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Collinearity and disequilibrium in irreversible thermodynamics of the steady state

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Abstract. This paper is a detailed development from two recent publications. One of these (Silver 1979) showed that conventional equations for entropy flux and mass flux as coupled linear functions of their conjugate forces necessarily imply the existence of an uncoupled set of fluxes and forces also. This paper generalises that result and derives an alternative set of flux force conjugates in which each flux is collinear with its conjugate force. This is valid irrespective of extent of departure from equilibrium. The other publication (Silver 1977) suggested the use of the concept of disequilibrium. This paper develops that concept rigorously to give a phenomenological model of the steady state, and so derives valid meanings for non-equilibrium properties irrespective of extent of departure from equilibrium. These properties are used in the proposed flux force conjugates and form the basis of equations for entropy generation in any steady state. The theory is consistent with conventional near-equilibrium theory, but capable of much wider application. The scope, indicated in a final section, includes thermoelectric effects, flow in porous media and membranes, and biophysical as well as engineering processes. The important principle established is a continuity of analysis over the whole range from reversible equilibrium to highly irreversible non-equilibrium steady states.

1. Introduction

Contemporary theory of non-equilibrium thermodynamics is founded on the work of Onsager and has been developed in very great detail by numerous workers over the last forty years. Among the main contributors to these developments have been Prigogine, De Groot, Meixner and Truesdell. The result has been the creation of an impressive distinct field of mathematical physics. Their work has recently been well presented and summarised by Lavenda (1978) who adds some valuable contributions in respect of extending the theory to nonlinear thermodynamics.

These sophisticated mathematical developments establish rigorously the logical validity of certain important properties and parameters, but in many of the actual applications of irreversible thermodynamics the phenomenological analysis which *uses* these properties and parameters is formally simple. This is well exemplified in contemporary treatment of the irreversible thermodynamics of the steady state. Irrespective of the underlying complexity, the overall steady-state situation is described in terms of a mass flux \mathbf{J}_m , which is constant, and an entropy flux \mathbf{J}_s , which increases. Interest centres on the rate of entropy generation, $\text{div } \mathbf{J}_s$, which is expressed in the form

$$T \text{ div } \mathbf{J}_s = \mathbf{J}_s \cdot \mathbf{X}_s + \mathbf{J}_m \cdot \mathbf{X}_m. \quad (1.1)$$

\mathbf{X}_s and \mathbf{X}_m are generalised 'forces', and the underlying concept is that \mathbf{X}_s is cognate to \mathbf{J}_s and \mathbf{X}_m to \mathbf{J}_m as shown by the form of the vector products in the entropy generation equation. However, it is a result of the fundamental mathematical analysis that \mathbf{J}_s and \mathbf{J}_m may be expressed as linear functions of \mathbf{X}_s and \mathbf{X}_m in the form

$$\mathbf{J}_s = \lambda_{ss}\mathbf{X}_s + \lambda_{sm}\mathbf{X}_m \quad \mathbf{J}_m = \lambda_{ms}\mathbf{X}_s + \lambda_{mm}\mathbf{X}_m. \quad (1.2)$$

Thus each of the two fluxes is affected by *both* forces, which are therefore said to be coupled. The coefficients λ_{sm} and λ_{ms} are called the cross-coupling coefficients.

The two important results of the underlying statistical analysis are

- (i) that each of the coefficients λ is an equilibrium property, and is therefore constant for a given p , T , independent of \mathbf{X}_s and \mathbf{X}_m ;
- (ii) that the cross-coupling coefficients are equal, i.e. that

$$\lambda_{sm} = \lambda_{ms}. \quad (1.3)$$

This simple linear relationship has served well for the treatment of many steady-state irreversible processes in physics and engineering and will be found exemplified in such text-books as Denbigh (1950), Zemansky (1957) and Benson (1967), while its relation to fundamental theory is discussed by De Groot (1961).

The application of this method is wholly dependent on the constancy of each λ and on the equality of the cross-coefficients. If neither of these can be assumed, the application cannot proceed. The validity of the fundamental analysis which establishes these propositions (i) and (ii) above is therefore essential to the utility of the method. Now the mathematical analysis can only be satisfactorily accomplished for perturbations not far removed from equilibrium, and hence the procedure outlined above cannot be used with confidence in situations known to be very far from equilibrium. Hence, although the theory is concerned with non-equilibrium, it assumes that *local* equilibrium exists at every location. The inherent inconsistency of this has been accepted on the presumption that it would not be applied to highly non-equilibrium situations. But, as has recently been remarked by Jaynes (1980), 'A local equilibrium approach has no criterion for judging its range of validity and provides no basis for further development, since it contains scarcely any quantity that has a precise meaning in a non-equilibrium state. The logic of using equilibrium relations in non-equilibrium situations was hardly an advance over that used by Thomson in 1854'. Moreover, in modern practical developments such as thermo-electric refrigeration, membrane purification processes, steady multi-phase flow, plasma flow, and the like to which the application of steady-state non-equilibrium thermodynamics could be expected to be beneficial, the conditions are usually very far removed from equilibrium. Some alternative procedure must be found to deal with such cases. Given the lack of fundamental statistical analysis of such situations, it is evident that we have to proceed, via macroscopic observables and phenomenological conceptualisation of non-equilibrium, to establish parameters which can be operationally measured.

It is, of course, obviously essential that the proposed development must satisfy all known macroscopic physical principles, and must, in the limit tending to near-equilibrium conditions, reduce to the accepted forms. The object of this paper is to present such a development with as much rigour as possible.

Two preliminary publications towards this end have already appeared. The first (Silver 1977) introduced formally a quantity termed *the disequilibrium* as a measure of the difference between the potential of a steady maintained non-equilibrium condition

and that of the equilibrium state at the same pressure and temperature. The second (Silver 1979) showed that the conventional equations of the form (1.1), (1.2) and (1.3) necessarily imply the simultaneous presence of an *uncoupled* set of fluxes and forces. It was also shown that the physical significance of the uncoupled set is quite clear, and it is rather surprising that this situation has not been noticed earlier. It raises several important questions on the relationship between the forms of equations and the macroscopic conceptual pattern.

The present paper proceeds from these two preliminary publications. Section 2 generalises the result of Silver (1979) and shows that the choice of flux-force relations for the steady state is much more open than has been supposed. Sections 3–7 develop a phenomenological model of the steady state in terms of the concept of disequilibrium initiated in Silver (1977), establish its quantitative definition more rigorously, and lead to the formation of an entropy generation equation which is not restricted to near-equilibrium conditions. Subsequent sections use the flux-force relations established in § 2 to discuss the behaviour in general.

2. General theory of flux-force relations

We begin by showing that the proposition established in Silver (1979) is merely a special case of a more general and indeed very elementary theorem. It is in fact rather puzzling that this appears to have escaped notice previously. The point will be realised by considering equations (1.2) as forming a matrix. It is then elementary that if the coefficients λ_{sm} and λ_{ms} are equal the matrix can be diagonalised. Physically this means that the set of equations in which each flux has to be expressed in terms of both forces can be replaced by a set in which each flux is collinear with its own conjugate force. Now that matrix theorem is valid for any number of elements so that, if for all pairs $\lambda_{ik} = \lambda_{ki}$, any number of fluxes can be expressed as collinear with their conjugate forces. But conventional Onsager-based theory has so far insisted always on the need to express each flux in terms of all forces, and the collinear sets have been neglected. There may be good reasons for that insistence in the general case for many fluxes and forces, and within the constraint of linear relations for near-equilibrium conditions, and also with the constraint of satisfying the entropy generation equation corresponding to equation (1.1). But, in the case of the non-equilibrium steady state which is describable in terms of only two fluxes \mathbf{J}_m and \mathbf{J}_s , there is no good reason for ignoring the possibility of collinear relations. Indeed, as will be shown, they bring many advantages.

There is also the more general point of considerable epistemological significance, which arises from the fact that the converse of the matrix theorem is also true. Thus if it is asserted as a macroscopic physical principle that the flux vector which responds to a force vector must be collinear with it, then any set of flux-force conjugate pairs which satisfies the same constraints must have equal cross-coefficients. The equality will arise directly from the assertion of the macroscopic physical concept and will not require foundation in statistical theory of underlying microscopic behaviour.

However, our main concern is with the advantage which can be gained in practice by using the collinear set for the non-equilibrium steady state which is describable in terms of only two fluxes \mathbf{J}_m and \mathbf{J}_s . To bring the matter out in its full physical significance, the following rather long derivation is given in place of the simple matrix theorem.

