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Nonequilibrium thermodynamics for multiphase reacting systems: an optimal control approach

Stanislaw Sieniutycz*

Faculty of Chemical and Process Engineering, Warsaw University of Technology, 1 Warynskiego Street, 00-645 Warsaw, Poland

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Abstract

This paper sets optimal control framework for balance and kinetic equations of multiphase reacting systems consistently with the second law of thermodynamics. Approaches effective in contemporary theory of nonequilibrium thermodynamics of single-phase systems are here extended to include interfacial discontinuities, surface reactions and interface transports which are phenomena typical of multiphase systems. We arrive at Lagrangian and Hamiltonian structures of transport equations and laws of chemical kinetics, which constitute efficient forms serving to generalize linear models to nonlinear regimes. Local disequilibria are predicted which are shown to be responsible for onset of interfacial and bulk instabilities.

Keywords: Thermodynamics; Multiphase reacting system; Control approach; Kinetic equations

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1. Introduction

The purpose of our presentation is a general thermodynamic approach to balance and kinetic equations of structured heterogeneous systems and chemical networks which is based on variational principles and is consistent with the second law of thermodynamics. Methods effective in classical irreversible thermodynamics of single-phase systems are here extended to include boundary discontinuities, surface reactions and interface transports in multiphase, multireaction systems. The network (system) theory is the helpful tool with which topological and graphical methods of electrical networks are extended to quite general energo-chemical systems. Chemical Ohms law links chemical force (affinity) and chemical flux (reaction rate), and chemical conversions follow simple rules of the algebra for chemical resistances. With these resistances as basic variables, there are two main methods coming from thermodynamics of single-phase systems, which can effectively be applied to complex structured systems. The first method starts with the derivation of balance equations for mass, energy and momentum and terminates at the entropy balance; from the knowledge of the entropy source σ_S kinetic laws are postulated. Yet, our main objective is the second (newer) method which is based on the variational formulation of second law and nonlinear chemical resistances. Through optimization an entropy functional is minimized to predict kinetic laws and secure appropriate balance equations. The method does not postulate linearity; rather it rests on state-dependent dissipation functions. It follows that this variational method assures classical nonlinear kinetics of mass action and nonlinear set of diffusion–reaction equations under the condition of local thermal equilibrium. Still local disequilibria can be predicted which are responsible for onset of interfacial and bulk instabilities. Lagrangian and Hamiltonian form of transport

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* Tel.: +48-22-8256340; fax: +48-22-8251440.
E-mail address: sieniutycz@ichip.pw.edu.pl (S. Sieniutycz).

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Nomenclature

$\mathbf{A}$	oriented area
$\mathcal{A}$	vector of chemical affinities
$\mathbf{c}$	matrix of thermostatic capacitances
H_σ	dissipative (thermodynamic) Hamiltonian
$\mathbf{i}$	flux density of electric current
$\mathbf{j}$	column matrix of independent diffusive fluxes
$\mathbf{j}_i$	flux density of *i*th component
$\mathbf{j}_q$	density of diffusive energy flux
$\mathbf{j}_s$	density of diffusive entropy flux
$\mathcal{J}$	mass flow across the interface
$\mathcal{J}_k$	mass flow of *k*th constituent across the interface
k	thermal conductivity
$\mathbf{L}$	Onsagerian matrix of phenomenological coefficients
L_σ	dissipative (thermodynamic) Lagrangian, $\Phi + \Psi$
M_k	molar mass of *k*th component
P	pressure
$\mathbf{r}$	vector of reaction rates
R	gas constant
R_j	resistance of *j*th reaction, component of matrix **R**
s_v	entropy of unit volume
S, S_σ	entropy and entropy production, respectively
t	time
T	temperature
$\mathbf{u}$	Gibbsian vector of independent thermodynamic intensities
$\mathbf{v}$	convection velocity
V	volume
$\mathbf{w}$	Onsager's vector of independent transport intensities or Lagrangian multiplier of conservation laws
$\mathbf{X}$	vector of independent thermodynamic forces
$\mathbf{y}$	vector of mass fractions

Greek symbols

δ	variational derivatives in space
Λ_σ	Lagrangian density of dissipative field
μ_k	molar chemical potential of *k*th component
$\tilde{\mu}_k = \mu_n M_k M_n^{-1} - \mu_k$	transfer potential of *k*th component ($\mu'_k \equiv -\tilde{\mu}_k$)
ν'	extended stoichiometric matrix
ξ	conversion variable
ρ	column vector of densities
ρ_e	energy of unit volume
σ	production term per unit volume
ϕ	electric potential
∇	nabla operator

Subscripts

e	total energy
i	*i*th component
q	diffusive energy
s	entropy
σ	dissipative property

Superscripts

s	entropy representation
γ	phase γ
δ	phase δ
T	transpose matrix; transformed quantity
$'$	extended quantity

equations and laws of chemical kinetics are valid, which are efficient to accommodate nonlinear effects. In the variational formalism, local disequilibria are shown to result from the difference between the Lagrange multipliers of balance laws and intensive parameters of Gibbs fundamental equation.

