THE ELEMENT POTENTIAL METHOD
FOR CHEMICAL EQUILIBRIUM ANALYSIS:

IMPLEMENTATION IN THE INTERACTIVE PROGRAM

STANJAN

VERSION 3

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JANUARY, 1986

THE ELEMENT-POTENTIAL METHOD FOR CHEMICAL EQUILIBRIUM ANALYSIS: IMPLEMENTATION IN THE INTERACTIVE PROGRAM STANJAN

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Summary

The element-potential method for chemical equilibrium analysis is a powerful technique that is is virtually unknown in the thermodynamics community. It provides a superior means for solution of complicated problems, especially those involving several phases. The concept of element potentials is so useful that it should be included, if not preferred, in any advanced instruction on chemical equilibrium.

This paper describes the basic method, a new algorithm for its effective computer implementation, and a general-purpose interactive freeware program that can be used to solve chemical equilibrium problems in single- or multi-phase systems. The method is extremely flexible and robust, and the programs have been tested by many users in difficult problems in sooting combustion, optical materials fabrication, and other multi-phase chemical problems.

1. Introduction

The solution of chemical equilibrium problems has posed a tough challenge for numerical computation. The problem may be formulated in several ways. If one uses the concept of equilibrium constants, then it is necessary to identify the set of reactions that take place and to determine the associated equilibrium constants. One then has to solve a set of nonlinear algebraic equations for the mol numbers of each species, a difficult task if the system is large. Other methods based on the minimization of the Gibbs function adjust the mols of each species, consistent with atomic constraints, until the minimum Gibbs function state is found. Again, there are many variables involved, and great care must be taken to be sure that all mols are non-negative. When there are important rare species in the system, this can be a very difficult task.

In search of a better way to solve combustion-equilibrium problems, the author reinvented what he later discovered to be a "lost" method, the so-called method of element potentials. Early development of the method was done by Powell[1]. The RAND method for equilibrium calculation described by Clasen[2] is essentially an early implementation of the method. White[3] pointed out some computational advantages of the method. Bigelow[4] extended the nonlinear programming theory of the method. The author's contribution is the development of the dual problem and a powerful numerical implementation. For pre-STANJAN history of the method, see Van Zeggeren and Storey[5]. The purpose of this paper is to make the method of element potentials known to the combustion community and to outline an interactive computer program based on the method that is available for solving chemical equilibrium problems.

The method of element potentials uses theory to relate the mol fractions of each species to quantities called element potentials. There is one element potential for each independent atom in the system, and these element potentials, plus the total number of mols in each phase, are the only variables that must be adjusted for the solution. In large problems this is a much smaller number than the number of species, and hence far fewer variables need be adjusted. There are many other advantages to the element-potential method that quickly become obvious when one begins to use it. We believe that element potentials should be part of modern instruction in thermodynamics, but the concept is not widely known or taught.

The present analysis, and the program, 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. The concept of element potentials is not limited to these models, and we believe that it may be very helpful in dealing with non-ideal systems.

The program, called STANJAN because of its roots at Stanford and its connection with the JANNAF thermochemical data tables, is an interactive program designed for use with either desktop 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, the user selects the species to be included in each phase of the system, sets the atomic populations and state parameters, and then STANJAN solves for the equilibrium state using the method of element potentials. This is extremely rapid, and, with an 8087 floating-point coprocessor on an IBM-PC, solutions for typical combustion problems are returned almost immediately. 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.

Thermodynamic cycle analysis is easily executed with STANJAN, because the user may specify the state parameters in a variety of ways, including

i) temperature and pressure,
ii) pressure and entropy,
iii) enthalpy and pressure same as last run,
iv) volume, entropy same as last run.

The equilibrium composition can be calculated, or a frozen composition can be specified.

STANJAN can be used to compute adiabatic flame temperatures for reactions at constant pressure (or volume). The approach is first to make a run with the reactants at the inlet (or initial) state, which calculates the enthalpy (and energy). This is followed by a run in which the products of combustion are considered, with the state specified as having the same pressure and enthalpy (or volume and energy) as the previous run.

A series of calculations can be made over a matrix of T and P values. These tabulated results can be stored in a file for later processing; special provisions are made for creating output tables readable by spreadsheet programs, particularly LOTUS-123.

In summary, STANJAN is a powerful and easy-to-use program for analysis of chemical equilibrium in single- or multiple-phase systems. The executable IBM-PC program disks are freeware and may be freely copied by any institution for its use. The FORTRAN source programs are also available at reasonable cost for users who wish to recompile for other machines or uses.

2. The Basic Theory of Element Potentials

The Gibbs function of a system is:

$$G = \sum_{j=1}^{s} \bar{g}_j N_j \tag{2.1}$$

where $\bar{g}_j$ is the partial molal Gibbs function and N_j is the number of mols of species j, and s is the total number of species in the system. Treating each phase as either a mixture of ideal gases or as an ideal solution, the partial molal Gibbs functions are given by:

$$\bar{g}_j = g_j(T,P) + RT \ln x_j \tag{2.2}$$

where $g_j(T,P)$ is the Gibbs function of pure j evaluated at the system temperature and pressure, x_j is the mol fraction of j in its phase, and R is the universal gas constant.

The atomic population constraints are:

$$\sum_{j=1}^{s} n_{ij} N_j = p_i \quad , \qquad i = 1, \ldots, a \tag{2.3}$$

where n_{ij} is the number of i atoms in a j molecule, p_i is the population (mols) of i atoms in the system, and a is the number of different elements (atom types) present in the system. The equilibrium solution at the given T and P is the distribution of N_j that minimizes G, subject to the atomic constraints (2.3), for non-negative N_j.

Minimization problems with constraints are best handled by the method of Lagrange multipliers. The development in this section does not assume knowledge of the method, but in essence develops the method for this particular problem. Since Lagrange multipliers may be unfamiliar to some readers and it is very important in the numerical solution, a brief review of the method is presented in Appendix A.

For convenience, we denote $\tilde{g}_j = g_j(T,P)/RT$, and seek the minimum of G/RT. Using (2.2) we find that, for arbitrary variations in the mol numbers,

$$d\left(\frac{G}{RT}\right) = \sum_{j=1}^{s} (\tilde{g}_j + \ln x_j)\, dN_j + \sum_{j=1}^{s} N_j \frac{1}{x_j}\, dx_j \tag{2.4}$$

We denote the number of mols in phase m by $\overline{N}_m$; then,

$$x_j = N_j/\overline{N}_{(j)} \tag{2.5}$$

where $\overline{N}_{(j)}$ is the number of mols in the phase containing species j (a species present in more than one phase is assigned distinct j indices for each phase). The second sum in (2.4) can therefore be replaced by

$$\sum_{m=1}^{p} \overline{N}_m \sum_{\substack{j=1 \\ \text{in } m}}^{s} dx_j$$

where p is the total number of phases which might be present. This vanishes, because the mol fractions in each phase always sum to unity.

Now the dN_j are not all independent, because of the atomic constraints. Relationships among the dN_j are obtained by differentiating (2.3):

$$\sum_{j=1}^{s} n_{ij} dN_j = 0 \quad , \quad i = 1, \ldots, a \tag{2.6}$$

We must solve for the a restricted dN_j in terms of the s−a free dN_j, and then substitute these relationships into (2.4) in order to express the G variation in terms of freely variable N_j. This process is equivalent to subtracting multiples of (2.6) from (2.4):

$$\begin{aligned} d\left(\frac{G}{RT}\right) = & \sum_{j=1}^{s} \left(\tilde{g}_j + \ln x_j\right) dN_j \\ & - \sum_{i=1}^{a} \lambda_i \sum_{j=1}^{s} n_{ij} dN_j \end{aligned} \tag{2.7}$$

The λ_i are the multipliers that are required to drop out the set of restricted dN_j from this equation. Thus, setting the coefficients of these dN_j to zero, one has

$$\tilde{g}_j + \ln x_j - \sum_{i=1}^{a} \lambda_i n_{ij} = 0 \tag{2.8}$$

for the restricted j. With these dN_j absent from (2.7), the remaining dN_j may be freely varied, and at the minimum G point there must be no variations that change G (to first order). This will be true only if the coefficient of each free dN_j is zero; hence, (2.8) also applies to the free j. So, for every species,

$$x_j = \exp\left(-\tilde{g}_j + \sum_{i=1}^{a} \lambda_i n_{ij}\right) \tag{2.9}$$

Equation (2.9) is the main result of the theory of element potentials for mixtures of ideal gases or for ideal solutions. It relates the phase mol fraction of each species to its value of $g(T,P)/RT$, to the atomic makeup of its molecule, and to a set of undetermined multipliers (the "Lagrange multipliers") to be determined from the atomic constraints. The multiplier λ_i is called the <u>element potential</u> for i atoms. Using (2.2), we see that

$$\bar{g}_j/RT = \sum_{i=1}^{a} \lambda_i n_{ij} \tag{2.10}$$

and hence λ_i represents the Gibbs function/RT per mol of i <u>atoms</u>. What is even more amazing is that each atom of an element contributes the same amount to the Gibbs function of the system, irrespective of which molecule or phase it is in! The λ_i are properties of the system, however, and cannot be tabulated as functions of the atom or molecule, as can the g_j. It is perhaps for this reason that the method of element potentials has not been widely used, although we believe it should be the method of choice today.

The values of the element potentials are determined by the atomic constraints (2.3), which we rewrite as

$$\sum_{j=1}^{s} n_{ij} \bar{N}_{(j)} x_j = p_i \quad , \quad i = 1, \ldots, a \tag{2.11}$$

Using (2.9), this becomes a set of a equations for the a unknown λ_i and the p unknown $\bar{N}_m$. To this we add the p equations

$$\sum_{\substack{j=1 \\ \text{in } m}}^{s} x_j = 1 \quad , \quad m = 1, \ldots, p \tag{2.12}$$

Equations (2.11) and (2.12) must be solved simultaneously to determine the element potentials and phase mols. This might appear to be a difficult task, but it is possible to do it accurately and quickly.

In many problems there will be a set of dominant species, the mol fractions of which can be estimated from simple balances. These can be used to estimate the element potentials, which can in turn be used to calculate the mol fractions of the minor species. As we shall see in examples to follow, this involves only the solution of linear algebraic equations. Thus there are advantages to the method of element potentials, even in "small" problems. Some examples are presented in the next section.

