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s_i should be replaced by $-s_i$ in Eqs. (10) and (11) and in the phrase immediately following Eq. (11).

Dissipation Potentials for Reaction-Diffusion Systems

J. D. Goddard*

University of California, San Diego Department of Mechanical and Aerospace Engineering, 9500 Gilman Drive, La Jolla, California 92093-0411, United States

ABSTRACT: This work considers strongly dissipative reaction−diffusion systems with constitutive equations given by Edelen's dissipation potentials, whose existence is tantamount to nonlinear Onsager symmetry. As the main goal of this work, it is shown that the associated extremum principle yields the relevant steady-state species balances and concentration fields for well-mixed reactors as well as for spatially inhomogeneous reactions accompanied by diffusion. The above principle is contrasted briefly with the popular notion of maximum entropy production. Potential applications of the theory to a wide range of reaction−diffusion systems are discussed, and questions are raised as to the possible breakdown of strong dissipation and nonlinear Onsager symmetry arising from reversible chemical or chemomechanical couplings.

■ INTRODUCTION

In a remarkable but much neglected series of papers, Edelen[5−7] shows that any *strictly dissipative* system with finite degrees of freedom is endowed with a *dissipation potential*. Such a system is defined by a finite set ("vector") of generalized "fluxes" $\mathbf{J} = [J_\alpha]$, $\alpha = 1, 2, ..., n$, given as functions $\mathbf{J}(\mathbf{X})$ of conjugate generalized "forces" $\mathbf{X} = [X^\alpha]$, whose *power* $\mathbf{X} \cdot \mathbf{J}$ defines a non-negative definite dissipation (rate):

$$\mathcal{D} = D(\mathbf{X}) = \mathbf{X} \cdot \mathbf{J} = \mathbf{J} \cdot \mathbf{X} \overset{\text{def}}{=} J_\alpha X^\alpha = D^*(\mathbf{J}) \geq 0 \qquad (1)$$

where equality occurs only for $\mathbf{J} = \mathbf{X} = 0$. Here, as below, brackets [ ] are employed to denote abstract-vector and matrix components, and sums are taken over pairs of identical superscripts and subscripts (the *tensor summation convention*—although not essential to the understanding of this article, the vector space $\mathbb{X}^*$ of fluxes $\mathbf{J}$ represents the dual of the vector space $\mathbb{X}$ of forces $\mathbf{X}$, and the above dot product defines the associated "pairing" or linear function $\mathbb{X}^* \times \mathbb{X} \to \mathbb{R}$, i.e. the map into real numbers representing power.[14]) Then, super-scripts and subscripts serve conveniently to distinguish nominal forces from fluxes.

Following Edelen, we assume that the dissipation rate is a *convex* function, which implies invertibility with $\mathbf{X} = \mathbf{X}(\mathbf{J})$, so that the $\mathcal{D}$ can be regarded as a function of either $\mathbf{X}$ or $\mathbf{J}$ as indicated in eq 1, either of which defines a *dissipation function*. We recall that the classical Rayleigh−Onsager dissipation function for linear systems is quadratic in $\mathbf{X}$ or $\mathbf{J}$, whereas the present theory applies to arbitrary nonlinear processes.

For the systems defined above, Edelen shows that there exist *dual* dissipation potentials, with

$$\mathbf{J} = [J_\alpha] = \partial_{\mathbf{X}} \varphi(\mathbf{X}) + \mathbf{U}(\mathbf{X}) = \left[\frac{\partial \varphi}{\partial X^\alpha} + U_\alpha \right],$$

and

$$\mathbf{X} = [X^\alpha] = \partial_{\mathbf{J}} \psi(\mathbf{J}) + \mathbf{V}(\mathbf{J}) = \left[\frac{\partial \psi}{\partial J_\alpha} + V^\alpha \right], \qquad (2)$$

$\mathbf{U}, \mathbf{V}$ are nondissipative ("powerless" or "gyroscopic") terms, such that

$$\mathbf{X} \cdot \mathbf{U} = 0 \text{ and } \mathbf{J} \cdot \mathbf{V} = 0 \qquad (3)$$

and Edelen shows how the potentials and the terms $\mathbf{U}, \mathbf{V}$ can be derived from the functions $\mathbf{J}(\mathbf{X})$ or $\mathbf{X}(\mathbf{J})$ by means of exterior calculus. His book[8] treats this in more mathematical detail, and in a recent article devoted to other applications, the present author[14] shows that Edelen's formulas can be derived by means of ordinary vector calculus. The interested reader is referred to these sources for more detail.

