

Analysis of parameter changes in chemical systems via geometric programming

J. J. DINKEL*

Department of Management Science and Organizational Behavior, The Pennsylvania State University, University Park, Pennsylvania 16802, USA

and

R. LAKSHMANAN

Department of Engineering, University of Quebec, Trois-Rivières, Quebec, Canada

(Received December 20, 1974)

SUMMARY

This paper exploits the relationship of chemical equilibrium problems to geometric programming in order to study the effect of changes in certain parameters on the equilibrium solution. As a result of analyzing these problems from the geometric programming point of view we develop efficient procedures for studying the effect of changes in pressure and/or temperature on the equilibrium solution. In particular we develop methods for determining allowable ranges of change and within those ranges we develop formulas for computing the new equilibrium solution. These developments are illustrated with an example.

1. Introduction

An important class of problems that can be viewed as constrained non-linear optimization problems can be categorized as chemical equilibrium problems. These problems consist of minimizing the Gibbs Free Energy of a system subject to a set of mass balance equations. The wide range of potential applications of these models has been demonstrated [1, 2, 6, 9]; also each chemical equilibrium problem is essentially a dual geometric program [6, 8]. It is the relationship of chemical equilibrium problems and geometric programming that will be exploited in this paper.

Since this class of problems deals with chemical thermodynamics the pressure and temperature of the system are two important parameters. To date, little has been said with respect to studying the effect of changes in these parameters on the equilibrium solution and what range of changes are possible *without* having to completely resolve the problem. The purpose of this paper is to present efficient procedures for performing such sensitivity (or post optimal) analysis on chemical equilibrium problems from a geometric programming point of view.

The calculation of the equilibrium composition of a system has been widely discussed in the literature. The classical method for solving this problem is the "equilibrium constant method" [7, 10]. In order to deal with more complex chemical reactions, for example organic compounds, the problem has been posed in the form of minimizing the free energy function; which can be dealt with using convex programming methods [1, 9]. In addition several authors [6, 8] have shown the relationship to geometric programming.

We give a brief discussion of the chemical equilibrium problem and its relation to geometric programming in order to motivate the development of the following sections.

The free energy of a mixture of n chemical containing x_i moles of the i th species can be expressed as:

$$F(x) = \sum_{i=1}^n f_i, \quad (1)$$

* This author's research was supported in part by the Center for the Study of Environmental Policy, The Pennsylvania State University.

where $x = (x_1, x_2, \dots, x_n)$ and $f_i = x_i [C_i + \ln(x_i/\bar{x})]$, $C_i = (F^0/RT)_i + \ln P$, $P =$ system pressure in atmospheres, $T =$ system temperature (Kelvin), $\bar{x} = \sum_{i=1}^n x_i$, $F^0/RT =$ Molal standard (Gibbs) free energy function.

The free energy, $(F^0/RT)_i$, of each species are obtainable directly from tables but are more often derived from the more commonly tabulated function $(T^{-1}F^0 - T^{-1}H^0)_i$ [10].

The determination of the equilibrium composition is equivalent to finding the *non-negative* set of values, x_i , which minimize (1) and satisfy the mass balance constraints

$$\sum_{i=1}^n a_{ij}x_i = e_j, \quad j = 1, \dots, m, \tag{2}$$

where $m =$ the number of chemical elements,

$a_{ij} =$ the number of atoms of element j in a molecule of species i ,

$e_j =$ initial number of moles of element j in the mixture.

The above is an example of a *homogenous or single phase* system; in order to allow for *heterogenous or multiple phase* models the development is extended by requiring $x_k = \sum_{[k]} x_i$ where $[k]$ indicates the k th = 1, ..., p phase.

Using the notation of Duffin, Peterson and Zener [6], that is $x_i = \delta_i$ and $\bar{x}_k \equiv \lambda_k$, the chemical equilibrium model is:

$$\min \frac{F}{RT} = \min \sum_{i=2}^n (\delta_i C_i + \delta_i \ln \delta_i) - \sum_{k=1}^p \lambda_k \ln \lambda_k, \tag{3}$$

$$\text{s.t.} : \sum_{i=2}^n a_{ij} \delta_i = e_j, \quad j = 1, \dots, m, \tag{4}$$

$$\delta_i \geq 0, \quad i = 2, \dots, n,$$

where

$$\frac{F}{RT} = \sum_{k=1}^p F^k / (RT) = \text{total free energy}.$$

The above model can be transformed to a dual geometric program (see [6, 8, 9] for complete details).