In problems with many species, the method has many significant advantages. There is no need to identify a set of reactions or to make use of the associated equilbrium constants. One has to deal only with $(a + p)$ variables, whereas other methods work with the s unknown mols as variables. In a gas-phase problem with 100 species containing C, H, O, and N, the element-potential method has only five unknowns, whereas mol-iteration methods must work with 100 unknowns. Mol-iteration methods must guard against negative mol fractions, which can never occur with mol fractions generated by (2.9). Furthermore, they can have serious problems when some species have very small mol fractions, but this is not a problem in a well-designed implementation of the method of element potentials. The power of the element-potential method is exceptional in dealing with systems containing multiple phases. This will be illustrated by examples after the dual problem and numerical solution method have been described.

3. Element Potentials in Hand Calculations

Two simple examples will illustrate the use of element potentials in hand calculations. Both involve the system consisting of CO, CO_2, O_2, and C(S) (solid carbon) at 3000°K and 1 atm, where these species have the following Gibbs functions:

Species	$\tilde{g} = g(T,P)/RT$
CO	-33.578
CO_2	-49.830
O_2	-30.273
C(S)	-3.686

(a) Same Number of Dominant Species as Elements

Suppose that the system contains 2 mols of C atoms and 1 mol of O atoms. Some solid carbon must therefore be present, and its mol fraction in the solid phase must be 1. Using (2.9) for C(S),

$$x_{C(S)} = 1 = \exp\left(-\tilde{g}_{C(S)} + \lambda_C\right) \tag{3.1}$$

The element potential for carbon can be found immediately from (3.1):

$$\lambda_C = \tilde{g}_{C(S)} + \ln(1) \tag{3.2}$$

If we can estimate one other mol fraction, we can calculate the element potential for oxygen. At first glance, it looks as though the dominant gas species should be CO_2, which has the lowest Gibbs function. Now, the dissociation of CO_2 gives 1 mol of CO and 0.5 mols of O_2, for which

$$G/RT = -33.578 + \ln(2/3) + 0.5 \times [-30.273 + \ln(1/3)] = -49.668$$

This is just slightly greater than the Gibbs function of the mol of CO_2, so there still appears to be a slight preference for CO_2. However, a half-mol of CO_2 can combine with a half-mol of C(S) to make a mol of CO. For the CO_2 and C(S),

$$G/RT = 0.5 \times [-49.830 + \ln(1/2)] + 0.5 \times (-3.868) = -25.455$$

which is much greater than that of the mol of CO. Hence, any free carbon will tend to react with CO_2 to form CO, and consequently we expect the dominant gas species to be CO. Assuming that the CO mol fraction is 1, (2.9) gives

$$x_{CO} = \exp\left(-\tilde{g}_{CO} + \lambda_C + \lambda_O\right) = 1 \tag{3.3}$$

from which we obtain our second <u>linear</u> equation in the element potentials:

$$\lambda_C + \lambda_O = \tilde{g}_{CO} + \ln(1) \tag{3.4}$$

Solving (3.2) and (3.4) simultaneously for the potentials, we have

$$\lambda_C = -3.686$$

$$\lambda_O = -29.892$$

From this we use (3.3) to estimate the mol fraction of CO_2

$$x_{CO_2} = \exp(-\tilde{g}_{CO_2} + \lambda_C + 2\lambda_O) = 0.1193 \times 10^{-5}$$

The assumption that CO was the dominant gas species was clearly correct. If we wished, we could correct our estimates by lowering the mol fraction of CO, but in this case we are so close to the exact solution that the iteration is not worthwhile. Indeed, this solution is exact to four decimal places!

Suppose at this point we wished to estimate the concentration of a species that we have not thus far included in the system, for example O. We can do this easily using the element potentials. At 3000°K and 1 atm, $\tilde{g}_O = - 12.951$, so

$$x_O = \exp(+ 12.951 - 29.892) = 2.38 \times 10^{-8}$$

This is a very accurate estimate, since the inclusion of O in the system with this mol fraction will not significantly influence the element potentials.

In summary, whenever we have a system in which one dominant species can be identified for each element in the system, the mol fractions of these species can be used to estimate the element potentials. With these element potentials, estimates of all of the other mol fractions can be made, and corrections can be made to the element potentials by iteration, if necessary. The element potentials can then be used to estimate the concentrations of minor species.

(b) Fewer Dominant Species than Elements

Suppose instead that the system contains 1 mol of C atoms and 2 mols of O atoms. Here the condensed phase will be almost absent and the gas phase will consist almost entirely of CO_2. Therefore, we have only one dominant mol fraction from which we want to estimate two element potentials. We can still do this using a concept called "balancing". The atomic constraints can be written as:

$$N_{CO} + N_{CO_2} + N_{C(S)} = 1 \tag{3.4}$$

$$N_{CO} + 2N_{CO_2} + 2N_{O_2} = 2 \qquad (3.5)$$

The idea of balancing is to select a set of <u>base species</u>, and then to recast the constraints so that each equation contains only one of these base species. The base set should include the dominant species. We select the dominant species CO_2 as one base, and O_2 as the other. Equation (3.4) contains only the base CO_2 and tells us that there is approximately 1 mol of CO_2 in the system. Combining the equations to eliminate CO_2 from (3.5), we obtain

$$2N_{O_2} - N_{CO} - 2N_{C(S)} = 0 \qquad (3.6)$$

This tells us that the second base species O_2 must be "balanced" by CO and/or C(S). Since CO has a much smaller Gibbs function that C(S), the balance will be primarily with CO, and so approximately

$$2N_{O_2} = N_{CO} \qquad (3.7)$$

Since both O_2 and CO are in the same phase, this translates into a requirement that the mol fraction of CO must be twice that of CO_2. Then, using (2.9) in (3.7) and taking the log of both sides, a linear equation relating the element potentials is obtained:

$$\ln(2) - \tilde{g}_{O_2} + 2\lambda_O = - \tilde{g}_{CO} + \lambda_C + \lambda_O \qquad (3.8)$$

A second linear equation relating the element potentials is obtained from the estimate that the mol fraction of CO_2 is unity,

$$- \tilde{g}_{CO_2} + \lambda_C + 2\lambda_O = \ln(1) \qquad (3.9)$$

We solve these two equations and obtain

$$\lambda_C = -18.351 \ , \qquad \lambda_O = -15.739$$

Using these potentials, the mol fractions are estimated as follows:

$$x_{CO} = 0.599 \ , \qquad x_{O_2} = 0.299 \ , \qquad x_{CO_2} = 1$$

Clearly, the assumption that CO and O_2 are rare species was not very good. However, we can correct our estimate by rescaling the x_j so that they sum to unity,

$$x_{CO} = 0.316 \ , \quad x_{O_2} = 0.158 \ , \quad x_{CO_2} = 0.526$$

These estimates are within 10% of the exact values. An improvement can be obtained by iterating, using our revised estimate for x_{CO_2} in (3.9). The result is:

$$\lambda_C = -18.565 \ , \quad \lambda_O = -15.953$$

and these produce

$$x_{CO} = 0.390 \ , \quad x_{O_2} = 0.195 \ , \quad x_{CO_2} = 0.526$$

These renormalize to give

$$x_{CO} = 0.352 \ , \quad x_{O_2} = 0.175 \ , \quad x_{CO_2} = 0.473$$

The exact solution is

$$x_{CO} = 0.3582 \ , \quad x_{O_2} = 0.1791 \ , \quad x_{CO_2} = 0.4627$$

and so we see that with only two iterations we are very close.

The iterative process used here might be used as the basis for a numerical method for general problems. However, a general method must work irrespective of the structure of any particular problem, and thus the multi-phase, many-species problem presents a greater challenge. The numerical method that we have developed to meet this challenge is based on the dual problem developed in the following sections.

4. The Dual Problem

The objective is to solve Eqs. (2.11) and (2.12) to determine the a unknown element potentials and the p unknown phase mols. A convergent algorithm exists for this purpose, based on a related max-min problem (the "dual" problem). We define three functions of the element potentials and phase mols:

$$W = \sum_{m=1}^{p} \bar{N}_m (Z_m - 1) - \sum_{i=1}^{a} \lambda_i p_i \qquad (4.1)$$

$$Z_m = \sum_{\substack{j=1 \\ \text{in } m}}^{s} x_j \tag{4.2}$$

$$H_i = \sum_{j=1}^{s} \overline{N}_{(j)} n_{ij} x_j - p_i \tag{4.3}$$

where x_j is defined in terms of the λ_i by (2.9). Note that $Z_m = 1$ for all phases present in the system when (2.12) is satisfied, and $H_i = 0$ for all atoms i when (2.11) is satisfied. Differentiating $W(\underline{\lambda},\overline{N})$,

$$\frac{\partial W}{\partial \lambda_i} = H_i \tag{4.4}$$

$$\frac{\partial W}{\partial \overline{N}_m} = Z_m - 1 \tag{4.5}$$

so that

$$dW = \sum_{i=1}^{a} H_i d\lambda_i + \sum_{m=1}^{p} \left(Z_m - 1\right) d\overline{N}_m \tag{4.6}$$

Note that, at constant $\overline{N}_m$, W will be stationary $(dW = 0)$ with respect to arbitrary variations in the element potentials at any state for which the atomic constraints are satisfied $(H_i = 0)$.

We define

$$D_{im} = \sum_{\substack{j=1 \\ \text{in } m}}^{s} n_{ij} x_j \tag{4.7}$$

$$Q_{ik} = \sum_{j=1}^{s} \overline{N}_{(j)} n_{ij} n_{kj} x_j \tag{4.8}$$

Then

$$dZ_m = \sum_{i=1}^{a} D_{im} d\lambda_i \tag{4.9}$$

and

$$dH_i = \sum_{k=1}^{a} Q_{ik} d\lambda_k + \sum_{m=1}^{p} D_{im} d\overline{N}_m \tag{4.10}$$

The nature of the stationary point in W is revealed by

$$\frac{\partial^2 W}{\partial\lambda_i \partial\lambda_k} = \frac{\partial H_i}{\partial\lambda_k} = Q_{ik} > 0 \qquad (4.11)$$

Since $Q_{ii} > 0$, W is a minimum at the extremum, and W is a concave function of the element potentials. This means that the minimum W point, where the population constraints are satisfied for fixed phase mols, can be found by the method of steepest descent, in which we move down the path in λ space along which W decreases most rapidly, until we find the minimum point.

