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An elegant and powerful technique for the analysis of chemical equilibrium exists but remains relatively unknown in the thermophysics community. The technique, known as the method of element potentials, provides a superior means for solving complicated problems, including those involving multiple phases. This paper describes the basic method, its origins and connection to probability theory, and various algorithms for its effective implementation in computer calculations. A sample of computer codes available are described. The simplicity and utility of the concept of element potentials makes a strong case that it may well be the preferred method of advanced instruction on chemical equilibrium. The method appears extremely flexible and robust. The various programs that have been developed and tested by many users in difficult problems in sooting combustion, optical materials fabrication, and other multi-phase chemical problems demonstrate its versatility and utility.

Nomenclature

A	Jacobian
G	total Gibbs functional
g	molal Gibbs functional
\mathcal{L}	Lagrangian
m	phase index
n	atomic population number per species
\mathcal{N}	moles
P	thermodynamic pressure
\mathcal{R}	universal gas constant
S	entropy
T	thermodynamic temperature
t	time
V	volume
α	atomic population constraint
δ	variation or infinitesimal difference
Δ	change in quantity
λ	Lagrange multiplier
\mathcal{X}	mole fraction

Subscripts

i,j,k,m index counters

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Introduction

Solving the problem of chemical equilibrium poses a difficult challenge for numerical computation. Formulation of the basic problem manifests itself in several ways. Traditionally, and what is taught in textbooks, one utilizes the concept of equilibrium constants. This makes it necessary to identify the set of reactions that occur and determine the associated equilibrium constants. A set of non-linear algebraic equations for the mol numbers of each species then requires a solution. This poses a very difficult task for anything but small systems. Other methods exist that require the minimization of the thermodynamic Gibbs functional by adjusting the mols of each species. This adjustment takes into account particular atomic constraints. Typically, many variables appear and one must take great care to insure non-negative calculated mols for each species. In the presence of important but rare species in the system, the difficulty of the task becomes evident.

In search of a better way to solve combustion-equilibrium problems, the thermodynamics community developed and occasionally re-invented a "lost method", the so-called method of element potentials. One of the early appearances of this technique was reported by Powell and Sarner¹ in 1959. The so-called RAND method for equilibrium calculation as described by Clasen² in 1965 develops a general algorithmic approach essential for effective implementation of the method. In 1967 White³ discussed the computational

advantages of the method, while Bigelow⁴ in 1970 extended the aspects of the method pertaining to non-linear programming. Also in 1970, Van Zeggeren and Story⁵ presented some of the history and details of the method's development. In the 1980's the basic method apparently was re-discovered by Reynolds⁶ of Stanford University and implemented for the numerical calculation of oxidation and vapor deposition processes by McAfee, et. al.^{7,8} Reynolds further developed the "dual problem" and authored a very robust numerical implementation into a computer program called STANJAN.⁶ More recently, Myers⁹ wrote the only textbook available, to the authors' knowledge, that described this method in detail suitable for course instruction. Myers also reported his classroom experiences and student response to the method of element potentials in his thermodynamics course at the University of Wisconsin.¹⁰

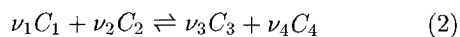
With this paper, we intend to (re-)acquaint the thermophysics community with the method of element potentials and to keep its utility, elegance, and power at the forefront of teaching and research in combustion and related thermophysical problems. Specifically, the author describes the basic method and algorithm for numerical implementation, some examples demonstrating the method, and a list of available computer programs suitable for classroom use. To serve an educational purpose, the paper will develop the theory and method from an elementary outline of Lagrange multipliers, followed by the use of this technique in element potentials.

The Equilibrium Constant Approach

The determination of chemical composition of a mixture of reactive species constitutes an important aspect of the theory of chemical reactions. Typically, conditions for equilibrium are desired at a given temperature and pressure. From the basic laws of thermodynamics a variational principle applies either to the mixture entropy or the potential function called the Gibbs function. At equilibrium conditions, the mixture entropy must be maximized while the corresponding Gibbs function must be minimized. Combining the first and second laws of thermodynamics with the definition for the Gibbs function, $G(T, P) = U + PV - TS$, the conditions for a minimum require that

$$\delta G - V\delta P + S\delta T \leq 0. \quad (1)$$

Consider a simple reactive mixture having a general chemical equation of the form



where ν_k and C_k represent the stoichiometric coefficients and chemical constituents respectively. At equilibrium, the mixture Gibbs function must be a

minimum. Therefore, any small variation in G is represented as

$$\delta G = \hat{\mu}_1 \delta \mathcal{N}_1 + \hat{\mu}_2 \delta \mathcal{N}_2 + \hat{\mu}_3 \delta \mathcal{N}_3 + \hat{\mu}_4 \delta \mathcal{N}_4 \quad (3)$$

where \mathcal{N}_k are the moles of species k and $\hat{\mu}_k$ represent the molal Gibbs functions which are constant for a given T, P . Balancing the chemical equation provides dependence relations among the moles:

$$\delta \mathcal{N}_2 = \frac{\nu_2}{\nu_1} \delta \mathcal{N}_1 \quad \delta \mathcal{N}_3 = -\frac{\nu_3}{\nu_1} \delta \mathcal{N}_1 \quad \delta \mathcal{N}_4 = -\frac{\nu_4}{\nu_1} \delta \mathcal{N}_1 \quad (4)$$

Since G must decrease, this implies that

$$(\hat{\mu}_1 \nu_1 + \hat{\mu}_2 \nu_2 - \hat{\mu}_3 \nu_3 - \hat{\mu}_4 \nu_4) \delta \mathcal{N}_1 \leq 0. \quad (5)$$

For arbitrary variations in \mathcal{N}_1 , the principle for minimum Gibbs function implies that the term in parentheses must vanish:

$$\hat{\mu}_1 \nu_1 + \hat{\mu}_2 \nu_2 = \hat{\mu}_3 \nu_3 + \hat{\mu}_4 \nu_4 \quad (6)$$

producing the equation of reaction equilibrium. For a perfect gas mixture the electrochemical potential for each species is given by

$$\hat{\mu}_i = \hat{g}_i(T, P) + \mathcal{R}T \ln \mathcal{X}_i \quad (7)$$

where \mathcal{X} represents the mol fraction of species i . For convenience, the change in the Gibbs function for the complete unit reaction is

$$\Delta G_r = \underbrace{\sum \nu_i \hat{g}_i}_{\text{products}} - \underbrace{\sum \nu_i \hat{g}_i}_{\text{reactants}} \quad (8)$$

