

ТЕРМОДИНАМІЧНИЙ АНАЛІЗ ТА МОДЕЛЮВАННЯ

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General thermodynamic relations for thermal variables formed by first-order partial derivatives and not mixed second-order derivatives

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The theory of differential equations is a powerful tool necessary for constructing mathematical models of various applied problems and their solution. The study and analysis of the general differential relations between the derivatives of the thermodynamic functions of substances is a new direction in the theory of their thermodynamic properties. This research is the development of thermodynamics associated with the establishment and use of differential equations. This paper presents two new thermodynamic relationships between thermal variables pressure, absolute temperature, and specific volume. They relate first-order partial derivatives with unmixed second-order derivatives for these variables. Revealing new general relations of thermodynamics made it possible to formulate and solve a number of problems, among which we can note: creation of algorithms for calculating second-order mixed derivatives for a given thermal equation of state; analysis of the features of the second mixed derivatives at the critical point of pure substance; investigations of the general thermodynamic equations with entropy. The procedure for establishing new equations is based on the use of a rigorous mathematical apparatus and Maxwell's differential equations. Therefore, they are of a general nature, that is, they are valid for any pure substance or any mixture of fixed composition. They are also applicable to any model of the equation of state of these substances. With a formal approach to the concept of the term "equation of state", the new relations themselves can be considered as the equation of state of substance. The obtained new relations can be used to develop the theory of the thermodynamic properties of substances. In particular, in this work it is shown that the ratios of two partial derivatives of pressure over the volume, which are zero critical conditions, have no singularities at the critical point itself.

Keywords: Thermodynamic properties; Maxwell equations; Pure substance; Thermal variables; Differential relationships.

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1. Introduction

The study and analysis of the general differential relations between the derivatives of the thermodynamic functions of substances is a new direction in the theory of their thermodynamic properties. These dependences were first published in [1, 2], where they

are represented by mixed second-order derivatives and ordinary first-order partial derivatives. These relations are based on Maxwell's differential thermodynamic equations and rigorous mathematical transformations of their derivatives. For this reason, the obtained dependences can be, like the Maxwell equations, may be applied to any pure substance or to a mixture of fixed

composition. Also they are available to any analytical equation of state (EOS) of a substance that describes its thermodynamic properties.

Each of the four general sets contains dependencies between three of the variables pressure p , absolute temperature T , molar (specific) volume v , and entropy s , which are included in the known Maxwell relations. Each of these sets contains two second-order differential equations. The most interesting of these is the relationships between thermal variables p , v , T , which are the most in practice types of EOS. These relations give reason to question the widespread statement about the impossibility of obtaining the equation of state of substance using a purely thermodynamic approach [8].

Revealing new general relations of thermodynamics made it possible to formulate and solve a number of problems, among which we can note:

- Creation of algorithms for calculating second-order mixed derivatives for a given thermal EOS $p = p(T, v)$ [3].

- Analysis of the features of the second mixed derivatives at the critical point of pure substance [4].

- Investigations of the general thermodynamic equations with entropy [5].

The aim of this work is to carry out studies of the obtained general differential relations [2] by transforming them due to previously unused dependencies between ordinary partial first-, second-order derivatives.

2. Mathematical relations between ordinary partial derivatives

These relations are based on the next well-known equality [6]

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

The relation (1) may be rewritten as

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

Formula (2) has been used for evaluation of indeterminate forms at the pure substance critical state by the analog of L'Hopital's rule [7]. Below it is applied

to obtain the equations for second-order mixed derivatives formed by p , v , and T variables.

Differentiation of both sides of equality (2) with respect to the variable T lead to the next equality

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

From the equation relating the inverse first-order partial derivatives

$$\left(\frac{\partial v}{\partial T}\right)_p = \frac{1}{\left(\frac{\partial T}{\partial v}\right)_p} \quad (4)$$

equality (3) can be rewritten as

$$\frac{\partial^2 p}{\partial v \partial T} = -\left[\left(\frac{\partial^2 p}{\partial T^2}\right)_v \left(\frac{\partial v}{\partial T}\right)_p - \left(\frac{\partial p}{\partial T}\right)_v \left(\frac{\partial^2 v}{\partial T^2}\right)_p\right] \left(\frac{\partial T}{\partial v}\right)_p^2 \quad (5)$$

After simple algebraic transformations the right side of equality (5) takes the form

