Int. J. Solids Structures Vol. 14, pp. 881–903
© Pergamon Press Ltd., 1978. Printed in Great Britain

0020-7683/78/1101-0881/$02.00/0

VARIATIONAL IRREVERSIBLE THERMODYNAMICS OF PHYSICAL-CHEMICAL SOLIDS WITH FINITE DEFORMATION

M. A. BIOT
Royal Academy of Belgium, Brussels, Belgium

(*Received 27 April 1978; received for publication 12 June 1978*)

Abstract—A new thermodynamics of open thermochemical systems and a variational principle of virtual dissipation are applied to the finite deformation of a solid coupled to thermomolecular diffusion and chemical reactions. A variational derivation is obtained of the field differential equations as well as Lagrangian equations with generalized coordinates. New formulas for the affinity and a new definition of the chemical potential are presented. An outline is given of an unusually large field of applications, such as active transport in biological systems, finite element methods, plastic properties as analogous to chemical reactions, phase changes and recrystalization, porous solids, heredity and initially stressed solids. A new and unified insight is thus provided in highly diversified problems.

1. INTRODUCTION

The variational Lagrangian thermodynamics formulated initially in 1954–55[1, 2] was extended more recently to nonlinear thermorheology[3]. At the same time a new approach to the thermochemistry of open systems was developed [4–6] which provides a new foundation of classical thermodynamics and avoids the traditional difficulties and ambiguities of Gibbs' classical treatment[7].

This paper is an application of this new thermodynamics to the problem of finite deformation of a solid, with substances in solution, subject to chemical reactions and thermomolecular diffusion. Two special cases of this problem have been developed earlier. One of these excludes chemical reactions and is presented in the context of the similar problem for porous solids[8]. The other includes chemical reactions but assumes small perturbations of a solid in the vicinity of a state of equilibrium with initial stress[9].

The basic concepts of the new thermodynamics of open systems such as the thermobaric potential are briefly recalled in Section 2. Their application to chemical reactions and a new expression for the affinity are developed in Section 3 along the lines developed earlier [4–6]. This is applied in Section 4 to an open solid undergoing homogeneous deformations while coupled chemical reactions are occurring internally. The analogy with nonlinear thermoviscoelasticity is pointed out.

The basic variational principle of virtual dissipation is formulated in Section 5 in the context of a deformable solid continuum with thermomolecular diffusion and chemical reactions. The differential field equations which govern the evolution of the continuum are *derived variationally* in Section 6.

The foregoing results are based entirely on classical thermodynamics. As shown in Section 7, two additional axioms, one of which involves Nernst's third principle, lead to a new definition of the chemical potential which bypasses the need of introducing the principles of quantum statistics. A complementary form of the field equations are then derived in Section 8.

Application of the principle of virtual dissipation in Section 9 to a system described by generalized coordinates as unknowns, leads directly to Lagrangian equations for those unknowns without recourse to the field equations. In Section 10 it is pointed out how the Lagrangian approach is particularly suited to the analysis of biological systems as already illustrated for the treatment of active transport in biological membranes[6]. Section 11 recalls that Lagrangian methods provide the foundation of a large variety of finite element methods. The analogy between plasticity and chemical reactions from the standpoint of internal coordinates is brought to light in Section 12. How the problems of creep and recrystalization under stress coupled to phase changes may be treated by the present methods is briefly discussed in

Section 13. Earlier treatments of porous solids, the thermodynamics of heredity and the solid under initial stress are recalled in Sections 14–16. The case of a solid under initial stress is not treated as a bifurcation and thereby is more general since it is not necessary to assume the existence of an unstressed state.

2. NEW THERMODYNAMICS OF AN OPEN CELL

A new approach to the thermodynamics of open systems has been introduced and discussed extensively in some earlier publications [4–6]. The development has been accomplished entirely within the framework of classical procedures and without recourse to the principles of statistical mechanics. The results are directly applicable to a deformable solid with pure substances in solution as already described in the similar case of a porous solid saturated by viscous fluids [8]. We shall briefly rederive here the essential concepts by using a slightly different and more direct approach.

We start by considering a cell C_p called a primary cell, which is first assumed rigid, containing a mixture of substances k at the temperature T. To this cell we adjoin large rigid reservoirs C_{sk} called supply cells, each containing a pure substance k at the pressure and temperature p_0T_0 the same for all supply cells. It was shown that this condition of uniform values p_0 and T_0, for C_{sk} is required in order to avoid Gibbs' paradox [4, 5]. We also adjoin to this system a large isothermal rigid reservoir at the temperature T_0 called a thermal well, TW. The total system $C_p + \Sigma^k C_{sk} + TW$ is called a hypersystem while the subsystem $C_p + \Sigma^k C_{sk}$ will be referred to as a collective system.

We have considered *reversible transformations of this hypersystem* whereby masses and heat are transferred within the system *by performing external work on the system.* This implies the use of reversible heat pumps. The supply cells C_{sk} and the thermal well are assumed large enough so that p_0 and T_0 remain constant in the process.

The increase of internal energy $\mathcal{J}$ of the hypersystem from a given initial state defines what we have called the collective potential of the primary cell C_p. The justification for this definition is derived from the fact that $\mathcal{J}$ is determined completely by the state variables of C_p. This can be seen as follows.

We shall first consider the case where the primary cell is rigid and contains a mixture of *non reacting* pure substances k at the temperature T. The cell C_p may be a solid in which the various substances are in solution. The case of reacting substances is considered in the next section.

The mass m_k of each substance in C_p is written

$$m_k = m_{0k} + M^k \tag{2.1}$$

where m_{0k} is the initial mass and M^k is the mass of each of the substances acquired by the open cell during a transformation. The state variables of C_p are the masses M^k, and the temperature T. Since the masses M^k are assumed to be provided entirely by the supply cells C_{sk}, the same variables M^k are also the state variables of the supply cells. Therefore *the state of the collective system $C_p + \overset{k}{\Sigma} C_{sk}$ is determined completely by the variables M^k and T.* As a consequence the increase of collective energy $\mathcal{U}$ and of collective entropy $\mathcal{S}$ of the system $C_p + \overset{k}{\Sigma} C_{sk}$ may be expressed as functions of M^k and T. We write

$$\begin{aligned} \mathcal{U} &= \mathcal{U}(M^k, T) \\ \mathcal{S} &= \mathcal{S}(M^k, T). \end{aligned} \tag{2.2}$$

We have defined the collective potential $\mathcal{J}$ as the increase of energy of the hypersystem $C_p + \overset{k}{\Sigma} C_{sk} + TW$ in the reversible transformation. Its value is

$$\mathcal{J} = \mathcal{U} + H_0 \tag{2.3}$$

where H_0 is the heat energy acquired by the thermal well. Since the transformation is reversible there is no entropy change of the hypersystem, $C_p + \overset{k}{\Sigma} C_{sk} + TW$, hence

$$\mathscr{S} = -\frac{H_0}{T_0} \tag{2.4}$$

and

$$\mathscr{J} = \mathscr{U} - T_0\mathscr{S}. \tag{2.5}$$

Since $\mathscr{U}$ and $\mathscr{S}$ are functions of the state variables M^k and T of the primary cell the collective potential $\mathscr{J}$ is also determined by the same variables.

$$\mathscr{J} = \mathscr{J}(M^k, T). \tag{2.6}$$

Because of these properties *we may drop the term collective and refer to $\mathscr{U}$, $\mathscr{S}$ and $\mathscr{J}$ respectively as the cell energy, the cell entropy and the cell potential,* keeping in mind of course that they are defined here in a new way as collective concepts.

The thermodynamic function (2.5) was introduced as a fundamental potential by the author [1,2] in a more restricted context and applied by Mindlin to piezoelectric crystals [10].

According to eqn (2.1)

$$M^k = m_k - m_{0k}. \tag{2.7}$$

Hence we may write

$$\mathscr{U} = \mathscr{U}(m_k, T), \qquad \mathscr{S} = \mathscr{S}(m_k, T), \qquad \mathscr{J} = \mathscr{J}(m_k, T) \tag{2.8}$$

as functions of the temperature and the total masses m_k of the substances k in solution in the cell.

In order to evaluate the changes of the thermodynamic functions $\mathscr{U}$, $\mathscr{S}$, $\mathscr{J}$ associated with a change of state of the open cell C_p we have introduced the new key concept of *thermobaric transfer* [4–6] described as follows. Consider a pure substance k in equilibrium with the primary cell C_p through a semipermeable membrane. In this equilibrium state the substance k is at a pressure p_k and at the same temperature T as C. The pressure p_k of the substance under these conditions is called the *partial pressure* of the substance in the mixture. The process of thermobaric transfer of a mass dM^k from the supply cell C_{sk} to the primary cell C_p is a reversible process by which the mass is first extracted from the supply cell, compressed and heated to the partial pressure p_k and temperature T and then injected reversibly and adiabatically through the semi-permeable membrane. The heating along this path is accomplished by a reversible pump operating between TW and dM^k and injecting a differential amount of heat into dM^k at each step. The process is described in more detail in Refs. [4, 5].

The increase of collective energy and entropy of the system $C_p + \overset{k}{\Sigma} C_{sk}$ in this process of thermobaric transfer are written

$$\begin{aligned} d\mathscr{U} &= \bar{\epsilon}_k \, dM^k \\ d\mathscr{S} &= \bar{s}_k \, dM^k \end{aligned} \tag{2.9}$$

where

$$\bar{\epsilon}_k = \int_{p_0T_0}^{p_kT} d\bar{\epsilon}_k \qquad \bar{s}_k = \int_{p_0T_0}^{p_kT} d\bar{s}_k. \tag{2.10}$$

The differential $d\bar{s}_k$ is the increment of entropy per unit mass of substance k at each step of the thermobaric transfer. Similarly

$$d\bar{\epsilon}_k = \frac{dp'_k}{\rho'_k} + T \, d\bar{s}_k = d\left(\frac{p'_k}{\rho'_k}\right) - p_k \, d\left(\frac{1}{\rho'_k}\right) + T' \, d\bar{s}_k \tag{2.11}$$

is the increment of enthalpy per unit mass of each substance at each step, at the variable pressure p'_k variable density ρ'_k and variable temperature T' along the path of integration.

