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A. PAGLIETTI

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On the mathematical formulation of the first principle of thermodynamics for non-uniform temperature processes

by

A. PAGLIETTI
Istituto di Scienza delle Costruzioni, Università di Cagliari, Italia

ABSTRACT. — In a system at non-uniform temperature some of the heat which flows from hotter regions to colder ones can produce non-thermal energy, quite apart from whether the system undergoes changes in its state or not. In this paper a general mathematical formulation of the first principle of thermodynamics is given which takes account explicitly of the non-thermal energy originating from the heat flow. Moreover, some restrictions imposed by the second principle of thermodynamics on this production of non-thermal energy are determined. Once the present formulation is adopted, it is shown that the energy of an amount of calories in motion in a non-uniform temperature field cannot be obtained simply by multiplying the number of calories times the Joule's equivalent of heat. An explicit expression of this energy is deduced for steady-state situation. Finally, the consequences of the proposed formulation on heat conduction problems are discussed, and some experimental evidence is given in support of the present approach.

RÉSUMÉ. — Dans un système à température non uniforme une partie de la chaleur qui s'écoule de zones plus chaudes à des zones plus froides peut produire de l'énergie non calorifique, même lorsque le système ne subit pas de changements d'état. Dans cet article on donne une formulation mathématique générale du premier principe de la thermodynamique qui tient compte de l'énergie non calorifique produite par le flux de chaleur. On détermine en outre certaines restrictions que le deuxième principe de la thermodynamique impose à cette production d'énergie non calorifique. Une fois que la présente formulation est adoptée, on montre que l'énergie

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d'un nombre de calories en mouvement dans un champ de température non uniforme ne peut pas être calculée en multipliant le nombre de calories par l'équivalent mécanique de Joule. On déduit d'ailleurs une expression explicite pour calculer cette énergie dans des situations stationnaires. On discute enfin les conséquences de la présente formulation sur le problème de conduction de chaleur et on donne un appui expérimental à l'approche présentée.

1. INTRODUCTION

When heat is transferred from a system R_1 at higher temperature to a system R_2 at lower temperature it can partially be transformed into non-thermal energy. The second principle of thermodynamics sets an upper bound L_{max} to the amount of non-thermal power which can thus be obtained. This bound is determined by Carnot's theorem according to the relation

$$L_{max} = Q\frac{\theta_1 - \theta_2}{\theta_1} \tag{1.1}$$

Here Q denotes the amount of heat per unit time lost by R_1, while θ_1 and θ_2 denote respectively the absolute temperatures of R_1 and R_2. As it is well-known, the above limitation refers to the case in which the transfer of heat from R_1 to R_2 does not produce any final change in the state of the medium through which it occurs. It is known, moreover, that although the classic proof of Carnot's theorem is based on considerations on ideal engines performing ideal cycles, it does not exclude that the same amount of non-thermal energy L_{max} can also be obtained as a result of a heat transformation process occurring in a system which does not contain any ideal engines. The system, however, must undergo a process in which all the heat absorbed is taken from the reservoir at higher temperature, while all the heat rejected is given up to the reservoir at lower temperature. For the validity of the limitation expressed by (1.1), of course, the process must not produce any final change in the system in which it takes place.

Carnot's theorem applies in particular when the transformation of heat into non-thermal energy occurs in a medium whose state remains unaltered during the whole heat transfer process. This is the case, for instance of a thermocouple whose ends are kept at constant different temperatures while the electric current produced in it is exploited to drive an electric engine. Once a steady-state condition is reached, the state of the thermocouple does not vary in time and all the produced electric energy originates from the heat which flows from the hotter end of the thermocouple to the colder one. The amount of non-thermal power so obtained cannot exceed the value (1.1). In this case θ_1 and θ_2 are the absolute temperatures of the ends of the thermocouple, while Q is the amount of heat lost per unit time by the reservoir connected with the end of the thermocouple at temperature θ_1.

In a system at non-uniform temperature there is always a flow of heat from hotter regions to colder ones. Consequently, in any element of the system where the temperature gradient does not vanish there can be transformations of heat into non-thermal energy; quite apart from whether the element undergoes changes in its state, or not. The aim of the present paper is to express the first principle of thermodynamics in a general form which accounts explicitly such a possibility and to find out the restrictions imposed on this expression by the second principle of thermodynamics. The analysis which follows should show that some conclusions, rather different from the standard ones, can in this way be obtained.

In the next section, after a review of the notions of state and process, the first principle of thermodynamics will be expressed in a global form that allows explicitly for the transformations of heat into non-thermal energy which do not entail changes in the state variables of the system. It will be apparent, however, that the proposed approach is more likely to yield non-trivial results if it is applied to systems at non-uniform temperature. These systems can be better studied by expressing the first principle of thermodynamics in a local form.

A general mathematical expression for the local form of the first principle of thermodynamics will be given in Section 4. Before doing this, however, it will be necessary to express the energy carried by the heat flux vector without introducing, *ab initio*, hypotheses that are strictly valid only for systems at uniform temperature. This expression will be proposed in Section 3. In Section 5 the limitations entailed by the second principle of thermodynamics on the term representing the local production of non-thermal energy due to the heat flow, will be derived. Also, an explicit expression for this term will be given which is valid when steady-state situations are considered.

In Section 6 the energy carried by an amount of heat in motion through a stationary non-uniform temperature field will be determined. This energy will be shown to be quite different from the one assumed by the classical theory. Finally, the possibility of an experimental check of the proposed theory and some experimental results already available will be discussed in Section 7.

2. GLOBAL EXPRESSION OF THE FIRST PRINCIPLE OF THERMODYNAMICS

From a macroscopic standpoint a system can be described by means of a set $\{ \underset{\sim}{\xi}^{(i)} \}$ of variables that are supposed to be sufficient to define its kinematical, physical and chemical situation. A set of values for the variables $\underset{\sim}{\xi}^{(i)}$ defines a *state* of the system. Accordingly, the variables $\underset{\sim}{\xi}^{(i)}$ themselves can be referred to as the *state variables* of the system. A *process* is an ordered succession of states. As discussed in [*10*, § 2] the notion of state in the broad sense given above is helpful when systems undergoing non-homogeneous and/or non-equilibrium processes are considered.

