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On nonlinear Onsager symmetry and mass-action kinetics

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ABSTRACT

This brief paper is a continuation of previous work (J.D. Goddard, "Dissipation potentials for reaction-diffusion systems." I&EC Res.,54.16,4078–4083, 2015) dealing with the application of Edelen's dissipation potentials to the irreversible thermodynamics of chemical-reaction networks. It is shown that one can achieve non-linear Onsager symmetry by means of constraints on a certain combination of Gibbs free energies dubbed *reactivity*, from which it follows that reaction rates are given simply as gradients of a dissipation potential. This may open the door to the application of thermodynamics and variational methods to combustion and biochemical reaction networks, including the possibility of enhanced derivation of reduced kinetic mechanisms. A graph-theoretical description of reaction networks is presented, which is based on stoichiometric hypergraphs and encompasses several past treatments in a more economical fashion. It may also suggest hypergraph optimization techniques to enhance the selection of reduced mechanisms.

Introduction

A preceding paper Goddard (2015),[1] hereinafter denoted by Ref. 1, considers the application of Edelen's theory of strictly dissipative (i.e. completely irreversible) systems to the description of multiple chemical reactions accompanied by heat and mass transfer. In particular, a certain variational principle was assumed whose validity requires non-linear Onsager symmetry. It was tacitly assumed that the irreversible processes involved in chemical kinetics were endowed with this symmetry, which among other things provides the desired variational principle.

Apart from the philosophical appeal of teleological principles, the existence of an extremum principle could be important for modeling various chemical and biochemical processes, not only for the derivation of approximate solutions to steady-state field equations, such as those describing steady laminar flames, but also for the development of reduced kinetic mechanisms, as studied extensively in the field of combustion (Fernández-Galisteo et al. 2019; Jiang et al. 2020; Millán-Merino et al. 2020, and references therein). When it comes to construction of reduced mechanisms for combustion reactions, variational methods grounded in thermodynamics seem physically more attractive than certain abstract optimization techniques proposed by others (Bhattacharjee et al. 2003).

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[1]A list of minor but previously unpublished corrigenda is given below in Appendix A.

Since mass-action kinetics are generally employed for the description of gaseous combustion reactions, the question naturally arises as to the underlying thermodynamics and the possible Onsager symmetry. To clarify the latter, we recall that Edelen (Edelen 1972; Goddard 2014) shows that any *strictly dissipative* system with finite degrees of freedom is endowed with a *dissipation potential*. To recapitulate, for systems defined by a finite set of generalized "fluxes" represented by an abstract vector $\mathbf{J} = [J_j]$, $j = 1, 2, \ldots, n$, given as functions $\mathbf{J}(\mathbf{X})$ of conjugate generalized "forces" $\mathbf{X} = [X^j]$, the *power* $\mathbf{X} \cdot \mathbf{J}$ defines a non-negative definite dissipation rate (or entropy-generation rate multiplied by absolute temperature):

$$\mathcal{D} = D(\mathbf{X}) = \mathbf{X} \cdot \mathbf{J} = \mathbf{J} \cdot \mathbf{X} \stackrel{\text{def}}{=} J_j X^j = D^*(\mathbf{J}) \geq 0, \tag{1}$$

where equality holds only if $\mathbf{J}$ or $\mathbf{X}$ vanishes. Then, superscripts and subscripts serve conveniently to distinguish nominal forces from fluxes (as dual vector spaces).

The functions D and D^* are assumed to be *convex*, which implies invertibility with $\mathbf{X} = \mathbf{X}(\mathbf{J})$, so that the $\mathcal{D}$ can be regarded as 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 Edelen's theory applies to arbitrary non-linear processes. This is the only situation for which dissipation function (or entropy generation rate) is basically identical with the dissipation potential to be discussed next.

