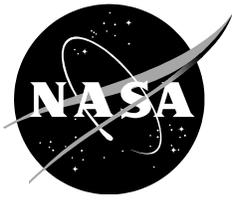


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Chemical Thermodynamics and the Mathematical Integration of Reaction Kinetics

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NASA Advanced Supercomputing Division

October 2023

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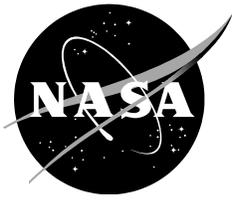
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Chemical Thermodynamics and the Mathematical Integration of Reaction Kinetics

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Abstract

Key advances in the development of numerical methods for non-reacting compressible flows have been enabled by translating physical requirements into concrete numerical guidelines, such as the satisfaction of entropy inequalities for shock-capturing techniques [Lax, *Contributions to Nonlinear Functional Analysis* (1971) 603-634]. In the present work, we present nonlinear numerical analysis tools that draw from *Chemical Thermodynamics*, the branch of *Nonequilibrium Thermodynamics* that deals with chemical reactions. Through Gibbs formalism, chemical thermodynamics provides a well-known theoretical expression for the chemical equilibrium constant of a reaction in terms of reduced chemical potentials. A less-known, yet extremely valuable result, due to [Krambeck, *Arch. Ration. Mech. Anal.*, 38 (1970) 317], states that when this expression is implemented, mass-action kinetic models are consistent with the dynamical prescriptions of the 2nd law of thermodynamics. For fixed-temperature ordinary differential equations modeling constant-volume reacting gas mixtures, this leads to a decreasing Helmholtz free energy. If the temperature is allowed to vary in accordance with conservation of energy (1st law), this leads to the statement of increasing entropy. These *nonlinear* prescriptions can, and should be, used to further develop temporal integration techniques for reaction kinetics. We demonstrate that Krambeck's result holds even when the equilibrium constants are approximated from data. We prove this result by constructing the *implicit free energy* and the *implicit entropy* inherent to a given approximation. This is first done for a 5-species, 17-reaction model problem for air. With this structure established, elements of *discrete entropy-stability theory* [Tadmor, *Acta Numer.*, 12 (2003) 451] are leveraged to examine the consistency of time-integration schemes with these prescriptions. Using chemical potentials, one can compute the respective contributions of the kinetics model and of the temporal scheme to free energy/entropy variations. We introduce a nonlinear-stable version of the Discontinuous-Galerkin (DG) scheme in time which shows robustness improvements over the standard linearly-stable version. Most notably, the maximum timestep that can be resolved with the nonlinearly-stable variant tends to grow with polynomial order, in contrast to the linearly-stable variant. We generalize our constructions to arbitrary systems of reversible chemical reactions, ultimately showing that the compressible reacting Euler system admits the opposite of the implicitly constructed thermodynamic entropy as a *mathematical entropy*. This lays important theoretical foundations towards robust scheme development [Harten, *J. Comput. Phys.* 49 (1983) 151-164].

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1 Introduction

The robust and accurate simulation of chemical nonequilibrium processes is a major research item in Computational Fluid Dynamics (CFD) [34, 33]. Chemical kinetics play an important role in a number of engineering applications such as combustion engine design [33] and hypersonic flight [27, 26, 28]. The small time scales involved make detailed simulations of these flows expensive, even with recent advances in computing power [33]. Within compressible flow models, the disparity in temporal scales cause the resulting system of equations to be stiff [29], motivating a long-time effort on developing robust high-resolution methods both in space and in time [34, 8, 32, 31, 30]. Another challenge lies in the chemical nonequilibrium model itself, which needs to be both accurate and affordable. These requirements are typically met through extensive data-driven modeling procedures [2] that generate nonequilibrium models that are difficult to analyze on paper.

The successful development of numerical methods is underpinned by our understanding of the mathematical structure of the physical model at hand, and by our ability to translate this knowledge into concrete numerical guidelines. CFD simulations of compressible flows have greatly benefited from the development of numerical schemes consistent with the notions of conservation [15], wave propagation [22], monotonicity [21] and entropy-stability [15, 18, 17]. The latter concept in particular has driven a number of advances in under-resolved simulations of compressible turbulent flows using high-order Discontinuous-Galerkin (DG) schemes over the last decade [11, 12, 34, 41, 45]. A number of studies [41, 45] report that enforcing consistency with the 2nd law of thermodynamics considerably improves stability. A less discussed, but equally valuable, feature of these schemes is their modular construction [11] which provides an exact measure of the amount of entropy produced at the discrete level and enables a better understanding of local behavior [35, 36, 37, 40]. The present work continues our recent efforts on the development of entropy-stable schemes for compressible multicomponent flow applications [38, 39]. Here we explore the integration of chemical kinetics from a mathematical modeling standpoint, and discuss some encouraging preliminary numerical results on a fixed-temperature kinetic system of Ordinary Differential Equations (ODEs) for air adapted from Park [27].

Numerical studies of chemical kinetics typically consider a homogeneous system evolving at fixed temperature and volume through a system of ODEs, and investigate the performance of time-integration schemes [2, 8, 32]. The stiffness of these systems is such that implicit schemes tend to perform better than explicit ones [29, 30]. The literature on this topic is rich [29, 30, 32, 31]) and a number of concepts such as *A-stability* have been introduced to support further developments. We note that the majority of these analysis techniques are based on a model linear system or some quasi-linear representation of nonlinear dynamics [32]. In this work, we demonstrate that *nonlinear* stability prescriptions can be drawn from *chemical thermodynamics* [3, 6, 4] and can be enforced at the discrete level [11]. For the fixed-temperature and fixed-volume system, the second law implies that the Helmholtz free energy is monotone decreasing [6, 23]. Entropy increase during chemical nonequilibrium applies when the temperature varies in time as to ensure conservation of energy (isolated system). In either configuration, an elegant proof by Krambeck [23, 1] establishes the consistency of the mass action kinetics with these prescriptions.

Krambeck’s proof allows the forward and backward reaction rates of the kinetic model to take arbitrary form as long as their ratio equals the reaction equilibrium constant. However, the proof does assume that the chemical equilibrium constants are evaluated in terms of the reduced chemical potentials, which characterize their internal energy structure. In practice, the equilibrium constants are evaluated using interpolation formulas that are fitted against either experimental data (through spectroscopic [10, 24] and calorimetric measurements [6]) or against data obtained through advanced quantum chemistry calculations [25, 7]. We show that these approximations of the equilibrium constants do not hamper nonlinear stability provided the equilibrium constants remain strictly positive. We prove these results by constructing the *implicit free energy* of the chemical models given their chemical equilibrium data. In the configuration where the gas temperature is allowed to vary in accordance with conservation of energy, we show that if the internal energy model satisfies the Van’t Hoff equations [3] one can construct an *implicit thermodynamic entropy*. This is first demonstrated for a model 5-species reacting system for Earth’s atmosphere [27].

With this structure established, discrete entropy-stability theory [11] can be leveraged to examine the consistency of time-integration schemes with the prescriptions of the 2nd law. We illustrate this with the 5-species model problem at fixed-temperature. Using chemical potentials, one can compute the respective

contributions of the kinetics model and of the temporal scheme to free energy/entropy variations. We introduce a nonlinearly-stable version of the DG scheme in time [14] which is more robust than its standard linearly-stable version. Most notably, the maximum time-step that can be resolved with the nonlinearly-stable variant tends to grow with polynomial order, in contrast to the linearly-stable variant. We also observe larger time-steps compared to the popular Diagonally Implicit Runge-Kutta (DIRK) methods developed for stiff ODEs [30, 31].

Following these preliminary results, we generalize our construction of the implicit free energy and implicit entropy to arbitrary sets of reversible chemical reactions through a few theorems and lemmas that detail straightforward linear algebra derivations, with compelling examples [27, 28]. An interesting result obtained is that the implicit free energy and the implicit thermodynamic entropy are functions of the ratio between the current and equilibrium compositions. Ultimately, we prove that for the compressible reactive multicomponent Euler equations, the opposite of the implicit entropy qualifies as a *convex extension* (or *mathematical entropy*) [17, 20, 1] of the associated system of conservation laws.

The present work is organized as follows. Section 2 provides a brief review of classical thermodynamics. Section 3 introduces Chemical Thermodynamics, the branch of nonequilibrium thermodynamics that deals with chemical processes, together with Krambeck’s proof. Section 4 introduces our model problem and details how to construct its implicit free energy and implicit thermodynamic entropy. In section 5, we show how to translate these concepts into a nonlinear discrete analysis framework. In section 6, we generalize the results of section 4 to arbitrary chemically reacting systems. In section 7, we consider compressible reacting flow and show that the opposite of the implicit thermodynamic entropy is a convex extension for the associated system of conservation laws.

2 Classical Thermodynamics

Classical thermodynamics is concerned with the evolution of systems in equilibrium through processes of exchange of matter and energy. While it will not provide the dynamical prescriptions we desire for the numerical study of chemical nonequilibrium, it does lay some of the foundations (formulation of entropy) of the formalism (Nonequilibrium Thermodynamics - Section 3) that will.

2.1 Equilibrium, system and process classifications

Classical thermodynamics assumes that systems can be described in terms of macroscopic or *state variables*. For gas mixtures, which we focus on, this requires some equilibrium to hold within the internal structure of the component species and between the gas as a whole and its surroundings. One can distinguish between three kinds of equilibrium [3]:

- *mechanical equilibrium*: there are no unbalanced forces within the system and between the system and its surroundings. A *pressure* p can be assigned to the system.
- *thermal equilibrium*: all internal degrees of freedom of the gas can be described by a (single) *temperature* which is the same as that of the system’s surroundings.
- *chemical equilibrium*: the gas mixture is not subject to spontaneous changes in its chemical composition. For a system that is homogenous in space, the chemical composition can be described by the number of moles of each species $(\mathcal{N}_k)_{1 \leq k \leq N_s}$.

Thermodynamic equilibrium is obtained when all three equilibrium conditions above are met. We refer to such states simply as equilibrium states from here onwards.

Systems are also classified in terms of the exchange processes they allow with their surroundings. A *closed* system does not exchange matter, an *open* system can exchange matter and energy, and an *isolated* system does not exchange matter nor energy.

A physical process that causes a system in equilibrium to transition to another state of equilibrium is said to be *reversible* if it can be described through a continuous succession of equilibrium states. The process is said to be *irreversible* otherwise.

2.2 Equation of State

The pressure, volume V , temperature T and molar composition $(\mathcal{N}_k)_{1 \leq k \leq N_s}$ of a gas mixture in equilibrium are assumed to be dependent of each other through an *equation of state* of the form:

$$p = p(V, T, \mathcal{N}_1, \dots, \mathcal{N}_{N_s}).$$

Throughout this work, we assume the ideal gas law to hold:

$$pV = \mathcal{N} \hat{R} T, \quad \mathcal{N} := \sum_{k=1}^{N_s} \mathcal{N}_k,$$

with $\hat{R} = 8.314 \text{ J.mol}^{-1}.\text{K}^{-1}$. For a mixture of gases, this can be expressed as Dalton's law of partial pressures:

$$p = \sum_{k=1}^{N_s} p_k, \quad p_k := \frac{\mathcal{N}_k}{V} \hat{R} T$$

Later in this work, we will work with molar concentration variables $[X_k] := \mathcal{N}_k/V$. We have:

$$p_k = [X_k] \hat{R} T. \quad (1)$$

2.3 Energy and Entropy

The first and second law of classical thermodynamics introduce two additional state variables that help study thermodynamic processes.

1st law: *There exists a state variable E called internal energy. For a closed system undergoing a reversible process, the infinitesimal change in internal energy is given by:*

$$dE = \delta Q - p dV,$$

where δQ is the heat received from the system's surroundings. In terms of the enthalpy $H := E + pV$, this relation writes:

$$dH = \delta Q - V dp.$$

2nd law: *There exists a state variable called entropy such that, for a closed system, we have:*

1. *For a reversible process between equilibrium states 1 and 2, the change in entropy is given by:*

$$S^1 - S^0 = \int_{T^0}^{T^1} \left(\frac{\delta Q}{T} \right)_{rev}.$$

2. *If the transition from equilibrium state 1 to equilibrium state 2 occurs through irreversible processes, the change in entropy satisfies the inequality:*

$$S^1 - S^0 > \int_{T^0}^{T^1} \left(\frac{\delta Q}{T} \right)_{rev}.$$

For a single-component thermally perfect gas, the internal energy and enthalpy are written as:

$$E^1 = \mathcal{N} \int_{T^0}^{T^1} \hat{c}_v(\tau) d\tau + E^0, \quad H^1 = \int_{T^0}^{T^1} \hat{c}_p(\tau) d\tau + H^0.$$

with constant volume heat per unit mole $\hat{c}_v(T)$ and constant pressure heat per unit mole $\hat{c}_p(T) = \hat{c}_v(T) + \mathcal{N} \hat{R}$. The second law gives, for a reversible process:

$$S^1 = \mathcal{N} \int_{T^0}^{T^1} \frac{\hat{c}_p(\tau)}{\tau} d\tau - \mathcal{N} \hat{R} \ln \left(\frac{p^1}{p^0} \right) + S^0.$$

For a mixture of thermally perfect gases satisfying Dalton's law of partial pressures, *Gibbs' theorem* gives the energy and enthalpy as the sum over species:

$$E := \sum_{k=1}^{N_s} \mathcal{N}_k \hat{e}_k = \sum_{k=1}^{N_s} \mathcal{N}_k \left(\int_{T^0}^T \hat{c}_{vk}(\tau) d\tau + \hat{e}_k^0 \right), \quad H = \sum_{k=1}^{N_s} \mathcal{N}_k \hat{h}_k = \sum_{k=1}^{N_s} \mathcal{N}_k \left(\int_{T^0}^T \hat{c}_{pk}(\tau) d\tau + \hat{h}_k^0 \right), \quad (2)$$

with specific molar quantities (\hat{e}_k, \hat{h}_k) and $(\hat{c}_{vk}, \hat{c}_{pk})$, and similarly, the entropy :

$$S := \sum_{k=1}^{N_s} \mathcal{N}_k \hat{s}_k = \sum_{k=1}^{N_s} \mathcal{N}_k \left(\int_{T^0}^T \frac{\hat{c}_{pk}}{\tau} d\tau - \hat{R} \ln \frac{p_k}{p^0} + \hat{s}_k^0 \right). \quad (3)$$

3 Chemical Thermodynamics

3.1 Nonequilibrium Thermodynamics

Classical thermodynamics provides a means of calculating entropy changes within a closed system due to reversible processes only. This limitation motivated the development of *Nonequilibrium Thermodynamics* by De Donder, Prigogine, and co-workers [4]. Nonequilibrium thermodynamics assumes that the states variables and equations of state used in the classical treatment can be used to describe systems out of equilibrium. It comprises the first law (conservation of energy) as given in the previous section, but uses a different version of the second law:

2nd law (Nonequilibrium Thermodynamics): *The entropy change dS within any system undergoing any process writes as the following combination:*

$$dS = dS_e + dS_i,$$

where dS_e is the flow of entropy into the system and $dS_i \geq 0$ is the production of entropy due to irreversible processes occurring within the system ($dS_i = 0$ for a reversible process). For a closed system, the entropy exchange term writes

$$dS_e = \frac{\delta Q}{T}.$$

This version of the second law is more general as it is not limited to closed systems. Its effective use requires explicit formulas for the entropy generation term dS_i . For chemical nonequilibrium, an expression for dS_i was derived by Gibbs and gave birth to the specialized branch of *Chemical Thermodynamics* [3, 4, 5].

3.2 Derivation of the Law of Mass Action

Chemical reactions between N_s species can be represented through:



where $(X_k)_{1 \leq k \leq N_s}$ denotes the set of species symbols, and $(\alpha_{r,k})_{1 \leq k \leq N_s}$ and $(\beta_{r,k})_{1 \leq k \leq N_s}$ denote the sets of stoichiometric coefficients for the reactants and products, respectively, and r is the reaction index. The law of mass action gives the equilibrium molar concentrations $[X_k]^*$ as:

$$\prod_{k=1}^{N_s} ([X_k]^*)^{\nu_{r,k}} = K_{eq,r}(T), \quad (5)$$

where $K_{eq,r}$ is the equilibrium constant associated with reaction r and $\nu_{r,k} = \beta_{r,k} - \alpha_{r,k}$.