In the first approach balance equations are first derived for mass, energy and momentum, and the combination of the energy and momentum equations leads to a balance equation for the internal energy. The internal energy balance is next combined with the Gibbs equation which describes the entropy as the state function; the result is an equation for entropy balance. From its source term kinetic laws are postulated. Approach of this sort was extended to multiphase heterogeneous systems by several researchers. Standard, [1,2], applied integral transformation theorems in the manner similar to that developed by Bird [3] for the homogeneous case. Further contributions of this sort are by Slattery and co-workers [4–6]. A recent statistical mechanics approach [7] applies a modified Boltzmann equation to derive multiphase flow equations by the Chapman–Enskog technique [8].

The main objective of our presentation is the second (newer) approach which is based on the variational formulation of second law and the concept of nonlinear chemical resistance. It is quite recent, and it is unknown to date for multiphase systems. It was originally set for single-phase systems by Sieniutycz and Berry [9] as four-dimensional extension of the Gyarmati's method [10] which is applicable in an exact way only to three-dimensional spaces and steady processes. We shall thus pursue an optimization or variational approach in which an entropy functional is minimized, to get kinetic laws and balance equations. The approach does not postulate linearity; rather it rests on the state-dependent dissipation functions from the beginning. Onsager [11,12], for example, restricted himself to linear relationships between thermodynamic fluxes and forces. Some authors [13,14] show that linearized equations yield results of excellent accuracy for engineering purposes even in situations involving the highest attainable composition gradients. However, whenever chemical reactions or phase changes are present, the nonlinearities play essential role, in particular because the mass action law describes nonlinear (in general) kinetics. Thus the reacting multiphase systems are particular systems where our variational method may be very helpful. In view of these positive features, we apply our approach to multiphase systems with possible chemical reactions and/or phase changes. Our derivations here are limited to systems in mechanical equilibrium moving with a constant velocity $\mathbf{v}$.

2. Variational approach

Each phase is an open, multicomponent system, of n components and N chemical reactions

$$\sum_{i=1}^{n} \nu_{ij}^{\mathrm{f}}[i] \leftrightarrow \sum_{i=1}^{n} \nu_{ij}^{\mathrm{b}}[i], \quad i=1,\ldots,n, \ j=1,\ldots,N$$

The system contains species i with chemical potential μ_i; T is the local temperature, and R the gas constant. The ν_{ij}^{f} and ν_{ij}^{b} are the forward and backward stoichiometric coefficients, respectively, for species i in reaction j. The advancement of the jth reaction is denoted by ξ_j, and its rate r_j. Each phase can be thermally inhomogeneous. When the state properties at the external boundary are fixed, we investigate a general entropy production functional

$$S_\sigma = \int L_\sigma \, \mathrm{d}x \, \mathrm{d}t = \int (\Phi + \Psi) \, \mathrm{d}x \, \mathrm{d}t \tag{1}$$

subject to the conservation law constraints. The properly expressed entropy source σ_{s}, or the sum of the flux-dependent and gradient-dependent dissipation functions, Φ and Ψ, respectively, is the thermodynamic Lagrangian L_σ. We use the mass fluxes rather than molar fluxes, the specific quantities, and the concentrations as independent mass fractions z_i. The notation for the vector set in each phase (phase superscript α omitted) is as follows:

$$\rho = \mathrm{col}(\rho_e, \rho_1, \rho_2, \ldots, \rho_{n-1}, \rho_{e1}), \text{ density matrix} \tag{2}$$

$$\mathbf{j} = \mathrm{col}(\mathbf{j}_q, \mathbf{j}_1, \mathbf{j}_2, \ldots, \mathbf{j}_{n-1}, \mathbf{i}_{e1}), \text{ diffusive flux matrix} \tag{3}$$

$$\mathbf{u} = (T^{-1}, \tilde{\mu}_1 T^{-1}, \tilde{\mu}_2 T^{-1}, \ldots, \tilde{\mu}_{n-1} T^{-1}, -\phi T^{-1}), \quad \text{transfer potential matrix} \tag{4}$$

with the relative chemical potential $\tilde{\mu}_k = \mu_n M_k M_n^{-1} - \mu_k$ and the matrix of entropic capacitances defined as $\mathbf{c} = \partial\rho/\partial\mathbf{u} = (\partial^2 s_v/\partial\rho_i \partial\rho_j)^{-1} \leq 0$.

