ON AXIOMS FOR HETEROGENEOUS CONTINUA

by

A. A. Hayday

UNIVERSITY OF ALABAMA RESEARCH INSTITUTE

Huntsville, Alabama

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**Associate Professor of Mathematics and Mechanics
University of Alabama Research Institute, Huntsville, Alabama, U.S.A.

Summary

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The paper deals with the derivation of general conservation equations for heterogeneous continua - substances consisting of several distinct, possibly interacting constituents. The analysis, resting for the most part on an admissible superposition of the diffusive motions on the postulated motion of the mixture, is based on axioms in integral form from which the basic differential equations are deduced. The treatment is a rigorous, direct generalization of the classical theory for simple continua. The main results are compared with those of Truesdell and found to be in entire agreement.

Author

1. Introduction

From the viewpoint of continuum physics, the behavior of many materials is well described by the properties of an ideal medium - the simple continuum; but this classical representation must be modified and extended in order that it suffice as a model for materials consisting of several distinct and mutually inter-acting constituents. A continuum theory describing such materials is called herein a heterogeneous continuum theory. In the broadest sense, it is not restricted to any particular state of continuously distributed heterogeneous matter and therefore covers,* for example, flows of reacting mixtures of gases, liquids containing small solid particles in suspension, and electrically conducting plasmas.

A general theory for heterogeneous continua was published by C. Truesdell [1, 2]. While rigorous, Truesdell's treatment is rather formal. He postulates the differential balance equations for the constituents and sums these over all constituents to obtain the equations for the medium as a whole. The summations are so performed that each of the resultant equations possesses the same mathe-matical form as the corresponding equation for a simple continuum. More recently, Kelly [3] gave a derivation of Truesdell's results starting from axioms in integral form and including electromagnetic effects. Basically, his formalism amounts to spatial integration and summation of the equations postulated by Truesdell, a certain degree of order being introduced into the summation procedures by what he calls a general balance principle stated for volumes fixed in space.

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*We are referring to general equations of balance that, for each particular continuum, must be developed and specialized further by including definite constitutive equations. This paper, as well as the first three quoted works, deals mainly with the derivation of the general balance equations and not the constitutive equations. Numerous earlier papers, usually of a more special nature, are not quoted herein because they are listed, together with critical evaluations, in the exhaustive bibliography of [2].

This paper, an extension of the author's earlier work [4], deals with the development of a different mathematical model for heterogeneous continua. The treatment is rigorous, yet simple and direct, and is closely related to the classical theory for simple continua. It rests for the most part on an admissible superposition of the diffusive motions of the components on the postulated motion for the mixture. Material properties ascribed to the medium as a whole are used consistently. In particular, the main axioms, unlike those in [1, 2] and [3], are stated in integral form in terms of well defined material volumes for the heterogeneous continuum. The differential balance equations for the medium as a whole are deduced from these axioms and shown to be in agreement with Truesdell's results. The reader, if he likes, may consider this formulation as an alternate to [1, 2] and in part to [3] and also as a generalized analog of the classical theory of one component fluid flow. An excellent treatment of the latter is due to J. Serrin [5].

2. Premises and Kinematical Definitions

The mathematical description of heterogeneous continua is based on identifying tangible portions of heterogeneous matter with sets of points in three-dimensional Euclidean space. The motion of the medium as a whole – the motion of a mixture – is represented herein by a one-to-one continuous transformation of the space into itself. The parameter t of this transformation represents time and its range is $-\infty < t < \infty$ where $t = 0$ specifies an arbitrary initial instant. Thus[*]

$$x_i = \phi_i (X_i, t); \qquad (2.1)$$

the spatial variables x_i denote the positions of mixture particles distinguished from all others by means of the material variables X_i conveniently chosen as the positions of mixture particles at $t = 0$. Hence t may be restricted to $0 \leq t < \infty$.

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[*]We use both Cartesian tensor notation and vector notation. Tensor indices appear as subscripts and vectors are distinguished from other quantities by bars above a letter. The superscripts are devoid of tensorial meaning and denote the components of the mixture. All functions appearing herein are assumed to be as many times continuously differentiable as required.

The Jacobian, J, of the mapping (2.1) is such that

$$0 < J \equiv \det\left(\frac{\partial x_i}{\partial X_i}\right) < \infty .$$ (2.2)

The terms "moving mixture particle" and moving point in space are synonymous. By definition, an arbitrary finite volume $V(t)$ is called material if it moves with the mixture; that is, every point of the bounding material surface S moves according to (2.1).

We will consider a heterogeneous continuum consisting of say N substances and distinguish it from a simple (one-component) continuum by the two following properties, regarded as explicit hypotheses.

1) There exist functions $\rho^k(\bar{x}, t) > 0$ such that the mass M^k of the kth component* is

$$M^k = \int_V \rho^k \, dv .$$ (2.3)

2) There exist vector fields $J_i^k(x_i, t)$ that are a priori known functions of certain well defined thermodynamic variables. These vector fields, called the diffusive (mass) fluxes, satisfy the condition

$$\sum_{k=1}^{N} J_i^k(x_i, t) = 0.$$ (2.4)

The total mass of the mixture is

$$M \equiv \sum_{k=1}^{N} M^k.$$ (2.5)

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*Hereafter $k \in \{1, 2, \ldots, N\}$ will always serve to identify a typical substance of the continuum.

