How Harmful Is the First Law?

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ABSTRACT: In his First Law (of thermodynamics), Clausius emphasized the equivalence of heat and work—conservation of energy was mentioned only indirectly. Today, the main emphasis is put on energy conservation, but the equivalence of heat and work has proven not only to be superfluous, but also highly destructive. Because of this emphasis, heat is no longer considered an independent entity. In the guise of the quantity Q heat acts in a strange double role—an entity equivalent to work, but also as something fundamentally different. The place formerly occupied by heat is now filled with an abstract quantity, the entropy S—a phantom without macroscopically relevant properties. By using a phenomenological approach to entropy, it can be shown that entropy S does indeed have easily comprehensible macroscopic properties. This approach can be used to simplify thermodynamic reasoning and to reduce the calculus of thermodynamics to a fraction of its usual extent.

KEYWORDS: entropy; heat; Clausius; quantity of heat; thermodynamics; work

PRELIMINARY REMARKS

The question in the title of this paper raises eyebrows. Today we accept the first law of thermodynamics as a statement of energy conservation. We have learned that conservation of energy is one of the fundamental laws of nature—proven to be valid in both the macrophysical and microphysical worlds. But there is a subtle and inconspicuous difference between the first law of thermodynamics and the principle of conservation of energy—a difference that has far-reaching consequences for the development and understanding of theories of heat, and for related disciplines such as chemical thermodynamics. We are not questioning the principle of the conservation of energy, but its special formulation as part of the First Law of Thermodynamics—with the *equivalence of heat and work* as its central idea since 1850. The statement of the First Law in terms of the equivalence of heat and work establishes a close link between two formerly completely independent concepts and treats the link as an underlying truth without serious examination. Classical thermodynamics is based on this foundation—its success is seen as proof beyond doubt that this was the right approach. For theories in natural sciences their success is often counted as the most important criterion for proving the correctness of underlying assumptions. Doubts

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about the meaning of the heat-work equivalence—accepted without question for one and a half centuries—appear hopeless and almost heretical.

Nonetheless, we hope to show that it is worthwhile to re-examine this point. From a philosophical standpoint, one can pose the question whether it is sufficient to show that a scientific theory is free of contradictions and confirmed by experience. Chemistry offers an interesting parallel, the phlogiston theory. That theory can be formulated in such a way that it is free of contradictions and in agreement with experience, yet it is totally unacceptable.

HISTORICAL BACKGROUND

The Period before 1850

The chemist Joseph Black (1728–1799) was one of the first who brought some order to thermodynamics, during the decades before 1800, by differentiating concepts such as temperature, heat quantity, and heat capacity. He thought of heat as a non-producible and indestructible entity—like a chemical element. He also taught that some substances contain more heat than others with the same temperature. When a substance changes from being thermally poor to thermally rich, like ice to water or water to steam, then the missing heat has to be supplied. When the same process runs in reverse, the excess heat has to be removed. It was realized in those days that it is impossible to create work from nothing—no perpetual motion machine could exist—but it was still believed that work could vanish without a trace. If a wheel with the brake applied has to be turned, work has to be done. Since this work is not retrievable, it was believed to be irreversibly lost. For our purposes, the most important features of pre-energetic thermodynamics are briefly summarized in TABLE 1.

Based on this foundation, in 1824, Sadi Carnot (1796–1832) developed his theory of heat engines by analogy to a water mill. In 1834, Benoit Clapeyron (1799–1864) introduced his equation for the increase in the pressure of steam as a function of temperature. In 1848 William Thomson (1824–1907) created the first universal definition of temperature that was independent of any thermometric material.

The Change

The year 1850 brought a decisive change. This change did not occur suddenly. It had a long history during which more and more facts became known that contradicted the predominant thinking. A simple example—namely, heat generation during abrasion—can clarify this change. This effect was attributed to a heat release from the material ground up during abrasion, which was thought to have a smaller heat capacity than the bulk material. In contradiction to this model, James Prescott Joule (1818–1889) proved in 1843 that there is a fixed relationship between the work expended and the heat generated,

$$W = \alpha \cdot Q \tag{1}$$

independent of the process of generation and of the amount of material ground up, if any. This finding indicates that heat is really generated and conversely, work does

TABLE 1. Main points of the historical development of thermodynamics

	Producible	Destroyable	
Thermodynamics before 1850			
Heat	No	No	Conservative
Work	No	Yes	Semi-conservative
Experimental findings lead to abandonment of pre-energetic thermodynamics			
Heat	No → yes	No	Semi-conservative
Work	No	Yes → no	Conservative
Thermodynamics after 1850			
Heat → entropy	Yes	No	Semi-conservative
Energy = work+heat	No	No	Conservative

not vanish, but that instead a well-defined equivalent entity is formed. Therefore, the old interpretation was wrong on two accounts (TABLE 1).

