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Comment on the paper: Ochrymiuk, T., Dudda, W., & Badur, J. (2023). On a Carnot working continuum with non-equilibrium state parameters. Archives of Thermodynamics, 44(4), 285−316. doi: 10.24425/ather.2023.149714

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Received: 22.06.2024; accepted: 29.10.2024

Vol. 45(2024), No. 4, 251–252; doi: 10.24425/ather.2024.152015

Cite this manuscript as: Gujrati, P.D. (2024). Comment on the paper: Ochrymiuk, T., Dudda, W., & Badur, J. (2023). On a Carnot working continuum with non-equilibrium state parameters. Archives of Thermodynamics, 44(4), 285−316. doi: 10.24425/ather.2023. 149714. *Archives of Thermodynamics*, 45(4), 251–252.

In a recent paper in this journal, Ochrymiuk, Dudda and Badur [1], to be denoted collectively by ODB in short here, have compared their results with a fundamental theorem of non-equilibrium thermodynamics that I had derived in 2011 [2]. The authors claim that it "is an unacceptable paradoxical result" to justify why their results do not agree with this theorem. This is unfortunate and is caused by their partial understanding of the first law as commonly stated in textbooks, see Callen [3], in terms of exchange heat $d_e Q$ and work $d_e W$ in Eq. (2), and not appreciating its subtle difference with the second law that is always stated in terms of system-intrinsic (SI) heat dQ and work dW. Correcting these deficiencies will show that the theorem is unassailable.

We will use the most common notation in [2], which can be expressed in terms of the notation by ODB as follows: d_e is d_{eq} and d_i is d_{irr}, here e refers to external or exchange with the outside and i refers to internal or irreversible. In contrast, d refers to SI changes so we have the operator identity $d = d_e + d_i$. Any irreversibility is due to processes that occur internally [4], so it is better to focus on an isolated system Σ for which $d = d_i$ as there is no outside to it, so that $dQ = d_i Q$ and $dW = d_i W$; similarly $dE = d_i E$, where $d_i E$ is the internal change in the energy E and $dS = d_i S$ for the entropy S.

Let E_k denote the SI energy of the kth microstate of the Hamiltonian of Σ, which occurs with probability p_k in the ensemble. Then

$$E \doteq \sum_k p_k E_k,$$

which is defined for any system, isolated or not and of any size, not necessarily macroscopic. From the definition, we obtain

$$dE \doteq \sum_k E_k dp_k + \sum_k p_k dE_k = dQ - dW, \tag{1}$$

where the first sum is the SI heat dQ that appears in the system, and the SI work dW done by the system; the latter follows immediately from the ensemble average of the work $dW_k = -dE_k$ done by the kth microstate, which happens at the cost of reducing E_k. Thus, Eq. (1) is nothing but a statement of energy conservation and represents the first law in terms of SI quantities, including the entropy governed by the second law through dQ. This is contrasted with the conventional form

$$dE \doteq d_e Q - d_e W \tag{2}$$

of the first law in terms of exchange quantities controlled by the outside and does not include the entropy as part of it. Therefore, dE here truly represents the energy change $d_e E$ due to exchange only. This will imply that $d_i E = 0$ due to internal processes, which is consistent with the well-known fact that internal processes cannot change the energy of any system [5]. For our isolated Σ, this means that $dE = d_i E = 0$. Using Eq. (1), this immediately proves the theorem

$$d_{\mathrm{i}}Q \equiv d_{\mathrm{i}}W \quad (3)$$

for Σ, whose physical significance is the following: the theorem finally justifies the well-known experimental result of classical thermodynamics that *any internal work is completely dissipated in the form of internal heat* as noticed by Count Rumford (Benjamin Thomson) [6] while drilling cannons to argue that heat could not be a caloric fluid. It is truly an irreversibility principle governing irreversible processes through the first law:

$$d_{\mathrm{i}}E \doteq \sum_k E_k d_{\mathrm{i}}p_k + \sum_k p_k\, d_{\mathrm{i}}\, E_k = d_{\mathrm{i}}Q - d_{\mathrm{i}}W = 0, \quad (1)$$

for any system, not necessarily an isolated one [7]. Thus, the theorem is not "(...) an unacceptable paradoxical result", and ODB is incorrect in the assessment. The first law in Eq. (2) makes no connection with the second law, but that in Eq. (1) is equivalent to the second law as claimed in [2].

