

The Triple Product Rule and the Subtleties of the Mathematical Tools Used in Thermodynamics

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Abstract: We have clarified several formulas from mathematics and physics. Specifically, we have shown that several standard concepts from thermodynamics, which have been recently investigated and rejected in some papers, continue to be valid. Thus, we have studied the triple product rule, the first law of thermodynamics, Mayer's relation, work, function of state, the relationship between the coefficient of thermal expansion, coefficient of isothermal compressibility and thermal coefficient of pressure. We have used multivariable calculus and properties of Jacobians and other mathematical tools. Likewise, we have provided several didactic examples concerning the interpretation of thermodynamical and mathematical formulas. We have concluded that the basement of several thermodynamical formulas is correct but full of subtleties. Thus, those formulas continue to be valid despite some claims in the recent literature.

Keywords: Triple Product Rule, Jacobians, Natural Variables, Work, Function of State.

I. INTRODUCTION

Firstly, let us remember that the American physicist Richard Feynmann considered that "Thermodynamics is a rather difficult and complex subject when we come to apply it," and "The subject of thermodynamics is complicated because there are so many different ways of describing the same thing" [1][12]. Nevertheless, we consider that thermodynamics is not a difficult subject to understand, as long as we pay attention to the details.

Secondly, some articles have been published not long ago [2-5][13], where it is claimed that many thermodynamical formulas are erroneous because the triple product rule and the first law of thermodynamics would be untrue and imprecise, respectively. Nonetheless these conclusions, those types of work are interesting because it tries to modify some standard concepts and results in physics (thermodynamics [6-9][14][15]) and mathematics (differential and integral calculus of several variables [10,11][16]).

In this research we will introduce several very didactic examples concerning paying attention to details and subtleties to consider when studying thermodynamics. We also will demonstrate that the triple product rule [12], also known as Euler's chain rule, is correct by using the properties of Jacobians [8,9]. Afterwards, specifically, we must also point out that we will refute in detail the arguments that appear in Stepanov (2021) [2], which is interesting research but with imprecise and erroneous conclusions.

II. THEORY/CALCULATION

A. Two Very Didactic Examples Concerning the Key Role of The Natural Variables in Thermodynamics

a. Example by Using the Internal Energy

Let there be an expanding gas whose internal energy is $U(T, V)$, where T is temperature and V , volume. Then, from pure mathematics we have as follows:

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \quad (1)$$

and from physics, namely, the first principle of thermodynamics (the conservation of energy) we have this way:

$$dU = \delta Q - PdV \quad (2)$$

where δQ is heat and P , pressure. Besides, we consider the heat capacity of the gas system $C = \frac{\delta Q}{dT}$, then $\delta Q = CdT$. Therefore,

$$dU = CdT - PdV \quad (3)$$

Indeed, if we were unaware of the subtleties of thermodynamics, we could equalise the prefactors of the respective differentials and would falsely obtain these two "equivalent formulas":

$$C = \left(\frac{\partial U}{\partial T}\right)_V \text{ and } \left(\frac{\partial U}{\partial V}\right)_T = -P \quad (4)$$

To explain the origin of these two inconsistencies, we must point out that we can add and subtract XdV in Eq. (1) (which could or could not have a physical meaning):

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT - XdV + XdV + \left(\frac{\partial U}{\partial V}\right)_T dV \quad (5)$$

by grouping terms, we get

$$dU = \left[\left(\frac{\partial U}{\partial T}\right)_V - X\frac{dV}{dT}\right] dT + \left[X + \left(\frac{\partial U}{\partial V}\right)_T\right] dV \quad (6)$$

Thus, it has become evident that we cannot equalise the prefactors of the differentials of Eq. (1) to the ones of Eq. (6); they are obviously different. This prohibition is valid even if the equations had a physical meaning like Eq. (3). Consequently, the two formulas of Eq. (4) are wrong. The solution to this apparent scientific enigma is to use the natural variables for U from the beginning, that is, starting from $U = U(S, V)$, where S is entropy and V , volume.