We set $M = \int_V \rho \, dv$ and thus

$$\rho = \sum_{k=1}^{N} \rho^k. \quad ^*$$

The concentrations of the components are defined as $w^k = \rho^k/\rho$. Clearly $\Sigma w^k = 1$.

The velocities and accelerations of the mixture are defined as

$$v_i \equiv \left. \frac{\partial \phi_i}{\partial t} \right|_{X_i} \tag{2.6}$$

and

$$a_i \equiv \left. \frac{\partial v_i}{\partial t} \right|_{X_i}. \tag{2.7}$$

The symbol $\left. \frac{\partial}{\partial t} \right|_{X_i}$ is henceforth replaced by $\frac{D}{Dt}$, and $\frac{\partial}{\partial t}$ represents the usual derivative holding x_i fixed.

From (2.1), (2.2), (2.6) and (2.7) we obtain $a_i = \frac{\partial v_i}{\partial t} + v_i v_{i,i}$. A more general formula is

$$\frac{DF}{Dt} = \frac{\partial F}{\partial t} + v_i F_{,i} \tag{2.8}$$

where F stands for a scalar or a component of a vector quantity associated with the motion.

The diffusive velocities v_i^k, defined as

$$v_i^k \equiv J_i^k / \rho^k , \tag{2.9}$$

are regarded as "carriers" of masses, momenta and energies for the individual components relative to the motion (2.1). They form the apparatus whereby masses, momenta, and energies are transported by diffusion into an arbitrary material

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*Henceforth we introduce a more compact notation: $\Sigma \equiv \sum\limits_{k=1}^{N}$, $\int \equiv \int\limits_V$ and $\oint \equiv \oint\limits_S$. While omitting the symbols S and V on integral signs, in the text we shall always emphasize our consistent use of material volumes and surfaces.

volume V. Scalar products of the v_i^k's with various forces shall be called work rates due to diffusion. With reference to an arbitrary material volume, we state the following superposition principle:

"Diffusive phenomena are superposed (added tensorially) on

the corresponding phenomena associated with the mixture motion."

This principle forms the basis for the axioms presented in the next section and, through their consequences, is shown to imply a definite interdependence of the mixture motion as a whole and the diffusive motions of the components.

In addition to the above, we shall frequently make use of the following well known theorem

Transport Theorem - Let V be an arbitrary material volume and

$F(\bar{x}, t)$ a scalar or vector function of position. Then

$$\frac{D}{Dt} \int F \, dv = \int (\frac{DF}{Dt} + Fv_{i,i}) \, dv \ . \tag{2.10}$$

The proof is standard and will not be given.

3. Conservation Principles

The differential equations governing the behavior of the mixture are deduced from the following postulates.

Postulate I:

The rate of change of mass of the kth component of the mixture within an arbitrary material volume V equals the sum of its diffusive mass flow into V and the rate of production* of mass of the kth component. This conservation principle is expressed by the statement

$$\frac{D}{Dt} \int \rho^k \, dv = -\oint J_i^k n_i \, da + \int K^k \, dv \tag{3.1}$$

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*Due to chemical reactions.

where n_i denotes the unit normal, positive outward, and K^k represents the mass rate of production per unit volume of the kth component. Now, from (2.10) and (3.1) it follows easily that

$$\int (\frac{D\rho^k}{Dt} + \rho^k v_{i,i} + J^k_{i,i} - K^k) \, dv = 0 \, ,$$

and since V is arbitrary this implies

$$\frac{D\rho^k}{Dt} + \rho^k v_{i,i} = K^k - J^k_{i,i} \, . \tag{3.2}$$

Summing (3.2) over all components and using (2.4), we obtain

$$\frac{D\rho}{Dt} + \rho v_{i,i} = \Sigma \, K^k \, . \tag{3.3}$$

Theorem I - The total mass M within an arbitrary material volume V is conserved,

$$\frac{D\rho}{Dt} + \rho v_{i,i} = 0 \tag{3.4}$$

if and only if

$$\Sigma \, K^k = 0 \, . \tag{3.5}$$

Henceforth we shall assume that whenever explicit formulas for the K^k are given their sum always vanishes. The statement (3.4) is then a direct consequence of (2.4), (3.1) and (3.5).

The local composition of a heterogeneous medium is usually expressed in terms of the concentrations w^k. The pertinent equation for the kth component is

$$\rho \frac{Dw^k}{Dt} + J^k_{i,i} = K^k \, , \tag{3.6}$$

easily obtained from (3.2) and (3.4).

Before we state the axioms expressing conservation of linear momentum and energy, we shall define a number of quantities appearing therein. The definitions are always consistent with the superposition principle.

The total linear momentum of an arbitrary material volume V is $\int \Sigma \rho^k (v_i + v_i^k) dv$; from (2.4), (2.9) and $\rho = \Sigma \rho^k$, it follows that the integral of the sum of diffusive momenta vanishes; that is, $\int \Sigma \rho^k v_i^k dv = 0$, and therefore

$$\int \Sigma \rho^k (v_i + v_i^k) dv = \int \rho v_i dv.$$

This quantity is influenced by the direct stress, $\oint \Sigma t_i^k ds$, and the body force $\int \Sigma \rho^k f_i^k dv$, where t_i^k denotes the direct component stress and f_i^k stands for the (body) force per unit mass acting on the kth component of the mixture. The force f_i acting on a unit mass of the mixture is defined as $f_i \equiv \Sigma w^k f_i^k$, and hence $\int \Sigma \rho^k f_i^k dv = \int \rho f_i dv$.

