Thermodynamic properties of ice, water and their mixture under high pressure

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ABSTRACT The equilibrium melting of ice under high pressure is analyzed. Experimental data from various authors is used to build a thermal equation of the state (TES) of ice. Observations of thermal properties of water are also used to construct the TES of water at temperatures below 0°C. This equation describes all anomalous properties of water and is in good agreement with Bridgman's data. Ice melting under high pressure is studied numerically by means of integrating the system of ordinary differential equations. Phase boundaries of pure ice and water on P-V diagram, isoentropes of ice-water mixture, and melting curve of ice are investigated.

INTRODUCTION

The models of deformation and flow of ice within the Greenland and Antarctic Ice Sheets, especially with respect to its compressibility, require information on thermodynamic properties of ice and water at temperature T < 0°C and under high pressure.

Static (Bridgman, 1911) and dynamic (Larson, 1984; Fomin, 1985) loading experiments helped distinguish a phase transition (melting) of ice in a certain domain of pressure and temperature variations. The resulting ice-water mixture may considerably change mechanical properties of material.

Using published data, we have constructed thermal equations of the state (TES) of ice I (in hydrostatic approximation) and water at T < 0°C and have determined their specific heat capacities. We have also numerically investigated the equation of the state of ice-water mixture in the domain of their equilibrium coexistence and have determined the bounds of phase equilibrium on the P-V diagram.

THERMODYNAMIC PROPERTIES OF ICE

TES of simple substances connects three thermodynamic parameters: pressure P, temperature T, and specific volume
V. When the equilibrium melting of ice is discussed, it is convenient to choose \( P \) and \( T \) as independent variables, for they are equal in both phases. Then the TES of ice has the following form:

\[
V_1 = V_1(P,T)
\]

Indices 1 and 2 in equation (1) and later in the text refer to ice and water, respectively.

Equation (1) is commonly used to describe the deformable solid body in case the loading stress is much greater than the strength of this solid body (hydrostatic approximation). The strength of ice with respect to compression, tension, and shear stress is not greater than several dozens of bars (Landolt-Bornstein, 1980) whilst the ice melting effects take place under the pressure of the order of \( 10^{-2} \) to \( 10^{3} \) bar. Such a pressure exists, for example, in Antarctic Ice Sheet at the depth of about 1 km. Below we shall neglect the possible effect of shear stresses on ice compression and will use hydrostatic approximation.

Equation (1) can be built using experimental data on the isothermal compressibility \( \beta_{T1} = -1/V_1(\partial V_1/\partial P) \) and coefficient of thermal expansion \( \alpha_{T1} = 1/V_1(\partial V_1/\partial T) \), by means of integrating the differential expression presented below

\[
\frac{dV_1}{V_1} = -\beta_{T1} dP + \alpha_{T1} dT
\]

The path of integration on \( P-T \) diagram of ice is shown on Fig. 1 (line ABC). Line 1 is the melting curve of ice I. The path starts at \( A \), where \( P = 0 \) bar, \( T = 0 \) °C and \( V_1 = 1.091 \times 10^{-3} \) m\(^3\) kg\(^{-1}\). The desired TES of ice should have the following form:

\[
V_1 = V_{10} \exp \left\{ - \int_{P_0}^{P} \beta_{T1}(P',T) \, dP' + \int_{T_0}^{T} \alpha_{T1}(P_0,T') \, dT' \right\}
\]

Here \( T \) is temperature in °C. We shall also denote absolute temperature as \( T' \).

The processing of experimental published data (Butkovich, 1959; Gammon et al., 1983; Brockamp & Von Ruter, 1969; Gagnon et al., 1986) made it possible to determine \( \alpha_{T1}(P_0,T) \) and \( \beta_{T1}(P,T) \). The expressions are as follows:

\[
\alpha_{T1}(P_0,T) = A_1 + A_2 T + A_3 T^2 + A_4 T^3
\]

\[
\beta_{T1}(P,T) = \frac{\beta_{T1}^o}{1 + m \beta_{T1}^o P}
\]
\[
\beta_{T1}^0 = \frac{\beta_1}{1 - \beta_2 T}
\]

where \( A_1 = 1.5756 \times 10^{-4}, A_2 = 5.556 \times 10^{-7}, A_3 = 2.655 \times 10^{-8}, A_4 = 7.11 \times 10^{-10}, \beta_1 = 1.1827 \times 10^{-5}, \beta_2 = 1.418 \times 10^{-3}. \)

