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A METHOD FOR DETERMINING THE CRITICAL DENSITY OF A SUBSTANCE IN THE STATE OF SATURATION FROM EXPERIMENTAL DATA

P. M. Kessel'man and P. A. Kotlyarevskii

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A new method for determining the critical density of a substance, based only on compressibility data in the saturation state, is proposed. Values of the critical density of CO_2 and H_2O are obtained.

The pressure of a saturated vapor $P_s = f(T_s)$ and its density d_s are usually established by separate measurements, data on the pressure curve being more accurate and usually encompassing a wide temperature range down to the critical point. In this connection, measurements of the parameters T_c and P_c can be reliably correlated using data on the pressure curve. At the same time, measurements of the density in the saturated state close to the critical point are very difficult and the accuracy of the data is inferior to the accuracy of measurements of the saturated vapor pressure.

For many substances the indicated region of the density saturation line $d_s = \varphi(T_s)$ has been little studied. Therefore indirect methods are used for determining the critical density d_c, the best of which, apparently, are those based on compressibility data, not only in the state of saturation but also in the supercritical region of parameters (methods based on the phenomenological law of Planck-Gibbs, on utilization of accurate compressibility measurements on the critical isotherm, and some others [1]). However, in the overwhelming majority of cases, when reliable experimental data in the supercritical region are absent, only density measurements in the saturated state are used for determining the critical density [2, 3, 4]. These different methods for determining d_c, which, as a rule, give results that differ greatly from each other (up to 5–7%), do not provide for the use of data on the pressure curve or the consistency of the complex of critical parameters T_c, P_c, and d_c. At the same time, it is very desirable to have more accurate values of d_c linked with P_c and T_c, since these three parameters determine the critical number $Z_c = (P_c/RT_c)(1/d_c)$ which is fundamental in the theory of thermodynamic similarity and in the investigation of properties of substances in the supercritical region.

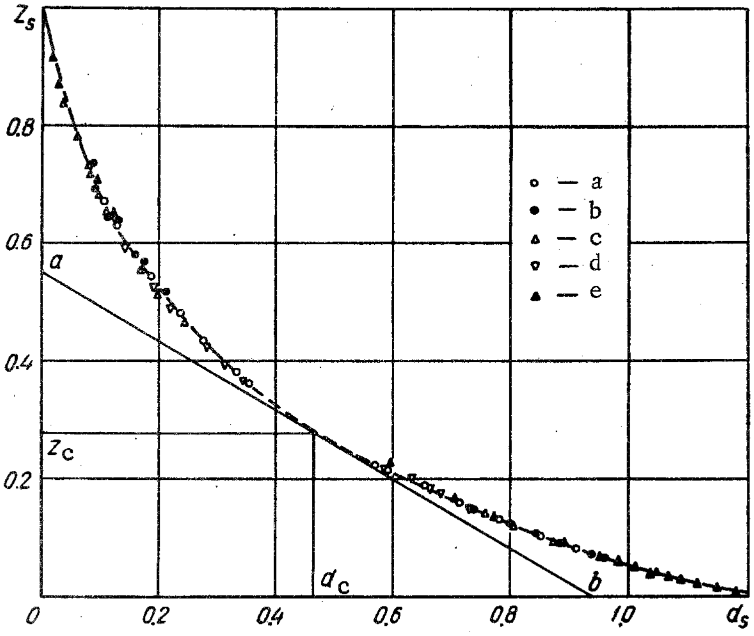

Fig. 1. Dependence of compressibility on density for CO_2 in the saturated state: a) from [7]; b) [11]; c) [4]; d) [12]; e) [6].

This paper proposes a new method for determining the critical density which makes possible the mutual correlation of the critical parameters and, at the same time, the supplementing, with reliable density data, of the little-investigated region of the saturation line immediately adjoining the critical point.

The essence of the method is as follows.

If the compressibility Z_s is plotted as a function of d_s from the experimental data of different authors, it can be represented as a curve passing smoothly from the gaseous to the liquid part through the critical point.* The corresponding curve $Z_s = f(d_s)$, constructed for CO_2, is shown in Fig. 1 (the relation $P_s = f(T_s)$ is taken from [5]). Having data on the saturation line for the gaseous and liquid phases, it is easy to extend the data on compressibility to the uninvestigated part of the curve adjoining the critical point. Using this graph, we can determine the critical density d_c with high accuracy. Mathematically, in the most general form, it is not difficult to show that the tangent drawn to this curve at the critical point satisfies the following condition: on the axes of ordinates and abscissas it makes intercepts equal, respectively, to double the values of the compressibility Z_c and density d_c. In fact, the slope of the tangent at the critical point is equal to

$$\left(\frac{\partial Z_s}{\partial d_s}\right)_c = \left[\frac{1}{RT_s}\frac{\partial}{\partial d_s}\left(\frac{P_s}{d_s}\right)\right]_c = \left[\frac{1}{RT_s}\left(-\frac{P_s}{d_s^2}+\frac{1}{d_s}\frac{\partial P_s}{\partial d_s}\right)\right]_c =$$

$$-\frac{P_c}{RT_c}\frac{1}{d_c^2}, \text{ since } \left(\frac{\partial P_s}{\partial d_s}\right)_c = 0.$$