The gyroscopic terms in eq 2 represent the breakdown of nonlinear Onsager symmetry, and when they are are absent, we call the system *strongly dissipative* (or *hyperdissipative* in analogy to *hyperelastic* in solid mechanics). Such a system represents the dissipative counterpart of reversible thermodynamic systems, with *force potential* φ and *flux potential* ψ corresponding, respectively, up to algebraic sign, to Gibbs and Helmhotz free energies. As with equilibrium thermodynamics, the constitutive theory connecting fluxes and forces in strongly dissipative systems *is completely determined by a single scalar potential*.

Table 1 displays examples of electrical, chemical, and mechanical systems which can exhibit strictly dissipative behavior (with $s_{ij} = v_{i,j} + \epsilon_{ijk}\omega^k$, where semicolons denote gradients). Applications to the mechanics of viscoplastic bodies are discussed elsewhere,[14,19] and the focus here is on chemical reactions and mass diffusion. As suggested by the table, the abstract enumerative index κ is to be replaced by the indices or collections of indices appropriate to the application at hand.

We recall that chemical reactions represent one of the earliest application of Edelen's potentials by Bataille et al.,[1] who do not pursue all the consequences and do not cite the contemporaneous body of cognate studies by others,[3,9,21,24,25] studies which do not consider Edelen's work. In the present article, we

Table 1. Examples of Dissipative Systems

system	force X^κ	flux J_κ	dissipation $\mathcal{D} = \mathbf{X} \cdot \mathbf{J}$
networks			
electrical resistors, $\kappa = 1n$	voltage V^κ	current I_κ	$-V^\kappa I_\kappa$
chemical reactions, $\kappa = 1n$	affinity A^κ	rate ω_κ	$-A^\kappa \omega_\kappa$
continuum mechanics	(hyper)stress	kinematics	stress-power
nonpolar continua, $n = 6$	$\sigma^{ij} = \sigma^{ji}$	$v_{i;j}$	$\sigma^{ij} v_{i;j}$
cosserat continua, $n = 18$	$\tau^{ij} \oplus m^{ij}$	$s_{ij} \oplus \omega_{i;j}$	$\tau^{ij} s_{ij} + m^{ij} \omega_{i;j}$
graded continua, $n = 27$	$\tau^{ij} \oplus \tau^{ijk}$	$v_{i;j} \oplus v_{i;jk}$	$\tau^{ij} v_{i;j} + \tau^{ijk} v_{i;jk}$

consider the implications of the associated extremum principle, which could have far reaching implications for reaction−diffusion and analogous systems. The main goal of the present papers is to present a sketch of general principles, without attempting a rigorous mathematical treatment and without detailed application to specific mathematical problems, although certain possibilities for the latter are mentioned below in the concluding section.

■ DISSIPATIVE REACTION−DIFFUSION SYSTEMS

Before formulating the reaction−diffusion problems, we recall that the potentials in eq 2 are (Legendre−Fenchel) convex conjugates, as noted elsewhere[14] (where it is also pointed out that for nondifferentiable potentials "max" is to be replaced by "sup" and partial derivatives by set-valued "sub-gradients"), with

$$\varphi(\mathbf{X}) = \max_{\mathbf{J}}\{\mathbf{X} \cdot \mathbf{J} - \psi(\mathbf{J})\} \text{ or } \psi(\mathbf{J}) = \max_{\mathbf{X}}\{\mathbf{X} \cdot \mathbf{J} - \varphi(\mathbf{X})\}$$

$$\text{and} \therefore \mathbf{J} = \xi^*(\mathbf{X}) = \partial_\mathbf{X}\varphi(\mathbf{X}), \ \mathbf{X} = \xi(\mathbf{J}) = \partial_\mathbf{J}\psi(\mathbf{J})$$

$$(4)$$

This leads to the *pseudolinear* relations with positive symmetric matrices $\mathcal{L} = \mathcal{L}^T = \mathcal{R}^{-1}$:

