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Kh. I. AMIRKHANOV, G. V. STEPANOV, B. A. MURSALOV

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Abstract

Full Text

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PHYSICAL CHEMISTRY

Academician of the Academy of Sciences of the Azerbaijan SSR Kh. I. AMIRKHANOV, G. V. STEPANOV, B. A. MURSALOV

THE HEAT CAPACITY C_V OF HEAVY WATER NEAR THE CRITICAL POINT

Experimental data on the properties of heavy water are available only for a limited range of temperatures and pressures, and data from a direct investigation of the heat capacity C_V are entirely absent from the literature. In this connection, in the present work an experimental study was carried out of the heat capacity at constant volume of heavy water containing 99.8% deuterium. The heat capacity C_V was measured along several isochores near the critical point by means of an adiabatic calorimeter described earlier in work ([1]).

The calorimeter was calibrated with ordinary water. Then, in order to reveal differences in the behavior of ordinary and heavy water, the study of C_V for D_2O was preceded by a study of the heat capacity of ordinary water along the very same isochores with one and the same calorimeter.

As follows from Fig. 1, the transition from the two-phase state to the single-phase state for the specific volume $V = 2.5$ cm^3/g for H_2O occurs abruptly, whereas for heavy water it is smooth, though sharp. For the specific volume $V = 2.7$ cm^3/g, the heat capacity C_V for H_2O and D_2O changes smoothly. As for the numerical difference in the values of the heat capacity C_V of H_2O and D_2O, as can readily be seen from Fig. 1, the values of C_V adjacent to the boundary curve from the side of the two-phase region are higher for deuterium oxide than the heat-capacity values of ordinary water on both of the indicated isochores. The heat capacity C_V in the single-phase region at temperatures 374-380° for D_2O is lower than for H_2O.

Fig. 1. Heat capacity C_V along isochores: *a*—heavy water, *b*—ordinary water

In order to determine whether, throughout the entire two-phase region, the value of the heat capacity of heavy water exceeds the value of C_V for H_2O, a study of C_V in the heterogeneous region was carried out for the specific volume $V = 2.5$ cm^3/g at $T = 300°$. It turned out that at this temperature the heat capacity C_V for D_2O is 1.318 cal/g $\cdot$ deg, and for H_2O 1.409 cal/g $\cdot$ deg, i.e., the heat capacity C_V of D_2O is lower than the heat capacity C_V of H_2O. The increase in the heat capacity C_V of heavy water (by 15%) in the immediate vicinity before

with the transition is apparently explained by the proximity of the isochores $V = 2.5$ cm^3/g and $V = 2.7$ cm^3/g to the critical specific volume.

Indeed, for a specific volume $V = 2.5$ cm^3/g of ordinary water the transition occurs abruptly and is removed from the critical isochore by an amount $\Delta V = 0.73$ cm^3/g ($V_k = 3.23$ cm^3/g). At the same time, along the isochore $V = 2.5$ cm^3/g for D_2O the transition occurs smoothly, and its possible distance from the critical isochore is 0.24–0.46 cm^3/g, depending on the value of V_k reported by various authors (2) (from $V_k = 2.74$ cm^3/g to $V_k = 2.96$ cm^3/g).

Since the heat capacity C_V of D_2O and H_2O was investigated with one and the same calorimeter under the same conditions, the errors in determining the heat capacity C_V in both cases will naturally be the same, since the power of the internal heater remains unchanged, the water equivalent is constant, and the temperature measurement is governed by a constant error. Consequently, with comparatively high accuracy, i.e., within the accuracy of the investigation of C_V for H_2O (1), one can find the values $\Delta C_V = C_V^{H_2O} - C_V^{D_2O}$.

Indeed, since $C_V = \frac{1}{m}\left(\frac{\Delta Q}{\Delta T} - A\right)$, where A is the water equivalent and m is the mass of the liquid under study, then

$$\Delta C_V = \frac{1}{m}\left(\frac{\Delta Q_1}{\Delta T} - \frac{\Delta Q_2}{\Delta T}\right) = \frac{ki\nu(\Delta\tau_1 - \Delta\tau_2)}{m \cdot \Delta T},$$

where $\Delta\tau_1$ and $\Delta\tau_2$ are, respectively, the heating times of ordinary and heavy water.

Consequently, an additional error in determining ΔC_V is introduced only by the heating time for one temperature step of the bridge circuit. Since the error in determining C_V caused by the inaccuracy of time recording is 0.03%, the overall error in determining ΔC_V increases correspondingly by this amount (1).

In this connection, it proved possible to determine the difference in heat capacities $C_V^{H_2O} - C_V^{D_2O}$ with sufficient accuracy. In the single-phase region studied by us, from 374 to 380°, it changes continuously and, for $V = 2.5$ cm^3/g, amounts to a decrease from 0.6 cal/g $\cdot$ deg at 380°, and for $V = 2.7$ cm^3/g, from 0.32 cal/g $\cdot$ deg at 374° to 0.053 cal/g $\cdot$ deg at 379°.

The temperature was determined with the aid of an individually calibrated copper-constantan thermocouple, preliminarily checked against a resistance thermometer at the transition points. The difference was 0.02–0.05°. Consequently, the transition temperature was recorded with precisely this accuracy. The transition temperature for ordinary water was recorded as the same as in the published work (3). The same thermocouple, for heavy water at the moment of transition along the isochore $V = 2.5$ cm^3/g, recorded the temperature $T = 371.0°$. For the specific volume $V = 2.7$ cm^3/g, $T = 371.24°$. Such a slight dependence of the transition temperature on the specific volume, as already noted earlier (3), is characteristic of the vicinity of the critical point. The magnitude of the critical temperature, on the basis of the above C_V data, cannot yet be established accurately. However, it may be assumed that the value of T_k must exceed 370.9°, which is given by some authors (4, 5).

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Note: Figure translations are in progress. See original paper for figures.

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