Now consider a path in $(\underline{\lambda}, \overline{\underline{N}})$ space along which the H_i all vanish. From (4.6), we see that W on this path is also stationary with respect to arbitrary variations $d\overline{N}_m$ when (2.12) is satisfied for all phases present. Along this path the λ_i are fixed by the $\overline{N}_m$, and we must consider this in the analysis.

Between any two states for which the H_i are zero, from (4.10),

$$\sum_{k=1}^{a} Q_{ik} d\lambda_k = - \sum_{m=1}^{p} D_{im} d\overline{N}_m \qquad (4.12)$$

This tells us how the W-minimizing λ_i will change when we change the $\overline{N}_m$. We define a matrix E_{im} such that

$$\sum_{k=1}^{a} Q_{ik} E_{km} = - D_{im} \qquad (4.13)$$

Then, between two nearby states where the H_i all vanish,

$$d\lambda_i = \sum_{m=1}^{p} E_{im} d\overline{N}_m \qquad (4.14)$$

Then, from (4.9), along the path of states where all $H_i = 0$ we have

$$dZ_m = \sum_{n=1}^{p} A_{mn} d\overline{N}_n \qquad (4.15)$$

where

$$A_{mn} = \sum_{i=1}^{a} D_{im} E_{in} \qquad (4.16)$$

Equation (4.16) tells how the Z_m change when we change the $\overline{N}_m$ along the path where all $H_i = 0$. Let $W^*(\overline{N})$ denote the value of W along such a path. Then, from (4.6),

$$\frac{\partial W^*}{\partial \overline{N}_m} = V_m \tag{4.17}$$

where

$$V_m = Z_m - 1 \tag{4.18}$$

Therefore, using (4.15),

$$\frac{\partial^2 W^*}{\partial \overline{N}_m \partial \overline{N}_n} = \frac{\partial Z_m}{\partial \overline{N}_n} = A_{mn} \tag{4.19}$$

Hence, using (4.16), (4.13), and (4.8),

$$\begin{aligned}\frac{\partial^2 W^*}{\partial \overline{N}_m \partial \overline{N}_m} &= \sum_{i=1}^{a} D_{im} E_{im} = -\sum_{i=1}^{a} \sum_{k=1}^{a} Q_{ik} E_{km} E_{im} \\ &= -\sum_{j=1}^{s} \sum_{i=1}^{a} \sum_{k=1}^{a} \overline{N}_{(j)} x_j n_{ij} n_{kj} E_{im} E_{km} \\ &= -\sum_{j=1}^{s} \overline{N}_{(j)} x_j \left(\sum_{i=1}^{a} n_{ij} E_{im} \right)^2 < 0\end{aligned} \tag{4.20}$$

Hence, W^* is a maximum at the stationary point; moreover, W^* is a convex function of the $\overline{N}_m$. This means that the method of steepest ascent, in which we move up the $W^*(\overline{N})$ surface along the most rapidly rising path, can be used to find the maximum.

Summarizing, W is a minimum for given phase mols at any state for which the atomic constraints are satisfied. We denote such states by W^*. W^* is in turn a maximum with respect to the phase mols when the mol-fraction-sum constraints are satisfied. These facts form the basis for a convergent solution algorithm.

At the equilibrium solution,

$$W^*_{max} = - \sum_{i=1}^{a} \lambda_i p_i \qquad (4.21a)$$

but, since λ_i is the G/RT per mol of i atoms,

$$W^*_{max} = - G/RT \qquad (4.21b)$$

The max-min problem for W is the "dual" of the Gibbs minimization problem, with the dual function W having physical significance only in the equilibrium state.

To help the reader understand this max-min problem, consider the one-species case; (2.9) becomes

$$x = e^{-\tilde{g}+n\lambda} \qquad (4.22)$$

and the atomic constraint is

$$\overline{N}\, n\, x = p \qquad (4.23)$$

For this case,

$$W = \overline{N}\left(e^{-\tilde{g}+n\lambda} - 1\right) - \lambda p \qquad (4.24)$$

At fixed $\overline{N}$, W is a concave function of λ, sketched in Fig. 4.1a. The atomic constraint (4.23) is satisfied when

$$\lambda = \frac{1}{n}\left[\tilde{g} + \ln\left(\frac{p}{nN}\right)\right] \qquad (4.25)$$

The path along which the constraints are satisfied is sketched in Fig. 4.1b. Thus,

$$W^* = \frac{p}{n} - \overline{N} - \frac{p}{n}\left[\tilde{g} + \ln\left(\frac{p}{\overline{N}n}\right)\right] \qquad (4.26)$$

W^* is sketched as a function of $\overline{N}$ in Fig. 4.1c. The maximum of W^* occurs when

$$\overline{N} = p/n \qquad (4.27)$$

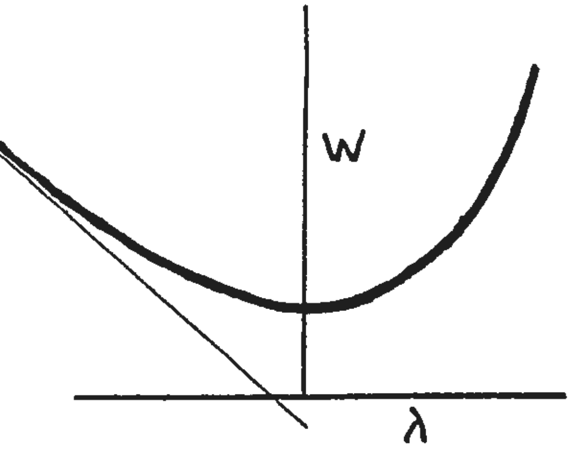

Figure 4.1a W at fixed $\overline{N}$

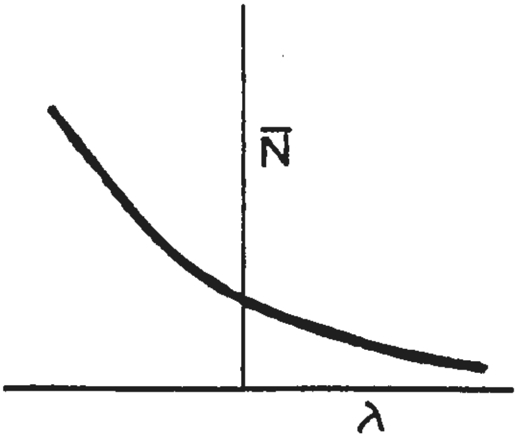

Figure 4.1b Path along which the population constraint is satisfied

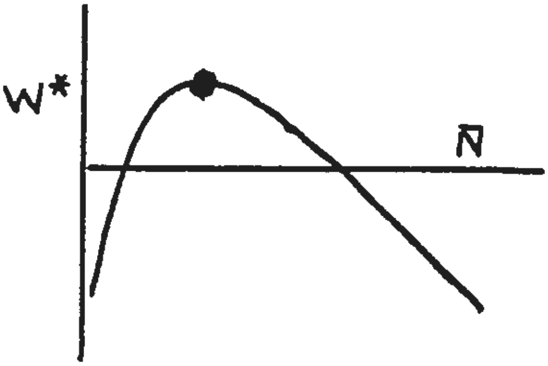

Figure 4.1c W* as a function of $\overline{N}$

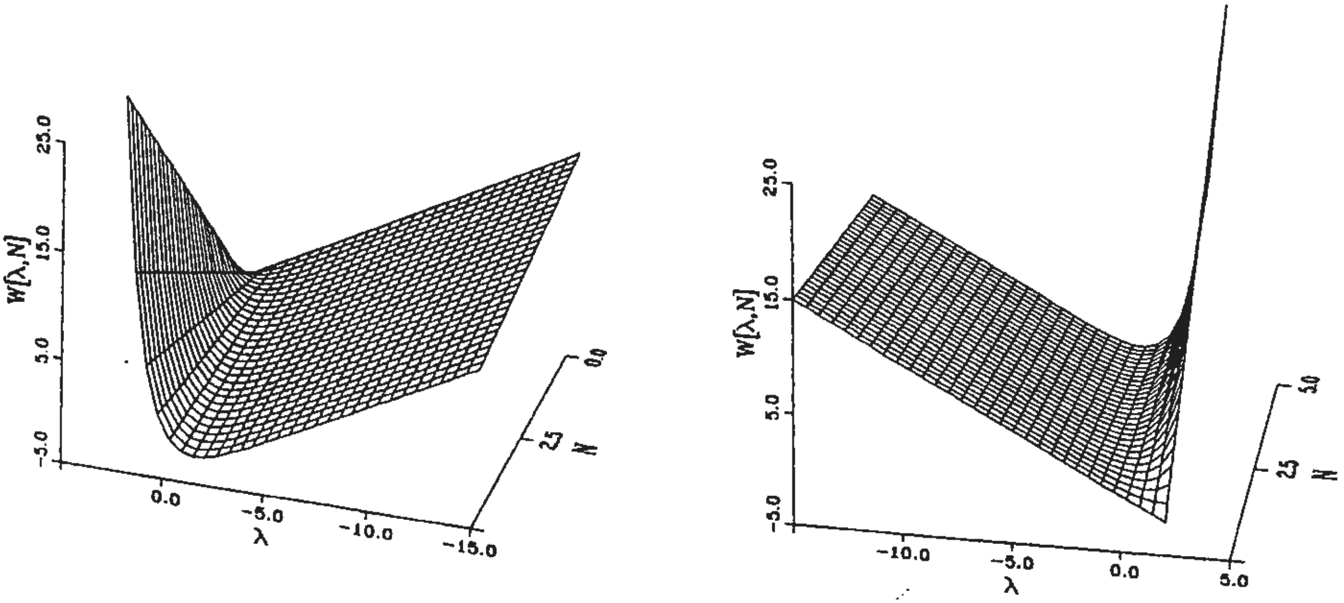

Figure 5.1 The W surface for $\tilde{g} = 0$, p = 1, n = 1

for which the element potential is, as expected,

$$\lambda = \frac{\tilde{g}}{n} \tag{4.28}$$

and the equilibrium value of W^* is

$$W^*_{max} = -\bar{N}\tilde{g} = -\bar{N}n\lambda \tag{4.29}$$

5. Dual-Problem Numerical Solution Details

The solution of the max-min problem proceeds in three modes. We shall first describe these graphically in terms of the previous example and its extension into more dimensions, and then present the analytical details.