$$\mathbf{J} = [J_\alpha] = \mathcal{L}\mathbf{X} = [\mathcal{L}_{\alpha\beta}X^\beta] = \partial_\mathbf{X}\varphi \text{ and } \mathbf{X} = [X^\alpha] = \mathcal{R}\mathbf{J}$$

$$= [\mathcal{R}^{\alpha\beta}J_\beta] = \partial_\mathbf{J}\psi \tag{5}$$

where the positive definite "Onsager conductance" $\mathcal{L}$ now depends on $\mathbf{X}$ and its reciprocal resistance $\mathcal{R}$ depends on $\mathbf{J}$. Their derivation is presented elsewhere,[14] and it is shown that the presence of gyroscopic terms in eq 2 lead to *asymmetric* matrices $\mathcal{L}$ and $\mathcal{R}$, representing a breakdown of hyper-dissipativity and the associated (nonlinear) Onsager symmetry.

As pointed out previously,[14] the above structure leads to a variational principle in which the dissipation potential is extremalized (mischaracterized as "maximized" in ref 14, since it depends on the potential being considered), an idea which is generally at odds with the "principle of maximum dissipation" (or maximum rate of entropy production) embraced by numerous investigators, particularly by Ziegler and contemporary adherents.[22,29,30] This divergence of principle was pointed out previously[1] for the case of chemical kinetics.

The present work is predicated on the principle of stationary or extremal dissipation potential and the implications for steady-state reaction-diffusion systems. Such systems, which represent the "stationary non-equilibrium state" of irreversible thermodynamics, are assumed to be strongly dissipative, with reservations to be discussed below in the conclusions. With this in mind, we consider first the case of homogeneous or "well-mixed states" such as are achieved ideally in the classical

CSTR,[11] and then we consider nonuniform states involving reaction in the presence of mass diffusion.

We shall have occasion to employ Edelen's formulas for dissipation potentials in terms of dissipation, given e.g. in ref 14 as

$$\varphi(\mathbf{X}) = \int_0^1 D(s\mathbf{X})\frac{ds}{s} \text{ or } \psi(\mathbf{J}) = \int_0^1 D^*(s\mathbf{J})\frac{ds}{s} \tag{6}$$

from which it follows that a dissipation function that is a homogeneous function gives rise to a dissipation potential that is simply proportional to the dissipation rate.[14] In the present article, we focus mainly on force potentials of the type φ.

Homogeneous Systems. We consider a chemical reaction involving n chemical species $\mathcal{S}_i$, $i = 1, ..., n$ with spatially uniform molar concentrations c_i [mol/vol], volumetric rates of reaction r_i [mol/vol-time] (production), and rate of external supply s_i [mol/vol-time]. Equating the abstract fluxes to the reaction rates, with $\mathbf{J} = [J_i] = [-r_i]$, we tentatively identify the conjugate forces with the chemical potentials (partial molar Gibbs free energies) μ^i, which we distinguish with superscripts. Whenever the quantity $D = -\mu^i r_i$ is non-negative definite, it represents the dissipation in the entropy balance (Clausius−Duhem) inequality. See, e.g., the classical treatment in ref 17, pp 702−703, and the more recent treatments,[9,13,15,21] each involving some nonessential differences in the thermodynamics. While many of the papers just cited assume that chemical kinetics are strictly dissipative, they do not avail themselves of Edelen's potentials. We note that Krambeck's assumption of the symmetry of the matrix $[\partial r_i/\partial \mu_j]$ is tantamount to nonlinear Onsager symmetry and to the current definition of strong dissipation, with rates given by Edelen's potential.

For the purposes of this analysis, we assume isothermal conditions with the μ^i given as invertible functions of $\mu^i(c_j) = \mu^i(c_1, c_2,..., c_n)$. The latter representation, previously adopted by others,[9,21] follows from the equation of state $\breve{a} = \breve{a}(c_1, c_2, ..., c_n, T)$ for the volumetric density of Helmholtz free energy, with

$$d\breve{a} = \mu^i dc_i - \breve{s}dT \tag{7}$$

where T is temperature and $\breve{s}$ is volumetric entropy density. The invertibility of $\mu^i(c_j)$ follows then from assumed convexity[21] of $\breve{a}$, which presumably rules out phase transitions. To obtain the usual description for isothermal and isobaric systems in terms of specific Gibbs free energy and n additional independent variables, we could adopt the stratagem proposed in eq 15, introducing an additional chemical species $\mathcal{S}_{n+1}$, e.g. an inert "solvent," along with the reduced chemical potentials given by $\mu^i - \mu^{n+1}$ in lieu of the μ^i.

