Gibbs function continuation for linearly constrained multiphase equilibria

James B. Scoggins[1],[*], Thierry E. Magin[1]

Aeronautics and Aerospace Department, von Karman Institute for Fluid Dynamics, Rhode-Saint-Genese, Belgium

A R T I C L E   I N F O

A B S T R A C T

The stable computation of linearly constrained, multiphase, chemical equilibrium compositions is an important topic for a wide range of industrial and academic applications. Numerous computational methods have been developed to solve such problems which are, in general, susceptible to failure under certain conditions due to numerical stiffness. In this work, we present a Gibbs function continuation method for linearly constrained multiphase equilibrium calculations. The method converts the nonlinear Element Potential Equations - derived from the minimization of the mixture Gibbs free energy using the Lagrange multiplier technique - into an initial value problem which can be stably integrated through the use of a property of linear least squares solutions. The stability and convergence properties of the proposed method are derived and it is shown that the single phase method arises as a special case of the multiphase algorithm when only one phase is considered. Two test cases are presented to clarify and demonstrate the accuracy and robustness of the method.

© 2015 The Combustion Institute. Published by Elsevier Inc. All rights reserved.

1. Introduction

The efficient and robust computation of multiphase, constrained equilibrium compositions is an important topic over a wide range of fields including combustion, aerospace and (bio)chemical engineering, metallurgy, paper processes, and the design of thermal protection systems for atmospheric entry vehicles (e.g., [1–6]). For a detailed history and list of applications, the reader is referred to the treatises by van Zeggeren and Storey [7] or Smith and Missen [8].

Prior to the work of White et al. [9], the equilibrium constant formulation was primarily used to compute equilibrium compositions for ideal, gas phase mixtures. The equilibrium constant formulation works by assigning formation reactions to each species based on a set of base or component species which are chosen *a priori* for the given reaction system. Kuo [10] cites several disadvantages that hindered researches using this method including difficulties in extending the method to non ideal equations of state, testing for the presence of condensed species and numerical complications with the use of component species.

In 1958, White et al. [9] introduced the concept of free-energy minimization and proposed a numerical solution technique using the method of steepest decent. White [11] later elaborated on the advantages of free-energy minimization and the use of element potentials in the solution of equilibrium compositions, including the possibility to treat any general chemical system without the necessity of specifying the formation reactions. In addition, the use of element potentials allowed for the solution of linear systems whose size scaled with the number of elements rather than species, present in the mixture. This fact alone offers a significant computational advantage when considering large chemical systems.

Today, both the equilibrium constant formulation and the free-energy minimization methods are widely used. Most commercial and general purpose research codes implement various numerical methods for solving the free-energy minimization problem, however the equilibrium constant formulation is still used in certain applications [4,12]. Perhaps one of the most widely used equilibrium codes today is the Stanford-JANAF (STANJAN) code by Reynolds [13] who popularized the element potential method for constrained Gibbs free-energy minimization by developing a numerical solution procedure to the minimization problem which solves the so-called dual problem. Part of the success of the STANJAN method lies in its powerful initialization and preconditioning procedures which help make STANJAN extremely robust for most problems. The Chemical Equilibrium with Applications (CEA) code developed by Gordon and McBride [14,15] is also used heavily, helped by the success of the detailed thermodynamic database developed at NASA Glenn Research Center [16], which it employs.

In addition to the normal mass balance constraints, so called "generalized constraints" [17] on the equilibrium solution have been used in a wide range of applications [3] and in particular, are an integral component of the Rate-Controlled Constrained Equilibrium (RCCE)

---

* Corresponding author.
E-mail addresses: scoggins@vki.ac.be (J.B. Scoggins), magin@vki.ac.be (T.E. Magin).
[1] Also at Laboratoire EM2C, Ecole Centrale Paris, France.

