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LETTER TO THE EDITOR

On the redundancy of the zeroth law of thermodynamics

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Abstract. Expositions of classical thermodynamics frequently include the so-called zeroth law amongst its 'fundamental principles'. It is shown here that, given only the first law and the second law (the latter in a formulation manifestly free of any explicit or implicit reference to temperature), the transitivity of the relation 'is in diathermic equilibrium with' can be deduced. The zeroth law which is an assertion of just this transitivity is therefore redundant. The existence of the absolute temperature function of course emerges directly, i.e. without appeal to a prior empirical temperature.

Classical thermodynamics is commonly held to be governed by four 'fundamental principles' known, for historical reasons, as its zeroth, first, second and third laws. The zeroth, first and second laws are usually taken to lie at the root of the definitions of temperature, energy and entropy, respectively, while the third bears a different character in as far as it expresses a limitation upon the behaviour of a function previously defined. It is not immediately clear why so privileged a status is granted to just this particular set of propositions. Various 'ancillary assumptions' are made in the course of exploring the consequences of the 'laws', but to none of these assumptions does one accord the status of a law. For example, in the context of standard systems (Buchdahl 1966)—these alone are contemplated here—the presupposition that any two states of such a system can always be linked adiabatically is crucial, but it is regarded as merely an ancillary assumption. Be that as it may, having singled out the zeroth, first and second laws as 'fundamental principles'—the third is not germane to the present issue—the question of their mutual independence arises.

Whether the first and second laws are viewed as independent of one another depends to some extent upon their formulation. If one takes the essence of the second law to be a characterisation of the relation of adiabatic inaccessibility, then, appropriately formulated (Carathéodory 1909), it is manifestly independent of the first law. Equivalently, one may simply introduce an empirical entropy function directly to reflect a certain ordering of the states of an adiabatically isolated system (Buchdahl 1962, Buchdahl and Greve 1962, see also Buchdahl 1966); and clearly there is no reference here to either the zeroth or the first law. The latter leads directly to—is equivalent to—the existence of an energy function; and here also there is no reference to the zeroth law. The original question is now reduced to this: is the zeroth law (a characterisation of mutual diathermic equilibrium) independent of the first and second laws? I shall show that it is not; that it is in fact already contained in them.

The zeroth law asserts the transitivity of the relation 'is in mutual diathermic equilibrium with': if K_A , K_B , K_C are three standard systems, such that K_B and K_C

are separately in diathermic equilibrium with K_A , then K_B and K_C are in diathermic equilibrium with each other. This conventional statement of the zeroth law (e.g. Woods 1975) needs to be supplemented with a general assumption. To state it succinctly, let it be agreed that, with the index J going over the range A, B, C , the system K_J shall have n_J coordinates, collectively denoted by X_J , exactly one of which is a non-deformation coordinate. Then

$$K_A \text{ and } K_B \text{ are in mutual diathermic equilibrium if and only if their states satisfy one condition } f_{AB}(X_A, X_B) = 0. \quad (\text{A})$$

In this context, even when K_A and K_B are spatially separated, equilibrium is said to be obtained when $f_{AB} = 0$; meaning that their states would be unaffected if mutual diathermic contact were established.

Remark. The assumption (A) has been stated in a generally accepted form. It is to be noted that it ostensibly concerns itself solely with the systems K_A and K_B . There is no explicit limitation as to whether the compound system made up of K_A and K_B is or is not adiabatically isolated from its surroundings, or whether possibly only K_A is so isolated, interacting merely indirectly with its surroundings, i.e. via K_B ; nor is the possibility excluded that K_A or K_B may be in contact (and in diathermic equilibrium) with a third system K_C . There is thus ostensibly the implication that the condition of being in mutual diathermic equilibrium is to be taken strictly as a two-term relation, and (A) is here to be understood in this sense.

On the basis of the first and second laws alone one concludes that there exist functions $q_J(X_J)$ and $s_J(X_J)$ such that

$$dQ_J = q_J ds_J. \quad (1)$$

q_J cannot be a function of s_J alone since otherwise dQ_J would be a total differential. Except possibly at isolated points, one can make a transformation of coordinates which amounts to the elimination of the non-deformation coordinate and one of the deformation coordinates from X_J in favour of q_J and s_J . The coordinates of K_J are therefore now q_J, s_J, x_J , where x_J stands collectively for the remaining $n_J - 2$ deformation coordinates of K_J . The condition of equilibrium (A) between K_A and K_B is now

$$g_{AB}(q_A, q_B, s_A, s_B, x_A, x_B) = 0. \quad (2)$$

Now let K^* be the compound (standard) system formed of K_A, K_B, K_C , with K_A lying between K_B and K_C , i.e. K_A is in diathermic equilibrium with K_B and with K_C . Therefore, the $n_A + n_B + n_C$ coordinates of the systems which make up K^* are subject to two conditions of the kind (2), i.e. $g_{AI} = 0$, the index I going over the range BC . Take the coordinates of K^* to be the remaining $n_A + n_B + n_C - 2$ independent variables $q_A, s_A, s_B, s_C, x_A, x_B, x_C$. q_I is a function of q_A, s_A, s_I, x_A, x_I alone: q_B , for instance, cannot depend on s_C and x_C , because of (A). Thus

$$q_I = \theta_{AI}(q_A, s_A, s_I, x_A, x_I). \quad (3)$$

The 'additivity of heat' is represented by the equation

$$dQ^* = \sum dQ_J. \quad (4)$$

There exist functions q^*, s^* of the coordinates of K^* such that $dQ^* = q^* ds^*$, so that

