

**PHASE TRANSFORMATION OF WATER
UNDER SHOCK COMPRESSION**

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UDC 539.893:620.181

The authors of [1-3] established that there is transformation of water into a solid phase (ice VII) under shock compression. It was shown that the shock adiabat of water splits into three separate parts (Figs. 1 and 2). In particular, in the coordinates wave velocity D vs. mass velocity u , these parts are rectilinear sections (Fig. 1) with their values of the coefficients C_0 and λ in the equation

$$D = C_0 + \lambda u. \tag{1}$$

The lower 1 and upper 3 sections are interpreted as corresponding to the liquid phase, and the intermediate 2 as corresponding to a mixture of the liquid phase and ice VII. To estimate temperatures two types of equation of state are used: the Mie-Gruneisen equation and the Zamyshlyayev-Menzhulin interpolation equation [4]. In the Mie-Gruneisen equation

$$P = P_c + P_T = P_c + \frac{\Gamma}{V} C_V T, \quad E = E_c + E_T = E_c + C_V T \tag{2}$$

the following expressions derived in [5] are used for the cold constituent of both the pressure P_c and the internal energy E_c

$$P_c = \frac{\rho_0 C_0^2}{4\lambda} \left[\exp \left(4\lambda \frac{\Delta\rho}{\rho} \right) - 1 \right], \quad E_c = \frac{C_0^2}{4\lambda} \left[\frac{P_c}{\rho_0 C_0^2} - \frac{\Delta\rho}{\rho} \right]. \tag{3}$$

Here P is the pressure; E is the internal energy; T is the temperature; C_V is the specific heat; Γ is the Gruneisen parameter; ρ is the density; $\Delta\rho = \rho - \rho_0$; the subscript 0 refers to the initial state under normal conditions; subscript c to cold constituents, and T to thermal constituents. The convenience of expressions (3) is that they contain the coefficients C_0 and λ entering into linear relation (1) between the wave and mass velocities. The latter are presented in tables for a large number of materials [6, 7], or can be calculated following the rules in [8, 9]. The shock adiabat of ice VII is obtained by processing of the experimental results of [10] on the isothermal compressibility of ice VII ($T = 298$ K and $P = 3-8$ GPa). The data of [10] are described by the Mie-Gruneisen equation with the cold constituent in the form of (3). As a result, the coefficients in linear relation (1) between the kinematic parameters of ice VII were evaluated as $C_{0VII} = 3.067$ km/sec and $\lambda = 1.968$, and the initial density of ice VII $\rho_{0VII} = 1.5198 \cdot 10^3$ kg/m³. It should be noted that this value is close to the density of ice VII $\rho = 1.5 \cdot 10^3$ kg/m³ given by Eisenberg and Kauzman [11] without specifying other parameters of state. Olinger and Halleck [10] obtained the value $V_0 = 1/\rho_0 = (0.696-0.731) \cdot 10^{-3}$ m³/kg and called it the ambient specific volume.

Further the mass fractions of the components (Fig. 3) are evaluated from known shock adiabats of both the mixture at section 2 and its components using the rule of additivity proved experimentally in [12, 13]. It is found that the shock adiabat of water in the temperature-pressure plane intersects twice the curve of liquid-ice VII phase equilibrium and is in the region of ice VII in the pressure range from 2.86 to 10.1 GPa. In this region the mass portion of ice VII increases from 0.8 at the lowest point to 27% at the highest point. The existence of a solid phase in shock-compressed water in the above pressure range was substantiated in [1-3] by the known data of other authors who studied properties of shock-compressed water such as viscosity [14], compressibility [15], and freezing [16]. However, the details of transition between three sections of the

Institute of Continuum Mechanics, Ural Division, Russian Academy of Sciences, Perm' 614061. Translated from *Prikladnaya Mekhanika i Tekhnicheskaya Fizika*, Vol. 37, No. 5, pp. 17-23, September-October, 1996. Original article submitted June 13, 1995.

