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NEW STABILITY CRITERIA FOR REACTION-DIFFUSION

M.A. BIOT

Royal Academy of Belgium, Brussels, Belgium

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New stability criteria are developed for steady state evolution of reaction-diffusion far from equilibrium. The derivation is based on the lagrangian equations of irreversible thermodynamics. A new and general expression is also developed for the affinity which embodies the chemical kinetics.

1. Introduction

A new variational approach to irreversible thermodynamics has been developed leading to lagrangian equations of evolution. The essential results have been presented recently in the form of a short monograph [1]. Its foundation rests on a fundamental principle of virtual dissipation.

Our purpose here is to derive new stability criteria for a steady state evolution based on lagrangian equations in the context of general reaction-diffusion. As a preliminary, the concepts of local energy and entropy per unit volume under irreversible evolution are given a precise definition and a new expression is also developed for the affinity which embodies chemical kinetics. A special derivation of the variational and the lagrangian equations is presented in the particular context of reaction-diffusion as well as a general expression for thermomolecular dissipation which is invariant under translation.

A new stability criterion is obtained which does not require "local equilibrium" and distinguishes between oscillatory and non-oscillatory stability. The lagrangian equations also lead directly to a stability criterion analogous to that proposed by Glansdorff and Prigogine [2] providing at the same time a precise definition of an associated condition of "local equilibrium".

2. Outline of a new thermochemistry

We shall briefly recall the new viewpoints and results introduced earlier in the analysis of open chemically reacting systems, and based on concepts which differ fundamentally from standard procedures [1].

Consider a rigid cell C_P containing a homogeneous mixture of pure substances k in equilibrium at a given temperature. It is subject to a transformation which brings it to a certain temperature T while masses M^k are added to it from outside. At the same time masses $\nu_k \xi$ are also added to it by a chemical reaction of coordinate ξ. We have shown that the same transformation may be obtained reversibly by a process called thermobaric transfer.

We refer to C_P as the primary cell and adjoin to it large rigid supply cells C_k each containing the substance k at the same pressure and temperature $p_0 T_0$. We also adjoin a chemical supply cell C_{ch} containing the reactants in chemical equilibrium along with a thermal well TW which is a large rigid reservoir at constant temperature T_0. The system $C_P + C_{ch} + \Sigma_k C_k + \mathrm{TW}$ is called a hypersystem.

In order to illustrate the process of thermobaric transfer we extract a mass $\mathrm{d}M^k$ from the supply cell, bring it reversibly to a state of equilibrium with the primary cell at the pressure p_k and temperature T and inject it isothermally and reversibly into it through a semipermeable membrane. The

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increase of energy of the system $C_P + \Sigma_k C_k$ is

$$d\mathscr{U}^M = \sum_k (\bar{\epsilon}_k + h_{vT}^k) dM^k, \tag{2.1}$$

with

$$\bar{\epsilon}_k = \int_{p_0 T_0}^{p_k T} (dp'_k/\rho'_k + T' d\bar{s}_k). \tag{2.2}$$

We have called $\bar{\epsilon}_k$ the injection enthalpy and p_k the injection pressure and denote by p'_k, ρ'_k, T' and $\bar{s}_k$ the pressure, density, temperature, and specific entropy of dM^k along the path of integration, respectively. The term $h_{vT}^k dM^k$ represents the heat to be added to C_P in order to maintain a constant temperature during injection.

We may also consider a reaction $d\xi$ to occur in the chemical cell C_{ch} at constant temperature T_{eq} which is maintained by injecting into it an amount of heat $\bar{h}_T^{eq} d\xi$. The masses $\nu_k d\xi$ produced are extracted from C_{ch} and injected by thermobaric transfer into C_P. Finally the temperature of C_P is increased by an amount dT.

Thus we end up with a system *whose final state is the same* as if masses dM^k had been transferred into the primary cell while a chemical reaction $d\xi$ takes place in it with an increase of temperature dT.

The increase of energy of the system $C_P + C_{ch} + \Sigma_k C_k$ in this combined process is

$$d\mathscr{U} = \sum_k (\bar{\epsilon}_k + h_{vT}^k) dM^k + \sum_k (\bar{\epsilon}_k - \bar{\epsilon}_k^{ch} + h_{vT}^k) \nu_k d\xi + \bar{h}_T^{eq} d\xi + C_{vm} dT. \tag{2.3}$$

In this expression $\bar{\epsilon}_k^{ch}$ is the injection enthalpy in C_{ch}. Similarly we obtain the increase of entropy of the system $C_P + C_{ch} + \Sigma_k C_k$ as

$$d\mathscr{S} = \sum_k (\bar{s}_k + h_{vT}^k/T) dM^k + \sum_k (\bar{s}_k - \bar{s}_k^{ch} + h_{vT}^k/T) \nu_k d\xi + (\bar{h}^{eq}/T_{eq}) d\xi + (C_{vm}/T) dT, \tag{2.4}$$

where

$$\bar{s}_k = \int_{p_0 T_0}^{p_k T} d\bar{s}_k \tag{2.5}$$

is the injection entropy and $\bar{s}_k^{ch}$ its value for the chemical cell.