The units of \( \alpha_{T1} \) and \( \beta_{T1} \) from above are \( ^\circ \text{K}^{-1} \) and \( \text{bar}^{-1} \), respectively. Coefficient \( m_1 \) is close to 5. According to Brockamp & Von Ruter (1969) \( m_1 = 4.4 \), while \( m_2 = 5.37 \) according to Gagnon et al. (1986).

\[\text{FIG. 1 Phase P-T diagrams of ice and water.} \]

Definitely the TES of ice I can be expressed as follows:

\[
V_1 = \frac{V_1^0(T)}{(1 + m_1 \beta_{T1}^0 P)^{1/m_1}} \\
V_1^0(T) = \int_0^T \alpha_{T1}(P_0, T') \, dT'
\]

The specific heat capacity of ice I is given by
\[ C_{P1}(P,T) = C_{P1}(P_0,T) - T \int_{P_0}^{P} V_1 \left( \frac{\partial \alpha_{T1}}{\partial T} + \alpha_{T1}^2 \right) \, dP \]

where \( C_{P1}(P,T) = 2.115 \times 10^3 + 7.78 \, T \, J \, (kg^{-1}K^{-1}) \); \( V_1 \) and \( \alpha_{T1} \) are obtained from equation (2).

thermodynamic properties of water

A thermal equation of the state of water at \( T < 0^\circ C \) was constructed, basing on works of Kell (1967), Minassian et al. (1981), Grindley & Lind (1971), Angel et al. (1973), Zemansky (1968), by means of integrating the expression

\[ \frac{dV_2}{V_2} = -\beta_{T2} \, dP + \alpha_{T2} \, dT \]

along the path A, B, C (see Fig. 1). The reference point is \( P = 0 \, \text{bar} \) and \( T_1 = 273.16^\circ \text{K} \). The result of integration is TES of water:

\[ V_2 = V_{20} \exp \left\{ -\int_{P_0}^{P} \beta_{T2}(P',T_{K1}) \, dP' \right\} + \int_{T_1}^{T} \alpha_{T2}(P,T_k) \, dT' \]  

(3)

where

\[ 10^4 \beta_{T2}(P,T_{K1}) = \sum_{i=0}^{4} b_i P^i \]

\[ 10^4 \alpha_{T2}(P,T_k) = A + \frac{B}{C + \Gamma} \]

\[ A = a_1 + a_2 T_k + a_3 T_k^2 \]

\[ B = a_4 + a_5 T_k + a_6 T_k^2 + a_7 T_k \Gamma + a_8 \Gamma \]

\[ C = a_9 + a_{10} T_k + a_{11} T_k^2 + a_{12} T_k^3 \]

\[ \Gamma = P + a_{13} P^2 + a_{14} P^3 \]

The expressions for \( \alpha_{T2} \) and \( \beta_{T2} \) were achieved by Minassian et al. (1981), Grindley & Lind (1971) by precise measurements. One may find the coefficients \( a_i \) (\( i = 1, 2, \ldots, 14 \)) and \( b_i \) (\( i = 0, 1, \ldots, 4 \)) in the work of Minassian et al. (1981). The specific heat capacity of water is given by:
\[
C_{P2}(P, T) = C_{P2}(P', T) - T_k \int_{P_0}^{P} \left( \frac{\partial \alpha_{T2}}{\partial T} + \alpha_{T2}^2 \right) \, dP'
\]

The observations of supercooled water's properties have indicated that specific heat of water at constant volume is very close to 4.206 \times 10^3 \, J \, kg^{-1} \, K^{-1} when T varies from -26 to 5°C and P = 0 bar. After that it may be determined from the following thermodynamic equation (Zemansky, 1968)

\[
C_{P2} - C_{V2} = \frac{T_k \alpha_{T2}^2 V_2^2}{\beta_{T2}}
\]

The received TES's of ice and water together with \( C_{Pi} \) \((i = 1, 2)\) is a sufficient basis for constructing all thermodynamic functions needed for mathematical simulations.