Using (7) and (6) for the simple reactive mixture and cancelling terms gives

$$\Delta G_r = \mathcal{R}T \ln \left\{ \frac{\mathcal{X}_1^{\nu_1} \mathcal{X}_2^{\nu_2}}{\mathcal{X}_3^{\nu_3} \mathcal{X}_4^{\nu_4}} \right\}. \quad (9)$$

From the definition of the partial molal Gibbs function, an arbitrary reference pressure P_0 may be used such that

$$\hat{g}(T, P) = \hat{g}_0(T) + \mathcal{R}T \ln \frac{P}{P_0}. \quad (10)$$

By substitution into 9 and rearranging, we get

$$\exp \left\{ -\frac{\Delta G_{r,0}(T)}{\mathcal{R}T} \right\} = \left[\frac{\mathcal{X}_3^{\nu_3} \mathcal{X}_4^{\nu_4}}{\mathcal{X}_1^{\nu_1} \mathcal{X}_2^{\nu_2}} \right] \left(\frac{P}{P_0} \right)^{\nu_3 + \nu_4 - \nu_2 - \nu_1} \quad (11)$$

Both sides of this expressions must now be functions of temperature only. Therefore, one defines the equilibrium constant for the reaction as

$$K_p(T) \equiv \left[\frac{\mathcal{X}_3^{\nu_3} \mathcal{X}_4^{\nu_4}}{\mathcal{X}_1^{\nu_1} \mathcal{X}_2^{\nu_2}} \right] \left(\frac{P}{P_0} \right)^{\nu_3 + \nu_4 - \nu_2 - \nu_1}. \quad (12)$$

For a given temperature and pressure, K_p is indeed a constant. An interesting though unexplored interpretation arises when we write K_p using the left-hand side of (11):

$$K_p(T) = \exp\left\{-\frac{\Delta G_{r,0}(T)}{\mathcal{R}T}\right\}. \quad (13)$$

This is the function tabulated in thermo-chemical books. The functional form of the expression suggests that K_p can be interpreted as a probability density functional for the energy $\epsilon = \Delta G_{r,0}$. In this case, the normalization condition

$$C_n = \int_0^\infty \exp\left\{-\frac{\epsilon}{\mathcal{R}T}\right\} d\epsilon \quad (14)$$

would apply, suggesting the PDF

$$\hat{K}_p(\epsilon|T) = \frac{1}{\mathcal{R}T} \exp\left\{-\frac{\epsilon}{\mathcal{R}T}\right\} \quad (15)$$

Without further elaboration, we will find inspiration in this expression when developing the numerical solution to the alternative method of element potentials below.

Solving a chemical equilibrium problem using the equilibrium constant method requires that we evaluate K_p using the right-hand side of Eqn (13). Tabulated values for the molal enthalpy and entropy exist, if tabulated values of \hat{g} are not available. So, for a given temperature, K_p is known. If the objective is to calculate the mole fractions of constituents, given the relative atomic abundance, then the additional equations provide enough information to obtain a unique solution. For the simple reactive mixture with m atomic elements composing all species present, we would have

$$K_p(T) = \frac{[\mathcal{X}_3^{\nu_3} \mathcal{X}_4^{\nu_4}]}{[\mathcal{X}_1^{\nu_1} \mathcal{X}_2^{\nu_2}]} \left(\frac{P}{P_0}\right)^{\nu_3 + \nu_4 - \nu_2 - \nu_1}, \quad (16)$$

the normalization constraint

$$\sum_{i=1}^4 \mathcal{X}_i = 1, \quad (17)$$

and m additional constraints representing the given abundance of atomic elements:

$$\mathcal{N} \sum_{i=1}^4 n_{ki} \mathcal{X}_i = \alpha_k, \quad k = 1, \dots, m \quad (18)$$

where $\mathcal{N} = \sum \mathcal{N}_i$ equals the total number of constituent moles. Let ζ represent the degree of reaction proceeding from reactants to products at equilibrium (*). The stoichiometric dependence conditions are then

$$\mathcal{N}_1^* = \mathcal{N}_1^0 - \zeta \nu_1 \quad (19)$$

$$\mathcal{N}_2^* = \mathcal{N}_2^0 - \zeta \nu_2 \quad (20)$$

$$\mathcal{N}_3^* = \mathcal{N}_3^0 + \zeta \nu_3 \quad (21)$$

$$\mathcal{N}_4^* = \mathcal{N}_4^0 + \zeta \nu_4 \quad (22)$$

Adding the total and simplifying gives the total number of moles in the mixture as

$$\mathcal{N} = \sum_{i=1}^4 \mathcal{N}_i^0 + \zeta (\nu_4 + \nu_3 - \nu_2 - \nu_1). \quad (23)$$

To solve a given problem, Eqn. (23) can be combined with (18) to eliminate \mathcal{N} . The atomic constraints (18) then may be solved for $\mathcal{X}_i(\zeta)$ if possible. Finally, Eqn. (16) is solved for ζ , by iteration if necessary. Examples using this procedure are given below.