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The Triple Product Rule and the Subtleties of the Mathematical Tools Used in Thermodynamics

This way the natural variables of the internal energy U play a key role in the solution to the puzzle. Then, considering $\delta Q = TdS$, from the first law of thermodynamics we solve for dU ,

$$dU = TdS - PdV \quad (7)$$

now let us consider that $S = S(T, V)$, then

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV \quad (8)$$

after replacing Eq. (8) in Eq. (7), we get

$$dU = T \left(\frac{\partial S}{\partial T}\right)_V dT + T \left(\frac{\partial S}{\partial V}\right)_T dV - PdV \quad (9)$$

Next, by considering the definition of thermodynamical temperature and a Maxwell relation, respectively,

$$T = \left(\frac{\partial U}{\partial S}\right)_V \text{ and } \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \quad (10)$$

we get, after replacing Eq. (10) in Eq. (9),

$$dU = \left(\frac{\partial U}{\partial S}\right)_V \left(\frac{\partial S}{\partial T}\right)_V dT + T \left(\frac{\partial P}{\partial T}\right)_V dV - PdV \quad (11)$$

now, we will apply the chain rule for the first addend and group the second and third addends. Thus, Eq. (11) transforms into

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left[T \left(\frac{\partial P}{\partial T}\right)_V - P\right] dV \quad (12)$$

where we can identify $\left(\frac{\partial U}{\partial T}\right)_V = C_V$. Consequently, this time we can equalise the prefactors of the differentials of Eq. (1) to the ones of Eq. (12), because we have taken account the natural variables from a beginning. Therefore, after the corresponding comparisons, the respective identities obtained are now the correct ones:

$$\left(\frac{\partial U}{\partial T}\right)_V = C_V \text{ and } \left(\frac{\partial U}{\partial V}\right)_T = \left[T \left(\frac{\partial P}{\partial T}\right)_V - P\right] \quad (13)$$

b. Example by using enthalpy

From mathematics and thermodynamics, respectively, for enthalpy H we have as follows:

$$dH = \left(\frac{\partial H}{\partial T}\right)_p dT + \left(\frac{\partial H}{\partial p}\right)_T dp \quad (14)$$

and

$$dH = CdT + Vdp \quad (15)$$

If we equalise the prefactors of the respective differentials in Eqs. (14) and (15), we will obtain these wrong formulas:

$$C = \left(\frac{\partial H}{\partial T}\right)_p \text{ and } V = \left(\frac{\partial H}{\partial p}\right)_T \quad (16)$$

In order to obtain the correct formulas, we start from $H = H(S, p)$ because the natural variables of enthalpy are entropy S and pressure p . Besides, we know that enthalpy is defined as

$$H = U + pV \quad (17)$$

then

$$dH = TdS + Vdp \quad (18)$$

now, by considering that $S = S(T, p)$, we have as follows:

$$dS = \left(\frac{\partial S}{\partial T}\right)_p dT + \left(\frac{\partial S}{\partial p}\right)_T dp \quad (19)$$

replacing Eq. (19) in Eq. (18) we obtain:

$$dH = T \left(\frac{\partial S}{\partial T}\right)_p dT + T \left(\frac{\partial S}{\partial p}\right)_T dp + Vdp \quad (20)$$

or

$$dH = T \left(\frac{\partial S}{\partial T}\right)_p dT + \left[T \left(\frac{\partial S}{\partial p}\right)_T + V\right] dp \quad (21)$$

but $T \left(\frac{\partial S}{\partial T}\right)_p = C_p$ and $\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p$. This last formula is a Maxwell relation. Therefore, Eq. (21) looks like this:

$$dH = C_p dT + \left[-T \left(\frac{\partial V}{\partial T}\right)_p + V\right] dp \quad (22)$$

or

$$dH = C_p dT + V[1 - \alpha T] dp \quad (23)$$

where α is the thermal expansion coefficient, $\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_p$.

Finally, we can equalize Eq. (23) with Eq. (14) and obtain

$$\left(\frac{\partial H}{\partial T}\right)_p = C_p \text{ and } \left(\frac{\partial H}{\partial p}\right)_T = V(1 - \alpha T) \quad (24)$$

These are the correct formulas for enthalpy because we began the calculations from its natural variables (S and p).