Chemical thermodynamics provides a derivation of $K_{eq,r}$ through the second law. Introduce the Gibbs

function $G := H - TS$. With the mixture's enthalpy and entropy given by equations (2) and (3), G can be expanded as:

$$G = \sum_{k=1}^{N_s} \mathcal{N}_k \hat{\mu}_k, \quad \hat{\mu}_k := \hat{h}_k - T \hat{s}_k = \int_{T^0}^T c_{pk}(\tau) \left(1 - \frac{T}{\tau}\right) d\tau + \hat{R}T \ln \left(\frac{p_k}{p^0}\right) + \left(\hat{h}_k^0 - T \hat{s}_k^0\right),$$

where $(\hat{\mu}_k)_{1 \leq k \leq N_s}$ is the set of molar chemical potentials. Gibbs formula for the entropy production due to chemical reactions [3, 4, 5] is:

$$dS_i = -\frac{1}{T} \sum_{k=1}^{N_s} \hat{\mu}_k d\mathcal{N}_k. \quad (6)$$

The system is in chemical equilibrium when $dS_i = 0$ and when for each reaction r the forward and backward reaction occur at the same frequency. This implies that the variations in number of moles satisfy a relation involving the *degree of advancement* $d\xi_r$ of the reaction:

$$\frac{d\mathcal{N}_1}{\nu_{r,1}} = \dots = \frac{d\mathcal{N}_{N_k}}{\nu_{r,N_s}} = d\xi_r, \quad (7)$$

where the proportionality constant $d\xi_r$ is the degree of advancement of the reaction. Combining these two relations leads to the affinity equation [4, 5]:

$$\sum_{k=1}^{N_s} \hat{\mu}_k \nu_{r,k} d\xi_r = 0 \iff \sum_{k=1}^{N_s} \hat{\mu}_k \nu_{r,k} = 0. \quad (8)$$

Introducing the reduced molar chemical potential $\hat{\mu}_k^0$:

$$\hat{\mu}_k^0(T) := \hat{\mu}_k - \hat{R}T \ln \left(\frac{p_k}{p^0}\right) = \int_{T^0}^T c_{pk}(\tau) \left(1 - \frac{T}{\tau}\right) d\tau + \left(\hat{h}_k^0 - T \hat{s}_k^0\right), \quad (9)$$

the affinity equation (8) can be rewritten as:

$$\begin{aligned} \sum_{k=1}^{N_s} \nu_{r,k} \ln \left(\frac{p_k}{p^0}\right) &= -\frac{1}{\hat{R}T} \sum_{k=1}^{N_s} \nu_{r,k} \hat{\mu}_k^0 \\ \iff \prod_{k=1}^{N_s} \left(\frac{p_k}{p^0}\right)^{\nu_{r,k}} &= \exp \left(-\frac{1}{\hat{R}T} \sum_{k=1}^{N_s} \nu_{r,k} \hat{\mu}_k^0 \right) \\ \iff \prod_{k=1}^{N_s} p_k^{\nu_{r,k}} &= (p^0)^{\sum_{k=1}^{N_s} \nu_{r,k}} \exp \left(-\frac{1}{\hat{R}T} \sum_{k=1}^{N_s} \nu_{r,k} \hat{\mu}_k^0 \right) \\ \iff \prod_{k=1}^{N_s} [X_k]^{\nu_{r,k}} &= \left(\frac{p^0}{\hat{R}T}\right)^{\sum_{k=1}^{N_s} \nu_{r,k}} \exp \left(-\frac{1}{\hat{R}T} \sum_{k=1}^{N_s} \nu_{r,k} \hat{\mu}_k^0 \right). \end{aligned}$$

By definition (5), this gives the equilibrium constant as a function of temperature and the reduced molar chemical potentials:

$$K_{eq,r}(T) = \left(\frac{p^0}{\hat{R}T}\right)^{\sum_{k=1}^{N_s} \nu_{r,k}} \exp \left(-\frac{1}{\hat{R}T} \sum_{k=1}^{N_s} \nu_{r,k} \hat{\mu}_k^0 \right). \quad (10)$$

For convenience, we will use a slightly different definition of the reduced molar chemical potential. We set:

$$\hat{\mu}_k^0(T) := \hat{\mu}_k - \hat{R}T \ln [X_k]. \quad (11)$$

With this definition, formula (10) simplifies to:

$$K_{eq,r}(T) = \exp \left(-\frac{1}{\hat{R}T} \sum_{k=1}^{N_s} \nu_{r,k} \hat{\mu}_k^0 \right). \quad (12)$$

3.3 Dynamical Prescriptions for Chemical Kinetics

Consider standard mass action kinetics modeled through an ODE system involving N_s species through N_R reactions (4):

$$\frac{d[X_k]}{dt} = \Omega_k, \quad \Omega_k := \sum_{r=1}^{N_R} \nu_{r,k} \omega_r, \quad \omega_r := K_r^f \prod_{k=1}^{N_s} [X_k]^{\alpha_{r,k}} - K_r^b \prod_{k=1}^{N_s} [X_k]^{\beta_{r,k}}, \quad (13)$$

where $K_r^f = K_r^f(T)$ and $K_r^b = K_r^b(T)$ are the forward and backward rates of reaction r . The volume of the gas mixture is assumed to be constant.

Through an elegant procedure, Krambeck [23] proved that if the forward and backward rates are related through equation (12)

$$\frac{K_r^f}{K_r^b} = K_{eq,r} = \exp\left(-\frac{1}{\hat{R}T} \sum_{k=1}^{N_s} \nu_{r,k} \hat{\mu}_k^0\right), \quad (14)$$

then the chemical nonequilibrium model (13) is consistent with the second law in that:

$$dS_i = -\frac{1}{T} \sum_{k=1}^{N_s} \hat{\mu}_k dN_k = -\frac{V}{T} \sum_{k=1}^{N_s} \hat{\mu}_k \Omega_k dt > 0.$$

We recall his proof here, as it will be used in our work. Through $\nu_{r,k} = \beta_{r,k} - \alpha_{r,k}$, equation (14) can be rewritten as:

$$\frac{K_r^f}{K_r^b} = \exp\left(-\frac{1}{\hat{R}T} \sum_{k=1}^{N_s} \beta_{r,k} \hat{\mu}_k^0\right) \Big/ \exp\left(-\frac{1}{\hat{R}T} \sum_{k=1}^{N_s} \alpha_{r,k} \hat{\mu}_k^0\right). \quad (15)$$

Using this relation, the chemical nonequilibrium model (13) can be rewritten in terms of the molar chemical potentials. The equilibrium relation (15) establishes the existence of an *auxiliary rate constant* K_r^S defined as:

$$K_r^S := K_r^f \exp\left(-\frac{1}{\hat{R}T} \sum_{k=1}^{N_s} \alpha_{r,k} \hat{\mu}_k^0\right) = K_r^b \exp\left(-\frac{1}{\hat{R}T} \sum_{k=1}^{N_s} \beta_{r,k} \hat{\mu}_k^0\right). \quad (16)$$

Using equation (11), the concentration products in equation (13) can be rewritten as:

$$\prod_{k=1}^{N_s} [X_k]^{\alpha_{r,k}} = \exp\left(\frac{1}{\hat{R}T} \sum_{k=1}^{N_s} \alpha_{r,k} (\hat{\mu}_k - \hat{\mu}_k^0)\right), \quad \prod_{k=1}^{N_s} [X_k]^{\beta_{r,k}} = \exp\left(\frac{1}{\hat{R}T} \sum_{k=1}^{N_s} \beta_{r,k} (\hat{\mu}_k - \hat{\mu}_k^0)\right) \quad (17)$$

Combining equations (16) and (17) leads to a remarkable formulation of mass action kinetics in terms of molar chemical potentials [1]:

$$\omega_r = K_r^S \left[\exp\left(\frac{1}{\hat{R}T} \sum_{k=1}^{N_s} \alpha_{r,k} \hat{\mu}_k\right) - \exp\left(\frac{1}{\hat{R}T} \sum_{k=1}^{N_s} \beta_{r,k} \hat{\mu}_k\right) \right] \quad (18)$$

Ultimately:

$$\begin{aligned}
dS_i &= -\frac{1}{T} \sum_{k=1}^{N_s} \hat{\mu}_k \sum_{r=1}^{N_r} \nu_{r,k} \omega_r dt \\
&= -\frac{1}{T} \sum_{r=1}^{N_r} K_r^S \sum_{k=1}^{N_s} \nu_{r,k} \hat{\mu}_k \left[\exp\left(\frac{1}{\hat{R}T} \sum_{k'=1}^{N_s} \alpha_{r,k'} \hat{\mu}_{k'}\right) - \exp\left(\frac{1}{\hat{R}T} \sum_{k'=1}^{N_s} \beta_{r,k'} \hat{\mu}_{k'}\right) \right] dt \\
&= \frac{1}{T} \sum_{r=1}^{N_r} K_r^S \left[\sum_{k=1}^{N_s} \alpha_{r,k} \hat{\mu}_k - \sum_{k=1}^{N_s} \beta_{r,k} \hat{\mu}_k \right] \left[\exp\left(\frac{1}{\hat{R}T} \sum_{k'=1}^{N_s} \alpha_{r,k'} \hat{\mu}_{k'}\right) - \exp\left(\frac{1}{\hat{R}T} \sum_{k'=1}^{N_s} \beta_{r,k'} \hat{\mu}_{k'}\right) \right] dt \\
&= \hat{R} \sum_{r=1}^{N_r} K_r^S \left[\left(\frac{1}{\hat{R}T} \sum_{k=1}^{N_s} \alpha_{r,k} \hat{\mu}_k \right) - \left(\frac{1}{\hat{R}T} \sum_{k=1}^{N_s} \beta_{r,k} \hat{\mu}_k \right) \right] \\
&\quad \times \left[\exp\left(\frac{1}{\hat{R}T} \sum_{k=1}^{N_s} \alpha_{r,k} \hat{\mu}_k\right) - \exp\left(\frac{1}{\hat{R}T} \sum_{k=1}^{N_s} \beta_{r,k} \hat{\mu}_k\right) \right] dt > 0.
\end{aligned}$$

At this juncture, an important question arises: *Does $dS_i > 0$ imply that the thermodynamic entropy of a chemically reacting system evolving through mass action kinetics always increases?* The answer depends on the kind of system defined by the reacting gas mixture.

The chemical reactions conserve mass, therefore the system is at least closed. Studies of time-integration schemes for chemical ODEs typically fix the temperature. For a constant volume system, this is only possible through heat exchanges with a reservoir/heat bath system (first law). The system is therefore not isolated and the second law does not support the prescription of increasing entropy as $dS_e \neq 0$. However, a dynamical prescription still exists. Following Zemansky [6] (section 16-8), one can consider the 'universe' system defined by the reservoir and gas mixture. This system is isolated and the second law gives:

$$dS_{universe} = dS_{reservoir} + dS > 0. \quad (19)$$

The reservoir's entropy changes can be modeled through heat transfer:

$$dS_{reservoir} = -\frac{\delta Q}{T}, \quad (20)$$

where δQ is the heat received by the reacting system (hence the minus sign). The first law applied to the gas mixture gives $dE = \delta Q$. Inequality (19) becomes:

$$dS_{universe} = \frac{dE}{T} - dS > 0 \iff dF < 0, \quad F := E - TS. \quad (21)$$

F is commonly known as the *Helmholtz free energy*. This prescription can also be found mathematically through:

$$\left(\frac{\partial F}{\partial \mathcal{N}_k} \right)_{\mathcal{N}_{k'}, V, T} = \hat{\mu}_k.$$

If instead of temperature, the pressure is set to a constant, the same reasoning leads to the prescription of decreasing Gibbs free energy:

$$\left(\frac{\partial G}{\partial \mathcal{N}_k} \right)_{\mathcal{N}_{k'}, V, p} = \hat{\mu}_k.$$

The requirement of entropy increase is a valid prescription when the system is isolated, i.e. $dS_e = 0$. This corresponds to the configuration where temperature evolves in time in such a manner that the internal energy of the system is conserved. Mathematically, we have:

$$\left(\frac{\partial S}{\partial \mathcal{N}_k} \right)_{\mathcal{N}_{k'}, V, E} = -\frac{1}{T} \hat{\mu}_k.$$

4 Implicit Chemical Thermodynamics

4.1 Working with Practical Models

Chemical kinetics models are defined by the forward & backward rates of each reaction, together with the corresponding chemical equilibrium constant. In practice, the model coefficients are designed in an *ad-hoc* manner through interpolation formulas fitted against experimental data relevant to the target application. In this section, we begin examining the extent to which this degree of empiricism may conflict with the dynamical prescriptions implied by chemical thermodynamics.

As model problem, we consider a 5-species $\{N_2, O_2, N, O, NO\}$ ($N_s = 5$) kinetic model for air, adapted from Park [27]. The model consists of a set of 17 reactions (dissociation and exchange) represented as:



where $M \in \{N_2, O_2, N, O, NO\}$ denotes the collision partner. The chemical equilibrium composition is determined by three independent chemical equilibrium relations

$$K_{eq,1}(T) := \frac{[N]^*[N]^*}{[N_2]^*}, \quad K_{eq,2}(T) := \frac{[O]^*[O]^*}{[O_2]^*}, \quad K_{eq,3}(T) := \frac{[O]^*[N]^*}{[NO]^*}. \quad (27)$$

coupled with two element conservation relations:

$$2[N_2]^* + [N]^* + [NO]^* = C_{(N)}, \quad (28)$$

$$2[O_2]^* + [O]^* + [NO]^* = C_{(O)}, \quad (29)$$

where $C_{(N)}$ and $C_{(O)}$ denote the molar concentrations of N elements and O elements, respectively. The equilibrium relations for exchange reactions (25) and (26), given by

$$K_{eq,4} := \frac{[O_2]^*[N]^*}{[O]^*[NO]^*}, \quad K_{eq,5} := \frac{[N]^*[NO]^*}{[N_2]^*[O]^*},$$

can be inferred from the first three. We have:

$$K_{eq,4}(T) = \frac{K_{eq,3}(T)}{K_{eq,2}(T)}, \quad K_{eq,5}(T) = \frac{K_{eq,1}(T)}{K_{eq,3}(T)}.$$

The forward reaction rates are of Arrhenius form:

$$K_f = CT^n \exp\left(-\frac{T_d}{T}\right).$$

The Arrhenius parameters (C , n , T_d) are taken from [27] (thermal equilibrium). The equilibrium constants are represented using analytical fits from [7]:

$$K_{eq}(T) = \exp\left[A_1\left(\frac{T}{10000}\right) + A_2 + A_3 \ln\left(\frac{10000}{T}\right) + A_4\left(\frac{10000}{T}\right) + A_5\left(\frac{10000}{T}\right)^2\right],$$

and are used to evaluate the backward rate coefficients.

Krambeck's proof allows the kinetic model's forward and backward reaction rates to have any form as long as their ratio equals the reaction's equilibrium constant. It does assume however that the chemical equilibrium constants are evaluated in terms of the reduced chemical potentials, which require a detailed knowledge

of their internal energy structure. In practice, the equilibrium constants are evaluated using interpolation formulas that are fitted against either experimental data (through spectroscopic [10, 24] and calorimetric measurements [6, 9]) or against data obtained through advanced quantum chemistry calculations [25, 7]. In the following sections, we demonstrate how the dynamical prescriptions of chemical thermodynamics hold with thermodynamic free energies and entropy *implicitly defined by the data*.

4.2 Implicit Free Energy

For the fixed-temperature system, the chemical equilibrium solution can be described as the solution of a constrained minimization problem. Define the free energy Lagrangian \tilde{F} :

$$\tilde{F}([X_k], \lambda_N, \lambda_O) := F - \lambda_N(2[N_2] + [N] + [NO] - C_{(N)}) - \lambda_O(2[O_2] + [O] + [NO] - C_{(O)}),$$

where λ_N and λ_O are Lagrange multipliers. The gradient equations with respect to the Lagrange multipliers give the element conservation constraints:

$$\left(\frac{\partial \tilde{F}}{\partial \lambda_N}\right)^* = 0, \quad \left(\frac{\partial \tilde{F}}{\partial \lambda_O}\right)^* = 0 \iff \begin{cases} 2[N_2]^* + [N]^* + [NO]^* = C_{(N)}, \\ 2[O_2]^* + [O]^* + [NO]^* = C_{(O)} \end{cases}$$

The gradient equations with respect to the concentrations give:

$$\left(\frac{\partial \tilde{F}}{\partial [X_k]}\right)^* = 0 \iff \begin{cases} \hat{\mu}_{N_2}^* - 2\lambda_N^* = 0, \\ \hat{\mu}_{O_2}^* - 2\lambda_O^* = 0, \\ \hat{\mu}_N^* - \lambda_N^* = 0, \\ \hat{\mu}_O^* - \lambda_O^* = 0, \\ \hat{\mu}_{NO}^* - \lambda_N^* - \lambda_O^* = 0. \end{cases}$$

This is equivalent to:

$$\hat{\mu}_{N_2}^* - 2\hat{\mu}_N^* = 0, \quad \hat{\mu}_{O_2}^* - 2\hat{\mu}_O^* = 0, \quad \hat{\mu}_{NO}^* - \hat{\mu}_N^* - \hat{\mu}_O^* = 0, \quad (30)$$

which is exactly the set of chemical equilibrium relations (27), if the equilibrium constants are computed through equation (12).