The Method of Lagrange Multipliers

Lagrange multipliers are used in the theoretical solution of problems of the form

$$F(\mathbf{x}) \implies \min \quad (24)$$

subject to the constraints

$$C_k(\mathbf{x}) = \alpha_k, \quad k = 1, \dots, m \quad (25)$$

In general, F and C_k may be nonlinear functions of the solution vector $\mathbf{x} = (x_1, x_2, \dots, x_n)$. The variation of F is

$$\delta F = \sum_{i=1}^n H_i \delta x_i \quad \text{where} \quad H_i \equiv \frac{\partial F}{\partial x_i} \quad (26)$$

For F to be a minimum with respect to arbitrary variations, δF must equal zero for arbitrary δx_i that satisfy the constraints

$$\delta C_k = \sum_{i=1}^n A_{ik} \delta x_i = 0 \quad \text{where} \quad A_{ik} \equiv \frac{\partial C_k}{\partial x_i} \quad (27)$$

If there are n variables and the system is subject to m constraints, only $n - m$ of the variables may be varied freely. To examine the conditions under which δF is zero for arbitrary variations of the free x_i , the changes in the restricted x_i must be represented in terms of the changes in the free ones and then substituted for the changes in the restricted variables in (26). This substitution is equivalent to subtracting a linear combination of the equations (27) from (26) such that the restricted δx_i drop out of the result. This yields

$$\delta F - \sum_{k=1}^c \lambda_k \delta C_k = \sum_{i=1}^n \left(H_i - \sum_{k=1}^c \lambda_k A_{ik} \right) \delta x_i \quad (28)$$

where the coefficients λ_k must be chosen to eliminate the restricted δx_i . To eliminate the restricted δx_i , the coefficient of each must be zero. So for these x_i ,

$$H_i - \sum_{k=1}^c \lambda_k A_{ik} = 0 \quad (29)$$

The remaining x_i can be varied freely, but there must be no variation that changes F to first order. So this

requires that the coefficient of these δx_i also to vanish in (28). Hence, (29) must hold for all i .

Equation (29) represents a set of n simultaneous equations for the solution vector \mathbf{x} . The constraints (25) provide m additional equations for the λ_k Lagrange multipliers.

If F and C_i are quadratic functions of the x_i , then (29) will be a linear equation system. In the element potential theory, F is the system Gibbs function, and the resulting equations are therefore non-linear.

The method of element potentials relates the mol fractions of each chemical species to quantities called element potentials. One element potential exists for each independent atom in the system and these potentials together with the total number of mols in each phase are the only variables requiring adjustment to obtain the solution. For large problems this number is much smaller than the number of species and hence far fewer variables need be adjusted. Many other advantages quickly become evident when one begins to use the method, although the method remains largely unknown and not widely taught.

The present analysis assumes that the gas phase is a mixture of ideal gases and that condensed phases are ideal solutions. These are good approximations for many practical problems of interest but the concept of element potentials is not limited to these models; it may also be very helpful in dealing with non-ideal systems.

Basic Theory of Element Potentials

Thermochemical equilibrium is characterized by the distribution of n species in a common phase at a given temperature T and pressure P that minimizes the Gibbs function:

$$G = \sum_{i=1}^n (\hat{h}_i - T\hat{s}_i) \mathcal{N}_i. \quad (30)$$

Let $\hat{g} = \hat{h} - T\hat{s}$ and $\tilde{g} \equiv \hat{g}/RT$. On making the Gibbs function non-dimensional, we have

$$\tilde{G}(\mathbf{x}|T, P) = \frac{G}{RT} = \sum_{i=1}^n \tilde{g}_i \mathcal{N}_i \quad (31)$$

For an ideal gas, the enthalpy depends only on temperature. Also, the entropy can be decomposed into

$$\hat{s}(T, P_i) = \hat{s}(T, P) + \ln(P_i/P) \quad (32)$$

From the ideal gas equation of state, one can establish the fact that $P_i/P = \mathcal{X}_i$. Thus,

$$\tilde{G}(\mathbf{x}|T, P) = \sum_{j=1}^n (\tilde{g}_j + \ln \mathcal{X}_j) \mathcal{N}_j \quad (33)$$

The objective function for thermochemical equilibrium is thus

$$\tilde{G}(\mathbf{x}|T, P) \implies \min. \quad (34)$$

The minimization problem is subject to the $m+1$ constraints

$$\mathcal{N} \sum_{i=1}^n n_{ki} \mathcal{X}_i = \alpha_k \quad k = 1, \dots, m. \quad (35)$$

where n_{ki} equals the number of k atoms in a molecule of i species and α_k equals the population in moles of k atoms in the system. The variable m equals the number of distinct elements (atom types) present in the system. For each phase,

$$\left(\sum_{i=1}^n \mathcal{X}_i \right)_j = 1 \quad j = 1, \dots, p \quad (36)$$

or

$$\sum_{i=1}^n \mathcal{N}_{i,j} = \mathcal{N}_j \quad (37)$$

For simplicity, let us assume for the moment that only one phase is present. For compact notation, define the following algebraic column vectors:

$$\mathbf{b} \equiv \begin{bmatrix} \tilde{g}_1 + \ln \mathcal{X}_1 \\ \vdots \\ \tilde{g}_j + \ln \mathcal{X}_j \\ \vdots \\ \tilde{g}_n + \ln \mathcal{X}_n \end{bmatrix}, \quad \mathbf{x} \equiv \begin{bmatrix} \mathcal{X}_1 \\ \vdots \\ \mathcal{X}_j \\ \vdots \\ \mathcal{X}_n \end{bmatrix}, \quad (38)$$

$$\boldsymbol{\alpha} \equiv \begin{bmatrix} \alpha_1 \\ \vdots \\ \alpha_i \\ \vdots \\ \alpha_m \end{bmatrix}, \quad \mathbf{N}^T \equiv \begin{bmatrix} n_{11} & \cdots & n_{1n} \\ \vdots & & \vdots \\ n_{m1} & \cdots & n_{mn} \end{bmatrix} \quad (39)$$

The minimization problem then can be stated in compact notation as

$$\tilde{G}(\mathbf{x}) = \mathcal{N} \mathbf{b}^T \cdot \mathbf{x} \implies \min \quad (40)$$

subject to the normalization condition

$$\mathbf{1}^T \cdot \mathbf{x} = 1 \quad (41)$$

and the m atomic constraints

$$\mathcal{N} \mathbf{N}^T \cdot \mathbf{x} = \boldsymbol{\alpha} \quad (42)$$

Forming the Lagrangian gives

$$\mathcal{L}(\mathbf{x}, \mathcal{N}, \boldsymbol{\lambda}) = \mathcal{N} \mathbf{b}^T \cdot \mathbf{x} - \lambda_0 (\mathbf{1}^T \cdot \mathbf{x} - 1) \mathcal{N} - \boldsymbol{\lambda}^T \cdot (\mathcal{N} \mathbf{N}^T \cdot \mathbf{x} - \boldsymbol{\alpha}) \quad (43)$$

