



Degree of Disequilibrium analysis for automatic selection of kinetic constraints in the Rate-Controlled Constrained-Equilibrium method[☆]



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ABSTRACT

The Rate-Controlled Constrained-Equilibrium (RCCE) model reduction scheme for chemical kinetics provides acceptable accuracies with a number of differential equations much lower than the number of species in the underlying Detailed Kinetic Model (DKM). To yield good approximations, however, the method requires accurate identification of the rate controlling constraints. So far, a drawback of the RCCE scheme has been the absence of a fully automatable and systematic procedure that is capable of identifying the best constraints for a given range of thermodynamic conditions and a required level of approximation. In this paper, we propose a new methodology for such identification based on a simple algebraic analysis of the results of a preliminary simulation of the underlying DKM, which is focused on the behaviour of the degrees of disequilibrium (DoD) of the individual chemical reactions. The new methodology is based on computing an Approximate Reduced Row Echelon Form of the Actual Degrees of Disequilibrium (ARREFADD) with respect to a preset tolerance level. An alternative variant is to select an Approximate Singular Value Decomposition of the Actual Degrees of Disequilibrium (ASVDADD). Either procedure identifies a low dimensional subspace in the DoD space, from which the actual DoD traces do not depart beyond a fixed distance related to the preset tolerance (ARREFADD methodology) or to the first neglected singular value of the matrix of DoD traces (ASVDADD methodology). The effectiveness and robustness of the method is demonstrated for the case of a very rapid supersonic nozzle expansion of the products of hydrogen and methane oxycombustion and for the case of methane/oxygen ignition. The results are in excellent agreement with DKM predictions. For both variants of the method, we provide a simple Matlab code implementing the proposed constraint selection algorithm.

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1. Introduction

According to the Rate-Controlled Constrained-Equilibrium (RCCE) theory, the reactions in a Detailed Kinetic Model (DKM) can be characterized in terms of the effectiveness with which they contribute to the spontaneous tendency to relax the composition towards chemical equilibrium. Loosely speaking, such effectiveness depends on the number of “kinetic bottlenecks” that the reaction needs to go through in order to advance and on how “narrow”

these bottlenecks are. Each kinetic bottleneck is characterized by a linear combination of the composition, called a “constraint”, which can be varied only by reactions that go through that particular bottleneck. Therefore, the “narrower” the bottleneck, the slower the rate of change of the associated rate-limiting constraint.

The general idea behind the RCCE method [1–14] is that for each particular problem, set of conditions, and acceptable degree of approximation there is a threshold time scale which essentially separates the “relatively fast” equilibrating kinetic mechanisms from those that slow down and control the spontaneous relaxation towards equilibrium. The “relatively slow” mechanisms control the interesting part of the non-equilibrium dynamics in that they effectively identify a low dimensional manifold in composition space, where, for the chosen level of approximation, the dynamics can be assumed to take place. In general, the rate controlling mechanisms are slow because they have to go through one or more bottlenecks. For example, the three-body reactions are slow because they

[☆] The authors wish to dedicate this paper to the memory of the brilliant founder of the rate-controlled constrained-equilibrium theory and their mentor, teacher, and coauthor, the late professor James C. Keck of the Massachusetts Institute of Technology, whose biography and scientific production is available at www.JamesKeckCollectedWorks.org.

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Nomenclature

$\mathbf{a} = [a_{ij}] = [a_{i1}, \dots, a_{i n_{sp}}]$	matrix of constraint coefficients
$A_\ell = RT\phi_\ell = -\sum_{j=1}^{n_{sp}} \nu_{j\ell} \mu_j$	de-Donder affinity of reaction ℓ
$A_\ell^+, b_\ell^+, E_\ell^+$	prefactor, temperature exponent, and activation energy of the forward rate constant of reaction ℓ
$c_i(\mathbf{N}) = \sum_{j=1}^{n_{sp}} a_{ij} N_j$	i th constraint functional of the composition vector \mathbf{N}
$\text{coker}(\mathbf{v})$	left null space (co-kernel) of matrix \mathbf{v} , often called the <i>inherent subspace</i>
$\text{DoD}_\ell = \phi_\ell = \ln(r_\ell^+/r_\ell^-)$	Degree of Disequilibrium of reaction ℓ , the same as ϕ_ℓ
$g_{jj}(T, p) = \mu_{jj}(T, p)$	Gibbs free energy of pure substance j at pressure p and temperature T (double subscript denotes pure substance)
$\Delta g_\ell^0(T) = \sum_{j=1}^{n_{sp}} \nu_{j\ell} g_{jj}(T, p_0)$	Gibbs free energy of reaction ℓ at standard pressure p_0 and temperature T
I_{sp}	nozzle thrust force per unit mass flow rate of the propellant
$k_\ell^+(T)$	forward rate constant of reaction ℓ at temperature T
$k_\ell^-(T)$	backward rate constant of reaction at temperature T
$K_\ell^{\text{co}}(T)$	equilibrium constant (based on concentration) of reaction ℓ at temperature T
$[N_j]$	concentration of species j
$N = \sum_{j=1}^{n_{sp}} N_j$	total number of moles
$\mathbf{N} = [N_1 \dots N_{n_{sp}}]$	vector of species mole numbers
p, p_0	pressure, atmospheric pressure
r_ℓ^+	forward rate of reaction ℓ
r_ℓ^-	reverse rate of reaction ℓ
R	universal gas constant
$\text{span}(\{\mathbf{v}_\ell\})$	column space of the stoichiometric matrix \mathbf{v} i.e., linear span of the set of vectors defined by its columns, often called the <i>reactive subspace</i>
T	temperature
$X_j = N_j/N$	mole fraction of species j
$\mathbf{X} = [X_1 \dots X_{n_{sp}}]$	vector of species mole fractions
$\ln(\mathbf{X}) = [\ln(X_1) \dots \ln(X_{n_{sp}})]$	vector of logarithms of the species mole fractions
Greek symbols	
γ_i	constraint potential, i.e., Lagrange multiplier associated with the i -th constraint
$\lambda_j = -\mu_j/RT$	entropic chemical potential of species j
$\mathbf{\Lambda} = [\lambda_1 \dots \lambda_{n_{sp}}]$	vector of entropic chemical potentials
$\mathbf{\Lambda}_\perp$	component of the row vector $\mathbf{\Lambda}$ orthogonal to $\text{span}(\{\mathbf{v}_\ell\})$
$\mathbf{\Lambda}_{\text{DoD}} = \mathbf{\Lambda} - \mathbf{\Lambda}_\perp$	vector that we call Overall Degree of Disequilibrium
$\mathbf{\Lambda}_{\text{DoD}}(z_p) = \mathbf{U}\mathbf{\Sigma}\mathbf{V}^T$	singular value decomposition of the $n_{sp} \times P$ matrix $\mathbf{\Lambda}_{\text{DoD}}(z_p)$

