

The Third-Order Derivatives For The Thermal Variables At The Critical State Of A Pure Substance

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Abstract—The object of the study was the third-order derivatives formed by pressure, temperature, and volume. The results of calculating the values of the third-order derivatives for the thermal variables at the critical state of a pure substance are presented. These calculations were carried out for a variety of low-temperature pure substances and they were used different models of the equation of state. In all the considered cases, this derivative took on finiteness values. Using this conclusion, the ratios between derivatives, which are critical conditions for pure substances, are analyzed.

Keywords—pure substance; equation of state; third-order derivatives, critical point.

I INTRODUCTION

One of the unsolved problems in the thermodynamics of the critical point of pure substance is to establish the value of the third derivative of pressure with respect to volume at a fixed temperature. For instance, in monograph [1], one of the topical problems is the question of whether the analyzed derivative being is equal to zero or different from it. Its solution will make it possible to reasonably approach the use of the expansion in a series of pressure as a function of volume on the isotherm for the vicinity of the critical point. This approach is widely used in the study of the features of the critical state [2, 3]. In addition, in the case of a finite value of the above derivative at the critical point, there is a basis for the statement about the finiteness of the quantities and similar derivatives of higher orders. Among the works in which this third-order derivative is considered, the article [4] should be noted. It analyzes the features of a number of thermodynamic functions under the assumption of its zero value. In the well-known course of theoretical physics [5], based on the analysis of the expansion of pressure in a series in powers of volume at a fixed temperature, it is concluded that the third-order derivative is negative at the critical point. This expansion was limited to two terms, and its convergence was not analyzed either. In the same work, the possibility of the derivative under study vanishing is rejected, proceeding from the fact that otherwise "three equations with two unknowns will be obtained, which have no general

solutions." The last conclusion is not confirmed by any analytical or numerical results.

The purpose of this work is to carry out a study at the critical state of the values of the some third-order derivatives for thermal independent variables. Equations of state (EOS), that describes vapour and liquid regions of thermodynamic surface, are used as models to calculate thermodynamic properties of pure substances.

II. ANALYSIS OF THE EXISTENCE OF A ZERO VALUE AT THE CRITICAL POINT FOR THE THIRD-ORDER DERIVATIVE OF PRESSURE WITH RESPECT TO VOLUME AT A FIXED TEMPERATURE BASED ON THE VAN DER WAALS EOS

This problem is to check the existence of equality

$$(\partial^3 p / \partial v^3)_T^c = 0, \quad (1)$$

where the symbols p , v , T - denote, respectively, pressure, specific (molar) volume, and absolute temperature. The superscript or subscript c in equality (1) and further refers the considered thermodynamic property to the critical state.

The choice of derivative (1) is due to the prevalence in practice of the EOS in the form $p=p(T, v)$.

When using this thermal EOS for the verification, it is necessary to have the critical parameters p_c , v_c , and T_c . Their values are the roots of the next system of equations

$$\begin{cases} p_c = p(T_c, v_c), \\ (\partial p / \partial v)_T^c = 0, \\ (\partial^2 p / \partial v^2)_T^c = 0. \end{cases} \quad (2)$$

A feature of the solution of system (2) is the possibility of determining the values of v_c , T_c from its last two equations (critical conditions) with the subsequent calculation of the critical pressure directly from the equality $p_c = p(T_c, v_c)$. In this case, another possibility appears for checking the general solutions of the critical conditions and equation (1). It consists in the successive replacement of each of the critical conditions by expression (1). In this work, this way is chosen.

Some difficulties arise with the choice of a EOS model to carry out such a check. It is due to the fact that in the general case it is impossible to identify the difference between calculated and reference values of critical parameters [6]. The calculated parameters mean the values obtained from the critical conditions, and the reference parameters mean the values adopted in the process of creating the EOS. For a correct verification, it is natural to use the calculated critical parameters as better corresponding to the used EOS model. Nevertheless, it must be noted that when applying numerical methods to find the design parameters, the obtained values are irrational numbers. As a result, incorrect conclusions are possible for strongly varying thermodynamic functions in the vicinity of the critical point.

The best option for carrying out this check should be considered the choice of the EOS model, in which the calculated and reference critical parameters coincide and at the same time an analytical solution of the problem under consideration is possible. This option can be practically implemented in the case of using cubic forms of EOS.

