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PHENOMENOLOGICAL APPROACH TO THE CALORIC THEORY OF HEAT

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THERMODYNAMICS, INFORMATION AND SOCIETY: FEATURED THOUGHTS

Jaroslav Šesták

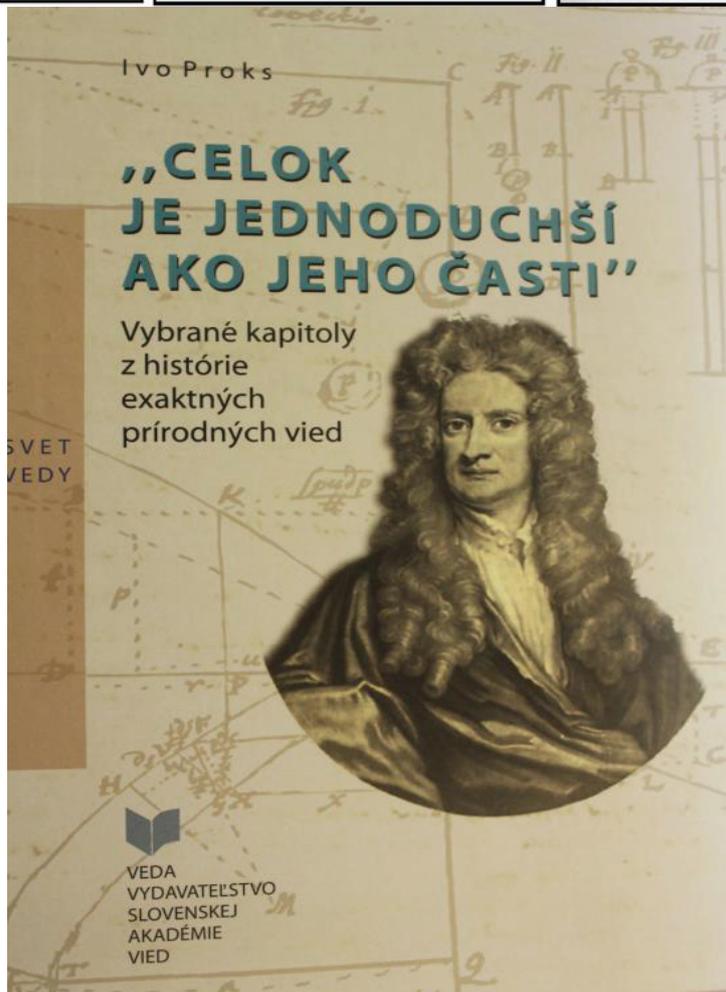
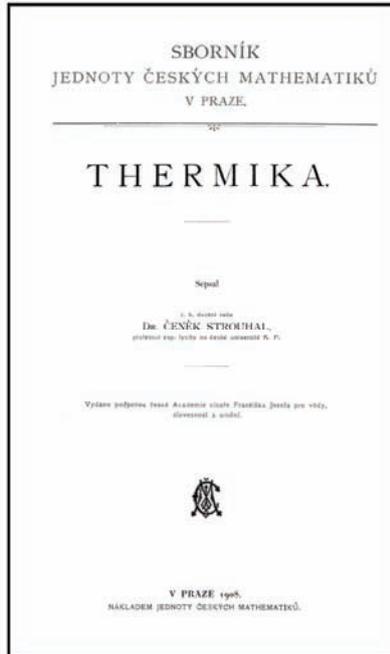
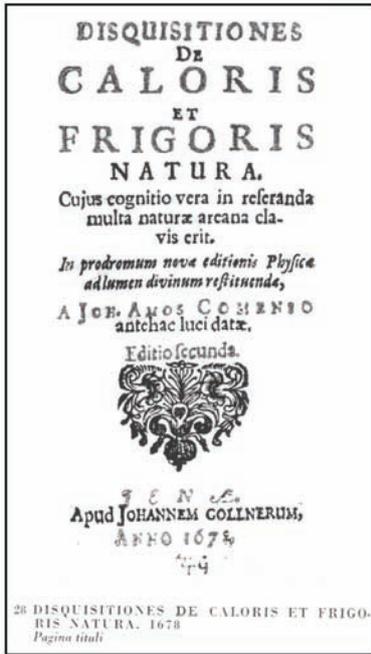
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HOTNESS MANIFOLD, PHENOMENOLOGICAL TEMPERATURE AND OTHER RELATED CONCEPTS OF THERMAL PHYSICS

J.J. Mareš,
Book Chapter

A THERMODYNAMIC FORMULATION OF ECONOMICS

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Book Chapter





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.

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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.

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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.

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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 fundamentals 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,

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).

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 cornerstone 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 bal-

ance 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

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, \dot{W} , and heat in calories, \dot{Q} .

JQ. The work W and the heat Q 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 ζ falling over a small temperature difference $d\theta$ can be expressed by the formula

$$dL = \zeta F'(\theta) d\theta, \quad (1a)$$

where $F(\theta)$ is so called Carnot’s function which must be determined experimentally respecting the operative definitions of quantities ζ 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 $d\theta$. 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 ζ from a hotter bath (by $d\theta$) into bulb of thermometer filled with the perfect gas is obviously equal to $p dV$. As in this case the empirical temperature scale θ is per definition identical with Kelvin’s perfect gas scale, T , we can write $dL = R dT = R d\theta$ 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 $R = \zeta F'(T)$. Taking into account the fact that caloric is conserved by reversible operations, the quantity ζ 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

$$dL = \zeta dT. \quad (1b)$$

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

³ We are using for caloric Greek final-letter ζ as this letter involves graphics of both, usual S for entropy and C for caloric. The caloric ζ 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 ζ 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 $T_1 - T_2$

$$L_W = \zeta(T_1 - T_2). \quad (2)$$

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 ζ' newly created at the temperature of cooler T_2 ; we thus have $\zeta' = L_W/T_2$ and for the thermal energy delivered at cooler we can write

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

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: $T_1 \rightarrow T + dT$, $dT > 0$, and $T_2 \rightarrow T$. For the caloric passing the leak we further write ζ and for the caloric delivered at the cooler $\zeta + \zeta' \rightarrow \zeta + d\zeta$. From this we obtain for such restricted case

$$dL_W = T d\zeta \quad (4)$$

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

$$dL = \zeta dT - T d\zeta. \quad (5)$$

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, $\delta\iota\acute{\alpha}$ = through, $\beta\alpha\lambda\upsilon\upsilon\epsilon\iota\upsilon$ = 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

$$p = p(V, T), \quad (6)$$

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

$$dL = p(V, T)dV \quad (7)$$

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

$$d\zeta = \Lambda_V(V, T)dV + K_V(V, T)dT \quad (8)$$

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/m³ mol] and [Cn/K mol], respectively. Basing on Eq. (8) and taking into account the fact that ζ 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

$$\Lambda_V = \left(\frac{\partial \zeta}{\partial V} \right)_T, \quad (9a)$$

$$K_V = \left(\frac{\partial \zeta}{\partial T} \right)_V. \quad (9b)$$

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 Λ s and K s. 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 ζ_C by a system in such a cycle can be reckoned as Stokes's integral

$$\zeta_C = \iint_{A(C)} \left\{ \left(\frac{\partial \Lambda}{\partial T} \right)_V - \left(\frac{\partial K}{\partial V} \right)_T \right\} dV dT, \quad (10)$$

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

$$L_C = \iint_{A(C)} \left(\frac{\partial p}{\partial T} \right)_V dV dT \quad (11)$$

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 ζ . 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 ζT .

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

$$\Lambda_V = \frac{R}{V}. \quad (12)$$

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 $dT=0$, we immediately obtain

$$\zeta = \int_{V_1}^{V_2} dV = R \ln \left(\frac{V_2}{V_1} \right). \quad (13)$$

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

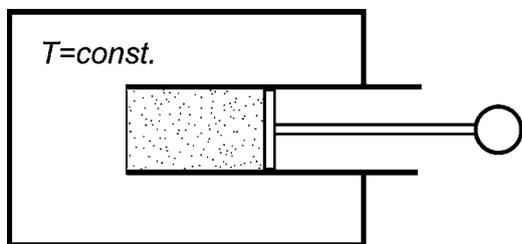


Fig. 1. Schematic view of the “caloric syringe”, a device for the direct measurement or dosage of caloric in terms of volume of ideal gas enclosed. $T = \text{const.}$, for details see the text.

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/m³ mol), the amount of caloric corresponding to the observed volume change ($V_1 - V_2$) can be easily computed by a formula

$$\zeta = \Lambda_V^*(V_1 - V_2). \quad (14)$$

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 $dL_W = Td\zeta$. 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

$$dT = \frac{d\zeta}{K_p} = \frac{dL_W}{K_p T}. \quad (15)$$

On the other hand, in accordance with the classical thermodynamics the dissipation of a given quantity of work dL_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 dQ (measured in calories) given by a relation

$$dL_W = JdQ. \quad (16)$$

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 dT 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

$$d\zeta = \frac{JdQ}{T}, \quad (17)$$

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

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

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 than 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 ζ 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/ζ (Ref. [11]) is then given simply by the temperature drop measured in the ideal gas temperature scale, i.e.

$$\eta_C = \frac{L}{\zeta} = (T_1 - T_2). \quad (19)$$

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

$$\eta_K = \left(1 - \frac{T_2}{T_1}\right). \quad (20)$$

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 ζ taken from the boiler kept at temperature T_1 is enhanced by passing the thermal resistance to the amount $\zeta + d\zeta$ but enters the heat engine at temperature $T < T_1$. Therefore, according to Eqs. (1b) and (3) we can write:

$$L = (\zeta + d\zeta)(T - T_2), \quad (21)$$

and

$$T(\zeta + d\zeta) = T_1\zeta, \quad (22)$$

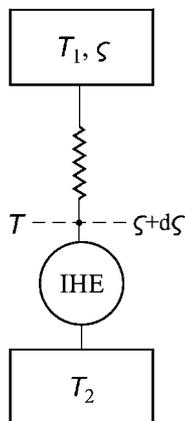


Fig. 2. More realistic caloric model of a heat engine; an ideal heat engine (IHE) impeded by a thermal resistance inserted between its input and the boiler kept at temperature T_1 . The temperature of the cooler is T_2 , temperatures are measured in Kelvin's absolute scale.

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

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

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

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

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

$$\zeta^u T_1 = \alpha(T_1 - T) \quad (25)$$

with $\alpha = \text{const.}$ was used. The condition for the optimum of the output power with respect to temperature T then reads $dL^u/dT = 0$, 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

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

corresponding obviously to Kelvin's dimensionless efficiency

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

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

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

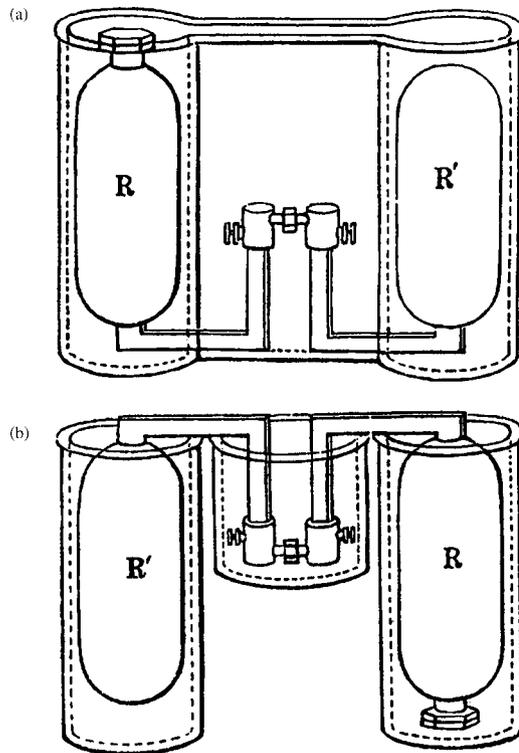


Fig. 3. Illustration to two-chamber Joule's experiment [37]. (a) First version of experimental set-up, with water calorimeter common for the whole system. (b) Second version, both receivers and stop-cocks with piping are submerged in their own calorimeters.

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 ($dL=0$) and that due to the thermal insulation the content of caloric in the enclosure remained constant ($\zeta = \text{const.}$, which is a rather bold and for clearly irreversible process an incorrect supposition), one obtains $\zeta dT=0$, 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]

$$TV^{\gamma-1} = \text{const.}, \quad (28)$$

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 $T_0V_0^{\gamma-1} = T_1(2V_0)^{\gamma-1}$, where T_0 , and T_1 are the starting and the end temperature, respectively. From this we obtain a formula

$$T_1 = \frac{T_0}{2^{\gamma-1}}. \quad (29)$$

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

$$L_W = \int_{V_0}^{2V_0} p dV = p_0 V_0^\gamma \int_{V_0}^{2V_0} \frac{dV}{V^\gamma} = \frac{nRT_0}{(1-\gamma)(2^{1-\gamma} - 1)} \quad (30)$$

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.

$$\gamma = \frac{K_p}{K_v}, \quad \text{and} \quad \frac{nR}{T} = n(K_p - K_v), \quad (31)$$

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

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

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 $\sim 2.38^\circ\text{F}$ (≈ 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 $V = 2.2 \times 10^{-3}$ m³, 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 than 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.

Acknowledgements

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CONTRIBUTION BY LAZARE AND SADI CARNOT TO THE CALORIC THEORY OF HEAT AND ITS INSPIRATIVE ROLE IN THERMODYNAMICS

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The works of Lazare and Sadi Carnots are reviewed emphasizing their contribution to the caloric theory of heat, which is consequently analyzed in terms of an alternative thermodynamic approach. In the framework of the caloric theory the elementary derivation of the efficiency of real heat engines, $\eta_{\kappa}=1-\sqrt{(T_2/T_1)}$, is given which is a direct consequence of linearity of Fourier's law of heat transfer.

Keywords: caloric as entropy, Carnot, efficiency, history, thermal analysis, thermodynamics

Introduction

It is worth of awareness to mention a remarkable forerunner in the early field of thermal physics but less-known Czech thinker and Bohemian educator, Comenius who in his book outlining contemporaneous physics [1] showed the importance of hotness and coldness in all natural processes envisaging caloric (as heat or better fire) to cause internal motions of things. In 1659 he succeeded to publish another treatise on the principles of heat and cold [2] but it is hard to guesstimate whether it was possible to circulate his ideas and terminology (e.g. caloric) from Amsterdam, where he mostly lived, to Scotland where a century later a substance, or better, a matter of fire, was consonantly called caloric by Black (1760) [3]. The practically same term was later also used by French chemist Lavoisier (1789). Caloric theory was perceptible for two centuries [3–8] assuming caloric to be a substantial kind of fluid which creeping among the elementary parts of matter causes changes of its temperature or aggregate state (melting, expansion, etc. [4]). Once enduring idea that heat in its common sense is a kind of energy survived until now [8, 9] in spite of that some annotations [10] already tried to associate heat with a somewhat artificial quantity called entropy as known from treaties of classical thermodynamics [8, 11–13] acknowledging that heat can be equally measured in the energy and entropy units. In the latter case (heat=entropy) the logical content of term heat is practically identical with the concept of Carnot's caloric [8, 10, 14–16].

This condition has opened possibility to reintroduce this old-new concept of caloric back into the phenomenological theory of thermal processes [14–16].

Lazare Carnot and his mechanical theory of machines

As a notable French citizen (born in Nolay 1753) Lazare [7, 17–19] attended the school for military engineering and than undertook military career (reorganizing army and later shortly becoming the Bonaparte's minister of war). In 1800 he was elected for a member of French Institute and five years later became its president. Scientifically he was most famous for his early published 'Memoir on the Theory of Machines' and its second version 'Fundamental principles of Equilibrium and Movement' [20] and for his theoretical works on mathematics as well [21]. Let us recall that the physics of the 18th century was developed under the influence of Newtonian concepts (1687) based on three fundamental commandment of motion: the principle of inertia, the law of motion (defining the quantity of 'force') and the law of action and reaction. Such a conception of mechanics was further elaborated along the same lines, let us just mention [17, 19] the system of mechanics of Euler (1736) and the dynamics of Baptiste d'Alembert (1743). The concept of energy, however, was yet missing. It was introduced only by Leibniz (1695) in the form of life force, vis viva, and dead force, vis mortua, which was latter renamed to

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'potential energy' by Rankine (1853) [22]. The first use of term 'energy' in its modern sense is, nevertheless, due to Young (1807). The quantity 'work' was also absent in mechanics and numerical analysis of mechanical processes, which was carried out without the use of algebraic formalisms for the vector analysis. Such was the state of art of mechanics when Lazare started his systematic studies trying to apply laws of physics to properties of mechanical devices.

Lazare's strategy actually showed to be suitable for an abstract description of mechanical devices. He defined the studied object as a set of its parts, which are either free or mutually connected to each other by a system of virtual joins (abstract mass-less rods known today as bonds) assuming them completely incompressible or, alternatively, elastic. He then asked what would be the 'resulting velocity' of a body as a whole, if each part of it will be permitted to perform its own 'geometric motion' compatible with the bonds. He named the difference between velocity without internal 'geometric motions' and 'resulting velocity' as a 'lost velocity'. On practical grounds he restricted his study of mechanical systems to two categories; first one, involving only life forces and second one, mixing both life and dead forces together. Furthermore, he subdivided the movements into two subcategories, namely, where the velocities undergo sudden changes (by impacts) or where changes continuously. He also found that the sum of products of mass and velocity taken over all parts of the body and projected into the direction of the lost velocity, remains equal zero during the motion. This corollary being also close to the famous law of the conservation of momentum was in fact a predecessor of the principle of 'virtual work'. Lazare conveyed the belief that the highest possible efficiency of the transfer of vis viva within mechanical devices is characterized by the absence of dissipation which was measured by the quantity of action, known as 'Carnot's moment of activity' and later labeled as the 'work' [23].

Concept of the work balance allowed Lazare to describe equilibrium in machines in terms of virtual displacements. There were another two quantities closely related to the 'work': 'power', a quantity without any further specification and 'efficiency', originally called 'effect'. For a comparison of efficiencies of ideal and real machines he also introduced the concept of 'mechanical inequalities'. His work in physics, however, remained without response in his milieu and it was also omitted by his followers, Lagrange and Laplace.

Sadi Carnot and his caloric concept of heat engines

Lazare's older son Leonard-Sadi Carnot [17, 24, 25] was born 1796 in Paris and until his age of sixteen he was conscientiously brought up and carefully educated by his father so that he could later transfer some of Lazare's ideas into his own thoughts on thermal physics. During this learning Sadi had to comprehend two co-existing concepts on the nature of heat. One introduced by a theory associating heat with the motion of elementary particles of bodies (later called kinetic theory) and the other regarding heat as a special substance (caloric theory). The protagonist of a rather complicated kinetic theory was Bernoulli, who already in his book on hydrodynamics (1738) derived the Boyle-Mariotte law originally known from the caloric-related works published by Newton and Euler. Much simpler caloric theory [5–8] was favored by Black and Irvin, who introduced quantities 'thermal capacity' and 'latent heat', experimentally measurable by the apparatus called calorimeter [3, 6, 8, 17]. Lavoisier and Laplace regarded both theories as equivalent hypotheses but preferred simpler equations for the heat balance derived on the basis of caloric concept, the density of which within the space in-between molecules corresponded to the macroscopically measured temperature. Moreover, Laplace (1816) successfully used the caloric theory for calculating corrections to Newton's expression for the speed of sound in air (physical model behind was already suggested by Lagrange).

In 1822, Fourier published an influential book on the analytical theory of heat [26], in which he developed methods for integration of partial differential equations, describing diffusion of the heat substance. Based on the yet inconsistent law of conservation of caloric, Poisson (1823) derived a correct and experimentally verifiable equation describing the relationship between the pressure and volume of an ideal gas undergoing adiabatic changes. In the year 1826 Clement defined the unit of heat (calorie) as the amount of caloric, necessary for heating 1 g of liquid water by 1°C. Though the expected temperature changes due to 'thickened caloric' did not experimentally occur (cf. measurements in 'Torricelli's vacuum' over mercury by Gay-Lussac) and in spite of that Thompson (Count Rumford, 1798) showed that the heat could be produced by friction ad infinitum, the caloric theory survived many defeats and its mathematical scheme is in fact applied for the description of heat flow until today.

In the light of Lazare's work on mechanical engines (co-opting ideas of equilibrium, infinitesimal

changes and imaginatively replicating the case of water fall from a higher level to a lower in a water mill, for caloric), Sadi was thinking about writing a book on the properties of heat engines applying caloric hypothesis generally accepted in that time within broad scientific circles. Instead, he wrote a slim book of mere 118 pages, published in 200 copies only, which he entitled as the ‘Reflections on the motive power of fire and on machines fitted to develop that power’ (1824) [27], which was based on his earlier outline dealing with the derivation of an equation suitable for the calculation of motive power performed by a water steam [18]. He explained comprehensively under what conditions it is possible to obtain useful work (‘motive power’) from a heat reservoir and how it is possible to realize a reversible process accompanied with heat transfer. Sadi also explained that a reversibly working heat engine furnished with two different working agents had to have the same efficiency related to the temperature difference, only. Among other notable achievements [17] there was the determination of the difference between the specific heats of gases measured at constant pressure and volume. He found that the difference was the same for all gases, anticipating thus the Mayer’s relation for ideal gas: $c_p - c_v = R$. Sadi also introduced the ‘Carnot’s function’ the inverse of which was later (1850) identified by Clausius (1822–1888), within the classical thermodynamics, with the absolute temperature T . Finally, Sadi adjusted, on the basis of rather poor experimental data that for the production of 2.7 mechanical units of ‘motive power’ it was necessary to destruct one caloric unit of heat, which was in a fair correspondence with the later mechanical equivalent of heat: (4.1 J cal⁻¹). It is worth noting that already when writing his book he started to doubt the validity of caloric theory [17, 24] because several of experimental facts seemed to him almost inexplicable. Similarly to his father, Sadi’s work remained unnoticed by contemporary physicists and permanently unjustly criticized for his principle of the conservation of caloric, which is, however, quite correct for any cyclic reversible thermal process.

Underlying laws of thermal physics within the caloric theory

Following the way of Carnot’s intuitive thinking [27], the small amount of work done dL (motive power in Carnot’s terms) is performed by caloric ζ falling over an infinitesimal temperature difference dT [14–16]

$$dL = \zeta F(T) dT \quad (1)$$

The function $F(T)$ here is the Carnot’s function, which has to be determined experimentally, certainly, with respect to the operative definitions of quantities ζ and T . It is a remarkable fact that according to Eq. (1) caloric is not consumed (produced) by performing work but only loses (gains) its temperature, by dT . Therefore, the caloric has there an extensive character of some special substance while the intensive quantity of temperature plays the role of its (thermal) potential; the thermal energy may be thus defined as the product, ζT . The perfect parallel with other potentials known from the physics, such as pressure – choric potential, gravitational potential for mass and electrostatic potential for charge, is evident.

