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## Abstract

## Full Text

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# INVESTIGATION OF THE HEAT CAPACITY $c_v$ OF WATER AND WATER VAPOR IN THE CRITICAL REGION

There are no data in the literature on the heat capacity $c_v$ of water and water vapor and its dependence on temperature and pressure, which is evidently explained by the methodological difficulties of the experiment ($^1$). To determine the heat capacity $c_v$, we used an adiabatic calorimeter with thermoelectric temperature regulation, previously described in ($^2$).

As is known, the study of the behavior of heat capacity, besides achieving adiabatic conditions in the calorimetric system, requires equilibrium of the temperature field; in the present case this is facilitated by the fact that in the critical region, where the coefficient of thermal expansion

$$\alpha = -\frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_p$$

attains very large values, the Grasshof number also acquires large values. For turbulent motion to arise in a liquid, it is necessary to satisfy the condition $\mathrm{Gr} \sim 5 \cdot 10^4$ ($^5$). In our experiment with a one-component substance, at a temperature difference of 0.01°, Gr reached $10^7$. Thus, the natural development of turbulent motion in the critical region contributes to the most rapid attainment of temperature equilibrium. The very design of the calorimeter we used, with metal walls of thickness reaching 7 cm, considerably accelerates the process of temperature equalization; this is confirmed by the identical readings obtained from three thermocouples arranged vertically along the height of the liquid in the calorimeter.

In the course of the experiment, temperature equilibrium between the phases ($T_1 = T_2$) was achieved by waiting according to the thermocouple readings and equality of pressures ($p_1 = p_2$); therefore it may be asserted that complete thermodynamic equilibrium was reached in the system, i.e., $\varphi_1(p, T) = \varphi_2(p, T)$, and that, consequently, the experiment could be carried out without stirring the liquid.

In the calorimeter of the described design ($^2$), the heat capacity $c_v$ of water and water vapor was determined at various specific volumes over temperature

Figure 1

Figure 1: Figure 1

intervals not exceeding 0.6°. For each specific volume the measurements were repeated several times. The total maximum error in determining the heat capacity $c_v$ is $\sim 2.5\%$.

## Experimental Results

Figure 1 shows the course of the change in the heat capacity of water during the transition from the two-phase state to the single-phase state. Far from the critical point, the heat capacity $c_v$, on crossing the boundary curve, undergoes an abrupt change (Fig. 1, 1), but as the critical point is approached, i.e., with increasing specific volumes, the discontinuous character of the change in $c_v$ is disturbed, although the absolute value of these jumps in the heterogeneous region continues to increase ($^{4-6}$).

Figure 2 gives the boundary curve of water in $(T-v)$ coordinates. The boundary curve in $(p-v)$ coordinates is constructed analogously, with the critical region clearly distinguished.

The method for constructing the boundary curve with the critical region indicated on it is based on the following experimental fact discovered by us (see Figs. 1, 2): far from the critical region, upon crossing the boundary curve, the heat capacity $c_v$ of the two-phase state drops discontinuously to the value of the heat capacity of the single-phase state, whereas in the critical region, beginning with a specific volume of 2.5 cm$^3$/g and up to a specific volume of 4.15 cm$^3$/g, the discontinuous change in $c_v$ is disrupted, and the transition is spread over a considerable temperature interval, reaching 4.5° for water. The temperature interval from the moment when the discontinuous change in the heat capacity $c_v$ is disrupted increases as the critical point is approached, reaching near it a maximum value of 4.5°. With a further increase in the specific volume the temperature interval decreases, reaching its minimum value of 0.6° at the specific volume $v = 4.15$ cm$^3$/g. A further increase in specific volume leads to a discontinuous change in $c_v$. Thus, for water the critical region is bounded in volume by the interval from $v = 2.5$ cm$^3$/g to $v = 4.15$ cm$^3$/g, and in temperature by the interval 4.5° ($^{12}$).

**Fig. 1.** Temperature dependence of the heat capacity of water in the critical region for various specific volumes: 1 –1.925, 2 –2.415, 3 –4.160, 4 –2.870, 5 –3.235 cm$^3$/g

The critical region of water found by us in the coordinates $(T, v)$, bounded by a temperature interval of 4.5°, is in satisfactory agreement with the theoretical calculations of Band, who gives for this region a temperature interval of 6.5°. The diagram in the coordinates $(P, v)$ is analogous to the diagram $(T, v)$.