B. Demonstration of the Triple Product Rule Based on the Properties of Jacobians

We begin from the following expression:

$$E = \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y \quad (25)$$

then, by considering the partial derivatives as Jacobians [8,9], we have

$$\left(\frac{\partial x}{\partial y}\right)_z = \frac{\partial(x,z)}{\partial(y,z)}, \left(\frac{\partial y}{\partial z}\right)_x = \frac{\partial(y,x)}{\partial(z,x)} \text{ and } \left(\frac{\partial z}{\partial x}\right)_y = \frac{\partial(z,y)}{\partial(x,y)} \quad (26)$$

thus expression E looks like this:

$$E = \frac{\partial(x,z)}{\partial(y,z)} \frac{\partial(y,x)}{\partial(z,x)} \frac{\partial(z,y)}{\partial(x,y)} \quad (27)$$

now, we will apply some properties of Jacobians, namely, we permute variables z and x , $\frac{\partial(y,x)}{\partial(z,x)} = -\frac{\partial(y,x)}{\partial(x,z)}$. Then

$$E = -\frac{\partial(x,z)}{\partial(y,z)} \frac{\partial(y,x)}{\partial(x,z)} \frac{\partial(z,y)}{\partial(x,y)} \quad (28)$$

next, for the two first factors, we will apply the rule of chain for Jacobians. Thus, we obtain

$$E = -\frac{\partial(y,x)}{\partial(y,z)} \frac{\partial(z,y)}{\partial(x,y)} \quad (29)$$

we again will permute, that is, we will use $\frac{\partial(y,x)}{\partial(y,z)} = -\frac{\partial(x,y)}{\partial(y,z)}$.

Then

$$E = -(-) \frac{\partial(x,y)}{\partial(y,z)} \frac{\partial(z,y)}{\partial(x,y)} \quad (30)$$

by using the rule of chain for Jacobians again, we get

$$E = \frac{\partial(z,y)}{\partial(y,z)} \quad (31)$$

and after making the final permutation, we obtain

$$E = -\frac{\partial(y,z)}{\partial(y,z)} = -1 \quad (32)$$

but $E = \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y$ therefore, we have demonstrated the triple product rule:

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1 \quad (33)$$

III. RESULTS AND DISCUSSION

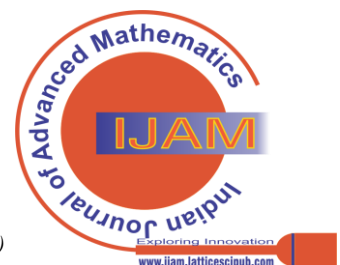
A. Analysis and Comments

Next, we will do an ordered and sequential analysis according to the content from Stepanov (2021) [2].

a. Concerning the non-strict derivation of the triple product rule, which appears in Stepanov (2021)

The non-strict derivation continues to be valid despite arguments from Stepanov (2021), since if we have a function $z = f(x, y)$ then equalise it to a constant k , $z = k$, implies that we now deal with a level curve with $[dz]_{z=k} = 0$. However, this does not imply that $\left[\left(\frac{\partial z}{\partial x}\right)_y\right]_{z=k} = 0$ and

$$\left[\left(\frac{\partial z}{\partial y}\right)_x\right]_{z=k} = 0.$$



Therefore, equation (6) from Stepanov (2021), which we will label as (S.6),

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

must be replaced by

$$[dz]_{z=k} = 0 = \left[\left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy\right]_{z=k} \quad (34)$$

Next, regarding this topic, we will give a specific example. Let $z = f(x, y) = (25 - x^2 - y^2)^{1/2}$ with $0 \leq z \leq 5$, that is, the equation of a quarter sphere centred at the origin and with radius 5. If we only consider the cross section for $z = 4$, we obtain a quarter circumference, $4 = (25 - x^2 - y^2)^{1/2}$ or $y = (9 - x^2)^{1/2}$ with $0 \leq x \leq 3$. Then, according to Eq. (34), we have

$$[dz]_{z=4} = \left[\frac{1}{2}(25 - x^2 - y^2)^{-\frac{1}{2}}(-2x)dx + \frac{1}{2}(25 - x^2 - y^2)^{-\frac{1}{2}}(-2y)dy\right]_{z=4} \quad (35)$$

after simplifying, we obtain

$$[dz]_{z=4} = - \left[(25 - x^2 - y^2)^{-\frac{1}{2}}(xdx + ydy)\right]_{z=4} \quad (36)$$

