

# Entropy, a resurrection of caloric—a look at the history of thermodynamics

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**Abstract** The entropy introduced into physics by Clausius was, contrary to general belief, not a new physical quantity but the reconstruction of the 'quantity of heat' conceived about one hundred years earlier by the Scottish chemist Black. The same quantity was also used under the name 'calorique' by Carnot in his work which laid the foundations of thermodynamics. That entropy and Black's 'quantity of heat' are only two names for the same physical quantity is not only of historical interest but is of significance to the teaching of thermodynamics as well. It asserts that entropy can be visualised as a kind of substance which obeys 'half a conservation theorem': it can be created but not destroyed.

**Zusammenfassung** Entgegen weitverbreiteter Lehrmeinung handelte es sich bei der durch Clausius eingeführten Entropie keineswegs um eine neue Größe der Physik, sondern um die Rekonstruktion einer viel älteren Größe, nämlich der hundert Jahre früher von dem schottischen Chemiker Black konzipierten 'quantity of heat'. Dieselbe Größe benutzte Carnot unter dem Namen 'calorique' in seiner berühmten Abhandlung, in der er die Grundlagen der Thermodynamik entwickelte. Daß Entropie und Wärmemenge (im Sinne Blacks) lediglich zwei verschiedene Namen für dieselbe Größe sind, ist nicht nur für die Geschichte der Physik von Bedeutung, sondern sollte es vor allem für ihre Didaktik sein—besagt es doch, daß die Entropie anschaulich verstanden werden kann als Menge der Wärme. Diese wie eine Art Substanz betrachtete Wärme befolgt einen 'halben' Erhaltungssatz: Sie kann zwar erzeugt, aber nicht vernichtet werden.

## 1. Introduction

Entropy is considered to be one of the important, but also most abstract and least visualisable quantities of physics. A closer look shows that this opinion can be attributed to historical chance and that entropy is not inherently difficult to visualise. It is no more difficult to visualise entropy than energy, and in some respect it is even easier. A simple picture of entropy is closely connected with the word 'heat'.

In common language 'heat' is pictured as residing in a body which it can leave or enter. This is expressed in sentences like 'the walls of a house prevent the heat from leaking out' or 'heat reservoirs are devices for storing heat'. In these statements heat is pictured as a kind of substance, once called 'caloric', which is localised and is able to flow.

For the physicist, however, heat is not a kind of

substance but a 'form of energy'. Mathematically this means that heat is represented by an 'incomplete differential' which implies that energy can flow into or out of a system in the form of heat but that it is wrong to imagine that energy is contained in the system as heat. Heat ceases to be heat as soon as it enters a system, it has then become just energy and is indistinguishable from energy transferred to the system in other energy forms (Falk *et al* 1983).

The concept of energy form was conceived by the discoverers of the energy principle. It turned out to be quite difficult to integrate it into a mathematical formulation of thermodynamics, an achievement due primarily to Rudolf Clausius. Ever since heat has lost the simple property of being a kind of substance, a property it has nevertheless retained in common language.

There is, however, a quantity characteristic of thermal phenomena which possesses all the properties associated with the word 'heat' in common language: the entropy. In fact, Clausius' entropy is just the old caloric once dismissed as being an invalid concept. This is difficult to recognise because the return of this concept to the roster of physical quantities was disguised by a mask of great abstraction and thus appeared as something new. From this point of view entropy is even older than energy and should therefore be no more difficult to comprehend. A look at the history of the theory of heat will document this.

## 2. Quantity and intensity of heat

The conceptual understanding of the phenomena of heat progressed differently from the understanding of motion. On the one hand, the theory of heat developed more slowly than mechanics. On the other hand, the essential conceptual contributions to the theory of heat came to a larger extent from chemists, physicians and engineers than from mathematically oriented physicists or mathematicians.

Historically the first outstanding figure in the conceptual clarification of the phenomenon of heat is the Scottish chemist and physician Joseph Black (1728–99). Black recognised (as did Johann Heinrich Lambert (1728–77)), that an understanding of heat required two different and independent concepts, namely, *quantity of heat* and *intensity of heat*. The following explanation of the first of these concepts is found in his *Lectures on the Elements of Chemistry* (edited by Black's pupil Robison four years after Black's death): 'If, for example, we have one pound of water in one vessel, and two pounds in another, and these two quantities of water are equally hot, as examined by a thermometer, it is evident, that the two pounds must contain twice the quantity of heat that is contained in one pound' (Black 1803).