Next, we introduce the definitions of several kinetic energies and rates of work. The total kinetic energy is $K_T \equiv \int \Sigma \rho^k \frac{|\bar{v} + \bar{v}^k|^2}{2} dv$; the kinetic energies of the mixture motion and the sum of diffusive motions are respectively $K \equiv \int \rho |\bar{v}|^2/2 \, dv$ and $K_D \equiv \int \Sigma \rho^k |\bar{v}^k|^2/2 \, dv$. As an immediate consequence of (2.4), (2.9) there follows $K_T = K + K_D$. The total rates of work due to surface and body forces are respectively expressed as $\oint \Sigma t_i^k (v_i + v_i^k) da$ and $\int \Sigma \rho^k f_i^k (v_i + v_i^k) dv$. Parts of the total rates of work enter the balances of K_D and K and so it is often convenient to write the contributions due to diffusive motions and the mixture motion separately, for example,

$$\int \Sigma \rho^k f_i^k (v_i + v_i^k) dv = \int \rho_i f_i v_i dv + \int \Sigma \rho^k f_i^k v_i^k dv.$$

We complete now our set of definitions. The total internal energy of a material volume is $\int \Sigma \rho^k E^k dv$ where E^k represents the internal energy per unit mass of the kth component. Alternately, with E, the internal energy per

unit mass of the mixture defined as $E \equiv \Sigma\, w^k E^k$, we have $\int \Sigma\, \rho^k E^k dv = \int \rho E\, dv$. This quantity is a part of the total energy, $\int \Sigma\, \rho^k (E^k + \frac{|\overline{v} + \overline{v}^k|^2}{2})\, dv$, having the decomposition

$$\int \Sigma\, \rho\, (E^k + \frac{|\overline{v} + \overline{v}^k|^2}{2})dv = \int \rho E dv + K + K_D.$$

The balance of total energy depends in part on the transport of heat into the volume, $-\oint \Sigma\, h_i^k n_i\, da$, and on the rate of generation of energy, $\int \Sigma\, \rho^k Q^k\, dv$; the latter integrals imply that with each component there is associated a flux of heat h_i^k and an energy source Q^k. With $h_i \equiv \Sigma\, h_i^k$ and $Q \equiv \Sigma\, w^k Q^k$ we have the obvious alternate expressions $-\oint h_i n_i\, da$ and $\int \rho Q dv$.

<u>Postulate II:</u>

The rate of change of total linear momentum of a material volume V equals the sum of the inward flux of total linear momentum and the forces acting on the volume. This principle may be otherwise expressed as

$$\frac{D}{Dt} \int \Sigma\, \rho^k (v_i + v_i^k) dv = -\oint \Sigma\, \rho^k (v_i + v_i^k) v_i^k n_i\, da$$

$$+ \oint \Sigma\, t_i^k\, da + \int \Sigma\, \rho^k f_i^k\, dv . \qquad (3.7)$$

We adopt now Cauchy's stress hypothesis, $t_i^k = t_i^k (x_i, n_i, t)$, and use it, together with (3.7) and the assumption of boundedness of integrands, to obtain the decomposition $t_i^k = T_{ij}^k n_i.$* On the basis of this relationship, previous definitions, Gauss' theorem and (2.10), we write (3.7) in the form

$$\int \{\rho \frac{Dv_i}{Dt} - \Sigma\, T_{ij,j}^k + \Sigma\, (\rho^k v_i^k v_j^k)_{,j} - \Sigma\, \rho^k f_i^k\} dv = 0$$

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*Henceforth we assume that the tensors T_{ij}^k are symmetric, but it is understood that many of the results remain valid without this assumption.

and since the volume is arbitrary, easily deduce the differential equation

$$\rho \frac{Dv_i}{Dt} = \Sigma T^k_{ij'j} - \Sigma (\rho^k v^k_i v^k_j)_{,j} + \Sigma \rho^k f^k_i . \tag{3.8}$$

Upon defining $t_i \equiv \Sigma t^k_i$ and writing the corresponding tensor as $T_{ij} = \Sigma T^k_{ij}$, this basic result takes the form

$$\rho \frac{Dv_i}{Dt} = T_{ij'j} - \Sigma (\rho^k v^k_i v^k_j)_{,j} + \rho f_i . \tag{3.9}$$

From (3.8) we now obtain easily a useful relationship for $\frac{DK}{Dt}$.