$$\max v(\delta) = \max \exp [-F/RT] = \prod_{i=1}^n (c_i/\delta_i)^{\delta_i} \prod_{k=1}^p \lambda_k^{\lambda_k}, \tag{5}$$

subject to: $\delta_1 = 1$,

$$\sum_{i=1}^n a_{ij} \delta_i = 0, \quad j = 1, \dots, m, \tag{6}$$

$$\delta_i \geq 0, \quad i = 1, \dots, n,$$

$$\text{where } c_i = \begin{cases} 1, & \text{for } i = 1, \\ \exp [-F_i^0/RT - \ln P], & i = 2, \dots, n, \end{cases} \tag{7}$$

$$a_{1j} = -e_j, \quad j = 1, \dots, m.$$

Several numerical procedures have been proposed as methods of obtaining solutions to these problems [1, 8, 9]. In this paper we are not concerned with the method of optimization and the procedures to be developed are independent of the method of optimization. We do assume the system (6) has been put into the form:

$$\delta = b^{(0)} + \sum_{j=1}^d r_j b^{(j)}, \tag{8}$$

where $d = n - m - 1$ is the *degree of difficulty* of the program [6]; the r_j are new independent

variables such that $(\delta) \geq 0$; and $b^{(j)}$ $j=0, 1, \dots, d$ are linearly independent nullity vectors [6]. For large problems the representation (8) can be obtained by using a Gauss–Jordan procedure. This representation plays a key role in the discussion that follows.

2. Sensitivity analysis via geometric programming

The original development of Duffin, Peterson and Zener [6] and the modifications of Dinkel [3, 4] with respect to the primal geometric program provide a systematic procedure for studying the effect of changes in pressure and temperature. The basis for this analysis is the following theorem which is a modified version of Theorem 1 [6].

Theorem 1. Let the $n \times m$ matrix (a_{ij}) have rank m and assume $d > 0$. If for some coefficients c_2^0, \dots, c_n^0 the dual program has optimal solution $\delta^* > 0$ and if the matrix $J(\delta^*)$ with elements

$$J_{ij}(\delta^*) = \sum_{g=1}^n \frac{b_g^{(i)} b_g^{(j)}}{\delta_g^*} - \sum_{k=1}^p \frac{\lambda_k^{(i)} \lambda_k^{(j)}}{\lambda_k^*}, \quad i, j = 1, \dots, d, \quad (9)$$

is non-singular, then the function which gives the optimal value of $v(\delta^*)$ in terms of variable coefficients c_2, \dots, c_n are differentiable with respect to c_i , $i=2, \dots, n$. At fixed, but arbitrary points c , these differentials are:

$$\frac{dv}{v^*} = \sum_{i=2}^n \delta_i^* \frac{dc_i}{c_i}, \quad (10)$$

$$d\delta_i = \sum_{j=1}^d \left\{ b_i^{(j)} \sum_{k=1}^d \left[J_{jk}^{-1}(\delta^*) \sum_{i=2}^n b_i^{(k)} \frac{dc_i}{c_i} \right] \right\}, \quad i = 2, \dots, n, \quad (11)$$

where the elements of $J(\delta^*)$ are given by (9).

As can be readily verified the above is a restatement of Theorem 1 [6] where (11) results from equations (9), (11), (12) [6] and since $c_1 = 1$ in all chemical equilibrium problems the term associated with $i=1$ has been deleted. In order to make use of this result we discuss the assumptions of Theorem 1 in terms of chemical equilibrium problems.

1. rank $(a_{ij}) = m$ implies the m chemical elements of the system are independent, which is the case by the definition of element.

2. $\delta^* > 0$ implies a strictly positive solution. Once again this is true for all well formed problems, for if some $\delta_i^* = 0$ then the associated $\lambda_k^* = 0$ which implies that phase is absent from the final solution. Thus in a correctly formulated p phase system all $\delta_i^* > 0$ in order that the system contain p phases at equilibrium.

3. The remaining assumption is that $J(\delta^*)$ is non-singular. Theorem 2 [6] gives a condition which guarantees the existence of $J(\delta^*)^{-1}$ (rank $(b_i^{(j)}) = d$, $i=1, \dots, n_0$; $j=1, \dots, d$). However this condition is rarely met in chemical equilibrium problems since $n_0 = 1$ and usually $d > 1$. Thus we must verify the non-singularity of $J(\delta^*)$. Once the representation (8) is known (9) provides a convenient means of constructing $J(\delta^*)$.

Also, as noted in [6], $J(\delta^*)$ is the Hessian matrix of $\log v(\delta)$ with respect to r_j . Thus if a second-order optimization technique (e.g. Newton–Raphson) [5] is employed to determine the optimal solution then $J(\delta^*)^{-1}$ will automatically be evaluated. For reasons to be discussed later we will use the construction given by (9).

We also note that formulas for changes in the primal variables t_j , $j=1, \dots, m$ can be developed [3, 6]; however since the dual program is the one of interest we do not pursue those relationships here.