This explanation is unambiguous and clear. Black's heat is a quantity which is *contained* in a body and can *flow* into or out of it, in short, it is an extensive quantity of a *substance-like* nature.

The second concept, the intensity of heat, was already known before Black's time as *temperature*. According to Black it is of the nature of a 'tension' or 'pressure' to which the heat contained in the body is subject. It expresses consequently, a general tendency of heat to leave the body in which it is contained. If two bodies are brought into contact (today we say 'thermal contact') then heat flows out of the body in which its intensity (temperature) is higher into the body in which its intensity is lower. The flow ceases when the heat has the same intensity in both bodies, that is, when both bodies are at the same temperature. Black calls this a state of *thermal equilibrium* between the bodies.

In the familiar symbolic method of description used today Black's ideas assert the existence of the following quantities:

$S$  = *quantity of heat*, in the following briefly called heat.  $S$  is contained in bodies, or more generally it is contained in physical systems and can be pictured as a localisable 'substance'.

$I_S$  = *heat current* or  $S$  current.  $I_S$  is counted positive when it flows out of a body.

$T$  = *temperature*, it measures the 'tension' to which  $S$  is subject in a physical system. The temperature scale can be chosen arbitrarily subject to two restrictions: (i) if two bodies are in thermal contact heat flows from the body that has the larger value of  $T$ ; (ii) if there is no  $S$  current when two bodies are in thermal contact they have the same value of  $T$  and are in thermal equilibrium.

It should be noted that the idea of heat as a substance also was developed by a number of investigators before Black in the 17th and 18th century. Initially this heat substance was called 'phlogiston' (Becher, Stahl, Scheele), later to the end of the 18th century 'calorique' (Lavoisier, Berthollet, de Fourcroy, de Morceau). In this picture, to be sure, the concern was less about the concept of the quantity of heat but rather the question of its connection with chemical combustion processes.

## 3. The heat capacity

The picture of heat as a substance residing in a body which is able to flow into or out of it strongly favours a picture in which an increase of the heat  $S$  contained in a body results in an increase of the 'tension' of the heat, that is an increase of its temperature. This is in agreement with the above statements concerning the flow of heat between two bodies and the state of thermal equilibrium which finally results. Expressed mathematically this means that

$$\Gamma = \frac{\partial S}{\partial T} > 0. \quad (1)$$

Black called the quantity  $\Gamma$  the *heat capacity* of the body. As expressed by equation (1),  $\Gamma$  cannot be negative. There is a simple reason for this. Suppose that a body of negative heat capacity is brought into thermal contact with a body of positive heat capacity and that the temperature of the second is larger than that of the first, then the temperature of both would decrease when heat flows from the second to the first body. Suppose further that the heat capacity of the second body is larger than the absolute value of the (negative) heat capacity of the first, then when thermal contact is established not only would the temperature of both bodies drop but the temperature difference

between them would also increase. Thus as a consequence of thermal contact the bodies would 'spontaneously' cool in such a manner that thermal equilibrium between them would never occur.

Within the framework of Black's description of heat phenomena these considerations show that the heat capacity is a useful quantity and that its positivity is of significance assuming that a free transfer of heat between bodies of different temperature leads to thermal equilibrium. According to Gibbs the condition that  $\Gamma$  is positive is a thermodynamic stability condition (Gibbs 1961).

It is historically remarkable that the concept of heat capacity was accepted so readily. The simple reason for this is that this quantity fits previously developed ideas in which a description of heat phenomena is based solely on the temperature concept. Besides it was hoped that the heat capacity would help find the 'true' or 'correct' temperature scale. The definition of temperature was felt to be unsatisfactory because it contained much that was arbitrary: (i) the choice of thermometer substance; (ii) the choice of the quantity  $X$  to be measured ( $X$  = pressure, volume, relative volume change etc.); (iii) fixing of the function  $T = f(X)$ . It was hoped that if heat capacities were measured using the 'correct' temperature scale, that they or rather the specific heat capacities  $\gamma = \Gamma/m$  ( $m$  = mass of the body) would turn out to be independent of temperature and thus be a characteristic material constant. This hope shrank progressively beginning with the investigation of Lavoisier and Laplace (1780–4) on the temperature dependence of the specific heat in the 1780s, and finally with the work of Dulong and Petit (1817). Meanwhile the concept of heat capacity took hold to the extent that it played a decisive and unfortunately sometimes and exaggerated role. According to current usage the product  $T\Gamma$  rather than  $\Gamma$  is called the heat capacity.