Throughout this paper, reference will be made to systems which do not exchange matter with their surroundings. For these systems the general expression of the energy conservation principle is given by the equation

$$\dot{K} + \dot{E} = W_T + Q \tag{2.1}$$

Here K denotes the kinetic energy of the system, E its internal energy while W_T and Q are respectively the total amount of non-thermal energy and the total amount of thermal energy absorbed per unit time by the system. The quantity W_T will also be referred to as the *total non-thermal power*.

Work can be done on a system either by mechanic forces or by non-mechanic (e. g. electric, magnetic, chemical, etc.) ones. Let W denote the power of all the forces acting on the system. It is customary to express W as an appropriate sum of products of intensive quantities $\underset{\sim}{F}^{(k)}$ *(generalised forces)* times the time-rate of extensive quantities $\underset{\sim}{s}^{(k)}$ *(generalised displacements)*. For homogeneous processes, therefore, W can be expressed as

$$W = \Sigma_k \underset{\sim}{F}^{(k)} . \dot{\underset{\sim}{S}}^{(k)} \tag{2.2}$$

When non-homogeneous processes are considered, $\underset{\sim}{F}^{(k)}$ and $\underset{\sim}{S}^{(k)}$ are not constant over the system. In this case the expression of W analogous to (2.2) is

$$W = \int_B w dV = \int_B \Sigma_k \underset{\sim}{F}^{(k)} . \dot{\bar{\underset{\sim}{S}}}^{(k)} dV \tag{2.3}$$

In this equation w denotes the specific power per unit volume, $\bar{\underset{\sim}{S}}^{(k)}$ is the specific generalised displacement per unit volume and the letter B appended to the integrals denotes integration over all the system. Explicit expression for $\underset{\sim}{F}^{(k)}$ and $\underset{\sim}{S}^{(k)}$ relevant to the more important thermodynamic systems are given in many textbooks, and in particular in the excellent treatises by Fast [*8*] and by Zemansky [7].

From the previous definition of state it follows that any change in an extensive quantity of a system entails a change in the state of the system. This implies that the quantities $\dot{\underset{\sim}{S}}^{(k)}$ and $\dot{\bar{\underset{\sim}{S}}}^{(k)}$ can be expressed in the form

$$\dot{\underset{\sim}{S}}^{(k)} = \Sigma_i A_i^{(k)} \dot{\underset{\sim}{\xi}}^{(i)} \qquad \text{and} \qquad \dot{\bar{\underset{\sim}{S}}}^{(k)} = \Sigma_i \bar{A}_i^{(k)} \dot{\underset{\sim}{\xi}}^{(i)}.$$

Equations (2.2) and (2.3) can, therefore, be read as

$$W = \Sigma_i \underset{\sim}{F}'^{(i)} . \dot{\underset{\sim}{\xi}}^{(i)} \tag{2.4}$$

and

$$W = \int_B w dV = \int_B \Sigma_i \underset{\sim}{\bar{F}}'^{(i)} . \dot{\xi}^{(i)} dV, \tag{2.5}$$

respectively. The quantities $\underset{\sim}{F}'^{(i)}$ and $\underset{\sim}{\bar{F}}'^{(i)}$ which appear in these equations are defined by $\underset{\sim}{F}'^{(i)} = \Sigma_k \underset{\sim}{F}^{(k)} A_i^{(k)}$ and $\underset{\sim}{\bar{F}}'^{(i)} = \Sigma_k \underset{\sim}{F}^{(k)} \bar{A}_i^{(k)}$. It should be clear that $\underset{\sim}{F}^{(k)}$, $A_i^{(k)}$ and $\bar{A}_i^{(k)}$, and hence $\underset{\sim}{F}'^{(i)}$ and $\underset{\sim}{\bar{F}}'^{(i)}$ are in general functions of the state variables of the system, of time and of the point of the system to which they are referred. It is not excluded, of course, that for certain systems some of the $A_i^{(k)}$ and $\bar{A}_i^{(k)}$ may possibly vanish identically.

The procedure usually followed in thermodynamics sets

$$W_T \equiv W \tag{2.6}$$

Once this relation is introduced, equation (2.1) becomes

$$\dot{K} + \dot{E} = W + Q. \tag{2.7}$$

It is found, however, that equations (2.6) and (2.7) cannot be valid in general. There are indeed situations in which non-thermal energy can be supplied or absorbed by a system even if $W \equiv 0$. In this case the total non-thermal power W_T cannot coincide with W and, therefore, equations (2.6) and (2.7) do not hold. To quote one of the many instances in which $W_T \neq W$, let us refer again to the thermocouple in steady-state situation at non-uniform temperature considered in Section 1. In this case some of the heat which flows through the thermocouple is converted into electric energy which can be supplied by the thermocouple to the surroundings. Since the thermocouple is in a steady-state situation, no one of its state variables varies in time and, therefore, from (2.4) or (2.5) we get that $W \equiv 0$. However, the total non-thermal power W_T supplied by the thermocouple does not vanish; which is in contradiction with (2.6). As a matter of fact we have in this case that $W_T = Q \neq 0$, and this is perfectly consistent with the general equation (2.1), because in the present case $\dot{K} \equiv \dot{E} \equiv 0$.

Usually, in order to correct equation (2.7) when it fails to be true, appropriate additional terms are introduced. The actual expression of these terms varies from case to case. In any case the correct expression of the first principle of thermodynamics can be thought as given in the form

$$\dot{K} + \dot{E} = W + Q - P, \tag{2.8}$$

where the quantity P, defined by

$$P = W - W_T, \tag{2.9}$$

represents the energy per unit time which the system supplies to its surroundings without suffering any change in its state variables. Of course P can be either positive or negative. While a positive value of P denotes an amount of energy which leaves the system, a negative value of P represents an amount of energy absorbed by the system. Explicit expressions for P in terms of other quantities that can directly be determined by experiments can be given only when the system and the process it undergoes are specified. In principle, however, P can assume any expression consistent with equation (2.9) and, therefore, equation (2.8) is as general as equation (2.1). The former, however, is more suitable for the forthcoming analysis in that it distinguishes explicitly between the non-thermal energy exchanges which entail changes in the state variables of the system and the ones which do not.

