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Peer Review

Review of: "Energeia Physics: An Amendment to the Joule-Thomson-Maxwell Energy Narrative"

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I normally find papers like this difficult to review because I disagree with the fundamental premise. However, it is not the job of a reviewer to recommend publication or not on the basis of whether he or she believes a paper to be incorrect unless there is an obvious flaw in the argument or the methodology. In this case, though, the paper is already available, and I am free to disagree with it. As I also have concerns over the historical accuracy of some of the ideas, and these are bound up with the wider issues on which I have a very different view from the author, I raise these in the following discussion alongside specific aspects of the content of the paper. On the correctness or otherwise of the paper, it is for individual readers to decide.

The first, and perhaps most trivial, issue that concerns me is the use of quotation marks in both the abstract and the opening paragraph of what follows. Presumably, these are quotes, but there are neither attributions nor references. Without these, the quotation marks serve no purpose. If the author is going to draw on other sources, the reader should know what these sources are.

The real issue for me as I read this paper is a possible misunderstanding of the foundations of thermodynamics. Take, for example, the paper's thesis, as described on page 3. The idea of compensating transformations relates firmly to cyclic processes. Clausius's theory of thermodynamics was built on two transformations: the transformation of heat to work and vice versa, and the transformation of heat at one temperature to heat at another. A cyclic process contains both types of transformation, and in Clausius's words, they compensate each other in a reversible cycle.

The transformation of heat at one temperature to heat at another has no meaning in modern thermodynamics, but early thermodynamicists sought to describe heat as a physical phenomenon and wrote about it as if bodies contained a definite quantity of heat. Even Planck, in the 1903 English edition

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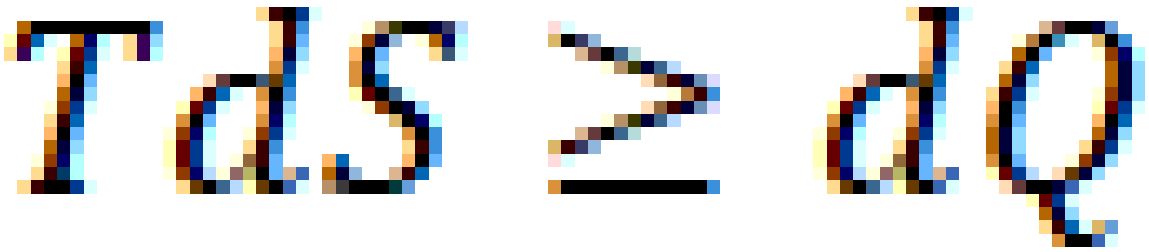
of his Treatise, wrote on the very first page, ... “of a body’s state with regard to heat”, and on the next page of comparing “the degree of heat of two bodies”. On page 35, section 51, Planck is explicit: “Since all calorimetric measurements, according to § 44, extend only to quantities of heat imparted to bodies or given out by them, they do not lead to any conclusion as to the total amount of heat *contained* in a body of given temperature”. The italics are Planck’s.

The idea of “heat at a given temperature” is an archaic notion, but one that is central to Clausius’s development of thermodynamics. His first formulation of the Second Law, that “heat can never pass from a colder to a warmer body without some other change, connected therewith, occurring at the same time”, depends on the notion of compensating transformations. Heat passes from a colder body to a hotter body in a refrigerator, but there is also a corresponding transformation of work into heat. Whether the notion of compensation can be successfully adapted to include chemical effects, I do not know. The paper was not that easy to follow.

