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Combustion and Flame 139 (2004) 222–226

Combustion and Flame
www.elsevier.com/locate/jnlabr/cnf

Gibbs function continuation for the stable computation of chemical equilibrium

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Received 20 January 2004; received in revised form 20 June 2004; accepted 21 July 2004

Abstract

We consider the computation of the chemical equilibrium state of an ideal gas mixture of given elemental composition, with and without general linear constraints on the species present. While computer programs to solve these problems have been available for more than 30 years, it is found that they are not always successful in determining the chemical equilibrium state in the presence of constraints. We present here the new method of *Gibbs function continuation*, which is guaranteed to determine the chemical equilibrium state for all well-posed constrained and unconstrained problems.

1. Introduction

For simple cases, the computation of the chemical equilibrium composition of ideal gas mixtures is a solved problem. Many codes are available for the purpose, notably the NASA equilibrium code [1] and STANJAN [2]. However, there are more complicated cases in which these methods fail. For example, in the method of rate-controlled constrained equilibrium (RCCE) [3,4], it is necessary to compute the equilibrium composition subject to linear constraints on the species. In some RCCE calculations [5], the equilibrium composition is determined subject to 20 constraints: some constraints are on individual species; others are linear combinations, such as the total moles and the active valence [4]. There are reports in the literature [6] that both codes mentioned above fail to determine the constrained equilibrium composition in some cases; and, similarly, in previous work on RCCE we encountered well-posed problems for which STANJAN is unable to determine the constrained equilibrium composition [7].

We present here the essence of a new algorithm for computing constrained and unconstrained compositions of ideal gas mixtures which is guaranteed to succeed for all well-posed problems. Full details of the algorithm are given elsewhere [8], and a Fortran implementation is available [9].

Like STANJAN, the new algorithm is based on the element potential method (or, more generally, the constraint potential method). Consequently, the nonlinear equations solved (which are reviewed in Section 2) are essentially the same as those in STANJAN. However, in place of Newton's method (which can be unstable), these equations are solved by a stable continuation method (described in Section 4), which is guaranteed to converge to the unique solution.

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doi:10.1016/j.combustflame.2004.07.008

2. The constraint potential equations

We consider an ideal gas mixture at fixed temperature T and pressure p consisting of n_{s} species which are composed of n_{e} elements. There are N_k moles of the kth species, and the moles of all species are represented by the n_{s} vector $\mathbf{N} \equiv [N_1\, N_2 \ldots N_{n_{\mathrm{s}}}]^T$. The total species moles is denoted by

$$\overline{N} \equiv \sum_{k=1}^{n_{\mathrm{s}}} N_k, \tag{1}$$

and the vector of mole fractions is

$$\mathbf{X} \equiv \mathbf{N}/\overline{N}. \tag{2}$$

Obviously the mole fractions sum to unity.

The species moles are subject to $n_{\mathrm{c}} \geqslant n_{\mathrm{e}}$ independent linear equality constraints, which are written

$$\mathbf{B}^T\mathbf{N} = \mathbf{c}, \tag{3}$$

where $\mathbf{B}$ is a given $n_{\mathrm{s}} \times n_{\mathrm{c}}$ matrix of full column rank, and $\mathbf{c}$ is a given vector of length n_{c}. For the unconstrained problem, n_{c} equals n_{e}, B_{kj} is the number of atoms of element j in a molecule of species k, so that c_j is the moles of atoms of element j. For constrained problems, $\mathbf{B}$ contains additional linearly independent columns.

For given $\mathbf{B}$ and $\mathbf{c}$, the *max–min composition* $\mathbf{N}^{\mathrm{mm}}$ is defined to be that which satisfies Eq. (3), and which maximizes $N_{\min}$, where $N_{\min}$ is defined to be the minimum (over all species) of the species moles. The constrained equilibrium problem is well-posed for all values of the constraint vector $\mathbf{c}$ for which $N_{\min}$ is strictly positive.

For fixed T and p, the constrained equilibrium composition is that which satisfies the constraints Eq. (3) and minimizes the Gibbs function G of the mixture. For an ideal gas mixture, G (normalized by the universal gas constant $\mathcal{R}$ and T) is given by

$$\widetilde{G} \equiv \frac{G}{\mathcal{R}T} = N_k(\tilde{g}_k + \ln X_k), \tag{4}$$

where the summation convention applies, and $\tilde{g}_k$ is the normalized molar-specific Gibbs function of species k (see [2,8]).

