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GENERALIZED LAGRANGIAN EQUATIONS OF NONLINEAR REACTION-DIFFUSION

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The principle of virtual dissipation for irreversible processes in open systems is given a new formulation where variations are unconstrained everywhere including the boundary. As a complementary development a new chemical thermodynamics of open systems initiated earlier is given a simplified derivation and new results are presented. A new evaluation of entropy production for fully nonlinear reaction-diffusion along with the variational principle provide field and lagrangian equations of evolution far from local equilibrium with inertia and gravity forces. The earlier inconvenient use of the entropy produced as an auxiliary state variable is eliminated. It is shown that the description by lagrangian equations is complete and rigorous and constitutes a universal formalism derived from first principles. It does not require prior knowledge of continuum field equations and leads directly to a large variety of finite element methods. Applications to internal relaxation with quantum kinetics are also indicated.

1. Introduction

Lagrangian equations of thermodynamic evolution were developed originally in the linear context [1, 2] with applications to viscoelasticity with heredity and internal coordinates. Extension to nonlinear phenomena was obtained later. In the context of chemistry this work embodies two distinct phases, which in addition to the lagrangian formulation itself provide a novel approach to the chemical thermodynamics of open chemical systems [3, 4].

Our purpose here is to present further generalizations and clarification of this dual development. In sections 2–5, the results of the new chemical thermodynamics are recalled. Their derivation is simplified and new methods are presented for the determination of thermodynamic functions, based on the concepts of "injection pressure" and "intrinsic heat of reaction".

This new thermodynamics is based on a novel choice of cell and reservoir model which involves a "chemical supply cell". The undetermined constants of the standard approach are eliminated without recourse to quantum cryogenic properties. A new form of the Gibbs-Duhem theorem which embodies these advantages is thereby obtained. The basic features of chemical thermodynamics are established by remarkably short procedures derived from an operational thought process called "thermobaric transfer" in contrast with standard formalism. Physical clarity is also thereby considerably improved. One of the key concepts is the "intrinsic" heat of reaction which is more representative of the true chemical energy than that derived from usual definitions.

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A generalization of the principle of virtual dissipation is developed in section 6 which avoids the constraints imposed upon the variations in earlier formulations [4, 7]. Section 7 shows how this leads to a general fundamental relation of entropy balance of biological systems which may be interpreted in terms of "equivalent" mechanical work.

Section 8 presents a novel evaluation of entropy production valid for fully nonlinear thermomolecular diffusion and reactions while sections 9 and 10 introduce new state variables which avoid the use of the entropy produced which was required in previous formulations in order to completely describe the system. Field and lagrangian equations are derived in sections 11 and 12 directly from the generalized variational principle for nonlinear evolution, far from local equilibrium, of reaction-diffusion systems including inertia and gravity forces.

The last two sections draw attention to the completeness and generality of the lagrangian equations as a universal mathematical framework unifying classical mechanics and thermodynamics. The completeness of the physical description by a finite number of cells of size above a resolution threshold may be extended to internal coordinates with relaxation effects and heredity by considering fictitious cells in the thermodynamic configuration space.

The methods stands in contrast to standard variational procedures which require prior knowledge of the boundary conditions and field differential equations of the continuum for each particular case. Application of the principle of virtual dissipation avoids this requirement. Field and lagrangian equations are derived directly from first principles. In particular the lagrangian equations yield also directly a large variety of finite element methods, with fluence vectors at the grid vertices as generalized coordinates, without the use of any field equations of the continuum.

2. Thermobaric transfer as a fundamental concept in the thermodynamics of open systems

A hypersystem is constituted by a set of primary cells, supply cells, and a thermal well. The set of primary cells $\sum C_P$ is called the primary system. The thermal well TW is a large rigid isothermal reservoir at a given temperature T_0 . The supply cells are of two types. The first are rigids cells C_{Sk} each containing a pure substance k at the pressure p_0 and the temperature T_0 the same for all supply cells of this type. They are assumed large enough so that a change of mass content affects the pressure and temperature in a negligible way. If a chemical reaction takes place between the various substances k, we adjoin to the supply cells a chemical supply cell C_{ch} . This is a rigid cell containing the reactants at a temperature and concentrations such that the reaction is in equilibrium. We may add as many chemical supply cells as the number of possible reactions. The particular choice of a unique pressure and temperature for the cells C_{Sk} is needed to avoid Gibbs' paradox [3].

Thermobaric transfer is defined as a *reversible* process by which masses are transferred from the supply cells into the primary cells while heat is added to various elements in a suitable way. We distinguish two kinds of thermobaric transfers. In the first kind the thermal well does not enter into play. In the second kind reversible heat pumps are used to inject heat mechanically by extraction from the thermal well.

The thermobaric transfer of the first kind is described as follows. Consider a single primary cell $C_{\rm P}$ whose walls are maintained rigid during the process. We extract adiabatically from a supply cell a small mass dM^k of substance at the pressure p_0 and temperature T_0 . By mechanical work on the mass dM^k and injection of heat into it, in a gradual reversible continuous process, we bring the mass to a temperature Tand a pressure p_k such that it is in equilibrium with the primary cell C_P through a semipermeable membrane. The mass dM^k is then injected reversibly and adiabatically into $C_{\rm P}$. We call p_k the *injection pressure*. In addition an amount of heat dh is injected reversibly into $C_{\rm P}$. By this reversible process, in a sequence of infinitesimal steps, we may add finite masses M_k to C_P and bring its temperature T to any desired value.

In the second kind of thermobaric transfer, the heat injected into dM^k and C_P is generated by using reversible heat pumps, extracting heat from the thermal well. In this case the thermobaric transfer is a reversible transformation obtained entirely through mechanical work on the hypersystem without any exchange of heat or matter with the environment. Thermobaric transfer of the second kind is important in relation with the concept of exergy and in the analysis of irreversible phenomena.

3. Energy entropy and affinity defined as collective concepts

Consider a single primary cell $C_{\rm P}$ and assume the cell to be rigid. Starting from a fixed initial state, any other state of the cell is determined by its temperature T and the masses M^k added to it. However if these masses have been added by thermobaric transfer from the supply cells C_{Sk} they also determine the state of C_{Sk} . Hence the state of $C_{\rm P}$ also determines the state of the collective system $C_{\rm P} + \sum C_{\rm Sk}$. Therefore we may define the energy U and entropy S of the primary cell $C_{\rm P}$ as the energy and entropy of the collective system $C_{\rm P} + \sum C_{\rm Sk}$. They are functions of M_k and T. This assumes that the change of state does not involve chemical reactions. Under this assumption as a first step we now evaluate the energy \mathcal{U} and the entropy \mathcal{S} of $C_{\rm P}$ as collective concepts by using a thermobaric transfer of the first kind. By this procedure we inject masses dM^{k} and heat dh into C_{P} and obtain for its increase of energy and entropy the expressions

$$\mathbf{d}\mathcal{U} = \sum_{k} \bar{\varepsilon}_{k} \, \mathbf{d}M^{k} + \mathbf{d}h, \tag{3.1}$$

$$\mathbf{d}\mathscr{S} = \sum_{k} \bar{s}_{k} \, \mathbf{d}M^{k} + \mathbf{d}h/T, \qquad (3.2)$$

where

$$\bar{s}_{k} = \int_{p_{0}T_{0}}^{p_{k}T} d\bar{s}'_{k},$$

$$\bar{\varepsilon}_{k} = \int_{p_{0}T_{0}}^{p_{k}T} (dp'_{k}/\rho'_{k} + T' d\bar{s}'_{k}).$$
(3.3)

We call p_k , \bar{s}_k and $\bar{\varepsilon}_k$ respectively the *injection* pressure, the *injection* entropy and the *injection* enthalpy. In the integrals we denote by $\bar{s}'_k p'_k \rho'_k$ and T' the specific entropy, pressure, density, and temperature of the mass dM^k along the path of integration in the thermobaric transfer. The term $T' d\bar{s}_k$ represents the heat injected continuously and reversibly into dM^k during the transfer process. The value of $\bar{\varepsilon}_k$ includes the work of extraction from the supply cells C_{Sk} and of injection into C_{P} .