Taking derivatives of the Lagrangian with respect to each of its arguments give

$$\frac{\partial \mathcal{L}}{\partial \mathbf{x}} = \left\{ \mathbf{b} + \frac{\partial \mathbf{b}}{\partial \mathbf{x}} \cdot \mathbf{x} - \lambda_0 \mathbf{1} - \mathbf{N} \cdot \boldsymbol{\lambda} \right\} \mathcal{N} \quad (44)$$

$$\frac{\partial \mathcal{L}}{\partial \mathcal{N}} = \mathbf{b}^T \cdot \boldsymbol{\mathcal{X}} - \lambda_0 (\mathbf{1}^T \cdot \boldsymbol{\mathcal{X}} - 1) - \boldsymbol{\lambda}^T \cdot \mathcal{N}^T \cdot \boldsymbol{\mathcal{X}} \quad (45)$$

$$\frac{\partial \mathcal{L}}{\partial \lambda_0} = (\mathbf{1}^T \cdot \boldsymbol{\mathcal{X}} - 1) \mathcal{N} \quad (46)$$

$$\frac{\partial \mathcal{L}}{\partial \boldsymbol{\lambda}} = \mathcal{N} \mathcal{N}^T \cdot \boldsymbol{\mathcal{X}} - \boldsymbol{\alpha} \quad (47)$$

Note the identity

$$\frac{\partial \mathbf{b}}{\partial \boldsymbol{\mathcal{X}}} \cdot \boldsymbol{\mathcal{X}} = \mathbf{1} \quad (48)$$

So that, on simplifying (47),

$$\frac{\partial \mathcal{L}}{\partial \boldsymbol{\mathcal{X}}} = (\mathbf{b} + (1 - \lambda_0)\mathbf{1} - \mathcal{N} \cdot \boldsymbol{\lambda}) \mathcal{N} \quad (49)$$

For non-trivial solutions the Lagrangian derivatives must vanish, implying that,

$$(\mathbf{b} + (1 - \lambda_0)\mathbf{1} - \mathcal{N} \cdot \boldsymbol{\lambda}) \mathcal{N} = 0 \quad (50)$$

$$\mathbf{b}^T \cdot \boldsymbol{\mathcal{X}} - \lambda_0 (\mathbf{1}^T \cdot \boldsymbol{\mathcal{X}} - 1) - \boldsymbol{\lambda}^T \cdot \mathcal{N}^T \cdot \boldsymbol{\mathcal{X}} = 0 \quad (51)$$

$$(\mathbf{1}^T \cdot \boldsymbol{\mathcal{X}} - 1) \mathcal{N} = 0 \quad (52)$$

$$\mathcal{N} \mathcal{N}^T \cdot \boldsymbol{\mathcal{X}} - \boldsymbol{\alpha} = 0 \quad (53)$$

Eqn.(50) provides the solution vector $\boldsymbol{\mathcal{X}}$ in terms of the Lagrange multipliers λ_0, λ_k :

$$\mathbf{b} = (\lambda_0 - 1)\mathbf{1} + \mathcal{N} \cdot \boldsymbol{\lambda} \quad (54)$$

By definition, $b_j = \tilde{g}_j + \ln x_j$, so that

$$\ln \mathcal{X}_j = (\lambda_0 - 1) - \tilde{g}_j + \sum_{k=1}^n \lambda_k n_{kj} \quad (55)$$

or, solving for \mathcal{X}_j , in vector form,

$$\boldsymbol{\mathcal{X}}(\boldsymbol{\lambda}) = e^{\lambda_0 - 1} \boldsymbol{\mathcal{Z}}(\boldsymbol{\lambda}) \quad (56)$$

where

$$\boldsymbol{\mathcal{Z}}_j = \exp \left(-\tilde{g}_j + \sum_{k=1}^n \lambda_k n_{kj} \right) \quad (57)$$

Putting this result back into the normalization constraint given by Eqn. (52) gives

$$e^{\lambda_0 - 1} = \frac{1}{\mathbf{1}^T \cdot \boldsymbol{\mathcal{Z}}} \quad (58)$$

By substitution, Eqn. (51) reduces to a normalization condition on the $\boldsymbol{\mathcal{Z}}_i$. The remaining equations (53) complete a non-linear system of $m + 1$ equations in $m + 1$ unknowns:

$$\mathbf{1}^T \cdot \boldsymbol{\mathcal{Z}} = 1 \quad (59)$$

$$\mathcal{N} \mathcal{N}^T \cdot \boldsymbol{\mathcal{Z}} - \boldsymbol{\alpha} = 0 \quad (60)$$

One more unknown, \mathcal{N} , can be eliminated by dividing the m -th constraint equation into the $m - 1$ equations remaining. Then we have reduced the problem to solving m equations for the m unknown λ_k :

$$\sum_{j=1}^n \mathcal{Z}_j = 1 \quad (61)$$

$$\alpha_m \sum_{j=1}^n n_{kj} \mathcal{Z}_j - \alpha_k \sum_{j=1}^n n_{mj} \mathcal{Z}_j = 0,$$

for $k = 1, \dots, m - 1$.

Solution by Iteration

Solving the reduced equations by iteration requires a good initial guess. Newton-Raphson iteration converges rapidly if the initial guess is “good enough”. In the next section, we will discuss a new approach for obtaining an initial guess that highlights the connection between the method of element potentials for the chemical equilibrium problem and a generalized entropy method used in modern optimization approaches. Obtaining a “good enough” approximation for the chemical equilibrium problem has relied on a linearization of the Gibbs equation with subsequent application of the simplex method to obtain initial estimates of the \mathcal{X}_i . This is the approach used by Prof. Reynold’s STANJAN program and as recommended by Clasen.² Other complicated methods have been proposed with varying degrees of success (see van Zeggeren & Storey⁵ and Smith & Missen¹⁸). In the following section, we present a simple and robust approach based on a least-squares solution for the Lagrange multipliers λ_k .

