	$8,2074 \cdot 10^{-3}$	$-5,0 \cdot 10^{-4}$	$-35,5$	$p_{56}(T_*)$

$$V_5 = [V_3(p_{35}(T), T) + \Delta V_{35}] \exp\left\{-\int_{p_{35}(T)}^{p} \beta_{T5}(p, T)\, dp\right\}. \tag{2.2}$$

We find the thermal equation of state for ice VI by the exact same method:

$$V_6 = [V_5(p_{56}(T), T) + \Delta V_{56}] \exp\left\{-\int_{p_{56}(T)}^{p} \beta_{T6}(p, T)\, dp\right\}. \tag{2.3}$$

We now examine available experimental results required for constructing thermal equations of state from Eqs. (2.1)-(2.3). The values of ΔV_{ij} for the jumps in the specific volume on the lines {13}, {35}, and {56} are given in [11]. We now analyze that data. First, we note that ΔV_{35} and ΔV_{56} change very little along the curves {35} and {56}, respectively. Thus, ΔV_{35} changes from $-5.446 \cdot 10^{-5}$ m³/kg at T = 238 K to $-5.469 \cdot 10^{-5}$ m³/kg at T = 253 K (the minus sign indicates a decrease in the specific volume in the phase change from ice III to ice V), and ΔV_{56} changes from $-3.809 \cdot 10^{-5}$ m³/kg at T = 253 K to $-3.886 \cdot 10^{-5}$ m³/kg at T = 273 K.

Information is also presented [11] on the change of ΔV_{13} along the curve {13}. However, we will show that using it leads to contradictory results. To do this we derive a formula which relates the value of the volumetric expansion coefficient of the two phases at the phase transition curve. For definiteness we examine the curve {13}. Let M_1 and M_2 be points on the curve {13} which correspond to temperatures T_1 and T_2; let $V_1^{(1)}$ and $V_1^{(2)}$ be the specific volumes of ice I at these points; let $\Delta V_{13}^{(1)}$ and $\Delta V_{13}^{(2)}$ be values of the jumps in the specific volume at the points M_1 and M_2; and let $\Delta T = T_2 - T_1$. The value $\alpha_{T3}^{(1)}$ — the volumetric expansion coefficient of ice III at point M_1 — can be estimated from the formula

$$\alpha_{T3}^{(1)} = \frac{1}{V_3^{(1)}}\left(\frac{\partial V_3}{\partial T}\right)_p \approx \frac{1}{V_3^{(1)}}\left[\frac{V_1^{(2)} - V_1^{(1)}}{\Delta T} + \frac{\Delta V_{13}^{(2)} - \Delta V_{13}^{(1)}}{\Delta T}\right].$$

By substituting the expression

$$V_1^{(2)} - V_1^{(1)} \approx V_1^{(1)}\left[-\beta_{T1}^{(1)}\Delta p + \alpha_{T1}^{(1)}\Delta T\right],$$

we obtain a function for estimating α_{T3} at point M_1:

$$\alpha_{T3}^{(1)} \approx \left(V_1^{(1)}/V_3^{(1)}\right)\left[-\beta_{T1}^{(1)}\Delta p/\Delta T + \alpha_{T1}^{(1)}\right] + \left(\Delta V_{13}^{(2)} - \Delta V_{13}^{(1)}\right)/\left(V_3^{(1)}\Delta T\right). \tag{2.4}$$

Here $\Delta p = p_{13}(T_2) - p_{13}(T_1)$. We use the data in [11] and choose $T_1 = 243$ K and $T_2 = 253$ K. We have $\Delta T = 10$ K, $\Delta p = -5$ MPa, $\Delta V_{13}^{(1)} = -0.1919 \cdot 10^{-3}$ m³/kg, and $\Delta V_{13}^{(2)} = -0.1773 \cdot 10^{-3}$ m³/kg. With the aid of Eq. (1.5) we find $\beta_{T1}^{(1)} = 1.01 \cdot 10^{-4}$ MPa⁻¹, $\alpha_{T1}^{(1)} = 1.17 \cdot 10^{-4}$ K⁻¹, $V_1^{(1)} = 1.062 \cdot 10^{-3}$ m³/kg; for the specific volume of ice III we take $V_3^{(1)} \approx 0.88 \cdot 10^{-3}$ m³/kg. The first term on the right side of (2.4) equals $2.02 \cdot 10^{-4}$, and the second equals $1.66 \cdot 10^{-3}$. Then from (2.4) it follows that according to data [11], $\alpha_{T3}^{(1)}$ will be on the order of 10^{-3}. Such a value of $\alpha_{T3}^{(1)}$ is unrealistic. Actually, it exceeds the estimate values of analogous coefficients for ice modifications by at least an order of magnitude; it is characteristic of liquids, but not solids [22]. Moreover, use of $\alpha_{T3}^{(1)} \approx 10^{-3}$ K⁻¹ along with established values [14] of the isothermal and adiabatic moduli K_T and K_S in the well-known thermodynamic formula