The variables $\bar{\epsilon}_k$ and $\bar{s}_k$ are independent of the path of integration and have been called respectively the *relative specific enthalpy and entropy of the substance in C_p. In contrast with traditional procedures these definitions do not involve any undetermined constants.*

The change in cell potential corresponding to the thermobaric transfer is according to (2.5)

$$d\mathcal{J} = d\mathcal{U} - T_0\, d\mathcal{S}. \tag{2.12}$$

Substitution of the values (2.9) yields

$$d\mathcal{J} = \psi_k\, dM^k \tag{2.13}$$

where

$$\psi_k = \bar{\epsilon}_k - T_0 \bar{s}_k \tag{2.14}$$

has been called the *thermobaric potential.*

From the definition of $\mathcal{J}$ we note that ψ_k represents the external work required for the thermobaric transfer of a unit mass of the particular substance. This may be verified by introducing the values (2.10) of $\bar{\epsilon}_k$ and $\bar{s}_k$ and putting $\theta' = T' - T_0$. We obtain

$$\psi_k = \int_{p_0 T_0}^{p_k T} \left(\frac{dp'_k}{\rho'_k} + \theta'\, d\bar{s}_k \right). \tag{2.15}$$

The first term represents the work of the pressure on the unit mass including the negative work of extraction from the supply cell and the positive work of injection into C_p. The second term $\theta\, d\bar{s}_k$ is the work of the heat pump at each step along the path. Hence ψ_k is effectively the external reversible work required in the thermobaric transfer.

If several masses are injected we write

$$d\mathcal{J} = \sum^{k} \psi_k\, dM^k. \tag{2.16}$$

we have assumed that no additional heat is added to C_p during the reversible injection of the mass dM^k. Consider now that by using a heat pump operating between C_p and TW we inject reversibly into C_p an amount of heat $T\, ds_T$ at the same time as the masses dM^k. We obtain

$$d\mathcal{U} = \sum^{k} \bar{\epsilon}_k\, dM^k + T\, ds_T \tag{2.17}$$

$$d\mathcal{S} = \sum^{k} \bar{s}_k\, dM^k + ds_T. \tag{2.18}$$

Substitution in expression (2.12) yields the increase of cell potential.

$$d\mathcal{J} = \sum^{k} \psi_k\, dM^k + \theta\, ds_T \tag{2.19}$$

where

$$\theta = T - T_0. \tag{2.20}$$

Again here we recognize the work $\theta\, ds_T$ accomplished by the heat pump to inject the heat $T\, ds_T$ into C_p operating between the temperatures T_0 and T.

The variable ds_T is not a state variable. Elimination of ds_T between eqn (2.19) and eqn (2.18) yields

$$\mathrm{d}\mathscr{J} = \sum^{k} \phi_k \,\mathrm{d}M^k + \theta \,\mathrm{d}\mathscr{S} \tag{2.21}$$

where

$$\phi_k = \psi_k - \theta \bar{s}_k = \bar{\varepsilon}_k - T\bar{s}_k \tag{2.22}$$

was introduced earlier as the *convective potential.*

We may obtain the value of $\mathscr{J}$ by integrating (2.19) along any convenient path. For example we first integrate at constant temperature $T = T_0$ then closing the cell ($\mathrm{d}M^k = 0$) we raise the temperature to T. This yields

$$\mathscr{J} = \mathscr{J}(M^k, T). \tag{2.23}$$

The same path of integration may be used to integrate eqn (2.18) for $\mathrm{d}\mathscr{S}$. We derive

$$\mathscr{S} = \mathscr{S}(M^k, T). \tag{2.24}$$

We note that along the path of integration the partial pressures p_k which appear in the differential coefficients are assumed to be known as functions of M^k and T. By eliminating T between eqns (2.23) and (2.24) we derive

$$\mathscr{J} = \mathscr{J}(M^k, \mathscr{S}). \tag{2.25}$$

3. NEW CHEMICAL THERMODYNAMICS OF AN OPEN CELL

The new concepts and results for open systems also lead to a new chemical thermodynamics [4, 5] which we shall briefly outline.

These fundamental results are obtained without the use of statistical mechanics. We consider again a rigid and open primary cell C_p with its adjoined supply cells C_{sk} and its thermal well TW. A chemical reaction may now take place between the various substance mixed in C_p. This chemical reaction is represented by the equation

$$\mathrm{d}m_k = \sum^{k} \nu_k \,\mathrm{d}\xi \tag{3.1}$$

where ξ is the reaction coordinate, and $\mathrm{d}m_k$ are the masses of the various substances "produced" by the reaction. The term "produced" is understood in a generalized sense so that negative values represent substances disappearing in the reaction. Conservation of mass implies the relation

$$\sum^{k} \mathrm{d}m_k = 0 \tag{3.2}$$

hence

$$\sum^{k} \nu_k = 0. \tag{3.3}$$

Since a chemical reaction is generally irreversible and associated with an entropy production, in order to evaluate the collective potential by the procedures outlined above, we must construct a system such that the change of state resulting from the chemical reaction may be obtained by an equivalent reversible process.

Such a process may be described as follows. Consider the reaction to occur in a rigid closed adiabatic cell. The reaction $\mathrm{d}\xi$ produces a change of composition and temperature of the cell from state (1) to state (2). In order to accomplish the same change of state reversibly we first bring the cell to an intermediate state (1) where the reaction is in equilibrium. This is obtained by using thermobaric transfers and heat pumps, while freezing the reaction. At equilibrium we allow the reaction $\mathrm{d}\xi$ to occur thus reaching the state (2′). We then bring the cell to the final state (2) again using thermobaric transfers and heat pumps.

It is important to note that during this reversible process the state of the supply cells is the same in the initial and final state since the masses extracted during one part of the process are restituted during the other. Hence the change in the collective system is the same as due to a reaction in the primary cell alone.

The work accomplished on the hypersystem during this process is the increase $\mathrm{d}\mathcal{J}_{ch}$ of cell potential. We may write

$$\mathrm{d}\mathcal{J}_{ch} = \mathrm{d}\mathcal{U}_{ch} - T_0\,\mathrm{d}\mathcal{S}_{ch} \tag{3.4}$$

where $\mathrm{d}\mathcal{U}_{ch}$ is the increase of internal energy and $\mathrm{d}\mathcal{S}_{ch}$ the increase of entropy as defined above in terms of collective concepts. However when the change occurs in the adiabatic closed cell as a chemical reaction, $\mathrm{d}\mathcal{U}_{ch} = 0$. Hence

$$\mathrm{d}\mathcal{J}_{ch} = -T_0\,\mathrm{d}\mathcal{S}_{ch} \tag{3.5}$$

where $\mathrm{d}\mathcal{S}_{ch}$ may be interpreted as the entropy "produced" by the reaction.

Following De Donder[11] the affinity A is defined by the relation

$$\mathrm{d}\mathcal{S}_{ch} = \frac{A}{T}\,\mathrm{d}\xi. \tag{3.6}$$

Hence

$$\mathrm{d}\mathcal{J}_{ch} = -\frac{T_0}{T}A\,\mathrm{d}\xi. \tag{3.7}$$

In the case of chemical equilibrium $\mathrm{d}\mathcal{S}_{ch} = A = 0$.

On the other hand for an open cell without chemical reaction we denote by $\mathrm{d}\mathcal{J}'$ and $\mathrm{d}\mathcal{S}'$ the values (2.18) and (2.19) found previously. We write

$$\begin{aligned} \mathrm{d}\mathcal{J}' &= \sum^{k} \psi_k\,\mathrm{d}M^k + \theta\,\mathrm{d}s_T \\ \mathrm{d}\mathcal{S}' &= \sum^{k} \bar{s}_k\,\mathrm{d}M^k + \mathrm{d}s_T. \end{aligned} \tag{3.8}$$

When adding a chemical reaction we find

$$\begin{aligned} \mathrm{d}\mathcal{J} &= \mathrm{d}\mathcal{J}' + \mathrm{d}\mathcal{J}_{ch} = -\frac{T_0}{T}A\,\mathrm{d}\xi + \sum^{k} \psi_k\,\mathrm{d}M^k + \theta\,\mathrm{d}s_T \\ \mathrm{d}\mathcal{S} &= \mathrm{d}\mathcal{S}' + \mathrm{d}\mathcal{S}_{ch} = \frac{A}{T}\,\mathrm{d}\xi + \sum^{k} \bar{s}_k\,\mathrm{d}M^k + \mathrm{d}s_T. \end{aligned} \tag{3.9}$$

Elimination of $\mathrm{d}s_T$ between these two equations yields

$$\mathrm{d}\mathcal{J} = -A\,\mathrm{d}\xi + \sum^{k} \phi_k\,\mathrm{d}M^k + \theta\,\mathrm{d}\mathcal{S}. \tag{3.10}$$

Note that the internal energy does not depend on $\mathrm{d}\xi$ since for a closed adiabatic cell no energy is provided to the cell ($\mathrm{d}M^k = \mathrm{d}s_T = 0$). Hence eqn (2.17) remains valid, i.e.

$$\mathrm{d}\mathcal{U} = \sum^{k} \bar{\epsilon}_k\,\mathrm{d}M^k + T\,\mathrm{d}s_T. \tag{3.11}$$

Based on these collective concepts and eqns (3.9) we have derived new expression for the heat of reaction and the affinity[4–6]. We shall briefly outline this derivation.

