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THE HEAT CAPACITY AT CONSTANT VOLUME OF WATER AND WATER VAPOR IN THE ONE- AND TWO-PHASE REGIONS ADJOINING THE BOUNDARY CURVE, INCLUDING THE CRITICAL POINT

In works (^{1}), the heat capacity c_v of water and water vapor was investigated in various regions of the phase diagram with a temperature interval of 0.32°, with an accuracy of 1.2–3.2%.

In the present work, in order to find hidden features of the behavior of the substance along the boundary curve near the critical point that had not been detected in previously published works, the heat capacity c_v was determined with the smallest possible temperature step, 0.08°. Taking the value of the heat capacity c_v obtained in this way as the true one, we can find its value in the immediate vicinity of the boundary curve (0.04°). Further, to reveal the dependence of c_v on the specific volume, which is sharply manifested near the critical point, the step in determining c_v with respect to specific volume was also reduced to the smallest possible value (0.1 cm^3/g).

An increase in the accuracy of measurement was achieved by further improving the integral adiabatic calorimeter: the wall thickness of the inner shell of the calorimeter was reduced to 1 mm, and the gap between the shells to 1.5 mm. This made it possible to reduce the heat capacity of the calorimeter to a value 7–8 times smaller than the heat capacity of the liquid under study, and thereby to increase the experimental accuracy along the left-hand boundary curve, including the critical region, to 0.3–1%, and along the right-hand curve to 1-2.5%.

The heat capacity c_v was investigated along the boundary curve for 48 isochores. For each isochore, two experimental points were determined on the side of the heterogeneous and homogeneous regions adjoining the boundary curve. Thus, near the boundary curve, 96 experimental points were obtained, 34 of which had previously been found experimentally (^{1}). A repeated study with the improved

Fig. 1. Family of curves of the temperature run of isochoric heat capacities near the critical point

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calorimeter showed that for all experimental points (^{1}), with the exception of one ($V = 21.64$ cm^3/g, $t = 300°$), the heat capacity did not fall outside the limits of measurement accuracy, which (within the error) confirms the correctness of the previously published data (^{1}).

Studies of the heat capacity were carried out along 15 isochores in the vicinity of the critical point; their results are presented in Fig. 1 as a family of curves of isochoric heat capacities as functions of temperature and specific volume when the substance passes from the heterogeneous state into the homogeneous one. The numerical value of the function $c_v(V,T)$ is given in detail in works (^{2}). A comparison of the results (^{1}), where it was possible to approach the boundary curve to within 0.16°, with the present experiment in the vicinity of the critical point shows that for volumes 2.6 cm^3/g $< V <$ 3.8 cm^3/g, when approaching the line of the beginning of the transition from the two-phase region by $0.16° - 0.04° = 0.12°$, c_v increases by 20-25%, which is hundreds of times greater than the increase in c_v when approaching the boundary curve far from the critical point by the same temperature increment. This fact suggests that at the critical point and near it, at the moment of transition, the heat capacity c_v increases to a very large value, not detectable by direct experiment—

that require measurements to be made with a very small temperature step.

For isochores $V \leqslant 2.6$ cm^3/g and $V \geqslant 3.8$ cm^3/g, the phase transition occurs discontinuously, whereas for isochores with specific volume 3.7 cm^3/g $>$ $V > 2.6$ cm^3/g the transition of the substance from the two-phase state to the single-phase state occurs smoothly, though sharply. Far from the critical point (2.6 cm^3/g $\geqslant V \geqslant 3.8$ cm^3/g), the beginning and end of the phase transition correspond to definite temperatures of the substance in the single-phase and two-phase states adjacent to the boundary curve. These characteristic temperatures, corresponding to the beginning and

Fig. 1. Family of curves of the temperature dependence of isochoric heat capacities near the critical point

the end of the transition for the given volumes for this substance, differ from the transition temperature by one half of the temperature step ΔT with which the heat capacity c_v was measured during the phase transition.

This indicates the existence of a sharp boundary curve separating the two-phase state of the substance from the single-phase state. Near the critical point, as well as far from it, the beginnings of the transitions for isochores 2.6 cm^3/g $<$ $V <$ 3.8 cm^3/g correspond to definite temperatures (Fig. 1) characteristic

Fig. 2

Figure 2: Fig. 2

of the given substance, but the ends of the transitions do not correspond to definite temperatures and heat capacities, because the transition occurs not discontinuously but smoothly, extended over a certain temperature interval until a pure phase is formed.

On moving away from the critical specific volume on both sides of it, owing to the decrease in the extent of the transition region (Fig. 1), the temperatures corresponding to the beginning of the pure phase decrease and, at specific volumes of 2.6 and 3.8 cm^3/g, become equal to the characteristic temperatures of the state of the substance on the side of the homogeneous region adjacent to the boundary curve.

This experimental fact gives us grounds to conclude that there is no sharp boundary curve separating the two-phase state of the substance from the single-phase state near the critical point in the interval of specific volumes from 2.6 to 3.7 cm^3/g, and to confirm the existence of a transitional (criti-

···region of the state of the substance (1). From the thermodynamic point of view, the state of the substance in the intermediate region is very mobile, since fluctuations are the primary cause of this type of transition.