The quantities $\bar{\epsilon}_k$, $\bar{s}_k$, h_{vT}^k and C_{vm} appearing in the coefficients of the differentials (2.3) and (2.4) may be determined as functions of the temperature and composition of C_P hence as functions of T and $M^k + \nu_k \xi$. By integration they yield

$$\mathscr{U} = \mathscr{U}(M^k, \xi, T), \quad \mathscr{S} = \mathscr{S}(M^k, \xi, T), \tag{2.6}$$

as function of $M^k \xi$ and T. These values may be *considered as defining the energy and entropy of the primary cell* although they involve the combined system $C_P + C_{ch} + \Sigma_k C_k$. As a consequence it is interesting to note that they depend not only on the composition $M^k + \nu_k \xi$ of the cell but also on M^k and ξ as separate independent variables.

After multiplying (2.4) by T and subtracting it from (2.3) we obtain

$$d\mathscr{U} = -A d\xi + \sum_k \phi_k dM^k + T d\mathscr{S}, \tag{2.7}$$

where

$$\phi_k = \bar{\epsilon}_k - T\bar{s}_k \tag{2.8}$$

was called the convective potential. The quantity A is

$$A = \sum_k [T(\bar{s}_k - \bar{s}_k^{ch}) - \bar{\epsilon}_k + \bar{\epsilon}_k^{ch}] \nu_k + \bar{h}_T^{eq} (T/T_{eq} - 1). \tag{2.9}$$

It represents the affinity since for an isolated system ($d\mathscr{U} = dM^k = 0$) eq. (2.7) yields

$$A = T d\mathscr{S}. \tag{2.10}$$

Eq. (2.10) is a new form of Gibbs' equation which avoids the use of the chemical potential. Thereby bypassing the difficulty due to the presence of undetermined constants in this potential.

When there are simultaneous chemical reactions of coordinates ξ_ρ eqs. (2.3) and (2.4) are readily generalized to this case by adjoining to the hypersystem chemical cells $C_{ch\rho}$ for each reaction. Eq. (2.7) is thus generalized to

$$d\mathscr{U} = -\sum_\rho A_\rho d\xi_\rho + \sum_k \phi_k dM^k + T d\mathscr{S}, \tag{2.11}$$

while expressions (2.6) become

$$\mathscr{U} = \mathscr{U}(M^k, \xi_\rho, T), \quad \mathscr{S} = \mathscr{S}(M^k, \xi_\rho, T). \tag{2.12}$$

3. Local energy and entropy of a continuous irreversible system

The energy and entropy of an open rigid cell have been defined above by a reversible process called thermobaric transfer. The volume of the cell is arbitrary and may be taken as unity. In that case $\mathscr{U}$ and $\mathscr{S}$ are the values of the energy and entropy per unit volume. The variables are now the temperature T and the masses M^k added by convection per unit volume while ξ defines the masses $\nu_k\xi$ produced by the chemical reaction also per unit volume. If we consider a *continuous system in irreversible evolution* occupying a domain Ω the energy and entropy of an elementary domain $\mathrm{d}\Omega$ are respectively $\mathscr{U}\mathrm{d}\Omega$ and $\mathscr{S}\mathrm{d}\Omega$ where *$\mathscr{U}$ and $\mathscr{S}$ are functions of the instantaneous local values of T and of M^k and ξ per unit volume.* The total energy U and entropy S of the domain Ω are then expressed by the volume integrals

$$U=\int_\Omega \mathscr{U}\mathrm{d}\Omega, \quad S=\int_\Omega \mathscr{S}\mathrm{d}\Omega. \tag{3.1}$$

Underlying this approach is the assumption that the domain may be divided into elements which are sufficiently small to be treated as infinitesimal while their actual size remains above a resolution threshold for which T, M^k and ξ retain their physical significance as defined above with reference to a unit volume. The local values of ϕ_k and A_ρ are intensive variables functions of the temperature T and

$$m_k=m_{0k}+\sum_\rho \nu_{k\rho}\xi_\rho+M^k, \tag{3.2}$$

where m_k is the mass of substance k per unit volume, m_{0k} being its initial value, while $\nu_{k\rho}\xi_\rho$ and M^k are the values added by chemical reaction and convection. Note that m_k may represent all the masses present in the system per unit volume or only those substances which participate in convection and reaction as solutes in a rigid neutral support.

