INTERSECTION OF TEMPERATURE DEPENDENCES OF VELOCITY OF SOUND IN LIQUID AND VAPOR PHASES OF FREON-12 ON SATURATION LINE NEAR CRITICAL POINT

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The intersection of the temperature dependences of the velocity of sound in vapor and liquid on the saturation line near the critical point was first discovered by Schneider for sulfur hexafluoride. His result, however, was for some time a matter of doubt, which was not really dispelled even after Trelin and Tannenberger obtained similar results for carbon dioxide and ethane. It has been suggested that the curves cannot intersect and the obtained intersection is due either to inaccurate measurement or to the effect of impurities.

Recently, however, A. A. Glinskii and I. S. Radovskii showed theoretically that intersection is possible and necessary, while Nozdrev and Stepanov [1] discovered experimentally the intersection of the curves for two substances – dimethylchlorosilane and trimethylchlorosilane. The relevant bibliography is given in [1].

Nevertheless, this question will probably not be conclusively answered for several reasons. 1) The theoretical deductions of Glinskii and Radovskii were based on certain not at all obvious assumptions; in particular, Glinskii's conclusions were based on the quite invalid assumption that the thermodynamic functions can be expanded in a series close to the critical point. Radovskii's work includes the assumption that the velocity of sound is not zero at the critical point. 2) In view of the small difference in the liquid and vapor phases close to the critical point it is not absolutely certain that the measurements were made in the phase to which they are assigned. The difficulty of the question is also indicated by the fact that in [2] Nozdrev claims that intersection of the curves cannot occur, but in [1] this intersection was discovered.

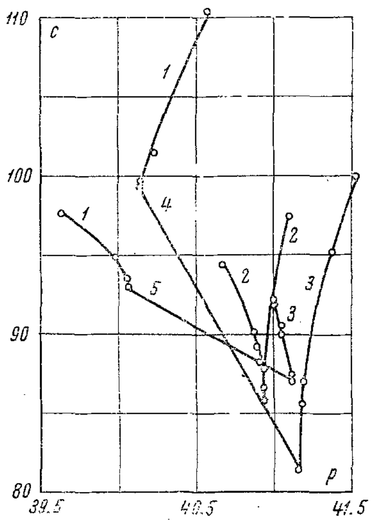

Fig. 1

To confirm the intersection of the curves in additional investigations by a method significantly different from those used earlier and to determine the parameters of the point of intersection and the increase in the velocity of sound in the vapor over that in the liquid we made measurements of the velocity of sound close to the critical point for Freon-12 (CF_2Cl_2). We paid particular attention to the purity of the investigated substance and the accuracy of the measurements of all the necessary parameters. The investigated Freon-12 was analyzed on a mass spectrometer. We did not detect any impurities.

The measurements were made by the ultrasonic-interferometer method at a frequency of 2.1 MHz on a considerably modified version of the apparatus described in [3]. A new temperature-regulating system enabled us to control the temperature to within 0.01° K. The temperature in the investigated volume was measured by a standard

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10-ohm platinum resistance thermometer made in the All-Union Scientific Research Institute of Physico-technical and Radiotechnical Measurements. To measure the pressure we designed an electric-contact membrane sensor (used in conjunction with a class 0.05 MP-60 piston pressure gauge) with high sensitivity (1 mm of water column at an absolute pressure of tens of atmospheres).

In view of the small difference between the vapor and liquid phases close to the critical point we made the measurements not on the saturation line, but on isotherms which intersected the saturation line. The high sensitivity of the pressure gauge enabled us to determine very accurately the points of intersection of the isotherms with the saturation line. This method ensured that the measured velocities of sound were assigned to the proper phase. The results of the measurements are shown in the figure, where 1 is the 383.56° K isotherm, 2 is the 384.44° K isotherm, 3 is the 384.94 isotherm, 4 is the velocity of sound in the liquid on the saturation line, and 5 is the velocity of sound in the vapor on the saturation line. These isotherms were chosen so that two of them were on the right of the postulated point of intersection and one on the left.

As the graph shows, near the critical point of Freon-12 the temperature dependences of the velocity of sound in the vapor and liquid phases on the saturation line intersect. The point of intersection is 0.9° K from the critical point. The error in determination of the velocity of sound does not exceed 0.5%. The maximum increase in the velocity of sound in vapor over that in liquid was 6.8% of the velocity in the liquid. The value for $\Delta c/c$ found by other authors varies in the range 0-3.5%, and the difference between the critical temperature and the temperature of the point of intersection of the curves is 0 to 2° K for different substances.

We previously carried out measurements in Freon-12 containing impurities. The presence of impurities was revealed by the too high value of the saturation pressure in comparison with the tabulated value. The impurities were also detected on the mass spectrometer. As the investigations showed, in the case of impure Freon-12 the curves also intersected. The increase in the velocity of sound in the vapor over that in the liquid was approximately the same as in pure Freon.

LITERATURE CITED

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