We consider a hypersystem constituted by two rigid cells C_p C_{eq} and a thermal well TW. The cell C_p is the primary cell and C_{eq} is a cell of composition and temperature such that the chemical reaction considered is in equilibrium. We assume a reaction $\mathrm{d}\xi$ to occur in C_p while the reverse reaction $-\mathrm{d}\xi$ occurs in C_{eq}. As the reaction proceeds we remove the products $\mathrm{d}m_k = \nu_k\,\mathrm{d}\xi$ from C_p and inject them by thermobaric transfer into C_{eq}. Using a heat pump we inject into C_p the amount of heat $\bar{h}_{pT}\,\mathrm{d}\xi$ required to maintain its temperature constant. The temperature of C_{eq} is also maintained constant by injecting the amount of heat $-\bar{h}^{eq}_{pT}\,\mathrm{d}\xi$. The composition and temperature hence also the pressure of the cells C_p and C_{eq} do not vary.

The supply cells remain unchanged since they are not involved in the process just described. If we denote by $\mathrm{d}\mathscr{U}$ and $\mathrm{d}\mathscr{U}^{eq}$ the change of energy of C_p and C_{eq} respectively, we may write

$$\mathrm{d}\mathscr{U} + \mathrm{d}\mathscr{U}^{eq} = 0 \tag{3.12}$$

since this is a consequence of the fact that no change occurs in the collective system $C_p + C_{eq} + \overset{k}{\Sigma}\, C_{sk}$. Applying eqn (3.11) with $\mathrm{d}M^k = -\nu_k\,\mathrm{d}\xi$ we obtain

$$\begin{aligned} \mathrm{d}\mathscr{U} &= -\sum^{k} \nu_k \bar{\epsilon}_k\,\mathrm{d}\xi + \bar{h}_{pT}\,\mathrm{d}\xi \\ \mathrm{d}\mathscr{U}_{eq} &= \sum^{k} \nu_k \bar{\epsilon}^{eq}_k\,\mathrm{d}\xi - \bar{h}^{eq}_{pT}\,\mathrm{d}\xi \end{aligned} \tag{3.13}$$

where $\bar{\epsilon}^{eq}_k$ is the relative specific enthalpy of each substance in C_{eq}. We substitute these values in eqn (3.12) taking into account the relation

$$\bar{\epsilon}_k - \bar{\epsilon}^{eq}_k = \int_{p_{keq}T_{eq}}^{p_kT} \mathrm{d}\bar{\epsilon}_k \tag{3.14}$$

where p_{keq} and T_{eq} are the partial pressures and temperature in C_{eq}. We derive

$$\bar{h}_{pT} - \bar{h}^{eq}_{pT} = \sum^{k} \nu_k \int_{p_{keq}T_{eq}}^{p_kT} \mathrm{d}\bar{\epsilon}_k. \tag{3.15}$$

In this expression, obtained earlier[4, 5], $\bar{h}_{pT}$ is a new concept called *intrinsic heat of reaction.* It is obtained by removing the products as the reaction proceeds at constant temperature. It is more representative of the chemical energy than the traditional concept which includes the heat of mixing as defined earlier [4, 5]. We may write (3.15) in differential form as

$$\mathrm{d}\bar{h}_{pT} = \sum^{k} \nu_k\,\mathrm{d}\bar{\epsilon}_k \tag{3.16}$$

which *generalizes completely and rigorously Kirchhoff's classical result* for the heat of reaction[12].

Consider now the entropy change of the collective system $C_p + C_{eq} + \overset{k}{\Sigma}\, C_{sk}$. The changes due to C_p and C_{eq} are respectively $\mathrm{d}\mathscr{S}$ and $\mathrm{d}\mathscr{S}_{eq}$. Since the collective system does not change we write

$$\mathrm{d}\mathscr{S} + \mathrm{d}\mathscr{S}_{eq} = 0. \tag{3.17}$$

Apply the second of eqns (3.9), we write

$$\begin{aligned} \mathrm{d}\mathscr{S} &= \frac{A}{T}\,\mathrm{d}\xi - \sum^{k} \nu_k \bar{s}_k\,\mathrm{d}\xi + \frac{\bar{h}_{pT}}{T}\,\mathrm{d}\xi \\ \mathrm{d}\mathscr{S}_{eq} &= \sum^{k} \nu_k \bar{s}^{eq}_k\,\mathrm{d}\xi - \frac{\bar{h}^{eq}_{pT}}{T_{eq}}\,\mathrm{d}\xi. \end{aligned} \tag{3.18}$$

In the second equation, $A = 0$, since the reaction is in equilibrium. The relative specific entropy in C_{eq} is denoted by $\bar{s}_k^{eq}$. We may write the relation

$$\bar{s}_k - \bar{s}_k^{eq} = \int_{p_{keq}T_{eq}}^{p_kT} \mathrm{d}\bar{s}_k. \tag{3.19}$$

Taking into account this relation after substituting the values (3.18) into eqn (3.17) we derive

$$\frac{A}{T} = \sum^{k} \nu_k \int_{p_{keq}T_{eq}}^{p_kT} \mathrm{d}\bar{s}_k + \frac{\bar{h}_{pT}^{eq}}{T_{eq}} - \frac{\bar{h}_{pT}}{T}. \tag{3.20}$$

This is the new expression for the affinity already obtained in earlier work[4, 5]

Elimination of $\bar{h}_{pT}$ between eqns (3.15) and (3.20) yields

$$A = -\sum^{k} \nu_k \phi'_k + \bar{h}_{pT}^{eq} \left(\frac{T}{T_{eq}} - 1\right) \tag{3.21}$$

where

$$\phi'_k = \int_{p_{keq}T_{eq}}^{p_kT} (\mathrm{d}\bar{\epsilon}_k - T'\,\mathrm{d}\bar{s}_k). \tag{3.22}$$

The value (3.21) of the affinity is a rigorous consequence of classical thermodynamics. We shall see below (Section 7) by the use of additional axioms how another expression may be derived in more familiar form.

When several reactions occur in the primary cell C_p the mass $\mathrm{d}m_k$ of a particular substance produced by the reactions is

$$\mathrm{d}m_k = \sum^{\rho} \nu_{k\rho}\,\mathrm{d}\xi_\rho \tag{3.23}$$

where ξ_ρ are the coordinates of the various reactions. Adding the effects of each reaction in eqns (3.9) we obtain

$$\mathrm{d}\mathcal{J} = -\frac{T_0}{T} \sum^{\rho} A_\rho\,\mathrm{d}\xi_\rho + \sum^{k} \psi_k\,\mathrm{d}M^k + \theta\,\mathrm{d}s_T$$

$$\mathrm{d}\mathcal{S} = \frac{1}{T} \sum^{\rho} A_\rho\,\mathrm{d}\xi_\rho + \sum^{k} \bar{s}_k\,\mathrm{d}M^k + \mathrm{d}s_T \tag{3.24}$$

where A_ρ is the affinity for each reaction.

Elimination of $\mathrm{d}s_T$ between these two equations yields

$$\mathrm{d}\mathcal{J} = -\sum^{\rho} A_\rho\,\mathrm{d}\xi_\rho + \sum^{k} \phi_k\,\mathrm{d}M^k + \theta\,\mathrm{d}\mathcal{S}. \tag{3.25}$$

In these expressions the state variables are ξ_ρ, M^k and $\mathcal{S}$. The masses M^k added by convection are considered as distinct and independent from those $\mathrm{d}m_k = \sum^{\rho} \nu_{k\rho}\,\mathrm{d}\xi_\rho$ produced by the reactions and which depend only on the chemical coordinates ξ_ρ.

4. THERMOMECHANICS AND CHEMICAL KINETICS OF AN OPEN DEFORMABLE CELL

In the foregoing analysis we have assumed the primary cell to be rigid. We shall now consider the cell to be deformable. In the initial state let it be a cube of unit size oriented along the coordinate axes x_i. It may be an open cell containing masses m_k of pure substances in solution at uniform temperature T. The state variables of this cell may be chosen to be the reaction coordinates ξ_ρ, the masses M^k added by convection, the entropy $\mathcal{S}$ and six strain components ϵ_{ij}. In this section we consider the strain to be homogeneous.

There are various ways of measuring the finite strain which have been the object of numerous discussions and applications by the author. We shall briefly recall the essential concepts.

The homogeneous deformation and solid rotation of the unit cube are represented by the affine transformation

$$\bar{x}_i = (\delta_{ij} + a_{ij})x_j \tag{4.1}$$

where x_i and $\bar{x}_j$ are the coordinates of material points before and after deformation.

Strain components may be defined in various ways. Green's tensor is

$$\epsilon_{ij} = \frac{1}{2}(a_{ij} + a_{ji}) + \frac{1}{2}a_{li} \cdot a_{lj}. \tag{4.2}$$

We may also use a definition introduced in 1939 by the author which avoids many of the difficulties attached to Green's tensor in applications and was developed extensively in a monograph[13]. In this definition we first perform an affinine transformation

$$\bar{x}_i = (\delta_{ij} + \epsilon_{ij})x_j \tag{4.3}$$

putting $\epsilon_{ij} = \epsilon_{ji}$ followed by a solid rotation such that the total transformation is equivalent to (4.1). The six independent values of ϵ_{ij} define the strain. They are functions of a_{ij}. To the second order we derive

$$\epsilon_{ij} = e_{ij} + \eta_{ij} \tag{4.4}$$

with

$$\eta_{ij} = \frac{1}{2}(e_{kj} \cdot \omega_{ki} + e_{ki} \cdot \omega_{kj} + \omega_{ki} \cdot \omega_{kj})$$

$$e_{ij} = \frac{1}{2}(a_{ij} + a_{ji}), \qquad \omega_{ij} = \frac{1}{2}(a_{ij} - a_{ji}). \tag{4.5}$$

Other similar definitions of ϵ_{ij} may be used which are non tensorial. For example in two dimensions we may write

$$\bar{x}_i = (1 + \epsilon_{11})x_1 + 2\epsilon_{12}x_2 \qquad \bar{x}_2 = (1 + \epsilon_{22})x_2 \tag{4.6}$$

and use ϵ_{11} ϵ_{22} ϵ_{12} as measure of the finite strain. To the second order their values were shown to be[14]

$$\begin{aligned} \epsilon_{11} &= a_{11} + \frac{1}{2}a_{21}^2 \\ \epsilon_{22} &= a_{22} - \frac{1}{2}a_{21}(2a_{12} + a_{21}) \\ \epsilon_{12} &= \frac{1}{2}(a_{12} + a_{21}) + \frac{1}{2}a_{21}(a_{22} - a_{11}). \end{aligned} \tag{4.7}$$

When using the general notation ϵ_{ij} for this case, we put $\epsilon_{21} = 0$. A large number of variations of this type of definition are possible in two and three dimensions as indicated[14]. The components thus defined are nontensorial but in many problems this is an advantage as illustrated by the derived nontensorial concept of slide modulus[13, 14]. The deeper reason for this usefulness is due to the fact that the local representation of stress and strain may be tailored to the physical anisotropy whether intrinsic or induced by the presence of initial stresses.

