A GENERALIZED TECHNIQUE FOR ELIMINATING SPECIES IN COMPLEX CHEMICAL EQUILIBRIUM CALCULATIONS

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This Memorandum is one in a continuing series of RAND publications* dealing with theoretical and computational questions which have arisen in connection with the RAND program of research on rocket fuels and propellents and in biology and physiology. It details a method by which a multi- or single-phase chemical equilibrium problem with a large number of different chemical species can be replaced by one with relatively few species. The purpose of this research is to find methods for transforming complex problems into problems which are more amenable to numerical solution.

This Memorandum is concerned with a technique first developed in an earlier Paper, On the Reduction of Certain Multiplicative Chemical Equilibrium Systems to Mathematically Equivalent Additive Systems, P-2419, by G. B. Dantzig and J. C. DeHaven. The present Memorandum generalizes the technique to systems more complex than those to which the technique of the earlier paper is readily applicable. The basic approach of the previous paper is described briefly,

*For example, see Refs. 2-8.
but the reader should be familiar with P-2419 for certain explanatory and illustrative material which has not been included in the present paper.
A GENERALIZED TECHNIQUE FOR ELIMINATING SPECIES IN COMPLEX EQUILIBRIUM CALCULATIONS

I. INTRODUCTION

We will consider multi- or single-phase chemical equilibrium problems, showing that, under certain circumstances, a problem involving a very large number of different chemical species may be replaced by one involving relatively few species. The new problem will then be much more amenable to numerical solution than the original problem. We will use the same approach in formulating complex chemical equilibrium problems as was used in [1]. It is briefly described here primarily in order to introduce our notation and terminology.

Consider a problem involving certain chemical species, $X_1, \ldots, X_L$, in one or more phases. It is no loss of generality to assume that no species can occur in more than one phase. For example, if $H_2O$ occurs in both a liquid phase and a gaseous phase, we assume, as is frequently done, that we are dealing with two distinct species, $H_2O$-liquid and $H_2O$-vapor, and we formulate the mass balance
equations (see below) in such a way that \( \text{H}_2\text{O}-\text{liquid} \) is transferable into or from \( \text{H}_2\text{O}-\text{vapor} \). Thus, we assume that species in distinct phases are distinct.

In [1] it was shown that any chemical equilibrium could be formulated from the following three types of information:

I. A specification of which species occur in which phases.

II. Certain constants \( \alpha_1, \ldots, \alpha_I, \ldots, \alpha_L \). For a discussion of the meanings and the various interpretations of these constants, as well as the methods by which they may be obtained, see [2]. Because one way of looking at the \( \alpha_I 's \) depends on the Gibbs free energy function, we will call \( \alpha_I \) the free energy parameter associated with \( \text{X}_I \). In fact, \( \alpha_I = \frac{\Delta F_0}{RT} \).

III. A set of \( N \) linear equations of the form

\[
\sum_{t=1}^{L} s_{t,n} x_{t} = s_{0,n}, \quad 1 \leq n \leq N
\]  

(1)

where \( x_{t} \) is the (unknown) number of moles of \( \text{X}_t \). Constraints of the type (1) may represent, for example, mass balance constraints, or may, for example, express the condition that a certain phase be electrically neutral.
Thus, if \( n \) of Eq. (1) is a mass balance constraint, \( 3 \), might be the number of atoms of some chemical element in each molecule of \( X \), and \( s_{0,n} \) would be the total number of atoms (measured in moles) of that element in the system under consideration. In practice, of course, it is ordinarily more convenient to base the mass balance equations on various radicals rather than on individual atoms. In any case, all the mass balance constraints are of the form (1); that is, they are linear equations in the \( x_l \)'s.

If equation \( n \) of (1) is an electro-neutrality condition on some phase, then \( s_{t,n} \) would be zero, except for those \( t \) for which \( X \) occurs in that phase, and \( X \) is an ion. In that case, \( s_{t,n} \) is the valence of \( X \), with the appropriate sign.

