

FEATURES OF SPECIFIC HEAT C_v AT THE CRITICAL POINT OF AN ASEOTROPIC MIXTURE

A. V. Voronel', V. G. Gorbunova and N. G. Shmakov
 All-union Research Institute of Physicotechnical and Radiotechnical Measurements
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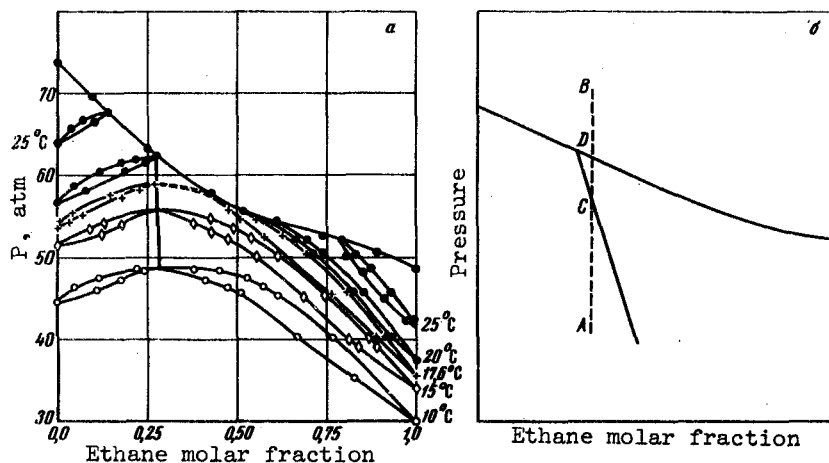
It was established in [1] that the specific heat C_v (more accurately, $C_{v,x}$, where x is the composition of the mixture) has no singularities at the critical point of binary mixtures, unlike the critical point of the pure substance [2]. A special position among mixtures is occupied by azeotropic mixtures [3], which behave to a considerable degree like the pure substance: the compositions of the vapor and liquid phases at the azeotropic point of such a mixture are identical, and therefore the process of condensation is simultaneously isobaric and isothermal. The compressibility and its derivative become infinite at the critical point of the azeotropic mixture ¹⁾:

$$\left(\frac{\partial P}{\partial V}\right)_T = 0; \quad \left(\frac{\partial^2 P}{\partial V^2}\right)_T = 0.$$

Were the specific heat C_v of an azeotropic mixture to become infinite at the critical point, as is the case at the critical point of the pure substance, then one could establish a connection between the anomaly of the isochoric specific heat and the anomaly of the compressibility of the system.

We measured the specific heat C_v of a mixture of carbon dioxide and ethane (0.719 CO_2 and 0.281 C_2H_6 in molar fractions), using the adiabatic calorimeter described in [6].

Figure 1a shows the phase diagram of the carbon dioxide - ethane system [4]. The isotrope line reaches the critical curve at an ethane concentration in the mixture 0.278 - 0.280. The real direction of our measurements is probably represented in the P-x diagram by the line AB (Fig. 1b).



The results of the

Fig. 1. a) P-x diagram for the ethane - carbon dioxide system, b) schematic representation of a section of the phase diagram.

1) The critical point of an azeotropic mixture is defined as the point at which the line of the azeotropes reaches the critical curve in the T-x or P-x diagram, see [4].

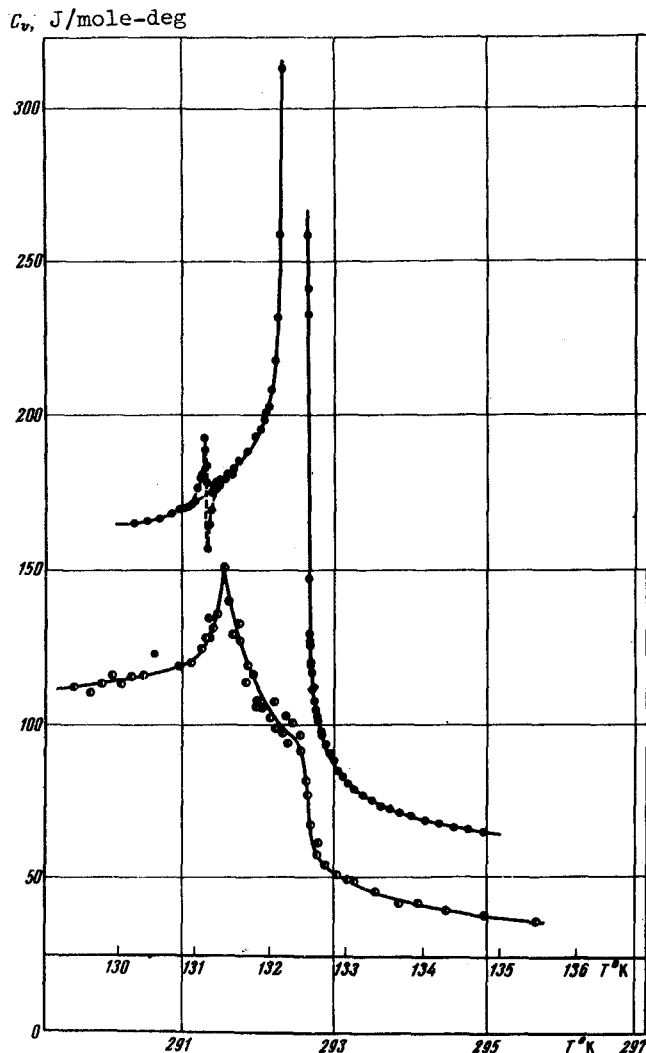


Fig. 2. Temperature dependence of the specific heat C_v : • - azeotropic mixture, o - air.