The surface $W(\lambda,\bar{N})$, for $n = 1$, $p = 1$, $\tilde{g} = 0$, is shown in Fig. 5.1. One way to solve the problem is to march down the surface at constant $\bar{N}$ until the minimum point is reached. The loci of such minima define a road that leads up the valley to the saddle point, where the the equilibrium solution is located.

Imagine that this surface is a hillside. On the hillside, a hiker has the choice of going up or down, and he must go down in $\underline{\lambda}$ space to reach the minimum W at fixed $\bar{N}$. If there were two λ's instead of just one, his downhill path could be taken in many ways; the fastest way down is the "path of steepest descent". Once at the roadway, the hiker has a choice of up or down, and he must go up in $\bar{N}$-space to reach the point of maximum W^* where the phase-mol-sums are all unity. But he must stay on the road, where the population constraints are satisfied. He would have a choice of several uphill roads if there were more than one $\bar{N}$, and he should choose the road of steepest ascent in order to reach the summit most quickly. This is the basis for the numerical method for solution of the max-min problem for W; steepest descent variation of the element potentials at constant phase mols, followed by steepest-ascent variation of the phase mols while maintaining the atomic constraints.

At the bottom of the valley, where the terrain is flat, it is hard to tell which way is down; here steepest descent methods often have difficulty, or are slow; but Newton-Raphson methods work well when we are close to a solution. So we use steepest descent to get close, and Newton-Raphson to zoom to the minimum. The same basic procedure is applied ascending towards the top.

The phase mols are adjusted by steepest ascent until we are very near the solution, at which point a Newton-Raphson iteration is employed.

In a two-phase problem, the hiker could be going nicely uphill, reducing the mols of one phase, and run abruptly into a fence labeled, "No more mols--keep out of negative mol-land!" At this point our hiker must turn and follow the fence uphill, maintaining zero mols for this phase, until the path of steepest ascent leaves the fence. This is the basic method by which the solution process decides which phases are present. We shall now outline the mathematics of these processes.

Mode 1: Steepest Descent of W in λ Space at Fixed $\bar{N}$

If a segment of the descent path in λ space has length ds, then

$$d\lambda_i = f_i ds \tag{5.1}$$

and

$$\sum_{i=1}^{a} f_i f_i = 1 \tag{5.2}$$

Then,

$$\frac{dW}{ds} = \sum_{i=1}^{a} H_i f_i \tag{5.3}$$

where the f_i are the direction cosines for the descent path. To find the path of steepest descent, we seek the f_i that maximize dW/ds, subject to (4.23). Thus, we put

$$d\left(\frac{dW}{ds} - \frac{\beta}{2} \sum_{i=1}^{a} f_i f_i\right) = 0 \tag{5.4}$$

where $\beta/2$ is a Lagrange multiplier for the normalizing constraint (5.2). Hence, the steepest descent path is that for which

$$\sum_{i=1}^{a} \left(H_i - \beta f_i\right) df_i = 0 \tag{5.5}$$

for arbitrary df_i. Thus, the direction cosines for the path of steepest descent are given by

$$f_i = H_i/\beta \tag{5.6}$$

Then (5.2) gives

$$\sum_{i=1}^{a} H_i H_i = \beta^2 \tag{5.7}$$

so that

$$\frac{dW}{ds} = \sum_{i=1}^{a} H_i H_i/\beta = \beta \tag{5.8}$$

which must be negative for descent. Hence, from (5.7)

$$\beta = -\sqrt{\sum_{i=1}^{a} H_i H_i} \tag{5.9}$$

For a given set of phase mols and potentials, we calculate the H_i and determine the path of steepest descent towards the set of λ_i which, for the given phase mols, will render all of $H_i = 0$. The distance that we should go along this path is estimated using a Taylor series expansion of dW/ds,

$$\frac{dW}{ds} = \left.\frac{dW}{ds}\right|_o + \left.\frac{d^2W}{ds^2}\right|_o \Delta s + \ldots \tag{5.10}$$

Since we seek $dW/ds = 0$, using (5.8) and (4.4),

$$0 = \beta + \sum_{k=1}^{a} \frac{\partial}{\partial \lambda_k}\left(\frac{dW}{ds}\right)\frac{d\lambda_k}{ds} = \beta + \sum_{k=1}^{a}\sum_{i=1}^{a} \frac{\partial^2 W}{\partial \lambda_k \partial \lambda_i} f_i f_k \Delta s \tag{5.11}$$

So, using (4.11)

$$\Delta s = \frac{-\beta}{\sum_{k=1}^{a}\sum_{i=1}^{a} Q_{ik} f_i f_k} \tag{5.12}$$

Since the matrix Q_{ik} is determined by the current values of the phase mols and element potentials, the path of steepest descent and the trial step we should take down it are easily calculated. This method for adjusting the element potentials is denoted as mode 1 in STANJAN.

In mode 1, the first thing done after the various quantities have been evaluated for the new potentials is to examine the behavior of W on the old path of steepest descent. If the minimum point has been passed, then a "valley interpolation" is made using both the old state and the new state to estimate the location between them on the descent path where the minimum W point occurs. This interpolated state is then used to start a fresh descent. If the trial points are jumping back and forth across a valley, overshooting the minimum point, then "damping" is turned on, in which the step along the path is reduced from that estimated above. This allows the trial point to descend down a steep hillside and then turn to follow the gentler downflow of the valley towards the point of minimum W.

Mode 1 is very robust and will work effectively, even when the trial state is far from the state of minimum W. For example, convergence has been obtained in cases where the initial mol fraction sum Z was as large as 10^{17}! Improvements occur along the descent path at the rate of a decade or two per step, and it is not long before the errors in the H_i become quite small. At this point an adjustment is made in the phase mols, and the solution process continues.

Mode 2: Newton-Raphson Adjustment of the λ at Fixed $\overline{N}$

Near the point of minimum W, it becomes difficult to tell the direction of steepest descent, and instead a Newton-Raphson iteration is used to find the point where the H_i all vanish. Equation (4.10) becomes, for fixed phase mols,

$$\sum_{k=1}^{a} Q_{ik}\Delta\lambda_k = -H_i \tag{5.13}$$

This is solved to obtain the desired changes. This procedure is denoted as mode 2 in STANJAN. It is adopted whenever the $\underline{H}$ errors are suitably small, and abandoned in favor of mode 1 if the computed changes are too large.

Phase Mols Adjustments in Modes 1 or 2

After a set of λ_i rendering the H_i all zero (approximately) has been found for a given set of $\overline{N}_m$, we must adjust the $\overline{N}_m$ for maximum W^*. When the solution is not close, a steepest ascent method is used to adjust the $\overline{N}_m$.

Let r_m represent the direction cosines in $\underline{\bar{N}}$ space, and ds^* an element of the path along which we seek the maximum of W^*. Then

$$d\bar{N}_m = r_m ds^* \qquad (5.14)$$

$$\sum_{m=1}^{p} r_m r_m = 1 \qquad (5.15)$$

From (4.17),

$$\frac{dW^*}{ds^*} = \sum_{m=1}^{p} V_m r_m \qquad (5.16)$$

To find the path of steepest ascent, we seek the r_n that maximize dW^*/ds^*, subject to (5.15). Thus we set

$$d\left(\frac{dW^*}{ds^*} - \frac{\alpha}{2} \sum_{m=1}^{p} r_m r_m\right) = 0 \qquad (5.17)$$

where $\alpha/2$ is a Lagrange multiplier for the normalizing constraint (4.34). Hence, the steepest ascent path is that for which

$$\sum_{m=1}^{p} \left(V_m - \alpha r_m\right) df_m = 0 \qquad (5.18)$$

for arbitrary dr_m. Thus, the direction cosines for the path of steepest ascent are given by

$$r_m = V_m/\alpha \qquad (5.19)$$

Then (5.15) gives

$$\sum_{m=1}^{p} V_m V_m = \alpha^2 \qquad (5.20)$$

so that

$$\frac{dW^*}{ds^*} = \sum_{m=1}^{p} V_m V_m/\alpha = \alpha \qquad (5.21)$$

which must be positive for ascent. Hence, from (5.20)

$$\alpha = \sqrt{\sum_{m=1}^{p} V_m V_m} \qquad (5.22)$$

The distance that we must go along the path is estimated from a Taylor's series expansion of dW^*/ds^*.

$$\frac{dW^*}{ds^*} = \left.\frac{dW^*}{ds^*}\right|_o + \left.\frac{d^2W}{ds^{*2}}\right|_o \Delta s^* + \ldots \qquad (5.23)$$

Since we scale the point $dW^*/ds = 0$, using (5.21),

$$0 = \alpha + \sum_{n=1}^{p} \frac{\partial}{\partial \bar{N}_m}\left(\frac{dW^*}{ds^*}\right)\frac{d\bar{N}_m}{ds^*} = \alpha + \sum_{n=1}^{p}\sum_{m=1}^{p} \frac{\partial^2 W^*}{\partial \bar{N}_n \partial \bar{N}_m} r_n r_m \cdot \Delta s^* \qquad (5.24)$$

So, using (4.19),

$$\Delta s^* = \frac{-\alpha}{\sum_{n=1}^{p}\sum_{m=1}^{p} A_{nm} r_n r_m} \qquad (5.25)$$

This is used to estimate the distance along the path to the maximum W^* point. If this distance would produce negative phase mols, then the changes are reduced to prevent this occurrence. Limits placed on the changes, "ridge interpolation", oscillation damping, and other numerical tricks add to the robustness of the program.

If is the path of steepest ascent reaches a state where one $\bar{N}_m$ is zero, then that phase will be absent in the system, and the phase is dropped from the phase sums. A new path of steepest ascent is then computed, and a step towards the maximum of W^* is taken. The possibility of inactive phases becoming active is considered in each phase adjustment.

Mode 3: Newton-Raphson Adjustment of the λ and $\bar{N}$

When the atomic poulation errors are small and the mol fraction sums for all active phases are very nearly unity, a Newton-Raphson scheme is used to adjust the λ_i and $\bar{N}_m$ simultaneously. The equation system (4.9), (4.10) is used to calculate the changes necessary to bring all H_i to zero and all Z_m

to unity. This mode is adopted whenever the solution is very near and abandoned whenever the changes it requests are too large. This mode is always the last mode used before a converged solution; it is called Mode 3 in STANJAN.