If, for each \( t, 0 \leq t \leq L \), we define a vector, \( S_t \), whose components are \( s_{n,t} \), \( 1 \leq n \leq N \), then Eq. (1) may be written as

\[
\sum_{t=1}^{L} x_t S_t = S_0. \tag{1'}
\]

Notice then, that \( S_t \) is essentially the "empirical formula" for \( X_t \).

We will call \( S_t \) the constraint vector associated with \( X_t \).
Repeating, a chemical equilibrium problem may be completely specified by the following three types of information:

I. The specification of which species occur in which phases.

II. An energy parameter, $\alpha_{t}$, for each species, $X_t$.

III. A constraint vector, $S_{t}$, for each species, $X_t$, and a vector $S_0$.

Note that the concentration * $[X_{t_0}]$ of each species $X_{t_0}$ can be calculated by dividing $x_{t_0}$ by the sum of all $x_{t_0}$'s for which $X_t$ occurs in the same phase as $X_{t_0}$ (this sum, of course, includes $x_{t_0}$ itself). Thus, the $[X_{t}]$'s are functions of the $x_{t}$'s (although each $[X_{t}]$ does not depend only on the corresponding $x_{t}$).

It was shown in [2] and [3] that the $x_{t}$'s may be efficiently determined, numerically, by minimizing the function

$$F = \sum_{t=1}^{L} x_{t} (\alpha_{t} + [X_{t}])$$

*Throughout this paper, we measure concentration in mole fractions.*
subject to the constraints that

$$\sum_{t=1}^{L} x_t S_t = S_0 .$$

(1')

Before stating and proving our results, we give an example of a typical and relatively simple situation to which they apply.

Consider a chemical equilibrium problem involving one or more phases. Consider some particular liquid phase, which we will arbitrarily call the first phase. Suppose that a certain chemical species, X, occurs in the first phase. Suppose also that X can combine with oxygen to form new species XO$_2$ and XO$_4$. Suppose that X has 50 distinct sites at which hydrogen ionization can occur, that XO$_2$ has 75 distinct sites at which hydrogen ionization can occur, and that XO$_4$ has 100 distinct sites at which hydrogen ionization can occur.

Suppose that all these sites are independent, in the same sense that ionization at one site does not influence the ease or difficulty of ionization at any other site on the same molecule. (Note: This assumption of complete independence is not necessary in order to apply the methods
of this paper. They would also be applicable if various types of systematic dependence were assumed.)

Suppose also that all these sites are of two distinct classes--sites of the first class being easier to ionize than sites of the second class. But, suppose that all sites of the first class are equally easy to ionize and that all sites of the second class are equally easy to ionize. Thus, each molecule of X might have 20 sites of the first class and 30 sites of the second class; each \( XO_2 \) molecule might have 30 sites of the first class and 45 sites of the second class. Each \( XO_4 \) molecule might have 50 sites of the first class and 50 sites of the second class.

Notice that two molecules ionized in different ways represent different species; hence, we are dealing with a total of \( 2^{50} \) different varieties of X, \( 2^{75} \) different varieties of \( XO_2 \), and \( 2^{100} \) different varieties of \( XO_4 \)--or a total of approximately \( 10^{30} \) distinct chemical species. It will turn out that we will be able to formulate a new problem which will be equivalent to the first problem, but one in which all these approximately \( 10^{30} \) species will be replaced by only seven species. Of course, the first phase may itself contain additional species and there may
be other phases. But we will have attained a significant reduction in problem complexity.

We will now leave this special example and proceed to state and prove our general results. Although we will not again refer to this example, the reader may wish to refer back to it from time to time in order to understand the applicability of the general and rather abstract discussion which follows. It should be emphasized that the example is not representative of either the complexity or the variety of the situations to which our results may be applied. The only purpose of the example is to enable the reader to more readily understand the statement of our results.
II. RESULTS

Let $\phi$ be some subset (or the entire set) of species in one of the phases (which we will arbitrarily call the first phase) of a multi- or single-phase equilibrium problem in the sense of [1]. Let $\phi$ be partitioned into various sets of species, $\phi_1, \ldots, \phi_i, \ldots, \phi_I$. That is, every species $\theta$ of $\phi$ is in exactly one of the sets, $\phi_i$.