Complex multiphase and multireaction systems can effectively by analyzed by applying methods developed in the network (system) theory and the theory of electric networks [15,16]. Extending topological and graphical methods of electrical networks to energy and chemical systems, the chemical resistances, $\mathbf{R}$, are introduced and used in system analysis and variational principles. In approaches using $\mathbf{R}$, chemical conversions follow rules of the algebra for resistances. Chemical Ohms law links the chemical force (affinity) and chemical flux (reaction rate). The use of chemical resistances is simple. An example is given.

Consider a system of enzyme reactions (three reactions between four components)

$$\begin{aligned}&\text{Reaction 1}: && \mathrm{e}+\mathrm{s} \leftrightarrow \mathrm{es},\\ &\text{Reaction 2}: && \mathrm{es} \leftrightarrow \mathrm{e}+\mathrm{p},\\ &\text{Reaction 3}: && \mathrm{s} \leftrightarrow \mathrm{p}\end{aligned} \tag{5}$$

aiming to evaluate ξ_{T}, the total conversion of s into p. There are two consecutive channels (1 and 2) and one parallel channel (3). For the total conversion ξ_{T}, Shiner [16] finds

$$\dot{\xi}_{\mathrm{T}} = \dot{\xi}_1 + \dot{\xi}_{\mathrm{C}} = \left(\frac{1}{R_1+R_2} + \frac{1}{R_3}\right)(\mu_{\mathrm{s}}^{\mathrm{e}} - \mu_{\mathrm{p}}^{\mathrm{e}}) \tag{6}$$

where the superscript e refers to chemical potentials fixed in an external world (in the stationary state $\dot{\xi}_{\mathrm{C}} = \dot{\xi}_1 = \dot{\xi}_2$). Essentially, all R_j can be nonlinear functions of state. This is simple; yet in this work we use nonlinear chemical resistances to accomplish a more difficult task: to derive a general structure of reaction–diffusion reactions in multiphase systems.

The variational form of the second law in the multiphase system has the general structure

$$S(t_2) = \min\{S(t_1) + S_{\otimes}^{\mathrm{e}} + S_{\sigma}^{\mathrm{b}} + S_{\sigma}^{\mathrm{i}}\} \tag{7}$$

where $S_\sigma = S_{\sigma}^{\mathrm{b}} + S_{\sigma}^{\mathrm{i}}$ is the total entropy production which comprises the effect of bulks and interfaces. Each of quantities, S_{σ}^{b} or S_{σ}^{i} is positive. Otherwise $S_{\otimes}^{\mathrm{e}}$ is the entropy exchanged by the system with its external word and its sign is undetermined. Eq. (7) provides the physical interpretation for the variational formulation of the second law (8) which proves that the entropy plays a role in thermodynamics similar to that of action in mechanics. The governing variational principle is set in the physical space–time rather than in the three-dimensional space and, as such, it substantiates the role of the entropy rather than the entropy production. For the prescribed states and/or fluxes at the system boundary (constant $S_{\otimes}^{\mathrm{e}}$) the principle implies a least possible production of entropy under constraints imposed by the conservation laws. We shall show that equations of transport, chemical kinetics and conservation laws follow from this entropy principle subject the conservation law constraints.

We shall prove the structure of Eq. (7) in an elementary way. When viscous phenomena are ignored and the problem is restricted to that with known constant velocities in each phase, the second law functional can be stated as

$$\begin{aligned} S(t_2) = \min\Bigg\langle & S(t_1) + \sum_\alpha \int_{t_1, A_\oplus^\alpha}^{t_2} - \mathbf{j}_s^\alpha(\mathbf{j},\mathbf{u})\,\mathrm{d}A_\oplus^\alpha\,\mathrm{d}t \\ & + \sum_\alpha \int_{t_1, V^\alpha}^{t_2} \bigg\{ \frac{1}{2}\mathbf{L}^{-1\alpha}(\mathbf{u}) : \mathbf{j}^\alpha \mathbf{j}^\alpha \\ & + \frac{1}{2}\mathbf{L}^{\alpha}(\mathbf{u}) : \nabla\mathbf{u}^\alpha \nabla\mathbf{u}^\alpha \bigg\}\,\mathrm{d}V^\alpha\,\mathrm{d}t \\ & + \sum_\alpha \int_{t_1, V^\alpha}^{t_2} \bigg\{ \frac{1}{2}\mathbf{R}^{\alpha} : \mathbf{r}^\alpha \mathbf{r}^\alpha \\ & + \frac{1}{2}\mathbf{R}^{-1\alpha} : (\nu'^{\mathrm{T}}\mathbf{u}^\alpha)(\nu'^{\mathrm{T}}\mathbf{u}^\alpha) + \mathbf{w}^\alpha \cdot \left(\frac{\partial \rho^\alpha(\mathbf{u})}{\partial t}\right. \\ & \left. + \nabla \cdot (\mathbf{j}^\alpha + \rho_m^\alpha \mathbf{v}^\alpha \mathbf{y}^\alpha - \mathbf{v}'\mathbf{r}^\alpha)\right)\bigg\}\,\mathrm{d}V^\alpha\,\mathrm{d}t \Bigg\rangle \end{aligned} \tag{8}$$

