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Table 1

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Abstract

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HEAT CAPACITY c_v OF WATER AND WATER VAPOR DURING PHASE TRANSITIONS AND AT SUPERCRITICAL PARAMETERS

In work ([1]) the heat capacity c_v of water and water vapor was investigated along the left part of the saturation curve. The present work is devoted to the heat capacity c_v in the two-phase region and in the region of superheated vapor (gas) along the right part of the saturation curve. The measurement method and the estimate of the error in determining the heat capacity c_v are given in work ([2]). In the temperature region where comparison with calculated data ([3]) was carried out, in the two-phase state of the substance and in the liquid phase the error is 2%, while in the vapor phase it reaches 3%. Table 1 gives the values of c_v found in work ([3]) by calculation along the right part of the saturation curve from the side of the two-phase and one-phase states of the substance, and their comparison with the experimental data of the present work. It is known that derivatives of a number of thermodynamic quantities, including those entering into the determination

Table 1

T_{sat}, °C	Two-phase region: exp.	Two-phase region: calc. ([3])	Two-phase region: $\frac{c_v \text{ exp} - c_v \text{ calc}}{c_v \text{ exp}} \times 100\%$	One-phase region: exp.	One-phase region: calc. ([3])	One-phase region: $\frac{c_v \text{ exp} - c_v \text{ calc}}{c_v \text{ exp}} \times 100\%$
300	4.890	4.859	0.633	0.820	0.715	12.8
320	4.272	4.355	−1.94	0.840	0.790	6.0
340	3.730	(3.862)	−3.53	0.901	(0.836)	7.21
360	3.33	–	–	1.075	–	–
370	3.26	–	–	1.174	–	–

of c_v, in the two-phase state of the substance are determined more accurately and more reliably than in the one-phase state. Evidently, on this basis and, perhaps, for a number of other reasons, the author of article ([3]) considers that

Figure 1 and Figure 2

Figure 1: Figure 1 and Figure 2

the calculated data for c_v along the saturation curve from the side of the two-phase region are more reliable than c_v in the liquid and vapor phases adjoining the saturation curve. Indeed, the experimental data on c_v in ([1]) and in the present work in the two-phase region agree well with the calculated data ([3]). In the liquid phase up to 100° the experimental data agree satisfactorily with the calculated data, while above 100° the discrepancy in c_v in the liquid and vapor phases increases systematically.

Figure 1 presents the change of c_v as a function of v and T during phase transitions and in the vapor phase along the right part of the saturation curve in the interval of specific volumes from 3.61 to 21.64 cm^3/g; the values of c_v in this interval of volumes have been obtained for the first time.

Figure 2 presents the isothermal change of c_v of superheated water vapor as a function of specific volume, with the right part of the saturation curve indicated (bold curve).

Figure 3 presents the change of the maxima of the heat capacity along the saturation curve from the side of the two-phase region on both sides of the critical point. It is seen from the figure that, with increasing transition temperature, c'_v along the left saturation curve from the side of the two-phase region increases, whereas c''_v along the right saturation curve from the side of the two-phase region, on the contrary,

increases, decreases, so that these curves smoothly approach one another up to the transition temperature of approximately 365–370°.

The middle line in Fig. 3 represents the half-sum of c'_v and c''_v in the temperature range under study. From the course of the dependence of c_v on v and T, one might expect that the curves of the heat-capacity maxima would follow the dashed curve, which is a continuation of the smooth curves along which c'_v and c''_v approach each other. However, the experimental data show that c''_v decreases with increasing temperature (upper curve), reaching a minimum value at a temperature of 370°, and with a further rise in temperature first slowly and then sharply increases, whereas c'_v, with increasing transition temperature all the way to the critical temperature, first slowly and then, beginning at

Fig. 1. Change in heat capacity c_v during phase transitions.
1 –$v = 3.61$ cm^3/g; 2 –4.93 cm^3/g;
3 –6.94 cm^3/g; 4 –10.48 cm^3/g;
5 –15.45 cm^3/g; 6 –21.64 cm^3/g.

Fig. 2. Character of the dependence of c_v on specific volume along isotherms.
1 –$T = 320°$; 2 –340°; 3 –360°;
4 –370°.

Fig. 3 and Fig. 4

Figure 2: Fig. 3 and Fig. 4

a temperature of 370°, increases sharply. Finally, the curves of the heat-capacity maxima meet the smooth heat-capacity curve corresponding to the critical specific volume $v = 3.23\ \text{cm}^3/\text{g}$, forming a maximum on the curve in the coordinates c_v, T.

As is seen from Fig. 3, for one and the same transition temperature on both sides of the critical point $c_v'' > c_v'$. Indeed, the heat capacity c_v of a two-phase system at constant volume, equal to the derivative $(\partial u/\partial T)_v$, will, according to the additivity property of the internal energy ([4]), also be additive and equal to

$$c_v = (1 - x)c_v' + xc_v'', \tag{1}$$

where x is the dryness fraction of wet steam. Differentiating (1) with respect to volume under the condition $t = \text{const}$ and taking into account that the known thermodynamic relation $(\partial c_v/\partial v)_T = T(\partial^2 P/\partial T^2)_v$ for a two-phase system takes the form $(\partial c_v/\partial v)_T = Td^2P/dT^2$, in work ([3]) it was obtained that

$$c_v'' - c_v' = (v'' - v')Td^2P/dT^2, \tag{2}$$

where v'' and v' are the specific volumes, respectively, of saturated vapor and of the liquid in equilibrium with it. Since for all substances on the phase-transition line $d^2P/dT^2 > 0$ and $v'' - v' > 0$, it follows from formula (2) that $c_v'' > c_v'$, which agrees with our experimental data up to the critical region.

