



Determination of the Second-Order Mixed Derivatives from Equations of State

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Abstract New method for the determination of second-order mixed derivatives from the equation of state with independent variables temperature and volume is proposed. It is based on Maxwell thermodynamic equations and on general relationships between second-order partial derivatives.

The results of finding of the mentioned derivatives are expressed by analytical forms. Usage of this method is demonstrated by the example of the Van der Waals equation of state. The features of the proposed approach for various types of equations of state are considered.

Keywords Chemical thermodynamics, equations of state, differential Maxwell equations, mixed derivatives

1. Introduction

The differential dependences for the mixed partial derivatives of the second order published in and have a general character [1]. They are based on Maxwell differential equations of thermodynamics and the strict mathematical apparatus. Therefore, these dependences can be used for any pure substance, as well as for any model of its equation of state (EOS), which connects the variables of the Maxwell equations.

It is essential that the relations obtained for the second mixed derivatives are valid for any point of the thermodynamic surface of substance. In particular, this concerns its critical state, for which many problems remain unresolved, including those related to mixed second-order derivatives. As it is noted in article [2], the study of these derivatives is not related with calculations of the thermodynamic properties of substance. It is intended for qualitative analysis of the features of the thermodynamic surface of substance and its special states.

Formally, the definition of general differential relations for three independent variables [2] doubt on the basic statement of thermodynamics about the impossibility of obtaining different forms of the EOS within the framework of this science. The equation of state of the system is not contained in the postulates of thermodynamics and can not be deduced from it. It must be taken from the experience or from a created model from statistical physics [3].

The problems associated with the second-order mixed derivatives have not actually been studied. There are only several results concerning the singularities of some such derivatives at the critical point [1]. The purpose of this paper is to develop and analyze a generalized method for determining the ratios for the second-order mixed derivatives based on the EOS with independent variables temperature and volume.

2. Use of General Relations in the Calculation of Second Mixed Derivatives for Thermal Equation of State

The most commonly used in practice thermal EOS is represented by the dependence

$$p=p(T,v), \quad (1)$$

where p , T , v – pressure, temperature, and molar (specific) volume. For the variables of this EOS, the following general differential relations are obtained [2]



$$\frac{\partial^2 T}{\partial p \partial v} = -\frac{\partial^2 v}{\partial T \partial p} \cdot \left(\frac{\partial T}{\partial v} \right)_p^2, \quad (2)$$

$$\frac{\partial^2 T}{\partial p \partial v} = -\frac{\partial^2 p}{\partial T \partial v} \cdot \left(\frac{\partial T}{\partial p} \right)_v^2. \quad (3)$$

The determination of the first and second order derivatives from the pressure with respect to temperature or volume does not cause difficulties and can be performed analytically. Establish the apparent dependence from the EOS (1) for a non-ideal gas

$$T = T(p, v) \quad (4)$$

is practically impossible. Special examples of a possible analytic expression for the function (4) from the equality (1) are the van der Waals [4] and Redlich-Kwong [5] equations of state. For modern multiparametric thermal EOS, obtaining analytic relationships for second-order mixed derivatives of temperature or volume is a problem.

Analytical finding of the mixed derivatives $\partial p \partial v$ and $\partial^2 v / \partial p \partial T$ from equation (1) may be solved by using expressions (2) and (3). So, from equation (3), transformed to the form

$$\frac{\partial^2 T}{\partial p \partial v} = -\frac{\partial^2 p}{\partial T \partial v} \left/ \left(\frac{\partial p}{\partial T} \right)_v^2 \right., \quad (5)$$

the value of the derivative $\partial^2 T / \partial p \partial v$ is directly determined.

In deriving the formula for the derivative $\partial^2 v / \partial p \partial T$ the equality of the left-hand sides of dependences (2) and (3) are used, from which it follows

$$\frac{\partial^2 v}{\partial T \partial p} \cdot \left(\frac{\partial T}{\partial v} \right)_p^2 = \frac{\partial^2 p}{\partial T \partial v} \cdot \left(\frac{\partial T}{\partial p} \right)_v^2. \quad (6)$$

From the relation (6) we obtain the following expression for determining the derivative $\partial^2 v / \partial p \partial T$

$$\frac{\partial^2 v}{\partial T \partial p} = \frac{\partial^2 p}{\partial T \partial v} \cdot \frac{\left(\frac{\partial T}{\partial p} \right)_v^2}{\left(\frac{\partial T}{\partial v} \right)_p^2}. \quad (7)$$