where the subscript α refers to phases, and the vector of Lagrange multipliers, $\mathbf{w}$, adjoints the constraints required by balance equations. The reaction stoichiometry is governed by the extended stoichiometric matrix, ν', which formally takes into account the vanishing sources of energy and electric charge in production terms. The first line contains the sum $\mathbf{A}_\oplus$ of the surface integrals over all closed areas, $\mathbf{A}_\oplus^\alpha$, which surround separate phases existing in the system. The subscript $\oplus$ stresses their closed and oriented nature. In our notation the entropy flux $\mathbf{j}_s(\mathbf{j},\mathbf{u})$ is simply the product $\mathbf{j}\cdot\mathbf{u}$. The derivation of such functional structure from an error criterion follows an earlier work [9,17]. For an isolated system the variational second law principle implies the least possible increase of the system entropy between any two successive configurations. For steady-state processes the principle implies the least possible entropy output for any input constant in time.

Now, in accordance with Fig. 1, the sum of all closed surface integrals can be split into components. The first component is the single closed integral over the external area, $\mathbf{A}_\oplus$,

$$S^{\mathrm{e}} = \int_{t_1, A_\oplus}^{t_2} - \mathbf{j}_s(\mathbf{j},\mathbf{u})\,\mathrm{d}A_\oplus\,\mathrm{d}t \tag{9}$$

It represents the exchange of entropy with an external word during the time $t_2 - t_1$. The second component

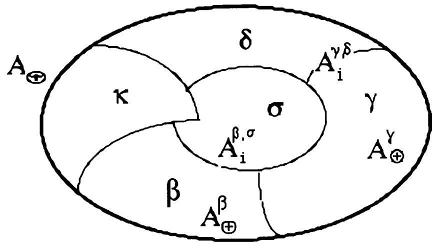

Fig. 1. Scheme of a general multiphase system and principle of designations.

is the sum of all nonclosed surface integrals over the internal interfaces, $\mathbf{A}_i^{\gamma,\delta}$,

$$S_\sigma^{\mathrm{i}} = \sum_{i(\gamma,\delta)}^{I} S_i^{(\gamma,\delta)} \equiv \sum_{i(\gamma,\delta)}^{I} \int_{t_1, A_i^{\gamma,\delta}}^{t_2} -\mathbf{j}_s^{\gamma,\delta}(\mathbf{j},\mathbf{u})\,\mathrm{d}A_i^{\gamma,\delta}\,\mathrm{d}t \qquad (10)$$

For steady interfaces, this integral sum expresses the entropy produced at interfaces. The entropy is also produced in bulks of each phase; this effect is represented by the integral

$$S_\sigma^{\mathrm{b}} = \sum_{\alpha=\gamma,\delta,\ldots} \int_{t_1, V^\alpha}^{t_2} \{\mathbf{j}^\alpha \cdot \nabla \mathbf{u}^\alpha + \mathbf{r}^\alpha \cdot \mathcal{A}^\alpha\}\,\mathrm{d}V^\alpha\,\mathrm{d}t \qquad (11)$$

The expressions in the first term refer to transport processes and those in the second to chemical reactions. Thus the structure of Eq. (7) is proved; this also proves the validity of the variational principle for the sum of Eqs. (9)–(11).

Specializing with systems in which the heat and mass transfers are essential, interface reactions are absent and viscous phenomena are negligible the dissipation function representation of the entropy production for interfaces can be presented in the form

$$S_\sigma^{\mathrm{i}} = \sum_{i(\gamma,\delta)}^{I} \int_{t_1, A_i^{\gamma,\delta}}^{t_2} [\tfrac{1}{2}\mathcal{C}_\infty^{\gamma,\delta} : \mathcal{J}\mathcal{J} + \tfrac{1}{2}\mathcal{C}_\infty^{\gamma,\delta} : (\mathbf{u}^\gamma - \mathbf{u}^\delta)(\mathbf{u}^\gamma - \mathbf{u}^\delta)]\,\mathrm{d}A_i^{\gamma,\delta}\,\mathrm{d}t \qquad (12)$$

