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New Variational Irreversible Thermodynamics of Open Physical-Chemical Continua

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ABSTRACT

An outline is presented of a new thermodynamics of open chemical systems combined with a principle of virtual dissipation which provides a unified approach in a large domain of continuum physics, including deformable solids and fluid mixtures.

1. INTRODUCTION

A new thermodynamics of open irreversible systems has been developed over the last twenty years. There are two complementary aspects to this development represented on the one hand by a variational principle of virtual dissipation and on the other by an original treatment of open systems based on new concepts which eliminate the traditional difficulties associated with the classical approach of Gibbs, while avoiding the ponderous statistical treatment. The variational analysis is based on fundamental physical invariants and generalizes d'Alembert's principle to all dissipative systems. Thus unifying thermodynamics and classical mechanics. Application of this variational principle yields directly the differential equations which govern physical systems. This variational approach turns out to be an essential feature in many problems and not just a formal accessory of the analysis. This is in contrast to usual variational procedures which are derived from the differential equations themselves as a prerequisite. The emergence of this new thermodynamics is particularly timely in view of the current interest in the economics of energy production in large complex systems. Our purpose here is to present a short review of this new development in the context of continuum physics.

2. THERMOBARIC TRANSFER: A NEW CONCEPT

The basic concept in the new analysis of open systems is derived by considering a hypersystem constituted by a primary cell C_p supply cells C_{Sk} and a thermal well TW (Fig. 1). The open primary cell C_p contains a mixture of substances k. Each of the large rigid supply cells C_{Sk} contains a substance k, all at the same pressure and temperature p_0T_0 . The choice of the same pressure and temperature for the supply cells is dictated by the requirement to avoid Gibbs' paradox [1]. The thermal well TW is a large rigid reservoir at a constant temperature T_0 . A mass dM^k of a substance is extracted from C_{Sk} and injected into C_p by a reversible process. We



Fig. 1. Hypersystem, primary cell C_p, supply cells C_{Sk}, thermal well TW.

call this a thermobaric transfer [1, 10].

Consider the thermobaric transfer of a unit mass of substance k. The mass is extracted from the supply cell compressed and heated to the pressure P_k and temperature T when it is in equilibrium with the mixture in C_p through a semipermeable membrane. It is then injected reversibly and adiabatically into C_p . This process is accomplished entirely through external work on the hypersystem. No external heat or matter is provided to the hypersystem from the outside. The heating of the mass transferred is accomplished by reversible heat pumps, extracting heat from TW. The work accomplished in the thermobaric transfer of this unit mass is

$$\psi_{\mathbf{k}} = \int_{\mathbf{p}_0^{\mathsf{T}_0}}^{\mathbf{p}_{\mathbf{k}}^{\mathsf{T}}} \left(\frac{d\mathbf{p}'}{\mathbf{p}'} + \theta' d\overline{\mathbf{s}}_{\mathbf{k}} \right) .$$
(2.1)

It defines the thermobaric potential [1, 10]. The pressure p'_k the density p' and temperature T' vary continuously along the path of integration. The heat added at each step is $T'ds_k$ where ds_k is the increase of specific entropy. The term $\theta'ds_k$ where $\theta' = T' - T_0$ represents the work of the heat pump at every step.

By definition the equilibrium pressure p_k of the substance with the mixture in C through a semipermeable membrane is the *partial pressure* of the substance in the mixture.

3. COLLECTIVE DEFINITION OF THE ENERGY AND ENTROPY OF AN OPEN CELL

The state variables of C_p also determine the state of the supply cells C_{Sk} since the masses added to C_p are equal to the masses extracted from C_{Sk} . We denote U and S respectively the collective energy and entropy of the system $C_p + \sum_{k} C_{Sk}$. These quantities depend only on the state variables of C_p . Hence we may consider U and S as defining the energy and entropy of C_p as an open cell [1, 10]. An initial state for which U = S = 0 may be chosen arbitrarily since U and S are defined as incremental quantities.

With these definitions the increase of entropy of ${\rm C}_{\rm p}$ due to thermobaric transfer of a mass ${\rm dM}^{\rm k}$ of a substance is

$$dS = \overline{s}_k dM^k , \qquad (3.1)$$

where

$$\overline{\mathbf{s}}_{\mathbf{k}} = \int_{\mathbf{p}_0 \mathbf{T}_0}^{\mathbf{r}_{\mathbf{k}}} d\overline{\mathbf{s}}_{\mathbf{k}}$$
(3.2)

is called the relative specific entropy of the substance in the mixture [1].

