



Second-Order Mixed Derivatives obtained from Equations of State with Entropy and Thermal independent Variables

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Abstract The explicit relationships for calculating and analyzing of the second-order mixed derivatives with entropy are obtained for some types of thermal equation of state. The entropy in these derivatives can be either a function or an argument. These expressions have been established on the basis of general differential Maxwell relations of thermodynamics and rigorous mathematical transformations. They may be applied to any pure substance and any model of equation of state. The determined formulas can be used to analyze the properties of a pure substance at special states of its thermodynamic surface.

Keywords Physical chemistry, thermodynamic properties, equation of state, pure substance, Maxwell equations, second-order differential relationships

1. Introduction

The thermodynamic relations between second-order partial derivatives, which have been published in articles [1-3], do not depend on the type of pure substance and the used model of the equation of state (EOS). Their generality is based on the application of rigorous mathematical transformations and Maxwell thermodynamic differential equations. Usage these relations gives the possibility to find the values of some mixed derivatives and to establish the ratio of the two mixed derivatives at the critical point of a pure substance [1]. Also the obtained dependencies between the three thermodynamic variables [2, 3] give grounds for doubt in the correctness of the statement that the equation of state of a pure substance can not be obtained within the framework of a strictly thermodynamic approach.

The method of determination of general analytical expressions to analyze and calculate various mixed second-order derivatives for thermal variables is proposed in the article [4]. The aim of this paper is to develop the above mentioned method to sets of independent thermodynamic variables that contain entropy.

2. General differential dependencies between three thermodynamic variables

Entropy s is the only caloric thermodynamic property of substance that is variable of Maxwell differential equation and of differential relations for second-order derivatives. All associated with entropy relations may be represented as sets $B = \{s, p, v\}$, $C = \{p, T, s\}$, and $D = \{v, T, s\}$, where symbols p , v , T denote correspondingly pressure, molar (specific) volume, and absolute temperature. These sets are named in accordance with the accepted notation in the work [3].



The complete list of relationships between three thermodynamic variables which obtained by usage of the Maxwell thermodynamic equation is given below [3].

Set B

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

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

Set C

$$\frac{\partial^2 p}{\partial T \partial s} = -\frac{\partial^2 T}{\partial s \partial p} \left(\frac{\partial p}{\partial T} \right)_s, \quad (3)$$

$$\frac{\partial^2 p}{\partial T \partial s} = -\frac{\partial^2 s}{\partial p \partial T} \left(\frac{\partial p}{\partial s} \right)_T. \quad (4)$$

Set D

$$\frac{\partial^2 v}{\partial T \partial s} = -\frac{\partial^2 T}{\partial v \partial s} \left(\frac{\partial v}{\partial T} \right)_s, \quad (5)$$

$$\frac{\partial^2 v}{\partial T \partial s} = -\frac{\partial^2 s}{\partial v \partial T} \left(\frac{\partial v}{\partial s} \right)_T. \quad (6)$$

Any from the presented set contains two equivalent equations for the second-order derivatives. Their equivalence is demonstrated by the examples published in reference [2] for the van der Waals and for the ideal gas equations of state.

Analyses and calculations of any second-order derivative from equalities (1) – (6) involves the usage of EOS. All these equalities depend on entropy and two thermal variables. Therefore, to obtain the explicit expression for second-order derivatives with entropy the corresponding thermal EOS will be attached.

Each of these set contains three mixed derivatives with entropy. In two equalities of the set, entropy is the independent variable, and in one of them it is considered as the function. All above mentioned derivatives are the objects for the next investigations.

3. Mixed second-order derivatives with entropy for set D

For this set is natural to take an thermal equation of state in the form

$$p = p(v, T). \quad (7)$$

Then the desired functions for the set D are derivatives $\partial^2 s / \partial v \partial T$, $\partial^2 v / \partial T \partial s$, $\partial^2 T / \partial v \partial s$. From known EOS (7) and ideal gas property of a substance it is not difficult to obtain the analytical dependence for function $s = s(T, v)$.

