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VARIATIONAL-LAGRANGIAN THERMODYNAMICS OF EVOLUTION OF COLLECTIVE CHEMICAL SYSTEMS

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New concepts in thermodynamics are further extended and combined with a principle of virtual dissipation to provide general equations of evolution of collective open chemical systems. A new definition of the chemical potential is introduced, and some new expressions for the affinity are discussed. Application of the principle of virtual dissipation leads very simply to quite general continuum field equations for thermomolecular diffusion coupled to chemical reactions in a body force field. An energy flux theorem is established. Complementary scalar field equations and corresponding variational principles are derived along with a general mathematical formulation of chemical waves. The power of the variational lagrangian formulation of thermodynamics is well illustrated by a simple and very general treatment of active transport in biological membranes. It is indicated how this lagrangian approach originated by the author in 1954 constitutes the fundamental conceptual and analytical tool unifying nonequilibrium thermodynamics and classical mechanics.

1. Introduction

Our purpose here is two-fold. First to further develop the concepts and results obtained earlier for open chemical collective systems [1,2]. Second to apply to such systems the principle of virtual dissipation introduced by the author [3,4,23] as a completely general and fundamental tool to obtain field differential equations as well as lagrangian equations with generalized coordinates.

Sections 2 and 3 recall briefly the new concepts and results for open systems. A new definition of the chemical potential in section 4 provides a formulation of the new results in a form directly comparable with traditional procedures. This requires the introduction of two axioms.

An interesting expression for the affinity obtained by de Rycker [9,10] is discussed in section 5. His expression uses the traditional definition of the heat of reaction and mixture properties. It is shown to be equivalent to the new value derived by this writer [1, 2] which is expressed in terms of intrinsic heat of reaction and the physical properties of the indivual reactants.

Section 6, discusses reactions in a single cell open or closed. The relation of availability to the affinity is illustrated. For the open cell it is shown how the equations constitute a particular case of the general lagrangian form.

The general entropy balance equation is derived in section 7, along the lines developed earlier [14,15,17]. In section 8 the principle of virtual dissipation [3,4, 23] is rederived in the particular context of the present paper, and applied in section 9 to obtain field differential equations for a continuum with thermomolecular diffusion coupled to chemical reactions. The equations are completely general, including heat transferred and generated as well as the influence of the gravity field. As shown in section 10 they lead to an energy flux theorem and the classical result for the Joule–Thomson expansion.

The field equations as well as the variational principle may be expressed in complementary form with scalar variables as shown in section 11. This provides a formulation of chemical waves as a mathematical problem of characteristic values.

Section 12 treats the problem of active transport of biological membranes in completely general form in the context of linear thermodynamics. It constitutes an ideal illustration of the power of the lagrangian formulation with internal coordinates as already derived by the author in 1954–55 [3,21].

The last section contains a brief outline whose purpose is to acquaint the reader with the broader aspects of the variational-lagrangian formulation of non-equilibrium thermodynamics and its relation to areas of physics other than those treated here.

2. New chemical thermodynamics of open systems

A fundamentally new approach to the chemical thermodynamics of open systems has been developed earlier [1,2]. We shall briefly recall the key results.

We have considered a hypersystem constituted by the three cells, a primary cell C_P, a chemical equilibrium cell C_{ch} and a thermal well TW. A chemical reaction "producing" masses $dm_k = \nu_k\, d\xi$ may occur in C_P at the temperature T. The same reaction is in equilibrium at the temperature T_{eq} in C_{ch}. The thermal well TW is a large isothermal reservoir at the constant temperature T_0. We have introduced an "intrinsic" heat of reaction $\bar{h}_{pT}$ [1,2] defined so that $\bar{h}_{pT}\, d\xi$ is the heat absorbed by the cell C_P undergoing a reaction $d\xi$, at constant pressure and temperature, the "products" of reaction *being removed* as the reaction proceeds. Under these conditions the composition, pressure and temperature of the cell remain constant. The masses "produced" by the reaction are positive or negative, to correspond to substances created or disappearing. The traditionally defined heat of reaction is denoted h_{pT} and differs from $\bar{h}_{pT}$ by an additional heat of reversible mixing at constant pressure and temperature [1,2].

The cells $C_P + C_{ch}$ represent a collective system.

We denote by $\bar{h}_{pT}^{eq}$ the intrinsic heat of the equilibrium reaction in C_{ch} at constant pressure p_{eq} and constant temperature T_{eq}. We have derived the relation [1,2],

$$\bar{h}_{pT} - \bar{h}_{pT}^{eq} = \sum_k \nu_k \int_{p_{k\,eq} T_{eq}}^{p_k T} (dp'_k/\rho'_k + T'\, d\bar{s}_k). \qquad (2.1)$$

The pressure p_k is the pressure of the pure substance in equilibrium with the cell C_P through a semipermeable membrane. By *definition* we call p_k the partial pressure of the substance in C_P. The pressure $p_{k\,eq}$ is the partial pressure of the substance in C_{ch}. The integral is applied to the pure substance through an arbitrary path of variable pressure, density, temperature $p'_k \rho'_k T'$ and entropy differential $d\bar{s}_k$ per unit mass.

We have also shown that it is possible to define the increase of entropy dS_{ch} of the collective system due to a chemical reaction $d\xi$, without recourse to any statistical definition of entropy, *by using an equivalent reversible process in the hypersystem.* Following de Donder [8], $dS_{ch}/d\xi = A/T$ defines the affinity A. The value of A/T was found to be [1,2]

$$\frac{A}{T} = \frac{dS_{ch}}{d\xi} = \sum_k \nu_k \int_{p_{k\,eq} T_{eq}}^{p_k T} d\bar{s}_k + \frac{\bar{h}_{pT}^{eq}}{T_{eq}} - \frac{\bar{h}_{pT}}{T}. \qquad (2.2)$$

The collective potential $\mathcal{V}$ of $C_P + C_{ch}$ also called cell potential of C_P is

$$\mathcal{V} = \mathcal{U} - T_0 \mathcal{S}, \qquad (2.3)$$

where $\mathcal{U}$ is the collective energy of $C_P + C_{ch}$ and $\mathcal{S}$ its collective entropy. If a reaction $d\xi$ occurs in C_P as a rigid adiabatic closed cell, there is no change in internal energy ($d\mathcal{U} = 0$) and

$$d\mathcal{V} = -T_0\, d\mathcal{S}_{ch} = -(T_0/T)A\, d\xi. \qquad (2.4)$$

Note that these quantities are defined by means of a reversible process which produces the same change of state as the chemical reaction. Hence when the change occurs purely through a reaction, the work $d\mathcal{V}$ of the corresponding reversible process is lost.

Consider now the primary cell to be open, non-rigid, and non-adiabatic. In order to deal with this case we have added to the hypersystem supply cells C_{Sk} each containing a pure substance k and all at the same pressure and temperature $p_0 T_0$. The collective system is now constituted by the cells $C_P + C_{ch} + \Sigma_k C_{Sk}$ and the hypersystem is obtained by adding the thermal well TW. The cell C_P at the pressure p may now exhibit a change of volume dv. An amount of heat $T\, ds_T$ may be injected into it by means of a heat pump between C_P and TW. Masses dM^k extracted from C_{Sk} may also be injected into C_P by a reversible process which we have called a *thermobaric transfer.* The mass increases dM^k are in addition to those $dm_k = \nu_k\, d\xi$ due to the chemical reaction $d\xi$. The resulting increase of cell potential was found to be [1,2]

$$d\mathcal{V} = -(T_0/T)A\, d\xi - p\, dv + \sum_k \psi_k\, dM^k + \theta\, ds_T, \qquad (2.5)$$

where

$$\theta = T - T_0. \tag{2.6}$$

The coefficient ψ_k was called the *thermobaric potential.* Its value [1,2] is

$$\psi_k = \int_{p_0 T_0}^{p_k T} (\mathrm{d}p'_k/\rho'_k + \theta' \,\mathrm{d}s_k), \tag{2.7}$$

with

$$\theta' = T' - T_0. \tag{2.8}$$

It represents the work required to transfer a unit mass of substance reversibly from its supply cell C_{Sk} to the primary cell C_P. The term $\theta \,\mathrm{d}s_T$ in (2.5) is the work required by a heat pump extracting heat from TW at the temperature T_0 and injecting an amount of heat $T\,\mathrm{d}s_T$ into C_P at the temperature T. The change of collective entropy $\mathrm{d}\mathcal{S}$ associated with $\mathrm{d}\mathcal{V}_k$ is defined as the change of entropy of the collective system $C_P + C_{ch} + \Sigma_k C_{Sk}$. We have called it the collective entropy of C_P because it is completely determined by the state variables of C_P. Its value [1,2] is

$$\mathrm{d}\mathcal{S} = (A/T)\,\mathrm{d}\xi + \sum_k \bar{s}_k \,\mathrm{d}M^k + \mathrm{d}s_T, \tag{2.9}$$

where

$$\bar{s}_k = \int_{p_0 T_0}^{p_k T} \mathrm{d}\bar{s}_k, \tag{2.10}$$

was called the "*specific relative entropy*" of substance k in C_P. We note that p_k is the partial pressure of substance k in C_P as defined previously. It was also noted that $\mathrm{d}s_T$ is not a state variable of the primary cell. However we may eliminate $\mathrm{d}s_T$ between eqs. (2.5) and (2.9). This yields

$$\mathrm{d}\mathcal{V} = -A\,\mathrm{d}\xi - p\,\mathrm{d}v + \sum_k \phi_k \,\mathrm{d}M^k + \theta\, d\mathcal{S}, \tag{2.11}$$

where

$$\phi_k = \psi_k - \bar{s}_k \theta, \tag{2.12}$$

was derived earlier [1,2] and called the *convective potential.* In expression (2.11) all differentials are now state variables. If several reactions take place, expression (2.11) becomes

$$\mathrm{d}\mathcal{V} = -\sum_\rho A_\rho \,\mathrm{d}\xi_\rho - p\,\mathrm{d}v + \sum_k \phi_k \,\mathrm{d}M^k + \theta \,\mathrm{d}\mathcal{S}. \tag{2.13}$$

Hence

$$\partial\mathcal{V}/\partial\xi_\rho = -A_\rho, \quad \partial\mathcal{V}/\partial v = -p,$$
$$\partial\mathcal{V}/\partial M^k = \phi_k, \quad \partial\mathcal{V}/\partial\mathcal{S} = \theta. \tag{2.14}$$

As already pointed out [1,2] the convective potential (2.12) is completely defined within the hypersystem and *does not involve any undetermined constant.* It may be written in more explicit form by introducing the value (2.7) for ψ_k. We find

$$\phi_k = \bar{\epsilon}_k - T\bar{s}_k, \tag{2.15}$$

with

$$\bar{\epsilon}_k = \int_{p_0 T_0}^{p_k T} (\mathrm{d}p'_k/\rho'_k + T' \,\mathrm{d}\bar{s}_k). \tag{2.16}$$

Integration by parts yields

$$\bar{\epsilon}_k = p_k/\rho_k - p_0/\rho_0 + \bar{u}_k, \tag{2.17}$$

where

$$\bar{u}_k = -\int_{p_0 T_0}^{p_k T} [p'_k \,\mathrm{d}(1/\rho'_k) + T' \,\mathrm{d}\bar{s}_k], \tag{2.18}$$

is the increase of internal energy, per unit mass transferred, of the collective system $C_P + C_{Sk}$ and $\bar{\epsilon}_k$ is the associated increase of enthalpy of the same system. We may call $\bar{u}_k$ and $\bar{\epsilon}_k$ the *specific relative energy and enthalpy* of the substance in k. They are called relative with reference to the state of the substance in the supply cell.

