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Phenomenological approach to the caloric theory of heat

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The paper is dedicated to the 70th birthday of our multi-year fellow worker in the Division of Solid-State Physics, Professor *Jaroslav Šesták*, accentuating his promoting assignment in thermal science and his activation role in founding Thermochimica Acta 40 years ago.

Keywords:
Caloric
Entropy
Heat
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ABSTRACT

This contribution presents an alternative approach to thermal physics and to its affiliated thermodynamics aiming to initiate a discussion concerning the related problems of its fundamental nature. We reason that the classical thermodynamics suffers considerably from a misinterpretation of experimental facts known as the *Principle of Equivalence of Energy and Heat* and from the resulting introduction of a troublesome quantity called entropy lacking clear physical meaning within the traditional thermodynamics. As this concept generates an endless chain of paradoxes connected mainly with the *Second Law of Thermodynamics*, we propose to change the structure and the conceptual basis of thermal physics prior to the solving of more complex problems involving, e.g., the application of quantum or stochastic electrodynamics to the relativistic thermal phenomena. We argue that a good candidate for such a more satisfactory theory is modified Carnot's theory reintroducing an old–new physical quantity historically named caloric. An introducing outline customizing the reader with the basic ideas of this alternative version of the classical thermodynamics is thus given. Principal relations of the caloric theory are presented, together with illustrative treatment of some common tasks of the thermal physics. Use of the caloric theory to description of real heat engines is also presented.

1. Introduction

The classical thermodynamics [1–7] is a phenomenological theory the foundations of which were basically laid down in the second half of the 19th century by *Carnot, Rankine, Joule, Mayer, Clausius, Kelvin* and *Gibbs* providing accordingly a most general description of thermal processes in real systems without making use of their molecular (atomic) structure. The classical thermodynamics is thus considered to be a well-established and logically closed theory above and beyond the disciplines of analytical mechanics and theory of electromagnetic field which is essentially free of arbitrary assumptions. Various axiomatic forms of classical thermodynamics together with the use of decidedly sophisticated mathematics seem to guarantee the absence of internal inconsistencies and absolute clearness of concepts involved. These are the reasons for widely admitted belief that this theory provides a reliable and quite general frame for further development of particular microscopic models enabling deeper understanding of the nature of real thermal processes.

That such belief may be mere an illusion has recently been revealed, e.g. during a rather confusing discussion concerning the validity of the *Second Law of Thermodynamics* for small quantum systems [8,9]. Moreover, the discussion evoked a strong suspicion that we have to do with a problem which is linked directly with possible flaws in the conceptual basis of classical thermodynamics.[1] Serious objections against the logical correctness of the fundaments of classical thermodynamics already exist and are relatively well documented [10–16]. In spite of that, these works are unjustly ignored in the relevant literature.

As we are convinced, the very origin of the difficult understanding of thermodynamics is connected just with an inconvenient choice of conceptual basis more than 150 years ago. Since the *Principle of Equivalence of Energy and Heat* looks quite plausible,

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[1] Let us recall that the history of science provides numerous examples of cognate situations where additional introduction of an abstract, as a rule not quite intelligible, mathematical structures, compensate, to a certain extent, for the mistakes in a construction of the conceptual basis of particular scientific theory. The resulting theory, of course, being free of internal contradictions and in reasonable agreement with the experience was, naturally, considered to be a "good" theory. In case, however, where a really complex problem had to be faced the accumulation of abstract entities effectively disabled its solution or even led to absurdity (e.g., let us recall in this connection the phlogiston theory).

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traditionally the most obscure is the revelation of the concept of entropy and rather an exceptional form of the *Second Law of thermodynamics*. Whereas the universal laws have mostly the form of conservation laws, the logical structure of the *Second Law* is quite different. Ultimately formulated, it is a law of irreparable waste of "something" (pessimistic version) or of creation of "something new" (optimistic version) in every real physical process.

In the recent decade an unprecedented number of challenges have been raised against the *Second Law* from the position of quantum mechanics [8]. However, these arguments are, as a rule, enormously complicated with numerous approximations and neglects and thus eventually questionable. Moreover, it is a very old empirical fact that the thermal processes in the nature are submitted to certain restrictions strongly limiting the class of possible processes. The exact and sufficiently general formulation of these restrictions is extremely difficult and sometimes, no wonder, incorrect (cf. e.g. the principle of *Antiperistasis* [17], or *Braun-le Chatelier's* principle [18]). In spite of that just these principles belong to the most inspiring achievements in the field. That is why the authors of this paper believe that the *Second Law,* or another law which puts analogous limitations on thermal processes, does reflect experimental facts with an appreciable accuracy and thus it should be incorporated into the formalism of thermal physics, as was already done in the case of thermodynamics.

On the other side, as we are convinced and as we discuss in the following section, the introduction of the *Principle of Equivalence of Energy and Heat* and of closely related *First Law of Thermodynamics* might be destructive for the development of an intelligible theory of thermal processes and should be avoided. Being then aware that the contemporary structure of thermodynamics with its rigid conceptual basis may have intrinsic difficulties, we claim that it has only a little sense to criticize or deny e.g. the *Second Law* from the positions of another disjunctive physical theory (e.g. quantum mechanics) prior to the correction of these imperfections is made within the theory of heat itself.

This paper thus deals with an alternative approach to the phenomenological theory of heat differing in fundamental assumptions from the classical thermodynamics. In Section 2 we consider the reasons why the principle of equivalence of work and heat led to inconvenient treatment of the quantity of heat in classical thermodynamics. Section 3 introduces a concept of caloric as a replacement of the usual concept of heat as energy. In Section 4, basic constitutive relations related to the caloric concept are outlined and fundamental laws of thermodynamics are reformulated in terms of caloric theory. The principal possibility to measure the quantity of caloric is discussed in Section 5. Finally, Section 6 presents elementary examples manifesting applicability of the caloric theory to common problems solved by traditional thermodynamics.