We recall that Edelen's theory requires that $\mathbf{J} = 0$ for $\mathbf{X} = 0$, which requires a shift of the origin of forces, with

$$X^i = \hat{\mu}^i = \mu^i - \mu_0^i, \text{ where } r_i(\mu_0^j) = 0; \ i = 0, 1, ..., n \tag{8}$$

with the μ_0^i, which may depend on the μ^i, denoting a referential state of chemical equilibrium, which is subject to stoichiometric and other constraints to be specified as needed. We may then take $\mu_0^i r_i = 0$ for any set of rates compatible with stoichiometry. Thus, the μ_0^i represent one special case of Edelen's "powerless" forces, associated here with stoichiometrically constrained equilibrium.

Then, with the assumption that the system of nonequilibrium reactions is strongly dissipative in its progress to equilibrium, the force−potential is given by the first member of eq 6 as

$$\varphi(\mu^i) = -\hat{\mu}^i \int_0^1 r_i(s\hat{\mu}^j) \, ds, \text{ with } r_i = -\frac{\partial \varphi}{\partial \mu^i} \qquad (9)$$

where a sum over i is implied. We consider below the dissipation potentials for some special kinetics, where we adopt reaction affinities as driving forces. First, however, we enunciate the following extremum principle in which δ denotes the usual symbol for variation arising from variation of variables or parameters: *The steady-state reaction system satisfies*

$$\delta(\varphi + \mu^j s_j) = 0 \qquad (10)$$

subject to constant supply rates s_i. As proof, note that the vanishing of the variation

$$\delta(\varphi + \mu^j s_j) = \left(\frac{\partial \varphi}{\partial \mu^i} + s_i\right)\delta\mu^i = (s_i - r_i)\frac{\partial \mu^i}{\partial c_j}\delta c_j \qquad (11)$$

gives the steady-state species balance $r_i = s_i$ since the Jacobian matrix $[\partial\mu^i/\partial c_j]$ is nonsingular.[21] That is to say, the stationarity of φ subject to a given external supply of the chemical species determines the mass balance and hence the state of the system through the constitutive equations $r_i(\mu^j)$ and $\mu^j(c_k)$.

The above results are rendered more evident by means of the standard decomposition of the reaction rates into r stoichiometrically independent reaction pathways with rates ω_j, $j = 1{:}r \leq n$:

$$\mathbf{r} = [r_i] = \mathbf{N}\boldsymbol{\omega} = [\nu_i^j \omega_j] \qquad (12)$$

where $\mathbf{N}$ is the rank-r, $n{\times}r$ matrix of stoichiometric coefficients ν_i^j (representing the number of moles of species i produced by reaction j, with negative values distinguishing reactants from products[11]). With this decomposition, the dissipation takes on a standard form:[1,24]

$$\mathcal{D} = -\mu^i r_i = -A^j \omega_j = -\boldsymbol{\alpha}\cdot\boldsymbol{\omega}, \text{ where } \boldsymbol{\alpha} = [A^i] = [\nu_j^i \mu^j]$$
$$= \mathbf{N}^T\mu \qquad (13)$$

corresponding to the form listed in Table 1, with vector α denoting the vector of *reaction affinities* (i.e., the chemical potential decrement along reaction path j). Thus, we should now employ reaction-path rates ω_i and conjugate affinities A^i instead of species rates and chemical potentials as respective flux and force, such that, provisionally,

$$\omega = [\omega_i] = -\partial_\alpha \varphi = -\left[\frac{\partial \varphi}{\partial A^i}\right] \qquad (14)$$

While numerous past works[9,24] have discussed reaction rate as a function of affinity, Bataille et al.[1] are ostensibly the first to employ Edelen's potentials. Note that the condition $\mu_0^i r_i = 0$ for all r_i compatible with stoichiometry can now be expressed as $A_0^i \omega_i = 0$ for all ω_i, where $A_0^i = \nu_i^j \mu_0^j$. This implies of course that $A_0^i = 0$ for all j, i.e. all equilibrium affinities must vanish.