Theorem II - The rate of change of K is

$$\frac{DK}{Dt} = \oint \Sigma t^k_i v_i \, da - \oint \Sigma \rho^k v^k_i v^k_i v_i n_j \, da - \int \Sigma T^k_{ij} v_{i'j} \, dv$$

$$+ \int \Sigma \rho^k v^k_i v^k_i v_{i'j} \, dv + \int \Sigma \rho^k f^k_i v_i \, dv . \tag{3.10}$$

To prove (3.10), it suffices to integrate the product of (3.8) with v_i and rearrange the result using (2.10) and (3.4). When $N = 1$, the medium is a simple continuum and (3.10) reduces to the well known formula

$$\frac{DK}{Dt} = \oint t_i v_i \, ds - \int T_{ij} v_{i'j} \, dv + \int \rho f_i v_i \, dv .$$

Otherwise, the general statement (3.10) always contains the terms $\oint \Sigma \rho^k v^k_i v^k_i v_i n_j \, da$ and $\int \Sigma \rho^k v^k_i v^k_i v_{i'j} \, dv$ that express, with respect to the mixture motion, the rate of work and dissipation due to diffusive stresses.

Postulate III:

The rate of change of total energy of an arbitrary material volume V equals the sum of the total rates of work of surface and body forces, the inward

flux of total energy, the inward flux of heat and the total heat generated within the volume. This principle may be written as

$$\frac{D}{Dt} \int \Sigma \; \rho^k \; (E^k + \frac{|\bar{v} + \vec{v}^k|^2}{2}) \; dv = \oint \Sigma \; t_i^k \; (v_i + v_i^k) da$$

$$+ \int \Sigma \; \rho^k \; f_i^k \; (v_i + v_i^k) dv - \oint \Sigma \; \rho^k \; (E^k + \frac{|\bar{v} + \vec{v}^k|^2}{2}) \; v_i^k n_i \; da$$

$$- \oint \Sigma \; h_i^k n_i \; da + \int \Sigma \; \rho^k Q^k \; dv. \tag{3.11}$$

Expanding* the total energy terms and combining the result with (3.10) gives after some obvious cancellations,

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*We write the left hand side of (3.11) in the form $\frac{D}{Dt} \int \Sigma \rho^k (E^k + |\vec{v}^k|^2/2) dv + \frac{DK}{Dt}$ and substitute (3.10) for $\frac{DK}{Dt}$; furthermore, we use

$$\oint \Sigma \; \rho^k \; (E^k + \frac{|\bar{v} + \vec{v}^k|^2}{2}) \; v_i^k n_i \; da = \oint \Sigma \; \rho^k E^k v_i^k n_i \; da$$

$$+ \oint \Sigma \; \rho^k |\vec{v}^k|^2/2 \; v_i^k n_i \; da + \oint \Sigma \rho^k v_i^k v_i v_i^k n_i da.$$

Note that while the rate of change of total energy equals the sum of the rates of change of $\int \rho E \, dv$, K and K_D, a similar decomposition of the integral expressing the transport of total energy into the volume by diffusion yields the cross term $\oint \Sigma \rho^k v_i^k v_i^k v_i n_i \, da$. From our viewpoint such terms are manifestations of various interactions among the constituents of a heterogeneous medium. Unfortunately, the precise nature of such interactions is unknown.

$$\frac{D}{Dt} \int \Sigma \rho^k (E^k + |v^k|^2/2) dv = \int \Sigma T^k_{ij} v_{i,j} dv - \int \Sigma \rho^k v^k_i v^k_i v_{i,j} dv$$

$$+ \int \rho^k f^k_i v^k_i dv + \oint \Sigma t^k_i v^k_i da - \oint \Sigma \rho^k (E^k + |\overline{v}^k|^2/2) v^k_i n_i da$$

$$- \oint \Sigma h^k_i n_i da + \int \Sigma \rho^k Q^k dv.$$

The above equation, written in terms of volume integrals, takes the form

$$\frac{D}{Dt} \int \Sigma \rho^k (E^k + |\overline{v}^k|^2/2) dv = \int \Sigma (T^k_{ij} - \rho^k v^k_i v^k_i) v_{i,j} dv$$

$$- \int \Sigma [h^k_i + \rho^k (E^k + |\overline{v}^k|^2/2) v^k_i - T^k_{ij} v^k_j]_{,i} dv + \int \Sigma (\rho^k Q^k + \rho^k f^k_i v^k_i) dv.$$

It is convenient now to introduce into this expression the definitions

$$\rho E^* \equiv \Sigma \rho^k (E^k + \frac{1}{2} |\overline{v}^k|^2),$$

$$T^*_{ij} \equiv T_{ij} - \Sigma \rho^k v^k_i v^k_j,$$

$$\xi^*_i \equiv \Sigma [h^k_i + \rho^k (E^k + \frac{1}{2} |\overline{v}^k|^2) v^k_i - T^k_{ij} v^k_j]$$

$$\rho Q^* \equiv \rho Q + \Sigma \rho^k f^k_i v^k_i,$$

suggested by the natural grouping of terms in the integrals and by the viewpoint adopted herein towards diffusive effects. Using (2.10), there follows

$$\int (\rho \frac{DE^*}{Dt} - T^*_{ij} v_{i,j} + \xi^*_{i,i} - \rho Q^*) dv = 0,$$

and since the volume is arbitrary this implies

$$\rho \frac{DE^*}{Dt} = T_{ii}^* - \xi_{i'_i}^* + \rho Q^* . \tag{3.12}$$

Equation (3.12) is a generalization of the energy equation for simple continua to which it reduces whenever $v_i^k \equiv 0$.