4. Entropy production and dissipation forces

In an irreversible process entropy is produced. It may be evaluated in several ways. In the present context of reaction-diffusion one of the simplest is the following.

We consider the mass flux $\dot{M}_i^k$ of substance k per unit area. If we denote by $\dot{H}_i$ the heat flux, the diffusive energy flux is (the dot indicates a time derivative)

$$\dot{\mathscr{F}}_i=\sum_k \bar{\epsilon}_k\dot{M}_i^k+\dot{H}_i. \tag{4.1}$$

We denote by $\mathscr{F}_iM_i^k$ and H_i the time integrals of $\dot{\mathscr{F}}_i\dot{M}_i^k$ and $\dot{H}_i$ with zero initial value and call them respectively energy, mass and heat fluence. They satisfy the relations

$$\mathscr{U}=-\sum_i \partial\mathscr{F}_i/\partial x_i, \quad M^k=-\sum_i \partial M_i^k/\partial x_i, \tag{4.2}$$

where x_i is the cartesian coordinate.

We now introduce arbitrary variations. Replacing differentials by variations in eq. (2.11) and solving for $\delta\mathscr{S}$ we obtain

$$\delta\mathscr{S}=(1/T)\delta\mathscr{U}+\sum_\rho (A_\rho/T)\delta\xi_\rho-\sum_k(\phi_k/T)\delta M^k. \tag{4.3}$$

We also write eq. (4.1) in variational form as

$$\delta\mathscr{F}_i=\sum_k \bar{\epsilon}_k\delta M_i^k+\delta H_i. \tag{4.4}$$

Hence using (4.2) we obtain

$$\delta\mathscr{U}=-\sum_i \frac{\partial}{\partial x_i}\left(\sum_k \bar{\epsilon}_k\delta M_i^k+\delta H_i\right),$$

$$\delta M^k=-\sum_i \frac{\partial}{\partial x_i}\delta M_i^k. \tag{4.5}$$

Substitution of these values into (4.3) yields an expression of the form

$$\delta\mathscr{S}=-\sum_i \frac{\partial}{\partial x_i}\delta S_i+\delta s^*, \tag{4.6}$$

where

$$\delta S_i=\sum_k \bar{s}_k\delta M_i^k+\delta H_i/T, \tag{4.7}$$

$$\delta s^*=\sum_\rho \frac{A_\rho}{T}\delta\xi_\rho-\sum_{ki}\frac{\partial}{\partial x_i}\left(\frac{\phi_k}{T}\right)\delta M_i^k+\sum_i \frac{1}{\partial x_i}\left(\frac{1}{T}\right)\delta\mathscr{F}_i. \tag{4.8}$$

The value (4.6) represents the variation of entropy per unit volume. The first term is due to the entropy flow while δs^* is the variation of entropy produced per unit volume.

Actually in the applications we use the virtual dissipation

$$T\delta s^* = \sum_\rho A_\rho \delta\xi_\rho - T\sum_{ki} \frac{\partial}{\partial x_i}\left(\frac{\phi_k}{T}\right)\delta M_i^k - \frac{1}{T}\sum_i \frac{\partial T}{\partial x_i}\delta\mathscr{F}_i. \tag{4.9}$$

The dissipative forces which generate entropy are

$$A_\rho, \quad -T\frac{\partial}{\partial x_i}\left(\frac{\phi_k}{T}\right), \quad -\frac{1}{T}\frac{\partial T}{\partial x_i}. \tag{4.10}$$

They provide a measure of the departure of the system from reversibility and may be called disequilibrium forces. They are conjugate to the coordinates ξ_ρ, M_i^k and $\mathscr{F}_i$.