At this stage the thermodynamic context is irrelevant and we consider any two force vectors \mathbf{X}_1 and \mathbf{X}_2 which act at a location in a reference space. Provided they are not

collinear, they define a plane. If \mathbf{J}_1 and \mathbf{J}_2 constitute a pair of flux vectors, equations of the *general* form

$$\mathbf{J}_1 = \lambda_{11}\mathbf{X}_1 + \lambda_{12}\mathbf{X}_2 \quad \mathbf{J}_2 = \lambda_{21}\mathbf{X}_1 + \lambda_{22}\mathbf{X}_2 \quad (2.1)$$

assert only that each flux vector lies in the plane defined by \mathbf{X}_1 and \mathbf{X}_2 . By *general* form we mean here that the λ coefficients need not be regarded as constants, i.e. they may be scalar functions of \mathbf{X}_1 , \mathbf{X}_2 . A set of the same form where each λ is constant is a special case.

The further assertion of the form

$$A = \mathbf{J}_1 \cdot \mathbf{X}_1 + \mathbf{J}_2 \cdot \mathbf{X}_2, \quad (2.2)$$

where A is a scalar constant, states a characteristic of the flux-force vector set \mathbf{J}_1 , \mathbf{X}_1 and \mathbf{J}_2 , \mathbf{X}_2 which must be preserved for any alternative set.

It is elementary to see that, by the introduction of a scalar quantity α , an alternative set \mathbf{J}'_1 , \mathbf{X}_1 and \mathbf{J}_2 , \mathbf{X}'_2 which preserves relation (2.2) can be obtained by writing

$$A = (\mathbf{J}_1 - \alpha\mathbf{J}_2) \cdot \mathbf{X}_1 + \mathbf{J}_2 \cdot (\alpha\mathbf{X}_1 + \mathbf{X}_2) \quad (2.3)$$

or

$$A = \mathbf{J}'_1 \cdot \mathbf{X}_1 + \mathbf{J}_2 \cdot \mathbf{X}'_2 \quad (2.4)$$

where

$$\mathbf{J}'_1 = \mathbf{J}_1 - \alpha\mathbf{J}_2 \quad \mathbf{X}'_2 = \alpha\mathbf{X}_1 + \mathbf{X}_2. \quad (2.5)$$

\mathbf{J}'_1 and \mathbf{X}'_2 are thus co-planar with \mathbf{J}_1 , \mathbf{J}_2 and \mathbf{X}_1 , \mathbf{X}_2 .

Combining equations (2.5) and (2.1), we find

$$\begin{aligned} \mathbf{J}'_1 &= [\lambda_{11} - \alpha(\lambda_{21} + \lambda_{12}) + \alpha^2\lambda_{22}]\mathbf{X}_1 + (\lambda_{12} - \alpha\lambda_{22})\mathbf{X}'_2 \\ \mathbf{J}_2 &= (\lambda_{21} - \alpha\lambda_{22})\mathbf{X}_1 + \lambda_{22}\mathbf{X}'_2. \end{aligned} \quad (2.6)$$

Thus if two co-planar fluxes \mathbf{J}_1 , \mathbf{J}_2 exist as conjugates to \mathbf{X}_1 and \mathbf{X}_2 to satisfy the constraint (2.2), there is a whole envelope of such possible co-planar sets which will satisfy the same constraint. That envelope can be generated by varying the coefficient α . The effect is that while the vectors \mathbf{X}_1 and \mathbf{J}_2 are retained, \mathbf{J}'_1 and \mathbf{X}'_2 can be given varying magnitude and direction by varying α . Thus \mathbf{J}'_1 and \mathbf{X}'_2 can be rotated in the defined plane.

Now we consider the implications of making the *additional* assertion that the cross-coefficients λ_{21} and λ_{12} are equal. It is immediately seen from equations (2.6) that the first implication is that, if the cross-coefficients are equal for *any* set in the co-planar envelope, they are equal for all sets, although the equal value will vary with α . Thus the property of equality of cross-coefficients is either possessed by the whole envelope, or it is not possessed at all. Again this conclusion is valid even if the various λ coefficients are not constants.

A further implication is also clear. Within an envelope of equal cross-coefficients there exists one set for which the equal value is zero. From equations (2.6) this occurs when the value of α is such that

$$\lambda_{12} = \lambda_{21} = \alpha\lambda_{22}. \quad (2.7)$$

For this set the flux \mathbf{J}'_1 is collinear with the force \mathbf{X}_1 , and the flux \mathbf{J}_2 is collinear with the force \mathbf{X}'_2 . Thus if it is asserted that the cross-coefficients for any set are equal, there

exists a set where each flux is collinear with its conjugate force. Conversely, if there is no collinear set, there can be no set with equal cross-coefficients. Again, all these statements are valid even if the λ coefficients are not constants, i.e. any of the coefficients λ_{11} , λ_{12} , λ_{21} , λ_{22} and the scalar quantity α may be scalar functions of \mathbf{X}_1 , \mathbf{X}_2 or \mathbf{X}_1 , \mathbf{X}'_2 . Thus the relations of equations (2.1) and (2.6) may be nonlinear. The theorem is concerned with the characteristics of co-planarity and *collinearity*, and not with linearity of relations.

In the thermodynamic context, this point is important because the conventional assumption of linear relations, i.e. of constant coefficients, means that coupling interactions between two forces do not appear in the set for which the fluxes are collinear with their conjugate forces. Thus accepted theory of the steady state, although it is based on the assumption of equality of cross-coefficients, has ignored the collinear set which is a necessary consequence of that same assumption. It is therefore likely that unnecessary complication has been introduced into the analysis of irreversible processes by using coupled flux-force sets in cases where, if the two assumptions of constant coefficients and equal cross-coefficients are actually valid, an uncoupled set must be available. The important point is that by allowing the coefficients to vary as scalar functions of the forces the collinear set may include coupling interactions, whereas so long as the coefficients are regarded as constant the collinear set is necessarily uncoupled.

The possible spectrum of generalisation can therefore be seen as ranging from, at one end, the conventional treatment where both the assumption of constancy of coefficients *and* that of equality of cross-coefficients are made, and to the other extreme where neither of these assumptions is used. The conventional extreme gives linear relations and a collinear set which has up to now been neglected. The other extreme would give nonlinear relations *and* would deny the existence of a collinear set. In between these two extremes, there is the possibility of abandoning the assumption of constant coefficients but retaining that of the equality of cross-coefficients. That is the procedure which we are now suggesting. It will form a continuity with conventional theory, coinciding with it in the limit where the coefficients are constant.

When a collinear set is chosen it may be given the following notation, where the primes could be dropped but are retained to avoid confusion:

$$\mathbf{J}'_1 = \lambda_1 \mathbf{X}_1 \quad \mathbf{J}_2 = \lambda_2 \mathbf{X}'_2.$$

By comparing with the coefficients of equation (2.6), we have

$$\lambda_{12} = \lambda_{21} = \alpha \lambda_2 \quad \lambda_{11} = \lambda_1 + \alpha^2 \lambda_2 \quad \lambda_{22} = \lambda_2.$$

The practical situation is always that we have to measure experimental quantities in order to find three parameters, which may be either the set λ_{11} , $\lambda_{12} = \lambda_{21}$, λ_{22} or λ_1 , λ_2 , α . The quantities which may possibly be accessible to experiment are the fluxes \mathbf{J}_1 , \mathbf{J}'_1 , \mathbf{J}_2 , and the forces \mathbf{X}_1 , \mathbf{X}_2 , \mathbf{X}'_2 .

It must be emphasised that, since either a collinear set or a non-collinear set is available under the constraint of equality of cross-coefficients, the decision as to which to use must be made on extraneous grounds. The neglect of the collinear set in conventional steady-state theory could perhaps be justified if there were apparent reasons for believing that no collinear set could be physically identified in the thermodynamic context. But it was shown in Silver (1979) that for the conventional near-equilibrium case such a set does have a clear physical identity and significance. It will be shown in this paper that this is still true for our more general development, and we shall

therefore give priority to the use of a collinear set. By adopting it, departures from linearity in the underlying phenomena can be accommodated by the greater generality which allows the coefficients to vary. Only experimental measurement can establish the extent to which this may be needed in steady-state conditions very far from equilibrium.

Perhaps it should be mentioned that in referring to a 'collinear set' only collinearity of conjugates is meant. The two forces are not in general collinear.

We now proceed to develop a phenomenological model of the steady state without restrictions to near-equilibrium to which the flux-force relations can be applied.