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

Using the general relation between second-order inverse derivatives [6],

$$\left(\frac{\partial^2 T}{\partial v^2}\right)_p = -\left(\frac{\partial^2 v}{\partial T^2}\right)_p \cdot \left(\frac{\partial T}{\partial v}\right)_p^3 \quad (7)$$

It is easy to establish that the result of two factors on the right-hand side of equation (6) is transformed to the equation

$$\left(\frac{\partial^2 v}{\partial T^2}\right)_p \cdot \left(\frac{\partial T}{\partial v}\right)_p^2 = -\left(\frac{\partial^2 T}{\partial v^2}\right)_p \cdot \left(\frac{\partial v}{\partial T}\right)_p \quad (8)$$

After substituting relation (8) into equality (6), the equation for the second mixed derivative $\partial^2 p / \partial v \partial T$ takes the form

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

In the process of deriving equation (9), only a strict mathematical apparatus have been used. It have no any thermodynamical sense about the meaning of variable functions of p , v , T . For this reason, the initial differential relations for these variables and their mathematical transformations are invariant under permutations of any two variables in equations (1) - (9). These circumstances make it possible to formally obtain relations for other mixed derivatives formed by the variables p , v , T .

From the interchanging in the equation (9) of the variables p and T it follows the next equation

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

From the interchanging in the formula (9) of the variables p and v it we can write the next equality

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

Equations (9) - (11) establish explicit dependences for second-order mixed derivatives as functions of two variables, which are ordinary derivatives of the first and second orders.

3. Analysis of differential dependencies using Maxwell thermodynamic equations

In contrast to relations (9) - (11), Maxwell thermodynamic equations are based on the I and II laws of thermodynamics. For the case of thermal variables p , v , T , which will be considered later, the general thermodynamic dependences presented in the paper [2] have the form

$$\frac{\partial^2 T}{\partial v \partial p} = - \frac{\partial^2 v}{\partial T \partial p} \cdot \left(\frac{\partial T}{\partial v} \right)_p, \quad (12)$$

$$\frac{\partial^2 T}{\partial v \partial p} = - \frac{\partial^2 p}{\partial T \partial v} \cdot \left(\frac{\partial T}{\partial p} \right)_v. \quad (13)$$

Equations (12), (13) are a consequence of transformations of the well-known Maxwell thermodynamic relations. Using equalities (9) - (11) and equations (12), (13) obtained in this paper, we will further consider the origin of the general relations between ordi-

nary derivatives of the first and second orders. Substitution of equations (10), (11) into equation (12) after some simplifications lead to the next equality

$$\left(\frac{\partial^2 T}{\partial p^2} \right)_v \cdot \left(\frac{\partial p}{\partial v} \right)_T + \left(\frac{\partial^2 p}{\partial v^2} \right)_T \cdot \left(\frac{\partial v}{\partial p} \right)_T \cdot \left(\frac{\partial T}{\partial p} \right)_v = - \left[\left(\frac{\partial^2 v}{\partial T^2} \right)_p \cdot \left(\frac{\partial T}{\partial p} \right)_v + \left(\frac{\partial^2 T}{\partial p^2} \right)_v \cdot \left(\frac{\partial p}{\partial T} \right)_v \cdot \left(\frac{\partial v}{\partial T} \right)_p \right] \cdot \left(\frac{\partial T}{\partial v} \right)_p^2. \quad (14)$$

After the disclosure of the square brackets, the right-hand side of equation (14) is transformed to the following record

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

Equation (15), using equalities (8) and (1), is simplified as

$$\left(\frac{\partial^2 T}{\partial v^2} \right)_p \cdot \left(\frac{\partial v}{\partial T} \right)_p \cdot \left(\frac{\partial T}{\partial p} \right)_v + \left(\frac{\partial^2 T}{\partial p^2} \right)_v \cdot \left(\frac{\partial p}{\partial v} \right)_T. \quad (16)$$

After substituting equation (16) into the right-hand side of equation (14), the equation (16) is rewritten as

$$\left(\frac{\partial^2 T}{\partial p^2} \right)_v \cdot \left(\frac{\partial p}{\partial v} \right)_T + \left(\frac{\partial^2 p}{\partial v^2} \right)_T \cdot \left(\frac{\partial v}{\partial p} \right)_T \cdot \left(\frac{\partial T}{\partial p} \right)_v = \left(\frac{\partial^2 T}{\partial v^2} \right)_p \cdot \left(\frac{\partial v}{\partial T} \right)_p \cdot \left(\frac{\partial T}{\partial p} \right)_v + \left(\frac{\partial^2 T}{\partial p^2} \right)_v \cdot \left(\frac{\partial p}{\partial v} \right)_T. \quad (17)$$