I do not make any inference of the theorem about other results ODB has obtained in [1].

References

[1] Ochrymiuk, T, Dudda, W., & Badur J. (2023). On a Carnot working continuum with non-equilibrium state parameters. *Archives of Thermodynamics*, 44(4), 285−316. doi: 10.24425/ather.2023.149714

[2] Gujrati, P.D. (2011). Generalized non-equilibrium heat and work and the fate of the Clausius inequality. *UATP/1103arXiv:1105.5549*. doi: 10.48550/arXiv.1105.5549

[3] Callen, H.B. (1985). *Thermodynamics and an Introduction to Thermostatistis* (2nd ed.). John Wiley, New York.

[4] de Groot, S.R., & Mazur, P. (1984). *Nonequilibrium Thermodynamics* (1st ed.) Dover, New York.

[5] Prigogine, I. (1971). *Thermodynamics of Irreversible Processes*. Wiley-Interscience, New York.

[6] Klassen, S., Dietrich, S., & Klassen, C.F. (2011). Biography: Sir Benjamin Thompson, Count Rumford. *Storytelling Teaching Model, http://science-story-telling.eu.* https://www.science-story-telling.eu/fileadmin/content/projekte/storytelling/biografien/biografien-eng/thompson-rumford-biografie-gb.pdf

[7] Gujrati, P.D. (2023). Foundations of nonequilibrium statistical mechanics in extended state space. *Foundations*, 3(3), 419−548. doi: 10.3390/foundations3030030

Answer of Authors of the original paper

Dear Editor-in-Chief,

In our paper *On a Carnot working continuum with non-equilibrium state parameters* published in your journal, we quoted a four-page work by Professor Gujrati under the title: *Generalized non-equilibrium heat and work and the fate of the Clausius inequality* from 2011.

The reason we quoted Gujrati's article was that we were looking for premises in the literature to justify different from the classical formulations of the first law of thermodynamics. Now, in Prof. Gujrati's article, we have found an extended form of the first law of thermodynamics, which has some analogies to our formulation of the first law of thermodynamics.

What was valuable to us was the fact that both our work and the work of Professor Gujrati are based on a new, hardly acceptable, surprising model postulate, requiring further justification, research and new premises. This new, hardly acceptable, element of the model is: our "uncompensated work transformation $\mathcal{N}_{work}$" and the "irreversible internal work d_iW", in the Gujrati's paper.

As for the unfortunate wording: "an unacceptable and paradoxical result". This was the wording originally used at the JETC 2023 conference at Salerno in relation to the concept of "uncompensated work transformation $\mathcal{N}_{work}$" that we have introduced.

We are glad that it was noted that our extended form of the first law of thermodynamics is based on this new element of $\mathcal{N}_{work}$ – which *per se* is difficult to be accepted and sounds paradoxical. Perhaps it is good that during the discussion with one of the authors, the strong words "an unacceptable and paradoxical result" were used – they are the best way to draw attention to the importance of the problem.

From the history of thermodynamics, we remember Lord Kelvin's words about the result of Davy's work as: "a lame and impotent conclusion" – it was not at all an unintentional harm to anyone. Rather, they were an indication of the place where we should focus our attention in the future.

Why did we also take the liberty of applying these words to Prof. Gujrati's result? Because we see many analogies between our extended formulation of the first law of thermodynamics and the extended formulation proposed by Prof. Gujrati.

This means that the criticisms are also similar. Therefore, we relate to Gujrati's irreversible internal work d_iW in an equivalent way as others relate to our $\mathcal{N}_{work}$. We understand well that d_iW is a novelty among thermodynamic proposals and we accept it – in our new explanatory paper, *Around the invalid formulations of the first law of thermodynamics*, we are proving that there is: a historical, logical and physical analogy of d_iW with our uncompensated transformation of the work $\mathcal{N}_{work}$.

After a series of discussions in the community, we know that both: d_iW and $\mathcal{N}_{work}$ are new, difficult to accept and paradoxically sounding proposals for thermodynamics. Therefore, we are glad that in his reply to our article, Prof. Gujrati gives one more premise for the validity of the d_iW – this time derived from statistical thermodynamics. We thank Professor Gujrati for putting the research focus at the heart of the problem, and we apologize for the linguistic misunderstanding.

Yours sincerely,
Tomasz Ochrymiuk, Waldemar Dudda and Janusz Badur