This section of the curve is shown dashed in the figure.

In spite of a certain gap in the low-temperature part of our curve, its comparison with the corresponding curve for air shows that even in this section the singularity of the specific heat C_v of an azeotropic mixture is much stronger than the C_v singularity of air. Whereas in the case of air the anomalous increase of the specific heat terminates at $t = 8.6 \times 10^{-3}$, for the azeotropic mixture the anomalous growth of the specific heat continues at any rate up to $t = 1.2 \times 10^{-3}$, where $t \equiv (T_j - T)/T_j$ (T_j - temperature of the jump, determined by the method of quasistatic thermograms) [2].

In the high-temperature part of our curve, the difference between the azeotropic mixture and air is even more pronounced. We can see clearly a strong increase of C_v , which can be interpreted as a logarithmic singularity.

measurements are shown in Figs. 2 and 3. In Fig. 2 the $C_v = C_v(T)$ curve is compared with the analogous curve for air [2]. Air is a non-azeotropic mixture having approximately the same component ratio as in our case. For convenience in comparison, the temperature axes of the curves are shifted relative to each other, so that the temperature "jumps of the specific heat" lie on the same vertical line.

The value of the specific heat of our mixture within the temperature interval 292.30 - 292.65°K are not plotted in the figures, since this interval corresponds to section CD of diagram 1b, which is difficult to interpret.

In the temperature interval 291 - 291.40°K there is a slight anomaly of the specific heat, similar to that noted on the specific-heat curve of oxygen [5]. It should be noted that a similar anomaly is also observed at a temperature 1 - 1.5° below the critical temperature on the curves of the isochoric specific heat of other substances (air, nitrogen, argon). The nature of this anomaly is now under additional study, but has no bearing on the phenomenon discussed in this article.

Figure 3 shows, in C_v and $\log t$ coordinates, the branch of our curve corresponding to the homogeneous substance. The temperature T_j is taken to be 293.672°K . The same figure shows for comparison the analogously constructed high-temperature branches of the curves of specific heat C_v of pure nitrogen, of nitrogen with small amounts of impurities, and of air [1,2,6].

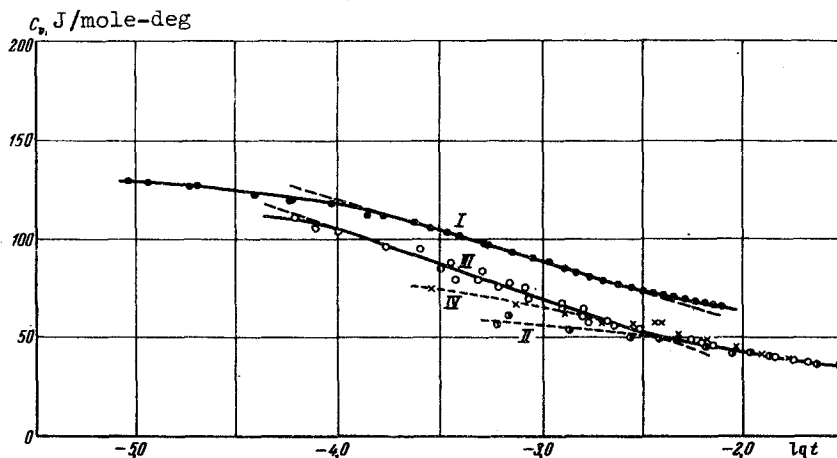


Fig. 3. Dependence of the specific heat C_v on $\log t$ at $T > T_j$: I - azeotropic mixture, II - air, III - nitrogen plus 0.05 - 0.1% impurities, IV - nitrogen plus 3.5% impurities.

It is seen from Fig. 3 that whereas in an ordinary mixture the law governing the increase of the specific heat C_v deviates more and more from logarithmic with increasing amount of impurities, the azeotropic mixture behaves practically like a pure substance. The small deviation from the logarithmic dependence in the direct vicinity of T_j ($\ln|(T_j - T)/T_j| < -3.8$) can be attributed to slight deviations of the composition from azeotropic. Comparison of our data with data on nitrogen containing 0.05 - 0.1% impurity [2] shows that the composition of our mixture apparently deviates from azeotropic by 0.1 - 0.2% ethane. This estimate may be too high, for owing to the insufficient accuracy of the P-V-T-x data our system corresponds only approximately to either a critical azeotropic composition (see the diagram in Figs. 1a and b) or to the critical density. In future experiments, the critical azeotropic composition and the critical density of the mixture will be refined, as a result of which we can expect a more complete agreement between $C_v = C_v(t)$ and the logarithmic formula.

Thus, an azeotropic mixture, which behaves thermodynamically like a pure substance, has the same singularity of specific heat as a pure substance, and thus the similarity in the behavior of the regular parts of the thermodynamic functions is accompanied by a similarity in the behavior of the singularities.

If one can speak of some model here, then apparently the behavior of the azeotropic mixture corresponds to the behavior of a compensated antiferromagnet; this analogy justifies the reference to what certainly seems to be a particular case.

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