$$c_p = K_T K_S T \alpha_T^2 V/(K_S - K_T) \tag{2.5}$$

leads to a specific heat of $c_p \approx 10^5$ J/(kg·K) for ice III at constant pressure which exceeds c_p for other solids by two orders of magnitude. Thus, the data [11] on the jump in the specific volume on the curve {13} lead to contradictory results. This has already been noted [18].

It is not hard to see that the source of such a large value of $\alpha_{T3}^{(1)}$ is the difference $\Delta V_{13}^{(2)} - \Delta V_{13}^{(1)}$. Such a significant change of ΔV_{13} is presented [11] only for the curve {13}; for curves {35} and {36}, the changes ΔV_{13} and ΔV_{35} are two orders of magnitude less, as noted above. For a comparable estimate of ΔV_{13} we turn to other experimental data. In [18] $\Delta V_{13} = -0.1847 \cdot 10^{-3}$ m³/kg at p = 210 MPa and T = 248 K, while a value 1.18 times higher than in [11] is established [2] at p = 200 MPa and T = 253 K. We know of no other sources except those cited above, in which ΔV_{13} could be determined along the curve {13}. Therefore, due to the

estimates of α_{T_3} and the scatter in experimental values of ΔV_{13} in the literature, we will take ΔV_{13} as a constant when we derive the thermal equation of state of ice III below; the value of ΔV_{13} will be chosen to give the best fit of the thermal equation of state to experiment. We make an analogous assumption with regard to ΔV_{35} and ΔV_{56} on the curves {35} and {56}, respectively. The choice of the values of ΔV_{13}, ΔV_{35}, and ΔV_{56} are shown in Table 4 in the column labeled ΔV_0.

Now we turn to measured data [2, 15] on the properties of ices III, V, and VI. The pressure-dependence of the density of ice III is determined at $T_* = -27.2°C$ [15], and the densities of ices V and VI are determined at $T_* = -35.5°C$, from which we can establish expressions for β_{Ti} at these temperatures:

$$\beta_{Ti} = b/(a + bp) \quad (i = 3, 5, 6). \tag{2.6}$$

Here p has units of MPa, and β_{Ti} has units of MPa^{-1}. The coefficients a and b are shown in Table 4. An important property of the isothermal moduli $K_T = 1/\beta_T$ [2] for different ice modifications is the following: K_T grows almost linearly with increasing pressure, and it decreases linearly with increasing temperature. Thus, by using (2.6), the form of the dependence of β_{Ti} on p and T can be written as

$$\beta_{Ti} = b/[a + bp + A(T_* - T_{1*})]. \tag{2.7}$$

In Eq. (2.7), $T_{1*} = -27.2°C$ for ice III, while $T_{1*} = -35.5°C$ for ices V and VI. According to what was stated above, $A < 0$ for all ice modifications. Experiments [2] showed that the values of A vary over a range of $-5 \cdot 10^{-4}$ to $-2 \cdot 10^{-3}$ and $A = -1.418 \cdot 10^{-3}$ for ice I [23]. We will use values $A = -2.0 \cdot 10^{-3}$, $-7.0 \cdot 10^{-4}$, and $-5.0 \cdot 10^{-4}$ for ices III, V, and VI.

Thus, all required quantities are now determined for constructing thermal equations of state for ices III, V, and VI in accordance with Eqs. (2.1)-(2.3). Having performed the integration, we come to the desired thermal equations of state:

$$V_i = \left(d_0 + d_1 T_* + d_2 T_*^2 + \Delta V_0\right) \frac{a + bp_0(T_*) + A(T_* - T_{1*})}{a + bp + A(T_* - T_{1*})}. \tag{2.8}$$

In Eq. (2.8) ΔV_0 and $p_0(T_*)$ should be replaced by ΔV_{13} and $p_{13}(T_*)$ for ice III, by ΔV_{35} and $p_{35}(T_*)$ for ice V and by ΔV_{56} and $p_{56}(T_*)$ for ice VI. The functions $p_{ij}(T_*)$ are given by Eq. (1.2). The values of the coefficients that enter into Eq. (2.8) are shown in Table 4.