The physical significance of the cell potential $\mathcal{V}$ should be clearly understood. We start from an initial state which is assumed to be the lowest state of energy attainable by the hypersystem. We then bring the cell C_P to a given state by thermobaric transfer and the use of heat pumps. The reversible work in this process defines the collective potential $\mathcal{V}$.

3. Generalized collective system and mixed collective potential

Instead of a single primary cell we may consider a large collection $\Sigma_\alpha C_{P\alpha}$ of such cells. We have defined [1–4] the collective potential of this system as

$$V = \sum_\alpha \mathcal{V}_\alpha, \tag{3.1}$$

where $\mathcal{V}_\alpha$ is the potential of each cell as defined by

(2.3). We may also write

$$V = U - T_0 S, \tag{3.2}$$

where U and S are the collective energy and entropy of the collective system

$$\mathrm{Sys} = \sum_\alpha \mathrm{C}_{\mathrm{P}\alpha} + \sum_k \mathrm{C}_{\mathrm{S}k} + \mathrm{C}_{\mathrm{ch}}. \tag{3.3}$$

The collective potential V is by definition the reversible work accomplished on the hypersystem Sys + TW in order to bring the system Sys to a given state starting from a suitably defined ground state for which we put $V = 0$. The entropy S of the system Sys is defined classically. Since the transformation in the hypersystem Sys + TW is reversible, its total entropy does not vary, hence the entropy S of Sys is simply the entropy lost by the thermal well TW. *Changes of state due to chemical reactions are included in this procedure since we have shown that we may produce the same change of state by an equivalent reversible process in the hypersystem.*

Consider a change of state in the system Sys alone without any involvement of TW, hence without any heat energy acquired or lost by Sys. If we neglect the kinetic energy, the work W done on Sys must be equal to its increase U of energy. Hence

$$U = W. \tag{3.4}$$

This relation is based on the first principle and is valid whether the transformation is reversible or not. With this value of U eq. (3.2) becomes

$$V = W - T_0 S. \tag{3.5}$$

Since no heat or matter is provided to the system Sys its entropy S represents the entropy produced in Sys. To indicate this we replace S by S^* and write

$$V = W - T_0 S^*. \tag{3.6}$$

For any change ΔV we may also write

$$-\Delta W = -\Delta V - T_0 \Delta S^*, \tag{3.7}$$

where $-\Delta W$ is the useful work provided by the system on its environment. By the second principle

$$\Delta S^* \geqslant 0 \tag{3.8}$$

and

$$-\Delta W \leqslant -\Delta V. \tag{3.9}$$

The useful work is therefore less or equal to the drop in value of V. Hence V is the maximum useful work available relative to the ground state, and $-\Delta V$ is the loss of "availability".

A generalization of these concepts is provided by considering that the work on the system is composed of three parts. The work $-p_a v$ of the atmospheric pressure p_a due to a change of volume v, the work $-G$ due to a force potential field such as gravity and the work W_e of the remaining external forces. Hence

$$W = -p_a v - G + W_e. \tag{3.10}$$

With this value eq. (3.6) becomes

$$\mathcal{P} = W_e - T_0 S^*, \tag{3.11}$$

where

$$\mathcal{P} = V + p_a v + G \tag{3.12}$$

was called a mixed collective potential [1,2,4] which embodies combined mechanical and thermodynamic properties. We may also consider $\mathcal{P}$ as a "generalized availability" of the collective system.

Mixed mechanical and thermodynamic stability criterion

If we take into account the kinetic energy $\mathcal{T}$, relation (3.4) must be replaced by

$$\mathcal{T} + U = W \tag{3.13}$$

and eq. (3.11) becomes

$$\mathcal{P} - W_e = -(T_0 S^* + \mathcal{T}). \tag{3.14}$$

If we consider a static equilibrium for which $\mathcal{T} = 0$, departure from this state requires a decrease of $\mathcal{P} - W_e$. Hence *if $\mathcal{P} - W_e$ is a minimum* this cannot happen and *the equilibrium is stable.* Note that this criterion is extremely general and involves, mechanical forces as well as thermal and chemical changes. Boundary and environmental conditions are included. For an open system we represent the environmental influence by considering as part of the collective system any number of cells which may exchange matter or heat with it. The potential of these cells is thus included in the total value of $\mathcal{P}$.

When dealing with a continuum in a domain Ω, the summation in (3.1) is replaced by a volume integral

$$V = \int_\Omega \mathcal{V}\, \mathrm{d}\Omega, \tag{3.15}$$

where $\mathcal{V}$ is the potential per unit volume. A particularly useful expression is obtained by considering a transformation in two steps. First at constant temperature T_0, in which case

$$F = U - T_0 S \tag{3.16}$$

is simply the classical Helmholtz free energy of the collective system. In the second step only the temperature is varied. Applying eq. (2.5) the collective potential becomes

$$V = F + \int_\Omega \mathrm{d}\Omega \int_{T_0}^{T} \theta \, \mathrm{d}s_\mathrm{T} = F + \int_\Omega \mathrm{d}\Omega \int_{T_0}^{T} (c\theta/T)\, \mathrm{d}T, \tag{3.17}$$

where c is the heat capacity per unit volume as a function of all state variables including the temperature. For quasi-isothermal transformations with small θ it becomes

$$V = F + \tfrac{1}{2} \int_\Omega (c\theta^2/T)\, \mathrm{d}\Omega. \tag{3.18}$$

The particular linearized case of a continuum under initial stress has been treated in detail [5,6].

4. New definition of the chemical potential

We may write (2.1) in differential form

$$\mathrm{d}\bar{h}_{pT} = \sum_k \nu_k \, \mathrm{d}\bar{\epsilon}_k, \tag{4.1}$$

which generalizes Kirchhoff's equation. We put

$$\bar{\epsilon}'_k = \int_{p_{k\,\mathrm{eq}} T_\mathrm{eq}}^{p_k T} \mathrm{d}\bar{\epsilon}_k, \quad \bar{s}'_k = \int_{p_{k\,\mathrm{eq}} T_\mathrm{eq}}^{p_k T} \mathrm{d}\bar{s}_k. \tag{4.2}$$

With these definitions eqs. (2.1) and (2.2) become

$$\bar{h}_{pT} - \bar{h}_{pT}^\mathrm{eq} = \sum_k \nu_k \bar{\epsilon}'_k, \tag{4.3}$$

$$A/T = \sum_k \nu_k \bar{s}'_k + \bar{h}_{pT}^\mathrm{eq}/T_\mathrm{eq} - \bar{h}_{pT}/T. \tag{4.4}$$

Elimination of $\bar{h}_{pT}$ between eqs. (4.3) and (4.4) yields

$$A = -\sum_k \nu_k \phi'_k + (T/T_\mathrm{eq} - 1)\bar{h}_{pT}^\mathrm{eq}, \tag{4.5}$$

where

$$\phi'_k = \bar{\epsilon}'_k - T\bar{s}'_k. \tag{4.6}$$

The quantities ϕ'_k, $\bar{\epsilon}'_k$ and $\bar{s}'_k$ are respectively the convective potential, specific enthalpy and entropy defined relative to the chemical equilibrium state as lower limit of integration. Eq. (4.5) is completely rigorous and based exclusively on the axioms of classical thermodynamics. It requires the knowledge of the temperature T_eq and intrinsic heat of reaction $\bar{h}_{pT}^\mathrm{eq}$ at chemical equilibrium.

In order to express the affinity in the traditional form in terms of chemical potentials we must introduce some new axioms:

(a) We integrate (4.1) with the absolute zero as the lower limit and write

$$\bar{h}_{pT} = \sum_k \nu_k \left[\int_0^{p_k T} \mathrm{d}\bar{\epsilon}_k + \bar{\epsilon}_k(0) \right]. \tag{4.7}$$

The value of the integral is obtained by extrapolating the experimental data to the absolute zero. It is assumed that the constant of integration may be written in the form $\Sigma_k \nu_k \bar{\epsilon}_k(0)$ where $\bar{\epsilon}_k(0)$ are constants characteristic of each substance and independent of the nature of the chemical reaction.

(b) It is assumed that

$$\bar{h}_{pT}^\mathrm{eq}/T_\mathrm{eq} = \sum_k \nu_k \left[\int_0^{p_{k\mathrm{eq}} T_\mathrm{eq}} \mathrm{d}\bar{s}_k + \bar{s}_k(0) \right]. \tag{4.8}$$

Again the value of the integral is obtained by extrapolation to the absolute zero and $\bar{s}_k(0)$ are constants characteristic of each substance and independent of the nature of the chemical reaction. Putting $\bar{s}_k(0) = 0$ amounts to assuming the validity of Nernst's theorem.

Substitution of expressions (4.7) and (4.8) into the value (4.5) yields the affinity in the traditional form

$$A = -\sum_k \nu_k \mu_k, \tag{4.9}$$

where

$$\mu_k = \bar{\epsilon}_k^\mathrm{abs} - T\bar{s}_k^\mathrm{abs}, \tag{4.10}$$

and

$$\bar{\epsilon}_k^\mathrm{abs} = \int_0^{p_k T} \mathrm{d}\bar{\epsilon}_k + \bar{\epsilon}_k(0), \quad \bar{s}_k^\mathrm{abs} = \int_0^{p_k T} \mathrm{d}\bar{s}_k + \bar{s}_k(0). \tag{4.11}$$

Eq. (4.10) provides a new and completely general definition of the chemical potential μ_k. Its use is only required for chemical reactions if we do not know $\bar{h}_{pT}^\mathrm{eq}$ and T_eq.