Let $A_1, \ldots, A_k, \ldots, A_K$ be classes of sites (these sites are actually abstract entities, and need not--but may--correspond to actual chemical sites). Suppose that a site in the class $A_k$ can have $J_k$ possible states: $B_{k1}, \ldots, B_{kj}, \ldots, B_{kJ_k}$. (For example, a class of sites might be the class of all oxylabile sites which are affected in a given manner by the presence of $O_2$; the possible states of a site in this class might then be an ionized state and an un-ionized state.)

Suppose further that for each $i$ and $k$, every species, $\theta$, in the set $\phi_i$ has exactly the same number of sites, $p_{ik}$, in the class $A_k$. That is, the classification of the sites of a species, $\theta$, depends only on which of the sets, $\phi_i$, that $\theta$ belongs to.
Suppose also, that any species, $\Theta$, of $\Phi$ is completely identified by stating the $\Theta_1$ of which it is a member and the states of each of its sites.

Suppose also, that for each $\Theta_1$, all logically possible assignments of states to sites (within the limitation that if a site is in the class $A_k$ then its state must be one of $B_{kl}, \ldots, B_{kj}, \ldots, B_{kj}$) actually occur among the species of $\Theta_1$.

Suppose, finally, that the free energy parameter, $a_{\Theta}$, and mass constraint vectors, $S_{\Theta}$, for each $\Theta$ of $\Phi$ depend only on which of the $\Theta_1$'s that $\Theta$ belongs to and on the states of the sites of $\Theta$; and, that this dependence is an additive dependence. To state this assumption more precisely, for each species $\Theta$ of $\Phi$, and for each site class $A_k$, and for each $j$, $1 \leq j \leq J_k$, let $h(\Theta, k, j)$ be the number of sites of $\Theta$ of class $A_k$ which are in the state $B_{kj}$. Our assumption then states that for each set $\Theta_1$ of species there is a vector $T_1$ and a number $\beta_1$, and that for each site class $A_k$ and each $j$, $1 \leq j \leq J_k$, there is a vector $T_{kj}$ and a number $\beta_{kj}$ such that

$$S_{\Theta} = T_1 + \sum_{k=1}^{K} \sum_{j=1}^{J_k} h(\Theta, k, j) T_{kj}, \text{ for all } \Theta \in \Theta_1$$

(2)
We may now state our results.

**Theorem 1.** Let \( x_\theta \) be the number of moles of species \( \theta \) present in the first phase at equilibrium. For each set \( \phi_i \) of species let

\[
y_i = \sum_{\theta \in \phi_i} x_\theta
\]  

and for each state \( B_{kj} \) let

\[
y_{kj} = \sum_{\theta \in \phi} h(\theta, k, j) x_\theta
\]  

(Note that \( y_i \) is then the total number of moles of species in \( \phi_i \), and that \( y_{kj} \) is the total number of sites in the state \( B_{kj} \) --measured in moles--regardless of the species on which these sites occur.)

Then, the following relationships hold:

\[
\sum_{i=1}^{I} y_i = \sum_{\theta \in \phi} x_\theta
\]
\[ J_k = \sum_{j=1}^{I} y_{kj} \sum_{i=1}^{p_{ik}} y_i \]  

(7)

for all site classes, \( A_k \);

\[ x_\theta = y_i \prod_{k=1}^{K} \prod_{j=1}^{J_k} \left( \frac{y_{kj}}{\sigma_k} \right)^{h(\theta,k,j)} \]  

(8)

for all sets \( \phi_i \) and all species \( \theta \in \phi_i \);

where \( \sigma_k \) denotes \( \sum_{j=1}^{J_k} y_{kj} \).