The values which are calculated from Eq. (2.8) for the specific volume of the ices are compared with data [11] along the melt curves. The relative error does not exceed 0.62, 0.47, and 0.32% for ices III, V, and VI, which indicates good agreement of (2.8) with experimental results.

3. Thermodynamic Functions of High-Pressure Ices.

We now calculate the heat capacity, the Gibbs thermodynamic potential, and the enthalpy of various ice modifications; these quantities can be used to determine all the other thermodynamic functions.

The heat capacity at constant volume c_V for crystalline solids can be approximated by $c_V = 6$ kcal/(mole·K) (Dulong and Petit's law), which in the case of H_2O is $1.39 \cdot 10^3$ J/(kg·K). This estimate is satisfactory if the temperature of the material is above the Debye temperature T_D [24], which is determined by the formula

$$T_D = \frac{h}{k} \left(\frac{9\rho}{4\pi m} \frac{v_l^3 v_t^3}{2v_l^3 + v_t^3} \right)^{1/3},$$

where h is Planck's constant; k is Boltzmann's constant; ρ is the density; m is the molecular weight; and v_l and v_t are the longitudinal and transverse sound speeds. By using data [14, 15], we obtain the following values of T_D for ices I, III, V, and VI: 206.5, 223.2, 255.4, and 279.6 K, respectively. From this it follows that if the required experimental data are missing, we can approximate $c_{Vi} = 1.39 \cdot 10^3$ J/(kg·K). The heat capacity c_{pi} is related to c_{Vi}: $c_{pi}/c_{Vi} = K_{Si}/K_{Ti}$, where K_{Si} and K_{Ti} are the adiabatic and isothermal bulk moduli; in this case c_{pi} differs from c_{Vi} by no more than 2-3%.

The value of c_p can be refined for ices I, III, and V. This has been done [10] for ice I. We determine the heat capacity for ices III and V by using Eq. (2.5) in which we insert known values [15] of K_{Si} and K_{Ti}; we compute V_i and α_{Ti} from the constructed thermal equations of state. We obtain $c_{p3} = 1.59 \cdot 10^3$ J/(kg·K) for $T_* = -27.2°C$ and p = 276 MPa, and $c_{p5} = 2.59 \cdot 10^3$ J/(kg·K) for $T_* = -35.5°C$ and p = 480 MPa. For other attainable values of T and P, we can calculate c_{pi} from the formula
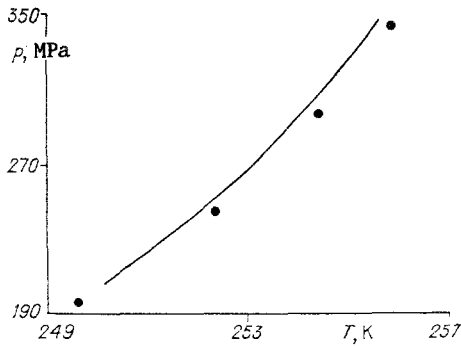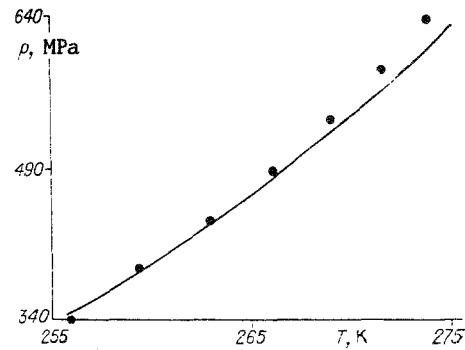
Fig. 2

Fig. 3

$$c_{pi}(p, T) = c_{pi}(p_1, T) - T \int_{p_1}^{p} V_i\left(\frac{\partial \alpha_{Ti}}{\partial T} + \alpha_{Ti}^2\right) dp,$$

where the integrand is computed from Eq. (2.8), and the first term on the right side is taken equal to the values found above.