4.1. Relation to the traditional formalism of chemical potentials

If we introduce the value (4.9) of the affinity in the differential (2.11) we obtain

$$\mathrm{d}\mathcal{V} = \sum_k \nu_k \mu_k \,\mathrm{d}\xi - p\,\mathrm{d}v + \sum_k \phi_k \,\mathrm{d}M^k + \theta\,\mathrm{d}\mathcal{S}. \tag{4.12}$$

The increase of mass of each species k is

$$\mathrm{d}m_k = \mathrm{d}M^k + \nu_k\,\mathrm{d}\xi, \tag{4.13}$$

where the first term is due to convection and the second due to the chemical reaction. Also by definition the convective potential is

$$\phi_k = \mu_k - \mu_{0k}, \tag{4.14}$$

where μ_{0k} is the chemical potential of the pure substance in the supply cell. Hence the differential (4.12) and $\mathrm{d}\mathcal{U} = \mathrm{d}\mathcal{V} + T_0\,\mathrm{d}\mathcal{S}$ become

$$\begin{aligned} \mathrm{d}\mathcal{V} &= \mathrm{d}\mathcal{V}^{\mathrm{tr}} - \sum_k \mu_{0k}\,\mathrm{d}M^k, \\ \mathrm{d}\mathcal{U} &= \mathrm{d}\mathcal{U}^{\mathrm{tr}} - \sum_k \mu_{0k}\,\mathrm{d}M^k, \end{aligned} \tag{4.15}$$

where

$$\begin{aligned} \mathrm{d}\mathcal{V}^{\mathrm{tr}} &= \sum_k \mu_k\,\mathrm{d}m_k - p\,\mathrm{d}v + \theta\,\mathrm{d}\mathcal{S}, \\ \mathrm{d}\mathcal{U}^{\mathrm{tr}} &= \sum_k \mu_k\,\mathrm{d}m_k - p\,\mathrm{d}v + T\,\mathrm{d}\mathcal{S}, \end{aligned} \tag{4.16}$$

are in traditional form. Note however that while the form is the same the definition of the chemical potential μ_k is obtained differently, and in addition $\mathcal{S}$ is a collective entropy.

Except for the difference of definition of the variables, $\mathrm{d}\mathcal{U}^{\mathrm{tr}}$ is expressed in the traditional form introduced by Gibbs [7].

If we deal with a single primary cell the values (4.15) are not equal to the traditional form (4.16). However it may be valid if we consider a collection of primary cells $C_{P\alpha}$. For each cell we write

$$\begin{aligned} \mathrm{d}\mathcal{V}_\alpha &= \mathrm{d}\mathcal{V}^{\mathrm{tr}}_\alpha - \sum_k \mu_{0k}\,\mathrm{d}M^{k\alpha}, \\ \mathrm{d}\mathcal{U}_\alpha &= \mathrm{d}\mathcal{U}^{\mathrm{tr}}_\alpha - \sum_k \mu_{0k}\,\mathrm{d}M^{k\alpha}. \end{aligned} \tag{4.17}$$

The differentials of the collective potential and energy of the whole system are

$$\begin{aligned} \mathrm{d}V &= \sum_\alpha \mathrm{d}\mathcal{V}^{\mathrm{tr}}_\alpha - \sum_{k\alpha} \mu_{0k}\,\mathrm{d}M^{k\alpha}, \\ \mathrm{d}U &= \sum_\alpha \mathrm{d}\mathcal{U}^{\mathrm{tr}}_\alpha - \sum_{k\alpha} \mu_{0k}\,\mathrm{d}M^{k\alpha}. \end{aligned} \tag{4.18}$$

If the exchange of matter occurs only between primary cells we may write

$$\sum_\alpha \mathrm{d}M^{k\alpha} = 0 \tag{4.19}$$

and the values (4.18) are reduced to the traditional form

$$\begin{aligned} \mathrm{d}V &= \sum_\alpha \mathrm{d}\mathcal{V}^{\mathrm{tr}}_\alpha, \\ \mathrm{d}U &= \sum_\alpha \mathrm{d}\mathcal{U}^{\mathrm{tr}}_\alpha. \end{aligned} \tag{4.20}$$

Hence the traditional form of these expressions applies only to closed systems under the condition stated.

5. Evaluation of the affinity by de Rycker's procedure

A very simple evaluation of the affinity was proposed by de Rycker [9,10] based also on the knowledge of the chemical equilibrium state. Consider a closed primary cell to go through a closed cycle *abcda* at constant pressure p with variable volume and variable reaction coordinate ξ. Along *ab* the reaction is frozen and the value $\xi = \xi_1$ is constant, while the temperature varies from T to the chemical equilibrium temperature T_{eq}. From b to c an infinitesimal reaction $\mathrm{d}\xi$ occurs at the equilibrium temperature T_{eq}. From c to d the reaction is again frozen at a constant value $\xi_2 = \xi_1 + \mathrm{d}\xi$ while the temperature is decreased from T_{eq} to T. Finally along *da* the value of ξ returns to ξ_1 while the temperature T is constant. The closed cycle returns the cell to its initial state. By integration of equation (2.9) along this cycle (with $\mathrm{d}M^k = 0$ since the cell is closed) we obtain

$$\oint_{abcda} [(A/T)\,\mathrm{d}\xi + \mathrm{d}s_{\mathrm{T}}] = 0. \tag{5.1}$$

Since $A = 0$ along the chemical equilibrium branch *bc*, relation (5.1) leads to

$$-\frac{A}{T}\,\mathrm{d}\xi + \int_a^b \mathrm{d}s_{\mathrm{T}} + \int_c^d \mathrm{d}s_{\mathrm{T}} + \left(\frac{h^{\mathrm{eq}}_{pT}}{T_{\mathrm{eq}}} - \frac{h_{pT}}{T}\right)\mathrm{d}\xi = 0, \tag{5.2}$$

where h_{pT} is the heat of reaction at constant pressure and temperature according to the traditional definition which includes the heat of mixing while h^{eq}_{pT} denotes the value of h_{pT} at chemical equilibrium. Also if $c_p\,(T,\xi)$ denotes the heat capacity of the cell at constant pressure we may write

$$\int_a^b \mathrm{d}s_{\mathrm{T}} + \int_c^d \mathrm{d}s_{\mathrm{T}} = -\mathrm{d}\xi \int_T^{T_{\mathrm{eq}}} \frac{1}{T'}\,\frac{\partial c_p(T',\xi)}{\partial\xi}\,\mathrm{d}T'. \tag{5.3}$$

Hence (5.2) becomes

$$\frac{A}{T} = \frac{h^{\mathrm{eq}}_{pT}}{T_{\mathrm{eq}}} - \frac{h_{pT}}{T} - \int_T^{T_{\mathrm{eq}}} \frac{1}{T'}\,\frac{\partial c_p(T',\xi)}{\partial\xi}\,\mathrm{d}T'. \tag{5.4}$$

Through the closed cycle there is no increase of cell energy, moreover the work done by the constant pressure on the cell is zero, since the volume returns to its initial value. Hence the total heat energy absorbed is zero, i.e.

$$h^{\mathrm{eq}}_{pT} - h_{pT} - \int_T^{T_{\mathrm{eq}}} \frac{\partial c_p}{\partial\xi}\,\mathrm{d}T' = 0. \tag{5.5}$$

Elimination of h_{pT} between eqs. (5.4) and (5.5) yields

$$A = \left(\frac{T}{T_{\mathrm{eq}}} - 1\right) h^{\mathrm{eq}}_{pT} + \int_T^{T_{\mathrm{eq}}} \left(1 - \frac{T}{T'}\right) \frac{\partial c_p}{\partial\xi}\,\mathrm{d}T'. \tag{5.6}$$

This is the value of the affinity derived by de Rycker [9,10]. He has also verified that in the temperature range of a large number of industrial problems we may neglect the last term in (5.6). For these cases he obtains the remarkably accurate simple approximation

$$A = (T - T_{\mathrm{eq}})h^{\mathrm{eq}}_{pT}/T_{\mathrm{eq}}, \tag{5.7}$$

which plots as a straight line versus T.

It is of interest to point out that eq. (5.1) applied along the branch ad yields the classical relation (see ref. [11, p. 48])

$$A = T(\partial\mathcal{S}/\partial\xi)_{pT} - h_{pT}. \tag{5.8}$$

Similar results for the case of constant volume instead of constant pressure are easily obtained by the same procedure. We derive

$$A = (T - T_{\mathrm{eq}})\,h^{\mathrm{eq}}_{vT}/T_{\mathrm{eq}}, \tag{5.9}$$

and

$$A = T(\partial\mathcal{S}/\partial\xi)_{vT} - h_{vT}, \tag{5.10}$$

where h_{vT} is the traditional heat of reaction at constant volume and temperature and h^{eq}_{vT} is its value at chemical equilibrium. Eq. (5.10) is also a classical relation (see ref. [11, p. 48]).

Note that h^{eq}_{pT} and T_{eq} are functions of all state variables except the temperature T. Hence they are functions of the chemical coordinate ξ, the volume v, and the masses M^k convected into the cell.

We will show that the affinity A derived from eqs. (5.4) and (5.5) by de Rycker's procedure is compatible with the value derived from eqs. (2.1) and (2.2). Consider a cell $\mathrm{C_P}$ without chemical reaction at the temperature T_{eq}. We go through a cycle at constant pressure p where the cell $\mathrm{C_P}$ is first brought to the temperature T. A mass $\mathrm{d}m_k$ is then extracted reversibly from $\mathrm{C_P}$ at the partial pressure p_k and constant temperature T. After this extraction the cell $\mathrm{C_P}$ is brought back to the temperature T_{eq}. The mass $\mathrm{d}m_k$ is also brought back to the temperature T_{eq} and partial pressure $p_{k\,\mathrm{eq}}$ and injected back reversibly at constant temperature T_{eq} into the cell. Through this cycle the system has not changed. There is no volume change, and no change of internal energy. Hence

$$\mathrm{d}m_k \int_{T_{\mathrm{eq}}}^{T} \frac{\partial c_p}{\partial m_k}\,\mathrm{d}T' + \mathrm{d}m_k \int_{p_kT}^{p_{k\,\mathrm{eq}}T_{\mathrm{eq}}} \mathrm{d}\bar{e}_k$$

$$- h^k_{pT}\,\mathrm{d}m_k + h^{k\,\mathrm{eq}}_{pT}\,\mathrm{d}m_k = 0, \tag{5.11}$$

where h^k_{pT} is the heat of mixing for substance k at constant pressure and temperature T as defined earlier [1,2] while $h^{k\,\mathrm{eq}}_{pT}$ is the similar quantity at the equilibrium temperature T_{eq}. We derive

$$\int_{T_{\mathrm{eq}}}^{T} \frac{\partial c_p}{\partial m_k}\,\mathrm{d}T' = \bar{e}'_k + h^k_{pT} - h^{k\,\mathrm{eq}}_{pT}. \tag{5.12}$$

In the same way expressing no change of entropy

$$\int_{T_{\mathrm{eq}}}^{T} \frac{1}{T'}\frac{\partial c_p}{\partial m_k}\,\mathrm{d}T' = \bar{s}'_k + \frac{h^k_{pT}}{T} - \frac{h^{k\,\mathrm{eq}}_{pT}}{T_{\mathrm{eq}}}. \tag{5.13}$$

We may also write

$$\sum_k \nu_k \frac{\partial c_p}{\partial m_k} = \sum_k \frac{\partial m_k}{\partial\xi}\,\frac{\partial c_p}{\partial m_k} = \frac{\partial c_p}{\partial\xi}, \tag{5.14}$$

as well as the following relations derived in [1,2]

$$h_{pT} = \bar{h}_{pT} + \sum_k \nu_k h^k_{pT}, \quad h^{\mathrm{eq}}_{pT} = \bar{h}^{\mathrm{eq}}_{pT} + \sum_k \nu_k h^{k\,\mathrm{eq}}_{pT}. \tag{5.15}$$

Using the values (5.12)–(5.15) in eqs. (5.4) and (5.5) of de Rycker we obtain eqs. (2.1) and (2.2) of this writer.