5. New expression of the affinity in terms of chemical kinetics

We may draw an analogy between viscous forces in mechanics and dissipative forces in irreversible thermodynamics. For the case of chemical reactions this analogy has never been formulated in a satisfactory way. For example in a viscous fluid mixture the viscous stress

$$\tau_{ij} = \tau_{ij}(m_k, T, \dot{\epsilon}_{\mu\nu}) \tag{5.1}$$

may be expressed as a function of the temperature T, the concentrations m_k of the constituents and the rate of deformation $\dot{\epsilon}_{\mu\nu}$. This relation embodies the kinetics of the dissipative process. A similar relation for chemical reactions may be derived as follows. We write the rate of reaction $\dot{\xi}_\rho$ and the affinity A_ρ as functions of m_k and T

$$\dot{\xi}_\rho = f_\rho(m_k, T), \quad A_\rho = A_\rho(m_k, T). \tag{5.2}$$

Assume that by adding masses $\sum_\sigma \nu_{k\sigma}\Delta\xi_\sigma$ to m_k we reach chemical equilibrium for which $\dot{\xi}_\rho$ and A_ρ vanish. Hence we may write (5.2) in the form

$$\dot{\xi}_\rho = f_\rho(m_k, T) - f_\rho(m_k + \textstyle\sum_\sigma \nu_{k\sigma}\Delta\xi_\sigma, T), \tag{5.3}$$

$$A_\rho = A_\rho(m_k, T) - A_\rho(m_k + \textstyle\sum_\sigma \nu_{k\sigma}\Delta\xi_\sigma, T). \tag{5.4}$$

We solve equations (5.3) for $\Delta\xi_\sigma$ and substitute the result into (5.4). This yields

$$A_\rho = \mathscr{R}_\rho(m_k, T, \dot{\xi}_\rho), \tag{5.5}$$

where the affinity $\mathscr{R}_\rho$ is now expressed as a function of m_k, T and $\dot{\xi}_\rho$. Relation (5.5) is entirely analogous to (5.1) and embodies the chemical kinetics.

In many cases we may approximate expression (5.5) by a linear function of $\dot{\xi}_\rho$ and write

$$\mathscr{R}_\rho = \sum_\sigma \mathscr{B}_{\rho\sigma}(m_k, T)\dot{\xi}_\sigma, \tag{5.6}$$

where $\mathscr{B}_{\rho\sigma}$ are functions of m_k and T. If in addition Onsager's reciprocity relations are verified we may introduce a dissipation function

$$\mathscr{D}^{\mathrm{ch}} = \tfrac{1}{2}\sum_{\rho\sigma} \mathscr{B}_{\rho\sigma}\dot{\xi}_\rho\dot{\xi}_\sigma \tag{5.7}$$

and write (5.6) as

$$\mathscr{R}_\rho = \partial\mathscr{D}^{\mathrm{ch}}/\partial\dot{\xi}_\rho. \tag{5.8}$$

Referring to relation (4.9), the virtual dissipation for chemical reactions is

$$T\delta s^{*\mathrm{ch}} = \sum_\rho \mathscr{R}_\rho \delta\xi_\rho \tag{5.9}$$

and the corresponding rate of dissipation is the positive expression

$$T\dot{s}^{*\mathrm{ch}} = \sum_\rho \mathscr{R}_\rho\dot{\xi}_\rho > 0. \tag{5.10}$$

In the linear case, with a dissipation function (5.7) the rate of dissipation becomes

$$T\dot{s}^{*\mathrm{ch}} = \sum_\rho \left(\partial\mathscr{D}^{\mathrm{ch}}/\partial\dot{\xi}_\rho\right)\dot{\xi}_\rho = 2\mathscr{D}^{\mathrm{ch}} > 0, \tag{5.11}$$

where $\mathscr{D}^{\mathrm{ch}}$ is a positive definite quadratic form in $\dot{\xi}_\rho$ with coefficients functions of m_k and T.

6. Kinetics of thermomolecular diffusion and invariance under translation

According to (4.9) the virtual dissipation due to thermomolecular diffusion may be written

$$T\delta s^{*\mathrm{TM}} = \sum_{ki} \mathscr{R}_i^k \delta M_i^k + \sum_i \mathscr{R}_i^{\mathrm{F}}\delta\mathscr{F}_i, \tag{6.1}$$

where the dissipative forces are expressed as

$$-T\frac{\partial}{\partial x_i}\left(\frac{\phi_k}{T}\right)=\mathscr{R}_i^k\left(m_k,\,T,\,\dot{M}_i^k,\,\dot{\mathscr{F}}_i\right), \tag{6.2}$$

$$-\frac{1}{T}\left(\frac{\partial T}{\partial x_i}\right)=\mathscr{R}_i^{\mathrm{F}}\left(m_k,\,T,\,\dot{M}_i^k,\,\dot{\mathscr{F}}_i\right). \tag{6.3}$$