Assuming the non-singularity of $J(\delta^*)$ we turn our attention to analyzing the effect of changes in pressure and/or temperature on the equilibrium solution. Since the assumptions of Theorem 1 are satisfied the following development is based on the maintenance of $\delta_i > 0$ for changes in P and/or T . Before giving this development it is necessary to point out the correct interpretation

of dv/v^* and dc_i/c_i in Theorem 1 for chemical equilibrium problems. From (7), we have $c_i = \exp(-C_i)$ where $C_i = F_i^0/RT + \ln P$; thus a change in P and/or T implies a change in $-C_i$ which in turn implies a change in $\ln c_i$ ($\ln c_i = -C_i$). Thus $dc_i/c_i = d[\exp(-C_i)]/\exp(-C_i) = d(-C_i)$ which will be interpreted as $\Delta(-C_i) = \Delta \ln c_i = \ln c'_i - \ln c_i$; where c'_i, c_i are the new and original coefficients. Similarly, since $v(\delta) = \exp(-F/RT)$, we have from (7), a change in $-C_i$ implies a change in $\ln v(\delta)$. Thus

$$d[\ln v(\delta^*)] = \frac{dv(\delta^*)}{v} = \frac{d[\exp(\sum \delta_i^*(-C_i) - \ln \delta_i^* + \sum \lambda_k^* \ln \lambda_k^*)]}{v} = \sum \delta_i^* d(-C_i).$$

In the results that follow dc_i/c_i will be interpreted as $\ln c'_i - \ln c_i$ and $dv(\delta^*)/v$ will be interpreted as $\ln v'(\delta) - \ln v(\delta)$ where the prime (') denotes the new value of coefficient or objective function. We also note that the above interpretations are obtainable directly from the free energy form by computing the difference between the new and old values.

At this point it is important to note the effect of the above interpretation of dc_i/c_i and its effect on Theorem 1; in particular the effect on equations (9)–(11). We see from Theorem 1 the results are stated in terms of differential changes in the coefficients and the evaluation of J^{-1} at the point δ^* for such changes. The above discussion has the effect of approximating these differential changes by the *difference form* $\ln c'_i - \ln c_i$ which from a practical point of view is important since we want to consider discrete changes in the parameters of the system. However we also note from equations (9)–(11) that the evaluation of J^{-1} remains at the point δ^* ; thus for “large” changes in the c_i the evaluation of J^{-1} at δ^* is a source of error in the results that follow. In order to compensate for this error we need to develop procedures that allow for the updating of the evaluation of J^{-1} . That is, since the value of J^{-1} depends on δ and δ is a function of c_i (for sensitivity analysis purposes) the evaluation of J^{-1} should be a function of changes in the coefficients. Specifically for a small change in the c_i we need to consider $J(\delta^* + d\delta)$ where $d\delta$ is determined via (11). Following the development of our initial results which will define approximate ranges of allowable changes we will develop an incremental procedure which will be used to refine these estimates through the updating of the evaluation of J^{-1} .

With these remarks in mind we begin our characterizations by determining the approximate range of allowable changes in the system pressure. In particular we suppose the system pressure, P , changes to $P + \Delta$ and we want to approximate the range of changes for which the analysis of Theorem 1 is valid and the effect of such changes on the equilibrium solution.

Theorem 2. *If the system pressure changes to $P + \Delta$ then each coefficient changes as: $dc_i/c_i = \ln P - \ln(P + \Delta)$ $i = 2, \dots, n$. Also the allowable range of changes is given by:*

$$\Delta > \max_{i: D_i < 0} \{P \exp(\delta_i^* D_i^{-1}) - P, -P\}, \quad \text{if } \ln P - \ln(P + \Delta) > 0, \tag{12}$$

$$\Delta < \min_{i: D_i > 0} \{P \exp(\delta_i^* D_i^{-1}) - P\}, \quad \text{if } \ln P - \ln(P + \Delta) < 0, \tag{13}$$

where

$$D_i = \sum_{j=1}^d \left\{ b_i^{(j)} \sum_{k=1}^d J_{jk}^{-1}(\delta^*) \sum_{i=2}^n b_i^{(k)} \right\}, \quad i = 2, \dots, n, \tag{14}$$

and if $D_i = 0$ then Δ is unrestricted.