In particular, they include the van der Waals equation, which in the reduced form $\pi = \pi(\varphi, \tau)$ is written as

$$\pi = \frac{8\tau}{3\varphi - 1} - \frac{3}{\varphi^2}, \quad (3)$$

where $\pi = p/p_c$, $\varphi = v/v_c$, $\tau = T/T_c$ are the values of pressure, volume and temperature referred to the corresponding critical parameters. The representation of the van der Waals EOS in dimensionless variables makes it possible to avoid the dependence of the results on the type of substance in the process of studying. At the same time, the qualitatively obtained conclusions do not change. The system of equations (1) for EOS (3) takes the form

$$\begin{cases} \pi(1,1) = 1, \\ (\partial\pi / \partial\varphi)_\tau^c = 0, \\ (\partial^2\pi / \partial\varphi^2)_\tau^c = 0. \end{cases} \quad (4)$$

The first check based on the van der Waals equation is to analyze the following records

$$\begin{cases} (\partial\pi / \partial\varphi)_\tau^c = 0, \\ (\partial^3\pi / \partial\varphi^3)_\tau^c = 0. \end{cases} \quad (5)$$

The analytical solution to the system of equations (5) has two roots. The first root corresponds to the following values of the variables τ and φ

$$\tau = \frac{27}{8} - \frac{27\sqrt{2}}{16}, \quad \varphi = \frac{2}{3} + \frac{\sqrt{2}}{3}.$$

The rounded values of these roots are $\tau = 0.989$ and $\varphi = 1.138$. Their substitution into expression (3) leads to the value $\pi_c = 0.961$. It contradicts the first equation of system (4).

The quantities τ and φ corresponding to the second root of system (5) are

$$\tau = \frac{27}{8} + \frac{27\sqrt{2}}{16}, \quad \varphi = \frac{2}{3} - \frac{\sqrt{2}}{3}.$$

For this case, the reduced pressure at the critical point takes on a non-physical value equal to $\pi_c = -189.951$.

In the system of equations formed by the second and third derivatives

$$\begin{cases} (\partial^2\pi / \partial\varphi^2)_\tau^c = 0, \\ (\partial^3\pi / \partial\varphi^3)_\tau^c = 0 \end{cases} \quad (6)$$

there is one analytically obtained root

$$\tau = \frac{2187}{2048}, \quad \varphi = \frac{4}{3}.$$

For approximate values of this root $\tau = 1.068$ and $\varphi = 1.333$, the value of the reduced pressure is $\pi_c = 1.161$. Thus, the solution of system (6) also does not satisfy to the critical conditions for a pure substance.

The facts that system of equations (5) and (6) have solutions is interesting. The point of the thermodynamic surface corresponding to system (5) is, most likely, in the region of unstable states. The same point for system (6) determines the gaseous state of the substance.

Thus, for the Van der Waals model, the systems of equations (4) - (6) do not have the same roots. This conclusion cannot be universal, since it was obtained by studying one specific equation of state. But it gives grounds for the assumption that the hypothesis of the existence of solutions satisfying the critical point of the substance for the analyzed third derivative as at least one of the critical conditions cannot be considered in general terms either.

III. DETERMINATION OF THE VALUES OF THE THIRD DERIVATIVE ON THE BASIS OF VARIOUS MODELS OF EQUATIONS OF STATE

In this section of the work, we will analyze the calculations obtained by using other thermal EOS that describe the thermodynamic properties in the regions of liquid and gaseous states of pure substances, as well as in the conditions of their vapour-liquid equilibrium.

The simplest way to study the derivative $(\partial^3p/\partial v^3)_T$ at the critical point is to directly calculate it from EOS. For the Van der Waals model (3), its reduced value, equalled to -9, is determined analytically. In fig. 1 is shown the nature of the change of the investigated derivative in the near-critical region.

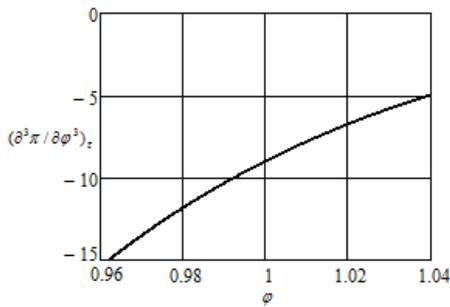


fig 1. Dependence of the reduced third derivative on the reduced volume at the critical isotherm for EOS (3)

As can be seen from the fig. 1, the curve represented on it is smooth, without any singularities at the critical point. In addition, in a fairly wide range of variation of ϕ , the values of the analyzed derivative remain negative.