This means that the segment $d_c - b$ is equal to the critical density and, consequently, the segment $0 - a = 2Z_c$. Hence follows the method of finding the critical density by construction of the tangent satisfying these conditions. For a final sharpening of the value found for d_c, it is convenient to use an additional graph of the relation $1/Z_s = f(d_s)$, constructed on the basis of the previous smoothed data (Fig. 2).

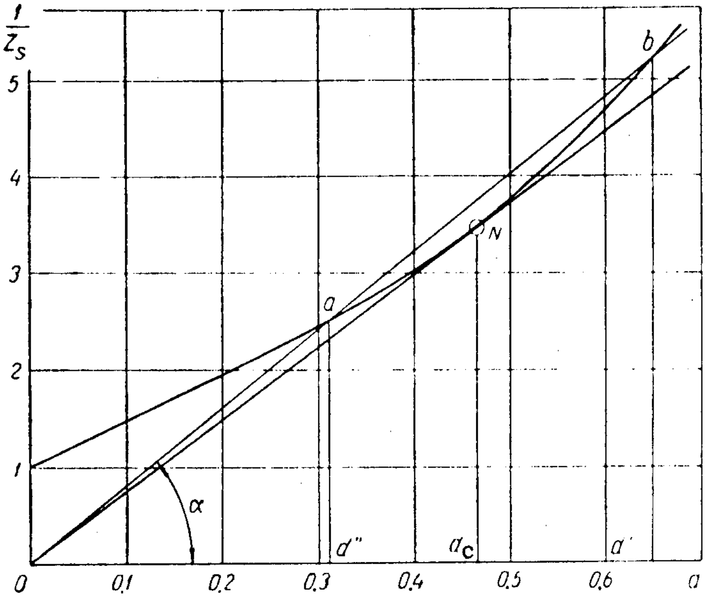

Fig. 2. Inverse compressibility as a function of density at CO_2 saturation (N is the critical point).

This curve possesses another remarkable property. If a secant is drawn from the origin at an angle whose tangent is $\tan\alpha = RT_s/P_s$, then it intersects the curve at points *a* and b, corresponding to values d" and d' at the given temperature T_s and corresponding saturation pressure P_s. When the secant tends to its limiting condition, i.e., tangency, points *a* and b converge at the point corresponding to the critical density d_c. Construction of this tangent from a fixed point at the origin gives an accurate value of d_c. It is necessary to point out that the slope of the tangent should be equal to RT_c/P_c. If the latter condition is fulfilled, then the value of d_c obtained is matched with the parameters P_c and T_c.

Data on the saturation line of CO_2 [4, 6–13] were processed by the method described above and a value of the critical density $d_c = 0.4682$ g/cm^3 was obtained. Values of the density in the saturated state, including the region adjoining the critical point, were obtained from a graph (Fig. 1) constructed to a suitable scale, in conjunction with data on the pressure curve plotted in coordinates P_s/RT_s and T_s.

The obtained value of the critical density of carbon dioxide agreed well with the data of [7, 11] and differed from [6] by 0.9 and from [13] by 1.8%. Using the proposed method to find the critical volume of water vapor from data in the International Skeleton Tables 1963, the authors obtained the value $V_c^{H_2O} = 3.18 \pm 0.01$ cm^3/g, which lies in sufficiently narrow limits. It agrees well with recent studies [1], which give $V_c^{H_2O} = 3.165 \pm 0.019$ cm^3/g.

Thus the method proposed makes it possible to determine the critical density of a substance with an accuracy suf-

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* It is assumed that after analysis and reduction of the data a relation $P_s = f(T_s)$ and critical parameters T_c and P_c have been adopted.

ficient for practical purposes, to correlate pressure curve data with values of the density on the boundary curve, and to supplement with reliable density data the rarely investigated region of the saturation line close to the critical point.

The analysis showed that, within the limits of the method, the accuracy of determination of d_c can be estimated at 0.3–1.0%. The proposed method is not based on empirical rules, but only on the fact that the saturation curve $Z_s = f(d_s)$ is monotonic.

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Lomonosov Technological Institute, Odessa