

Second critical point and low-temperature anomalies in the physical properties of water

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A metastable P - T phase diagram is calculated for water on the basis of a two-level model. The line of transitions between low-density amorphous ice and high-density amorphous ice terminates at a critical point with the coordinates $T_c = 225$ K, $P_c = 0.33$ kbar. The proximity of this critical point to atmospheric pressure is responsible for the low-temperature anomalous behavior seen in the physical properties of water at standard pressure. The temperature dependence of the specific volume and that of the specific heat calculated in this model agree well with experimental data. © 1994 American Institute of Physics.

Anomalies in the physical properties of water near the crystallization point at standard pressure and at elevated pressures have attracted research interest for a long time now. Measuring these anomalies has been the goal of a huge number of studies (see some reviews^{1,2}). Nevertheless, there are still no models which yield quantitative descriptions or even qualitative explanations of the physical nature of these anomalies. The numerous equations of state which have been proposed for water are purely empirical^{2,3} and have little in the way of physical content.

Some important experimental results have recently been published by Whalley's group.⁴⁻⁷ In studying the behavior of ice at low temperatures and high pressures, they observed two modifications of amorphous ice, which differ in density by 20%: low-density amorphous ice (lda) and high-density amorphous ice (hda). It was established that the lda-hda conversion is a reversible first-order phase transition with significant thermal and volume effects. An attempt was made to construct a metastable phase diagram of water, but the lda-hda equilibrium line proposed in Ref. 7 had a shaky experimental foundation, and it ran to a stability region of water, where no anomalies are observed.

A further step toward an understanding of the experimental results on the different types of amorphous ice was taken by Pool *et al.*,⁸ who suggested that the lda-hda phase-transition line terminates at a critical point, at a pressure slightly above atmospheric and at a temperature below 0 °C. They suggested that the anomalies observed in various physical properties of water in its supercooled state were due to supercritical phenomena. Using a molecular-dynamics method, Pool *et al.*⁸ and Stanley *et al.*⁹ calculated the lda-hda phase-transition line, determined the coordinates of the critical point and of the lines at which both phases lose their stability in the P - T region, and achieved a fairly good agreement between theory and experiment in terms of anomalies in the density, the isothermal compressibility, and the specific heat of water.⁹

While quite versatile, the molecular-dynamics method has several serious shortcomings. In order to derive correct results by this method it is necessary to have some initial data on the interatomic potentials. These data must generally be refined in the course of the calculations. For a final choice of the shape of the potentials it is necessary to carry out trial calculations with various values of the coefficients, at the cost of considerable computer time. In addition, this method does not generate simple analytic expressions for the thermodynamic potential or for the changes in the anomalous behavior of various physical properties with the temperature and the pressure.

In this letter we propose the use of a two-level model which is far simpler and no less effective, for calculating a metastable P - T phase diagram and anomalies in the temperature dependence of the specific volume and specific heat at atmospheric pressure. This model has previously proved successful in describing the phase diagram of the isomorphic conversion of cerium.¹⁰

Here are the basic positions of the model:

- (1) Two types of clusters, differing in atomic configuration and energy, exist in water in its normal and supercooled states.
- (2) The atomic configurations of the clusters correspond to the structure of the short-range order of the lda and hda modifications of amorphous ice.
- (3) The difference between the energies of the clusters is a linear function of the degree of excitation of the system, i.e., of the concentration of the clusters with the higher energy.
- (4) Water may be thought of as a mutual solution of these clusters, which are then taken to be the "components" of a binary system.
- (5) The expression for the thermodynamic potential yielded by this model is valid for both the liquid and amorphous states of water.

As was shown in Ref. 10, the Gibbs thermodynamic potential of such a system can be written

$$G = G_1 c + G_2 (1 - c) + U c (1 - c) + RT \{ c \ln c + (1 - c) \ln (1 - c) \},$$

where G_1 and G_2 are the Gibbs potentials of the pure lda and hda components, c and $(1 - c)$ are the respective concentrations by volume of these components, and U is the mixing energy.

In contrast with solutions of ordinary two-component systems, for which c is an external parameter, the quantity c in this model is an internal parameter. It is found by minimizing the thermodynamic potential G with respect to c , i.e., from the condition

$$\frac{\partial G}{\partial c} = (\Delta E^0 - T \Delta S^0 + P \Delta V^0) + (1 - 2c)U + RT \ln \frac{c}{1 - c} = 0,$$

where $\Delta E^0 = E_2 - E_1$, $\Delta S^0 = S_2 - S_1$, and $\Delta V^0 = V_2 - V_1$. The subscripts 1 and 2 refer to the lda and hda states, respectively. Following the customary procedure in calculations of the properties of regular binary solutions, we assume that ΔE^0 , ΔV^0 , ΔS^0 , and U are independent of T and P within the P - T region under consideration. In this case all we need to calculate the Gibbs potential $G(T, P, c)$ and thus all other thermodynamic properties of water are the values of these four constants.

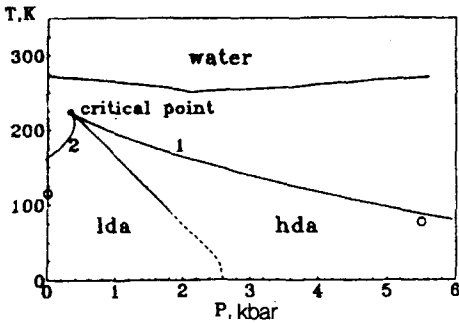


FIG. 1. Metastable P - T phase diagram of water at low temperatures. 1—Line at which the lda phase loses its stability; 2—line at which the hda phase loses its stability; open circles—experimental data.^{5,6} The proposed lda-hda transition line at low temperatures is shown by the dashed line.