CALCULATION OF ICE-MELTING UNDER HIGH PRESSURE

Line 1 in Fig. 1 is the melting curve of ice I. It corresponds to such values of P and T when coexistence of ice I and water in the form of a two-phase mixture is permissible. Let Z be the mass share of water in the mixture. The specific volume \( V \) and specific entropy \( S \) are presented as follows:

\[
V = (1 - Z) V_1 + Z V_2
\]

\[
S = (1 - Z) S_1 + Z S_2
\]

Below we give the equation connecting the parameters of pure phases and the mixture:

\[
\left( \frac{\partial V}{\partial P} \right)_s = (1 - Z) \left[ \left( \frac{\partial V_1}{\partial P} \right)_T + \frac{2 T_k}{q} \left( \frac{\partial V_1}{\partial T} \right)_P (V_2 - V_1) - \frac{C_{P1} T_k}{q^2} (V_2 - V_1)^2 \right] + Z \left[ \left( \frac{\partial V_2}{\partial P} \right)_T + \frac{2 T_k}{q} \left( \frac{\partial V_2}{\partial T} \right)_P \right] x
\]

\[
x (V_2 - V_1) - \frac{C_{P2} T_k}{q} (V_2 - V_1)^2 \]

where q is the specific heat of melting of ice I.

We have investigated the process of adiabatic loading of ice-water mixture, when S = const. In such case the partial derivative in equation (4) may be replaced by dV/dP. With attention fixed on the parameters of mixture during adiabatic loading we invoke two additional
conditions of equilibrium: Clausius-Clapeyron equation
\[
\frac{dT}{dP} = \frac{T_k (V_2 - V_1)}{q} \quad (5)
\]
and the equation for the specific heat of melting
\[
\frac{dq}{dP} = \left[ C_{p2} - C_{p1} + \frac{q}{T_k} - \frac{q (V_2 \alpha_{T2} - V_1 \alpha_{T1})}{V_2 - V_1} \right] \times
\]
\[
\times \frac{T_k (V_2 - V_1)}{q} \quad (6)
\]

The system of ordinary differential equations (4)-(6) has been solved numerically by Runge-Kutta method. The values of \( P \) changed from \( P = 0 \) to \( P = 2100 \) bar by step \( \Delta P = 100 \) bar. The initial conditions at \( P = 0 \) were \( T = 0^\circ C \) and \( q = 333.7 \times 10^3 \) J kg\(^{-1}\). The initial value of specific volume varied from \( V = 1.091 \times 10^{-3} \) m kg\(^{-1}\) (ice; \( Z = 0 \)) to \( V = 1.082 \times 10^{-3} \) m kg\(^{-1}\) (mixture; \( Z = 0.8 \)). The bounds of mixture on P-V diagrams - left bound \( V_2 = V(P,T(P)) \) and right bound \( V = V(P,T(P)) \) - were determined together with calculations of \( V(P) \), \( T(P) \), \( q(P) \) and \( Z(P) \). The relations \( V = V(P) \) and \( T = T(P) \) are the adiabatic equations of state of mixture and the melting curve, respectively.

\[\text{FIG. 2 Phase P-V diagrams of ice-water mixture. Solid lines - phase boundaries of ice water; dashed lines 1-5 - isoentropes of ice-water mixture under various initial conditions.}\]
RESULTS

We have compared the calculated values of specific volumes $V_1$ and $V_2$ with experimental observations of Bridgman and other researchers. The results agree quite well: the relative error of $V_1$ is about 1-2% and that of $V_2$ is a share of percent.

Fig. 2 displays the P-V diagram of ice-water mixture. Left and right curves are the bounds of ice-water mixture area. Dashed lines are isoentropes at $P = 0$ bar, $T = 0^\circ$C and initial values of $Z$: $1 - Z = 0.0$, $2 - Z = 0.2$, $3 - Z = 0.4$, $4 - Z = 0.6$, $5 - Z = 0.8$. The final values of $Z$ on lines 1-4 at $P = 2100$ bar are 0.19, 0.49, 0.65 and 0.88 respectively. Hence, if the sample of ice, initially at $P = 0$ bar, $T = 0^\circ$C, is subjected to quasistatic adiabatic compression along the melting curve, only about 20% of ice will transfer into water.

The obtained isoentropes satisfy the inequality $(\delta^2 V/\delta P^2) < 0$. It points out the transformation of shock wave into continuous wave of compression while it travels through the ice sample. Larson’s (1984) experiments confirm such an inference.

The repeated results may form the basis for processing experimental data on the properties of ice within ice sheet and for mathematical simulations of ice behavior under high pressure with respect to its compressibility and phase transitions.

REFERENCES