2. Equivalence of energy (work) and heat: principal corner stone of classical thermodynamics

Decisive for the establishment of dynamic theory of heat in the second half of the 19th century was the formulation of the *First Law of Thermodynamics* which is logically fully dependent on the acceptance of the *Principle of Equivalence of Energy and Heat*. Indeed, on the basis of this principle it is assumed that work and heat are quantities of the same physical nature, i.e. that they have particularly the same physical dimension, energy. Therefore, these two quantities can, with proper signs, directly enter the energy balance equation describing a given process. The kernel of the *First Law of Thermodynamics* is, however, the introduction of a new state function known as the *internal energy* completing the said energy balance equation. As the *First Law* is mostly expressed just in the form of such a balance equation it is frequently believed that it is nothing but the universal *Law of Conservation of Energy* in thermal physics.[2]

The first step toward the *Principle of Equivalence of Energy and Heat* was probably made by *Benjamin Count of Rumford* by the generalization of his observations made at an arsenal in Munich (1789) [19]. Accordingly, it was possible to produce practically unlimited quantity of heat only by mechanical action, i.e. by boring cannon barrels by a blunt tool and this experimental fact was analyzed by *Rumford* as follows: *"It is hardly necessary to add, that any thing which any insulated body, or system of bodies, can continue to furnish without limitations, cannot possibly be a material substance: and it appears to me extremely difficult, if not quite impossible, to form any distinct idea of anything, capable of being excited and communicated, in the manner the heat was excited and communicated in these experiments, except it be motion"*. The same idea that heat absorbed by a body, which is particularly responsible e.g. for the increase of its temperature, is identical with the kinetic energy of its invisible components, was about 50 years later apparently supported by arguments due to *J.P. Joule* [20]. Results of his famous paddle-wheel experiment have been summarized into two points: *The quantity of heat produced by the friction of bodies, whether solid or liquid is always proportional to the quantity of force expended. The quantity of heat capable of increasing the temperature of a pound of water by 1 °F requires for its evolution expenditure of a mechanical force represented by the fall of 772 lbs through the space of one foot.* (Notice, here the term "force" has evidently meaning of mechanical energy.) In spite of clearness of these correct statements, Joule did not stress out explicitly important facts that his experiment was performed only at a single (room) temperature and that we have to do only with one-way transformation of work into the heat there. Instead he tacitly treated throughout the paper the heat as if it were a physical entity fully equivalent or identical with mechanical energy being interested mainly in obtaining the absolute value of conversion factor between work and heat. Therefore, we claim that Joule, in fact, rather postulated then proved this principle (Notice, once anticipated the equivalence between energy and heat this conversion factor between different kinds of energy has to be automatically universal and temperature independent.) His way of thinking was probably due either to influence of Rumford or to the reasoning that in the experiment heat appears just when mechanical work disappears and *ipso facto* these two entities must be identical. Such an extremely suggestive but logically incorrect conclusion was later, probably under the strong influence of kinetic theory of gases, boldly canonized by *Clausius* [21] who proclaims a subject of thermodynamics to be *"die Art der Bewegung, die wir Wärme nennen"*, i.e. the kind of motion we call heat [22].

In the history of thermodynamics objections appeared against such an interpretation of the heat. Unfortunately, these objections were only rare and with no adequate response. One of the earliest ones is due to *E. Mach* [10,12]. Accordingly, it is quite easy to realize a device of Joule's type where a given amount of energy is completely dissipated and simultaneously "equivalent" amount of heat

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[2] There are numerous forms of the First Law which, however, are all in some way related to the principle of equivalence of heat and work. Modern representative version of the First Law, using time parameterization [4], is a postulate of the existence of a certain state function, internal energy, the rate of which is the sum of "working" and "heating", i.e. of independent time derivatives of work, $\overset{\bullet}{W}$, and heat in calories, $\overset{\bullet}{J}Q$. The work W and the heat JQ then have a character of transfer quantities depending on the way how they are supplied in or extracted from the system. The analysis of various formulations of the First Law in thermodynamics is not the subject of this contribution; it deals only with the precursor of the First Law, the Principle of Equivalence of Energy and Heat.

is evolved. On the other side, as far as it is known, there is no single real case where the same amount of heat is transformed back into mechanical work only by reversion of the original process. Similarly useless for work production is "*the heat of a closed, throughout equally heated system of bodies*." Mach thus concluded that "*Considering the things unbiased, one has to ask, whether it ever has a scientific meaning and purpose, the heat which can no more be transformed into the work still treat as energy"*. This groundlessly ignored argument should be, as we are convinced, taken quite seriously. It is, namely, not a marginal fact that the very generic property of the energy, its principal convertibility into another form of energy without *any limitation*, logically excludes the possibility that the heat is a kind of energy. Of course, postulating, in spite of that, the equivalence of energy and heat, we are simultaneously defining a set of special operative methods and units for the measurement of heat and a meaningful mathematical theory of thermal processes can be and actually has been established in this way (the classical thermodynamics serves as an example!). The price paid for the *Principle of Equivalence of Energy and Heat* is, however, rather high. The energy being heat attains exclusive properties, which the entity called energy has not in other branches of physics. Why it should be so, is answered neither by experiments nor theory of thermodynamics. Moreover, together with the equivalence principle entered into thermodynamics a highly abstract quantity, *entropy*, lacking, in contrast to statistical physics, clear physical content there.

3. Caloric concept

3.1. Heat as entropy: introduction of caloric

Astonishingly an elegant way leading out of the problems mentioned above was very likely for the first time suggested by *Callendar* [11] and later in a more sophisticated and complete form worked out by Job in his impressive book [13]. The main idea is that the heat in common sense (i.e. a cause of temperature elevation, of the change of dimensions or aggregation state of bodies exposed to the heating) should not be identified with a kind of energy but rather with entropy as is known from classical thermodynamics. It was further shown by *Larmor* [23] and especially by *Lunn* [24] in a very pregnant way that the heat can be measured in energy and entropy units as well. In the latter case the heat = entropy concept attains the content almost identical with the concept of *Carnot's* "*caloric*". This circumstance opens a possibility to reintroduce this old–new romantic concept of caloric back into the phenomenological theory of thermal processes [25,26] and simultaneously, it enables one completely to avoid an inadequate use of term entropy. This term, namely, playing at present an important role in different branches of science, mathematics and even in the humanities has there, as a rule, not exactly the same content. The confusion of formally similar but in nature essentially different concepts having the same name, is obviously harmful, tempts to unjustified generalizations and may be totally destructive especially in solving interdisciplinary problems [27].