3. Description of steady-state non-equilibrium

In general qualitative terms, the steady-state non-equilibrium is observed in what is, to macroscopic observation, a continuum, when at any location the macroscopically observed values of pressure, temperature and constitution are constant in time but vary with location, so that steady gradients of these properties are also maintained. If isolated, such a situation could not persist, and its maintenance requires the provision of fluxes of energy and/or mass through the continuum from sources to sinks.

To formulate a detailed quantitative description of this steady state we consider a representative unit mass at a location to be heterogeneous and non-uniform. By heterogeneous and non-uniform we imply that it has within it distinguishable elements which are themselves internally homogeneous and uniform, and which we shall term homogeneities. Each such homogeneity will be identified by its subscript i as an individual element homogeneous in its constitution and phase, and uniform in pressure, temperature and velocity. The mass concentration of homogeneity of kind i will be denoted by b_i , so that $b_1, b_2, \dots, b_i, \dots$ etc are the masses of kind i contained in the representative unit heterogeneous non-uniform mass. Each homogeneity is a bulk element, i.e. it is presumed to contain a sufficient number of molecules to have the properties pressure, temperature and constitution properly ascribed to it, and therefore its velocity is a bulk velocity. Elements which differ in any one or more of the characteristics constitution, phase, pressure, temperature, velocity, will be regarded as different homogeneities having a different subscript.

The description of a homogeneity as homogeneous in constitution does not necessarily imply that it contains only a single chemical species. It may be a mixture of different species but, as defined, the proportions of these species throughout the extent of the homogeneity are uniform. Thus if z_j denotes the mass fraction of an individual species j per unit mass of the heterogeneous whole, we may presume that the mass $z_{j,i}$ of that particular species is present in b_i . We then have the relations

$$b_i = \sum_j z_{j,i} \quad \text{for all } i \quad z_j = \sum_i z_{j,i} \quad \text{for all } j. \quad (3.1)$$

Also

$$\sum_i b_i = 1 \quad \sum_j z_j = 1. \quad (3.2)$$

Now in general it would be possible for such a mixture, although uniformly mixed, to be not in equilibrium proportions and for reaction to be occurring within it. For the present discussion we shall exclude that possibility and assume that each homogeneity is internally at equilibrium, each at its own value of pressure p_i and temperature T_i . Thus each $z_{j,i}/b_i$ is an equilibrium proportion of the substance j within the homogeneity i at

the conditions p_i, T_i . The non-equilibrium consists in the co-existence within the heterogeneous mass of these individual internally equilibrated homogeneities. The resultant reactions and interactions between them occur in the steady state, accompanied by fluxes of mass and energy, in such a way that the non-equilibrium condition at each location is constant in time but varies with location.

With this model it follows that each homogeneity has a set of specific thermodynamic properties U_i, V_i, S_i , etc which are functions of p_i, T_i and the (equilibrium) proportions $z_{i,i}/b_i$. Each homogeneity will also have kinetic energy $\frac{1}{2}v_i^2$ per unit of its mass independent of its constitution. Moreover, if potential fields are present, each homogeneity will also have potential energy ϕ_i per unit of its mass. This potential ϕ_i will in general depend on the constitution, unless the field is purely gravitational, and, if the field includes magnetic as well as electric potential, may also depend on v_i .

Hence we can ascribe to each homogeneity the specific energy content per unit of its mass

$$\epsilon_i = U_i + \phi_i + \frac{1}{2}v_i^2. \quad (3.3)$$

It follows that the representative heterogeneous non-equilibrium mass at a location has an energy per unit mass given by

$$\bar{\epsilon} = \sum b_i \epsilon_i = \bar{U} + \bar{\phi} + \frac{1}{2}\bar{v}^2 + \frac{1}{2}\sigma^2 \quad (3.4)$$

where

$$\bar{v} = \sum b_i v_i \quad (3.5)$$

and

$$\sigma^2 = \sum b_i (v_i - \bar{v})^2. \quad (3.6)$$

The velocity \bar{v} is the mean velocity of the heterogeneous mass flow. It is helpful also to define the relative velocity v_{ri} of any individual homogeneity to the mean mass flow as

$$v_{ri} = v_i - \bar{v}. \quad (3.7)$$

The following thermodynamic properties are also attributable to the heterogeneous mass flow per unit mass:

specific internal energy	$\bar{U} = \sum b_i U_i$	(3.8)
specific volume	$\bar{V} = \sum b_i V_i$	
specific entropy	$\bar{S} = \sum b_i S_i$	
specific enthalpy	$\bar{H} = \sum b_i (U_i + p_i V_i) = \bar{U} + \sum b_i p_i V_i$	
specific Gibbs potential	$\bar{G} = \sum b_i (U_i + p_i V_i - T_i S_i) = \bar{H} - \sum b_i T_i S_i$	

In this model a homogeneity at a location flowing with velocity v_i and having a specific volume V_i constitutes a stream occupying a fraction a_i of unit cross-sectional area of the continuum. Thus there is a homogeneous stream mass flux \mathbf{J}_i of amount

$$\mathbf{J}_i = a_i v_i / V_i. \quad (3.9)$$

Now we presume that the situation is isomorphic, so that the fraction a_i is equal to the volume fraction occupied, so that

$$a_i = b_i V_i / \bar{V}. \quad (3.10)$$

Thus

$$\mathbf{J}_i = b_i v_i / \bar{V}. \quad (3.11)$$

The total mass flux of all streams is therefore

$$\mathbf{J}_m = \sum \mathbf{J}_i = \bar{v} / \bar{V}. \quad (3.12)$$

The relative flux of any individual stream is defined by

$$\mathbf{J}_{r,i} = b_i v_{ri} / \bar{V} = \mathbf{J}_i - b_i \mathbf{J}_m \quad (3.13)$$

and of course

$$\sum \mathbf{J}_{r,i} = 0. \quad (3.14)$$

The total enthalpy flux due to the various streams is given by

$$\sum \mathbf{J}_i (H_i + \phi_i + \frac{1}{2} v_i^2) = \mathbf{J}_m (\bar{H} + \bar{\phi} + \frac{1}{2} \bar{v}^2 + \frac{1}{2} \sigma^2) + \sum \mathbf{J}_{r,i} (H_i + \phi_i + \frac{1}{2} v_i^2). \quad (3.15)$$

Thus the total enthalpy flux appears in two separable components, namely the mean enthalpy carried along with the overall mass flux \mathbf{J}_m , and a component arising from the effects of all the individual relative mass fluxes $\mathbf{J}_{r,i}$. Since $\sum \mathbf{J}_{r,i}$ is zero, this latter component is not associated with any macroscopically observable mass flow, and therefore must appear as what we normally call heat flux. We therefore designate it as heat flux arising from relative mass motion and denote it by the symbol $\mathbf{J}_{q,r}$, writing

$$\mathbf{J}_{q,r} = \sum_i \mathbf{J}_{r,i} (H_i + \phi_i + \frac{1}{2} v_i^2). \quad (3.16)$$

Recognition of $\mathbf{J}_{q,r}$ reminds us that in a general description of the non-equilibrium steady state we should include the presence of heat fluxes. We therefore allow that there may be present various heat fluxes $\mathbf{J}_{q,k}$, each having its individual temperature T_k . The total heat flux present in the steady state will be denoted by \mathbf{J}_q and its amount is given by

$$\mathbf{J}_q = \sum_k \mathbf{J}_{q,k} + \mathbf{J}_{q,r}. \quad (3.17)$$

This total heat flux in the non-equilibrium steady state has associated with it all the individual temperatures T_k and T_i .

We may also note the total entropy flux \mathbf{J}_s . This will be given by

$$\mathbf{J}_s = \sum_k \mathbf{J}_{q,k} / T_k + \sum_i \mathbf{J}_i S_i = \sum_k \mathbf{J}_{q,k} / T_k + \sum_i \mathbf{J}_{r,i} S_i + \mathbf{J}_m \bar{S}. \quad (3.18)$$

To conclude the description of the non-equilibrium steady state we give the mass conservation and energy conservation equations,

$$\text{div } \mathbf{J}_m = 0, \quad (3.19)$$

while in general for each individual stream

$$\text{div } \mathbf{J}_i \neq 0. \quad (3.20)$$

The energy equation is

$$\text{div} \left(\sum_k \mathbf{J}_{q,k} + \sum_i \mathbf{J}_i (H_i + \phi_i + \frac{1}{2} v_i^2) \right) = -\dot{W}_d. \quad (3.21)$$

Using equations (3.15)–(3.17), this becomes

$$\operatorname{div} \mathbf{J}_q = -\overset{0}{W}_d - \mathbf{J}_m \cdot \operatorname{grad}(\bar{H} + \bar{\phi} + \frac{1}{2}\bar{v}^2 + \frac{1}{2}\bar{\sigma}^2). \tag{3.22}$$

It will be understood that in this model of the steady state interactions, including chemical interactions, are presumed to occur as the individual streams flow with changing T_i and p_i . These interactions are subject to the constraint of *internal* equilibrium at T_i and p_i , and to the overall conservation equations (3.19) and (3.22). But there is no other limitation on the variety nor range of T_i and p_i which may occur from stream to stream, and hence no constraint on the extent of non-equilibrium. We now seek a means of describing this non-equilibrium quantitatively, and to do so we first study the exergy characteristics of the steady state.