For equilibrium constants approximated through curve-fits, the Lagrangian formalism can be used infer an equivalent Helmholtz Free Energy. The chemical equilibrium relations (27) can be rewritten as:

$$2\hat{R}T \ln [N]^* - \hat{R}T \ln [N_2]^* = \hat{R}T \ln (K_{eq,1}), \quad (31)$$

$$2\hat{R}T \ln [O]^* - \hat{R}T \ln [O_2]^* = \hat{R}T \ln (K_{eq,2}), \quad (32)$$

$$\hat{R}T \ln [N]^* + \hat{R}T \ln [O]^* - \hat{R}T \ln [NO]^* = \hat{R}T \ln (K_{eq,3}). \quad (33)$$

We introduce a family of chemical potentials $\hat{\mu}_k^b$ parametrized by two functions of temperature \hat{b}_N and \hat{b}_O

$$\hat{\mu}_k^b([X_k], T) := \hat{\mu}_k^{0,b}(T) + \hat{R}T \ln [X_k] \quad \text{with} \quad \begin{cases} \hat{\mu}_N^{0,b} := \hat{b}_N, \\ \hat{\mu}_O^{0,b} := \hat{b}_O, \\ \hat{\mu}_{N_2}^{0,b} := 2\hat{b}_O + \hat{R}T \ln (K_{eq,1}), \\ \hat{\mu}_{O_2}^{0,b} := 2\hat{b}_O + \hat{R}T \ln (K_{eq,2}), \\ \hat{\mu}_{NO}^{0,b} := \hat{b}_N + \hat{b}_O + \hat{R}T \ln (K_{eq,3}). \end{cases} \quad (34)$$

This representation satisfies the relations (31) - (33). From there it follows that the function F^b defined by:

$$F^b([X_k], T) := \sum_{k=1}^{N_s} [X_k] \hat{f}_k^b, \quad \hat{f}_k^b := \hat{\mu}_k^b - \hat{R}T = \hat{\mu}_k^{0,b} + \hat{R}T(\ln [X_k] - 1), \quad (35)$$

is an equivalent free energy for the reacting ODE with equilibrium constants $(K_{eq,1}, K_{eq,2}, K_{eq,3})$. Expanding expression (35), we get:

$$F^b = \hat{R}T \left[\sum_{k=1}^{N_s} [X_k] \left(\ln [X_k] - 1 \right) + \left([N_2] \ln (K_{eq,1}) + [O_2] \ln (K_{eq,2}) + [NO] \ln (K_{eq,3}) \right) \right] + \left(C_{(N)} \hat{b}_N + C_{(O)} \hat{b}_O \right) \quad (36)$$

One can verify that the chemical equilibrium solution minimizes the corresponding Lagrangian $\tilde{F}^b([X_k], \lambda_N, \lambda_O)$:

$$\left(\frac{\partial \tilde{F}^b}{\partial [X_k]} \right)^* = 0 \iff \begin{cases} \ln [N_2]^* + \ln (K_{eq,1}) - 2\lambda_N^* = 0, \\ \ln [O_2]^* + \ln (K_{eq,2}) - 2\lambda_O^* = 0, \\ \ln [N]^* - \lambda_N^* = 0, \\ \ln [O]^* - \lambda_O^* = 0, \\ \ln [NO]^* + \ln (K_{eq,3}) - \lambda_N^* - \lambda_O^* = 0, \end{cases}$$

and that F^b is monotone decreasing for the kinetic system (see section 5.1):

$$\frac{dF^b}{dt} = \sum_{k=1}^{N_s} \hat{\mu}_k^b \Omega_k < 0.$$

At this stage, the only requirement on the equilibrium constants is that they are strictly positive. The characterization of (\hat{b}_N, \hat{b}_O) arises when the temperature-varying case is considered.

4.3 Implicit Entropy

For an isolated reacting system, the temperature evolves according to conservation of energy:

$$\frac{dT}{dt} = - \frac{1}{\sum_{k=1}^{N_s} \hat{c}_{v,k} [X_k]} \sum_{k=1}^{N_s} \hat{e}_k \Omega_k. \quad (37)$$

The equilibrium composition and temperature satisfy conservation of energy in addition to chemical equilibrium and element conservation. It can be described as the solution of a maximization problem. Consider the entropy Lagrangian:

$$\tilde{S}([X_k], T, \lambda_N, \lambda_O, \lambda_E) := S - \lambda_N \left(2[N_2] + [N] + [NO] - C_{(N)} \right) - \lambda_O \left(2[O_2] + [O] + [NO] - C_{(O)} \right) - \lambda_E \left(\sum_{k=1}^{N_s} [X_k] \hat{e}_k(T) - E \right).$$

The gradient equation with respect to temperature yields:

$$\left(\frac{\partial \tilde{S}}{\partial T} \right)^* = 0 \iff \sum_{k=1}^{N_s} \frac{\hat{c}_{v,k}(T^*)}{T^*} [X_k]^* = \lambda_E^* \sum_{k=1}^{N_s} [X_k]^* \hat{c}_{v,k}(T^*) \iff \lambda_E^* = \frac{1}{T^*}.$$

This relation is key as it enables the gradient equations with respect to the concentrations to simplify to the chemical equilibrium relations at $T = T^*$. Through $\hat{\mu}_k = \hat{e}_k + \hat{R}T - T\hat{s}_k$, we have:

$$\left(\frac{\partial \tilde{S}}{\partial [X_k]} \right)^* = 0 \iff \begin{cases} \hat{s}_{N_2}^* - \hat{R} - 2\lambda_N^* - \lambda_E^* \hat{e}_{N_2}^* = 0 \\ \hat{s}_{O_2}^* - \hat{R} - 2\lambda_O^* - \lambda_E^* \hat{e}_{O_2}^* = 0 \\ \hat{s}_N^* - \hat{R} - \lambda_N^* - \lambda_E^* \hat{e}_N^* = 0 \\ \hat{s}_O^* - \hat{R} - \lambda_O^* - \lambda_E^* \hat{e}_O^* = 0 \\ \hat{s}_{NO}^* - \hat{R} - \lambda_N^* - \lambda_O^* - \lambda_E^* \hat{e}_{NO}^* = 0 \end{cases} \iff \begin{cases} \hat{\mu}_{N_2}^* - 2\hat{\mu}_N^* = 0 \\ \hat{\mu}_{O_2}^* - 2\hat{\mu}_O^* = 0 \\ \hat{\mu}_{NO}^* - \hat{\mu}_N^* - \hat{\mu}_O^* = 0. \end{cases}$$

The gradient equation with respect to the Lagrange multipliers yield element and energy conservation equations.

As for the fixed-temperature system, we can show that given equilibrium constants ($K_{eq,1}$, $K_{eq,2}$, $K_{eq,3}$) and an internal energy model $(\hat{e}_k)_{1 \leq k \leq N_s}$, there exists an implicit thermodynamic entropy. Taking the logarithm of equation (12) gives:

$$\ln K_{eq,r} = -\frac{1}{\hat{R}T} \sum_{k=1}^{N_s} \nu_{r,k} \hat{\mu}_k^0.$$

Differentiating with respect to temperature gives the well-known Van't Hoff equation [3]:

$$\frac{d}{dT} \ln K_{eq,r} = \frac{1}{\hat{R}T^2} \sum_{k=1}^{N_s} \nu_{r,k} \hat{e}_k. \quad (38)$$

We require that the given $(K_{eq,r})_{1 \leq r \leq 3}$ and $(\hat{e}_k)_{1 \leq k \leq N_s}$ be consistent with equation (38), namely

$$\hat{e}_{N_2} = 2\hat{e}_N - \hat{R}T^2 \frac{d}{dT} \ln(K_{eq,1}), \quad (39)$$

$$\hat{e}_{O_2} = 2\hat{e}_O - \hat{R}T^2 \frac{d}{dT} \ln(K_{eq,2}), \quad (40)$$

$$\hat{e}_{NO} = \hat{e}_N + \hat{e}_O - \hat{R}T^2 \frac{d}{dT} \ln(K_{eq,3}). \quad (41)$$

This constraint implies that given the equilibrium constants and their derivatives, the specific internal energies are fully determined from that of the atomic species (\hat{e}_N , \hat{e}_O). We consider the candidate entropy S^b defined as:

$$S^b := \frac{1}{T} (E - F^b) = \sum_{k=1}^{N_s} [X_k] \hat{s}_k^b, \quad \hat{s}_k^b := \frac{1}{T} (\hat{e}_k - \hat{f}_k^b). \quad (42)$$

where the specific free energies \hat{f}_k^b follow the previous representation (34). Expanding, we get:

$$\begin{aligned} S^b = & -\hat{R} \sum_{k=1}^{N_s} [X_k] \left(\ln [X_k] - 1 \right) + \frac{E}{T} - \frac{1}{T} \left(C_{(N)} \hat{b}_N + C_{(O)} \hat{b}_O \right) \\ & - \hat{R} \left([N_2] \ln K_{eq,1} + [O_2] \ln K_{eq,2} + [NO] \ln K_{eq,3} \right) \end{aligned} \quad (43)$$

We require that the thermo-chemical equilibrium solution be found by maximizing S^b under constraints. The gradient of the corresponding Lagrangian \tilde{S}^b with respect to temperature is:

$$\begin{aligned} \frac{\partial \tilde{S}^b}{\partial T} = & \left(\frac{1}{T} - \lambda_E \right) \sum_{k=1}^{N_s} [X_k] \hat{c}_{v,k} - \frac{E}{T^2} + \frac{1}{T^2} \left(C_{(N)} \left(\hat{b}_N - T \frac{d\hat{b}_N}{dT} \right) + C_{(O)} \left(\hat{b}_O - T \frac{d\hat{b}_O}{dT} \right) \right) \\ & - \hat{R} \left([N_2] \frac{d \ln K_{eq,1}}{dT} + [O_2] \frac{d \ln K_{eq,2}}{dT} + [NO] \frac{d \ln K_{eq,3}}{dT} \right) \end{aligned}$$

Using the Van't Hoff equations (39)-(41) and the conservation equations to simplify the last three terms above, we get:

$$\frac{\partial \tilde{S}^b}{\partial T} = \left(\frac{1}{T} - \lambda_E \right) \sum_{k=1}^{N_s} [X_k] \hat{c}_{v,k} + \frac{C_{(N)}}{T^2} \left(\hat{b}_N - T \frac{d\hat{b}_N}{dT} - \hat{e}_N \right) + \frac{C_{(O)}}{T^2} \left(\hat{b}_O - T \frac{d\hat{b}_O}{dT} - \hat{e}_O \right).$$

This equation leads to $\lambda_E^* = 1/T^*$ if \hat{b}_N and \hat{b}_O satisfy:

$$\frac{d}{dT} \left(\frac{\hat{b}_N}{T} \right) = -\frac{\hat{e}_N}{T^2}, \quad \frac{d}{dT} \left(\frac{\hat{b}_O}{T} \right) = -\frac{\hat{e}_O}{T^2}. \quad (44)$$

This is equivalent to:

$$\frac{\hat{b}_N(T)}{T} = - \int_{T^0}^T \frac{\hat{e}_N(\tau)}{\tau^2} d\tau + \frac{\hat{b}_N(T^0)}{T^0}, \quad \frac{\hat{b}_O(T)}{T} = - \int_{T^0}^T \frac{\hat{e}_O(\tau)}{\tau^2} d\tau + \frac{\hat{b}_O(T^0)}{T^0}, \quad (45)$$

where T^0 is a reference temperature. Equation (45) completes the characterization of $(\hat{\mu}_k^b)_{1 \leq k \leq N_s}$. We recover the chemical equilibrium equations through:

$$\left(\frac{\partial \tilde{S}^b}{\partial [X_k]} \right)^* = 0 \iff \begin{cases} \ln [N_2]^* + \ln K_{eq,1}(T^*) - 2\lambda_N^* = 0, \\ \ln [O_2]^* + \ln K_{eq,2}(T^*) - 2\lambda_O^* = 0, \\ \ln [N]^* - \lambda_N^* = 0, \\ \ln [O]^* - \lambda_O^* = 0, \\ \ln [NO]^* + \ln K_{eq,3}(T^*) - \lambda_N^* - \lambda_O^* = 0. \end{cases} \implies (31) - (33) \text{ at } T = T^*.$$

Finally, S^b is monotone increasing for the kinetic system defined by equations (13) and (37). We have:

$$\frac{\partial S^b}{\partial [X_k]} = \frac{1}{T} (\hat{e}_k - \hat{\mu}_k^b).$$

We can show (lemma 6.7) that the completed representation of the reduced chemical potentials $(\hat{\mu}_k^b)_{1 \leq k \leq N_s}$ implies:

$$\frac{\partial S^b}{\partial T} = \frac{1}{T} \sum_{k=1}^{N_s} \hat{c}_{vk} [X_k] \implies \frac{dS^b}{dt} = -\frac{1}{T} \sum_{k=1}^{N_s} \hat{\mu}_k^b \Omega_k > 0.$$

Ultimately, the implicit entropy writes (we drop the b superscript and ignore the integration constants (45)):

$$\begin{aligned} S = & - \hat{R} \sum_{k=1}^{N_s} [X_k] \left(\ln [X_k] - 1 \right) + \frac{E}{T} + \left(C_{(N)} \int_{T^0}^T \frac{\hat{e}_N(\tau)}{\tau^2} d\tau + C_{(O)} \int_{T^0}^T \frac{\hat{e}_O(\tau)}{\tau^2} d\tau \right) \\ & - \hat{R} \left([N_2] \ln K_{eq,1} + [O_2] \ln K_{eq,2} + [NO] \ln K_{eq,3} \right). \end{aligned} \quad (46)$$

These derivations are generalized in section 6.

5 Numerical Analysis

In this section, we briefly outline how the analysis of sections 3 and 4 can be used for numerical purposes. For simplicity, we consider the model 5-species system of section 4.1 at fixed temperature $T = 10000 \text{ K}$. We represent the kinetic system (13) in vector form:

$$\frac{d\mathbf{X}}{dt} = \mathbf{\Omega}(\mathbf{X}), \quad (47)$$

with $\mathbf{\Omega} := (\Omega_k)_{1 \leq k \leq N_s}$ and $\mathbf{X} := ([X_k])_{1 \leq k \leq N_s}$. The initial total number of moles is $N_{tot} = 10^{18}/N_A$, with $N_A = 6.023 \cdot 10^{23}$. The initial molar fractions $\chi_k := [X_k]/N_{tot}$ are set to $(\chi_{N_2}, \chi_{O_2}, \chi_N, \chi_O, \chi_{NO}) = (0.78, 0.21, 0.001, 0.001, 0.008)$. The temporal evolution of the molar fractions is shown in figure 1.

For this system, the free energy F is the relevant thermodynamic function (section 3.3). From section 4.2, we can define the implicit free energy:

$$F := \sum_{k=1}^{N_s} [X_k] (\ln [X_k] - 1) + [N_2] \ln K_{eq,1} + [O_2] \ln K_{eq,2} + [NO] \ln K_{eq,3}.$$

F is a convex function of \mathbf{X} . Its hessian \mathbf{B} given by:

$$\mathbf{B} := \frac{\partial^2 F}{\partial \mathbf{X}^2} = \text{diag} \left[\left([X_k]^{-1} \right)_{1 \leq k \leq N_s} \right],$$

is symmetric positive definite (we assume $[X_k] > 0$). The vector of implicit chemical potentials $\boldsymbol{\mu}$ is given by:

$$\boldsymbol{\mu} := \left(\frac{\partial F}{\partial \mathbf{X}} \right)^T = (\hat{\mu}_k)_{1 \leq k \leq N_s}.$$

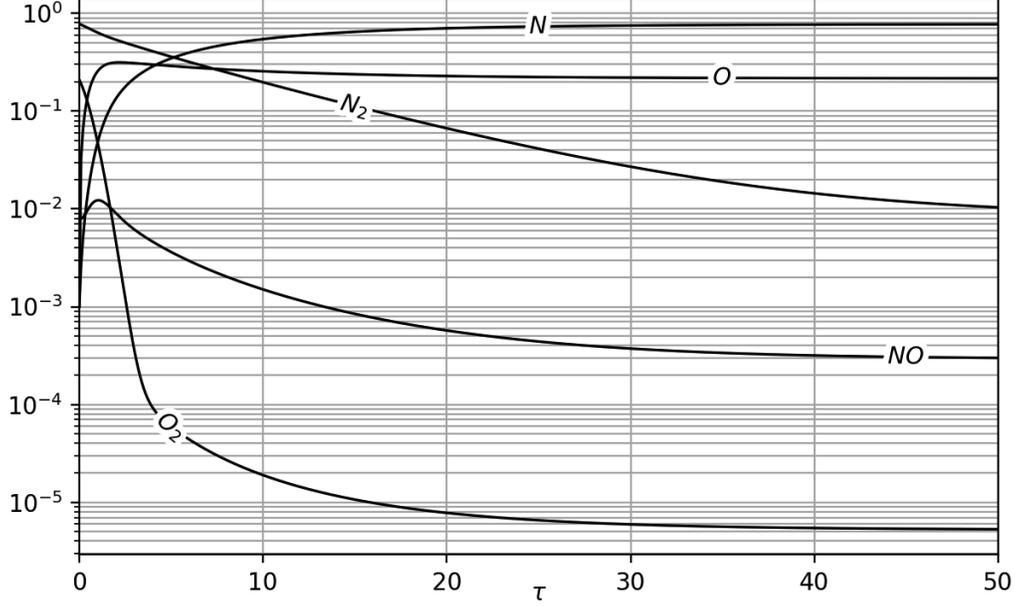


Figure 1: Constant-temperature evolution of molar fractions over time for the 5-species air system. ODE system integrated with backward Euler at $\Delta t = 10^{-1}\tau$. $\tau = 8.2210^{-8}s$ is a characteristic time obtained by taking the inverse of the largest eigenvalue of the Jacobian at $t = 0s$.

5.1 Free Energy Breakdown

The discrete evolution of F over time can be decomposed into contributions from the model (source terms) and contributions from the temporal integration scheme used.