There is an enormous amount of confusion around the basics of thermodynamics, and in my view, this paper does nothing to clarify the basic concepts. The author quotes Britannica’s version of the Second Law. Admittedly, the author did not write it (as far as I know), but it is flawed, and the author seems to be unaware of the flaw. It manages to combine 3 supposed statements of the 2nd Law: Clausius's original, Kelvin's statement, and the law of entropy increase, which is a separate, later development due to Clausius. The first two relate to cyclic processes and only cyclic processes, but the explicit mention of cycles is absent. Perhaps this is not such an issue with the Clausius statement, as the idea of transferring heat from hot to cold implies a refrigerator, but it is an enormous omission for the Kelvin statement. The third version of the law, due to Clausius, purports to be more general and is the basis of modern irreversible thermodynamics, but in this framework, entropy is separated from heat via an inequality,



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Thus, the concept of heat energy per unit temperature has no meaning in the modern understanding of entropy increase.

By way of example, consider the free, or Joule, expansion in which a gas expands freely into a larger volume. There is no heat flow, no work done, and no change in internal energy, but entropy is believed to increase. As the temperature remains constant (in the case of an ideal gas), the quantity TdS, where dS is the increase in entropy, can be meaningfully defined. This has the units of energy, but no quantity governed by the First Law changes.

This, to me, is the central issue. If energy is conserved in all transformations or is considered to be "a numerical quantity which does not change when something happens", as quoted in this paper, then the production out of nothing of a quantity with the units of Joules/Kelvin cannot be consistent with the notion of energy. There seem to be two mechanisms of entropy production described in the literature. One arises from dissipative processes, like friction, in which lost energy raises the temperature of some part of the system and heat flows in response. The other is more problematic. It arises because entropy is a state function, and the transition to a different state with a higher entropy means that the entropy must increase. However, there is no apparent physical mechanism or cause associated with this increase, which happens solely because entropy is a state function.

A state function is a mathematical concept that describes a path-independent integral. The total heat exchanged and work done between any two states gives the total change in internal energy, but in order to integrate the quantities mathematically, the precise path taken between the two states needs to be known. However, an integrating factor, the inverse of absolute temperature, converts these inexact integrals into a path-independent integral. Thus, there is a quantity that can be defined for every state in p-V-n space. The question is, though, is this quantity also a physical property of a body in the same thermodynamic state? The standard view in thermodynamics is that entropy as a state function is also a physical property, but this is precisely what leads to the difficulty described above in relation to the free expansion. In fact, it applies to any irreversible process because for such a process $TdS>dQ$. In short, entropy is dissociated from heat flow and can no longer be regarded as heat energy per unit temperature.

As described above, in any such irreversible process, entropy increases for no other reason than that it is a state function. There is no identifiable physical cause and no identifiable physical effect. We don't even know the nature of the property that is supposedly increasing. As a physicist, this troubles me deeply. The most obvious answer is that entropy is not a property of a body. The concept was formulated at a time when physicists believed that a body contained a definite amount of heat, and it is clear from Clausius's

writings that he believed this to be the case. It makes sense in this view of heat to regard a function comprising a change in heat divided by temperature as a property of a body, as both heat and temperature were also regarded as properties of a body in a given thermodynamic state. However, the development of the concept of energy, in which heat is seen as an exchange of energy, should, logically, mean that entropy is connected with an exchange of heat and only with an exchange of heat.

I appreciate that this is my view and that it is not standard, but if I am correct, then the whole premise of this paper is rendered invalid. However, it is for the wider scientific community to make that judgement. As for myself, I remain concerned about the accuracy of some of the statements and their possibility to sow further confusion in a field in which such confusion is already widespread. I have seven specific concerns.

1. Kelvin did not formulate his version of the Second Law in terms of the Kelvin-Planck statement. Planck came after Kelvin, who formulated the law in his own terms. Kelvin's own statement is contained in a paper of his under his original name of William Thomson entitled, "On the dynamical theory of heat" and contained in a book by Magie, (New York and London, 1899, pub by Harper & Brothers) entitled simply, The Second Law of Thermodynamics. In the opening paragraph of part 1, (p114), Kelvin writes,

"According to an obvious principle, first introduced, however, into the theory of the motive power of heat by Carnot, mechanical effect produced in any process cannot be said to have been derived from a purely thermal source, unless at the end of the process all the materials used are in precisely the same physical and mechanical circumstances as they were at the beginning."