Proof

We have already shown that $dc_i/c_i = \ln c'_i - \ln c_i$ when $\ln c_i = -F_i^0/RT + \ln P$; thus $dc_i/c_i = \ln P - \ln(P + \Delta)$. Since $\delta'_i = \delta_i^* + d\delta_i$ we need to determine those changes which will maintain $\delta'_i > 0$. That is, since the hypothesis of Theorem 1 are satisfied we need only maintain a strictly positive solution. Thus, from (11), we have:

$$\begin{aligned} 0 &= \delta'_i = \delta_i^* + d\delta_i = \delta_i^* + \sum_{j=1}^d \left\{ b_i^{(j)} \sum_{k=1}^d \left[J_{jk}^{-1} \sum_{i=2}^n b_i^{(k)} \right] \right\} [\ln P - \ln(P + \Delta)] \\ &= \delta_i^* + D_i [\ln P - \ln(P + \Delta)] = \delta_i^* + D_i \ln(P/P + \Delta). \end{aligned} \tag{15}$$

Now if $\ln(P/P + \Delta) > 0$ (i.e. $\ln P > \ln(P + \Delta)$) we need evaluate those changes for which $D_i < 0$; for if $D_i > 0$ then δ'_i is always strictly positive. If, in addition, $D_i \neq 0$ then $\ln(P/P + \Delta) = -\delta_i^* D_i^{-1}$ or $\Delta = P \exp(\delta_i^* D_i^{-1}) - P$.

Thus in order to maintain $\delta'_i > 0$ we obtain

$$\Delta > \max_{i: D_i < 0} \{P \exp(\delta_i^* D_i^{-1}) - P, -P\},$$

where the $-P$ has been added to the above operation to insure that $\ln(P + \Delta)$ is well defined. If $D_i = 0$ we note from (15) that $\delta'_i = \delta_i^*$ and thus the equilibrium solution does not change.

Similarly, if $\ln(P/P + \Delta) < 0$ we evaluate $D_i > 0$ to obtain:

$$\Delta < \min_{i: D_i > 0} \{P \exp(\delta_i^* D_i^{-1}) - P\}.$$

Combining these results completes the proof of the theorem.

The above result presents a range of allowable changes in the system pressure and within this range the representation (10), (11) can be used to compute the new equilibrium solution. For any Δ satisfying (12), (13) the new solution can be computed as:

$$\delta'_i = \delta_i^* + [\ln P - \ln(P + \Delta)] D_i, \quad i = 2, \dots, n, \tag{16}$$

for the new equilibrium composition

$$\ln v' = \ln v^* + [\ln P - \ln(P + \Delta)] \sum_{i=2}^n \delta_i^* \tag{17}$$

for the new value of the objective function.

At this point we note that the use of the above results and those to follow must be used within an additional assumption implicit in the model formulation. This assumption is that the system obeys the perfect gas law and clearly large changes in the system pressure can violate this assumption. Also large changes in pressure and/or temperature may cause the original reactions to be altered. Thus even though the above analysis indicates a large range of allowable changes, for example see Example 1 of the next section, one must take into account the above remarks.

A similar analysis can be applied to study changes in temperature and pressure and temperature. However we note that changes in temperature also cause a change in each F_i^0 as well and this change does not allow the separability apparent in Theorem 2. Nevertheless it is possible to use the preceding development to study such changes. In fact the preceding development is directly applicable with some minor modifications.

If T changes to $T + \Delta T$ then F_i^0 also changes to $F_i^0 + \Delta F_i^0$. Let the new value of C_i be denoted as $C'_i = C_i + \gamma_i$ where γ_i reflects both of the above changes.

Following the development preceding Theorem 2 it follows that

$$\frac{dc_i}{c_i} = (-C'_i) - (-C_i) = -\gamma_i. \tag{18}$$

If, in addition to a change in T , we also have a change in pressure to $P + \Delta$ then (18) becomes:

$$\frac{dc_i}{c_i} = \ln P - \ln(P + \Delta) - \gamma_i. \tag{19}$$

We obtain the following version of Theorem 2 for changes in temperature or both pressure and temperature by substituting the above relationships into Theorem 1.

Theorem 3. *If the system pressure changes to $P + \Delta$ and the system temperature changes to $T + \Delta T$ under the conditions of Theorem 1 then the change in the equilibrium solution is computed as:*

$$d\delta_i = \sum_{j=1}^d \left\{ b_i^{(j)} \sum_{k=1}^d \left[J_{jk}^{-1} \sum_{i=2}^n b_i^{(k)} [\ln P - \ln(P + \Delta) - \gamma_i] \right] \right\}, \quad i = 2, \dots, n. \tag{20}$$

Moreover if the changes are such that $\delta_i^* + d\delta_i > 0$ for all i then the new equilibrium solution is:

$$\delta'_i = \delta_i^* + d\delta_i, \quad i = 2, \dots, n, \tag{21}$$

$$\ln v' = \ln v^* + \sum_{i=2}^n \delta_i^* [\ln P - \ln(P + \Delta) - \gamma_i]. \tag{22}$$

This result follows from a substitution of (18), (19) into (10), (11). We note that we do not obtain the range analysis of Theorem 2 due to the dependence of γ_i on F_i^0 and as a result the analysis is better suited to a *point wise analysis*. That is, for a given change in temperature and/or pressure one can readily determine via (20) whether all $\delta'_i > 0$. If this condition is satisfied then the new solution is computed via (21) and (22).