It is important to emphasise that P can be greater than zero even when the system is in a steady-state situation, and hence $\dot{K} \equiv \dot{E} \equiv W \equiv 0$. This happens for instance in the above quoted example of a thermocouple in steady-state situation at non-uniform temperature. In this case the amount of non-thermal energy P supplied by the system equals Q and originates entirely from the transformation of the thermal energy absorbed by the system. Since every transformation of heat into non-thermal energy must meet the requirements imposed by the second principle, it follows that in similar circumstances the quantity P cannot be greater than the upper bound L_{max} given by (1.1), θ_1 and θ_2 being in this case the temperatures of the hotter point of the system and the one of the colder one. It should be apparent, therefore, that while there are no bounds to the negative values that P can assume, there are situations in which the second principle of thermodynamics sets limitations to the positive values of P.

As it follows from equation (1.1), no transformation of heat into non-thermal energy can occur in a system when its temperature is uniform and all its state variables are kept unaltered. It can be inferred, therefore, that in such a situation the quantity P must be less than or equal to zero. Since $\dot{E} \equiv \dot{K} \equiv W \equiv 0$ when the state variables of the system are kept unaltered, it follows from (2.8) that in the considered situation $Q = P \leq 0$. The case $Q = P < 0$ is relevant to a system which, while keeping unaltered its state, absorbs non-thermal energy from the surroundings and dissipates it into heat, which is then supplied to the surroundings. This is the case, for instance, of an electric conductor which in steady-state conditions in a non-uniform electric field transform into heat part of the energy carried by the electric current flowing through it.

While the actual expression of P in terms of other quantities characterising the system and the process it undergoes depends on the particular system and process considered, the limitations imposed on the positive values of P by the second principle of thermodynamics apply to every system and process. Since P can be greater than zero in systems at non-uniform temperature only, to find out the above limitations it will be convenient to express equation (2.8) in a local form. This will be done in Section 4. To achieve an adequate extent of generality, however, a preparatory discussion on the energy carried by the heat flux vector will now be introduced.

3. ON THE ENERGY OF THE HEAT FLUX VECTOR

Work and heat are different modes of energy transfer between a system and its surroundings. From the operational standpoint various equivalent definitions of heat and work can be given. Since every kind of work can entirely be used to lift weights, the definition of work usually adopted is that of a force times a distance. Heat, on the other hand, can always be used to raise the temperature of a body. By means of a calorimeter and by prescribing an appropriate experimental procedure, therefore, one can give an operational definition of heat as that entity which produces changes in the equilibrium temperature of the calorimeter. Moreover, a quantitative determination of the amount of heat can be obtained from measurements of temperature changes of the calorimeter. As it is well-known, from the above definitions of work and heat it is a straightforward matter to define the relevant units, such as the *joule* and the *calorie*.

From Joule's celebrated experiments on the equivalence of heat and work we know that for any system at any temperature one calorie is always equivalent to $\underline{J}$ units of work, $\underline{J}$ being a constant which is often referred to as the mechanical equivalent of the calorie or Joule's constant. Strictly speaking the above equivalence is valid only when reference is made to amounts of heat absorbed or supplied by systems at uniform temperature. Indeed, the experiments of Joule, as well as the analogous ones which were subsequantly devised to check the equivalence between heat and work, refer to system at uniform temperature (or, at least, to system whose temperature is uniform at the time in which the measurements are taken). To apply the first principle of thermodynamics to a system which is not in thermal equilibrium, however, one has to know what is the energy of an amount of heat in motion through the system owing to the non-vanishing temperature gradient field. The hypothesis which is currently, though implicitly, made is that the mechanical equivalent of a moving amount of heat is the same as the one determined by Joule's experiments. A direct experimental proof of the validity of this hypothesis is, however, lacking. Since the analysis of this paper will show that such a hypothesis cannot hold true in general, a different a more general hypothesis will be formulated in what follows.

Let $\underset{\sim}{q}^*$ denote that *total heat flux* vector at a generic point R of a system.

The vector $\underset{\sim}{q}^*$ is defined as being equal in magnitude to the number of calories which by radiation and by conduction cross per unit time an infinitesimal unitary area normal to the direction of the heat flow at R. The convention will be made, moreover, that the direction of $\underset{\sim}{q}^*$ is the same as that of the heat flow. Let dA denote an area element of a surface Σ belonging to the system and let $\underset{\sim}{n}$ be the outward oriented unit normal vector to dA. From the above definition of total heat flux vector and from the adopted convention on its direction it follows that the total amount of heat which per unit time flows through the area element dA into the space enclosed by Σ is given by

$$q^* dA = - \underset{\sim}{q}^* . n dA \qquad (3.1)$$

The quantity q^* defined by this equation will be referred to as the *total heat flow* per unit area relevant to the direction $\underset{\sim}{n}$. Of course, both q^* and $\underset{\sim}{q}^*$ vanish when no heat currents are present in the system.

Let $\theta = \widehat{\theta}(\underset{\sim}{X}; t)$ denote the temperature field of a system. Here $\underset{\sim}{X}$ is the position vector of the generic point of the system, while t is time. Since, as remarked before, the present experimental knowledge does not allow to draw any definite conclusion concerning the energy of an amount of heat in motion owing to a non-uniform temperature field, we shall introduce the somewhat general hypothesis that the energy e_q of q^* is given by

$$e_q = \widehat{f}[\widehat{\theta}(\underset{\sim}{X}; t)] q^* . \qquad (3.2)$$

The scalar-valued function $f = \widehat{f}[\widehat{\theta}]$ which appears in this equation is a function of the temperature field $\widehat{\theta}(\underset{\sim}{X}; t)$. It is a positive-valued function and it can be measured in joule over calorie. Its explicit expression should be determined by appropriate experimental and theoretical considerations. For the time being, however, the function $\widehat{f}[\widehat{\theta}]$ will be left undefined. Later on it will be found that when steady-state non-uniform temperature fields are considered, the function $\widehat{f}[\widehat{\theta}]$ must have the form

$$f = \widehat{f}[\widehat{\theta}] = A\theta^2, \qquad (3.3)$$

where A is a constant. In more general situations the quantity f may be a function both of θ and of its derivatives with respect to $\underset{\sim}{X}$ and t. No attempt will be made, however, to determine the general expression of the function $\widehat{f}[\widehat{\theta}]$, since this would be far beyond the scope of the present paper.