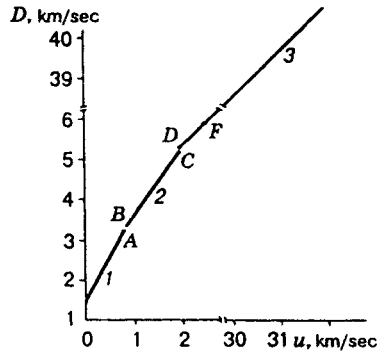


Fig. 1

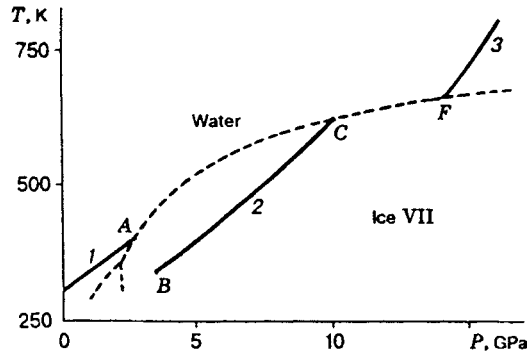


Fig. 2

TABLE 1

State	<i>u</i>	<i>D</i>	ρ , 10 ⁻³ kg/m ³	<i>V</i> , 10 ³ m ³ /kg	<i>P</i>	<i>P_c</i>	<i>E</i>	<i>E_c</i>	<i>T</i> , K	α , %
	km/sec				GPa		10 ⁻⁵ J/kg			
A	0.843	3.276	1.3633	0.7335	2.76	2.20	3.678	1.892	400	0
B	0.858	3.320	1.3484	0.7416	2.85	2.46	3.681	2.300	315	0.8

shock adiabat of water, i.e., between the pairs of points A–B and C–D in Figs. 1 and 2 in wave velocity–mass velocity and temperature–pressure planes, and the structure of water at upper section 3 are unknown.

In this work, we attempt to find answers to these questions. First we turn to the transition at low temperatures and pressures, i.e., consider the transition from section 1 to section 2 and determine the values of some parameters of water and mixture at states A and B. The point A in the temperature–pressure plane is the point of intersection of the shock adiabat at section 1 with the curve of phase equilibrium of liquid and solid phases (ice VII). The density ρ , or specific volume $V = 1/\rho$, pressure P , internal energy E in the state A as in all other states at section 1 are evaluated using the laws of conservation of mass, momentum, and energy at a shock-wave front. The values of cold constituents of pressure P_c and internal energy E_c are found using relations (3), and the temperature T using the equation of state (2) in the form of the Mie–Grüneisen equation with a constant heat capacity of the liquid phase (water). The results are presented in Table 1.

If the transition from the liquid to solid state (ice VII) with passage through the curve of phase equilibrium of these phases occurred under static conditions, then, first, one could expect complete transformation of the liquid phase into the solid one, and second, jump-wise changes in the density $\Delta\rho$, or specific volume ΔV , internal energy ΔE , and entropy ΔS would be related by the equations of the first principle of thermodynamics, Clausius–Clapeyron and Simon's equations. However, as is obvious from Fig. 3, the state of mixture at section 2 at low temperatures and pressures is characterized by a low concentration of the solid phase (ice VII) in the mixture. Recall Bridgman's doubt [17]: whether phase transitions are realized completely under shock-wave action over such short times. If the shock-wave front thickness is assumed to be equal to several free paths, in our case the time of passage of a particle through the shock-wave front is $\sim 10^{-6}$ sec. According to Kormer [18], under conditions close to those considered the time of phase transition is equal to $\sim 10^{-6}$ – 10^{-7} sec.

Thus, in state B we have a partial and insignificant transformation of water into ice VII. On the one hand, points A and B are in the regions of different phases. On the other hand, A and B are successive points on the shock adiabat. Therefore, in particular, the values of internal energy for these states should be rather close and differ by the amount of energy required for solidification of the amount of water that is sufficient for obtaining fraction α of ice VII:

$$E_A + \Delta E_A \alpha \rho = E_B. \quad (4)$$

TABLE 2

State	u	D	$\rho,$	$V,$	P	P_c	E	E_c	$T,$	$\alpha,$
	km/sec		10^{-3} kg/m ³	10^3 m ³ /kg	GPa		10^{-6} J/kg		K	%
C	1.960	5.170	1.6103	0.6210	10.10	6.18	1.921	0.721	620	27.1
D	1.960	5.290	1.5893	0.6292	10.36	7.86	1.921	0.972	~ 620	> 27