For the systems defined above, there exist a potential function $\varphi(\mathbf{X})$ such that

$$\mathbf{J} = [J_j] = \partial_{\mathbf{X}} \varphi(\mathbf{X}) + \mathbf{J}^o(\mathbf{X}) = \left[\frac{\partial \varphi}{\partial X^j} + J_j^o \right], \tag{2}$$

and a dual relation with the role of force and flux reversed, which we do not need for the present analysis. The flux $\mathbf{J}^o$ is non-dissipative ("powerless" or "gyroscopic"), such that:

$$\mathbf{X} \cdot \mathbf{J}^o = X^i J_i^o = 0, \tag{3}$$

and both $\varphi(\mathbf{X})$ and $\mathbf{J}^o(\mathbf{X})$ can be derived from the function $\mathbf{J}(\mathbf{X})$ (Edelen 1972; Goddard, 2014). We recall that a discussion of non-dissipative fluxes in chemical kinetics is given by Bataille, Edelen, and Kestin (1978).

When gyroscopic terms are absent, one obviously has the Maxwell-type relations

$$\frac{\partial J_i}{\partial X^j} = \frac{\partial J_j}{\partial X^i}, \ \text{ for } \ i, j = 1, 2, \cdots, n, \tag{4}$$

which are not satisfied by $\mathbf{J}^o$. Thus, the occurrence of non-zero gyroscopic terms in Eq (2) represents the breakdown of non-linear Onsager symmetry. When such terms are absent, we say the system is *strongly dissipative, hyperdissipative*, or simply *Onsager-symmetric*.

The dissipation potentials for Onsager-symmetric systems represent the dissipative analogs of the potentials describing equilibrium-thermodynamic systems. Thus, the constitutive equations connecting generalized displacements or fluxes to conjugate forces in such systems are completely determined by convex-conjugate scalar potentials. Moreover, in perfect analogy to equilibrium systems, certain conservation laws or balance equations arise from the minimization of potential. We refer the reader to Ref. 1 and references therein while focusing attention here on the issue of Onsager symmetry of the mass-action form of chemical kinetics.

In the interest of a reasonably self-contained exposition, certain material from previous publications is restated in the following presentation. As a word on notation, we shall employ bold upper case Greek and Roman font for matrices, with bold lower case generally reserved for the special case of column or row vectors, and with the rules of matrix multiplication for their products. (As the sole exception, we employ Onsager's upper-case notations for general forces and fluxes.) We indicate the components of vectors and matrices by letters with superscripts and subscripts, all in light font, enclosed in square brackets [ ]. Superscripts generally denote forces and subscripts their conjugate rates (as members of dual spaces), with summation over pairs of repeated superscript and subscript (as tensor summation convention), except where otherwise indicated. Partial derivatives are most often denoted by subscripted symbol ∂.

Irreversible thermodynamics of mass-action kinetics

We shall have occasion to employ Edelen's construct for the force potential in terms of dissipation rate as outlined in Ref. 1

$$\varphi(\mathbf{X}) = \int_0^1 D(s\mathbf{X})\frac{ds}{s} = \mathbf{X} \cdot \int_0^1 \mathbf{J}(s\mathbf{X})ds, \tag{5}$$

whereas we will not need related formula for $\mathbf{J}^o$. It is obvious from the preceding relation that the dissipation function is generally not the same as the dissipation rate $\mathbf{X} \cdot \mathbf{J}$ except for the case where $\mathbf{J}$ is linear in $\mathbf{X}$, which represents the classical Rayleigh-Onsager form.

We consider a chemical reaction or network of reactions involving $n = S$ chemical species $\mathcal{S}_i$, $i = 1, \ldots, S$ with molar concentrations C_i [moles /vol.], volumetric rates of production by reaction r_i [moles /vol.-time], and with abstract fluxes given by the reaction rates, with $\mathbf{J} = [J_i] = [-r_i]$, we provisionally identify the conjugate forces X^i with the chemical potentials (partial molar Gibbs free energies) μ^i. Adopting the postulate of several past works and Ref. 1, the quantity $D = -\mu^i r_i$ is assumed to represent a non-negative dissipation rate.