The notation ϵ_{ij} for the strain used hereafter includes any of the various definitions of strain described above. The corresponding stress components is defined by virtual work, so that

$$T_{ij}\delta\epsilon_{ij} \tag{4.8}$$

represents the virtual work associated with the virtual deformation $\delta\epsilon_{ij}$. We omit the summation sign although ϵ_{ij} is not necessarily a tensor, with the understanding that the summation is extended to all six independent variables ϵ_{ij}.

According to the definition of $\mathscr{J}$ its differential in the case of a deformable cell is obtained by simply adding the external work $T_{ij}\,\mathrm{d}\epsilon_{ij}$ performed by the stresses T_{ij} under the conditions $\mathrm{d}\xi = \mathrm{d}M^k = \mathrm{d}s_T = 0$. By adding this term to the values (3.25) of $\mathrm{d}\mathscr{J}$ we obtain

$$\mathrm{d}\mathscr{J} = T_{ij}\,\mathrm{d}\epsilon_{ij} - \frac{T}{T_0}\sum^{\rho} A_\rho\,\mathrm{d}\xi_\rho + \sum^{k} \psi_k\,\mathrm{d}M^k + \theta\,\mathrm{d}s_T. \tag{4.9}$$

The value of $\mathrm{d}\mathscr{S}$ remains the same as (3.24)

$$\mathrm{d}\mathscr{S} = \frac{1}{T}\sum^{\rho} A_\rho\,\mathrm{d}\xi_\rho + \sum^{k} \bar{s}_k\,\mathrm{d}M^k + \mathrm{d}s_T. \tag{4.10}$$

Elimination of $\mathrm{d}s_T$ between (4.19) and (4.10) yields

$$\mathrm{d}\mathscr{J} = T_{ij}\,\mathrm{d}\epsilon_{ij} - \sum^{\rho} A_\rho\,\mathrm{d}\xi_\rho + \sum^{k} \phi_k\,\mathrm{d}M^k + \theta\,\mathrm{d}\mathscr{S}. \tag{4.11}$$

We note that according to eqns (2.10), (2.15), (2.22) and (3.21) the quantities $\bar{e}_k$, $\bar{s}_k$, ψ_k, ϕ_k and A_ρ are functions of the partial pressures p_k and the temperature T. In turn p_k is a function of T, ϵ_{ij} and the masses m_k of each substance in solution. This mass is given by

$$m_k = m_{0k} + M^k + \sum^{\rho} \nu_{k\rho}\xi_\rho \tag{4.12}$$

where m_{0k} is the initial value of m_k. Hence $\bar{e}_k$, $\bar{s}_k$, ψ_k, ϕ_k and A_ρ may be expressed as functions of ϵ_{ij}, T, M^k and ξ_ρ.

The values of $\mathscr{J}$ and $\mathscr{S}$ may be conveniently obtained by integrating (4.9) and (4.10) first at constant temperature T_0 then heating the cell to the temperature T maintaining constant the values ϵ_{ij}, ξ_ρ and M^k. We obtain

$$\begin{gathered}\mathscr{J} = \mathscr{J}(\epsilon_{ij}, \xi_\rho, M^k, T)\\ \mathscr{S} = \mathscr{S}(\epsilon_{ij}, \xi_\rho, M^k, T).\end{gathered} \tag{4.13}$$

Elimination of T between these two relations yields

$$\mathscr{J} = \mathscr{J}(\epsilon_{ij}, \xi_\rho, M^k, \mathscr{S}) \tag{4.14}$$

where $\mathscr{J}$ is now a known function of ϵ_{ij}, ξ_ρ, M^k and $\mathscr{S}$.

From the differential (4.11) we derive

$$\frac{\partial\mathscr{J}}{\partial\epsilon_{ij}} = T_{ij} \qquad \frac{\partial\mathscr{J}}{\partial M^k} = \phi_k \qquad \frac{\partial\mathscr{J}}{\partial\mathscr{S}} = \theta \tag{4.15}$$

and a fourth one which plays a special role

$$\frac{\partial\mathscr{J}}{\partial\xi} = -A_\rho. \tag{4.16}$$

We denote by Q_i the quantities T_{ij}, ϕ_k and θ and by q_i the corresponding variables ϵ_{ij}, M^k and $\mathcal{S}$. Equations (4.15) are then written

$$\frac{\partial \mathcal{G}}{\partial q_i} = Q_i. \tag{4.17}$$

The quantities Q_i may be considered as mixed mechanical thermodynamic driving forces which are known functions of time imposed by the environment.

Equations (4.16) and (4.17) are not sufficient to determine the unknown variables q_i and ξ_ρ because A_ρ is not known. The additional relations are provided by chemical kinetics by which reaction rates are given as (the dot denotes a time derivative),

$$\dot{\xi}_\rho = f_\rho(\epsilon_{ij}, m_k, T). \tag{4.18}$$

This may be expressed in terms of ϵ_{ij}, ξ_ρ, M^k and $\mathcal{S}$ using the value (4.12) of m_k and writing

$$T = T(\epsilon_{ij}, \xi_\rho, M^k, \mathcal{S}) \tag{4.19}$$

obtained by solving for T the value (4.13) of $\mathcal{S}$. The rates of reaction become

$$\dot{\xi}_\rho = f_\rho(\epsilon_{ij}, \xi_\rho, M_k, \mathcal{S}). \tag{4.20}$$

Equations (4.17) and (4.20) now constitute a complete system for the chemical kinetics of the deformable open cell.

We may write these equations in a form which corresponds to a general Lagrangian formulation of irreversible thermodynamic systems. As already pointed out, the affinity is a function of the partial pressures and the temperature

$$A_\rho = A_\rho(p_k, T). \tag{4.21}$$

Since p_k is a function of ϵ_{ij}, m_k, T using eqns (4.12) and (4.19) we write

$$A_\rho = A_\rho(\epsilon_{ij}, \xi_\rho, M^k, \mathcal{S}). \tag{4.22}$$

Elimination of ξ_ρ between eqns (4.20) and (4.22) yields

$$A_\rho = \mathcal{R}_\rho(\epsilon_{ij}, \dot{\xi}_\rho, M^k, \mathcal{S}) \tag{4.23}$$

where the affinity is now expressed in terms of reaction rates $\dot{\xi}_\rho$ by what we have called a *rate function* [4–6], $\mathcal{R}_\rho$.

Introducing into (4.16) the value (4.23) of A_ρ we obtain the system of differential equations

$$\frac{\partial \mathcal{G}}{\partial q_i} = Q_i$$

$$\frac{\partial \mathcal{G}}{\partial \xi_\rho} + \mathcal{R}_\rho = 0 \tag{4.24}$$

which govern the time evolution of the open deformable cell. These equations are now in the Lagrangian form introduced by the author. A particular case of interest is obtained by assuming that the system, while nonlinear and irreversible, is never very far from equilibrium. For such a quasi-irreversible system Onsager's principle[15, 16] applies to the chemical reactions.

This is expressed by writing the rate functions in the form

$$\mathcal{R}_\rho = \frac{\partial D}{\partial \dot{\xi}_\rho} \tag{4.25}$$

where

$$D=\frac{1}{2}\sum^{\rho\sigma} b_{\rho\sigma}(\epsilon_{ij}, M^k, \mathscr{S})\dot{\xi}_\rho\dot{\xi}_\sigma \tag{4.26}$$

is a *positive quadratic form in* $\dot{\xi}_\rho$ *with coefficients dependent on the state of the system.* Equations (4.24) are now

$$\frac{\partial \mathscr{V}}{\partial q_i}=Q_i$$

$$\frac{\partial \mathscr{V}}{\partial \xi_\rho}+\frac{\partial D}{\partial \dot{\xi}_\rho}=0. \tag{4.27}$$

For a closed cell ($M^k=0$) these equations are the same as obtained in the analysis of nonlinear thermoviscoelasticity where the role of internal coordinates is played by the chemical variables ξ_ρ [3].

5. PRINCIPLE OF VIRTUAL DISSIPATION FOR CONTINUOUS SYSTEMS

We may consider a continuum as a collection of infinitesimal primary cells. An important property of the collective potential is its additivity. Hence the collective potential of a continuum may be written

$$V=\int_\Omega \mathscr{V}\,\mathrm{d}\Omega \tag{5.1}$$

where Ω is the domain before deformation and $\mathscr{V}$ is the cell potential per unit initial volume. The elementary initial volume is $\mathrm{d}\Omega=\mathrm{d}x_1\mathrm{d}x_2\mathrm{d}x_3$ with initial coordinates x_i. Similarly the collective energy and entropy are

$$U=\int_\Omega \mathscr{U}\,\mathrm{d}\Omega$$

$$S=\int_\Omega \mathscr{S}\,\mathrm{d}\Omega. \tag{5.2}$$

Because of eqn (2.5) we may write

$$V=U-T_0\mathscr{S}. \tag{5.3}$$

We also assume that the continuum is subject to a potential force field such as gravity. The potential field per unit mass is a function $\mathscr{G}(\bar{x}_i)$ of the coordinates. If we call ρ the mass per unit initial volume at a displaced point $\bar{x}_i$ the mechanical potential energy of the continuum is

$$G=\int_\Omega \rho\mathscr{G}(\bar{x}_i)\,\mathrm{d}\Omega. \tag{5.4}$$

We define

$$\mathscr{P}=V+G \tag{5.5}$$

as a *mixed collective potential* which embodies mixed mechanical and thermodynamic properties.