Joule believed that his research had validated the hypothesis, advocated by him and some of his contemporaries, that heat and work are two forms of the same unchangeable entity occurring in nature. He called it *power, motive force,* or *vis viva* —we refer to it as *energy* today. The thought that the amount of work necessary for the generation of a specific amount of heat could depend on temperature did not occur to him. In that case, the factor α in Equation (1) would not be constant. His simple experimental setup did not allow him to address this problem.

It was known at that time that heat generated at a high temperature could be used to perform more work in a heat engine than heat generated at a lower temperature. Apparently, heat is more valuable at a high temperature than the same amount of heat at a lower temperature—the idea that it takes more work to generate a given heat quantity at a high temperature than at a lower one was therefore close at hand.

Joule's experiments provided evidence for heat generation but not for heat loss. It was known that heat generation depends on the consumption of work. Rudolf Clausius (1822–1888) thought it was justified to assume the inverse also to be true —that a heat engine consumes heat in producing work.[1] With this argument he justified a basic assumption about the nature of heat that later became generally known as the First Law of Thermodynamics. It is worthwhile to mention here that, in the same scientific essay that announces what came to be known as the First Law, Clausius introduced an additional quantity that later came to be called "entropy." Entropy was assigned the same properties as those suggested for heat by the experiments (TABLE 1).

Period after 1850

The old theory of heat had numerous early successes, but was not sustainable in the presence of contradictory new observations. Clausius showed that not all of the old discoveries had to be discarded in order to reconcile the theory with experience. He showed that a few basic assumptions about the nature of heat are sufficient to reach this goal. These are in summary:

- Heat and work are interchangeable in a fixed relationship (the First Law).
- Heat does not flow by itself from low-temperature objects to high-temperature objects.

Please note that the First Law makes a statement about heat while energy conservation is only implied. This version of the First Law allows work to be destroyed in a process where heat plays no role. Conversely, it is possible to formulate the energy principle for example, as Max Born[2] did—without referring to the heat concept. The assumption, commonly made today, that the First Law is equivalent to the principle of the conservation of energy, obscures this distinction: a small distinction but one that is important for us. From his second basic assumption Clausius derived a quantity, later called entropy, which is only a function of the system's state and thus independent of the process used to reach this state. This new quantity was defined by the following integral,

$$S(p, T) = S_0 + \int_{p_0, T_0}^{p, T} \frac{dQ_{rev}}{T} \tag{2}$$

Clausius showed that this quantity has a remarkable property:

- The entropy of a closed system increases but never decreases (Second Law).

W. Thomson, who resisted accepting Joule's interpretation of heat for a long time, was persuaded to develop the theory of heat further, starting with the foundation suggested by Clausius. Also Hermann von Helmholtz (1821–1894), Josiah Gibbs (1839–1903), and others expanded the theoretical framework in various directions. For our purposes, the most salient features of "classical thermodynamics" after 1850 are roughly summarized in TABLE 1.

The changes made covered more than that necessary to accommodate the experimental findings:

- Heat was combined with work into a new quantity called "energy" and thus lost its role as an individual entity.
- The newly created, and purely mathematical, quantity *entropy* takes the place of heat.

PROPERTIES OF ENTROPY

Phenomenological Approach to Entropy

Classical thermodynamics is categorized as a phenomenological theory. It has the special advantage of yielding important results without making use of the existence of atoms. In the 20th century, the phenomenological theory was extended to irreversible processes, and thus not limited to equilibrium conditions. Entropy was thought of as something distributed in matter, like a thermal fluid that is producible but cannot be destroyed. It was likened, in some ways, to the electrical charge or a diffusing substance. These comparisons were prompted by the similarities in the differential equations for entropy, electrical charge, and material flows. It is noteworthy that, in

this case, entropy is treated, at least formally, as an object with physical properties, not purely a mathematical invention.

The list of properties is still too small to present a picture of entropy that is of practical use. In describing a person, we usually compile a list of "phenomenological" attributes that allow us to evaluate his or her appearance, place of residence, skills, and so on. The conjunction of these attributes is basically what makes up a person; his or her name is only an abbreviation for this list. Data such as fingerprints, blood type, or passport number are important to find and identify a person, but they are no substitute for the "phenomenological" attributes. The "wanted poster" for a person is an example of a concise list of such attributes.