Note further that eq 13 represents a special case of a more general force-flux transformation that preserves dissipation:

$$\mathbf{X} = \mathcal{N}\mathbf{X}', \quad \mathbf{J}' = \mathcal{N}^*\mathbf{J}, \text{ with } \mathcal{D} = \mathbf{J}\cdot\mathbf{X} = \mathbf{J}'\cdot\mathbf{X}' \qquad (15)$$

where the * represents the *dual* or transpose. In the present case, the transformation matrix $\mathcal{N} = \mathbf{N}$ has rank less than n, which means that straightforward variation of φ in terms of the affinities A^i would result in fewer than the n equations necessary to specify the species concentrations. Hence, there is a restriction of the degrees of freedom arising from stoichio-

metric constraints, and the problem must be reformulated to allow for the specification of a set of concentration variables that includes *reaction invariants* or "generalized inerts." The underlying mathematical techniques are subsumed in numerous previous analyses.[9,12,21,24]

In particular, one may express the vector of chemical potentials $\mu = [\mu^i]$ as $\hat{\mu} = \mathbf{N}^{-T}\alpha + \lambda$, where $\mathbf{N}^{-T} = \mathbf{N}(\mathbf{N}^T\mathbf{N})^{-1}$ denotes the *pseudoinverse* of $\mathbf{N}^T$ which, like the vector of reaction affinities $\boldsymbol{\alpha} = [A^i] = [\hat{\mu}^j \nu_j^i] = \mathbf{N}^T\hat{\mu}$, with $i = 1,...,r$, lies in the r-dimensional range of $\mathbf{N}^T$, whereas the vector $\lambda = [\Lambda^i]$ lies in the $(n-r)$-dimensional null space of $\mathbf{N}^T$ and, hence, is orthogonal (in the sense of linear functions) to the range of $\mathbf{N}$, i.e. $\lambda\mathbf{N} = \mathbf{0}$. (Certain other works[9,21] assume that the forces denoted here by α, λ lie in the same Euclidean space as the fluxes, whereas technically they should be regarded as dual spaces, distinguished here by superscripts and subscripts.) The vector $\lambda = [\lambda^i]$ is in essence the set of Lagrange multipliers or "reactive" forces associated with the conservation of atoms or, more precisely, any independent set of $n - r$ reaction invariants.[12] Accordingly, it seems proper to replace eq 9 by

$$\varphi(\mu^i) = -\boldsymbol{\alpha}\cdot\int_0^1 \boldsymbol{\omega}(\lambda, s\boldsymbol{\alpha}) \, ds = -A^i \int_0^1 \omega_i(\Lambda^j, sA^j) \, ds,$$
$$\text{with } \mathbf{r} = [r_i] = -\frac{\partial \varphi}{\partial \alpha} = -\left[\frac{\partial \varphi}{\partial A^i}\right] \qquad (16)$$

This is perhaps made more evident by a simple mechanical analog involving dissipative (Coulomb) sliding between solid surfaces with dependence on slip velocity and normal force, where λ represents the powerless normal force, $\boldsymbol{\alpha}$ the active tangential force, and ω the slip velocity. Thus, in the variation $\delta\mu$, we must treat λ as constant, with $\delta\lambda = 0$.

Reaction–Diffusion Systems. We are concerned here with spatial region $\mathcal{R}$ (the "reactor"), in which spatially distributed reactions and diffusion occur with $4n$ local fluxes and $4n$ local forces given respectively by

$$\mathbf{J}(\mathbf{x}) = [-r_i(\mathbf{x}), \mathbf{j}_i(\mathbf{x})] \text{ and } \mathbf{X}(\mathbf{x}) = [\mu^i(\mathbf{x}), \mathbf{g}^i(\mathbf{x})],$$
$$\text{with } \mathbf{g}^i = -\nabla\mu^i(\mathbf{x}) \qquad (17)$$

at spatial position $\mathbf{x} \in \mathcal{R}$, where $\mathbf{j}_i$ [mol/area-time] is the space-vector representing diffusional flux of species i and ∇ denotes spatial gradient. In essence, we are now dealing with an *infinite-dimensional function space* (e.g., a *Banach* space), such that the dissipation rate for a strictly dissipative system is a *functional* on the spatial fields, with

$$D[\mu^i] = \int_{\mathcal{R}} (\mathbf{j}_i\cdot\mathbf{g}^i - \mu^i r_i) \, dV(\mathbf{x}) \qquad (18)$$