Taking into account that caloric is conserved during reversible operations, the quantity ζ must be independent of temperature and, consequently, Carnot’s function $F(T)$ has to be also constant. Putting the function equal identically 1 the unit of caloric fully compatible with the SI system is defined. Such a unit, according to Callendar [28], can be appropriately called ‘Carnot’ (abbreviated as ‘Cn’ or ‘Ct’). One ‘Cn’ unit is then such a quantity of caloric, which is during 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. (1) may be rewritten in a very simple form [15]

$$dL = \zeta dT \quad (2)$$

On the other hand, in accordance with the classical thermodynamics the dissipation of a given quantity of work dL_w in an apparatus brings it into a new state, which is characterized by ‘internal energy’ and which is just the same as if the system were supplied by an ‘equivalent’ amount of heat dQ (measured in calories) according to the following relation

$$dL_w = J dQ \quad (3)$$

The temperature independent universal conversion factor ($J \sim 4.185 \text{ J cal}^{-1}$) is the mechanical equivalent of heat, which can be then determined from the observed temperature increase and from 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 suitable for conversion between both ‘languages’ of complementary theories may be thus established. Comparing Eq. (2) with Eq. (3), we immediately obtain the relation between heat (measured as energy) and caloric in the form

$$d(\zeta T) = J dQ \quad (4)$$

which, at first glance, resembles the famous formula for entropy, certainly if we measure the heat in energy

units. This correspondence between entropy and caloric, may serve as a very effective heuristic tool for finding the properties of caloric by exploitation the results known hitherto from classical thermodynamics. From this point of view it is clear that the caloric theory is not at any odds with experimental facts, which are only anew explained (see e.g. paddle-wheel experiment [15]). The factor J historically determined by Joule should have been rather related with the establishment of a particular system of units then with a general proof of the equivalence between heat and energy.

One of the central questions of the Carnot's theory of heat engines is the evaluation of engine efficiency. In the caloric theory the solution is given directly by a slightly modified principal Eq. (2). Accordingly, the amount of caloric, ζ , which is entering the completely reversible and continuously working heat engine at temperature T_1 and leaving it at temperature T_2 will produce a motive power of amount Carnot's efficiency η_C defined as a ratio L/ζ is then given by a plain temperature drop $\Delta T=(T_1-T_2)$ (as measured in the ideal gas temperature scale). Transforming the incoming caloric into thermal energy $T_1\zeta$, we obtain immediately Kelvin's dimensionless efficiency η_K of the ideal reversible heat engine, $\eta_K=\{1-(T_2/T_1)\}$, which is well-known from textbooks of thermodynamics.

However, η_K is nearly useless for the practical 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 it may be taken an ideal heat engine impeded by a thermal resistance** (Fig. 1) [15]. The effect of thermal resistance can be understood within the caloric theory in such a way that the original quantity of caloric ζ , taken from the boiler kept at temperature T_1 , increases, by passing across a thermal resistance, to the new quantity equal to $\zeta+\Delta\zeta$, entering than the ideal heat engine at temperature $T<T_1$. Therefore, using Eq. (2) in the integral form, we can write for the motive power:

$$L=(\zeta+\Delta\zeta)(T-T_2) \tag{5a}$$

Simultaneously, because of preservation of thermal energy, the following equation holds:

$$T(\zeta+\Delta\zeta)=T_1\zeta \tag{5b}$$

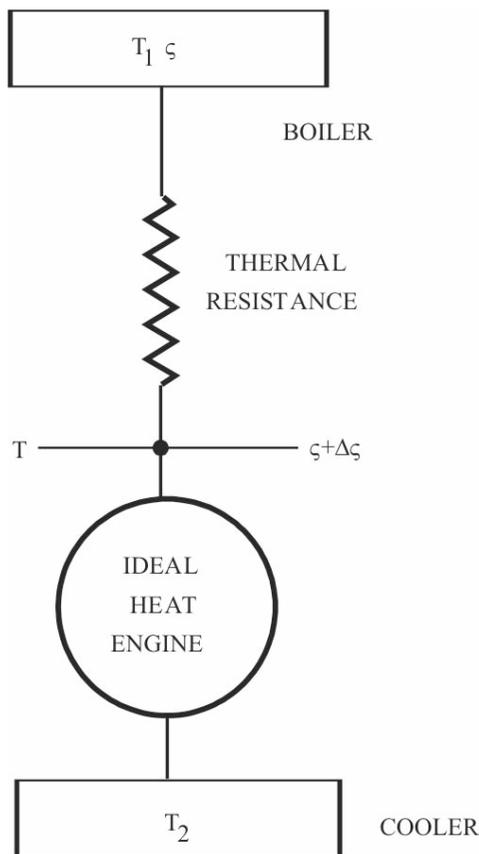


Fig. 1 Simplified outline of a real heat engine

then from Eqs (5a) and (5b) we immediately obtain the following relation expressing the Carnot's efficiency $\eta_C=L/\zeta=T_1\{1-(T_2/T)\}$.

If we relate the quantities L and ζ to an arbitrary time unit (we conveniently use for this purpose a superscript u), Eq. (5a) becomes effectively the rate equation

$$L^u=k(T_1-T)(T-T_2)/T \tag{6}$$

where for the evaluation of temperature drop across the thermal resistance we can apply the Fourier law [26] $\zeta^u T_1=k(T_1-T)$, where k is a constant representing the inverse of thermal resistance. The condition for the optimum of the output power with respect to temperature T then reads $dL^u/dT=0$, from which we obtain $T=\sqrt{(T_1 T_2)}$. Consequently, the Carnot's true efficiency of such a system with optimized output power is thus given by a formula

$$\eta_C=T_1\{1-\sqrt{(T_2/T_1)}\} \tag{7}$$

Such a root square dependence, which is the direct consequence of linearity of Fourier's law, is

** We consider here only the case where the thermal resistance appears just between the boiler and the heat engine; in fact a resistance to the cooler and/or other thermal leakages should be in a more realistic model taken into account. If we consider, however, only Fourier's linear heat resistances in series with ideal heat engine, it can be shown by a little algebra that resulting Eq. (7) for the efficiency remains valid

also obviously repeated for the above mentioned dimensionless Kelvin's efficiency, η_K . Because of enormous effort of engineers to optimize the real output power of concrete heat engines, Eq. (7) describes the actual efficiencies quite well as interestingly shown by Curzon and Ahlborn [29].

Acknowledgements

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Thermodynamics, Information and Society: featured thoughts

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1. Preface

Thermodynamics [1,2] (from the Greek *thermos* = heat and *dynamis* = force) is closely associated with *energy*, E (*ergon* = action and *energia* = activity) and with efficiency limiting the production possessions of all heat engines (in a specific meaning of 'energy transducer') whose manufacturing know-how has gradually developed along with the societal information content of progressively civilized society. The capability to represent time and space and number has become the precondition for having any experience whatsoever. The domain of thermodynamics thus bears the specific characteristics of human cognition resulting from our capability to imagine abstractly, either with numbers or mere words, which is a key feature of our societal consciousness. To try to deal seriously with energy problems is, however, like trying to write an objective political treatise on any controversial subject. Nevertheless, we can trace in the history of the human race that all major advances in civilization have been accompanied by increases in the rate of energy consumption retaining, however, a historical understanding of heat (and temperature). In many instances the availability of low-cost energy and its inconsiderate and inefficient utilization has led to disastrous ecological effects albeit securing luxurious life. Therefore energy must be understood in its wider thermodynamic scale, possibly related to its information content. It is assumed that the energy of any macro-system which is used to transform it to more likely forms exhibits its lowest Gibbs (free) energy, G , and the reason for its availability is certain storage of improbability. The fight of a man against nature is therefore a fight for lower entropy, S (and consequently better information), not merely for energy which is, more or less, plentiful.

2. Heat: a historical introduction

The classical Greek classification of the surrounding world [2,3] probably arose in India (60BC) and consisted of the four basic elements: (-dry-) *fire* (-hot-) *air* (-wet-) *water* (-cold) *earth* (-dry-), all things being their combinations. It, however, did not distinguish energy and matter so that when heating a metal one was simply adding more "fire" to it. *Plato* (427-347) seemed to distinguish between fire and heat and *Aristotle* (383 – 322 BC) apparently differentiated temperature from the quantity of heat even though the same word was used for both. Aristotle and later philosophers paid attention to the notions "spirit, breath" which by some were identified with ether and by others with fire, which was always considered as a basic compositional element. *Demokritos* (460-370 BC (and his teacher *Leukippos*) already tried to assume its dependence on the shape and arrangements of elementary particles (atoms). *Theophrastos* [5] (287 BC) proposed three stages of fire: glow, flame and lightening while *Galen* (129-199 AD) brought out an idea of four degrees for becoming warm and cold with a "neutral point", which were equal parts of ice and boiling water. Practical knowledge of the effects of fire progressed more in the time between *Theophrastos* and the later architect *Vitruvius* (27 BC) than it had had in several

centuries previously, as would be expected in a highly developed civilization such as that of Rome (assuming its aesthetic aspects and personal comfort of life). The *Pythagoreans* distinguished the notions of matter and form, linked through a process of development. In contrast to Plato and Aristotle they believed that form had no separate existence but was immanent in matter; their philosophy and scientific ideas dominated Western thoughts for two thousand years until a radical change was brought about by new discoveries in physics, astronomy and mathematics (e.g. *Copernicus, Galilei, Descartes and Newton*) assuming the world as a perfect machine governed by exact mathematics.

The need of controlled fire became important in regulating the temperature regime of furnaces (*Norton* [6]) necessary in early metallurgy (*Agricola* [7]). About two centuries after the foundation of the Charles University (Prague 1348), *Stolcius* [8] introduced a world first specialization called "*chimiatrie*". The Bohemian educator *Comenius* (1592-1670) distinguished three degrees of heat (*calor, fervor and ardor*) and cold (*frigus, algor* and one unnamed) with a reference norm (*tepor*), and the highest stage "ardor" meant an internal degradation into atoms". He stated [9] an almost modern definition of thermal analysis [1] "*..to observe clearly the effect of heat and cold, let us take a visible subject and let us observe the changes that occur while heated or cooled, so that the effect of heat and cold are apparent to our senses...*". About the same time *Mylius* proposed that the highest stage of fire is melting, and he emphasized that the value of effects is multiplied with increasing temperature. *Comenius* [9] also first observed non-equilibrium character of such thermal treatment and analysis "*...by a well burning fire we can melt ice to water and heat it quickly to very hot water, but there is no means of converting hot water to ice quickly enough even when exposed to very intense frost ..*" noting thus the phenomenon nowadays called undercooling. It, however, is difficult to trace and thus hard to say if it was possible (though likely) to disseminate the idea of caloric from Amsterdam (when *Comenius* mostly lived and also died) to Scotland where a century later a new substance, or better a matter of fire, likewise called *caloric* was thoroughly introduced by *Joseph Black* (1728-1799, and his student *Irvine*. It was assumed, e.g., that caloric creeps between the constituent parts of a substance causing its expansion and thus explaining the resistance of the particles to crush together under the ever presented force of gravity [3,4].

In accordance with *Bacon, Boyle* (1627 - 1691, a cofounder of the British Royal Society in 1662 and the journal *Philosophical Transactions* in 1665), who is known for introducing the theory of gases, tried to change the traditional alchemistic assumption of four basic elements, and he almost approached the current roots of these theories, namely that fire is equated with heat and the other three elements with the traditional macroscopic phases of gas, liquid and solid. Together with *Hooke, Locke* and *Newton* they stated that heat was caused by certain vibrations of inherent particles which idea, however, was rejected in favor of the still persisting erroneous assumption that there was a certain material basis to heat (fluid theory). A self-consistent continuum theory of matter can thus be taken into consideration and traced from ancient times, based on macroscopic experience only [2,3].

The phenomenon of combustion was known for many centuries but its widely accepted theory, put forward by *Becher* (1635-1682) and *Stahl* (1660-1734) [10], assumed that all inorganic substances consist of three 'earths': the *mercurial, vitreous* and *combustible*. The latter was termed by *Becher* "*terra pinquis*" and the essential part of *Stahl's* subsequent theory was that when substances were burnt, the *terra pinquis* (called '*phlogiston*') escaped, and readily combustible substances were supposed to contain large portion of it [11]. During the so called 'phlogistic' period, which may be taken to be the period of about one hundred and twenty years after the year 1660, no attention was paid at first to the relation between the weights of reactants and products, and an attempt was

made to explain the inherent puzzle that phlogiston could possess a negative weight. In 1773 *Priestley* isolated a gas that supported combustion which was named "fire air" commonly called "dephlogisticated air" which is nowadays known as oxygen. *Cavendish* (1731-1810) discovered "inflammable air" (hydrogen) and *Lavoisier* (1743-1794) determined the compound nature of water. They both contributed more than others toward the overthrow of the phlogistic theory whose absurdities now seem to be ridiculous, but it should be borne in mind that such an idea was at that time undoubtedly valuable and, moreover, is closely allied to the modern concept of energy.

Quantitative experiments with heat began after the invention of a reliable thermometer (closed capillary, liquid-in-glass) and *Richmann* (1744) established the calorimetric mixing formula that expressed how bodies at different temperatures are balanced at an intermediate temperature. Until the work of the Scot *Black* (1728 - 1799), the notions of *heat* and *temperature* were not distinguished, and together with *Magellan* (1722 - 1790) he introduced the concepts of *latent heat* and *heat capacity*, respectively, to explain how heat is absorbed without change in temperature and what heat is needed to increase a body's temperature by one unit. They, however, still maintained the material basis of heat although *Black* saw the great advantages of the progressive *Lavoisierian* theory of combustion and gradually released himself from the fetters of phlogistonism. However, a mathematical theory of the caloricum was presented as late as in 1824 year by *Carnot*, based on the efficiency of a reversible heat engine and assuming a conserved heat material.

The early basis of *thermodynamics* can be found in the first formulation of *conservation laws* (*Descartes* [12] assuming conservation as something general between and within the systems) which was probably first discovered by the little known Bohemian physician *Marek* (*Marcus Marci*, 1596-1667) [13]. The amount of motion was expressed by the product of mass and velocity. The *Bernoullis* (*Johann*) 1735 (as well as *Daniel* in his book *Hydrodynamica* 1738) stated the conservation law of *vital force* ('*vis viva*' used simultaneously with the Newton's force called '*vis mortua*') which had been introduced and explained by *Leibniz* 1686 in the case of the "vital" force conservation during the elastic collision of balls by its transformation into deformation. Obviously it failed, however, in all cases when heat appeared as a result of inherent friction [14].

Even in the modern recent thermodynamics there are many yet unclear aspects, besides an extensive work concerning Brownian motion and noise phenomena there is a stochastic interpretation of quantum mechanics [15]. Accordingly to this theory, the Schrödinger equation is nothing but the classical diffusion equation with complex diffusion constant $\sim j/2m$ [3]. This statement became later a corner-stone of so called *stochastic electrodynamics*, which provides an alternative to quantum mechanics and initiated further studies in applied quantum physics (self-organized oscillatory processes and the inner role of classical and quantum diffusion) [16,17].

Worth noting is the so called *Planck-Einstein* transformation formula for temperature, which reads $T = T_0 \sqrt{[1 - (v/c)^2]}$ [18], which means that the temperature of a body observed from the system moving with a relative velocity, v , is lower than the temperature in rest system. On the other hand, *Planck* assumed that the First and Second Law of thermodynamics keep their form in all inertial frames. In the year 1953, however, *Einstein* doubted the correctness of this formula and rather speculated about a modulus operandi using the inverse form (i.e., the temperature as observed in moving system is higher). This statement, which was later proved by *Ott* [18], thus reads as $T = T_0 / \sqrt{[1 - (v/c)^2]}$. In both these cases, information about the temperature is regarded to be mediated

by the coherent electromagnetic radiation. Interestingly, in the case, where temperature is considered to be essentially a local property and the thermometer reading is transferred to a moving system, e.g., by means of digital coding, the temperature, in the contrast to the both above formulae, must be seemingly considered as *relativistically invariant* as all other intensive properties of fields (pressure, etc.) are. Therefore, we need to look for an alternative relativistic transformation aimed towards the habitually adjusted meaning of certain physical constant, such as the traditional thermal constant viewed as a substitute, $k \cong k_0 \sqrt{[1 - (v/c)^2]}$, etc., [18].

3. Roots of classical thermodynamics – entropy

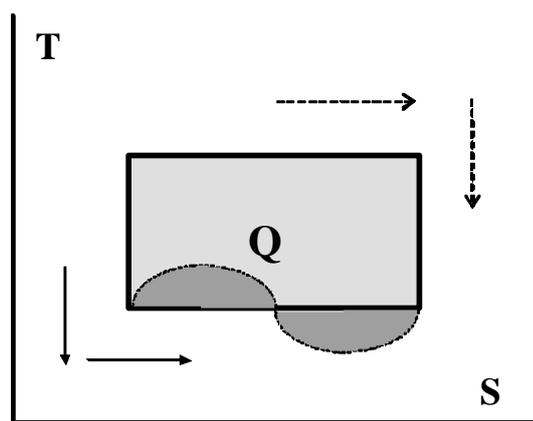
Towards the end of eighteenth century *Lavoisier, Helmholtz and Laplace* described both theories of heat equally suitable to comply with a theory of temperature measurements because it was only determined by the state of the system under study (introduction of the term '*calorimetr*'). Also the founder of *theory of heat engines*, *Sadi Carnot* [19,20] (1796-1832) first explained the motion of a piston in his thermal engine by transport of heat as a fluid (conservation of caloric) from a state of lower to higher "tension" and this idea was supported also by *Clapeyron* (1799 - 1864). *Rumford* in 1798 was first to evaluate the mechanical equivalent of heat, but this was not accepted until proved by *Mayer* (1814 - 1878) and by *Joule* (1818 - 1889 who also applied it to the transformation of electrical work) as well as by *Helmholtz* (1821-1894), better known for stating *that energy can neither be created nor destroyed*. Following a textbook by *Poncelot* (1826), *Rankine* introduced the term '*energy*' (1853, but this was not generally accepted for vital force = actual energy, which was later renamed as today's *kinetic energy* and its meaning transposed to all forces expressing the capability of a system to perform a mechanical motion and consequently producing a motion measured by the product of a force and trajectory: *potential energy* (*William Thomson* 1824-1907 who actually introduced the term *thermodynamics*). The term force remained reserved for Newtonian systems only if having sustained to be within a science of changes and developments valid until today.

A similar understanding was anticipated for the internal motion of particles (i.e., molecules and atoms) because heat was also a measure of transfer of motion from one system to another. Between the kinetic and potential energies of macroscopic bodies and those assumed at the level of a molecular motion within the bodies there is, however, an essential difference because they are qualitatively different forms of motion, differing in *the degree of self-organization*. In contrast to *mechanical motion*, treating bodies as uniformly moving particles (which affect the state of a collective system moving in the ordered direction as whole), the transfer of heat is seen as a change of *random motion* of inherent particles (regarding the initial and final states that differ in the degree of particles disorder). It was necessary to develop such a description for the practical need of transformation of heat into work as applied to machines in then arising spheres of manufacturing. *Boyle and Mariot* (1679) introduced the constancy of the product of pressure, P, and volume, V. This was later improved by accounting for a temperature, T, effect by *Amontons* (1702), *Charles, Dulong, Gay-Lussac and Regnault* (1847), in the form of so called state equation of gases: $P \times V \approx T$. Finally it was found that the same change of a system's energy can be achieved by various combinations of thermal and mechanical transfers yielding the definition of a state function called '*internal energy*' U, (*Clausius* 1851) depending exclusively thus on the state of the system regardless the way through which the final state was achieved [12].

Consequently the way for a practical utilization was opened by *Carnot* (1824) who proposed a *four-cycle engine* (see below Figure) based on two (non-identical) isothermal and adiabatic terms. For a unidirectional (ordered) motion of a piston there arose the validity of the notion that the change of internal energy ΔU equals $P \times \Delta V$ defining thus the *state variables P and V*. Similarly for multi-directional (disordered) heat motion (flow) we can analogously write $\Delta U = T \times \Delta S$ which then necessarily leads to the definition of a new extensive variable called *entropy, S, to complete the pair with the already known intensive temperature, T*. Consequently it has followed that any such a thermal engine can work only between two heat reservoirs (having definite input and output at the different temperatures T_1 and T_2) providing the 'efficiency' never exceeding $\xi = (T_2 - T_1)/T_2$ (while the entropy in such a reversible process is conserved). However, a new target has been focused toward alternative thermodynamics based on the historical caloric in the meaning of entropy [1-3, 14,15,22]. In the framework of the caloric theory [14] the elementary derivation of the efficiency of *real* heat engines reads $\eta_K = 1 - \sqrt[3]{(T_2/T_1)}$ showing that its formulae is a direct consequence of the linearity of *Fourier's law* of heat transfer [22].

If there is an alteration in the system forcing it to go away from equilibrium than such a change can occur only at the expense of the displacement of another coupled system in the opposite direction towards equilibrium. If such a system proceeds in a given direction while opposed continuously by a force field tending to reverse it, the system can produce useful work done on the expense of disordering entropy. It is covered by the second law of thermodynamics, which it is frequently expressed in terms of the Gibbs' energy using equation, $\Delta G = \Delta H - T \Delta S$, where ΔG has the form of above mentioned Gibbs (free) energy change representing a maximum work so far attainable and H is the enthalpy change (i.e., the change in system heat content, Q, at constant pressure as a result of energy absorbed and/or evolved). Although the changes can be measured, the entropy itself appears as an abstract mathematical quantity whose reality is difficult directly measure, likewise visualize because entropy is somehow outside the range of our common sense and experience. Entropy should be understood, however, as a function of internal make up (structure) of the system, its organization and disorganization [1-3], rather than merely a phenomenological function of the system heat content and temperature (Q/T).

Carnot textbook thermodynamic cycle [1-4] on the classically assumed temperature, T,



versus entropy, S. Solid arrows show the power cycle while the dashed arrows show the opposite heat pump (refrigeration cycle). Similarly assumed business cycle (replacing conditions of the minimum Gibbs energy by the maximum economic prosperity [26], can be anticipated by using a non-conventional representation of T (= Tolerance) as the mean property of a society. Imagining that products are manufactured in a cheap (lower) market and then sold in a more affluent market (at a higher T).The shaded area represents useful work (either energy (heat= Q) or simply profit

(money=Q). Become familiar with the dotted line illustrating a non-equilibrium processing due to the delays caused by, e.g., thermal conductivity (Cruzon-Ahlborn diagram) similar to the s-shaped background of a DTA (Differential thermal analysis) peak [1-3] being the consequence of efficiency of real heat engines, $\eta_K = 1 - \sqrt[3]{(T_2/T_1)}$,

In conclusion we can remind an often cited humorous abbreviation of the energy consequences of the three laws of thermodynamics saying what cannot be done:

"In the heat-to-work conversion game the first law says that we cannot win, in best we can reach an equal result, the second one says that an equal result can be achieved at absolute zero only and the third law says that the absolute zero can never be attained"

4. Logarithmic measure and statistical approach

The logarithm (as well as the exponential function) has become one of the most frequent and important mathematical operate [2,3]. Its history dates back to the early demand for a reliable computation (navigation, astronomy, trade) which led to the discovery of a logarithmic function (*Kepler* and his reckoner *Burgi* in Prague 1603-1612) upon a comparison of arithmetic and geometrical progressions. It was later improved by *Napier* (1614) and *Briggs* (1628) until its functional approval by and *Mercator* (1628) and *Jacob Bernoulli* (1745, studying the logarithmic spiral, followed by *Huygens*). In order to make logarithms easier *Napier* had already devised rectangular rods inscribed with numbers, which became known as "*Napier's Bones*". By 1620 *Gunter* had devised another scale plotting logarithms on a line. Using two of these inscribed on a rule, multiplication and division could be done by simple adding and subtracting lengths using a pair of dividers. Shortly afterwards *Oughtred* placed the two scales side by side so that one could slide the other one relatively each other making thus the first *slide rule*, which has become a widely applied standard *hand-held* device, which was extremely useful logistic gadget keeping the brainpower involved (preceding manual exploit invented by the era of computers).