Accuracy and Convergence

The element potentials and phase mols are adjusted to accuracy of 1 part in 10^8, and the mol fraction sums are made unity to 1 part in 10^{10}. This accuracy is maintained, even in nearly singular cases, with the help of the matrix conditioning procedure described below.

On an IBM-PC, mol fractions as small as 10^{-300} are displayed. On most mainframes the mol fractions can be no smaller than 10^{-68}. Thus, more acccurate results can actually be obtained in some problems using the smaller desktop computers!

6. Independent Atoms, Basis Species, and Matrix Conditioning

In some syatems the atoms are not independently variable; for example, in a system consisting of CO, COS, and S, the atoms C and O are not independently variable. In order to avoid singular matrices in the solution, we must work only with the independent atoms. These are identified in the STANJAN initializer, described below. The atom sums above are then carried out only over the independent atoms, and only the element potentials of independent atoms are computed.

In any system there will be a small set of base species which together could contain all of the atoms. While there is one base species per independent atom, there need not be a one-to-one correspondence between the independent atoms and base species. Usually there are many possible sets of base species; the most useful are those that dominate the system, and the STANJAN initializer identifies these. For example, in a system containing a mixture of CO, CO_2, O_2, and C(S) at 3000°K and 1 atm, with a C:O ratio of 2:1, the base species will be C(S) and CO (see example in Section 3).

The base species play a key role in obtaining accurate solutions when the matrices are nearly singular. This is accomplished by a process we call matrix conditioning, an idea closely related to the balancing concept used in the second example of Section 3. For example, consider a system containing

CO, CO_2, and O_2, with a C:O ratio of 1:2, at a low temperature. The system will consist almost entirely of CO_2, and the population equations will be

$$N_{CO_2} + N_{CO} = 1 \tag{6.1}$$

$$2N_{CO_2} + N_{CO} + 2N_{O_2} = 2 \tag{6.2}$$

Since N_{CO} and N_{O_2} are both very small, these two equations are very nearly the same, i.e., the system is very nearly linearly dependent. Conditioning removes this difficulty.

We need to solve equations of the form

$$\sum_{i=1}^{a} Q_{ik}X_k = Y_i \tag{6.3}$$

where X_k denotes the solution vector and Y_i the right-hand side (see (4.19) and (4.21)). The Q_{ik} matrix associated with this system is

$$Q_{ik} = \bar{N}\begin{bmatrix} x_{CO_2} + x_{CO} & 2x_{CO_2} + x_{CO} \\ 2x_{CO_2} + x_{CO} & 4x_{CO_2} + x_{CO} + 4x_{O_2} \end{bmatrix} \tag{6.4}$$

because $x_{CO_2} \simeq 1$, and the other x_j are very small, this matrix is very nearly singular, and hence the solutions of (4.13) and (5.13) are very hard to construct accurately.

The idea of matrix conditioning is to form linear combinations of the equations that remove all but one base species from each equation. This is equivalent to multiplying the (6.4) by a conditioning matrix C_{ni}; this produces

$$\sum_{i=1}^{a}\sum_{k=1}^{a}\sum_{j=1}^{s} C_{ni}\,\bar{N}_{(j)}\,n_{ij}\,n_{kj}\,x_j\,X_k = \sum_{i=1}^{a} C_{ni}Y_i \tag{6.5}$$

Now, for the n^{th} equation, we select C_{ni} such that the only base species retained is the n^{th};

$$\sum_{i=1}^{a} C_{ni} n_{ij} = \begin{cases} 1 & \text{if } j \text{ is the } n^{th} \text{ base species,} \\ 0 & \text{if } j \text{ is any other base species.} \end{cases} \tag{6.6}$$

Then, instead of solving (6.4), we solve the conditioned equations

$$\sum_{k=1}^{a} Q^{*}_{ik} X_k = Y^{*}_{i} \tag{6.7}$$

where the conditioned matrix and right-hand side are

$$Q^{*}_{ik} = \sum_{n=1}^{a} C_{in} Q_{nk} \tag{6.8}$$

$$Y^{*}_{i} = \sum_{k=1}^{a} C_{ik} Y_k \tag{6.9}$$

In the C-O example above, we take CO_2 and O_2 as the base species. The first equation does not contain the base O_2, and hence is already conditioned. The second conditioned equation is formed by subtracting the first of (6.3) from half of the second. Thus, the two conditioned equations are

$$(N_{CO_2} + N_{CO})X_1 + (2N_{CO_2} + N_{CO})X_2 = Y_1 \tag{6.10}$$

$$(-N_{CO})X_1 + (2N_{O_2} - N_{CO})X_2 = - Y_1 + \frac{1}{2} Y_2 \tag{6.11}$$

This pair of equations will be linearly independent and will yield accurate numerical results, even when the mols of CO and O_2 are very small.

STANJAN computes Q_{ik} exactly, so that the base species vanish completely from other than their own equations. The conditioned versions of equations (4.19-4.21) are solved, rather than the primitive equations. The bases are reviewed and changed if necessary whenever a phase appears or disappears during the solution, and a new conditioning matrix is calculated.

This matrix conditioning allows STANJAN to solve accurately, even when two original equations differ by as little as one part in 10^{20} or more! The matrix-conditioning process is also used in the phase-redistribution process in the initializer (Section 7) to help maintain high accuracy in nearly singular systems.

The population equations may also be conditioned, producing

$$\sum_{k=1}^{a} \sum_{j=1}^{s} C_{ik} \overline{N}_{(j)} n_{kj} x_j = \sum_{k=1}^{a} C_{ik} p_k = p_i^* \tag{6.12}$$

Note that, by (6.6), all but one of the base species drop out from each of these conditioned population equations. For example, the conditioning of Eqs. (6.1) and (6.2) produces

$$N_{CO_2} + N_{CO} = 1 \tag{6.13}$$

$$-\frac{1}{2} N_{CO} + N_{O_2} = 0 \tag{6.14}$$

The right-hand sides of these equations (the "conditioned populations") are just the mols of the base species, and this fact is used to compute the conditioned populations. The balancing procedure described in Section 3 is required whenever one of the conditioned populations p_i^* is zero, and the conditioned population equation provides this balance. Note that (6.14) is the balance equation (3.7).

7. Initialization

The solution requires an initial guess, and a good guess leads to a fast solution. The STANJAN initializer is one of the most important reasons for its success in treating general problems. Problems that could not be initialized by early STANJAN versions now run nicely, and problems that took dozens of iterations are now initialized so well that only a few iterations are required. Thus, the STANJAN initializer may be of considerable interest to those who prefer to use other methods for equilibrium solution.

The basic idea of the initializer is to create an approximate distribution of the atoms from which the phase mols and mol fractions of key species can be estimated. These estimated mol fractions are then used to estimate the element potentials, in much the same way as the examples in Section 3. The initializer does this in a way that works for an arbitrary problem.

The initializer begins by distributing the system atoms to a set of base species in a way that makes an approximate Gibbs function as small as possible. This approximate Gibbs function is that obtained by neglecting the $\ln x_j$ corrections to the Gibbs functions (see 2.2). The initializer minimizes

$$\frac{G^*}{RT} = \sum_{j=1}^{s} \tilde{g}_j N_j \tag{7.1}$$

subject to the atomic constraints (2.3) and to the constraints

$$N_j \geq 0 \quad , \qquad j = 1, \ldots , s \tag{7.2}$$

This minimization problem is a classic problem in linear programming, and is solved by the simplex method. Because the simplex method may not be familiar to readers, a brief description of it is given here; for more detail see Appendix B, and for a full account see Veinott[6].

The theorems of linear programming show that the solution will be one where only a small set of species have non-zero mols (in the approximation (7.1)). At each step in the simplex process one has identified a set of "base species" that contain the atoms, with all other species having zero mols. The simplex process is a base-species-replacement process in which the function to be minimized is continually reduced by changing the base species set until no further reductions are possible. There are always as many base species as there are independent atoms in the system, and the base species mols together contain all of the atoms.

The process begins by placing all atoms in "false" monatamic species. The atoms are transferred to the real species by a simplex minimization of the total number of false mols. Important conclusions are drawn at the end of this simplex process. If it is impossible to eliminate the false species, then the assigned populations were impossible. If a false species remains as a base with zero mols, then that atom is not linearly independent in the system. This is the process by which independent atoms are identified.

Once the atoms are placed in real species, the simplex minimization process continues until no further reduction in G^* can be achieved. The dominant species are then identified as the base species; the mols of all other species are zero at this point. The conditioning matrix is calculated for this set of base species.

The initial distribution of atoms to the base species allows estimation of the phase mols and mol fractions of the base species, with one base species per independent atom. In order to estimate the element potentials, one linear equation in the element potentials must be obtained for each independent atom in the system (i.e., for each base species). For each base there are two primary possibilities:

i) If the estimated mol fraction is greater than zero, this value is used to derive one linear equation relating the element potentials (see examples in Section 3).

ii) If the base species was estimated to have zero mols, then the dominant balancing species is identified. The balancing species is a secondary species that appears in the conditioned population equation with a negative coefficient; the one with the largest expected mol fraction is chosen as the dominant balancing species. Four possible events are then possible:

a) If no balancing species can be found, then the species is excluded and the initialization is repeated.

b) If the balancing species is in the same phase as the zero-mols base species, then the balance equation is used to derive a linear equation relating the potentials (see example in Section 3). If the phase has zero mols, the "phase-redistribution" flag is set.

c) If the balancing species is in another phase, then the other zero-mols base species are examined and the bases are reordered so that the dominant zero-mols base is considered first.

d) If the zero-mols base is the dominant zero-mols base in a phase containing zero mols, then its mol fraction is set to unity and this value is used to derive a linear equation relating the element potentials, and the phase-redistribution flag is set.

The conditioning matrix is recomputed whenever the bases are changed. These processes produce a set of linear algebraic equations, which is solved for the estimated element potentials.

In determining the balancing species, estimates of the element potentials are used to estimate the species mol fractions. The simplex Lagrange multipliers themselves provide the first estimates of the element potentials for purposes of selecting the balancing species. Then, after a set of element potentials has been obtained from the process described above, the selection of balancing species is repeated using these potentials, and different balancers are chosen if appropriate. Thus, the final element potentials are consistent with the choices of balancing species used to generate them.