The fraction on the right-hand side of (7) can be represented as

$$\frac{\left(\frac{\partial T}{\partial p} \right)_v^2}{\left(\frac{\partial T}{\partial v} \right)_p^2} = -\left(\frac{\partial v}{\partial p} \right)_T = -\frac{1}{\left(\frac{\partial p}{\partial v} \right)_T}. \quad (8)$$

On the basis of equations (8), the final expression for determining the derivative $\partial^2 v / \partial p \partial T$ takes the form

$$\frac{\partial^2 v}{\partial T \partial p} = -\frac{\partial^2 p}{\partial T \partial v} \cdot \frac{1}{\left(\frac{\partial p}{\partial v} \right)_T}. \quad (9)$$

Thus, in order to derive analytical dependences for the derivatives $\partial^2 T / \partial p \partial v$ and $\partial^2 v / \partial p \partial T$, it is necessary to have formulas for calculating the derivatives $\partial^2 p / \partial T \partial v$, $(\partial p / \partial T)_v$, $(\partial p / \partial v)_T$.

It should be noted that expressions (5) and (9) can be considered as thermodynamic constraints in the form of Maxwell equations on the relationships between second-order partial derivatives.



3. Determination of Mixed Second-Order Derivatives for Different Forms of the Equation of State

The van der Waals equation of state, despite its low accuracy in determining the properties of substances, remains in demand for testing a wide variety of thermodynamic problems. In particular, this equation can be used for direct character verification of expressions (5) and (9). Below, in order to exclude the influence of the kind of substance, this EOS is represented in the reduced coordinates

$$\pi = \frac{8\tau}{3\varphi - 1} - \frac{3}{\varphi^2}, \quad (10)$$

where π , φ , τ are the reduced values of pressure, volume and temperature of the substance, related to its corresponding critical parameters. For the equation of state (10), direct derivation gives

$$\left(\frac{\partial\pi}{\partial\tau}\right)_{\varphi} = \frac{8}{3\varphi - 1}, \quad \frac{\partial^2\pi}{\partial\tau\partial\varphi} = -\frac{24}{(3\varphi - 1)^2}. \quad (11)$$

From the expression (5) written in the dimensionless form

$$\frac{\partial^2\tau}{\partial\pi\partial\varphi} = -\frac{\partial^2\pi}{\partial\tau\partial\varphi} / \left(\frac{\partial\pi}{\partial\tau}\right)_{\varphi}^2, \quad (12)$$

and, using the substitution of (11) into (12), it is easy to obtain

$$\frac{\partial^2\tau}{\partial\pi\partial\varphi} = \frac{3}{8}. \quad (13)$$

The same equality as expression (13) takes place if we use the direct dependence $\tau = \tau(\pi, \varphi)$ for the Van der Waals equation of state. It is interesting to note, that the numerical value of the derivative $\partial^2\tau/\partial\varphi\partial\pi$ coincides with the value of the compressibility factor of the substance z at its critical point.

In the reduced coordinates, formula (9) for finding the derivative $\partial^2v/\partial p\partial T$ takes the form

$$\frac{\partial^2\varphi}{\partial\tau\partial\pi} = -\frac{\partial^2\pi}{\partial\tau\partial\varphi} \cdot \frac{1}{\left(\frac{\partial\pi}{\partial\varphi}\right)_{\tau}}. \quad (14)$$

For the EOS (10) the derivative $(\partial\pi/\partial\varphi)_{\tau}$, written in the right-hand side of equation (14), has the form

$$\left(\frac{\partial\pi}{\partial\varphi}\right)_{\tau} = \frac{6}{\varphi^3} - \frac{24\tau}{(3\varphi - 1)^2}. \quad (15)$$

Substituting the second of equalities (11) and the dependence (15) into formula (14), we obtain an analytic expression for the derivative $\partial^2\varphi/\partial\tau\partial\pi$

$$\frac{\partial^2\varphi}{\partial\tau\partial\pi} = \frac{24}{(3\varphi - 1)^2} \cdot \left(\frac{6}{\varphi^3} - \frac{24\tau}{(3\varphi - 1)^2}\right)^{-2}. \quad (16)$$

The above example clearly demonstrates the procedure for determining the second mixed derivatives of thermal quantities $\partial^2T/\partial p\partial v$, $\partial^2v/\partial p\partial T$ under the condition that the expressions for the pressure derivatives $\partial^2p/\partial T\partial v$, $(\partial p/\partial T)_v$, $(\partial p/\partial v)_T$ can be analytically obtained. The restriction on the analyticity of the pressure derivatives is satisfied for all the commonly used EOS except their special types, designed to describe the near-critical region of the thermodynamic surface of a pure substance [6, 7].