The specific Gibbs thermodynamic potential for the i-th phase $G_i = H_i - TS_i$ plays an important role in phase-transition problems, where H_i and S_i are the specific enthalpy and entropy of the material. From thermodynamics we know that $G_i(p, T) = G_j(p, T)$ along the phase-transition curve {ij}. Whenever the phase-transition kinetics must be considered, it is assumed that the transition rate is determined by the difference in the Gibbs functions $G_i - G_j$ of the interacting phases [9, 21].

In order to construct the Gibbs potential of the high-pressure ices, we introduce the functions G(p, T) and V(p, T), which are determined in the region Ω by assuming that G(p, T) $\equiv G_i(p, T)$ and V(p, T) $\equiv V_i(P, t)$ in $\Omega_i \subset \Omega$. Here G(p, T) is continuous and V(p, T) is piecewise continuous in Ω. The points of discontinuity of V(p, T) are concentrated on the phase transition curves {ij}. If $H_0(T)$ and $S_0(T)$ are known at some pressure $p = p_0$, then G(p, T) can be found from the formula

$$G(p, T) = H_0(T) - TS_0(T) + \int_{p_0}^{p} V(p, T) dp. \tag{3.1}$$

The jump in the function V(p, T) must be considered when the phase transition curve crosses the isotherm used in performing the integration on the right side of (3.1). As an example, we examine the isotherm RR' (see Fig. 1). It intersects the curves {1w} and {5w}, where the point R' is located in the region Ω_5. Then we find from (3.1)

$$G(p, T) = H_0(T) - TS_0(T) + \int_{p}^{p_{1w}(T)} V_1(p, T) dp + \int_{p_{1w}(T)}^{p_{5w}(T)} V_w(p, T) dp + \int_{p_{5w}(T)}^{p} V_5(p, T) dp.$$

The equations $p = p_{ij}(T)$ of the melt curves {ij} (i = 1, 3, 5, and 6) are described by Eqs. (1.1), the equations of the curves {13}, {35}, and {56} are described by Eqs. (1.2). The specific volumes of the ices I, III, V, and VI are computed from (1.5) and (2.8). The function $V_w(p, T)$ has been examined in detail [10].

We return to establishing the functions $H_0(T)$ and $S_0(T)$. Because the enthalpy H and the entropy S are determined relative to a constant, we use as a basis for H = S = 0 the point in the region Ω at which $p_0 = 0.1$ MPa and $T_0 = 273.15$ K. We compute H_0 and S_0 from the formula

$$H_0 = \int_{T_0}^{T} c_p(p_0, T) dT, \quad S_0 = \int_{T_0}^{T} \frac{c_p(p_0, T)}{T} dT. \tag{3.2}$$

The dependence $c_p(p_0, T)$ on T for ice I (for $T < T_0$) is determined by the formula $c_{pi}(p_0, T) = 2.115 \cdot 10^3 + 7.79 \cdot T_*$ J/(kg·K) [12]; the expression for liquid water, which we obtained from data [19], has the form $c_{pw}(p_0, T) = 4.2153 \cdot 10^3 - 2.2584 \cdot T_* + 3.2069 \cdot 10^{-2} T_*^2$ J/(kg·K). The function $H_0(T) - TS_0(T)$, which is continuous at $T = T_0$, can easily be found explicitly from (3.2). Thus, the Gibbs thermodynamic potential of all examined phases of H_2O is completely determined.
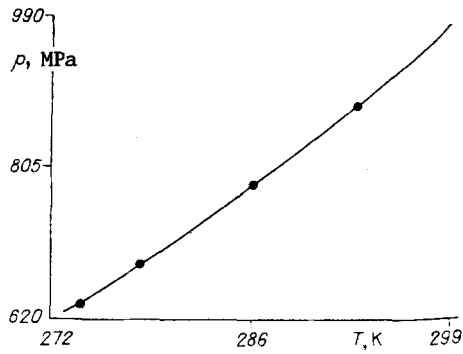
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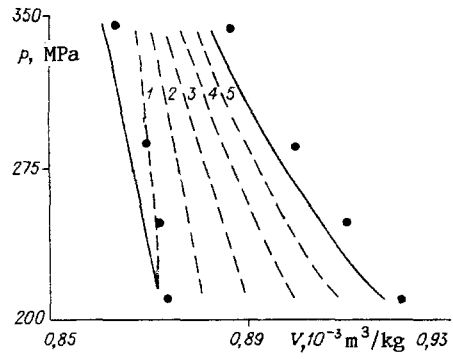
Fig. 4