4. CELL POTENTIAL

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From U and S as collective concepts we derive another collective concept

$$V = U - T_0 S \tag{4.1}$$

which we have called the cell potential [1]. With the collective definition of U and S it extends the concept of generalized free energy which I have shown to be the basic thermodynamic function of nonequilibrium thermodynamics in 1954-55 [6, 7]. An important property of the cell potential is derived by considering a reversible transformation of the hypersystem obtained entirely through external work on the system, no masses or heat being exchanged with the environment. Since the transformation is reversible there is no change of total entropy of the hypersystem, hence

$$S + \frac{n_0}{T_0} = 0 , \qquad (4.2)$$

where H_0 is the heat energy acquired by the thermal well. Elimination of S between (4.1) and (4.2) yields

$$V = U + H_0$$
 (4.3)

Hence for a reversible transformation V represents the energy of the hypersystem [1].

5. DEFORMABLE OPEN CELL

When a chemical reaction occurs in the cell the masses "produced" by the reaction ξ are given by

$$dm_k = v_k d\xi , \qquad (5.1)$$

where the condition $\Sigma v_k = 0$ is imposed by mass conservation. The state of the cell is determined by the six strain components $\varepsilon_{\mu\nu}$, the masses M^k added by convection into C_p , the temperature T and the reaction coordinate ξ . Any differential change of state is the sum of the change due to the chemical reaction d ξ and the change due to other variables. For a chemical reaction occurring in a rigid closed adiabatic cell we may write

$$du_{\rm ch} = 0$$
, $dv = -T_0 dS_{\rm ch}$, (5.2)

where

$$S_{\rm ch} = \frac{A}{T} d\xi \tag{5.3}$$

is the entropy produced by the reaction. The quantity A is the affinity as defined by De Donder [2]. If several reactions ξ_{ρ} may occur, A denotes the affinity of each reaction.

For a general change of state the increase of cell potential is the sum of increases due to each variable

$$dN = \tau_{\mu\nu} d\varepsilon_{\mu\nu} + \sum_{k}^{k} \psi_{k} dM^{k} + \theta ds_{T} - \frac{T_{0}}{T} \sum_{\rho}^{\rho} A_{\rho} d\xi_{\rho} . \qquad (5.4)$$

The first three groups of terms in accordance with (4.3) represent the reversible work accomplished on the hypersystem. The first group $\tau_{\mu\nu} d\epsilon_{\mu\nu}$ is the work accomplished by stresses applied to the cell. It represents a summation for all possible values of the indices, where $\epsilon_{\mu\nu}$ are six parameters defining the deformation and $\tau_{\mu\nu}$ corresponding forces defined by virtual work. They are not necessarily tensors. The second group $\Sigma \psi_k dM^k$ is the reversible work accomplished by thermobaric transfer of masses dM^k into C_p . The term θds_T with $\theta = T - T_0$ is the work of the heat pump required to inject reversibly into C_p an amount of heat Tds_T. Taking into account equations (3.1) and (5.3) the increase of entropy of C_p is

$$dS = \frac{A}{T} d\xi + \sum_{k=1}^{k} \overline{s}_{k} dM^{k} + ds_{T} .$$
(5.5)

Note that ds_T is not a state variable. Elimination of ds_T between (5.4) and (5.5) yields

$$dV = \tau_{\mu\nu} d\epsilon_{\mu\nu} + \sum_{k=0}^{k} dM^{k} + \theta dS - \sum_{\rho=0}^{\rho} A_{\rho} d\xi_{\rho} , \qquad (5.6)$$

where

$$\phi_{\mathbf{k}} = \psi_{\mathbf{k}} - \theta_{\mathbf{s}} \tag{5.7}$$

defines a new concept, the convection potential: which replaces the chemical potential. Note that in contrast to traditional concepts $\phi_k \psi_k$ and s_k do not contain any undetermined constants.