now, since $y = (9 - x^2)^{\frac{1}{2}}$, then $dy = \frac{1}{2}(9 - x^2)^{-\frac{1}{2}}(-2x)dx$, and by replacing these expressions in Eq. (36), we get as follows:

$$[dz]_{z=4} = - \left[(25 - x^2 - y^2)^{-\frac{1}{2}}[xdx + (9 - x^2)^{\frac{1}{2}} \frac{1}{2}(9 - x^2)^{-\frac{1}{2}}(-2x)dx]\right]_{z=4} \quad (37)$$

thus,

$$[dz]_{z=4} = - \left[(25 - x^2 - y^2)^{-\frac{1}{2}}(xdx - xdx)\right]_{z=4} \quad (38)$$

that is,

$$[dz]_{z=4} = 0 \quad (39)$$

Now, we will come back to the non-strict derivation of the triple product rule. Since $z = k$ is a level curve and not a plane (for $z = f(x, y)$), then

$$[dy]_{z=k} = \left[\left(\frac{\partial y}{\partial x}\right)_z\right]_{z=k} [dx]_{z=k} \quad (40)$$

by replacing Eq. (40) into Eq. (34), we get

$$0 = \left[\left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z dx\right]_{z=k} \quad (41)$$

now, we factor out dx ,

$$0 = \left[\left(\frac{\partial z}{\partial x}\right)_y + \left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z\right]_{z=k} [dx]_{z=k} \quad (42)$$

consequently

$$0 = \left[\left(\frac{\partial z}{\partial x}\right)_y + \left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z\right]_{z=k} \quad (43)$$

or

$$\left[\left(\frac{\partial z}{\partial x}\right)_y\right]_{z=k} = - \left[\left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z\right]_{z=k} \quad (44)$$

finally, we obtain

$$\left[\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y\right]_{z=k} = -1 \quad (45)$$

Usually, in the literature, the square brackets and evaluation at $z = k$ are omitted.

b. Concerning the stricter derivation of the triple product rule, which appears in Stepanov (2021)

The two formulas of Eq. (8) from Stepanov (2021), which we will label as (S.8),

$$dx = [dx]_{z=\text{const}} + [dx]_{y=\text{const}} = \left(\frac{\partial x}{\partial y}\right)_z dy + \left(\frac{\partial x}{\partial z}\right) dz_y \quad (S.8)$$

require clarification: formula

$$dx = \left(\frac{\partial x}{\partial y}\right)_z dy + \left(\frac{\partial x}{\partial z}\right) dz \quad (46)$$

is standard, generic and correct, but regarding formula

$$dx = [dx]_{z=\text{const}} + [dx]_{y=\text{const}} \quad (47)$$

it is only valid on a certain path in the ZY plane (see Fig. 1). Thus, if we have a function $x = f(y, z)$, Eq. (47) is only valid for the path drawn in Fig. 1. Likewise, for the path in Fig. 2, the following equation is valid:

$$dx = \left[\left(\frac{\partial x}{\partial y}\right)_z dy + \left(\frac{\partial x}{\partial z}\right)_y dz\right]_{z=my} \quad (48)$$

In thermodynamics of reversible processes, we must consider x, y , and z as functions of state, that is, it does not matter which path we follow to go from an initial state to a final state: the difference of the respective variable is always the same. Therefore, regarding the stricter derivation of the triple product rule, appearing in Stepanov (2021), but which is not his authorship, it is valid because it is always possible to find a way that allows us to reach the correct result, that is, the triple product rule.

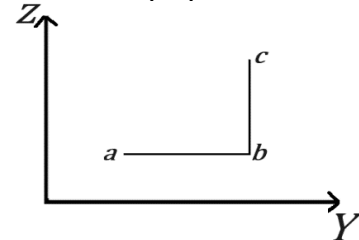


Figure 1. The ZY Plane Showing a Path Where Variables z and y are Independent

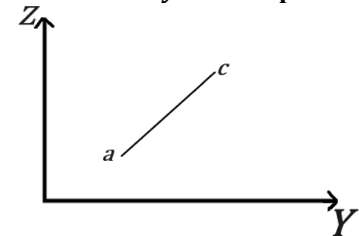


Figure 2. The ZY Plane Showing a Path Where Variables z and y are Dependent

c. Concerning equation (19) of Stepanov (2021)

