A GENERALIZED TECHNIQUE FOR ELIMINATING SPECIES IN COMPLEX CHEMICAL EQUILIBRIUM CALCULATIONS

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PREFACE AND SUMMARY

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,

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[*]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.

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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, $X_1, \ldots, X_\ell, \ldots, X_L$, 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 H_2O-liquid is transferable into or from H_2O-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 $\alpha_1, \ldots, \alpha_l, \ldots, \alpha_L$. 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 α_l's depends on the Gibbs free energy function, we will call α_l the free energy parameter associated with X_l. In fact, $\alpha_l = \dfrac{\Delta F_l^0}{RT}$.

III. A set of N linear equations of the form

$$\sum_{l=1}^{L} s_{l,n} x_l = s_{0,n}, \quad 1 \le n \le N \tag{1}$$

where x_l is the (unknown) number of moles of X_l. 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, $s_{\ell,n}$ might be the number of atoms of some chemical element in each molecule of X_ℓ, 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 $s_{\ell,n}$ would be zero, except for those ℓ for which X_ℓ occurs in that phase, and X_ℓ is an ion. In that case, $s_{\ell,n}$ is the valence of X_ℓ, with the appropriate sign.

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

$$\sum_{\ell=1}^{L} x_\ell S_\ell = S_0 . \tag{1'}$$

Notice then, that S_ℓ is essentially the "empirical formula" for X_ℓ.

We will call S_ℓ the <u>constraint vector</u> associated with X_ℓ.

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, α_i, for each species, X_i.

III.   A constraint vector, S_i, for each species, X_i, and a vector S_0.

Note that the concentration[*] $[X_{i_0}]$ of each species X_{i_0} can be calculated by dividing x_{i_0} by the sum of all x_i's for which X_i occurs in the same phase as X_{i_0} (this sum, of course, includes x_{i_0} itself). Thus, the $[X_i]$'s are functions of the x_i's (although each $[X_i]$ does not depend only on the corresponding x_i).

It was shown in [2] and [3] that the x_i's may be efficiently determined, numerically, by minimizing the function

$$F = \sum_{i=1}^{L} x_i \, (\alpha_i + [X_i])$$

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[*]Throughout this paper, we measure concentration in mole fractions.

subject to the constraints that

$$\sum_{\ell=1}^{L} x_\ell S_\ell = S_0 \ .$$

(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 $\emptyset$ 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 $\emptyset$ be partitioned into various sets of species, $\emptyset_1, \ldots, \emptyset_i, \ldots, \emptyset_I$. That is, every species θ of $\emptyset$ is in exactly one of the sets, $\emptyset_i$.

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, θ, in the set $\emptyset_i$ has exactly the same number of sites, P_{ik}, in the class A_k. That is, the classification of the sites of a species, θ, depends only on which of the sets, $\emptyset_i$, that θ belongs to.

Suppose also, that any species, θ, of ϕ is completely identified by stating the ϕ_i of which it is a member and the states of each of its sites.

Suppose also, that for each ϕ_i, 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 $B_{k1}, \ldots, B_{kj}, \ldots, B_{kJ_k}$) actually occur among the species of ϕ_i.

Suppose, finally, that the free energy parameter, a_θ, and mass constraint vectors, S_θ, for each θ of ϕ depend only on which of the ϕ_i's that θ belongs to and on the states of the sites of θ; and, that this dependence is an additive dependence. To state this assumption more precisely, for each species θ of ϕ, and for each site class A_k, and for each j, $1 \le j \le J_k$, let $h(\theta,k,j)$ be the number of sites of θ of class A_k which are in the state B_{kj}. Our assumption then states that for each set ϕ_i of species there is a vector T_i and a number β_i, and that for each site class A_k and each j, $1 \le j \le J_k$, there is a vector T_{kj} and a number β_{kj} such that

$$S_\theta = T_i + \sum_{k=1}^{K} \sum_{j=1}^{J_k} h(\theta,k,j) T_{kj} \ , \quad \text{for all } \theta \epsilon \phi_i \qquad (2)$$

and

$$\alpha_\theta = \beta_i + \sum_{k=1}^{K} \sum_{j=1}^{J_k} h(\theta,k,j)\beta_{kj} \ , \ \text{for all } \theta \epsilon \emptyset_i \ . \tag{3}$$

We may now state our results.

<u>Theorem 1</u>. Let x_θ be the number of moles of species θ present in the first phase at equilibrium. For each set $\emptyset_i$ of species let

$$y_i = \sum_{\theta \epsilon \emptyset_i} x_\theta \tag{4}$$

and for each state B_{kj} let

$$y_{kj} = \sum_{\theta \epsilon \emptyset} h(\theta,k,j)x_\theta \ . \tag{5}$$

(Note that y_i is then the total number of moles of species in $\emptyset_i$, 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:

$$\sum_{i=1}^{I} y_i = \sum_{\theta \epsilon \emptyset} x_\theta \ ; \tag{6}$$

$$\sum_{j=1}^{J_k} y_{kj} = \sum_{i=1}^{I} p_{ik} y_i \qquad\qquad (7)$$

for all site classes, A_k;

$$x_\theta = y_i \prod_{k=1}^{K} \prod_{j=1}^{J_k} \left(\frac{y_{kj}}{\sigma_k}\right)^{h(\theta,k,j)} \qquad\qquad (8)$$

for all sets $\emptyset_i$ and all species $\theta \epsilon \emptyset_i$;

where σ_k denotes $\displaystyle\sum_{j=1}^{J_k} y_{kj}$.