At the minimum of $\widetilde{G}$, Eq. (4), subject to the constraints $\mathbf{B}^T\mathbf{N} = \mathbf{c}$, Eq. (3), the quantity

$$\overline{G} \equiv \widetilde{G} - \boldsymbol{\lambda}^T\left(\mathbf{B}^T\mathbf{N} - \mathbf{c}\right) \tag{5}$$

is stationary with respect to infinitesimal changes $d\mathbf{N}$ and $d\boldsymbol{\lambda}$, where $\boldsymbol{\lambda}$ is the n_{c} vector of Lagrange multipliers, or *constraint potentials*. It follows from Eqs. (4) and (5) that the corresponding infinitesimal change in $\overline{G}$ is

$$d\overline{G} = (\ln X_k + \tilde{g}_k - B_{kj}\lambda_j)\, dN_k - (B_{kj}N_k - c_j)\, d\lambda_j \tag{6}$$

(since $N_k\, d\ln X_k$ is zero). At the minimum of $\overline{G}$, $d\overline{G}$ is zero for all $d\boldsymbol{\lambda}$ and $d\mathbf{N}$, which imposes the conditions that the multipliers of $d\lambda_j$ and dN_k in Eq. (6) are zero. The first of these conditions is simply a statement of the imposed constraints; the second is

$$\ln X_k + \tilde{g}_k - B_{kj}\lambda_j = 0, \tag{7}$$

which, when exponentiated, yields

$$X_k = \exp(-\tilde{g}_k + B_{kj}\lambda_j). \tag{8}$$

This is an explicit expression for the n_{s} equilibrium mole fractions in terms of the n_{c} constraint potentials, which can alternatively be written

$$\mathbf{X} = \exp(-\tilde{\mathbf{g}} + \mathbf{B}\boldsymbol{\lambda}), \tag{9}$$

where $\exp(\mathbf{f})$ denotes the vector whose ith component is $\exp(f_i)$.

In the constrained equilibrium state, in addition to being given by Eq. (9), the mole fractions satisfy the normalization condition

$$\sum_{k=1}^{n_{\mathrm{s}}} X_k = 1, \tag{10}$$

and the constraint equation (3) which can be reexpressed as

$$\mathbf{v} \equiv \mathbf{B}^T\mathbf{X} = \mathbf{c}/\overline{N}. \tag{11}$$

These last three equations summarize the mathematic problem to be solved in the constraint-potential approach: with $\mathbf{X}$ being given by Eq. (9), the $n_{\mathrm{c}} + 1$ unknowns $\boldsymbol{\lambda}$ and $\overline{N}$ are to be determined so that the $n_{\mathrm{c}} + 1$ equations (10) and (11) are satisfied. Then the moles of species at equilibrium are given by $\mathbf{N} = \overline{N}\mathbf{X}$.

3. Infinitesimals

The essence of the numerical problems involved in the constraint-potential equations and the key to overcoming them are revealed by the consideration of infinitesimal changes in the variables. Specifically, we consider infinitesimal changes $d\boldsymbol{\lambda}$ and $d\tilde{\mathbf{g}}$ (in $\boldsymbol{\lambda}$ and $\tilde{\mathbf{g}}$), and examine the corresponding changes $d\mathbf{X}$ and $d\mathbf{v}$ (in $\mathbf{X}$ and $\mathbf{v}$).

It happens that, in this analysis, natural variables are the square roots of the mole fractions. Thus, $\mathbf{y}$ is defined as the n_{s} vector with components $y_k \equiv \sqrt{X_k}$, and $\mathbf{Y}$ is defined as the $n_{\mathrm{s}} \times n_{\mathrm{s}}$ diagonal matrix formed from $\mathbf{y}$.