#### 4. Latent heat

If equation (1) is written in the form

$$\Delta S = \Gamma \Delta T \quad (2)$$

it might be concluded that the heat contained in a body and its temperature can always be related by an equation of the form (2) so that  $\Delta S$  could be defined by equation (2). This, however, is not always possible, the processes of melting and evaporation—generally phase changes—are evidence of this. For Black they were direct proof of the independence and priority of the quantity  $S$ . In a series of ingenious experiments and observations Black was able to show that the melting of ice and the evaporation of water at constant pressure, i.e. under conditions familiar to everyone, proceed without temperature change but nevertheless require the supply of considerable quantities of heat.

Now, melting is a process in which a body, for example a quantity of liquid water, is generated or 'created' whilst another body, namely ice, is destroyed or 'annihilated'. The creation of the liquid water is tantamount to generating all the physical quantities contained in it: the mass  $\Delta m$  of the water, the amount of heat  $\Delta S$  contained in the water and many others (which are of no immediate interest to us). Thus, for water as for any other piece of matter there must be a relation of the form

$$\Delta S = \sigma \Delta m \quad (3)$$

( $\Delta T = 0$ ), where  $\Delta m$  and  $\Delta S$  represent the changes of its mass and heat and  $\sigma$  expresses the relation between  $\Delta m$  and  $\Delta S$  (at constant temperature) characteristic for the material which constitutes the matter under consideration. A relation like equation (3) exists, therefore, for liquid water as well as for ice with corresponding values  $\sigma_{\text{water}}$  and  $\sigma_{\text{ice}}$  of the quantity  $\sigma$ . The difference  $\Lambda = \sigma_{\text{water}} - \sigma_{\text{ice}}$  is what Black named the *latent heat* of the phase transition ice–water and—if multiplied by  $T$ —is still called so today. Equation (3) can also be written

$$\sigma = \frac{\partial S(T, m)}{\partial m}. \quad (4)$$

The reason why the partial differential symbol was used in equation (1) is now evident for the first time: the heat  $S$  contained in a body is connected with more physical quantities than  $T$  alone, at least also with  $m$  as is evident from Black's procedure. In fact, as we shall see,  $S$  is connected with other physical quantities of the body as well, especially with volume and pressure. The dependence of the heat  $S$  on several quantities proved historically to be a serious obstacle which was decisive, not only for the fate of Black's system of concepts but also for the theory of heat in the following century.

#### 5. Adiabatic processes

The problem of finding those physical quantities of a body which are connected with the heat  $S$  contained in it is rendered difficult because there is no evident means of measuring  $S$  and its changes directly. There is, however, a way out of this difficulty by keeping  $S$  constant and looking for those quantities which show a coupling due to this constraint. This idea immediately suggests the following experiment: enclose the body in an envelope impenetrable to heat (=adiabatic enclosure)—assuming for the moment that  $S$  can be kept constant this way—and study all changes of the body which are still permissible in such an enclosure.

Such experiments were never performed. However Gay-Lussac (1807) published an experiment, the so-called 'free expansion' of a gas, which can be considered as a special (extreme) case of adiabatic

expansion—in which, as we shall see,  $S$  does not stay constant, but increases—but which was not recognised as such. Adiabatic processes in gases were not explained until Poisson (1823), and Carnot (1824) also recognised the significance of these processes for the theory of heat.

