

# The Triple Product Rule is Incorrect

Igor A. Stepanov



**Abstract:** The triple product rule, also known as the cyclic chain rule, cyclic relation, cyclical rule or Euler's chain rule, relates the partial derivatives of three interdependent variables, and often finds application in thermodynamics. It is shown here that its derivation is wrong, and that this rule is not correct; hence, the Mayer's relation and the heat capacity ratio, which describe the difference between isobaric and isochoric heat capacities, are also untrue. Also, the relationship linking thermal expansion and isothermal compressibility is wrong. These results are confirmed by many experiments and by the previous theoretical findings of the author.

**Keywords:** Cyclic chain rule; Cyclic relation; Mayer's relation; Heat capacity ratio; Isochoric heat capacity; Compressibility

## I. INTRODUCTION

Functions theory contains the triple product rule, also known as the cyclical relation, cyclic chain rule or Euler's chain rule [1–4]. Suppose that there is a function  $f(x, y, z) = 0$  and this implicit equation can be solved for each of the variables  $x$ ,  $y$ , and  $z$  as a differentiable function of the other two. The triple product rule is a formula that relates the partial derivatives of these functions, and is given by

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

It is often used in thermodynamics, for example in the derivation of formulae for the difference between isobaric and isochoric heat capacities. It can be shown that there is a mistake in the derivation of the triple product rule, and that this rule is invalid. As a consequence, these thermodynamic formulae are also wrong. The results obtained are confirmed by many experimental results and previous outcomes reported by the author.

## II. THEORY

Let us perform a non-strict derivation of (1) [1,2,4]. The total differential of  $z$  is:

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy. \quad (2)$$

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

$$dy = \left(\frac{\partial y}{\partial x}\right)_z dx. \quad (3)$$

Introducing (3) into (2) at constant  $z$ , we obtain

$$0 = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z dx. \quad (4)$$

Since (4) must be true for all  $dx$ , rearranging its terms gives

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

From this, the triple product rule follows.

It can be seen that there are flaws in this derivation. For constant  $z$ , (2) becomes

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

and both terms on the right-hand side become zero. Furthermore, the differential  $dy$  in the second term on the right-hand side of (2) is taken at constant  $x$ :  $dy = dy(x = \text{const})$ . Therefore, at constant  $z$ , we may introduce (3) into (2) only when  $dy$  in (3) is also taken at constant  $x$ :

$$dy(x = \text{const}) = \left(\frac{\partial y}{\partial x}\right)_{zx} dx, \quad (7)$$

which does not make sense.

Let us perform a stricter derivation of (1) [3,4]. We can write

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

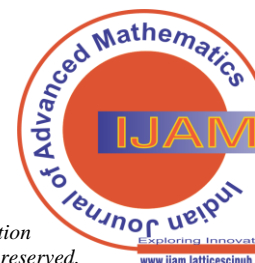
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\* Correspondence Author

Igor Stepanov\*, Scholar/Institute of Science and Innovative Technologies, Liepaja University, Liepaja, Latvia, LV-3401. Email: [istepanov2001@gmail.com](mailto:istepanov2001@gmail.com)

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

Substituting (9) into (8), we obtain

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

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

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

From this, the triple product rule can easily be obtained.

The flaw in this derivation is as follows. Equation (9) cannot be substituted into (8), since  $dy$  in (8) is taken at constant  $z$ :  $dy = dy(z = \text{const})$ , while  $dy$  in (9) is for varying  $z$ .

A specialist in mathematical physics sent me the following “mathematically rigorous proof” of (1): “Assume there are an open set  $\Omega$  of  $(x, y, z)$  and three differentiable functions  $\xi, \eta$ , and  $\zeta$  such that on  $\Omega$ , the equation  $f(x, y, z) = 0$  is equivalent to

$$x = \xi(y, z), \quad y = \eta(x, z), \quad z = \zeta(x, y) \quad (12)$$

Since all three equations hold on  $\Omega$ , each one can be substituted in the others. So

$$y = \eta(x, \zeta(x, y)) \quad (13)$$

and for a constant  $y$ , differentiation with respect to  $x$  gives

$$0 = \partial_1 \eta(x, \zeta(x, y)) + \partial_2 \eta(x, \zeta(x, y)) \partial_1 \zeta(x, y), \quad (14)$$

where  $\partial_1$  and  $\partial_2$  are the derivatives with respect to the first and second argument of the function, respectively. Moreover

$$x = \xi(\eta(x, z), z), \quad (15)$$

so differentiation with respect to  $x$  gives

$$1 = \partial_1 \xi(\eta(x, z), z) \partial_1 \eta(x, z). \quad (16)$$

Combining (14) and (16) gives

$$-1 = \partial_1 \xi(\eta(x, z), z) \partial_2 \eta(x, \zeta(x, y)) \partial_1 \zeta(x, y). \quad (17)$$

and thus

$$-1 = \partial_1 \xi(y, z) \partial_2 \eta(x, z) \partial_1 \zeta(x, y). \quad (18)$$

In the usual (admittedly sometimes confusing) notation, this is (1).” Really, only two cases are possible on the left-hand side of (14):  $\left(\frac{\partial y}{\partial x}\right)_z$  or  $\left(\frac{\partial y}{\partial x}\right)_y$ . In the former one, the last term in (14) becomes zero.