In (5.6) all differentials are now state variables. Integrating along any arbitrary path we obtain

$$V = V(\varepsilon_{\mu\nu}, M^k, S, \xi_{\rho})$$
(5.8)

with the property

$$\frac{\partial V}{\partial \varepsilon_{\mu\nu}} = \tau_{\mu\nu} \frac{\partial V}{\partial M} = \phi_k \quad \frac{\partial V}{\partial S} = \theta \quad \frac{\partial V}{\partial \xi_{\rho}} = -A_{\rho} \quad .$$
(5.9)

6. NEW EXPRESSIONS FOR THE AFFINITY AND HEAT OF REACTION

The thermobaric transfer procedure provides immediately a new expression for the affinity. We consider two rigid cells C_p and C_{eq} where a reaction of coordinate ξ may occur. In C_{eq} the reaction is in equilibrium at the temperature T_{eq} and partial pressures p_{keq} . The reaction d ξ takes place in C_p and a reversed reaction $-d\xi$ takes place in C_{eq} . The masses $dm_k = v_k d\xi$ produced in C_p are extracted from C_p and injected into C_{eq} by thermobaric transfer. At the same time the temperatures of C_p and C_{eq} are maintained constant by injecting respectively into C_p and C_{eq} amounts of heat equal to $\overline{h_{pT}}d\xi$ and $-\overline{h_{pT}}^{eq}d\xi$ using heat pumps. Hence the composition and temperature of C_p and C_{eq} do not change in this process. Since the reaction in C_{eq} is in equilibrium it does not produce any entropy. However the reaction C_p produces the entropy $(A/T)d\xi$.

This must be equal to the entropy increase of the thermal well [1] as expressed by the relation

$$\frac{A}{T} = \sum_{k=1}^{k} v_{k} \int_{p_{keq}}^{p_{k}T} d\bar{s}_{k} - \frac{\bar{h}}{T} pT + \frac{\bar{h}}{T} pT + \frac{\bar{h}}{T} pT + \frac{\bar{h}}{T} pT$$
(6.1)

Similarly there is no change of collective energy of the system. This yields the relation [1].

$$\overline{h}_{pT} - \overline{h}_{pT}^{eq} = \sum_{k}^{k} v_{k} \int_{p_{keq}^{T}eq}^{p_{k}T} d\overline{\varepsilon}_{k} , \qquad (6.2)$$

where

$$d\overline{\varepsilon}_{k} = \frac{dp'}{\rho' k} + T' d\overline{s}_{k}$$
(6.3)

is the differential of the specific enthalpy of each substance.

The intrinsic heat of reaction \overline{h}_{pT} is a new concept [1]. It is the heat absorbed per unit change of the reaction coordinate ξ while the state of the system remains unchanged by removing the reaction products (positive or negative) and maintaining the temperature constant. It is more representative of the true chemical energy than the traditional heat of reaction which includes the heat of mixing. Equation (6.2) yields \overline{h}_{pT} which introduced in (6.1) provides the value of the affinity A.

In differential form equation (6.2) is

$$d\bar{h}_{pT} = \sum v_k d\bar{\epsilon}_{T}$$
(6.4)

which generalizes rigorously the classical Kirchhoff relation for the heat of reaction.

7. NEW DEFINITION OF THE CHEMICAL POTENTIAL

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We assume that in integral form we may write (6.4) as

$$\overline{h}_{pT} = \sum_{k}^{k} v_{k} \int_{0}^{p_{k}T} d\overline{\varepsilon}_{k} + \sum_{k}^{k} v_{k} \overline{\varepsilon}_{k}^{(0)} , \qquad (7.1)$$

where the lower limit is extrapolated to the absolute zero, with a constant of integration $k = \sum v_k \overline{\epsilon}_k(0)$ such that $\overline{\epsilon}_k(0)$ is characteristic of the pure substance and independent of the reaction involved. Moreover we assume the validity of the relation

$$\frac{\overline{h}^{eq}}{T_{eq}} = \sum_{k}^{k} v_{k} \int_{0}^{p_{k}T} d\overline{s}_{k}$$
(7.2)

whose justification is related to Nernst's principle. Substitution of expressions (7.1) and (7.2) into (6.1) yields

$$A = -\sum_{k=1}^{\infty} v_{k}^{\mu} k$$
(7.3)

with

$$\mu_{k} = \overline{\epsilon}_{k}^{abs} - T\overline{s}_{k}^{abs} ,$$

$$\epsilon_{k}^{abs} = \int_{0}^{p_{k}T} d\overline{\epsilon}_{k} + \overline{\epsilon}_{k}(0) , \quad \overline{s}_{k}^{abs} = \int_{0}^{p_{k}T} d\overline{s}_{k} .$$
(7.4)

Equation (7.3) provides a new definition of the chemical potential μ_k [3, 14]. Use of the chemical potential is of course not necessary if we know the reference equilibrium state of equations (6.1) and (6.2), which are rigorous consequences of the first and second principle in classical form.