What was the reason for the neglect of the important processes with  $S = \text{constant}$ ? A possible answer is that the restriction to fluid and solid bodies does not suggest such experiments since the adiabatic isolation practically fixes the volume of such systems and apparently decouples the pressure from the volume. However, this cannot have been the decisive reason because work with gases had been going on for a long time. It was known since the 1780s that gases which expand into the free atmosphere cool off. The reverse process, the heating of air, for example, during adiabatic compression, an effect which can be considerable, was not discovered by a physicist, chemist or physician. In 1803 a worker at the French rifle factory at Etienne en Forez made a practical application of the effect by inventing the pneumatic lighter (Mach 1919). Only then did scientists begin to take interest. The main reason that the adiabatic processes were practically ignored is that presumably of all of Black's concepts those that were 'derived', particularly the heat capacity, were more readily accepted and were held to be more important than the basic quantity  $S$ , the heat. Thus the logic of Black's conceptual scheme was up-ended.

From the point of view of Black's conceptual scheme the pneumatic lighter proved that the heat  $S$  contained in a gas depends on the temperature  $T$ , the pressure  $p$ , and the quantity of gas measured by the mass  $m$ , and that therefore  $S = S(T, p, m)$ . If  $m$  and  $S$  are fixed it follows from  $S(T, p, m) = \text{constant}$  that, as observed,  $T$  is a function of  $p$ . Furthermore, it follows from  $S = S(T, p, m)$ , that

$$\frac{dS}{dT} = \frac{\partial S(T, p, m)}{\partial T} + \frac{\partial S(T, p, m)}{\partial p} \frac{dp(T)}{dT}. \quad (5)$$

This relation is difficult to verify for solids or liquids because of a weak dependence of the heat  $S$  on the pressure. Thus the second term of equation (5) can be neglected so that it appears as if there were only a single heat capacity. For gases, however, the second term is not negligible.

## 6. The producibility of heat $S$

It is by no means obvious that the heat  $S$  contained in a gas depends not only on  $T$  and  $m$  but on  $p$  as well. This difficulty would have been exacerbated by Gay-Lussac's experiment of 1807, had it been recognised for what it is, namely that the heat  $S$  of a system can be increased not only by influx but by the production of heat in the system as well. The phenomenon we are concerned with is easily

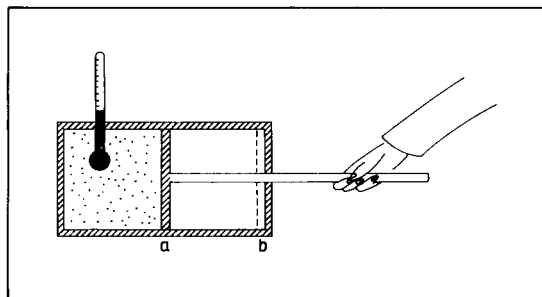


Figure 1 Realisation of adiabatic processes (see text).

demonstrated by an adiabatic expansion process. Let a gas be enclosed in a cylinder with a moveable piston. Let the walls of the cylinder and the piston be fabricated of heat insulating material so that the following processes occur in adiabatic isolation (figure 1).

Consider the following process: the piston is moved from an initial position  $a$  to an intermediate position  $b$  and is then moved again from  $b$  back to  $a$ . Suppose that the temperature of the gas can be read at the different positions of the piston. The experiment yields the following results:

(i) If the piston is moved sufficiently slowly from  $a$  to  $b$  the gas cools from an initial temperature  $T_a$  to the temperature  $T_b$ , which will turn out to be a minimum as compared to values resulting from processes subsequently discussed so that we call it  $T_b(\text{min}) < T_a$ . If the piston is moved, again slowly, from  $b$  to  $a$  the gas assumes the initial  $T_a$ .

(ii) If the piston is moved rapidly from  $a$  to  $b$ , the gas is cooled less, in fact the faster the piston is moved the less the gas is cooled. The final temperature  $T_b$  obtained is a direct measure of how rapidly the piston was moved from  $a$  to  $b$ . A motion from  $a$  to  $b$  that is 'infinitely rapid' (realised, for example, by breaking the piston at  $a$ ) yields the maximum temperature  $T_b(\text{max}) \leq T_a$ . The final temperatures which are attainable this way cover the interval  $[T_b(\text{min}), T_b(\text{max})]$ . Gay-Lussac actually tried to determine the temperature  $T_b(\text{max})$  in his free expansion-experiment and concluded from his measurements that  $T_b(\text{max}) = T_a$  for an ideal gas (which is negligible in our considerations).