We will show that it is possible to develop a wanted poster or fact file for entropy. This description will focus on phenomenologically relevant attributes that are sufficient to define entropy as a measurable physical quantity—while omitting the usual purely mathematical traits using statistical methods for describing atomic behavior. For our approach, it is not required to quantify temperature. As such, it makes it easy to define temperature on the absolute scale by means of entropy.

Attributes of Entropy

Two important mathematical features of entropy are that it is an extensive quantity and a function of the system state. By comparing the entropy of each of two equal systems in the same state, we find that they have the same value. If the entropy is greater or smaller, then the state of the system is different. The entropy contained in a body is not without effect; it changes the condition of that body. One objective of this section is to describe such observable changes more precisely. Along the same lines, we can translate other abstract statements about entropy into simpler language.

(1) *Entropy as an extensive state function:* Each object contains more or less entropy depending on its state. Objects of the same kind and under the same conditions contain equal amounts of entropy. The entropy of a system of objects is equal to the sum of the entropies of its parts.

(2) *Generation:* Entropy is generated in a variety of ways; for example by rubbing, passage of an electric current, or a chemical reaction.

(3) *The Second Law:* Entropy cannot penetrate thermally insulated walls. Therefore, the amount of entropy in a thermally insulated body cannot decrease but can only increase.

(4) *Heating:* The main effect of an entropy increase is that the body becomes warm. For objects of the same kind, the one with the most entropy is the warmest. A body without entropy is absolutely cold. Entropy flows spontaneously only from hotter to colder bodies. In a body entropy spreads out uniformly until all parts are equally warm.

(5) *Side effects*: An entropy increase causes numerous side effects, including changes in volume, shape, state of aggregation, and magnetism. As an example, let us consider the general effects on a substance of continuously increasing entropy—it does not matter whether the entropy source is internal or external. (*a*) Volume increases for most cases. One could say that entropy requires space. Volume decreases when ice melts to produce water. This is one of only a few exceptions. (*b*) When a solid reaches its melting

point, the additional entropy cumulates in the resulting melt and therefore the body does not become any warmer. The melted substance contains more entropy than the original solid. (c) When a liquid reaches its boiling point, the resulting vapor absorbs the additional entropy and therefore the liquid does not become any warmer. The entropy increases further when the steam vapor with the surrounding air.

(6) *Reciprocal effects:* A substance that expands with an entropy input—almost all substances do—becomes warmer upon compression and colder upon expansion according to the Le Chatalier principle.

Working with Entropy

The properties described above make it practical to work with entropy. Entropy can be transferred, poured out, cumulated, distributed...and therefore treated like a physical object.

1. *Controlled exchange:* Let us consider two touching and equally warm bodies. Compressing one body makes it warmer and it gives off entropy to the other one. Expanding the same body makes it colder and then entropy flows in the opposite direction. Entropy can be "squeezed out" and "sucked up" like water by a sponge.

2. *Transfer:* With the aid of an "entropy sponge" one can transfer entropy from a cold to a warmer object or vice versa. By repeating the same procedure, any desired amount of entropy can be transferred.

3. *Preservation of entropy:* In order to guarantee that entropy does not increase during an operation, one has to insist that all operational steps are reversible. This condition is easily stated, but very difficult to satisfy in practice, but methods to circumvent this restriction are known.

4. *Measuring entropy:* The volume loss of ice while melting is proportional to the amount of entropy added. This fact can be used to construct a simple entropy-measuring instrument: a bottle equipped with an inserted capillary tube and filled with an ice-water mixture (ice calorimeter). When care is taken that no entropy is generated or lost during the measurement, then the amount of entropy added is proportional to the water level change of the capillary tube.

TEMPERATURE AND WORK

Definition of Temperature

Entropy always flows in the direction of decreasing temperatures. In other words, temperature difference causes an entropy flow that seeks to equalize those temperatures. One can say that temperature creates a kind of thermal tension for moving entropy, similar to the effect of pressure on a fluid. Already in the 18th century, Johann Lambert (1728–1777) presented this explanation for the expansion of heat.

It takes work to overcome this tension and force entropy into a body. The higher the tension, or the hotter the body, the more work is required. Energy conservation

demands that the energy increase in a body is independent of the source; it can be internal or external, as long as the total energy is conserved.