3.2. Basic relations for caloric: an intuitive approach

Caloric as a physical quantity corresponding to the common term heat can be introduced without *a-priori* knowledge of entropy using *Carnot's* principle which is an early generalization of experience with optimizing the motive power gain of heat engines. The principle can be stated as follows [28]:

Carnot's principle (postulate)

> "*The motive power of heat is independent of the agents set at work to realize it; its quantity is fixed solely by the temperatures of the bodies between which, in the final result, the transfer of the caloric occurs.*"

Notice that such a formulation having some features of universality is in fact related to a special class of periodic processes known as *Carnot's* cycles and that the principle is logically closed only if heat and caloric are synonyms. In such a case is the principle not dependent on an *a-priori* definition of physical quantity measuring caloric (heat) or definition of temperature, either; every empirical temperature scale θ is thus usable [11]. Following then *Carnot*'s more or less intuitive way of thinking, the small amount of work dL ("motive power") done by caloric ς falling over a small temperature difference dθ can be expressed by the formula

$$\mathrm{d}L = \varsigma F'(\theta)\mathrm{d}\theta, \tag{1a}$$

where $F'(\theta)$ is so called *Carnot's* function which must be determined experimentally respecting the operative definitions of quantities ς and θ.[3] It is a remarkable fact that according to Eq. (1a) caloric is not consumed in producing work but only loses its temperature by dθ. Therefore, the caloric has there a character of some special substance, temperature plays the role of its thermal potential and the thermal energy may be defined as a product caloric time temperature. If, moreover, the conservation of caloric takes place during transferring it back to the boiler at the expense of external work, the process is *reversible*. The perfect analogy with other potentials known from the physics, such as gravitational for mass and electrostatic potential for charge, is evident. As is shown below, such a view of caloric must be somewhat corrected in case where the dissipative, essentially irreversible, process (friction, heat transport) is involved.

As we have already noticed, prior to the practical use of Eq. (1a) or its integration it is necessary to determine *Carnot's* function experimentally. It is an empirical result of research into rarefied gases that *Carnot's* function $F'(\theta)$ can be reduced to the universal constant = 1 using, instead of arbitrary empirical temperature scale θ, the perfect (ideal) gas temperature scale T equivalent to the absolute *Kelvin* scale [29]. Indeed, the amount of motive power dL extracted reversibly by means of a constant pressure gas thermometer (serving here as a peculiar heat engine) by transferring caloric ς from a hotter bath (by dθ) into bulb of thermometer filled with the perfect gas is obviously equal to $p\,\mathrm{d}V$. As in this case the empirical temperature scale θ is per definition identical with *Kelvin's* perfect gas scale, T, we can write $\mathrm{d}L = R\,\mathrm{d}T = R\,\mathrm{d}\theta$ where R is a certain constant (in SI units for 1 mol of gas in bulb it equals universal gas constant ≈ 8.31 J/mol K). The comparison of these relations with formula (1a) gives $R = \varsigma F'(T)$. Taking into account the fact that caloric is conserved by reversible operations, the quantity ς must be independent of temperature and, consequently, *Carnot's* function $F'(T)$ has to be also constant. Putting then $F' = 1$, one defines the unit of caloric fully compatible with the SI system which may be, according to *Callendar's* [11] suggestion, appropriately called "Carnot" (Abbreviation "Cn"). 1 Cn is then that quantity of caloric which is in a reversible process capable of producing 1 J of work per 1 K temperature fall. Simultaneously, if such a system of units is used, Eq. (1a) may be rewritten in a very simple form

$$\mathrm{d}L = \varsigma \mathrm{d}T. \tag{1b}$$

As was mentioned above, Eq. (1b) is valid only for the case where no irreversible process is present. Taking into account the

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[3] We are using for caloric Greek final-letter ς as this letter involves graphics of both, usual S for entropy and C for caloric. The caloric ς is in contrast to Clausius's entropy, an entropy-like quantity for which is the "arbitrary" additional constant identically equal to zero.

fact that the friction and heat leakage cannot be avoided in any real device, this equation representing an ideally reversible case should be corrected. Such a correction was in fact already introduced by *Carnot* and can be found in his posthumously edited works [30]. The main idea is that the caloric circumventing heat engine by some side channel uselessly falling from a higher to a lower temperature has to produce an additional amount of caloric just equivalent to the motive power which would be otherwise produced, i.e. to the "wasted motive power". Alternatively, the motive power of the engine may be wasted also by friction. In this case the part of motive power already produced is immediately destroyed by friction, and we can imagine that the developed caloric is conveyed to a sink kept at a lower temperature. This is obviously nothing but another type of realization of a side channel for the transfer of an original amount of caloric from high temperature to the cooler. Generalizing, the increase of caloric in a dissipative irreversible process due to the heat conduction or friction is measured by the wasted motive power not realized in an engine simply because of its non-ideal nature. In order to describe the role of thermal leakage quantitatively, let us assume that an amount of caloric ς taken from the boiler of temperature T_1 is conveyed directly to the cooler kept at slightly lower temperature $T_2 < T_1$. The motive power which might be potentially delivered from such a process is given by expression (1b) where we insert instead of dT a finite difference $T_1 - T_2$

$$L_{\mathrm{W}} = \varsigma(T_1 - T_2). \tag{2}$$

This motive power L_{W}, being not re-established in the form of macroscopically observable useful mechanical, electric or magnetic work is, however, "wasted". The only remaining form in which the energy L_{W} can reappear is thus the potential energy of caloric ς' newly created at the temperature of cooler T_2; we thus have $\varsigma' = L_{\mathrm{W}}/T_2$ and for the thermal energy delivered at cooler we can write

$$T_2(\varsigma + \varsigma') = T_2\varsigma + T_2\left[\frac{\varsigma(T_1 - T_2)}{T_2}\right] = \varsigma T_1. \tag{3}$$