We now consider the continuum to undergo a completely general transformation which *may be irreversible.* With a virtual infinitesimal transformation we may write d'Alemberts principle as

$$\sum^{i} I_i\delta q_i+\delta U+\delta G=\delta W \tag{5.6}$$

where δW is the virtual work of external forces in addition to the potential forces and $\overset{i}{\Sigma} I_i \delta q_i$ the virtual work of the inertia forces with generalized inertia forces I_i corresponding to generalized coordinates q_i. The variables must of course be varied subject to certain constraints which we shall specify. Elimination of U between eqns (5.3) and (5.6) yields

$$\sum^{i} I_i \delta q_i + \delta \mathcal{P} + T_0 \delta S = \delta W. \tag{5.7}$$

Consider now that there is *no variational flow of matter or heat across the boundary of* Ω. In this case δS represents the *entropy produced in* Ω. To indicate this we write S^* instead of S and eqn (5.7) becomes

$$\sum^{i} I_i \delta q_i + \delta \mathcal{P} + T_0 \delta S^* = \delta W. \tag{5.8}$$

The term $T_0 \delta S^*$ represents a virtual dissipation and eqn (5.8) is the general form of the *principle of virtual dissipation* [3] generalizing d'Alembert's principle to irreversible thermodynamic systems.

The principle may be written in an alternate form particularly useful for continuous systems as follows. It was shown earlier [3] that we may write

$$\delta \mathcal{P} + T_0 \delta S^* = \delta_R \mathcal{P} + \int_\Omega T \delta s^* \, \mathrm{d}\Omega \tag{5.9}$$

where δs^* is the entropy produced and $T \delta s^*$ is the virtual dissipation, both per unit initial volume.

The term $\delta_R \mathcal{P}$ is

$$\delta_R \mathcal{P} = \int_\Omega [\delta_R \mathcal{J} + \delta(\rho \mathcal{G})] \, \mathrm{d}\Omega \tag{5.10}$$

where δ_R denotes a variation obtained by excluding the variation δs^* of entropy produced. The principle of virtual dissipation (5.8) thus becomes [3].

$$\sum^{i} I_i \delta q_i + \delta_R \mathcal{P} + \int_\Omega T \delta s^* \, \mathrm{d}\Omega = \delta W. \tag{5.11}$$

Note that T is the local temperature. We have called $T\delta s^*$ the intrinsic dissipation.

We must now define the variables to be varied and the constraints which they must obey. One of the variables is the field of displacements u_i of the solid. The new coordinates become $\bar{x}_i = x_i + u_i$. Another field is the mass displacement vector M_i^k of each substance relative to the solid. It is defined as the total mass which has flowed across a material area initially perpendicular to the x_i axis and initially equal to unity. It obviously satisfies the mass conservation constraint

$$M^k = -\frac{\partial M_i^k}{\partial x_i}. \tag{5.12}$$

Summation signs are omitted for tensorial quantities.

An equation of entropy balance is also obtained by considering the rate of increase of entropy in an arbitrary domain Ω'. It may be written

$$\int_{\Omega'} \dot{\mathcal{S}} \, \mathrm{d}\Omega' = \int_{\Omega'} \left(\overset{*}{\dot{s}}_{NT} + \frac{\dot{h}}{T} \right) \mathrm{d}\Omega' - \int_{A'} \sum^{k} \bar{s}_k \dot{M}_i^k n_i \, \mathrm{d}A'. \tag{5.13}$$

In this equation, $\dot{h}$ is the rate of the heat acquired per unit initial volume of Ω', $\overset{*}{\dot{s}}_{NT}$ is the rate of entropy produced per unit initial volume which is not due to pure thermal conduction and

$\bar{s}_k \dot{M}_i^k$ is the rate of convected entropy per unit area of the initial boundary A'. We write

$$\dot{h} = -\frac{\partial \dot{H}_i}{\partial x_i} \tag{5.14}$$

where $\dot{H}_i$ is the rate of heat flow per unit initial area across a face initially perpendicular to x_i. By integration by parts eqn (5.13) may be transformed to

$$\int_{\Omega'} \dot{\mathscr{S}} \, d\Omega' = \int_{\Omega'} \left(\dot{s}^* - \frac{\partial \dot{S}_i}{\partial x_i} \right) d\Omega' \tag{5.15}$$

where

$$\dot{s}^* = \dot{s}^*_{NT} - \frac{\dot{H}_i}{T^2} \frac{\partial T}{\partial x_i} \tag{5.16}$$

$$\dot{S}_i = \sum^k \bar{s}_k \dot{M}_i^k + \dot{S}_i^T$$

$$\dot{S}_i^T = \frac{\dot{H}_i}{T}. \tag{5.17}$$

The domain Ω' being arbitrary the integral (5.15) implies

$$\dot{\mathscr{S}} = \dot{s}^* - \frac{\partial \dot{S}_i}{\partial x_i}. \tag{5.18}$$

This generalizes Meixner's result[17] which is restricted to thermal flow. Time integration with zero initial values yields

$$\mathscr{S} = s^* + s \tag{5.19}$$

where

$$s = -\frac{\partial S_i}{\partial x_i} \tag{5.20}$$

is the *entropy supplied.* The vector S_i is the total entropy displacement due to convection and conduction. Relation (5.19) expresses the basic entropy balance, while relation (5.20) is a holonomic constraint analogous to (5.12) for the masses. The rate of entropy production $\dot{s}^*$ per unit initial volume (5.16) may also be written

$$\dot{s}^* = \dot{s}^*_{NT} + \lambda_{ij} \dot{S}_i^T \dot{S}_j^T \tag{5.21}$$

where λ_{ij} is the thermal resistivity tensor of a *deformed element of solid*, relating $\dot{H}_i$ and $\partial T / \partial x_i$.

The variables u_i, M_i^k, S_i, s^* and ξ_ρ completely define the state of the deformable solid with thermomolecular diffusion and chemical reactions.

The strain components ϵ_{ij} may be chosen according to any of the particular definitions described in Section 4. They may be tensorial or non tensorial functions of a_{ij}. we write

$$\epsilon_{ij} = \epsilon_{ij}(a_{\mu\nu}) \tag{5.22}$$

with the property of invariance under a rigid rotation. For a non homogeneous deformation a_{ij} are the gradients.

$$a_{ij} = \frac{\partial u_i}{\partial x_j}. \tag{5.23}$$

The total rate of intrinsic dissipation per unit initial volume is the *positive definite* expression

$$T\dot{s}^* = \sum^{\rho} \mathcal{R}_\rho \dot{\xi}_\rho + 2\mathcal{D} \tag{5.24}$$

where $\mathcal{R}_\rho$ is the rate function defined by (4.23) and $\mathcal{D}$ is a dissipation function

$$\mathcal{D} = \frac{1}{2}\sum^{lk} C_{ij}^{lk} \dot{M}_i^l \dot{M}_j^k + C_{ij}^{k} \dot{M}_i^k \dot{S}_j + \frac{1}{2} T\lambda_{ij} \dot{S}_i \dot{S}_j \tag{5.25}$$

which is a quadratic function of $\dot{M}_i^k$ and S_i with coefficients dependent on the local state. This quadratic form represents thermomolecular diffusion with the local validity of Onsager's principle[15, 16]. The coefficients C_{if}^{k} represent the coupling between mass and entropy flow *including entropy convection.*

The virtual dissipation is immediately derived from these results. It is written

$$T\delta s^* = \sum^{\rho} \mathcal{R}_\rho \, \mathrm{d}\xi_\rho + \sum^{k} \frac{\partial \mathcal{D}}{\partial \dot{M}_i^k} \delta M_i^k + \frac{\partial \mathcal{D}}{\partial \dot{S}_i} \delta S_i. \tag{5.26}$$

6. VARIATIONAL DERIVATION OF FIELD EQUATIONS FOR COUPLED THERMOMOLECULAR DIFFUSION AND CHEMICAL REACTIONS IN A DEFORMABLE SOLID CONTINUUM

We consider a deformable solid which undergoes a deformation described by the material displacement field u_i. The coupled thermomolecular diffusion *relative to the solid* is described by the vectors S_i and M_i^k. The vector S_i is the entropy displacement due to conduction and convection, while M_i^k is the mass displacement relative to the solid of the various substances in solution. The scalar field ξ_ρ represents the distribution of chemical coordinates, and s^* is the entropy produced per unit initial volume. These unknown fields are to be determined as functions of the initial coordinates x_i and the time t.

Equations governing these fields are readily obtained by applying the principle of virtual dissipation assuming arbitrary variations which vanish at the boundary. In this case the virtual work of external boundary forces vanishes ($\delta W = 0$) and the variational principle (5.11) is written

$$\sum^{i} I_i \delta q_i + \int_\Omega [\delta_R \mathcal{J} + \delta(\rho \mathcal{G}) + T\delta s^*] \, \mathrm{d}\Omega = 0. \tag{6.1}$$

The variation $\delta_R \xi$ is obtained by varying only ϵ_{ij}, M^k, ξ_ρ and s (excluding s^*). We find

$$\delta_R \mathcal{J} = \frac{\partial \mathcal{J}}{\partial \epsilon_{ij}} \delta\epsilon_{ij} + \sum^{k} \frac{\partial \mathcal{J}}{\partial M^k} \delta M^k + \frac{\partial \mathcal{J}}{\partial \mathcal{S}} \delta s + \sum^{\rho} \frac{\partial \mathcal{J}}{\partial \xi_\rho} \delta\xi_\rho. \tag{6.2}$$

According to (4.15) and (4.16) this may be written

$$\delta_R \mathcal{J} = T_{\mu\nu} \frac{\partial \epsilon_{\mu\nu}}{\partial a_{ij}} \delta a_{ij} + \sum^{k} \phi_k \delta M^k + \theta \delta s - \sum^{\rho} A_\rho \, \mathrm{d}\xi_\rho. \tag{6.3}$$

Since ρ is independent of the chemical reaction we write

$$\rho = \sum^{k} (\rho_0 + M^k) \tag{6.4}$$

where ρ_0 is the initial mass per unit volume.