Although the quantity f represents a mechanical equivalent of heat, equation (3.2) should not be interpreted as a generalisation of the classical result of Joule. The latter refers to amounts of heat absorbed or lost by systems at uniform temperature, while equation (3.2) refers to amounts of heat in motion in non-uniform temperature fields. Equation (3.2) cannot contain as a particular case the result of Joule, since for systems at uniform temperature $\underset{\sim}{q}^*$ and hence q^* vanish. Instead, equation (3.2) should be interpreted as a statement—complementing that of Joule—which applies in situations of non-thermal equilibrium and, thus, outside the range of applicability of Joule's result.

From equations (3.1) and (3.2) a *thermal energy flux* vector e_q relevant to the heat flux vector $\underset{\sim}{q}^*$ can be defined by the relation

$$\underset{\sim}{e}_q = \widehat{f}[\widehat{\theta}]\underset{\sim}{q}^* \tag{3.4}$$

From this definition it follows that the vector $\underset{\sim}{e}_q$ has the same direction as the vector $\underset{\sim}{q}^*$ and that its modulus equals the amount of thermal energy which per unit time crosses the infinitesimal unitary area which is orthogonal to the heat flow at the point to which the vector $\underset{\sim}{q}^*$ is referred.

4. LOCAL EXPRESSION OF THE FIRST PRINCIPLE OF THERMODYNAMICS

To deal with non-homogeneous processes and/or non-homogeneous systems a local expression of the first principle of thermodynamics is needed. This expression is usually derived from (2.7) by introducing appropriate smoothness hypotheses on the quantities appearing there and by applying a standard analytical procedure. Once the equation of balance of momentum and that of balance of moment of momentum are exploited, the above procedure leads to the conclusion that for any volume element the following energy balance equation

$$\rho\dot{\varepsilon} = w - \operatorname{div} \underset{\sim}{q}^* \tag{4.1}$$

must be valid. This equation is commonly regarded as expressing in local form the first principle of thermodynamics in many practical situations. The quantities ρ, ε and w appearing in it are respectively the mass density, the specific internal energy per unit mass and the work per unit time and per unit volume performed by the surface forces acting on the volume element to which equation (4.1) is referred. The validity of the following equations

$$\mathrm{E} = \int_v \rho\dot{\varepsilon} d\mathrm{V} \quad \text{and} \quad \mathrm{W} = \int_v w d\mathrm{V} \tag{4.2}$$

is of course, assumed; V being the volume occupied by the system. The latter will be supposed to be bounded by a closed surface ∂V.

A clear exposition of the usual procedure to derive equation (4.1) from equation (2.7) can be found, though for a more particular case than the one considered here, in [*6*, Chap. 12]. Its generalisation to the more general systems considered here is straightforward. In continuum mechanics the term div $\underset{\sim}{q}^*$ appearing in (4.1) is often expressed as div $\underset{\sim}{q} + \rho s$, where $\underset{\sim}{q}$ is the heating conduction vector while s is the radiation heat supply per unit time and per unit mass. Such a notation is obviously equivalent to the more compact one adopted here.

Equation (4.1) relies upon equation (2.7), which as pointed out in Section 2 may not hold true when systems at non-uniform temperature are considered. Moreover, to derive equation (4.1) the assumption must be made that the energy of an amount of heat in motion owing to a non-uniform temperature field is the same as that of the same amount of heat when it is absorbed or lost by a system at uniform temperature. Only if this assumption is valid can the total amount of thermal energy per unit time Q be expressed as

$$Q = -\int_{\partial v} \underset{\sim}{q}^* . \underset{\sim}{n} dA = -\int_v \text{div}\, \underset{\sim}{q}^* dV, \tag{4.3}$$

and thus can equation (4.1) be derived from (2.7). However, under the more general hypothesis introduced in Section 3, the energy flux relevant to the heat flux $\underset{\sim}{q}^*$ is given by (3.4). Therefore, the following equation

$$Q = -\int_{\partial v} \underset{\sim}{e}_q . \underset{\sim}{n} dA = -\int_v \text{div}\, (f\underset{\sim}{q}^*) dV \tag{4.4}$$

should be introduced instead of (4.3). The negative sign which appears before the integrals in (4.3) and (4.4) is a consequence of the adopted conventions for the sign of Q and the direction of $\underset{\sim}{q}^*$.

To find a local expression for the first principle of thermodynamics which is valid in general, let us start from equation (2.8) and observe that since P is an extensive quantity it can be expressed as

$$P = \int_v p dV, \tag{4.5}$$

where p is the specific value of P per unit volume. The physical meaning of p is, of course, analogous to that of P. It represents the amount of energy per unit time and per unit volume which the element supplies to its surroundings without suffering changes in its state variables. Analogously to what has been observed for P, the quantity p can be expressed as a function of other quantities characterising the system and the processes it undergoes, when system and process are specified. Moreover, at a point of a system the quantity p can be greater than zero, only if the temperature gradient at that point does not vanish.

It will henceforth be assumed that in the domain V the quantity p is a continuous function of the points of the system. This hypothesis is consistent with the analogous one generally adopted for $\dot{\varepsilon}$ and does not imply any serious restriction. By introducing equations (4.5) and (4.4) in equation (2.8) and by following the same procedure as that adopted to derive (4.1) from (2.7), the following equation can easily be obtained

$$\rho\dot{\varepsilon} = w - \operatorname{div}(f\underset{\sim}{q}^*) - p \tag{4.6}$$

This equation will be regarded as the general expression of the first principle of thermodynamics in local form.

