Academician of the Academy of Sciences of the Azerbaijan SSR Kh. I. AMIRKHANOV and A. M. KERIMOV

![Fig. 1. Diagram of the calorimeter](image)

1961

SovietRxiv

Fig. 1. Diagram of the calorimeter

Figure 1: Fig. 1. Diagram of the calorimeter

Figure 2

Figure 2: Figure 2

Abstract

Full Text

PHYSICAL CHEMISTRY

Academician of the Academy of Sciences of the Azerbaijan SSR Kh. I. AMIRKHANOV and A. M. KERIMOV

THE HEAT CAPACITY c_v OF WATER AND WATER VAPOR AT HIGH TEMPERATURES AND HIGH PRESSURES

The present work, which is a continuation of work (^{1}), contains new data on the direct determination of the heat capacity c_v of water and water vapor at high temperatures (up to 500°) and high pressures (up to 800 atm.).

Fig. 1. Diagram of the calorimeter

The method used for determining c_v is the same as before, but, in contrast to work (^{1}), all measurements were carried out with continuous and intensive stirring not only of the liquid under investigation in the calorimeter, but also of the thermostating liquid.

Special measures were taken to eliminate heat removal along the lead-in wires to the protective capillary. Despite the high working pressures, reaching 1000 atm., the water equivalent of the calorimeter did not exceed 1/5 of the average amount of heat supplied per measurement, which was achieved by reducing the thickness of the calorimeter walls to

1.5 mm, which is quite permissible owing to the natural transfer of part of the pressure to the outer shell (see Fig. 1). All these measures were undertaken in order to obtain more reliable data. At the same time, along with the agreement of a number of results in the two works, data were also obtained showing discrepancies between them, mainly in the direction of underestimation. For the control isochore $v = 1.235$ cm^3/g, the underestimation reached 5%; for isochores with a larger specific volume this discrepancy was still somewhat greater.

Fig. 2. Change in the heat capacity c_v in the two-phase and single-phase regions for isochores:

Figure 3

Figure 3: Figure 3

$v_1 = 1.012$ cm^3/g; $v_2 = 1.043$ cm^3/g; $v_3 = 1.091$ cm^3/g; $v_4 = 1.156$ cm^3/g

Figure 2 presents data on the heat capacity c_v for four isochores (the isochores of specific volumes v_1 and v_2 contain data on the heat capacity c_v in the liquid phase from 1 to 800 atm). As is evident from Fig. 2, after crossing the boundary curve from the two-phase region into the single-phase region, for all specific volumes v_1, v_2, v_3, and v_4 the heat capacity c_v decreases as pressure and temperature increase. The rate at which the heat capacity decreases with temperature for the specific volume v_1 is greater than for the specific volume v_2.

Figure 3 shows the changes in the heat capacity c_v upon transition from the two-phase region into the single-phase region for the isochores v_5, v_6, and v_7. For these isochores as well, after the boundary curve is crossed, the heat capacities c_v decrease as temperature and pressure increase. For all 7 isochores obtained, the rate of decrease of the heat capacity with temperature diminishes as the specific volume increases.

Figure 4 shows the change in heat capacity for the isochores described above and, in addition, for the isochores v_8 (2.7 cm^3/g) and v_9 (3.23 cm^3/g). For the latter two isochores, the heat capacity c_v upon transition from the two-phase region into the single-phase region changes smoothly, but sharply. This proves the existence of the critical region, since, unlike the transitions up to the critical region, where the heat capacities after and before the transition give separate, nearly straight lines (Figs. 2 and 3), in the critical region the curves of the heat capacity c_v upon transition from the two-phase region into the single-phase region have a characteristic rounding near the equilibrium curve, which, on the critical isochore and on isochores near it, has the character of a continuous smooth curve (Fig. 4, v_8 and v_9). This feature is so characteristic that all precautionary measures undertaken to eliminate this effect as a trivial one did not lead to positive results, and it consistently accompanied all measurements in this region, objectively proving the existence of the region of the critical state of the substance. The course of the section of the curves of dependence of the heat–

Fig. 3. Change in the heat capacity c_v in the two-phase and single-phase regions for isochores:
$v_5 = 1.251$ cm^3/g; $v_6 = 1.404$ cm^3/g; $v_7 = 1.741$ cm^3/g

capacity c_v on temperature is, in all likelihood, a consequence of the residual microheterogeneity of the system, which tends to decrease rapidly with increasing temperature and, in doing so, absorbs some additional energy for the further fragmentation of microscopic droplets. As a result, the system will possess a certain additional heat capacity until this process is completed, i.e., until a fully homogeneous phase is formed.