Elimination of dh between eqs. (3.1) and (3.2) yields

$$\mathrm{d}\mathcal{U} = \sum_{k} \phi_{k} \, \mathrm{d}M^{k} + T \, \mathrm{d}\mathcal{S}, \tag{3.4}$$

where

$$\phi_k = \bar{\varepsilon}_k - T\bar{s}_k \tag{3.5}$$

was called the *convective potential* [3]. It replaces the Gibbs chemical potential. By contrast with standard procedures it contains no undetermined constant, while eq. (3.4) is not used to define ϕ_k but constitutes a theorem.

An important remark is in order here. The undetermined constants of standard methods have been eliminated from the present definitions of $\bar{\varepsilon}_k$, \bar{s}_k and ϕ_k . In the classical approach even the differential $d\phi_k =$ $d\bar{\varepsilon}_k - T d\bar{s}_k - \bar{s}_k dT$ involves the undetermined constant in \bar{s}_k except for an isothermal transformation. This was well recognized by Gibbs himself in his famous paper [13] and remains so in standard textbooks [14, 15].

Consider now the case where a chemical reaction occurs in $C_{\rm P}$. The masses produced by the reaction are $dm_k = v_k d\xi$ where ξ is the reaction coordinate. An increase of temperature dT is also produced by the reaction. The same change of state of the system may be obtained by thermobaric transfer as follows. We assume a reaction d ξ to produce the masses $dm_k = v_k d\xi$ in the chemical supply cell C_{ch} . Taking into account their sign they are "extracted" from C_{ch} and injected by thermobaric transfer into $C_{\rm P}$ where the reaction is assumed frozen. At the same time we inject into C_{ch} an amount of heat \bar{h}_T^{eq} such that its temperature remains constant and equal to T_{eq} . Hence the injection pressures p_{keq} of C_{ch} also remain constant. Into C_{P} we inject an amount of heat dh such that the temperature change dT is the same as if a chemical reaction $d\xi$ had actually taken place in it. Obviously the state of C_{ch} does not vary since its composition and temperature remain constant. On the other hand the change of state of $C_{\rm P}$ obtained by

thermobaric transfer is the same as produced by an actual chemical reaction. However this equivalent thermobaric transfer is a completely reversible process since the chemical reaction in C_{ch} is in equilibrium. The corresponding increase of energy $d\mathcal{U}_{ch}$ and entropy $d\mathcal{G}_{ch}$ of the collective system $C_P + C_{ch}$ may thus be derived by applying eqs. (3.1) and (3.2) replacing dM^k by $\nu_k d\xi$ and dh by $\bar{h}_T^{eq} d\xi$ and dh. We obtain

$$d\mathcal{U}_{\rm ch} = \sum_{k} \nu_k \, d\xi \int_{p_{k\,\rm eq}T_{\rm eq}}^{p_k T} d\bar{\varepsilon}'_k + \bar{h}_T^{\rm eq} \, d\xi + dh = 0, \quad (3.6)$$

$$d\mathscr{S}_{ch} = \sum_{k} \nu_{k} d\xi \int_{p_{keq}T_{eq}}^{p_{k}T} d\bar{s}'_{k} + \frac{\bar{h}_{T}^{eq}}{T_{eq}} d\xi + \frac{dh}{T}, \qquad (3.7)$$

where

$$\mathrm{d}\bar{\varepsilon}_{k}^{\prime} = \mathrm{d}p_{k}^{\prime}/\rho_{k}^{\prime} + T^{\prime}\,\mathrm{d}\bar{s}_{k}^{\prime}.\tag{3.8}$$

We note that $d\mathcal{U}_{ch} = 0$ since otherwise by repeated cycling of a chemical reaction cancelled by an equivalent thermobaric transfer we could extract energy indefinitely from the system. Elimination of dh between eqs. (3.6) and (3.7) yields $d\mathcal{G}_{ch}$ which we write as

$$\mathrm{d}\mathscr{G}_{\mathrm{ch}} = (A/T)\,\mathrm{d}\xi,\tag{3.9}$$

where

$$A = \sum_{k} \nu_{k} \left[T \int_{p_{keq}T_{eq}}^{p_{k}T} d\bar{s}'_{k} - \int_{p_{keq}T_{eq}}^{p_{k}T} d\bar{\varepsilon}'_{k} \right]$$
$$+ \bar{h}_{T}^{eq} \left(T/T_{eq} - 1 \right)$$
(3.10)

expresses the affinity [3] as defined by De Donder's relation (3.9) [5]. The quantity \bar{h}_T^{eq} is the intrinsic heat of reaction at chemical equilibrium (see section 5 below). Since $d\mathcal{U}_{ch} = 0$ eq. (3.4) for $d\mathcal{U}$ remains unchanged when a chemical reaction takes place in addition to a mass and heat transfer. However we may write it in an equivalent form

$$d\mathcal{U} = -A \, d\xi + \sum \phi_k \, dM^k + T \, d\mathcal{S}, \qquad (3.11)$$

where $d\mathcal{S}$ now denotes the total change of entropy including the term $(A/T) d\xi$ due to the chemical reaction. Adding eqs. (3.2) and (3.9) the total entropy change is obtained as

$$\mathrm{d}\mathscr{S} = \frac{A}{T} \mathrm{d}\xi + \sum \bar{s}_k \, \mathrm{d}M^k + \frac{\mathrm{d}h}{T}. \tag{3.12}$$

For simultaneous chemical reactions of affinity A_{ρ} and reaction coordinate ξ_{ρ} the foregoing results are valid after replacing $A d\xi$ by $\sum_{\rho} A_{\rho} d\xi_{\rho}$. From (3.3) we also note the important differential relation

$$\mathrm{d}\bar{\varepsilon}_k = \mathrm{d}p_k / \rho_k + T \,\mathrm{d}\bar{s}_k. \tag{3.13}$$

We have assumed a rigid primary cell. Generalization to a cell of variable volume v and pressure p is trivial, and is obtained by simply adding a term -p dv to the value of $d\mathcal{U}$ [3].

4. Chemical potential

Eq. (3.10) shows that the affinity for any arbitrary state of the cell may be derived once we know the intrinsic heat of reaction \bar{h}_T^{eq} for an equilibrium state of the reaction. This involves a knowledge of the properties of the pure reactants within the range of temperatures of practical interest.

Knowledge of \bar{h}_T^{eq} may be avoided by using a standard expression for the affinity written as

$$A = -\sum_{k} \nu_k \mu_k, \tag{4.1}$$

where μ_k are the chemical potentials. However their values require the knowledge of cryogenic properties of the reactants down to absolute zero. This is shown as follows.

The value (3.10) of A may be written in the form (4.1) by putting

$$\bar{h}_{T}^{\text{eq}} = \sum_{k} \nu_{k} \bigg[\int_{0}^{p_{k \text{ eq}} T_{\text{eq}}} \mathrm{d}\bar{\varepsilon}_{k}' + \bar{\varepsilon}_{k}(0) \bigg], \qquad (4.2)$$

$$\frac{\bar{h}^{\rm eq}}{T_{\rm eq}} = \sum_{k} \nu_{k} \left[\int_{0}^{\nu_{k\,\rm eq} T_{\rm eq}} \mathrm{d}\bar{s}'_{k} + \bar{s}_{k}(0) \right].$$
(4.3)

The integrals at the lower limit of absolute zero are evaluated by extrapolating to the absolute zero, classical properties of the substances in the gaseous state while $\bar{e}_k(0)$ and $\bar{s}_k(0)$ are constants assumed to be characteristic of the substance and independent of any particular chemical reaction. We may consider *this assumption as a basic axiom*. The constants $\varepsilon_k(0)$ and $s_k(0)$ are then determined experimentally from chemical reactions. Substitution of the values (4.2) and (4.3) into eq. (3.10) for the affinity yields an expression of the form (4.1) where

$$\mu_k = \int_{0}^{p_k T} \mathrm{d}\bar{\varepsilon}'_k - T \int_{0}^{p_k T} \mathrm{d}\bar{s}'_k + \bar{\varepsilon}_k(0) - T\bar{s}_k(0). \quad (4.4)$$

This provides a novel and very general definition of the chemical potential [4].

For some simple substances the constants $\bar{\varepsilon}_k(0)$ and $\bar{s}_k(0)$ may be obtained by integration through the cryogenic range down to absolute zero by using the actual physical properties of these substances derived from the axioms of quantum statistics [6]. However this is not generally feasible in practice.

The value of $\bar{s}_k(0)/\mathcal{M}_k R$ where \mathcal{M}_k is the molecular weight and R the molar gas constant represents the so-called chemical constant of standard theories.

