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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, $\eta_K=1-\sqrt{(T_2/T_1)}$, 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]

$$\mathrm{d}L=\zeta F(T)\mathrm{d}T \qquad (1)$$

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]

$$\mathrm{d}L=\zeta\mathrm{d}T \qquad (2)$$

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 thr following relation

$$\mathrm{d}L_w=J\mathrm{d}Q \qquad (3)$$

The temperature independent universal conversion factor (J~4.185 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

$$\mathrm{d}(\zeta T)=J\mathrm{d}Q \qquad (4)$$

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:

$$L=(\zeta+\Delta\zeta)(T–T_2) \qquad (5a)$$

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

$$T(\zeta+\Delta\zeta)=T_1\zeta \qquad (5b)$$

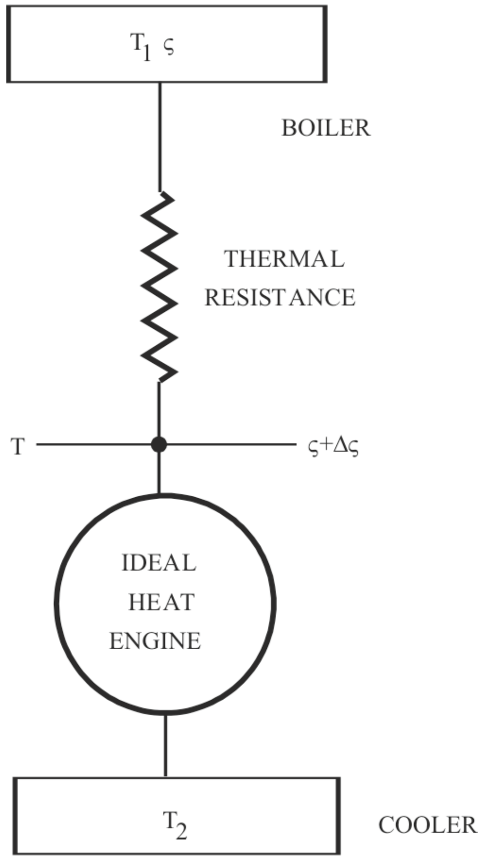

Fig. 1 Simplified outline of a real heat engine

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

$$L^u=k(T_1–T)(T–T_2)/T \qquad (6)$$

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

$$\eta_C=T_1\{1–\sqrt{(T_2/T_1)}\} \qquad (7)$$

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].

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References

1 J. A. Comenius, Physicae Synopsis, Leipzig 1633.
2 J. A. Comenius, Disquisitiones de Caloris et Frigoris Natura, Amsterdam, 1659.
3 J. Šesták and J. J. Mareš, J. Therm. Anal. Cal., 88 (2007) 764.
4 J. Šesták, Heat, Thermal Analysis and Society, Nukleus, Hradec Králové 2004.
5 R. Fox, The Caloric Theory of Gases, Claredon Press, Oxford 1971.
6 S.G. Brush, Kind of Motion we call Heat, Vol. I and II, North Holand, Amsterdam 1976.
7 I. Proks, Evaluation of the Knowledge of Phase Equilibria in Kinetic Phase Diagrams, (Z. Chvoj, J. Šesták and A.Tříska, Eds) Elsevier, Amsterdam 1991, p. 1.
8 J. Šesták, Science of Heat and Thermophysical Studies: a generalized approach to thermal analysis, Elsevier, Amsterdam 2005.
9 J. J. Mareš, J. Therm. Anal. Cal., 60 (2000) 1081.
10 G. Job, Neudarstellung der Wärmelehre – Die Entropie als Wärme, Akad. Verlagsges., Frankfurt am Main 1972.
11 P. Kelland, Theory of Heat, Cambridge 1837.
12 R. Clausius, Mechanische Wärmetheorie, Viewg und Sohn, Braunschweig 1876.
13 H. B. Callen, Thermodynamics: an introduction to the physical theories of equilibrium thermostatics and irreversible thermodynamics, Wiley, New York 1960.
14 J. J. Mareš, J. Šesták, V. Špička, P. Hubík and J. Krištofik, Key lecture, Phenomenological Approach to the Caloric Theory of Heat, Int. Seminary on Calorimetry in Medlov, Proc. by Universita Pardubice (Z. Černošek and E. Černoškova, Eds), Pardubice 2007, p. 43.
15 J. J. Mareš, P. Hubík, J. Šesták, V. Špička, J. Krištofik and J. Stávek, Thermochim. Acta, 474 (2008) 16.
16 J. J. Mareš, J. Šesták, V. Špička, P. Hubík and J. Krištofik, Key lecture, Temperature transformation and Mosengeil-Ott's antinomy, Int. Conf. Frontiers of Quantum and Mesoscopic Thermodynamics, Prague 2008, Book of Abstracts, p. 81.
17 I. Proks, Lazare and Sadi Carnots, in Personalities of Historical Thermodynamics, (J. J. Mareš and J. Šesták, Eds), Slovak Academy of Sciences, Bratislava 2009.
18 R. B. Lindsey, Energy: historical development of the concept, Dowden, Stroudburg 1975.
19 C. C. Gillipsie, Lazare Carnot Savant, Princeton University Press, New York 1971.
20 L. Carnot, Principes fondamentaux d'équilibre et du mouvement, Paris 1803.
21 L. Carnot, Course de mathématique, géométrie et application de l'algebra à la géométrie, Paris 1800 and Géométrie de position, Paris 1803.
22 W. J. M. Rankine, Phil Mag., 5 (1853) 106.
23 J. V. Poncelet, Traité de mécanique appliqué aux machines, Bruxelles 1845.
24 D. S. L. Cardwell, From Watt to Clausius, Cornel University Press, New York 1971.
25 M. J. Klein, Physics Today, 27 (1974) 23.
26 J. B. J. Fourier, Théorie analytique de la chaleur, Paris 1822.
27 S. Carnot, Réflexions sur la puissance motrice du feu et sur les machines propres à développer cette puissance, Bachelier, Paris 1824, German translation: Ostwald's Klassiker, Nr. 37, Engelmann, Leipzig 1909.
28 H. L. Callendar, Proc. Phys. Soc. London, 23 (1911) 153.
29 F. L. Curzon and B. Ahlborn, Am. J. Phys., 43 (1975) 22.

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