with bold-face brackets [ ] denoting the arguments of functionals as spatial fields. We assume smooth fields that possess gradients, such that specification of $\mu^i(\mathbf{x})$ also specifies $\nabla\mu^i(\mathbf{x})$. Given strong dissipation at all points $\mathbf{x} \in \mathcal{R}$, it is plausible if not certain that eq 18 can be expressed as the functional derivative of a global dissipation potential given by the functional

$$\Phi[\mu^i] = \int_{\mathcal{R}} \varphi\{\mu^i(\mathbf{x}), \mathbf{g}^i(\mathbf{x})\} \, d\mathbf{V}, \text{ with } \varphi(\mu^i, \mathbf{g}^i)$$
$$= \varphi_D(\mathbf{g}^i) + \varphi_R(\mu^i) \qquad (19)$$

involving local reaction and diffusion potentials as

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$$\varphi_R(\mu^i), \text{ with } r_i = -\partial_{\mu i}\varphi_R \text{ and } \varphi_D(\mathbf{g^i}) \text{ with } \mathbf{j}_i = \partial_{\mathbf{g}^i}\varphi_D \tag{20}$$

The latter is not restricted to classical linear diffusion laws (the analog of linear Darcy flow in porous media, which can also be extended to nonlinear flow[19]) and the associated quadratic form for φ_D. Although by no means necessary, we have assumed an "uncoupled" form of $\varphi(\mu^i, \mathbf{g}^i)$ via the last equation in eq 19.

Substituting the Edelen formulas 6–9 into eq 19 gives formally

$$\Phi[\mu^i] = \int_0^1 \int_{\mathcal{R}} [\mathbf{g}^i(\mathbf{x}) \cdot \mathbf{j}_i\{s\mathbf{g}_j(\mathbf{x})\} - \mu^i(\mathbf{x})r_i\{s\hat{\mu}^j(\mathbf{x})\}]$$
$$dV(\mathbf{x}) \, ds$$
$$= \int_0^1 D[s\hat{\mu}^i]\frac{ds}{s} \tag{21}$$

the analog of a result given elsewhere.[19] That is, the functional specifying the global dissipation potential is given by the functional for the global dissipation, which represents the infinite-dimensional analog of the finite-dimensional Edelen relation 6.

Of interest here is the variation of the functional

$$F[\mu^i] = \Phi[\mu^i] - \iint_{\partial\mathcal{R}} \mu^i \mathbf{j}_i \cdot \mathbf{n} \, dS(\mathbf{x}) \tag{22}$$

involving an integral over the boundary $\partial\mathcal{R}$ of $\mathcal{R}$, whose unit outer normal is denoted by $\mathbf{n}$. With $\mathbf{j}_i \cdot \mathbf{n}$ fixed at all points $\mathbf{x} \in \partial\mathcal{R}$, this variation is found to be

$$\delta F[\mu^i] = \int_{\mathcal{R}} (\partial_{\mathbf{g}^i}\varphi_D\delta\mathbf{g}^i(\mathbf{x}) - \partial_{\mu^i}\varphi_R\delta\mu^i(\mathbf{x})\}) \, dV$$
$$= \int_{\mathcal{R}} (\nabla \cdot \mathbf{j}_i - r_i)\delta\mu^i \, dV(\mathbf{x}) \tag{23}$$

where we employ the relation $\delta\mathbf{g}^i = -\delta(\nabla\mu^i) = -\nabla(\delta\mu^i)$ and the (Gauss) divergence theorem. Hence, the stationarity of Φ requires that the right-hand side of eq 23 vanishes for all admissible variations $\delta\mu^i$.

Note that in the case of a homogeneous reactor where all fields in $\mathcal{R}$ are independent of $\mathbf{x}$, this reduces to eq 11, provided we identify the volumetric supply rates as

$$s_i = -\frac{1}{V}\int_{\partial\mathcal{R}} \mathbf{j}_i \cdot \mathbf{n} \, dS(\mathbf{x}) \tag{24}$$

Otherwise, for the nonhomogeneous case, we obtain the steady-state species mass balance $\nabla \cdot \mathbf{j}_i = r_i$. That is, stationarity of the dissipation functional Φ subject to fixed species input at all points of $\partial\mathcal{R}$ yields the steady-state mass balances and presumably also the concentration fields from the constitutive equation for $\varphi(\mu^i, \mathbf{g}^i)$. The converse seems obvious.