5. Evaluation of the thermodynamic functions

We shall consider again the case of a rigid open primary cell C_P . Note that the rigid boundaries may be fictitious and represented by fixed coordinate planes. Generalization to a cell of variable volume is trivial [3]. As already stated the energy and entropy of the cell are defined as collective concepts for the system C_P + $\sum C_{Sk} + C_{ch}$. They are functions of the temperature T of C_P , the masses M_k added to it by convection, and the reaction coordinate ξ giving the masses $\nu_k \xi$ added to it by the chemical reaction. As shown above the chemical reaction $d\xi$ in C_P is equivalent to producing a reaction $d\xi$ in $C_{\rm ch}$ extracting the masses $\nu_k d\xi$ from $C_{\rm ch}$ at constant temperature and injecting them in $C_{\rm P}$ by thermobaric transfer. Constancy of the temperature $T_{\rm eq}$ of $C_{\rm ch}$ is obtained by injecting into it an amount of heat $\bar{h}_T^{\rm eq} d\xi$. At the same time an amount of heat dh is injected into $C_{\rm P}$ to generate any desired increase of temperature. In this process the state of $C_{\rm ch}$ does not change. Applying equations (3.1) and (3.2) to the subsystem $C_{\rm P} + \sum C_{\rm Sk} + C_{\rm ch}$ we derive its collective increment of energy and entropy as

$$d\mathcal{U} = \sum_{k} \nu_{k} d\xi \int_{p_{keq}T_{eq}}^{p_{k}T} d\bar{\varepsilon}'_{k} + \bar{h}_{T}^{eq} d\xi$$

$$+ \sum_{k} \bar{\varepsilon}_{k} dM^{k} + dh, \qquad (5.1)$$

$$d\mathcal{S} = \sum_{k} \nu_{k} d\xi \int_{p_{keq}T_{eq}}^{p_{k}T} d\bar{s}'_{k} + \frac{\bar{h}_{T}^{eq}}{T_{eq}} d\xi$$

$$+ \sum_{k} \bar{s}_{k} dM^{k} + dh/T. \qquad (5.2)$$

The heat dh injected may be written as

$$dh = \sum_{k} h_{vT}^{k} (dM^{k} + \nu_{k} d\xi) + C_{Vm} dT, \qquad (5.3)$$

where C_{Vm} is the heat capacity of the cell C_P for $d\xi = dM^k = 0$ and constant volume, while $h_{vT}^k dM^k$ is the amount of heat which must be added to the cell to maintain constant its temperature when injecting the mass dM^k at constant volume [7]. We have called h_{vT}^k the heat of mixing at constant volume and temperature. We have shown that its value is obtained without calorimetric measurement as [7]

$$h_{vT}^{k} = -T/\rho_{k} \ (\partial p_{k}/\partial T)_{vm}.$$
(5.4)

It is given in terms of the injection pressure

$$p_k = p_k(v, m_k, T) \tag{5.5}$$

expressed as a function of the volume v of the cell, of its temperature T and the total mass

$$m_k = \nu_k \xi + M^k \tag{5.6}$$

of each substance added by the chemical reaction and convection. Relations (5.5) are derived either experimentally or from kinetic theories, and may be considered as additional equations of state. The derivative in (5.4) is for constant volume v and m_k , and ρ_k is the density of the pure substance at the temperature T and pressure p_k .

Using the value (5.3) of dh we may integrate (5.1) and (5.2) over an arbitrary path and obtain the energy and entropy of the cell,

$$\mathcal{U} = \mathcal{U}(\xi, M^k, T), \quad \mathcal{S} = \mathcal{S}(\xi, M^k, T), \quad (5.7)$$

as functions of ξ , M^k and T. We may arbitrarily choose $\mathcal{U} = \mathcal{S} = 0$ for any initial state of the cell. Using the values (3.10), (5.1) and (5.2) we derive

 $d\mathcal{U} - T d\mathcal{G} = -A d\xi + \sum \phi_k dM^k, \qquad (5.8)$

which checks with (3.11)

Evaluation of the thermodynamic functions for the case where the cell contains only an homogeneous mixture of fluids was also obtained by thermobaric transfer. We shall only recall here the result for the case $\xi = 0$. The entropy and energy were found to be [7]

$$\mathscr{S} = \sum_{k} \mathscr{S}_{k} m_{k}, \quad \mathscr{U} = \sum_{k} \mathscr{U}_{k} m_{k} - pv, \qquad (5.9)$$

where

$$\mathscr{G}_{k} = \bar{s}_{k} + h_{pT}^{k}/T \quad \mathscr{U}_{k} = \bar{\varepsilon}_{k} + h_{pT}^{k}, \qquad (5.10)$$

and m_k is the total mass of each substance in the cell of volume v under the pressure p. The heat of mixing of each substance at constant pressure and temperature with $d\xi = 0$ is denoted by h_{pT}^k . Its value was obtained as [7]

$$h_{pT}^{\kappa} = -T/\rho_k (\partial p_k / \partial T)_{pm}, \qquad (5.11)$$

where the derivative is for $dp = d\xi = dM^k = 0$. For a mixture of perfect gases this result yields $h_{pT}^k = 0$. Hence in this case

$$\mathscr{S} = \sum_{k} \bar{s}_{k} m_{k}, \quad \mathscr{U} + pv = \sum_{k} \bar{\varepsilon}_{k} m_{k}, \quad (5.12)$$

showing the additive property of entropy and enthalpy of perfect gas mixtures.

A new form of the Gibbs-Duhen theorem was also derived [7] as

$$\sum_{k} m_k \, \mathrm{d}\phi_k + \mathscr{S} \, \mathrm{d}T = v \, \mathrm{d}p, \qquad (5.13)$$

where \mathscr{S} is given by (5.9) and m_k includes the masses produced by chemical reactions.

Intrinsic heat of reaction. It is denoted by \bar{h}_T and was defined by the heat $\bar{h}_T d\xi$ to be added in a reaction $d\xi$, where the positive or negative products of the reaction are removed as the reaction proceeds and the temperature is kept constant [3, 7]. As a consequence the volume, pressure and composition also remain constant. When \bar{h}_T is known it yields the standard heats of reaction as

the first at constant volume and temperature and the second at constant pressure and temperature. The values of h_{vT}^k and h_{pT}^k are given by (5.4) and (5.11) without calorimetric measurements, while \bar{h}_T may be evaluated from the rigorous and general relation [4, 7]

$$\mathrm{d}\bar{h}_T = \sum_k \nu_k \, \mathrm{d}\bar{\varepsilon}_k. \tag{5.15}$$

For a perfect gas mixture $h_{pT}^k = 0$ and $h_{pT} = \bar{h}_T$. Since the intrinsic heat of reaction does not involve the heat of mixing it is more representative of the true chemical energy than the standard concepts (5.14).

6. Generalized principle of virtual dissipation

A generalized formulation of the principle of virtual dissipation may be obtained directly and very simply from the concept of thermobaric transfer of the second kind in a hypersystem.

Consider a primary system constituted by a set of cells $\sum C_P$. Arbitrary variations are then given to the state variables in such a way that continuity of mass and heat flow between primary cells is preserved. In such a variation, masses are exchanged only between primary cells. At the boundary there are variations of heat and mass injected into the primary system. They represent an exchange of the open primary system with the environment. However instead of the heat and masses being provided by the environment we may assume that they are injected at the boundary by thermobaric transfer of the second kind by extraction from supply cells and the thermal well. Hence we obtain an *equivalent variation of state of the primary system entirely within the hypersystem without involving the environment.*

Obviously the virtual work accomplished in this variation is equal to the variation of energy of the hypersystem. This energy variation is

$$\delta U + \delta U_{\rm TW} = \delta W^{\rm TH} + \delta W^{\rm M} \tag{6.1}$$

where U is the energy of the primary system defined as a collective concept hence as the energy of the system $\sum C_P + \sum C_{Sk} + C_{ch}$ while U_{TW} is the energy of the thermal well. On the right side δW^{TH} is the variation of the work performed in the thermobaric transfer at the boundary and δW^M is the virtual mechanical work of all other forces acting on the hypersystem. If S_{TW} denotes the entropy of the thermal well we have

$$\delta U_{\rm TW} = T_0 \, \delta S_{\rm TW}. \tag{6.2}$$

Hence (6.1) may be written

$$\delta V + T_0 \,\delta S^* = \delta W^{\rm TH} + \delta W^{\rm M},\tag{6.3}$$

where

 $V = U - T_0 S, \tag{6.4}$

$$S^* = S + S_{\rm TW},\tag{6.5}$$

and S denotes the entropy of the primary system defined as a collective concept. The expression V was shown in 1954-55 to be the fundamental thermodynamic function of irreversible thermodynamics [1, 2]. It was later given the name exergy. The virtual entropy produced in the hypersystem is δS^* .