One can show that this derivation is wrong. If on the left-hand side of (14)  $y$  is constant, then  $y$  is constant also on its right-hand side. Consequently, both terms on the right-hand side of (14) turn to zero. Furthermore, as the first term on the right-hand side of (14) is zero, one may not introduce (16) into (14) because the last factor in (16) is not zero.

### A. Discussion and Conclusions

The triple product rule is used in the derivations of the Mayer's relation and the heat capacity ratio [5,6], which relate the isobaric and isochoric heat capacities  $C_P$  and  $C_V$ . According to the Mayer's relation,  $C_P - C_V > 0$ , and from the heat capacity ratio,  $C_P/C_V > 1$ . In [5,6], it was shown that the calculation of heat capacities with the Mayer's relation and the heat capacity ratio gives wrong results; for example, the isochoric heat capacity becomes greater than the isobaric one [5].

In thermodynamics there is a relation that connects the thermal expansion coefficient and the isothermal compressibility [6]:

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

It follows from (1). Let us check (19) for a gas. Let us heat a gas by the heat exchange (introducing a quantity of heat  $\delta q$  into it). Its temperature and volume will then increase and the derivative on the left-hand side of (19) will be positive. The increase in temperature also causes an increase in pressure and therefore both derivatives on the right-hand side of (19) are positive. (The volume in the numerator of the derivative on the right-hand side of (19) increases because of heating.) This is a contradiction, since both sides of (19) must have equal signs.

Now let us heat the gas with compression. In this case, one can write the following equation:

$$\left(\frac{\partial V}{\partial P}\right)_T = -\left(\frac{\partial T}{\partial P}\right)_V \left(\frac{\partial V}{\partial T}\right)_P \quad (20)$$

Here, on the left-hand side, the derivative is negative, the first derivative on the right-hand side is positive, and the second derivative is negative because the decrease in volume leads to the temperature increase. Here, it is necessary to note that in this derivative, the volume in the numerator is the argument and the temperature in the denominator is the function [7].

The change in the volume causes the change in the temperature. Again, both sides of (20) have different signs, which is a clear contradiction. The authors of [8] performed an experimental check of (1) and (19), assuming that  $x = F$  was the tension of a rubber band,  $y = L$  was its length, and  $z = T$  was the absolute temperature, and found that the right-hand side of (1) was equal to  $-0.88$ . In [6], an analysis of their work was given and a mistake was found: from their experiment, it follows that the right-hand side must be positive. Its absolute value is still not clear, and the conclusion in [6] that it is equal to  $0.88$  is premature, although plausible. The signs of the partial derivatives in (19) obtained in [8] have been confirmed by many other papers [9,10]. Hence, numerous experimental results support the findings of the present paper: the triple product rule is not valid.

In [11], it was shown that the first law of thermodynamics for an isobaric process is:

$$dQ = dU + PdV, \quad (21)$$

and for an isochoric process:

$$dQ = dU + VdP \quad (22)$$

(note that in this case,  $dQ$  is an exact differential), and the isobaric heat capacity is therefore equal to the isochoric one:  $C_p = C_v$ . The result of the present paper is further evidence that (21) and (22) are true.

In [12], it also was shown using a lot of experimental data that in heating of gases by compression, the isobaric and isochoric heat capacity are equal to each other, and they are equal to  $(\partial U / \partial T)_V$ .

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## AUTHORS PROFILE



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

- The 3-dimensional Ising model was solved exactly. This solution is published in *Nano Science and Nano Technology: An Indian Journal*. 2012. Vol 6. No 3. 118, free online.
- Explanation of the size effect in physics of strength and prediction of the cells with independent entropy was done.
- Heats of reactions measured experimentally differ from those measured by the Van't-Hoff equation by  $P \square V$ . This result was nominated for a scientific discovery by the Russian Academy of Natural Sciences.
- The mathematical law of scatter in strength of solids and some composite materials was discovered.
- The theory "Iodine is a covalent crystal, not a molecular one" - was proposed by me.
- A new molecular phase in solid iodine was predicted.
- An increase in the entropy always leads to an increase in the temperature – this was proposed.