From Eq. (8) we obtain

$$dX_k = X_{(k)}(-d\tilde{g}_k + B_{kj}\, d\lambda_j), \tag{12}$$

where suffixes in parentheses are excluded from the summation convention. With the definition

$$\mathbf{H} \equiv \mathbf{Y}\mathbf{B}, \tag{13}$$

Eq. (12) can be reexpressed as

$$d\mathbf{X} = -\mathbf{Y}^2\, d\tilde{\mathbf{g}} + \mathbf{Y}\mathbf{H}\, d\boldsymbol{\lambda}. \tag{14}$$

And given the relation $d\mathbf{X} = 2\mathbf{Y}\, d\mathbf{y}$, we also obtain

$$2\, d\mathbf{y} = -\mathbf{Y}\, d\tilde{\mathbf{g}} + \mathbf{H}\, d\boldsymbol{\lambda}. \tag{15}$$

The constraint equation (11) amounts to the statement that the vector

$$\mathbf{v} \equiv \mathbf{B}^T\mathbf{X} = \mathbf{H}^T\mathbf{y} \tag{16}$$

is parallel to the given constraint vector $\mathbf{c}$. For the infinitesimal $d\mathbf{v}$, from Eqs. (14) and (16) we obtain

$$d\mathbf{v} = -\mathbf{H}^T\mathbf{Y}\, d\tilde{\mathbf{g}} + \mathbf{H}^T\mathbf{H}\, d\boldsymbol{\lambda}. \tag{17}$$

As is done in STANJAN, it is natural to consider Newton's method (or a variant thereof) to find a solution to Eqs. (9)–(11). That is, $\boldsymbol{\lambda}$ is set to an initial guess, $\tilde{\mathbf{g}}$ takes its known fixed value (i.e., $d\tilde{\mathbf{g}} = 0$), and then $\boldsymbol{\lambda}$ is changed iteratively to satisfy Eqs. (10) and (11). On each Newton iteration, to effect the required change $d\mathbf{v}$ (so that $\mathbf{v} + d\mathbf{v}$ is parallel to $\mathbf{c}$), changes in the constraint potentials are required to satisfy

$$d\mathbf{v} = \mathbf{H}^T\mathbf{H}\, d\boldsymbol{\lambda}, \tag{18}$$

i.e., Eq. (17) with $d\tilde{\mathbf{g}} = 0$. Clearly, the success of this approach depends crucially on the conditioning of the matrix $\mathbf{H}^T\mathbf{H}$; for if it is singular, then there is no value of $d\boldsymbol{\lambda}$ that can effect a change in all components of $d\mathbf{v}$.

In exact arithmetic, the matrix $\mathbf{H} \equiv \mathbf{Y}\mathbf{B}$ has full column rank, and hence $\mathbf{H}^T\mathbf{H}$ is symmetric positive definite. This follows from the facts that $\mathbf{B}$ has full column rank and that $\mathbf{Y}$ is nonsingular, since it is a diagonal matrix with strictly positive diagonal components, $y_k = \sqrt{X_k}$. However, in chemical equilibrium, it is not unusual to have extremely small species mole fractions, e.g., $X_i = 10^{-40}$, and hence $\mathbf{H}^T\mathbf{H}$ can be numerically singular.

Suppose, for example, that the first two columns of $\mathbf{B}$ are identical except for one row, denoted by k. Suppose further that X_k is extremely small, e.g., 10^{-40}. Then, numerically, the first two columns of $\mathbf{H}$ are identical. As a consequence, any value of $d\boldsymbol{\lambda}$ has the same effect on the first two constraints: dv_1 and dv_2 cannot be changed independently.

In STANJAN "matrix conditioning" is used to address this problem (see Section 6 of [2]). This depends on performing exact arithmetic operations on the matrix $\mathbf{B}$, which is assumed to have (small) integer components. The method is not applicable to general linear constraints in which case components of $\mathbf{B}$ are not necessarily integer.