Here $\Delta E_A = 0.387 \cdot 10^5$ J/kg and $\alpha = 0.8\%$. Using this assumption we evaluated the parameters of state B in a similar way as was done for state A. Their numerical values are also presented in Table 1. When determining ΔE in (4) we used the Simon equation for the melting curve of ice VII obtained in [19] and written here in the form

$$P = 2.154 + 0.503 \left[\left(\frac{T}{354.8} \right)^{5.135} - 1 \right] \quad (5)$$

(P in gigapascals and T in kelvins). The entropy jump $\Delta S = 153$ J/K. Eisenberg and Kauzman [11] give the mean value $\Delta S = 186$ J/K for transition through phase boundaries of different structures of ice.

The change in the mass fraction α of ice VII in the mixture with water at section 2 of the shock adiabat can be represented as a function $\alpha(P)$, which is independent of the time of phase transition. The fact is that in shock-wave studies, water with different properties (compressibility, viscosity, transparency, etc.) remains in a shock-compressed state for practically the same time ($\sim 10^{-6}$ sec), although experiments are performed in different laboratories using different techniques and setups.

All parameters (except for temperature) in state C are determined in the same way as was done for state A taking into account the numerical values of the coefficients in (1) for section 2. To estimate the temperature, the thermal constituents in Eqs. (2) are changed so as to take into account the presence of two components, for example:

$$E = E_c + [C_{V\text{H}_2\text{O}}(1 - \alpha) + C_{V\text{II}}\alpha]\rho T. \quad (3a)$$

Numerical values of the parameters in state C are presented in Table 2. The thermal energy $E_T = 1.20 \cdot 10^6$ J/kg of the state C enables one to expect melting of 27% of ice VII from the mixture. It should be noted that this amount of E_T is insufficient to evaporate all water after melting of fraction α of ice VII ($\Delta E_{\text{vap}} = 2.26 \cdot 10^6$ J/kg), i.e., to break intermolecular bonds. In fact, at point C in the curve of phase equilibrium, $\Delta E = E_{\text{mel}} = 3.14 \cdot 10^5$ J/kg, so that melting of 27% of ice VII requires $0.92 \cdot 10^5$ J/kg.

However, by analogy with the foregoing, one could expect that states C and D in the vicinity of the shock adiabat have close structures and close values of internal energy. As will be shown below, there is one more argument in favor of these assumptions. Therefore, we assume that $E_D \simeq E_C$. The resulting values of the parameters in state D are presented in Table 2.

For the region of high pressures and temperatures of section 3 of the shock adiabat, the authors of [18, 20] performed experiments on measuring the temperature of shock-compressed water. Figure 4 gives the results of these experiments approximated for the range under study by the linear relation

$$T = -316 + 68.8P \quad (6)$$

(T in kelvins and P in gigapascals). Extrapolating relation (6) up to the intersection with the melting curve of ice VII, we obtain point F with coordinates $T = 661$ K and $P = 14.2$ GPa. These values are close to the parameters $T = 650$ K and $P = 13$ GPa of the "freezing" point (the term of Schroeder and MacMaster [16]) of shock-compressed water. The temperatures studied in [18, 20], on the one hand, are fairly high, and, on the other hand, are much lower than those at which thermal excitation of electrons starts. The latter are on the order of several electron-volts, i.e., tens of thousands of degrees [21]. Therefore, to describe the states of shock-compressed water within this temperature and pressure range, one can use, as before, the equation of state in the form of (2) and (3) and obtain the values of heat capacity.

The thus obtained values of heat capacity are shown along the approximation curve $T(P)$ in Fig. 4.