5.1.1 Model Contribution

Following the procedure of section 3.3, one can prove that $\boldsymbol{\Omega}$ always dissipates F . This contribution is represented by the free energy dissipation term \mathcal{E}^Ω defined as:

$$\mathcal{E}^\Omega := -\boldsymbol{\mu}^T \boldsymbol{\Omega} > 0.$$

Introducing the auxiliary rate constants:

$$\begin{aligned} K_{1,k}^S &:= K_{1,k}^f / K_{eq,1} = K_{1,k}^r, & K_{2,k}^S &:= K_{2,k}^f / K_{eq,2} = K_{2,k}^r, & K_{3,k}^S &:= K_{3,k}^f / K_{eq,3} = K_{3,k}^r, \\ K_4^S &:= K_4^f / K_{eq,3} = K_4^r / K_{eq,2}, & K_5^S &:= K_5^f / K_{eq,1} = K_5^r / K_{eq,3}, \end{aligned}$$

one can rewrite the 17 reaction source terms (section 4.1) in potential form:

$$\begin{aligned}
\text{Reactions (22)} &\rightarrow \omega_{1,k} = [X_k] \left(K_{1,k}^f [N_2] - K_{1,k}^r [N]^2 \right) = [X_k] K_{1,k}^S \left(\exp(\hat{\mu}_{N_2}) - \exp(2\hat{\mu}_N) \right), \\
\text{Reactions (23)} &\rightarrow \omega_{2,k} = [X_k] \left(K_{2,k}^f [O_2] - K_{2,k}^r [O]^2 \right) = [X_k] K_{2,k}^S \left(\exp(\hat{\mu}_{O_2}) - \exp(2\hat{\mu}_O) \right), \\
\text{Reactions (24)} &\rightarrow \omega_{3,k} = [X_k] \left(K_{3,k}^f [NO] - K_{3,k}^r [N][O] \right) = [X_k] K_{3,k}^S \left(\exp(\hat{\mu}_{NO}) - \exp(\hat{\mu}_O + \hat{\mu}_N) \right), \\
\text{Reaction (25)} &\rightarrow \omega_4 = K_4^f [NO][O] - K_4^r [O_2][N] = K_4^S \left(\exp(\hat{\mu}_{NO} + \hat{\mu}_O) - \exp(\hat{\mu}_{O_2} + \hat{\mu}_N) \right), \\
\text{Reaction (26)} &\rightarrow \omega_5 = K_5^f [N_2][O] - K_5^r [NO][N] = K_5^S \left(\exp(\hat{\mu}_{N_2} + \hat{\mu}_O) - \exp(\hat{\mu}_{NO} + \hat{\mu}_N) \right).
\end{aligned}$$

The solution of system (47) satisfies

$$\frac{dF}{dt} = -\mathcal{E}^\Omega = -\sum_{k=1}^{N_s} \mathcal{E}_{1,k} - \sum_{k=1}^{N_s} \mathcal{E}_{2,k} - \sum_{k=1}^{N_s} \mathcal{E}_{3,k} - \mathcal{E}_4 - \mathcal{E}_5 < 0. \quad (48)$$

with:

$$\begin{aligned}
\mathcal{E}_{1,k} &:= (\hat{\mu}_{N_2} - 2\hat{\mu}_N) \omega_{1,k} > 0, \\
\mathcal{E}_{2,k} &:= (\hat{\mu}_{O_2} - 2\hat{\mu}_O) \omega_{2,k} > 0, \\
\mathcal{E}_{3,k} &:= (\hat{\mu}_{NO} - \hat{\mu}_N - \hat{\mu}_O) \omega_{3,k} > 0, \\
\mathcal{E}_4 &:= (\hat{\mu}_{NO} + \hat{\mu}_O - \hat{\mu}_{O_2} - \hat{\mu}_N) \omega_4 > 0, \\
\mathcal{E}_5 &:= (\hat{\mu}_{N_2} + \hat{\mu}_O - \hat{\mu}_{NO} - \hat{\mu}_N) \omega_5 > 0.
\end{aligned}$$

The relative contributions of these terms are shown in figure 2.

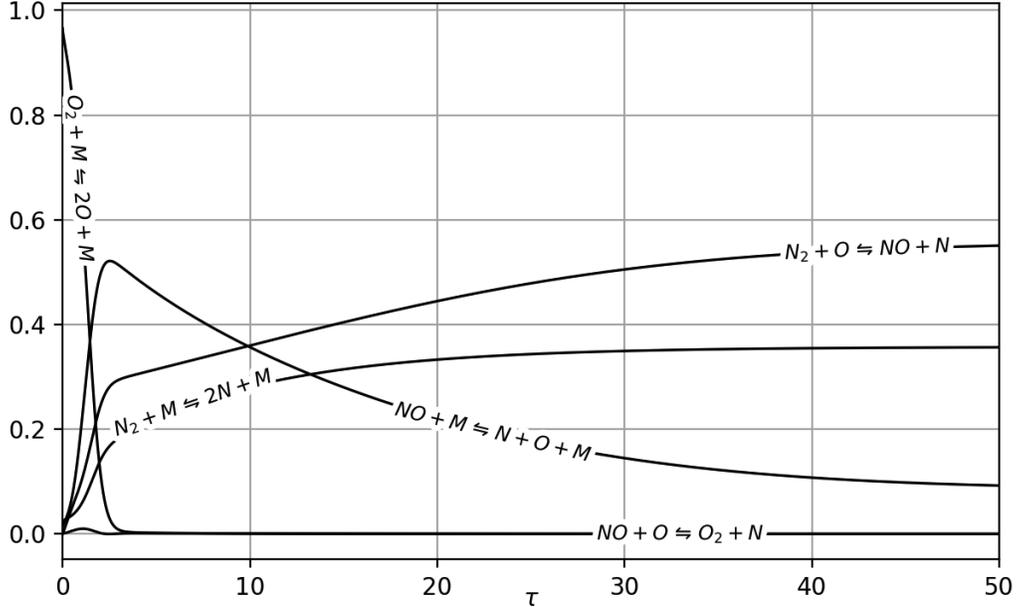


Figure 2: Relative contributions of the different reactions to the overall model dissipation of free energy over time. The ODE system integrated with backward Euler at $\Delta t = 10^{-1}\tau$.

5.1.2 Discrete Contributions

In order to complete the picture drawn by equation (48), we need to integrate the contribution (positive or negative) of the temporal scheme. Since F is convex, Tadmor's analysis [11] can be used for that purpose.

Consider the Backward Euler (BE) scheme:

$$\mathbf{X}^{n+1} - \mathbf{X}^n = \Delta t \Omega(\mathbf{X}^{n+1}). \quad (49)$$

Taking the dot product with the vector of chemical potential at instant $n + 1$ gives:

$$(\boldsymbol{\mu}^{n+1})^T (\mathbf{X}^{n+1} - \mathbf{X}^n) = -\Delta t \mathcal{E}^\Omega(\mathbf{X}^{n+1}).$$

Tadmor showed (example 7.1 in [11]) that the left hand side term above can be rewritten as:

$$(\boldsymbol{\mu}^{n+1})^T (\mathbf{X}^{n+1} - \mathbf{X}^n) = F(\mathbf{X}^{n+1}) - F(\mathbf{X}^n) + \mathcal{E}^{BE}(\boldsymbol{\mu}^n, \boldsymbol{\mu}^{n+1}). \quad (50)$$

with:

$$\begin{aligned} \mathcal{E}^{BE}(\boldsymbol{\mu}^n, \boldsymbol{\mu}^{n+1}) &:= (\Delta \boldsymbol{\mu}^{n+\frac{1}{2}})^T \int_{-1/2}^{1/2} \left(\frac{1}{2} - \xi \right) \mathbf{B}(\boldsymbol{\mu}^{n+\frac{1}{2}}) \Delta \boldsymbol{\mu}^{n+\frac{1}{2}} d\xi > 0, \\ \Delta \boldsymbol{\mu}^{n+\frac{1}{2}} &:= \boldsymbol{\mu}^{n+1} - \boldsymbol{\mu}^n, \quad \boldsymbol{\mu}^{n+1/2}(\xi) := \frac{1}{2}(\boldsymbol{\mu}^n + \boldsymbol{\mu}^{n+1}) + \xi \Delta \boldsymbol{\mu}^{n+\frac{1}{2}}. \end{aligned}$$

Therefore, equation (49) implies:

$$F(\mathbf{X}^{n+1}) - F(\mathbf{X}^n) = -\Delta t \mathcal{E}^\Omega(\mathbf{X}^{n+1}) - \mathcal{E}^{BE}(\boldsymbol{\mu}^n, \boldsymbol{\mu}^{n+1}) < 0.$$

In other words, the BE scheme always dissipates free energy. Consider the Forward Euler (FE) scheme:

$$\mathbf{X}^{n+1} - \mathbf{X}^n = \Delta t \Omega(\mathbf{X}^n). \quad (51)$$

Tadmor showed (example 7.2 in [11]):

$$(\boldsymbol{\mu}^n)^T (\mathbf{X}^{n+1} - \mathbf{X}^n) = F(\mathbf{X}^{n+1}) - F(\mathbf{X}^n) - \mathcal{E}^{FE}(\boldsymbol{\mu}^n, \boldsymbol{\mu}^{n+1}), \quad (52)$$

with:

$$\mathcal{E}^{FE}(\boldsymbol{\mu}^n, \boldsymbol{\mu}^{n+1}) := (\Delta \boldsymbol{\mu}^{n+\frac{1}{2}})^T \int_{-1/2}^{1/2} \left(\frac{1}{2} + \xi \right) \mathbf{B}(\boldsymbol{\mu}^{n+\frac{1}{2}}) \Delta \boldsymbol{\mu}^{n+\frac{1}{2}} d\xi > 0.$$

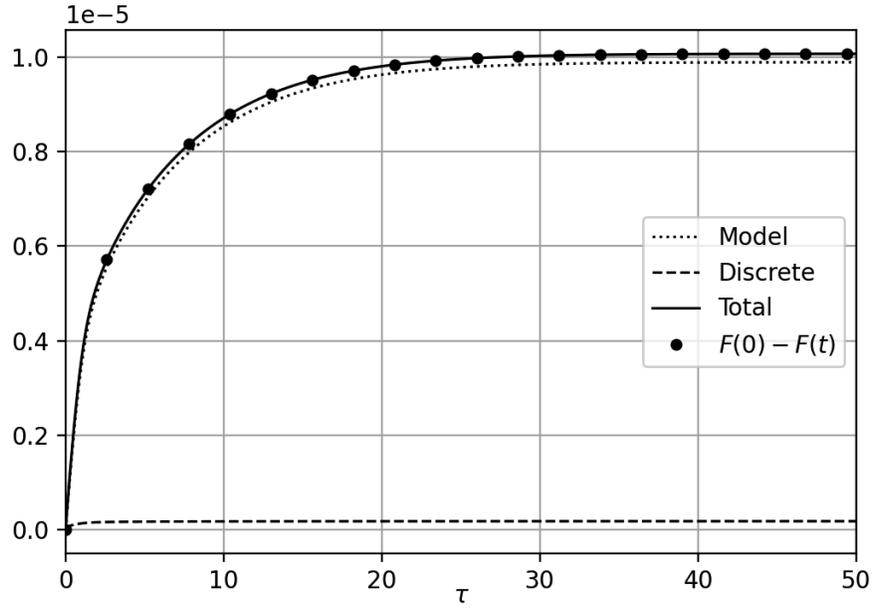
Therefore, equation (51) implies:

$$F(\mathbf{X}^{n+1}) - F(\mathbf{X}^n) = -\Delta t \mathcal{E}^\Omega(\mathbf{X}^n) + \mathcal{E}^{FE}(\boldsymbol{\mu}^n, \boldsymbol{\mu}^{n+1}). \quad (53)$$

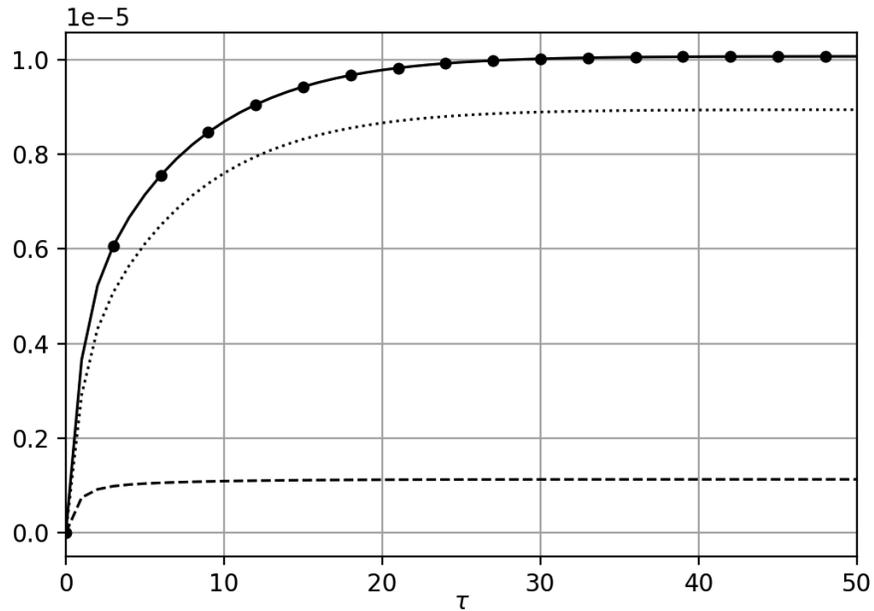
The sign of the right-hand side term is not fixed. In principle, \mathcal{E}^{FE} could become larger than $\Delta t \mathcal{E}^\Omega$ for a large enough time step. In practice however, Δt cannot be arbitrarily large. For the present kinetic system and configuration (τ depends on the initial composition and temperature), the forward Euler scheme eventually yields negative concentrations past a threshold time step $\Delta t_{max}^{FE} \approx 0.123\tau$. Instabilities can still develop when the right-hand side of equation (53) is negative.

Figures 3 and 4 show the respective contributions of the model ($\Delta t \mathcal{E}^\Omega$) and the temporal scheme over time for the backward Euler and forward Euler schemes, respectively. For the backward Euler scheme, the discrete contribution to free energy decay is always positive (nonlinear stability) and grows with Δt until a threshold value $\Delta t_{max}^{BE} \approx 1.103\tau$ for which the nonlinear solve fails to converge. As Δt grows, we see that the model contribution actually decreases. This is consistent with the dynamical prescription of decreasing free energy (section 3.3) and the definition of chemical equilibrium as a free energy minimizer (section 4.2). Conversely, as the free energy produced by the forward Euler scheme grows with Δt , the model contribution actually increases.

Similar free energy breakdowns can be achieved for higher-order temporal schemes that can be construed as composite forward/backward Euler schemes. An example derivation can be found in Gouasmi *et al.* (section 4.1 in [37]). Unless the temporal scheme is constructed specifically with equations (50) and (52) in mind, the discrete contributions will be of unknown sign a priori.

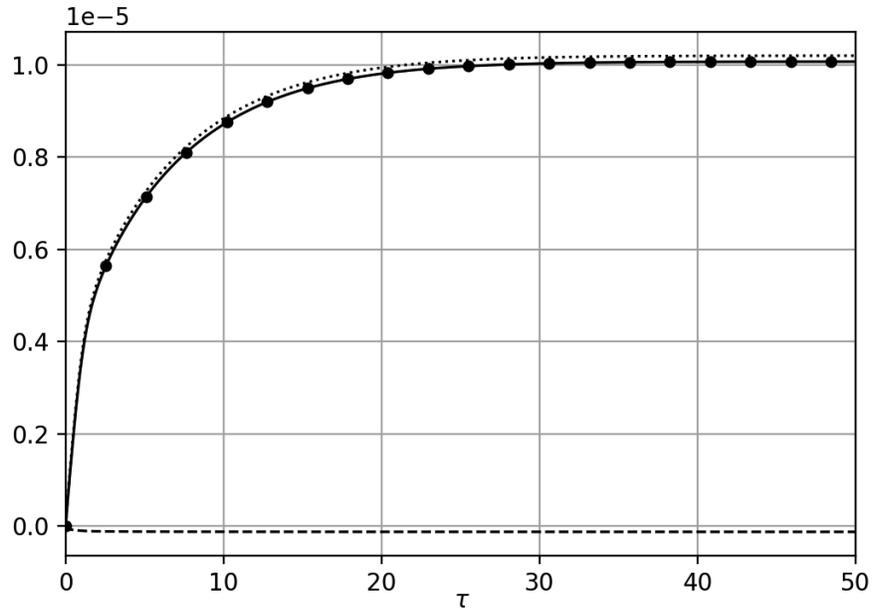


(a) $\Delta t = 0.1\tau$

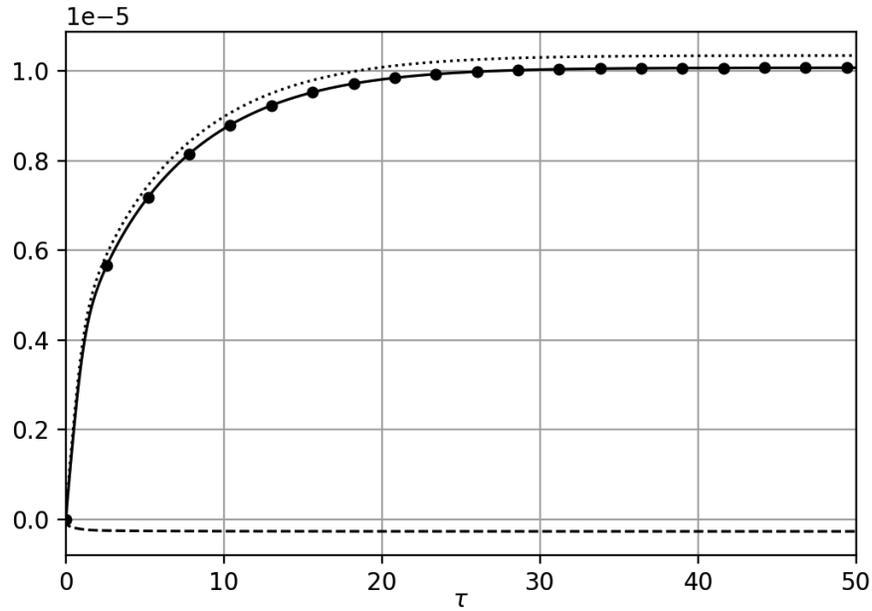


(b) $\Delta t = \tau$

Figure 3: Cumulative model (dotted line) and discrete (dashed line) contributions to free energy decay with backward Euler in time. The full line is the addition of the model and discrete contributions to free energy variations. The full circle markers represent the decay of free energy directly computed from solution snapshots (it matches the full line). The backward Euler scheme dissipates free energy, and this contribution grows with Δt . The model contribution decreases with Δt .



(a) $\Delta t = 0.05\tau$



(b) $\Delta t = 0.1\tau$

Figure 4: Model and discrete contributions to free energy decay with forward Euler in time (same legend as figure 3). The forward Euler scheme produces free energy, and as Δt grows, the dissipation of free energy due to the model grows to compensate the discrete production.