The functions $\mathscr{R}_i^k$ and $\mathscr{R}_i^{\mathrm{F}}$ embody the irreversible kinetics of the thermomolecular diffusion. They are functions of the local state m_k and T and the mass and energy fluxes $\dot{M}_i^k\dot{\mathscr{F}}_i$. In general they will be linear functions of the fluxes and obey Onsager's reciprocity principle. Hence they may be written in the form

$$\mathscr{R}_i^k=\partial\mathscr{D}^{\mathrm{TM}}/\partial\dot{M}_i^k,\quad \mathscr{R}_i^{\mathrm{F}}=\partial\mathscr{D}^{\mathrm{TM}}/\partial\dot{\mathscr{F}}_i, \tag{6.4}$$

with a thermomolecular dissipation function

$$\mathscr{D}^{\mathrm{TM}}=\tfrac{1}{2}\sum_{ik}C^{lk}\dot{M}_i^l\dot{M}_i^k+\sum_{ik}C^{k\mathrm{F}}\dot{M}_i^k\dot{\mathscr{F}}_i+\tfrac{1}{2}\sum_i C^{\mathrm{F}}\dot{\mathscr{F}}_i\dot{\mathscr{F}}_i. \tag{6.5}$$

It is a positive definite quadratic form in $\dot{M}_i^k$ and $\dot{\mathscr{F}}_i$ with coefficients $C^{lk}(m_k,\,T)$, $C^{k\mathrm{F}}(m_k,\,T)$ $C^{\mathrm{F}}(m_k,\,T)$ functions of m_k and T.

In many cases the mixture is a fluid medium with intermolecular diffusion. In that case the dissipation function must be invariant under a uniform translation. A uniform increase of velocity v_i adds $m_k v_i$ to $\dot{M}_i^k$ and $\dot{\mathscr{F}}_{v_i}^{\mathrm{c}}$ to $\dot{\mathscr{F}}_i$, where

$$\mathscr{F}^{\mathrm{c}}=\sum_k m_k\left(\bar{\epsilon}_k+h_{pT}^k\right). \tag{6.6}$$

The quantity $\bar{\epsilon}_k+h_{pT}^k$ is the energy required to inject a unit mass of substance isothermally into the mixture and h_{pT}^k is the additional heat to be injected in order to maintain the temperature and pressure constant. A dissipation function which satisfies the condition of invariance under translation is obviously of the form

$$\mathscr{D}^{\mathrm{TM}}=\tfrac{1}{2}\sum_{lki}C^{lk}\left(\dot{M}_i^l/m_l-\dot{M}_i^k/m_k\right)^2+\tfrac{1}{2}\sum_{ki}C^k\left(\dot{M}_i^k/m_k-\dot{\mathscr{F}}_i/\mathscr{F}^{\mathrm{c}}\right)^2. \tag{6.7}$$

That this is the only form satisfying the invariance condition can be seen by adding to (6.7) the terms needed in order to obtain the most general quadratic form in $\dot{M}_i^k$ and $\dot{\mathscr{F}}_i$. These terms are

$$\sum_{ik}A_k\left(\dot{M}_i^k\right)^2+\sum_i\mathscr{B}_i\dot{\mathscr{F}}_i^2. \tag{6.8}$$

However, they must vanish since they are not invariant under translation.

An invariant expression for $\mathscr{D}^{\mathrm{TM}}$ was also derived earlier using the entropy flux $\dot{S}_i$ instead of $\dot{\mathscr{F}}_i$ [1].

7. Principle of virtual dissipation and lagrangian equation of reaction-diffusion

For reaction-diffusion the principle of virtual dissipation developed earlier in a broader context [1] may be derived as follows. We consider a hypersystem constituted by a primary system, supply cells C_k, chemical cells $\mathrm{C}_{\mathrm{ch}\rho}$ and a thermal well TW. The primary system is a continuous system occupying the domain Ω whose energy and entropy are defined by (3.1).

We consider an arbitrary irreversible evolution of the primary system determined by a time sequence of ξ_ρ, M_i^k and $\mathscr{F}_i$. By eqs. (2.12) and (4.2) this also determines the time sequence of ξ_ρ, M^k and T. We freeze the system at any particular time and consider arbitrary variations $\delta\xi_\rho$, δM_i^k, $\delta\mathscr{F}_i$ in the vicinity of a frozen state. In this variation no heat or matter is exchanged between the hypersystem and the environment, and the variation is generated by the virtual work δW performed by external forces on the hypersystem. The work is the purely mechanical work necessary to inject masses and heat into Ω as required by the values δM_i^k and δH_i at the boundary of Ω, using supply cells as a source of matter and TW as a source of heat for mechanical heat pumps.