4. Exergy in the steady state

The exergy of a thermodynamic system is defined, with reference to an arbitrary reservoir at stated temperature T_0 and pressure p_0 , as the maximum work which the system could produce in changing from its initial state to a final state in equilibrium with the reservoir. Thus the exergy is a function of both the system and the reservoir.

We now consider the exergy of the steady-state non-equilibrium condition which we have described in § 3. There are various contributions to be taken into account. First we have the heat flux contributions. Each flux $\mathbf{J}_{q,k}$ at temperature T_k gives an exergy flux contribution of

$$\mathbf{J}_{\Lambda,k} = \mathbf{J}_{q,k}(1 - T_0/T_k). \tag{4.1}$$

Then we have the contributions arising from the mass fluxes. If we denote by Λ_i the exergy of unit mass in the condition i , each mass flux \mathbf{J}_i will give an exergy flux contribution

$$\mathbf{J}_{\Lambda,i} = \mathbf{J}_i \Lambda_i. \tag{4.2}$$

The total exergy flux is therefore

$$\mathbf{J}_{\Lambda} = \sum_k \mathbf{J}_{q,k} - T_0 \left(\sum_k \mathbf{J}_{q,k}/T_k \right) + \sum_i \mathbf{J}_{r,i} \Lambda_i + \mathbf{J}_m \bar{\Lambda}. \tag{4.3}$$

Now it can be shown that the exergy of unit mass of the homogeneity in the condition i is given by

$$\Lambda_i = H_i + \phi_i + \frac{1}{2}v_i^2 - T_0 S_i - (\bar{\phi}_0 + \bar{g}_0). \tag{4.4}$$

The quantity \bar{g}_0 in equation (4.4) is the mean Gibbs potential per unit mass in the final equilibrium at T_0, p_0 . At this equilibrium the mass fractions z_j for each species j will have changed to equilibrium proportions $z_{j,0}$ and so give the equilibrium set of Gibbs partial potentials for each species. These partial potentials are denoted by $g_{j,0}$ and the mean value is \bar{g}_0 given by

$$\bar{g}_0 = \sum_j z_{j,0} g_{j,0}. \tag{4.5}$$

Correspondingly we have

$$\bar{\phi}_0 = \sum_j z_{j,0} \phi_j. \tag{4.6}$$

ϕ_j is the field potential per unit mass of species j , and is independent of thermodynamic conditions. But because of the constitution proportions $\bar{\phi}_0$ does depend on the thermodynamic condition.

For convenience we introduce the combined potential $\bar{\psi}_0$ which is defined by

$$\bar{\psi}_0 = \bar{\phi}_0 + \bar{g}_0. \quad (4.7)$$

We can now use these relations in substituting from equation (4.4) into (4.3) and find

$$\mathbf{J}_\Lambda = \sum_k \mathbf{J}_{q,k} + \sum \mathbf{J}_{r,i} (\mathbf{H}_i + \phi_i + \frac{1}{2} v_i^2) - T_0 (\sum \mathbf{J}_{q,k} / T_k + \sum \mathbf{J}_{r,i} \mathbf{S}_i) + \mathbf{J}_m \bar{\Lambda}. \quad (4.8)$$

Now of course from equation (4.4) we also have

$$\bar{\Lambda} = \sum b_i \Lambda_i = \bar{H} + \bar{\phi} + \frac{1}{2} \bar{v}^2 + \frac{1}{2} \bar{\sigma}^2 - T_0 \bar{S} - \bar{\psi}_0. \quad (4.9)$$

With this, and referring back to equations (3.16), (3.17), and (3.18), the exergy flux equation becomes

$$\mathbf{J}_\Lambda = \mathbf{J}_q + \mathbf{J}_m (\bar{H} + \bar{\phi} + \frac{1}{2} \bar{v}^2 + \frac{1}{2} \bar{\sigma}^2) - T_0 \mathbf{J}_s - \mathbf{J}_m \bar{\psi}_0. \quad (4.10)$$

Combining this relation with the energy equation (3.22), we find

$$\text{div } \mathbf{J}_\Lambda = -\overset{0}{W}_d - T_0 \text{div } \mathbf{J}_s - \mathbf{J}_s \cdot \text{grad } T_0 - \mathbf{J}_m \cdot \text{grad } \bar{\psi}_0. \quad (4.11)$$

However, in the conventional treatment of exergy the reservoir conditions are considered to be a fixed reference base, so that the last two terms of equation (4.11) vanish, leaving

$$\text{div } \mathbf{J}_\Lambda = -T_0 \text{div } \mathbf{J}_s - \overset{0}{W}_d. \quad (4.12)$$

In the steady state $\text{div } \mathbf{J}_s$ is the rate of entropy creation per unit volume, and must be positive. Equation (4.12) is a familiar form, showing that the loss of exergy appears either as work output or as entropy creation. In a continuum where there is no means of work interaction $\overset{0}{W}_d$ is zero, and the loss of exergy on a reference base T_0 appears entirely as creation of entropy multiplied by that base temperature. The derivation given above shows that the results are valid in the presence of many different heat and mass fluxes, with widely differing temperatures and pressures, and with no restriction on the extent of chemical reaction which may occur as the fluxes move through the reference continuum. We make use of this fact to introduce the new concept which we term *disequilibrium*.

5. The concept of disequilibrium

It is common experience that in a steady state which is known not to be in equilibrium, appropriate sensors may nevertheless record steady mean values of temperature and of pressure, and hence steady values of the gradients of these properties. Without at present exploring the relation which will be shown to exist between these steady observed values, which we denote by T and p respectively, and the many different T_k and T_i and p_i included in the actual detail of the fluxes, we temporarily accept, on the basis of such experience, the hypothesis that T and p are observable. We then propose

to define a measure of the extent of non-equilibrium which exists at the location where T and p are observed, by the exergy in relation to a reservoir for which $T_0 = T$ and $p_0 = p$. This is a valid procedure since the choice of a reference reservoir is arbitrary. The important distinction is that the exergy determined on this basis is a function of the non-equilibrium condition alone, since along with all T_k and all T_i and p_i it uses the observed T and p , instead of an extraneous reference base.

Hence, for distinction, we adopt the name *disequilibrium* for this characteristic, and denote it by the distinct symbol η in place of Λ . The whole analysis proceeds precisely as in § 4 up to and including the result corresponding to equation (4.11),

$$\operatorname{div} \mathbf{J}_\eta = -\overset{0}{W}_d - T \operatorname{div} \mathbf{J}_s - \mathbf{J}_s \cdot \operatorname{grad} T - \mathbf{J}_m \cdot \operatorname{grad} \bar{\psi}_0. \tag{5.1}$$

The suffix zero retained on $\bar{\psi}_0$ denotes that it is an equilibrium value assessed now at T, p . Hence the terms in $\operatorname{grad} T$ and $\operatorname{grad} \bar{\psi}_0$ do not vanish and we do not proceed to a relation corresponding to equation (4.12). Instead, we have to consider the physical significance of the concept of disequilibrium in the steady state.

When a steady state is established the conditions throughout the reference space remain constant in time, no matter how diverse and non-uniform they may be. The fluxes of energy and matter from sources to sinks proceed steadily with generation of entropy. We know that if the fluxes were not maintained the system must decay to equilibrium. The meaning of a steady state is that the non-equilibrium condition can be maintained for the duration of that state. On this reasoning we suggest, as a physical principle, that when a steady state is set up the various reactions and interactions of the heat and mass fluxes occur in such a way that *there is no generation nor reduction of disequilibrium anywhere in the reference space*; i.e. that

$$\operatorname{div} \mathbf{J}_\eta = 0. \tag{5.2}$$

The constraint imposed by adopting equation (5.2) may be regarded either, as we have suggested, as the actual physical condition set up by the processes which occur in any steady state, or as a special case which is assumed for further development. Certainly equation (5.2) does provide a basis for very important and useful results, as will be seen in the following material.