We derive

$$\delta[\rho \mathcal{G}(\bar{x}_i)] = \mathcal{G} \delta\rho + \rho \frac{\partial \mathcal{G}}{\partial \bar{x}_i} \delta u_i = \mathcal{G} \sum^{k} \delta M^k + \rho \frac{\partial \mathcal{G}}{\partial \bar{x}_i} \delta u_i \tag{6.5}$$

hence

$$\delta_R \mathscr{J} + \delta(\rho \mathscr{G}) = T_{\mu\nu} \frac{\partial \epsilon_{\mu\nu}}{\partial a_{ij}} \delta a_{ij} + \sum^{k} \varphi_k \delta M^k + \rho \frac{\partial \mathscr{G}}{\partial \bar{x}_i} \delta u_i + \theta \delta s - \sum^{\rho} A_\rho \delta \xi_\rho \tag{6.6}$$

where

$$\varphi_k = \phi_k + \mathscr{G} \tag{6.7}$$

defines a *mixed convective potential* which takes into account the body force potential $\mathscr{G}$.

Finally we consider the inertia forces. In order to avoid undue complications which do not add significantly to the physical accuracy we introduce some simplifying assumptions. A more accurate evaluation of the inertia forces will be found in an earlier paper dealing with fluid saturated porous solids [8]. We shall assume that the inertia forces are due mainly to the acceleration $\ddot{u}_i$ and the time derivative of the momentum $\rho \dot{u}_i$ of the solid. Per unit initial volume the virtual work of the inertia forces is

$$\frac{\mathrm{d}}{\mathrm{d}t}(\rho \dot{u}) \delta u_i + \ddot{u}_i \sum^{k} \int_\Delta \rho_k \delta u_i^k \, \mathrm{d}\bar{x}_1 \, \mathrm{d}\bar{x}_2 \, \mathrm{d}\bar{x}_3. \tag{6.8}$$

In this expression Δ is the domain occupied after deformation by an element of the solid initially of unit volume, $\rho_k = m_k/\Delta$ is the partial density of substance k after deformation and δu_i^k is the virtual displacement of the substance in cartesian coordinates. It was shown that [8]

$$\int_\Delta \rho_k \delta u_i^k \, \mathrm{d}\bar{x}_1 \, \mathrm{d}\bar{x}_2 \, \mathrm{d}\bar{x}_3 = \frac{\partial \bar{x}_i}{\partial x_j} \delta M_j^k. \tag{6.9}$$

We derive for the virtual work of the inertia forces

$$\sum^{i} I_i \delta q_i = \int_\Omega \left[\frac{\mathrm{d}}{\mathrm{d}t}(\rho \dot{u}_i) \delta u_i + \sum^{k} \ddot{u}_i \frac{\partial \bar{x}_i}{\partial x_j} \delta M_j^k \right] \mathrm{d}\Omega. \tag{6.10}$$

We now substitute the values (5.26), (6.6) and (6.10) in the principle of virtual dissipation (6.1). From relations (5.12), (5.20) and (5.23) we derive the variations

$$\delta s = -\frac{\partial}{\partial x_i} \delta S_i \qquad \delta M^k = -\frac{\partial}{\partial x_i} \delta M_i^k \qquad \delta a_{ij} = \frac{\partial}{\partial x_j} \delta u_i \tag{6.11}$$

and we integrate by parts the terms in (6.1) which contains these variations. In the final result we cancel the factors multiplying the arbitrary variations. This yields

$$\frac{\partial}{\partial x_j}\left(T_{\mu\nu} \frac{\partial \epsilon_{\mu\nu}}{\partial a_{ij}} \right) - \rho \frac{\partial \mathscr{G}}{\partial \bar{x}_i} = \frac{\mathrm{d}}{\mathrm{d}t}(\rho \dot{u}_i), \qquad \frac{\partial \varphi_k}{\partial x_i} + \frac{\partial \mathscr{D}}{\partial \dot{M}_i^k} = -\ddot{u}_j \frac{\partial \bar{x}_j}{\partial x_i},$$

$$\frac{\partial \theta}{\partial x_i} + \frac{\partial \mathscr{D}}{\partial \dot{S}_i} = 0, \qquad -A_\rho + \mathscr{R}_\rho = 0. \tag{6.12}$$

These equations along with (5.24) for $\dot{s}^*$ namely

$$T \dot{s}^* = \sum^{\rho} \mathscr{R}_\rho \xi_\rho + 2\mathscr{D} \tag{6.13}$$

constitute a complete set of differential equations for the time evolution of the variables u_i, M_i^k, S_i, ξ_ρ and s^*. The value of $\mathscr{S}$ is determined from equation (5.19) while M^k is derived from (5.12).

7. ADDITIONAL AXIOMS AND NEW DEFINITION OF THE CHEMICAL POTENTIAL

The thermodynamic functions derived in the foregoing analysis are based exclusively on the axioms of classical thermodynamics. It is possible to proceed further and derive thermodynamic functions analogous to those associated with the axioms of quantum statistics. However in deriving these results we may bypass completely the statistical treatment by introducing two very simple axioms and by this process obtain a new definition of the chemical potential.

Let us go back to expressions (3.15) and (3.20) for the affinity and the heat of reaction. We assume that we may write

$$\text{Axiom (a)} \qquad \bar{h}_{pT} = \sum^{k} \nu_k \int_0^{p_kT} \mathrm{d}\bar{\epsilon}_k + \sum^{k} \nu_k \bar{\epsilon}_k(0) \tag{7.1}$$

$$\text{Axiom (b)} \qquad \frac{\bar{h}^{eq}_{pT}}{T_{eq}} = \sum^{k} \nu_k \int_0^{p_{keq}T_{eq}} \mathrm{d}\bar{s}_k. \tag{7.2}$$

Note that Axiom (b) implies *Nernts' third principle.* The lower limit of the integrals in (7.1) and (7.2) is the state of absolute zero and it is assumed that the integration may be performed as a limiting process by extrapolation. We further assume that the constants of integration $\bar{\epsilon}_k(0)$ are *characteristic of the pure substances and independent of the chemical reactions.* These constants are considered to be derived by measuring heats of reaction for a sufficient number of cases. In principle they may also be obtained from quantum statistics but in fact this is seldom practical.

Substitution of the values (7.1) and (7.2) into expression (3.20) for the affinity yields

$$A = -\sum^{k} \nu_k \mu_k \tag{7.3}$$

where

$$\mu_k = \bar{\epsilon}^{abs}_k - T\bar{s}^{abs}_k \tag{7.4}$$

with

$$\bar{\epsilon}^{abs}_k = \int_0^{p_kT} \mathrm{d}\epsilon_k + \bar{\epsilon}_k(0) \qquad \bar{s}^{abs}_k = \int_0^{p_kT} \mathrm{d}\bar{s}_k. \tag{7.5}$$

Equation (7.3) expresses the affinity in the traditional form *with a new definition* (7.4) *of the chemical potential.*

In the previous sections we have defined the entropy $\mathcal{S}$ as a collective concept which depends on the state of the supply cells. We may consider the particular case where the supply cells are all in the state of absolute zero temperature and extrapolate to this case the results obtained in Section 3 from classical thermobynamics. To simplify the writing consider the case of a single reaction ξ. The entropy differential (3.9) becomes

$$\mathrm{d}\mathcal{S} = \frac{A}{T}\mathrm{d}\xi + \sum^{k} \bar{s}^{abs}_k \, \mathrm{d}M^k + ds_T \tag{7.6}$$

where $\bar{s}_k$ has been replaced by $\bar{s}^{abs}_k$ as expressed by (7.5). We may also write relation (3.20) in the form

$$\frac{A}{T} = \sum^{k} \nu_k \bar{s}^{abs}_k - \frac{\bar{h}_{pT}}{T}. \tag{7.7}$$

Substituting this value into (7.6), taking into account the relation

$$\mathrm{d}m_k = \mathrm{d}M^k + \nu_k \, \mathrm{d}\xi \tag{7.8}$$

we obtain

$$\mathrm{d}\mathscr{S} = \sum^{k} \bar{s}_k^{abs}\,\mathrm{d}m_k - \frac{\bar{h}_{pT}}{T}\,\mathrm{d}\xi + \mathrm{d}s_T. \tag{7.9}$$

On the other hand we may write

$$T\,\mathrm{d}s_T = h_{pT}\,\mathrm{d}\xi + \sum^{k} h_k{}^m\,\mathrm{d}M^k + h_{ij}\,\mathrm{d}\epsilon_{ij} + C\,\mathrm{d}T. \tag{7.10}$$

Also by definition

$$\bar{h}_{pT}\,\mathrm{d}\xi = \left(h_{pT} - \sum^{k} \nu_k h_k{}^m\right)\mathrm{d}\xi. \tag{7.11}$$

Using relations (7.8), (7.10) and (7.11), the value (7.9) of the entropy differential becomes

$$\mathrm{d}\mathscr{S} = \sum^{k}\left(\bar{s}_k^{abs} + \frac{h_k{}^m}{T}\right)\mathrm{d}m_k + \frac{h_{ij}}{T}\,\mathrm{d}\epsilon_{ij} + \frac{C}{T}\,\mathrm{d}T. \tag{7.12}$$