As a matter of interest in 1848 *Thompson-Kelvin* suggested a logarithmic temperature scale "Th" based on the formula of the Carnot cycle efficiency, $\xi = \Delta T/T = \text{const}_1 \Delta \text{Th}$. After integration for $\xi = \text{const}_1 d\text{Th} = dT/T$ one can obtain $\text{Th} = \text{const}_1 \log T + \text{const}_2$ where both constants are determinable by means of the conventional fixed points, e.g., freezing and boiling points of water, having thus the Th unit equal to 1. Although complicating the description of the mechanical energy of a molecule, it, however, would solve the difficult authentication of the validity of third law of thermodynamic because $T = 0$ would be replaced by $\text{Th} = \infty$, a more realistic approach toward inaccessible zero.

On the other hand, logarithmic functions played a significant role in describing the natural increments. The most important milestone was the comparison of a phenomenological definition of entropy, S, as introduced by *Clausius* with a statistically defined analogous quantity by *Boltzmann* (1879) defined as a logarithm of the number of microstates (W) corresponding to a given macro state. It enabled a generalized view to thermodynamics and reaction kinetics revealing purpose of logarithmization, in which we have achieved an important procedure enabling the combination of two subsystems into the total one ensuing summation of two partial disorders ($S' + S''$) while the final number of microstates is the product of entering microstates of the respective subsystems (W's).

Another important discovery was the physiological law by *Weber* (1846) and *Fechner* (1860), which stated that a logarithmic function describes in general the responses of living creatures to external excitations. By a thoroughgoing analysis of conflicts it was proved that the measure of a psychological category called *conviction* have got to be the logarithm of the number of *reasons* as also introduced by a less well known Czech priest *Šimerka* (1882) [23]. Correspondingly, investigation of the transmission of telegraph signals led to the theory of information defined as a logarithm of the number of possible messages, *Hartley* (1928) and *Shannon* (1948). A unifying mathematical description due to *Markoff* (1907), *Chinchin* (1953) and *Kolmogoroff* (1947) showed that all these

processes observed and connected with information, entropy and chaos had a common *statistical nature*. It evoked an idea that all the natural processes taking place not only within thermodynamic structures but also in nature biology, chemistry, psychology and information have a deeper connection than was ever thought before.

As a matter of interest, the microscopic understanding of entropy ($S \approx \log W_p$, where W_p is the number of possible particles' ordering) can be presented in a certain correlation with the Weber-Fechner law for logarithmic responses of organisms, i.e., *feelings* (p) versus *stimulus* (i) in the form of $\Delta p = (p_1 - p_2) = \log (i_1/i_2)$. Such a global logarithmic relation (assuming, e.g., generalized information content [2,3,24] where $I \approx -k \log W_C$ where W_C is the number of possible message coding) has thus a common feature differing only in the *value of the multiplying constant*, k , and its physical meaning (i.e., units). In statistical physics, k is equal to the classical *Boltzmann constant* ($K=1.38 \times 10^{-23}$ Joule/Kelvin), while for the case of information, k can be expressed as the ratio $1/\log 2$ called '*bites*' or simply made equal to a less convenient unit called '*nats*'. Consequently the above mentioned thermodynamic efficiency of a thermodynamic engine, most useful in the advancement of human race, can be transformed into *information gain*, I_{gain} , based on the actual and maximum efficiency, $I_{\text{gain}} = \log (1 - \xi_{\text{act}} / \xi_{\text{max}})$ which one can ever achieve and can be enumerated to the conversion factor for one [Joule/Kelvin] unit to equal 10^{23} bits. .

5. Statistical thermodynamics and information

As shown, the above mentioned entropy can be analyzed not only in classical terms of heat content of a system within traditional domain of thermodynamics but also in terms of the system *probability* (statistical physics, again applied to thermodynamics) and/or toward the *organization structure* ('information content'). Recalling the third law of thermodynamics (*Nernst* 1864-1941) we know that when temperature is approaching the value of absolute zero ($K = 0$), entropy also diminishes ($S = 0$). However, it was experimentally shown that for certain inorganic molecules that there can exist exemption for a particular modification, such as that for N_2O , which can have either $S=0$ or $S=5.76$ [J/K] at $T=0$. Therefore we cannot completely exclude a concept of introducing more complexity into the zero temperature state of a perfect crystal, thus violating its traditional understanding. It can be imagined as adding more information to an already perfectly ordered system by making it more *organized* [25]. Therefore we cannot reflect the idea of the existence of a kind of hypothetical conversion of energy to structural information and hence the possibility of accepting the concept of negative entropy (*negentropy*) [3,25,26].

We may disorganize a system by applying heat or alternatively by otherwise disordering its structure upon *withdrawing information of (its inner) ordering*. For example, when ice is heated, it first melts, then boils, and on further heating it provides steam and above the melting point of platinum (2000 K) it becomes a plasma of ions and electrons. At an even higher energy level, the integrity of the atoms themselves becomes compromised, and at a sufficiently high temperature, nuclear matter can be observed to "boil" again to yield a plasma of quarks and gluons (a '*quagma*'); with entropy eventually approaching almost an infinite value. On the other hand, if we cool ice down to the temperature of absolute zero where entropy become zero (reaching an ideally ordered crystal with no thermal vibrations), its energy apparently cannot be decreased by further withdrawal of heat. There, however, remains information about its (perfect) structure, its *occupation of space*, and there is no theoretical reason why one may not further decrease entropy by the "*addition of information*". It looks impossible, but we can equally well imagine a force field, which would "*freeze*" the constituents to total immobility at higher temperatures, too, as we know it from the subject of constrained glasses. In fact, we can actually identify

such a phenomenon as we can approximate an imagined force field holding atoms in a relatively immobile state at elevated temperatures, recalling certain organic molecules in which the resonating "pi" clouds of electrons act as an inter-atomic force stabilizing the positions of atoms. The best examples, however, are met in all biological systems that, for example, absorb heat not to provide energy but to maintain a stable temperature so as to minimize externally induced entropy changes. Whether looking at the DNA molecules and related genetic or metabolic systems, cellular organization, the evolution of organisms, or ecosystems, the process is the same: there is an entropy modification by inserting information as the simple systems become more complex, more differentiated, integrated, both within the internal organization and with the environment outside the system, evolving itself to become *thermodynamically increasingly improbable*.

Let us continue to analyze the meaning of entropy by beginning with Boltzmann's investigations, later modified by *Schroedinger* (1944) [26], who suggested that a living organism is "fed upon a negative entropy", arguing if the W is a measure of disorder, D , its reciprocal $1/D$ can be considered a direct *measure of order* (Or). According to *Stonier* (1990) [25] organization or structure is a reflection of order. Organization and information, I , can be assumed to be closely interwoven although information is both a more general and abstract quantity bearing a conceptual necessity to be freely altered from one form to another (the structure of a written text can be different due to various alphabets but the information contained remains the same). Upon a first approximation assuming a linear dependence, d , than $I = d \text{ Or}$ or $D = 1/\text{Or} = d/I$. By a rearrangement when $S = k \log (d/I)$ we can define the fundamental *relationship between information and entropy* as follows: $I = d \exp (-S/k)$. The consequence of such a fundamental equation and the related plots is the fact that the inherent constant, d , represents the information constant of the system at zero entropy, recalling a perfect crystal of ice at 0 K, $d = I_0$, which is not so hypothetical, assuming that I_0 is a constant for all values of I and S within the system, but it may not be constant across systems. This becomes intuitively apparent when one compares such a single crystal of ice with that of DNA. Surely at any comparable temperature below melting or dissociation, including 0 K, the DNA will definitely contain more information than ice. Returning to the fundamental equation rewritten as $S = k \log (I/I_0)$, which emphasize a quantitative expression of order/disorder, the ratio between the information content of the system when its entropy is zero, and the actual information content of the system at any given entropy value may be restated as a generalized probability function to correspond to Boltzmann's original W (originally derived, however, for gases in which I would never exceed I_0 and therefore S would have never become negative).

Let us calculate the change of entropy between a perfect crystal of ice at 0 K ($S=0$), and its vapor state (S_{vap}) at the boiling point (373 K) which is equal to about $200 \text{ [J K}^{-1} \text{ mol}^{-1}]$ of H_2O . Using the relationship between information and entropy and the Boltzmann's constant ($K=1.38 \times 10^{-23} \text{ [J/K]}$) we obtain $I = I_0 \exp (-1.45 \times 10^{25})$ or in the binary base $I = I_0 2^{-(2.1 \times 10^{25})}$. Note that the increase in entropy is shown by negative sign in the exponent indicating a loss of information. Because the exponent is to the base 2, assume that this exponent may be stated as a bit and then, on contrary, the information needed to organize a mole of water steam into a perfect crystal of ice would require an input of $\sim 10^{25}$ bits or on average of about 35 bits per single molecule. It covers, however, a complicated process of trapping gaseous molecules existing in a "cloud" state by means of a complex arrangement of electric and magnetic fields. The randomly moving molecules become fixed by the force fields into a regular array. This is a general characteristic for crystalline state formation in general and there is a spectrum of crystalline states ranging from a powder upto a perfect crystal usually classified by its X-ray diffraction (XRD) pattern.

Moreover, a gas consisting of molecules contains also an information residue because the organization intrinsic to molecules affects their behavior as a gas, similar to that of ions in plasma.

6. Biology and information content

However, we are not always aware that any organization of a system drives it away from equilibrium into a less disordered state, which does require the application of energy to a system which may result in one of the four possible changes [25]:

** The energy is merely absorbed as non-specific heat thereby increasing the entropy.*

**The input of energy causes the system itself to become more highly organized (for example, when a phonon is absorbed, an electron is shifted to an outer shell, causing the atom to achieve a more improbable thermodynamic state)*

**The system performs physical (mechanical, electrical) work mostly on the basis of human innovative ideas*

**The system performs information work by creating an organized (organic) living cell.*

The growth of organic nuclei is metabolic and interstitial and far more complex. For example, the DNA molecule produced, from a string of simpler molecules of nucleotides, aminoacids whose sequences represent a series of messages, may be isolated in a test tube as a crystal containing all the necessary information for reproducing a virus or a baby. Here we can envisage that such a structure, thermodynamically as improbable as a perfect crystal at absolute zero, can be created to exist at room temperature in the form of a perfectly organized organic crystal. Restricting our protein to be composed of the 21 essential aminoacids only, we arrive at 21^{200} possible primary structures being equivalent in binary terms to approximately 878 bits per molecule. (In contrast if language consisted of only ten-letters words, the total vocabulary available would amount to 26^{10} requiring a mere 47 bits per word). The entropy change can also be measured for denaturation of a molecule of enzyme from biologically active to inactive states, which involves about 900 [J/K]. The exponent of the information ratio can be interpreted again to represent an information change of 155 bits per molecule. If these information assumptions prove to be correct, that the bits per molecule lost when a perfect ice crystal is vaporized =35 or when a trypsin molecule inactivated =155, then one may calculate that an entropy change of approximately 6 [J/K] is required to bring about the required loss, an average of one bit per molecule, so that we can assume that a single [J/K] = 10^{23} bits.

The information which is processed by a human cell interacting with a strand of DNA is the organizational pattern of the carrier of information independent of human minds. Information existed for billion years prior to the advent of the human species, and for million years that information has been processed. DNA itself would be useless unless the information is semantically processed by a living cell. If information has an independent pattern meaning (reality), it may not involve any interpretation in relation to the inherent text (i.e., *semantics*). Information can thus be considered to be somehow distinct from the system which interprets it (yet assuming a dichotomy between the information intrinsically contained in a system and the information, which may be conveyed by the system to some acceptor). Thus *information may even organize information*, which is a process occurring in our brains, or may take place in the process of self-organization in nature and likely in advanced computers in some (near/distant) future.

In regard to paternal interpretation we can venture to say that information appears to be like energy [25]; both exist independently of our existence and both do not need to be

perceived to exist or to be understood. Energy is defined as the capacity to perform work and it is the nature of energy supplied or withdrawn which determines the nature of the changes occurring in the system acted upon. *Information is defined as the capacity to organize a system or maintain it in an organized state.* Similarly to the existence of different forms of energy (mechanical, chemical, electrical, heat, light) there exist different forms of information. Energy is capable of being transferred from system to another likewise information may be transformed from one form to another. The information contained by a system is a function of the linkage binding simpler into more complex units. Thus all organized structures contain information, and on the contrary no organized structure can exist without containing some form of information. Information is an implicit component of virtually every single equation and constants governing the laws of physics. To measure distance and time properly, an organized frame of references must be available and thus the measurements of space and time establish information about the distribution and organization of matter and energy. An organized system occupies space and time, therefore, the information content of a system is also proportional to the space it occupies: "*the universe appears to be organized into a hierarchy of information levels*" as proposed by Stonier in 1994 [26,27].

7. Thermodynamic laws, irreversibility and systems' behavior

The recent impact of computers has changed our perception of information as something purely static because inside computer information appears to have a dynamics of its own. Traditional physics learned in this century to accept the surprising idea that energy may be converted into matter. It brought an important consequence into nuclear physics with the possibility of gaining new forms of energy. This relativistic theory, however, left a problem how to explain motion solely in terms of matter. This new knowledge certainly has not affected our experience of how to obtain work: one always needs to apply energy. However, it gradually become evident that for obtaining useful work, one needs to apply not only energy but also information, and the applied energy must *either contain information itself, or act on some organized subject* and/or device (thermodynamic engine/machine as energy 'metamorphoser'), which then takes the action of a basically unchanging edifice called '*energy transducer*', which is commonly developed and invented through the skill and experience of mankind generations and thus necessarily containing information. Information-less heat can thus be transformed to the other form of (information containing) energy. Beside thermodynamics there arose and is growing a new category casually called *information physics*.

As shown the above mentioned systematic can be analyzed not only in classical terms of heat content and heat transfers treated within traditional thermodynamics but also in terms of *organization structure* (information content). Similarly to heat engines (understandable as information transducers) we can analyze the way how material properties are monitored during an experimental investigation. For example in a widely used thermo analytical (TA) experiment, measuring the temperature difference between the sampled material and an inert standard (DTA), we can compare various instrumentation means (i.e. similarly to various organizations available for information transducers). Although temperature is always an unavoidable (basic) parameter we can see that there is not too many alternatives for its controlling, i.e., isothermal ($dT/dt = 0$), nonisothermal ($dT/dt = \text{constant}$) and/or superimposed various oscillation modes (eventually to be added with sharp temperature changes due to quenching or explosions). It is because we can only improve TA intelligent instrumentality employing temperature (DTA) and/or heat (DSC) monitoring system but we cannot change the information content of the entirely applied *reagent*, i.e., heat (because it equals zero). On the other hand, we can mention another well-known

technique traditionally used to classify structures (XRD) where, measuring directional distribution of x-rays as diffracted by matter, one obtains not only information on the level of molecular structure but also on the level of superstructures (the supramolecularity as expressed by the arrangement of molecules in a crystal and the assembly of crystals in polycrystalline bulk) including special aspects of orientations, size and defects of individual crystalline blocks. In addition we can simultaneously play with temperature (using a low or high temperature chamber) not mentioning the know-how state of the XRD instrumentation itself. Although the temperature, as the above emphasized widespread and obligatory parameter, has universal applicability in all physical/chemical measurements, it is generally seen too vague to gather interested scientists (such as those involved in thermal analysis) in a more wider membership while a more specialized XRD can count their active members in higher orders showing different stages of information capabilities as accepted within societal culture, too.

In the above mentioned classical thermodynamics [1-4,28], irreversibility, although an important feature, is always associated with energy losses and wastes due to flows, hysteresis, etc., (cf. previous figure). *Prigogine* (1971) [30] introduced a fundamental change of this view in his theory of *dissipative structures* by showing its applicability in living systems operating far from equilibrium. The characteristics of a dissipative structure cannot be merely derived from the properties of its parts being a consequence of self-organization. The system's flow processes are interwoven through multiple feedback loops, and the corresponding mathematical equations are nonlinear. In the theory of *chaos* [29,30], the linear equations of classical thermodynamics can also be analyzed in terms of point attractors and whatever the initial conditions are, the system will be driven (attracted) towards a stationary state of a minimum entropy production to be as close to an equilibrium state as possible. Such a system is completely predictable by the above mentioned thermodynamic laws which are valid even for the conditions of steady states close to equilibrium, not only for constant T ($dT/dt = 0$) but also for its steady increase and/or decrease ($dT/dt = \text{constant}$, [2,3]). Outside the linear region (arbitrary dT/dt) the situation dramatically changes because the arising nonlinear equations have often more than one solution. This means that a new situation may merge at any moment, which mathematically means, that the system encounters *bifurcation points* [31] at which it may branch off into an entirely new states which are often dependent on the previous history. It provides a key characteristics for a biological system [32,33] being thus sensitive to small changes in the environment, the relevance of previous development, existence of critical points during its progression and last but not least unpredictability of the future.

Going further, there is another restriction for obtaining an useful technical work provided by man regarding the critical flux density of energy as presented by *Kapica* (1894 -1984). It limits the speed for an energy transfer between systems, which is very important for the construction of advanced heat engines, such as turbines etc., and their practical applications (e.g., the altitude at which the jet-airplane can fly). It certainly cannot be separated from other conditioning given by the level of technology (suitable material availability) and the possible impact to the *environment* (due to the finiteness of the Earth surface and its biosphere in which we are living). No less important became the description of the organization of our human race itself although not well developed yet and thus being made on a very simplified mathematical level.

Viewing perceptible activities of human population on the surface of earth from a greater distance, it would be possible to observe and compare the behavior of societies as systems of thermodynamic-like particles. Metals, a similarly viewed society of different species of atoms, can be described by *functions* derived long ago within thermodynamics so far well

determining the state of integration and/or segregation of resulting mixtures (alloys). In analogy to the vast variety of problems analyzed in the associated field of material science, similar rules can be established useful for the applications to various problems in segregated societies now governed, however, not by mathematically well defined functions but by ‘*human feelings*’ (sociology) and, however, not convenient to consider as yet. For example, it may be the integration of foreign workers in different states or integration of women in leading positions of politics, business or science. It may help to give solutions to long-lasting conflicts in binary societies like former Northern Ireland or Africa colonies, nonexistent USSR or the Yugoslavia, etc. It may be extended to develop transitional terms of traditional thermodynamics in to sociology, economy or even to some military thoughts [34]. The societies would exhibit different states depending to the degree of their development and organization and can show characteristic quantities, which may appear to have a certain similarity to those features already known in thermodynamics.

Therefore, let us move to the matching area of our interest which is closely related to the established field of *phase diagrams* [2,35] as well as to problems associated with energy absorption and liberation during the formation of mixtures (*solutions*). Mixing (mix) pure components of A (x %) and B ((1-x)%) is accompanied by a change of the Gibbs (free) energy, $\Delta G_{\text{mix}} = \Delta H_{\text{mix}}^{\text{ex}} - T\Delta S_{\text{mix}}^{\text{id}}$ being composed of two terms expressing its non-ideal (ex - excess) and ideal (id) contributions. Then, because $\Delta H_{\text{mix}}^{\text{id}} = 0$, we can traditionally write, $\Delta G_{\text{mix}}^{\text{id}} = -T\Delta S_{\text{mix}} = RT(x \ln x + (1-x) \ln(1-x))$. Assuming a so-called *regular solution* we have $\Delta H_{\text{mix}}^{\text{ex}} = x(1-x)\omega$. Whereas the *mole fraction*, x (concentration), can be directly measured, certain assumptions must be made regarding the *interaction parameter*, ω , which must evidently be zero for the mixture exhibiting ideal behavior because the components A and B behave equally.

Such a simple model of regular A-B mixtures is conveniently based on the logarithmic law of entropy with the addition of the non-ideality term, $\Delta H_{\text{mix}}^{\text{ex}}$, which is usually dealt with in terms of *cohesive energy*, E, providing that $\omega = (E_{AB} + E_{BA} - E_{AA} - E_{BB})$ which, in addition, expresses the *interactions* between the inherent pairs of components A and B. Therefore the entire meaning of the functions describing ΔS and ω depend only on the particular system under observation. For example an A-B alloy will be stable, if G (depending on the alloy composition x) is at its maximum, (resulting from either the positive or negative interaction energy between the A-A, A-B and B-B neighbors. For a strong A-B interaction ω will be positive; a strong A-A and/or B-B attraction will lead to a negative sign resulting in a limited alloy solubility, all well described in the textbooks of metallurgical thermodynamics [35]. (Certainly, we are not considering here further complications, what it could be called “the oil and water model”, where one group, the water, wants to get rid of the other group, the oil, while oil does not particularly want to be with its own kind and would stay mixed with water, as happens when an *emulsifier* is used to amend the interaction conditions).

8. Thermodynamics of societies

Surprisingly, there can be found statistically well compiled evidence (*Mimkes* 1993) [34] that such a regular solution model can also be satisfactorily applied to describe the intermarriage data of binary societies consisting of *partners* (= *components*), e.g., girls and boys in different *societies* (= *mixtures*) such as: immigrant foreigners and domestic citizens in the middle Europe, religious Catholics and non-Catholics inhabitants of British islands or African (black) and non-black citizens of the USA. The observed structural analogy is due to the general validity of mathematical laws of statistics of mixing which allows one to translate the well-established laws of thermodynamics into the social science

where the state of binary societies is determined by above mentioned feelings, i.e., the maximum of mutual *happiness and/or satisfaction*.

Case A, Order and sympathy, $\omega > 0$:

Crystal: In rock salt the attraction of the ion components A (sodium-Na) and B (chlorine-Cl) is much stronger than the attraction between the similar pairs of Na-Na and Cl-Cl. The maximum of the (negative) Gibbs energy is given for equal numbers of both components at $x=0.5$. It is well-known that due to the strong Na-Cl attraction the rock salt crystallize in a well ordered ABABAB... structure. This is associated with a negative enthalpy change accompanied with the heat liberation.

Society: A group of English-speaking tourist is visiting Japanese fair. They are more attracted to English-speaking sellers and domestic buyers to Japanese speaking sellers. Mutual happiness (including economic gain) will be low if there are few sellers or few buyers. The maximum of mutual satisfaction will be at equal numbers of all kinds of buyers and sellers. Each group gets a certain degree of excitement from the shopping process when buying and selling; emotion possibly bears a certain analogy with (or relation to) the above mentioned heat of mixing.

Ancient philosophy: water and wine, fire together with air

Case B, Disorder, integration, indifference and apathy , $\omega = 0$:

Alloys: There are no interactions between the neighbors at all. The Gibbs energy is negative as a result of entropy disordering effect, only. Such an ideal solution can be exemplified for silicon (Si) and germanium (Ge) in which the arrangement is random.