The results presented so far deal with changes in the coefficients of the primal GP which reflect changes in the system pressure and/or temperature and result directly from the original works of Duffin, Peterson and Zener [6]. Another set of parameters of interest is the initial concentration of the various elements; that is, we want to be able to study variations in the $e_j, j=1, \dots, m$ of (4). As can be seen from (7) such variations imply the changing of the primal GP exponents, a situation not treated by the results of [6]. The special structure of (4) will enable us to develop results for analyzing such changes. The analysis that follows is based on the following result [6]:

$$\text{Let } \ln K_j = \sum_{i=1}^n b_i^{(j)} \ln c_i, \quad j = 0, 1, \dots, d, \tag{23}$$

and using the representation (5) we have:

$$\ln v(\delta) = \ln K_0 + \sum_{j=1}^d r_j \ln K_j - \sum_{i=2}^n \delta_i(r) \ln \delta_i(r) + \sum_{k=1}^p \lambda_k(r) \ln \lambda_k(r). \tag{24}$$

Then r is an optimizing point of $\ln v(\delta)$ if and only if

$$\ln K_j = \sum_{i=2}^n b_i^{(j)} \ln \delta_i(r) - \sum_{k=1}^p \lambda_k^{(j)} \ln \lambda_k(r), \quad j = 1, \dots, d. \tag{25}$$

We use the above to state the result of interest:

Theorem 4. *Suppose the e_j of (4) change by some differential amount such that in (8) no $b^{(j)}, j=1, \dots, d$ changes. The change in the equilibrium solution is:*

$$d \ln v = \sum_{i=2}^n d\delta_i [\ln c_i - \ln \delta_i - 1] + \sum_{k=1}^p d\lambda_k [\ln \lambda_k + 1], \tag{26}$$

where

$$\delta_i = b_i^{(0)} + \sum_{j=1}^d r_j b_i^{(j)}.$$

Moreover the new equilibrium solution satisfies:

$$dr = J^{-1}(\delta^*)M, \tag{27}$$

where

$$M_j = - \left\{ \sum_{i=2}^n \frac{b_i^{(j)}}{\delta_i^*} db_i^{(0)} - \sum_{k=1}^p \frac{\lambda_k^{(j)}}{\lambda_k^*} d\lambda_k^{(0)} \right\}, \quad j = 1, \dots, d.$$

Proof

Equation (26) is a direct result of considering the logarithm of (5) and differentiating the result with respect to e_j and setting $db^{(j)} = 0, j=1, \dots, d$. Equation (27) results from differentiating (25) with respect to e_j and noting that if no $b^{(j)}, j=1, \dots, d$ changes then $d[\ln K_j]/de_j = 0, j=1, \dots, d$. Also the resulting terms in $d[\ln K_j]$ form the elements of $J^{-1}(\delta^*)$; for example see equation (11), [6].

Once the solution to (27) has been determined the new equilibrium solution is computed as:

$$d\delta_i = db_i^{(0)} + \sum_{j=1}^d dr_j b_i^{(j)}, \quad i = 2, \dots, n. \tag{28}$$

As in the analysis of changes in pressure and/or temperature we will replace $db_i^{(0)}$ by the difference from $b_i^{(0)'} - b_i^{(0)}$ representing discrete changes in the e_j .

As noted previously these approximations and the evaluation of J^{-1} at δ^* is a source of error in the calculations; also from (27) we see that with respect to changes in the e_j the error is compounded since M is also a function of δ^* . In order to deal with this error we introduce a procedure which updates the evaluation of J^{-1} and M . The procedure is readily incorporated into the results of the previous theorems to yield improved estimates on the ranges of allowable changes and the new equilibrium solution.

The basic idea of this *incremental procedure* is to divide a particular change, in the coefficients or e_j , into a sequence of small changes. The new solution is computed for each element of the sequence and this is used to update the evaluation of J^{-1} . That is, suppose $\ln c_i' - \ln c_i = \Delta$, some arbitrary change, choose a positive integer K and define the incremental change Δ/K and the associated sequence of changes $\ln c_i^{(k+1)} = \ln c_i^{(k)} + k \Delta/K$ for $k = 1, \dots, K$. The choice of K is arbitrary and should be such that Δ/K represents a small percentage change in the coefficient (say 10%). Clearly the larger the value of K the smaller the increment and the number of times the evaluation of J^{-1} is updated will be increased. The results presented so far assume $K = 1$ and we now suppose $K > 1$. The incremental procedure is:

for $k = 1$ determine the change in the equilibrium solution via (11) as $d\delta^{(1)}$ which is used to compute the new equilibrium solution $\delta^* + d\delta^{(1)}$. For $k = 2$ the new change in the equilibrium solution (for a change in the coefficient of Δ/K) is computed as before except that in (11) the evaluation of J^{-1} is at the point $\delta^* + d\delta^{(1)}$. The new change $d\delta^{(2)}$ is used to compute the equilibrium solution $\delta^* + d\delta^{(1)} + d\delta^{(2)}$ and the procedure is repeated a total of K times.