If the phase redistribution flag was set by the element potential estimating process described above, then it is necessary to redistribute the atoms to populate an empty phase. The idea is to redistribute so that the balancing species are present in about the right amount, which will force the species that they balance to be present. The first step is to estimate the mol fractions of the balancing species using the estimated element potentials. Then the atoms are redistributed amongst the set of species consisting of the original base species plus the balancing species, seeking to bring the mol fractions of the balancing species as close to their targets as possible. This is accomplished by a second simplex calculation in which the sum of the differences between the target mol fractions and actual mol fractions is minimized, subject to the atomic constraints, to the constraint that all mols must be non-negative, and to the constraint that the target mol fraction can not be exceeded. Usually these targets are met precisely. The net effect is that approximately the right number of atoms are put into the phases which, on first estimation, had zero mols. This intricate simplex process is described in more detail below.

If a phase redistribution is required, the element potentials are reestimated using the revised mol distribution, following the procedure described above. On each pass the base set is checked to see that they are the dominant species, and if necessary bases are changed. Thus, at the end the phase mols and element potentials are all based on a consistent set of dominant species. These initial estimates of the phase mols and element potentials will generate approximately the correct mol fractions, and so the equilibrium solution by the method described in Section 5 usually converges to high accuracy in just a few iterations.

When running a sequence of calculations involving the same species and atomic populations at nearby states, the full initialization process is avoided. The mol fractions of the base species from the previous run are instead used to estimate the element potentials, and the phase mols of the previous run are used. STANJAN also provides the option of freezing the composition, and these runs do not require initialization or equilibrium solution.

The phase-redistribution simplex process uses the variables

$$y_j = -N_j + \overline{N}_{(j)} x_j^* \quad \text{(balancers)} \tag{7.3a}$$

for the balancing species assigned target mol fractions x_j^*, and

$$y_j = N_j \quad \text{(bases)} \tag{7.3b}$$

for the base species. Equation (7.3a) is rewritten as

$$y_j = x_j^* \left(\sum_{\substack{j'o \\ \text{in } (j)}} y_{j'} + \sum_{\substack{j''b \\ \text{in } (j)}} N_{j''} \right) - N_j \tag{7.4}$$

where the sum over $j'o$ denotes a sum over the base species, and $j''b$ denotes a sum over the balancing species, in the phase of balancing species j. The set of (7.4) for the balancing species (there may be more than one) is inverted to give, for the balancing species,

$$N_j = \sum_{j''b} T_{jj''} y_{j''} + \sum_{j'o} B_{jj'} y_{j'} \quad \text{(balancers)} \tag{7.5a}$$

where $j''b$ denotes a sum over balancing species and $j'o$ denotes a sum over base species and $\underline{T}$ and $\underline{B}$ result from the inversion. Then, for the base species,

$$N_j = y_j \quad \text{(bases)} \tag{7.5b}$$

Equations (7.5) allow expression of the N_j in terms of the simplex variables y_j. The atomic constraints (2.3) can then be expressed in the form

$$\sum_{jbo} R_{ij} y_j = p_i \quad , \quad i = 1, \ldots , a \tag{7.6}$$

where jbo denotes a sum over all variables in this simplex problem (the base and balancing species); R_{ij} is computed from $T_{jj''}$, $B_{jj'}$, and n_{ij}. Finally, the simplex variables also satisfy

$$y_j \geq 0 \quad \text{for all } j \tag{7.7}$$

Note that (7.7) keeps the balancing mol fractions no greater than their targets.

The simplex process is initiated by establishing a feasible set using additional false monatomic species having $y_j = N_j$ and minimizing the sum of the false mols, subject to the constraints. Then the problem described above is solved.

In order to improve the accuracy in nearly singular problems, the atomic constraint equations (7.6) are multiplied by the conditioning matrix C_{ik} discussed in Section 6. In some problems with very rare balancing species, the constraint equations may not be very well satisfied after some simplex base change. A correction is then made. The approach is to select the constraint equation best satisfied, and then to treat that simplex base as a known quantity in a smaller set of equations for the other simplex bases. The net result is a remarkable increase in accuracy.

In summary, the initializer is a sophisticated program that makes a very good guess as to the distribution of atoms to dominant species and phases in the system. It possesses remarkable accuracy in very-nearly-singular situations. The importance of the initializer cannot be overemphasized.

8. Examples

a) Carbon-Rich C-O System

The first example involves a carbon-rich mixture of CO, CO_2, O_2, and O, with the possibility of a solid carbon phase. The full output log of this run is presented to give the reader a flavor of STANJAN. The user begins by calling STANJAN. After an opening opportunity to see a brief description of the element potential method, the dialog begins. The user's responses are underlined in the log in Fig. 8.1. The margin numbers refer to the notes that follow. This example is similar to the first two examples in Section 3, and the reader may find it useful to make the comparison.

1) Note that the first step is to get the data for the species to be used. In this case the user selects the general-purpose combustion file COMB.DAT, from which he selects the desired species. When running a lot of problems with the same species, it is faster to first use the program JANNFILE to set up a data set containing only the desired species, and then use the single-keystroke defaults * and # to make the phase selection from this species set.

2) In this example the user had made a previous run with the same atoms, and so is given a choice of using the same populations or making a setup change. In the first run STANJAN offered two ways to specify the atom

populations, either by giving them directly or by naming some reactants in the data file and then specifying the number of mols of each put into the system.

3) The isentropic sound speed, defined as

$$c = \sqrt{\left(\frac{\partial P}{\partial \rho}\right)_s} \tag{8.1}$$

is calculated. Equilibrium states will be used to calculate c unless the frozen composition option is selected, in which case it becomes the sound speed with frozen chemistry.

4) STANJAN includes an optional instructive monitor, which can be used to learn about the method. It is included here to display the features of the initializer and dual problem solution described in previous sections.

5) This is what the user would have seen had he chosen to check the atomic composition.

6) These are the properties as computed from the JANNAF table data.

7) The initializer first finds that CO will be the dominant species. The balancing requires the presence of CO_2, in the amount estimated. The initializer then redistributes the atoms to the phases to provide the target mol fraction of the balancing species CO.

8) Note how close the solution is after the initialization. Only two iterations are required to reach a solution accurate in mol fractions to one part in 10^8.

9) These are the data taken from the JANNAF tables.

10) This is the primary output.

Figure 8.1 Example run log for carbon-rich C-O system

1)

```
You may now select a species data file.  The file  COMB.DAT  contains a set
of species for combustion analysis.  Just <return> if no file is desired.

  Species data file?  COMB.DAT

Getting species data file COMB.DAT                              PLEASE WAIT!
C
C(S)
CH4
CO
CO2
H
H2
H2O
H2O(L)
HO
N
N2
NO
NO2
O
O2

Species data file: COMB.DAT

 C          C(S)       CH4        CO         CO2        H          H2         H2O
 H2O(L)     HO         N          N2         NO         NO2        O          O2

Type the species in phase  1, separated by commas.  When typing
file species above, be sure to use EXACTLY the same characters.
If you enter other species you will need their thermochemical data.
Type * to include all gas species above,  # for all condensates.
Just <return> if you are finished specifying phases.


CO,CO2,O,O2

Type the species in phase  2, separated by commas.  When typing
file species above, be sure to use EXACTLY the same characters.
If you enter other species you will need their thermochemical data.
Type * to include all gas species above,  # for all condensates.
Just <return> if you are finished specifying phases.

C(S)

Type the species in phase  3, separated by commas.  When typing
file species above, be sure to use EXACTLY the same characters.
If you enter other species you will need their thermochemical data.
Type * to include all gas species above,  # for all condensates.
Just <return> if you are finished specifying phases.

 _


Do you want to CHECK the ATOMS in the molecules? N

<return> may be used for "no"
```

(continued)

Figure 8.1 (continued)

```
    The mixture has the SAME ATOMS as in the last run.

2)  This is the CURRENT SETUP:

    Phase  1 species:
     CO         CO2        O          O2
    Phase  2 species:
     C(S)

    Atom   relative population
      C        1.00000000E+00
      O        1.00000000E+00

    Do you want to make any SETUP CHANGES? N

    <return> may be used for "no"


    Run mode options:

      0    Abort and redo setup
      1    Specified T and P
      2    Specified T and V
      3    Specified T and S
      4    Specified P and V
      5    Specified P and H
      6    Specified P and S
      7    Specified V and U
      8    Specified V and H
      9    Specified V and S
     10    A matrix of specified P,T cases (LOTUS file option)
     11    P and H same as last run
     12    V and U same as last run
     13    Specified T, S same as last run
     14    Specified P, S same as last run
     15    Specified V, S same as last run
     16    One of the above at a specified frozen composition

    Enter run mode option: 1

    Enter T (K): 3000

    Enter P (atm): 1

3)  The sound speed can be calculated, but then the calculations take longer.

    Do you want the SOUND SPEED? __

    Do you want to SAVE the run OUTPUT in a file? __

4)  Do you want to MONITOR the run (probably not)? Y

    Monitor levels:
      0 none
      1 (T,P) state iteration monitor
      2 method instruction monitor
      3-9 trouble diagnostic monitor
    Monitor level? 2

    Do you want the MONITOR OUTPUT in a FILE? __
```

(continued)