Eq. (3) can be, for the sake of compatibility with Eq. (1b), recast back into the terms of infinitesimally small increments of temperature or caloric by making the following substitutions: $T_1 \to T + \mathrm{d}T$, $\mathrm{d}T > 0$, and $T_2 \to T$. For the caloric passing the leak we further write ς and for the caloric delivered at the cooler $\varsigma + \varsigma' \to \varsigma + \mathrm{d}\varsigma$. From this we obtain for such restricted case

$$\mathrm{d}L_{\mathrm{W}} = T\mathrm{d}\varsigma \tag{4}$$

i.e. the wasted motive power can be expressed as $T\mathrm{d}\varsigma$ where T is the temperature of the cooler and $\mathrm{d}\varsigma$ the increment of caloric there. Generalizing thus Eq. (1b) for the net motive power delivered in an irreversible process, the wasted power $\mathrm{d}L_{\mathrm{W}}$ must be subtracted and we eventually obtain the fundamental relation of the caloric cyclic process in the frame of intuitive approach

$$\mathrm{d}L = \varsigma\mathrm{d}T - T\mathrm{d}\varsigma. \tag{5}$$

Besides, comparing both sides of Eq. (3), we can conclude that the thermal energy reaching the cooler by the thermal conduction is exactly the same as that leaving the boiler. This fact may be expressed in the form of

Corollary 1. *"By thermal conduction the energy flux remains constant".*

This corollary, belonging to both, caloric and dynamic theory of heat, plays an important role in calorimetry, as established by *Black* and *Richman* [10] the gist of which is the preservation of total amount of energy in an enclosed calorimeter during the equalization of temperature. From this point of view the realization of zero energy flux condition at boundary of the calorimeter is essential. The technical mean preventing during a thermal process the unwanted exchange of energy between the system and its environment is known as an adiabatic (or thermal) insulation ("adiabatic" is a word of Greek origin meaning "impassable", *α* = negation, *διά* = through, *βαίνειν* = to go). In case where the adiabatic insulation of the system is complete, the thermal process taking there place is called adiabatic.

4. Outline of caloric theory

4.1. Constitutive relations of caloric theory

Building caloric theory of heat, relations (1b) and (5) introduced in the preceding paragraph and specifying very intuitively the properties of caloric should serve as a guide for a more systematic treatment of constitutive relations controlling the real systems. Constitutive relations which are determined experimentally depend sensitively on definitions of relevant quantities and measurement methods; as these are to some extent arbitrary, very different descriptions of thermal phenomena can be created, in principle. Not only for practical reasons, but also not to deny great achievements of our predecessors, have we preferred to follow the lines of classical thermodynamics as close as possible [31].

In the following treatment, limited only to the simplest case of isotropic fluid, the existence of the *thermal equation of state* is assumed. It is a relation defined in the positive quadrant of V–T (volume–temperature) plane by a relation

$$p = p(V, T), \tag{6}$$

where "p" means the pressure. It is an experimental fact that this relation cannot be always inverted for V (cf. anomalous behavior of water). Therefore, p and T cannot be, in general, used as independent variables for the description of a thermal process. The pressure function p representing an intensive parameter conjugate [32] to the extensive parameter V, volume, enables moreover to evaluate the "motive power" dL in terms known from fluid mechanics as

$$\mathrm{d}L = p(V, T)\mathrm{d}V \tag{7}$$

The net gain of a caloric by a given body in any thermal process, $\mathrm{d}\varsigma$, entering e.g. Eq. (5), can be expressed using certain functions of V and T as follows:

$$\mathrm{d}\varsigma = \Lambda_{\mathrm{V}}(V, T)\mathrm{d}V + K_{\mathrm{V}}(V, T)\mathrm{d}T \tag{8}$$

These constitutive functions, Λ_{V} and K_{V}, which are assumed to be continuous together with their partial derivatives, are called *latent caloric with respect to volume* and *caloric capacity for constant volume* of a given body, respectively. These quantities may be specified also with respect to another variable (e.g. pressure) or special conditions. A corresponding subscript is then used.

As we assume that caloric scales linearly with the amount of material involved in the system under investigation, i.e. being an extensive quantity, it may be related to e.g. 1 mol and the physical dimensions of Λ_{V} and K_{V} in SI will be then [Cn/m^3 mol] and [Cn/K mol], respectively. Basing on Eq. (8) and taking into account the fact that ς should be, according to Carnot's principle a state function, we may express the functions Λ and K also in differential forms, for particular case related to volume V, as

$$\Lambda_{\mathrm{V}} = \left(\frac{\partial\varsigma}{\partial V}\right)_{\mathrm{T}}, \tag{9a}$$

$$K_{\mathrm{V}} = \left(\frac{\partial\varsigma}{\partial T}\right)_{V}. \tag{9b}$$

Notice, Λ_V represents a "structural" part of the caloric at a given temperature which varies with changes of volume (or another extensive parameter) while K_V represents a "kinetic" part of the caloric the manifestations of which are the changes of temperature. It is an important feature of caloric that it consists of two ingredients indistinguishable without *a-priori* knowledge of Λs and Ks. In the light of this fact, such phrases traditionally closely related to interpretation of classical thermodynamics, as e.g. "the kind of motion we call heat", "kinetic theory of matter", look somewhat misleading.

Of an appreciable theoretical importance are thermal processes corresponding to a closed path C in the positive quadrant of the V–T plane called cycles, or cyclical processes. Taking into account the above assumed properties of the derivatives of functions Λ and K, the net gain of caloric ς_C by a system in such a cycle can be reckoned as Stokes's integral

$$\varsigma_C = \iint_{A(C)} \left\{ \left(\frac{\partial \Lambda}{\partial T} \right)_V - \left(\frac{\partial K}{\partial V} \right)_T \right\} \mathrm{d}V\mathrm{d}T, \tag{10}$$

where $A(C)$ is the area in the V–T plane encircled by a path C. The work done in a cycle may then be evaluated by an integral formula which is a generalization of relation (7), namely

$$L_C = \iint_{A(C)} \left(\frac{\partial p}{\partial T} \right)_V \mathrm{d}V\mathrm{d}T \tag{11}$$

If a body undergoes transformations which bring it back to its original state (the same coordinates in the V–T plane and the same aggregation state), the content of caloric which is according to Eq. (8) fully determined by constitutive functions of state will have to be also the function of state. In other words, the following corollary for caloric can be formulated

Corollary 2. *"The quantity of caloric in a body is solely a function of its state".*

As was already pointed out by *Carnot* and discussed in preceding paragraph the caloric is conserved only in a restricted case, if all the changes are reversible. It may be expressed in a form of

Corollary 3. *"In any reversible cycle the caloric absorbed is just equal to that abstracted".*

It should be stressed here that this statement is mathematically, but not semantically, equivalent to Joule's proposition about reversible cycles according to which the heat = energy absorbed exceeds that abstracted by just the equivalent work done. Reversible (i.e. "isocaloric") cycle is obviously nothing but an abstraction. There is no exactly reversible process which can be observed in the nature. This concept may, however, serve as a theoretical mean which enables one to make and analyze thought experiments ("*Gedankenversuchen*") providing useful relations applicable to real systems.