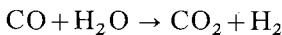
If we have chosen Δ as the original bounds from Theorems 1 and 2 the above procedure will indicate if these bounds are overestimates of the true bounds. For example, if at some point in the above process some $\delta^{(k)} \leq 0$ the procedure is stopped and new bounds are computed from the point $\delta^{(k-1)}$. On the other hand if $\delta^{(k)} > 0$ Theorems 1 and 2 can be applied at the point $\delta^* + \sum_{k=1}^K d\delta^{(k)}$ to obtain an improved set of bounds. This procedure improves the results of equations (9) and (11) since in place of evaluating J^{-1} at δ^* we obtain updated values as $J^{-1}(\delta^* + d\delta^{(1)})$, $J^{-1}(\delta^* + d\delta^{(1)} + d\delta^{(2)})$ and so on. Also the evaluation of M in (27) is similarly updated for changes in the e_j .

3. Numerical results

In order to illustrate the development of the preceding section we present a small example. While this is a small example it does illustrate the computation procedures.

3.1. Water-gas reaction [10]

According to the above reference [10] we consider the reaction



at $P = 1$ atmosphere, $T = 1095^\circ\text{K}$ with a starting state of 1 mole each of CO and H₂O. The geometric program associated with this reaction, according to (5-7), is:

$$\begin{aligned} \max v(\delta) &= \prod_{i=1}^5 (c_i/\delta_i)^{\delta_i} \lambda_1^{\lambda_1}, \\ \text{subject to } \delta_1 &= 1, \quad -\delta_1 + \delta_3 + \delta_5 = 0, \\ &-\delta_1 + \delta_2 + \delta_4 = 0, \quad \delta_i > 0, \quad i = 2, \dots, 5, \\ &-2\delta_1 + \delta_2 + \delta_3 + 2\delta_4 = 0, \end{aligned} \tag{29}$$

TABLE 1

$F_i^0/RT + \ln P$ for water-gas reaction

i Species	$P = 1 \text{ atm.}$ $T = 1095^\circ \text{K}$	$P = 2 \text{ atm.}$ $T = 1095^\circ \text{K}$	$P = 1 \text{ atm.}$ $T = 1200^\circ \text{K}$	$P = 2 \text{ atm.}$ $T = 1200^\circ \text{K}$	$P = 1 \text{ atm.}$ $T = 1271^\circ \text{K}$	$P = 2 \text{ atm.}$ $T = 1371^\circ \text{K}$
2 CO	-57.4239	-56.7307	-56.6705	-55.3773	-55.7447	-55.3515
3 H ₂ O	-50.3023	-49.6091	-48.4106	-47.7175	-46.0221	-45.3290
4 CO ₂	-70.8924	-70.1992	-67.6020	-66.9089	-63.4167	-62.7235
5 H ₂	-16.7936	-16.1004	-17.1604	-16.4673	-17.5876	-16.8945

TABLE 2

Equilibrium solutions for water-gas reaction

δ_i^* Species	$P = 1$ $T = 1095^\circ \text{K}$	$P = 2$ $T = 1095^\circ \text{K}$	$P = 1$ $T = 1200^\circ \text{K}$	$P = 2$ $T = 1200^\circ \text{K}$	$P = 1$ $T = 1371^\circ \text{K}$	$P = 2$ $T = 1371^\circ \text{K}$
2 CO	0.505025	0.505025	0.53975	0.53975	0.59417	0.59417
3 H ₂ O	0.505025	0.505025	0.53975	0.53975	0.59417	0.59417
4 CO ₂	0.494975	0.494975	0.46025	0.46025	0.40583	0.40583
5 H ₂	0.494975	0.494975	0.46025	0.46025	0.40583	0.40583
λ_1 Total	2.	2.	2.	2.	2.	2.
Moles						
$\ln v(\delta^*)$	90.478789	89.092406	87.700687	86.31439	84.194276	82.807978

where $c_1 = 1$ and the other constants for various system conditions are given in Table 1.