In closing here, we note that the issue of stoichiometric constraints raised above is now resolved in principle by appropriate specification of boundary conditions on $\partial\mathcal{R}$ for c_i and/or $\mathbf{j}_i$.

APPLICATIONS, EXTENSIONS, AND CONCLUSION

As a concrete illustration of the above theory, we derive the dissipation potential for a simplified version of mass-action kinetics. In particular, we consider the case of a single reaction among reactants with $\nu_i \leq 0$ for $i \in \mathbf{R} = \{1, 2, ..., R\}$ and products with $\nu_i \geq 0$ for $i \in P = \{R + 1, 2, ..., n\}$, and with rate

$$r_i = \nu_i\omega, \text{ where } \omega = k\left(\Pi_P - \frac{1}{K}\Pi_R\right), \Pi_Q = \prod_Q c_i^{|\nu_i|},$$
$$\text{for } Q = R, P \tag{25}$$

where $\prod$ denotes a product and k and k/K are the respective kinetic coefficients for forward and reverse reactions.

We consider the case of ideal solutions for which we may set $c_i/c = \exp\{\beta(\mu^i - g^i)\}$ where $\beta = 1/RT$ and g^i is the molar free energy of the pure species. Evaluating the equilibrium constant K at the equilibrium state $\omega = 0$, $\mu^i = \mu_0^i$, we can reduce eq 25 to the form

$$\omega = k_0\left[\left(\frac{c}{c_0}\right)^{\Delta n/2}e^{\beta A/2} - \left(\frac{c}{c_0}\right)^{-\Delta n/2}e^{-\beta A/2}\right],$$

$$\text{with } k_0 = kc^{n/2}c_0^{\Delta n/2}\exp\beta\{\hat{A}/2 + \sum_R |\nu_i|(\mu_0^i - g^i)\},$$

$$n_Q = \sum_Q |\nu_i|, \hat{A}_Q = \sum_Q \hat{\mu}^i|\nu_i|, \text{ for } Q = P, R,$$

$$n = n_P + n_R, \Delta n = n_P - n_R, \hat{A} = \hat{A}_P + \hat{A}_R,$$
$$A = \hat{A}_P - \hat{A}_R \tag{26}$$

where c_0 is the value of total molar density c at the equilibrium state and the $\hat{A}_Q$ represent "partial" reaction affinities. Here and in the passages immediately following, we suspend our summation convention on repeated indices.

It is easy to show that the expression for $A\omega$ (eq 26) will be positive, hence dissipative, only if $k_0 > 0$ and $c = c_0$. The last condition implies that the hypothetical equilibrium state must be subject to the constraint of constant c. For an ideal gas, this implies that this equilibrium state is achieved under isobaric and isothermal conditions. The condition is also is also realized in the important special case of a nominally incompressible solution in a solvent $\mathcal{S}_{n+1}$.

We note that the kinetics of an irreversible reaction with $K \to \infty$ is formally represented by $c_i = 0$ or $\mu_0^i \to -\infty$ for some $i \in P$. On the other hand, the limit $k \to \infty$ leads generally to a condition of chemical equilibrium $A = \mu^i\nu_i = 0$ representing a (linear) constraint on the μ^i. Accordingly, this engenders an additional nondissipative flux proportional to ν_i. We note that the prefactor k_0 involves quantities that depend on $\hat{\mu}^i$, and in order to achieve an explicit form of the integral 16, we shall assume that further restrictions on the kinetic coefficient k and the hypothetical equilibrium state μ_0^i can render this quantity dependent only on the $n - 1$ constraint variables $\lambda = [\Lambda^i]$ appearing in eq 16. Then, eq 16 gives

$$\varphi = 4\frac{k_0}{\beta}[\cosh(\beta A/2) - 1] \tag{27}$$

In the case of small affinities, one recovers the well-known (Rayleigh–Onsager) quadratic form $\varphi = k_0\beta A^2/2$.

Having derived eq 27 by a thermodynamic route, we can now recast it in terms of concentration variables c_i. This restores the latter as primary variables, with $\varphi(c_1, c_2,..., c_n)$ being the proper object of the extremum principle. Without further detailed analysis, it seems plausible that one should be able to handle the above diffusion laws by the same artifice, providing a direct variational principle for concentration fields. Certain special cases are apparent for diffusion described by Fick's law.