This thought process suggests that the expended energy W can be used as a measurement of temperature. This can be readily accomplished by entropy generation. Since an increase in entropy drives up the temperature, the created entropy quantity S_e has to remain small. The smaller this quantity, the less energy is required. Therefore, W by itself does not provide a proper temperature measurement, but the proportionality factor (T) between W and S_e:

$$W = T \cdot S_e \quad \text{(for } S_e \to 0) \tag{3}$$

Work for Entropy Transfer

If entropy is transferred from a colder to a warmer object—by means of our test aid—then two work contributions have to be considered. First, the work required to force the entropy quantity S into the warmer object against the thermal tension T_2, $T_2 \cdot S$, and secondly, the work output from the colder object, $T_1 \cdot S$. The difference of both contributions is equal to the work W that has to be performed:

$$W = (T_2 - T_1) S \tag{4}$$

It is assumed that no additional entropy is generated by friction or any other means. That would require more work.

If entropy is transferred from a higher to a lower temperature, $T_2 < T_1$, then W becomes negative and work is delivered as in a heat engine. Entropy generation during this operation lowers the work output and therefore, the efficiency.

Entropy Generation in an Entropy Flow

Entropy can be easily generated by passing an electrical current through a resistance. If we know the charge q, the driving voltage $\Delta\varphi$, and the existing temperature T, then we can compute the produced entropy S_e from the energy balance, where $q \cdot \Delta\varphi$ represents the energy from the potential drop and $T \cdot S_e$ denotes the energy required for entropy generation:

$$T \cdot S_e = q \cdot \Delta\varphi \tag{5}$$

It is not commonly known that entropy is also generated by driving it through a thermal resistance. The produced quantity S_e can be computed from a similar energy balance:

$$T \cdot S_e = S \cdot \Delta T \tag{6}$$

In the above equation $S \cdot \Delta T$ represents the energy released by the entropy flow across the temperature drop ΔT, and T is the temperature of the colder side through which both the initial S and newly generated entropy S_e flow. This kind of entropy production can be shown experimentally. For the sake of simplicity, we use the following idealized process (FIG. 1).
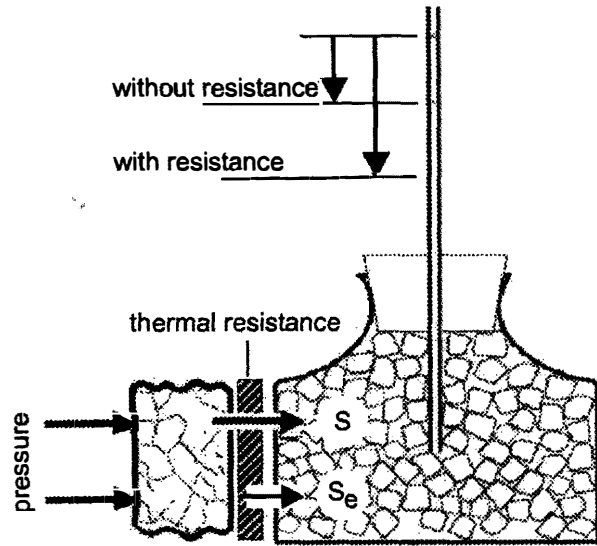
FIGURE 1. Entropy flow through a thermal resistance generates entropy.

1. *Entropy flow without resistance:* By squeezing the "sponge," it remains cold because entropy S is transferred to the bottle. The ice melts and the water level in the capillary tube falls.
2. *Entropy flow through a resistance:* By squeezing the "sponge" as before, it warms up because entropy escapes very slowly. Both S and S_e (generated in the resistance) trickle over to the bottle, the ice melts, and the water level in the capillary tube drops but lower than before! Although the "sponge" released the same amount of entropy for both cases, the bottle now indicates more entropy.

THE FIRST LAW AND ITS CONSEQUENCES

Conservation of Work

Clausius makes a basic assumption about the nature of heat in his First Law—the statement of the equivalence of heat and work. It is not necessary to make this assumption in formulating the principle of energy conservation. It suffices to realize that all work, gained or expended, has an equivalent and the sum of these equivalents remains constant in all processes. Work-equivalents like *potential, kinetic, electrical, internal energy*... can be interpreted as a measure of stored work. We have seen that the energy $W = T \cdot S_z$ can be interpreted as work against the thermal tension T while the entropy S_z is pressed into a body. This energy, which we could call *thermal work* for convenience, flows into a body along with the entropy S_z and was interpret-

ed by Clausius as *heat Q*. If we avoid the exclusion of the quantity Q as "non-work" and treat it as work, then the energy principle can be simply stated as conservation of work:

Work cannot be created nor destroyed.