5.2 Nonlinear Stability at High Order

Drawing from [12, 14], we introduce a high-order temporal scheme that always dissipates free energy. Consider a piecewise polynomial representation \mathbf{q}_I of the approximate solution on the interval $I := [t^n, t^{n+1}]$:

$$\mathbf{q}_I(t) := \sum_{p=1}^P \varphi_p(t) \mathbf{q}_p, \quad (54)$$

where P is the polynomial order and $(\varphi_p)_{1 \leq p \leq P}$ is the temporal basis. The DG temporal discretization of equation (47) writes:

$$\int_I \left(\frac{d\varphi_p}{dt} \right) \mathbf{X}(\mathbf{q}_I(\tau)) d\tau - [\varphi_p(t^{n+1,-}) \mathbf{X}(\mathbf{q}_I^{n+1,-}) - \varphi_p(t^{n,+}) \mathbf{X}(\mathbf{q}_I^{n,-})] = - \int_I \varphi_p(\tau) \Omega(\mathbf{X}(\mathbf{q}_I(\tau))) d\tau, \quad (55)$$

$$\mathbf{q}_I^{n,-} := \mathbf{q}_I(t^{n,-}), \quad \mathbf{q}_I^{n+1,-} := \mathbf{q}_I(t^{n+1,-}), \quad 1 \leq p \leq P.$$

In reference coordinates $\tau := \frac{2}{\Delta t}(t - \frac{1}{2}(t^n + t^{n+1})) \in [-1, 1]$, this gives:

$$\int_{-1}^1 \left(\frac{d\varphi_p}{d\tau} \right) \mathbf{X}(\mathbf{q}_I(\tau)) d\tau - [\varphi_p(1) \mathbf{X}(\mathbf{q}_I^{n+1,-}) - \varphi_p(-1) \mathbf{X}(\mathbf{q}_I^{n,-})] = - \frac{\Delta t}{2} \int_{-1}^1 \varphi_p(\tau) \Omega(\mathbf{X}(\mathbf{q}_I(\tau))) d\tau.$$

Using a quadrature rule $(\tau_q, w_q)_{1 \leq q \leq n_q}$ for the temporal integrals, leads the discrete system:

$$\sum_{q=1}^{n_q} w_q \left(\frac{d\varphi_p}{d\tau} \right)_{\tau=\tau_q} \mathbf{X}(\mathbf{q}_I(\tau_q)) - [\varphi_p(1) \mathbf{X}(\mathbf{q}_I^{n+1,-}) - \varphi_p(-1) \mathbf{X}(\mathbf{q}_I^{n,-})] = - \frac{\Delta t}{2} \sum_{q=1}^{n_q} w_q \varphi_p(\tau_q) \Omega(\mathbf{X}(\mathbf{q}_I(\tau_q))), \quad (56)$$

which we solve with $n_q = 2P$, Legendre basis functions and Gauss-Legendre quadrature rules. The solution at time instant $n + 1$ is obtained by solving the system (56), and evaluating the representation (54) at $t = t^{n+1}$.

Setting $\mathbf{q} := \mathbf{X}$ leads to the standard DG scheme in time, which is linearly stable [48]. Early work by Hughes *et al.* [12] and Barth [14] demonstrated that a nonlinearly stable variant can be obtained by assigning a polynomial form to the *entropy variables* (see section 7.1). In the present context, this is equivalent to assigning a polynomial form to the chemical potentials:

$$\boldsymbol{\mu}_I(t) := \sum_{p=1}^P \varphi_p(t) \boldsymbol{\mu}_p.$$

This is proved as follows. First, consider an equivalent weak form obtained by integrating equation (55) by parts:

$$\int_I \varphi_p \left(\frac{d\mathbf{X}(\mathbf{q}_I)}{dt} \right) d\tau - \varphi_p(t^{n,+}) (\mathbf{X}(\mathbf{q}_I^{n,+}) - \mathbf{X}(\mathbf{q}_I^{n,-})) = \int_I \varphi_p(\tau) \Omega(\mathbf{X}(\mathbf{q}_I(\tau))) d\tau \quad (57)$$

Injecting the representation $\mathbf{q} := \boldsymbol{\mu}$ and multiplying by each modal equation by corresponding degree of freedom, we get, for $1 \leq p \leq P$:

$$\int_I \varphi_p \boldsymbol{\mu}_p^T \left(\frac{d\mathbf{X}(\boldsymbol{\mu}_I)}{dt} \right) d\tau - \varphi_p(t^{n,+}) \boldsymbol{\mu}_p^T (\mathbf{X}(\boldsymbol{\mu}_I^{n,+}) - \mathbf{X}(\boldsymbol{\mu}_I^{n,-})) = \int_I \varphi_p(\tau) \boldsymbol{\mu}_p^T \Omega(\mathbf{X}(\boldsymbol{\mu}_I(\tau))) d\tau.$$

Summing over all degrees of freedom, we get:

$$\begin{aligned} & \int_I \boldsymbol{\mu}_I^T \left(\frac{d\mathbf{X}(\boldsymbol{\mu}_I)}{dt} \right) d\tau - (\boldsymbol{\mu}_I^{n,+})^T (\mathbf{X}(\boldsymbol{\mu}_I^{n,+}) - \mathbf{X}(\boldsymbol{\mu}_I^{n,-})) = \int_I \boldsymbol{\mu}_I^T \Omega(\mathbf{X}(\boldsymbol{\mu}_I(\tau))) d\tau, \\ \iff & \int_I \left(\frac{dF(\boldsymbol{\mu}_I)}{dt} \right) d\tau - (\boldsymbol{\mu}_I^{n,+})^T (\mathbf{X}(\boldsymbol{\mu}_I^{n,+}) - \mathbf{X}(\boldsymbol{\mu}_I^{n,-})) = - \int_I \mathcal{E}^\Omega(\boldsymbol{\mu}_I)(\tau) d\tau, \\ \iff & F(\boldsymbol{\mu}_I^{n+1,-}) - F(\boldsymbol{\mu}_I^{n,+}) - (\boldsymbol{\mu}_I^{n,+})^T (\mathbf{X}(\boldsymbol{\mu}_I^{n,+}) - \mathbf{X}(\boldsymbol{\mu}_I^{n,-})) = - \int_I \mathcal{E}^\Omega(\boldsymbol{\mu}_I(\tau)) d\tau. \end{aligned}$$

Using equation (50):

$$(\boldsymbol{\mu}_I^{n,+})^T (\mathbf{X}(\boldsymbol{\mu}_I^{n,+}) - \mathbf{X}(\boldsymbol{\mu}_I^{n,-})) = F(\boldsymbol{\mu}_I^{n,+}) - F(\boldsymbol{\mu}_I^{n,-}) + \mathcal{E}^{BE}(\boldsymbol{\mu}_I^{n,-}, \boldsymbol{\mu}_I^{n,+}), \quad (58)$$

we have, finally:

$$F(\boldsymbol{\mu}_I^{n+1,-}) - F(\boldsymbol{\mu}_I^{n,-}) = -\mathcal{E}^{BE}(\boldsymbol{\mu}_I^{n,-}, \boldsymbol{\mu}_I^{n,+}) - \int_I \mathcal{E}^\Omega(\boldsymbol{\mu}_I) d\tau. \quad (59)$$

Equation (59) is satisfied provided the integrals are evaluated accurately enough. Since the right-hand side terms of equation (59) can be readily computed, we can use the above relation to assess the reliability of a quadrature rule (good agreement is found with $n_q = 2P$).

For stiff systems, implicit schemes are preferred to explicit ones [29, 30, 32]. That is because explicit schemes have stringent time step restrictions. This is commonly established through a model scalar ODE:

$$\frac{dx}{dt} = kx, \quad x(0) = x_0.$$

where $k \in \mathbb{C}$ is such that $Re(k) < 0$, guaranteeing a stable solution. A temporal scheme is termed linearly stable if it satisfies $|x^{n+1}| < |x^n|$ for any such k . Explicit schemes are only stable if $z = k\Delta t$ lies in a certain region of the complex left half plane. Implicit schemes are found to be either unconditionally stable or stable within regions that are typically larger than that of explicit schemes. Such analyses have driven many advances in time integration techniques for stiff systems (see Kennedy & Carpenter [32] for an extensive review). However, their scope is limited.

For problems of engineering interest such as reacting flows, executing an implicit scheme requires a system of nonlinear equations to be solved using iterative methods. Here we use a Newton method coupled with a standard line search (the Jacobians are evaluated analytically and directly inverted). Linear stability analysis can hardly predict whether a solution to the nonlinear system actually exists for a given Δt . In practice, one finds that the larger Δt , the less likely the nonlinear solve will converge below a set threshold residual value. This limitation can be tied to the accuracy of the temporal scheme itself. For chemically reacting systems, this practical limitation is easy to comprehend. For example, our model kinetic system has an equilibrium solution \mathbf{X}^* which cancels out $\boldsymbol{\Omega}$. The backward Euler scheme is unconditionally stable yet it cannot reach the equilibrium composition in one single step. Setting $\mathbf{X}^{n+1} = \mathbf{X}^*$ in equation (49) leads to $\mathbf{X}^n = \mathbf{X}^*$.

The implicit nonlinearly stable DG scheme we introduced has similar time step limitations. However, we report that the maximum time step that can be resolved is larger than for the standard DG scheme and some DIRK schemes taken from the literature [30, 31]. In addition, the maximum resolved time step tends to grow with the polynomial order P . This is shown in figure 5. Future work will examine the performance of these schemes in more detail.

6 Generalization

6.1 Model assumptions

We consider reacting systems of the form (13), with the forward and backward reaction rates (K_r^f, K_r^b) related through the corresponding equilibrium constant $K_{eq,r}$. The gas mixture consists of N_s species made up of $N_L < N_s$ elements. At least $N_{IR} = N_s - N_L$ independent chemical reactions are involved. We index the species as follows:

- The linear independence of the element conservation equations implies the existence of N_L distinct species $(X_l)_{1 \leq l \leq N_L}$ such that $[X_l]$ features in the l -th element conservation equation. These species are indexed from 1 to N_L .
- The remaining N_{IR} species are indexed from $N_L + 1$ to N_s .

We consider the evolution of the ODE (13) with a fixed-temperature and with a temperature that varies. In either configuration, we assume the existence of a unique strictly positive chemical equilibrium solution

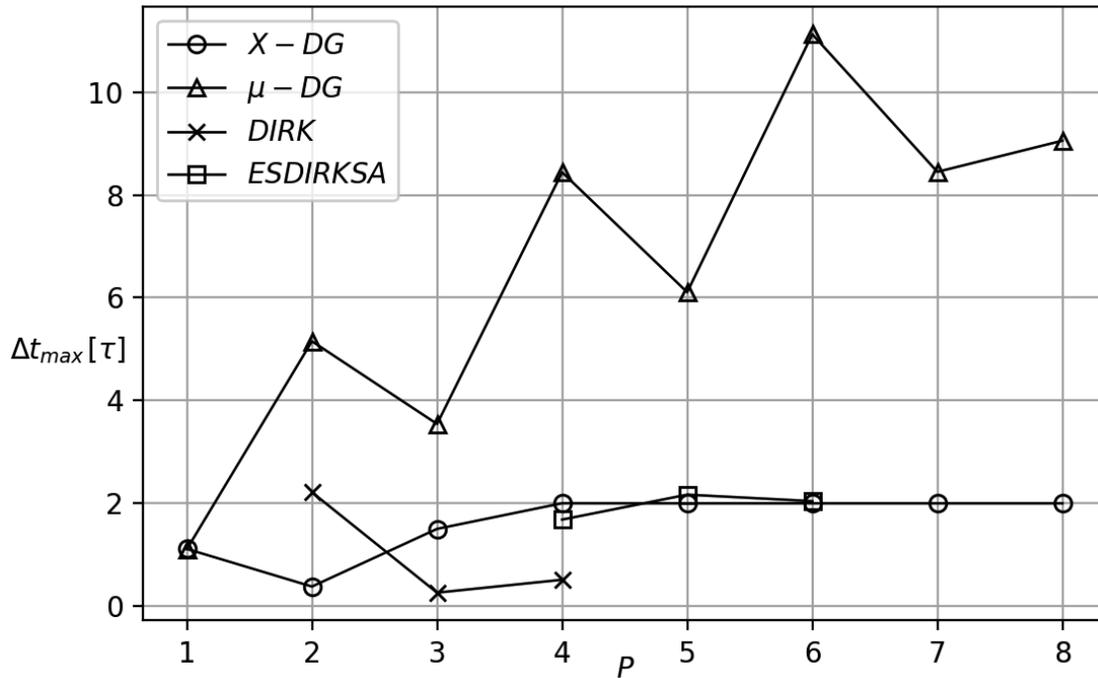


Figure 5: Largest resolved time-step (1000 Newton iterations, residual tolerance 10^{-15}) for different temporal schemes of varying orders of accuracy P . The standard DG scheme (polynomial representation of $[X_k]$) is represented by the circle marker. Its nonlinearly stable variant (polynomial representation of $[\hat{\mu}_k]$) is represented by the triangle marker. The DIRK schemes of Crouzeix [30] ($2 \leq P \leq 4$) are represented by the cross marker. The ES-DIRK-SA schemes ($4 \leq P \leq 6$) recently introduced by Kennedy & Carpenter [31] are represented by the square marker.

$([X_k]^*)_{1 \leq k \leq N_s}$ that is the solution of N_{IR} independent chemical equilibrium equations

$$\sum_{k=1}^{N_s} \nu_{r,k} \ln [X_k]^* = \ln K_{eq,r}, \quad 1 \leq r \leq N_{IR}, \quad (60)$$

coupled with N_l linearly independent element conservation equations

$$\sum_{k=1}^{N_s} c_{l,k} [X_k] = C_{(l)}, \quad 1 \leq l \leq N_L. \quad (61)$$

In the temperature-varying case, the equilibrium temperature at which the chemical equilibrium relations are to hold is determined by the energy conservation equation:

$$\sum_{k=1}^{N_s} [X_k]^* \hat{e}_k(T^*) = E. \quad (62)$$

We assume the chemical equilibrium constants to be strictly positive. For the temperature-varying configuration, we require that they satisfy the Van't Hoff equations (38), which can be thought of as consistency relations between the internal energy model and the chemical equilibrium model.

We reckon the above assumptions to be reasonable for a large class of reacting systems. We refer the reader to Krambeck's work [23], Giovangigli's book [1] and references therein for detailed analyses of the well-posedness of reaction kinetics.

6.2 Convergence to Equilibrium

The procedure we introduced in section 4 can be generalized by formally introducing the equilibrium composition into the derivations. For the fixed-temperature case, we rewrite equation (36) without the $\hat{R}T$ factor and the last two terms:

$$F = \sum_k [X_k] \left(\ln [X_k] - 1 \right) + \left([N_2] \ln K_{eq,1} + [O_2] \ln K_{eq,2} + [NO] \ln K_{eq,3} \right) \quad (63)$$

The last three terms above can be rewritten in terms of the equilibrium concentrations through:

$$\ln K_{eq,1} = 2 \ln [N]^* - \ln [N_2]^*, \quad \ln K_{eq,2} = 2 \ln [O]^* - \ln [O_2]^*, \quad \ln K_{eq,3} = \ln [N]^* + \ln [O]^* - \ln [NO]^*.$$

Therefore

$$[N_2] \ln K_{eq,1} + [O_2] \ln K_{eq,2} + [NO] \ln K_{eq,3} = - \sum_k [X_k] \ln [X_k]^* + C_{(N)} \ln [N]^* + C_{(O)} \ln [O]^*, \quad (64)$$

and equation (63) simplifies to:

$$F = \sum_k [X_k]^* \mathcal{X}_k \left(\ln \mathcal{X}_k - 1 \right) + C_{(N)} \ln [N]^* + C_{(O)} \ln [O]^*$$

where $\mathcal{X}_k := [X_k]/[X_k]^*$ denotes the ratio between the current composition and the equilibrium one. The remaining two terms can be discarded. We have the following theorem:

Theorem 6.1 (Relative Free Energy). *Under the assumptions of section 6.1, the function \mathcal{F} defined by:*

$$\mathcal{F} := \sum_{k=1}^{N_s} [X_k]^* \mathcal{X}_k (\ln \mathcal{X}_k - 1).$$

is monotone decreasing for the reacting system (13) evolving at fixed temperature. \mathcal{F} converges to its value at chemical equilibrium.

Proof. The monotonicity of \mathcal{F} can be proved in a way similar to Krambeck's proof (section 3.3). By definition, we have:

$$K_r^f(T) \prod_{k=1}^{N_s} ([X_k]^*)^{\alpha_{r,k}} = K_r^b(T) \prod_{k=1}^{N_s} ([X_k]^*)^{\beta_{r,k}}. \quad (65)$$

Therefore, we can rewrite the source term ω_r as:

$$\omega_r = -K_r^* \left[\exp \left(\sum_{k=1}^{N_s} \alpha_{r,k} \ln \mathcal{X}_k \right) - \exp \left(\sum_{k=1}^{N_s} \beta_{r,k} \ln \mathcal{X}_k \right) \right], \quad K_r^* := \left[K_r^f(T) \prod_{k=1}^{N_s} ([X_k]^*)^{\alpha_{r,k}} \right].$$

and we obtain the desired result:

$$\begin{aligned} \frac{d\mathcal{F}}{dt} &= \sum_{k=1}^{N_s} \ln \mathcal{X}_k \sum_{r=1}^{N_r} \nu_{r,k} \omega_r \\ &= \sum_{r=1}^{N_r} \left[\sum_{k=1}^{N_s} \alpha_{r,k} \ln \mathcal{X}_k - \sum_{k=1}^{N_s} \beta_{r,k} \ln \mathcal{X}_k \right] \omega_r \\ &= - \sum_{r=1}^{N_r} K_r^* \left[\sum_{k=1}^{N_s} \alpha_{r,k} \ln \mathcal{X}_k - \sum_{k=1}^{N_s} \beta_{r,k} \ln \mathcal{X}_k \right] \\ &\quad \times \left[\exp \left(\sum_{k=1}^{N_s} \alpha_{r,k} \ln \mathcal{X}_k \right) - \exp \left(\sum_{k=1}^{N_s} \beta_{r,k} \ln \mathcal{X}_k \right) \right] \leq 0. \end{aligned}$$

\mathcal{F} converges because, as a function of \mathcal{X}_k , it is bounded from below (\mathcal{F} writes as a positive combination of $x \ln x - x \geq -1$ functions). \mathcal{F} converges to the composition that cancels out the sum of negative terms above. This completes the proof.