5. UPPER BOUNDS TO THE VALUES OF p AND P

Since a positive value of p represents an amount of non-thermal energy produced in an element as a result of the transformation of part of the heat flowing through the element, it cannot exceed the limits imposed by the second principle of thermodynamics. To determine these limits let us consider an infinitesimal volume element dV at a generic point R of a system at non-uniform temperature. The shape of this element will be defined in the following way. Its lateral surface is a portion of tube of flux of infinitesimal cross-section relevant to the vector field $\underset{\sim}{q}^*$. On the other hand, the bases of dV are two infinitesimal area elements dA and dA′ resulting from the intersection of the above tube of flux with two isothermal surfaces at infinitesimal distance dx from each other. The absolute temperature of these surfaces will be denoted by θ and θ', respectively. It will be assumed moreover, that $\theta > \theta'$ and that the point R belongs to dA. Let $\underset{\sim}{ds}$ be the infinitesimal vector respresenting the arch element of a line of flux of $\underset{\sim}{q}^*$ between dA and dA′. Suppose that $\underset{\sim}{ds}$ is oriented as the vector $\underset{\sim}{q}^*$ itself. Since the flow of heat occurs from hotter regions to colder ones, the angle between grad θ and $\underset{\sim}{q}^*$ (and hence the angle between grad θ and $\underset{\sim}{ds}$) will be greater than $\pi/2$. It follows, therefore, that the temperature difference between dA and dA′ can be expressed as

$$\theta - \theta' = -\operatorname{grad}\theta . \underset{\sim}{ds}, \tag{5.1}$$

where the vector grad θ is understood to be calculated at R and it is assumed that grad $\theta \neq \underset{\sim}{0}$. Since $\theta > \theta'$ and since no flow of heat can occur through the lateral surface of the element dV, all the heat which flows into the element is the one which crosses the surface dA, while all the outflow of heat from the element occurs through the surface dA′ only. Therefore, from equation (3.4) we get that the amount of thermal energy Q which pei unit time enters the element is given by

$$Q = -\hat{f}[\hat{\theta}]\underset{\sim}{q}^*.\underset{\sim}{n}dA = -\underset{\sim}{e_q}.\underset{\sim}{n}dA. \tag{5.2}$$

Here $\underset{\sim}{n}$ is the outward oriented unit normal vector to dA. In the present case this vector can be expressed as

$$\underset{\sim}{n} = \text{grad}\,\theta/|\,\text{grad}\,\theta\,|. \tag{5.3}$$

By applying equation (1.1) to the considered element and by exploiting (5.1) and (5.2) we obtain

$$\bar{L}_{max} = Q\frac{\theta - \theta'}{\theta} = \underset{\sim}{e_q}.\underset{\sim}{n}dA\,\frac{1}{\theta}\,\text{grad}\,\theta.\underset{\sim}{ds}, \tag{5.4}$$

where $\bar{L}_{max}$ denotes the value of L_{max} relevant to the case considered here. But, in view of (5.3) we get that

$$\text{grad}\,\theta.\underset{\sim}{ds} = |\,\text{grad}\,\theta\,|\,\underset{\sim}{n}.\underset{\sim}{ds}. \tag{5.5}$$

Moreover, since the considered element is a cylindrical one, we have that

$$dV = dxdA = -\,n.\underset{\sim}{ds}dA. \tag{5.6}$$

From (5.5) and (5.6) it follows that

$$\text{grad}\,\theta.\underset{\sim}{ds} = -\,|\,\text{grad}\,\theta\,|\,\frac{dV}{A}. \tag{5.7}$$

Therefore, from (5.3) (5.4) and (5.7) the equation

$$\bar{L}_{max} = -\,\frac{1}{\theta}\underset{\sim}{e_q}.\text{grad}\,\theta dV \tag{5.8}$$

can be inferred.

The value of $\bar{L}_{max}$ determined by (5.8) represents the maximum amount of non-thermal power which could be produced by the considered element as a result of the transformation of part of the heat which flows through it, when this transformation does not require any change in the state variables of the element. By denoting by $\bar{l}_{max}$ the specific value of $\bar{L}_{max}$ per unit volume, we get from (5.8)

$$\bar{l}_{max} = -\,\frac{1}{\theta}\underset{\sim}{e_q}.\text{grad}\,\theta, \tag{5.9}$$

which, in view of (3.4), can also be read

$$\bar{l}_{max} = -\,\frac{1}{\theta}\hat{f}[\hat{\theta}]\underset{\sim}{q}^*.\text{grad}\,\theta. \tag{5.10}$$

The quantity p cannot, of course, be greater than $\bar{l}_{max}$. The latter, therefore, represents the upper bound to p we were looking for:

$$p \leq \bar{l}_{max} = -\frac{1}{\theta}\widehat{f}[\widehat{\theta}]\underset{\sim}{q}^* . \text{grad } \theta. \tag{5.11}$$

The analogous upper bound to P follows immediately by integration:

$$\text{P} = \int_{\text{V}} p d\text{V} \leq \int_{\text{V}} \bar{l}_{max} d\text{V} = -\int_{\text{V}} \frac{1}{\theta}\widehat{f}[\widehat{\theta}]\underset{\sim}{q}^* . \text{grad } \theta d\text{V}. \tag{5.12}$$

In view of (5.11) and without any loss in generality, we can express p in the form

$$p = \bar{l}_{max} - c = -\frac{1}{\theta}\widehat{f}[\widehat{\theta}]\underset{\sim}{q}^* . \text{grad } \theta - c, \tag{5.13}$$

where $c = c(\underset{\sim}{\text{X}}, t)$ is an appropriate scalar field over V such that

$$c = c(\underset{\sim}{\text{X}}, t) \geq 0 \tag{5.14}$$

at each time and at each point of the system. It will henceforth be assumed that there is no supply of non-thermal energy to the elements of the system, beside the one due to the transformation of the heat that flows through the element. In these circumstances a physical interpretation of c is obtained by observing that the maximum amount of non-thermal power $\bar{l}_{max}$ can be supplied by an element of unitary volume to its surroundings, only if the element itself does not absorb any of the non-thermal energy produced in it by the heat flow. Otherwise, of course, the amount of non-thermal energy available from the element could not reach its maximum value. It is apparent from (5.13), therefore, that the quantity c can be thought as representing that part of the non-thermal energy $\bar{l}_{max}$—virtually available from the heat flow—which is absorbed per unit time and per unit volume by the same element in which it is produced.