8. COLLECTIVE POTENTIAL

Consider a continuous system composed of elementary primary cells of volume $d\Omega$ in the initial state of coordinates x_1 . The collective potential of the continuum is

$$V = \int_{\Omega} V d \Omega , \qquad (8.1)$$

where V is the cell potential in the final state per unit initial volume. Similarly

$$U = \int_{\Omega} U d\Omega , \quad S = \int_{\Omega} S d\Omega , \qquad (8.2)$$

where U and S are collective values per unit initial volume. Hence according to (4.1)

$$V = U - T_0 S$$
 (8.3)

If the continuum is in a body force field of potential $G(\overline{x}_i)$ per unit mass at the point \overline{x}_i , its total potential in the field is

$$G = \int_{\Omega} m G(\overline{x}_{i}) d\Omega$$
(8.4)

with

m

$$= m_0 + \sum_{k=1}^{k} M^k$$
, (8.5)

where m_0 is the initial mass per unit initial volume, and M^k is the mass of each substance injected into the element also per unit initial volume. The element initially at point x_1 is displaced to the point

$$\overline{\mathbf{x}}_{\mathbf{i}} = \mathbf{x}_{\mathbf{i}} + \mathbf{u}_{\mathbf{i}}$$
 (8.6)

The mixed collective potential as introduced earlier [1, 4, 5] is defined as

$$P = V + G ag{8.7}$$

It constitutes an extension of the generalized free energy which, as shown originally in 1954-55 [6, 7], provided the basic potential in a new and systematic treatment of nonequilibrium thermodynamics. The concept has been applied repeatedly in many problems including those of dissipative piezoelectric crystals [8, 9].

9. PRINCIPLE OF VIRTUAL DISSIPATION

Extension of d'Alembert's principle of classical mechanics leads to a new variational principle [5] applicable to irreversible thermodynamic systems called the *principle of virtual dissipation*. It is expressed for continuous systems in the form [5]

$$\sum_{i=1}^{I} \delta q_{i} + \delta_{R} P + \int_{\Omega} T \delta s^{*} d\Omega = \delta W .$$
(9.1)

The arbitrary variations to be applied are specified as follows.

The term δW is the virtual work of external forces applied to the continuum in addition to

those due to the potential field G, while $\sum_{i} \delta q_{i}$ represents the virtual work of the inertia forces according to d'Alembert's definition. The variable s* denotes the entropy produced per unit initial volume, and T is the temperature of the displaced element. The entropy S per unit initial volume is

$$S = s + s^{*}$$
, (9.2)

where s is the entropy acquired by convection and conduction. We remember that this entropy is defined as a "collective" concept. The symbol δ_R indicates a restricted variation which assumes that in varying S in P we put $\delta s^* = 0$ hence $\delta S = \delta s$. The integrand is the local virtual dissipation as explained below.

Independent variables to be varied arbitrarily are the solid displacement u_i the entropy displacement S_i the mass displacements M_i^k of each substance and the reaction coordinates ξ_ρ . The rate of mass flow is \dot{M}_i^k (dot = time derivative) at the displaced point across a material surface initially of unit area and initially perpendicular to x_i . The rate of entropy flow is similarly defined. It is equal to [10]

$$\dot{s}_{i} = \sum_{k}^{k} \frac{\dot{s}_{k}}{s_{k}} \dot{M}_{i}^{k} + \dot{H}_{i}^{T} ,$$
 (9.3)

where \dot{H}_{i} is the rate of heat flow across the same material area and $\Sigma \underset{k}{s} \dot{M}_{i}^{k}$ is the convective entropy flux. The variables satisfy the holonomic conservation constraints

$$M^{k} = -\frac{\partial M_{i}^{k}}{\partial x_{i}}, \qquad s = -\frac{\partial S_{i}}{\partial x_{i}}$$
(9.4)

(summation sign omitted). The six strain components $\varepsilon_{uv}(a_{ij})$ are expressed as functions of

$$a_{ij} = \frac{\partial u_i}{\partial x_j} .$$
 (9.5)

The strain components may be defined in a very general way either as Green's tensor, or as a cartesian tensor relative to rotating cartesian coordinates or in nontensorial fashion as explained in more detail elsewhere [4, 10].

When applying the variational principle to the domain Ω the variations $\delta u_{i} \delta M_{i}^{k} \delta S_{i} \delta \xi_{\rho}$ are arbitrary except for one restriction, namely that the normal components of δM_{i}^{k} and δS_{i} vanish at the boundary of Ω . Note that only the variations vanish and not the values of M_{i}^{k} and S_{i} themselves.