Further transformations of equation (17) consist in reducing both parts of the terms with derivatives $(\partial^2 T / \partial p^2)_v$ and multiplying these parts by $(\partial p / \partial v)_T$. These transformations lead to the following notation of equation (17)

$$\left(\frac{\partial^2 p}{\partial v^2} \right)_T \cdot \left(\frac{\partial v}{\partial p} \right)_T \cdot \left(\frac{\partial p}{\partial v} \right)_T \cdot \left(\frac{\partial T}{\partial p} \right)_v = \left(\frac{\partial^2 T}{\partial v^2} \right)_p \cdot \left(\frac{\partial v}{\partial T} \right)_p \cdot \left(\frac{\partial T}{\partial p} \right)_v \cdot \left(\frac{\partial p}{\partial v} \right)_T. \quad (18)$$

Using the differential relation (1), it is easy to obtain from the equation (18) the result of the transformation of equation (12) represented by the next formula

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

The equality (19) may be rewritten as

$$\frac{\left(\frac{\partial^2 p}{\partial v^2}\right)_T}{\left(\frac{\partial^2 T}{\partial v^2}\right)_p} = -\left(\frac{\partial p}{\partial T}\right)_v. \quad (20)$$

Formula (20) was first established by evaluation of indeterminate forms of type 0/0 at the critical state of a substance. These studies used the analogue of L'Hopital's rule applied to mixed derivatives [6].

In work [6] it is obtained from the Maxwell general thermodynamic relations. Therefore, we can conclude that the equation (20) is valid not only the critical point of pure substance or of mixture of fixed content, but also at any stable states of these substances.

The algorithm for analyzing equation (13) is identical to the above study of equation (12). Since the left-hand sides of these two equalities are the same, further mathematical transformations concerning relation (13) will be carried out with its right-hand side

$$-\frac{\partial^2 p}{\partial T \partial v} \cdot \left(\frac{\partial T}{\partial p}\right)_v^2. \quad (21)$$

Equation (21) takes the following form after substituting the right-hand side of equality (9) into it

$$\left[-\left(\frac{\partial^2 p}{\partial T^2}\right)_v \cdot \left(\frac{\partial T}{\partial v}\right)_p + \left(\frac{\partial^2 T}{\partial v^2}\right)_p \cdot \left(\frac{\partial v}{\partial T}\right)_p \cdot \left(\frac{\partial p}{\partial T}\right)_v \right] \cdot \left(\frac{\partial T}{\partial p}\right)_v^2. \quad (22)$$

The expansion of square brackets in equation (22) leads to the following notation

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

Using the equation connecting the direct and inverse ordinary second-order partial derivatives, represented as

$$\left(\frac{\partial^2 p}{\partial T^2}\right)_v \cdot \left(\frac{\partial T}{\partial p}\right)_v^2 = -\left(\frac{\partial^2 T}{\partial p^2}\right)_v \cdot \left(\frac{\partial p}{\partial T}\right)_v, \quad (24)$$

and after obvious transformations of the second term of equation (23), it is written as

$$\left(\frac{\partial^2 T}{\partial p^2}\right)_v \cdot \left(\frac{\partial p}{\partial T}\right)_v \cdot \left(\frac{\partial T}{\partial v}\right)_p - \left(\frac{\partial^2 T}{\partial v^2}\right)_p \cdot \left(\frac{\partial v}{\partial T}\right)_p \cdot \left(\frac{\partial T}{\partial p}\right)_v. \quad (25)$$

By multiplying both terms of equation (25) by $(\partial p/\partial v)_T (\partial v/\partial p)_T$ that equal to 1, we have

$$\begin{aligned} & \left(\frac{\partial^2 T}{\partial p^2}\right)_v \cdot \left(\frac{\partial p}{\partial T}\right)_v \cdot \left(\frac{\partial T}{\partial v}\right)_p \cdot \left(\frac{\partial p}{\partial v}\right)_T \cdot \left(\frac{\partial v}{\partial p}\right)_T \\ & - \left(\frac{\partial^2 T}{\partial v^2}\right)_p \cdot \left(\frac{\partial v}{\partial T}\right)_p \cdot \left(\frac{\partial T}{\partial p}\right)_v \cdot \left(\frac{\partial p}{\partial v}\right)_T \cdot \left(\frac{\partial v}{\partial p}\right)_T. \end{aligned} \quad (26)$$