From what has already been observed for p and from equation (5.13) it should be clear that the function $c = c(\underset{\sim}{\text{X}}, t)$ can be specified only when the system and the processes it undergoes are specified. There are, however, important instances in which the knowledge of the function $c(\underset{\sim}{\text{X}}, t)$ can altogether be dispensed with. Let us consider the case of a system in steady-state situation, that is in a situation in which no one of its state variables varies in time. If we assume, as it seems reasonable, that a system cannot absorb energy when all its state variables remain unaltered, then from the interpretation of c given above it follows that c must vanish at each point of the system where the state variables do not vary in time. For systems in steady-state situations, therefore, the relation

$$p \equiv \bar{l}_{max} = -\frac{1}{\theta}\widehat{f}[\widehat{\theta}]\underset{\sim}{q}^* . \text{grad } \theta \tag{5.15}$$

must be valid. This result appears to be consistent also with the fact that, if the state variables of a system do not vary, the system cannot dissipate energy and, consequently, the amount of non-thermal power produced by the heat which flows through the system must be equal to the maximum theoretically admissible.

6. DETERMINATION OF THE FUNCTION $\hat{f}[\hat{\theta}]$ FOR STEADY-STATE SITUATIONS

Let us apply the energy balance equation (4.6) to a unitary volume element in steady-state situation at non-uniform temperature (grad $\theta \neq \underset{\sim}{0}$ at the element). Since in a steady-state situation no change in the state variables occurs, we have that $\dot{\varepsilon} = w = 0$. Therefore, by applying (5.15) we get from (4.6) that

$$- \operatorname{div} \{ \hat{f}[\hat{\theta}] \underset{\sim}{q}^* \} + \frac{1}{\theta} \hat{f}[\hat{\theta}] \underset{\sim}{q}^* . \operatorname{grad} \theta = 0 \qquad (6.1)$$

The first term in the left-hand side of this equation is the difference between the thermal energy which enters the element and the one which leaves it, while the second term denotes the energy produced at the element by the heat flow. The latter is a negative quantity, since $\hat{f}[\hat{\theta}] > 0$ and since $\underset{\sim}{q}^* . \operatorname{grad} \theta < 0$. It represents, therefore, an outflow of energy, which may be exploited to perform work or to produce heat in other points of the system or even outside the system.

Equation (6.1) applies, for instance, to a unitary volume element of a wire belonging to a thermocouple in steady-state situation when its junctions are kept at different constant temperature. In this case the energy $- \frac{1}{\theta} \hat{f}[\hat{\theta}] \underset{\sim}{q}^* . \operatorname{grad} \theta$ flowing out a thermocouple element is exploited (or at least partially exploited) to generate electric current. The latter can perform work in an electric engine connected with the thermocouple. It may be interesting to observe that, once it is generated, the energy represented by the second term in the left-hand side of (6.1) can flow in any direction and, in particular, in the opposite direction to that of the heat flow from which it originates.

Let us now consider a particular system in which the energy produced by the heat flow in an element to which equation (6.1) applies is entirely dissipated (that is transformed again into heat) in the same element in which it is produced. In this case the term $\frac{1}{\theta} \hat{f}[\hat{\theta}] \underset{\sim}{q}^* . \operatorname{grad} \theta$ becomes an amount of thermal energy which is produced in the element and flows out of it.

That is a source for the vector field $\underset{\sim}{q}^*$ at the point where the considered element is. At the same point, therefore, the divergence of the vector field $\underset{\sim}{q}^*$ must be equal to the heat produced by the source, no absorption or loss of heat occurring in the element in a steady-state situation. The heat produced by this source, however, is in motion through a medium at non-uniform temperature. Its energy, therefore, must be given by $\widehat{f}\,[\widehat{\theta}]$ div $\underset{\sim}{q}^*$ in accordance with the hypothesis introduced in Section 3. This energy must, of course, be equal to the energy $-\frac{1}{\theta}\widehat{f}\,[\widehat{\theta}]\underset{\sim}{q}^*.\text{grad}\,\theta$ which is turned into heat. This clearly means that

$$\widehat{f}[\widehat{\theta}]\,\text{div}\,\underset{\sim}{q}^* = -\frac{1}{\theta}\widehat{f}[\widehat{\theta}]\underset{\sim}{q}^*.\text{grad}\,\theta \tag{6.2}$$

and, therefore, that

$$\text{div}\,\underset{\sim}{q}^* = -\frac{1}{\theta}\underset{\sim}{q}^*.\text{grad}\,\theta. \tag{6.3}$$

By observing that equation (6.1) can be written in the form

$$-\widehat{f}[\widehat{\theta}]\,\text{div}\,\underset{\sim}{q}^* - \underset{\sim}{q}^*.\text{grad}\,\widehat{f}[\widehat{\theta}] + \frac{1}{\theta}\widehat{f}[\widehat{\theta}]\underset{\sim}{q}^*.\text{grad}\,\theta = 0 \tag{6.4}$$

and by exploiting (6.2) or (6.3), it follows that the energy balance equation (6.1) can be satisfied only if

$$\text{grad}\,\widehat{f}[\widehat{\theta}] = \frac{2}{\theta}\widehat{f}[\widehat{\theta}]\,\text{grad}\,\theta. \tag{6.5}$$

By a separation of variables this differential equation can be written as

$$\frac{1}{\widehat{f}[\widehat{\theta}]}\,\text{grad}\,\widehat{f}[\widehat{\theta}] = \frac{2}{\theta}\,\text{grad}\,\theta, \tag{6.6}$$

whose general solution is

$$f = \widehat{f}[\widehat{\theta}] = \text{A}\theta^2, \tag{6.7}$$

A being a constant of integration.

To derive relation (6.7) the particular case has been considered in which all the non-thermal power $\frac{1}{\theta}\widehat{f}\,[\widehat{\theta}]\underset{\sim}{q}^*.\text{grad}\,\theta$ produced in an element of a system in steady-state situation is entirely turned into heat in the same element in which it is produced. The function $\widehat{f}\,[\widehat{\theta}]$, however, depends on the temperature field of the system, and not on the particular system which is considered. Since there is nothing which prevents from considering a system in which the non-thermal energy produced by the heat flow is exploited as in the instance considered above, it follows that the above result (6.7) must be valid in general whenever steady-state situations are considered.

Since relation (6.7) is valid for every system in steady-state situation, the constant A appearing in it plays the role of a universal physical constant. It is worth remarking, moreover, that the compatibility between equation (6.1) and equation (6.2) or (6.3) could not subsist, should it be assumed that the energy per unit time carried by a flowing amount of heat is given by the product of $\underset{\sim}{q}^*$ times Joule's constant $\underline{J}$, rather than by equation (3.4).