The coefficients $\bar{s}_k^{abs}$, $h_k{}^m$, h_{ij} and C are functions only of m_k, ϵ_{ij} and T. Hence integration of (7.12) yields

$$\mathscr{S} = \mathscr{S}(m_k, \epsilon_{ij}, T) \tag{7.13}$$

as a function of the same variables. This expression is *valid whether m_k results from chemical reactions or convection.*

We may also derive the cell potential in terms of the chemical potential μ_k by writing the convective potential as

$$\phi_k = \mu_k - \mu_{0k} \tag{7.14}$$

where μ_{0k} is the chemical potential of the substance in the supply cell. With the value (7.3) of A and taking into account relation (7.8) we write (3.10) in the form

$$\mathrm{d}\mathscr{J} = \sum^{k}\mu_k\,\mathrm{d}m_k + \theta\,\mathrm{d}\mathscr{S} - \sum^{k}\mu_{0k}\,\mathrm{d}M^k. \tag{7.15}$$

If we assume the supply cells to be at absolute zero, this becomes

$$\mathrm{d}\mathscr{J} = \sum^{k}\mu_k\,\mathrm{d}m_k + \theta\,\mathrm{d}\mathscr{S} - \sum^{k}\epsilon_k(0)\,\mathrm{d}M^k. \tag{7.16}$$

Hence the value of $\mathscr{J}$ still depends on M^k unless we neglect $\epsilon_k(0)$. On the other hand if we consider a continuum with zero variation of the total mass of each substance in the domain Ω,

$$\int_\Omega \delta M^k\,\mathrm{d}\Omega = 0 \tag{7.17}$$

we obtain for the variation of the total collective potential

$$\delta V = \int_\Omega \left(\sum^{k}\mu_k\delta m_k + \theta\delta\mathscr{S}\right)\mathrm{d}\Omega \tag{7.18}$$

This value depends only on δm_k and $\delta\mathscr{S}$.

8. COMPLEMENTARY FORM OF THE FIELD EQUATIONS

Let us neglect the inertia term—$\ddot{u}_j \partial \bar{x}_j / \partial x_i$ in the field equations (6.12). Physically this means that we neglect the effect of inertia forces on the diffusion process. The second and third equations (6.12) become

$$\frac{\partial \mathscr{D}}{\partial \dot{M}_i^k} = X_i^k \qquad \frac{\partial \mathscr{D}}{\partial \dot{S}_i} = X_i \tag{8.1}$$

where

$$X_i^k = -\frac{\partial \varphi_k}{\partial x_i}, \qquad X_i = -\frac{\partial \theta}{\partial x_i}. \tag{8.2}$$

Equations (8.1) are linear in $\dot{M}_i^k$ and $\dot{S}_i$. They may be solved for $\dot{M}_i^k$ and $\dot{S}_i$ and the solution may be written

$$\dot{M}_i^k = \frac{\partial \mathscr{D}^c}{\partial X_i^k} \qquad \dot{S}_i = \frac{\partial \mathscr{D}^c}{\partial X_i} \tag{8.3}$$

where $\mathscr{D}^c$ is the dissipation function $\mathscr{D}$ expressed as a quadratic form in X_i^k and X_i instead of $\dot{M}_i^k$ and $\dot{S}_i$. By substituting the values (8.3) into (5.12) and (5.20) we obtain

$$\dot{M}^k = -\frac{\partial}{\partial x_i}\left(\frac{\partial \mathscr{D}^c}{\partial X_i^k}\right), \qquad \dot{s} = -\frac{\partial}{\partial x_i}\left(\frac{\partial \mathscr{D}^c}{\partial X_i}\right). \tag{8.4}$$

On the other hand the time derivation of (4.12) yields

$$\dot{m}_k = \dot{M}^k + \sum^{\varrho} \nu_{k\rho} \dot{\xi}_\rho = \dot{M}^k + \sum^{\varrho} \nu_{k\rho} f_\rho \tag{8.5}$$

where $f_\rho(\epsilon_{ij}, m_k, T)$ is the rate of reaction (4.18). Also from (5.19) and (5.24) substituting $A_\rho(\epsilon_{ij}, m_k, T)$ instead of $\mathscr{R}_\rho$ and f_ρ for $\dot{\xi}_\rho$ we write

$$\dot{\mathscr{S}} = \dot{s} + \frac{1}{T}\sum^{\varrho} A_\rho f_\rho + \frac{2\mathscr{D}}{T}. \tag{8.6}$$

Combining equations (8.4)–(8.6) and adding the first group of the field equations (6.12) we obtain

$$\frac{\partial}{\partial x_j}\left(T_{\mu\nu}\frac{\partial \epsilon_{\mu\nu}}{\partial a_{ij}}\right) - \rho\frac{\partial \mathscr{G}}{\partial \bar{x}_i} = \frac{\mathrm{d}}{\mathrm{d}t}(\rho \dot{u}_i)$$

$$\dot{m}_k = -\frac{\partial}{\partial x_i}\left(\frac{\partial \mathscr{D}^c}{\partial X_i^k}\right) + \sum^{\varrho} \nu_{k\rho} f_\rho$$

$$\dot{\mathscr{S}} = -\frac{\partial}{\partial x_i}\left(\frac{\partial \mathscr{D}^c}{\partial X_i}\right) + \frac{1}{T}\left(\sum^{\varrho} A_\rho f_\rho + 2\mathscr{D}^c\right). \tag{8.7}$$

The entropy $\mathscr{S}$ as well as other variables in these equations are expressed in terms of the unknowns u_i, m_k and T. The time evolution of these variables is governed by the complementary form (8.7) of the field equations[6].

9. LAGRANGIAN EQUATIONS

The principle of virtual dissipation (5.11) may be applied to derive directly Lagrangian equations which govern the evolution of complex systems described by generalized coordinates. The fields are approximated by the expressions

$$\begin{aligned} u_j &= u_j(q_i, x_l, t) \\ M_j^k &= M_j^k(q_i, x_l, t) \\ S_j &= S_j(q_i, x_l, t) \\ \xi_\rho &= \xi_\rho(q_i, x_l, t) \end{aligned} \tag{9.1}$$

where q_i are generalized coordinates to be determined as functions of time. In a large number of problems the entropy produced s^* does not contribute significantly to the values of the state variables. Hence in this case suitably chosen generalized coordinates q_i are sufficient to describe the state of the system. The mixed collective potential is evaluated as

$$\mathscr{P} = \mathscr{P}(q_i, t) \tag{9.2}$$

and the rate of dissipation expressed in generalized coordinates is

$$\int_\Omega T\dot{s}^* \,\mathrm{d}\Omega = \sum^i R_i \dot{q}_i + 2D \tag{9.3}$$

where

$$R_i = \int_\Omega \sum^\rho \mathcal{R}_\rho \frac{\partial \xi_\rho}{\partial q_i} \,\mathrm{d}\Omega \qquad D = \int_\Omega \mathscr{D} \,\mathrm{d}\Omega. \tag{9.4}$$

The virtual dissipation is then

$$\int_\Omega T\delta s^* \,\mathrm{d}\Omega = \sum^i \left(R_i + \frac{\partial D}{\partial \dot{q}_i} \right) \delta q_i. \tag{9.5}$$

The virtual work of the inertia forces is approximated as

$$\sum^i I_i \delta q_i = \int_\Omega \frac{\mathrm{d}}{\mathrm{d}t}(\rho \dot{u}_j)\, \delta u_j \,\mathrm{d}\Omega = \sum^i \delta q_i \int \frac{\mathrm{d}}{\mathrm{d}t}(\rho \dot{u}_j) \frac{\partial u_j}{\partial q_i} \,\mathrm{d}\Omega. \tag{9.6}$$

Hence the generalized inertia is

$$I_i = \int_\Omega \frac{\mathrm{d}}{\mathrm{d}t}(\rho \dot{u}_j) \frac{\partial u_j}{\partial q_i} \,\mathrm{d}\Omega. \tag{9.7}$$

special care must be exercised in evaluating the variation $\delta \mathscr{P} = \delta_R \mathscr{P}$ since the variational principle assumes that the normal components of δM_i^k and δS_i are zero at the boundary of Ω a condition which is not obeyed by using expressions (9.1) in evaluating the variations. Hence δM_i^k and δS_i are now discontinuous at the boundary and the terms containing δM^k and δs are infinite and yield a finite contribution at this boundary. This contribution is easily evaluated by integrating by parts. We derive

$$\delta_R \mathscr{P} = \delta \mathscr{P} = \sum^i \frac{\partial \mathscr{P}}{\partial q_i} \delta q_i + \sum^i \int_A \delta q_i \sum^{ki} \left(\varphi_k \frac{\partial M_j^k}{\partial q_i} + \theta \frac{\partial S_j}{\partial q_i} \right) n_j \,\mathrm{d}A \tag{9.8}$$

where A is the boundary of the initial domain and n_j its unit outward normal.

Finally the virtual work of the surface tractions f_j per unit initial area is

$$\delta W = \int_A f_j \delta u_j \,\mathrm{d}A = \sum^i \delta q_i \int_A f_j \frac{\partial u_j}{\partial q_i} \,\mathrm{d}A. \tag{9.9}$$

Substitution of expressions (9.5), (9.6), (9.8) and (9.9) into the variational principle (5.11) with arbitrary variations δq_i yields the Lagrangian equations

$$I_i + R_i + \frac{\partial D}{\partial \dot{q}_i} + \frac{\partial \mathscr{P}}{\partial q_i} = Q_i \tag{9.10}$$

where

$$Q_i = \int_A \left(f_j \frac{\partial u_j}{\partial q_i} - \sum^{k} \varphi_k \frac{\partial M_j^k}{\partial q_i} n_j - \theta \frac{\partial S_j}{\partial q_i} n_j \right) \mathrm{d}A \tag{9.11}$$

is a mixed mechanical and thermodynamic driving force which represents the effect of the environment. Equations (9.10) are in the same form as derived from the general Lagrangian thermodynamics[3, 6, 8, 9].