By extending d'Alemberts principle to the case where U is not merely the mechanical potential but the thermodynamic energy we may apply eq. (6.3) to dynamics by considering reversed inertia forces as being equivalent to external force acting on the system, and included in δW^{M} . Hence we may write (6.3) as

$$\sum_{i} I_{i} \,\delta q_{i} + \delta V + T_{0} \,\delta S^{*} = \delta W^{\mathrm{TH}} + \delta W^{\mathrm{M}}, \qquad (6.6)$$

where $I_i \,\delta q_i$ is the virtual work of the inertia forces and δW^M that due to the mechanical forces acting directly on the primary system.

The variational equation (6.6) constitutes the fundamental generalized form of the *principle of virtual dissipation*. Except of the continuity of mass and heat flow between primary cells *the variations are unrestricted anywhere including the boundary*. The principle is thus freed from the constraints imposed in previous formulations [4, 7].

The exergy of a single primary cell is

$$\mathscr{V} = \mathscr{U} - T_0 \mathscr{S} \tag{6.7}$$

and the total exergy is

$$V = \sum \mathcal{V},\tag{6.8}$$

where the summation is extended to all primary cells.

From (3.11) and (6.7) for the case of multiple reactions we obtain

$$d\mathcal{V} = -\sum_{\rho} A_{\rho} d\xi_{\rho} + \sum_{k} \phi_{k} dM^{k} + \theta d\mathcal{S}, \qquad (6.9)$$

where $\theta = T - T_0$

The exergy may be given an important physical interpretation in terms of thermobaric transfer of the second kind. Consider an infinitesimal transformation without chemical reaction $(d\xi = 0)$. The change of exergy is

$$\mathrm{d}\mathcal{V} = \mathrm{d}\mathcal{U} - T_0 \,\mathrm{d}\mathcal{G}.\tag{6.10}$$

The transformation may be obtained by a thermobaric transfer of the second kind. Since it is a reversible transformation which occurs entirely within the hypersystem without exchange of matter or heat with the environment the total entropy of the hypersystem is constant Therefore $-d\mathcal{S}$ is the increase of entropy of the thermal well and $-T_0 d\mathcal{S}$ its increase of energy. Hence $d\mathcal{V}$ is the increase of energy of the hypersystem and is equal to the work on it by the external forces including the work of the heat pumps. On the other hand substituting into (6.10) the values (3.1) and (3.2) of $d\mathcal{U}$ and $d\mathcal{S}$ we obtain

$$\mathrm{d}\mathcal{V} = \sum_{k} \psi_{k} \, \mathrm{d}M^{k} + (\theta/T) \, \mathrm{d}h, \qquad (6.11)$$

where

$$\psi_k = \bar{\varepsilon}_k - T_0 \bar{s}_k = \phi_k + \theta \bar{s}_k \tag{6.12}$$

is the *thermobaric potential* [3, 7]. We note that ψ_k may be defined entirely mechanically as the work required to inject a unit mass of pure substance into the primary cell by thermobaric transfer of the second kind. The term $(\theta/T) dh$ in (6.11) is the mechanical work of a heat pump, required to inject a quantity of heat dh into the cell.

The importance of the thermobaric potential ψ_k is due to its physical significance in terms of mechanical work. By contrast with ϕ_k it does not involve the entropy. It is also of importance in linear theories for small perturbations near equilibrium. In that case to the first order dh is a state variable. The general analysis may then be developed based on expression (6.11) for d \mathcal{V} using ψ_k instead of ϕ_k , resulting in considerable simplification and physical clarity [8].

Using these results, we may now derive explicitly the value of dW^{TH} in the general variational principle (6.6) as,

$$\delta W^{\rm TH} = -\int_{A} \begin{bmatrix} \xi \\ \psi_k & \delta M_i^k + (\theta/T) & \delta H_i \end{bmatrix} n_i \, dA$$
$$= -\int_{A} (\phi_k & \delta M_i^k + \theta & \delta S_i) n_i \, dA. \qquad (6.13)$$

The integrals are extended to the boundary A of the primary system with unit normal n_i , while $-\delta M_i^k$ and $-\delta H_i$ represent the variations of masses and heat injected through the boundary. We have put

$$\delta S_i = \sum_k \bar{s}_k \, \delta M_i^k + \delta H_i / T \tag{6.14}$$

as the variation of the entropy injected at the boundary. The boundary integral (6.13) represents the mechanical work required to inject at the boundary by thermobaric transfer of the second kind masses $-\delta M_i^k n_i$ and the heat $-\delta H_i n_i$. This thermobaric transfer obtained by purely mechanical work within the hypersystem is completely equivalent to an actual exchange with the environment. Hence δW^{TH} may be considered as the virtual work of *thermodynamic forces* exerted by the environment on the primary system.

When the system is in a gravity field with no other forces acting on the system we replace δW^{M} by

$$-\delta G - \int_{A} \mathscr{G} \sum_{k} \delta M_{i}^{k} n_{i} \, \mathrm{d}A$$

where G is the potential energy of the system in the gravity field, and \mathscr{G} is the gravity field potential per unit mass. The supply cells are assumed located on the equipotential surface $\mathscr{G} = 0$. The surface integral is the work against the gravity field in the boundary thermobaric transfer. The principle of virtual dissipation (6.6) then becomes

$$\sum_{i} I_{i} \,\delta q_{i} + \delta \mathcal{P} + T_{0} \,\delta S^{*}$$

$$= -\int_{A} \left[\sum_{k} \varphi_{k} \,\delta M_{i}^{k} + \theta \,\delta S_{i} \right] n_{i} \,\mathrm{d}A,$$

$$\mathcal{P} = V + G, \qquad \varphi_{k} = \phi_{k} + \mathscr{G}. \qquad (6.15)$$

we have called \mathcal{P} the mixed collective potential and φ_k the mixed convective potential [7].

We have considered variations δM_i^k and δH_i of mass and heat transfer per unit area. We may replace δ by time derivatives and consider the mass flux \dot{M}_i^k and heat flux \dot{H}_i . The dot denotes a time derivative. Expression (6.14) becomes the entropy flux

$$\dot{S}_{i} = \sum_{k} \bar{s}_{k} \dot{M}_{i}^{k} + \dot{H}_{i} / T.$$
(6.16)

Within a flowing continuous system we consider a fixed surface of normal n_i . If we imagine the surface as a fictitious boundary we must inject through it masses $\dot{M}_i^k n_i$ and heat $\dot{H}_i n_i$ if the flow field is to remain undisturbed. This must be true for all orientations n_i . Hence it defines the heat flux \dot{H}_i . By time integration of \dot{M}_i^k , \dot{H}_i and \dot{S}_i with zero initial values we obtain the mass fluence M_i^k the heat fluence H_i and the entropy fluence S_i . With cartesian coordinates x_i , conservation of mass is expressed by

$$\boldsymbol{M}^{k} = -\partial \boldsymbol{M}_{i}^{k} / \partial \boldsymbol{x}_{i}. \tag{6.17}$$

7. Fundamental entropy balance of biological systems

We neglect inertia forces and replace variations by time derivations in eq. (6.3). We obtain

$$T_0 \dot{S}^* - \dot{W}^{\rm M} = \dot{W}^{\rm TH} - \dot{V}. \tag{7.1}$$

On the left we have $T_0 \dot{S}^*$ representing the useful energy dissipated by entropy production and the work $-\dot{W}^{M}$ accomplished against the environment. The expression on the right side is

$$W^{\rm TH} = -\int_{A} \left[\psi_k \dot{M}_i^k + (\theta/T) \dot{H}_i \right] n_i \, \mathrm{d}A - \dot{V}, \qquad (7.2)$$

where $-\psi_k \dot{M}_i^k n_i$ is the positive chemical contribution of matter acquired and lost. It is represented here by the mechanical work of thermobaric transfer for an equivalent hypersystem. The term $\theta \dot{H} n_i / T$ carried to the left side of (7.2) represents the useful energy lost to the environment in the form of heat. It is equal to the equivalent mechanical work of a heat pump. The concept of thermobaric transfer thus provides a vivid illustration of entropy balance in biological systems in terms of equivalent mechanical work.