From considered partial derivatives, the dependence $\partial^2\varphi(\tau, \pi)/\partial\tau\partial\pi$ is most difficult to obtain and interesting for the study. The use of expression (16) makes it possible to graphically represent its characteristic curves in the reduced coordinates, which are shown in Fig. 1 and in Fig. 2.



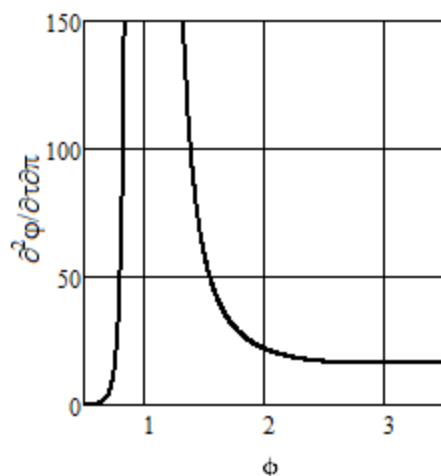


Figure 1: Partial derivative $\partial^2\varphi(\tau,\pi)/\partial\tau\partial\pi$ for the critical isotherm

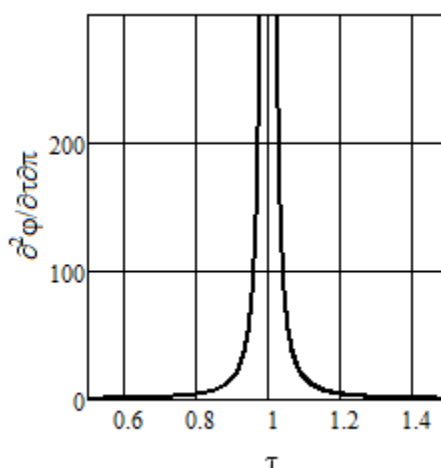


Figure 2: Partial derivative $\partial^2\varphi(\tau,\pi)/\partial\tau\partial\pi$ for the critical isobar

As can be seen from the figures, at the critical point of pure substance this derivative has an infinite discontinuity of the second kind. The existence of a discontinuity in this derivative is analytically proved in article [1], but its concrete form is presented in this paper.

Summarizing the features of the proposed method for determining the mixed partial derivatives of the second order, we can conclude that it enables us to:

- Get the desired derivatives $\partial^2T/\partial p\partial v$, $\partial^2v/\partial p\partial T$ as formulas, which makes it possible to carry out with them symbolic mathematical transformations and create graphs of functions.
- Refuse the use of the explicit functions $T=T(p,v)$ and $v=v(p,T)$ for derivation of the relations for $\partial^2T/\partial p\partial v$, $\partial^2v/\partial p\partial T$, obtaining of which for most EOS is difficult.

The approach described in this paper is applicable not only to the equation of state (1), but also to its other forms. For example, the virial [8] or the Benedict-Webb-Rubin [9] EOS are often written as

$$z=z(T, \rho), \quad (17)$$

where ρ - is the density of substance. Usage relations

$$\rho = \frac{1}{v}, \quad z = \frac{pv}{RT}, \quad (18)$$

it is not difficult to pass from equation (17) to a dependence of the form (1). Another variant of obtaining mixed derivatives is to transform the equalities (5) and (9) to the variables z , T , ρ , using the relations (18).



The method of finding the mixed derivatives considered in this paper can be applied to the fundamental EOS [10]

$$a = a(T, \rho), \quad (19)$$

where a – specific Helmholtz free energy. From the general relationship for the thermodynamic potential

$$p = - \left(\frac{\partial a}{\partial v} \right)_T \quad (20)$$

It is not difficult to receive expressions for the calculation of derivatives $\partial^2 p / \partial T \partial v$, $(\partial p / \partial T)_v$, $(\partial p / \partial v)_T$, and, consequently, for mixed derivatives $\partial^2 T / \partial p \partial v$ и $\partial^2 v / \partial p \partial T$. At the same time, it is impossible to obtain expressions similar to (5) and (9) for the function $a(T, \rho)$.

4. Conclusion

At present time, the determination of the second mixed derivatives of thermodynamic functions has no significant interest, since they are not used either in calculating the thermal and caloric properties of pure substances, nor in studying the qualitative features of their thermodynamic surface.

Nevertheless, the method of obtaining analytical expressions for determining second mixed derivatives based on the thermal equation of state that proposed in this paper is a step for analyzing the singularities of thermodynamic functions at the critical point of a pure substance. Now there is no research in this direction.

The identical approach to obtaining the second mixed derivatives can in principle be realized for EOS expressed as explicit definable functions $T = T(p, v)$ or $v = v(p, T)$.

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