A METHOD OF DETERMINING THE CRITICAL TEMPERATURE FROM EXPERIMENTAL DATA ON A ρ_S(T) BOUNDARY CURVE

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We present the basis of an analytical method for determining the critical temperature from experimental data on a boundary curve in ρ,T-coordinates. We show that our method for determining T_{crit} is accurate to within 0.1%.

It is a known fact [1, 2] that the most accurate values of critical parameters are determined in special experiments where the unknown quantities T_{crit}, ρ_{crit}, P_{crit} vary directly. Owing to the specific peculiarities in the behavior of a material at a critical point, setting up such experiments is complicated and does not always lead to the desired results. In our judgment, the problem of determining the critical temperature can be solved analytically over a wide range of temperature variation by using experimental data on a boundary curve in ρ,T-coordinates.

Data characterizing the boundary curve ρ_S(T) are usually obtained in studies of the thermodynamic properties of materials (P, ρ, T-data) by extrapolating either the isochore P(T) to the elastic curve P_S(T) or the isotherm P(ρ) to the isobars P_S = const. In a region of temperatures far from the critical point the isolines, in passing from a homogeneous to a heterogeneous region, show a well-defined break, the location of which can be determined very accurately. The closer the approach to T_{crit} the closer the angles of inclination of the curves in the single and two-phase regions approach one another, leading thereby to the appearance of an indeterminacy in the determination of the break location. The boundary curve, constructed from the experimental data, has thus the form of a truncated parabola, the position of whose vertex, i.e., the critical parameters, cannot be determined graphically with sufficient accuracy. This problem lends itself to an analytical treatment, the basis for which resides in the properties of the material on the boundary curve in a neighborhood of the critical point.

A general form for the boundary curve ρ_S(T) throughout the region in which liquid and vapor exist is a rather complicated one. However, in a neighborhood of the critical point it turns out to be possible, owing to the satisfaction of the well-known conditions (see, for example, [3, 4]) $(\partial P/\partial v)_{T_{crit}} = (\partial^2 P/\partial v^2)_{T_{crit}} = 0$; $(\partial^3 P/\partial v^3)_{T_{crit}} < 0$, to establish the form of the boundary curve. It was shown in [3, 4] that by expanding the state parameters in a Taylor series in the small increments $v_{crit} - v$, $t_{crit} - t$, $P_{crit} - P$ the boundary curve must have the form of a symmetric second-degree parabola, i.e., $v_V - v_{crit} = v_{crit} - v_L \sim (T_{crit} - T)^{1/2}$ and $v_V - v_L \sim (T_{crit} - T)^{1/2}$, or, since we are dealing with small increments, we can write

$$\rho_L - \rho_V \sim (T_{crit} - T)^{1/2}. \tag{1}$$

An analysis of experimental data for orthobaric densities for a number of nonconducting liquids leads to the establishment of the one-third power law [5, 6] for the boundary curve instead of the law (1):

$$\rho_L - \rho_V \sim (T_{crit} - T)^{1/3}. \tag{2}$$

Careful experimental investigations, made in recent years with a series of materials, show that the best approximation to the experimental data for ρ_V and ρ_L, close to the critical point, is given by the more general relationship

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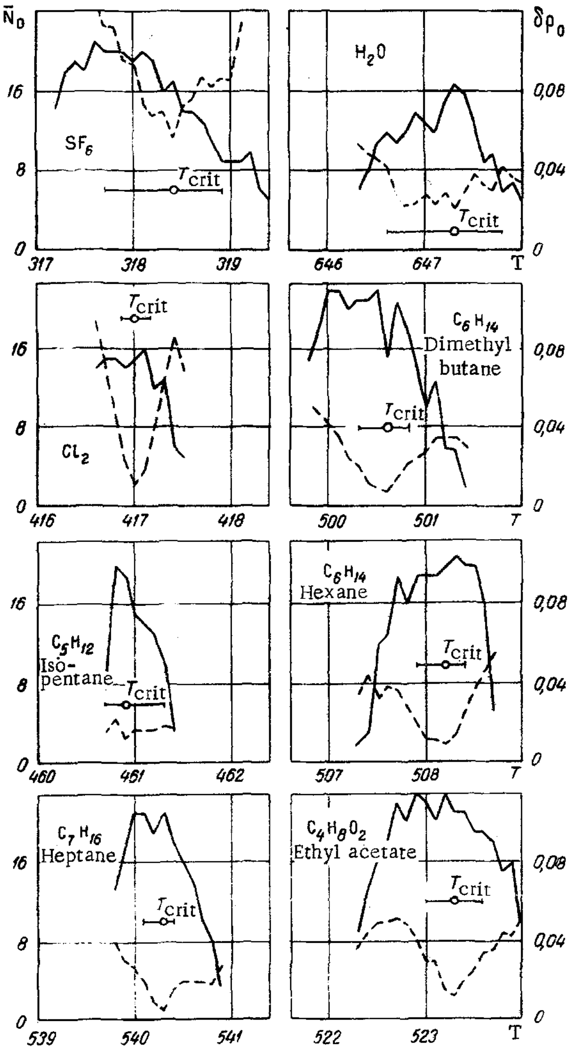