4.2. Fundamental laws of thermodynamics in terms of caloric theory

Keeping the line, we can close this section by reformulation of two fundamental laws of classical thermodynamics in terms of the caloric theory. After the proper terminological substitution of caloric (i.e. heat = entropy) for heat = energy it is only a technical problem to express these fundamental laws in a manner which is usual in classical axiomatic thermodynamics [31], namely:

Theorem I. *"Energy is conserved in any real thermal process".*

Theorem II. *"Caloric cannot be annihilated in any real thermal process".*

It is worth noticing that the *First* (Theorem I) and *Second* (Theorem II) *Laws*, formulated in such a way are conceptually disjunctive. It makes difference in comparison with classical thermodynamics where both fundamental laws deal in fact with the same quantity—heat. In the caloric theory the physical entity, energy, is liberated from limitations not existing in other branches of physics and its role of heat takes caloric. The link between *First* and *Second Laws* is looser, provided by formulae (1b) or (5). Moreover, as the *First Law* in the caloric theory is, in contrast to classical thermodynamics, *exactly* identical with the general *Law of Conservation of Energy*, its explicit formulation is thus somewhat redundant.

5. Measurement of caloric

Till now we have tacitly assumed the possibility of measurement of the central physical quantity of the caloric theory—caloric ς. As the implicit definition of this physical quantity and the corresponding unit (Carnot, Cn compatible with SI) has already been given, it remains to provide a description of techniques enabling one to measure caloric, even though only in principle.

Recall first that we have to our disposal various instruments measuring energy content or energy fluxes (calorimeters, energy-meters and power-meters) and temperature (thermometers, pyrometers). On the other side, devices for the direct measurement of caloric (i.e. heat = entropy, "entropy-meters") are not in general use. This circumstance is, beside the technical problems, probably due to the fact that in the science of thermal phenomena the measurements of temperature historically preceded the definition of the meaningful concept of heat [17], which eventually, becomes identical with energy. In thermodynamics, in measuring the heat, the energy is measured, but it is necessary to subtract the amount of energy for which there are good experimental reasons that is not "transformed" into the heat in a given process. Quite an analogous method may be used in experiments arranged according to the caloric theory because of the identity of the thermal energy with product ςT.

There are, however, more direct methods enabling one to measure or to dose caloric, utilizing the changes of the "structural" part of caloric bound to a suitably chosen substance with respect to an extensive state parameter (e.g. volume). For example, let us use as a standard substance a mole of an ideal, i.e. sufficiently rarefied gas for which the latent caloric with respect to volume Λ_V is given simply by

$$\Lambda_V = \frac{R}{V}. \tag{12}$$

The content of caloric in such a system is then, at constant temperature, solely determined by its volume. Indeed, by integration of Eq. (8) for $\mathrm{d}T = 0$, we immediately obtain

$$\varsigma = \int_{V_1}^{V_2} \mathrm{d}V = R \ln \left(\frac{V_2}{V_1} \right). \tag{13}$$

A corresponding device which may be tentatively called a "caloric syringe" is depicted in Fig. 1. It is a tube provided with a movable piston and a diathermic bottom which is in contact with the system under investigation. Changing the volume of the gas enclosed in the tube a well-defined amount of caloric may be thus injected in or extracted from the system. Of course, the "caloric syringe", because of a lot of technical problems involved, is a device of a little practical use. Nevertheless, the same idea of the conversion of caloric measurements to the measurements of some

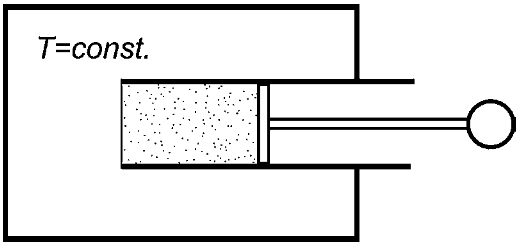

Fig. 1. Schematic view of the “caloric syringe”, a device for the direct measurement or dosage of caloric in terms of volume of ideal gas enclosed. T = const., for details see the text.

extensive state parameter of a system containing a substance with an already known constitutive function Λ may be very fruitful e.g. for research into magnetic or dielectric materials.

As an example of practical device measuring the caloric with an appreciable accuracy on the same principle as “caloric syringe”, we can mention the so called *Bunsen's* ice calorimeter [33]. It is a device enabling a very precious measurements of total volume of co-existing solid (ice) and liquid phases of water. The exchange of caloric between the system under investigation and Bunsen's calorimeter taking place at the melting temperature of ice (~273 K) is accompanied by a phase change resulting in a volume change of the water–ice system. As the latent caloric of fusion of ice is a known constant ($\Lambda_V^* \sim 1.35 \times 10^{-2}$ Cn/m^3 mol), the amount of caloric corresponding to the observed volume change ($V_1 - V_2$) can be easily computed by a formula

$$\varsigma = \Lambda_V^*(V_1 - V_2). \tag{14}$$

6. Basic properties of caloric in examples

6.1. Joule's paddle-wheel experiment

The somewhat controversial touching point between classical thermodynamics and caloric theory is related to the interpretation of Joule's paddle-wheel experiment [18] where the dissipation of measured quantity of work in a fluid system has as a consequence a certain, well-defined increase of its temperature. Within the frame of caloric theory the dissipated (wasted) mechanical work should correspond to the isothermal caloric production which is according Eq. (4) given by $\mathrm{d}L_\mathrm{W} = T\mathrm{d}\varsigma$. As the experiment is performed at constant external pressure the following increase of temperature should be given by Eq. (8) rewritten in terms of K_p

$$\mathrm{d}T = \frac{\mathrm{d}\varsigma}{K_\mathrm{p}} = \frac{\mathrm{d}L_\mathrm{W}}{K_\mathrm{p}\,T}. \tag{15}$$

On the other hand, in accordance with the classical thermodynamics the dissipation of a given quantity of work $\mathrm{d}L_\mathrm{W}$ in the apparatus brings it into a new state characterized by internal energy which is just the same as if the system were reversibly supplied by an “equivalent” amount of heat $\mathrm{d}Q$ (measured in calories) given by a relation

$$\mathrm{d}L_\mathrm{W} = J\mathrm{d}Q. \tag{16}$$

The temperature independent universal conversion factor $J > 0$ ($J \sim 4.185$ J/cal) called the mechanical equivalent of heat can be then determined from the observed temperature increase $\mathrm{d}T$ and from the *a-priori* known thermal capacitance of the device. Comparing formulae describing the same experimental situation within the frame of caloric theory and of thermodynamics some useful relations for “translation” between languages of both theories may be established.