For the purposes of this analysis, we assume isothermal conditions with the μ^i given as invertible functions of S species concentrations $\mu^i(C_j) = \mu^i(C_1, C_2, \ldots, C_S)$. More detail is given in Ref. 1, where, to satisfy the condition $\mathbf{J} = 0$ for $\mathbf{X} = 0$, the force is defined as

$$X^i = \hat{\mu}^i = \mu^i - \mu_o^i, \text{ where } r_i(\mu_0^j) = 0, \ i = 0, 1, \ldots, S, \tag{6}$$

with μ_o^i denoting a fixed referential state of chemical equilibrium. Artificial values of y_i and μ^i may need to be imposed at the nominal equilibrium state in the case of reactions like those of combustion, where the amounts of certain species such as oxidant or fuel may be completely consumed. With these understandings, we drop the hats $\widehat{}$ on μ.

The standard decomposition of the species reaction rates into R stoichiometrically independent kinetic pathways with rates ω_j, $j = 1, 2, \ldots, R \leq S$ is given by

$$\mathbf{r} = [r_i] = \mathbf{N}\omega = [\nu_i^j \omega_j] \tag{7}$$

where $\mathbf{N} = [\nu_i^j]$, of rank R, is the $S \times R$ 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. Hence, the dissipation rate takes on a standard form:

$$\mathcal{D} = -\mu^i r_i = \alpha^j \omega_j = \alpha \cdot \omega, \ \text{where} \ \alpha = [A^i] = -[\nu_j{}^i \mu^j] = -\mathbf{N}^T \mu, \tag{8}$$

where the *affinity* A^i represent the decrement of chemical potential along reaction path i (*vide infra*). Thus, in lieu of species rates and chemical potentials, we can now adopt rates ω_i and conjugate affinities A^i as respective fluxes and forces with a corresponding form for the dissipation potential φ. However, the relation proposed provisionally in Ref. 1

$$\omega = [\omega_i] = \partial_\alpha \varphi = \left[\frac{\partial \varphi}{\partial A^i} \right], \tag{9}$$

is subject to qualifications that are illustrated by the special case of mass-action kinetics considered next.

From single to multiple reactions

Following others, e.g. Fogler (2021), we employ the term *elementary reaction* to denote a reaction subject to mass-action kinetics, for which the rate of a reaction step is proportional to the concentrations of each participating species raised to a power of the magnitude of its stoichiometric coefficient, for both forward and reverse reactions. Thus, for the elementary reaction among chemical species $A, B, C, D, \ldots$ involving a molecules of A, b molecules of B, etc., which in elementary chemical notation reads

$$aA + bB + \ldots \rightleftharpoons cC + dD + \ldots, \tag{10}$$

the forward rate is proportional to $[A]^a [B]^b \ldots$ and the reverse rate to $[C]^c [D]^d \ldots$ where square brackets, otherwise reserved herein for other usage, denote molar concentrations for this example.

To introduce a more general and convenient notation, we begin by considering the case of a single elementary reaction among various species, with certain modifications of the treatment given in Ref. 1. However, we adopt the same assumption of ideal solutions, a generally excellent approximation for the gaseous reactions involved in combustion. Then, the partial molar Gibbs free energies μ^i, rendered nondimensional by RT, are given in terms of species concentrations C_i by

$$\mu^i = \ln y_i, \ \text{where} \ y_i = C_i/C \ \text{and} \ C = \sum_{i=1}^{S} C_i, \tag{11}$$

where C is total molar density and y_i is mole fraction. Hence, the generalized force defined in Eq (6) is given by $\hat{\mu}^i = \ln y_i/y_{i,o}$ where the equilibrium mole fractions $y_{i,o}$ are function of $C_1, \ldots, C_S$. To avoid implicit restrictions on y_i or μ^i as independent variables, we may assume the existence of a fictitious or real inert diluent (such as nitrogen in certain combustion reactions and interstitial fluid or plasma for biochemical reactions). We further note that non-ideal solutions could be treated by means of activity coefficients.