6. Chemical reaction in a closed or open cell. Lagrangian formulation

We shall consider first a closed adiabatic primary cell. Its volume v may vary and a single reaction ξ may take place in the cell. The cell potential

$$\mathcal{V} = \mathcal{V}(v, \xi) \tag{6.1}$$

is a function of its volume v and the reaction coordinate ξ. Since the cell is closed and adiabatic we put

$$\mathrm{d}M^k = \mathrm{d}s_{\mathrm{T}} = 0 \tag{6.2}$$

in eq. (2.5). Hence

$$\mathrm{d}\mathcal{V} = -(T_0/T)A\,\mathrm{d}\xi - p\,\mathrm{d}v, \tag{6.3}$$

and

$$\partial\mathcal{V}/\partial v = -p, \qquad \partial\mathcal{V}/\partial\xi = -(T_0/T)A. \tag{6.4}$$

Since $\mathcal{V}$ is defined by means of A the second equations constitutes an identity, so that eqs. (6.4) are not sufficient to determine the two unknowns v and ξ as functions of the pressure p. The additional equation is provided by chemical kinetics where the rate of reaction $\dot{\xi}$ is given in terms of ξ and v. We write

$$\dot{\xi} = f(\xi, v). \tag{6.5}$$

Eqs. (6.4) and (6.5) may be given in a different form which is a particular case of a more general formulation, by evaluating the affinity

$$A = A(\xi, v) \tag{6.6}$$

as a function of ξ and v. We then eliminate ξ between eqs. (6.5) and (6.6). This yields

$$A = R(\dot{\xi}, v). \tag{6.7}$$

We note the fundamental property

$$\dot{\xi}R(\dot{\xi}, v) \geqslant 0. \tag{6.8}$$

Eqs. (6.4) then take the form

$$\partial\mathcal{V}/\partial v = -p, \qquad \partial\mathcal{V}/\partial\xi = -(T_0/T)R(\dot{\xi}, v). \tag{6.9}$$

Since the temperature T may be evaluated as a function of ξ and v eqs. (6.9) govern the two unknowns ξ and v. If v is given as a function of time then the second equation contains the single unknown ξ. As an illustration we plot $\mathcal{V}$ as a function of ξ for various values of the volume v (fig. 1).

Consider the curves v_1 = Const and v_2 = Const with $v_1 < v_2$. These curves show a minimum on the line $ab(A = 0)$ which corresponds to chemical equilibrium. If we decrease the volume slowly, $\mathcal{V}$ and ξ will vary along this line ab. Since $A = 0$ along this line eq. (6.3) yields

$$\mathcal{V}_a - \mathcal{V}_b = \int_a^b p\,\mathrm{d}v. \tag{6.10}$$

Hence the lost availability $\mathcal{V}_a - \mathcal{V}_b$ is exactly equal to the work provided by the cell. On the other hand if the change of volume is accomplished very fast, we move along the line ac with $\mathrm{d}\xi = 0$. Hence

$$\mathcal{V}_a - \mathcal{V}_c = \int_a^c p\,\mathrm{d}v. \tag{6.11}$$

The loss of availability $\mathcal{V}_a - \mathcal{V}_c$ along this line is also equal to the work provided but its value is smaller than (6.10). If the reaction is then allowed to proceed at constant volume v toward equilibrium b we obtain from (6.3)

$$\mathcal{V}_c - \mathcal{V}_b = \int_b^c (T_0/T)A\,\mathrm{d}\xi. \tag{6.12}$$

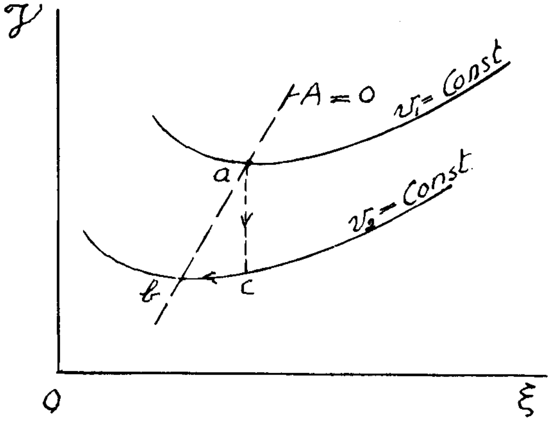

Fig. 1. Plot of the cell potential $\mathcal{V}$ as a function of v and ξ.

Hence there is further loss of availability $\mathcal{V}_c - \mathcal{V}_b$ with no work accomplished.

Consider now the general case of an open non-adiabatic cell where several reactions ξ_ρ may take place. We may evaluate the affinity

$$A = A(\xi_\rho, v, M^k, \mathcal{S}) \tag{6.13}$$

as a function of the reaction coordinates ξ_ρ the volume v the masses M^k injected and the entropy $\mathcal{S}$. On the other hand from chemical kinetics we write the reaction rates as

$$\dot{\xi}_\rho = f_\rho(\xi_\sigma, v, M^k, \mathcal{S}). \tag{6.14}$$

We then eliminate ξ_ρ between eqs. (6.13) and (6.14). This yields

$$A_\rho = R_\rho(\dot{\xi}_\sigma, v, M^k, \mathcal{S}). \tag{6.15}$$

Again the functions R_ρ obey the fundamental inequality

$$\sum_\rho \dot{\xi}_\rho R_\rho \geqslant 0. \tag{6.16}$$

With these functions R_ρ, eqs. (2.14) are written

$$\begin{aligned} &\partial \mathcal{V}/\partial v = -p, && \partial \mathcal{V}/\partial M^k = \phi_k, \\ &\partial \mathcal{V}/\partial \mathcal{S} = \theta, && \partial \mathcal{V}/\partial \xi_\rho = -R_\rho. \end{aligned} \tag{6.17}$$

If $\mathcal{V}$ has been evaluated as a function of v, M^k, $\mathcal{S}$ and ξ_ρ eqs. (6.17) constitute a complete system for the time evolution of these variables, for given values p, θ and ϕ_k.

We may write these equations in the fundamental lagrangian form introduced by the author in irreversible thermodynamics [3,4,21]. If we denote the variables v, M^k and $\mathcal{S}$ by q_i and the corresponding variables $-p$, ϕ_k and θ by Q_i we may write eqs. (6.17) in the abreviated form

$$\partial \mathcal{V}/\partial Q_i = Q_i, \qquad \partial \mathcal{V}/\partial \xi_\rho + R_\rho = 0. \tag{6.18}$$

In the author's general lagrangian thermodynamics Q_i plays the role of generalized driving forces and ξ_ρ that of internal coordinates [3,4,21].

These equations also govern the evolution of the system if any three of the six variables v, M^k, $\mathcal{S}$, p, ϕ_k and θ are prescribed functions of time. If the system is weakly irreversible, i.e. if during its evolution the system remains close to an equilibrium state we may apply Onsager's principle [12,13] and write

$$A_\rho = R_\rho = \partial D/\partial \dot{\xi}_\rho \tag{6.19}$$

where

$$D = \tfrac{1}{2} B_{\rho\sigma} \dot{\xi}_\rho \dot{\xi}_\sigma, \tag{6.20}$$

is a quadratic form in $\dot{\xi}_\rho$ whose coefficients

$$B_{\rho\sigma} = B_{\sigma\rho} = B_{\rho\sigma}(q_i, \xi_\rho), \tag{6.21}$$

are functions of the state variable q_i, ξ_ρ. Eqs. (6.18) become

$$\partial \mathcal{V}/\partial q_i = Q_i, \qquad \partial \mathcal{V}/\partial \xi_\rho + \partial D/\partial \dot{\xi}_\rho = 0. \tag{6.22}$$

These equations are similar to those which govern nonlinear viscoelasticity [4] where Q_i are applied stresses and ξ_ρ are internal coordinates. [See also eqs. (13.3) below.]

7. Fundamental entropy balance in a continuum with entropy production, diffusion and convection

In the foregoing development we considered finite cells. We shall now apply the newly developed methods and concepts to a continuum. The collective entropy of the continuum is written

$$S = \int_\Omega \mathcal{S}\, \mathrm{d}\Omega, \tag{7.1}$$

where the volume integral is extended to a domain Ω and $\mathcal{S}\, \mathrm{d}\Omega$ represents the collective entropy of the elementary cell of volume $\mathrm{d}\Omega = \mathrm{d}x_1\, \mathrm{d}x_2\, \mathrm{d}x_3$. Hence $\mathcal{S}$ is the local entropy per unit volume. It is important to note that eq. (2.9) for $\mathrm{d}\,\mathcal{S}$ is not valid here because it assumes that there is no gradient of $\bar{s}$ across the cell. A new entropy balance equation was derived [14] and developed subsequently [15]. The procedure is to write the rate of increase $\dot{S}$ of the total entropy S as (the dot represents a time differential)

$$\dot{S} = \int_\Omega (\dot{s}^*_{\mathrm{NT}} + \dot{h}/T)\, \mathrm{d}\Omega - \sum_{ik} \int_A \bar{s}_k \dot{M}^k_i n_i\, \mathrm{d}A. \tag{7.2}$$

In this equation $\dot{s}^*_{\mathrm{NT}}$ is the rate of entropy production per unit volume which is not due to thermal diffusion, and $\dot{h}$ is the rate of energy supplied to a unit volume by thermal conduction at the temperature T. The second integral is evaluated at the boundary A of Ω with a unit normal n_i and represents the entropy supplied to Ω by convection. The rate of mass flow of substance k per unit area is $\dot{M}_i^k$ and $\bar{s}_k$ is the specific relative entropy of a unit mass of the substance in equilibrium with the medium through a semipermeable membrane at the point considered.

Conservation of energy requires

$$\dot{h} = -\sum_i \partial \dot{H}_i / \partial x_i, \tag{7.3}$$

where $\dot{H}_i$ is the rate of heat flow per unit area. The surface integral in (7.2) may be written as a volume integral. After substitution of the value (7.3) for $\dot{h}$ eq. (7.2) may be written

$$\dot{S} = \int_\Omega \left(\dot{s}^* - \sum_i \partial \dot{S}_i / \partial x_i \right) \mathrm{d}\Omega, \tag{7.4}$$

where

$$\dot{S}_i = \sum_k \bar{s}_k \dot{M}_i^k + \dot{S}_i^{\mathrm{T}}, \quad \dot{S}_i^{\mathrm{T}} = \dot{H}_i / T,$$
$$\dot{s}^* = \dot{s}^*_{\mathrm{NT}} - \sum_i \frac{\dot{H}_i}{T^2} \frac{\partial T}{\partial x_i}. \tag{7.5}$$

The vector $\dot{S}_i$ is the total rate of entropy flow, $\dot{S}_i^{\mathrm{T}}$ the rate of entropy flow by conduction and $\dot{s}^*$ the total rate of entropy production per unit volume including the entropy produced by thermal flow. From (7.4) the rate of entropy increase per unit volume is

$$\dot{\mathcal{S}} = \dot{s}^* - \sum_i \partial \dot{S}_i / \partial x_i. \tag{7.6}$$

This is the basic entropy balance equation, generalizing the result of Meixner [16] for thermal flow.