Now if the piston is brought back to  $a$  after one of the rapid expansions (appropriately slowly so that nothing unexpected occurs), the gas will always have the temperature  $T' > T_a$ . The gas can be brought again to its initial temperature  $T_a$  by the withdrawal of a certain quantity of heat  $\Delta S'$  which is determined by  $T' - T_a$ . Since the gas was enclosed by a heat insulating envelope during the whole process of expansion and subsequent compression, so that heat was neither supplied nor withdrawn, we must conclude: The heat  $\Delta S'$ , which must be withdrawn from the gas in order to return it to its initial state, was produced.

A further conclusion to be drawn from the experiment described above is that the enclosure of a body in a heat insulating envelope by no means ensures that the heat  $S$  contained in the body retains its value, i.e.  $S = \text{constant}$ . The latter is the case only if the processes possible under adiabatic isolation proceed 'slowly' (more exactly: if they proceed so that all differences of intensive quantities involved are kept sufficiently small). In fact, the second law of thermodynamics is expressed here: in any process possible under adiabatic isolation the heat  $S$  contained in the system may increase, but can never decrease. A decrease of  $S$  is possible only if the  $S$  impenetrable envelope is opened to let heat flow out of the system. Thus the heat produced in any manner can be removed if it is transferred from the system under consideration to another one, usually called the surroundings. However, the heat created in any process cannot be destroyed, in physical terminology, the production of heat is irreversible.

The experiment described above never took place, either as a thought experiment or in reality, even though two experiments at hand are parts of it and therefore suggest it. The two partial experiments are the compression corresponding to a piston motion of the pneumatic lighter and the infinitely rapid piston motion corresponding to the 'free expansion' of Gay-Lussac. Thus conditions were at hand to support the considerations presented above. Furthermore, the production of heat had already been achieved in Gay-Lussac's experiment. Nevertheless the obvious conclusions concerning the properties of heat were not drawn. Let us suppose for the moment that it was concluded that heat is created. The reaction would probably have been the same as it was thirty years later: Black's  $S$ , then called 'caloric', was declared to be a wrong concept since it 'disagreed with the facts'. At that time the old philosophical doctrine (prejudice) that anything substance-like necessarily obeys a conservation law was very strong. The idea that substance can be created and annihilated may be part of the literary phantasy of man, as shown by fairy tales, for example, but such 'unsound' ideas have no place in scientific thought.

### 7. Carnot: heat and work

Carnot (1824) raised a new question about heat: how are heat and work connected? This question was triggered by the great economic significance which the English steam engines had already achieved. Carnot was motivated by the practical problem of improving these machines, namely, the delivery of a given amount of work—usually measured by pumping a given quantity of water from the bottom of a shaft—with the combustion of the least amount of coal. He turned the question into the scientific problem: what determines the upper limit

for the work delivered by a heat engine?

Opinions about Carnot's essay have differed widely during the course of history. At first, for a decade, it was completely ignored by the scientific world. Then it was taken up and propagated by Clapeyron (1834), a mining and railroad engineer, without any noticeable response. In the 1840s it was even considered erroneous and it was dismissed. It was finally recognised by Thomson (later Lord Kelvin) in his work (Thompson 1848) on the construction of the absolute temperature scale in which he applied Carnot's line of thinking, which was followed by another paper (Thomson 1849). Today it is beyond question that Carnot's essay belongs to the greatest works of science. It contains no less than the foundations of present-day thermodynamics. Of the results of Carnot's considerations two are of primary interest to us:

(i) Black's arbitrary temperature scale was replaced by an absolute temperature scale (as shown by Thomson).

(ii) Besides the heat  $S$ —which Carnot calls 'calorique' and which is called *entropy* today—a second extensive quantity  $E$  can be constructed within Carnot's theory (but was not constructed by Carnot himself) which is independent of  $S$  and is called *energy* today.

We emphasise that the heat  $S$  and the energy  $E$  are two different extensive quantities in Carnot's theory. Just as the heat  $S$ , the energy  $E$  can be imagined to reside as a 'substance' in the body, and just as  $S$  can flow into or out of a body the energy  $E$  can also flow into or out of a body. Thus in addition to a heat current  $I_S$  there is an energy current  $I_E$ .