The temperature-varying case is more subtle. Using an integral form of the Van't Hoff equation (38):

$$\ln \left(\frac{K_{eq,r}}{K_{eq,r}^*} \right) = \frac{1}{\hat{R}} \sum_{k=1}^{N_s} \nu_{r,k} \int_{T^*}^T \frac{\hat{e}_k}{\tau^2} d\tau, \quad (66)$$

where $K_{eq,r} := K_{eq,r}(T)$ and $K_{eq,r}^* := K_{eq,r}(T^*)$, we can rewrite and simplify equation (46) ($T^0 := T^*$) to

$$S = -\hat{R} \sum_{k=1}^{N_s} [X_k]^* \mathcal{X}_k \left[\left(\ln \mathcal{X}_k - \frac{1}{\hat{R}} \int_{T^*}^T \frac{\hat{e}_k(\tau)}{\tau^2} d\tau \right) - 1 \right] + \frac{E}{T}. \quad (67)$$

We can prove that S defined by equation (67) is monotone increasing for the kinetic system (13) whose temperature varies according to equation (37). Here again, we can adapt Krambeck's derivations. We have to work with equation (65) evaluated at T^* , that is:

$$K_r^f(T^*) \prod_{k=1}^{N_s} ([X_k]^*)^{\alpha_{r,k}} = K_r^b(T^*) \prod_{k=1}^{N_s} ([X_k]^*)^{\beta_{r,k}}. \quad (68)$$

We rewrite the source term ω_r in two steps. First, using equation (68), we have:

$$\begin{aligned} \omega_r &= -K_r^{**} \left[\mathcal{K}_r^f(T) \exp \left(\sum_{k=1}^{N_s} \alpha_{r,k} \ln \mathcal{X}_k \right) - \mathcal{K}_r^b(T) \exp \left(\sum_{k=1}^{N_s} \beta_{r,k} \ln \mathcal{X}_k \right) \right], \\ K_r^{**} &:= \left[K_r^f(T^*) \prod_{k=1}^{N_s} ([X_k]^*)^{\alpha_{r,k}} \right], \quad \mathcal{K}_r^f(T) := \frac{K_r^f(T)}{K_r^f(T^*)}, \quad \mathcal{K}_r^b(T) := \frac{K_r^b(T)}{K_r^b(T^*)}. \end{aligned}$$

Second, the nonequilibrium rate ratios \mathcal{K}_r^f and \mathcal{K}_r^b are related through the Van't Hoff equation (38). We have:

$$\frac{\mathcal{K}_r^f(T)}{\mathcal{K}_r^b(T)} = \frac{K_{eq,r}(T)}{K_{eq,r}(T^*)} = \exp\left(\frac{1}{\hat{R}} \sum_{k=1}^{N_s} \nu_{r,k} \int_{T^*}^T \frac{\hat{e}_k(\tau)}{\tau^2} d\tau\right).$$

We then introduce another auxiliary rate constant \mathcal{K}_r^S :

$$\mathcal{K}_r^S := \mathcal{K}_r^f \exp\left(\frac{1}{\hat{R}} \sum_{k=1}^{N_s} \alpha_{r,k} \int_{T^*}^T \frac{\hat{e}_k(\tau)}{\tau^2} d\tau\right) = \mathcal{K}_r^b \exp\left(\frac{1}{\hat{R}} \sum_{k=1}^{N_s} \beta_{r,k} \int_{T^*}^T \frac{\hat{e}_k(\tau)}{\tau^2} d\tau\right),$$

which leads to:

$$\omega_r = -K_r^{**} \mathcal{K}_r^S \left[\exp\left(\sum_{k=1}^{N_s} \alpha_{r,k} \left(\ln \mathcal{X}_k - \frac{1}{\hat{R}} \int_{T^*}^T \frac{\hat{e}_k(\tau)}{\tau^2} d\tau\right)\right) - \exp\left(\sum_{k=1}^{N_s} \beta_{r,k} \left(\ln \mathcal{X}_k - \frac{1}{\hat{R}} \int_{T^*}^T \frac{\hat{e}_k(\tau)}{\tau^2} d\tau\right)\right) \right]. \quad (69)$$

That S is monotone decreasing follows from equation (69) and

$$\frac{\partial S}{\partial [X_k]} = \hat{R} \ln \mathcal{X}_k - \int_{T^*}^T \frac{\hat{e}_k(\tau)}{\tau^2} d\tau - \frac{\hat{e}_k}{T}, \quad \frac{\partial S}{\partial T} = -\frac{1}{T} \sum_{k=1}^{N_s} \hat{c}_{v,k} [X_k].$$

To conclude regarding convergence, we need to show that S is bounded from above. This is accomplished by noting that conservation of energy implies:

$$\sum_{k=1}^{N_s} [X_k] \int_{T^*}^T \frac{\hat{e}_k(\tau)}{\tau^2} d\tau = E \int_{T^*}^T \frac{d\tau}{\tau^2} = \frac{E}{T^*} - \frac{E}{T}. \quad (70)$$

Using equation (70), we can rewrite S as:

$$S = -\hat{R} \sum_{k=1}^{N_s} [X_k]^* \mathcal{X}_k (\ln \mathcal{X}_k - 1) + \frac{E}{T^*}.$$

The last term above is a constant of the system, therefore S is bounded from above. This proves the following theorem:

Theorem 6.2 (Relative Entropy). *Under the assumptions of section 6.1, the function S defined by:*

$$S = -\sum_{k=1}^{N_s} [X_k]^* \mathcal{X}_k \left[\left(\ln \mathcal{X}_k - \frac{1}{\hat{R}} \int_{T^*}^T \frac{\hat{e}_k(\tau)}{\tau^2} d\tau \right) - 1 \right] + \frac{E}{\hat{R}T}.$$

is monotone increasing for the reacting system (13) whose temperature varies according to conservation of energy (37). S converges to its value at chemical equilibrium $([X_k]^)_{1 \leq k \leq N_s}$. S also writes:*

$$S := -\sum_{k=1}^{N_s} [X_k]^* \mathcal{X}_k (\ln \mathcal{X}_k - 1) + \frac{E}{\hat{R}T^*}. \quad (71)$$

6.3 Algebraic Constructions

We now detail the construction of the implicit free energy and implicit entropy of chemically reacting systems from their equilibrium data. The idea is to break down the sums in theorems 6.1 and 6.2 as:

$$\sum_{k=1}^{N_s} [X_k]^* \mathcal{X}_k (\ln \mathcal{X}_k - 1) = \sum_{k=1}^{N_s} [X_k] (\ln [X_k] - 1) - \sum_{k=1}^{N_s} [X_k] \ln [X_k]^*.$$

and demonstrate that the second sum on the right hand side is a function of known quantities. For the fixed-temperature configuration, we have:

Lemma 6.3. *Under the assumptions of section 6.1, the chemical equilibrium composition $([X_k]^*)_{1 \leq k \leq N_s}$ of the reacting system (13) evolving at a fixed temperature satisfies:*

$$-\sum_{k=1}^{N_s} [X_k] \ln [X_k]^* = -\sum_{k=1}^{N_L} \left(\sum_{l=1}^{N_L} d_{k,l} C_{(l)} \right) \ln [X_k]^* - \sum_{k=N_L+1}^{N_s} [X_k] \left(\sum_{r=1}^{N_{IR}} a_{k-N_L,r} \ln K_{eq,r} \right), \quad (72)$$

with constant coefficients $(a_{q,r})_{1 \leq q,r \leq N_{IR}}$ and $(d_{k,l})_{1 \leq k,l \leq N_L}$ determined by the stoichiometric coefficients $(\nu_{r,k})_{1 \leq r \leq N_{IR}, 1 \leq k \leq N_s}$ and element conservation coefficients $(c_{l,k})_{1 \leq l \leq N_L, 1 \leq k \leq N_s}$.

Proof. Using the indexing introduced in section 6.1, we rewrite equation (60) as:

$$\sum_{k=N_L+1}^{N_s} \nu_{r,k} \ln [X_k]^* = \ln K_{eq,r} - \sum_{l=1}^{N_L} \nu_{r,l} \ln [X_l]^* \quad (73)$$

and equation (61) as:

$$\sum_{k=1}^{N_L} c_{l,k} [X_k] + \sum_{k=N_L+1}^{N_s} c_{l,k} [X_k] = C_{(l)}. \quad (74)$$

We introduce the following vectors:

$$\begin{aligned} \mathbf{X}_L &:= \left([X_l] \right)_{1 \leq l \leq N_L} \in \mathbb{R}^{N_L \times 1}, \quad \mathbf{X}_R = \left([X_k] \right)_{N_L+1 \leq k \leq N_s} \in \mathbb{R}^{N_{IR} \times 1}, \\ \mathbf{G}_L &:= \left(\ln [X_l]^* \right)_{1 \leq l \leq N_L} \in \mathbb{R}^{N_L \times 1}, \quad \mathbf{G}_R = \left(\ln [X_k]^* \right)_{N_L+1 \leq k \leq N_s} \in \mathbb{R}^{N_{IR} \times 1}, \\ \mathbf{K} &:= \left(\ln K_{eq,r} \right)_{1 \leq r \leq N_{IR}} \in \mathbb{R}^{N_{IR} \times 1}, \quad \mathbf{C}_0 = (C_{(l)})_{1 \leq l \leq N_L} \in \mathbb{R}^{N_L \times 1}, \end{aligned}$$

and the following matrices:

$$\begin{aligned} \mathbf{V}_L &:= (\nu_{r,k})_{1 \leq r \leq N_{IR}, 1 \leq k \leq N_L} \in \mathbb{R}^{N_{IR} \times N_L}, \quad \mathbf{V}_R := (\nu_{r,N_L+k})_{1 \leq (r,k) \leq N_{IR}} \in \mathbb{R}^{N_{IR} \times N_{IR}}, \\ \mathbf{C}_L &:= (c_{l,k})_{1 \leq l \leq N_L, 1 \leq k \leq N_L} \in \mathbb{R}^{N_L \times N_L}, \quad \mathbf{C}_R := (c_{l,k})_{1 \leq l \leq N_L, N_L+1 \leq k \leq N_s} \in \mathbb{R}^{N_L \times N_{IR}}. \end{aligned}$$

With these we rewrite equation (73) as:

$$\mathbf{V}_R \mathbf{G}_R = \mathbf{K} - \mathbf{V}_L \mathbf{G}_L, \quad (75)$$

and equation (74) as:

$$\mathbf{C}_L \mathbf{X}_L + \mathbf{C}_R \mathbf{X}_R = \mathbf{C}_0. \quad (76)$$

A key relation is the consistency of every reaction with element conservation:

$$\sum_{k=1}^{N_s} \nu_{r,k} c_{l,k} = 0, \quad 1 \leq r \leq N_{IR}, \quad 1 \leq l \leq N_L \iff \mathbf{V}_L \mathbf{C}_L^T + \mathbf{V}_R \mathbf{C}_R^T = 0. \quad (77)$$

In the above, \mathbf{V}_R and \mathbf{C}_L are invertible matrices. Multiplying equation (77) on the right by $\mathbf{C}_L^{-T} := (\mathbf{C}_L^T)^{-1}$ and on the left by \mathbf{V}_R^{-1} , we obtain the remarkable relation:

$$-\mathbf{V}_R^{-1} \mathbf{V}_L = \mathbf{C}_R^T \mathbf{C}_L^{-T} \quad (78)$$

Through equations (75), (78) and (76), we show:

$$\begin{aligned}
-\sum_{k=1}^{N_s} [X_k] \ln [X_k]^* &= -\mathbf{X}_L^T \mathbf{G}_L - \mathbf{X}_R^T \mathbf{G}_R \\
&= -\mathbf{X}_L^T \mathbf{G}_L - \mathbf{X}_R^T (\mathbf{V}_R^{-1} \mathbf{K} - \mathbf{V}_R^{-1} \mathbf{V}_L \mathbf{G}_L) \\
&= -(\mathbf{X}_L^T - \mathbf{X}_R^T \mathbf{V}_R^{-1} \mathbf{V}_L) \mathbf{G}_L - \mathbf{X}_R^T \mathbf{V}_R^{-1} \mathbf{K} \\
&= -(\mathbf{X}_L^T + \mathbf{X}_R^T \mathbf{C}_R^T \mathbf{C}_L^{-T}) \mathbf{G}_L - \mathbf{X}_R^T \mathbf{V}_R^{-1} \mathbf{K} \\
&= -(\mathbf{X}_L^T \mathbf{C}_L^T + \mathbf{X}_R^T \mathbf{C}_R^T) \mathbf{C}_L^{-T} \mathbf{G}_L - \mathbf{X}_R^T \mathbf{V}_R^{-1} \mathbf{K} \\
&= -(\mathbf{C}_L^{-1} \mathbf{C}_0)^T \mathbf{G}_L - (\mathbf{V}_R^{-1} \mathbf{K})^T \mathbf{X}_R.
\end{aligned}$$

This completes the proof. The $d_{k,l}$ are the coefficients of \mathbf{C}_L^{-1} , and the $a_{q,r}$ are the coefficients of \mathbf{V}_R^{-1} . As a direct consequence of theorem 6.1 and lemma 6.3, we have:

Theorem 6.4 (Implicit Free Energy). *Under the assumptions of section 6.1, there exists constant coefficients $(a_{q,r})_{1 \leq q, r \leq N_{IR}}$ such that the following functional*

$$\frac{F}{\hat{R}T} = \sum_{k=1}^{N_s} [X_k] (\ln [X_k] - 1) - \sum_{k=N_L+1}^{N_s} [X_k] \sum_{r=1}^{N_{IR}} a_{k-N_L, r} \ln K_{eq, r},$$

is monotone decreasing for the reacting system (13) at fixed-temperature. The chemical equilibrium composition $([X_k]^*)_{1 \leq k \leq N_s}$ minimizes F under element conservation constraints. F is called an implicit free energy of the system.

For the isolated reacting system, we have

Lemma 6.5. *Under the assumptions of section 6.1, the chemical equilibrium composition $([X_k]^*)_{1 \leq k \leq N_s}$ of the reacting system (13) whose temperature evolves according to conservation of energy (37) (denote T^* its equilibrium value) satisfies the relation:*

$$\begin{aligned}
\sum_{k=1}^{N_s} [X_k] \ln [X_k]^* &= \sum_{k=N_L+1}^{N_s} [X_k] \left(\sum_{r=1}^{N_{IR}} a_{k-N_L, r} \ln K_{eq, r} \right) + \frac{E}{\hat{R}} \left(\frac{1}{T} - \frac{1}{T^*} \right) \\
&\quad + \sum_{k=1}^{N_L} \left(\sum_{l=1}^{N_L} d_{k,l} C_{(l)} \right) \left(\ln [X_k]^* + \frac{1}{\hat{R}} \int_{T^*}^T \frac{\hat{c}_k}{\tau^2} d\tau \right) \quad (79)
\end{aligned}$$

with the same constant coefficients $(a_{q,r})_{1 \leq q, r \leq N_{IR}}$ and $(d_{k,l})_{1 \leq k, l \leq N_L}$ as in lemma 6.3.