Fig. 5

The enthalpy H_i can be calculated by using the formula

$$H_i(p, T) = H_0(T) + \int_{p_0}^{p} [V - T(\partial V/\partial T)_p]\, dp + \sum_k \Delta H_k,$$

where the last term is the sum of enthalpy changes where the isotherms intersect the phase transition curves. The quantity ΔH_k is the specific phase transition energy q with the proper sign. The value of q_{ij} can be determined on the curve $\{ij\}$ by the Clapeyron–Clausius equation

$$q_{ij} = T\Delta V_{ij} dp_{ij}/dT,$$

by using (1.1), (1.2) and the resultant thermal equations of state.

4. Calculating the Equilibrium Melting Ices at High Pressure. We use the resultant thermal equations of state to calculate the equilibrium melting of ices III, V, and VI under a quasi-static load along the melt curves $\{3w\}$, $\{5w\}$, and $\{6w\}$. We apply the method used earlier [10] for ice I.

The curve $\{iw\}$ (i = 1, 3, 5, and 6) corresponds to the p and T values at which ice and water are thermodynamically allowable as a two-phase mixture. Let z be the mass fraction of water in the mixture. Then the specific volume of the mixture V and its entropy S are computed as

$$V = (1 - z) V_i + z V_w, \quad S = (1 - z) S_i + z S_w. \tag{4.1}$$

We now examine the adiabatic loading process of the mixture by assuming S = const. Then, in analogy to [10], we use the equations for the adiabatic compressibility of the mixture

$$dV/dp = (1 - z)\left[(\partial V_i/\partial p)_T + (2T/q_{iw})(\partial V_i/\partial T)_p (V_w - V_i) - c_{pi}T(V_w -\right.$$
$$\left. - V_i)^2/q_{iw}^2\right] + z\left[(\partial V_w/\partial p)_T + (2T/q_{iw})(\partial V_w/\partial T)_p (V_w - V_i) - c_{wi}T(V_w - V_i)^2/q_{iw}^2\right]; \tag{4.2}$$

the Clapeyron–Clausius equation

$$dT/dp = T(V_w - V_i)/q_{iw} \tag{4.3}$$

and the equation which describes the change in the specific heat of melt q_{ij} along the curve $\{iw\}$

$$\frac{dq_{iw}}{dp} = \left[c_{pw} - c_{pi} + \frac{q_{iw}}{T} - \frac{q_{iw}(V_w a_{Tw} - V_i a_{Ti})}{V_w - V_i}\right]\frac{T(V_w - V_i)}{q_{iw}}. \tag{4.4}$$

Thus, we have a system of ordinary differential equations (4.2)-(4.4) with respect to V, T, and q_{iw}. Once they are solved along with (4.1) for given initial conditions, we can determine the adiabatic dependence of V(p) (the isentrope of the mixture) and also compute T(p) numerically, i.e., determine the melt curve. All quantities which enter into the right sides of (4.2)-(4.4) are obtained in Secs. 1-3 of this article. The thermodynamic properties of water are described in [10].

The system (4.1)-(4.4) was integrated numerically by the Runge–Kutta method. The values of the required functions at the triple points $\{13w\}$, $\{35w\}$, and $\{56w\}$ of ices III, V, and VI were chosen as the starting values. In each series of calculations we varied the initial values of z from 0.0 to 0.8 with a step of 0.2. The results of the calculations are shown in Figs. 2-7.
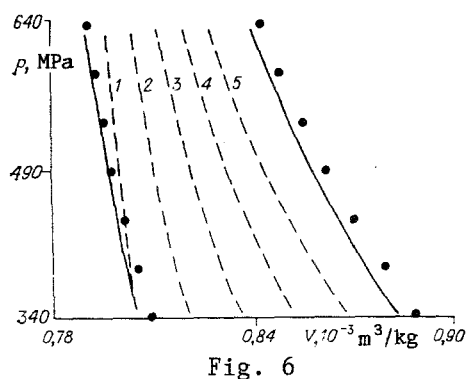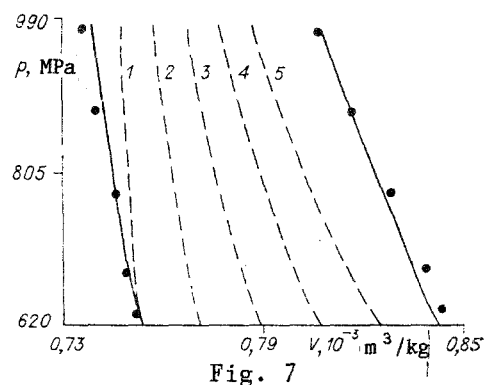
Fig. 6