Now a central assertion of Carnot's theory is that  $I_S$ ,  $I_E$  and  $T$  are connected with each other by the following general rule: if a heat current  $I_S$  flows out of (or into) a body of absolute temperature  $T$ , then this heat current is always accompanied by an energy current  $I_E$  which has the value

$$I_E = TI_S. \quad (6)$$

From this relation follows that if a heat current  $I_S$  flows out of a body 2 of (fixed) temperature  $T_2$  an energy current of the amount  $T_2 I_S$  must also leave the body. If the total quantity of heat which has left the body, increased if need be, by an additional heat quantity produced (outside body 2), is transferred to another body 1 of temperature  $T_1 < T_2$  (also fixed), a heat current  $I'_S (\geq I_S)$  and with it an energy current  $T_1 I'_S$  flows into this body. Thus there is a difference  $\Delta I_E$  between the energy current given off by body 2 and taken up by body 1

$$\begin{aligned} \Delta I_E &= T_2 I_S - T_1 I'_S = (T_2 - T_1) I_S - T_1 (I'_S - I_S) \\ &= \frac{T_2 - T_1}{T_2} (T_2 I_S) - T_1 I_S \text{ (produced)}. \end{aligned} \quad (7)$$

Now, as is well known, the quotient  $\Delta I_E / (T_2 I_S)$  is

called the efficiency  $\eta$  of a machine which delivers an energy current  $\Delta I_E$  by using the transfer of heat from a body of higher temperature  $T_2$  to a body of lower temperature  $T_1$ . Equation (7) shows that the efficiency  $\eta$  is equal to Carnot's maximum efficiency  $(T_2 - T_1)/T_2$  less the 'irreversibility contribution'  $T_1 I_S$  (produced)/( $T_2 I_S$ ). The latter vanishes for a machine working reversibly.

The property of the energy manifested by equation (6), namely, to be transported together with other extensive quantities (in this case with the quantity  $S$ ) is valid generally. An energy current is always accompanied by at least one further current of an extensive quantity, or following Herrmann (1979): flowing energy is always 'carried' by another extensive quantity. Different 'forms of energy' are nothing other than energy which is accompanied or carried by different extensive quantities and in a transformation of energy the carriers of the energy are changed (Falk *et al* 1983, Falk and Herrmann 1981).

### 8. The development of the theory of heat after 1840

The development of the theory of heat as it had progressed for a century was abruptly cut off by Mayer's and Joule's discovery of the conservation of energy. From here on the fate of the theory of heat is familiar to every physicist. The newly discovered energy became a centrepiece in rebuilding the theory. Besides its basic conservation property energy had (allegedly) another fundamental property which distinguishes it from the other quantities of physics: it can appear in different forms and convert from one form into another. Henceforth the word 'heat' was used for one of these energy forms. Analogously, work denoted another energy form, the 'mechanical energy'. In looking at it this way a heat engine is a device which takes up energy in the form of heat at the temperature  $T_2$  and delivers energy in the form of work and heat at the temperature  $T_1$ . In general, any physical process, particularly cyclical processes, consist of such a transformation of energy.

It was considered a scientific event of particular significance when Clausius constructed a new physical quantity which he called *entropy*. This is the (slightly modified) Greek word for 'transformation' (German 'Verwandlung'). Clausius sought a quantitative measure for a transformation (of work into heat and *vice-versa*). He wrote: 'We have now to find the law according to which the transformation must be expressed mathematically, so that the equivalence of two transformations may appear from the equality of their values. The mathematical value of a transformation may be termed, thus determined, its 'equivalence-value' (Clausius 1887). Entropy is just the technical term for this equivalence-value. Clausius used three concepts for

the construction of the entropy: The energy form heat, the absolute temperature, and the concept of a reversible process. Setting aside for the moment the abstractness of Clausius' procedure the most difficult hurdle for the beginner is that the entropy which is constructed by expressly using reversible processes is not restricted to reversible processes but is a 'state function' of the physical system under consideration and therefore a valid concept for any process of the system, reversible or not.

The most peculiar feature of entropy was considered to be its increase in an irreversible process. The phrase 'heat death of the universe' is an example. However, the substance-like nature of entropy and, therefore, its property to be localised in and flow through space was not clearly recognised. Clausius put forward an additional hurdle with the remark that the value of entropy (as well as that of energy) could not be determined absolutely during a process, only its incremental change could be found. It is most remarkable that it was not recognised, and is not so even today, that the entropy constructed by Clausius with great effort and admirable scientific tact is nothing but Black's  $S$  of old†.