Societies: There can be found two kinds of solution:

Indifference: Equal partners are as attractive or repellent as different partners which leads to $(\omega = 0) E_{AB} + E_{BA} - E_{AA} - E_{BB} = 0$.

Apathy: The attraction of all partners is zero so that

$(\omega = 0) E_{AB} = E_{BA} = E_{AA} = E_{BB} = 0$.

In a downtown supermarket in Kyoto we will find a random distribution of men and women. For busy shoppers a short cashier line will be more important than male and/or female neighborhoods. It corresponds to indifference, and the society of shoppers is mixed by chance or is integrated.

Case C, Segregation and antipathy, $\omega < 0$:

Alloys: The mixture of gold (Au) and platinum (Pt) will segregate into two different phases. The (negative) Gibbs energy exhibits two maxima, one for Au with few Pt atoms, the other with Pt and few Au atoms. The degree of segregation is not generally a full 100% unless the equilibrium temperature is close to absolute zero. On the other hand there is a $T_{\max}(x)$ temperature needed to completely dissolve or integrate a given composition x of two components which can be derived upon the derivation dG/dx yielding $T_{\max}(x)$.

Societies: Mutual happiness of a society of e.g. black and white neighbors would again show two maxima: one maximum is obtained if the percentage of black neighbors is low and the white people feel at home, on the contrary, the other maximum is obtained at a high percentage of black neighbors, where blacks feel at home. To attain a maximum of happiness the town will segregate into areas mostly white with just few black renters and the areas mostly black and few white renters. In this way, both the black and white people would *feel* mostly at home. In general, the degree of neighborhood segregation will not be 100%. This can happen only if tolerance between different groups is close to zero; thus resulting in ghettos, e.g., the pure ethnic Moslem and/or Serbia homeland areas.

Ancient philosophy: water and oil, water against fire

The above grouping can further be discussed in more detail in terms of the extreme values of interactions, e.g., when ξ is much greater than zero, it yields a *hierarchy*, and for its highly negative values, it result in an aggressive society [26]. Upon simulating the classical (T-P) phase diagram of matter (solid-liquid-gas), we can define analogous states of societies, i.e., *hierarchy-democracy-anarchy* [26], cf. end table. Such thermodynamic-like considerations offer, certainly, a wider source of inspiration relating, for example, P to *political pressure* and V to *freedom*, the constancy of their multiplication showing (similar to Boyle's law) for the higher pressure, a lower freedom and vice versa. Associating P with the pressure of political relations, then temperature can also be characterized as a measure of extent of internal proceedings: the warmer the international proceedings the lower the number of possible collisions. Two neighboring states developing with different speed would mutually interact (quicker accelerating the slower and vice versa) and the warmer the international proceedings the slower would be the possible number of collisions.

9. Extended thermodynamic thoughts – economy

In like manner to assuming above that feelings govern the behavior of societies, we can broaden our considerations to economics where the achievements of best prosperity can be assumed to be similar to the minimum of free energy, see end Table [36]. For example, if two markets with different standards of living (with the *mean property designated as T*) are combined, the new standard of living would fall in between the former values. A good case can be shown by the unification of Germany where a uniform standard of living can only be obtained by stirring and mixing partners from the both sides. Let us recall the Carnot cycle in the previous figure. Manufacturing a product like cars, furniture or other advanced goods from single input parts requires comparable labor (assumed as a change of entropy) in any country. The price of merchandise, however, depends on the quality of labor, tools and generally on the living and technology standards, T. This may be pictured in the same diagram, just replacing thermal power cycle by an assumed economy profit sequences. The useful work extracted from the heat Q may then represents money gained by producing in a cheap market and selling in a more affluent market at the difference ΔT (of unequal economies) and (dashed) a non-equilibrium delay caused by transfer of matter replaced by economic hindrance. It implies that the rich are becoming richer ($\xi >$) but, on the other hand, job creation or agriculture support may install equalization ($\xi <$).

It certainly does not include all inevitable complications when assuming boundary conditions. Property known in physics as viscosity can be renamed within international relations as *hesitation*, a function of the density of population, speed of the information progress and the distance of possible collision centers from the places of negotiations (past East-West Germany relations stirred via Moscow communistic administration or Middle East conflicts taking place on the Arab-Jews territories but negotiated as far away as in New York). Understanding the free roadway as the mean distance between two potential ignition of collisions, we can pass to the area of transport phenomena observing *inner friction* as hindrance to the streaming forward characteristic, e.g., for the migration of people from the East/South to West. We can imagine a technology transfer which depends not only on the properties of state boundary (surface energy standing for the transferred meaning of administration obstacles) but also on the driving force which is proportional to the difference of the technology levels (North and South Korea) bearing in mind that the slower brakes the quicker and vice versa. Like in chemistry, nucleation agents (ideas, etc.) can help formation of societal embryos capable of further spontaneous growth. Surfactants are often use to decrease the surface energy similarly to the methods of

implantation of production factories or easing of customs procedures (Well-developed western Europe against post-communistic eastern Europe). Human society often suffers disintegration, but the overall development can be seen in open loops (or spirals) which finally tend to unification upon increasing the *information treasure* of civilization. It is alike a technological process where the raw material first undergoes through disintegration followed by separation, flotation and other enrichments to upgrade the quality for an efficient stage of final production of new quality material.

Such examples of brief trips to the nature of sociology could give us certain thoughts for improving the art of both the *natural and humanistic sciences whose interconnections were natural until the past century* where the notion of heat had been analyzed to become the natural roots of thermodynamics. Researching the analogy of physical chemistry to sociological studies of human societies is a very attractive area particularly assuming the role of thermodynamic links which, however, can be functional until the relation between inherent particles, independent people, is overcome by the conscious actions of humans [36-42] because people are not so easily classified as are mere chemicals. Such a feedback between the human intimate micro-world to the societal macro-state can change the traditional form of thermodynamic functions which, nevertheless, are here considered only in a preparatory stage of feelings. Therefore this sociology-like contribution can be classified as a first and simplified approach to a problem that's more adequate solution will, hopefully, not take another century as was the development of the understanding of heat and the development of thermodynamics [1-3].

Table 1

<i>Symbols</i>	<i>Natural science</i>	<i>Social Science</i>	<i>Economy</i>	<i>Military</i>
A-B	gold-platinum silicon-germanium natrium-chlorine	black-white Catholic-Protestant male-female	sell-buy rich-poor Europe-USA	NATO-Russia North-South SEATO-China
x	concentration (%)	minority size (%)	demand/supply	relation of forces
<i>ordering</i>				
$\omega > 0$	compound	sympathy	trade links	military treaty
$\omega = 0$	ideal solution	indifference	free market	neutrality <
$\omega < 0$	segregation	antipathy	business/competition	military block
<i>functions</i>				
G	Gibbs energy	satisfaction/happiness	prosperity	security
T	temperature	tolerance to chaos	mean property	reconciliation
Q	heat	selfrealization/health	money	weapons
E_{AA}	cohesive E	tradition/heritage	profit/earnings	friendship
$E_{AB} > 0$	binding E	curiosity/love	investment	joint activity
$E_{AB} < 0$	repelling E	distrust/hate	cost	hostility
$E=0$	indifference	apathy	stagnation	neutrality
stages				
	<i>metallurgy</i>		<i>anthropology</i>	
	disordering/solubility		integration	
	solubility limit		segregation	
	phase diagram		intermarriage diagram	

← states and state diagrams ⇒		
<i>ancient philosophy</i>	<i>pressure vs temperature</i>	<i>political pressure vs living standard</i>
air	gases	anarchy
water	liquids	democracy
earth	solids	hierarchy

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20 Hotness Manifold, Phenomenological Temperature and Other Related Concepts of Thermal Physics

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20.1 Introduction

Although the operative methods of temperature measurement are well-known and described in detail in various practical instructions [1,2] and discussed in many textbooks [3-10], the systematic treatment of the central concept of thermal physics, the *temperature* itself, is paradoxically almost lacking in the current literature. The temperature, namely, is there at present defined mostly from the theoretical positions of statistical physics and not as a phenomenological quantity. Nevertheless, the predominant majority of practical measurements in physics, chemistry and technology or in thermal analysis and calorimetry particularly are performed by means of macroscopic devices (thermometers) yielding as a result the *phenomenological temperature*, and not by means of statistical analysis of properties of ensembles of particles and excitations. It is thus evident that prior to the identification of the temperature defined in the frame of statistical theory with the phenomenological temperature, the latter has to be satisfactorily defined first.

The purpose of this contribution is thus to re-examine a fundamental concept of thermal physics, *phenomenological temperature*, from the logical, epistemological and partially also from historical points of view. The mathematical structure of the precursor of temperature, *hotness manifold*, is, as far as we know, for the first time discussed here in terms of *elementary set theory*. In the exposition of the subject the emphasis is put on experiment, elucidation of allied concepts and on generalization of empiric data while the reader must confer with special references already given on mathematical proofs of some statements.

20.2 Early Thermal Measurements, Thermoscope

The first devices known as *thermoscopes* appeared during the later Renaissance in connection with the first edition of Latin translation of Hero's "*Pneumatica*" by F.

Commandino Urbinate (1575) [11]. The influence of this book dealing with various unexplained natural phenomena and curious contrivances worked by air, water or steam was so general that it is almost impossible to tell whether a particular device was directly derived from Hero's descriptions or whether it is an original invention. Therefore one can find in the literature a long series of "inventors of thermometer", e.g. Cardano, Galileo, Sanctorius, Besson, de la Porta, Drebbel, Fludd, Leurechon, Ens, Harsdoerfer, Kirchner etc. [12,13], but to decide about the priority of any one of them is a very difficult task. Quite early it was recognized that these devices, having various forms of fluid or air dilatometers, enabled the objectification of the subjective feelings of hot and cold. Almost simultaneously appeared an idea that the thermal states of bodies which were in common terms described by means of ordered series of terms cold, cool, tepid, warm, hot, could be characterized by the ordered series of thermoscope readings as well. The substitution of *thermoscope* for human *sensations* in experiments leads finally to the conviction that the thermal state of bodies or of environment can be characterized by thermoscope readings incomparably better than by means of sensation in itself. The thermoscope typically a glass tube provided with an arbitrary scale and bottom opened vessel filled with wine, the upper bulb of which contained a mixture of air with water and alcohol vapours, was thus promoted to the device apt to indicate with certain "absolute exactness" the thermal state of vicinal bodies. Such a (of course, very optimistic!) belief reflects also famous Fludd's quotation [14] "*Weather-glass (i.e. thermoscope) became a mighty weapon in the Herculean fight between Truth and Falsehood*". However, the principles behind the operation of thermoscope remain for a long time unclear and the conditions for its proper application were discovered only step-by-step by means of painful experimental work. Let us now summarize the fundamental concepts of thermometry in terms of modern language.

20.3 Introduction of Phenomenological Conjugate Variables and Thermal Equilibrium

The basic task of any mathematical theory of material systems is to establish general rules for the further treatment of *empirical constitutive relations* describing the state of a body in terms of suitably chosen parameters. We do not mean here the parameters specific for the description of thermal effects but just the parameters already introduced in other branches of physics and generally known as the *phenomenological variables* [15]. The existence of such variables, playing the roles of macroscopic conditions which are compatible with a huge number of parameters describing each microscopic component of the body, is clearly a matter of experience. Usually, there is an appreciable number of various phenomenological variables determining the state of the body but fixing a chosen one by external means, this number can ever be diminished by one. Continuing such a procedure,

the number of significant phenomenological variables can be finally reduced to two. It is a fact worth noticing that the two-parameter system is the simplest model of a real system because it enables one to construct a meaningful constitutive relation and, simultaneously, it is apt for straightforward generalization, e.g. by adding another pair of independent variables. In order to ensure easy perceptibility of mathematical description of two-parameter systems a special form of phenomenological variables was found to be desirable. It is a well known fact that the terms entering the energy balance equations in mechanics and electrodynamics have a canonical form which may be characterized by means of the following dimensional relation,

$$[\text{Energy}] = [X] \times [Y], \quad (20.1)$$

where square brackets mean the physical dimension of the quantities enclosed. As the energy is an extensive quantity, it is favourable to choose for the first phenomenological variable also an extensive quantity, say X . In such a case, however, the second parameter has to be inevitably an intensive quantity, Y [16]. Such a couple of quantities obeying relation (20.1) is then called a couple of *conjugate variables*. For example, extensive quantities are volume V , momentum G , electrical charge Q , mass M , and paired, conjugate, intensive quantities are pressure p , velocity v , electrical potential ϕ , and gravitational potential γ . The existence of the intensive and extensive “aspects” of heat which was already recognized by J. Black [17] is thus in this context the discovery of primary importance for the formalization of theory of heat and its compatibility with other branches of physics. His “intensity of heat” and “matter of heat” can be, namely, quite naturally assigned to a certain couple of conjugate variables, which may be tentatively called “temperature” and “heat”. Formal compatibility of these two quantities with the system of quantities already introduced in other branches of physics is thus only a matter of proper choice of suitable operative definitions and units.

The idea to treat a real system in terms of conjugate variables enables one to introduce some fundamental concepts of thermal physics in a quite systematic way and, somewhat astonishingly, without a priori reference to the thermal phenomena *per se*, particularly to the quantities of temperature and heat [18]. The important role plays here the so called *correlation test*. It is the procedure frequently used in the practical thermometry which enables one to check whether the thermometer is in proper thermal contact with the measured body. Simultaneously, it provides the basis for the following operational definition of diathermic and adiabatic partitions (walls), viz: Let us have two systems characterized by couples of conjugate variables (X, Y) and (X', Y') , respectively, and separated by a macroscopically firm material partition (wall) defining their common boundary. Such a partition is called *diathermic* if the changes of the variables (X, Y) induce the changes of the variables (X', Y') and vice versa, i.e. if the changes of both otherwise separated systems are correlated (“diathermic” originates from Greek $\delta\acute{\iota}\alpha$ = through, $\theta\epsilon\rho\mu\acute{\iota}\omicron\varsigma$ = warm). A concept complementary to that of diathermic partition is the *adiabatic*

partition (from Greek α - = negation, $\delta\acute{\iota}\alpha$ = through, $\beta\acute{\alpha}\lambda\upsilon\epsilon\iota\nu$ = to go) which prevents the thermal contact of neighbouring bodies, i.e. ensures their thermal insulation. Obviously this concept is a limiting one, depending to an appreciable extent on the accuracy of the correlation test. The adiabatic partition is, namely, any partition for which the experimental proof of its ability to realize the diathermic contact by the said test failed.

Using then the language of the two-parameter description, the general definition of the equilibrium state as known from other branches of physics can be extrapolated also to the region of thermal phenomena. Let us recall first what the equilibrium state means e.g. in mechanics. Standard formulation for the two-parameter system reads: Any state of a body in which the conjugate coordinates X and Y remain constant in time so long as the external conditions are unchanged is called *equilibrium state* [19]. Combining then this definition with that of the diathermic partition, we can immediately define the concept of thermal equilibrium, which already belongs to the scope of thermal physics, namely:

If two bodies being in diathermic contact are both in equilibrium state, they are in thermal equilibrium.

Let us then call *thermoscope* any two-parameter system in which one of the conjugate parameters, say Y , can be fixed, $Y = Y_0$. It is further assumed that thermoscope can be brought into a diathermic contact with other bodies and that it is sufficiently “small” in comparison with these bodies in order to not appreciably disturb their thermal equilibrium. The second conjugate real parameter X , which is called in this connection *thermoscopic variable*, is generally of quite a diverse physical nature and dimension. It may be length, volume, resistance, voltage, frequency and many others. In order to distinguish formally among various thermoscopic variables, differently constructed thermoscopes and physical conditions under which they operate, a small Latin index is used. Applying this convention, reading $X_k(P)$ of the k -th thermoscope which is in diathermic contact with a body under investigation defines the *thermoscopic state* P of the body. The corresponding set of the thermoscopic states which can be observed in this way is then marked as \mathbf{H}_k . Notice that the readings X_k are related to the thermoscope while the indicated thermoscopic state such as $P \in \mathbf{H}_k$, already relates to the body. It is a matter of fact that the phenomenological parameters were introduced into classical mechanics and electrodynamics as continuous quantities covering certain closed intervals of real axis. Therefore, according to our definitions, such a property is transferred also to the thermoscopic variables X_k . We will thus assume that the numerical values of quantity X_k also continuously cover a certain closed interval \mathbf{I}_k , operation range of the k -th thermoscope, which is a proper part of the set of real numbers, \mathbf{E}_1 . In usual symbols we can thus write: $X_k \in \mathbf{I}_k \subset \mathbf{E}_1$. If it is further for every couple $P, Q \in \mathbf{H}_k$, $P \neq Q$, $\Leftrightarrow X_k(P) \neq X_k(Q)$, the set \mathbf{H}_k can be ordered in accordance with the intrinsic order already existing in real interval $\mathbf{I}_k \subset \mathbf{E}_1$.

This provides basis for the construction of a primitive temperature scale. Indeed, unambiguous assignment of a certain value $X_k(P)$ to every state $P \in \mathbf{H}_k$ is nothing but realisation of a *local empirical temperature scale* in terms of thermoscopic variable X_k . It is, however, an important fact belonging rather to the scope of epistemology that although the empirical scales enable one to characterize the thermal states of bodies, for the revealing of the very nature of the physical quantity called temperature are almost useless and further development of more involved concepts is thus necessary.

There is another requirement ensuring the objectivity of the above conception. It is so called *Principle of indifference* [20] according to which different thermoscopes k, j operating in the common range of thermoscopic states should distinguish any two different states $P \neq Q, P, Q \in (\mathbf{H}_k \cap \mathbf{H}_j)$, regardless of their construction, thermometric substances, variables X and other physical conditions used. A procedure worked out by Dulong and Petit [21] is used in practical thermometry for the comparison of different empirical temperature scales. So called Dulong-Petit plot is a locus of readings X_k of one thermoscope versus readings X_j of another thermoscope both being in thermal contact with the same body (thermal bath). Evidently, in terms of such a plot the Principle of indifference may be formulated simply as follows: Two empirical temperature scales agree with the Principle of indifference just if their Dulong-Petit plot is monotonic. Interestingly, very similar method was used much earlier by savants of *Accademia del Cimento* who discovered in this way, just above the freezing point of water its anomaly, i.e. non-monotonic Dulong-Petit plot with respect to the other at that time known thermoscopes [14,22], which excludes water from being in this range a suitable thermometric substance.

20.4 Fixed Thermometric Points, Mach's Postulates

A serious obstacle for the development of non-peripatetic thermal physics was an appreciable irreproducibility of early thermoscopes used. There were attempts to improve the situation by making exact copies of a standard instrument and by sending them to the various laboratories where they were intended to serve as secondary standards [23]. This, theoretically correct approach had nevertheless lot of practical limitations. It required a really high reproducibility of glass-blowing and preparation of glass and thermometric substances. Consequently, standard "thermometers" were very expensive and the transport of such delicate instruments over the long distances was quite risky. Therefore an important qualitative step toward the scientific thermometry was done when the so called *fixed thermometric points* were discovered and came into general use.

The fixed point is called a body prepared by a definite prescription revealing by some observable qualitative property its physical state (e.g. boiling point

of helium, melting point of water, melting point of platinum – all at normal atmospheric pressure) and which being in thermal equilibrium with other bodies defines unambiguously their thermoscopic state.

Fixed points thus may serve as a mean for the realization of fiducial points on empirical temperature scales corresponding to the different thermoscopes. Decisive steps in this direction were made by Danish astronomer O. Rømer, and especially by his immediate follower, German instrument maker G. D. Fahrenheit who used large deal of Rømer's know-how [24]. He devoted an enormous care to the purification of thermometric substance, improvements of glass-blowing procedure and exact specification of conditions for realization of fixed points. As a result, Fahrenheit's thermometers were much admired throughout the scientific community for their accuracy and extraordinary reproducibility and became thus for a long time a thermometric standard.

As was recognized very early the fixed points are of crucial significance for sewing together local thermometric scales. In order to cover much larger range of thermoscopic states it is, namely, necessary to combine the thermoscopes of different construction and sometimes of different physical nature of thermoscopic variables. It is then obvious that just the existence of a common fixed point incident with two different local empirical scales ensures that these scales really overlap and that they can be sewn at this point together.

Importance of fixed points for thermometry is, however, not confined only to the calibration of thermoscopes but as was recognized not before the end of the 19th century their theoretical significance is much more general. Quite interestingly, it has been originally taken for a self-evident empirical fact that it is always possible to find, in an operation range of any thermoscope, a sufficient number of fixed points enabling calibration of a local empirical scale. The very fact that such a liberty of choice can only be a consequence of the existence of enormous (if not infinite) number of fixed points falling into any interval of thermoscopic states remained for a long time quite unnoticed. Similar fate, i.e., being effectively undiscovered, has also the fact that the fixed points can be always found out of any interval of thermoscopic states.

These and other experimentally observed properties of fixed points have been generalized by means of the method of incomplete induction, the reasoning according to which the conclusion related even to the infinite number of cases is drawn from the knowledge of a finite number of cases provided that they, without exception, imply the same conclusion. Such a type of generalization of experience resulting into certain verities or postulates is quite analogous to that made e.g. prior to the axiomatic construction of Euclidean geometry. As the propositions given below received their first explicit formulation in the hands of E. Mach [21], we suggest calling them tacitly *Mach's postulates* (M1 – M5).

First of all, as every fixed point defines unambiguously a certain thermoscopic state and because the set of thermoscopic states \mathbf{H}_k is ordered by means of relation (\prec, \succ) , the *set of fixed points* \mathbf{F} ($\mathbf{F} = \cup \mathbf{F}_k$, where \mathbf{F}_k are sets of fixed points related

to \mathbf{H}_k) can be also ordered just according to the same relation. Giving a physical meaning to such an idea, we can say that calibration of empirical scales by means of fixed points can be interpreted as an ordering of fixed points. This fact then enables one to postulate:

M1) The set of fixed points \mathbf{F} is ordered by means of binary relation (\prec, \succ) .

The generalizations of experience with experimental establishment of new fixed points and of making their inventory list lead then to the following three postulates¹:

M2) To every fixed point $P \in \mathbf{F}$ there exists at least one fixed point Q such that $Q \succ P$.

M3) To every fixed point $R \in \mathbf{F}$ there exists at least one fixed point S such that $S \prec R$.

M4) For every couple of fixed points $P \prec R$ there exists at least one interlaying point Q such that the relations $P \prec Q$ and $Q \prec R$ are simultaneously valid.

There is another remarkable empirical property of the set of thermoscopic states closely related to that of fixed points which can be formulated as follows:

M5) Let A and B be two different fixed points such that $A \prec B$. Then if the body changes its thermoscopic state from the state corresponding to a fixed point A to that represented by a fixed point B , it must inevitably pass through all the interlaying thermoscopic states P , for which $A \prec P \prec B$.