8. New evaluation of entropy produced

Systematic and general methods of evaluation of entropy production are illustrated hereafter by considering the particular case of a continuous system with heat and mass transfer in the presence of chemical reactions. The flow is referred to a fixed coordinate system which may or may not be identified with a rigid material through which diffusion takes place. Hence the treatment includes the particular case of a fluid mixture [7]. For a continuous primary domain Ω we denote by \mathcal{U} , \mathcal{S} and \mathcal{V} the energy, entropy and exergy per unit volume.

The variation of entropy is obtained from (3.12) as

$$\delta \mathscr{S} = \sum_{\rho} \left(A_{\rho} / T \right) \, \delta \xi_{\rho} + \sum_{k} \bar{s}_{k} \, \delta M^{k} + \delta h / T. \tag{8.1}$$

It is important to remember that δh is the heat added *reversibly* per unit volume. In terms of the heat fluence H_i it is written

$$\delta h = \delta h^{P} - \partial \, \delta H_{i} / \partial x_{i}, \qquad (8.2)$$

where δh^P is the heat which must be injected reversibly in addition to $-\partial \delta H_i/\partial x_i$ in order to obtain the same change of state as in an actual irreversible process. Hence h^P may be called the heat produced by the irreversibility. It corresponds to the "uncompensated heat" of Clausius. After substituting the values (6.17) of M^k and the value (8.2) of δh we may write (8.1) as

$$\delta \mathscr{G} = -\partial \, \delta S_i / \partial x_i + \delta s^*. \tag{8.3}$$

where δS_i is equal to (6.14). The variation of entropy produced per unit volume is δs^* . Using (8.1) and (8.2) it is given by

$$T\delta s^* = \sum_{\rho} A_{\rho} \,\delta \xi_{\rho} + T \sum_{k} \frac{\partial s_{k}}{\partial x_{i}} \,\delta M_{i}^{k} \\ + \delta h^{P} - \frac{1}{T} \frac{\partial T}{\partial x_{i}} \,\delta H_{i}.$$
(8.4)

On the other hand the variation of energy is obtained from (3.1). Substituting the value (8.2) of δh we write

$$\delta U = \sum_{k} \bar{\varepsilon}_{k} \, \delta M^{k} + \delta h^{P} - \partial \, \delta H_{i} / \partial x_{i}. \tag{8.5}$$

Again substituting the value (6.17) and integrating over the domain Ω we obtain

$$\int_{\Omega} \delta \mathcal{U} \, \mathrm{d}\Omega = \int_{\Omega} \left[-\frac{\partial}{\partial x_i} \left\langle \bar{\varepsilon}_k \, \delta M_i^k + \delta H_i \right\rangle \right]$$

$$+ \frac{\partial \bar{\varepsilon}_k}{\partial x_i} \delta M_i^k + \delta h^P \, \mathrm{d}\Omega, \qquad (8.6)$$

where $\bar{e}_k \, \delta M_i^k + \delta H_i$ is the variation of energy flow. On the other hand conservation of energy is expressed by

$$\int_{\Omega} \delta \mathcal{U} \, \mathrm{d}\Omega = \int_{\Omega} \left[-\frac{\partial}{\partial x_i} \left(\bar{\varepsilon}_k \, \delta M_i^k + \delta H_i \right) \right]$$

+ $\sum_k \mathcal{B}_i \, \delta M_i^k \, \mathrm{d}\Omega, \qquad (8.7)$

where \mathcal{B}_i is the body force per unit mass and $\sum_k \mathcal{B}_i \delta M_i^k$ is the virtual work of these forces. Comparing expressions (8.6) and (8.7) which are valid for an arbitrary domain Ω we conclude

$$\sum_{k \in \mathcal{A}} (\partial \bar{\varepsilon}_k / \partial x_i) \, \delta M_i^k + \delta h^P = \sum_k \mathcal{B}_i \, \delta M_i^k.$$
(8.8)

By elimination of $\delta h^{\rm P}$ between eqs. (8.4) and (8.8) taking into account the differential relation (3.13) we obtain

$$T\delta s^* = \sum_{\rho} A_{\rho} \,\delta\xi_{\rho} + \sum_k X_i^k \,\delta M_i^k + X_i^T \,\delta H_i \tag{8.9}$$

where

$$X_{i}^{k} = \mathcal{B}_{i} - (1/\rho_{k}) \, \partial p_{k} / \partial x_{i},$$

$$X_{i}^{T} = -(1/T) \, \partial T / \partial x_{i}$$
(8.10)

are disequilibrium forces along with A_{ρ} . An important step is to express these forces in terms of rate variables. Consider first the chemical reaction. From chemical kinetics we may determine the reaction rates $\dot{\xi}_{\rho}$ as functions of the state variables ξ_{ρ} , M^k and T of the cell. Solving these relations for ξ_{ρ} and substituting these values into A_{ρ} we write

$$A_{\rho} = \mathcal{R}_{\rho}(\dot{\xi}_{\sigma}, M^{k}, T). \tag{8.11}$$

Hence the disequilibrium chemical forces \mathcal{R}_{ρ} are now expressed in terms of the rates $\dot{\xi}_{\sigma}$ and involve chemical kinetics. As can be seen these chemical forces are the scalar equivalent of viscous stresses expressed in terms of strain rates.

We imagine that we may freeze the chemical reactions and obtain either experimentally or theoretically the relations between the disequilibrium forces and the flow rates \dot{M}_{i}^{k} and \dot{H}_{i} . They are written

$$\boldsymbol{X}_{i}^{k} = \mathcal{R}_{i}^{k}(\dot{\boldsymbol{M}}_{j}^{l},\dot{\boldsymbol{H}}_{j}), \qquad \boldsymbol{X}_{i}^{T} = \mathcal{R}_{i}^{T}(\dot{\boldsymbol{M}}_{j}^{l},\dot{\boldsymbol{H}}_{j}). \quad (8.12)$$

Eq. (8.9) then becomes

$$T\,\delta s^* = \sum_{\rho} \mathcal{R}_{\rho}\,\delta\xi_{\rho} + \sum_{k} \mathcal{R}_{i}^{k}\,\delta M_{i}^{k} + \mathcal{R}_{i}^{T}\,\delta H_{i}. \qquad (8.13)$$

Instead of H_i and \dot{H}_i as variables we may introduce the entropy fluence S_i and the entropy flux \dot{S}_i . Solving eqs. (6.14) and (6.16) for δH_i and \dot{H}_i and substituting these values into (8.13) we obtain

$$T\,\delta s^* = \sum_{\rho} \mathcal{R}_{\rho}\,\delta\xi_{\rho} + \sum_{k} \mathcal{R}_{i}^{Sk}\,\delta M_{i}^{k} + \mathcal{R}_{i}^{ST}\,\delta S_{i}, \quad (8.14)$$

where

$$\mathscr{R}_{i}^{Sk}(\dot{M}_{i}^{l},\dot{S}_{i}) = \mathscr{R}_{i}^{k} - T\bar{s}_{k}\mathscr{R}_{i}^{T}, \qquad (8.15)$$

$$\mathcal{R}_{i}^{ST}(\dot{M}_{i}^{l}, \dot{S}_{i}) = T\mathcal{R}_{i}^{T}$$

$$(8.16)$$

Note that the rate functions \mathcal{R}_i^k and \mathcal{R}_i^T depend not only on the fluxes \dot{M}_i^k and \dot{H}_i but also on the local state variables although this is not indicated explicitly.

The present derivation of entropy produced is fully general and does not assume linearity or any dependence on Onsager's principle.

Replacing the variations by time derivatives, (8.14) becomes the rate of dissipation

$$T\dot{s}^{*} = \sum_{\rho} \mathcal{R}_{\rho} \dot{\xi}_{\rho} + \sum_{k} \mathcal{R}_{i}^{\mathrm{S}k} \dot{M}_{i}^{k} + \mathcal{R}_{i}^{\mathrm{S}T} \dot{S}_{i}.$$
(8.17)

It is a function of the rates $\dot{\xi}_{\rho}$, \dot{M}_{i}^{k} and \dot{S}_{i} with the property $T\dot{s}^{*} \ge 0$.