### 9. The role of the laws of thermodynamics

In order to further clarify the logical relation between the Black-Carnot way of building up thermodynamics and the 'classical' way which gives particular emphasis to the first and second law we pose the following question: are there statements in thermodynamics which would not be affected if the two laws, that is the conservation of energy and the indestructibility of entropy, would be violated? The answer is as simple as it is surprising: any mathematical relationship between physical quantities of a physical system describing its properties would not be affected. Expressed more poignantly: Almost all the formulae appearing in textbooks of physics and especially thermodynamics are independent of the two laws. Thus these formulae are not proved wrong if it were discovered some day that energy is not always conserved or that entropy is sometimes destroyed (Falk and Ruppel 1976, Falk 1968).

What then is the purpose of the two laws in the theory? They represent statements on how changes of the entropy or the energy of a system can be brought about. Thus the energy of a system can be

† In this connection a remark by K Schreber, the German translator of Clapeyron's paper, deserves a mention. He writes (Schreber 1926): 'It seems to me that a more appropriate translation for calorique would be entropy for then the difference between Carnot's presentation and today's views of the general theory of heat would be much diminished'. Cf, however, the note added in proof at the end of this article.

changed only if a second system is at hand to deliver or take up the change  $\Delta E$  of the energy of the system. However, the changes of other quantities of the system connected with the change  $\Delta E$  of its energy (due to the internal structure of the system) have nothing to do with the way the change  $\Delta E$  is brought about. In the case of a change  $\Delta S$  of the entropy of a system the presence of a second system is not absolutely necessary if  $\Delta S > 0$  but it is if  $\Delta S < 0$ . The system is not 'aware' that an increase  $\Delta S$  of its entropy takes place because the entropy amount  $\Delta S$  flows from a second system into the first or  $\Delta S$  is created within the system (or that a combination of both takes place). The system only notices that its entropy experiences the change  $\Delta S$  but does not 'know' how this change was made. Consequently any relationship which connects the entropy of a system with its other physical quantities cannot depend on whether entropy is generated internally or even if it can be generated at all.

Thus the property of entropy to reside in a body and to be able to flow into and out of it is not logically connected with its indestructibility asserted by the second law. The substance-like property of entropy, which is so important if it is to be visualised, is not aided by emphasising as dominant its property of being produced in irreversible processes.

The fact that there are general physical quantities and that any physical system can be described by interrelating these quantities in a way typical for each system is logically independent of the existence of a general ban on the creation or/and annihilation of some of these quantities. For this reason the mutual relations between thermodynamic quantities derived from Carnot's ideas are valid even though Carnot's personal views on conservation of the quantities he operated with were partly wrong.

### 10. Didactic conclusions

Our considerations have made it plausible that the notoriety of entropy as being unvisualisable and incomprehensible is due to historical accident, namely that the Black-Carnot theory was held to be wrong by the discoverers of the energy principle. The idea of classifying energy into energy forms and calling one of them 'heat', in a sense entirely different from that used formerly, seemed very plausible at the time but turned out to be unfortunate. First the concept of heat lost its simple visualisability and became an 'incomplete differential', that is a 'process quantity' (as opposed to a 'state quantity'). However, as was already recognised by Black and Carnot, since a single quantity does not suffice for the description of heat phenomena it became necessary to introduce the old  $S$  of Black somehow. Clausius succeeded in this with his

complicated and opaque construction of entropy. Basically one had arrived where one had been before after a difficult and steep detour. Of course we do not mean to belittle the contributions of the physicists after Carnot or imply that nothing essential was learned. Quite the contrary, a mighty expansion of the scientific horizon was achieved. However, the detour regarding the concepts entailed an unnecessary complication of the description.

From this point of view it seems worthwhile to consider the suggestion of Job (1972) to use the word 'heat' as it had been used earlier, namely as a synonym for entropy. This endows entropy with the elementary visualisability possessed by Black's heat or Carnot's caloric. In common language the word 'heat' immediately implies a quantity which resides in bodies and is able to flow into or out of them. It is thus possible even without previous knowledge to form a picture of entropy and a feeling for its handling. This picture of entropy is not only qualitatively useful but it is also viable for handling the quantitative details of physical as well as chemical and biological processes.