7. AN EXPERIMENTAL CHECK OF THE PROPOSED THEORY

When a system in steady-state situation is considered, equations (4.6), (5.15) and (6.7) allow us to express the first principle of thermodynamics in the form

$$- \operatorname{div} (\theta^2 \underset{\sim}{q}^*) + \theta \underset{\sim}{q}^* . \operatorname{grad} \theta = 0 \tag{7.1}$$

that is

$$\operatorname{div} \underset{\sim}{q}^* + \frac{1}{\theta} \underset{\sim}{q}^* . \operatorname{grad} \theta = 0. \tag{7.2}$$

In the same circumstances the classical local form of the first principle (4.1) yields the well-known equation

$$\operatorname{div} \underset{\sim}{q}^* = 0, \tag{7.3}$$

which is markedly different from (7.2). The difference between (7.2) and (7.3) allows for a direct experimental check of the proposed theory.

Let us refer, for simplicity's sake, to the case of a cylindrical bar of homogeneous heat-conducting material. Suppose that the lateral surface of the bar is thermally insulated and that, moreover, the ends of the bar are respectively kept at the constant temperatures θ_1 and $\theta_2 (< \theta_1)$ by putting them in thermal contact with two appropriate heat reservoirs. After a sufficiently long time the bar reaches a steady-state situation in which a certain amount of heat flows steadily from the hotter reservoir to the colder one. Since in the present case the heat transfer due to radiation can be neglected, we can set $\underset{\sim}{q}^* \equiv \underset{\sim}{q}$, where $\underset{\sim}{q}$ is the heating conduction vector. We shall assume that the length l of the bar is much grater than the maximum width of its cross-section, so that the heat-transfer phenomenon can be studied as a one-dimensional one. By fixing a reference axis $\underset{\sim}{x}$ coinciding with the axis of the bar, having the origin at its hotter end and, moreover, pointing towards the colder end, we can express equation (7.2) in the form

$$\frac{dq_x}{dx} + \frac{1}{\theta} q_x \frac{d\theta}{dx} = 0. \tag{7.4}$$

Here, of course, q_x denotes the component of the vector $\underset{\sim}{q}$ along the axis $\underset{\sim}{x}$.

To proceed further the constitutive equation for q has to be specified. There are numbers of experiments to determine the amount of thermal energy Q which crosses per unit time the unit area of a prescribed material. From these experiments it is found that for an isotropic material the above amount of thermal energy Q can be expressed as

$$\mathrm{Q} = \widehat{k}(.) \,|\, \mathrm{grad}\ \theta . \underset{\sim}{n} \,|, \tag{7.5}$$

where $k = \widehat{k}(.)$ is a scalar function of the state variables of the material, while $\underset{\sim}{n}$ is the unit normal to the surface through which the flow of heat occurs. For many materials the function $\widehat{k}(.)$ is found to be a function of θ only, and for certain materials the relation of $\widehat{k}(.) = k =$ const. holds over a wide range of temperatures. Often the quantity Q is determined by conveying to a calorimeter the heat flowing through a specimen of the material to be tested. By multiplying the coefficient of Joule $\underline{\mathrm{J}}$ times the number of calories which the calorimeter absorbs from the specimen per unit time and per unit area, the value of Q can thus be obtained.

Since in the present case $\underset{\sim}{q}^* \equiv \underset{\sim}{q}$, the amount of heat q which crosses per unit time a unitary area element can be calculated from (3.1) and reads

$$q = |\, \underset{\sim}{q} . \underset{\sim}{n} \,|. \tag{7.6}$$

Therefore, if according to the classical procedure we set

$$\mathrm{Q} = \underline{\mathrm{J}}q = \underline{\mathrm{J}} \,|\, \underset{\sim}{q} . \underset{\sim}{n} \,|, \tag{7.7}$$

if we compare this equation with (7.5) and if, moreover, we remember that the direction of $\underset{\sim}{q}$ is discordant to that of grad θ, we get

$$\underset{\sim}{q} = -\frac{1}{\underline{\mathrm{J}}} \widehat{k}(.)\ \mathrm{grad}\ \theta. \tag{7.8}$$

This is the constitutive equation for $\underset{\sim}{q}$ which is usually adopted in thermodynamics. Equation (7.7), however, is valid under the hypothesis that the energy of a moving amount of heat q is given by $\underline{\mathrm{J}}q$. According to the present theory, however, the energy of a moving amount of heat q is given by (3.2) and reads $\hat{f}[\hat{\theta}]q$. If the present theory is adopted, therefore, the following equation

$$Q = \hat{f}[\hat{\theta}]q = \hat{f}[\hat{\theta}]\,|\,\underset{\sim}{q}.\underset{\sim}{n}\,| \tag{7.9}$$

has to be introduced instead of (7.6). Accordingly, the constitutive equation for $\underset{\sim}{q}$ which can be deduced from the expiremental result (7.5) is

$$\underset{\sim}{q} = -\frac{1}{\hat{f}[\hat{\theta}]}\hat{k}(.)\ \mathrm{grad}\ \theta. \tag{7.10}$$

For the one-dimensional process considered in this section we get from equations (7.10) and (6.7) the relation

$$q_x = -\frac{1}{A\theta^2}\hat{k}(.)\frac{d\theta}{dx}. \tag{7.11}$$

If, moreover, the particular case in which $\hat{k}(.) = k =$ const. is considered, then equations (7.4) and (7.11) yield

$$\frac{d}{dx}\left(-\frac{k}{A\theta^2}\frac{d\theta}{dx}\right) - \frac{k}{A\theta^3}\left(\frac{d\theta}{dx}\right)^2 = 0 \tag{7.12}$$

That is

$$\frac{d^2\theta}{dx^2} - \frac{1}{\theta}\left(\frac{d\theta}{dx}\right)^2 = 0. \tag{7.13}$$

The general solution of this differential equation is

$$\theta = \theta(x) = be^{ax}, \tag{7.14}$$

where, of course, a and b are two integration constants that are to be determined by the boundary conditions $\theta(0) = \theta_1$ and $\theta(l) = \theta_2$.