Next, we obtain from (3.12) an expression for $\rho \frac{DE}{Dt}$ to be used in the subsequent discussion on thermodynamics. For this purpose, we define* the set of scalars $\{\lambda^k\}$

$$\lambda^k \equiv \frac{D}{Dt} (\rho^k |\overline{v}^k|^2/2) + (\rho^k |\overline{v}^k|^2/2 \ v_i^k)_{,i} + \rho^k |\overline{v}^k|^2/2 \ v_{i'_i}$$

$$-K^k |\overline{v}^k|^2/2 + \rho^k v_i^k v_i^k v_{i'_i} + T_{ii}^k v_{i'_i}^k - \rho^k f_i^k v_i^k - (T_{ii}^k v_i^k)_{,i} ; \tag{3.13}$$

substituting (3.13) into (3.12) yields the required equation

$$\rho \frac{DE}{Dt} = T_{ii} \ v_{i'_i} + \Sigma T_{ii}^k v_{i'_i}^k - (\Sigma h_i^k + \rho^k E^k v_i^k)_{,i} + \rho Q + F \tag{3.14}$$

where

$$F \equiv - \Sigma (\lambda^k + K^k |\overline{v}^k|^2/2) .$$

The results (3.14), (3.12), (3.9) are in entire agreement with Truesdell's.**

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* This is necessary because, other than a formal integral of (3.13), no explicit formula for DK_D/Dt is available.

**While the derivations differ, they are not entirely unrelated. A somewhat closer connection between the two may be established as follows. We suppose that the chemical reactions and possible other interactions among the constituents result in productions of total momentum and total energy, this being expressed by including on the right hand sides of the axioms (3.7), (3.11) the integrals $\int \Sigma \rho [p_i^k + \tilde{K}^k (v_i^k + v_i)] dv$, $\int \Sigma \rho [e^k + \tilde{K}^k (E^k + |\overline{v}^k + \overline{v}^k|^2/2)] dv$; $\tilde{K}^k \equiv \rho K^k$, and p_i^k, e^k denote respectively productions of kth total momentum and k^{th} total energy due to interactions. Because $\Sigma \tilde{K}^k = \Sigma K^k = 0$, contributions due to the mixture motion vanish. The remaining portions of the integrands may be set equal to zero on the basis of the same sort of theorems as in [1,2], the latter expressing the requirement that each differential equation for the medium as a whole possess the same mathematical structure as the corresponding equation for simple continuum. Since this leaves the main results unaltered, we have chosen not to pursue this course.

4. Thermodynamics

The purpose of this section is to join the preceding development with the necessary thermodynamical considerations. This is done by deriving from postulated equations of state for the constituents an equation of state for the medium as a whole, by deducing several forms of the Gibbs equation, and by deriving the equation expressing the balance of total entropy of a heterogeneous continuum. The latter suggests then several candidates for a possible general postulate of irreversibility. Our treatment is a simpler and somewhat modified version of that due to Truesdell [1, 2]. The fundamental ideas go back to the classical work of J. W. Gibbs.*

We state now the basic assumptions. The main hypothesis is that E^k - the specific internal energy of the kth component - is influenced by the totality of parameters consisting of all partial specific volumes, $\{v^1, \ldots, v^N\}$ where $v^k \equiv 1/\rho^k$, and that these together with one additional scalar parameter s^k are sufficient to determine E^k independently of time, motion and stress; s^k, dimensionally independent from all other parameters, is called the kth specific entropy. The set $\{s^k, v^1, \ldots, v^N\}$ is said to constitute the thermodynamic state of the kth component and its subset $\{v_1, \ldots, v^N\}$ is called the thermodynamic substate. The thermodynamic state is specified by a definite functional relationship

$$E^k = E^k(s^k, v^1, \ldots, v^N) , \qquad (4.1)$$

herein referred to as a caloric equation of state. It is assumed that all such relationships are differentiable as many times as required and may be inverted to yield any one variable in terms of the remaining ones. Therefore

$$dE^k = \frac{\partial E^k}{\partial s^k} ds^k + \sum_{p=1}^{N} \frac{\partial E^k}{\partial v^p} dv^p \qquad (4.2)$$

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*The reader is referred to [6], [7] and [8]. An exhaustive list of pertinent papers may be found in [2].

and since (4.1) is valid for any motion (4.2) expresses a general change in the state of the kth constituent. The particular change associated with the mixture motion is given by

$$\frac{DE^k}{Dt} = \frac{\partial E^k}{\partial s^k} \frac{Ds^k}{Dt} + \sum_{p=1}^{N} \frac{\partial E^k}{\partial v^p} \frac{Dv^p}{Dt} \, . \tag{4.3}$$

An alternate expression is

$$\frac{DE^k}{Dt} = T^k \frac{Ds^k}{Dt} + \sum_{p=1}^{N} \frac{\partial E^k}{\partial v^p} \frac{Dv^p}{Dt} \tag{4.4}$$

where

$$T^k \equiv \frac{\partial E^k}{\partial s^k} \bigg|_{v^1, \ldots, v^N} \qquad *$$

is the temperature of the kth constituent.