The foregoing considerations suggest that teaching of entropy should primarily aim at the picture of entropy as a kind of substance residing in the bodies. This picture seems to be indispensable if entropy is to be used in practical work. On the other hand this picture seems to imply that entropy is also conserved as is the case, for example, with electric charge. It takes special pains to point out that the substance-like nature of a physical quantity does not necessarily entail its conservation. Therefore it is not contradictory if entropy obeys 'half a conservation law'—it can be created but not destroyed—thus yielding a conceptual means for the description of irreversible processes. If one proceeded the other way around and began with the property of entropy to increase in irreversible processes it would be difficult to comprehend its substance-like nature. As shown above, it is logically impossible to derive this property of the entropy from its capability to be produced.

### Note added in proof

One of the referees of this paper called the author's attention to H L Callendar's presidential address to the Physical Society of London in 1911 (*Proc. Phys. Soc. London* **23** 153–89). In this address on 'The Caloric Theory of Heat and Carnot's Principle' Callendar arrives at essentially the same conclusions as those presented here, namely that entropy is just another name for an age old quantity called 'caloric' by Carnot (and, as pointed out here, 'quantity of heat' by Black). In Callendar's own words this reads as follows:

Since Carnot's equation... was adopted without material modification into the mechanical theory... it was inevitable that Carnot's caloric should make its reappear-

ance sooner or later in the mechanical theory. It first reappears, disguised as a triple integral, in Kelvin's solution (1852 *Phil. Mag.* **4** 305) of the problem of finding the available work in an unequally heated body. The solution (as corrected later) is equivalent to the statement that the total quantity of caloric remains constant when the equalisation of temperature is effected reversibly. Caloric reappeared next as the "thermodynamic function" of Rankine, and the "equivalence-value of a transformation" (Clausius 1854 *Pogg. Ann.* **93** 497). Finally, in 1865, when its importance was more fully recognised, Clausius (*Pogg. Ann.* **125** 390) gave it the name of 'entropy', and defined it as the integral of  $dQ/T$ . Such a definition appeals to the mathematician only. In justice to Carnot, it should be called caloric, and defined directly by his equation . . . . ., which any schoolboy could understand. Even the mathematician would gain by thinking of a caloric as a fluid, like electricity, capable of being generated by friction or other irreversible processes.

I very much regret that Callendar's paper escaped my attention and I am thankful for the referee's hint. In view of Callendar's essay, the above statement that the identity of entropy with Black's heat and Carnot's caloric was not recognised must of course be corrected. It remains, however, a remarkable—and most regrettable—fact that despite its unquestionable scientific merit Callendar's work has never been incorporated in textbooks on thermodynamics. This is the more astonishing, since there have been other noteworthy attempts in the meantime to promote views similar to those of Callendar, such as Joseph Larmor's *On the Nature of Heat, as Directly Deducible from the Postulate of Carnot* (1918 *Proc. Roy. Soc. A* **94** 326) and Arthur C Lunn's *The measurement of heat and the scope of Carnot's principle* (1919 *Phys. Rev.* **14** 1).

It should be added that these papers—including Callendar's—can be seen as pursuing two objectives which should be carefully kept apart. The first objective is to show that entropy is identical with the once discredited caloric. This can be *proved* to be true (or false). The second objective is of a much less stringent character. It is meant to assure that Carnot fully anticipated in his essay the two historical ways of defining the concept of heat: either to identify heat with caloric (i.e. entropy)—as was done by Black and Carnot—or to make it a 'form of energy', as was put forward by the discoverers of the energy principle. Although it cannot be denied that Carnot's treatise can be read this way it is nevertheless hard to believe that Carnot was truly aware of the enormous implications entailed in his theory. It certainly does no harm to Carnot's scientific stature when assuming that he was led by a

strong physical instinct rather than by a complete insight into all consequences of his ideas. By disentangling these two different objectives it might be easier to accept what should long have been accepted, namely that Callendar's penetrating identification of entropy and caloric is a definite scientific truth.

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