20.5 Hotness Manifold and Definition of Temperature

It is a matter of historical fact that formulation of Mach' postulates (1896, [21]) and establishment of Cantor's set theory (1895, [25]) were practically contemporaneous events. That is probably why the mathematical structure of hotness mani-

¹Speaking for a while in terms of Kelvin's temperature which will be specified later, the temperatures observed range from $\sim 10^{-10}$ K (Low Temperature Lab, Helsinki University of Technology) up to $\sim 10^9$ K (supernova explosion) without any traces that the ultimate limits were actually reached. Speculative upper limit provides only the so called Planck temperature $T_P = \sqrt{(\hbar c/G)} \times (c^2/k) \approx 1.417 \times 10^{32}$ K, hypothetically corresponding to the first instant of Big Bang and depending on the assumption that the constants c , G and k involved are really universal. Therefore the conjecture referred to as Mach's postulates M2 and M3, i.e. that the hotness manifold has no upper or lower bound, is obviously operating at least for all phenomena already known.

fold has not been fully appreciated and, as far as we know, has never been systematically analyzed from the point of view of the set theory. In terms of this theory (e.g. [26,27]) Mach's postulates may be interpreted in the following way.

Taking first into account the fact that the realizations of fixed points are real bodies, their number must be either finite or equivalent to the set of natural numbers, i.e. \mathbf{F} must be countable. In the 4th Mach's postulate one can easily recognize the definition of dense sets belonging to Cantor's theory; from this we can immediately conclude that \mathbf{F} is also dense. Postulates 2 and 3 then mean that the set \mathbf{F} has no upper or lower bound. Any ordered countable dense set is, however, called rational series or a set of rational numbers. We can thus summarize, the set of fixed points \mathbf{F} is equivalent to an unbounded set of rational numbers.

The mathematical structure of *hotness manifold* \mathbf{H} , which is a union of all sets of thermoscopic states \mathbf{H}_k , $\mathbf{H} = \cup \mathbf{H}_k$, is not as simple as the structure of \mathbf{F} . It is necessary first to make clear the operational method (i.e. a method related to the experimental procedures which can be really performed) enabling sewing-up the overlapping sets of thermal states and matching of corresponding empirical temperature scales. Let us assume that two sets of thermal states, \mathbf{H}_k , \mathbf{H}_{k+1} , overlap, i.e. that $\mathbf{H}_k \cap \mathbf{H}_{k+1} \neq \emptyset$. In order to realize this fact in experiment one has to find a fixed point $R \in \mathbf{F}$ belonging to both these sets, i.e. $R \in \mathbf{H}_k$, $R \in \mathbf{H}_{k+1}$. Theoretically the possibility of such an operation is ensured by 4th Mach's postulate M4. For the sake of definiteness and without loss of generality we can further construct the subsets $\mathbf{H}'_k \subset \mathbf{H}_k$, and $\mathbf{H}'_{k+1} \subset \mathbf{H}_{k+1}$ in such a way that $Q \prec R$ for every $Q \in \mathbf{H}'_k$ and $P \succ R$ for every $P \in \mathbf{H}'_{k+1}$. Evidently, the empirical temperature scale for thermal states from $\mathbf{H}_k \cup \mathbf{H}_{k+1} = \mathbf{H}'_k \cup \mathbf{H}'_{k+1}$ below R corresponds to the empirical scale in \mathbf{H}_k and above R to that in \mathbf{H}_{k+1} . Moreover, in order to assign the same value of empirical temperature to the common point R , it is necessary to make formal changes at least in one of the empirical scales. Applying the procedure just described and simultaneously looking for new fixed points and for new physical effects enabling the construction of new kinds of thermoscopes, we can build a chain of \mathbf{H}_k 's more and more extending the region of accessible thermal states. We are obliged to Professor Mach for belief that such a procedure is limited only by our skills. Taking now into account the fact that every \mathbf{H}_k is equivalent to a real interval $\mathbf{I}_k \subset \mathbf{E}_1$, it is obvious that \mathbf{H}_k is a continuous set. Furthermore, fixed points, such as R , are then nothing but rational cuts in sets \mathbf{H}_k and \mathbf{H}_{k+1} [27]. Analyzing these circumstances, we can conclude that the properties of the hotness manifold $\mathbf{H} = \cup \mathbf{H}_k$ discussed above can be put in the form of two axioms already well-known from the set theory, namely

Dedekind's axiom: If \mathbf{H}_1 and \mathbf{H}_2 are any two non-empty parts of \mathbf{H} , such that every element of \mathbf{H} belongs either to \mathbf{H}_1 or to \mathbf{H}_2 and every element of \mathbf{H}_1 precedes every element of \mathbf{H}_2 , then there is at least one element $R \in \mathbf{H}$ such that:

- i) any element that precedes R belongs to \mathbf{H}_1 ,
- ii) any element that follows R belongs to \mathbf{H}_2 .

Axiom of linearity: The hotness manifold \mathbf{H} contains countable subset $\mathbf{F} \subset \mathbf{H}$ in such a way that between any two points $P \prec Q \in \mathbf{H}$ there is a point $R \in \mathbf{F}$ such as $P \prec R$ and $Q \succ R$.

As the second axiom ensures that the requirements of 5th Mach's postulate are automatically satisfied, the couple of Dedekind's axiom and axiom of linearity may be regarded as a concise reformulation of Mach's postulates. The simultaneous validity of both these axioms, however, defines in set theory the class of sets which are equivalent to the set of real numbers \mathbf{E}_1 . The mathematical structure of hotness manifold may thus be summarized as follows:

Hotness manifold (a set of all accessible thermoscopic states) \mathbf{H} is a set topologically equivalent to the set of all real numbers (real axis) \mathbf{E}_1 . It contains a countable, dense and unbounded subset of all fixed points $\mathbf{F} \subset \mathbf{H}$, realizing the skeleton of \mathbf{H} .

As we have seen above, the construction of this manifold is based on well-defined operational methods specifying conditions and procedures necessary for determination or reestablishment of a particular thermoscopic state. Manifold \mathbf{H} is just the experimentally accessible entity enabling one to judge how hot or cold the bodies are. Therefore, it is this entity which is right to be regarded as an entity objectively existing in the Nature and representing the universal Platonic idea behind the usual concept of temperature, in philosophical jargon, the *temperature "an sich"*. Of course, as the set \mathbf{H} has no intrinsic *metric properties*, it yields directly no physical quantity [16,28]. Introduction of corresponding physical quantity, tacitly called temperature, thus requires special definition which obviously has to involve all the properties of hotness manifold.

As has been shown in previous paragraphs, the temperature and even the hotness manifold cannot be taken for primary concepts of thermal physics but are in fact the subjects of somewhat convoluted constructions. In the hierarchy of conceptual basis of thermal physics, however, the concept of temperature plays the role subordinate to that of hotness manifold \mathbf{H} , which is characterized just only by its topological properties. On the other hand, it is quite clear that hotness manifold alone is not sufficient for the development of quantitative theory of thermal effects. For such a purpose, namely, a regular physical quantity [16] preserving simultaneously all essentials of hotness manifold, is necessary. Keeping the sufficient generality, such requirements may be satisfied by the following definition:

Temperature is any continuous one-to-one order preserving mapping of hotness manifold on a simple connected subset of real numbers.

20.6 Kelvin's Temperature Scale

It is quite obvious that the definition of temperature given in the preceding paragraph offers an enormous liberty for the construction of temperature scale. It is thus necessary to rationally choose the limitations which will be decisive for intelligibility of the future theory of thermal effects. Traditionally the safest guide for the introduction of new concepts into science is the so called *anthropomorphic principle* respecting the commonly accepted patterns of thinking and involving also practical and cultural aspects. The special mapping of the hotness manifold on an ordered subset of real numbers defining the operating temperature scale T was thus chosen on the more-or-less historical and practical grounds, in other words, on the basis of fully arbitrary anthropomorphic criteria. One of such restrictions having in fact no physical reason but which significantly simplifies the mathematical operations with temperature concerns the class of *absolute temperature scales* defined as follows [29]:

Any temperature scale which is chosen in such a way that their functional values have the highest lower bound equal to zero (i.e. T is always positive) is called absolute temperature scale and the corresponding temperatures are called absolute temperatures².

Notice that the possible value $T = 0$ (equal to the highest lower bound) is already excluded by our definition of temperature because due to the absence of the lowest hotness level in the hotness manifold any continuous one-to-one order-preserving transformation on the set with lower bound = 0 has inevitably to map its improper point (e.g. $-\infty$) just on the point corresponding to absolute zero. *Nernst's law* of unattainability of absolute zero of temperature (the "Third Law of Thermodynamics") [30] is thus together with its consequences intrinsically involved in these definitions of temperature and absolute temperature and as such needs no additional, sometimes very curious, justifications or "proofs" [31].

It is a result of rather a complicated historical development that the present temperature scale (Kelvin's international temperature scale ITS [1]) is based on *two independent anthropomorphic idealizations*, namely, idealized substance, *ideal (perfect) gas* and idealized process, *Carnot's reversible cycle*. It is an important provable fact with large practical impact that both approaches define the identical scales which can thus be in particular cases used alternatively.

The first approach is based on the idealization of the most salient common features of the constitutive relations of real gases. The behaviour of majority of real gases is, namely, almost the same in cases where the gases have sufficiently low density. This fact was used for the definition of the perfect gas and later for the

²Notice that this definition of absolute temperature scale differs from that due to Lord Kelvin who related the adjective "absolute" rather to the independence of temperature scale of thermometric substance than to the existence of lower bound of temperature values.

construction of the *ideal (perfect) gas temperature scale* T . The equation controlling the behaviour of the ideal gas, which is a hypothetical substance or concept rather than a real thing, reads:

$$T = pV / nR, \quad (20.2)$$

where p and V are respectively the pressure and the volume of the ideal gas which may both alternatively play the role of thermoscopic variables. As the hypothetical thermoscope a conventional gas thermometer [2] filled with n moles, $n > 0$, of ideal gas is considered. The constant R on the right side, has then a form of product $R = k N$ where k and N are Boltzmann's and Avogadro's constants, respectively (in SI system of units $k = 1.38 \times 10^{-23}$ J/K, $N = 6.02 \times 10^{23}$ mol $^{-1}$). The scale defined by means of equation (20.2) has some other remarkable properties. For example, as both quantities p and V have a natural lower bound = 0 (this very fact was already recognized by Amontons [21] and formulated as the hypothesis of *l'extrême froid*), the temperature T has also this lower bound and thus automatically belongs to the class of absolute temperatures. Moreover constitutive relation (20.2) reveals remarkable symmetry with respect to quantities p and V . We can thus exploit anyone of these two quantities as a thermoscopic variable keeping the other one constant. Comparing these two cases it must be inevitably:

$$T_p = T_v = T, \quad (20.3)$$

where T_p and T_v are temperatures of a body (e.g. corresponding to temperature of a certain fixed point) determined by means of constant pressure and constant volume method, respectively. The exact realization of condition (20.3) in experiments with real gases and with prescribed high accuracy (typically of the order of 0.1%) is very difficult if not impossible. However, Berthelot [32] devised a simple graphical method based on plausible assumptions which enables one to extrapolate experimental data obtained on real gases at finite pressures to the case corresponding to the ideal gas and finally determine also the value of T satisfying conditions (20.3). From these facts it is thus apparent that the ideal gas temperature scale can be in principle realized in the range where the gaseous phase of real gases and, of course, also the gas thermometer itself, can exist.

20.7 Carnot's Theorem and Kelvin's Proposition

Reasonably chosen temperature function which maps the hotness manifold on a subset of real numbers E_1 should be, as was already mentioned, conformal with other terms entering the energy balance equation. In such a case temperature (intensive quantity T) and heat (extensive quantity ζ) will make up a couple of conjugate variables obeying dimensional equation (20.1), i.e.

$$[\text{Energy}] = [T] \times [\zeta]. \quad (20.4)$$

The principal possibility to write down the thermal energy term just in this form was confirmed by early experiments on the development of mechanical work by means of heat engines. In spite of the fact that these experiments were backed by a rather primitive technique (e.g. temperatures were measured by roughly calibrated mercury thermometers and heat by the weight of burned coal), being thus of doubtful accuracy, their analysis enabled S. Carnot to introduce some new theoretical concepts and to draw out definite conclusions. In the present context among new Carnot's concepts the most important roles play two idealizations of real thermal process taking place in the heat engine, namely, the *cyclic process* and *reversible process*. By cyclic process (*cycle*) is meant any thermal process in which initial and final physical state of the heat engine are the same. The reversible process is then a thermal process in which the heat engine works without wastes of heat. For the heat engines utilizing the cyclic reversible process (so called *ideal heat engines*) Carnot was able to formulate a theorem which in its archaic version reads³ [33]

“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 caloric is done.” (S. Carnot, 1824)

Of course, from the modern point of view Carnot's theorem is rather a desideratum than piece of scientific knowledge. (Remarkable is also a somewhat inconsequent use of heat and caloric as synonyms.) On the other hand, it has a form of the energy balance postulate we are searching for. Indeed, if we, namely, transform the theorem into mathematical symbols we can write it in terms of finite differences [34]

$$\Delta L = \zeta F'(t) \Delta t, \quad (20.5)$$

where ζ means the quantity of heat regardless of the method of its measurement, ΔL is the motive power (i.e. useful work done by heat engine) and Δt is the difference between empirical temperatures of heater and cooler. The unknown function $F'(t)$ called *Carnot's function* should be for a concrete empirical scale determined by experiment [36, 37]. As the gained work ΔL has a dimension of energy and as this energy must be for reversible cycle equal per definition to the thermal energy of heat ζ supplied to the ideal heat engine, we can conclude that the terms suitable

³ It should be stressed here that there exist in the literature a lot of various arbitrarily changed forms of “Carnot's theorem” or “principle” which are not equivalent one to each other and which essentially differ in their very content from the original formulation. As was thus quite correctly pointed out by H. L. Callendar [35] distinguished researcher into the vapour turbines and president of Royal Society, the original oldest Carnot's formulation of his principle is at the same time the best one.

for insertion into the energy balance equation have to have a form of products $\zeta\Delta t$ properly modified by Carnot's function.

A revolutionary step toward the definition of the temperature scale independent of particular type of thermometer and thermometric substance was made in 1848 by Lord Kelvin [38]. He proposed to treat Carnot's theorem not as a heuristic statement deduced from experiments of rather a limited accuracy but as a fundamental postulate of absolute validity. He further pointed out that the very purpose of Carnot's function is to modify or correct the difference of temperatures measured in a particular empirical temperature scale in such a way that it could serve as an exact proportionality factor between work, ΔL , and heat, ζ . As this factor has to be according to Carnot's postulate the same for all substances and reversible cycles, Kelvin, inverting the logics of reasoning, suggested to define a universal (in his terminology "absolute", see footnote²) temperature scale just by *prescribing* a proper analytical form of Carnot's function. For example, giving to Carnot's function the simplest permissible analytical form, namely, $F(*T) = 1$ (so called "*caloric gauge*"), we are in fact defining a new temperature scale $*T$ in terms of which equation (20.5) reads:

$$\Delta L = \zeta (*T_2 - *T_1). \quad (20.6)$$

It is immediately seen that using such a definition of the temperature scale the energy terms have the desired form of a product of two conjugate variables ζ and $*T$. Interestingly enough, equation (20.6) is simultaneously a fundamental relation of the caloric theory of heat (cf. [39, 34]). Accordingly, from the phenomenological point of view the heat is a kind of substance or fluid, caloric (*calorique*, *Wärmestoff*, *менлоподъ*, *teplík*), which being dissolved in all bodies is responsible for their thermal state. It is treated as an indestructible fluid (recall that the only method of how to get rid of heat is to convey it away), which is created in every irreversible processes such as rubbing, chemical reactions, burning, absorption of radiation and eating during which "something" simultaneously disappears for ever. The properties of so defined quantity are thus very near to the concept of heat in a common sense [40]. Taking further into account the structure of equation (20.6), we can also conclude that the development of moving force in an ideal heat engine is not connected with some actual consumption of heat as is claimed in thermodynamics but rather with its transfer from hotter body to a colder one (water-mill analogy [33]). At the same time, equation (20.6) defines an entropy-like unit of heat fully compatible with the SI system which may be, according to *Callendar's* suggestion, appropriately called "Carnot" (Abbreviation "Ct") [35]. 1 Ct is then that quantity of heat which is in a reversible process capable of producing 1 J of work per 1 K temperature fall.

Nevertheless, in the present context another aspect of equation (20.6) is far more important. Accordingly, namely, the temperature difference $*T_2 - *T_1$ between two bodies used e.g. as "heater" and "cooler" of an ideal heat engine, is identical with the ratio $\Delta L/\zeta$ where both of these quantities are measurable in prin-

ciple; ΔL by means of standard methods well-known from mechanics and ζ e.g. by the amount of fuel consumed by heating the heater or, if the cooler is kept at freezing point of water, by amount of ice melted during the cycle. It is quite obvious that such a technique of temperature measurement, although possible in principle, is rather a curiosity which would be very difficult to realize with sufficiently high accuracy in practice. The idea of this method is, however, of primary importance for theory. Obviously, due to Carnot's postulate, equation (20.6) has to be valid for any ideal heat engine regardless of its construction and working substance used. Analyzing thus one particular representative case of the ideal heat engine, general conclusions can be made. For example, if we imagine an ideal heat engine driven by perfect gas and working in cycles which consist of two isothermal and two isochoric reversible processes, the useful work can be easily computed, provided that the temperatures are measured in terms of perfect gas scale. The result of such a computation reads

$$\Delta L = nR \ln(V_2/V_1) (T_2 - T_1), \quad (20.7)$$

where V_1 and V_2 are the limits of volume between which the engine operates. It is apparent at first glance that the last equation is fully congruent with equation (20.6) with the proviso that the heat (measured in entropy units, e.g. Ct) transferred from heater to cooler per cycle is given by $\zeta = nR \ln(V_2/V_1)$. The congruence of these equations means that the system of units can be always chosen in such a way that scales *T and T will be identical [16]. Expressing this fact more physically, we can say:

The measurement of temperature by means of ideal gas thermometer is equivalent to the measurement of temperature by means of ideal heat engine.

The theoretical significance of this theorem is enormous because it enables one to relate without ambiguity the ideal gas (Kelvin) temperature scale to the temperatures defined by other types of ideal heat engines, e.g. "*gedanken*" reversible cycles, in systems controlled by electric, magnetic or electrochemical forces. Besides, it should be stressed that this theorem, although based on arbitrary assumptions, is by no means accidental. The idealization of the constitutive relation of real gases and the idealization involved in Carnot's postulate have the same anthropomorphic roots, namely, the feeling that the thermal dilation of bodies must be linearly dependent on their thermal state. Incidentally, in the range between 0°C and 100°C the air scale and the mercury temperature scale, prevalingly used in experiments related to establishment of Carnot's theorem, are almost identical.

For the sake of completeness we have to mention here also the so called "*thermodynamic gauge*" of Carnot's function. The general acceptance of this gauge in *classical thermodynamics* was, however, not a result of a free choice but a direct consequence of admittance of *Joule-Mayer's Principle* of equivalence of work (energy) and heat. This Principle which is till now in practically all modern text-

books on thermodynamics treated as an experimentally proved “truth” was, however, quite correctly from the very beginning criticized by M. Faraday [41] as an absolutely wrong “*strange conclusion*” which was “*deduced most illogically*” on the basis of fatal misinterpretation of Joule’s paddle-wheel experiment. Accordingly, namely, the existence of exchange rate between two different quantities, mechanical work and heat, called mechanical equivalent of heat, $J \approx 4.2 \text{ J/cal}$, is confused with the experimental proof of identity of these two entities. Thus in such a context Joule-Mayer’s Principle has rather a character of arbitrary redundant postulate than that of experimental result [42]. Nevertheless, once this Principle is accepted, Carnot’s function, in terms of ideal gas temperature scale T , has to have inevitably the form $F(T) = J/T$ (*thermodynamic gauge*) [36], cf. also [43]. Such a gauge, however, enormously complicates the formalism of classical thermodynamics, because it requires introducing into the thermal term (4) of balance equation, instead of “quantity of heat” already associated with the energy, another somewhat artificial physical quantity, *entropy*, which has no clear phenomenological interpretation [40]. Typical claims which can thus be found in the current literature on thermodynamics sound “*Joule’s experiment conclusively established that heat is a form of energy...*” It is, however, worth mentioning here some remarkable facts which undermine the credibility of such statements. For example, practically all measurements (i.e. more than about 30 serious extensive works Joule’s works including from the second half of the 19th to the end of the 20th centuries) of mechanical equivalent of heat were made at only *single* temperature. It is thus quite evident that the experimentalists tacitly assumed, prior making the experiment, the validity of Joule-Mayer’s Principle, being convinced that the measured equivalent is nothing but a conversion factor between two different energy units, which has to be inevitably temperature independent. “Derivation” of Joule-Mayer’s Principle from such an experimental data is obviously nothing but a case of circular reasoning. Moreover, the mechanical equivalent of heat was (with much smaller accuracy but in the correct way) determined by Carnot [33] more than 20 years before Joule within the frame of caloric theory, i.e. without any possible reference to Joule-Mayer’s Principle.

Interestingly enough, the choice of particular gauge does not directly influence the properties of Kelvin’s temperature scale itself but it is quite decisive for the mathematical behaviour and physical interpretation of corresponding conjugate extensive quantity.

20.8 Problem of Distant Measurements of Temperature

Under the term “*distant measurements*” in a restricted sense we mean the determination of a physical quantity belonging to a certain moving inertial frame by means of measurements made in the rest system. The operational methods for distant measurements of e.g. length, time, frequency and intensity of fields are gener-

ally known from the Special Theory of Relativity. In the case of temperature, however, due to its peculiar physical nature, we encounter serious difficulties which result into quite controversial solutions of the problem [44]. At first glance it may seem that the problem of distant measurement of temperature belongs to the scope of practical calorimetry and thermal analysis performed in laboratories only marginally, being of primary importance only for thermo-physical processes taking place on remote objects like stars or spacecrafts. It should be stressed, however, that the considerations dealing with relativistic transformations of thermal quantities reveal their physical structure and are thus quite crucial for a consistent interpretation of these quantities even under the terrestrial conditions.

The main difficulty in distant measurement of temperature is the principal impossibility of realization of correlation test and establishment of thermal equilibrium between two relatively moving inertial systems. Indeed, the relative movement of systems A and B prevents one from answering without ambiguity, on the basis of correlation test, the question of whether the common boundary is diathermic or not, which makes any judgment on the thermal equilibrium between A and B quite questionable. It is further clear that the boundary between two relatively moving systems has to move at least with respect to one of them. In such a case, however, the interaction between these systems can exist even if the boundary is non-diathermic (adiabatic). For example, the moving boundary can exert a pressure on one of the systems without changing the state of the other and/or a charged system A surrounded by a metallic envelope, regardless of the fact whether it is diathermic or adiabatic, can induce dissipative equalization currents in system B without affecting the charge distribution inside system A. In order to exclude such cases, the temperature of any body must be measured only by means of a thermometer which is in the rest with respect to the body, and this operation cannot be, in principle, performed by a relatively moving observer (cf. also [45]). Hence the temperature cannot be the subject of a direct distant measurement in principle. It can only be the result of local measurement and subsequent data transfer into another inertial system. (If possible, the digital mailing of the data would be the best choice.) Of course, as the theoretical basis for the determination of temperature of moving objects equation $T = T_0$, expressing the Lorentz invariance of temperature, has to be simultaneously taken into account. The operational rules for distant measurement of temperature may then be formulated as follows:

- 1) Bring the body under investigation into diathermic contact with the thermometer placed in the same inertial frame
- 2) Reconstruct in another (e.g. rest) inertial system the reading of the thermometer applying transformation rules relevant to the thermoscopic variable used

Having already at our disposal the prescription defining the temperature in mathematical terms, it is in principle possible to perform the Lorentz transformation of the left-hand side of equation (20.2) and to obtain in this way the formula

for the relativistic transformation of temperature T . However, in order to be able to analyze also other temperature measuring methods (using e.g. platinum resistance, black-body radiation, thermoelectric voltage) in a sufficient generality a methodical approach is more relevant.