Fig. 1. Plots of the quantities $\delta\rho_0$ (shown dashed) and N_0 versus the parameter T_0 for eight materials.

$$\rho_L - \rho_V \sim (T_{crit} - T)^{\beta}, \tag{3}$$

where the value for the critical exponent β is equal to 0.357 for CO_2 and 0.345 for Xe (see [5, 6]); 0.358 for heptane [7] and nitrogen [8], and 0.333 for SF_6 (see [9]), i.e., as before, β is close to 1/3. It should be pointed out that only the differences of the orthobaric densities enter into the expressions (2) and (3), thereby making it impossible to make a judgment concerning the symmetry of the boundary curve with respect to the critical point [which contrasts with the expression (1)].

The form of the boundary curve in a neighborhood of T_{crit} can be established experimentally through a study of the isochoric heat capacity C_V in passing from a heterogeneous region into a homogeneous one. The value of the jump in the heat capacity in this transition, namely, ΔC_V, can, as shown in [10], uniquely determine the form of the boundary curve:

$$\Delta C_v \sim \lim (\rho_{crit} - \rho)\, d\rho/dT, \quad \rho \to \rho_{crit}. \tag{4}$$

In their investigations of the heat capacity some authors observed a finite value for the jump $\Delta C_V \neq 0$ (see [10]), which corresponds to a value of the coefficient β in the expression (3) equal to 1/2; other authors (see [5]) assume that $\Delta C_V \to \infty$ as $T \to T_{crit}$ ($\beta < 1/2$), and, finally, a third group of authors give $\Delta C_V = 0$ ($\beta > 1/2$, see [11]).

Thus, the question as to the form of the boundary curve in a neighborhood of the critical point has as yet not been answered fully. However, unquestionably the following conditions characterizing the continuity of the transition from a liquid to a gaseous state must be satisfied for the boundary curve for T_{crit}:

TABLE 1. Calculated Values of the Critical Temperature for Various Materials

Material	ω	$T_{crit} \pm \partial T_{crit}$	ΔT_{crit}	$(\delta\rho_*/\rho_*)_{min}$
CO_2	0,56	305,1±0,7	0,9	6,5
H_2O	0,47	647,3±0,6	0,0	6,5
Cl_2	0,40	417,0±0,2	—0,1	1,8
SF_6	0,62	318,4±0,6	—0,3	7,6
C_3H_8	0,67	368,7±0,4	—1,3	2,2
iso-C_5H_{12}	0,34	460,9±0,3	—0,1	5,6
C_6H_{14}	0,46	508,2∓0,3	0,3	4,3
C_6H_{14}	0,46	500,6±0,3	0,3	2,9
C_7H_{16}	0,39	540,3±0,2	0,1	8,5
C_8H_{18}	0,86	569,0±1,2	—0,4	8,5
C_2H_6	0,92	303,2±1,9	—2,2	15
CH_4O	0,75	513,0±0,6	—0,2	7,3
$C_4H_8O_2$	0,51	523,3±0,3	0,0	3,2
CF_3Cl	0,86	301,9±1,1	0,0	6,9

1) the curve must pass through the critical point

$$(\rho_V)_{T_{crit}} = (\rho_L)_{T_{crit}} = \rho_{crit}; \tag{5a}$$

2) the curve must be of the form

$$\rho_L - \rho_V \sim (T_{crit} - T)^\beta, \tag{5b}$$

where the value of the critical exponent $\beta \cong 1/3$;

3) at least the first derivatives of the density with respect to the temperature must be infinite:

$$(d\rho_V/dT)_{T_{crit}} = -(d\rho_L/dT)_{T_{crit}} = \infty, \tag{5c}$$

which corresponds to the condition of infinite compressibility of the material at the critical point.

Since the equilibrium densities are continuous functions of the temperature, they can be described with sufficient accuracy (within the limits of precision of the experiment) throughout the temperature interval in question by power series of the form

$$\rho_V = A_0 + \sum_1^m A_m (T_0 - T)^{m/n}, \tag{6}$$

$$\rho_L = C_0 + \sum_1^m C_m (T_0 - T)^{m/n}. \tag{7}$$

In Eqs. (6) and (7) the physical meaning of the coefficients A_0 and C_0 is that of critical density, while the quantity T_0, treated henceforth as a parameter, has the significance of a critical temperature, not as yet known accurately.

The choice of the form of the polynomials (6) and (7) is not a random one but is stipulated so as to guarantee, on the one hand, the best approximation to the experimental data, and, on the other hand, to satisfy the conditions (5) at the critical point. The latter is necessary, since the determination of T_{crit} by our method amounts, in effect, to an extrapolation of the polynomials (6) and (7) to the critical temperature. The experimental data for the equilibrium densities are, in the general case, not necessarily orthobaric; therefore, in approximating them, we used independent equations. However, this does not contradict the conditions (5), for whose satisfaction, besides the equality of the coefficients A_0 and C_0, the exponent n must have the same value in both equations. In accordance with what was said above, we take the value of n henceforth equal to three. According to the conditions (5) and the choice determined for the approximating polynomials (6) and (7), our method has made it possible, along with a determination of T_{crit}, to calculate the value of the critical density ρ_{crit}.