Using condition (5.2) in equation (5.1), we can proceed immediately to the entropy generation equation

$$T \operatorname{div} \mathbf{J}_s = -\overset{0}{W}_d - \mathbf{J}_s \cdot \operatorname{grad} T - \mathbf{J}_m \cdot \operatorname{grad} \bar{\psi}_0. \tag{5.3}$$

For a continuum in which no means of work action exists, this becomes

$$T \operatorname{div} \mathbf{J}_s = -\mathbf{J}_s \cdot \operatorname{grad} T - \mathbf{J}_m \cdot \operatorname{grad} \bar{\psi}_0. \tag{5.4}$$

Equation (5.4) will be recognised immediately as a form familiar in contemporary theory of irreversible thermodynamics. But although the form is identical, the significance of our development is substantial. In contemporary theory the relation (5.4) is derived only on the basis of assuming local equilibrium at the observed T, p at every location, and is valid only for near-equilibrium conditions. In contrast our development has placed no restriction on the extent of non-equilibrium which may be present, other than the proposition that the steady state, no matter how great a disequilibrium is set up anywhere in the reference space, behaves so that no further change of disequilibrium occurs. This proposition is obviously physically consistent

with the concept of 'steadiness'. It is also evident that the conventional assumption of local equilibrium is an unnecessary constraint and limitation. The theory now proposed removes that limitation and opens the way for the application of equation (5.4) to situations grossly far from equilibrium.

However, it may be argued that observed values of T and p are more acceptable when local equilibrium can be assumed than in the highly non-equilibrium conditions which we have described in terms of various T_k , T_i and p_i , unless some relationship can be derived between these various values and the values T , p recorded by appropriate sensors. We therefore proceed to show in the next section that such relationships can indeed be found.

6. The reference temperature and pressure for disequilibrium

In § 3 we found that the total heat flux, including the contribution arising from the relative mass motion, was given by equations (3.17) and (3.16) as

$$\mathbf{J}_q = \sum_k \mathbf{J}_{q,k} + \sum_i \mathbf{J}_{r,i} (H_i + \phi_i + \frac{1}{2}v_i^2). \quad (6.1)$$

It is also apparent from equation (3.18) that the entropy flux associated with all the contributions to \mathbf{J}_q , which we may denote by $\mathbf{J}_{s,q}$, is given by

$$\mathbf{J}_{s,q} = \mathbf{J}_s - \mathbf{J}_m \bar{S} = \sum_k \mathbf{J}_{q,k}/T_k + \sum_i \mathbf{J}_{r,i} S_i. \quad (6.2)$$

It is therefore possible to use equations (6.1) and (6.2) to define quite precisely a temperature such that if it were applicable to the whole of \mathbf{J}_q the entropy flux would agree with the actual value arising from all the individual contributions. Let us denote this temperature by T_q ; its defining equation is

$$\mathbf{J}_q/T_q = \mathbf{J}_{s,q}. \quad (6.3)$$

The detail of equations (6.1) and (6.2) shows that the definition of T_q given by (6.3) fully subsumes all the individual T_k and T_i .

The exergy of \mathbf{J}_q with respect to a reservoir at T_0 is now simply $\mathbf{J}_q(1 - T_0/T_q)$, and is of course zero with respect to T_q . Thus if a sensor inserted at the location remained at a temperature below T_q it could extract work from the heat flux, while if it attained a temperature greater than T_q work could be supplied. In this sense T_q is a temperature which is in 'equilibrium' with all the actual T_k and T_i , and on this basis we now assume that the observed value T of temperature in the steady state will be equal to T_q as defined by equation (6.3).

This argument may be summed up in the statement that we shall assume that the value of temperature T observed by an appropriate sensor in the non-equilibrium steady state is given by the equation

$$\sum_k \mathbf{J}_{q,k} + \sum_i \mathbf{J}_{r,i} (H_i + \phi_i + \frac{1}{2}v_i^2) = T \left(\sum_k \mathbf{J}_{q,k}/T_k + \sum_i \mathbf{J}_{r,i} S_i \right). \quad (6.4)$$

It is this temperature T as defined by equation (6.4) which is the basis for the measurement of the disequilibrium η . Using equation (4.4), the disequilibrium per unit mass of an individual stream is given by

$$\eta = H_i + \phi_i + \frac{1}{2}v_i^2 - TS_i - \bar{\psi}_0. \quad (6.5)$$

Correspondingly the mean value of disequilibrium per unit mass of the heterogeneous non-equilibrium flow is

$$\bar{\eta} = \bar{H} + \bar{\phi} + \frac{1}{2}\bar{v}^2 + \frac{1}{2}\bar{\sigma}^2 - T\bar{S} - \bar{\psi}_0. \quad (6.6)$$

It should be remarked that although the exergy and disequilibrium expressions contain only the reference temperature explicitly, the reference pressure is also present implicitly, since the equilibrium constitution, and hence the potential $\bar{\psi}_0$, depends upon pressure as well as on temperature. For the disequilibrium the reference pressure must be p , where p is the observable pressure resulting from all the individual p_i . The appropriate value may be established as follows.

Each individual p_i acts over the area cross-section a_i occupied by the stream J_i . Hence the effective pressure over unit area is

$$p = \sum_i p_i a_i. \quad (6.7)$$

Using equation (3.10) for a_i gives

$$p\bar{V} = \sum_i b_i p_i V_i. \quad (6.8)$$

Equation (6.8) defines the pressure p observable in the non-equilibrium condition, which along with T gives the reference base for the disequilibrium.

It is evident that there are two very different circumstances under which the mean disequilibrium $\bar{\eta}$ will be zero. One of these is obviously when each individual η_i is zero for all i . This is the case of true equilibrium, implying uniformity of p_i and T_i for all i at the macroscopically observed values p and T . The second possibility is that although all η_i are not uniformly zero, their weighted sum $\bar{\eta} = \sum b_i \eta_i = 0$. This forms a local quasi-equilibrium giving the zero value of disequilibrium. Now it is suggested that although conventional irreversible thermodynamics of the steady state is usually said to be based on the assumption of local equilibrium, it must actually correspond to local *quasi-equilibrium* as described in the second case where $\bar{\eta}$ is zero despite individual variations. The first case, with all η_i individually zero, cannot seriously be expected to be true for any real irreversible steady state.

For any condition, no matter how far from equilibrium, the mean values of any of the specific properties entropy, enthalpy, etc, are given in general by $\bar{S} = \sum b_i S_i$, $\bar{H} = \sum b_i H_i$ etc. For the special case of local quasi-equilibrium where $\bar{\eta} = 0$, we may usefully adopt the special symbols \bar{S}_0 , \bar{H}_0 , etc. At true equilibrium the corresponding values would of course be S_0 , H_0 , etc.

We now note an important consequence of the definition of T . Referring back to the exergy flux equation (4.8) in terms of a reference base T_0 , we observe that if equation (6.4) were satisfied by $T_0 = T$, the exergy flux would reduce simply to $J_m \bar{\Lambda}$. It follows therefore that the disequilibrium flux is always simply $J_m \bar{\eta}$, and hence the assumed steady-state condition of equation (5.2), that $\text{div } J_\eta$ must be zero, means that the disequilibrium $\bar{\eta}$ attains a uniform value throughout the reference space in the steady state. Conventional theory has a similar but more restrictive condition, since the assumption of local equilibrium means that disequilibrium is uniform, at the particular value zero.

The useful conclusions of this section are that the values of T , p and $\bar{\eta}$ are well defined characteristics of the actual non-equilibrium condition, and so validate the applicability of the entropy generation equation (5.4) derived in the previous section.

As already noted, the form of that equation is identical to that familiar in accepted Onsager-based theory, but the significance has important differences. These are discussed in the next section.

7. Correspondence of parameters

In this section we note the correspondences and differences between the concepts and parameters used in contemporary accepted theory of the steady state, and those which arise from the treatment we propose. Particular attention must be devoted to those parameters appearing in the entropy generation equation (5.4).