With the above understanding, we write the $S \times 1$ vector of stoichiometric coefficients

$$\nu = [\nu_i] = \nu_P + \nu_R, \tag{12}$$

where v_R is an $S \times 1$ vector with components v_i that are negative for the nominal reactants and zero otherwise, while v_P is an $S \times 1$ vector with components v_i that are positive for the nominal products and zero otherwise. We then introduce the vector of absolute values

$$\overline{v} = [|v_i|] = v_P - v_R, \tag{13}$$

With account taken of the vanishing of rate with vanishing affinity the rate of an elementary reaction is given by Ref. 1

$$\begin{aligned} &\omega(\mu) = \omega(A, \overline{A}) = k(e^{A_R} - e^{A_P}) = 2ke^{\overline{A}/2}\sinh(A/2), \\ &\text{where } A_R = -v_R \cdot \mu, \ A_P = v_P \cdot \mu, \\ &A = -v \cdot \mu = A_R - A_P, \ \text{and } \overline{A} = \overline{v} \cdot \mu = A_P + A_R, \end{aligned} \tag{14}$$

where k is a kinetic constant depending on C, which is assumed constant.

With the conventional designation of A as *affinity*, the quantity $\overline{A}$ might be dubbed *reactivity*, motivated to a certain extent by the Mechanical analogy presented below. Note that the quantities A_R and A_P represent affinities for irreversible reactions of the nominal reactants or products and that the equations are invariant under reversal of roles, with $v \rightarrow -v$ under exchange of subscripts P & R.

From the above, we find that

$$\partial_\mu \omega = [\partial_{\mu^i} \omega] = -(\partial_A \omega)v + (\partial_{\overline{A}} \omega)\overline{v} \tag{15}$$

Moreover, it follows from $\mathbf{r} = v\omega$ and the Eqs (12) and (13) that

$$\partial_\mu \mathbf{r} - (\partial_\mu \mathbf{r})^T = [\partial_i r_j - \partial_j r_i] = 2(v_P \otimes v_R - v_R \otimes v_P)\partial_{\overline{A}}\omega, \tag{16}$$

where $\mathbf{a} \otimes \mathbf{b} = [a_i b_j]$ denotes the tensor product. Unless this antisymmetrical form vanishes, it represents the breakdown of Onsager symmetry. In the present case, this breakdown arises from the dependence on $\overline{A}$, i.e from the dependence of reactant rates on the concentrations or free energies of the products. As suggested in Ref. 1, the form of Eq (14) is analogous to pressure- and rate-dependent sliding friction, with sliding force represented by A dependent on the reactive orthogonal pressure force represented by $\overline{A}$.

The case of a nominal irreversible reaction, discussed further below, corresponds to $A_P \rightarrow 0$, with degeneracy $\overline{A} \rightarrow A_R \rightarrow A$ and limit $\omega = k(\exp A - 1)$, which is Onsager-symmetric with dissipation potential $\breve{\varphi} = k(\exp A - 1 - A)$. Consistent with this definition of irreversibility we must take $A = 0$ for the state of nominal equilibrium where one or more reactants are exhausted, such that $y_i \rightarrow 0$, $\mu_i \rightarrow -\infty$, and therefore $A_R \rightarrow -\infty$.

Following Ref. 1, we may define an effective dissipation potential for a set of reversible reactions by the following modification of Edelen's formula (5):

$$\hat{\varphi}(A, \overline{A}) = A \int_0^1 \omega(sA, \overline{A})ds = 4ke^{\overline{A}/2}(\cosh(A/2) - 1), \ \text{with } \omega = (\partial_A \hat{\varphi})_{\overline{A}}, \tag{17}$$

and

$$\overline{v} \cdot d\mu = 0 \ \text{and} \ d\mu = d\hat{\mu} - \overline{v}^*(\overline{v} \cdot d\hat{\mu}), \ \text{where} \ \overline{v} \cdot \overline{v}^* = 1, \tag{18}$$

where $d\hat{\mu}$ is an arbitrary $S \times 1$ vector. Eq (18) represents a projection normal to $\overline{v}$ (i.e. onto the null space of the linear function defined by $\overline{v}$).