Integration with respect to time yields

$$\mathcal{S} = s^* + s, \tag{7.7}$$

where

$$s = -\sum_i \partial S_i / \partial x_i, \tag{7.8}$$

is the entropy supplied and S_i is a vector introduced earlier as the entropy displacement [4,14,15]. Note that the mass displacement vector M_i^k also satisfies a similar holonomic constraint

$$M^k = -\sum_i \partial M_i^k / \partial x_i, \tag{7.9}$$

where M^k is the mass acquired by convection per unit volume.

In the presence of chemical reactions the conservation of mass condition is written

$$m_k = M^k + \sum_\rho \nu_{k\rho} \xi_\rho = -\sum_i \partial M_i^k / \partial x_i + \sum_\rho \nu_{k\rho} \xi_\rho, \tag{7.10}$$

where m_k is the mass increase of substance k per unit volume and ξ_ρ are reaction coordinates.

8. Principle of virtual dissipation

Let us apply eq. (3.13) to a rigid continuum Ω. We assume no volume change, no external work except that of the potential $G(v = W_{\mathrm{e}} = 0)$ and negligible inertia forces. We write

$$V = \int_\Omega \mathcal{V} \mathrm{d}\Omega, \quad S^* = \int_\Omega s^* \mathrm{d}\Omega, \quad G = \int_\Omega \rho \mathcal{G} \mathrm{d}\Omega, \tag{8.1}$$

where

$$\mathcal{V} = \mathcal{V}(\xi_\rho, M^k, \mathcal{S}), \tag{8.2}$$

is the potential per unit volume, $\mathcal{G}$ the scalar potential of body forces per unit mass and ρ the mass per unit volume. Eq. (3.11) becomes

$$\frac{\mathrm{d}}{\mathrm{d}t} \int_\Omega (\mathcal{V} + \rho \mathcal{G} + T_0 s^*) \mathrm{d}\Omega = 0. \tag{8.3}$$

This equation is applicable assuming no heat or mass flows through the boundary, hence the normal components of S_i and M_i^k vanish at the boundary. The equation is also valid for arbitrary variations $\delta\xi_\rho$, δS_i, δM_i^k and δs^* which satisfy the holonomic constraints (7.8) and (7.9) hence

$$\delta s = -\sum_i \partial\, \delta S_i / \partial x_i,$$
$$\delta M^k = -\sum_i \partial\, \delta M_i^k / \partial x_i. \tag{8.4}$$

We also satisfy

$$\delta\rho = -\sum_k \delta M^k = -\sum_{ik} \partial \delta M_i^k / \partial x_i. \tag{8.5}$$

In variational form eq. (8.3) becomes

$$\int_\Omega (\delta \mathcal{V} + \mathcal{G} \delta\rho + T_0 \delta s^*) \mathrm{d}\Omega = 0. \tag{8.6}$$

From (7.7) we derive $\delta\mathcal{S} = \delta s + \delta s^*$. Hence

$$\delta\mathcal{V} = \delta_{\mathrm{R}}\mathcal{V} + (\partial\mathcal{V}/\partial\mathcal{S})\delta s^*, \tag{8.7}$$

where

$$\delta_{\mathrm{R}}\mathcal{V} = \sum_k \frac{\partial\mathcal{V}}{\partial M^k}\delta M^k + \frac{\partial\mathcal{V}}{\partial\mathcal{S}}\delta s + \sum_\rho \frac{\partial\mathcal{V}}{\partial\xi_\rho}\delta\xi_\rho, \tag{8.8}$$

is a restricted variation obtained by not varying s^* in $\mathcal{S}$. On the other hand, from eqs. (2.14) we write

$$\partial\mathcal{V}/\partial\mathcal{S} = \theta = T - T_0. \tag{8.9}$$

Substitution of the value (8.7) of $\delta\mathcal{V}$ into (8.6) yields

$$\int_\Omega (\delta_{\mathrm{R}}\mathcal{V} + \mathcal{G}\delta\rho + T\delta s^*)\,\mathrm{d}\Omega = 0. \tag{8.10}$$

This relation expresses the principle of virtual dissipation [4,23] as applied to the assumed continuous system. For simplicity we have neglected the inertia forces. These have been included in the general formulation [4,23] and applied to thermomolecular diffusion [15,17].

The term $T\delta s^*$ is what we have called the *virtual dissipation.* Its evaluation is obtained as follows. We may write

$$T\dot{s}^* = \sum_\rho \mathcal{R}_\rho\dot{\xi}_\rho + 2\mathcal{D}, \tag{8.11}$$

where $(1/T)\Sigma_\rho\mathcal{R}_\rho\dot{\xi}_\rho$ and $(2/T)\mathcal{D}$ are the rates of entropy production respectively by the chemical reactions and the thermomolecular diffusion. The coefficients

$$\mathcal{R}_\rho = \mathcal{R}_\rho(\dot{\xi}_\sigma, M^k, \mathcal{S}) \tag{8.12}$$

are defined as in (6.7) and in the present case are functions of the reactions rates, the masses M^k injected per unit volume, and $\mathcal{S}$.

The dissipation due to thermomolecular diffusion is expressed by the dissipation function

$$\mathcal{D} = \frac{1}{2}\sum_{lkij} C_{ij}^{lk}\dot{M}_i^l\dot{M}_j^k + \sum_{kij} C_{ij}^k\dot{M}_i^k\dot{S}_j + \tfrac{1}{2}T\sum_{ij}\lambda_{ij}\dot{S}_i\dot{S}_j. \tag{8.13}$$

It is a quadratic form in the rate variables and thereby embodies the Onsager principle [12,13] for thermomolecular diffusion. The last term which contains the thermal resistivity λ_{ij} expresses the dissipation for the case of pure thermal diffusion ($\dot{M}_i^k = 0$).

The coefficients C_{ij}^{lk} C_{ij}^k and λ_{ij} are functions of the local state variables $\xi_\rho M^k$ and $\mathcal{S}$. The coefficient C_{ij}^k represents a coupling term between mass flow and thermal flow which includes convection. This is discussed in more detail elsewhere [15,17].

With these definitions the virtual dissipation is expressed by

$$T\delta s^* = \sum_\rho \mathcal{R}_\rho\delta\xi_\rho + \sum_{ki}\frac{\partial\mathcal{D}}{\partial\dot{M}_i^k}\delta M_i^k + \sum_i \frac{\partial\mathcal{D}}{\partial\dot{S}_i}\delta S_i. \tag{8.14}$$

9. Variational derivation of field equations for thermomolecular diffusion and coupled chemical reactions

The unknown field variables to be determined are the reaction coordinate ξ_ρ the vectors M_i^k and S_i and the entropy produced s^*. We shall apply the principle of virtual dissipation (8.10). With the value (8.8) for $\delta_{\mathrm{R}}\mathcal{V}$ and (8.14) for $T\delta s^*$ we may write

$$\begin{aligned}\int_\Omega\Big[&\sum_k \frac{\partial\mathcal{V}}{\partial M^k}\delta M^k + \frac{\partial\mathcal{V}}{\partial\mathcal{S}}\delta s + \sum_\rho \frac{\partial\mathcal{V}}{\partial\xi_\rho}\delta\xi_\rho + \mathcal{G}\delta\rho \\ &+ \sum_\rho \mathcal{R}_\rho\delta\xi_\rho + \sum_{ki}\frac{\partial\mathcal{D}}{\partial\dot{M}_i^k}\delta M_i^k + \sum_i \frac{\partial\mathcal{D}}{\partial\dot{S}_i}\delta S_i\Big]\mathrm{d}\Omega = 0.\end{aligned} \tag{9.1}$$

We introduce the values (8.4) and (8.5) for the variations $\delta s\,\delta M^k$ and $\delta\rho$ and integrate by parts. Since the variations $\delta M_i^k\,\delta S_i\,\delta\xi_\rho$ are arbitrary, we cancel the coefficients of these variations and obtain

$$\begin{gathered}\frac{\partial}{\partial x_i}\left(\frac{\partial\mathcal{V}}{\partial M^k} + \mathcal{G}\right) + \frac{\partial\mathcal{D}}{\partial\dot{M}_i^k} = 0, \\ \frac{\partial}{\partial x_i}\left(\frac{\partial\mathcal{V}}{\partial\mathcal{S}}\right) + \frac{\partial\mathcal{D}}{\partial\dot{S}_i} = 0, \\ \partial\mathcal{V}/\partial\xi_\rho + \mathcal{R}_\rho = 0.\end{gathered} \tag{9.2}$$

These equations along with (8.11) constitute a complete system governing the time evolution of the unknowns. They may be written in a simpler form by taking into account eqs. (2.14) we find

$$\begin{gathered}\partial\varphi_k/\partial x_i + \partial\mathcal{D}/\partial\dot{M}_i^k = 0, \\ \partial\theta/\partial x_i + \partial\mathcal{D}/\partial\dot{S}_i = 0, \\ A_\rho = \mathcal{R}_\rho,\end{gathered} \tag{9.3}$$

where

$$\varphi_k = \phi_k + \mathcal{G}, \tag{9.4}$$

was introduced earlier as a mixed convective potential. It takes into account the work $\mathcal{G}$ due to the potential forces on the unit mass.