Proof. Adapting lemma 6.3, we can write:

$$\sum_{k=1}^{N_s} [X_k] \ln [X_k]^* = \sum_{k=1}^{N_L} \left(\sum_{l=1}^{N_L} d_{k,l} C_{(l)} \right) \ln [X_k]^* + \sum_{k=N_L+1}^{N_s} [X_k] \left(\sum_{r=1}^{N_{IR}} a_{k-N_L, r} \ln K_{eq, r}^* \right) \quad (80)$$

The last term on the right-hand side can be decomposed as follows

$$\begin{aligned}
\sum_{k=N_L+1}^{N_s} [X_k] \left(\sum_{r=1}^{N_{IR}} a_{k-N_L, r} \ln K_{eq, r}^* \right) &= \sum_{k=N_L+1}^{N_s} [X_k] \left(\sum_{r=1}^{N_{IR}} a_{k-N_L, r} \ln K_{eq, r} \right) \\
&\quad - \sum_{k=N_L+1}^{N_s} [X_k] \left(\sum_{r=1}^{N_{IR}} a_{k-N_L, r} \ln \left(\frac{K_{eq, r}}{K_{eq, r}^*} \right) \right) \quad (81)
\end{aligned}$$

We introduce the following vectors:

$$\mathbf{H} := \left(\ln \left(\frac{K_{eq,r}}{K_{eq,r}^*} \right) \right)_{1 \leq l \leq N_{IR}} \in \mathbb{R}^{N_{IR} \times 1},$$

$$\mathbf{Q}_L := \left(\int_{T^*}^T \frac{\hat{e}_l(\tau)}{\tau^2} d\tau \right)_{1 \leq l \leq N_L} \in \mathbb{R}^{N_L \times 1}, \quad \mathbf{Q}_R := \left(\int_{T^*}^T \frac{\hat{e}_k(\tau)}{\tau^2} d\tau \right)_{N_L+1 \leq k \leq N_s} \in \mathbb{R}^{N_{IR} \times 1}$$

The Van't Hoff equation (38) writes:

$$\mathbf{H} = \mathbf{V}_L \mathbf{Q}_L + \mathbf{V}_R \mathbf{Q}_R \quad (82)$$

Conservation of energy (62) implies the matrix equation:

$$\mathbf{X}_L^T \mathbf{Q}_L + \mathbf{X}_R^T \mathbf{Q}_R = E \left(-\frac{1}{T} + \frac{1}{T^*} \right) \quad (83)$$

Through equations (76), (78), (82), and (83) we show:

$$\begin{aligned} - \sum_{k=N_L+1}^{N_s} [X_k] \left(\sum_{r=1}^{N_{IR}} a_{k-N_L,r} \ln \left(\frac{K_{eq,r}}{K_{eq,r}^*} \right) \right) &= -\frac{1}{\hat{R}} \mathbf{X}_R^T \mathbf{V}_R^{-1} \mathbf{H} \\ &= -\frac{1}{\hat{R}} \mathbf{X}_R^T \mathbf{V}_R^{-1} (\mathbf{V}_L \mathbf{Q}_L + \mathbf{V}_R \mathbf{Q}_R) \\ &= -\frac{1}{\hat{R}} (\mathbf{X}_R^T \mathbf{V}_R^{-1} \mathbf{V}_L \mathbf{Q}_L + \mathbf{X}_R^T \mathbf{Q}_R) \\ &= -\frac{1}{\hat{R}} \left(\mathbf{X}_R^T \mathbf{V}_R^{-1} \mathbf{V}_L \mathbf{Q}_L - E \left(\frac{1}{T} - \frac{1}{T^*} \right) - \mathbf{X}_L^T \mathbf{Q}_L \right) \\ &= \frac{1}{\hat{R}} \left(E \left(\frac{1}{T} - \frac{1}{T^*} \right) + \mathbf{X}_L^T \mathbf{Q}_L + \mathbf{X}_R^T \mathbf{C}_R^T \mathbf{C}_L^{-T} \mathbf{Q}_L \right) \\ &= \frac{1}{\hat{R}} \left(E \left(\frac{1}{T} - \frac{1}{T^*} \right) + \mathbf{C}_0 \mathbf{C}_L^{-T} \mathbf{Q}_L \right) \end{aligned}$$

Combining equations (80), (81) and the above completes the proof. As a direct consequence of theorem 6.2 and lemma 6.5, we have:

Theorem 6.6 (Implicit Entropy). *Under the assumptions of section 6.1, there exists constant coefficients $(a_{q,r})_{1 \leq q,r \leq N_{IR}}$ and $(d_{k,l})_{1 \leq k,l \leq N_L}$ such that the following functional:*

$$\begin{aligned} \frac{S}{\hat{R}} &= - \sum_{k=1}^{N_s} [X_k] (\ln [X_k] - 1) + \sum_{k=N_L+1}^{N_s} [X_k] \sum_{r=1}^{N_{IR}} a_{k-N_L,r} \ln K_{eq,r} + \frac{E}{\hat{R}T} \\ &\quad + \frac{1}{\hat{R}} \sum_{k=1}^{N_L} \left(\sum_{l=1}^{N_L} d_{k,l} C_{(l)} \right) \int_{T_0}^T \frac{\hat{e}_k}{\tau^2} d\tau, \quad (84) \end{aligned}$$

is monotone increasing for the reacting system (13) whose temperature evolves according to conservation of energy (37). The equilibrium composition $([X_k]^*)_{1 \leq k \leq N_s}$ and temperature T^* maximize S under element and energy conservation constraints. S is called an implicit entropy of the system.

6.3.1 Example applications

For the 5-species model of section 4.1, the implicit free energy and entropy of sections 4.2 and 4.3 are recovered through:

$$(X_1, X_2, X_3, X_4, X_5) := (N, O, N_2, O_2, NO)$$

$$\implies \mathbf{V}_R = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} = \mathbf{V}_R^{-1}, \quad \mathbf{C}_L = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} = \mathbf{C}_L^{-1}.$$

For kinetic models that include ionization reactions, the same formalism can be used by assimilating the charge conservation equation as an element conservation equation. For an 11-species air model [27] (N_2 , N , O_2 , O , NO , N_2^+ , N^+ , O_2^+ , O^+ , NO^+ , e^-) where e^- represents free electrons, chemical equilibrium is characterized by three conservation equations:

$$2[N_2]^* + 2[N_2^+]^* + [N]^* + [N^+]^* + [NO]^* + [NO^+]^* = C_{(N)}, \quad (85)$$

$$2[O_2]^* + 2[O_2^+]^* + [O]^* + [O^+]^* + [NO]^* + [NO^+]^* = C_{(O)}, \quad (86)$$

$$[N_2^+]^* + [O_2^+]^* + [N^+]^* + [O^+]^* + [NO^+]^* - [e^-]^* = C_{(e)}, \quad (87)$$

and eight independent chemical equilibrium relations. We can define:

$$\begin{aligned} \ln K_{eq,1} &:= 2 \ln [N]^* - \ln [N_2]^*, \quad \ln K_{eq,2} := 2 \ln [O]^* - \ln [O_2]^*, \\ \ln K_{eq,3} &:= \ln [N]^* + \ln [O]^* - \ln [NO]^*, \quad \ln K_{eq,4} := \ln [N_2^+]^* + \ln [e^-]^* - \ln [N_2]^*, \\ \ln K_{eq,5} &:= \ln [O_2^+]^* + \ln [e^-]^* - \ln [O_2]^*, \quad \ln K_{eq,6} := \ln [NO^+]^* + \ln [e^-]^* - \ln [NO]^*, \\ \ln K_{eq,7} &:= \ln [N^+]^* + \ln [e^-]^* - \ln [N]^*, \quad \ln K_{eq,8} := \ln [O^+]^* + \ln [e^-]^* - \ln [O]^*. \end{aligned}$$

With the following indexing:

$$(X_1, X_2, X_3) := (N, O, e^-)$$

$$(X_4, X_5, X_6, X_7, X_8, X_9, X_{10}, X_{11}) := (N_2, O_2, NO, N_2^+, O_2^+, NO^+, N^+, O^+)$$

the matrices $\mathbf{V}_R \in \mathbb{R}^{8 \times 8}$ and $\mathbf{C}_L \in \mathbb{R}^{3 \times 3}$ write:

$$\mathbf{V}_R = \begin{bmatrix} -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 \\ -1 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} = \mathbf{V}_R^{-1}, \quad \mathbf{C}_L = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} = \mathbf{C}_L^{-1}. \quad (88)$$

An implicit free energy F^{11} is given by:

$$\begin{aligned} \frac{F^{11}}{\hat{R}T} &= \sum_{k=1}^{11} [X_k] (\ln [X_k] - 1) + \left([N_2] \ln (K_{eq,1}) + [O_2] \ln (K_{eq,2}) + [NO] \ln (K_{eq,3}) \right. \\ &+ [N_2^+] \ln \left(\frac{K_{eq,1}}{K_{eq,4}} \right) + [O_2^+] \ln \left(\frac{K_{eq,2}}{K_{eq,5}} \right) + [NO^+] \ln \left(\frac{K_{eq,3}}{K_{eq,6}} \right) - [N^+] \ln (K_{eq,7}) - [O^+] \ln (K_{eq,8}) \left. \right) \\ &\quad - \int_{T^0}^T \frac{1}{\tau^2} (C_{(N)} \hat{e}_N + C_{(O)} \hat{e}_O - C_{(e)} \hat{e}_{e^-}) d\tau, \quad (89) \end{aligned}$$

and an implicit entropy S^{11} given by:

$$\frac{S^{11}}{\hat{R}} = \frac{1}{\hat{R}T} (E - F^{11}).$$

A model for Mars' atmosphere [28] complements that of air with (Ar , Ar^+ , C , C_2 , CN , CO , CO_2 , CNO , C^+ , C_2^+ , CN^+ , CO^+) for a total of 23 species. Chemical equilibrium is defined by five conservation equations:

$$\begin{aligned} 2[N_2]^* + 2[N_2^+]^* + [N]^* + [N^+]^* + [NO]^* + [NO^+]^* + [CN]^* + [CNO]^* + [CN^+]^* &= C_{(N)}, \\ 2[O_2]^* + 2[O_2^+]^* + [O]^* + [O^+]^* + [NO]^* + [NO^+]^* + [CNO]^* + [CO]^* + 2[CO_2]^* + [CO^+]^* &= C_{(O)}, \\ [C]^* + 2[C_2]^* + [CN]^* + [CO]^* + [CO_2]^* + [CNO]^* + [C^+]^* + 2[C_2^+]^* + [CN^+]^* + [CO^+]^* &= C_{(C)}, \\ [Ar]^* + [Ar^+]^* &= C_{(Ar)}, \\ [N_2^+]^* + [O_2^+]^* + [N^+]^* + [O^+]^* + [NO^+]^* + [Ar^+]^* + [C^+]^* + [C_2^+]^* + [CN^+]^* + [CO^+]^* - [e^-]^* &= C_{(e)}, \end{aligned}$$

and eighteen chemical equilibrium relations:

$$\begin{aligned}
\ln K_{eq,9} &:= 2 \ln [C]^* - \ln [C_2]^*, \quad \ln K_{eq,10} := \ln [C]^* + \ln [N]^* - \ln [CN]^*, \\
\ln K_{eq,11} &:= \ln [C]^* + \ln [O]^* - \ln [CO]^*, \\
\ln K_{eq,12} &:= \ln [C_2^+]^* + \ln [e^-]^* - 2 \ln [C]^*, \quad \ln K_{eq,13} := \ln [CN^+]^* + \ln [e^-]^* - \ln [C]^* - \ln [N]^*, \\
\ln K_{eq,14} &:= \ln [CO^+]^* + \ln [e^-]^* - \ln [C]^* - \ln [O]^*, \quad \ln K_{eq,15} := \ln [CO]^* + \ln [O]^* - \ln [CO_2]^*, \\
\ln K_{eq,16} &:= \ln [N_2]^* + \ln [CO]^* - \ln [CNO]^* - \ln [N]^*, \\
\ln K_{eq,17} &:= \ln [C^+]^* + \ln [e^-]^* - \ln [C]^*, \quad \ln K_{eq,18} := \ln [Ar^+]^* + \ln [e^-]^* - \ln [Ar]^*.
\end{aligned}$$

With the following indexing:

$$\begin{aligned}
(X_1, X_2, X_3, X_4, X_5) &:= (N, O, C, Ar, e^-) \\
(X_6, X_7, X_8, X_9, X_{10}, X_{11}, X_{12}, X_{13}) &:= (N_2, O_2, NO, N_2^+, O_2^+, NO^+, N^+, O^+) \\
(X_{14}, X_{15}, X_{16}, X_{17}, X_{18}, X_{19}, X_{20}) &:= (C_2, CN, CO, C_2^+, CN^+, CO^+, CO_2) \\
(X_{21}, X_{22}, X_{23}) &:= (CNO, C^+, Ar^+)
\end{aligned}$$

Here $\mathbf{V}_R \in \mathbb{R}^{18 \times 18}$, $\mathbf{C}_L \in \mathbb{R}^{5 \times 5}$. An implicit free energy F^{23} is given by:

$$\begin{aligned}
\frac{F^{23}}{\hat{R}T} &= \sum_{k=1}^{23} [X_k] (\ln [X_k] - 1) + \left([N_2] \ln (K_{eq,1}) + [O_2] \ln (K_{eq,2}) + [NO] \ln (K_{eq,3}) \right. \\
&+ [N_2^+] \ln \left(\frac{K_{eq,1}}{K_{eq,5}} \right) + [O_2^+] \ln \left(\frac{K_{eq,2}}{K_{eq,5}} \right) + [NO^+] \ln \left(\frac{K_{eq,3}}{K_{eq,6}} \right) - [N^+] \ln (K_{eq,7}) - [O^+] \ln (K_{eq,8}) \\
&+ [C_2] \ln (K_{eq,9}) + [CN] \ln (K_{eq,10}) + [CO] \ln (K_{eq,11}) - [C_2^+] \ln (K_{eq,12}) - [CN^+] \ln (K_{eq,13}) \\
&\quad - [CO^+] \ln (K_{eq,14}) + [CO_2] \ln (K_{eq,15} K_{eq,11}) + \\
&\quad \left. [CNO] \ln (K_{eq,16} K_{eq,11} K_{eq,1}) - [C^+] \ln (K_{eq,17}) - [Ar^+] \ln (K_{eq,18}) \right) \\
&\quad - \int_{T^0}^T \frac{1}{\tau^2} (C_{(N)} \hat{e}_N + C_{(O)} \hat{e}_O + C_{(C)} \hat{e}_C + C_{(Ar)} \hat{e}_{Ar} - C_{(e)} \hat{e}_{e^-}) d\tau, \quad (90)
\end{aligned}$$

and an implicit entropy S^{23} by:

$$\frac{S^{23}}{\hat{R}} = \frac{1}{\hat{R}T} (E - F^{23}).$$

6.4 Final Characterization

Theorem 6.6 provides the general form of the reduced chemical potential functions introduced in section 4. We can rewrite equation (84) as:

$$S = \sum_{k=1}^{N_s} [X_k] \hat{s}_k, \quad \hat{s}_k = \frac{1}{T} (\hat{e}_k - \hat{\mu}_k) + \hat{R}, \quad \hat{\mu}_k = \hat{\mu}_k^0 + \hat{R}T \ln [X_k],$$

with:

$$\hat{\mu}_k^0 := -T \int_{T^0}^T \frac{\hat{e}_k}{\tau^2} d\tau, \quad 1 \leq k \leq N_L \quad (91)$$

$$\hat{\mu}_k^0 := -T \sum_{l'=1}^{N_L} \left(\sum_{l=1}^{N_L} d_{l',l} c_{l,k} \right) \int_{T^0}^T \frac{\hat{e}_{l'}}{\tau^2} d\tau - \hat{R}T \sum_{r=1}^{N_{IR}} a_{k-N_L,r} \ln K_{eq,r}, \quad N_L + 1 \leq k \leq N_s. \quad (92)$$

To reach this expression, the molar element concentrations $(C_{(l)})_{1 \leq l \leq N_L}$ have been substituted with their expression in terms of the species concentrations (equation (61)). This is a necessary step towards the mathematical modeling of compressible reacting flows discussed in the next section. The following lemma will prove useful:

Lemma 6.7. *The reduced chemical potential functions $(\hat{\mu}_k^0)_{1 \leq k \leq N_s}$ defined by equations (91) and (92) satisfy the following relations:*

$$\sum_{k=1}^{N_s} [X_k] \left(\frac{d\hat{\mu}_k^0}{dT} - \frac{\hat{\mu}_k^0}{T} \right) = - \frac{1}{T} \sum_{k=1}^{N_s} [X_k] \hat{e}_k, \quad (93)$$

$$\frac{d}{dT} \left(\frac{\hat{\mu}_k^0}{T} \right) = - \frac{\hat{e}_k}{T^2}. \quad (94)$$

Proof. Equation (93) is equivalent to:

$$\sum_{k=N_L+1}^{N_s} [X_k] \sum_{r=1}^{N_{IR}} a_{k-N_L,r} \hat{R}T^2 \frac{d \ln K_{eq,r}}{dT} + \sum_{l=1}^{N_L} \left(\sum_{\nu=1}^{N_L} d_{l,\nu} C(\nu) \right) \hat{e}_l = \sum_{k=1}^{N_s} [X_k] \hat{e}_k. \quad (95)$$

We introduce the following vectors:

$$\mathbf{E}_L := (\hat{e}_l)_{1 \leq l \leq N_L} \in \mathbb{R}^{N_L \times 1}, \quad \mathbf{E}_R := (\hat{e}_k)_{N_L+1 \leq k \leq N_s} \in \mathbb{R}^{N_{IR} \times 1}.$$

By definition, we have:

$$\mathbf{X}_L^T \mathbf{E}_L + \mathbf{X}_R^T \mathbf{E}_R = \sum_{k=1}^{N_s} [X_k] \hat{e}_k.$$

The left hand side term in (95) writes:

$$\sum_{k=N_L+1}^{N_s} [X_k] \sum_{r=1}^{N_{IR}} a_{k-N_L,r} \hat{R}T^2 \frac{d \ln K_{eq,r}}{dT} + \sum_{l=1}^{N_L} \left(\sum_{\nu=1}^{N_L} d_{l,\nu} C(\nu) \right) \hat{e}_l = \mathbf{X}_R^T \mathbf{V}_R^{-1} \left(\hat{R}T^2 \frac{d\mathbf{K}}{dT} \right) + (\mathbf{C}_L^{-1} \mathbf{C}_0)^T \mathbf{E}_L$$

The Van't Hoff equation (38) also writes:

$$\hat{R}T^2 \frac{d\mathbf{K}}{dT} = \mathbf{V}_R \mathbf{E}_R + \mathbf{V}_L \mathbf{E}_L. \quad (96)$$

Using equations (76), (78) and (96), we reach the desired result:

$$\begin{aligned} \mathbf{X}_R^T \mathbf{V}_R^{-1} \left(\hat{R}T^2 \frac{d\mathbf{K}}{dT} \right) + (\mathbf{C}_L^{-1} \mathbf{C}_0)^T \mathbf{E}_L &= \mathbf{X}_R^T (\mathbf{E}_R + \mathbf{V}_R^{-1} \mathbf{V}_L \mathbf{E}_L) + (\mathbf{X}_L + \mathbf{C}_L^{-1} \mathbf{C}_R \mathbf{X}_R)^T \mathbf{E}_L \\ &= \mathbf{X}_L^T \mathbf{E}_L + \mathbf{X}_R^T \mathbf{E}_R + \mathbf{X}_R^T (\mathbf{V}_R^{-1} \mathbf{V}_L + \mathbf{C}_R^T \mathbf{C}_L^{-T}) \mathbf{E}_L \\ &= \mathbf{X}_L^T \mathbf{E}_L + \mathbf{X}_R^T \mathbf{E}_R. \end{aligned}$$

To prove relation (94), we introduce the following vectors:

$$\mathbf{M}_L := \left(\frac{\hat{\mu}_l}{T} \right)_{1 \leq l \leq N_L} \in \mathbb{R}^{N_L \times 1}, \quad \mathbf{M}_R := \left(\frac{\hat{\mu}_k}{T} \right)_{N_L+1 \leq k \leq N_s} \in \mathbb{R}^{N_{IR} \times 1}.$$

We already have the desired result for the first N_L species, namely:

$$\frac{d\mathbf{M}_L}{dT} = - \frac{1}{T^2} \mathbf{E}_L.$$

For the remaining N_{IR} species, we have:

$$\begin{aligned} \frac{d\mathbf{M}_R}{dT} &= - \frac{1}{T^2} (\mathbf{C}_L^{-1} \mathbf{C}_R) \mathbf{E}_L - \hat{R} \mathbf{V}_R^{-1} \frac{d\mathbf{K}}{dT} \\ &= - \frac{1}{T^2} \left((\mathbf{C}_L^{-1} \mathbf{C}_R) \mathbf{E}_L + \mathbf{V}_R^{-1} \left(\hat{R}T^2 \frac{d\mathbf{K}}{dT} \right) \right) \\ &= - \frac{1}{T^2} \left((\mathbf{C}_L^{-1} \mathbf{C}_R + \mathbf{V}_R^{-1} \mathbf{V}_L) \mathbf{E}_L + \mathbf{E}_R \right) \\ &= - \frac{1}{T^2} \mathbf{E}_R. \end{aligned}$$

This completes the proof.