Multiple reactions

The generalization to R stoichiometrically independent, thermodynamically uncoupled, and reversible reactions is given by

$$
\begin{aligned}
&\hat{\varphi}(\alpha, \overline{\alpha}) = k_j B^j, \;\; \text{where (with no sum on } k) \;\; B^k = 4e^{\overline{A}^k/2}(\cosh(A^k/2) - 1),\\
&\alpha = [A^i] = -\mathbf{N}^T \mu = -[v_j^i \, \mu^j], \;\; \overline{\alpha} = [\overline{A}^i] = \overline{\mathbf{N}}^T \mu = [v_j^i \, \mu^j],\\
&\text{and} \;\; \omega = [\omega_i] = \partial_\alpha \hat{\varphi} = [\partial_{A^i} \hat{\varphi}] = [2k_i e^{\overline{A}^i/2} \sinh(A^i/2)] \;\; (\text{no sum on } i),\\
&\text{with} \;\; d\overline{\alpha} = \overline{\mathbf{N}}^T d\mu = 0 \;\; \text{and} \;\; d\mu \in \ker(\overline{\mathbf{N}}^T),
\end{aligned} \tag{19}
$$

with ker denoting the null space of the linear transformation represented by $\mathbf{N}^T$.

Thus, as generalization of Eq (18), we may write $d\mu = \mathbf{P}d\hat{\mu}$ where matrix $\mathbf{P}$ represents the projection onto $\ker(\overline{\mathbf{N}}^T)$. Since $\overline{R} = \text{rank}\,(\overline{\mathbf{N}}^T) \leq R$, it follows that $d\alpha = -\overline{\mathbf{N}}^T \mathbf{P}d\hat{\mu}$ and, hence, α are restricted to a space of dimension $= \min(R, S - \overline{R})$. Therefore, in order that the degrees of freedom represented by α be at least equal to the number of independent reactions R, we must require that $\text{rank}\,(\overline{\mathbf{N}}) + \text{rank}\,(\mathbf{N}) = \overline{R} + R \leq S$. Since this is not generally guaranteed, this condition must be confirmed for given stoichiometry $\mathbf{N}$, perhaps serving as restriction on any reduced kinetic mechanism with number of independent reactions.

A graph-theoretical view of reaction networks

Some of the earliest applications of graph theory to chemical reaction networks are found in the works of Oster and coworkers, notably Perelson and Oster (1974) and references therein. In the author's opinion, the graph-theoretical treatment presented here, together with the existence of a dissipation potential, provides a more economical and perhaps clearer treatment than that of most previous works, including that of Goddard (2002).

Thus, a dissipative network of R independent chemical reactions among S distinct chemical species may be viewed as a *bipartite graph* with a set of S nodes or *vertices* connected solely by multiple bonds or *edges* to a second set of R nodes, as depicted schematically in Figure 1, where one set of nodes, labeled alphabetically, represents chemical species and is connected to a second distinct set of nodes, labeled numerically and representing reactions.

Alternatively, the above bipartite graph may also be viewed as a *directed hypergraph* (Berge 1973) with the R nodes 1, 2, ... representing *hyperedges* connecting *hypervertices* or *hypernodes* as subsets of A, B, ... Note that the exceptional Edge 5 does not represent a valid chemical reaction but might represent an exchange with the surroundings. Although connected to a nonparticipating or "inert" species in the figure, similar connections to a reactive species could also represent non-trivial external exchanges or network "multiports." (In the special case of a *simple graph* each edge 1, 2, ...,with 5 excluded, connects a unique pair of distinct nodes from the set A, B, ...).

By associating positive weights ω_i to the nodes i = 1, 2, ... and by decorating the connecting edges with arrows to indicate direction and with stoichiometric coefficients to indicate edge weights, one obtains a *weighted, directed hypergraph* which has found applications in other fields (Ausiello and Laura 2017; Gallo et al. 1993).
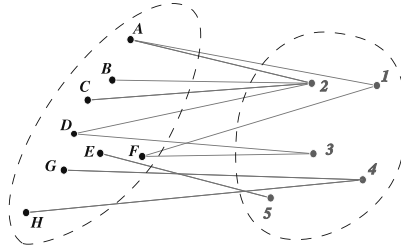
Figure 1. Bipartite species-reaction graph.