The derivative $\partial^2 s / \partial v \partial T$ may be rewritten as

$$\frac{\partial^2 s}{\partial T \partial v} = \frac{\partial}{\partial T} \left[\left(\frac{\partial s}{\partial v} \right)_T \right]. \quad (8)$$

According to the Maxwell differential equation the expression for the derivative in square brackets of the relation (8) is represented as

$$\left(\frac{\partial s}{\partial v} \right)_T = \left(\frac{\partial p}{\partial T} \right)_v. \quad (9)$$

Substitution of equality (9) for equality (8) provides an opportunity to write the next analytical dependence for the derivative $\partial^2 s / \partial v \partial T$

$$\frac{\partial^2 s}{\partial T \partial v} = \left(\frac{\partial^2 p}{\partial T^2} \right)_v. \quad (10)$$

Taking into account the relations (9) and (10), the derivative $\partial^2 v / \partial T \partial s$ can be directly obtained from the expression (6) according to the formula

$$\frac{\partial^2 v}{\partial T \partial s} = - \left(\frac{\partial^2 p}{\partial T^2} \right)_v \cdot \left(\frac{\partial p}{\partial T} \right)_v^{-2}. \quad (11)$$

The only mixed derivative $\partial^2 T / \partial v \partial s$ is unknown in the set D . The expression for this derivative follows from the relation (5) transformed to the form

$$\frac{\partial^2 T}{\partial v \partial s} = - \frac{\partial^2 v}{\partial T \partial s} \cdot \left(\frac{\partial T}{\partial v} \right)_s^{-2}. \quad (12)$$

From differential equation of thermodynamics [5]

$$\left(\frac{\partial T}{\partial v} \right)_s = - \frac{T}{c_v} \cdot \left(\frac{\partial p}{\partial T} \right)_v, \quad (13)$$

where c_v – isochoric heat capacity, that is the function of temperature and volume.

Substitution of equalities (11) and (13) for equality (12) gives the next analytical expression for derivative $\partial^2 T / \partial v \partial s$

$$\frac{\partial^2 T}{\partial v \partial s} = - \left(\frac{T}{c_v} \right)^2 \left(\frac{\partial^2 p}{\partial T^2} \right)_v. \quad (14)$$

Dependence (7) is the most common form in practice of the equation of state. Among other forms of EOS with independent variables T and v , we can note the relations written as $z = z(T, \rho)$, where z, ρ – are correspondingly compressibility factor and density of a substance. The example of such equation of state is virial [6] or the Benedict-Webb-Rubin [7] EOS. By simple mathematical transformations $z = p \cdot v / (R \cdot T)$, $\rho = 1/v$, the function $z(T, \rho)$ reduces to the expression (7). Thus, the above equations of state can be used directly to find the desired derivatives from formulas (10) – (12).

A similar conclusion can be obtained by using modern fundamental equations of state [4, 8].

For the set D may be established analytical dependencies for considered above the second-order mixed derivatives by using another types of thermal equation of state. This procedure ground on the next general mathematical relation between direct and inverse second-order derivatives

$$\left(\frac{\partial^2 p}{\partial T^2} \right)_v = - \left(\frac{\partial^2 T}{\partial p^2} \right)_v \cdot \left(\frac{\partial p}{\partial T} \right)_v^3. \quad (15)$$

Obtaining the expressions for the quantities $\partial^2 s / \partial v \partial T$, $\partial^2 v / \partial T \partial s$, $\partial^2 T / \partial v \partial s$ by usage equality (15) means that EOS takes the form

$$T = T(p, v). \quad (16)$$

Substitutions of equality (15) for relations (10), (11), (14) and some mathematical transformations give the opportunity to write down

$$\frac{\partial^2 s}{\partial T \partial v} = - \left(\frac{\partial^2 T}{\partial p^2} \right)_v \cdot \left(\frac{\partial T}{\partial p} \right)_v^{-3}, \quad (17)$$

$$\frac{\partial^2 v}{\partial T \partial s} = \left(\frac{\partial^2 T}{\partial p^2} \right)_v \cdot \left(\frac{\partial T}{\partial p} \right)_v^{-1}, \quad (18)$$

$$\frac{\partial^2 T}{\partial v \partial s} = \left(\frac{T}{c_v} \right)^2 \left(\frac{\partial^2 T}{\partial p^2} \right)_v \cdot \left(\frac{\partial T}{\partial p} \right)_v^{-3}. \quad (19)$$

The equalities (17) - (19) determine second-order mixed derivatives with entropy for thermal variables of the set B . So, the heat capacity c_v in the formula (19) is the function of variables p and v .



4. Mixed second-order derivatives with entropy for set C

Natural form of a thermal equation of state for the set C is

$$v = v(p, T), \quad (20)$$

and the desired derivatives are $\partial^2 s / \partial p \partial T$, $\partial^2 p / \partial T \partial s$, $\partial^2 T / \partial p \partial s$. From known EOS (20) and ideal gas property of a substance it is not difficult to obtain the analytical dependence for function $s = s(p, T)$.