Entropy Optimization Method

Principles of optimization have reached a level of maturity sufficient to provide general guidelines for dealing with problems of constrained optimization. A powerful and quite general principle developed in the last fifty years grew from the work done by Shannon at the conception of information theory. The principle of maximum entropy as championed by E. T. Jaynes¹¹ stands as a notable hallmark in the theory. Its generalization and subsequent development finds widespread application as the principle of minimum cross-entropy or Kullback-Liebler entropy (also known by other names). The basic idea utilizes an abstract distance measure between two distributions defined as

$$D(\mathbf{p}, \mathbf{q}) = \sum_i p_i \ln \frac{p_i}{q_i} \quad (62)$$

where p_i, q_i represent two discrete probability distributions and D effectively measures the relative “distance” from \mathbf{q} to \mathbf{p} . Other measures exist but so far this one has proven the most general and useful.

Kapur and Kesavan¹² provide a very readable and detailed introduction. When the q_i represent the uniform distribution $q_i = 1/n$ where n equals some finite number, the principle of minimum cross-entropy reduces to Jayne's principle of maximum entropy. The idea finds widespread use beyond probability theory and in fact will prove useful in the analysis of the chemical equilibrium problem and is easy enough to understand that a working familiarity should be accessible to most students, even undergraduates. The basic and most general optimization problem is this: Given three of the following mathematical entities

- a set of moment constraints C ;
- a measure of entropy or cross-entropy M ;
- the *a priori* probability distribution q ; and
- the *a posteriori* probability distribution p ;

Determine the fourth such that $D(p, q)$ is minimized. In the direct optimization method, a set of constraints, a measure of entropy or cross-entropy, and q are given. The objective function D is minimized so as to obtain the probability distribution p . For the inverse optimization problem, the distribution p is given together with two of the remaining statements and the objective is to find the fourth. Chemical equilibrium belongs to the class of problems dealing with direct optimization.

Consider the Gibbs function per mol given by

$$\frac{\tilde{G}(\mathcal{X}|T, P)}{\mathcal{N}} = \sum_{j=1}^n (\tilde{g}_j + \ln \mathcal{X}_j) \mathcal{X}_j \quad (63)$$

Define the distribution $q_j = \exp\{-\tilde{g}_j\}$ and substitute. The objective functional for chemical equilibrium becomes

$$\frac{\tilde{G}(\mathcal{X}|T, P)}{\mathcal{N}} = \sum_{j=1}^n \mathcal{X}_j \ln \frac{\mathcal{X}_j}{q_j} \quad (64)$$

Now, given the normalization and atomic constraints, the chemical equilibrium problem is mathematically identical direct optimization. The distribution q_j can easily be normalized without affecting the general solution procedure. Since the \tilde{g}_j are known at given (T, P) , this adds only a constant to (64) and does not affect the final solution. Reasoning that the chemical equilibrium problem seeks the minimum measure \tilde{G} , manifested as a distance functional between \mathcal{X} and the q_i computed a priori, one might presume that normalized q_i would make a good candidate as an initial guess for an iterative solution of the problem. Unfortunately, the normalized q_i are not suitable for this. The key to a robust and easy to implement method is to realize that the problem as set in the last section gives a way to use the ideas generated by the optimization problem. Directly from (50), it is possible to replace the unknown b_j with a known distribution

and then obtain an estimate for the Lagrange multipliers λ_k (we know already that $\lambda_0 = 1$ on account of the normalization condition for the Z_j). Assuming we have a known distribution, we may write, using (50), the matrix equation

$$\mathcal{B} = \mathcal{N} \cdot \lambda \quad (65)$$

Since $m \leq n$, the matrix \mathcal{N} is not invertible in general. We can generate an approximate estimate for the λ_k by using the least-squares solution to (65):

$$\hat{\lambda} = (\mathcal{N}^T \cdot \mathcal{N})^{-1} \cdot \mathcal{N}^T \cdot \mathcal{B} \quad (66)$$

Once an approximate estimate for the λ_k is obtained, iterative methods will converge to a quick solution if the initial calculation is "good enough". The key then is finding a reasonable distribution \mathcal{B}_j that will give good estimates for the unknown λ_k .

As already mentioned, a potential candidate is the q_i defined above. If unnormalized, this will give the zero vector for \mathcal{B} and λ , not a good choice. When normalized, the distribution tends to assign a lion's share of the mol fraction to the single q_j that has the largest \tilde{g}_j in magnitude. This tends to give poor initial estimates for the least-squares λ_k and the iterative solution does not converge. Following the insight gained from noting that the exponential distribution tends to hold a central place in optimization theory (and physics in general, actually), several other distributions were considered before reaching some tentative conclusions and recommendations. Thus, inspired by the interpretation of the equilibrium constant K_p given by Eqn. (15), consider the initial PDF given by

$$\mathcal{B}_j = q_j / \sum_j q_j, \quad q_j = \exp\{-\frac{\tilde{g}_j}{\bar{g}}\} \quad (67)$$

where $\bar{g} = \frac{1}{n} \sum_j \tilde{g}_j$. When plotted against the magnitude $|\tilde{g}_j|$, this PDF follows a nice exponentially decreasing trend with increasing ordinate. Another possibility might be

$$\mathcal{B}_j = q_j / \sum_j q_j, \quad q_j = \exp\{-\frac{\Delta \hat{h}_j}{RT}\} \quad (68)$$

where the Δh_j equals the (tabulated) enthalpy change for a given species from reference (formation) conditions to the required temperature. This is the same quantity used to obtain the molal Gibbs function (chemical potential): $\hat{g} = \hat{h}_j^0 + \Delta \hat{h} - T\hat{s}$. Again, this has a smooth exponential trend with increasing ordinate. Finally, one might simply consider the uniform distribution $\mathcal{B}_j = 1/n$ in deference to the optimization principle that stipulates maximum uncertainty when nothing is known about the \mathcal{B}_j other than the "natural" constraint that their sum equals one. After testing all these possibilities, we found that:

- Using the initial guess $q_j = \exp\{-\tilde{g}_j\}$ (normalized or not) gave poor least-squares estimates for the λ_k and iterative methods did not converge.
- Using any of the other three possibilities gave good estimates and Newton–Raphson iteration of Eqns. (61) converged quickly to a (presumably) unique solution.