Figure 8.1 (continued)

```
    Start of run monitor output

5)  Atomic compositions:

                C   O
    CO          1   1
    CO2         1   2
    O           0   1
    O2          0   2
    C(S)        1   0

6)  Properties for T = 3000.000 K,  P =  1.0133E+05 Pa
    species       h, kcal/mol     s, cal/mol-K       g/RT
    CO               -4.063          65.370         -33.578
    CO2             -57.519          79.848         -49.830
    O                73.081          50.096         -12.951
    O2               23.446          67.973         -30.273
    C(S)             14.412          12.129          -3.686

    Initialization:

    Independent atom    population
                 C       1.00000E+00
                 O       1.00000E+00

    Estimated distribution:
      Phase  1 mols = 1.00000E+00
7)    Phase  2 mols =  .00000E+00
             CO          CO2          O            O2           C(S)
      mols: 1.00000E+00  .00000E+00  .00000E+00  .00000E+00  .00000E+00
         X:  .10000E+01  .00000E+00  .00000E+00  .00000E+00  .00000E+00

    Phase redistribution:
      Target mol fraction =  .11932E-05 for CO2

    Estimated distribution:
      Phase  1 mols = 9.99999E-01
      Phase  2 mols = 1.19321E-06
             CO          CO2          O            O2           C(S)
      mols: 9.99998E-01 1.19321E-06  .00000E+00  .00000E+00 1.19321E-06
         X:  .10000E+01  .11932E-05  .00000E+00  .00000E+00  .10000E+01

8)   Equilibrium solution monitor:

     EQUIL pass   1;   dual function W =  3.457765381675E+01
       phase  1 mols = 9.99998807E-01;  mol fraction sum Z =  1.00000043932E+00
       phase  2 mols = 1.19320842E-06;  mol fraction sum Z =  1.00000000000E+00
       element potential for C  = -3.6861558095 40E+00; population error = -2.845E-12
       element potential for O  = -2.9891497963 28E+01; population error =  4.393E-08
             CO           CO2          O            O2           C(S)
        X:  .10000E+01  .11932E-05  .43935E-07  .15276E-12  .10000E+01
     Element potentials and phase mols adjusted by Newton-Raphson

     EQUIL pass   2;   dual function W =  3.4577653860 69E+01
       phase  1 mols = 9.99998807E-01;  mol fraction sum Z =  1.00000000000E+00
       phase  2 mols = 1.23714086E-06;  mol fraction sum Z =  1.00000000000E+00
       element potential for C  = -3.686155809540E+00; population error =  1.281E-15
       element potential for O  = -2.989149800721E+01; population error =  1.281E-15
             CO           CO2          O            O2           C(S)
        X:  .10000E+01  .11932E-05  .43935E-07  .15276E-12  .10000E+01
     Element potentials and phase mols adjusted by Newton-Raphson

     Final distribution:
             CO           CO2          O            O2           C(S)
       mols: 9.99998E-01 1.19321E-06 4.39351E-08 1.52763E-13 1.23714E-06


     End of run monitor output
```

(continued)

Fig 8.1 (concluded)

```
    OUTPUT READY. Note: <ctrl-s> stops/starts IBM-PC display.

    Do you want to see the JANNAF data used? Y_

    On IBM-PC, use <ctrl-PrtSc> to start printer (optional). __
    Please press <return> to continue. __

9)  JANNAF table data:                        For T = 3000.00 K
    species      mol. mass  enth. form      SO          H-HO
                   g/mol     kcal/mol    cal/mol-K    kcal/mol
    Phase  1;  Gas species:
    CO           28.01054     -26.420      65.370       22.357
    CO2          44.00995     -94.054      79.848       36.535
    O            16.00000      59.559      50.096       13.522
    O2           31.99879        .000      67.973       23.446
    Phase  2;  Condensed species:                                   Density, g/cc
    C(S)         12.01100        .000      12.129       14.412          2.700

10) Independent        relative          element
    system atom       population        potential
         C          1.00000000E+00        -3.6862
         O          1.00000000E+00       -29.8915

    Composition at T =   3000.00 K    P =  1.000E+00 atmospheres
     species          mol fraction    mol fraction     mass fraction       mols*
                      in the phase    in mixture       in mixture
    Phase  1:  Molal mass, g/mol =    28.011
     CO                .10000E+01      .10000E+01       .10000E+01      9.99998E-01
     CO2               .11932E-05      .11932E-05       .18748E-05      1.19321E-06
     O                 .43935E-07      .43935E-07       .25096E-07      4.39351E-08
     O2                .15276E-12      .15276E-12       .17451E-12      1.52763E-13
    Phase  2:  Molal mass, g/mol =    12.011
     C(S)              .10000E+01      .12371E-05       .53049E-06      1.23714E-06

    * Species mols for the atom populations in mols.

    Mixture properties:   molal mass =   28.011 kg/kmol
       T = 3000.000 K            P = 1.0133E+05 Pa      V = 8.7884E+00 m**3/kg
       U =-1.4974E+06 J/kg       H =-6.0691E+05 J/kg    S = 9.7645E+03 J/kg-K

    Made  0 (T,P) iterations;   2 EQUIL iterations.


    On IBM-PC, use <ctrl-PrtSc> to stop printer (optional).
    Please press <return> to continue. __
```

b) Example with Two Complex Phases

The next example is taken from the field of fiber optics manufacture. It involves a complex set of species in the gas phase, and a condensed phase, treated here as an ideal solution. The JANNAF data and operating conditions were provided to the author by the AT&T Bell Laboratories. For brevity only the final output is given in Fig. 8.2. Note that only five iterations were required.

c) Gas Turbine Engine Example

This example shows how STANJAN can be used to calculate the adiabatic flame temperature in a gas turbine engine combustor, and then the composition after isentropic expansion in the turbine nozzle.

The first step is to get the enthalpy of the reactants by a run at the combustor inlet state. Here we took $T = 400°K$, $P = 6$ atm, and assumed that the reactants were

$$CH_4 + 2O_2 + 7.52\ N_2$$

The results are shown in Fig. 8.3.

The next step is to get the adiabatic flame temperature by finding the state of the products at the same enthalpy and pressure as the last run. The reactants and a set of products are allowed species. The results are shown in Fig. 8.4.

The final step is to get the temperature following isentropic expansion in the turbines by finding the equilibrium state for the same species at the same entropy and a specified pressure (here 1 atm.). The results are given in Fig. 8.5.

Figure 8.2 Output for example with two complex phases

```
Independent        relative           element
system atom       population         potential
     Ar         1.00000000E-01        -25.7075
     Cl         6.06000000E+00        -16.2887
     O          2.88340000E+01        -14.1651
     Si         1.00000000E+00        -50.0253
     Ge         5.15000000E-01        -43.8678
     P          2.30000000E-02        -37.3859

Composition at T =    1650.00 K     P =  1.000E+00 atmospheres
 species          mol fraction    mol fraction     mass fraction       mols*
                  in the phase     in mixture       in mixture
Phase  1:  Molal mass, g/mol =    38.255
 Ar                .59712E-02      .54758E-02       .52939E-02       1.00000E-01
 Cl                .56748E-01      .52040E-01       .44650E-01       9.50359E-01
 ClO               .10439E-02      .95729E-03       .11920E-02       1.74821E-02
 Cl2               .15201E+00      .13940E+00       .23921E+00       2.54579E+00
 Cl4Si             .47293E-07      .43370E-07       .18882E-06       7.92022E-07
 GeO               .17976E-10      .16484E-10       .35342E-10       3.01041E-10
 GeO2              .13847E-12      .12698E-12       .32141E-12       2.31896E-12
 O                 .22737E-04      .20851E-04       .80737E-05       3.80779E-04
 O2                .78362E+00      .71861E+00       .55651E+00       1.31233E+01
 OSi               .82707E-12      .75845E-12       .80921E-12       1.38510E-11
 O2Si              .95361E-10      .87450E-10       .12869E-09       1.59701E-09
 Cl4Ge             .28651E-08      .26274E-08       .13593E-07       4.79825E-08
 Cl3OP             .11617E-04      .10653E-04       .39530E-04       1.94545E-04
 OP                .15489E-08      .14204E-08       .16140E-08       2.59397E-08
 O2P               .31089E-03      .28510E-03       .43449E-03       5.20647E-03
 O10P4             .26269E-03      .24090E-03       .16550E-02       4.39927E-03
 ClGe              .17509E-13      .16057E-13       .41983E-13       2.93228E-13
Phase  2:  Molal mass, g/mol =    75.214
 GeO2(1)           .33993E+00      .28201E-01       .71380E-01       5.15000E-01
 O2Si(1)           .66007E+00      .54758E-01       .79626E-01       9.99999E-01
 O3P(1)            .12491E-05      .10362E-06       .19804E-06       1.89240E-06

* Species mols for the atom populations in mols.

Mixture properties:   molal mass =   41.321 kg/kmol
   T = 1650.000 K          P = 1.0133E+05 Pa      V = 3.0048E+00 m**3/kg
   U =-5.4778E+05 J/kg     H =-2.4331E+05 J/kg   S = 6.2782E+03 J/kg-K

Made  0 (T,P) iterations;   5 EQUIL iterations.
```

Figure 8.3 First step in the turbine example:

Calculation of the enthalpy of the reactants

```
Independent       relative          element
system atom      population        potential
     H         4.00000000E+00       -11.4094
     O         4.00000000E+00       -12.3340
     N         1.50400000E+01       -10.8571

 Dependent
system atom
     C         1.00000000E+00

Composition at T =    400.00 K    P =  6.000E+00 atmospheres
 species        mol fraction    mol fraction    mass fraction     mols*
                in the phase     in mixture      in mixture
Phase  1:  Molal mass, g/mol =   27.633
 CH4             .95057E-01      .95057E-01      .55187E-01     1.00000E+00
 O2              .19011E+00      .19011E+00      .22015E+00     2.00000E+00
 N2              .71483E+00      .71483E+00      .72466E+00     7.52000E+00

* Species mols for the atom populations in mols.

Mixture properties:   molal mass =   27.633 kg/kmol
   T =  400.000 K          P = 6.0795E+05 Pa     V = 1.9796E-01 m**3/kg
   U =-2.6694E+05 J/kg     H =-1.4659E+05 J/kg   S = 7.0201E+03 J/kg-K

Made  O (T,P) iterations;   1 EQUIL iterations.
```

Figure 8.4 Second step in the turbine example:

Calculation of the adiabatic flame temperature

```
Independent         relative              element
system atom        population            potential
      C          1.00000000E+00           -20.4676
      H          4.00000000E+00           -11.9990
      O          4.00000000E+00           -16.5667
      N          1.50400000E+01           -12.9931

Composition at T =    2316.31 K     P =  6.000E+00 atmospheres
 species          mol fraction    mol fraction     mass fraction       mols*
                  in the phase    in mixture        in mixture
Phase  1:  Molal mass, g/mol =   27.466
 C                 .55358E-16      .55358E-16       .24209E-16      5.85920E-16
 CH4               .25808E-15      .25808E-15       .15074E-15      2.73153E-15
 CO                .75620E-02      .75620E-02       .77120E-02      8.00375E-02
 CO2               .86918E-01      .86918E-01       .13927E+00      9.19962E-01
 H                 .22987E-03      .22987E-03       .84361E-05      2.43302E-03
 H2                .28857E-02      .28857E-02       .21181E-03      3.05426E-02
 H2O               .18475E+00      .18475E+00       .12118E+00      1.95542E+00
 HO                .24233E-02      .24233E-02       .15006E-02      2.56492E-02
 N                 .15822E-07      .15822E-07       .80693E-08      1.67459E-07
 N2                .70944E+00      .70944E+00       .72358E+00      7.50883E+00
 NO                .21100E-02      .21100E-02       .23053E-02      2.23330E-02
 NO2               .67724E-06      .67724E-06       .11345E-05      7.16807E-06
 O                 .13180E-03      .13180E-03       .76780E-04      1.39501E-03
 O2                .35539E-02      .35539E-02       .41404E-02      3.76148E-02
Phase  2:  Molal mass, g/mol =     .000
 H2O(L)            .00000E+00      .00000E+00       .00000E+00       .00000E+00
Phase  3:  Molal mass, g/mol =     .000
 C(S)              .00000E+00      .00000E+00       .00000E+00       .00000E+00

* Species mols for the atom populations in mols.

Mixture properties:   molal mass =   27.466 kg/kmol
   T = 2316.309 K          P = 6.0795E+05 Pa      V = 1.1534E+00 m**3/kg
   U =-8.4777E+05 J/kg     H =-1.4659E+05 J/kg    S = 9.3791E+03 J/kg-K

Made  4 (T,P) iterations;  25 EQUIL iterations.
```