Employing the optimization procedure described by Dinkel *et al.* [5] we obtain the equilibrium solutions listed in Table 2. We note these results agree with those obtained via the classical "equilibrium constant method" [10]. These results are presented as a basis for comparison of our sensitivity analysis.

To begin our analysis we note the reduced form (8) of the system (23) is:

$$\delta = b^{(0)} + r_1 b^{(1)} = \begin{pmatrix} 1 \\ 1 \\ 1 \\ 0 \\ 0 \end{pmatrix} + r_1 \begin{pmatrix} 0 \\ -1 \\ -1 \\ 1 \\ 1 \end{pmatrix}$$

Since $d = 1$ the matrix $J(\delta)$ is 1×1 and is constructed as:

$$J_{11} = \sum_{g=1}^5 \frac{b_g^{(1)} b_g^{(1)}}{\delta_g^*} - \frac{\lambda_1^{(1)} \lambda_1^{(1)}}{\lambda_1^*} = \frac{0}{1} + \frac{(-1)(-1)}{0.505025} + \frac{(-1)(-1)}{0.505025} + \frac{1}{0.494975} + \frac{1}{0.494975} - \frac{0}{2} = 8.00081. \text{ Thus } J_{11}^{-1} = 0.12499.$$

We begin by studying changes in the system pressure. As can be seen from Table 2 changes in the system pressure from 1 to 2 atmospheres do not effect the equilibrium solution; in fact we know from thermodynamic principles that any change in system pressure, so long as the perfect gas law assumption is met, will not change the equilibrium solution. These facts are recoverable via our analysis as follows:

If P changes to $P + \Delta$ we compute from (11) and Theorem 2:

$$d\delta_i = b_i^{(1)} J_{11}^{-1} \sum_{i=2}^5 b_i^{(1)} \frac{dc_i}{c_i} = D_i [\ln P - \ln(P + \Delta)].$$

However since $\sum_{i=2}^5 b_i^{(1)} = -1 - 1 + 1 + 1 = 0$, we have $d\delta_i = 0, i = 2, \dots, 5$, and thus the equi-

librium solution does not change for a pressure change $-P < \Delta$. For the objective function we have from (17):

$$\ln v' - \ln v^* = \sum_{i=2}^5 \delta_i^* \frac{dc_i}{c_i} = \ln 2 \sum_{i=2}^5 \delta_i^* = -1.38629$$

which agrees with the results of Table 2.

For changes in the system temperature it follows from Theorem 3 that

$$\begin{aligned} d\delta_2 &= b_2^{(1)} J_{11}^{-1} \{b_2^{(1)}(-\gamma_2) + b_3^{(1)}(-\gamma_3) + b_4^{(1)}(-\gamma_4) + b_5^{(1)}(-\gamma_5)\} \\ &= -0.125 \{\gamma_2 + \gamma_3 - \gamma_4 - \gamma_5\}, \\ d\delta_4 &= 0.125 \{\gamma_2 + \gamma_3 - \gamma_4 - \gamma_5\}, \\ d\delta_3 &= d\delta_2 \text{ and } d\delta_5 = d\delta_4. \end{aligned}$$

Thus

$$0 = \delta_2' = \delta_2^* + d\delta_2 \text{ implies } \gamma_2 + \gamma_3 - \gamma_4 - \gamma_5 = 4.04,$$

and

$$0 = \delta_4' = \delta_4^* + d\delta_4 \text{ implies } \gamma_2 + \gamma_3 - \gamma_4 - \gamma_5 = -3.96.$$

Thus the range of allowable changes is:

$$-3.96 < \gamma_2 + \gamma_3 - \gamma_4 - \gamma_5 < 4.04. \tag{30}$$

For each of the temperature changes of Table 1 the corresponding values of (24) are:

$$\begin{aligned} T = 1095 \text{ to } T = 1200: \gamma_2 + \gamma_3 - \gamma_4 - \gamma_5 &= -0.27844, \\ T = 1200 \text{ to } T = 1371: \gamma_2 + \gamma_3 - \gamma_4 - \gamma_5 &= -0.44385, \\ T = 1095 \text{ to } T = 1371: \gamma_2 + \gamma_3 - \gamma_4 - \gamma_5 &= -0.72229. \end{aligned}$$

For the first case we compute the new solution as:

$$\begin{aligned} d\delta_2 = d\delta_3 &= -0.125(-0.27844) = 0.034805, \\ d\delta_4 = d\delta_5 &= 0.125(-0.27844) = -0.034805, \\ \ln v' - \ln v^* &= -2.7829, \end{aligned}$$

which is comparable to the results of Table 2. To illustrate the effect of the iterative procedure suggested as the end of Section 2 we note that if we compute according to Theorem 3 $\ln v' - \ln v^*$ for $T=1095$ to $T=1371$ we obtain 6.3169; while if we compute first for $T=1095$ to $T=1200$ and then $T=1200$ to $T=1371$ we obtain 6.30149 which is closer to the value 6.2845 obtained from Table 2.