Then, the $R \times S$ matrix $\boldsymbol{\Delta} = \mathbf{N}^T$, a generalization of the *incidence* matrix for simple directed graphs (*digraphs*), represents a differential operator such that the $R \times 1$ vector $\boldsymbol{\Delta}\mu = -\alpha$ yields R differences of nodal potentials defined by $S \times 1$ vector μ. Furthermore, the $S \times R$ matrix $-\boldsymbol{\Delta}^T$ is the analog of a divergence operator, such that $\boldsymbol{\Delta}^T \omega = \mathbf{r}$ represents the rate of nodal accumulation due to fluxes or currents given by the $R \times 1$ vector ω. Note that $\boldsymbol{\Delta}$ and $\boldsymbol{\Delta}^T$ represent the respective *boundary* and *coboundary* operators of cohomology (Barile 2021; Slepian 2012), as recognized by Perelson and Oster (1974), but overlooked by (Goddard (2002) who nevertheless points out the connection between stoichiometry and the differential operators. Note also that the matrix $\overline{\mathbf{N}}$, which possesses only positive elements, represents an undirected hypergraph and a generalization of the *adjacency matrix* for a simple graph, while serving to define the reactivity vector $\overline{\alpha}$.

The reaction rates ω, which represent flows on the associated network, are now given by the *pseudo-linear* Onsager form (Goddard 2014)

$$
\begin{aligned}
&\omega = \partial_\alpha \hat{\varphi} = [\omega_i] = \mathbf{L}\alpha = -\mathbf{L}\boldsymbol{\Delta}\mu, \ \text{ with } \ \mathbf{L}(\alpha, \overline{\alpha}) = \text{diag}[\lambda^i], \\
&\text{where } \lambda^i = 2k_i e^{\overline{A}^i/2} \sinh(A^i/2)/A^i \ \text{ (no sum on } i)
\end{aligned}
\tag{20}
$$

The diagonal form for the conductance $\mathbf{L}$ reflects the fortuitous status of the conjugate pair $\{\alpha, \omega\}$, which represent non-linear analogs of the normal modes of the linear system that arises asymptotically for $\| \alpha \| \to 0$. Under a dissipation-preserving transformation to a pair $\{\mathbf{Q}^T\alpha, \mathbf{Q}^{-1}\omega\}$ the matrix $\mathbf{L}$ takes on a more general symmetric, positive, and non-diagonal form. A different expression for λ^i applies to non-elementary reactions and to the irreversible reactions considered below.

The above graph-theoretical description of flow on a resistive network offers an appealing conceptualization of the dissipation that governs that flow, as is the case with current flow on electrical networks of non-linear resistors.

However, it should be carefully noted that it is the dissipation potential and *not* the dissipation (or entropy generation) rate that is minimized by that flow, the exception being linear or power-law resistances for which dissipation rate is equal to or proportional to dissipation potential (Goddard 2014). In particular, dissipation potential is minimized with respect to variations of affinity α or chemical potential μ subject to the constraint of constant reactivity $\overline{\alpha}$, together with other constraints, such as specification of a subset of the species potentials μ or of the external rate of supply of certain species. The relation to conservation laws is discussed in Ref. 1.

Irreversible reactions, partitions, and linearization

We now assume that the above set of R reactions includes $R - R'$ irreversible reactions. The analysis given above holds for the rates and affinities $\{\omega_i, A^i\}$, $i = 1, 2, \ldots, R'$, of the R' reversible reactions, whereas it follows from the above discussion that the remaining rates and affinities are for $i = R' + 1, \ldots R$ given by

$$\omega_i = k_i(e^{A^i} - 1) = \partial_{A^i}\breve{\varphi} \text{ (no sum on } i\text{),}$$
$$\text{where } \breve{\varphi} = k_i E^i, \text{ and } E^i = (e^{A^i} - 1 - A^i), \tag{21}$$

which shows clearly that irreversible reactions are Onsager-symmetric.