We come now to the first important result of this section ascertaining under what conditions there exists an equation of state for the mixture of the form

$$E = E(s, v^1, \ldots, v^N) \tag{4.5}$$

compatible with the given equations of state (4.1);

$$s \equiv \sum_{k=1}^{N} w^k s^k$$

is called the total specific entropy of the mixture and, as before,

$$E \equiv \sum_{k=1}^{N} w^k E^k.$$

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*Henceforth we omit the subscripts because it is clear from a given functional relationship and its partial derivatives which variables are held fixed.

Theorem 1 - A mixture whose constituents have equations of state of the form (4.1) possesses an equation of state (4.5) if and only if the local thermodynamic states described by $s^1, \ldots, s^N, v^1, \ldots, v^N$, are subject to the following conditions:

1. L components have the same temperature $T^1 = T^2 = \ldots T^L = T$,

2. The concentrations of the remaining $N - L$ components are zero,
$$w^{L+1} = w^{L+2} = \ldots w^N = 0 .$$

The proof is simple since, for fixed $v^1, \ldots, v^N$, a necessary condition for

$$dE = \sum_{k=1}^{N} w^k T^k ds^k = T \, ds,$$

is $T^k = T \equiv \dfrac{\partial E}{\partial s}$ (or the particular $w^k = 0$). The reader can easily complete the proof.

In practice it is not so much the equations of state (4.1), (4.5) that are used but rather the rate equations typified by (4.4). Such an equation for the mixture is obtained in a straightforward way from (4.5) and previous hypotheses. It suffices to put $v^k \equiv v/w^k$ into (4.5), form the differential expressing the general change in E and then observe that, for the special change following the motion of the mixture, this implies

$$\frac{DE}{Dt} = T \frac{Ds}{Dt} - \pi \frac{Dv}{Dt} + \sum_{k=1}^{N} \mu^k \frac{Dw^k}{Dt} \tag{4.6}$$

where

$$T \equiv \frac{\partial E}{\partial s}, \qquad \pi \equiv -\frac{\partial E}{\partial v}, \qquad \mu^k \equiv \frac{\partial E}{\partial w^k} .$$

Equation (4.6) is called the Gibbs equation; the coefficients T, π, μ^k are respectively the mixture temperature, total pressure and chemical potential. The latter are now

given explicitly in terms of the constituent quantities. We multiply (4.3) with ρ^k, use previous hypotheses and some rearrangement to obtain

$$\frac{DE}{Dt} = T\frac{Ds}{Dt} + \frac{Dv}{Dt} \sum_{k=1}^{N} \sum_{p=1}^{N} \frac{w^k}{w^p} \frac{\partial E^k}{\partial v^p} - \frac{1}{\rho} \sum_{k=1}^{N} \sum_{p=1}^{N} \frac{w^k}{w^{p^2}} \frac{\partial E^k}{\partial v^p} \frac{Dw^p}{Dt}$$

$$+ \sum_{k=1}^{N} (E^k - Ts^k) \frac{Dw^k}{Dt} . \tag{4.7}$$

Equation (4.7) is precisely of the form (4.6) provided

$$\mu^k \equiv E^k - Ts^k - \frac{v^k}{w^k} \sum_{p=1}^{N} w^p \frac{\partial E^p}{\partial v^k} , \qquad \pi \equiv - \sum_{k=1}^{N} \sum_{p=1}^{N} \frac{w^k}{w^p} \frac{\partial E^k}{\partial v^p} . \tag{4.8}$$

It is important to note that the validity of (4.7) with coefficients (4.8) is not an assumption but a consequence of the caloric equations of state of the constituents and the condition $T^k = T$. In the special case when $E^k = E^k(s^k, v^k)$ we have

$$\pi = \sum_{k=1}^{N} \pi^k , \qquad \mu^k = E^k - Ts^k + \pi^k v^k ,$$

where the partial (or component) pressures π^k are defined as

$$\pi \equiv - \frac{\partial E^k}{\partial v^k} .$$

The last statement is summarized in the following theorem:

Theorem 2 – If the components satisfy equations of state $E^k = E^k(s^k, v^k)$ and if at each instant of time t at a place x_i the component temperatures are identical then there is a Gibbs equation such that

1. The total pressure is equal to the sum of the partial pressures,
2. The chemical potentials are $\mu^k = E^k - Ts^k + \pi^k v^k$.

The Gibbs equations discussed thus far require $T^k = T$. It is worthwhile to consider here a more general Gibbs equation not subject to this requirement, namely, one that admits at a place x_i, $T^A \neq T^B$. For this purpose we retain the constituent equations of state (4.1) but do not demand an equation of state for the mixture of the form (4.5). At each point x_i in space at each instant of time t we define a mean temperature $\tilde{T}$ for the mixture as

$$\sum_{k=1}^{N} T^k w^k ds^k \equiv \tilde{T} \sum_{k=1}^{N} w^k ds^k.$$

Clearly,

$$\tilde{T} ds = \tilde{T} \{ \sum_{k=1}^{N} w^k ds^k + \sum_{k=1}^{N} s^k dw^k \}.$$

Computations similar to those yielding (4.7), (4.8) give now

$$\frac{DE}{Dt} = \tilde{T} \frac{Ds}{Dt} - \pi \frac{Dv}{Dt} + \sum_{k=1}^{N} \tilde{\mu}^k \frac{Dw^k}{Dt}$$

where

$$\tilde{\mu}^k \equiv E^k - \tilde{T} s^k - \frac{v^k}{w^k} \sum_{p=1}^{N} w^p \frac{\partial E^p}{\partial v^k}.$$

and the total pressure π is the same as in (4.8). Of course, $\widetilde{T}$ is not a state variable in the usual sense and therefore the applicability of the above formulation needs further examination. Subsequent discussion is always consistent with Theorem 1 and no further mention of $\widetilde{T}$ is made.