This statement alone is sufficient to imply a cyclic process, but just a few lines further on, Kelvin was explicit:

"In any such engine the series of motions performed during a period, at the end of which the materials are restored to precisely the same condition as that in which they existed at the beginning, constitutes what will be called a complete cycle of its operations. Whenever in what follows, the work done or the mechanical effect produced by a thermo-dynamic engine is mentioned without qualification, it must be understood that the mechanical effect produced, either in a non-varying engine, or in a complete cycle, or any number of complete cycles of a periodical engine, is meant."

It seems to me that the central notion of a cyclic process, or a periodic engine, is often overlooked in relation to Kelvin's statement. For example, in section #108 of Planck's Treatise, he writes,

"We often find the second law stated as follows : The change of mechanical work into heat may be complete, but, on the contrary, that of heat into work must needs be incomplete, since, whenever a certain quantity of heat is transformed into work, another quantity of heat must undergo a corresponding and compensating change; e.g. transference from higher to 'lower temperature."

As a statement of the Second Law, this seems to be an amalgamation of both Kelvin (the incomplete conversion of heat into work) and Clausius (an associated compensating change). However, as both the Kelvin statement and Clausius' first statement are equivalent, as shown by Zemansky in his fifth edition of Heat and Thermodynamics, there is no difficulty, providing the necessity of a cyclic process is accepted. However, Planck asserts that this statement is valid in limited circumstances and goes on to consider a single, non-cyclic expansion as an example of a process in which heat is completely converted to work. Needless to say, as this does not apply to a periodic engine, it does not violate Kelvin's statement of the Second Law.

Following on from this, Planck develops over the next few pages his own version of the Second Law: "It is impossible to construct an engine which will work in a complete cycle, and produce no effect except the raising of a weight and the cooling of a heat-reservoir." This is just a different way of saying that heat cannot be completely converted into work in a cyclic process in the absence of other effects, which is commonly accepted as Kelvin's statement of the Second Law. The author's assertion that Kelvin formulated the Law in terms of the Kelvin-Planck statement should either be amended or omitted to avoid a historically misleading idea.

2. On page 5, the author writes, "It is worth noting that, though the idea of entropy and the definite second law of thermodynamics as the entropy law are attributed to Carnot (1824), Clausius (1854-1865), and Gibbs (1875-1878), an earlier 1852 version of the second law of thermodynamics was established by William Thomson in a four-page paper ..., as the principle of the degradation of energy". From a historical perspective, this seems to me to be wide of the mark. Kelvin's paper on the dynamical theory of heat referred to above, in which he set out his statement of the Second Law, was published in 1851. He does not appear to have explicitly stated that heat cannot be converted completely into work, but much of the discussion around Carnot's principle asserts as much. Instead, he proposed the axiom: "It is impossible, by means of inanimate material agency, to derive mechanical effect from any portion of matter by cooling it below the temperature of the coldest of the surrounding objects"

This is the version mentioned by Zemansky (Heat and Thermodynamics, 5^{th} Edition p178). Maxwell, writing in 1888, (Theory of Heat, Dover pub. Inc 2001, originally published 1888) states that "the law from

which Carnot's principle is deduced has been called the Second Law of Thermodynamics". Moreover, the Second Law "asserts that it is impossible, by the unaided action of natural processes, to transform any part of the heat of a body into mechanical work, except by allowing heat to pass from that body into another at lower temperature". He then cites both Clausius's original form and Kelvin's form given above. Therefore, there is no evidence that Kelvin regarded the Second Law as anything other than a restriction on the conversion of heat to work in cyclic heat engines. Any suggestion that he regarded his 1852 paper on dissipation as an expression of a later development of the Second Law seems to me to be very much a modern interpretation. Likewise, Carnot was concerned only with cyclic, reversible engines. The association of entropy and dissipation with the Second Law is due to Clausius and Clausius alone, although dissipation did not feature explicitly in his derivation. His principal motivation seems to have been to understand what he called "internal work", which was the motion of atoms within inter-particle force fields and the inter-conversion of potential energy and kinetic energy, or vis viva, which was thought by Clausius to be heat.