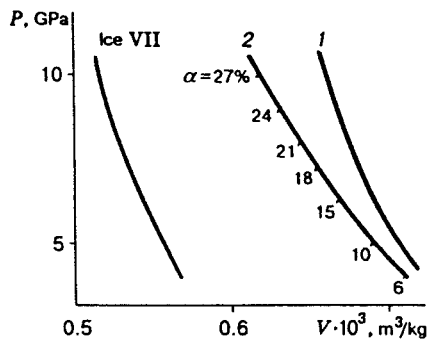


Fig. 3

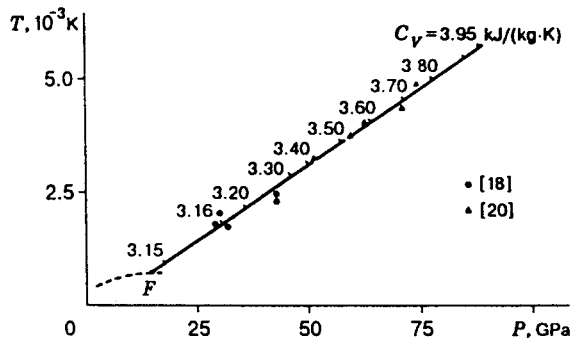


Fig. 4

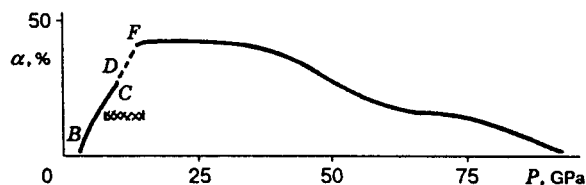


Fig. 5

One can see that the heat capacity increases from ~ 3.15 to 4 $\text{kJ}/(\text{kg} \cdot \text{K})$, which is characteristic of liquid water. One can assume that the lower values of C_V are caused by a mixture of liquid water and another phase whose heat capacity is lower than that of the liquid. This second phase can be either a vapor or a solid phase, for example, ice VII. As was noted above, the thermal energy in state C is insufficient for water to be evaporated. Therefore, we assume that at section 3 of the shock adiabat in the pressure range up to ~ 90 – 100 GPa there is also a mixture of water with ice VII with a variable fraction of the latter.

As was mentioned above, the time (the duration of a shock wave) of realization of a shock-compressed state with certain parameters is comparable with the time of phase transition. Because of this, one can expect that states with the same parameters (for example, P , V , and T) under dynamic compression can differ from those under static compression. In particular, either an incomplete phase transformation with a new-phase concentration less than unity, or the formation of a new phase in states with significantly higher parameters than those in statics can occur in dynamics. In other words, under shock-wave compression the formation of a new phase can be "retarded," i.e., the region of the existence of a new phase is shifted toward higher values of state parameters, in particular, pressure and temperature. Thus, one can expect inertial conservation of the previous phase and retardation of the appearance of a new phase, i.e., inertial retardation of the phase transition. Let us use the well-known proposition that a shock adiabat is not an aggregate of successive states of the tested material, but an aggregate of states such that the material can be transferred into each of these from the initial state by an individual shock-wave action. This circumstance assists in understanding the effect of "retarded" formation of a new phase under dynamic, in particular, shock-wave compression as opposed to static compression of material, which is supported by the double intersection of the shock adiabat of water and the melting curve of ice VII (the pairs of points A–B and C–D).

We assume, as before, that the heat capacity of the mixture is the additive sum of the products of heat capacities of the mixture components by their mass fractions. In this case, one can obtain a change in the mass fraction of ice VII with pressure $\alpha(P)$ for the pressure range under study in section 3 of the shock adiabat of water. Figure 5 shows the curve of $\alpha(P)$. As the pressure increases from 14.2 GPa in state F to 90 – 100 GPa, α decreases from $\sim 42\%$ to 0 . Figure 5 also shows the change in α for section 2 of the shock adiabat and states B, C, D, and F. Section DF in Fig. 5 is shown by a broken curve, since no quantitative data on the

concentration of ice VII in this section has been obtained. However, the existence of ice VII at this section can be confirmed by the experimental results of Mineev [14] on measuring the viscosity of shock-compressed water. He studied the pressure of range 4–15 GPa [14] and concluded that, at least, in the range of 7–15 GPa the solid phase of ice VII is present in shock-compressed water (shaded region in Fig. 5).

The author does not deny other possible mechanisms of the behavior of shock-compressed water at the upper section, for which, in particular, the question on the structure of water remains open.

The author is indebted to Prof. O. B. Naimark for interest in the work and valuable discussion of particular aspects and the entire work.

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