We obtain now the differential equation expressing the local balance of total specific entropy s and from it deduce an integral equation for the balance of total entropy $\int \rho s\, dv$; guided by the procedures established in the theory of simple continua we suggest then certain inequalities regarded as possible general postulates of thermodynamic irreversibility.

Equations (3.14) and (4.6) are rewritten as

$$\rho \frac{DE}{Dt} = P_E + Q_E \tag{4.7}$$

and

$$\rho \frac{DE}{Dt} = \rho T \frac{Ds}{Dt} + P_I \tag{4.8}$$

where

$$P_E \equiv T_{ij} v_{i'j} + \sum_{k=1}^{N} T_{ij}^{k} v_{i'j}^{k} \ ,$$

$$Q_E \equiv \rho Q - \rho \sum_{k=1}^{N} (\lambda^k + K^k \tfrac{1}{2} |\overrightarrow{v}^k|^2) - (h_i + \sum_{k=1}^{N} \rho^k E^k v_i^k)_{,i} \ ,$$

and

$$P_I \equiv \rho \sum_{k=1}^{N} \mu^k \frac{Dw^k}{Dt} - \pi \rho \frac{Dv}{Dt} \ .$$

The terms P_E, Q_E and P_I are called[*] respectively the external power, the external non-mechanical supply of energy and the inner power. Eliminating $\rho \frac{DE}{Dt}$ between (4.7) and (4.8) gives us the equation for the production of total specific entropy,

$$\rho T \frac{Ds}{Dt} = P_E - P_I + Q_E$$

that may be expressed as

$$\rho \frac{Ds}{Dt} = \frac{P_E - P_I}{T} - \left(\frac{h_i + \sum_{k=1}^{N} \rho^k E^k v_i^k}{T} \right)_{,i} - \frac{1}{T^2} T_{,i} \left(h_i + \sum_{k=1}^{N} \rho^k E^k v_i^k \right)$$

$$+ \frac{\rho Q - \rho \sum_{k=1}^{N} (\lambda^k + K^k \frac{1}{2} |\vec{v}^k|^2)}{T}. \qquad (4.9)$$

We integrate (4.9), use the transport theorem and after some obvious rearrangement obtain the corresponding integral equation for the balance of total entropy,

$$\frac{D}{Dt} \int \rho s \, dv = - \oint \frac{(h_i + \sum_{k=1}^{N} \rho^k E^k v_i^k)}{T} n_i \, da + \int (\Delta + \frac{\rho Q}{T}) \, dv, \qquad (4.10)$$

where

$$T\Delta = P_E - P_I - \frac{1}{T} T_{,i} (h_i + \sum_{k=1}^{N} \rho^k E^k v_i^k) - \rho \sum_{k=1}^{N} (\lambda^k + K^k \frac{1}{2} |\vec{v}^k|^2) \quad (4.11)$$

The theory of simple continua suggests[*] that we may set

$$T \Delta \geq 0$$

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[*]We follow the treatment of Truesdell [2]. For a simple continuum which obeys a caloric equation of state $E = E(s, a^k), k = 1, \ldots, K$ we have

$$\rho \frac{dE}{dt} = \rho T \frac{ds}{dt} + P_I$$

where $P_I \equiv \rho \sum_{k=1}^{K} \tau^k \frac{da^k}{dt}$; the quantities $\tau^k \equiv \frac{\partial E}{\partial a^k}$ are called thermodynamic tensions. Eliminating $\rho \frac{dE}{dt}$ between the above equation and the equation

$$\rho \frac{dE}{dt} = P_E + Q_E$$

where $P_E \equiv T_{ij} D_{ij}$, $Q_E \equiv \rho Q - h_{i,i}$, gives

$$\rho T \frac{ds}{dt} = P_E - P_I + Q_E$$

Integration of

$$\rho \frac{ds}{dt} = \frac{P_E - P_I}{T} - \left(\frac{h_i}{T}\right)_{,i} - \frac{h_i T_{,i}}{T^2} + \frac{\rho Q}{T}$$

leads to

$$\frac{d}{dt} \int \rho s \, dv = -\oint \frac{h_i}{T} n_i \, da + \int \left(\Delta + \frac{\rho Q}{T}\right) dv$$

where

$$T \Delta \equiv (P_E - P_I) - \frac{h_i T_{,i}}{T}$$

On the basis of physical arguments we have

$$P_E - P_I \geq 0 \quad \text{when } Q = 0 \text{ and } T = \text{const},$$

and

$$h_i T_{,i} \geq 0 \quad \text{when } Q = 0 \text{ and } P_E - P_I = 0.$$

Therefore $T \Delta \geq 0$ and for $T > 0$ the above expression is equivalent to

$$\frac{d}{dt} \int \rho s \, dv \geq - \oint \frac{h_i n_i}{T} \, da + \int \frac{\rho Q}{T} \, dv$$

The last statement is adopted as a postulate of irreversibility.

and adopt the equivalent inequality

$$\frac{D}{Dt} \int \rho s \, dv \geq - \oint \left[\frac{h_i + \sum_{k=1}^{N} \rho^k E^k v_i^k}{T} \right] n_i \, da + \int \frac{\rho Q}{T} \, dv \qquad (4.12)$$

as a general postulate of irreversibility.

