ON THE SHAPE OF THE CRITICAL ISOTHERM NEAR THE CRITICAL POINT

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The quantity $B \equiv (\partial^3 p / \partial V^3)_{T_c}$, which characterizes the shape of the critical isotherm near the critical point that terminates the liquid-vapor equilibrium, is calculated for five simple substances and for water. The agreement of the results obtained by four different methods enables us to assert that $B < 0$ for simple liquids and that this quantity can be reliably estimated. It is shown that rough approximate values of B for simple substances can be obtained from known values of the critical parameters p_c and V_c.

THE character of the singularity which occurs in the thermodynamic quantities at the critical point at the end of the curve of phase equilibrium between liquid and vapor for a pure substance has not been elucidated up to the present. If we assume that the thermodynamic quantities at the critical point can be expanded in power series in the small deviation of the density, then we can write for this point the following conditions (cf. reference 1):

$$(\partial p / \partial V)_{T_c} = 0, \tag{1}$$

$$(\partial^2 p / \partial V^2)_{T_c} = 0, \tag{2}$$

$$(\partial^3 p / \partial V^3)_{T_c} < 0. \tag{3}$$

The condition (3) requires experimental verification.[1] The quantity $(\partial^3 p / \partial V^3)_{T_c}$ (which we denote by B for brevity), if it is not zero, determines the shape of the critical isotherm, which is a third-degree parabola in the neighborhood of the critical point if the condition (3) is satisfied.

In the present work our purpose has been to get estimates of the values of B for various substances by different methods. It must be agreed that the least reliable method for obtaining this quantity is direct repeated differentiation of the p-V-T data obtained experimentally. By this method one can at best get the order of magnitude of the quantity desired. Values obtained by this method for several simple substances are given in the second column of the table under the heading p-V-T. For comparison with these values, values for water are included in the table which differ from these values by more than an order of magnitude.

In a paper by Habgood and Schneider[1] graphical differentiation gave for xenon $B = 0$, but a detailed analysis shows that the error in this estimate is not less than 1×10^{-5} atm-mole^3/cm^9.

Values of $(\partial^3 p / \partial V^3)_{T_c}$, atm-mole^3/cm^9

Substance	$p - V - T$	ΔC_v	g	l. c. s.
Xe	0—1	3.5	4	
CO_2	1—6	12	11	10
C_2H_4	3—5	—	3,5	2.5
C_2H_6	—	—	2,3	2
SF_6	0.2—0.5	—	0,7	0.5
H_2O	50—150	140	—	130
N_2	—	—	—	5.5
Ar	—	—	—	13
H_2	—	—	—	5.4
CH_4	—	—	—	5.7

The quantity B can be found more accurately from the data on the specific heat at constant volume near the critical point, as is shown in a paper by the writer.[3]

The third column of the table, headed ΔC_v, gives the results of calculations from the experimental data of references 3 — 9. The possible error of the values in this column is about 50 percent, and is due both to the error in the determination of the discontinuity of the specific heat from the experimental data and to that in the determination (from p-V-T data) of the coefficient $(\partial^2 E / \partial V^2)_{T_c}$, which appears in the formula for calculating B.

Evidently the greatest accuracy for the quantity B can be obtained from measurements of the hydrostatic effect, by a method previously described by the writer.[10] Values so obtained are given in the fourth column of the table under the arbitrary heading g. Experimental data from references 11 — 13 have been used here.

We note that the critical isotherm is precisely the sort of thing that obeys the law of corresponding states, and consequently in reduced coordinates the data for the various substances fit on a single

curve. This means that for this class of substances the third derivative in the reduced coordinates will have the same value, i.e.,

$$\frac{V_c^3}{p_c}\left(\frac{\partial^3 p}{\partial V^3}\right)_{T_c} = \alpha, \qquad (4)$$

where α is a constant which does not depend on the substance. Now if we know the third derivative for one substance, we can find its value for all others.

Of course the accuracy of this method is not high, since the substances obey the law of corresponding states only to a very rough approximation. It seems very natural, however, that the values of B, if they are not zero, will be of the order of the combination of the critical parameters that has the same dimensions, p_c/V_c^3.

Taking the data for Xe as the most reliable, we get for this substance $\alpha = 1.2$. The van der Waals equation gives $\alpha = 9$. The difference between these numbers characterizes the degree of applicability of the van der Waals equation at the critical point.

The values of B calculated for the various substances by using Eq. (4) are given in the fifth column of the table, under the heading l.c.s. (law of corresponding states). Evidently the accuracy of these data is of the same order as the accuracy of the data in the second column.

An examination of the table shows that the condition (3) is satisfied for a broad class of substances. In all cases considered the third derivative of the critical isotherm at the critical point is different from zero. Moreover, the rather good agreement of the values obtained by the various methods, and the roughly equal orders of magnitude for the various substances, show that the numerical values of B have evidently been correctly determined.

Thus the equation of the critical isotherm near the critical point can be written in the form $p - p_c = (B/6)(V - V_c)^3$, and the table given here provides a qualitative characterization of the differences of shape of the critical isotherm for the different substances. The numerical values of B determine the radii of curvature of the curve near the critical point.

By means of the relation (4) we can calculate the required quantity and reconstruct the curve for many simple substances.

We can evidently assert that the singularity of the thermodynamic potential at the critical point is such that it does not affect the first four terms of the expansion in powers of the departure of the density from its critical value.

In conclusion the writer thanks M. Sh. Giterman for a discussion of the results of this work.

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257