3. The idea of a workless heat transfer on page 7 is confusing, and the later description of the process is unphysical. A hot reservoir in contact with a cooler reservoir will not transmit a given amount of energy. The whole idea of a reservoir is that its temperature does not change. It has to be so big relative to any other sources of heat in a system that its temperature does not change upon heat flow, either in or out. The only natural process that would cause heat flow between two bodies to be limited in the sense that a definite quantity is transmitted from one to the other is their eventual equilibration, but then they cease to be reservoirs and become normal sources of heat. It is simply not possible to envisage a definite quantity of heat passing directly from one reservoir to another in the way described by the author. In a Carnot engine, heat extracted from the hot reservoir does work, but work done on the piston to restore the starting volume does work on the gases inside, and this work is transformed into heat which is passed into the cold reservoir. The operation of an engine is central to the so-called "transfer" of heat from one reservoir to another, but in reality, a quantity of heat is not transferred directly from one reservoir to another.

4. In discussing Maxwell's treatment leading to what is now regarded as the Helmholtz free energy, based on figure 1, the author introduces combustion as the mechanism by which the initial state is created. In the context of Maxwell's treatment, this is unnecessary, as Maxwell is concerned not with how the gas came to be in its initial state, but how it cools from that state to another at a smaller volume and lower temperature. The rationale for the additional combustion step is not clear.

5. Likewise, the author claims that combustion is required to make the Carnot cycle more realistic and claims, in consequence, that the Carnot cycle is not a truly reversible cycle. The whole point of the Carnot cycle is that it is an ideal, reversible cycle. If irreversibility is introduced into it, whether in the form of chemical combustion as a heat source or something else, it is no longer a Carnot cycle. Cycles that incorporate combustion include the Otto and Diesel cycles, but there are others, such as the Brayton cycle. These are not reversible and are intended to represent the real processes that occur in real engines.

6. On page 12, the author re-words the Britannica version of the Second Law, but still retains the essential errors I have discussed above. In particular, he does not appear to recognise that Clausius's two formulations of the Second Law were not only separated by a number of years, they are conceptually distinct. Kelvin's formulation, the Kelvin-Planck statement, and Clausius's first formulation all relate to cyclic processes. Clausius's second formulation was specifically intended to describe non-cyclic processes and related to individual systems. Only Clausius's extension of the Second Law, known as the law of entropy increase, can be used to describe the entropy of an isolated system. As I have described, this version of the Second Law conflicts with the notion of energy conservation.

7. On page 13, the authors write of the Second Law that, 'the law, together with the first law, is applied to determine the "quantity of work a body can do"'. The inner quotation marks around quantity of work are the author's. Again, there is no attribution, but the quotation suggests to me that it came originally from Clausius's Sixth Memoir of 1862. This is the paper in which he attempted to extend the 2nd law through the development of the function that came to be known as entropy. Central to his argument was the idea that work done by a gas is always algebraically smaller than the work done in an ideal, reversible process, and he substituted the latter into an equation essentially expressing energy conservation in order to develop his inequality. He re-worded his law to speak of the work that "can be done", by which he meant in an ideal, reversible process, rather than the work that is done during a real process. It is this, I believe, that underlies the conflict between Clausius' inequality and energy conservation. By way of example, in a free expansion, as alluded to earlier, the work that can be done is given by the integral of pdV over the volume change, whereas the work that is actually done is zero. The former is used to calculate the entropy change, whereas the latter is consistent with energy conservation.

The lack of an appropriate attribution for this seeming quote means that it is impossible to know exactly what the author intended, but if it is indeed a quote from Clausius that pertains to increasing entropy, I question how it can be used in conjunction with the First Law, as it is, in my view, incompatible with it.

Declarations

Potential competing interests: No potential competing interests to declare.