The virtual dissipation is derived from the rate of dissipation expressed as

$$T\dot{s}^{*} = \sum_{\rho}^{P} R_{\rho} \dot{\xi}_{\rho} + 2D_{T} , \qquad (9.6)$$

where

$$\mathcal{D}_{T} = \frac{1}{2} \sum_{ij}^{k} C_{ij}^{kk} \dot{M}_{i}^{k} \dot{M}_{j}^{k} + \sum_{ij}^{k} C_{ij}^{k} \dot{M}_{i}^{k} \dot{S}_{j} + \frac{1}{2} T \lambda_{ij} \dot{S}_{i} \dot{S}_{j}$$
(9.7)

is a quadratic form in \dot{M}_{i}^{k} and \dot{S}_{i} with coefficients dependent on the local state variables $\varepsilon_{\mu\nu}$, M^{k} , S and ξ_{ρ} , while λ_{ij} represents the local thermal resistivity. The quadratic form implies the local validity of Onsager's principle [11, 12]. It generalizes Meixner's result [13] which is restricted to thermal conduction. The coefficient c_{ij}^{k} represent a coupling which includes entropy convection. The second principle of thermodynamics implies

$$\mathcal{D}_{\mathrm{T}} > 0 \quad . \tag{9.8}$$

The coefficient $R_{\rho}(\epsilon_{\mu\nu}M^{k}S\dot{\xi}_{\rho})$ embodies the chemical kinetics. It is obtained by writing the rate of reaction as

$$\dot{\xi}_{\rho} = f_{\rho}(\varepsilon_{\mu\nu}, M^{k}, S, \xi_{\rho})$$
(9.9)

and the affinity

$$A_{\rho} = A_{\rho}(\epsilon_{\mu\nu}, M^{K}, S, \xi_{\rho}) .$$
(9.10)

Elimination of ξ_0 between these two relations yields

$$A_{\rho} = R_{\rho}(\epsilon_{\mu\nu}, M^{k}, S, \dot{\xi}_{\rho}) . \qquad (9.11)$$

The virtual dissipation is obtained from (9.6) as

$$T\delta s^{*} = \sum_{i}^{\rho} R_{\rho} \delta \xi_{\rho} + \sum_{i}^{k} \frac{\partial \mathcal{D}_{T}}{\partial \dot{M}_{i}^{k}} \delta M_{i}^{k} + \frac{\partial \mathcal{D}_{T}}{\partial \dot{S}_{i}} \delta S_{i} . \qquad (9.12)$$

As a consequence of the second principle the function R_{a} has the properties

$$R_{\rho} = 0 \quad \text{for } \dot{\xi}_{\rho} = 0 \tag{9.13}$$

$$\sum_{\rho}^{\rho} R_{\rho} \dot{\xi}_{\rho} > 0 .$$

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10. FIELD DIFFERENTIAL EQUATIONS FOR A DEFORMABLE PHYSICAL-CHEMICAL SOLID WITH BODY FORCES

The variational principle (9.1) is applied to a deformable solid with chemical reactions and thermomolecular diffusion putting $\delta W = 0$. For simplicity we shall not include the inertia forces. A more complete analysis is presented elsewhere [10, 14]. The variations under the integral sign are evaluated using the holonomic constraints (9.4) and (9.5). We then integrate by parts and put equal to zero the coefficients of the arbitrary variations $\delta u_i \delta M_i^k \delta S_i$ and

 $\delta\xi_{0}$. Using the values (5.9) for the partial derivatives of V we obtain

$$\frac{\partial}{\partial \mathbf{x}_{j}} \left(\tau_{\mu\nu} \frac{\partial \varepsilon_{\mu\nu}}{\partial \mathbf{a}_{\mathbf{i}\mathbf{j}}} \right) - \mathbf{m} \frac{\partial G}{\partial \mathbf{x}_{\mathbf{i}}} = 0 , \quad \frac{\partial \phi_{\mathbf{k}}}{\partial \mathbf{x}_{\mathbf{i}}} + \frac{\partial \mathcal{D}_{\mathbf{T}}}{\partial \mathbf{M}_{\mathbf{i}}^{\mathbf{k}}} = 0 ,$$
$$- A_{\rho} + R_{\rho} = 0 , \quad \frac{\partial \theta}{\partial \mathbf{x}_{\mathbf{i}}} + \frac{\partial \mathcal{D}_{\mathbf{T}}}{\partial \mathbf{S}_{\mathbf{i}}} = 0 .$$
(10.1)

We have put

$$\varphi_{\mathbf{k}} = \varphi_{\mathbf{k}} + G \tag{10.2}$$

which has been called *mixed convective potential* [3, 10]. The unknown field variables governed by equations (10.1) are $u_i \stackrel{M^k}{i} S_i \xi_{\rho}$ and s*. A complete set of equations is obtained by adding equation (9.6). Attention is called to the remarkable simplicity symmetry and generality of the field equations (10.1) in spite of the physical complexity of the system.