Isothermal case

Assuming that all transformations occur isothermally at the constant temperature T_0 amounts to putting $\theta = 0$ in eqs. (9.3) and eliminating $\dot{S}_i$ from the equations. The result may however be obtained directly and very simply by introducing the condition $\theta = 0$ from the start in the principle of virtual dissipation. For $\theta = 0$ eqs. (2.14) yield

$$\partial \mathcal{V} / \partial \mathcal{S} = 0. \tag{9.5}$$

This determines $\mathcal{S}$ as an implicit function of ξ_ρ and M^k. Hence

$$\mathcal{V} = \mathcal{V}(\xi_\rho, M_k). \tag{9.6}$$

The dissipation function with suitable coefficients is

$$\mathcal{D} = \frac{1}{2} \sum_{klij} K_{ij}^{lk} \dot{M}_i^l \dot{M}_j^k . \tag{9.7}$$

The unknowns are now ξ_ρ and M_i^k. By varying these unknowns, the principle of virtual dissipation (8.10) yields

$$\begin{gathered} \frac{\partial}{\partial x_i}(\psi_k + \mathcal{G}) + \frac{\partial \mathcal{D}}{\partial \dot{M}_i^k} = 0, \\ A_\rho = \mathcal{R}_\rho . \end{gathered} \tag{9.8}$$

Since $\theta = 0$ the thermobaric potential ψ_k is reduced to

$$\psi_k = \int_{\rho_0 T_0}^{p_k T_0} \mathrm{d}p'_k / \rho'_k . \tag{9.9}$$

10. Energy flux theorem

A fundamental energy flux theorem may be derived by adding the field equations (9.3) after multiplying the first group by $\dot{M}_i^k$ the second group by $\dot{S}_i$ and the third group by $\dot{\xi}_\rho$. Using relations

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

$$= \sum_{ki} \frac{\partial \mathcal{D}}{\partial \dot{M}_i^k} \dot{M}_i^k + \sum_i \frac{\partial \mathcal{D}}{\partial \dot{S}_i} \dot{S}_i + \sum_\rho \mathcal{R}_\rho \dot{\xi}_\rho , \tag{10.1}$$

derived from (8.11) and Euler's theorem on quadratic forms, we obtain (since $\partial\theta/\partial x_i = \partial T/\partial x_i$)

$$\sum_{ik} \left(\dot{M}_i^k \frac{\partial \varphi_k}{\partial x_i} + \frac{\partial T}{\partial x_i} \dot{S}_i \right) - \sum_\rho A_\rho \dot{\xi}_\rho + T\dot{s}^* = 0. \tag{10.2}$$

From (7.6) and (7.9) we may write

$$\dot{M}^k = -\sum_i \partial \dot{M}_i^k / \partial x_i, \quad \dot{\mathcal{S}} = -\sum_i \partial \dot{S}_i / \partial x_i + \dot{s}^* . \tag{10.3}$$

Hence eq. (10.2) becomes

$$\sum_i \frac{\partial F_i}{\partial x_i} + \sum_k \varphi_k \dot{M}^k + T\dot{\mathcal{S}} - \sum_\rho A_\rho \dot{\xi}_\rho = 0 \tag{10.4}$$

with

$$F_i = \sum_k \varphi_k \dot{M}_i^k + T\dot{S}_i . \tag{10.5}$$

The last terms of eq. (10.4) may be written as

$$\begin{aligned} &\sum_k \varphi_k \dot{M}^k + T\dot{\mathcal{S}} - \sum_\rho A_\rho \dot{\xi}_\rho \\ &\quad = \sum_k (\phi_k + \mathcal{G}) \dot{M}^k + \theta \dot{\mathcal{S}} - \sum_\rho A_\rho \dot{\xi}_\rho + T_0 \dot{\mathcal{S}} \end{aligned} \tag{10.6}$$

or according to eqs. (2.3) and (2.14)

$$\begin{aligned} &\sum_k \varphi_k \dot{M}^k + T\dot{\mathcal{S}} - \sum_\rho A_\rho \dot{\xi}_\rho \\ &\dot{\mathcal{V}} + T_0 \dot{\mathcal{S}} + \sum_k \mathcal{G} \dot{M}^k = \dot{\mathcal{U}} + \sum_k \mathcal{G} \dot{M}^k . \end{aligned} \tag{10.7}$$

Hence eq. (10.4) becomes

$$\sum_i \partial F_i / \partial x_i + \dot{\mathcal{U}} + \sum_k \mathcal{G} \dot{M}^k = 0. \tag{10.8}$$

The terms $\dot{\mathcal{U}} + \Sigma_k \mathcal{G} \dot{M}^k$ represent the rate of increase of energy per unit volume, and F_i is the energy flux vector. Eq. (10.8) constitutes an energy flux theorem. Using relations (2.15) and (7.5) we write

$$\varphi_k = \phi_k + \mathcal{G} = \bar{\epsilon}_k - T\bar{s}_k + \mathcal{G},$$

$$\dot{S}_i = \sum_k \bar{s}_k \dot{M}_i^k + \dot{S}_i^{\mathrm{T}} = \sum_k \bar{s}_k \dot{M}_i^k + \frac{\dot{H}_i}{T} . \tag{10.9}$$

With these values the energy flux vector (10.5) becomes

$$F_i = \sum_{\kappa} (\bar{\epsilon}_k + \mathcal{G})\dot{M}_i^k + \dot{H}_i. \tag{10.10}$$

For a single substance and one-dimensional rate of mass flow and heat flow $\dot{M}$ and $\dot{H}$ in steady state, eq. (10.8) yields

$$F = (\bar{\epsilon} + \mathcal{G})\dot{M} + \dot{H} = \text{Const.} \tag{10.11}$$

If we apply this to an entrance and exit point for which $\dot{H} = 0$ we obtain (since $\dot{M}$ = Const)

$$\bar{\epsilon} + \mathcal{G} = \text{Const}, \tag{10.12}$$

which is the classical relation for the Joule–Thomson effect in terms of the enthalpy $\bar{\epsilon}$.

The kinetic energy has been neglected in the foregoing derivation. It has been included in a more elaborate treatment of thermomolecular diffusion [17].

11. Complementary variational principle and corresponding field equations. Chemical waves

Eqs. (9.3) are linear in $\dot{M}_i^k$ and $\dot{S}_i$. They may be solved for these unknowns. Because of the symmetry of the coefficients we may write the solution in the form

$$\dot{M}_i^k = -\partial\mathcal{D}^c/\partial X_i^k, \quad \dot{S}_i = -\partial\mathcal{D}^c/\partial X_i, \tag{11.1}$$

where

$$X_i^k = \partial\varphi_k/\partial x_i, \quad X_i = \partial\theta/\partial x_i, \tag{11.2}$$

are dissipative forces and

$$\mathcal{D}^c = \frac{1}{2}\sum_{lkij} L_{ij}^{lk} X_i^l X_j^k + \sum_{kij} L_{ij}^k X_i^k X_j + \frac{1}{2}\sum_{ij} L_{ij} X_i X_j$$

is a quadratic form in X_i^k, X_i whose coefficients depend on the local state variables ξ_ρ M^k and $\mathcal{S}$. From Euler's theorem and eqs. (11.1) and (11.2) we derive

$$\begin{aligned} 2\mathcal{D}^c &= \sum_{ik} \frac{\partial\mathcal{D}^c}{\partial X_i^k} X_i + \sum_i \frac{\partial\mathcal{D}^c}{\partial X_i} X_i \\ &= -\sum_{ik} \dot{M}_i^k \frac{\partial\varphi_k}{\partial x_i} - \sum_i \dot{S}_i \frac{\partial\theta}{\partial x_i}. \end{aligned} \tag{11.3}$$

Introducing relations (9.3) this becomes

$$2\mathcal{D}^c = \sum_{ik} \dot{M}_i^k \frac{\partial\mathcal{D}}{\partial\dot{M}_i^k} + \sum_i \dot{S}_i \frac{\partial\mathcal{D}}{\partial\dot{S}_i} = 2\mathcal{D}. \tag{11.4}$$

Hence

$$\mathcal{D}^c = \mathcal{D}. \tag{11.5}$$

The dissipation function $\mathcal{D}^c$ is the same as $\mathcal{D}$ but is expressed in terms of dissipative forces X_i^k and X_i. From (7.7)–(7.9) and (8.11) we have the relations

$$\begin{aligned} \dot{M}^k &= -\sum_i \partial\dot{M}_i^k/\partial x_i, \\ \dot{\mathcal{S}} &= -\sum_i \partial\dot{S}/\partial x_i + 2\mathcal{D}^c/T + \sum_\rho A_\rho\dot{\xi}_\rho/T. \end{aligned} \tag{11.6}$$

Substitution of expressions (11.1) into these equations yields

$$\dot{M}^k = \sum_i \frac{\partial}{\partial x_i}\left(\frac{\partial\mathcal{D}^c}{\partial X_i^k}\right),$$

$$\dot{\mathcal{S}} = \sum_i \frac{\partial}{\partial x_i}\left(\frac{\partial\mathcal{D}^c}{\partial X_i}\right) + \frac{1}{T}\left(2\mathcal{D}^c + \sum_\rho A_\rho f_\rho\right), \tag{11.7}$$

$$\dot{\xi}_\rho = f_\rho(\xi_\sigma, M^k, \mathcal{S}). \tag{11.8}$$

The last set of equations for $\dot{\xi}_\rho$ is analogous to (6.14) and is derived from chemical kinetics.

11.1. Complementary variational principles

We may also consider θ, φ_k and ξ_ρ as the unknown variables. It is immediately verified that in this case eqs. (11.7) and (11.8) are equivalent to the variational principle

$$\begin{aligned} &\int_\Omega \Big[\sum_k \dot{M}^k \delta\phi_k + (\dot{\mathcal{S}} - \dot{s}^*)\,\delta\theta \\ &\quad - \sum_\rho (\dot{\xi}_\rho - f_\rho)\delta\xi_\rho + \delta_L\mathcal{D}^c\Big]\,\mathrm{d}\Omega \\ &\quad + \int_A \Big[\sum_{ik} \dot{M}_i^k \delta\phi_k + \sum_i \dot{S}_i \delta\theta\Big] n_i\,\mathrm{d}A = 0, \end{aligned} \tag{11.9}$$

with arbitrary variations $\delta\phi_k = \delta\varphi_k$, $\delta\theta$ and $\delta\xi_\rho$. The vector n_i is the unit normal at the boundary A of Ω, and we have put

$$\dot{s}^* = T^{-1}\left(2\mathcal{D}^c + \sum_\rho A_\rho f_\rho\right). \tag{11.10}$$

The symbol δ_L indicates that in $\mathcal{D}^c$ the coefficients L are not varied. Another formulation is obtained by replacing $\delta\xi_\rho$ by δA_ρ. This can always be done since

$\delta\xi_\rho$ is arbitrary. Taking into account the relation

$$\sum_k \dot{M}^k \delta\phi_k + \dot{\mathcal{S}}\delta\theta - \sum_\rho \dot{\xi}_\rho \delta A_\rho$$

$$= \sum_k \dot{M}^k \delta \frac{\partial \dot{\mathcal{V}}}{\partial \dot{M}^k} + \dot{\mathcal{S}}\, \delta \frac{\partial \dot{\mathcal{V}}}{\partial \dot{\mathcal{S}}} + \sum_\rho \dot{\xi}_\rho \delta \frac{\partial \dot{\mathcal{V}}}{\partial \dot{\xi}_\rho} = \delta_t \dot{\mathcal{V}}, \tag{11.11}$$

where the symbol δ_t indicates that in $\dot{\mathcal{V}}$ the time derivatives $\dot{M}^k$, $\dot{\mathcal{S}}$ and $\dot{\xi}_\rho$ are not varied, we write

$$\int_\Omega \left(\delta_t \dot{\mathcal{V}} + \delta_L \mathcal{D}^c - \dot{s}^* \delta\theta + \sum_\rho f_\rho \delta A_\rho\right) \mathrm{d}\Omega$$

$$+ \int_A \left(\sum_{ik} \dot{M}_i^k \delta\phi_k + \sum_i \dot{S}_i \delta\theta\right) n_i \,\mathrm{d}A = 0. \tag{11.12}$$

This constitutes an alternative form of the complementary variational principle (11.9).