The alternative method presented here—*Gibbs function continuation*—is based on the observation that for arbitrary $d\tilde{\mathbf{g}}$, and for $d\mathbf{v}$ being parallel to $\mathbf{v}$, a corresponding value of $d\boldsymbol{\lambda}$ can always be stably determined, even if $\mathbf{H}$ is rank deficient. For an infinitesimal scalar $d\varepsilon$, we consider $d\mathbf{v}$ given by

$$d\mathbf{v} = \mathbf{v}\, d\varepsilon, \tag{19}$$

i.e., parallel to $\mathbf{v}$. Then from Eqs. (16) and (17) we obtain

$$d\mathbf{v} = \mathbf{v}\, d\varepsilon = \mathbf{H}^T\mathbf{y}\, d\varepsilon = -\mathbf{H}^T\mathbf{Y}\, d\tilde{\mathbf{g}} + \mathbf{H}^T\mathbf{H}\, d\boldsymbol{\lambda}, \tag{20}$$

and, rearranging the last equation, we further obtain

$$\mathbf{H}^T(\mathbf{H}\, d\boldsymbol{\lambda} - \mathbf{Y}\, d\tilde{\mathbf{g}} - \mathbf{y}\, d\varepsilon) = 0. \tag{21}$$

The essential observation is that (for arbitrary $d\tilde{\mathbf{g}}$ and $d\varepsilon$) a least-squares solution for $d\boldsymbol{\lambda}$ to

$$\min_{d\boldsymbol{\lambda}} \|\mathbf{H}\, d\boldsymbol{\lambda} - \mathbf{Y}\, d\tilde{\mathbf{g}} - \mathbf{y}\, d\varepsilon\|_2 \tag{22}$$

satisfies Eq. (21) even if $\mathbf{H}$ is rank deficient; for it is a general property of such least-squares solutions that the residual

$$d\boldsymbol{\gamma} \equiv \mathbf{H}\, d\boldsymbol{\lambda} - \mathbf{Y}\, d\tilde{\mathbf{g}} - \mathbf{y}\, d\varepsilon, \tag{23}$$

is orthogonal to the columns of $\mathbf{H}$, and hence

$$\mathbf{H}^T\, d\boldsymbol{\gamma} = \mathbf{H}^T(\mathbf{H}\, d\boldsymbol{\lambda} - \mathbf{Y}\, d\tilde{\mathbf{g}} - \mathbf{y}\, d\varepsilon) = 0, \tag{24}$$

in satisfaction of Eq. (21).

4. Gibbs function continuation

Continuation methods have previously been used in several different combustion applications (see, e.g., [10]). In the Gibbs function continuation method, the solution to the constraint potential equations (9)–(11), is obtained by integrating a set of ordinary differential equations (ODEs) in pseudo-time, s. As functions of s, we introduce the pseudo-Gibbs function $\bar{\mathbf{g}}(s)$, and the constraint potentials $\bar{\boldsymbol{\lambda}}(s)$. The pseudo-Gibbs function is prescribed to vary linearly with s, from a specified initial condition at $s = 0$ to the true value of the Gibbs function at $s = 1$:

$$\bar{\mathbf{g}}(s) = \bar{\mathbf{g}}(0) + s\big[\tilde{\mathbf{g}} - \bar{\mathbf{g}}(0)\big]. \tag{25}$$

From a specified initial condition $\bar{\boldsymbol{\lambda}}(0)$, the constraint potentials $\bar{\boldsymbol{\lambda}}(s)$ are obtained by integrating a set of ODEs that are constructed (as described below) so that the final solution $\bar{\boldsymbol{\lambda}}(1)$ is the value of the constraint potentials $\boldsymbol{\lambda}$ that satisfy Eqs. (9)–(11).

Based on $\bar{\mathbf{g}}(s)$ and $\bar{\boldsymbol{\lambda}}(s)$, we define

$$\overline{\mathbf{X}}(s) \equiv \exp\bigl(-\bar{\mathbf{g}}(s) + \mathbf{B}\bar{\boldsymbol{\lambda}}(s)\bigr) \tag{26}$$

(cf. Eq. (9)); and then we redefine $\mathbf{y}(s)$, $\mathbf{Y}(s)$, $\mathbf{H}(s)$, and $\mathbf{v}(s)$ in an obvious way based on $\overline{\mathbf{X}}(s)$.

By construction, the Gibbs function continuation method has the following properties:

(1) For all s (i.e., $0 \leqslant s \leqslant 1$), the mole fractions $\overline{\mathbf{X}}(s)$ satisfy the normalization condition

$$\sum_{k=1}^{n_s} \overline{X}_k = \mathbf{y}^T\mathbf{y} = 1. \tag{27}$$

(2) For all s, the vector

$$\mathbf{v}(s) \equiv \mathbf{B}^T\overline{\mathbf{X}}(s) = \mathbf{H}^T\mathbf{y} \tag{28}$$

is parallel to the specified constraint vector $\mathbf{c}$.