Given equality (1), equation (26) has the following final form for the right-hand side of formula (13)

$$-\left(\frac{\partial^2 T}{\partial p^2}\right)_v \cdot \left(\frac{\partial p}{\partial v}\right)_T + \left(\frac{\partial^2 T}{\partial v^2}\right)_p \cdot \left(\frac{\partial v}{\partial p}\right)_T. \quad (27)$$

Formula (13) itself, taking in account equality (19), is written as

$$\begin{aligned} & \left(\frac{\partial^2 T}{\partial p^2}\right)_v \cdot \left(\frac{\partial p}{\partial v}\right)_T + \left(\frac{\partial^2 p}{\partial v^2}\right)_T \cdot \left(\frac{\partial v}{\partial p}\right)_T \cdot \left(\frac{\partial T}{\partial p}\right)_v = \\ & = -\left(\frac{\partial^2 T}{\partial p^2}\right)_v \cdot \left(\frac{\partial p}{\partial v}\right)_T + \left(\frac{\partial^2 T}{\partial v^2}\right)_p \cdot \left(\frac{\partial v}{\partial p}\right)_T. \end{aligned} \quad (28)$$

After simplification, equation (28) takes the next final form

$$2 \left(\frac{\partial^2 T}{\partial p^2}\right)_v \cdot \left(\frac{\partial p}{\partial v}\right)_T + \left(\frac{\partial^2 p}{\partial v^2}\right)_T \cdot \left(\frac{\partial v}{\partial p}\right)_T \cdot \left(\frac{\partial T}{\partial p}\right)_v = \left(\frac{\partial^2 T}{\partial v^2}\right)_p \cdot \left(\frac{\partial v}{\partial p}\right)_T. \quad (29)$$

Formula (29) is obtained on the basis of the general thermodynamic relation (13). Carrying out algebraic transformations of this formula, we can obtain its other records using equality (18).

4. Conclusions

The main results of this paper are the derivation of two general differential thermodynamic relations connecting ordinary derivatives of the first and second orders for thermal variables. Using one of them, it was possible to establish that the previously discovered relation of two second-order partial derivatives, which

are critical conditions, have a general nature. So, it relates not only to the critical state of matter.

The obtained equations are the basis for solving various problems of the theory of thermodynamic properties of pure substances.

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Загальні термодинамічні співвідношення для теплових змінних, утворених частними похідними першого порядку і не змішаними похідними другого порядку

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Теорія диференціальних рівнянь є потужним інструментом, необхідним для побудови математичних моделей різноманітних прикладних задач та їх вирішення. Вивчення і аналіз загальних диференціальних співвідношень між похідними термодинамічних функцій речовин є новим напрямком в теорії їх термодинамічних властивостей. Ці дослідження є розвитком термодинаміки, пов'язаним зі створенням і використанням диференціальних рівнянь. У цій статті представлено два нових термодинамічних співвідношення між тепловими змінними: тиском, абсолютною температурою та питомим об'ємом. Вони пов'язують часткові похідні першого порядку з незмішаними похідними другого порядку для цих змінних. Виявлення нових загальних співвідношень термодинаміки дозволило сформулювати та вирішити низку завдань, серед яких можна відзначити: створення алгоритмів обчислення змішаних похідних другого порядку для заданого теплового рівняння стану; аналіз особливостей других змішаних похідних у критичній точці чистої речовини; дослідження загальних рівнянь термодинаміки з ентропією. Процедура створення нових рівнянь заснована на використанні строгого математичного апарату і диференціальних рівнянь Максвелла. Тому вони мають загальний характер, тобто справедливі для будь-якої чистої речовини або будь-якої суміші фіксованого складу. Вони також застосовні до будь-якої моделі рівняння стану цих речовин. При формальному підході до поняття терміну «рівняння стану» самі нові співвідношення можна розглядати як рівняння стану речовини. Отримані нові співвідношення можуть бути використані для розвитку теорії термодинамічних властивостей речовин. Зокрема, у цій роботі показано, що відношення двох частних похідних тиску за об'ємом, які є нульовими критичними умовами, не мають особливостей у самій критичній точці.

Ключові слова: Термодинамічні властивості; Рівняння Максвелла; Чиста речовина; Теплові змінні; Диференціальні відносини.

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