Comparing thus Eqs. (4) and (15) with Eq. (16), we immediately obtain the relation between equivalent heat (=energy) and produced caloric in a form

$$\mathrm{d}\varsigma = \frac{J\mathrm{d}Q}{T}, \tag{17}$$

which is at first glance formally resemble to the famous formula for reversibly exchanged entropy in which the heat is measured in energy units. This correspondence between equivalent entropy and produced caloric, may serve as a very effective heuristic tool for finding the properties of caloric by exploitation of results known from classical thermodynamics. The peculiar form of (17) is in fact due to the cunning identification of empirical temperature scale with *Kelvin's* absolute (ideal gas) scale in classical thermodynamics and caloric theory as well. In both these cases, namely, the special choice of just this temperature scale T effectively simplifies Carnot's function $F(\theta)$ connecting “heat” and “work” in formula (1a). As was already shown in Section 3.2, in caloric theory in this case $F'(\theta)$ is reduced to a constant. In thermodynamics, quite similar considerations [3] then lead to the result

$$F'(T) = \frac{J}{T}, \tag{18}$$

fully compatible with Eq. (17). From this point of view it is clear that the caloric theory is not at odds with the results of paddle-wheel experiment and that factor J determined by Joule had rather to do with the establishment of a particular system of units then with the general proof of equivalence between heat and energy.

6.2. Efficiency of heat engines

Central question of the theory of heat engines is the evaluation of their efficiencies. In the caloric theory the solution is given directly by slightly modified principal Eq. (1b). Accordingly, the amount of caloric ς entering the ideal reversible continuously working heat engine at temperature T_1 and leaving it at temperature T_2 will produce a motive power of amount L there. Carnot's efficiency η_C defined as a ratio L/ς (Ref. [11]) is then given simply by the temperature drop measured in the ideal gas temperature scale, i.e.

$$\eta_\mathrm{C} = \frac{L}{\varsigma} = (T_1 - T_2). \tag{19}$$

Transforming the entering caloric into thermal energy $T_1\varsigma$, we obtain immediately *Kelvin*'s dimensionless efficiency of the ideal reversible heat engine well-known from thermodynamics,

$$\eta_\mathrm{K} = \left(1 - \frac{T_2}{T_1}\right). \tag{20}$$

Formula (20) being frequently used for the theoretical analysis of idealized reversible processes is of great significance in theoretical thermal physics. However, it is practically useless for the evaluation of the performance of real heat engines which are optimized not with respect to their efficiency but rather with respect to their available output power. As a convenient model for such a case may be taken an ideal heat engine impeded by a thermal resistance (see Fig. 2) which can be within the caloric theory treated as follows.

The original quantity of caloric ς taken from the boiler kept at temperature T_1 is enhanced by passing the thermal resistance to the amount $\varsigma + \mathrm{d}\varsigma$ but enters the heat engine at temperature $T < T_1$. Therefore, according to Eqs. (1b) and (3) we can write:

$$L = (\varsigma + \mathrm{d}\varsigma)(T - T_2), \tag{21}$$

and

$$T(\varsigma + \mathrm{d}\varsigma) = T_1\varsigma, \tag{22}$$

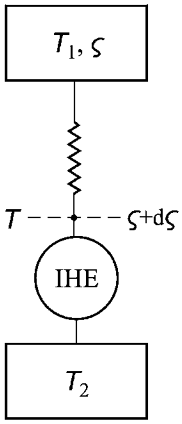

Fig. 2. More realistic caloric model of a heat engine; an ideal heat engine (IHE) impeded by a thermal resistance inserted between its input and the boiler kept at temperature T_1. The temperature of the cooler is T_2, temperatures are measured in *Kelvin's* absolute scale.

from which we immediately obtain the following relation for *Carnot's* efficiency

$$\eta_C = T_1\left(1 - \frac{T_2}{T}\right) . \tag{23}$$

If we relate the quantities L and ς to an arbitrary time unit (we use for this purpose superscript u), Eq. (21) becomes effectively a rate equation, namely

$$L^u = \frac{\alpha(T_1 - T)}{T}(T - T_2), \tag{24}$$

where for the evaluation of temperature drop across the thermal resistance the Fourier law [34]

$$\varsigma^u T_1 = \alpha(T_1 - T) \tag{25}$$

with α = const. was used. The condition for the optimum of the output power with respect to temperature T then reads $\mathrm{d}L^u/\mathrm{d}T = 0$, from which we obtain $T = \sqrt{T_1 T_2}$. *Carnot's* efficiency of such a system with optimized output power is thus given by a formula

$$\eta_C = T_1\left(1 - \sqrt{\frac{T_2}{T_1}}\right) , \tag{26}$$

corresponding obviously to *Kelvin's* dimensionless efficiency

$$\eta_K = \left(1 - \sqrt{\frac{T_2}{T_1}}\right) . \tag{27}$$

Interestingly, as was shown by *Curzon and Ahlborn* [35] this formula describes, probably because of enormous effort of engineers optimizing the output power of real heat engines, their actual efficiencies quite well. The most "effective" engine with efficiency given by (19) or (20), must be reversible, i.e. must work infinitesimally slowly being thus of no practical use. On the other side, any real machine of reasonable performance, has to be irreversible with the efficiency approaching the value given by (26) or (27) in best.