As is seen from Fig. 1, the transition energy Q for isochores $V \leq 2.5$ cm^3/g and $V \geq 3.8$ cm^3/g is equal to zero, since the transition occurs discontinuously. It appears beginning with the isochore $V = 2.6$ cm^3/g and increases as the critical point is approached. In the transition along the critical isochore it reaches its maximum value. As one moves away from the critical isochore toward larger volumes, the magnitude of the transition energy decreases and, in the transition along the isochore $V = 3.8$ cm^3/g, disappears. Thus, the transition region of the state of the substance covers a rather broad interval of specific volumes and separates the two-phase region from the one-phase region. It begins 0.15–0.2° below the critical temperature and disappears above it.

Fig. 2. Maximum of the heat capacity in the two-phase region adjacent to the boundary curve

The smooth change of the heat capacity near the critical point during the transition to one phase cannot be explained by the effect of gravity. This effect leads to a dependence of the density on the height of the vessel in which the experiment is carried out. It is necessary to note that the investigation of the heat capacity c_v is performed with intensive mixing not only in the horizontal layers of the liquid, but also, by means of a serpentine heater, over the height of the calorimeter, in contrast to visual investigations of density, which require the substance in the vessel to be at absolute rest. In addition, investigations of the heat capacity c_v over a number of years were carried out with a spherical calorimeter of different diameter (for d from 35 to 90 mm), and, despite the fact that the height of the vessel in the limiting cases differed by approximately a factor of 3, the results of the investigation show that the temperature dependence of c_v, without undergoing a discontinuity, is accompanied by a smooth change during phase transitions near the critical point. Consequently, it may be asserted that the smooth temperature dependence of the heat capacity c_v is not connected with the influence of gravity, but is inherent in the behavior of the substance itself, proving the existence of a transition region between the heterogeneous and homogeneous phases.

It is known that determining the critical volume of a substance is a rather difficult problem. In work (3) we determined the critical isochore

$V = 3.23$ cm^3/g. The present work made it possible to determine more accurately the value of the critical specific volume. For this purpose the maxima of c_v along isochores were determined: $V = 3.23$; 3.24; 3.25; 3.26 cm^3/g. As can be seen from Fig. 1, the maximum of the maxima of the isochoric heat capacities for the isochore $V = 3.26$ cm^3/g is too low and lies outside the limits of the experimental error. Consequently, the volume $V = 3.26$ cm^3/g, accepted in the literature as critical, does not correspond to reality. The heat-capacity maxima c_v corresponding to the indicated isochores ($V = 3.23$; 3.24; 3.25 cm^3/g) differ from one another practically within the limits of the experimental error. To refine the value of the critical isochore, the transition-energy values along these isochores were additionally compared. The calculation showed that for the isochore $V = 3.23$ cm^3/g the transition energy $\Delta Q = 1.30$ cal/g, for the isochore $V = 3.24$ cm^3/g ΔQ reaches the maximum value 1.38 cal/g, and for the isochore $V = 3.25$ cm^3/g $\Delta Q = 1.35$ cal/g, which gives grounds for taking $V = 3.24$ cm^3/g as the critical isochore.

According to the theory of V. K. Semenchenko (^{4}), and also from the data of Fig. 1, in the interval of specific volumes 2.5—3.8 cm^3/g the smooth temperature course of c_v along 15 isochores crosses the critical isotherm, and in doing so the state of the substance is not accompanied by any changes. This fact, and the results of the investigation (^{1}), show that the critical isotherm has no physical meaning and, consequently, as is unfortunately erroneously stated in textbooks and monographs, it cannot be the boundary line between liquid and vapor.

Figure 2 presents the maxima of the heat capacity c_v along the boundary curve from the side of the two-phase region in the coordinates (c_v, T) and (c_v, V). The linear dependence of the half-sum of c_v' and c_v'' on the mean density of the liquid —vapor, similar to the rectilinear diameter, is determined in (^{1b}). Owing to the absence of sufficient experimental data, it was not possible to establish its course exactly near the critical point. As can be seen from Fig. 2a, it deviates from the straight line, bending upward, and ends at the point of intersection of the curves c_v' and c_v'', the temperature of which is 374.03°. As indicated above, this temperature is 0.04° below the temperature of the point lying on the line of the beginning of transition along the critical isochore. Consequently, the true temperature of the beginning of transition along the critical isochore will be

374.07°. This temperature is 0.08° below the critical temperature accepted in the literature. It should be noted that far from the critical point the transition temperatures were determined as the half-sums of the temperatures corresponding to the beginning and end of the transitions of the isochoric heat capacity. Near the critical point, in connection with the smooth transition of the substance into the homogeneous state, as indicated above, the end of the transition and its temperature can be determined only arbitrarily, and if the temperature of the end of the sharp change in c_v is taken as the temperature of the end of transition, then the critical temperature of water will be 374.21°.

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