[17–31] method. Some important examples of constraints used in the RCCE method include constraints on the total number of moles, the number of free valence electrons, and the number of O-O bonds, among many others [3,30]. Bishnu et al. [32,33] added the ability to include general linear constraints on the equilibrium solutions to both STANJAN and CEA. They found that, under certain conditions, both the constrained versions of STANJAN and CEA failed to converge to a solution. In general, these situations arise when the linear constraints force the equilibrium composition near the boundary of the feasible region imposed by the hyperplane defined by the constraints.

In an effort to provide a provably robust, constrained equilibrium solver, Pope [34,35] developed the Gibbs Function Continuation (GFC) method which solves the Element Potential Equations for an ideal gas mixture under general linear constraints. Since its development, the GFC method has been successfully embedded into a variety of more complex turbulent combustion modeling algorithms, including the eddy dissipation concept (EDC) [36,37], RCCE using a greedy algorithm with local improvement (RCCE-GALI) [29], and the Relaxation–Redistribution method (RRM) [38]. One drawback of the GFC method however, is that it is only capable of computing equilibrium compositions of gas phase mixtures.

The purpose of this paper is to generalize the GFC method to mixtures with multiple ideal phases and to provide a more rigorous mathematical analysis of its robustness and stability. The new method is referred to as the multiphase Gibbs function continuation (MPGFC) method. In Section 2, the necessary equations to describe constrained chemical equilibrium for any number of ideal phases are reviewed. Section 3 develops the mathematical basis of the MPGFC method, followed by a detailed overview of a practical implementation of the algorithm in Section 4. Finally, two numerical test cases will be presented to demonstrate some key features of the algorithm in Section 5 before a few concluding remarks.

2. Constrained chemical equilibrium

2.1. Free energy minimization

Consider a chemical system composed of any number of ideal phases. The set of indices which denote all species in this system is $\mathcal{S} = \{1, \ldots, n^{\mathcal{S}}\} = \cup_{m \in \mathcal{P}} \mathcal{S}_m$ where $n^{\mathcal{S}}$ is the total number of species considered, $\mathcal{P} = \{1, \ldots, n^{\mathcal{P}}\}$ is the set of phase indices with $n^{\mathcal{P}}$ the number of phases, and $\mathcal{S}_m$ denotes the set of species indices belonging to phase m. Note that each species belongs to a single phase. If a particular chemical species occurs in (for example) three phases, then it is treated as three different species. Since all phases are ideal, the normalized Gibbs function for this system is

$$\tilde{G} \equiv \frac{G}{RT} = \sum_{m \in \mathcal{P}} \sum_{j \in \mathcal{S}_m} N_j \big(\tilde{g}_j + \ln N_j - \ln \bar{N}_m \big), \tag{1}$$

where N_j is the number of moles of species j and $\tilde{g}_j(T, p)$ is the non-dimensional Gibbs function of pure species j at the system temperature T and pressure p, R is the molar universal gas constant, and $\bar{N}_m$ is the total moles in phase m, sometimes referred to as the phase moles of phase m.

$$\bar{N}_m = \sum_{j \in \mathcal{S}_m} N_j, \quad \forall\, m \in \mathcal{P}. \tag{2}$$

The vector of $n^{\mathcal{P}}$ phase moles, $\bar{N}$, can thus be expressed as

$$\bar{N} = \mathbf{P}^T N, \tag{3}$$

where $N \in \mathbb{R}^{n^{\mathcal{S}}}$ is the vector of species moles and $\mathbf{P} \in \mathbb{R}^{n^{\mathcal{S}} \times n^{\mathcal{P}}}$ is a "phase summation matrix" whose elements are defined as

$$P_{jm} \equiv \delta_{p_j m}. \tag{4}$$

The symbol $\delta_{p_j m}$ is the familiar Kronecker Delta function and the subscript p_j is used to denote the index of the phase in $\mathcal{P}$ to which the species j belongs. In other words, for all m in $\mathcal{P}$ and all j in $\mathcal{S}_m$, $p_j = m$.

Table 1
Example constraint matrices $\mathbf{B}$ and $\mathbf{P}$ for a 5-species CO_2 mixture with constraints placed on the total mixture moles, $\bar{N}_{\text{mix}}$.