**Theorem 2.** If we replace the original problem by a new problem, as follows:

a) Eliminate all the species \( \theta \) of \( \phi \) from the first phase;

b) For each \( \phi_i \), add to the first phase a new species \( i \) with constraint vector \( T_i \) and energy parameter \( \beta_i \). Let \( y_i \) then be the number of moles of species \( i \) in the new problem;

c) For each \( k, 1 \leq k \leq K \), introduce a new phase whose species will be the states \( B_{kj} \), the constraint
vector and energy parameter associated with B_kj being T_kj and \( \beta_{kj} \), respectively. Let \( y_{kj} \) then be the number of moles of species B_kj in the new problem;

d) All the species of the original problem (except those in \( \emptyset \)) will be retained in the new problem with their original constraint vectors and energy parameters;

e) For each A_k, a new constraint, Eq. (7), is introduced;

then, the two problems will be equivalent in the following senses:

I. The minimum free energy of the original problem is the same as the minimum free energy for the new problem.

II. The number of moles of all the species (and their concentrations), except for those species in \( \emptyset \) which do not occur in the new problem, will be the same at equilibrium in the two problems.

III. If \( x_\emptyset \) is the amount of species \( \emptyset \) in the first problem at equilibrium, and if \( y_i \) and \( y_{kj} \) are the amounts of species i and B_kj, respectively, in the new problem at equilibrium, then these quantities are related by Eqs. (4)-(8). (Equation (7) holds, of course, simply because
it was imposed as a constraint on the new problem.)

Note: It should be observed that having replaced the old problem by the new problem and having solved the new problem, we may recover the original $x_9$'s by direct substitution in Eq. (8).
III. PROOFS

Throughout this section we will assume that each \( T_i \) and each \( T_{kj} \) is a given vector and that the \( S_\theta \)'s are given by Eq. (2). We will also assume that each \( \beta_i \) and each \( \beta_{kj} \) is a given number and that the \( \alpha_\theta \)'s are given by Eq. (3).

We will allow the \( y_i \)'s, \( y_{kj} \)'s, and \( x_\theta \)'s to be variables. We will make explicit various different assumptions about the manner in which they are related to each other in the various lemmas. Thus, at times we will assume that the \( y \)'s are defined in terms of the \( x \)'s by Eqs. (4) and (5); and, at times we will assume that the \( x \)'s are defined in terms of the \( y \)'s by Eq. (8).

However, we will always regard \( \sigma_k \) as being defined by

\[
\sigma_k = \sum_{j=1}^{J_k} y_{kj} .
\]

Lemma 1. \( \sum_{j=1}^{J_k} h(\theta,k,j) = p_{ik} \), for all \( \theta \) in the set \( \Phi_i \) and for all \( k \).

Proof. This is simply a restatement of the assumption that a species in \( \Phi_i \) has \( p_{ik} \) sites in the class \( A_k \) of sites.

We will find it convenient to introduce a polynomial in several variables, \( R(z) \), where the components of \( z \) are
\[ z_i, \text{ for } i=1,\ldots,I, \text{ and } z_{kj}, \text{ for } k=1,\ldots,K \text{ and } j=1,\ldots,J_k; \]

thus, \( z \) has a total of \( I + \sum_{k=1}^{K} J_k \) components. We define:

\[
R(z) = \sum_{i=1}^{I} \sum_{\theta \in \Omega_i} \prod_{k=1}^{K} \prod_{j=1}^{J_k} z_{kj} h(\theta, k, j). \tag{9}
\]

**Lemma 2.**

\[
z_{kj} \frac{\partial R}{\partial z_{kj}} = \sum_{i=1}^{I} \sum_{\theta \in \Omega_i} h(\theta, k, j) \prod_{k=1}^{K} \prod_{j=1}^{J_k} z_{kj} h(\theta, k, j).
\]

**Proof.** By calculation from 9.

**Lemma 3.**

\[
R(z) = \sum_{i=1}^{I} \prod_{k=1}^{K} \left( \sum_{j=1}^{J_k} z_{kj} \right) p_{ik}.
\]