Since dissipation is additive over reactions, the dissipation potential is given by the total $\varphi = \hat{\varphi}(\alpha_{rev}, \overline{\alpha}_{rev}) + \breve{\varphi}(\alpha_{irr})$, where

$$\alpha_{rev} = \left[A^i\right], 1mu\overline{\alpha}_{rev} = [\overline{A}^i], 1mui = 1, \ldots R', \alpha_{irr}$$
$$= \left[A^i\right], 1mui = R' + 1, \ldots R, \tag{22}$$

with partial derivatives taken at constant reactivity $\overline{\alpha}_{rev} = N_{rev}^T \mu$, where N_{rev} is determined by the stoichiometry of these reactions. Eq (20) now apply to the reversible reactions, $i = 1, \ldots R'$, whereas $\lambda^i = k_i(e^{A^i} - 1)/A^i$ (with no sum on i) for the irreversible reactions, $i = R' + 1, \ldots, R$.

The reader may have noted that the above decomposition of reactions into two kinetic classes is a special case of decomposition into any number of kinetic classes which corresponds mathematically to the idea of the decomposition of ω and dual α into direct sums of independent subspaces, with additivity of dissipation and dissipation potential over subspaces. This is perhaps most easily visualized in terms of the standard partition of matrices and vectors, with partition by column of $\mathbf{N}$, or by row of $\mathbf{N}^T$, and partition by row of the column vectors ω and α.

In addition to partition into kinetic classes there is an additional partition into classes of chemical species, for example, stable molecules and unstable intermediates, which is represented by partition by row of $\mathbf{N}$. It is obvious then that there exists a two-way partition of matrices representing the simultaneous decomposition into distinct classes of species and of reaction kinetics.

In closing here it is worth noting that the above relations can in an obvious way be linearized in a small perturbation α' of a given α, e.g. the equilibrium state $\alpha = \mathbf{0}$. In this case one has recourse to more or less standard linear network analysis.

We recall that the near-equilibrium approximation has been employed by Friedlander and Keller (1965) in a study of the effects of chemical reaction on biological mass transfer. Since this approximation does not require the restriction to constant reactivity, it might be employed as a test of the non-linear theory proposed above, and it might provide useful approximate analytical or numerical solutions. While it may be implausible to speak of near-equilibrium perturbations for combustion reactions, the linearized equations could still offer clues as to optimal reaction pathways. With that in mind, Appendix B, added in the proof to this paper, suggests a possible algorithm.

Summary and potential applications

The preceding analysis shows how one may obtain a dissipation potential and nonlinear Onsager symmetry for chemical kinetics, provided the dissipation potential is treated as a constrained function of the chemical potentials of reagents, namely, a function of reaction affinities with *reactivities* held constant. This may open the door to the application of variational principles to complex networks of chemical reactions, including those involving diffusion of heat and mass discussed in Ref. 1. Although detailed applications are relegated to future work, it is worth mentioning potential applications to reduction of kinetic mechanisms in combustion.

The current approach to reduced mechanisms appears to be based largely on the so-called *quasi-steady state hypothesis*, whereby reactions involving unstable or highly reactive radicals and similar species are assumed to be at equilibrium.[2] This partial equilibrium condition provides equations that allows for the elimination of those species with consequent reduction of the ostensible kinetic pathways. A basic introduction is given in Chapt. 9 of the textbook by Fogler (2021) along with some important examples, and an abstract treatment is provided by Goddard (1990). The technique has received extensive application in the field of combustion by F. Williams and coworkers in works mentioned above in the Introduction (Fernández-Galisteo et al. 2019; Jiang et al. 2020; Millán-Merino et al. 2020).