11. LAGRANGIAN EQUATIONS

We may represent the variables as

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$$u_{j} = u_{j}(q_{i}, x_{\ell}, t) , \quad M_{j}^{k} = M_{j}^{k}(q_{i}, x_{\ell}, t) ,$$

$$S_{j} = S_{j}(q_{i}, x_{\ell}, t) , \quad \xi_{\rho} = \xi_{\rho}(q_{i}, x_{\ell}, t) , \qquad (11.1)$$

$$s^{*} = s^{*}(q_{i}^{*}, x_{\ell}, t) ,$$

where q_1 and q'_1 are unknown generalized coordinates. By varying q_1 , and again neglecting the inertia forces for simplicity, the principle of virtual dissipation (9.1) yields directly the Lagrangian equations

$$\frac{\partial P}{\partial q_{i}} + R_{i} + \frac{\partial D}{\partial \dot{q}_{i}} = Q_{i} , \qquad (11.2)$$

where

$$\mathbf{R}_{\mathbf{i}} = \int_{\Omega} \sum_{\boldsymbol{\alpha}} R_{\boldsymbol{\rho}} \frac{\partial \boldsymbol{\varsigma}_{\boldsymbol{\rho}}}{\partial \mathbf{q}_{\mathbf{i}}} d\Omega , \qquad \mathbf{D} = \int_{\Omega} \mathcal{D}_{\mathbf{T}} d\Omega , \qquad (11.3)$$

$$Q_{i} = \int_{A} \left(f_{j} \frac{\partial u_{i}}{\partial q_{i}} - \sum_{k}^{k} \varphi_{k} \frac{\partial M_{j}^{k}}{\partial q_{i}} n_{j} - \theta_{k} \frac{\partial S_{k}}{\partial q_{i}} n_{j} \right) dA . \qquad (11.4)$$

The mixed mechanical thermodynamic driving forces Q_i represent the effect of the environment. The vector f_i is the force per unit initial area at the boundary A of Ω and n_j is the unit normal at the boundary.

Note that δM_{i}^{k} and δS_{i} due to δq_{i} do not satisfy the condition that the normal components vanish at the boundary. As shown elsewhere [14, 15] taking this into account yields the terms containing M_{j}^{k} and S_{j} in expression (11.4) of Q_{i} . They represent the effect of the environment at the boundary of the open diabatic medium. Equations (11.2) are the same in number as the variables q_{i} . Additional equations for q'_{i} are obtained by writing relation (9.6) at a sufficient number of points in the domain Ω .

The Lagrangian equations (11.2) provide the foundation of a large variety of *finite element* methods or local interpolation methods by using as generalized coordinates values of the field as discrete points with expressions (11.1) used as interpolation formulas.

12. EVOLUTION OF A DEFORMABLE OPEN CELL: VISCOELASTICITY, PLASTICITY AND HEREDITY

The case of a single open cell undergoing an homogeneous deformation with matter and heat injection in the presence of chemical reactions is expressed by combining equations (5.9) and (9.11). The result may be written in Lagrangian form as

$$\frac{\partial V}{\partial q_1} = Q_1, \quad \frac{\partial V}{\partial \xi_0} + R_\rho = 0, \quad (12.1)$$

where q_i denotes the variables $\epsilon_{\mu\nu} \stackrel{k}{}^{k}$ and S and Q_i the corresponding force variables $\tau_{\mu\nu} \phi_k \theta$. If the cell remains sufficiently close to an equilibrium we may write

$$T\dot{s}^* = \sum_{i}^{\rho} R_{\rho} \dot{\xi}_{\rho} = \sum_{i}^{\sigma\rho} B_{\sigma\rho} \dot{\xi}_{\sigma} \dot{\xi}_{\rho} = 2D_{ch} , \qquad (12.2)$$

where $B_{\sigma\sigma}$ are functions of q_i . In this case equations (12.1) become

$$\frac{\partial V}{\partial q_{i}} = Q_{i}, \quad \frac{\partial V}{\partial \xi_{\rho}} + \frac{\partial D}{\partial \xi_{\rho}} \stackrel{ch}{=} \mathcal{O}, \qquad (12.3)$$

These equations are analogous to those obtained earlier for nonlinear viscoelasticity [5, 16] where ξ_o play the role of internal coordinates which embody heredity properties.