The quantity Q is a strange mixture of energy and entropy attributes. If we transfer the energy Q to a body, its entropy increases while the entropy of its surroundings decreases. The body becomes warmer and its surroundings colder. However, this phenomenon is not described as entropy flow but as a peculiarity of the energy Q that produces these specific effects. In other words, heating is not considered as caused by an entropy flow, but as a consequence of the unique features of the energy Q that other forms of energy do not possess. Heat is thus "fundamentally" different from other kinds of work. The entropy increase is treated and calculated as a secondary result from this special form of energy transfer. These peculiarities of the quantity Q require unique terminology, calculations, conclusions and a number of supporting mathematical quantities that are not found in other fields of physics. They make the thermodynamics structure strange and confusing.

Entropy as Heat

Naturally, entropy influences everyday activities. Entropy is something that flows into a pot of soup to warm its contents, is lost from a cup of coffee as it cools down, is produced by an electric stove, a microwave oven, and an oil-burning heater. It is delivered via hot water, distributed by radiators, contained by insulated walls in a room and stored by woolen clothing on a body. In short, it is what an unbiased layman calls "heat."

The commonly held concept of "heat" is quite broad and mixes physical aspects like temperature, heat quantity, and thermal energy together with physiological and psychological ones. Therefore, it is not feasible to simply equate entropy and heat based on everyday perceptions without providing precise descriptions. The narrower concept of "quantity of heat" has a better chance. The direct metrication (a philosophical procedure for connecting qualitative concepts like length, time, mass ... with their metrical counterparts l, t, m ...) of the notion "quantity of heat" yields a quantity in full conformance with entropy—as long as the same units and null references are established for both.[3]

H. Callendar[4] already claimed in 1911 that entropy is nothing more than the reconstruction of the heat quantity used by Carnot, with the exception that entropy can be produced while Carnot's heat cannot. From this viewpoint Equation (3) corresponds to Joule's relationship (1), except that the factor α there is not constant, but depends on temperature. Due to a cunning definition of temperature, it is identical with the absolute temperature T.

Consequences

All these observations are incompatible with the equivalence of heat and work assumed by the First Law. Not only that, but the standard interpretation of the First Law precludes a simple interpretation of entropy, by assigning its attributes to the energy quantity Q. As a result, entropy is reduced to a lifeless ghost without concrete

physical properties, while Q assumes a schizophrenic double role that it cannot fulfill.

The quantities Q and S are in a relationship similar to that of phlogiston and oxygen at the beginning of modern chemistry. According to phlogiston theory, removing all the phlogiston from a metal yields a heavy, earthy calx (the metal oxide, from the modern point of view), which can readily be transformed again into the (obviously lighter) metal by adding phlogiston.

$$\text{metal} \rightleftharpoons \text{calx} + \text{phlogiston} \quad (\text{today: metal} + \text{oxygen} \rightleftharpoons \text{oxide} \tag{7}$$

The entity that was later called oxygen is described in the phlogiston theory by its negative—a phantom with fantastic properties, only known in its bound state, but intangible itself, with a negative weight. Before 1800, Lavoisier finally put an end to this "spook." More than 50 years later, Clausius created a similar phantom with his definition of entropy.

H. Fuchs[5] demonstrated the creation of such a phantom in his satirical article "A surrealistic tale of electricity" by demanding electricity and work to be equivalent, analogous to the First Law. Starting from this point, mathematics transforms *charge* into an abstract entity similar to entropy.

Future Outlook

In this text we have tried to show that the treatment of heat as a form of energy by the First Law is more of a disaster than a benefit for thermodynamics. A few modest changes in the assumptions of pre-energetic thermodynamics, as shown in TABLE 1, would have been sufficient to make it consistent with experience. Many difficulties that resulted from this historical arrangement could have been avoided. Within the limited scope of this paper we cannot fully address such questions as how well the new approach holds up under scrutiny, how useful it is for practical applications, and how compatible it is with statistical interpretations. Our investigations over several decades have not encountered any serious difficulties. On the contrary, they show that:

(1) long derivations can often be reduced to one or two lines;

(2) many results are intuitively predictable without any calculations; and

(3) the approach is compatible with microphysical models.

The First Law marks a consequential turning point in the history of thermodynamics, where this science forfeited its heavenly naturalness, perhaps forever—analogous to the Fall of Man.
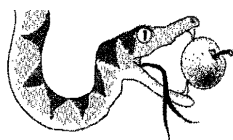
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