The rate functions introduced here do not assume any linear dependence of the forces on the fluxes. For example they may include the nonlinear diffusion of a non-newtonian fluid through a porous medium.

In the case of a linear dependence, and in the absence of a temperature gradient, we write the linear relations

$$\mathcal{R}_{i}^{T}(\dot{M}_{i}^{l},\dot{H}_{i})=0.$$
 (8.18)

If we solve these relations for \dot{H}_i the coefficients of \dot{M}_i^k constitute what is generally called the "heat of transport".

When in addition to being linear the relations between fluxes and forces satisfy Onsager's reciprocity properties [9, 10] the value (8.14) becomes [4]

$$T \,\delta s^{*} = \sum_{\rho} \frac{\partial \mathscr{D}^{ch}}{\partial \dot{\xi}_{\rho}} \,\delta \xi_{\rho} + \sum_{k} \frac{\partial \mathscr{D}^{TM}}{\partial \dot{M}_{i}^{k}} \,\delta M_{i}^{k} + \frac{\partial \mathscr{D}^{TM}}{\partial \dot{S}_{i}} \,\delta S_{i}, \qquad (8.19)$$

where \mathscr{D}^{ch} is a quadratic form in the reaction rates $\dot{\xi}_{\rho}$ and \mathscr{D}^{TM} a quadratic form in the fluxes \dot{M}_{i}^{k} and \dot{S}_{i} . Replacing the variations by time derivatives and applying Euler's theorem for quadratic forms we derive the rate of dissipation as

$$T\dot{s}^* = 2\mathscr{D}^{\rm ch} + 2\mathscr{D}^{\rm TM}. \tag{8.20}$$

The coefficients of the quadratic forms depend on the local state.

We note that S_i and s^* assuming zero initial values satisfy a fundamental entropy balance equation

$$\mathcal{G} = -\partial S_i / \partial x_i + s^* \tag{8.21}$$

whose variational form was already expressed by (8.3).

The total entropy produced to be used in the variational principle (6.15) is

$$\delta S^* = \int_{\Omega} \delta s^* \, \mathrm{d}\Omega. \tag{8.22}$$

9. Alternative choices of state variables

Equations of evolution of the thermodynamic system are obtained in various forms depending on the choice of state variables to describe the system.

A simple approximate description is obtained by neglecting the entropy produced s^* . We may then write (8.21) as

$$\mathcal{G} = -\partial S_i / \partial x_i \tag{9.1}$$

and use the entropy fluence S_i along with M_i^k and ξ_o as state variable.

Another possibility is to neglect the entropy produced by thermomolecular diffusion. In that case we introduce a pseudo-fluence of entropy S_i^+ as state variable and write

$$\mathcal{G} = -\partial S_i^+ / \partial x_i, \tag{9.2}$$

along with

$$-\partial \dot{\mathbf{S}}_{i}^{+}/\partial x_{i} = -\partial \dot{\mathbf{S}}_{i}/\partial x_{i} + \sum_{\rho} \left(\mathcal{R}_{\rho}/T \right) \dot{\boldsymbol{\xi}}_{\rho}.$$
(9.3)

Hence

$$\dot{S}_i = \dot{S}_i^+ + \int_{\Omega^+} g_i(x_j, x_j^+) \sum_{\rho} \frac{\mathscr{R}_{\rho}}{T} \dot{\xi}_{\rho} \, \mathrm{d}\Omega^+, \qquad (9.4)$$

where $g_i(x_i, x_i^+)$ is any flux due to a unit concentrated source at the point x_i^+ . Replacing the time derivatives by variations,

$$\delta S_i = \delta S_i^+ + \int_{\Omega^+} g_i(x_j, x_j^+) \sum_{\rho} \frac{\mathcal{R}_{\rho}}{T} \, \delta \xi_{\rho} \, \mathrm{d}\Omega^+. \tag{9.5}$$

With this value in (8.14) the virtual dissipation $T\delta s^*$ is expressed in terms of the state variables S_i^+ , M_i^k and ξ_{ρ} . A procedure which does not involve any approximation is obtained as follows. Replacing differentials by variations and introducing the value (8.2) of δh , eq. (3.1) is written,

$$\delta \mathcal{U} = \sum_{k} \bar{\varepsilon}_{k} \, \delta M^{k} + \delta h^{P} - \partial \, \delta H_{i} / \partial x_{i}.$$
(9.6)

Equating the values (8.4) and (8.13) of $T\delta s^*$, taking into account relations (8.10), (8.11) and (8.12) we obtain

$$T\sum_{k} \left(\partial \bar{s}_{k} / \partial x_{i} + \delta h^{\mathrm{P}} = \sum_{k} \mathcal{R}_{i}^{k} \, \delta M_{i}^{k}.$$

$$(9.7) \mathcal{E} \mathcal{M} \mathcal{R}_{i}^{k}$$

Elimination of δh^{P} between eqs. (9.6) and (9.7) yields

$$\delta \mathcal{U} = \sum_{k} \bar{\varepsilon}_{k} \, \delta M^{k} - T \sum_{k} \frac{\partial s_{k}}{\partial x_{i}} \, \delta M^{k}_{i} + \sum_{k} \mathcal{R}^{k}_{i} \, \delta M^{k}_{i} - \partial \, \delta H_{i} / \partial x_{i}.$$
(9.8)

Further transformation is obtained by applying the mass conservation equations (6.17) in variational form. Hence

$$\delta \mathcal{U} = -\frac{\partial}{\partial x_i} \left[\sum_k \bar{\varepsilon}_k \, \delta M_i^k + \delta H_i \right] \\ + \sum_k \left[\frac{\partial \bar{\varepsilon}_k}{\partial x_i} - T \frac{\partial \bar{s}_k}{\partial x_i} \right] \delta M_i^k \\ + \sum_i \mathcal{R}_i^k \, \delta M_i^k.$$
(9.9)

Applying eq. (3.13) to the bracket in the second term yields

$$\delta \mathcal{U} = -\frac{\partial}{\partial x_i} \left[\sum_k \bar{\varepsilon}_k \, \delta M_i^k + \delta H_i \right] + \sum_k f_i^k \, \delta M_i^k, \quad (9.10)$$

where

$$f_i^k = \frac{1}{\rho_k} \frac{\partial p_k}{\partial x_i} + \mathcal{R}_i^k.$$
(9.11)

We now introduce an energy fluence \mathcal{F}_i as a state variable such that

$$\mathscr{U} = -\partial \mathscr{F}_i / \partial x_i. \tag{9.12}$$

Eq. (9.10) becomes

$$\frac{\partial}{\partial x_i} \left[\sum_k \bar{\varepsilon}_k \, \delta M_i^k + \delta H_i - \delta \mathscr{F}_i \right] = \sum_k f_i^k \, \delta M_i^k. \qquad (9.13)$$

In integral form this may be written

$$\delta H_i = \delta \mathscr{F}_i - \sum_k \bar{\varepsilon}_k \, \delta M_i^k + \int_{\Omega^+} g_i(x_j, x_j^+) \sum_k f_j^k \, \delta M_j^k \, \mathrm{d}\Omega^+.$$
(9.14)

Also using (3.5) and (6.14) this becomes

$$T \,\delta S_{i} = \delta \mathscr{F}_{i} - \sum_{k} \phi_{k} \,\delta M_{i}^{k} + \int_{\Omega^{+}} g_{i}(x_{j}, x_{j}^{+}) \sum_{k} f_{j}^{k} \,\delta M_{j}^{k} \,\mathrm{d}\Omega^{+}.$$
(9.15)

An important remark must be made here regarding the functional nature of f_j^k . We note that the second equation (8.10) may be written

$$-(1/T) \partial T/\partial x_i = \mathcal{R}_i^T(\dot{M}_i^l, \dot{H}_i).$$
(9.16)

It may be solved for \dot{H}_i in terms of $\partial T/\partial x_i$ and \dot{M}_j . Substituting this value of \dot{H}_i into \mathcal{R}_i^k all rate variables except \dot{M}_j^k are eliminated from the functional dependence. The same property applies to f_i^k . Hence we write

$$f_{i}^{k} = f_{i}^{k} (\dot{M}_{j}^{l}). \tag{9.17}$$

It should be understood of course that f_i^k also depends on the local state variables and their gradients.