**Proof.** Note that we have assumed that all the \( \theta \)'s in the same \( \Phi_i \) have the same classification of sites. Imagine that for each \( \theta \) of \( \Phi_i \) and for each site of \( \theta \) we write (with a very small pen!) the sum
if the site is in the class $A_k$. Note that we will have written each sum $p_{ik}$ times on each $\Theta$ of $\Phi_i$. Let us then develop the product

$$\prod_{k=1}^{K} \left( \sum_{j=1}^{J_k} z_{kj} \right)^{p_{ik}}$$

as follows.

For each $\Theta$ of $\Phi_i$, write a product of $z$'s over the sites of $\Theta$ by choosing at each site the term $z_{kj}$ corresponding to the state $B_{kj}$ that the site is in. Let us then add the resulting products for all $\Theta$ of $\Phi_i$. On the one hand it is clear, from the definition of $h(\Theta, k, j)$, that the resulting sum will be:

$$\sum_{\Theta \in \Phi_i} \prod_{k=1}^{K} \prod_{j=1}^{J_k} z_{kj} h(\Theta, k, j).$$

On the other hand, since we have assumed that as $\Theta$ varies over $\Phi_i$ all possible permissible assignments of sites to states occur exactly once, it is not hard to see that the
process has also evaluated the product, (10). Thus, the quantities (10) and (11) are equal.

If (10) and (11) are set equal and multiplied by $z_i$, and the result is added over $i$, we arrive at the identity asserted in Lemma 3.

**Lemma 4.** If the relationships of Eqs. (4) and (5) hold, then:

$$\sum_{i=1}^{I} y_i T_i + \sum_{k=1}^{K} \sum_{j=1}^{J_k} y_{kj} T_{kj} = \sum_{\theta \in \Phi} x_{\theta} S_{\theta}.$$

**Proof.** This follows by expanding $S_{\theta}$, using Eq. (2), and from Eqs. (4) and (5).

**Lemma 5.** If the relationships of Eqs. (4) and (5) hold, then

$$\sum_{i=1}^{I} y_i \beta_i + \sum_{k=1}^{K} \sum_{j=1}^{J_k} y_{kj} \beta_{kj} = \sum_{\theta \in \Phi} x_{\theta} \alpha_{\theta}.$$

**Proof.** From (3), (4), and (5).

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*Recall that as $\theta$ varies over $\Phi_1$, each possible assignment of states to sites is attained exactly once.*
Lemma 6. If Eqs. (4) and (5) hold, then so does Eq. (7).

Proof. Lemma 1.

Lemma 7. If Eq. (4) holds, then so does Eq. (6).

Lemma 8. If the \( x_\theta \)'s are the quantities associated with the original problem and if the \( y \)'s are defined by Eqs. (4) and (5), then Eq. (8) holds.

Proof. We know that for an appropriate Lagrangian vector, \( \pi \),

\[
\alpha_\theta + \log \frac{x_\theta}{a} = \pi \cdot S_\theta \text{ for all } \theta \in \Phi.
\]

Here, \( a \) denotes the total number of moles at equilibrium in compartment one of the first problem.

Hence, using Eqs. (2) and (3) (and letting \( \theta \) be in \( \Phi_1 \)):

\[
\log \frac{x_\theta}{a} = \pi \cdot S_\theta - \alpha_\theta = (\pi \cdot T_{i_1} - \beta_{i_1}) + \sum_{k=1}^{K} \sum_{j=1}^{J_k} h(\theta, k, j) (\pi \cdot T_{kj} - \beta_{kj});
\]

or, letting

\[
v_i = e^{\pi \cdot T_{i_1} - \beta_{i_1}} > 0
\]
and letting

\[ v_{kj} = e^{-\beta_{kj}} > 0 , \]

we get

\[ x_\theta = a v_i \prod_{k=1}^{K} \prod_{j=1}^{J_k} v_{kj} h(\theta, k, j) , \text{ for } \theta \in \Phi_i . \]  \hspace{1cm} (12)