The variational principle is obtained by writing that the variations obey a virtual conservation of energy of the hypersystem. This is written

$$\delta U+T_0\delta S_{\mathrm{TW}}=\delta W. \tag{7.1}$$

In this expression δS_{TW} represents the increase of entropy of TW, hence $\delta U+T_0\delta S_{\mathrm{TW}}$ is the increase of energy of the hypersystem. By introducing the exergy

$$V=U-T_0\,S \tag{7.2}$$

(7.1) becomes

$$\delta V + T_0 \delta S^* = \delta W, \tag{7.3}$$

where

$$\delta S^* = \delta S + \delta S_{\mathrm{TW}} \tag{7.4}$$

is the total virtual entropy produced in the hyper-system.

Eq. (7.3) expresses the principle of virtual dissipation. It remains to show how to evaluate δW and δS^* for reaction-diffusion.

We write δW as a surface integral extended to the boundary A of the domain Ω with a unit normal n_i. This value is

$$\delta W = -\int_A \sum_{ki} \left[\psi_k \delta M_i^k + (\theta/T) \delta H_i \right] n_i \, \mathrm{d}A, \tag{7.5}$$

where $\theta = T - T_0$. The mass injected into Ω per unit area is $-\sum_i \delta M_i^k n_i$. It is extracted from the supply cell at the pressure and temperature $p_0 T_0$, then heated and compressed to a suitable pressure and temperature p_k and T, then injected reversibly into Ω at the boundary. The purely mechanical work to accomplish this, including the use of heat pumps, per unit mass, was called thermobaric potential [1]. Its value was found to be

$$\psi_k = \int_{p_0 T_0}^{p_k T} (\mathrm{d}p'_k/\rho'_k + \theta' \mathrm{d}\bar{s}'_k) = \bar{\epsilon}_k - T_0 \bar{s}_k. \tag{7.6}$$

The path of integration is arbitrary and corresponds to what we have called a thermobaric transfer. The values of the pressure, density, specific entropy, and temperature along the path are p'_k, ρ'_k, $\bar{s}'_k$ and T' with $\theta' = T' - T_0$. In (7.5) the term $(-\theta/T)\delta H_i n_i$ is the work of a heat pump extracting heat from TW and injecting the heat $\delta H_i n_i$ through the boundary at the temperature $T = T_0 + \theta$.

Substitution in (7.5) of the value (7.6) of ψ_k and the value δH_i extracted from (4.4) yields

$$\delta W = -\int_A \sum_i \left[(T_0/T) \sum_k \phi_k \delta M_i^k + (\theta/T) \delta \mathscr{F}_i \right] \times n_i \mathrm{d}A. \tag{7.7}$$

The virtual dissipation is

$$T_0 \delta S^* = T_0 \int_\Omega (\delta s^{*\mathrm{ch}} + \delta s^{*\mathrm{TM}}) \mathrm{d}\Omega, \tag{7.8}$$

where $\delta s^{*\mathrm{ch}} + \delta s^{*\mathrm{TM}}$ is the total virtual entropy produced per unit volume. Using the values (5.9) and (6.1) and the values (6.4) for $\mathscr{R}_i^k$ and $\mathscr{R}_i^{\mathrm{F}}$ we obtain

$$T_0 \delta S^* = T_0 \int_\Omega \frac{1}{T} \left(\sum_\rho \mathscr{R}_\rho \delta \xi_\rho + \sum_{ki} \frac{\partial \mathscr{D}^{\mathrm{TM}}}{\partial \dot{M}_i^k} \delta M_i^k + \sum_i \frac{\partial \mathscr{D}^{\mathrm{TM}}}{\partial \mathscr{F}_i} \delta \mathscr{F}_i \right) \mathrm{d}\Omega. \tag{7.9}$$

Applying the principle of virtual dissipation (7.3) we may derive the evolution of a reaction-diffusion field in terms of generalized coordinates by proceeding as follows. The reaction-diffusion field is given by the vector fields $\mathscr{F}_i$ and M_i^k and the scalar fields ξ_ρ. They may be expressed in the form

$$\mathscr{F}_j = \sum_i u_{ij}^{\mathrm{F}} q_i, \quad M_j^k = \sum_i u_{ij}^k q_i, \quad \xi_\rho = \sum_i u_i^\rho q_i, \tag{7.10}$$

where $u_{ij}^{\mathrm{F}}(x_l)$, $u_{ij}^k(x_l)$, $u_i^\rho(x_l)$ are suitable chosen functions of the coordinates x_l while q_i are generalized coordinates to be determined as functions of time. Once we know q_i we obtain from (4.2)

$$\mathscr{U} = -\sum_j \partial \mathscr{F}_j / \partial x_j = \sum_i w_i^{\mathrm{F}} q_i,$$

$$M^k = -\sum_j \partial M_j^k / \partial x_j = \sum_i w_i^k q_i, \tag{7.11}$$

where

$$w_i^{\mathrm{F}} = -\sum_j \partial u_{ij}^{\mathrm{F}} / \partial x_j, \quad w_i^k = -\sum_j \partial u_{ij}^k / \partial x_j. \tag{7.12}$$