The temperature T and pressure p carry the same significance intrinsically in both cases, of being macroscopically observable characteristics. The combined potential $\bar{\psi}_0$ is also the same in both cases, being the value for equilibrium at T, p . In conventional theory, however, it is assumed that all properties can be taken as having equilibrium values for the temperature and pressure at the location, and that the actual conditions are never very far from equilibrium at any point. On this basis, as is well known, the fundamental statistical mechanics upon which accepted theory is based predicts the existence of certain parameters, usually denoted by S^*, H^* , etc, which are also properties of the equilibrium state. Their values, which characterise the response to small near-equilibrium perturbations, can be calculated from the statistics of specific microscopic models, and usually differ in value from the corresponding S_0, H_0 , etc. In contrast, our model puts no constraint on the extent of non-equilibrium, and gives the disequilibrium $\bar{\eta}$ as a quantitative measure of that extent. However, we do adopt the constraint that, whatever the value of $\bar{\eta}$, it is uniform throughout the reference space of the steady state. Conventional theory has the similar but more restricting condition of limiting the uniform value to zero.

The general values \bar{S}, \bar{H} , etc of our phenomenological model when $\bar{\eta}$ is not zero must be regarded as quite distinct from the parameters S^*, H^* , etc of conventional theory. However, in our theory we recognise the possibility of a quasi-equilibrium condition where $\bar{\eta} = 0$, and it can be surmised that the values \bar{S}_0, \bar{H}_0 , etc in that condition may be identified with S^*, H^* , etc.

We now turn to comparison of the theories in respect of entropy generation, as given in equation (5.4). For convenience we repeat that equation and renumber it here:

$$T \operatorname{div} \mathbf{J}_s = -\mathbf{J}_s \cdot \operatorname{grad} T - \mathbf{J}_m \cdot \operatorname{grad} \bar{\psi}_0. \quad (7.1)$$

As noted already, the form of the equation is the same as that of accepted theory. But despite the formal identity there are very substantial differences. The extent of non-uniformity in the various p_i and T_i , and the differing values of T_k , are not allowed for at all in accepted theory, nor is the non-zero uniform disequilibrium. As a result of the presence of these features in our case there is an important difference in the meaning of the entropy flux \mathbf{J}_s . In our case we have, with complete generality,

$$\mathbf{J}_s = \mathbf{J}_q/T + \mathbf{J}_m \bar{S} \quad (7.2)$$

while in accepted theory

$$\mathbf{J}_s = \mathbf{J}_q/T + \mathbf{J}_m S^*. \quad (7.3)$$

However, when $\bar{\eta} = 0$ we have in our case

$$\mathbf{J}_s = \mathbf{J}_q/T + \mathbf{J}_m \bar{S}_0. \quad (7.4)$$

Thus, if we accept the identification of \bar{S}_0 with S^* as suggested above, our phenomenological treatment gives an entropy generation equation which is fully consistent with accepted theory for the case of zero disequilibrium, but which may be extended to conditions far from equilibrium. The quantity \bar{S} in our case is the specific entropy of the heterogeneous unit mass and as such its meaning is continuous from the true equilibrium value S_0 through the quasi-equilibrium value \bar{S}_0 to the general non-equilibrium value. However large, or small, $\bar{\eta}$ may be, the analysis gives a precise meaning to \bar{S} as $\sum b_i S_i$. Although it may not be possible to determine its value by statistical mechanics for conditions far from equilibrium, its existence and significance are well defined by the present theory.

This is as far as the introduction of the concept of disequilibrium alone can take us. In essence its contribution is to enable a reinterpretation of the usual form of the entropy generation equation (7.1). To make further progress we now transform that equation, by applying the general considerations on collinearity of flux-force vector pairs which we established in § 2 and have not yet used.

8. Flux-force relations in entropy generation

We can now consider the entropy generation equation (7.1) in the light of the general discussion on flux-force relations given in § 2. Recalling that

$$\mathbf{J}_s = \mathbf{J}_q/T + \mathbf{J}_m \bar{S},$$

we see that equation (7.1) can be written in either of the two alternative forms

$$T \operatorname{div} \mathbf{J}_s = -\mathbf{J}_s \cdot \operatorname{grad} T - \mathbf{J}_m \cdot \operatorname{grad} \bar{\psi}_0 \tag{8.1}$$

or

$$T \operatorname{div} \mathbf{J}_s = -(\mathbf{J}_q/T) \cdot \operatorname{grad} T - \mathbf{J}_m \cdot (\bar{S} \operatorname{grad} T + \operatorname{grad} \bar{\psi}_0). \tag{8.2}$$

Comparison with the general theory in § 2 shows the following correspondences.

$T \operatorname{div} \mathbf{J}_s$	corresponds to	A
\mathbf{J}_s	corresponds to	\mathbf{J}_1
$-\operatorname{grad} T$	corresponds to	\mathbf{X}_1
\mathbf{J}_m	corresponds to	\mathbf{J}_2
$-\operatorname{grad} \bar{\psi}_0$	corresponds to	\mathbf{X}_2
$\mathbf{J}_q/T \equiv \mathbf{J}_s - \bar{S} \mathbf{J}_m$	corresponds to	\mathbf{J}'_1
$-(\bar{S} \operatorname{grad} T + \operatorname{grad} \bar{\psi}_0)$	corresponds to	\mathbf{X}'_2
\bar{S}	corresponds to	α .

Since the flux \mathbf{J}_s includes the contribution $\bar{S} \mathbf{J}_m$, \mathbf{J}_s and \mathbf{J}_m are not mutually exclusive. In contrast, the fluxes \mathbf{J}_q and \mathbf{J}_m are mutually exclusive since \mathbf{J}_q was carefully defined to exclude any and all energy or enthalpy carried along with \mathbf{J}_m . The fact that \mathbf{J}_q includes contributions carried along with each of the subordinate relative mass fluxes $\mathbf{J}_{r,i}$ is irrelevant in this connection, since $\sum \mathbf{J}_{r,i} = 0$ whatever the value of \mathbf{J}_m .

We now suggest that the mutual exclusion property of the vectors \mathbf{J}_q and \mathbf{J}_m gives an acceptable reason for assuming that these form the possible collinear set with respective conjugate forces discussed in § 2. Thus we write

$$\mathbf{J}_q = -\lambda_q \text{grad } T \quad (8.3)$$

$$\mathbf{J}_m = -\lambda_m (\bar{S} \text{grad } T + \text{grad } \bar{\psi}_0). \quad (8.4)$$

It is then merely formal to show that the set with equal cross-coefficients discussed in § 2 is

$$\mathbf{J}_s = -(\lambda_q/T + \lambda_m \bar{S}^2) \text{grad } T - \lambda_m \bar{S} \text{grad } \bar{\psi}_0 \quad (8.5)$$

$$\mathbf{J}_m = -\lambda_m \bar{S} \text{grad } T - \lambda_m \text{grad } \bar{\psi}_0. \quad (8.6)$$

Equations (8.5) and (8.6) may be compared with the results of conventional theory for the near-equilibrium steady state, which are

$$\mathbf{J}_s = -(K/T + S^{*2}/r) \text{grad } T - (S^*/r) \text{grad } \bar{\psi}_0 \quad (8.7)$$

$$\mathbf{J}_m = -(S^*/r) \text{grad } T - (1/r) \text{grad } \bar{\psi}_0. \quad (8.8)$$

In these equations S^* is the entropy transport parameter already discussed in § 7. It was shown therein that \bar{S} corresponds in our general theory to S^* , with its particular value \bar{S}_0 at quasi-equilibrium being identified with S^* . The coefficient K is the thermal conductivity *measured* under conditions of zero mass flux, while r is the resistance to mass flux *measured* under conditions of zero temperature gradient. Since in the conventional theory S^* , K and r are all equilibrium properties, they are constants in these equations and assumed to be valid under any conditions.

It is evident from equations (8.3) and (8.4) that λ_q is a concept of thermal conductivity corresponding to K and that λ_m is a concept of reciprocal of resistance to mass flux corresponding to $1/r$. Thus our results (8.5) and (8.6) correspond phenomenologically with the accepted results (8.7) and (8.8), with \bar{S} , λ_q and λ_m taking the place of S^* , K and $1/r$ respectively. They will therefore agree precisely at near-equilibrium conditions if, as suggested in § 7, \bar{S}_0 is identified with S^* .

The practical difference and advantage is that the whole conceptual pattern can now be extended without misgiving to conditions far from equilibrium, where \bar{S} , λ_q and λ_m need not be constant. The value of λ_q can be obtained without restriction to zero mass flow and that of λ_m without restriction to zero temperature gradient, and experimental results will determine the extent to which the three parameters may in fact be variable.