The algorithm of establishing explicit analytical expressions for the above derivatives is similar to that used for the set D. The expression for derivative $\partial^2 s / \partial p \partial T$ may be represented as

$$\frac{\partial^2 s}{\partial p \partial T} = \frac{\partial}{\partial T} \left[\left(\frac{\partial s}{\partial p} \right)_T \right]_p. \quad (21)$$

According to the Maxwell differential equation

$$\left(\frac{\partial s}{\partial p} \right)_T = - \left(\frac{\partial v}{\partial T} \right)_p. \quad (22)$$

Substitution of equality (22) for equality (21) leads to the next analytical expression for the derivative $\partial^2 s / \partial p \partial T$

$$\frac{\partial^2 s}{\partial p \partial T} = - \left(\frac{\partial^2 v}{\partial T^2} \right)_p. \quad (23)$$

Using the relations (22), (23), and, (4) the expression for derivative $\partial^2 p / \partial T \partial s$ takes the form

$$\frac{\partial^2 p}{\partial T \partial s} = \left(\frac{\partial^2 v}{\partial T^2} \right)_p \cdot \left(\frac{\partial v}{\partial T} \right)_p^{-2}. \quad (24)$$

The explicit expression for derivative $\partial^2 T / \partial p \partial s$, that follows from the relation (3), can be written down as

$$\frac{\partial^2 T}{\partial p \partial s} = - \frac{\partial^2 p}{\partial T \partial s} \cdot \left(\frac{\partial T}{\partial p} \right)_s^2. \quad (25)$$

From differential equation of thermodynamics [5]

$$\left(\frac{\partial T}{\partial p} \right)_s = - \frac{T}{c_p} \cdot \left(\frac{\partial v}{\partial T} \right)_p, \quad (26)$$

where c_p – isobaric heat capacity considered as the function of temperature and pressure.

Substitution of equalities (24) and (26) for equality (25) gives the next analytical expression for derivative $\partial^2 T / \partial v \partial s$

$$\frac{\partial^2 T}{\partial v \partial s} = - \left(\frac{T}{c_p} \right)^2 \left(\frac{\partial^2 v}{\partial T^2} \right)_p. \quad (27)$$

From the general mathematical relation between direct and inverse second-order derivatives

$$\left(\frac{\partial^2 v}{\partial T^2} \right)_p = - \left(\frac{\partial^2 T}{\partial v^2} \right)_p \cdot \left(\frac{\partial v}{\partial T} \right)_p^3 \quad (28)$$

can be obtained the next expressions for derivatives $\partial v \partial T$, $\partial^2 v / \partial T \partial s$, $\partial^2 T / \partial v \partial s$. that are based on EOS (16).

Substitutions of equality (28) for relations (23), (24), (27) and some transformations lead the next explicit expressions

$$\frac{\partial^2 s}{\partial p \partial T} = \left(\frac{\partial^2 T}{\partial v^2} \right)_p \cdot \left(\frac{\partial T}{\partial v} \right)_p^{-3}, \quad (29)$$



$$\frac{\partial^2 p}{\partial T \partial s} = - \left(\frac{\partial^2 T}{\partial v^2} \right)_p \cdot \left(\frac{\partial T}{\partial v} \right)_p^{-1}, \quad (30)$$

$$\frac{\partial^2 T}{\partial v \partial s} = \left(\frac{T}{c_p} \right)^2 \cdot \left(\frac{\partial^2 T}{\partial v^2} \right)_p \cdot \left(\frac{\partial T}{\partial v} \right)_p^{-3}. \quad (31)$$

5. Conclusion

Each of the considered set *C* or *D* contains the entropy and two different thermal variables from thermodynamical Maxwell differential equations. These two variables determine the form of the natural thermal EOS that will be used to find the dependencies of the second-order mixed derivatives with entropy. The entropy in these derivatives can be either a function or an argument. For thermal EOS with independent variables, temperature and volume, as well as temperature and pressure, explicit expressions are obtained for calculating and analyzing of the second-order mixed derivatives with entropy.

But the set *B* can not be used to reveal any explicit dependence for a mixed second-order derivative with entropy. A possible explanation of this fact is that the temperature does not enter into the list of the element of this set, nor in the number of Maxwell differential equations.

The total number of second-order mixed derivatives formed from the sets *B*, *C*, *D*, and three possible types of the thermal equation of state is equal to 27. The non-revealed such derivatives in this work are subjects of further research.

It should be noted that any expression for the derivative with entropy does not contain a term corresponding for the ideal gas state of substance. Therefore, EOS with a linear dependency between temperature and pressure (for instance, ideal gas and van der Waals equations of state) can not be applied for testing of the obtained relationships. In this case, the use of mixed second-order derivatives leads to trivial results.

The derived formulas can be used to analyze the properties of a pure substance in special state of its thermodynamic surface. First of all, this concerns problems related to the critical point of a pure substance.

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