11.2. *Isothermal case and chemical waves*

Consider the particular isothermal case where the temperature $T = T_0$ is constant ($\theta = X_i = 0$). The unknowns in this case are M^k and ξ_ρ since $\mathcal{S}$ is now a known function of these variables through the relation $\partial\mathcal{V}/\partial\mathcal{S} = 0$. Eqs. (11.7) are reduced to

$$\dot{M}^k = \sum_i \frac{\partial}{\partial x_i}\left(\frac{\partial \mathcal{D}^c}{\partial X_i^k}\right), \quad \dot{\xi}_\rho = f_\rho(\xi_\sigma, M^k). \tag{11.13}$$

These equations are further simplified by noting that the local state is determined by the variables

$$m_k = \sum_\rho \nu_k \xi_\rho + M^k. \tag{11.14}$$

Hence we may write

$$\dot{\xi}_\rho = f_\rho(m_k). \tag{11.15}$$

The coefficients of $\mathcal{D}^c$ as well as ϕ_k are also functions of m_k. Therefore eqs. (11.13) imply

$$\dot{m}_k = \sum_i \frac{\partial}{\partial x_i}\left(\frac{\partial \mathcal{D}^c}{\partial X_i^k}\right) + \sum_\rho \nu_{k\rho} f_\rho, \tag{11.16}$$

which constitute a complete set of equations for the unknowns m_k.

Chemical waves correspond to periodic solutions in space and time. For simplicity consider a one-dimensional distribution along x without external force field ($\mathcal{G} = 0, \varphi_k = \phi_k$). Eqs. (11.16) become

$$\dot{m}_k = \frac{\partial}{\partial x}\left(\frac{\partial \mathcal{D}^c}{\partial X^k}\right) + \sum_\rho \nu_{k\rho} f_\rho, \tag{11.17}$$

with $X^k = \partial\phi_k/\partial x$. We put

$$m_k = m_k(\zeta), \tag{11.18}$$

as periodic solutions of the single variable

$$\zeta = x - \upsilon t, \tag{11.19}$$

where υ is the velocity of propagation. Substitution of (11.18) into (11.17) yields

$$-\upsilon \frac{\mathrm{d}m_k}{\mathrm{d}\zeta} = \frac{\mathrm{d}}{\mathrm{d}\zeta}\left(\frac{\partial \mathcal{D}^c}{\partial X^k}\right) + \sum_\rho \nu_{k\rho} f_\rho, \tag{11.20}$$

a set of ordinary differential equations with the independent variable ζ. Chemical waves are thus given by characteristic values of υ for which eqs. (11.20) have periodic solutions in ζ.

The treatment of chemical waves illustrated here on a particular case is derived from a general and systematic process, in contrast to current procedures [18].

12. Variational-lagrangian thermodynamics of active transport in biological membranes

A thin membrane separates two reservoirs of cell potentials $\mathcal{V}^-$ and $\mathcal{V}^+$ which represent the outside environment. *An external mass flow occurs through* the faces of the membrane. An internal mass flow through "carrier" molecules as well as coupled chemical reactions take place inside the membrane. These chemical reactions produce a strong coupling between external mass flows, some of which may be in opposition to the concentration gradient. This so-called active transport has been the subject of extensive studies by a number of biochemists and particularly by Katchalsky and Spangler [20].

This phenomenon is a particular case of coupled diffusion and chemical reactions obeying the general equations of the preceding sections. However the variational-lagrangian analysis developed earlier [3,4, 21] for collective thermodynamic systems is particularly suited to the treatment of active transport (see section 13 below). An essential feature of the method is the description of the continuous field by a discrete set of variables called generalized coordinates.

From the standpoint of the physicist this representation is completely general since the number of coordinates may be arbitrarily large up to a "resolution threshold" as pointed out earlier [19]. The membrane being thin we consider the system to be isothermal at the temperature T_0 ($\theta = 0$). We also assume that there is no external body force field ($\mathcal{G} = 0$), and that the system is linear in the vicinity of equilibrium.

The membrane is considered to be a one-dimensional system with the coordinate x normal to the faces which are located at $x = -a$ and $x = a$.

Lagrangian equations which govern the time evolution of general linear thermodynamic system were developed and applied by the author in 1954–55 [3, 21]. They are *directly applicable to the present case* and are written

$$\frac{\partial}{\partial q_i}(V + \mathcal{V}_{\text{ext}}) + \frac{\partial D}{\partial \dot{q}_i} = 0, \tag{12.1}$$

where

$$V = \int_{-a}^{+a} \mathcal{V}\,\mathrm{d}x, \quad D = \tfrac{1}{2} T_0 \int_{-a}^{+a} \dot{s}^*\,\mathrm{d}x. \tag{12.2}$$

The collective potential V of the membrane is a quadratic form in the generalized coordinates q_i and the dissipation function D is a quadratic form in $\dot{q}_i$. The quadratic forms have constant coefficients and are positive definite. The collective potential of the environment is

$$\mathcal{V}_{\text{ext}} = \mathcal{V}^- + \mathcal{V}^+, \tag{12.3}$$

where $\mathcal{V}^-$ and $\mathcal{V}^+$ are respectively the potential of reservoirs in contact with the faces at $x = -a$ and $x = a$. We may write (12.1) as

$$\partial V/\partial q_i + \partial D/\partial \dot{q}_i = Q_i, \tag{12.4}$$

with thermodynamic driving forces $Q_i = -\partial \mathcal{V}_{\text{ext}}/\partial q_i$. The lagrangian eqs. (12.1) may also be considered as a consequence of the principle of virtual dissipation (8.10) written in the form

$$\delta \mathcal{V}_{\text{ext}} + \int_{-a}^{+a} (\delta \mathcal{V} + T_0 \delta s^*)\,\mathrm{d}x = 0. \tag{12.5}$$

The state of the membrane is described by $M_x^k(x)$ the mass displacement distribution of each chemical species along x and by the reaction coordinate ξ_ρ for each reaction. The membrane being thin we shall neglect the mass storage m_k. Hence putting $m_k = 0$ in eq. (7.10) we derive the mass conservation constraint in the form

$$\partial M_x^k/\partial x = \sum_\rho \nu_{k\rho} \xi_\rho, \tag{12.6}$$

which establishes a coupling between the mass transport and the chemical reactions. Putting $m_k = 0$ also implies $\mathcal{V} = 0$. Hence the lagrangian eqs. (12.4) are reduced to

$$\partial D/\partial \dot{q}_i = Q_i. \tag{12.7}$$

The dissipation function is

$$D = \int_{-a}^{+a} \mathcal{D}\,\mathrm{d}x, \tag{12.8}$$

where

$$\mathcal{D} = \tfrac{1}{2} T_0 \dot{s}^* = \frac{1}{2} \sum_k C_k (\dot{M}_x^k)^2 + \frac{1}{2} \sum_{\sigma\rho} B_{\sigma\rho}\, \dot{\xi}_\sigma\, \dot{\xi}_\rho. \tag{12.9}$$

The coefficients C_k represent uncoupled molecular diffusion. We assume homogeneous properties so that C_k and $B_{\sigma\rho}$ are constants.

We now introduce generalized coordinates q_k q_ρ and $\zeta_{\alpha\rho}$ by writing M_x^k in the form

$$M_x^k = q_k - x \sum_\rho \nu_{k\rho} q_\rho + \sum_{\alpha\rho} \nu_{k\rho} \zeta_{\alpha\rho}\, \mathcal{F}_{\alpha\rho}(x), \tag{12.10}$$

where $\mathcal{F}_{\alpha\rho}$ are suitably chosen functions of x with the property

$$\mathcal{F}_{\alpha\rho}(-a) = \mathcal{F}_{\alpha\rho}(a) = 0. \tag{12.11}$$

For example we may choose trigonometric functions of the type

$$\sin(n\pi x/a), \quad \cos[(n + \tfrac{1}{2})\pi x/a], \quad n = 0, 1, 2, \ldots, . \tag{12.12}$$

Substitution of expressions (12.10) into the mass conservation constraint (12.6) shows that it is satisfied if we put

$$\xi_\rho = -q_\rho + \sum_\alpha \zeta_{\alpha\rho}\, \mathrm{d}\mathcal{F}_{\alpha\rho}/\mathrm{d}x. \tag{12.13}$$

It is convenient to separate the functions $\mathcal{F}_{\alpha\rho}(x)$ into a symmetric group where $\mathcal{F}_{\alpha\rho}(x) = \mathcal{F}_{\alpha\rho}(-x)$ and an antisymmetric group where $\mathcal{F}_{\alpha\rho}(x) = -\mathcal{F}_{\alpha\rho}(-x)$. We also use i as a single index to indicate all pairs of indices $\alpha\rho$. The variables $\zeta_{\alpha\rho}$ are then denoted by ζ_i and ζ_i' depending on whether associated with symmetric or antisymmetric functions $\mathcal{F}_{\alpha\rho}$. By substituting the values (2.10) and (12.13) in the dissipation function (12.9) it separates into two uncoupled terms

$$D = D_s + D_a, \tag{12.14}$$

where

$$D_s = \frac{1}{2}\sum_k C_k \dot{q}_k^2 + \sum_{\kappa i} b_{ki}\dot{q}_k\dot{\zeta}_i + \frac{1}{2}\sum_{ij} b_{ij}\dot{\zeta}_i\dot{\zeta}_j,$$

$$D_a = \frac{1}{2}\sum_\rho b'_\rho \dot{q}_\rho^2 + \sum_{\rho i} b'_{\rho i}\dot{q}_\rho\dot{\zeta}'_i + \frac{1}{2}\sum_{ij} b'_{ij}\dot{\zeta}'_i\dot{\zeta}'_j. \tag{12.15}$$

The corresponding lagrangian equations are also uncoupled. They are

$$\begin{aligned} &\partial D_s/\partial \dot{q}_k = Q_k, \qquad \partial D_a/\partial \dot{q}_\rho = Q'_\rho, \\ &\partial D_s/\partial \dot{\zeta}_j = 0, \qquad \partial D_a/\partial \dot{\zeta}'_j = 0. \end{aligned} \tag{12.16}$$