7 Compressible Flow

We are ultimately interested in the development of CFD algorithms for compressible reacting flows. In this final section, we establish that the thermodynamic entropy we constructed from equilibrium data is compatible with the mathematical structure that underlies numerical schemes for (non-reacting) compressible flows. The integration of multi-component and radiative transport phenomena will be treated in future work.

7.1 Mathematical Entropy

A number of systems of conservation laws, represented as

$$\frac{\partial \mathbf{u}}{\partial t} + \sum_{j=1}^d \frac{\partial \mathbf{f}_j}{\partial x_j} = 0, \quad (97)$$

where $\mathbf{u} \in \mathbb{R}^N$ is the vector of conserved variables and $(\mathbf{f}_j(\mathbf{u}))_{1 \leq j \leq d} \in \mathbb{R}^{N \times d}$ is the set of flux vectors in d spatial dimensions, are known to imply an additional conservation equation for a convex scalar function U of the conserved variables [17, 20, 16]:

$$\frac{\partial U}{\partial t} + \frac{\partial F_i}{\partial x_i} = 0, \quad F_i = F_i(\mathbf{u}) \in \mathbb{R}. \quad (98)$$

When these conditions are met, U is termed a *mathematical entropy* of the system (97). Mathematical entropies are paramount in the analysis of such systems, especially when it comes to their *well-posedness* (the existence of U implies the system is symmetric hyperbolic [20, 16]) and the selection of physically relevant *weak solutions* through *entropy inequalities* [18]:

$$\frac{\partial U}{\partial t} + \frac{\partial F_i}{\partial x_i} < 0. \quad (99)$$

Mathematical entropies are key in the development of robust numerical schemes. For flows involving strong discontinuities, schemes that satisfy a discrete version of (99) are preferred. Such schemes are termed *entropy stable*. This guideline guided the development of the popular upstream-based and Godunov-type schemes in the 80s [19]. A different approach to enforcing entropy-stability at the discrete level [12, 11] has gained significant attention over the last decade [35, 36, 34, 41, 45] in the context of under-resolved turbulent flow simulation (inequality (99) can imply *integral nonlinear stability* depending on the boundary conditions). It makes an extensive use of the so-called *entropy variables* $\mathbf{v} \in \mathbb{R}^N$ defined by:

$$\mathbf{v} := \left(\frac{\partial U}{\partial \mathbf{u}} \right)^T. \quad (100)$$

The present work is part of an effort to develop this framework towards reacting flows (mathematical and numerical developments for non-reacting multicomponent flows can be found in [38, 39]). A compressible reacting flow can be represented as system (97) complemented with a chemical source term $\mathbf{R}(\mathbf{u}) \in \mathbb{R}^N$:

$$\frac{\partial \mathbf{u}}{\partial t} + \sum_{j=1}^d \frac{\partial \mathbf{f}_j}{\partial x_j} = \mathbf{R}. \quad (101)$$

We emphasize the distinction between the concepts of mathematical entropy (proper to systems of conservation laws) and of thermodynamic entropy. For compressible flows, these two concepts are tightly linked [12, 1, 13, 38]. Our goal here is to find $U(\mathbf{u})$ convex such that system (101) implies:

$$\frac{\partial U}{\partial t} + \frac{\partial F_i}{\partial x_i} = \mathbf{v}^T \mathbf{R} \quad \text{with} \quad \mathbf{v}^T \mathbf{R} < 0. \quad (102)$$

7.2 Multicomponent Reacting Flow

In three dimensions ($d = 3$), the compressible reacting Euler system [1] is defined by:

$$\begin{aligned}\mathbf{u} &:= \left[(\rho_k)_{1 \leq k \leq N_s} \quad \rho u \quad \rho v \quad \rho w \quad \rho e^{tot} \right]^T, \\ \mathbf{f}_1 &:= \left[(\rho_k u)_{1 \leq k \leq N_s} \quad \rho u^2 + p \quad \rho uv \quad \rho uw \quad (\rho e^{tot} + p)u \right]^T, \\ \mathbf{f}_2 &:= \left[(\rho_k v)_{1 \leq k \leq N_s} \quad \rho uv \quad \rho v^2 + p \quad \rho vw \quad (\rho e^{tot} + p)v \right]^T, \\ \mathbf{f}_3 &:= \left[(\rho_k w)_{1 \leq k \leq N_s} \quad \rho uw \quad \rho vw \quad \rho w^2 + p \quad (\rho e^{tot} + p)w \right]^T, \\ \mathbf{R} &:= \left[(R_k)_{1 \leq k \leq N_s} \quad 0 \quad 0 \quad 0 \quad 0 \right]^T.\end{aligned}$$

The species partial densities are denoted by $(\rho_k)_{1 \leq k \leq N_s}$ and are related to molar concentrations through $\rho_k = m_k [X_k]$, where m_k is the molar mass of species k . $\rho := \sum_{k=1}^{N_s} \rho_k$ denotes the total density, and $Y_k := \rho_k / \rho$ denotes the mass fraction of species k . The mean flow velocities are represented by the vector $\vec{\mathbf{u}} := [u \ v \ w]$. The total energy per unit volume is defined by $\rho e^{tot} := \rho e + \frac{1}{2} \rho \|\vec{\mathbf{u}}\|^2$, where $\rho e := \sum_{k=1}^{N_s} \rho_k e_k$. The source terms are related by those of equation (13) through $R_k := m_k \Omega_k$.

If the equilibrium constants embedded in \mathbf{R} are evaluated through the law of mass action, an admissible mathematical entropy for this system is given by:

$$U := -\rho s, \quad \rho s := \sum_{k=1}^{N_s} \rho_k s_k, \quad s_k := \int_{T^0}^T \frac{c_{vk}}{\tau} d\tau - r_k \ln \left(\frac{\rho_k}{\rho_k^0} \right) + s_k^0, \quad r_k := \hat{R}/m_k. \quad (103)$$

In this section, the proof of this result [1] is reviewed. In order to prove that U satisfies a conservation equation, one begins by expressing the flow equations in total derivatives:

$$\begin{aligned}\frac{D\rho}{Dt} &= -\rho \nabla \cdot \vec{\mathbf{u}}, \quad \frac{DY_k}{Dt} = \frac{1}{\rho} R_k, \quad \frac{De}{Dt} = -\frac{p}{\rho} \nabla \cdot \vec{\mathbf{u}}, \\ \frac{D}{Dt} &:= \frac{\partial}{\partial t} + \vec{\mathbf{u}} \cdot \nabla.\end{aligned} \quad (104)$$

The Gibbs differential equation writes:

$$T ds = de - \frac{p}{\rho^2} d\rho - \sum_{k=1}^{N_s} \mu_k dY_k, \quad \mu_k := \frac{1}{T} (e_k - s_k) + r_k. \quad (105)$$

Equations (105) and (104) imply the transport equation:

$$\frac{Ds}{Dt} = -\frac{1}{\rho T} \sum_{k=1}^{N_s} m_k \mu_k \Omega_k, \quad (106)$$

which combined with conservation of total mass yields the conservation equation:

$$\frac{\partial(\rho s)}{\partial t} + \nabla \cdot (\rho \vec{\mathbf{u}} s) = -\frac{1}{T} \sum_{k=1}^{N_s} m_k \mu_k \Omega_k = -\frac{1}{T} \sum_{k=1}^{N_s} \hat{\mu}_k \Omega_k > 0. \quad (107)$$

Using the relation between the specific entropies and specific chemical potentials:

$$s_k = \frac{1}{T} (e_k - \mu_k) + r_k, \quad (108)$$

one can show that the Gibbs equation (105) is equivalent to

$$Td(\rho s) = d(\rho e) - \sum_{k=1}^{N_s} \mu_k d\rho_k \iff TdU = -d(\rho e) + \sum_{k=1}^{N_s} \mu_k d\rho_k \quad (109)$$

To obtain the differential relation with respect to \mathbf{u} , use:

$$d(\rho e) = d(\rho e^{tot}) + ud(\rho u) + vd(\rho v) + wd(\rho w) - \frac{1}{2} \sum_{k=1}^{N_s} \|\bar{\mathbf{u}}\|^2 d\rho_k.$$

This leads to the following expression for the entropy variables:

$$\mathbf{v} = \frac{1}{T} \left[(\mu_k - \frac{1}{2} \|\bar{\mathbf{u}}\|^2)_{1 \leq k \leq N_s} \quad \bar{\mathbf{u}} \quad -1 \right]. \quad (110)$$

The convexity of U is established through its Hessian matrix \mathbf{G}

$$\mathbf{G} := \frac{\partial^2 U}{\partial \mathbf{u}^2} = \frac{\partial \mathbf{v}}{\partial \mathbf{u}}.$$

which needs to be positive definite. This is shown by congruence [16, 1, 38] through the matrix H defined by:

$$\mathbf{H} := \left(\frac{\partial \mathbf{u}}{\partial \mathbf{z}} \right)^T \mathbf{G} \left(\frac{\partial \mathbf{u}}{\partial \mathbf{z}} \right), \quad \mathbf{z} := \left[(\rho_k)_{1 \leq k \leq N_s} \quad \bar{\mathbf{u}} \quad T \right].$$

With s_k defined by equation (103), this gives:

$$\mathbf{H} = \left(\frac{\partial \mathbf{u}}{\partial \mathbf{z}} \right)^T \frac{\partial \mathbf{v}}{\partial \mathbf{z}} = \text{diag} \left(\left[(\rho_k)_{1 \leq k \leq N_s} \quad \left(\frac{\rho}{T} \right)_{1 \leq j \leq d} \quad \rho c_v / T^2 \right] \right), \quad (111)$$

and convexity is obtained provided $\rho_k > 0$, $c_{vk} > 0$ and $T > 0$.

7.3 Implicit Mathematical Entropy

In the proof we just reviewed, the chemical potential are defined by the specific entropies (equation (105)). Conversely, the implicit thermodynamic entropy we introduced is derived from the chemical potentials $\mu_k := \mu_k^0 + r_k T \ln \rho_k$ with:

$$\mu_k^0 := -T \int_{T^0}^T \frac{e_k}{\tau^2} d\tau, \quad 1 \leq k \leq N_L \quad (112)$$

$$\mu_k^0 := -T \sum_{l'=1}^{N_L} \left(\sum_{l=1}^{N_L} d_{l',l} c_{l,k} \right) \int_{T^0}^T \frac{e_{l'}}{\tau^2} d\tau - r_k T \sum_{r=1}^{N_{IR}} a_{k-N_L,r} \ln K_{eq,r}(T), \quad N_L + 1 \leq k \leq N_s \quad (113)$$

We consider the same candidate mathematical entropy $U = -\rho s$ with the implicit definition of s_k instead. The flow equations (104) and the relation (108) between s_k and μ_k still hold. Therefore, the conservation (107) holds if the differential relation (109) holds. We have:

$$\begin{aligned} Td(\rho s) &= Td\left(\frac{1}{T} \sum_{k=1}^{N_s} \rho_k e_k\right) - Td\left(\frac{1}{T} \sum_{k=1}^{N_s} \rho_k \mu_k\right) + Td\left(\sum_{k=1}^{N_s} r_k \rho_k\right) \\ &= d(\rho e) - \sum_{k=1}^{N_s} \mu_k d\rho_k - \sum_{k=1}^{N_s} \rho_k d\mu_k + T \sum_{k=1}^{N_s} r_k d\rho_k + \frac{dT}{T} \sum_{k=1}^{N_s} \rho_k (e_k - \mu_k) \end{aligned}$$

The last three sum terms cancel out as we have:

$$\begin{aligned} \sum_{k=1}^{N_s} \rho_k d\mu_k - T \sum_{k=1}^{N_s} r_k d\rho_k - \frac{dT}{T} \sum_{k=1}^{N_s} \rho_k (e_k - \mu_k) &= \sum_{k=1}^{N_s} \rho_k d\mu_k^0 - \frac{dT}{T} \sum_{k=1}^{N_s} \rho_k (e_k - \mu_k + r_k T \ln \rho_k) \\ &= \sum_{k=1}^{N_s} \rho_k d\mu_k^0 - \frac{dT}{T} \sum_{k=1}^{N_s} \rho_k (e_k - \mu_k^0) \\ &= \left[\sum_{k=1}^{N_s} \rho_k \left(\frac{d\mu_k^0}{dT} - \frac{\mu_k^0}{T} \right) - \frac{1}{T} \sum_{k=1}^{N_s} \rho_k e_k \right] dT \\ &= 0 \quad (\text{Lemma 6.7}) \end{aligned}$$

This proves conservation. Similarly, the convexity of U is established through the congruence transform (111) which yields the exact same diagonal matrix (it can be shown that the off-diagonal terms of \mathbf{H} cancel out if and only if the reduced chemical potentials satisfy relation (94) in lemma 6.7). This proves the final result:

Theorem 7.1 (Implicit Mathematical Entropy). *The compressible reacting Euler system whose chemical nonequilibrium model $(\Omega_k)_{1 \leq k \leq N_s}$ satisfies the assumptions of section 6.1 admits the mathematical entropy*

$$U := - \sum_{k=1}^{N_s} \rho_k s_k, \quad s_k(\rho_k, T) := \frac{1}{T} (e_k(T) - \mu_k(\rho_k, T)) + r_k.$$

with $\mu_k(\rho_k, T) := \mu_k^0(T) + r_k T \ln \rho_k$ and $\mu_k^0(T)$ defined by equations (112)-(113). The corresponding entropy variables are given by equation (110).

8 Conclusions

In the present work, we demonstrated that chemical thermodynamics can be used as a nonlinear analysis tool in the temporal integration of reaction kinetics. For ODE systems that fix the temperature, the second law imposes a free Helmholtz energy that is monotone decreasing. If the temperature varies as to make the gas mixture isolated, the second law imposes that the thermodynamic entropy is monotone increasing. These prescription are nonlinear and can be probed and enforced at the discrete level, thanks to well-established results [14, 11]. Preliminary numerical experiments with a DG in time scheme based on a polynomial representation of the chemical potentials shows improved robustness and larger resolvable time steps compared to its standard version and some DIRK-type schemes designed for stiff systems. In addition, the respective contributions of the physical model and the discretization to free energy decay, a measure of convergence to equilibrium, can be computed and compared. These insights will play an important role in improving numerical methods for chemical kinetics and, more broadly, to relaxation dynamics.

A significant contribution of this work is the finding that the chemical equilibrium constants of the kinetics model do not need to be evaluated following Gibbs' formalism for these prescriptions to be applicable. We demonstrated how one can actually infer the implicit chemical thermodynamics embedded in a chemical equilibrium model built from data, provided reasonable conditions are met. We believe these derivations will spur progress in the development of advanced chemistry models for reacting flows. The prescriptions of this work can be leveraged by the reduced-order and data-driven modeling communities, as optimization constraints for example.

While the present work was mainly concerned with chemical relaxation, it has also laid theoretical ground for compressible fluid dynamics simulations. We proved that the implicit thermodynamic entropy we constructed can also be used as a mathematical entropy, a core concept for systems of conservation laws [16, 20, 17, 12, 1], shock-capturing [18] and entropy-stable discretizations [11, 39, 45]. Continuing on our recent work on entropy-stable schemes [38, 39], we will explore the long-time challenge of integrating compressible flow physics and chemical relaxation together [43, 44, 46]. We will seek to leverage the knowledge of discrete entropy dynamics [40] to develop more efficient time-integration and solution methods within a multi-physics space-time Finite-Element Solver under development at NASA Ames Research Center [42].

For flows in strong thermo-chemical non-equilibrium, thermal relaxation time scales become comparable to the chemical time scales, and the common assumption of one single temperature characterizing the internal energy distributions of the entire gas mixture is no longer valid (early work by Candler [47] shows errors in shock standoff distance predictions). Multi-Temperature models [7, 26] are currently standard for these applications, and a characteristic feature of their formulation is that for some reactions the forward and reverse rates are no longer related by an equilibrium constant at all times. In this configuration, Krambeck's proof does not apply anymore and classical thermodynamics shows its limits [5, 13]. We address these issues through a self-consistent statistical approach in a forthcoming paper.

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