We will label the equation as (S.19),

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

It relates the coefficient of thermal expansion $\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P$, coefficient of isothermal compression $\beta = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T$ and thermal coefficient of pressure $\gamma = \frac{1}{P} \left(\frac{\partial P}{\partial T}\right)_V$. Formula (S.19) usually is expressed as $\alpha = \beta\gamma P$ and it remains valid despite the arguments that Stepanov (2021) used. To clarify this matter, we can guide ourselves with equations of state. For example, we can use the Clapeyron equation for an ideal gas, the van der Waals equation, Dieterici's equations or modified Berthelot equation for a real gas. All of them satisfy Eq. (S.19).



The Triple Product Rule and the Subtleties of the Mathematical Tools Used in Thermodynamics

Likewise, when we heat the gas by using compression, we have Eq. (20) of Stepanov (2021), which we will label as (S.20),

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

it is also verified by the equations of state of Clapeyron, van der Waals, Dieterici, and Berthelot, respectively. Eq. (S.20) can be expressed as $\beta = \frac{\alpha}{P\gamma}$.

d. Regarding formulas (21) and (22) of Stepanov (2021), for isobaric and isochoric processes, respectively

These formulas are as follows:

$$dQ = dU + PdV \quad (\text{S.21})$$

$$dQ = dU + VdP \quad (\text{S.22})$$

Formula (S.21) is correct but misinterpreted. It is valid for a process in which P could or could not be a constant; an isobaric process is not the only option. And formula (S.22) is false, since for an isochoric process the work is zero and according to the first law of thermodynamics, we have

$$dQ = dU \quad (49)$$

Specifically, the misinterpretation in formulas (S.21) and (S.22) is to assume wrongly that work is defined as

$$W = PV \quad (50)$$

and from here the product of two functions could be derived to obtain falsely the work differential. Work must be defined as

$$W = \int PdV \quad (51)$$

and when P is constant, we have $W = PV$. Therefore, to make physical interpretations, there is a sequence of steps we must necessarily respect.

e. Concerning the claim that Mayer's relation is untrue because it has been demonstrated by using the triple product rule

There are several demonstrations in the literature that are still valid because the triple product rule is correct. Next, we show a demonstration by using the properties of Jacobians [8,9]. Based on Bazarov (1964) [8], we begin from

$$C_P - C_V = T \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P \quad (52)$$

now we use

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{\partial(P,V)}{\partial(T,V)} = -\frac{\partial(V,P)}{\partial(T,V)} \frac{\partial(T,V)}{\partial(T,P)} \frac{\partial(T,P)}{\partial(T,V)} \quad (53)$$

simplifying, we have

$$\left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial V}{\partial T}\right)_P \frac{\partial(T,P)}{\partial(T,V)} = -\frac{\left(\frac{\partial V}{\partial T}\right)_P}{\frac{\partial(T,P)}{\partial(T,V)}} = -\frac{\left(\frac{\partial V}{\partial T}\right)_P}{\left(\frac{\partial P}{\partial T}\right)_T} \quad (54)$$

replacing Eq. (54) in Eq. (52) we have

$$C_P - C_V = -T \frac{\left[\left(\frac{\partial V}{\partial T}\right)_P\right]^2}{\left(\frac{\partial V}{\partial P}\right)_T} = -T \frac{\left[\frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P\right]^2}{\frac{1}{V} \left[\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T\right]} \quad (55)$$

or

$$C_P - C_V = -T \frac{\alpha^2}{\frac{1}{V}\beta} = -TV \frac{\alpha^2}{\beta} \quad (56)$$

This way we have obtained the Mayer's relation for heat capacities.

IV. CONCLUSIONS

All conclusions appearing in Stepanov (2021) are not precise. Specifically, it continues to be valid the triple product rule, Mayer's relation. Likewise, it continues to be valid the relationship between the coefficient of thermal

expansion, coefficient of isothermal compressibility and thermal coefficient of pressure.

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Authors Contributions	Felipe A. Reyes Navarro conceived, designed, analysed, and wrote the manuscript. Rafael E. Carlos Reyes analysed and interpreted the results of the manuscript. Furthermore, he corrected its final version.

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