In Fig. 4 the curve constructed from the maximum values of c_v along the boundary curve on the side of the two-phase region shows that the maxima of the heat capacity c_v, as the critical point is approached, increase,

reaching its greatest value in it. With a further increase in the specific volume, the absolute values of the maxima of c_v at first decrease and then begin to increase again. Thus, the heat-capacity maxima are located in the vicinity of the critical point (c.p.) on both sides of the largest maximum, corresponding to the critical specific volume ([5]).

On the basis of thermodynamic conclusions, the boundary curve in the vicinity of the c.p. should be symmetric with respect to the critical isochore and have the form of a parabola. Therefore $v'' - v_\text{k} = v_\text{k} - v'$. Consequently, near the c.p. the specific volumes v' and v'' on the left and on the right should approach each other symmetrically, and at the c.p. their difference should become zero, i.e., $v'' - v' = 0$; $v'' = v' = v_\text{k}$; the second derivative

Fig. 3. Curve of heat-capacity maxima c_v along the boundary curve

Fig. 4. Curve of heat-capacity maxima c_v along the boundary curve on the side of the two-phase region

$\partial^2 P/\partial T^2$ at the c.p. of water has a value equal to zero or very close to zero, regardless of whether we approach it along the boundary curve from the right or from the left. Therefore, from equation (2) it follows that, with approach to the c.p., the difference between the quantities c'_v and c''_v decreases and only at the c.p. becomes zero.

However, from the location of the maxima c'_v and c''_v in the vicinity of the c.p., corresponding to one and the same transition temperature on both sides of it, it is seen that for $v' < v_{\text{k}} < v''$, i.e., for specific volumes $v' \neq v''$, the difference between c'_v and c''_v, contrary to equation (2), becomes equal to zero. In other words, in a fairly wide interval of specific volumes, where $v'' > v'$, the heat capacities $c'_v = c''_v$. This experimental fact indicates the inapplicability of equation (2) to the state of a substance in the critical region. Thus, in order to obtain correct ideas about the properties of a substance near the c.p., it is necessary to take into account the structural features of the substance in the vicinity of the c.p. The principal structural feature of a substance near the c.p. is the microheterogeneity of the system, in which the distinction between the liquid and the vapor in equilibrium with it disappears.

Equation (2) can describe the indicated feature of c'_v and c''_v near the c.p. only if it is assumed that d^2P/dT^2 not only at the c.p., but also over a considerable interval of specific volumes in the vicinity of the c.p., has a value close to zero (in the present work $d^2P/dt^2 < 0.0004$).

Let us try to explain the features of the change in the function $c_v(v, T)$ near the critical point.

It is known from statistical physics that energy fluctuations are related to the magnitude of the heat capacity at constant volume by the relation $c_v = (\overline{E^2} - \overline{E}^2)/kT^2$. At temperatures slightly below the critical temperature, the surfac-

the surface tension at the boundary of the two phases and the difference between their densities are substantial; as a result, there are no sufficient conditions for the development of fluctuations, and therefore the latter increase only weakly with temperature and their role is not observed in these transitions, while the main mass of the substance undergoes a phase transition discontinuously.

As the critical temperature is approached, owing to the decrease in surface tension and in the difference between the densities of the phases, heterophase fluctuations near the transition line increase, which promotes the formation of microscopic droplets of liquid with its saturated vapor, and the system passes into a microheterogeneous state.

For such a system the surface of all the microdroplets becomes very large and, consequently, the surface energy in these processes plays an essential role. It is true that, as the critical point is approached, the surface tension decreases;

but the number of fragmented microdroplets reaches such a large value that the total surface energy increases, which explains the steep rise of the heat capacities near the critical temperature (Fig. 3).

With the development of microheterogeneous fluctuations and the fragmentation of microdroplets down to the critical size, the energy absorbed by the system reaches its maximum value at a quite definite temperature and specific volume (Fig. 3, $T = 373.95^\circ$, $v = 3.23$ cm^3/g), where the heat capacities c_v'' and c_v' have the greatest value and become equal.

With a further increase in temperature, the increase in surface energy due to the fragmentation of droplets can no longer compensate for the loss of energy due to the sharp decrease with temperature of the surface tension of all droplets. On the other hand, when the substance passes from the microheterogeneous state into the homogeneous state, the microheterogeneous fluctuations weaken because the substance passes into the homogeneous state. Thus, during the transitions the role of surface energy and fluctuations decreases with increasing temperature and, consequently, so does the additional energy absorbed by the system; this leads to a smooth decrease in the heat capacity c_v (Fig. 3, $v = 3.23$ cm^3/g) during the transition near the critical point over a certain temperature interval. This process continues until the entire system has passed completely into the homogeneous state.

Thus, the jump-like transition of the heat capacity on both sides of the critical point and its smooth change during the transition from the two-phase region into the single-phase region near the critical point give the authors sufficient grounds to conclude that, alongside the critical point, there exists a critical region of continuous change in the properties of the substance, bounded for water in the interval of specific volume v from 2.70 to 3.61 cm^3/g.

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