(3) At $s = 1$ we have

$$\bar{\mathbf{g}}(s) = \tilde{\mathbf{g}}. \tag{29}$$

It follows from properties (1) and (2) that (for all s) $\overline{\mathbf{X}}(s)$ are the constrained-equilibrium mole fractions of pseudo-species with Gibbs function $\bar{\mathbf{g}}(s)$; and then from property (3) it follows that $\bar{\boldsymbol{\lambda}}(1)$ is the required solution for $\boldsymbol{\lambda}$.

The simplest way to specify the initial conditions is

$$\overline{\mathbf{X}}(0) = \mathbf{X}^{\mathrm{mm}}, \tag{30}$$

where $\mathbf{X}^{\mathrm{mm}}$ are the mole fractions of the max–min composition;

$$\bar{\boldsymbol{\lambda}}(0) = 0; \tag{31}$$

and

$$\bar{\mathbf{g}}(0) = -\ln \mathbf{X}^{\mathrm{mm}}. \tag{32}$$

The max–min composition is readily determined by linear programming (see [8]), and $\mathbf{X}^{\mathrm{mm}}$ automatically satisfies properties (1) and (2). Given the specifications $\bar{\boldsymbol{\lambda}}(0) = 0$ and $\overline{\mathbf{X}}(0) = \mathbf{X}^{\mathrm{mm}}$, then Eq. (26) determines that $\bar{\mathbf{g}}(0)$ is given by Eq. (32).

As s increases from zero, property (2) is enforced by requiring $\mathbf{v}(s)$ to evolve by

$$\frac{d\mathbf{v}(s)}{ds} = \alpha(s)\mathbf{v}(s), \tag{33}$$

for some scalar $\alpha(s)$. This equation ensures that $\mathbf{v}(s)$ remains parallel to $\mathbf{v}(0)$, which is parallel to $\mathbf{c}$. It follows from Eqs. (20) and (21) that Eq. (33) is satisfied if and only if $d\bar{\boldsymbol{\lambda}}(s)/ds$ satisfies the equation

$$\mathbf{H}^T\left(\mathbf{H}\frac{d\bar{\boldsymbol{\lambda}}}{ds} - \mathbf{Y}\frac{d\bar{\mathbf{g}}}{ds} - \mathbf{y}\alpha\right) = 0. \tag{34}$$

This equation is indeed satisfied by

$$\frac{d\bar{\boldsymbol{\lambda}}}{ds} = \dot{\boldsymbol{\lambda}}^g + \alpha\dot{\boldsymbol{\lambda}}^y, \tag{35}$$

where $\dot{\boldsymbol{\lambda}}^g$ and $\dot{\boldsymbol{\lambda}}^y$ are the least-squares solutions of

$$\min_{\dot{\boldsymbol{\lambda}}^g} \left\| \mathbf{H}\dot{\boldsymbol{\lambda}}^g - \mathbf{Y}\frac{d\bar{\mathbf{g}}}{ds} \right\|_2, \tag{36}$$

and

$$\min_{\dot{\boldsymbol{\lambda}}^y} \left\| \mathbf{H}\dot{\boldsymbol{\lambda}}^y - \mathbf{y} \right\|_2. \tag{37}$$

The scalar variable $\alpha(s)$ is determined by the normalization condition, property (1). Differentiating Eq. (27) with respect to s, we obtain

$$\begin{aligned} 0 &= \frac{d}{ds}\bigl(\mathbf{y}^T\mathbf{y}\bigr) = 2\mathbf{y}^T\frac{d\mathbf{y}}{ds} = -\mathbf{y}^T\mathbf{Y}\frac{d\bar{\mathbf{g}}}{ds} + \mathbf{y}^T\mathbf{H}\frac{d\bar{\boldsymbol{\lambda}}}{ds} \\ &= -\overline{\mathbf{X}}^T\frac{d\bar{\mathbf{g}}}{ds} + \mathbf{y}^T\mathbf{H}\dot{\boldsymbol{\lambda}}^g + \alpha\mathbf{y}^T\mathbf{H}\dot{\boldsymbol{\lambda}}^y, \end{aligned} \tag{38}$$