The variables ζ_i and $\dot{\zeta}_i$ play the role of internal variables [see eq. (13.3) below]. The driving forces are

$$Q_k = -\partial \mathcal{V}_{\text{ext}}/\partial q_k = \phi_k^- - \phi_k^+,$$

$$Q'_\rho = -\partial \mathcal{V}_{\text{ext}}/\partial q_\rho = \sum_k a(\phi_k^- + \phi_k^+)\nu_{k\rho}, \tag{12.17}$$

where ϕ_k^- and ϕ_k^+ are the convective potentials of the environment at the faces $x = -a$ and $x = a$. Consider for example the first group of eqs. (12.16) for q_k and ζ_i. They are written

$$C_k \dot{q}_k + \sum_i b_{ki}\dot{\zeta}_i = Q_k, \tag{12.18}$$

$$\sum_l b_{lj}\dot{q}_l + \sum_i b_{ij}\dot{\zeta}_i = 0. \tag{12.19}$$

The matrix b_{ij} being positive definite its inverse Δ_{ij} is also positive definite. The set of eqs. (12.19) may be solved for ζ_i as

$$\dot{\zeta}_i = -\sum_{jl} \Delta_{ij} b_{lj}\dot{q}_l. \tag{12.20}$$

Substitution of this value in eqs. (12.18) yields

$$C_k \dot{q}_k \overset{\ell}{\sum} K_{lk}\dot{q}_l = Q_k, \tag{12.21}$$

where

$$K_{lk} = K_{kl} = \sum_{ij} \Delta_{ij} b_{ki} b_{lj}. \tag{12.22}$$

These equations constitute a particular case of the general impedance derived from linear thermodynamic systems in 1954–55 [3,21] with internal coordinates as explained in section 13 below. Since the matrix Δ_{ij} is positive definite the matrix K_{lk} is also positive definite. This can be seen by writing

$$\sum_{lk} K_{lk} z_l z_k = \sum_{ij} \Delta_{ij} Z_i Z_j > 0, \tag{12.23}$$

where

$$Z_i = \sum_k b_{ki} z_k. \tag{12.24}$$

If the functions $\mathcal{F}_{\alpha\rho}$ are chosen to be the orthogonal trigonometric functions (2.12) multiplied by suitable coefficients they may be normalized so that

$$\begin{aligned} &\frac{1}{2}\sum_{ij} b_{ij}\zeta_i\zeta_j = \frac{1}{2}\sum_i \zeta_i^2, \\ &\frac{1}{2}\sum_{ij} b'_{ij}\zeta'_i\zeta'_j = \frac{1}{2}\sum_i \zeta_i'^2, \end{aligned} \tag{12.25}$$

and the coupling coefficient becomes the simple expression

$$K_{lk} = \sum_i b_{li} b_{ki}. \tag{12.26}$$

These results lead to the important conclusion that the product

$$Q_k \dot{q}_k = C_k \dot{q}_k^2 - \sum_l K_{lk}\dot{q}_l\dot{q}_k, \tag{12.27}$$

may be negative. The driving force Q_k is the difference $\phi_k^- - \phi_k^+$ of the convective potentials of the substance at each faces. Since this potential increases with the concentration, a negative value of $Q_k \dot{q}_k$ represents a "contragradient" flow in the direction of the concentration gradient. This effect along with the presence of a strong coupling coefficient K_{lk} is known as "active transport".

Note that from eqs. (12.16) we derive

$$\sum_k \dot{q}_k \frac{\partial D_s}{\partial \dot{q}_k} + \sum_i \dot{\zeta}_i \frac{\partial D_s}{\partial \dot{\zeta}_i} = 2D_s = \sum_k Q_k \dot{q}_k. \tag{12.28}$$

The total dissipation and entropy production remains positive as should be. As a consequence a negative value of $Q_k \dot{q}_k$ requires the *simultaneous coupled flow of at least two substances.*

The symmetric coordinate q_k represents a substance for which the same amount of flow occurs at each face. Substance for which $q_k = \Sigma_\rho \nu_{k\rho} q_\rho = 0$ do not flow across the faces and correspond to "*carrier molecules*" which are present only in the membrane. Their behavior is represented entirely by the internal coordinates ζ_i and ζ'_i.

We have assumed a membrane of homogeneous properties across the thickness. The same linear analysis may be carried out if the membrane is inhomogeneous. In this case the coefficients of $\mathcal{D}$ depend on x. However the equations will not separate into uncoupled symmetric and antisymmetric groups.

Periodic solutions cannot occur in the linear case. Such periodic solutions associated with some cases of active transport require an analysis based on the non-linear equations developed in the two preceding sections.

13. General variational-lagrangian thermodynamics of collective systems

In the foregoing analysis we have stressed chemical applications. However the methods are completely general and are applicable to all thermodynamic systems of macroscopic physics. This development was initiated by the author in 1954 and further extended and applied in a large number of publications. This development is briefly summarized hereafter.

13.1. Linear lagrangian thermodynamics

The development was initiated in the context of linear thermodynamics [3,21,22], and leads to the lagrangian equations

$$(\mathrm{d}/\mathrm{d}t)\,(\partial \mathcal{T}/\partial \dot{q}_i) + \partial D/\partial \dot{q}_i + \partial \mathcal{P}/\partial q_i = Q_i, \qquad (13.1)$$

where q_i are perturbations from an equilibrium state. The kinetic energy $\mathcal{T}$ the dissipation function D and the mixed collective potential $\mathcal{P}$ are expressed by quadratic forms with constant coefficients.

$$\mathcal{T} = \frac{1}{2}\sum_{ij} m_{ij}\dot{q}_i\dot{q}_j, \quad D = \frac{1}{2}\sum_{ij} b_{ij}\dot{q}_i\dot{q}_j,$$

$$\mathcal{P} = \frac{1}{2}\sum_{ij} a_{ij} q_i q_j, \qquad (13.2)$$

and Q_i are generalized mixed mechanical and thermodynamic driving forces. They may include non-mechanical forces generated at the boundary by driving cells of potential $\mathcal{P}'$ which contribute terms $-\partial\mathcal{P}'/\partial q_i$ to the value of Q_i. The inertia terms are represented by $(\mathrm{d}/\mathrm{d}t)\,(\partial \mathcal{T}/\partial \dot{q}_i)$. The forms $\mathcal{T}$ and D are positive-definite while $\mathcal{P}$ may be non-definite depending on the stability of the equilibrium state.

In many problems we may distinguish external and internal coordinates q_k and q_α. The lagrangian equations for this case are

$$\begin{aligned}&(\mathrm{d}/\mathrm{d}t)\,(\partial \mathcal{T}/\partial \dot{q}_k) + \partial D/\partial \dot{q}_k + \partial \mathcal{P}/\partial q_i = Q_i,\\ &\partial D/\partial \dot{q}_\alpha + \partial \mathcal{P}/\partial q_\alpha = 0.\end{aligned} \qquad (13.3)$$

It was shown [19,21] that driving forces may be expressed in terms of the external coordinates q_k as

$$Q_l = \sum_k (Z_{lk} + p^2 m_{lk})\,q_k, \qquad (13.4)$$

where

$$Z_{lk} = \sum_s \frac{p}{p + r_s} D^{(s)}_{lk} + D'_{lk}\,p + D_{lk}, \qquad (13.5)$$

and $p = \mathrm{d}/\mathrm{d}t$ is the time differential operator. The fractional operator expresses the following integral operation,

$$\frac{p}{p + r_s} f(t) = \int_0^t \exp[r_s(t' - t)]\,\frac{\mathrm{d}f}{\mathrm{d}t'}\,\mathrm{d}t'. \qquad (13.6)$$

In these expressions $r_s > 0$ and the matrices $D^{(s)}_{lk}$, D'_{lk} and D_{lk} are positive definite. These results were applied to viscoelasticity [3,21,22].

The treatment of active transport in section 12 constitutes a particular case of eqs. (13.4).

13.2. Nonlinear collective systems

In the general nonlinear case the variational principle of virtual dissipation takes the form [4,23]

$$\delta_{\mathrm{R}}\mathcal{P} + \sum_i I_i\,\delta q_i + \sum_i X_i\,\delta q_i - Q_i\,\delta q_i = 0, \qquad (13.7)$$

where δ_{R} is a restricted variation which does not include the entropy produced, and I_i are generalized inertia forces. The forces X_i are generalized dissipative forces defined variationally by

$$\sum_i X_i\,\delta q_i = \int_\Omega T\,\delta s^*\,\mathrm{d}\Omega, \qquad (13.8)$$

which represents the virtual dissipation in the domain Ω to which the variational principle is applied. The variational equation (13.7) constitutes and *extension of d'Alembert's principle* to dissipative thermodynamic collective systems.

We may express the dissipative force in terms of q_i and rate variables $\dot{q}_i$ as

$$X_i = R_i(q_l, \dot{q}_l). \tag{13.9}$$

The general equations of evolution of the system derived from (13.7) are

$$\partial \mathcal{P}/\partial q_i + I_i + R_i - Q_i = 0. \tag{13.10}$$

A large number of thermodynamic systems are governed by these equations, which in many cases may be written in the lagrangian form [4,23].

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial \mathcal{T}}{\partial \dot{q}_i}\right) - \frac{\partial \mathcal{T}}{\partial q_i} + \frac{\partial \mathcal{P}}{\partial q_i} + R_i = Q_i. \tag{13.11}$$

For quasi-reversible systems we may write

$$R_i = \partial D/\partial \dot{q}_i, \quad D = \frac{1}{2}\sum_{ij} b_{ij}(q_l)\,\dot{q}_i\dot{q}_j, \tag{13.12}$$

where the dissipation function D is now a quadratic form with coefficients functions of q_i. How to apply such equations in systems with large entropy production s^* has been described in ref. [15] by introducing additional variables q'_i describing the scalar field s^*.

13.3. New heat transfer

For non-inertial systems with transport and diffusion the lagrangian equations are of the type

$$\partial V/\partial q_i + \partial D/\partial \dot{q}_i = Q_i. \tag{13.13}$$

Its application to heat transfer has been presented in detail in a monograph [19]. It leads to a new approach eminently suited to systems analysis without using traditional heat transfer coefficients. Simple approximations lead to remarkably accurate results. Among the numerous applications we may cite also the work of Lardner [24], Prasad and Agrawal [25], Chung and Yeh [26].

13.4. Instability and dissipative structures

For small deviations from an equilibrium state the perturbations satisfy eq. (13.1). For constant forces Q_i we may incorporate the terms $-\Sigma_i Q_i q_i$ into the value of $\mathcal{P}$ and the equation takes the form

$$(\mathrm{d}/\mathrm{d}t)(\partial \mathcal{T}/\partial \dot{q}_i) + \partial D/\partial \dot{q}_i + \partial \mathcal{P}/\partial q_i = 0. \tag{13.14}$$

If $\mathcal{P}$ may become negative the state of equilibrium is unstable. It was shown that dissipative structures appear in this case and that their amplitude is proportional to real increasing exponentials, i.e. they are *nonoscillatory* [4,5]. The existence of such dissipative structures for *small deviations from a state of static equilibrium has been overlooked* in the current literature [18,27] under the erroneous assumption that such structures require the system to be nonlinear while they appear as linear perturbations of a non-equilibrium state of flow. The perturbations in the latter case may be oscillatory.

In the nonlinear case an interesting example is given by a layered viscous medium in steady compressive flow in the direction of the layers. Folding of the layers with a definite wavelength represents a dissipative structure. It was shown [4] that this may be derived by applying the nonlinear lagrangian equation

$$\partial D/\partial \dot{q}_i = 0, \tag{13.15}$$

with the dissipation function (13.12) and considering small perturbations around the state of steady flow. A large number of references regarding such problems may be found in ref. [28].

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