6.3. Two-chamber experiment

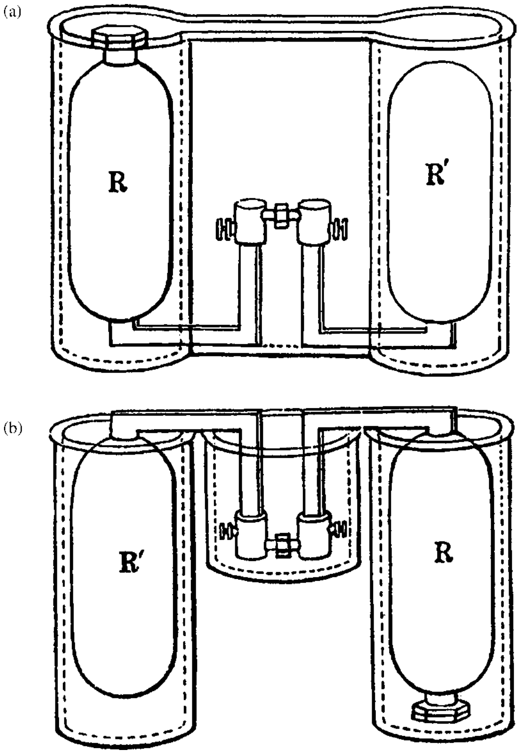

Fig. 3. Illustration to two-chamber *Joule's* experiment [37]. (a) First version of experimental set-up, with water calorimeter common for the whole system. (b) Second version, both receivers and stop-cocks with piping are submerged in theirs own calorimeters.

Very instructive for the comparison of dynamic and caloric theory of heat is the analysis of so called two-chamber experiment concerning free expansion of perfect gas into vacuum. As a rule, this subject serves in standard textbooks of thermodynamics [1,2,5,6] as a starting point for discussion of Joule-Thompson's effect which is of primary importance for liquefaction of gases. Let us assume that a thermally insulated enclosure is divided by a partition into two chambers of the same volume, V_0, one of which is filled with perfect gas of pressure p_0 at temperature T_0, and the other is evacuated. If the partition is suddenly removed, e.g. by its spontaneous rupture, then the gas is allowed to expand freely into the vacuum space. The end-state of such a spectacularly irreversible process may be predicted using Eq. (5). Taking into account, namely, that no external work was done ($\mathrm{d}L = 0$) and that due to the thermal insulation the content of caloric in the enclosure remained constant (ς = const., which is a rather bold and for clearly irreversible process an incorrect supposition), one obtains $\varsigma \mathrm{d}T = 0$, or equivalently $T = T_0$. The zero change of temperature of an ideal gas expanding into vacuum, reputedly observed in experiments, is e.g. frequently used for mathematical proof of independency of its internal energy of volume.

An actual experiment made by *Gay-Lussac* [36] and in a more sophisticated form by *Joule* [37] exhibits, however, not so simple picture. The two said chambers were in *Joule's* experiment realized by metallic receivers, one pressurized and the other evacuated, connected by piping with valves. The whole system was placed in a common water calorimeter or alternatively, every receiver and the connecting piece with stop-cock were submerged into their own separate calorimeters (see Fig. 3a and b). In the experiment with a common calorimeter, after the equalization of pressure in both chambers and before reading the temperature, the water surrounding the whole system was thoroughly stirred for some time. In this case a negligible change of temperature with respect to its original value was indicated. On the other hand, the experiment performed with the chambers and piping in separate calorimeters showed a clear decrease of temperature in calorimeter with the originally pressurized chamber and temperature increase in calorimeters containing the valves and the second chamber. Moreover, the observed temperature decrease and increase corresponding to the first and the second chambers, respectively, seems to compensate each other. These experiments, which are not so easy to treat within the frame of elementary thermodynamics using e.g. concept of internal energy, may be described by the caloric theory as follows.

First, let us imagine that the evacuated chamber is cylindrical in form and provided with a piston moving freely without the friction inside the chamber. If we open the stop-cock (with the piston by the side where the connecting pipe mouths) the gas will start to expand adiabatically until the piston reaches the opposite side of the chamber. The work done in this chamber bears evidently character of wasted motive power, because the piston is backed only by vacuum and eventually by the firm wall. Such a waste must be compensated by rise of a certain amount of caloric which increases the temperature of the gas in this chamber. On the other hand, the cooling of the gas in the originally pressurized chamber is due to the adiabatic expansion controlled by *Poisson's* constitutive formula [10]

$$TV^{\gamma-1} = \text{const.,} \tag{28}$$

where γ is a temperature independent constant. The caloric process in the system may thus be described as follows. Cooling of the gas appearing in the first chamber just after the full expansion can be computed from the relation $T_0 {V_0}^{\gamma-1} = T_1(2V_0)^{\gamma-1}$, where T_0, and T_1 are the starting and the end temperature, respectively. From this we obtain a formula

$$T_1 = \frac{T_0}{2^{\gamma-1}}. \tag{29}$$

On the other side, the increase of temperature of gas entering the second chamber can be computed directly from the wasted power and calorimetric properties of the gas involved. For the power wasted by adiabatic expansion we can obviously write

$$L_{\mathrm{W}} = \int_{V_0}^{2V_0} p\mathrm{d}V = p_0 V_0^{\gamma} \int_{V_0}^{2V_0} \frac{\mathrm{d}V}{V^{\gamma}} = \frac{nRT_0}{(1-\gamma)(2^{1-\gamma}-1)} \tag{30}$$

where we use the ideal gas equation of state for n mol $p_0V_0 = nRT_0$ Taking now into account Poisson's relations valid for the ideal gas, i.e.

$$\gamma = \frac{K_{\mathrm{p}}}{K_{\mathrm{V}}}, \text{ and } \frac{nR}{T} = n(K_{\mathrm{p}} - K_{\mathrm{V}}), \tag{31}$$

we immediately obtain for the end temperature in the second chamber a value

$$T_2 = 2T_0[1 - 2^{-\gamma}]. \tag{32}$$

As the experiment was conducted with air ($\gamma = 1.4$) and started at room temperature ($T_0 = 300$ K), we immediately obtain estimates $T_1 = 227$ K and $T_2 = 372$ K. Notice that according to formulae (29) and (32) the resulting temperatures are independent of initial pressure (i.e. of the amount of gas involved) and that the computed differences with respect to the room temperature ($T_0 - T_1 \approx T_2 - T_0 = 73$ K) are much larger than those observed by Joule ~2.38 °F (≈1.32 K). It is evidently due to the large thermal capacity of water calorimeters used. Indeed, if we take Joule's own figures into account (volume of the receiver $V = 2.2 \times 10^{-3}\ \mathrm{m}^{-3}$, water content of the calorimeter ~3.7 kg, and initial pressure in the first chamber 2.2×10^{6} Pa), we obtain the differences of order of ~1 K in a satisfactory agreement with Joule's observation. The cancellation of temperature differences in the experiment with common calorimeter cannot thus be interpreted as a preservation of temperature during the free expansion of perfect gas because it is rather due to the stirring of water in the calorimeter and back-conveying of caloric already transferred by the process of pressure equalization.