where the second line follows from the analog of Eq. (15), and the final line from Eq. (35). This equation can then be solved to determine $\alpha(s)$ as

$$\alpha(s) = \left(\overline{\mathbf{X}}^T\frac{d\bar{\mathbf{g}}}{ds} - \mathbf{y}^T\mathbf{H}\dot{\boldsymbol{\lambda}}^g\right)/D, \tag{39}$$

where the denominator is

$$D \equiv \mathbf{y}^T\mathbf{H}\dot{\boldsymbol{\lambda}}^y. \tag{40}$$

It is necessary to show that the denominator D is strictly positive. To this end, we decompose $\mathbf{y}$ as

$$\mathbf{y} = \mathbf{y}^{\parallel} + \mathbf{y}^{\perp}, \tag{41}$$

where

$$\mathbf{y}^{\parallel} \equiv \mathbf{H}\dot{\boldsymbol{\lambda}}^y \tag{42}$$

is in the subspace spanned by the columns of $\mathbf{H}$, and

$$\mathbf{y}^{\perp} \equiv \mathbf{y} - \mathbf{y}^{\parallel} \tag{43}$$

is orthogonal to $\mathbf{H}$, so that $\mathbf{H}^T\mathbf{y}^{\perp} = 0$ and $(\mathbf{y}^{\parallel})^T\mathbf{y}^{\perp} = 0$. We then obtain from Eq. (40)

$$D = \bigl(\mathbf{y}^{\parallel}\bigr)^T\mathbf{y}^{\parallel} = \bigl|\mathbf{y}^{\parallel}\bigr|^2 \geqslant 0. \tag{44}$$

From the definition of $\mathbf{v}$, Eq. (16), we obtain

$$0 < |\mathbf{v}|^2 = \mathbf{y}^T\mathbf{H}\mathbf{H}^T\mathbf{y} = \bigl|\mathbf{H}^T\mathbf{y}^{\parallel}\bigr|^2, \tag{45}$$

from which it follows that $|\mathbf{y}^{\parallel}|$ and hence D are strictly positive.

In summary, the Gibbs function continuation method consists of:

(1) Solving the linear program (maximize the minimum component of $\mathbf{N}$ subject to the constraints $\mathbf{B}^T\mathbf{N} = \mathbf{c}$) to obtain the min–max moles, $\mathbf{N}^{\mathrm{mm}}$, and mole fractions, $\mathbf{X}^{\mathrm{mm}}$.

(2) Specifying initial conditions $\bar{\boldsymbol{\lambda}}(0)$ and $\bar{\mathbf{g}}(0)$ by Eqs. (31) and (32).
(3) Specifying $\bar{\mathbf{g}}(s)$ by Eq. (25) so that $\bar{\mathbf{g}}(1) = \tilde{\mathbf{g}}$.
(4) Integrating Eq. (35) from $s = 0$ to $s = 1$ to obtain $\boldsymbol{\lambda} = \bar{\boldsymbol{\lambda}}(1)$, where $\dot{\boldsymbol{\lambda}}^g$, $\dot{\boldsymbol{\lambda}}^y$, and α are stably obtained from Eqs. (36), (37), and (39) (for all values of s required in the numerical integration).

Thus the method consists of solving a well-posed set of ordinary differential equations from realizable initial conditions, the solution to which exists and is unique. As a consequence, the method is guaranteed to obtain the required solution.

5. Conclusions

Gibbs function continuation is a stable method to solve the constraint-potential equations to determine the chemical equilibrium composition of ideal gas mixtures. The method is guaranteed to yield the equilibrium solution for all well-posed problems. No "matrix condition" is required, and the constraint matrix can have noninteger components. An efficient algorithm based on Gibbs functions continuation is described by Pope [8] and has been implemented in a Fortran library [9].

Acknowledgments

This article is dedicated to the memory of W.C. (Bill) Reynolds, the pioneer of the element potential method, who taught me the subtleties of this method, and much more besides. The work was supported in part by DOE Office of Basic Energy Sciences Grant DE-FG02-90ER14128.

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