Let \( c_k, 1 \leq k \leq K, \) be arbitrary positive numbers and set \( w_{kj} = c_k v_{kj} . \) Also, set

\[ w_i = a \prod_{k=1}^{K} c_k \; ; \]

then, using Lemma 1, Eq. (12) becomes

\[ x_\theta = w_i \prod_{k=1}^{K} \prod_{j=1}^{J_k} w_{kj} h(\theta, k, j) , \text{ for } \theta \in \Phi_i . \]  \hspace{1cm} (13)

Now, by taking

\[ c_{kj} = \left( \sum_{j=1}^{J_k} v_{kj} \right)^{-1} \]
we have

$$\sum_{j=1}^{J_k} w_{kj} = 1 . \quad (14)$$

From Eq. (14) and from Lemma 3 we get

$$R(w) = \sum_{i=1}^{I} w_i . \quad (15)$$

$$\frac{\partial R(w)}{\partial w_i} = 1 \quad (16)$$

$$\frac{\partial R(w)}{\partial w_{kj}} = \sum_{i=1}^{I} p_{ik} w_i . \quad (17)$$

From Eqs. (4) and (13) it follows that

$$y_i = w_i \sum_{\theta \in \phi_i} \prod_{k=1}^{K} \prod_{j=1}^{J_k} v_{kj} h(\theta, k, j)$$
\[ = (\text{From the definition of } R) \ w_i \frac{\partial R(w)}{\partial w_i} \]

\[ = (\text{From (16)}) \ w_i . \quad (18) \]

Next, by using Eqs. (5) and (13), we get

\[ y_{kj} = \sum_{i=1}^{I} w_i \sum_{\theta \in \phi_i} h(\theta, k, j) \prod_{\tilde{k}=1}^{J_k} \prod_{\tilde{j}=1}^{J_{\tilde{k}}} w_{\tilde{j}} h(\theta, \tilde{k}, \tilde{j}) \]

\[ = (\text{By Lemma 2}) \ w_{kj} \frac{\partial R(w)}{\partial w_{kj}} . \quad (19) \]

Combining (17), (18), and Lemma 6

\[ \frac{\partial R(w)}{\partial w_{kj}} = \sum_{\tilde{j}=1}^{J_{\tilde{k}}} y_{k\tilde{j}} = \sigma_k . \quad (20) \]

Combining (20) and (19)

\[ w_{kj} = \frac{y_{kj}}{\sigma_k} ; \quad (21) \]

then, (18), (21), and (13) yield (8). \textit{QED}
Lemma 9. If Eqs. (7) and (8) hold, so do Eqs. (4) and (5).

Proof. Let \( w_{kj} = \frac{y_{ki}}{\sigma_k} \) and let \( w_i = y_i \). Then

\[
\sum_{j=1}^{J_k} w_{kj} = 1 \tag{22}
\]

and Eq. (8) becomes

\[
x_{\theta} = w_i \prod_{k=1}^{K} \prod_{j=1}^{J_k} w_{kj} h(\theta, k, j) \text{ for all } \theta \in \phi_i . \tag{23}
\]

Next

\[
\sum_{\theta \in \phi_i} h(\theta, k, j) x_{\theta} = \sum_{i=1}^{I} w_i \sum_{\theta \in \phi_i} h(\theta, k, j) \prod_{k=1}^{K} \prod_{j=1}^{J_k} w_j h(\theta, \bar{k}, \bar{j})
\]

\[
= (\text{By Lemma 2}) w_{kj} \frac{\partial R(w)}{\partial w_{kj}} . \tag{24}
\]

By Lemma 3 and Eq. (22)

\[
\frac{\partial R(w)}{\partial w_{kj}} = \sum_{i=1}^{I} p_{ik} w_i = \sum_{i=1}^{I} p_{ik} y_i = (\text{By Lemma 6}) \sum_{j=1}^{J_k} y_{kj} = \sigma_k .
\]
This and Eq. (24) yield (5).