We may note for later use that when equations (8.3) and (8.4) are used, the entropy generation rate becomes

$$T \text{div } \mathbf{J}_s = \mathbf{J}_q^2/\lambda_q T + \mathbf{J}_m^2/\lambda_m, \quad (8.9)$$

i.e. the contributions from \mathbf{J}_q and \mathbf{J}_m are individual. If any coupling exists between these contributions it is catered for by variations in λ_q and λ_m .

It is noteworthy that although the conventional theory emphasises coupling between \mathbf{J}_s and \mathbf{J}_m and uses the forms of equations (8.7) and (8.8) in the entropy generation equation of the form (8.1), the final result gives exactly the same:

$$T \text{div } \mathbf{J}_s = \mathbf{J}_q^2/KT + r\mathbf{J}_m^2. \quad (8.10)$$

The formal equivalence of λ_q and K , and of $1/\lambda_m$ and r has already been noted.

It is unnecessary to develop these correspondences much further in detail. It is sufficient to remark that every phenomenon discussed by conventional theory in terms

of S^* can be equally well discussed in terms of \bar{S} and its range of applicability very much extended. The expansion of $\text{grad } \bar{\psi}_0$, which is common to both conventional theory and our equations, gives

$$\text{grad } \bar{\psi}_0 = V_0 \text{grad } p - S_0 \text{grad } T + \sum g_{i,0} \text{grad } z_{i,0} + \text{grad } \bar{\phi}_0. \quad (8.11)$$

When this is inserted into equation (8.4), we have the condition that J_m can be zero when

$$V_0 \text{grad } p + \text{grad } \bar{\phi}_0 + \sum g_{i,0} \text{grad } z_{i,0} = (\bar{S} - S_0) \text{grad } T. \quad (8.12)$$

Conventional theory gives the same result with S^* instead of \bar{S} .

This is the equation which accounts for the existence of a pressure gradient or a potential gradient as a result of a temperature gradient. It is inherently a non-equilibrium effect since it vanishes when \bar{S} , or S^* in conventional theory, is equal to S_0 .

It is obvious that the familiar 'heat of transport' $T(S^* - S_0)$ of conventional theory is generalised in our case to $T(\bar{S} - S_0)$. Moreover, recalling the discussion of the potential ϕ_i in § 3, it will be realised that where electromagnetic effects are present the relative directions of the underlying individual streams will have significance.

The important conclusion of the whole theory is that, if we accept the descriptive model of the steady state in terms of uniform disequilibrium, as developed in §§ 3–7 inclusive, all the consequent steady-state phenomena can be discussed in terms of the experimentally accessible parameters λ_q , λ_m and \bar{S} , and such that discussion is continuous with conventional theory, reducing to the latter for near-equilibrium conditions. Evidently the actual utility of this in steady-state applications known to be very far from equilibrium, such as turbulent multi-phase multi-component flows, MHD plasmas and the like, can only be tested by experimental work, but at least it provides a reasonable ground for extension of irreversible thermodynamics to these fields of work. These possibilities will be further studied in future papers. Meanwhile a brief indication of the scope for applications, and some preliminary results, are given in the next section.

9. Applications and scope

The previous sections have established the main objectives of this study, namely (a) that the choice of fluxes of heat and mass collinear with their respective conjugate forces is as valid as the conventional choice of a non-collinear set, and (b) that a phenomenological model of the steady state can be developed to give valid meaning to the specific properties entropy, enthalpy, etc, under steady-state non-equilibrium conditions. It has also been shown in § 8 that the use of this treatment gives the same results as conventional theory for totally dissipative flows at near-equilibrium conditions, but is capable of extension to conditions far from equilibrium. It is therefore worthwhile to add a brief concluding section illustrating the possible scope of the theory.

First we establish certain interesting interrelations. We may expand the entropy generation rate as follows:

$$\begin{aligned} T \text{div } J_s &= T \text{div} (J_q/T + J_m \bar{S}) \\ &= \text{div } J_q - (J_q/T) \cdot \text{grad } T + T J_m \text{grad } \bar{S}. \end{aligned} \quad (9.1)$$

Then using equation (8.9) and (8.3) we find

$$-\text{div } J_q + J_m^2/\lambda_m = T J_m \cdot \text{grad } \bar{S}. \quad (9.2)$$

The LHS of equation (9.2) is the sum of the heat absorption plus dissipation due to mass flow, per unit volume. Note that the dissipation $\mathbf{J}_q^2/\lambda_q T$ is not included.

Now let us define a property τ as the sum of heat absorption plus frictional dissipation per unit mass per unit temperature rise, i.e. the definition of this property is

$$\tau \equiv \frac{-\operatorname{div} \mathbf{J}_q + \mathbf{J}_m^2/\lambda_m}{\mathbf{J}_m \cdot \operatorname{grad} T}. \quad (9.3)$$

Equation (9.2) shows therefore that

$$\tau = T \, d\bar{S}/dT. \quad (9.4)$$

Similarly, if the mass flux crosses a constant temperature discontinuity from a region A to a region B , we may define a property Π as the sum of the heat absorption plus frictional dissipation per unit mass in crossing from A to B , i.e. the definition of this property is

$$\Pi_{ab} \equiv \frac{-\int_A^B \operatorname{div} \mathbf{J}_q \, dl + \int_A^B (\mathbf{J}_m^2/\lambda_m) \, dl}{\mathbf{J}_m}. \quad (9.5)$$

Equation (9.2) shows that

$$\Pi_{ab} = T(\bar{S}_b - \bar{S}_a). \quad (9.6)$$

Finally, if we define the total integral of heat absorption plus frictional dissipation per unit mass making one circuit of a closed loop, as a property denoted by ξ , equation (9.2) shows that

$$\xi = \oint T \, d\bar{S} = -\oint \bar{S} \, dT. \quad (9.7)$$

Now if the loop contains two distinguishable portions A and B and is such that \mathbf{J}_m flows from A to B at T_1 and from B to A at T_2 , we have

$$\xi_{ab} = -\int_1^2 \bar{S}_b \, dT - \int_2^1 \bar{S}_a \, dT = \int_2^1 (\bar{S}_b - \bar{S}_a) \, dT. \quad (9.8)$$

Thus we see that if T_2 is kept constant and T_1 varied, and denoted by the general symbol T ,

$$d\xi_{ab}/dT = \bar{S}_b - \bar{S}_a = \Pi_{ab}/T. \quad (9.9)$$

Also from equations (9.6) and (9.4) we see that

$$T \frac{d}{dT} \left(\frac{\Pi_{ab}}{T} \right) = T \frac{d\bar{S}_b}{dT} - T \frac{d\bar{S}_a}{dT} = -(\tau_a - \tau_b). \quad (9.10)$$

Thus the following interrelations are established:

$$\Pi_{ab} = T \, d\xi_{ab}/dT \quad \tau_a - \tau_b = -T \, d^2\xi_{ab}/dT^2. \quad (9.11)$$

Equations (9.11) are immediately recognisable as the familiar so-called 'thermocouple relations', and we have used familiar symbols. But, as shown, they are completely general for any loop circuit in the steady state, irrespective of the nature of the mass flux, irrespective of load and irrespective of extent of departure from equilibrium. When the mass flux carries a charge, the results give electrical current and potential. There are several other important points to note in comparison with the present state of thermocouple theory.

First of all, when \mathbf{J}_m is zero we have the value τ^0 as

$$\tau^0 = T \, d\bar{S}^0/dT. \quad (9.12)$$

We have correspondingly

$$\Pi_{ab}^0 = T(\bar{S}_b^0 - \bar{S}_a^0) \quad (9.13)$$

$$\xi_{ab}^0 = \int_2^1 (\bar{S}_b^0 - \bar{S}_a^0) \, dT. \quad (9.14)$$

The superscript 0 on these values denotes the condition when the mass flux is zero. This must not be regarded as necessarily a near-equilibrium state, for with a high temperature difference the heat flux may be substantial and the situation highly irreversible. The thermal dissipation $\mathbf{J}_q^2/\lambda_q T$ is active throughout, and without it the circuit conditions could not be maintained. But it requires experiment or statistical theory to relate it to the value of $\bar{S}^0 - S_0$ which is maintained. Phenomenological theory cannot accomplish this. (It must be recalled that the definitions do not require any of the properties to be constant independent of fluxes and forces.)

In contrast, accepted contemporary theory assumes near-equilibrium conditions with constant properties and is only valid for such situations. This is met by our case by using the value \bar{S}_0 instead of \bar{S} or \bar{S}^0 . Conventional theory has the same results with S^* , confirming our view that \bar{S}_0 is identical with S^* .