The volume change ΔV^0 in the lda \rightarrow hda transition found at $P \approx 5.5$ kbar is, according to Ref. 5, -4.0 ± 0.3 cm³/mole. The equilibrium pressure of this transition at 77 K was taken to be ~ 2 kbar in Ref. 7. Correcting ΔV^0 to equilibrium pressure, we find -3.8 cm³/mole, which is the figure used in the calculations. An extrapolation of the lda \rightarrow hda equilibrium line to atmospheric pressure should occur in a temperature interval corresponding to the most pronounced low-temperature anomalies in thermodynamic properties, which is near 228 K (Refs. 1 and 11). On the basis of the coordinates of these two points of the proposed equilibrium line, we estimated the values of the parameters ΔE^0 and ΔS^0 for use in the initial iterations in the calculation of the metastable diagram for water. The actual calculations of the T - P phase diagram and of the equilibrium properties on the basis of the model proposed here are described in detail in Refs. 12 and 13. Here we would simply point out that the function $G_{T,P}(c)$ is a curve with either one or two minima, depending on the values of the parameters T and P . The $T(P)$ curves along which one of the minima becomes degenerate determine the lines at which the corresponding phase loses its stability. The condition $G^{\min}(c_1) = G^{\min}(c_2)$ determines the line of the phase equilibrium in the T - P plane, which terminates at the critical point. The critical temperature and the mixing energy are related by $T_c = U/2R$, so the parameter U can be estimated from the value $T_c \approx 228$ K. The optimum values of the parameters ΔE^0 , ΔS^0 , and U , found by minimizing the deviation of the calculated anomalous part of the specific volume, $V = f(T)$, from the experimental result, are 250 cal/mole, 1.0 cal/(mole·K), and 900 cal/mole, respectively. These values were used in the subsequent

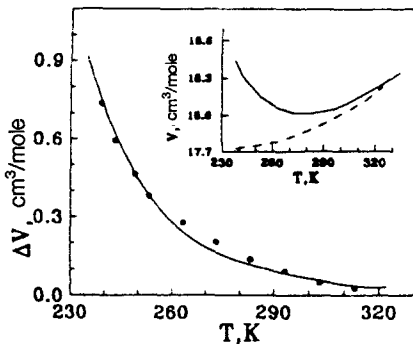


FIG. 2. Temperature dependence of the anomalous part of the specific volume at atmospheric pressure. Points—Experimental data;^{3,14} solid curve—theoretical. The inset shows the temperature dependence of the total specific volume (solid curve) and an extrapolation of the normal component to low temperatures (dashed curve).

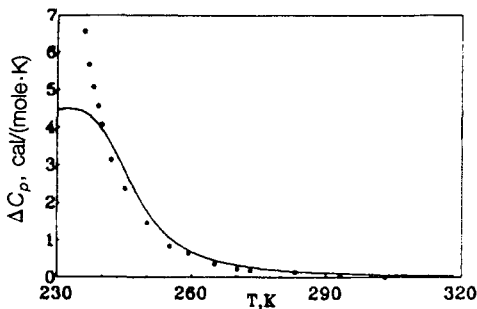


FIG. 3. Temperature dependence of the anomalous part of the specific heat at atmospheric pressure. Points—Experimental data;¹¹ solid curve—theoretical.

calculations. The anomalous part of the volume, $\Delta V(T)$, was found by subtracting from the experimental $V=f(T)$ dependence^{3,14} the normal component extrapolated from a region far from the critical point and far from supercritical anomalies.

Figure 1 shows the lda-hda phase-equilibrium line in the $P-T$ plane, along with the instability lines of the lda phase (curve 1) and of the hda phase (curve 2). The refined coordinates of the critical point are $T_c=225$ K, $P_c=0.33$ kbar. These values are significantly different from the values found in Ref. 9 (185 K and ~ 1.5 kbar according to Fig. 9 of that paper). Figure 2 shows the temperature dependence of the anomalous part of the specific volume constructed from the experimental and theoretical results. Over the entire range of the anomalous behavior of the volume of water we see a good quantitative agreement between theory and experiment. A more sensitive test of the applicability of the model is the behavior of thermodynamic properties which are determined by the second derivatives of the thermodynamic potential. Accordingly, we also show results calculated for the anomalous part of the specific heat of water at low temperatures. Figure 3 shows experimental and theoretical values of the specific heat at low temperatures. To determine the anomalous part of the specific heat from the experimental data, we used a procedure like that used for the specific volume; we also used results from Ref. 11, where there was a detailed discussion of the validity of this type of data analysis. The agreement between theory and experiment is good over the entire temperature interval 240–320 K. The deviation of the theoretical values from the experimental values at lower temperatures is apparently due to an increased role of fluctuations as the critical point is approached. Fluctuations are ignored in this model. The calculated anomalies in the compressibility and thermal expansion of water also agree well with experimental data. The two-level model proposed here thus gives a completely satisfactory description of all the principal anomalies in the thermodynamic properties of water in its supercooled state.

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