Fortunately, the properties of hotness manifold enable one to make the following fairly general considerations. First of all, it is evident that in order not to violate the Principle of Relativity the behaviour of bodies realizing fixed thermometric points has to be the same in all inertial frames (cf. [46]). For example, it would be absurd to admit an idea that the water violently boiling in its rest system can simultaneously⁴ look calm if observed from another relatively moving inertial system. In other words, any fixed point has to correspond to the same hotness level regardless of the inertial frame used for the observation. Assigning, by means of some convention, to each body realizing the fixed point a certain “inventory entry”, the resulting, by pure convention established list of numbers cannot be changed by a mere transfer from one inertial system to another.

For example, using thus as an operative rule for stocktaking of fixed points formula (20.2) (in SI units with $R = 8.3145 \text{ J/K mol}$) and assigning to the triple point of water an inventory entry 273.16 K, we obtain an ordered table of fiducial points of ideal gas scale (similar to the ITS [1]) which must be valid in all inertial frames. As the set of fixed points provides a dense subset (skeleton) in continuous hotness manifold, such a Lorentz-invariant table can be extended and made finer as we like and consequently, any hotness level can be, by means of this table, approximated with arbitrary accuracy. Due to the continuity of prescription (20.2) the whole *ideal gas (Kelvin) scale T is then inevitably Lorentz invariant*.

The invariance of Kelvin scale has, however, a very interesting and far reaching consequence. Let us make the following thought experiment with two identically arranged gas thermometers both filled with one mole of ideal gas which are in two relatively moving inertial systems in diathermic contact with the same fixed point bath (for definiteness, with triple point of water) placed in their own frames. As the pressure in both devices is Lorentz invariant [47,48], we can write:

$$p = p_0, \quad (20.8)$$

$$T = T_0, \quad (20.9)$$

where index 0 is related, as above, to the quantities measured in the a-priori chosen rest system. Taking now the well-known Lorentz transformation of volume into account, we obtain from (20.8) and (20.9) the following series of equations

$$pV = p_0 V_0 \sqrt{(1 - v^2/c^2)} = RT = R_0 T_0 \sqrt{(1 - v^2/c^2)}, \quad (20.10)$$

⁴ Notice that we have to do here with the essentially time-independent stationary process where the Lorentz transformation of time plays no role. Let us also recall that the pressure, controlling e.g. boiling point of water, may be proved independently to be Lorentz invariant [47,48]

from which a somewhat astonishing relation immediately follows:

$$R = R_0 \sqrt{1 - v^2/c^2}. \quad (20.11)$$

The physical meaning of this formula is really far reaching. Taking into account, namely, that R is an entropy unit, equation (20.11) must simultaneously enter the transformation formulae for entropy in general. This is, however, in severe contradiction with *Planck's Ansatz* claiming that the entropy is Lorentz invariant. We have to recall here that this Ansatz, serving as a starting point of numerous considerations in relativistic thermodynamics, has never been proved with sufficient exactness but from the beginning it was mere an intuitive conjecture [49]. It was namely argued that the entropy has to be invariant, because it is the logarithm of a discrete number of states which is "naturally" Lorentz invariant. Nevertheless, such a seemingly transparent argument cannot be true in general as can be shown by means of the following consideration. Let us imagine first that a sample of paramagnetic salt is submerged in a bath of boiling helium kept at normal atmospheric pressure realizing the Lorentz invariant fixed point corresponding to the temperature of 4.2 K [8]. At zero magnetic fields certain entropy can be ascribed to such a state of paramagnetic salt independently of the fact in what inertial system the experiment is performed. Let us further assume that there is distributed static electric charge in the rest system not affecting the entropy of paramagnetic salt. As is well known from the special theory of relativity, however, the magnetic field is nothing but the electrostatic field observed from the relatively moving inertial system [50]. Therefore, the observer in the relatively moving inertial frame has to detect magnetic field, and the entropy of the said paramagnetic sample kept at 4.2 K must be smaller than that in the rest system. In other words, because the entropy in this particular case depends on the choice of inertial system of observation, it cannot be generally Lorentz invariant. If we thus once admit the relativistic invariance of temperature, we have to reject Planck's conjecture as unsound and particularly, we can also no more treat various entropy pre-factors, e.g. gas constant R and Boltzmann's constant k , as universal constants.

20.9 Summary

In conclusion, the central concept of thermal physics, *temperature*, is defined in terms of the set theory as an arbitrary one-to-one order preserving continuous mapping of the so-called *hotness manifold (set)* \mathbf{H} on a certain simple connected open subset of real numbers. It has been shown that the hotness manifold representing all in the Nature existing thermoscopic (thermal) states is the only entity accessible to direct physical observation. This set which was further proved to be topologically equivalent to the set of all real numbers (real axis) \mathbf{E}_1 , contains a countable, dense and unbounded subset of all *fixed points* $\mathbf{F} \subset \mathbf{H}$. Any fixed point

is realized by means of a specially prepared body which defines just one thermal state. The properties of the set \mathbf{F} and its relation to the manifold \mathbf{H} are specified by means of Mach's postulates which are generalizations of empirical facts. As was further shown, the special mapping of \mathbf{H} on the set of all positive real numbers known as the *International Kelvin Temperature Scale* T was chosen on the grounds of two essentially anthropomorphic idealizations providing a concordant result, namely, on ideal substance, *perfect gas* and on ideal process in heat engine, *reversible cycle*. Finally, on the basis of simple physical arguments taking into account the mathematical structure of the hotness manifold the Lorentz invariance of the temperature was proved. Consequently, the variable conjugate to temperature, i.e. entropy-like heat, cannot be Lorentz invariant in severe contradiction to Plank's Ansatz claiming the Lorentz invariance of entropy in general.

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1

A Thermodynamic Formulation of Economics*Juergen Mimkes*

The thermodynamic formulation of economics is based on the laws of calculus. Differential forms in two dimensions are generally not exact forms (δQ), the integral from (A) to (B) is not always the same as the integral from (B) to (A). It is possible to invest little in one way and gain a lot on the way back, and to do this periodically. This is the mechanism of energy production in heat pumps, of economic production in companies and of growth in economies. Not exact forms may be turned into exact forms (dS) by an integrating factor T , $dS = \delta Q/T$. The new function (S) is called entropy and is related to the probability (P) as $S = \ln P$. In economics the function (S) is called production function. The factor (T) is a market index or the standard of living, GNP/capita, of countries. The dynamics of economic growth is based on the Carnot process, which is driven by external resources. Economic growth and capital generation – like heat pumps and electric generators – depend on natural resources like oil. GNP and oil consumption run parallel for all countries. Markets and motors, economic and thermodynamics processes are all based on the same laws of calculus and statistics.

1.1

Introduction

In the last ten years new interdisciplinary approaches to economics and social science have been developed by natural scientists. The problems of economic growth, distribution of wealth, and unemployment require a new understanding of markets and society. The dynamics of social systems has been introduced by W. Weidlich (1972) [17] and H. E. Stanley (1992) [15] has coined the term econophysics. A thermodynamic approach to socio-economics has been favored by D. K. Foley (1994) [4], J. Mimkes (1995) [10] and Drăgulescu and V. M. Yakovenko (2001) [3]. Financial markets have been discussed by M. Levy et al. (2000) [8], S. Solomon and Richmond (2001) [14], Y. Aruka (2001) [1] and many others. Many conferences have been held to enhance the communication between natural and socio-economic sciences with topics like

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econophysics, complexity in economics and socio-economic agent systems. In the first chapter, the mechanism of economic production is discussed on the basis of calculus and statistics. The two mathematical fields will be applied to economics in a similar way to thermodynamics, this is the thermodynamic formulation of economics.

1.2 Differential Forms

1.2.1 Exact Differential Forms

The total differential of a function $f(x, y)$ is given by (see, e.g., W. Kaplan [6])

$$df = (\partial f / \partial x) dx + (\partial f / \partial y) dy \quad (1.1)$$

The second (mixed) derivative of the function $f(x, y)$ is symmetric in x and y ,

$$\frac{\partial^2 f}{\partial x \partial y} = \frac{\partial^2 f}{\partial y \partial x} \quad (1.2)$$

In the same way every differential form

$$df = a(x, y) dx + b(x, y) dy \quad (1.3)$$

is called total or exact, if the second derivatives

$$\partial a(x, y) / \partial y = \partial b(x, y) / \partial x \quad (1.4)$$

are equal. Exact differential forms are marked by the “ d ” in df . The function $f(x, y)$ exists and may be determined by a line integral,

$$\int_A^B df = \int_A^B \left(\frac{\partial f}{\partial x} dx + \frac{\partial f}{\partial y} dy \right) = f(B) - f(A) \quad (1.5)$$

The closed integral of an exact differential form is zero: The closed integral may be split into two integrals from A to B on path (1) and back from B to A on path (2). Reversing the limits of the second integral changes the sign of the second integral. Since both integrals depend on the limits A and B only, the closed integral of an exact differential is zero:

$$\oint df = \int_A^B df_{(1)} + \int_B^A df_{(2)} = \int_A^B df_{(2)} - \int_A^B df_{(2)} = 0 \quad (1.6)$$

Example:

$$\begin{aligned}
 f(x, y) &= x^3 y^5 \\
 df &= (3x^2 y^5) dx + (5x^3 y^4) dy \\
 \frac{\partial^2 f}{\partial x \partial y} &= 3 \cdot 5 \cdot x^2 y^4 = \frac{\partial^2 f}{\partial y \partial x} \\
 \oint df &= 0
 \end{aligned} \tag{1.7}$$

1.2.2

Not Exact Differential Forms

In one dimension all differential forms are exact. A two-dimensional differential form δg

$$\delta g = a(x, y) dx + b(x, y) dy \tag{1.8}$$

is not always an exact differential form. The second derivatives are generally not equal,

$$\partial a(x, y) / \partial y \neq \partial b(x, y) / \partial x \tag{1.9}$$

These differential forms are called not exact and are marked by the “ δ ” in δg . A function $g(x, y)$ does not exist in general and may not be determined by a line integral, because the line integral of not exact differential forms depends on the integral limits A and B and on the path of integration. Any different path of integration will lead to a new function $g(x, y)$. A closed integral from A to B along path (1) and back from B to A along path (2) will not be zero,

$$\oint \delta g = \int_A^B \delta g_{(1)} - \int_A^B \delta g_{(2)} \neq 0 \tag{1.10}$$

Example: We may construct a non exact differential form by dividing df (1.7) by y :

$$\delta g = df(x, y) / y = (3x^2 y^4) dx + (5x^3 y^3) dy \tag{1.11}$$

$$12x^2 y^3 = \partial a(x, y) / \partial y \neq \partial b(x, y) / \partial x = 15x^2 y^3$$

In Fig. 1.1. the closed integral of δg is calculated for path (1) from point $A = (1; 1)$ along the line ($y = 1$) to $B = (2; 1)$ and then along the line ($x = 2$) to point $C = (2; 2)$.

$$\begin{aligned}
 \int_{1;1}^{2;2} \delta g_1 &= \int_1^2 (3x^2 (y=1)^4) dx + \int_1^2 5(x=2)^3 y^3 dy \\
 &= (2^3 - 1^3) + 5 \cdot 2^3 (2^4 - 1^4) / 4 = 157
 \end{aligned}$$

The second integral of δg is calculated for path (2) from point $A = (1;1)$ along the line ($x = 1$) to point $D = (1;2)$ and then along the line ($y = 2$) to point $C = (2;2)$:

$$\begin{aligned}\int_{1;1}^{2;2} \delta g_2 &= \int_1^2 (3x^2(y=2)^4) dx + \int_1^2 5(x=1)^3 y^3 dy \\ &= 2^4(2^3 - 1^3) + 5 \cdot 1^3(2^4 - 1^4)/4 = 130,75\end{aligned}$$

The closed line integral along path (1) from $A = (1;1)$ via $B = (2;1)$ to $C = (2;2)$ and back along path (2) from C via $D = (1;2)$ to $A = (1;1)$ – see Fig. 1.1 – is

$$\oint \delta g = \int_A^B \delta g_{(1)} + \int_B^A \delta g_{(2)} = 157 - 130,75 = 26,25 \neq 0$$

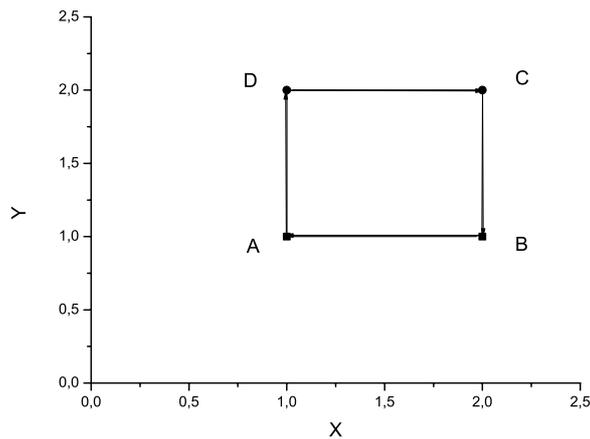


Fig. 1.1 The closed line integral along path (1) from $A = (1;1)$ via $B = (2;1)$ to $C = (2;2)$ and back along path (2) from C via $D = (1;2)$ to A is not zero!

1.2.3

The Integrating Factor

A two-dimensional differential form δg may be made exact by an integrating factor $1/T$:

$$df = \delta g/T = [a(x,y) dx + b(x,y) dy]/T \quad (1.12)$$

(Sometimes the integrating factor is also called λ , but with respect to thermodynamics the factor $1/T$ will be used here.) In two dimensions this factor always exists.

Example: The non total differential form δg (1.11) has been obtained by dividing the exact form df (1.7) by “ y ”. Accordingly, $y = 1/T$ will be the integrating factor of δg .

1.2.4

The First and Second Law of Differential Forms

The results above may be stated in two laws for differential forms:
The first law of differential forms:

Two-dimensional differential forms δg will generally not be exact.

The second law of differential forms:

A not exact differential form may be made exact by an integrating factor $1/T$.

1.2.5

Not Exact Differential Forms in Thermodynamics and Economics

Why are differential forms and calculus of not exact forms so important for thermodynamic and economics?

1. Thermodynamics. Heat is a function of at least two variables, temperature and pressure. According to the first law of differential forms, heat (δQ) will be a non exact differential form. The value of the integral from (A) to (B) will not be the same as from (B) to (A). This makes the first law of differential forms so important in the application to periodic machines: it is possible to invest little heat in one way and gain a lot of heat on the way back and to do this periodically.

Heat pumps. *A heat pump or generator may periodically invest 1 kWh of energy in one way and gain 5 kWh on the way back!*

The second law makes it possible to calculate a complicated technical process of not exact differential forms by a simple function. This makes thermodynamics so important for theory and application (see, e.g. R. Fowler and Guggenheim (1960) [5]).

2. Economics. Economic growth is a function of at least two variables, labour and capital. According to the first law of differential forms profit (δQ) will not be an exact differential form. The value of the integral from (A) to (B) will not be the same as from (B) to (A). This makes the first law of differential forms so attractive in the application to periodic production: it is possible to invest little capital in one way and gain a lot of capital on the way back and to do this periodically:

Banks. A bank may periodically invest 4% of interest in savings and collect 10% interest from investors.

Companies. A company may periodically pay as little as possible to workers and collect periodically as much as possible from customers.

The second law makes it possible to calculate a complicated technical process of not exact differential forms by a simple function. This makes the thermodynamic formulation of economics so important for theory and application in economics and business.

1.3

The First Law of Economics

1.3.1

The First Law: Capital Balance of Production

Economic production in farms, automobile plants, medical offices or banks is achieved by hard work, but the output will be different for each type of production. The output depends on each specific production process, or in mathematical terms, on the path of integration. Production may be modeled by calculus of not exact differential forms,

$$-\oint \delta W = \oint \delta Q \quad (1.13)$$

The surplus (Q) is a result of work input ($-W$). The cyclic process of economic production Eq. (1.13) may be split into two parts, the integral from A to B and back from B to A ,

$$-\oint \delta W = \oint \delta Q = \int_A^B \delta Q_{(1)} - \int_A^B \delta Q_{(2)} = Y - C = \Delta Q \quad (1.14)$$

The economic process consists of output (Y) and input (C), the difference is the surplus ΔQ . (The letter S for surplus in standard economics has been replaced by ΔQ .) Income (Y) and costs or consumption (C) are both part of the same production cycle, and depend on the specific production and consumption processes. Surplus and economic growth cannot be calculated in advance (*ex ante*), unless the whole process is entirely known.

Equation (1.14) may be written in differential forms. If two not exact differentials ($-\delta W$) and (δQ) are equal along the same path of integration, they may differ only by a total differential form (dE), which will always vanish for closed integrals,

$$\delta Q = dE - \delta W \quad (1.15)$$

This is the first law of economics in differential form. It is a capital balance of production. The surplus (δQ) will increase the capital (dE) and requires

the input of work ($-\delta W$). The main feature of this first law of economics is the fact that the capital balance of production cannot be expressed by definite functions. The capital balance can only be given by not exact differential forms! Eq. (1.13) will be discussed in more detail below.

1.3.2

Work (W)

Work (W) is the effort and know-how which we invest in our job. The function (W) does not exist as a general function, it always depends on the path of integration, the production process. Accordingly, (W) cannot be calculated “*ex ante*”. Work is not equivalent to labor, which defines the number and kind of people in the production process. Work is equivalent to the production process. The dimension of (W) is capital, the same as capital (E) and surplus (Q). In thermodynamics the function (W) refers to work of machines. In economics the function (W) may refer to people as well as to machines! The thermodynamic formulation of economics reveals a problem of modern production namely that people and machines work according to the same laws, Eq. (1.13). If people do not work efficiently, they may be replaced by machines: in construction labor will be taken over by cranes and motors, in offices work may be done by computers.

1.3.3

Surplus (ΔQ)

The surplus (ΔQ) is the result of work (W), Eq. (1.13), and again cannot be calculated “*ex ante*”, as (δQ) is a not exact differential form. The integral depends on the path of integration, the surplus depends on the production process. The thermodynamic formulation of economics makes it possible to compare economic production to work in thermodynamics.

Heat pumps. *A heat pump is close to the energy reservoir of a river or garden. A heat pump or generator may periodically invest 1 kWh of energy one way and gain 5 kWh on the way back! The heat output (Q) is larger than the work input (W). Where does the heat come from?*

In each cycle the heat (ΔQ) is pumped from the environment, the garden or river, which will be cooled down when the heat pump is operating. In gardens or rivers the energy loss will be filled up from the reservoir of the environment.

Banks. *A bank is close to the capital reservoir of savers. A bank may periodically invest 4% of interest in savings and collect 10% interest from investors. The output (Q) is larger than the input (W)! Where does the surplus come from?*

For banks the surplus capital for each cycle is taken from the growth of the saving community. It is not only the first member of an economic chain which

exploits nature and the environment, but all other members of an economic chain do the same in each production cycle. This mechanism of economic growth will be discussed in more detail in the Carnot process, below.

1.3.4

Capital (E)

The capital (E) is the basis of economic production (W). The farm is the capital of the farmer, the production plant is the capital of a company, the investment the capital of investors.

Without labour (W) capital cannot grow. Only by an input of work may the capital increase. Of course, capital may also decrease by mismanagement or failures. But every economic system has to produce positive surplus in order to survive. After each production cycle the surplus (ΔQ) has to be in a reasonable relationship to the invested capital (E). The relation

$$r = - \oint \delta W / E = \oint \delta Q / E = \Delta Q / E \quad (1.16)$$

is called the efficiency of the production cycle (δW). The ratio “ r ” is called the interest rate and is given in percent. The efficiency or interest rate measures the success of a production cycle (δW) and determines, whether people or machines will be employed in a specific production process.

1.4

The Second Law of Economics

1.4.1

The Second Law: Existence of a System Function (S)

The not exact differential form δQ may be changed into an exact differential form dS by an integrating factor T . This is called the second law:

$$dS = \frac{1}{T} \delta Q \quad (1.17)$$

Equation (1.17), is a law for the existence of a system function (S), which is called entropy in physics and information science. Economists usually call this function the production or utility function. $1/T$ is the integrating factor.

1.4.2

The Integrating Factor (T)

$1/T$ is the integrating factor of the capital balance (1.13). T is proportional to the mean capital (E) of N agents of the specific economic system,

$$E = cNT \quad (1.18)$$

c is a proportional factor. T may be regarded as an “economic temperature”. In a market of N commodities, T is proportional to the mean price level. In a society of N households T is proportional to the mean capital per household, or standard of living. In countries, T is proportional to the GDP per capita. T is introduced by the second law as the main variable in all economic functions.

1.4.3

Entropy and Production Function (S)

Inserting Eq. (1.17) into (1.13) we find

$$-\oint \delta W = \oint T dS \quad (1.19)$$

The entropy or production function (S) is closely related to the work function (W). But in contrast to (W) the function (S) is independent of the production process, it has the dimension of a (production) number and may be calculated “*ex ante*”. The functions (W) and (S) represent mechanism and calculation in all economic processes:

The work function (W). The work function (W) is defined by the production process and may be different for each process. This makes it possible to invest little in one part of the process and gain much in another part of the production process in order to obtain a surplus.

The production function (S). The entropy or production function (S) depends on the system and makes it possible to calculate the economic process “*ex ante*”.

1.4.4

Pressure and Personal Freedom

In Eq. (1.17) the non exact form δQ has been expressed by dS : $\delta Q = T dS$. In the same way the non exact form of production (δW) may be expressed by the exact differential form dV ,

$$\delta W = -p dV \quad (1.20)$$

The parameter p may be called the pressure, V may be regarded as space or personal freedom, which may be reduced due to the external economics or social pressure.

1.4.5

The Exact Differential ($dS(T, V)$)

According to Eq. (1.17) and (1.20) the entropy (dS) may be written as an exact differential form of T and V :

$$dS(T, V) = \frac{\partial S}{\partial T} dT + \frac{\partial S}{\partial V} dV = \frac{1}{T} (dE(T, V) + p(T, V) dV)$$

$$dS(T, V) = \frac{1}{T} \frac{\partial E}{\partial T} dT + \frac{1}{T} \left(\frac{\partial E}{\partial V} + p \right) dV \quad (1.21)$$

The exact differential dS may be integrated independent from the path of integration. The production function $S(T, V)$ depends on capital $E(T, V)$ and economic pressure $p(T, V)$. However, other variables, like $S(T, p)$ are also possible, they require additional calculations and will be discussed at a later point.