The viscoelastic heredity may be due to a large category of internal variables and a completely general theory has been developed along this line for the nonlinear case [5]. They generalize earlier results obtained in 1954-55 for linear viscoelasticity [6, 7]. The latter are expressed as

$$r_{ij} = z^{\mu\nu}_{ij} \epsilon_{\mu\nu}, \qquad z^{\mu\nu}_{ij} = \sum_{j}^{s} \frac{D_{ij}^{s\mu\nu}}{p + r_{s}} + \frac{D^{\mu\nu}_{ij}}{p + r_{s}} + \frac{D^{\mu\nu}_{ij}}{p + r_{s}} + \frac{D^{\mu\nu}_{ij}}{p + r_{s}}, \qquad (12.4)$$

where τ and ε are stress and strain components $p = \frac{d}{dt}$ (the time derivative) or $p = i\omega$ ($\omega = circular$ frequency), $r_{c} > 0$ and the coefficients are nonnegative matrices.

Plasticity properties may be expressed in a similar way [5] by introducing internal dislocation motion q_{11}^S as internal coordinates with

$$T_{s}^{*} = \sum_{ij}^{s} R_{ij}^{s} q_{ij}^{is}$$
(12.5)

representing the rate of dissipation. The indices correspond to various locations and orientations. The principle of virtual dissipation yields the additional equations

$$\frac{\partial V}{\partial q_{ij}^s} + R_{ij}^s = 0$$
(12.6)

for the internal plastic variables. We note that R_{ij}^s is the tensor equivalent of the affinity R_{0} .

As pointed out [14] coupled diffusion and crystalization leading to creep deformation, may be treated similarly by using internal coordinates to represent the microthermodynamics of the deformable solid.

13. VISCOUS FLUID MIXTURES WITH THERMOMOLECULAR DIFFUSION

The principle of virtual dissipation has been applied to viscous compressible heat conducting fluids for the case of a material description [5] and a Eulerian description [17]. The analysis has recently been extended to mixtures with viscosity and thermomolecular diffusion [15]. In this case the rate of dissipation is

$$T\dot{s}^* = 2D_{_{\rm T}} + 2D_{_{\rm T}}$$
, (13.1)

where

$$\mathcal{D}_{v} = \frac{1}{2} \sum_{k}^{\ell k} \lambda^{\ell k} r^{\ell} r^{k} + \frac{1}{2} \sum_{k}^{\ell k} \lambda^{\ell k} v^{\ell}_{\mathbf{i}\mathbf{j}} v^{k}_{\mathbf{i}\mathbf{j}} + \frac{1}{2} \sum_{k}^{\ell k} \lambda^{\ell k} v^{\ell}_{\mathbf{i}\mathbf{j}} v^{k}_{\mathbf{j}\mathbf{i}}$$
(13.2)

is the dissipation function due to the viscosity. In this expression

$$\mathbf{v}_{ij} = \frac{\partial \mathbf{v}_{i}^{k}}{\partial \mathbf{x}_{i}}, \quad \mathbf{r}^{k} = \delta_{ij} \quad \mathbf{v}_{ij}^{k}, \qquad \mathbf{v}_{i}^{k} = \dot{\mathbf{M}}^{k} / \mathbf{m}_{k} \quad .$$
(13.3)

The local mass of each substance per unit volume is $\mathtt{m}_k^{}$ and \mathtt{v}_i^k is its velocity.

The dissipation function due to thermomolecular diffusion is

$$\mathcal{D}_{T} = \frac{1}{2} \sum_{i}^{k} C^{kk} \dot{M}_{i}^{k} \dot{M}_{i}^{k} + \sum_{i}^{k} C^{k} \dot{M}_{i}^{k} \dot{s}_{i} + \frac{T}{2k} \dot{s}_{i} \dot{s}_{i} , \qquad (13.4)$$

where k is the thermal conductivity of the mixture.

The coefficients in \mathcal{D}_{V} and \mathcal{D}_{T} are functions of the local state, and it has been shown how those of \mathcal{D}_{T} must be chosen in order to satisfy invariance under translation [15].