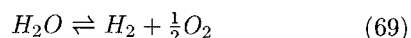
Due to its simplicity and effectiveness, the uniform distribution emerged as the recommended PDF for the least-squares solution (66) to initialize the λ_k . Subsequently, iterative techniques can be used to solve (61). For the examples considered, we encountered no difficulties in obtaining a converged solution even with a large number of species. Use of the uniform distribution in this sense has not been noted before. Typically, the uniform distribution has been used as an initial guess for the mol fractions coupled with initial guesses for other parameters and then attempts to solve the equations by iterations. Van Zeggeren and Storey⁵ note this use (pp. 55–56) with more complicated approaches requiring careful attention to convergence criteria and singularities, especially when a constituent species is present in very small amounts. Many unsuccessful methods failed because the calculations resulted in negative mol fractions. The method of element potentials does not suffer from this deficiency, as Eqn. (57) clearly indicates.

Sample Calculations

We will give in this section only a few examples of the many that we actually calculated. The commercial software package MATHEMATICA¹³ was used because of familiarity and availability. Any other software package with the capability to solve systems of equations can easily be used (e.g., MATHCAD, MATLAB, EES, etc.). The first example analyzes the dissociation of water vapor at high temperature. Both methods handle this simple chemical reaction easily. The second example analyzes the reaction of hydrogen with carbon dioxide producing carbon monoxide and water vapor. For complete analysis this case actually requires up to eight chemical species plus the possible presence of carbon in the solid phase and water in the liquid phase. A third example more clearly demonstrates the power of the method of element potentials by analyzing the combustion of octane. The final example accounts for constituents in multiple phases.

Example 1: Dissociation of Water Vapor

As a first example for comparison consider the dissociation of water at $T = 3000$ K and $P = 1$ atm. With the K_p method, the reaction equation is



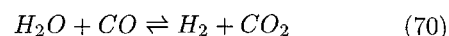
and assume 1 mol of water vapor initially. Let the mol fractions for species H_2O , H_2 , and O_2 be indexed

by 1,2,3 respectively. For this simple case the mol fractions can be uniquely expressed in terms of ζ the degree of reaction towards equilibrium. Then the expression for K_p given by Eqn. (16) can be solved for ζ by numerical iteration. For this case, the MATHEMATICA function NSolve was used, which requires no initial guess to obtain numerical estimates of polynomial equations. It is also possible to solve four equations for the four unknowns $\mathcal{X}_1, \mathcal{X}_2, \mathcal{X}_3, \zeta$ or even three equations for the three unknown mol fractions directly. In each case the result obtained was the same: $\mathcal{X}_1 = 0.793819, \mathcal{X}_2 = 0.137454, \mathcal{X}_3 = 0.068727$. The default accuracy on the MATHEMATICA functions was used.

The element potential method does not require a reaction equation, simply: What are the mol fractions of the desired species at the given T, P and given the mols of atomic elements present in the system? Proceeding as recommended above, we first obtain a least-squares estimate for the Lagrange multipliers λ_1 (for H) and λ_2 (for O) from the uniform distribution for the same three species as before. The least-squares estimates for this case (with 2 mols of H and 1 mol of O) are $\lambda_1 = -11.5378$ and $\lambda_2 = -15.9791$. Next, these are used as initial values for the numerical solution of Eqns. (61). A converged solution gives $\lambda_1 = -11.4147$ and $\lambda_2 = -16.4865$ using the MATHEMATICA function FindRoot which utilizes the Newton–Raphson iteration technique. The final result is almost identical to that given by Reynold’s STANJAN program for the element potentials. The computed mol fractions, $\mathcal{X}_1 = 0.794132, \mathcal{X}_2 = 0.137245, \mathcal{X}_3 = 0.0686225$ differ insignificantly from those given by the K_p method.

Example 2: Hydrogen and Carbon Dioxide

Consider now the reaction between hydrogen gas and carbon dioxide at $T = 3000$ K and $P = 1$ atm. With the K_p method, the reaction equation is



and assume 1 mol of H_2O with one mole of CO initially. For this simple case the mol fractions of the constituent species cannot be uniquely expressed in terms of ζ because the stoichiometric coefficients add up to one and the resulting matrix from the constraints is singular. To solve, we use the mol fraction for one species, say \mathcal{X}_4 , as a base then solve for the remaining mol fraction in terms of that base. The expression for K_p given by Eqn. (16) can then be solved for \mathcal{X}_4 by numerical iteration if necessary. In this case, the resulting expression is quadratic in \mathcal{X}_4 and one must decide which sign appropriate. The MATHEMATICA function NSolve was also used and it gave both possible solutions to \mathcal{X}_4 , including one that was negative. So we pick the positive one and compute the remaining three. This shows some of the ambiguity and possible problems that arise with the equilibrium constant method. The

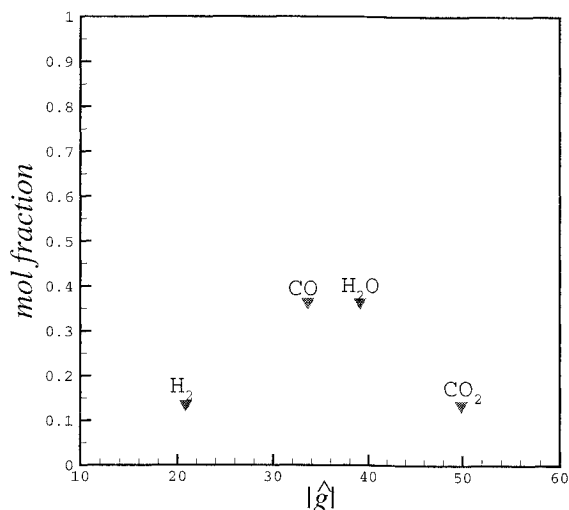


Figure 1 Mol fractions of constituent species for CO₂ plus H₂ reaction at 3000K and 1 atm as calculated with the equilibrium constant method.

correct solution gave equal amounts of CO₂ and H₂ (0.1356) completed by equal amounts of CO and H₂O (0.3643). These are shown in Figure 1 as mol fractions plotted against the absolute value of the molal Gibbs energy. Such a tidy result is obviously suspect. The method of element potentials indicates why.