$\mu_j = \mu_{j,\text{off}}(T, p, \mathbf{N})$	chemical potential of species j in a non-reacting mixture of “frozen” composition \mathbf{N} (hence the “off” subscript) in stable equilibrium at temperature T and pressure p
$\nu_{j\ell}^+$	forward stoichiometric coefficient of species j in reaction ℓ
$\nu_{j\ell}^-$	reverse stoichiometric coefficient of species j in reaction ℓ
$\nu_{j\ell} = \nu_{j\ell}^- - \nu_{j\ell}^+$	net stoichiometric coefficient of species j in reaction ℓ
$\mathbf{v} = [\nu_{j\ell}]$	matrix of stoichiometric coefficients
$\mathbf{v}_\ell = [\nu_{1\ell} \dots \nu_{n_{sp}\ell}]$	vector of the stoichiometric coefficients of reaction ℓ , defined by the ℓ -th column of the matrix \mathbf{v} of stoichiometric coefficients
$\phi_\ell = \ln(r_\ell^+/r_\ell^-) = \langle \mathbf{\Lambda} \mathbf{v}_\ell \rangle$	Degree of Disequilibrium of reaction ℓ , same as DoD_ℓ
$\mathbf{X}_k = [\chi_{1k} \dots \chi_{n_{sp}k}]$	a basis for $(\{\mathbf{v}_\ell\})$
Acronyms	
ARREFADD	Approximate Reduced Row Echelon Form of the Actual Degrees of Disequilibrium
ASVDADD	Approximate Singular Value Decomposition of the Actual Degrees of Disequilibrium
DKM	Detailed Kinetic Model
DoD	Degree of Disequilibrium
RCCE	Rate-Controlled Constrained-Equilibrium

require three-body collisions which occur much less frequently than two-body collisions. As a result, the bottleneck mechanism is that of three-body collisions and the associated rate-limiting constraint is the total number of moles, which would not change if all three-body reactions were frozen. The “narrowness” of each bottleneck can be measured by the characteristic time with which the associated constraint would relax towards its equilibrium value in the absence of interactions sustaining the non-equilibrium state.

As emphasized for example in Ref. [12], the RCCE method enjoys a very appealing built-in general feature of strong thermodynamic consistency. However, the main difficulties in its practical use have been: (a) identifying the kinetic bottlenecks and (b) constructing an efficient set of constraints implied by them. Several efforts have addressed these problems with varying degrees of success [15]. The Greedy algorithm [16] and its extension including local improvements [17] select, one at a time, the most effective single-species constraints by cyclic execution of the DKM. This approach has shown to be efficient for turbulent flames in conjunction with in situ adaptive tabulation. Level of Importance (LOI) [18] picks up single species as constraints from the top of the list of species which are sorted based on their time scales. The method has demonstrated acceptable agreements with DKM calculations. Nonetheless, as shown in [17], time-scale based methods for the selection of constraints do not necessarily identify the most effective set of constraints. The analysis of the DoD traces of all the chemical reactions obtained from a full DKM calculation was shown in Ref. [19] to provide important information for selecting constraints. However, it ultimately fell short to be fully rationalized and automated for a general case. It is the aim of this paper to present a methodology to fully rationalize the idea presented in [19], regardless of the complexity of the mechanism, in a truly algorithmic manner. The proposed methodology, therefore, holds the promise to resolve the difficulties involved with the lack of a systematic way to choose constraints, which has long represented the main obstacle toward a widespread use of the RCCE method.

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