Finally if both P and T change we have from Theorem 3 and employing the fact that $\sum b_i^{(1)} \ln(1 + \Delta) = 0$ the same representation (24) as for changes in temperature only. The use of the other formulas of Theorem 3 yield results comparable to the results of Table 2.

To illustrate the results of Theorem 4 and the potential of the incremental procedure suppose we change the initial concentration to 2 moles of CO and 1 mole of H₂O. Changing the concentration of CO changes e_1 to 2, e_2 to 3 while e_3 remain at 1. The new $b^{(0)}$ is given by:

$$b^{(0)} = \begin{pmatrix} 1 \\ 2 \\ 1 \\ 0 \\ 0 \end{pmatrix} \text{ with } b^{(1)} \text{ as given before.}$$

Treating the above change $db_2^{(0)} = 1$ as a single increment ($K = 1$) we compute the new equilibrium solution according to (27) where

$$M_1 = -(b_2^{(1)} db_2^{(0)} / \delta_2^*) = 1.980198, \quad J_{11}^{-1} = 0.12499.$$

TABLE 3

Equilibrium solution for 2 moles CO, 1 mole H₂O

	<i>GP Solution</i>	1 <i>Increment</i>	10 <i>Increments</i>
δ_2	1.339302	1.257575	1.3319611
δ_3	0.339302	0.257575	0.3319611
δ_4	0.660698	0.7424247	0.6680389
δ_5	0.660698	0.7424247	0.6680389
$\ln v(\delta)$	128.9425	129.27901	129.0286

Thus $dr=0.2475247$ and employing (28) the new equilibrium solution is computed. These results are given in Table 3 along with the *GP* solution for the problem. As can be seen from the results of the table the sensitivity analysis results contain a good deal of error. In order to refine these results we employ the incremental procedure with $K=10$. That is, we consider the sequence of problems with the incremental change of 0.1; thus the values of $b_2^{(0)}$ are 1.1, 1.2, ..., 2. Table 3 also contains the results for these computations and as is readily apparent provides very accurate results.

As noted previously these improved results are due to the updating of the evaluation of the matrix J^{-1} from δ^* to $\delta^* + d\delta$. In terms of the example this procedure reduced the error by a factor of 10 and for problems where the degree of difficulty is large (and hence J is $d \times d$) this procedure should greatly improve the accuracy of the results.

4. Conclusions

The results of the preceding sections demonstrate an efficient procedure for determining the effect of changes in system parameters in the context of chemical equilibrium problems. The authors have tested the above procedures on more complex problems, e.g. the combustion of propane [7], with similar results. Thus the geometric programming approach to chemical equilibrium problems in addition to providing a means for obtaining equilibrium solutions also provides a convenient method for analyzing changes in the system parameters. The use of such analysis would seem to be of particular importance with respect to mathematical models of biological systems [2].

REFERENCES

- [1] R. J. Clasen, *The Numerical Solution of the Chemical Equilibrium Problem*, The Rand Corporation, RM-4345-PR, January (1965).
- [2] G. B. Dantzig, J. C. DeHaven and C. F. Sams, A Mathematical Model of the Chemistry of the External Respiratory System, *Proceedings of 4th Berkeley Symposium on Mathematical Statistics*, June-July (1960).
- [3] John J. Dinkel, *Sensitivity Analysis in Geometric Programming*, Submitted for publication.
- [4] John J. Dinkel and G. A. Kochenberger, A Note on Substitution Effects in Geometric Programming, *Management Science*, 20, 7 (1974).
- [5] John J. Dinkel, G. A. Kochenberger and B. McCarl, An Approach to the Numerical Solutions of Geometric Programs, *Mathematical Programming*, Vol. 7 (1974).
- [6] R. J. Duffin, E. L. Peterson and C. Zener, *Geometric Programming*, John Wiley and Sons, Inc., New York (1967).
- [7] H. J. Kandimer and S. R. Brinkley, Calculation of Complex Equilibrium Relations, *Ind. Eng. Chem.*, Vol. 42 (1950).
- [8] U. Passy and D. J. Wilde, A Geometric Programming Algorithm for Solving Equilibrium Problems, *SIAM J. Applied Mathematics*, March (1968).
- [9] N. A. Shapiro and L. S. Shapley, Mass Action Laws and the Gibbs Free Energy Function, *SIAM J. Applied Mathematics*, Vol. 13, No. 2, June (1965).
- [10] J. M. Smith, *Introduction to Chemical Engineering Thermodynamics*, McGraw-Hill, Inc., New York (1949).