Application of the principle of virtual dissipation including the inertia forces yields the field equations $a_k^k = a_k^k + a_k^k$

$$a_{i}^{k} - \frac{1}{m_{k}} \frac{\partial \sigma_{ij}}{\partial x_{j}} + \frac{\partial \phi_{k}}{\partial x_{i}} + \frac{\partial \nu_{T}}{\partial \dot{M}_{i}^{k}} = 0 ,$$

$$\frac{\partial \theta}{\partial x_{i}} + \frac{\partial p}{\partial S_{i}} = 0$$
(13.5)

to which we must add equation (13.1). The unknowns are $M_1^k S_1$ and s*. The acceleration of each substance is a_1^k expressed in terms of the velocity field v_1^k . The body force such as gravity is included in φ_k . The viscous stresses are defined as

$$\sigma_{ij}^{k} = \frac{\partial \mathcal{D}_{v}}{\partial v_{ij}^{k}}$$
(13.6)

purely in terms of the dissipation while the partial pressures represented in ϕ_k are defined thermodynamically.

Again the simplicity and symmetry of the field equations stands in contrast to the complexity of the system. The corresponding Lagrangian equations have also been derived directly from the variational principle [15].

14. GENERAL APPLICABILITY

The variational-Lagrangian procedure here described is applicable to a large category of problems. A few of these are mentioned here.

Linear Thermodynamics

The method was originally developed in the linear context in 1954-55 [6, 7]. The Lagrangian equations in this case are

$$\frac{\mathrm{d}}{\mathrm{dt}} \left(\frac{\partial T}{\partial \dot{\mathbf{q}}_{i}}\right) + \frac{\partial D}{\partial \dot{\mathbf{q}}_{i}} + \frac{\partial P}{\partial q_{i}} = Q_{i} , \qquad (14.1)$$

where T (the kinetic energy) and D are quadratic forms in q'_i while P is a quadratic form in q_i .

The coefficient of these forms are constants. The theory has been applied to solids under initial stress [4] and extended more recently to include thermomolecular diffusion and chemical reactions [18].

Piezoelectric Crystals

Applications to piezoelectric crystals [8, 9] make use of the potential (4.1) by including the electric terms.

Porous Solids

An extremely general theory of porous solids, linear [19] and nonlinear [10, 20] has been developed on the basis of nonequilibrium thermodynamics.

Geothermal Systems and Aquifers

The porous solid theory leads to a variational analysis of porous geothermal systems [21] including two-phase liquid vapor transition as well as nonequilibrium adsorption. The treatment of aquifers constitutes a particular case. New Heat Transfer

A new approach to heat transfer based on the equation

$$\frac{\partial \mathbf{V}}{\partial \mathbf{q}_{\mathbf{i}}} + \frac{\partial \mathbf{D}}{\partial \dot{\mathbf{q}}_{\mathbf{i}}} = \mathbf{Q}_{\mathbf{i}}$$
(14.2)

was presented in a monograph [22]. Equation (14.2) was shown to be a consequence of the principle of virtual dissipation [5]. It avoids the use of heat transfer coefficients by direct systems analysis. Its superior accuracy has been well illustrated [22-30] and its invariant property has been used to derive a self-similar formulation of heat conduction [31].

Rock Mechanics, Geophysical and Geological Applications

The thermodynamics of porous solids leads to a new rock mechanics. In addition the Lagrangian approach to viscous solids provides a unified foundation in the theory of salt dome formation and geological folding. In particular it was shown that dissipative folding of layered structures result from instabilities around steady state solutions of the nonlinear Lagrangian equation [5]

$$\frac{\partial \mathbf{D}}{\partial \dot{\mathbf{q}}_{\star}} = \mathbf{0} \tag{14.3}$$

which expresses minimum dissipation.

Unified Thermodynamics of Stability

The Lagrangian equations (14.1) of linear thermodynamics provide a completely general approach to the stability theory of elastic thermoelastic and viscoelastic continua in equilibrium un-der initial stress [4, 32, 33]. This type of instability is non-oscillatory and is not a bifurcation. It must be distinguished from bifurcation instability in the vicinity of a stationary flow as mentioned above in connection with the nonlinear equation (14.3) and exemplified by folding of stratified viscous solids in compression [5] along the layers.

Biological Applications

The variational treatment of deformable solids with simultaneous diffusion and chemical reactions [3, 14] provides a powerful tool in the analysis of coupled biomechanical systems. Of particular interest is a new systematic approach to active transport in biological membranes simplifying and generalizing existing treatments [34]. The case of active transport is a good illustration of the fact that the variational approach is essential and not just a formal accessory of the analysis.

Because of the scope and wide generality of the subject the foregoing account is necessarily incomplete. It is restricted to essential concepts and highlights along with some typical results without the required elaboration for full understanding. The latter may not be acquired without a detailed acquaintance with the relevant publications.

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