It is a straightforward matter to apply the above formulas to a system of multiple simultaneous reactions with rates $r_i = \nu_i^j \omega_j$ and partial affinities $\hat{A}_Q^j = \sum_Q \hat{\mu}^i |\nu_i^j|$, allowing one to treat reaction networks of reactions governed by mass-action kinetics. Moreover, the above theory is readily extended to nonisothermal systems involving nonuniform temperature field $T(\mathbf{x})$, heat of reaction, and diffusive heat flux $\mathbf{q}$ [energy/area-time]. To this end, it suffices to enlarge the set of generalized forces to include $\mathbf{g}^0 = -\nabla T$ and the set of fluxes to include $\mathbf{j}_0 = \mathbf{q}/T$. The diffusion potential φ_D depends now on all the forces $\mathbf{g}^i$ and allows for the coupled heat and mass diffusion envisaged in linear irreversible thermodynamics (LIT), but without the restriction to linear processes.

The theory can also be extended to heterogeneous reactions by simply replacing the three-dimensional domain by a two-dimensional reactive surface, with

$$\mathrm{d}V(\mathbf{x}) \to \mathrm{d}S(\mathbf{x}), \text{ and } \int_{\partial \mathcal{R}} \mu^i \mathbf{j}_i \cdot \mathbf{n}\, \mathrm{d}S(\mathbf{x}) \to [\![\mu^i \mathbf{j}_i \cdot \mathbf{n}]\!]$$

in eq 23, where $[\![\ ]\!]$ denotes a discontinuity across $\mathcal{R}$ determined by external mass transfer from the surrounding bulk phases, which may also be subject to strongly dissipative mass-transfer relations. The flux $[r_i, \mathbf{j}_i]$ now refers to surface quantities, i.e. surface reaction rate and surface diffusion. Clearly, one can also treat the case of coupled homogeneous and heterogeneous reactions with a dissipative transfer of mass and heat, including diffusion and reaction in porous media and catalysts.

Finally, we note that the nominal reaction rates in the above model can be identified with irreversible dissolution processes of the type studied for asphaltenes and zeolites by Fogler and co-workers.[16,18,26] Although these involve phase change associated with nonconvexity of thermodynamic potentials, this does not rule out convex dissipation potentials.

In sum, the above theory reduces the problem of determining concentration fields in steady-state systems involving complex chemical reaction networks to a variational problem. This is the dissipative analog of the determination of equilibrium concentrations by extremalization of the appropriate thermodynamic potential.

As other possible applications, we recall that variational methods have found extensive use in numerical analysis, e.g. in finite-element methods, and in approximate solutions based on *Galerkin* techniques. Moreover, such methods have already been applied to the *homogenization* (derivation of continuum from discrete models) of dissipative mechanical and chemical systems,[4,19,20] not to mention a large amount of literature on elastic composites endowed with elastic potentials.

A superficial survey of the vast and ever expanding field of biochemical and metabolic reaction networks reveals early studies[23−25] that appeal to the idea of maximum dissipation and contemporary investigations[2,27,28] that are based heavily on stoichiometric considerations. One is therefore led to wonder if extremum principles based on Edelen potentials might not be more relevant to the overall kinetics of such systems.

To close with a major reservation, we note that the above analysis is restricted to strongly dissipative systems, whereas one cannot generally rule out gyroscopic forces of the kind displayed in eq 2. The present analysis indicates that stoichiometric constraints may be viewed formally as a special case, for which one can effectively eliminate such forces by change of variables. More generally, and as conjectured elsewhere,[14] gyroscopic effects may arise from reversible couplings between fluxes or forces. In the case of chemical reaction networks, this might be realized by the coupling of reversible or nearly reversible reactions, with possible implications for biosynthetic processes. Similar questions arise for otherwise dissipative biochemo-mechanical processes, a matter which warrants further investigation that would go beyond the scope of the present paper.

■ AUTHOR INFORMATION

Corresponding Author
*Phone: +1 858 534 4508. Fax: +1 858 5534 4543. E-mail: jgoddard@ucsd.edu.

Notes
The authors declare no competing financial interest.

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