The approach just described might be qualified as *kinetic*, to be distinguished from the *thermodynamic* approach based on dissipation. From a physics perspective, the former might be regarded as more general since it deals directly with concentrations of reactants and involves detailed identification of reactive intermediates to be eliminated. Concomitantly, it requires a considerable degree of insightful guess-work as suggested by the revision of mechanism proposed by Millán-Merino et al. (2020). Based on these considerations, the aforementioned approaches might be viewed as complementary, with the reaction times in the kinetic approach being analogs of the network resistances in the thermodynamic approach. Hence, the question arises as to whether thermodynamics can facilitate the choice of reduced mechanisms. For example, the minimum dissipation potential, subject to constraints based on prescribed chemical potentials of key reagents such as fuel and air together with reactivity constraints could provide one criterion for choosing from among various reduced mechanisms, despite the somewhat artificial nature of the reactivity constraints. In this context, the relation to optimal paths on weighted hypergraphs (Ausiello and Laura 2017; Gallo et al. 1993) might be worth considering. The selection of optimal paths may be connect to the algorithm suggested below in Appendix B.

In any event, there remains a crucial open question as to whether the constraint on reactivities allows for sufficient degrees of freedom for the specification of affinities for all stoichiometrically independent reactions. If so, the dissipation potential could be extended to include dissipation associated with heat and mass transfer, which would also allow for an assessment of their possible influence on the reduced kinetic mechanism (Goddard 1990, 2015). This and related issues for biochemical reaction networks are matters worthy of further investigation.

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[2]The frequent characterization of this partial equilibrium as a condition of vanishing reaction rate is more appropriately stated as a vanishing of reaction affinity, which tends to zero with the reciprocal of large kinetic constant representing large conductance.

Acknowledgments

It is a distinct privilege and pleasure to offer the above paper as a tribute to the memory of Professor Paul A. Libby, renowned researcher and respected departmental colleague, with whom I became a close friend over the thirty year period from June 1991 until his demise in November of 2021. Although emeritus professor during that period, he maintained an admirable level of scientific activity, collaborating with various visitors from abroad. Paul was also participant in a daily coffee klatch, involving myself and two or three other colleagues in wide-ranging discussion of politics, history, and science. As perhaps the most serious-minded of the group Paul strove, sometimes without success, to keep our discussions on a high plane, adjourning the gathering with coffee cup as gavel whenever he felt we might be more productively engaged at our offices.

Beyond the sadness at the loss of a colleague and friend, I share the regrets of other contributors to this volume that Paul will not be with us to enjoy the fruits of our labors.

I note that three bound volumes of Paul's collected works have been assembled by departmental colleagues and that digital copies may be made available to researchers and scholars by contacting the Department of Mechanical and Aerospace Engineering in the University of California, San Diego.

Disclosure statement

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Appendix A. Minor corrigenda for Ref. 1

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

(2) Eq. (13) should read

$$\mathcal{D} = -\mu^i r_i = A^j \omega_j = \alpha \cdot \omega, \;\; \text{where} \;\; \alpha = [A^j] = -[\nu_i^j \mu^j] = -\mathbf{N}^T \mu,$$

as indicated by Eq. (8) of the present paper.

(3) Eq. (14) should be replaced by Eq. (9) of the present paper.

Appendix B. Possible algorithm

The dissipation potential φ for a given set of R independent reactions can be written as the sum $\sum_i \varphi_i$ of dissipation potentials of the individual reactions. This set can be partitioned into a set of R' nominally rapid reactions and a remaining set of $R - R'$ slow steps. This partition can be provisionally based on the magnitude of the effective rate constants $k' = k \exp(\overline{A}/2)$ defined by (19) for which according to (21) we may take $\overline{A} = 0$ for irreversible reactions.

Assuming that the fast reaction are driven toward their equilibrium state $A = 0$, we may provisionally linearize their potential about this state to obtain an approximately quadratic dissipation potential $\tilde{\varphi} \propto k' A^2$. It follows that the validity of the equilibrium approximation will then depend on $\tilde{\varphi}$. Note that by linearization of all reactions one can create a hierarchy of values $\tilde{\varphi}$ with a nominal cutoff $\tilde{\varphi}'$ defining fast reactions for which we take $A \equiv 0$ with $\varphi \equiv 0$. By lowering the cutoff one obviously reduces the overall dissipation potential $\sum_i \varphi_i$. Note that the condition $\alpha = -\nu \cdot \mu$ for the set of independent equilibrium reaction provides restrictions on the the Gibbs free energies and concentrations, which appears equivalent to the usual kinetic technique for eliminating intermediate species.