Again, the element potential method does not require a reaction equation, simply: What are the mol fractions of the desired species at the given T, P and given the mols of atomic elements present in the system? Proceeding as recommended above, we first obtain a least-squares estimate for the Lagrange multipliers λ_1 (for C), λ_2 (for H), and λ_3 (for O) from the uniform distribution with all possible species, including O₂, HO, O, and H. The least-squares estimates for this case (with 2 mols of H and O and 1 mol of C) are obtained. Next, these are used as initial values for the numerical solution of Eqns. (61). A converged solution gives $\lambda_1 = -17.1566$, $\lambda_2 = -11.4327$, and $\lambda_3 = -17.4506$ using MATHEMATICA's FindRoot function. The final result indicates that the species neglected by analyzing only those in the chemical reaction (70) are present in significant amounts, as shown in Figure 2. The advantage of the element potential method is that one could solve the problem using the same four species as with the K_p method then test for the presence of other species. Since the resulting element potentials (the λ_k) do not change significantly, the test gives fairly accurate estimates for the presence of species not initially included. The power of the method of element potentials is already evident in this case because it is just as easy to include all possible species without considering any chemical reactions. Using STANJAN, we verified that no liquid water or solid carbon were present at these conditions.

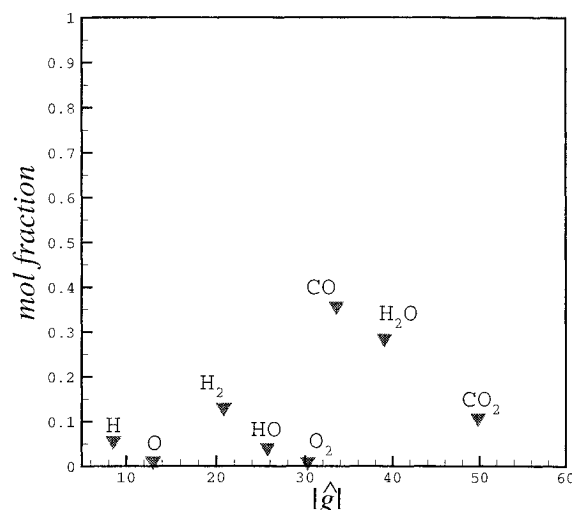


Figure 2 Mol fractions for 8 species for the complete CO₂ plus H₂ reaction at 3000K and 1 atm as calculated with the method of element potentials.

Example 3: Combustion of Octane Fuel

Probably the advantages of the method of element potentials becomes clear when dealing with complex systems composed of many components. The combustion of hydrocarbon fuels for example contains many more degrees of freedom than the simple reaction equations typically contained in textbooks for equilibrium analysis. With the equilibrium constant method, the task becomes daunting (but still possible). Consider the combustion of octane and theoretical air resulting in products at 3000 K and 100 atm and suppose only 10 component species are considered: O₂, N₂, CO₂, CO, H₂O, H₂, HO, NO, NO₂, CH₄. Tabulated values for the required Gibbs functions are found in Myers' book⁹ pp. 760–770. Given the atomic population in mols of C, H, O, and N as 8, 18, 25, and 94.35 respectively for the mix, the method of element potentials easily converges to a solution. With a least-squares estimate for the four element potentials required, the complete solution accurately predicts the mol fractions of the ten species. With the current method, the element potentials for C, H, O, and N converge to $\{-17.3755, -10.7052, -15.1329, -12.06\}$ respectively. These compare quite well to the more complicated techniques used in other programs. The resulting mol fractions are represented by the graph shown in Figure 1, inspired by the probabilistic interpretation of the problem. The mol fractions are plotted against the absolute value of the molal Gibbs energy, thus representing a discrete distribution over its range. This figure provides an interesting visual representation of the data, suitable for easy viewing and definitely useful in the classroom experience.

To test for the presence of solid carbon in the mix, one simply calculates the total Gibbs function with

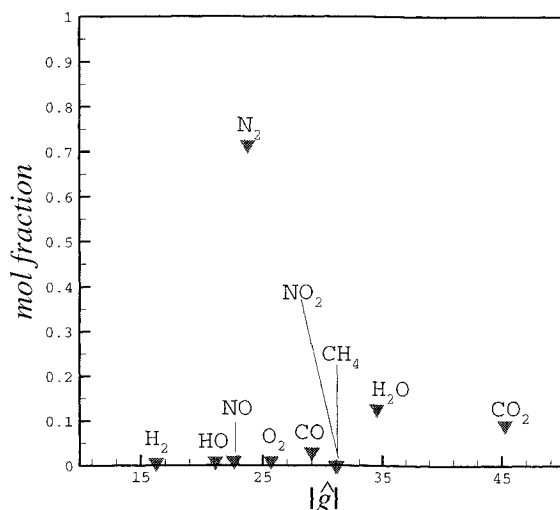


Figure 3 Mol fractions for 10 species produced by the combustion of octane at 3000K and 100 atm calculated with the method of element potentials.

and without carbon. If the Gibbs function is less with a solid carbon phase present, then this should be the equilibrium state and the results modified; otherwise the equilibrium state contains no solid carbon. Myers⁹ (pp. 911-915) describes this example more fully for products at 1 atm. However, the method used by Myers solves for the full set of equations resulting from taking derivatives of the Lagrangian, Eqns. (47-50) so that initial guesses for the mol fractions of the species are also required and a larger number of equations solved. Here we take further advantage of the power intrinsic in the method of element potentials by reducing the number of equations solved to the minimum and using a simple least-squares technique for the initial estimates. To the authors' knowledge of the literature, this technique has escaped previous efforts in the field.