Fig. 4

Figure 4: Fig. 4

The critical specific volume $v_{\text{cr}} = v_9 = 3.23$ cm^3/g was determined by us earlier (1), on the basis of the theory of V. K. Semenchenko (2).

The critical temperature in the present work was determined graphically. On the curve of the dependence of c_v on temperature along the critical isochore there is a segment of an almost vertical drop in heat capacity and a segment of a rectilinear dependence of the heat capacity c_v on temperature after the transition into the homogeneous phase, between which the curve is rounded. The linear continuations of these segments intersect at a point whose temperature we take as critical and which is equal to $T_{\text{cr}} = 374.34°$.

From the lower curve in Fig. 4 it is seen that the heat capacity along the boundary curve on the liquid side, with an increase in specific volume from v_1 to v_7, for which the transition temperatures are $T_1 = 50°$ and $T_7 = 350°$,

Fig. 4. Change in the heat capacity c_v along the left-hand boundary curve from the side of the two-phase and one-phase regions. v_1–v_7 are the same as in Figs. 2 and 3. $v_8 = 2.7$ cm^3/g; $v_9 = 3.23$ cm^3/g

decreases from 0.975 to 0.752 cal/g · deg. After the minimum at 350°, with a further increase in specific volume and in the transition temperature up to the critical point, the heat capacity c_v on the liquid side along the boundary curve increases sharply, reaching a maximum at the critical point: $c_v = 1.69$ cal/g · deg.

Table 1

T, °C	Two-phase region: c_v, kcal/g · deg, exp.	Two-phase region: c_v, kcal/g · deg, calc.(3)	Two-phase region: discrepancy, %	One-phase region: c_v, kcal/g · deg, exp.	One-phase region: c_v, kcal/g · deg, calc.(3)	One-phase region: discrepancy, %
50	1.000	0.9986	0.15	0.975	0.963	1.24
100	1.008	1.0065	0.15	0.930	0.900	3.3
150	1.036	1.0268	0.8	0.885	0.840	5.3
200	1.079	1.0628	0.58	0.837	0.782	5.8
250	1.132	1.1223	0.8	0.800	0.755	5.9
300	1.240	1.2393	0.72	0.760	0.721	5.4
340	1.467	1.418	3.4	0.754	0.701	7.7

From the upper curve in Fig. 4, which represents the change in heat capacity in the two-phase region and adjoins the boundary curve, it is seen that the heat capacity in the two-phase region increases with increasing specific volume and transition temperature up to the critical point; moreover, the rate of increase rises sharply at temperatures above 350°.

A comparison of the experimental values of the heat capacity c_v with the calculated values(3) in the two-phase and single-phase regions adjoining the boundary curve is given in Table 1. It is seen from this table that in the two-phase region, up to a transition temperature of 300°, the discrepancy between the experimental data and the calculated values does not exceed 0.8%, while at a transition temperature of 340° it reaches 3.4%. In the single-phase region adjoining the left boundary curve, at a transition temperature of 50° the discrepancy between the experimental data and the calculated values is 1.24%, and with increasing temperature it rises to 7.7% for a transition temperature of 340°.

From a comparison of the results obtained by us with the calculated ones, it may be concluded that in the two-phase region above 300°, calculation of c_v from caloric and thermal quantities and from the values of their derivatives leads to a noticeable error; and in the single-phase region adjoining the boundary curve, determination of c_v by calculation is altogether inadmissible.

Dagestan Branch
Academy of Sciences of the USSR

Received
21 III 1961

REFERENCES

[1] Kh. I. Amirkhanov, A. M. Kerimov, *DAN*, **113**, No. 2 (1957); *Teploenergetika*, No. 9 (1957). [2] V. K. Semenchenko, *ZhFKh*, **26**, 1337 (1952); **21**, 1461 (1947). [3] V. V. Sychev, *Inzh.-fiz. zhurn.*, **3**, No. 7 (1960).

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.