whereas for the bulk

$$S_\sigma^{\mathrm{b}} = \sum_{\alpha=\gamma,\delta,\ldots} \int_{t_1, V^\alpha}^{t_2} \{\tfrac{1}{2}\mathbf{L}^{-1\alpha}(\mathbf{u}) : \mathbf{j}^\alpha \mathbf{j}^\alpha + \tfrac{1}{2}\mathbf{L}^\alpha(\mathbf{u}) : \nabla \mathbf{u}^\alpha \nabla \mathbf{u}^\alpha + \tfrac{1}{2}\mathbf{R}^\alpha : \mathbf{r}^\alpha \mathbf{r}^\alpha + \tfrac{1}{2}\mathbf{R}^{-1\alpha} : (\nu'^{\mathrm{T}}\mathbf{u}^\alpha)(\nu'^{\mathrm{T}}\mathbf{u}^\alpha)\}\,\mathrm{d}V^\alpha\,\mathrm{d}t \qquad (13)$$

The expressions with **L** refer to transport processes and those with **R** to chemical reactions. The above two integrals enable us to apply the variational principle of Eq. (7); their sum with Eq. (9) is, in fact, contained in the functional (8).

3. Results: variational and classical

Let us compare results of the macroscopic balance approach and the variational approach in the bulk of each phase for the resting system in mechanical equilibrium (ignored effects of hydrodynamic motion). In the matrix notation, the macroscopic balance approach yields the set of Eqs. (14)–(16). The set, respectively, incorporates the conservation laws, the standard linear laws of coupled Onsager's transport (postulated by the entropy source analysis and the first laws of Fourier and Fick) and (as the basic flaw) the laws of *linear* chemical kinetics. An extra (dependent) equation of the set is a matrix equation of change found as the combination of conservation and kinetic equations. With the neglected phase superscript, α, the set is

$$\frac{\partial \rho(\mathbf{u})}{\partial t} + \nabla \cdot \mathbf{j} = \mathbf{v}'\mathbf{r} \qquad (14)$$

$$\mathbf{L}_0^{-1} \cdot \mathbf{j} = \nabla \mathbf{u}; \quad \mathbf{R}_0 \cdot \mathbf{r} = \nu'^{\mathrm{T}}\mathbf{u}\ (= \mathcal{A}^s) \qquad (15)$$

$$\mathbf{c}(\mathbf{u})\frac{\partial \mathbf{u}}{\partial t} = \nabla \cdot (\mathbf{L}_0 \nabla \mathbf{u}) - \mathbf{R}_0^{-1}\mathcal{A}^s(\mathbf{u}) \qquad (16)$$

where $\mathbf{c}(\mathbf{u}) = -\partial\rho(\mathbf{u})/\partial\mathbf{u}$ is the capacity matrix and $\mathcal{A}^s = \nu'^{\mathrm{T}}\mathbf{u}$ is the vector of affinities; both these quantities are in the entropy representation. The conservation laws (14) contain production terms which are nonvanishing for $i = 1, \ldots, n$. The subscript zero stresses the constancy of coefficients and resulting linearity. The formal macroscopic balance approach and the related linear kinetics predicted from the entropy source are not capable of assuring any nontrivial information about true, nonlinear chemical kinetics.

On the other hand, the result of vanishing first variation of the entropy source S_σ or the Euler–Lagrange equations for functional (8) with respect to the variables **w**, **j**, **r** and **u** are, respectively, nonlinear equations

$$\frac{\partial \rho(\mathbf{u})}{\partial t} + \nabla \cdot \mathbf{j} = \mathbf{v}'\mathbf{r} \tag{17}$$

$$\mathbf{L}(\mathbf{u})^{-1} \cdot \mathbf{j} = \nabla \mathbf{w}; \quad \mathbf{R}(\mathbf{u}) \cdot \mathbf{r} = \nu'^{\mathrm{T}}\mathbf{w} \tag{18}$$

$$\begin{aligned} \mathbf{c}(\mathbf{u})\frac{\partial \mathbf{w}}{\partial t} &= \nabla \cdot (\mathbf{L}\nabla \mathbf{u}) - \nu'\mathbf{R}^{-1}\mathcal{A}^{s}(\mathbf{u}) \\ &\underset{\mathbf{u}=\mathbf{w}}{\Rightarrow} \nabla \cdot (\mathbf{L}\nabla \mathbf{u}) - \nu'\mathbf{r} \end{aligned} \tag{19}$$