Finally, from (23),

\[ \sum_{\theta \in \Theta} x_{\theta} = \sum_{\theta \in \Theta} \sum_{k=1}^{K} \sum_{j=1}^{J_k} w_{kj} h(\theta, k, j) \]

= (From the definition of R) \[ w_i \frac{\partial R(w)}{\partial w_i} \].

But, Lemma 3 and Eq. (22) yield \( \frac{\partial R(w)}{\partial w_i} = 1 \). This and the fact that \( w_i = y_i \) yield (4).

**Lemma 10.** (A) If Eqs. (4) and (5) hold and if the \( x_{\theta} \) are those associated with the equilibrium solution in the original problem; or (B) if Eqs. (7) and (8) hold, then:

\[ \sum_{\theta \in \Theta} x_{\theta} = \sum_{i=1}^{I} y_i T_i + \sum_{k=1}^{K} \sum_{j=1}^{J_k} y_{kj} T_j \]

(25)

and

\[ \sum_{\theta \in \Theta} \left( \alpha_{\theta} + \log \frac{x_{\theta}}{a} \right) = \sum_{i=1}^{I} \left( \beta_i + \log \frac{y_i}{a} \right) \]

\[ + \sum_{k=1}^{K} \sum_{j=1}^{J_k} y_{kj} \left( \beta_{kj} + \log \frac{y_{kj}}{\sigma_k} \right) \]

(26)
where by "a" we mean the sum of all amounts of all species in the first compartment of the original problem.

**Note 1:** By Lemmas 6 and 8, (A) implies (B). Hence, we need only prove that (B) implies (25) and (26). But, by Lemma 9, (B) implies Eqs. (4) and (5) and by Lemma 7 Eqs. (4) and (5) imply Eq. (6). Hence, in proving Lemma 10 we may assume Eqs. (4), (5), (6), (7), and (8).

**Note 2:** By Eq. (6), a is also the sum of all the amounts of all the species in the first phase in the new problem.

Equation (25) follows at once from Lemma 4.

To prove Eq. (26), observe that by employing Lemma 5 and Eq. (26) we need only prove that

\[ \sum_{\theta \in \Phi} x_\theta \log x_\theta = \sum_{i=1}^{I} y_i \log y_i + \sum_{k=1}^{K} \sum_{j=1}^{J_k} y_{kj} \log \frac{y_{kj}}{\sigma_k} \quad (27) \]

To prove Eq. (27), note that from Eq. (8) we get

\[ \log x_\theta = \log y_i + \sum_{k=1}^{K} \sum_{j=1}^{J_k} h(\theta, k, j) \log \frac{y_{kj}}{\sigma_k} \]
for \( \theta \) in \( \Phi_i \), and hence

\[
\sum_{\theta \in \Phi} x_\theta \log x_\theta = \left( \sum_{i=1}^{I} \log y_i \sum_{\theta \in \Phi_i} x_\theta \right) \\
+ \sum_{k=1}^{K} \sum_{j=1}^{J_k} \left( \log \frac{y_{kj}}{\sigma_k} \sum_{\theta \in \Phi} h(\theta, k, j) x_\theta \right)
\]

\[
= \sum_{i=1}^{I} y_i \log y_i + \sum_{k=1}^{K} \sum_{j=1}^{J_k} y_{kj} \log \frac{y_{kj}}{\sigma_k}
\]

which is Eq. (27). \textbf{QED.}

Theorem 1 follows from Lemmas 7, 6, and 8.

To prove Theorem 2, observe that, given a solution of the old problem, we may define the \( y \)'s by means of Eqs. (4) and (5) to obtain a solution to the new problem. Conversely, by means of Eq. (8) we may obtain a solution to the old problem given a solution to the new problem. Lemmas 4, 6, 8, 9, and 10 assure the validity of this process and of the various assertions of Theorem 2.
REFERENCES