A special program was written for an electronic digital computer for the determination of the critical temperature in which the parameter T_0 passed through a series of values with a step of size δT_0 (usually, $\delta T_0 = 0.1°K$), while the degree m of the polynomials varied from 1 to 14. Along with the coefficients A_0 and C_0 (the coefficients A_m and C_m were of no special concern to us) the program calculated, for each m, the values of the dispersion of the polynomials (6) and (7). For each value of the parameter T_0 there was thus obtained a series of values of the coefficients A_0 and C_0, constituting a function of degree m and determining, generally speaking, a critical density. According to [12], the unknown value of the critical density ρ_0 (for given T_0) can be found by averaging the values of A_0 and C_0 on sections of stability, i.e., the dispersion constants of the polynomials (6) and (7). From the A_0 and C_0 values corresponding to the stability sections for the determination of ρ_0, we selected only those which were included between the experimental data for the vapor and the liquid, i.e., $(\rho_V)_{max} < A_0$, $C_0 < (\rho_L)_{min}$. Thus, finally, to each value of the parameter T_0 there correspond N_1 values of the coefficients A_0 and N_2 values of the coefficients C_0, which, treated jointly, yield a value of the desired density:

$$\rho_0 = \left(\sum_1^{N_1} (A_0)_i + \sum_1^{N_2} (C_0)_j\right) / N_1 + N_2$$

and its error $\delta\rho_0$, defined as the averaging error.

As a result of these calculations, we determined the dependence of the quantities ρ_0, $\delta\rho_0$, $N_1 + N_2 = N_0$ on the parameter T_0. We found that the functions $N_0(T_0)$ and $\delta\rho_0(T_0)$ have an extremal nature with maximum and minimum values, respectively (see Fig. 1). On the contrary, the curve $\rho_0(T)$ has a more or less stable character (within the limits of the error $\delta\rho_0$), a result, evidently, of the validity of the rectilinear diameter rule. The smallest value of the error in the critical density, $(\delta\rho_0)_{min}$, for a sufficiently large number of points close to N_{0max}, must correspond, according to [12], to optimal values of the critical temperature T_{crit} and the critical density ρ_{crit}. In calculating the errors in the value of the critical temperature, namely, δT_{crit}, we assumed that the boundaries of a possible variation in the value of T_{crit} lie between the values of the parameter T_0 closest to T_{crit}, which correspond to one half the height of the peaks of $\delta\rho_0(T_0)$ or $N_0(T_0)$.

Our method was tried out on 14 different materials for which experimental data are available for the equilibrium densities over a wide range of temperatures and values of the critical parameters [13]. We illustrate the method by presenting in the figure the functions $\delta\rho_0(T_0)$ and $N_0(T_0)$, obtained for eight materials. The results of the calculations are shown in Table 1. In this table we give, for each material, the value of $\omega = [(\rho_L - \rho_V)/{}^1\!/_2(\rho_L + \rho_V)]_{min}$ characterizing the degree of constriction of the experimental boundary curve or proximity of the experimental data to the critical point. The calculated value of the critical temperature T_{crit} and its error δT_{crit}, and also the value of the deviation of our results from those given in the literature (see [13]), namely, $\Delta T_{crit} = (T_{crit})_{cal} - (T_{crit})_{lit}$, are given in °K. In the last column we give the percent relative error in the determination of the critical density corresponding to the minimum of the curve $\delta\rho_0(T_0)$.

It can be seen from the table that the value of the deviation ΔT_{crit} lies, for the majority of the materials, within the limits of the mean error δT_{crit} of the calculated T_{crit} values, i.e., $\Delta T_{crit} < \delta T_{crit}$, which testifies to the reliability of the results calculated by our method. It is also evident that the magnitude of the absolute error δT_{crit} that is obtained depends strongly on the proximity ω of the experimental data to the critical point. Thus, our method for determining the critical temperature from the experimental data on the boundary curve $\rho_S(T)$, for ω less than 0.8 to 0.9, guarantees an accuracy in the calculations of T_{crit} no worse than 0.1%, and, at the same time, it enables us to determine the critical density to within 5%. A more accurate (apparently, to within 1%) value of the critical density can be had upon extrapolating the rectilinear diameter to the already known value of the critical temperature.

We note, in conclusion, that the method we have descibed above was applied to determine the critical temperature of hexafluorides of molybdenum, tungsten, and uranium from experimental data on the boundary curve [14-16]. The values of T_{crit} turned out to be equal to 485.2 ± 1.0; 452.7 ± 0.7; and 504.5 ± 1.0°K, respectively, while the values of the critical density ρ_{crit}, calculated according to the rectilinear diameter rule, turned out to be 0.916 ± 0.008; 1.28 ± 0.015; and 1.38 ± 0.012 g/cm^3, respectively.

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