To prove that the true (nonlinear and nontruncated) chemical kinetics is now assured, we first use the property of the equilibrium constant for the *j*th reaction K_j as the ratio of the forward and backward reaction rate constants, $k_j^{\mathrm{f}}/k_j^{\mathrm{b}}$; then the chemical affinity of the *j*th reaction is

$$\begin{aligned} \mathcal{A}_j^{s} &= \sum_{i=1}^{n} \frac{(\nu_{ij}^{\mathrm{f}} - \nu_{ij}^{\mathrm{b}})\mu_i}{T} = -\sum_{i=1}^{n} \frac{\nu_{ij}\mu_i}{T} \\ &= R \ln\left[k_j^{\mathrm{f}} \prod_{i=1}^{n} a_{\mathbf{i}}^{\nu_{ij}^{\mathrm{f}}}\right] - \ln\left[k_j^{\mathrm{b}} \prod_{i=1}^{n} a_{\mathbf{i}}^{\nu_{ij}^{\mathrm{b}}}\right] \end{aligned} \tag{20}$$

Next we use the definition of the chemical resistances, that obey the formula

$$R_j(\rho) = R \ln\left[\left(k_j^{\mathrm{f}} \prod_{i=1}^{N} a_i^{\nu_{ij}^{\mathrm{f}}}\right) \Big/ \left(k_j^{\mathrm{b}} \prod_{i=1}^{N} a_i^{\nu_{ij}^{\mathrm{b}}}\right)\right] \Big/ \; k_j^{\mathrm{f}} \prod_{i=1}^{N} a_i^{\nu_{ij}^{\mathrm{f}}} - k_j^{\mathrm{b}} \prod_{i=1}^{N} a_i^{\nu_{ij}^{\mathrm{b}}} \tag{21}$$

[15,18,19] with the activities $a_i = a_i(\rho)$ expressed as functions of the actual state. It then follows from Eqs. (18)–(21) that the variational method assures classical nonlinear kinetics of mass action and nonlinear set of diffusion–reaction equation under the subsidiary condition of local thermal equilibrium (LTE), i.e. when $\mathbf{u} = \mathbf{w}$. (See a good discussion of LTE in Ref. [20].) This proves that the variational approach is reacher than that based on balance equations; once the variational principle is stated, it lives its own life and, whenever suitable nonlinear resistances are applied, true nonlinear kinetics (Guldberg and Waage kinetics, Langmuir kinetics, or other) can be secured along with nonlinear diffusion–reaction sets. The distinction between the Gibbsian intensities **u** and Lagrange multipliers of conservation laws **w** plays, in particular, a role in explaining the origin and development of thermo-hydrodynamic instabilities by tracing the growing differences between the Gibbsian intensities **u** and **w** on unstable trajectories.

3.1. Generalized description

Below we adduce *generalized* equations for multiphase systems, which hold when our restriction of trivial hydrodynamics is relaxed. In comparison with single-phase systems, the surface continuity relations are extra terms of basic importance in the analysis of transports and chemical reactions at the phase boundaries of multiphase systems. For conserved fluxes an equation states that the normal component (subscript n) of the surface vector or tensor flux is an invariant which is continuous through the phase boundary. This is valid whether or not the surface transport process is reversible. Owing to these facts, we do not need generally assume that pressure, temperature and the chemical potentials of the constituents are continuous across the phase boundary. Assuming that a surface chemical reaction occurs on the δ side of the interface, the balance equations of the mass energy and momentum across the interface (subscript i) follow in the form given below. To write down these equations we first define the barycentric velocity of the mixture and the mass flow $\mathcal{J}$ across the interface (γ, δ)

$$\mathcal{J} = \rho(\mathbf{v} - \mathbf{v}_{\mathrm{i}}^{\gamma,\delta}) = \sum_{k=1} \mathcal{J}_k \tag{22}$$

where $\mathbf{v}_{\mathrm{i}}$ is the velocity of the interface boundary between phases γ and δ, and the mass flux of the *k*th constituent is

$$\mathcal{J}_k = \rho(\mathbf{v}_k - \mathbf{v}_{\mathrm{i}}^{\gamma,\delta}) \tag{23}$$

As this holds for each phase (α, β, γ, ...), the phase index is neglected in symbols ($\mathcal{J}$, **v**, etc.) which are contained in formulas of this sort. The other basic fluxes are the momentum and energy fluxes $\mathcal{P}$ and $\mathcal{Q}$; their suitable forms are:

$$\begin{aligned} \mathcal{P} &= \rho(\mathbf{v} - \mathbf{v}_{\mathrm{i}}^{\gamma,\delta})(\mathbf{v} - \mathbf{v}_{\mathrm{i}}^{\gamma,\delta}) + p\mathbf{U} + \tau \\ &\equiv \frac{1}{\rho}\mathcal{J}\mathcal{J} + p\mathbf{U} + \tau \end{aligned} \tag{24}$$