When the effect of entropy produced, on the state variable, is not negligible we may introduce additional generalized coordinates q_i' and write

$$s^* = s^*(q_i', x_l, t). \tag{9.12}$$

The unknowns q_i' are now included in the Lagrangian equations (9.10). Additional equations for q_i' are then obtained by writing eqn (6.13)

$$Ts^* = \sum^{\rho} \mathscr{R}_\rho \dot{\xi}_\rho + 2\mathscr{D} \tag{9.13}$$

at suitably chosen points equal in number to the number of additional coordinates q_i'.

We may also express the generalized inertia force I_i approximately by means of the kinetic energy as follows. We integrate eqn (9.6) with respect to time assuming the variations to vanish at the limits of integration. We derive

$$\sum^{i} \int_t I_i \delta q_i \, \mathrm{d}t = -\int_t \mathrm{d}t \int_\Omega \rho \dot{u}_j \delta \dot{u}_j \, \mathrm{d}\Omega. \tag{9.14}$$

We denote by

$$\mathscr{T} = \frac{1}{2} \int_\Omega \rho \dot{u}_j \dot{u}_j \, \mathrm{d}\Omega \tag{9.15}$$

the approximate kinetic energy and by $\delta\mathscr{T}$ the variation of $\mathscr{T}$ due only to the variation of $\dot{u}_i$. Equation (9.14) may then be written

$$\sum^{i} \int_t I_i \delta q_i \, \mathrm{d}t = -\int_t \delta\mathscr{T} \, \mathrm{d}t = \int_t \left[\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial \mathscr{T}}{\partial \dot{q}_i}\right) - \frac{\partial \mathscr{T}}{\partial q_i} \right] \delta q_i \, \mathrm{d}t. \tag{9.16}$$

This relation being valid for arbitrary variation δq_i implies

$$I_i = \frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial \mathscr{T}}{\partial \dot{q}_i}\right) - \frac{\partial \mathscr{T}}{\partial q_i}. \tag{9.17}$$

The derivative $\partial\mathscr{T}/\partial q_i$ is evaluated by assuming ρ independent of q_i. With this value of I_i the Lagrangian equations (9.10) are written

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial \mathscr{P}}{\partial \dot{q}_i}\right) - \frac{\partial \mathscr{P}}{\partial q_i} + R_i + \frac{\partial D}{\partial \dot{q}_i} + \frac{\partial \mathscr{P}}{\partial q_i} = Q_i. \tag{9.18}$$

10. APPLICATION TO BIOLOGICAL SYSTEMS

Biological systems are open deformable systems exchanging matter work and energy with the environment, while chemical reactions coupled to thermomolecular diffusion occur internally. Such systems of considerable complexity are eminently suited to a simplified description by generalized coordinates whose evolution obeys the Lagrangian equations (9.18). In particular this Lagrangian formulation has been applied by the author to biological membranes with active transport[6]. Theories developed by Katchalsky[18] and others are shown to be considerably simplified by the Lagrangian formulation which in addition attains a high degree of generality. The example treated provides an excellent illustration of the power of the method by providing an easy evaluation of the coupling eoefficients between external flows through the membrane as influenced by coupled internal chemical reactions. The phenomenon is called active transport because some of the flows occur against the concentration gradient.

11. FINITE ELEMENT METHODS

The Lagrangian formulation provides the foundation of a large variety of finite element methods, choosing as generalized coordinates, values of the field variables at the vertices of a lattice dividing the continuum into finite elements. Equations (9.1) and (9.12) may then be considered as interpolation formulas giving the values of the field in the finite elements or in small groups of such elements. All kinds of interpolation formulas may be used, such as linear quadratic or others, leading to a large variety of techniques.

12. APPLICATION TO PLASTICITY AND ANALOGY WITH CHEMICAL REACTIONS

A natural extension of the technique of internal coordinates as introduced by the author[1–3] was applied to describe plastic properties[3]. It is of interest to point out that this may be achieved by including in the virtual dissipation terms of the type

$$T\delta s^* = \mathcal{R}_{ij}\delta q_{ij} \tag{12.1}$$

where δq_{ij} is the variation of an *internal plastic strain* due to dislocation motion and $\mathcal{R}_{ij}$ is a function of the local state and $\dot{q}_{ij}$. The variables q_{ij} are treated as internal generalized plastic coordinates. Comparing with expression (5.26) the analogy with chemical reactions is obvious and $\mathcal{R}_{ij}$ *is the tensor equivalent of the affinity* $\mathcal{R}_\rho$.

13. PHASE CHANGES AND CRYSTALIZATION UNDER STRESS

When the solid contains small crystal grains it may be approximated as a continuum. The state of an element of this continuum may then be defined by the external variables and by a large number of generalized internal variables which describe the microthermodynamic state of the element. These variables may correspond to crystal geometry, local strains and temperatures. There may also be present a number of different phases containing each a certain number of pure substances. The cell potential may then be expressed in terms of these external and internal variables, and the rate of dissipation in terms of these variables and their time derivatives. Application of the principle of virtual dissipation to this case yields field equations of the same type as (6.12) including the internal coordinates of the microthermodynamics. Creep may result due to crystals dissolving at some points and recrystalizing at others, because of disequilibrium in the microthermodynamics.

14. APPLICATION TO POROUS SOLIDS

The foregoing results are applicable to a large category of porous solids when the motion of the pore fluid relative to the solid may be treated thermodynamically as a diffusion. This problem has been discussed in more detail earlier[8].

15. HEREDITY AS A RESULT OF THE PRESENCE OF INTERNAL COORDINATES

The variational principle applied to a system with internal coordinates yields for the response of external coordinates a response which exhibits heredity. This approach was initiated for linear viscoelasticity in 1954[1] and extended to non linear viscoelasticity[3, 19]. Equations (4.24) for the response of a deformable cell govern a system where the *heredity* is the result of internal chemical reactions. With quasi reversible reactions (4.27) it behaves as a nonlinear viscoelastic solid[3].

16. SOLID UNDER INITIAL STRESS

A particular case of the present theory is that of a solid in thermodynamic and mechanical equilibrium under initial stress. Small departures from equilibrium are then considered, with small displacements and small perturbations of the thermodynamic variables, including thermomolecular diffusion and chemical reactions. The problem has been analyzed in detail[9] and constitutes a direct application of the linear thermodynamics developed already in 1954–55[1, 2]. A considerable simplification results in this case due to the fact that s_T, the entropy due to thermal convection, is a state variable replacing the cell entropy $\mathcal{S}$. It is also important in this case to use the definition (4.1) of the strain or definitions of the type (4.7). *Green's tensor* (4.2) *is not suitable* because it leads to spurious complications. The theory of initially stressed solids, for isothermal or adiabatic deformations without chemical reactions or molecular diffusion, was treated extensively in a monograph[13]. Note that the problem *is not treated as a bifurcation but as a small deviation from an equilibrium state.* The theory is therefore more general since no reference is required to an originally unstressed state which may not exist physically.

REFERENCES

1. M. A. Biot, Theory of stress–strain relations in anisotropic viscoelasticity and relaxation phenomena. *J. Appl. Phys.* **25**, 1385–1391 (1954).
2. M. A. Biot, Variational principles in irreversible thermodynamics with application to viscoelasticity. *Phys. Rev.* **97**, 1463–1469 (1955).
3. M. A. Biot, Variational Lagrangian irreversible thermodynamics of nonlinear thermorheology. *Q. Appl. Math.* **34**, 213–248 (1976).
4. M. A. Biot, New chemical thermodynamics of open systems, thermobaric potential a new concept. *Bull. Acad. R. de Belgique (Classes des Sciences)* **62**, 239–257 (1976).
5. M. A. Biot, New fundamental concepts and results in thermodynamics with chemical applications. *Chem. Phys.* **22**, 183–198 (1977).
6. M. A. Biot, Variational-Lagrangian thermodynamics of evolution of collective chemical systems. *Chem. Phys.* **29**, 97–115 (1978).
7. J. W. Gibbs, *Thermodynamics*, Vol. 1. Longmans, London (1906).
8. M. A. Biot, Variational-Lagrangian thermodynamics of nonisothermal finite strain mechanics of porous solids and thermomolecular diffusion. *Int. J. Solids Structures* **13**, 579–597 (1977).
9. M. A. Biot, Variational-Lagrangian irreversible thermodynamics of initially stressed solids with thermomolecular diffusion and chemical reactions. *J. Mech. Phys. Solids* **25**, 289–307 (1977); and Errata **26**, 29 (1978).
10. R. D. Mindlin, Equations of high frequency vibrations of thermopiezo-electric crystal plates. *Int. J. Solids. Structures* **10**, 625–637 (1974).
11. Th. De Donder, *L'Affinité.* Gauthier-Villars, Paris (1934).
12. I. Prigogine and R. Defay, *Chemical Thermodynamics.* Longmans, London (1965).
13. M. A. Biot. *Mechanics of Incremental Deformations.* Wiley, New York (1965).
14. M. A. Biot, Buckling and dynamics of multilayered and laminated plates under initial stress. *Int. J. Solids Structures.* **10**, 419–451 (1974).
15. L. Onsager, Reciprocal relations in irreversible processes-I. *Phys. Rev.* **37**, 405–426 (1931).
16. L. Onsager, Reciprocal relations in irreversible processes—II. *Phys. Rev.* **38**, 2265–2279 (1931).
17. J. Meixner. Zur thermodynamik der thermodiffusion. *Ann. der Physik* **39**, 333–356 (1941).
18. A. Katchalsky and R. Spangler. Dynamics of membrane processes, *Q. Rev. Biophys.*, 127–175 (1978).
19. R. A. Schapery, A Theory of Nonlinear Thermoviscoelasticity Based on Irreversible Thermodynamics. In *Proc. 5th U.S. Congress Appl. Mech.* 511–530 (1966).