Perhaps the most important result of our treatment is to show that the *interrelations* are totally independent of the value of \bar{S} , although the numerical values of τ , Π and ξ will be dependent on the actual value. Hence the *interrelations* could be derived by treating the circuit as if it were in equilibrium, i.e. using S_0 throughout instead of \bar{S} . This is essentially what Kelvin did, although he did not use the entropy concept, and our analysis explains fully why he obtained the correct results. He was fully aware that the thermocouple was merely one example of a convective circuit and indeed in one little known paper (Thomson 1882) discussed it as an analogue to a thermosyphon hot water system.

Another important feature is that the Thomson effect, Peltier effect and Seebeck effect are all functions of \bar{S} and *not* of the difference between \bar{S} and S_0 . Unfortunately some writers in their accounts of the thermocouple imply that the effects arise because of this difference, via the pressure gradient or potential gradient set up by a temperature gradient according to equation (8.12). But equation (9.2) shows quite clearly that although these effects do exist the heat absorption is related to \bar{S} irrespective of the difference between \bar{S} and S_0 . The property τ is quite simply the non-equilibrium value of specific heat, having the limiting equilibrium value $T \, dS_0/dT$ for ideal equilibrium conditions, and $T \, d\bar{S}_0/dT$ for quasi-equilibrium. Thus the pre-Onsager writers who referred to the Thomson coefficient as the 'specific heat of electricity' were essentially correct, although they tend to be scorned by the more sophisticated attitudes of today.

In this connection it can be seen that the conventional presentation of Thomson and Peltier effects in physics texts obscures their real nature. Typically the Thomson effect is discussed in terms of 'maintaining a particular temperature distribution' in a wire. It is said that if that distribution is noted at zero current and then a current is supplied along the wire 'the heat that must be supplied or extracted at all places along the wire to restore the initial temperature distribution is called the Thomson heat. If the current in one direction requires heat to be supplied to maintain the distribution, current in the

reverse direction will require heat to be extracted to maintain the distribution so the effect is reversible.'

But this is just the same as a fluid flowing along a tube with heat supplied all along the tube, although no-one would describe it in such terms. We simply say that we heat it or cool it, but we could use the same vocabulary as is conventionally used for the thermocouple as follows. At a steady state we establish a definite temperature distribution along the tube. If we increase the mass flow rate we have to increase the heat supply rate to maintain the same temperature distribution. If we reverse the flow we have to extract heat to maintain the same distribution. In short, the Thomson phenomena of heat rate and flow rate in a thermocouple wire are exactly those familiar in a heat exchanger tube. The correspondence is really trivial, but it is rather a pity that the discussion of thermoelectric phenomena usually obscures it.

However there are important differences within this correspondence. (i) Usually the resistive dissipation effects are proportionally much greater in the case of current flow in a wire than in fluid flow in a tube. (ii) Because of the much higher thermal conductivity of the wire, and the proportionally much lower rate of lateral heat absorption than in the fluid flow case, the heat absorption in an element length dx in the wire case has to include a significant proportion from the variation of axial heat flux which in the fluid flow case is usually negligible. (iii) Because of these differences, it is hardly possible to maintain the temperature distribution along a tube with extremely low fluid flow rates approaching zero, whereas in a wire we can easily have zero current with a given temperature distribution.

But in fluid flow along very fine capillaries, and in flow through porous materials and membranes, these differences will become less marked. In such applications, therefore, it may be useful to bear in mind the correspondence with thermoelectric phenomena. This may have special relevance in biophysics, and may be useful for analogue modelling.

The above remarks refer to the Thomson effect, or Peltier effect, considered singly. The interrelations, and the Seebeck effect of a completed loop circuit, will have obvious relevance wherever capillary fluid circuits occur. Again these may arise in biophysics applications.

Finally it is easy to show that if $\overset{0}{W}_d$ is retained in equation (7.1) instead of being put equal to zero, the whole analysis still applies and the entropy generation equation (8.2) contains only a single additional term:

$$T \operatorname{div} \mathbf{J}_s = -\overset{0}{W}_d - (\mathbf{J}_q/T) \cdot \operatorname{grad} T - \mathbf{J}_m \cdot (\bar{\mathbf{S}} \operatorname{grad} T + \operatorname{grad} \bar{\psi}_0). \quad (9.15)$$

This, together with the fact that the theory is applicable to steady states, however great the irreversibility or non-equilibrium condition, should enable it to be used profitably in application to many situations in mechanical, electrical, chemical and process engineering.

The important point of principle is the continuity of the analysis over the whole range from equilibrium thermodynamics to highly irreversible steady states.

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Appendix 1. List of symbols

a_i	fraction of cross-sectional area occupied by homogeneity of kind i	U_i	internal energy of unit mass of homogeneity i
A	general scalar	$\bar{U} \equiv$	$\Sigma b_i U_i$
b_i	mass concentration of homogeneity i	v_i	velocity of stream J_i
$g_{i,0}$	partial chemical potential per unit mass of species j at equilibrium	\bar{v}	$\Sigma b_i v_i$
$\bar{g}_0 =$	$\Sigma z_{j,0} g_{j,0}$	$v_{r,i}$	$v_i - \bar{v}$
G_i	chemical potential of unit mass of homogeneity i	V_i	volume of unit mass of homogeneity i
$\bar{G} \equiv$	$\Sigma b_i G_i$	$\bar{V} \equiv$	$\Sigma b_i V_i$
H_i	enthalpy of unit mass of homogeneity i	$\overset{0}{W}_d$	rate of work delivered from unit volume
$\bar{H} \equiv$	$\Sigma b_i H_i$	z_j	mass concentration of species j in unit heterogeneous mass
J_1, J_2, J'_1	flux symbols for general discussion	$z_{j,i}$	mass of species j in the homogeneity b_i
J_i	mass flux rate of stream of homogeneity i	$z_{j,i,0}$	mass of species j in the homogeneity b_i when at equilibrium within b_i
J_m	total mass flux rate $\equiv \Sigma J_i$	$z_{j,0}$	mass concentration of species j at final equilibrium
$J_{r,i} \equiv$	$J_i - b_i J_m$ relative mass flux rate	X_1, X_2, X'_2	force symbols for general discussion
J_s	total entropy flux rate	X_s	force conjugate to J_s
$J_{q,k}$	heat flux rate entirely unassociated with any mass motion (occurring at temperature T_k)	X_m	force conjugate to J_m
$J_{q,r}$	heat flux rate arising from relative mass motion $\equiv \Sigma J_{r,i} (H_i + \Phi_i + \frac{1}{2} v_i^2)$	α	scalar property defined in § 2
J_q	total heat flux rate $\equiv \Sigma_k J_{q,k} + J_{q,r}$	ϵ_i	energy of unit mass of homogeneity i
K	thermal conductivity	$\bar{\epsilon} \equiv$	$\Sigma b_i \epsilon_i$ energy of unit heterogeneous mass
p	observed steady state pressure at reference location	ϕ_i	field potential of unit mass of homogeneity i
p_0	pressure in reservoir	$\bar{\phi} \equiv$	$\Sigma b_i \phi_i$ field potential of unit heterogeneous mass
p_i	pressure of homogeneity i	ϕ_j	field potential of unit mass of species j
r	dissipative resistance to mass flux	$\phi_0 =$	$\Sigma z_{j,0} \phi_j$ field potential of unit heterogeneous mass at equilibrium
S_i	entropy of unit mass of homogeneity i	Λ_i	exergy of unit mass of b_i
$\bar{S} \equiv$	$\Sigma b_i S_i$	$\bar{\Lambda}$	exergy of unit heterogeneous mass
\bar{S}^0	value of \bar{S} with zero mass flux	η_i	disequilibrium of unit mass of homogeneity i
\bar{S}_0	value of \bar{S} at quasi-equilibrium	$\bar{\eta}$	mean disequilibrium of unit heterogeneous mass
S_0	value of \bar{S} at true equilibrium	λ	with various suffixes defined in text—
S^*	entropy transport parameter	τ, Π, ξ	generalised properties corresponding respectively to Thomson, Peltier and Seebeck properties in a thermocouple
$T =$	temperature defined by equation (6.4) and shown in § 6 to be observed temperature	$\bar{\psi}_0 \equiv$	$\bar{\phi}_0 + \bar{g}_0$
$T_k =$	temperature associated with the heat flux $J_{q,k}$		
T_0	temperature in reservoir		
T_i	temperature of homogeneity i		

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