1.4.6

The Maxwell Relation

The functions E and p cannot be chosen arbitrarily, as the mixed differentials of the exact form dS in Eq. (1.21) have to be equal. This leads to (*exercise!*)

$$\frac{\partial p}{\partial T} = \frac{1}{T} \left(\frac{\partial E}{\partial V} + p \right) = \frac{\partial S}{\partial V} \quad (1.22)$$

These “Maxwell relations” are general conditions for all model functions $E(T, V)$, $p(T, V)$ and $S(T, V)$.

Equation (1.21) leads to the existence of a function $F(T, V)$,

$$F(T, V) = E(T, V) - TS(T, V) \quad (1.23)$$

(see exercise). F may be called the “effective costs” function, which will be a minimum for stable economic systems. The function F corresponds to the “Helmholtz free energy” function of thermodynamics.

Exercise: The total differential $dF = d(E - TS) = dE - TdS - SdT$ may be transformed by Eqs (1.15), (1.17) and (1.20) into

$$dF = -p dV - T dS$$

The mixed second derivative of dF is given by the Maxwell relation Eq. (1.22).

1.4.7

Lagrange Function

Dividing the function $F(T, V)$ in Eq. (1.23) by $(-T)$ we obtain

$$L(T, V) = S(T, V) - (1/T)E(T, V) \rightarrow \text{maximum!} \quad (1.24)$$

L is the Lagrange function which maximizes the production function (S) under constraints of costs (E) with a Lagrange multiplier $\lambda = (1/T)$. This is the result of the first and second law. The discussion of the Lagrange function will be continued in Section 1.5.4.

1.5 Statistics

1.5.1

Combinations

The distribution of decisions is given by the mathematics of combinations. For two possible decisions – left/right or yes/no – we find the probability P

$$P(N_L; N_R) = \frac{N_0!}{N_L! N_R!} \cdot \frac{1}{2^N} \quad (1.25)$$

N_L is the number of decisions for the left side and N_R the number of decisions for the right side, $N_L + N_R = N_0$. ($N!$ stands for the product $4! = 1 \cdot 2 \cdot 3 \cdot 4$ and $0! = 1$).

1.5.2

Normal Distribution

For large numbers N_0 the probability function $P(N_L, N_R)$ in Eq. (1.25) leads to a normal distribution,

$$P(N) = \frac{1}{\sqrt{2\pi}\sigma} \cdot e^{-\frac{(N-\bar{N})^2}{2\sigma^2}} \quad (1.26)$$

with $0 \leq N \leq N_0$, $\bar{N} = N_0/2$ and $2\sigma = \sqrt{N}$. The normal distribution is one of the most important probability functions in the natural, social and economic sciences.

1.5.3

Polynomial Distribution

In many cases we have more than two decisions, e.g., we can choose the color of a car to be black, white, red, blue, etc. For $N_0 = N_1 + \dots + N_K$ and K possible equal decisions we obtain

$$P(N_1; \dots; N_K) = \frac{N_0!}{N_1! \cdot \dots \cdot N_K!} \cdot \frac{1}{K^N} \quad (1.27)$$

If the probability of the decisions is not equal, we have to introduce the probability q_k of the decision k . The sum of all q_k will be equal to one, $\sum q_k = 1$:

$$P(N_1; \dots; N_K) = \frac{N_0!}{N_1! \cdot \dots \cdot N_K!} \cdot q_1^{N_1} \cdot \dots \cdot q_K^{N_K} \quad (1.28)$$

If we have N_0 cars with K different colors and each color has the probability q_k , then $P(N_1; \dots; N_K)$ is the probability to find, in a street with N cars, N_1 cars of color 1, N_2 cars of color 2 and N_k cars of color k .

1.5.4

Lagrange Function in Stochastic Systems

What is the most probable distribution of apples, pears and bananas under given prices (E)? Or, what is the most probable distribution of N goods in K different price categories?

The probability (P) will always tend to be a maximum. The most probable distribution of N commodities with constraints of price E may be calculated by the Lagrange function (L),

$$L(N_k) = \ln P(N_k) - (1/T)\sum N_k E_k \rightarrow \text{maximum!} \quad (1.29)$$

$P(N_k)$ is the probability according to Eq. (1.28), N_k is the number of goods, E_k the price in price class (k), $(1/T)$ is the Lagrange multiplier. Equation (1.29) is the Lagrange function Eq. (1.24) of systems that follow the laws of probability.

Example: The Munich beer garden.

1. A Munich beer garden has N_1 permanent and N_2 temporary employees. The wages are $E_1 = 15\text{€}$ per hour for the permanent and $E_2 = 7,5\text{€}$ per hour for the temporary staff. The Lagrange function calculates the optimal output per hour under the constraints of wages E ,

$$E = N_1 E_1 + N_2 E_2 = N(x_1 E_1 + x_2 E_2) \quad (1.30)$$

where $x_k = N_k/N$ is the relative number and N the total number of staff. The entropy for two types of employees is given by

$$S = N \ln N - N_1 \ln N_1 - N_2 \ln N_2 = -N(x_1 \ln x_1 + x_2 \ln x_2) \quad (1.31)$$

The Lagrange function is maximized,

$$L = N \ln N - N_1 \ln N_1 - N_2 \ln N_2 - (1/T)(N_1 E_1 + N_2 E_2) = \text{max!} \quad (1.32)$$

At a maximum the derivatives with respect to N_1 and N_2 will be zero. The relative numbers of permanent and temporary staff x_1 and x_2 follow a Boltzmann distribution. With the given values of E_1 and E_2 we obtain

$$x_1 = \exp(-E_1/T) = 0.38$$

$$x_2 = \exp(-E_2/T) = 0.62$$

$$T = 15.8$$

$$S/N = 0.664$$

$$E/N = 10.35$$

The relative numbers of permanent and temporary staff x_1 and x_2 , the Lagrange parameter T , the mean output per person S/N and the mean wages per person may be calculated from the wages E_1 and E_2 without any further assumptions.

2. In standard economics the Cobb Douglas production function U

$$U = N_1^\alpha N_2^{1-\alpha} = N x_1^\alpha x_2^{1-\alpha} \quad (1.33)$$

is often used in the Lagrange function. In addition to wages E_i , the employees x_i are rated by an additional elasticity parameter α . For an arbitrary value $\alpha = 0.7$ we obtain

$$x_1 = \alpha / [\alpha / E_1 + (1 - \alpha) / E_2] / E_1 = 0.538$$

$$x_2 = \alpha / [\alpha / E_1 + (1 - \alpha) / E_2] / E_2 = 0.462$$

$$T = (E_1 / \alpha) (N_2 / N_1)^{1-\alpha} = 22.44$$

$$S / N = x_1^\alpha x_2^{1-\alpha} = 0.5141$$

$$E / N = (E_1 x_1 + E_2 x_2) = 11.54$$

For all values of α the mean output S/N is lower and the mean wage costs E/N are higher compared to the entropy $S = \ln P$. The Cobb Douglas function is obviously not the optimal production function. The entropy and Cobb Douglas function look very similar and differ by a factor of about 1.4, this is shown in Figs 1.2 and 1.3.

1.5.5

Boltzmann Distribution

In Fig. 1.4 we have $N = 10$ buyers looking for automobiles. There are now $K = 5$ different car models on the market with the attractiveness $q_k = 1$. The constraint for each model is the price E_k . As a result we find N_k buyers for each car model k .

What is the most probable distribution?

The problem is solved by the Lagrange function (1.29). The probability $P(N_k)$ is given by (1.28):

$$L(N_k) = \ln\{N! / (\prod N_k!) \prod q_k^{N_k} - (1/T) \sum_k (N_k E_k)\} = \text{maximum!} \quad (1.34)$$

For large numbers N the faculty may be replaced by the Stirling formula

$$N! = N \ln N - N \quad (1.35)$$

where N may be replaced by $N = (\sum N_k)$. The Lagrange function is now given by

$$L(N_k) = \left\{ (\sum N_k) \ln(\sum N_k) - \sum (N_k \ln N_k) + \sum (N_k \ln q_k) - (1/T) \sum N_k E_k \right\} \rightarrow \text{maximum!} \quad (1.36)$$

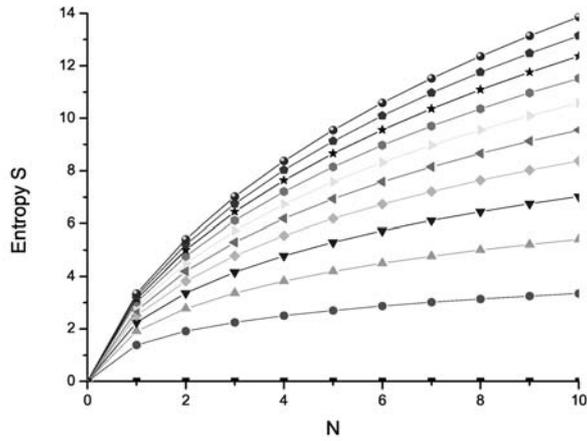


Fig. 1.2 The entropy $S(N_2) = (N_1 + N_2) \ln(N_1 + N_2) - N_1 \ln N_1 - N_2 \ln N_2$ plotted versus N_2 in the range from 0 to 10. The parameter is N_1 in the range from 0 to 10.

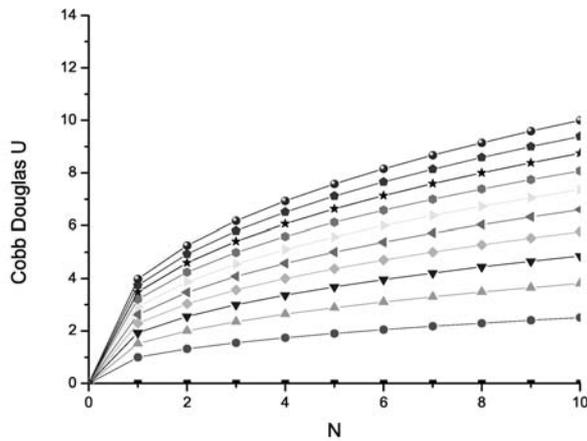


Fig. 1.3 The Cobb Douglas function $U(N_2) = N_1^\alpha N_2^{1-\alpha}$ plotted versus N_2 in the range from 0 to 10. The parameter is N_1 in the range from 0 to 10. In this range the Cobb Douglas Function is smaller than entropy by a factor of about 1.4 for all values of α . The closest match between the functions is obtained for $\alpha = 0.4$.

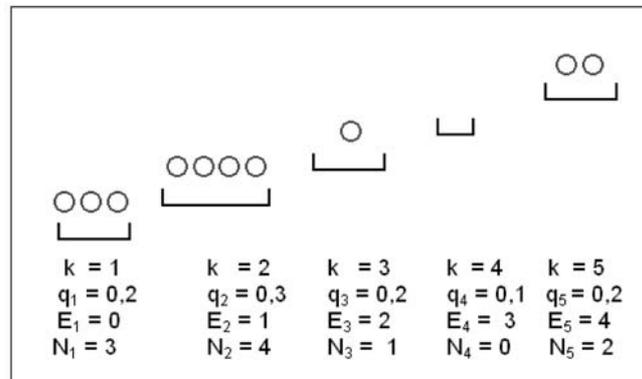


Fig. 1.4 $N = 10$ identical buyers are looking for automobiles. There are now $K = 5$ different car models on the market with the attractiveness $q_k = 1$. The constraint for each model is the price E_k . As a result we find N_k buyers for each car model.

At equilibrium the Lagrange function may be differentiated with respect to N_k ,

$$\partial L / \partial N_k = \{\ln(\sum N_k) - \ln N_k\} + \ln q_k - E_k / T = 0 \quad (1.37)$$

This leads to the distribution of N_k different objects as a function of price E_k ,

$$N_k / N = q_k \exp(-E_k / T) \quad (1.38)$$

The Boltzmann distribution is the most probable distribution of N elements in K categories under constraints (E).

Figure 1.5 shows the distribution of cars sold in the German automobile market in 1998. According to the German tax laws there are four classes of cars, 1.5 liters, 1.8 liters, 2.4 liters and above. The diamond points in Fig. 1.5 are the data of cars sold in Germany in 1998 as given by the automobile industry. The distribution does not yield a Boltzmann distribution, nearly six million units are missing in the lowest category at 1.5 liters or 20 000 DEM. However, the number of seven million used cars is reported for Germany in 1998 by the German Automobile Agency in Flensburg. If this number is added to the new cars of 1998 in the lowest price category, a Boltzmann distribution is obtained. Obviously, the complete automobile market is determined by new and used cars!

Figure 1.6 shows traffic violators given by the German Traffic department in Flensburg, in 2000. The number of repeated violators is shown as a function of the fine (in number of points proportional to a fine in €). The number of violators decreases with a growing fine according to the Boltzmann distribution, Eq. (1.38). The data in Fig. 1.6 exactly follow the calculations. Decisions on

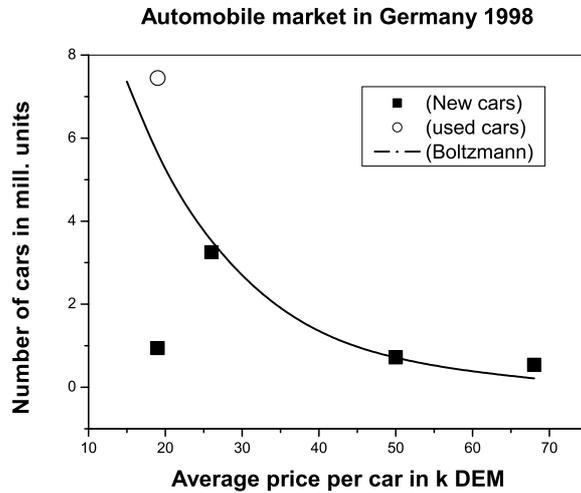


Fig. 1.5 Production of new cars in Germany 1998. According to the German tax classes four types of cars are reported by the industry, 1.5 liters, 1.8 liters, 2.4 liters and above. A Boltzmann distribution, Eq. (1.38), is obtained only if the number of seven million used cars is added to the lowest price category. The complete automobile market is only given by new and used cars!

buying cars or violating traffic rules depends exponentially on the price (E) in relation to the standard of living (T).

1.6 Entropy in Economics

1.6.1 Entropy as a Production Function

In stochastic systems the production function (S) is given by

$$S(N_k) = \ln P(N_k). \quad (1.39)$$

The term entropy (S) is used in mathematics, physics and information science, and has been first introduced to economics by N. Georgescu-Roegen (1974) [7] and more recently by D. K. Foley and J. Mimkes (1994) [4]. In stochastic systems, entropy replaces the Cobb Douglas function of standard economics as a production function. There are several reasons for this replacement.

1. Entropy is a natural system function without additional parameters. The Cobb Douglas function has an arbitrary "elasticity parameter" α .

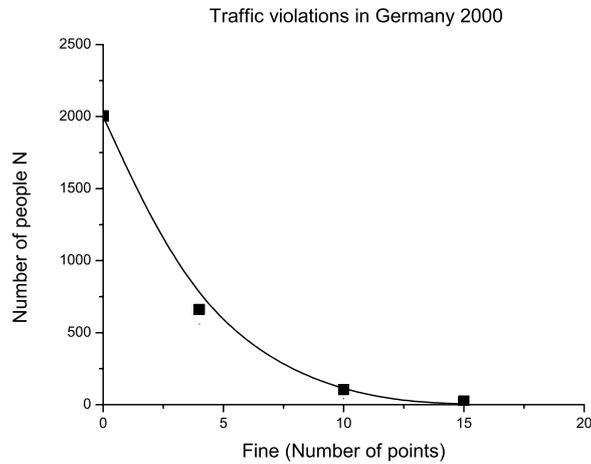


Fig. 1.6 The Boltzmann distribution of repeated traffic violating agents as a function of fine (in points) in Germany 2000. Decisions on violations depend exponentially on the fine (E).

2. The Cobb Douglas function has been found by fitting data, there is no theoretical foundation for this function. The similarity between the functions in Figs 1.2 and 1.3 suggests that entropy would fit the data as well.
3. Figure 1.2 and 1.3 indicate that entropy leads to higher values of production and lower values of costs than does the Cobb Douglas function.
4. In the Lagrange principle the value of different groups of labor are characterized by their wages. They do not need an additional characterization by a parameter α . The Lagrange function with entropy is a sufficient characterization of labor groups.
5. Entropy has a very great significance in production and trade, entropy characterizes the change in the distribution of commodities and money during the process of production and trade. This will be discussed in the following section.

1.6.2

Entropy of Commodity Distribution

We will now discuss the significance of entropy in economics in more detail.

Example: A farmer sells ten apples. Before the transaction the apples are unevenly distributed, the customers have none and the farmer has all the apples, Fig. 1.7.

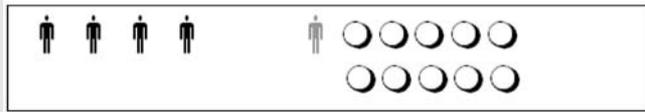


Fig. 1.7 Before selling the ten apples are unevenly distributed, the customers have none and the farmer has all the apples.

The probability for the distribution of ten apples to one out of five persons is given by Eq. (1.28):

$$P_1 = 10! / (0!0!0!0!10!) / 5^{10} = 5^{-10}$$

$$S_1 = -10 \ln 5 = -16.094$$

The farmer sells two apples to each customer and keeps two for himself, Fig. 1.8. Probability and entropy are now

$$P_2 = 10! / (2!2!2!2!) / 5^{10} = 0.0116$$

$$S_2 = \ln(0.0116) = -4.557$$

The entropy of these distributions is negative, since the probability is always $P \leq 1$.

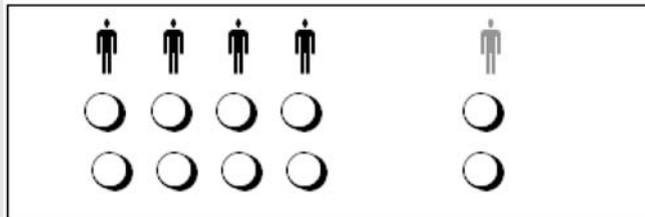


Fig. 1.8 After selling, the apples are evenly distributed, the farmer and each customer has two apples.

In the process of selling, the entropy of apple distribution has changed by

$$\Delta S = S_2 - S_1 = -4.557 + 16.094 = 11.437$$

Selling (distribution) of commodities is equivalent to an increase in entropy. At the end of the sale the distribution of apples has reached equilibrium, all have the same number of apples and the probability and entropy are at a max-

imum,

$$S_2 = \ln P_2 = \text{maximum!}$$

The trade of commodities is generally finished when equilibrium has been reached.

1.6.3

Entropy of Capital Distribution

Example: The farmer sells his ten apples for 1 € each. Before the transaction the farmer and each of his four customers have two 1 € coins in their pockets. The coins are evenly distributed, Fig. 1.9.

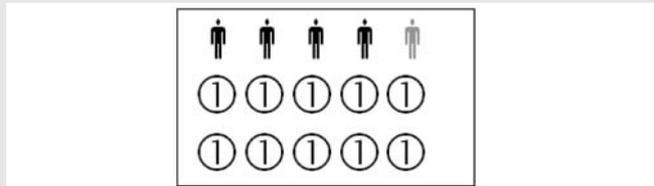


Fig. 1.9 Before selling the ten 1 € coins are evenly distributed: all five persons have two 1 € coins each in their pocket.

The probability for a distribution of two 1 € coins for each of five person is given by

$$P_1 = 10! / (2!2!2!2!) / 5^{10} = 0.0116$$

$$S_1 = \ln(0.0116) = -4.557$$

The farmer sells two apples to each customer and keeps two for himself, Fig. 1.10. He collects 2 € from each customer. The farmer has now 10 € in his pocket, the customers have no more 1 € coins. The probability and entropy are now

$$P_2 = 10! / (0!0!0!0!10!) / 5^{10} = 5^{-10}$$

$$S_2 = -10 \ln 5 = -16.094$$



Fig. 1.10 After selling the apples the 1 € coins are unevenly distributed: the farmer has all coins and the customers have none.

In the process of selling, the entropy of the 1 € coins distribution has changed by

$$\Delta S = S_2 - S_1 = -16.094 + 4.557 = -11.437$$

The negative entropy difference indicates that the coins have been collected. The example shows a new aspect of entropy (S). A positive change of entropy in a system of elements (commodities, capital) is equivalent to distributing, while a negative change of entropy corresponds to collecting elements (commodities, capital). In trading the entropies of commodities and capital change in the opposite direction, the absolute entropy difference of commodities and capital is the same.

1.6.4

Entropy of Production

In the production line of an automobile plant, workers have to assemble parts of a car according to the construction plan. In Fig. 1.11 there are still N different parts, which may be assembled in $P = N!$ possible ways. Assembling means ordering N parts together in one and only one way according to the construction plan.

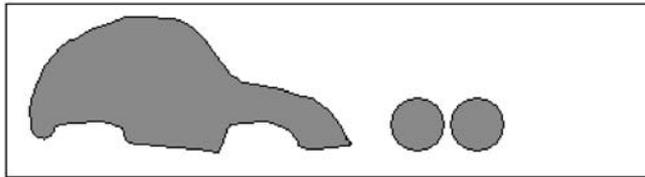


Fig. 1.11 Before assembling N parts of a product there are still $P = N!$ possibilities. Before production the car is still in disorder.

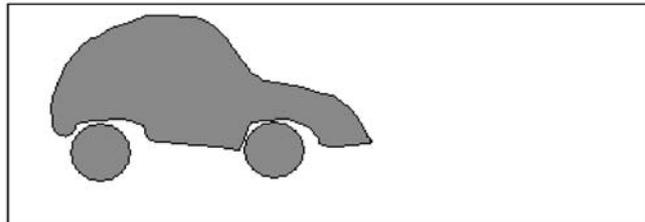


Fig. 1.12 Assembling means ordering N parts in one and only one way according to the construction plan. Production is ordering.

Assembling and ordering according to a plan means entropy reduction, $\Delta S < 0$. Work and production are always accompanied by entropy reduc-

tion. This applies to manual work as well as mental work. A puzzle

$$d+i+c+n+o+o+p+r+t+u = \text{production}$$

may be rearranged into a meaningful word. Mental work is ordering many ideas into one meaningful master plan or theory.

1.6.5

Summary of Entropy

Entropy may have many different aspects, but the main result for entropy may be stated as follows.

$$\Delta S = S_2 - S_1 > 0 \quad (1.40)$$

corresponds to distributing elements like commodities or money and creating disorder.

$$\Delta S = S_2 - S_1 < 0 \quad (1.41)$$

corresponds to collecting elements like commodities or money and creating order.

1.7

Mechanism of Production and Trade

1.7.1

The Carnot Process

The mechanism of production and trade is based on the Carnot process. Equation (1.19) may be integrated along the closed path with $T = \text{constant}$ and $S = \text{constant}$ in the T - S diagram, Fig. 1.13

$$-\oint \delta W = \oint \delta Q = \oint T dS = \int_1^2 T_1 dS + \int_3^4 T_2 dS = Y - C = \Delta Q \quad (1.42)$$

Automobile production is a typical economic process that can be modeled by the Carnot process in Fig. 1.13. The cycle of production starts and ends at point (1).

Example: Carnot cycle of automobile production.