Fig. 7

In Figs. 2-4, the solid lines show the calculated melt curves of the ices III, V, and VI, and the points show Bridgman's data [11]. The good agreement of the calculation with the experimental data can be seen for ice VI (Fig. 4). For ices III and V some deviation of the calculated curves from the data [11] can be explained by the fact that the initial value of the heat of melt q for subsequent curves was chosen from the previous curve according to Eq. (4.4). These initial values differ from [11] by roughly 10-15%, which is caused by the deviations from data [11] of the calculated q_{1w} on curve {1w} (see the discussion in [10]).

Figures 5-7 show the calculated isentropes $V(p)$ of ice-water mixtures for ices III, V, and VI, respectively. The solid lines to the right and left are the boundaries of the region occupied by the two-phase mixture in the $p - V$ diagram, and the dashed curves 1-5 are isentropes of the mixture which correspond to initial water fractions $z = 0$, 0.2, 0.4, 0.6, and 0.8. The points are data [11] which correspond to the boundaries of the two-phase region. As noted in [10], the isentropes of the two-phase mixture of ice I and water have the property $(\partial^2 V/\partial p^2)_s < 0$ (the curves on the $p-V$ diagram are convex upwards). Conversely, the calculated isentropes of mixtures with ice V and ice VI are convex downward, while the mixture with ice III and water is convex upwards for $z = 0$, 0.2, and 0.4, but downwards for $z = 0.6$ and 0.8. Such a behavior of isentropes of mixtures of water and ice of different modifications indicates the complexity of the wave picture formed when compression waves are propagated through a sample of ice I loaded to pressures p on the order of 10^2-10^3 MPa, as indicated by experimental data [5, 6].

5. Conclusions. We used the experimental data of different authors to do a comparative analysis of the thermodynamic characteristics of ices I, III, V, and VI for temperatures of 233-293 K and pressures of 0-10^3 MPa and to construct new thermal equations of state for ices III, V, and VI. A critical analysis of previous results [11] on the jumps in the specific volume on the phase transition curves {13}, {35}, and {56} showed that the data on the changes in the specific volume on the curve {13} lead to contradictory results. In constructing the thermal equations of state of the high-pressure ice phases we assumed that the changes in the specific volume are constant on the curves {13}, {35}, and {56}. These thermal equations of state can be improved and their range of application can be expanded if data on the temperature-dependence of the volumetric expansion coefficient and the isothermal compressibility of the ice phases at various pressures are refined. Here we note that other forms of the so-called isothermal equation of state are sometimes used [25] because of the relationship between the lack of experimental data and the quality of the ice thermal equations of state.

The Debye temperatures of the ice phases computed from experimental data show that the value $c_V = 1.39 \cdot 10^3$ J/(kg·K) is a satisfactory approximation. Refined values of c_p were obtained for ices III and V. The Gibbs thermodynamic potential, which plays an important role in studying phase change kinetics, was constructed for various ice modifications and liquid water. We examined the calculation of the specific enthalpy of various ice phases.

The thermodynamic functions of liquid water for T > 273 K have been extensively studied, and results continue to be published [26]. Here the thermal equation of state of water and its thermodynamic functions were used, which were examined in [10] and which are applicable to T < 273 K, where all the melt curves for the ice phases I, III, and V are located.

The equilibrium melt of ices III, V, and VI were investigated. The melt curves were calculated numerically, and the bounds of the two-phase regions of the $p-V$ diagram were

determined. The calculated isentropes of water mixtures of ice V and ice VI have the property $(\partial^2 V/\partial p^2)_S > 0$, as opposed to ice III, for which $(\partial^2 V/\partial p^2)_S < 0$ in the two-phase region. The mixture of ice III phases and water shows a different behavior of the isentropes, depending on the initial water fraction. This indicates a complex wave picture when compressive waves propagate through a sample during impact and explosive loading.

These results can serve as a basis for mathematical modeling in studying the quasistatic and dynamic deformation of various H_2O phases and for interpreting corresponding experimental data.

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