Example with Multiple Phases

Consider the system consisting of CO, CO₂, O₂, and C(s) (solid carbon) at 3000 K and 1 atm, where these species have the Gibbs functions given in Table 1. Suppose the system contains 2 mols of C atoms and 1 mol of O atoms. Some solid carbon must be present and its mol fraction in the solid phase should equal 1. From this knowledge, one could immediately calculate the element potential for carbon and then that of oxygen by guessing the dominant gas species to be CO. Instead, let us use the modified methods recommended here by simply including the solid carbon as a separate species. The least-squares estimates for the element potentials are then $\lambda_1 = -11.3891$ for carbon and $\lambda_2 = -18.3604$ for oxygen. Using the fact that the mol fraction of carbon in its phase equals one, the numerical solution of the remaining equations easily converges to give $\lambda_1 = -3.586$ and $\lambda_2 = -30.0147$.

Table 1 Non-Dimensional Gibbs Function for Selected Species for Example with Two Phases.

No.	Species	$\tilde{g} = g(T, P)/RT$
1	CO	-33.578
2	CO ₂	-49.830
3	O ₂	-30.273
4	C(s)	- 3.586

These in turn yield 0.999999 as the mol fraction for CO, which is indeed the dominant gas species under these conditions. The mol fractions for CO₂ and O₂ are 1.06672×10^{-6} and 1.21901×10^{-13} respectively.

Suppose at this point that we want an estimate for the concentration of a species that has not been included in the system, for example atomic oxygen. This is easily accomplished using element potentials. At 3000 K and 1 atm, $\tilde{g}_O = -12.951$, so using the calculated element potential λ_2 for oxygen,

$$x_O = \exp(12.951 - 30.0147) \doteq 3.88 \times 10^{-8}$$

This estimate is very accurate since the inclusion of oxygen in the system with such a minute mol fraction will not significantly influence the element potentials.

When less carbon is present in the system, the method of element potentials still applies for this case. What happens now is that a trace amount of solid carbon is predicted and the element potentials converge to values not significantly different than those obtained by assuming no solid carbon phase, as in the case when we have only 1 mol of carbon with 2 mols of oxygen. Here the method predicts 0.462895 mols of CO₂, 0.35807 mols of CO, and 0.179035 mols of O₂. Difficulty occurs only when one assumes a single gaseous phase when there is an over-abundance of carbon: the method will not converge. This is in fact a desirable trait because it warns us that we have not used all of the information available or that we have not posed the problem properly. STANJAN also gives a warning if a single phase is specified when more might actually be present. The success of our current method indicates that the methodology introduced here can be generalized to account for multiple phases without significant difficulty.

Available Software

Here we briefly describe available software that implements the method of element potentials in various ways and with different objectives. For educational use, Reynold's STANJAN program is highly recommended. The version used for comparison with this work dates from 1989. The newest version can be obtained from Prof. Reynolds at Stanford University at a reasonable cost (not known at this time and probably subject to change without notice). The other programs are intended for industrial use and are probably much more sophisticated than what a classroom requires. Many other programs exist, probably more than what are known to the authors. Using the simple techniques described in this work, an instructor also has the option of letting student write their own programs using available computer resources. Once the basic theory and method for implementing a solution is understood, the time required to solve a particular problem is minimal.

STANJAN

The program STANJAN (due to its roots at Stanford and its connection with the JANNAF thermochemical data tables), is an interactive program designed for use with either desk-top or mainframe computers. The basic data are taken from the JANNAF tables, and data for a selection of species accompany the program. A companion program, JANFILE, can be used to prepare data for other species from the JANNAF table data. Both are very robust, user-friendly interactive programs.

With STANJAN, users select the species to be included in each phase of the system, set the atomic populations and state parameters. Then STANJAN solves for the equilibrium state using the method of element potentials. The results include the composition of each phase (mols and mol fractions) and the thermodynamic properties of the system, including (if desired) the speed of sound. STANJAN can also execute thermodynamic cycle analysis because the user may specify the state parameters in a variety of ways, including (T, P) , (P, S) , and (H, P) or (V, S) . The equilibrium composition can be calculated or a frozen composition specified. Users can also apply STANJAN to compute adiabatic flame temperature for reactions at constant pressure or volume.

RAND SOLVER

A full description of the RAND method can be found in the memorandum by Clasen.² The basic algorithm is very similar to that of STANJAN: apply the simplex method to obtain initial estimates then use Newton-Raphson to converge the solution. The program requires the user to input the Gibbs free energy functions for each species at the specified temperature and pressure of interest and it permits only isothermal computations.

NASA-LEWIS CODE

The NASA-Lewis code also known as the "Gordon-McBride" program¹⁴ was developed at the NASA Lewis (now Glenn) Research Center, Cleveland, OH. The program is specifically intended for use in the propellant and aerospace industries. Thermodynamic and propulsion characterizations can be made for multi-component reacting mixtures. Only ideal gas phases are modeled and phases other than gases are restricted to pure compounds. Thermodynamic and transport properties are available at high temperatures. Both adiabatic and isothermal reactions can be specified. For additional details on the development of the NASA-Lewis code, Gordon¹⁵ (1970) and Zeleznik & Gordon¹⁶ (1960) and the references therein provide well-documented critiques of the various techniques chosen for implementation. The interested reader is referred also to Straub's book¹⁷ on some of the limitations and modifications for improvement of the Lewis code that are beyond the scope of this work.

Closing Remarks

We have presented pedagogical descriptions of two methods for obtaining chemical equilibrium compositions, the equilibrium constant method and the method of element potentials. Both methods are based on the same fundamental principle for the condition of equilibrium, minimum free energy but they differ in the development of that principle. Computer implementation of these methods requires attention to mathematical and numerical details such as iteration techniques, convergence controls, and singularities in order to obtain a unique solution. Although the two formulations reduce to the same number of iterative equations in general, the equilibrium constant method suffers from disadvantages not found in the method of element potentials. We have presented an interesting implementation of the latter method with insight gained from generalized optimization techniques and probability theory. The algorithmic development of the method reduces the chemical equilibrium problem to a reduced set of equations with Lagrangian multipliers. We then employ a least-squares approximation to initialize a more accurate, convergent solution by iteration. The methodology is easy to implement using existing commercial software for solving systems of equations and appears to be accurate and robust. For practical and aesthetic reasons, the method of element potentials is recommended as suitable and advantageous for classroom use and beyond.

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Notes

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