Below is a three-parameter cubic EOS, which ensures the coincidence of all reference and calculated critical parameters

$$p = RT \left[\frac{1}{v-b} - \frac{a(T)}{v(v+c)} \right], \quad (7)$$

where b , c are constants, $a(T)$ is the temperature function, R is universal gas constant.

The method for determining the constants of this equation is given in [7]. For exact correspondence to the accepted reference critical parameters of the substance p_c , v_c , T_c , it is convenient to represent the temperature function $a(T)$ as

$$a(T) = a_c \cdot \alpha(T),$$

where a_c is a parameter calculated from the critical conditions. In this case, the choice of the form of the temperature function $\alpha(T)$ is limited by the condition

$$\alpha(T_c) = 1.$$

Since the derivative $(\partial^3 p / \partial v^3)_T$ is analyzed at a constant critical temperature, then Eq. (7), when solving the problem under consideration, and taking into account the last equality, is convenient to write in the form

$$p = RT \left[\frac{1}{v-b} - \frac{a_c}{v(v+c)} \right]. \quad (8)$$

In its reduced form, equation (8) is written as

$$\pi = \frac{\tau}{z_c} \left[\frac{1}{\phi - b_r} - \frac{a_{cr}}{\phi(\phi + c_r)} \right], \quad (9)$$

where z_c is the compressibility factor of the substance at the critical point. The subscript r at the parameters of the

equation of state (9) means that their values are referred to the value of the critical volume.

Table 1 shows the results of calculations of the reduced derivative $(\partial^3 \pi / \partial \phi^3)_{\tau c}$ for 24 pure substances used in low-temperature technology. In this table Subst means the name of substance

Table 1. Values of analyzed parameters for pure substances

Subst	z_c	$(\partial^3 \pi / \partial \phi^3)_{\tau c}^c$	Subst	z_c	$(\partial^3 \pi / \partial \phi^3)_{\tau c}^c$
CH ₄	0,280	-4,554	R115	0,288	-4,554
N ₂	0,241	-4,784	C ₂ H ₆	0,274	-4,784
R14	0,280	-4,090	R12	0,266	-4,090
H ₂	0,300	-5,150	R11	0,233	-5,150
C ₃ H ₈	0,286	-4,228	R21	0,280	-4,228
CO ₂	0,276	-3,990	R22	0,241	-3,990
O ₂	0,292	-4,442	R23	0,280	-4,442
iC ₄ H ₁₀	0,274	-4,263	R142	0,300	-4,263
R218	0,253	-4,124	R13B1	0,286	-4,124
R114	0,243	-4,023	R143	0,276	-4,023
C ₃ H ₆	0,280	-4,023	R13	0,292	-4,023
Ar	0,276	-4,863	Ne	0,274	-4,863

As follows from this table, for all the presented substances, the inequality $(\partial^3 \pi / \partial \phi^3)_{\tau c}^c < 0$ takes place. These negative values exceed the value obtained for the van der Waals EOS. For this EOS, as it is known, the value of $z_c=0.375$ does not depend on the type of pure substance. At the same time, as our studies show [7], the parameters of the equation of state (9) a_c , b_r , c_r can be analytically expressed as the functions of variable z_c . Thus, for EOS (9), the effect of the type of substance is determined by the value of z_c .

The plot shown in fig. 2 is based on the data in table 1. In this figure, the circles indicate the values of the coefficient z_c given in table 1, and the solid curve is the analytical dependence following from the EOS (9).

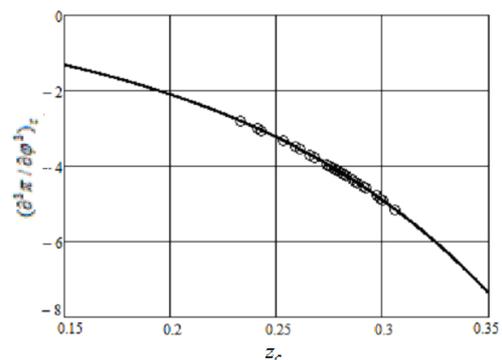


fig. 2. Dependence of the reduced third derivative as a function of the compressibility factor at the critical point for the EOS (9)

As seen from fig. 2, the dependence shown on it is a monotonically decreasing function of the variable z_c . It is essential that the value $(\partial^3 \pi / \partial \phi^3)_{\tau c}^c$ remains negative even outside the range of variation of the coefficient z_c for real substances, which is 0.23 - 0.33 [8].