Figure 8.5 Third step in the turbine example:

Calculation of the nozzle exit state

```
Independent        relative           element
system atom       population          potential
     C          1.00000000E+00         -24.7380
     H          4.00000000E+00         -13.7096
     O          4.00000000E+00         -18.3106
     N          1.50400000E+01         -13.3409

Composition at T =   1674.93 K     P =  1.000E+00 atmospheres
 species         mol fraction    mol fraction    mass fraction       mols*
                 in the phase     in mixture      in mixture
Phase  1:  Molal mass, g/mol =   27.625
 C                 .15608E-23      .15608E-23      .67862E-24     1.64248E-23
 CH4               .93925E-20      .93925E-20      .54545E-20     9.88372E-20
 CO                .33225E-03      .33225E-03      .33688E-03     3.49629E-03
 CO2               .94697E-01      .94697E-01      .15086E+00     9.96504E-01
 H                 .16438E-05      .16438E-05      .59977E-07     1.72976E-05
 H2                .20251E-03      .20251E-03      .14778E-04     2.13099E-03
 H2O               .18982E+00      .18982E+00      .12379E+00     1.99747E+00
 HO                .74204E-04      .74204E-04      .45683E-04     7.80848E-04
 N                 .27866E-11      .27866E-11      .14130E-11     2.93239E-11
 N2                .71458E+00      .71458E+00      .72462E+00     7.51956E+00
 NO                .84518E-04      .84518E-04      .91807E-04     8.89380E-04
 NO2               .83678E-08      .83678E-08      .13936E-07     8.80548E-08
 O                 .48685E-06      .48685E-06      .28197E-06     5.12314E-06
 O2                .20673E-03      .20673E-03      .23946E-03     2.17541E-03
Phase  2:  Molal mass, g/mol =     .000
 C(S)              .00000E+00      .00000E+00      .00000E+00      .00000E+00
Phase  3:  Molal mass, g/mol =     .000
 H2O(L)            .00000E+00      .00000E+00      .00000E+00      .00000E+00

* Species mols for the atom populations in mols.

Mixture properties:   molal mass =   27.625 kg/kmol
   T = 1674.929 K          P = 1.0133E+05 Pa      V = 4.9750E+00 m**3/kg
   U =-1.7272E+06 J/kg     H =-1.2231E+06 J/kg    S = 9.3791E+03 J/kg-K

Made  3 (T,P) iterations;  24 EQUIL iterations.


Calculating the sound speed;    PLEASE WAIT!


Sound speed (isentropic) =   794.9 m/s
```

d) Other Applications

An early version of STANJAN was used for fiber-optics fabrication analysis by McAffee et al.[7] This version, which did not use the full dual problem, had difficulties in converging with multiple phases, and had to be extended by them to cover ideal solutions. The present version runs their problems very quickly, with no difficulty.

More recently, McAffee et al.[8] studied other such problems using the element potential method. At that time, the full dual problem had not yet been developed, so they developed their own algorithm for making the steepest descent.

9. Availability and Implementation of STANJAN

STANJAN and an associated data file-managing program, JANFILE, have been compiled using MICROSOFT(c) FORTRAN for use on the IBM-PC or compatible desktop computers. These programs run with or without the floating point coprocessor. This version can handle up to twenty species, in up to six phases, containing up to eight different elements.

The user disk, containing the compiled programs, data files, and examples, is available for educational use as freeware. An institution desiring to use this program for instructional use should send a blank formatted disk to the author in a floppy disk mailer. The disk will be returned with these files. This disk may be freely copied, and faculty members are encouraged to help spread STANJAN by sending copies to colleagues at other institutions.

The FORTRAN source programs are also available on IBM-PC floppy disk, at a reasonable cost. For details contact the author. These may be recompiled for use on larger computers, and can be easily modified to handle larger problems. These programs are good examples of modern, structured FORTRAN programs, are very well documented internally, and may themselves be useful as educational tools.

An early version of the equilibrium routine of the parent STANJAN, which did not use the full dual problem, was incorporated in Sandia's widely used CHEMKIN program as "the Stanford Equilibrium Solver". Users of that program will find the present equilibrium solver more robust and faster, especially if used with the current STANJAN initializer.

Acknowledgments

The author is indebted to K. B. McAffee for motivating the extension to ideal solutions, to P. E. Dimotakis for suggestions on FORTRAN program style, and to C. H. Kruger, C. T. Bowman, A. K. Oppenheim, I. Glassman, H. Dwyer, G. Gavalas, A. Acrivos, P. A. Libby, R. Key, E. C. Rea, Jr., and numerous students at Stanford and elsewhere for many useful suggestions for STANJAN improvements.

Mrs. Ruth Korb's patience in preparing this $(n+1)^{th}$ version of the paper, and that of the author's wife during the long nights of STANJAN development, are most sincerely appreciated.

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Appendix A

The Method of Lagrange Multipliers

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

$$F(\underline{x}) = \min \tag{A.1}$$

subject to the constraints

$$C_k(x) = \text{constant} \quad , \qquad k = 1, \ldots , c \tag{A.2}$$

In general, F and C_k may be nonlinear functions of the solution vector $x = (x_1, x_2, \ldots , x_n)$.

Taking the differential of F,

$$dF = \sum_{i=1}^{n} H_i dx_i \tag{A.3}$$

where

$$H_i = \frac{\partial F}{\partial x_i} \tag{A.4}$$

Now, for F to be a minimum with respect to arbitrary variations, $dF = 0$ for arbitrary dx_i that satisfy the constraints

$$dC_k = 0 = \sum_{i=1}^{n} A_{ik} dx_i \tag{A.5}$$

where

$$A_{ik} = \frac{\partial C_k}{\partial x_i} \tag{A.6}$$

If we have n variables and c constraints, only $n-c$ of the variables may be freely varied. Before examining the conditions under which dF is zero for arbitrary variations of the free x_i, we need to represent the changes in the restricted x_i in terms of the changes in the free ones, and then substitute for the changes in the restricted variables in (A.3). This substitution is equivalent to subtracting a linear combination of the equations (A.5) from

(A.3) such that the restricted dx_i drop out of the result. This subtraction yields:

$$dF - \sum_{k=1}^{c} \lambda_k dC_k = \sum_{i=1}^{n} \left(H_i - \sum_{k=1}^{c} \lambda_k A_{ik}\right) dx_i \tag{A.7}$$

where the coefficients λ_i must be chosen to drop out the restricted dx_i. In order for the restricted dx_i to drop out, the coefficient of each must be zero, so for these i,

$$H_i - \sum_{k=1}^{c} \lambda_k A_{ik} = 0 \tag{A.8}$$

For the remaining freely varied x_i, there must be no variation that changes F (to first order) which requires that the coefficient of these dx_i also vanish in (A.7). Hence, (A.8) must hold for all i.

Equation (A.8) represents a set of n simultaneous equations for the solution vector x_i. The constraints (A.2) provide c additional equations for the λ_k, called the "Lagrange multipliers".

If F and C_i are quadratic functions of the x_i, then (A.8) will be a linear equation system; this is the case in the applications to finding the paths of steepest descent described in Section 5 above. In the element potential theory, F is the system Gibbs function, and the resulting equations are nonlinear.

The Simplex Method

The Simplex method finds the solution vector y_j that minimizes

$$F(\underline{y}) = \sum_{j=1}^{n} w_j y_j \tag{B.1}$$

Subject to the constraints

$$\sum_{j=1}^{n} A_{ij} y_j = C_i \;, \qquad i = 1, \ldots , c \tag{B.2}$$

$$y_j \geq 0 \tag{B.3}$$

The method solves this problem simultaneously with a "dual" problem of maximizing

$$\sum_{j=1}^{n} \lambda_k C_k = \max \tag{B.4}$$

subject to

$$\sum_{k=1}^{c} \lambda_k A_{kj} \leq w_j \tag{B.5}$$

The method rests on the fact that the final solution will contain only as many non-zero y_j as there are constraints (B.2). These are the "base variables" for the problem. The solution involves starting with a trial set of bases and then replacing one base at a time. Each replacement results in a reduction in the value of the objective function F. The process terminates when no further changes are possible.

On each simplex pass, the first step is to determine the n "simplex Lagrange multiplers" λ_k by solving

$$\sum_{k=1}^{n} A_{kj} \lambda_k = w_j \tag{B.6}$$

where (B.6) applies only to the current base set. Then, for each variable y_j that is not a current base, one computes

$$S_j = \sum_{k=1}^{n} A_{kj}\lambda_k - w_j \tag{B.7}$$

for each j that is a candidate as a better base; S_j represents the reduction in F per unit of y_j added to the system. The j having the largest $S_j > 0$ is chosen as a new base to replace one of the old bases.

The direction of changes in the space $\underline{y}$ is then calculated from (B.2),

$$\sum_{jOB} A_{ij}\Delta y_j + A_{ik}\Delta y_k = 0 \tag{B.8}$$

where jOB denotes a sum over the old bases, and k denotes the new base member. This determines the directions $\Delta y_j/\Delta y_k$. Then the change in each old base along this path is examined, and the first point along the path at which one of the old y_j drops to zero is found. This determines the value of y_k in the new base set, and hence the changes in the other bases y_j. The process ends when there is no possible base change.

The simplex method requires a "feasible solution" (an initial base set) to start. This can be generated using the same simplex process by extending the system to include a set of non-negative false variables, one for each constraint. The feasible solution is then obtained using the simplex process to minimize the sum of the false variables.