(1) \rightarrow (2): Automobile production starts at point (1). Workers with a low standard of living (T_1) produce the automobile according to the production plan (ΔS). The total production costs are given by material (E) and labor: $C = E + T_1 \Delta S$. The costs could be reduced by building the cars

- according to the same production plan (ΔS) and same material (E) in a place with low standard of living (T_1).
- (2) \rightarrow (3): Transport of cars from production plant (T_1) to market (T_2).
- (3) \rightarrow (4): The automobiles are sold to customers at a market with a high standard of living (T_2). The sales price is given by the material and the market: $Y = E + T_2\Delta S$.
- (4) \rightarrow (1): The cycle is closed by recycling the automobile.

The surplus is $\Delta Q = Y - C = \Delta T\Delta S$ and corresponds to the enclosed area in Fig. 1.13.

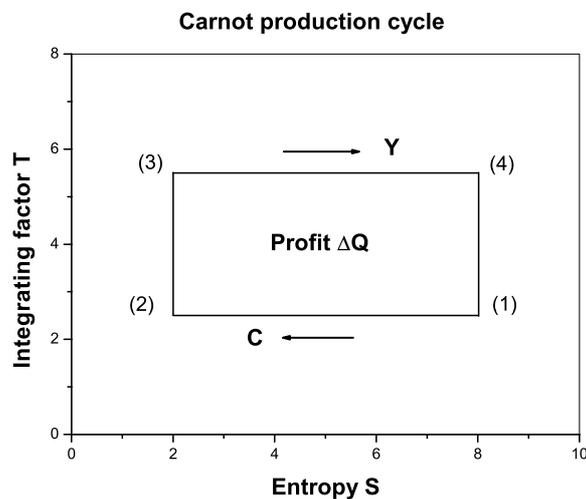


Fig. 1.13 In the Carnot production cycle the flow of goods starts and ends at point (1), (see text).

Example: Carnot cycle of apple farming.

- (1) \rightarrow (2): In the fall a farmer collects apples from his trees and stores them in his cellar. The work of collecting apples from the trees leads to a reduction of entropy of apple distribution, ($\Delta S < 0$). The production costs are $C = T_1\Delta S$. T_1 is the price level of apples in the fall.
- (2) \rightarrow (3): The apples are stored in the cellar without changing the distribution, $S = \text{constant}$.
- (3) \rightarrow (4): In spring the apples are distributed ($\Delta S > 0$) from the farm to the market at the higher price level (T_2) of apples, the total amount of income from the apples is $Y = T_2\Delta S$.

- (4) → (1): The apples are sold and there is no change in the distribution of apples until the fall, $S = \text{constant}$. The cycle starts again. The surplus of the apple production cycle is $\Delta Q = Y - C = \Delta T \Delta S$ and corresponds to the enclosed area in Fig. 1.2. The capital flow starts from point (1) and ends at point (1), but capital flow is opposite to the flow of apples, the work (W) and the profit (Q) in Eq. (1.42) have the opposite sign.
- (1) → (4): The apple farmer goes to the market. The money in his pocket does not change, ($\Delta S = 0$).
- (4) → (3): At the market the apple farmer collects ($\Delta S < 0$) money from the customers.
- (3) → (2): The apple farmer returns home without spending the money in his pocket, ($\Delta S = 0$).
- (2) → (1): At home the apple farmer distributes ($\Delta S < 0$) part of the money to the apple pickers.

Income (Y), costs (C) and profits (ΔQ) of labor are determined by

$$Y = E + T_2(S_4 - S_3) \quad (1.43)$$

$$C = E + T_1(S_2 - S_1) \quad (1.44)$$

$$\Delta Q = Y - C = \Delta T \Delta S \quad (1.45)$$

$\Delta Q = Y - C$ is the profit given by the enclosed area of Fig. 13. The materials (E) are the same in production and consumption and do not enter the calculations in a closed cycle. The Carnot process is the basis of all economic processes and will now be discussed in more detail. In economics every company, bank, and every person is a Carnot-like machine. In thermodynamics every motor and energy generator is a Carnot-like machine. In biology every living cell is a Carnot-like machine. The Carnot process is the common mechanism in economics, thermodynamics and biology.

1.7.2

The Origin of Growth and Wealth

What is the mechanism of economic interaction? If a baker sells bread to his customers, where does the wealth come from? From his work? From his customers?

If buyers and sellers just exchange values, there is no change in wealth and nobody will become richer. Since people make profit and do get rich by economic interactions, agents must take it from somewhere. If one agent takes it from the other agent, there will be no economic transactions, nobody wants to go to a market where he gets robbed.

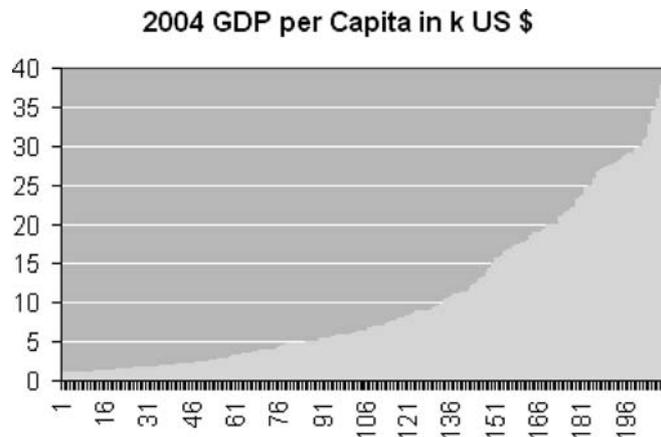


Fig. 1.14 shows the world GDP per capita in US\$ for all countries in 2004. South Asian countries have the lowest and North America the highest GDP per capita.

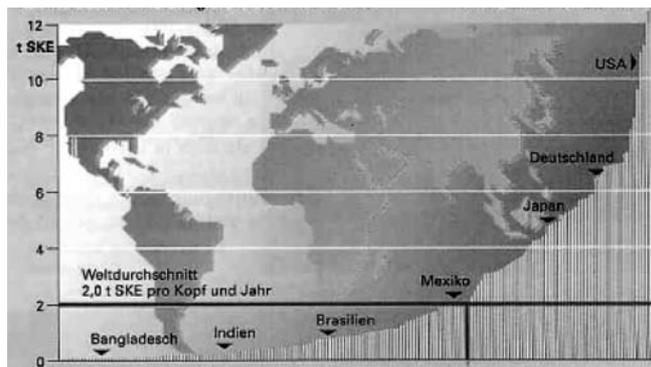


Fig. 1.15 shows the energy consumption in tons of coal in 122 countries in 1991. South Asian countries have the lowest and North America the highest energy consumption. (UN Statistical Yearbook 1991). The shape of the functions in Figs 1.14 and 1.15 are very similar and correspond to nearly the same countries.

The answer is the Carnot process. A heat pump extracts heat from a cold river and heats up a warm house. A bank may extract capital from poor savers and give it to rich investors. Economic interaction of two partners is only possible by exploitation of a third party due to clever manipulation (work). The most common objects of exploitation are natural resources, the environment and common property like water, air, coal and oil. A motor runs on oil, industrial production also runs on oil. Figure 1.14 and 1.15 show the world distribution of wealth (GDP per capita) and the world energy consumption per capita. Both run nearly parallel in all countries. This shows indeed that

all wealth comes from exploitation. And this is not only true for the first person in the economic chain (like miners and farmers), but for everybody in the economic chain who wants to make a profit.

1.7.3

World Trade Mechanism

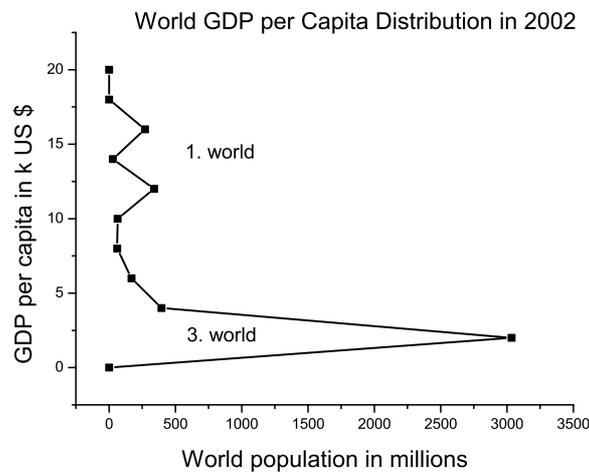


Fig. 1.16 shows the distribution of wealth in the world (CIA World Factbook, USA, 2004). The number of people in different income classes is given by the gross domestic product (GDP) per person. The distribution is clearly divided into two parts. The majority of people (about three billion) in the “third world” live below or close to 2 000 US\$ per person.

The minority of about one billion people in the “first world” have an income between 12 000 and 15 000 US\$ per capita. (The gap at 14 000 US\$ per capita is an artifact and due to US–EU currency fluctuations.) About two billion people, the “second world” live in between the two extremes.

Machines like motors or heat pumps always require or create two different temperatures (T). Inside the motor it is hot and therefore it needs water or air cooling outside. The heat pump works with a cold river and a warm house, the refrigerator has a cold inside and a warm outside. This difference in temperatures is necessary to make the Carnot process work. The areas of different temperatures have to be separated. If the door of the refrigerator stays open, it will not work, the efficiency is $r = 0$.

In all economic systems, work (W) according to the Carnot process always creates two different price or income levels (T). Buying and selling must create two price levels, otherwise there is no reason to do business. But also within a country, production (W) will create poor workers and rich capitalists.

The two-level system is also observed in the world distribution of wealth. Figure 1.16 shows the GDP distribution of the world and the corresponding number of people. The wealth of nations is clearly divided into two parts. In the “third world” more than three billion people live below or close to a GDP of 2 000 US\$ per capita (1995). And in the “first world” about one billion people live between 12 000 and 16 000 US\$ per capita. (The small dip at 14 000 US\$ per capita is more or less artificial and due to fluctuations of the US\$ and EU currencies.)

The Carnot process will stabilize the two different standards of living in the world population. The lower standard will grow with time, but also the difference will grow in order to enhance the efficiency. But the distribution of countries does not have to stay that way for ever. Some countries like China and India will emerge from the bottom and come closer to the top after a decade or two. Some richer countries may stay in the same position or even drop their standard of living. This will be discussed in Section 1.8 on the economic growth of interdependent systems.

1.7.4

Returns

Profits $\Delta Q = \Delta T \Delta S$ rise with the difference in price and costs ΔT of the product. The ideal efficiency of production in Eq. (1.16) may now be given by

$$r = \frac{Y - C}{C} = \frac{T_2 - T_1}{T_1} \quad (1.46)$$

Example: Dutch Importation of furniture from Indonesia

The GDP per capita in Holland and Indonesia are

$$T_{\text{Holland}} = 12\,000 \text{ US\$ per capita and}$$

$$T_{\text{Indonesia}} = 3\,000 \text{ US\$ per capita.}$$

Importing local commodities like furniture from Indonesia to Holland leads to an (ideal) efficiency

$$r = (12\,000 - 3\,000)/3\,000 = 3 \text{ or } 300\%.$$

Returns are ideally independent of the type of commodity. The efficiency is determined only by the difference in the standard of living ΔT .

The difference in complexity ΔS does not appear in efficiency calculations. For this reason the entropy function (S) has little importance in macro economics. However, in micro economics, the entropy (S) is linked to the prob-

ability (P) of the system. This is important for stock markets. A high entropy difference ΔS indicates a high probability of continuity or security of a share. A company with simple products may quickly be replaced. A company with complex products will last longer. Production (ΔW) creates a certain area $\Delta T\Delta S$, Fig. 1.13. The area with a large ΔT and a small ΔS will be highly efficient but less secure. A large ΔS and a small ΔT indicates that this company creates complex products with less efficiency and high security. The area $\Delta T\Delta S$ is determined by the work invested in the product. The shape of the area indicates whether a share is speculative and (perhaps) profitable or secure and less profitable. The optimum for a portfolio of stocks may be a nearly square area $\Delta T\Delta S$ with medium efficiency and medium security.

1.8

Dynamics of Production: Economic Growth

1.8.1

Two Interdependent Systems: Industry and Households

The dynamics of economic systems is again based on the Carnot process. So far all equations have been static, as in the thermodynamic formulation of economics the first and second laws do not contain time. But the length of a Carnot cycle is a natural time scale; a day, a month or a year. Economic growth may be handled like a starting motor. Both the inside and outside of the motor will get warmer, depending on how the heat is distributed. In economic systems the profit of each cycle has to be divided between the two sides of the production cycle, Y and C . If the lower level (C) gets the share “ p ” and the higher level (Y) the share $(1 - p)$ of the profit (ΔQ), we obtain:

$$dY_1 = p\Delta Q dt \quad (1.47)$$

$$dY_2 = (1 - p)\Delta Q dt \quad (1.48)$$

$$\Delta Q = Y_2 - Y_1 \quad (1.49)$$

The solution of this set of differential equations is:

$$Y_1(t) = Y_0 + p[Y_{20} - Y_{10}][\exp(\alpha t) - 1] \quad (1.50)$$

$$Y_2(t) = Y_{20} + (1 - p)[Y_{20} - Y_{10}][\exp(\alpha t) - 1] \quad (1.51)$$

with

$$\alpha = (1 - 2p) \quad (1.52)$$

According to Eqs (1.47)–(1.52) a rising standard of living (Y) in two interdependent economic systems is determined by the share of the profit “ p ” of the group at the lower level (Y_1). The results are shown in Figs 1.17–1.22.

1. $p = 0$; Fig. 1.17. If all profit goes to the richer party (Y_2), the standard of living of group (2) will grow exponentially, the standard of living of the first party stays constant, (Y_{10}).
2. $p = 0.25$; Fig. 1.17. at 25% of the profit for the poorer party (Y_1) and 75% for the rich party (Y_2) both parties will grow exponentially. Examples are Japan and Germany after World War II, both economies were depending on the US and were growing exponentially, this is indicated in Fig. 1.18.
3. $p = 0.50$; Fig. 1.17. An even split between the two parties leads to a linear growth of both parties. The efficiency of the interaction is reduced with time.
4. $p = 0.75$; Fig. 1.19. The growth of both parties is leveling off not much above the initial standard of living. An example is the present US–Japanese economic relationship; both economies are close to each other without much economic growth, as shown in Fig. 1.20.
5. $p = 1.00$; Fig. 1.19. If all profit goes to the poor side, the standard of living of the poor party soon reaches the constant standard of living of the rich party.
6. $p = 1.25$; Fig. 1.21. If more than 100% of the profit goes to the poor party, (Y_2) will decrease, and (Y_1) will catch up with (Y_2). This has been observed in the relationship of West and East Germany after reunion in 1990, Fig. 1.22.

The data in Figs 1.17–1.22 can only indicate the results of Eqs (1.47)–(1.52), as all countries also have other (less important) interactions with other countries. The results may also be applied to other binary interactive economic systems like industry and households, or in trade. For industries and households the distribution of profit p is determined by the interacting agents of unions and industry, whereas in trade we have buyer and seller. This is now discussed in more detail.

1.8.2

Linear and Exponential Growth ($0 < p < 0.5$)

Figure 1.17 shows the problem of unions and industry in more detail. Unions tend to ask for high raises in payments, industry urges to invest the profits. Indeed, the fair deal, a split of profits 50:50 between workers and industry (dashed line) in Fig. 1.17 is not the best deal and will only result in linear growth. Workers and industry are much better off in a deal where 90% of the profits are reinvested (solid lines). Low increase in wages will lead to exponential growth for industry and later for workers as well. But workers

(as well as their managers) will have to be more patient with pay raises, as in Germany or Japan after World War II, Fig. 1.18.

1.8.3

Trailing Economies: USA and Japan ($0.5 < p < 1$)

The opposite picture is shown in Fig. 1.19. A high factor p leads to decreasing efficiency, (Y_1) is trailing a decreasing (Y_2). After Japan and Germany have acquired many production plants, the factor p has grown and the efficiency of the exports has started to decrease. In Fig. 1.20 the economic level (Y_1) of Japan is now trailing the slowly decreasing level (Y_2) of the USA.

1.8.4

Converging Economies, West and East Germany ($p > 1$)

If the poor side (Y_1) profits very much, $p = pN_1/(N_1 + N_2) > 1$, both parties will converge, as shown in Fig. 1.21. This happened during the reunification of West and East Germany, Fig. 1.22. The standard of living in East Germany grew by 100% within six years, as the standard of living in West Germany was declining. The economic levels (Y_1) and (Y_2) in East and West Germany have nearly converged and differ now, after more than 15 years, by only 20%.

1.9

Conclusion

In the thermodynamic formulation of economics, the laws of markets and societies have been derived from calculus and statistical laws. No further assumptions have been used to derive the laws of economics. The calculated functions are supported by data, which all seem to agree very well. Many arguments indicate that the thermodynamic formulation of economics is a very general approach, which fits the data very well and explains economics and economic growth on the basis of natural science.

However, economic interactions are not only governed by statistical laws. Many economic interactions are restricted by traditional customs, civil laws or by agreements between trading partners. These additional laws will influence the interactions of free economic agents. How will they affect the results above? This will be discussed in more detail in the chapter on "The Thermodynamic Formulation of Social Science".

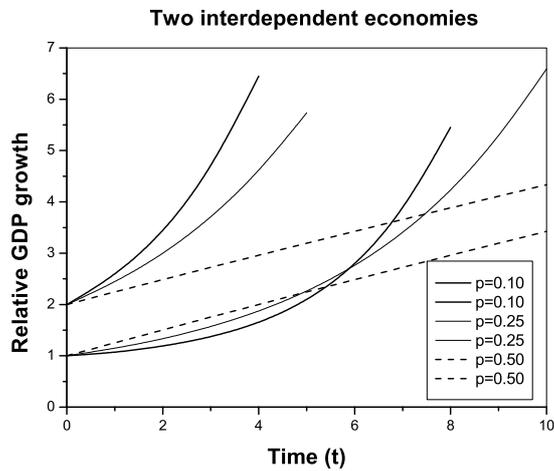


Fig. 1.17 The development of the standard of living of two interdependent economic systems starting at $Y_1 = 1$ and $Y_2 = 2$. The profit for the poor side varies from $p = 0.10$ to $p = 0.40$. After some time the standard of living of workers (Y_1) will grow with a lower pay raise p !!

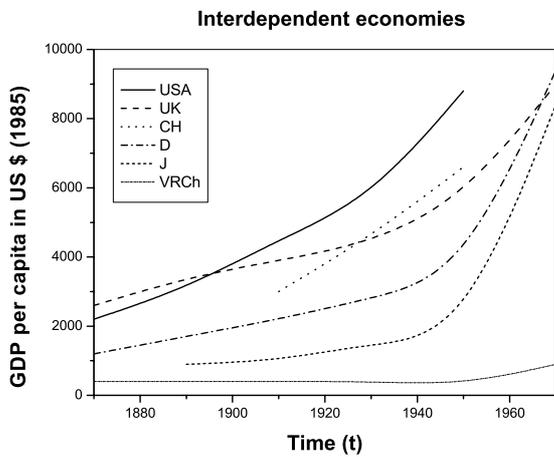


Fig. 1.18 Economic growth of US, UK, Switzerland, Japan, Germany and China between 1870 and 1990. The victorious allies USA and UK have grown exponentially. Japan and Germany only started to grow exponentially after World War II by international trade at low wages. China was excluded and did not take part in economic growth at that stage.

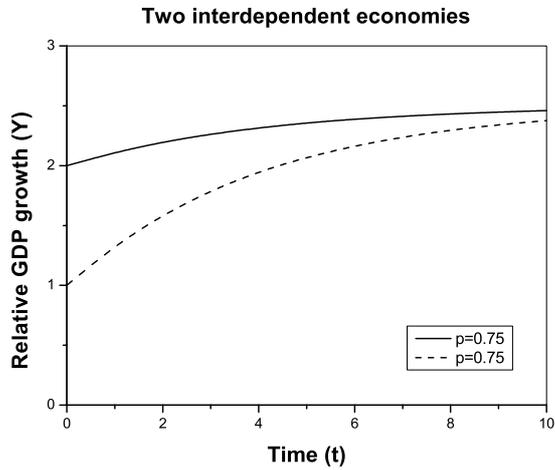


Fig. 1.19 The development of the standard of living of two interdependent economic systems starting at $Y_1 = 1$ and $Y_2 = 2$. At high values of profit for the poor side, $p = 0.75$, economic growth is declining with time.

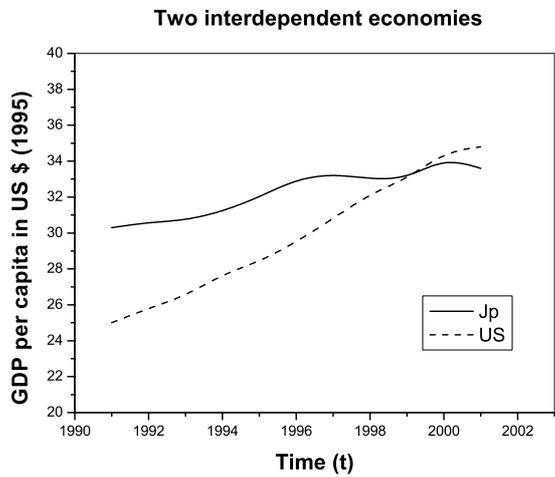


Fig. 1.20 The development of the standard of living (GDP/person) of the USA and Japan in quarters between 1980 and 2000. The interdependent economic systems are declining with time.

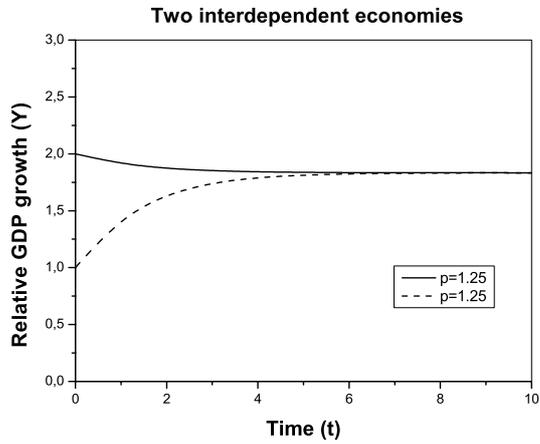


Fig. 1.21 The development of the standard of living of two interdependent economic systems starting at $Y_1 = 1$ and $Y_2 = 2$. At very high values of profit for the poor side, $p > 1$ both economies will converge below $Y_2 = 2$.

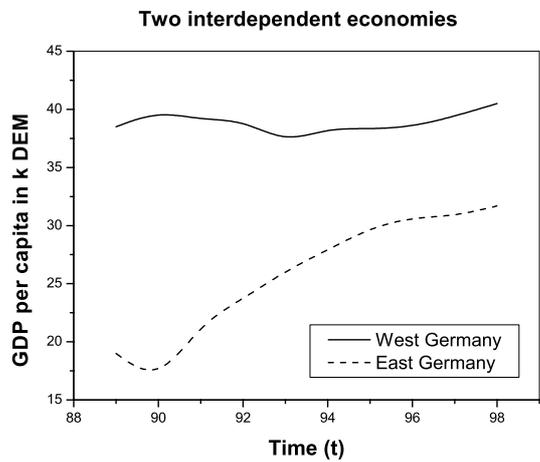


Fig. 1.22 Real standard of living in West and Germany between 1989 and 1998 due to productivity and capital transfer. In 1998 East Germany reached about 80% of the living standard in West Germany.

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