Figure 2

Figure 2: Figure 2

Fig. 3

Figure 3: Fig. 3

**Fig. 2.** Boundary curve of water, constructed from the behavior of the heat capacity $c_v$ during the transition from the heterogeneous phase to the homogeneous one

In Fig. 3 the dependence of $c_v$ of water in the supercritical region on the specific volume is shown for three isotherms. The experimental curves have the following character. As the critical volume is approached along the isotherms, the heat capacity increases, reaching finite maximum values; moreover, like the heat capacity $c_p$ in the supercritical region ([7]–[10]), the heat capacity $c_v$ has a maximum.

With a further increase in the specific volume, i.e., as one moves away from the critical point, the heat capacity decreases sharply. At the critical point the absolute value of the maxima of the heat capacity $c_v$ is attained. At temperatures above the critical value the relative maxima decrease. As is seen from Fig. 3, the heat capacity, contrary to the theory of van der Waals, is a function not only of temperature but also of volume.

In Fig. 4 are given the maximum values of the heat capacity $c_v$ upon crossing the boundary curve. According to the theory of V. K. Semenchenko ([5], [11]), the heat capacity upon crossing the boundary curve reaches its maximum value at the critical point. Hence it follows that the critical volume must correspond to the maximum of this “cri-

maximums.” For water this maximum corresponds to the volume $v_k = 3.23$ cm$^3$/g.

Thus, the value of the critical volume of water obtained by us, equal to $v_k = 3.23$ cm$^3$/g, differs by 2.5% from the exactly coinciding values of the critical specific volume ($v_k = 3.30$ cm$^3$/g) according to the VTI tables, the new table of M. P. Vukalovich ([12]), and the determination of V. A. Kirillin and V. N. Zubarev ([13]).

**Fig. 3.** Dependence of the heat capacity $c_v$ of water on specific volume along critical and supercritical isotherms: 1—381°, 2—773°, 3—374.2°.

## Discussion of results

The results of our experiments show that, far from the critical point, the heat capacity of water, when it passes from the two-phase state into the single-phase state, changes discontinuously; moreover, the absolute magnitude of these jumps

Fig. 4

Figure 4: Fig. 4

increases as the critical region is approached, reaching its maximum at the critical point. From the classical point of view, the increase in the heat capacity $c_v$ of water in the two-phase state with increasing temperature and the discontinuous drop in $c_v$ upon its transition to the single-phase state can be explained by the fact that, in the transition region, the amount of heat supplied is spent not only on increasing the temperature of the separate phases, but also on the breaking of molecular bonds of a multimolecular compound, which occurs in the process of dissociation of molecules. The heat of vaporization cannot substantially affect the course of the heat capacity, since its magnitude tends to zero as the critical point is approached ([14]), whereas the magnitude of the jump in $c_v$ increases. Upon transition to the single-phase state the processes of dissociation and vaporization suddenly cease, which leads to a discontinuous lowering of $c_v$. The breaking of molecular bonds, which amounts to a decrease in the degree of association, naturally depends on temperature and pressure. Therefore, at the critical point the number of bonds being broken and their intensity reach a maximum, which leads to the maximum increase in the value of $c_v$. For liquids the region of dispersion, i.e., the region in which the process of dissociation takes place, must depend on the degree of association of the molecules. Therefore, for different liquids the region of the critical state must be different. The molecular mechanism of the maxima of the heat capacity at supercritical temperatures (see Fig. 3) should be analogous to that described above. With the aid of the van der Waals equation it is impossible to explain, either qualitatively or quantitatively, the behavior of the substance considered above at temperatures different from the critical one.

**Fig. 4.** Maximum values of the heat capacity $c_v$ of water in the heterogeneous region for different specific volumes.

Indeed, rewriting the van der Waals equation in the form

$$p = \frac{RT}{v-b} - \frac{a}{v^2},$$

we find

$$\left(\frac{\partial^2 p}{\partial T^2}\right)_v = 0.$$

Consequently,

$$\left(\frac{\partial c_v}{\partial v}\right)_T = T\left(\frac{\partial^2 P}{RT^2}\right)_v = 0,$$

i.e., the heat capacity $c_v$ should not depend on volume and may be a function only of temperature. Experiment shows (see Fig. 3) that this condition is satisfied only for the maxima of the critical and supercritical isotherms.

For any other specific volume the condition $\left(\frac{\partial c_v}{\partial v}\right)_T = 0$ is not satisfied for the critical and supercritical isotherms, i.e., the van der Waals equation is not applicable to them.

It is evident from Fig. 3 that the maxima of $c_v(v)$ lie on the critical isochore, which is almost rectilinear.

The presence of maxima of the heat capacity $c_v$ in the supercritical region as a function of temperature at constant volume, analogous to what occurs for $c_p$ (8–11), confirms the existence of anomalous behavior of the heat capacity in this region.

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