Knowing $\mathscr{U}$, M^k and ξ_ρ we determine the temperature T from relations (2.12).

The generalized coordinates as functions of time are governed by a system of differential equations called lagrangian equations. They are obtained from the variational principle (7.3) by introducing arbitrary variations δq_i in the values (7.10). The exergy (7.2) may be considered as a function $V(q_i)$ of the generalized coordinates q_i. We may write

$$\delta V = \sum_i (\partial V / \partial q_i) \delta q_i, \quad T_0 \delta S^* = \sum_i R_i \delta q_i,$$

$$\delta W = \sum_i Q_i \delta q_i. \tag{7.13}$$

Substituting the values (7.13) into the variational principle (7.3) with arbitrary variations δq_i yields the lagrangian equations of reaction-diffusion as

$$\partial V/\partial q_i + R_i = Q_i. \tag{7.14}$$

It is easily shown that $\partial V/\partial q_i$ may be obtained without actually evaluating $V(q_i)$ as an explicit function of q_i. The generalized driving force $Q_i(t)$ is a given function of time if the values ϕ_k and the temperature T are determined as functions of time at the boundary. The combined generalized thermomolecular and chemical dissipative force

$$R_i = R_i(q_l, \dot{q}_l) \tag{7.15}$$

is a function of q_l and $\dot{q}_l$ with the fundamental property

$$\Sigma R_i \dot{q}_i > 0. \tag{7.16}$$

8. New stability criteria of evolution

Consider a system where the values ϕ_k and the temperature T are time independent at the boundary. A possible evolution of the system is a steady state where the temperature T and the masses m_k per unit volume are also time independent along with the time derivatives $\dot{\mathscr{F}}_i$, $\dot{M}_i^k$ and $\dot{\xi}_\rho$ throughout the system.

The question is to evaluate the stability of such a steady state far from equilibrium. The lagrangian equations (7.14) provide a completely general tool for such a stability analysis. The steady state field may be represented by putting

$$q_1 = \alpha t, \quad q_2 = q_3, \ldots, q_n = 0 \tag{8.1}$$

in expressions (7.10) where the steady state corresponds to the value $q_1 = \alpha t$ proportional to the time t. A perturbed field is represented in terms of small perturbations Δq_i by putting

$$q_1 = \alpha t, \quad q_2 = \Delta q_2, \quad q_3 = \Delta q_3, \ldots, q_n = \Delta q_n.$$

If the values of the temperature and ϕ_k remain unperturbed at the boundary, Q_i remains unperturbed. In that case the lagrangian eqations (7.14) for small perturbations become

$$\sum_j \left(\partial^2 V/\partial q_i \partial q_j\right) \Delta q_j + \Delta R_i = 0, \tag{8.2}$$

where

$$\Delta R_i = \sum_j \left(\partial R_i/\partial \dot{q}_j\right) \Delta \dot{q}_j + \sum_j \left(\partial R_i/\partial q_j\right) \Delta q_j,$$
$$j = 2, 3, \ldots, n. \tag{8.3}$$

Putting

$$\partial^2 V/\partial q_i \partial q_j = a_{ij} = a_{ji},$$
$$c_{ij} = \partial R_i/\partial q_j, \quad r_{ij} = \partial R_i/\partial \dot{q}_j, \tag{8.4}$$

the perturbation equations (8.2) are written

$$\sum_j (a_{ij} + c_{ij}) \Delta q_j + \sum_j r_{ij} \Delta \dot{q}_j = 0. \tag{8.5}$$

The coefficients (8.4) are evaluated for unperturbed values (8.1) of q_i and it is easily seen that they are constants for a steady state.

The stability analysis of the steady state reaction-diffusion in the general case is thus reduced to solving a system of homogeneous differential equations with constant coefficients. The system will be stable if all characteristic roots have negative real parts.