Equation (7.14) states that if the bar is made of a material exhibiting a constant heat conduction coefficient, then the temperature of its cross-sections must decay with an exponential law. Under the same circumstances, the classical theory based upon (7.3) and (7.8) yields the well-known result

$$\theta = \theta(x) = \bar{a}x + \bar{b} \tag{7.15}$$

where $\bar{a}$ and $\bar{b}$ are two constants of integration. The discrepancy between (7.14) and (7.15) allows for a direct experimental check of the proposed theory. Of course, similar discrepancies can be found also when k is a non-constant function of θ. For instance, when k is a linear function of θ, that is when

$$k = k_0(1 + \alpha\theta), \tag{7.16}$$

k_0 and α being two constants coefficients, equations (7.4) and (7.10) yield

$$\theta e^{\alpha\theta} = be^{ax}, \tag{7.17}$$

whilst the classical result derived from (7.3) and (7.8) is

$$\frac{\alpha}{2}\theta^2 + \theta = \bar{a}x + \bar{b}. \tag{7.18}$$

In what follows some experimental results obtained by A. Berget [5] will be reported and will be shown to be in a remarkable agreement with the theoretical values foreseen by (7.17).

To determine the thermal conductivity of mercury, Berget performed a series of accurate experiments on a specimen of liquid mercury contained in a cylindrical vessel. The specimen was subjected to the same boundary conditions as that of the cylindrical bar considered earlier in this Section. A complete account of these experiments is contained in the original paper [5]. A less extensive description of the experimental apparatus adopted by Berget as well as of the results he obtained at various stages of his experiments can also be found in [1]-[4]. Berget introduced the so-called guard-ring method to obtain an adequate lateral lagging of the specimen he tested. The effectiveness of this method was checked accurately by Berget himself. To measure the temperature differences between the various points of the specimen, Berget adopted a system of thermocouple suitably connected with a galvanometer, by means of which he was able to detect temperature differences of about 1/100 K. Operating in steady-state conditions, Berget found that when the ends of the specimen were kept at constant temperature of about 273 K and 573 K respectively, the temperature of the cross-sections of the specimen decreased with a non-linear law from the hotter end to the colder one. Since greater temperature gradients were exhibited where the temperature of the specimen was higher, by applying equations (7.3) and (7.8) Berget argued that the thermal conductivity coefficient k of mercury was a decreasing function of temperature. He then assumed as valid for k the linear relation (7.16)—which is a reasonable assumption since the range of temperatures he considered was relatively small—and from his experimental data derived a negative value for the coefficient α.

A great number of experiments performed in this century on specimens of mercury by quite different methods than the one adopted by Berget, however, have shown that the thermal conductivity of liquid mercury increases with temperature. In the linear approximation (7.16), therefore, the coefficient α must be greater than zero in contradiction with the inferences by Berget.

The competence of Berget as experimenter is acknowledged in this and in other fields of physics. Moreover, the experiments reported in [5] show a standard of accuracy and a wealth of ancillary precautions, which match the best experiments performed today. Yet, as far as I can see, no further experiments are available to check the values of temperature that Berget found at the cross-sections of his specimen. The validity of Berget's experimental data might, therefore, be questioned. It is interesting to observe, however, that the theory presented in this paper and, in particular, equations (7.2) and (7.10) yield results which are in agreement not only with Berget's experimental data but also with the today's evidence that liquid mercury exhibits a positive coefficient α. Whereas, according to the classical theory based upon (7.3) and (7.8), Berget's findings are in contradiction with the fact that $\alpha > 0$.

From the experimental data on the conductivity coefficient of mercury reported in [9], it follows that in the range of temperature between 273 K and 573 K equation (7.16) particularizes as

$$k = 1.1126(1 + 0.0214\theta)[wm^{-1}\mathrm{K}^{-1}], \qquad (7.19)$$

which means that $\alpha = 0.0214$. If the theory of this paper is accepted, the temperatures of the cross-sections of the mercury specimen considered by Berget must be calculated from (7.17). On the other hand, if the classical theory is assumed as valid, the above temperatures must be calculated from (7.18). In the following Table I the experimental results by Berget are compared with those obtained by applying (7.17) and the ones foreseen by (7.18). The agreement of the present theory with the experiments by Berget appears to be rather good. The Table shows that the difference between the values of temperature calculated from (7.17) does not exceed in mean the 0.68 % of the experimental values by Berget. The analogous average difference between the temperatures calculated from the classical relation (7.18) and the experimental ones is greater than the 4.3 %.

The slight discrepancy between present theory and experimental results can further be reduced by assuming a slightly different value of α than the one obtained from [9]. No matter what is the actual value of α, however, the classical theory can never be in agreement with the above experiments if $\alpha > 0$.

It may be worth remarking, finally, that in the temperature interval between 273 K and 373 K and by operating with a temperature gradient of about 7.5 K/cm, Berget [1] [4] [5] found that the temperature of the cross-section of his specimen varied almost linearly along the axis. With the above value of α, the maximum deviation from linearity obtained by applying (7.17) and (7.18) to this situation turns out to be about -0.15 % and 1.05 %, respectively. This should provide a further experimental support to the present theory.

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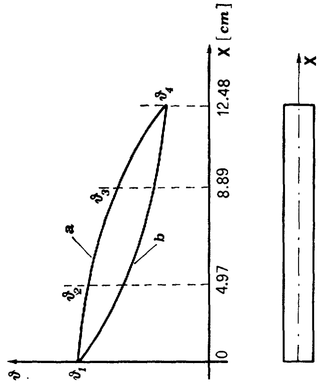
TABLE I

	Absolute temperatures [K]							
	$\theta_1 = 572.0$ $\theta_4 = 321.0$		$\theta_1 = 568.0$ $\theta_4 = 320.0$		$\theta_1 = 523.0$ $\theta_4 = 311.3$		$\theta_1 = 514.0$ $\theta_4 = 310.9$	
	θ_2	θ_3	θ_2	θ_3	θ_2	θ_3	θ_2	θ_3
Experimental (Berget [5]).	472.6	388.3	464.5	386.0	436.0	365.1	430.5	364.0
Present theory [eq. (7.17)]	470.4	391.7	467.6	389.8	437.4	370.9	431.9	368.2
Classical theory [eq. (7.18)].	486.4	407.7	483.7	405.5	449.6	383.0	449.6	383.0



curve a : classical theory ($a > 0$)
curve b : present theory ($a > 0$)

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