$$\mathcal{Q}=\sum_k \rho_k h_k(\mathbf{v}_k-\mathbf{v}_{\mathrm{i}}^{\gamma,\delta})+q+(\mathbf{v}-\mathbf{v}_{\mathrm{i}}^{\gamma,\delta})\cdot\Pi_{\mathrm{i}} \equiv \sum_k h_k\mathbf{J}_k+q+(\mathbf{v}-\mathbf{v}_{\mathrm{i}}^{\gamma,\delta})\cdot\Pi_{\mathrm{i}} \tag{25}$$

where Π_{i} is the interface stress tensor

$$\Pi_{\mathrm{i}} \equiv \frac{1}{2}\rho(\mathbf{v}-\mathbf{v}_{\mathrm{i}}^{\gamma,\delta})(\mathbf{v}-\mathbf{v}_{\mathrm{i}}^{\gamma,\delta})+\tau_{\mathrm{i}} \equiv \frac{1}{2\rho}\mathcal{J}\mathcal{J}+\tau_{\mathrm{i}} \tag{26}$$

In terms of these basic fluxes, all balance equations across the interface are expressed. The global mass balance or the continuity equation for the mass flow $\mathcal{J}$ across the interface is

$$\mathcal{J}_{\mathrm{n}}^{\gamma}=\mathcal{J}_{\mathrm{n}}^{\delta}\equiv\mathcal{J}_{\mathrm{n}} \quad \left(=\sum_{k=1}\mathcal{J}_{\mathrm{n}k}\right) \tag{27}$$

where $\mathbf{v}_{\mathrm{i}}$ is the interface velocity. The mass flux of the kth constituent $\mathcal{J}_k$ is nonconservative

$$\mathcal{J}_{k\mathrm{n}}^{\delta}=\mathcal{J}_{k\mathrm{n}}^{\gamma}+\sum_j \nu_{kj}r_j^{\delta} \tag{28}$$

where the surface chemical reactions are assumed to occur on the δ-side of the phase boundary. The momentum and energy balances across the interface are

$$\mathcal{P}_{\mathrm{n}}^{\gamma}=\mathcal{P}_{\mathrm{n}}^{\delta}\equiv\mathcal{P}_{\mathrm{n}} \tag{29}$$

$$\mathcal{Q}_{\mathrm{n}}^{\gamma}=\mathcal{Q}_{\mathrm{n}}^{\delta}\equiv\mathcal{Q}_{\mathrm{n}} \tag{30}$$

Using in the latter equation the definitions of chemical potentials $\mu_{\mathrm{i}}=h_{\mathrm{i}}-Ts_{\mathrm{i}}$ and the balances of constituents, the second law of thermodynamics at the interface γ, δ is found in the form

$$\begin{aligned}\sum_k(\mathcal{J}_{k\mathrm{n}}^{\delta}s_k^{\delta})-\sum_k^{\gamma}(\mathcal{J}_{k\mathrm{n}}^{\gamma}s_k^{\delta})+\frac{q_{\mathrm{n}}^{\gamma}}{T}-\frac{q_{\mathrm{n}}^{\delta}}{T} &= -\sum_k\mathcal{J}_{k\mathrm{n}}^{\gamma}\left(\frac{\mu_k^{\delta}}{T^{\delta}}-\frac{\mu_k^{\gamma}}{T^{\gamma}}\right)+\mathcal{Q}_n^{\gamma}\left(\frac{1}{T^{\delta}}-\frac{1}{T^{\gamma}}\right)\\ &\quad+\sum_j\frac{\mathcal{A}_j^{\delta}r_j^{\delta}}{T^{\delta}}+\sum_j\frac{\mathcal{A}_j^{\gamma}r_j^{\gamma}}{T^{\gamma}}-\left[\frac{(v^{\delta}-v^{\gamma})\cdot\Pi_{\mathrm{n}}}{T^{\delta}}\right]\geq 0\end{aligned} \tag{31}$$

where $\mathcal{A}_j^{\delta}$ is the affinity of jth surface chemical reaction on the δ side of the interface. This serves to postulate the kinetic equations consistent with the second law. Separating processes of different tensorial nature, in agreement with Curie's theorem, we may write separate inequalities for the surface chemical reactions, surface energy and mass transfer and surface frictional effects.