Species	B columns			P columns	
	C	O	$\bar{N}_{\text{mix}}$	Gas	C(gr)
C	1	0	1	1	0
CO	1	1	1	1	0
CO_2	1	2	1	1	0
O_2	0	2	1	1	0
C(gr)	1	0	1	0	1

The two notations of the phase index are used for convenience, depending on the situation. For instance, Eq. (1) may be equivalently written as

$$\tilde{G} = \sum_{j \in \mathcal{S}} N_j \Big(\tilde{g}_j + \ln N_j - \ln \sum_{k \in \mathcal{S}_{p_j}} N_k \Big). \tag{5}$$

The non-dimensional Gibbs function for a pure species j is given by

$$\tilde{g}_j(T, p) = \frac{H_j(T)}{RT} - \frac{S_j^\circ(T)}{R} + \begin{cases} \ln \dfrac{p}{p^\circ}, & j \in \text{gas phase} \\ 0, & \text{otherwise} \end{cases}, \tag{6}$$

where H_j is the molar enthalpy of pure species j and S_j°, its molar entropy evaluated at the standard state pressure p°.

If the total moles of each element i in the mixture is denoted by c_i^{e}, then conservation of mass dictates that

$$\sum_{j \in \mathcal{S}} B_{ji}^{\text{e}} N_j = c_i^{\text{e}} \quad \forall\, i \in \mathcal{E}, \tag{7}$$

where B_{ji}^{e} is the stoichiometric coefficient for the ith element in species j. $\mathcal{E} = \{1, \ldots, n^{\mathcal{E}}\}$ denotes the set of element indices for the $n^{\mathcal{E}}$ considered elements in the mixture. Eq. (7) is often referred to as the mass balance relations or constraints. It states that the available atoms in a mixture must be shared amongst each of the species in the mixture (regardless of phase). In addition to these physically imposed constraints, it is often useful to impose other constraints on the system. Therefore, we consider the set of $n^{\mathcal{G}}$ additional linear constraints on the number of moles of each species, $\mathcal{G} = \{1, \ldots, n^{\mathcal{G}}\}$, such that

$$\sum_{j \in \mathcal{S}} B_{ji}^{\text{g}} N_j = c_i^{\text{g}} \quad \forall\, i \in \mathcal{G}. \tag{8}$$

Using matrix notation, the total constraints imposed on the composition are thus given by

$$\mathbf{B}^T N = c, \tag{9}$$

where

$$\mathbf{B} = \begin{bmatrix} \mathbf{B}^{\text{e}} & \mathbf{B}^{\text{g}} \end{bmatrix} \in \mathbb{R}^{n^{\mathcal{S}} \times n^{\mathcal{C}}}, \quad c = \begin{bmatrix} c^{\text{e}} \\ c^{\text{g}} \end{bmatrix} \in \mathbb{R}^{n^{\mathcal{C}}}, \tag{10}$$

and $n^{\mathcal{C}} = n^{\mathcal{E}} + n^{\mathcal{G}}$ are the total number of linear constraints whose indices compose the set $\mathcal{C} = \{1, \ldots, n^{\mathcal{C}}\}$. As a clarifying example, consider a 5-species mixture composed of four gaseous species, C, CO, CO_2, and O_2, and solid graphite, C(gr), with an imposed constraint on the total mixture moles, $\bar{N}_{\text{mix}}$. Table 1 shows the corresponding $\mathbf{B}$ and $\mathbf{P}$ matrices associated with this system. Note that the first two columns of $\mathbf{B}$ correspond to the mass balance constraints in Eq. (7) while the last column corresponds to the constraint on the total mixture moles.

For a given $\mathbf{B}$, c, and a fixed temperature and pressure, the local thermodynamic equilibrium (LTE) composition for a chemical system is the one which minimizes $\tilde{G}$, Eq. (1), while satisfying the linear constraints in Eq. (9).

2.2. Constraint potentials

The Lagrange multiplier method is a well known technique for solving constrained minimization problems and will be used here. To