There is, however, a particular case where it is possible to take advantage of the thermodynamic properties to derive a direct stability criterion. Let us assume that the affinities are linear functions of the reaction rates, i.e.

$$\mathscr{R}_\rho = \sum_\sigma \mathscr{B}_{\rho\sigma}(m_k, T) \dot{\xi}_\sigma. \tag{8.6}$$

Since the thermomolecular dissipative forces (6.4) are linear functions of the rates $\dot{\mathscr{F}}_i$ and $\dot{M}_i^k$, the total dissipative generalized forces R_i are also linear functions of $\dot{q}_i$. Hence we may write

$$R_i = \sum_j r_{ij}(q_l) \dot{q}_j, \tag{8.7}$$

where the coefficients r_{ij} are functions of the generalized coordinates q_l. An important property here is the positive-definiteness (7.16) of

$$\sum_i R_i \dot{q}_i = \sum_{ij} r_{ij}(q_i) \dot{q}_i \dot{q}_j. \tag{8.8}$$

In addition we shall also assume that $\mathscr{R}_\rho$ is expressed by (5.8). Due to expressions (6.4) for $\mathscr{R}_i^k$ and $\mathscr{R}_i^{\mathrm{F}}$ this implies $r_{ij} = r_{ji}$.

In the present case the perturbed value (8.3) of R_i becomes

$$\Delta R_i = \sum_j (\partial r_{i1}/\partial q_j)\dot{q}_1 \Delta q_j + \sum_j r_{ij}(q_l)\Delta \dot{q}_j. \tag{8.9}$$

Hence

$$c_{ij} = (\partial r_{i1}/\partial q_j)\dot{q}_1, \tag{8.10}$$

while r_{ij} is a constant obtained by substituting for q_l the values q_1 and $q_2 = q_3, \ldots, q_n = 0$. According to (8.8) the coefficients r_{ij} are positive-definite i.e

$$\sum_{ij} r_{ij}\Delta q_i \Delta q_j > 0. \tag{8.11}$$

This important relation based on irreversible thermodynamics leads to a new stability criterion obtained as follows. Multiply eqs. (8.5) by Δq_i and add the results. We obtain

$$\sum_{ij} (a_{ij} + c_{ij})\Delta q_i \Delta q_j + \sum_{ij} r_{ij}\Delta q_i \Delta \dot{q}_j = 0. \tag{8.12}$$

This may be written

$$\sum_{ij} (a_{ij} + c_{ij})\Delta q_i \Delta q_j + \tfrac{1}{2}\mathrm{d}D'/\mathrm{d}t = 0, \tag{8.13}$$

where

$$D' = \sum_{ij} r_{ij}\Delta q_i \Delta q_j. \tag{8.14}$$

According to (8.11) it is positive-definite. Let us assume that

$$\sum_{ij} (a_{ij} + c_{ij})\Delta q_i \Delta q_j > 0, \tag{8.15}$$

i.e. that it is also positive-definite. In that case eq. (8.13) shows that $\mathrm{d}D'/\mathrm{d}t < 0$. Since D' is positive-definite it means that the perturbations Δq_i tend to zero. As a consequence condition (8.15) *is a sufficient condition for the steady state to be stable.*

If condition (8.15) is not fulfilled the perturbations may be unstable and contain exponentially increasing solutions. Whether the perturbed solution is stable or unstable two cases may be distinguished.

(1) If $c_{ij} = c_{ji}$ all characteristic roots are real and the perturbations are non-oscillatory.

(2) If $c_{ij} \neq c_{ji}$ some of the perturbation terms may be oscillatory.

An interesting stability criterion may also be derived under fixed boundary conditions by multiplying eqs. (8.2) by $\Delta \dot{q}_i$ and adding the results. We obtain

$$\sum_{ij} \left(\partial^2 V/\partial q_i \partial q_j\right)\Delta \dot{q}_i \Delta q_j + \sum_i R_i \Delta \dot{q}_i = 0. \tag{8.16}$$

If we assume

$$\sum_i R_i \Delta \dot{q}_i > 0 \tag{8.17}$$

and

$$\sum_{ij} \left(\partial^2 V/\partial q_i \partial q_j\right)\Delta q_i \Delta q_j > 0 \tag{8.18}$$

by an argument similar to that used above for equation (8.12) we conclude that Δq_i must tend to zero. Hence when the two inequalities (8.17) and (8.18) are verified simultaneously the steady state evolution is stable. Condition (8.17) is similar to the one derived by Glansdorff and Prigogine [2]. However, it is obtained here by a very simple and general direct procedure. The additional condition (8.18) required may be considered as expressing in precise form the assumption of so-called "local equilibrium" implicit in current procedures.

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