Calculations of the analyzed derivative were also carried out according to the reliable polynomial form of EOS [9], written in the form

$$z(\varphi, \tau) = 1 + \sum_{i=1}^m \sum_{j=0}^n b_{i,j} \varphi^{-i} \tau^{-j}, \quad (10)$$

where $b_{i,j}$ is an element of the array of coefficients of the equation (10), determined from various thermodynamic properties of substances. For the convenience of calculating the analyzed derivative, EOS (10) was represented as

$$\pi(\varphi, \tau) = \frac{z(\varphi, \tau) \cdot \tau}{z_c \cdot \varphi}. \quad (11)$$

Table 2 below shows the results of obtaining the values of derivatives $(\partial^3 \pi / \partial \varphi^3)_\tau^c$ based on EOS (10).

Table 2. Values of the third derivatives at the critical point for cryogenic substances, calculated from the EOS (11)

Substance	N ₂	O ₂	Ar
$(\partial^3 \pi / \partial \varphi^3)_\tau^c$	-3,377	-5,025	-3,493

As follows from all the presented data, the values of the derivative $(\partial^3 \pi / \partial \varphi^3)_\tau^c$ significantly depend on both the type of substance and the type of the EOS used. But at the same time:

1. the fact of the presence of a zero value in the investigated derivative was not established;
2. all calculated values of the derivative $(\partial^3 \pi / \partial \varphi^3)_\tau^c$ are negative values.

IV. GENERAL THERMODYNAMIC RELATIONS ASSOCIATED WITH THIRD-ORDER DERIVATIVES

This section of the work contains a discussion of questions related to the presence of general thermodynamic dependences, which include the third-order derivatives of thermal quantities. It was shown in [10] that at the critical point of pure substance take place the equalities

$$\frac{(\partial p / \partial v)_T^c}{(\partial^2 p / \partial v^2)_T^c} = \frac{(\partial^2 p / \partial v^2)_T^c}{(\partial^3 p / \partial v^3)_T^c} = \dots = 0. \quad (12)$$

The first fraction in equalities (12) is the ratio of two critical conditions, that it is an indeterminate form 0/0 type. The three dots in these equalities mean that, in the general case, the chain of fractions is limited by the appearance in the denominator the first non-zero derivative. This condition is due to the method of evaluation of indeterminacy, based on the use of an analogue of L'Hospital rule for a function of two variables [10], applied to the critical point. Assuming the validity of next inequality not refuted by the above studies

$$(\partial^3 p / \partial v^3)_T^c < 0, \quad (13)$$

the number of fractions in (12) must be limited by two equalities. This makes it impossible to apply the approach proposed in [10] for the analysis at the critical state of the highest derivatives of pressure with respect to volume at a fixed temperature.

In article [10], when evaluating indeterminate forms at the critical point of a pure substance, the following general relations were obtained between various sets of critical conditions

$$\begin{aligned} \frac{(\partial p / \partial v)_T^c}{(\partial T / \partial v)_p^c} &= \frac{(\partial^2 p / \partial v^2)_T^c}{(\partial^2 T / \partial v^2)_p^c} = \frac{(\partial^3 p / \partial v^3)_T^c}{(\partial^3 T / \partial v^3)_p^c} \\ &= - \left(\frac{\partial p}{\partial T} \right)_v^c. \end{aligned} \quad (14)$$

The last fraction in equalities (14) in accordance with the Planck-Gibbs rule is the slope of the elasticity curve of pure substance at the critical point. It was theoretically [11] and experimentally [1] substantiated that this slope obeys the inequality

$$(\partial p / \partial v)_T^c > 0. \quad (15)$$

From the analysis of relations (14), (15), it is easy to conclude that when inequality (13) is satisfied, the third derivative $(\partial^3 T / \partial v^3)_p^c$ has a positive value.

CONCLUSION

All the results presented in this work indicate the finiteness of the values of the analyzed third derivatives at the critical point of pure substances. At the same time, one cannot speak of the generality of these results, since general results can be obtained only by using undoubted assumptions about the features of the critical state and the laws of thermodynamics. Further research is needed to solve the problem considered in this paper.

Nevertheless, the obtained conclusions doubt on the possibility of categorical statements contradicting the above results. First of all, this concerns the zero or infinite value of the derivative $(\partial^3 p / \partial v^3)_T^c$.

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