(4) becomes

$$q^* ds^* = \sum q_J ds_J. \quad (5)$$

Since only the three differentials ds_J appear on the right, s^* can only be a function of $s_A, s_B, s_C (=s)$ alone. This implies that q_J/q^* depends only on these variables. In particular, the absence of q_A, x_A, x_B, x_C from q_A/q^* entails that q^* must have q_A as a factor, while the other factor depends on s alone:

$$q^* = q_A \chi^*(s). \quad (6)$$

In turn, since $\theta_{AI}/q_A \chi^*(s)$ depends only on s , θ_{AI} must be free of x_A, x_I and it must have q_A as a factor:

$$\theta_{AI} = q_A \phi_{AI}(s_A, s_I). \quad (7)$$

Consequently (5) now reads

$$\chi^*(s) ds^* = ds_A + \phi_{AB}(s_A, s_B) ds_B + \phi_{AC}(s_A, s_C) ds_C. \quad (8)$$

The form on the right is integrable. The condition of integrability reduces to

$$\phi_{AB} \partial \phi_{AC} / \partial s_A - \phi_{AC} \partial \phi_{AB} / \partial s_A = 0$$

i.e. ϕ_{AB}/ϕ_{AC} is independent of s_A . It follows that there are functions $\psi_A(s_A), \psi_{AI}(s_I)$ such that

$$\phi_{AI}(s_A, s_I) = \psi_{AI}(s_I) / \psi_A(s_A)$$

or equivalently

$$q_A / \psi_A(s_A) = q_B / \psi_{AB}(s_B) = q_C / \psi_{AC}(s_C). \quad (9)$$

The first of these equations reflects the equilibrium between K_A and K_B . Bearing (A) in mind, the lack of symmetry of this equation implicit in the appearance of the index A on the right must be rejected, i.e. ψ_{AB} must be independent of A and likewise ψ_{AC} must be independent of A . In other words, there are functions $\psi_J(s_J)$ such that (in place of (9))

$$q_A / \psi_A(s_A) = q_B / \psi_B(s_B) = q_C / \psi_C(s_C). \quad (10)$$

It is natural to define

$$q_J / \psi_J(s_J) =: \tau_J(q_J, s_J). \quad (11)$$

Then the mutual diathermic equilibrium of K_A and K_B is characterised by the equality of τ_A and τ_B . Here τ_A is a function which belongs exclusively to K_A in the sense that its structure is determined by K_A alone and it depends solely on the coordinates of K_A . Likewise τ_B belongs exclusively to K_B and τ_C to K_C . On the other hand K_A can be any standard system at all, i.e. if K^\dagger is such a system, K^\dagger is in diathermic equilibrium with K_B if and only if $\tau_B = \tau^\dagger$, where τ^\dagger is a function which belongs exclusively to K^\dagger . Then, choosing K^\dagger to be K_C , τ^\dagger must be just the function τ_C , since otherwise there would be two distinct conditions governing the mutual diathermic equilibrium between K_A and K_C . Therefore K_B and K_C are in equilibrium if $\tau_B = \tau_C$. According to the second of equations (10), however, $\tau_B = \tau_C$ here. Therefore K_B and K_C are in mutual diathermic equilibrium as a consequence of K_B and K_C being separately in diathermic equilibrium with K_A . This conclusion has been reached without any appeal to the zeroth law, and the latter is therefore redundant.

From (1) and (10) it follows that

$$dQ_J = \tau_J(q_J, s_J) \psi_J(s_J) ds_J$$

or, if $\Psi_J(s_J) := \int \psi_J(s_J) ds_J$,

$$dQ_J = \tau_J(q_J, s_J) d\Psi_J(s_J). \quad (12)$$

τ_J is thus an integrating denominator of dQ_J and it has the same value for all systems in mutual diathermic equilibrium. Evidently τ_J is the absolute temperature (function) and Ψ_J the metrical entropy of K_J . Absolute temperature has thus appeared directly, i.e. without prior reference to empirical temperature, consistent with the redundancy of the zeroth law.

Finally, granted the validity of (A), including the interpretation which forms the subject of the remark stated above and having shown that the zeroth law in its traditional form is redundant one may well take the position that (A) should be taken as one of the basic 'laws'—the 'zeroth law'—rather than as an 'ancillary assumption'. That, however, is just an example of the kind of semantic issue which was raised at the beginning of this letter.

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