Having expressed δS_i as a linear function of the state variables $\delta \mathcal{F}_i$, δM_i^k expression (8.14) yields the virtual dissipation as a linear function of the same state variables plus $\delta \xi_{\rho}$. This value may then be substituted in the variational principle. Note that (9.15) also yields the entropy flux \dot{S} in terms of \dot{F}_i and \dot{M}_i^k by replacing the variations by time derivatives. We obtain

$$T\dot{S}_{i} = \dot{\mathscr{F}} - \sum_{k} \phi_{k} \dot{M}_{i}^{k} + \int_{\Omega^{+}} g_{i}(x_{j}, x_{j}^{+}) \sum_{k} f_{j}^{k} \dot{M}_{j}^{k} d\Omega^{+}.$$
(9.18)

10. Simplification for negligible inertia and body forces

When body or inertia force are negligible, we may put $\mathcal{B}_i = 0$ in eqs. (8.10). In this case

$$X_i = \mathcal{R}_i^k = -(1/\rho_k) \,\partial p_k / \partial x_i. \tag{10.1}$$

Hence the disequilibrium force is entirely due to the gradient of the injection pressures. In this case from eq. (9.11) we derive

$$f_i^{\kappa} = 0.$$
 (10.2)

As a consequence eqs. (9.15) and (9.18) are greatly simplified and become

$$T\delta S_i = \delta \mathscr{F}_i - \sum_k \phi_k \, \delta M_i^k, \qquad (10.3)$$

$$T\dot{S}_{i} = \dot{\mathscr{F}}_{i} - \sum_{k} \phi_{k} \dot{M}_{i}^{k}.$$
(10.4)

By substitution of the value (3.5) and (6.16) for ϕ_k and \dot{S}_i eq. (10.4) yields

$$\dot{\mathscr{F}}_i = \sum \bar{\varepsilon}_k \dot{M}_i^k + \dot{H}_i. \tag{10.5}$$

We recognize on the right side the *diffusive* energy flux due to the mass flux \dot{M}_i^k and the heat flux \dot{H}_i . We thus obtain in this case a physical interpretation of $\dot{\mathcal{F}}_i$ as an actual energy flux.

11. Variational derivation of field equations for reaction-diffusion with gravity and inertia

We shall consider a system with simultaneous reaction-diffusion and derive the field equations including the effect of inertia and gravity. The gravity potential per unit mass at the point x_i is denoted by \mathscr{G} . Hence the mixed collective potential is

$$\mathcal{P} = \int_{\Omega} \left[\mathcal{V} + \mathcal{G} \sum^{k} M^{k} \right] \mathrm{d}\Omega.$$
 (11.1)

The virtual work of the inertia forces is

$$\sum I_i \, \delta q_i = \int_{\Omega} \sum_k a_i^k \, \delta M_i^k \, \mathrm{d}\Omega, \qquad (11.2)$$

where a_i^k is the acceleration of the substance k. It may be expressed as

$$a_{i}^{k} = \partial v_{i}^{k} / \partial t + v_{j} \left(\partial v_{i}^{k} / \partial x_{j} \right),$$

$$v_{i}^{k} = \dot{M}_{i}^{k} / m_{k}$$
(11.3)

where v_i^k is the velocity of the mass m_k of diffusing substance. Following an earlier remark [7] regarding the definition of the acceleration of reacting substances inconsistencies are avoided by using the barycentric velocity of each group of reacting substances to define the acceleration of each substance. It can be shown that this procedure satisfies energy conservation.

In applying the variational principle we may choose to vary any suitable variables. In the present case it is convenient to vary ξ_{ρ} , M_i^k and S_i . The variations will be applied only inside the domain Ω so that δW^M and δW^{TH} vanish at the boundary. The variational principle (6.15) then becomes.

$$\int_{\Omega} (a_i^k \,\delta M_i^k + \delta \mathcal{V} + \mathcal{G} \sum_k \delta M^k + T_0 \,\delta s^*) \,\mathrm{d}\Omega = 0.$$
(11.4)

Referring to eq. (8.3) we may write

$$\delta \mathcal{V} + \mathcal{G} \sum_{k} \delta M^{k} = -\sum_{\rho} A_{\rho} \, \delta \xi_{\rho} + \sum_{k} \varphi_{k} \, \delta M^{k} + \theta (-\partial \, \delta S_{i} / \partial x_{i} + \delta s^{*}).$$
(11.5)

We have put in accordance with (6.15)

$$\varphi_k = \phi_k + \mathscr{G}. \tag{11.6}$$

From (6.17) we also write $\delta M^k = -(\partial/\partial x_i) \, \delta M_i^k$.

Hence the variational equation (11.4) becomes

$$\int_{\Omega} \left[\sum_{k} a_{i}^{k} \,\delta M_{i}^{k} - \sum_{\rho} A_{\rho} \,\delta \xi_{\rho} - \sum_{k} \varphi_{k} \,\frac{\partial \,\delta M_{i}^{k}}{\partial x_{i}} - \theta \,\frac{\partial \,\delta S_{i}}{\partial x_{i}} + Ts^{*} \right] \mathrm{d}\Omega = 0.$$
(11.7)

We integrate by parts and insert the value (8.14) of $T \delta s^*$. Cancelling the coefficients of the arbitrary variations $\delta \xi_{\rho}$, δM_i^k and δS_i we obtain

$$a_{i}^{k} + \partial \varphi_{k} / \partial x_{i} + \mathcal{R}_{i}^{Sk} = 0,$$

$$\partial \theta / \partial x_{i} + \mathcal{R}_{i}^{ST} = 0,$$

$$-A_{\rho} + \mathcal{R}_{\rho} = 0.$$
(11.8)

These field equations contain the variable \dot{S}_i which is a state variable only if s^* may be neglected in eq. (8.21). In earlier work we added the auxiliary equation (8.17) to determine the entropy production s^* which along with S_i yields the entropy \mathscr{S} through eq. (8.21). With the new procedure developed above, this is not necessary, since the value (9.18) of \dot{S}_i may be introduced in eqs. (11.8). The only unknowns are then the state variables ξ_{ρ} , \mathscr{F}_i and M_i^k . The field equations (11.8) thus become integro-differential equations in these state variables.

An analogous approach is also obtained by neglecting the contribution of diffusion to the value of s^* using S_i^+ of eq. (9.2) as a state variable.

The field equations (11.8) are applicable to nonlinear diffusion such as represented by a mixture of non-newtonian fluids in a porous medium.

The dynamical case of a reacting gas mixture with newtonian viscosity, thermomolecular diffusion and radiation pressure has been developed in detail earlier [7].

12. Generalized lagrangian equations far from local equilibrium with gravity and inertia

In previous work lagrangian equations were discussed in the particular case where the local

irreversible process is linear and near equilibrium [4].

The present treatment opens the way to a completely general lagrangian analysis of reaction-diffusion phenomena which are nonlinear and far from equilibrium. The state variables are the fields

$$\mathcal{F}_{j} = \mathcal{F}_{j}(q_{1}, q_{2}, ..., x_{l}),$$

$$M_{j}^{k} = M_{j}^{k}(q_{1}, q_{2}, ..., x_{l}),$$

$$\xi_{\rho} = \xi_{\rho}(q_{1}, q_{2}, ..., x_{l}),$$
(12.1)

as given functions of the coordinates x_i and a finite number of unknown parameters q_i , functions of time, called generalized coordinates. In the completely general case the functions (12.1) may also contain the time explicitly.

