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Comment on 'The Triple Product Rule and the Subtleties of the Mathematical Tools Used in Thermodynamics' by Felipe Américo Reyes Navarro and Rafael Edgardo Carlos Reye

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***Abstract:** It is shown that much of the criticism of my paper 'The Triple Product Rule is Incorrect' Indian Journal of Advanced Mathematics (IJAM), Vol. 1, No. 2, 2021. 1 – 3, https://doi.org/10.35940/ijam.B1102.101221 presented in [1] is incorrect.*

***Keywords:** Triple Product Rule, Natural Variables, Work, Compression, Function of Stat.*

I. INRODUCTION

The authors of [1] rebut my criticism in [2] of the derivation of the triple product rule, which was given in [3, 4, 6]. One can see that there are mistakes in their rebuttal.
The derivation in [3, 4, 6] goes as follows:
The total differential of z is:

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy\,. \quad \ldots \quad (1)$$

We suppose that z is constant, which means that $y = y(x)$ and

$$dy = \left(\frac{\partial y}{\partial x}\right)_z dx\,. \quad \ldots \quad (2)$$

Introducing equation (2) into equation (1) with constant z, we obtain

$$0 = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z dx\,. \quad \ldots \quad (3)$$

Since equation (3) must be true for all dx, rearranging its terms gives

$$\left(\frac{\partial z}{\partial x}\right)_y = -\left(\frac{\partial z}{\partial y}\right)_x\,. \quad \ldots \quad (4)$$

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From this, the triple product rule follows:

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1\,. \ldots \quad (5)$$

It can be seen that there are flaws in this derivation. For constant z, equation (1) becomes

$$0 = \left(\frac{\partial z}{\partial x}\right)_{yz} dx + \left(\frac{\partial z}{\partial y}\right)_{xz} dy, \quad \ldots \quad (6)$$

and both terms on the right-hand side become zero.
The authors of [1] disagree that both derivatives in equation (6) are zero.
I consulted Prof. A. V. Ovchinnikov, one of Russia's leading mathematicians, who serves as Deputy Editor-in-Chief of the Russian Abstract Journal *Matematika*. He wrote to say that if z=const, then not only is dz zero, but also $\left(\frac{\partial z}{\partial x}\right)_{yz} = \left(\frac{\partial z}{\partial y}\right)_{xz}$ =0 because a derivative of a constant is zero. Therefore, if one introduces the relation $dy = \left(\frac{\partial y}{\partial x}\right)_z dx$ Into the previous formula, one can obtain only 0=0 and nothing else!
The authors of [1] proposed a function:

$$z = (25 - x^2 - y^2)_z dx. \quad \ldots \quad (7)$$

They perform a formal differentiation of the right-hand side of this for a constant z and obtain a derivative that is not equal to 0. However, in an exact differentiation, one has to consider that the right-hand side is also constant and that its derivative is 0.
A stricter derivation of the triple product rule is given in [5] (p. 391), [6]. We can write

$$dx = dx|z = \text{const} + dx|y = \text{const} = \left(\frac{\partial x}{\partial y}\right)_z dy + \left(\frac{\partial x}{\partial z}\right)_y dz, \quad \ldots \quad (8)$$

and

$$dy = \left(\frac{\partial y}{\partial x}\right)_z dx + \left(\frac{\partial y}{\partial z}\right)_x dz. \quad \dots \quad (9)$$

Substituting equation (9) into equation (8), we obtain

$$dx = \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial x}\right)_z dx + \left[\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x + \left(\frac{\partial x}{\partial z}\right)_y\right] dz. \quad \dots \quad (10)$$

The first term on the right-hand side equals dx, and hence

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x + \left(\frac{\partial x}{\partial z}\right)_y = 0. \quad \dots \quad (11)$$

From this, the triple product rule in Equation (5) can be easily obtained.

The flaw in this derivation is as follows. Equation (9) cannot be substituted into equation (8), since dy in equation (8) is taken at constant z: dy = dy(z = const), while dy in equation (9) is for varying z. The differential dy in equation (9) at constant z will look like:

$$dy = \left(\frac{\partial y}{\partial x}\right)_z dx \quad \dots \quad (12)$$

and its substitution into equation (8) will not lead to success.

Finally, equation (S20) in [1] describes the compression of a gas. It contains the derivative:

$$\left(\frac{\partial V}{\partial T}\right)_P. \quad \dots \quad (13)$$

At a compression, the temperature of a gas increases, but its volume decreases; hence, this derivative must be negative. Nevertheless, the authors of [1] use another derivative, namely:

$$\left(\frac{\partial V}{\partial T}\right)_P = \alpha V \quad \dots \quad (14)$$

where the thermal expansion coefficient is involved, one cannot use equation (14) to describe mechanical compression. The derivative must be rederived.

II. FINDING AND DISCUSSION

It is shown that the derivation of the triple product rule given in [3, 4, 6] is indeed wrong. Equation (20) in [2] is demonstrated to be unsuitable for describing the compression process.

III. CONCLUSION

The thermodynamic identity, Eq. (19) in [2], which results from the triple product rule, is not always correct. Before applying Eq. (19), it is necessary to check every derivative in it. Here is that identity:

$$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial V}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V. \quad \dots \quad (19)$$

DECLARATION STATEMENT

Some of the references cited are older, noted explicitly as [3], [4], and [5]. However, these works remain significant for the current study, as they are pioneering in their fields.

I must verify the accuracy of the following information as the article's author.

- **Conflicts of Interest/ Competing Interests:** Based on my understanding, this article has no conflicts of interest.
- **Funding Support:** This article has not been funded by any organizations or agencies. This independence ensures that the research is conducted with objectivity and without any external influence.
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- **Data Access Statement and Material Availability:** The adequate resources of this article are publicly accessible.
- **Author's Contributions:** The authorship of this article is contributed solely.

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Igor Stepanov got an MSc in physics from the University of Latvia in 1982 and an MPhil from the University of Sheffield in 2012. Currently, I work as a researcher at Liepaja University, Latvia. Some of my critical findings are:

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- This solution is published in the JP Journal of Heat and Mass Transfer. 2023. Vol 33. No 1. 51 – 70.