7. Conclusions

It has recently been recognized that the treatment of some complex problems belonging to the scope of small quantum systems or stochastic electrodynamics by means of traditional tools of thermodynamics, leads to numerous antinomies. We claim that the source of much confusion and serious obstruction for the further development of theory of thermal processes in quantum systems may be due just to the inconvenient conceptual basis of classical thermodynamics as established in the second half of the 19th century. Therefore, we have suggested modifying the structure of classical thermodynamics, which is essentially based on the interpretation of heat as a special kind of energy controlled by the *First* and the *Second Laws*, in favor of an alternative admissible system where heat is regarded as an entropy-like quantity. In order not to perplex this quantity with entropy known from classical thermodynamics and other branches of science a historical term "caloric" was reintroduced. In the present paper we prefer to show the viability of caloric theory of heat rather then to give its rigorous exposition. Therefore, besides the sketch of basic ideas of caloric theory a few simply solved examples are added. These examples simultaneously illustrate the relation between caloric and dynamical theory of heat although no systematic comparison is made.

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References

[1] J.K. Roberts, Heat and Thermodynamics, fourth ed., Blackie and Son Ltd., Glasgow, 1951.
[2] P.S. Epstein, Textbook of Thermodynamics, J. Wiley and Sons, New York, 1954.
[3] H. Cullen, Thermodynamics: an Introduction to Thermostatics, Wiley, New York, 1960.
[4] C. Truesdell, Rational Thermodynamics, McGraw-Hill, New York, 1969.
[5] M. Bailyn, A Survey of Thermodynamics, AIP Press, New York, 1990.
[6] S.J. Blundell, K.M. Blundell, Concepts in Thermal Physics, Oxford University Press, Oxford, 2006.
[7] G.M. Barrow, Physical Chemistry, sixth ed., McGraw-Hill, New York, 1996.
[8] D.P. Sheehan (Ed.), Proceedings of the 1st IC on Quantum limits to the Second Law, San Diego 2002 by AIP, T.M. Nieuwenhuizen, P.D. Keefe, V. Špička (Eds.), Melville 2002 and that of the IC on Frontiers of Mesoscopic and Quantum Thermodynamics, Prague 2004, Physica E 29 (2005) 1–442.
[9] J. Gemmer, M. Michel, G. Mahler, Quantum Thermodynamics: Emergence of Thermodynamic Behavior Within Composite Quantum Systems, Springer, Heidelberg, 2004.
[10] E. Mach, Die Principien der Wärmelehre, Verlag von J. A. Barth, Leipzig, 1896.
[11] H.L. Callendar, Proc. Phys. Soc. Lond. 23 (1911) 153.
[12] E. Mach, Populär-Wissenschaftliche Vorlesungen, Verlag von J. A. Barth, Leipzig, 1923.
[13] G. Job, Neudarstellung der Wärmelehre – Die Entropie als Wärme", Akad. Verlagsges., Frankfurt am Main, 1972.
[14] G. Job, T. Lankau, Ann. N.Y. Acad. Sci. 988 (2003) 171.
[15] G. Falk, Eur. J. Phys. 6 (1985) 108.
[16] J.J. Mareš, J. Šesták, J. Therm. Anal. Calorim. 82 (2005) 681.
[17] J.J. Mareš, J. Therm. Anal. Calorim. 60 (2000) 1081.
[18] T. Ehrenfest-Afanassjewa, G.L. De Haas-Lorentz, Physica 2 (1935) 743.
[19] B. Count of Rumford, Philos. Trans. 88 (1789) 80.
[20] J.P. Joule, Philos. Trans. 140 (1850) 61.
[21] R. Clausius, Ann. Phys. Chem. (Leipzig) 142 (1871) 433.
[22] S.G. Brush, The Kind of Motion we Call Heat, vol. I & II, North Holand, Amsterdam, 1976.
[23] J. Larmor, Proc. R. Soc. Lond. A 194 (1918) 326.
[24] A.C. Lunn, Phys. Rev. 14 (1919) 1.

[25] R. Fox, The Caloric Theory of Gases: from Lavoisier to Regnault, Claredon Press, Oxford, 1971.
[26] R.B. Lindsey, Energy: Historical Development of the Concept, Dowden, Stroudburg, 1975.
[27] J.S. Wicken, Philos. Sci. 54 (1987) 176.
[28] S. Carnot "Réflexions sur la puissance motrice du feu et sur les machines propres à développer cette puissance" Bachelier, Paris 1824, German translation, Ostwald's Klassiker, Nr. 37, Engelmann, Leipzig1909.
[29] H.T. Wensel, J. Appl. Phys. 11 (1940) 373.
[30] V.K. La Mer, Am. J. Phys. 22 (1954) 20.
[31] C. Truesdell, The Tragicomical History of Thermodynamics, Springer Verlag, New York, 1980.
[32] J. Palacios, Dimensional Analysis, Macmillan & Co. Ltd., London, 1964.
[33] R. Bunsen, Calorimetrische Untersuchungen, Ann. Phys. Chem. 141 (1870) 1.
[34] J.-B.J. Fourier, Théorie analytique de la chaleur" Paris 1822, English translation "The Analytical Theory of Heat, Dover Publications, Mineola, New York, 2003.
[35] F.L. Curzon, B. Ahlborn, Am. J. Phys. 43 (1975) 22.
[36] L.J. Gay-Lussac, Mém. de la Société d'Arcueil 1 (1807) 180, see also ref. 10., p.198.
[37] J.P. Joule, Phil. Mag. 26 (1845) 369.