3.2. Hamiltonian structure

Finally, we have shown that the structure of the transport–reaction equations obtained by the variational method is Hamiltonian. For this purpose, the "dissipative" momenta are evaluated as the derivatives $\partial L_\sigma/\partial\mathbf{j}$ and $\partial L_\sigma/\partial\mathbf{r}$, with which the "thermodynamic Hamiltonian" follows in terms of the physical variables as

$$H_\sigma=\tfrac{1}{2}\mathbf{L}^{-1}(\mathbf{u}):\mathbf{jj}+\tfrac{1}{2}\mathbf{R}:\mathbf{rr}-\tfrac{1}{2}\mathbf{L}(\mathbf{u}):\nabla\mathbf{u}\nabla\mathbf{u} -\tfrac{1}{2}\mathbf{R}^{-1}:(\nu'^{\mathrm{T}}\mathbf{u})(\nu'^{\mathrm{T}}\mathbf{u}) \tag{32}$$

In terms of H_σ the divergenceless part of the entropy functional takes the form

$$S_\sigma^{\mathrm{T}}=-\int\left[H_\sigma(\mathbf{u},\mathbf{w},\nabla\mathbf{u},\nabla\mathbf{w})+\rho(\mathbf{u})\cdot\frac{\partial\mathbf{w}}{\partial t}\right]\mathrm{d}\mathbf{x}\,\mathrm{d}t \tag{33}$$

The first canonical equation is obtained by taking the variational derivative for the above integral with respect to the intensity $\mathbf{u}$

$$-c(\mathbf{u})\frac{\partial\mathbf{w}}{\partial t}=-\frac{\delta H_\sigma}{\delta\mathbf{u}}=-\nabla\cdot(\mathbf{L}\nabla\mathbf{u})+\mathbf{v}'\mathbf{R}^{-1}\mathcal{A}^s(\mathbf{u}) \tag{34}$$

This is the vector representation of all equations of change. The second canonical equation or the stationarity condition of the integral S_σ^{T} with respect to the multiplier $\mathbf{w}$ is the set of conservation equations for energy, mass and electric charge

$$\frac{\partial\rho(\mathbf{u})}{\partial t}=\frac{\delta H_\sigma}{\delta\mathbf{w}}=-\nabla\cdot(\mathbf{L}\nabla\mathbf{w})+\nu'\mathbf{R}^{-1}(\nu'^{\mathrm{T}}\mathbf{w}) =-\nabla\cdot\mathbf{J}+\nu'\mathbf{r} \tag{35}$$

The two canonical equations (34) and (35) coincide at the local equilibrium, and the result can be written in terms of the variables $\mathbf{u}$ only, as the nonlinear equation of change

$$c(\mathbf{u})\frac{\partial\mathbf{u}}{\partial t}=\nabla\cdot(\mathbf{L}\nabla\mathbf{u})-\mathbf{v}'\mathbf{R}^{-1}\mathcal{A}^s(\mathbf{u}) \tag{36}$$

It incorporates the Fourier–Onsager transports, Ohm's electric conductivity and nonlinear chemical kinetics of Guldberg and Waage. They are shown here to have variational background subject the assumption that reduction of variables takes place on Gibbs manifold. It follows from the Hamilton's equations that the variational method assures classical nonlinear kinetics and nonlinear set of diffusion–reaction equation under the condition of LTE, $\mathbf{u} = \mathbf{w}$. The variational approach is reacher than classical and, for suitable resistances, true nonlinear chemical kinetics (Guldberg and Waage kinetics, Langmuir kinetics, or other) is secured along with nonlinear diffusion–reaction equations.

3.3. Example of application

As an example of the process in which the theory can successfully be applied we consider the description of new phase creation (vapor) during flashing, that is, boiling of expanding water in a nozzle in which intense evaporation occurs caused by the large pressure drop and consistent increase of the velocity. Production of vapor in the flashing zone and its later disappearance in the "shock wave" are described by a relaxation–diffusion model [21]. Assuming that the disequilibrium caused by the creation of vapor bubbles is defined as the difference in the dryness fraction $x^e - x$, the vapor production can be treated as a chemical reaction described by the resistance equation

$$R(x) = R \ln \frac{k^{\mathrm{f}}(1-x)/(k^{\mathrm{b}}x)}{k^{\mathrm{f}}(1-x) - k^{\mathrm{b}}x} \tag{37}$$

After introducing the equilibrium dryness fraction $x^e = k^{\mathrm{f}}/(k^{\mathrm{f}} + k^{\mathrm{b}})$, the kinetics of the phase change during flashing or condensation becomes described by the expression $r = (k^{\mathrm{f}} + k^{\mathrm{b}})(x^e - x)$, which constitutes a well-known relaxational formula with the relaxation time $\theta_x = (k^{\mathrm{f}} + k^{\mathrm{b}})^{-1}$. Consequently, the second law variational principle which uses the resistance (21) in its particular form (37) applies to pseudohomogeneous mixture of water and vapor. This leads to the description of flashing as an interface chemical reaction.

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