It must be emphasized that $T\Delta \geq 0$, and hence (4.12) are merely suggested as possible hypotheses. Other candidates for a "general postulate of irreversibility" are easily obtained because the terms which enter Δ are not uniquely defined. For example, we may write (4.9) in the form

$$\rho \frac{Ds}{Dt} = - \left[\frac{h_i + \sum_{k=1}^{N} \rho^k (E^k - \mu^k) v_i^k}{T} \right]_{,i} + \frac{\rho Q}{T} + \Delta' \qquad (4.13)$$

where

$$T\Delta' \equiv \sum_{k=1}^{N} T_{ij}^k (v_{i,j} + v_{j,i}^k) + \pi v_{i,i} - \frac{1}{T} T_{,i} \left(h_i + \sum_{k=1}^{N} \rho E^k v_i^k \right)$$

$$- \rho \sum_{k=1}^{N} \{ \lambda^k + K^k (\frac{1}{2} |\overline{v}^k|^2 + \mu^k) + \rho^k v_i^k (\frac{\mu^k}{T})_{,i} \}. \qquad (4.14)$$

The assumption

$$T\Delta' \geq 0$$

is equivalent to

$$\frac{D}{Dt} \int \rho s \, dv \geq - \oint \left[\frac{h_i + \sum_{k=1}^{N} \rho^k (E^k - \mu^k) v_i^k}{T} \right] n_i \, da + \int \frac{\rho Q}{T} \, dv. \qquad (4.15)$$

The inequality $T\Delta' \geq 0$ is the same as Truesdell's [1,2] and clearly different from $T\Delta \geq 0$. Of course, this difference is also reflected in the corresponding integral statements (4.15) and (4.11). We may, if we wish, construct still other inequalities, group the thermodynamic variables into "forces" and "fluxes" and obtain agreement with the results given by various writers on "irreversible thermodynamics." (For example, in [4], a Δ is used which leads to the results of S. R. De Groot [9] and H. A. Toelhoeck and S. R. De Groot [10], proper interpretation of terms being made where necessary.) Writers on that subject go one step further and require that partial sums occurring in a particular Δ be separately non-negative. The arguments advanced for the support of such steps do not appear to us very convincing.* What is fundamentally lacking is the knowledge of the appropriate group of transformations of the thermodynamic variables and the invariance which we are to require. It appears therefore that further progress towards a rigorous theory of thermo-mechanics must wait until such time when this question is settled in sufficient generality.

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A general critical evaluation of "irreversible thermodynamics" may be found in [1]. An illuminating critique directed at the well known reciprocal relations of Onsager was given by D. B. Coleman and C. Truesdell [11]. For a rigorous modern work on classical thermostatics the reader is referred to the work of D. B. Coleman and W. Noll [12].

References

1. Truesdell, C., "Sulle Basi della Termomeccanica," Accademia Dei Lincei, Atti Rendiconti di Science Fisiche, Matematiche e Naturali, (8), 22, 33-38, 158-166, (1957).

2. Truesdell, C. and R. Toupin, "The Classical Field Theories," Handbuch der Physik III/1, Springer Verlag, Berlin, (1960).

3. Kelly, P. D., "A Reacting Continuum," Int. Journal Engng. Sci., Vol. 2, pp. 129-153, Pergamon Press, (1964).

4. Hayday, A. A., "Governing Equations for Multicomponent Fluid Continua With Chemical Reactions," University of Illinois, Project Squid Rep. Nonr. 1858 (25) Nr-098-038, (1962).

5. Serrin, J. "Mathematical Principles of Classical Fluid Mechanics," Handbuch der Physik, Bd. VIII/1, Springer Verlag, Berlin, (1959).

6. Gibbs, J. W., "Graphical Methods in the Thermodynamics of Fluids," Trans. Connecticut Acad. 2, 309-342, (1873).

7. Gibbs, J. W., "A Method of Geometrical Representation of the Thermodynamic Properties by Means of Surfaces," Trans. Connecticut Acad. 2, 382-404, (1873).

8. Gibbs, J. W., "On the Equilibrium of Heterogeneous Substances," Trans. Connecticut Acad. 3, (1875-1878), 108-248, 343-524.

9. De Groot, S. R. "Thermodynamics of Irreversible Processes," North-Holland Publishing Company, Amsterdam, (1958).

10. Tolhoeck, H. A., and De Groot, S. R., "A Discussion of the First Law of Thermodynamics for Open Systems," Physica, Vol. 18, No. 10, October 1952.

11. Coleman, D. B. and Truesdell, C., "On the Reciprocal Relations of Onsager," Journal of Chemical Physics, Vol. 33, No. 1, July 1960.

12. Coleman, D. B. and Noll, W., "On the Thermostatics of Continuous Media," Archive for Rational Mechanics and Analysis, Vol. 4, No. 2, 1959.