The only external forces are gravity forces, and the variational principle (6.15) is applicable. We write

$$\sum_{i} I_{i} \, \delta q_{i} + \delta \mathscr{P} + T_{0} \int_{\Omega} \delta s^{*} \, \mathrm{d}\Omega = \delta W^{\mathrm{TG}}, \qquad (12.2)$$

with

$$\delta W^{\mathrm{TG}} = -\int_{A} \left[\sum_{k} \varphi_{k} \, \delta M_{i}^{k} + \theta \, \delta S_{i} \right] n_{i} \, \mathrm{d}A.$$

The value $\mathscr{P}(q_i)$ is a function of the generalized state variables q_i . By varying q_i we obtain

$$\delta \mathcal{P} = \sum_{i} \frac{\partial \mathcal{P}}{\partial q_{i}} \, \delta q_{i}. \tag{12.3}$$

The field variations due to δq_i are

$$\delta \mathscr{F}_{j} = \sum_{i} \frac{\partial \mathscr{F}_{j}}{\partial q_{i}} \delta q_{i}, \qquad \delta M_{j}^{k} = \sum_{i} \frac{\partial M^{k}}{\partial q_{i}} \delta q_{i},$$
$$\delta \xi_{\rho} = \sum_{i} \frac{\partial \xi_{\rho}}{\partial q_{i}} \delta q_{i}. \qquad (12.4)$$

Similarly the time derivatives are

$$\dot{\mathscr{F}}_{j} = \sum_{i} \frac{\partial \mathscr{F}_{j}}{\partial q_{i}} \dot{q}_{i}, \qquad \dot{M}_{j}^{k} = \sum_{i} \frac{\partial M^{k}}{\partial q_{i}} \dot{q}_{i},$$
$$\dot{\xi}_{\rho} = \sum_{i} \frac{\partial \xi_{\rho}}{\partial q_{i}} \dot{\xi}_{\rho}. \qquad (12.5)$$

Using eqs. (9.15) and (9.18) the variation δS_i and the entropy flux \dot{S}_i are obtained from

$$T \,\delta S_j = \sum_i \mathscr{L}_{ji} \,\delta q_i, \qquad T \dot{S}_j = \sum_i \mathscr{L}_{ji} \dot{q}_i, \qquad (12.6)$$

where

$$\mathcal{L}_{ii}(q_{\nu}, \dot{q}_{\nu}, x_{l}) = \frac{\partial \mathcal{F}_{j}}{\partial q_{i}} - \sum_{k} \phi_{k} \frac{\partial M_{j}^{k}}{\partial q_{i}} + \int_{\Omega} g_{i}(x_{l}, x_{l}^{+}) \sum_{k} f_{\mu}^{k} \frac{\partial M_{\mu}^{k}}{\partial q_{i}} d\Omega^{+}.$$
(12.7)

The virtual dissipation is derived by substituting the values (12.4), (12.5) and (12.6) in expression (8.14) for $T\delta s^*$. This yields

$$T_0 \int_{\Omega} \delta s^* \, \mathrm{d}\Omega = \sum_i R_i \, \delta q_i, \qquad (12.8)$$

where the generalized dissipative force is

$$R_{i}(q_{\nu}, \dot{q}_{\nu}) = \int_{\Omega} \frac{T_{0}}{T} \left[\sum_{\rho} \mathscr{R}_{\rho} \frac{\partial \xi_{\rho}}{\partial q_{i}} + \sum_{k} \mathscr{R}_{j}^{Sk} \frac{\partial M_{j}^{k}}{\partial q_{i}} + \mathscr{R}_{j}^{ST} \mathscr{L}_{ji} \right] \mathrm{d}\Omega.$$
(12.9)

It is a function of q_i and their time derivatives \dot{q}_i . The generalized inertia forces as given by (11.2) are

$$I_i = \int_{\Omega} \sum_k a_j^k \frac{\partial M_j^k}{\partial q_i} \mathrm{d}\Omega.$$
(12.10)

The virtual work δW^{TG} of the gravitythermodynamic forces at the boundary A is obtained from (12.2). We write

$$\delta W^{\rm TG} = \sum_{i} Q_i \, \delta q_i, \qquad (12.11)$$

where Q_i is given by the boundary integral

$$Q_{i}(q_{\nu}, \dot{q}_{\nu}) = -\int_{A} \left[\sum_{k} \varphi_{k} \frac{\partial M_{j}^{k}}{\partial q_{i}} + \frac{\theta}{T} \mathscr{L}_{ji} \right] n_{j} \, \mathrm{d}A.$$
(12.12)

It is a function of q_i and \dot{q}_i . Its dependence on \dot{q}_i is due solely to the fact that f_j^k in the value of \mathscr{L}_{ji} depends on the set of flux variables \dot{M}_j^k .

Substituting expressions (12.3), (12.8), (12.10) and (12.11) in the variational principle (12.2) yields the lagrangian equations

$$I_i + \partial \mathcal{P} / \partial q_i + R_i = Q_i. \tag{12.13}$$

They govern the time evolution of the generalized coordinates describing the state of the reaction-diffusion system. They belong to the same general type as those governing the evolution of a large class of thermodynamic systems. The kinetics and dissipation are embodied in the term R_i which satisfies the inequality

$$\sum_{i} R_{i} \dot{q}_{i} \ge 0. \tag{12.14}$$

If inertia effects and gravity forces are negligible we put $I_i = 0$, $\mathcal{P} = V$. Also we have shown that in this case $f_i^k = 0$. Hence a simplified value of \mathcal{L}_{ii} is obtained as

$$\mathscr{L}_{ji} = \partial \mathscr{F}_{j} / \partial q_{i} - \sum_{k} \phi_{k} \, \partial M_{j}^{k} / \partial q_{i}, \qquad (12.15)$$

and the lagrangian equations become

$$\partial V/\partial q_i + R_i = Q_i. \tag{12.16}$$

Note that in many problems even when the inertia and body forces are not negligible the value of f_i^k remains small so that putting $f_i^k = 0$ as an approximation will be justified especially since the formulation is thereby considerably simplified. In this case Q_i does not depend on \dot{q}_i .

13. Completeness of macrophysical description by generalized coordinates – Resolution threshold of cells

The present treatment of thermodynamics emphasizes the description of a complex system as an assemblage of cells. From a fundamental viewpoint the size of these cells may be chosen extremely small remaining above a *resolution threshold* below which the statistical average definitions of temperature and entropy break down, and fluctuations enter into play. From the macroscopic viewpoint the system of cells is determined by a finite number of generalized coordinates, which as pointed out earlier [11] provide a complete physical description. As a consequence the corresponding lagrangian equations describe rigorously the evolution of the system. It is important to note that the use of a continuum model is an extrapolation beyond the validity of physical laws. While fashionable with the mathematician the continuum model which implies spatial derivatives and the concepts of measure is not more rigorous. Moreover it introduces spurious difficulties regarding completeness and measure which are irrelevant in the physical context. These remarks find confirmation in recent work by Woods [12] who has demonstrated lack of physical validity in the formalism of the current fashionable continuum mechanics and thermodynamics.

By contrast the lagrangian equations provide a rigorous universal mathematical framework for the evolution of macrophysical systems. A deep and unified insight is thus achieved which brings to light common types of behavior shared by all such systems.

Finally one should add that the principle of virtual dissipation provides directly either the field equations or the lagrangian equations from first principles using fundamental physical invariants and including boundary conditions. Great flexibility is thereby achieved in the choice of variables and coordinate systems without using tensor analysis. The procedure constitutes a complete reversal from standard methods which derive variational principles by requiring prior knowledge of the differential equations and boundary conditions for each individual case.

The lagrangian equations also provide the foundation for a large variety of finite element methods, where the state of the finite cells is described by generalized coordinates which may be fluence vectors at the grid vertices. The evolution of the system with a finite number of these coordinates is governed by the corresponding lagrangian equations obtained directly without prior knowledge of the field differential equations of the continuum.

14. Lagrangian equations with resolution threshold in configurational subspace. Internal relaxation, order disorder phenomena and quantum kinetics

The concept of threshold minimum size of cells as described above for physical three dimensional space may be extended to subspaces in the abstract multidimensional configurational thermodynamic space. For example we may consider the translational, rotational, and vibrational degrees of freedom of gas molecules as constituting distinct subspaces, which are then divided into cells above minimum threshold size each with their own entropy and temperature. The state of an assembly of such cells is then determined by mass and energy fluence between these fictitious cells. Following the same procedures as used for cells in physical space completely general lagrangian equations of evolution may be formulated including the exchanges between cells represented by internal fluence coordinates. In particular this approach is applicable to internal relaxation effect due to molecular rotation and vibration in gases.

This procedure with lagrangian equations and internal coordinates has been used to establish a general thermodynamic theory of relaxation and heredity in viscoelasticity [1].

The concept of subspace cells may be extended to quantum levels, with their own

temperature and entropy. The kinetics of exchanges obeyed by the fluence coordinates is then obtained from transition probabilities and quantum statistics.

The same procedures may also be used for order-disorder phenomena in metal alloys where the order-disorder state is described by internal fluence coordinates.

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