<u>Theorem 2</u>. If we replace the original problem by a new problem, as follows:

a) Eliminate all the species θ of $\emptyset$ from the first phase;

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

c) For each k, $1 \le k \le K$, 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 β_{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_θ is the amount of species θ 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_θ'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_θ's are given by Eq. (2). We will also assume that each β_i and each β_{kj} is a given number and that the α_θ's are given by Eq. (3).

We will allow the y_i's, y_{kj}'s, and x_θ'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 σ_k as being defined by

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

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

and for all k.

Proof. This is simply a restatement of the assumption that a species in ϕ_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, for $i=1,\ldots,I$, and z_{kj}, for $k=1,\ldots,K$ and $j=1,\ldots,J_k$;

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

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

Lemma 2.

$$z_{kj} \frac{\partial R}{\partial z_{kj}} = \sum_{i=1}^{I} z_i \sum_{\theta \in \emptyset_i} h(\theta,k,j) \prod_{\bar{k}=1}^{K} \prod_{\bar{j}=1}^{J_k} z_{\bar{k}\bar{j}}^{h(\theta,\bar{k},\bar{j})} .$$

Proof. By calculation from 9.

Lemma 3.

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

Proof. Note that we have assumed that all the θ's in the same $\emptyset_i$ have the same classification of sites. Imagine that for each θ of $\emptyset_i$ and for each site of θ we write (with a very small pen!) the sum

$$\sum_{j=1}^{J_k} z_{kj}$$

if the site is in the class A_k. Note that we will have written each sum p_{ik} times on each θ of ϕ_i. Let us then develop the product

$$\prod_{k=1}^{K} \left(\sum_{j=1}^{J_k} z_{kj} \right)^{p_{ik}} \tag{10}$$

as follows.

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

$$\sum_{\theta \in \phi_i} \prod_{k=1}^{K} \prod_{j=1}^{J_k} z_{kj}^{h(\theta,k,j)} . \tag{11}$$

On the other hand, since we have assumed that as θ varies over ϕ_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.

<u>Lemma 4</u>. If the relationships of Eqs. (4) and (5) hold, then:

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

<u>Proof</u>. This follows by expanding S_θ, using Eq. (2), and from Eqs. (4) and (5).

<u>Lemma 5</u>. If the relationships of Eqs. (4) and (5) hold, then

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

<u>Proof</u>. From (3), (4), and (5).

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[*]Recall that as θ varies over ϕ_i, 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_θ'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, π,

$$\alpha_\theta + \log \frac{x_\theta}{a} = \pi \cdot S_\theta \text{ for all } \theta \in \emptyset .$$

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 θ be in $\emptyset_i$):

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

or, letting

$$v_i = e^{\pi \cdot T_i - \beta_i} > 0$$

and letting

$$v_{kj} = e^{\pi \cdot T_{kj} - \beta_{kj}} > 0 \; ,$$

we get

$$x_\theta = av_i \prod_{k=1}^{K} \prod_{j=1}^{J_k} v_{kj}^{h(\theta,k,j)} \; , \quad \text{for } \theta \epsilon \phi_i \; . \qquad (12)$$

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

$$w_i = a \prod_{k=1}^{K} c_k^{-p_{ik}} \; ;$$

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

$$x_\theta = w_i \prod_{k=1}^{K} \prod_{j=1}^{J_k} w_{kj}^{h(\theta,k,j)} \; , \quad \text{for } \theta \epsilon \phi_i \; . \qquad (13)$$

Now, by taking

$$c_{kj} = \left(\sum_{j=1}^{J_k} v_{kj} \right)^{-1}$$

we have

$$\sum_{j=1}^{J_k} w_{kj} = 1 \ . \tag{14}$$

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

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

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

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

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

$$y_i = w_i \sum_{\theta \in \phi_i} \prod_{k=1}^{K} \prod_{j=1}^{J_k} w_{kj}^{h(\theta,k,j)}$$

$$= \text{(From the definition of R)} \quad w_i \frac{\partial R(w)}{\partial w_i}$$

$$= \text{(From (16))} \quad w_i \ . \tag{18}$$

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

$$y_{kj} = \sum_{i=1}^{I} w_i \sum_{\theta \in \phi_i} h(\theta,k,j) \prod_{\bar{k}=1}^{K} \prod_{\bar{j}=1}^{J_{\bar{k}}} w_{\bar{j}}^{h(\theta,\bar{k},\bar{j})}$$

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

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

$$\frac{\partial R(w)}{\partial w_{kj}} = \sum_{\bar{j}=1}^{J_k} y_{k\bar{j}} = \sigma_k \ . \tag{20}$$

Combining (20) and (19)

$$w_{kj} = \frac{y_{kj}}{\sigma_k} \ ; \tag{21}$$

then, (18), (21), and (13) yield (8).   QED

Lemma 9. If Eqs. (7) and (8) hold, so do Eqs. (4) and (5).

Proof. Let $w_{kj} = \dfrac{y_{kj}}{\sigma_k}$ and let $w_i = y_i$. Then

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

and Eq. (8) becomes

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

Next

$$\sum_{\theta \epsilon \phi_i} h(\theta,k,j)x_\theta = \sum_{i=1}^{I} w_i \sum_{\theta \epsilon \phi_i} h(\theta,k,j) \prod_{\bar{k}=1}^{K} \prod_{\bar{j}=1}^{J_{\bar{k}}} w_j^{h(\theta,\bar{k},\bar{j})}$$

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

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),

$$\sum_{\theta \in \phi_i} x_\theta = w_i \sum_{\theta \in \phi_i} \prod_{k=1}^{K} \prod_{j=1}^{J_k} w_{kj}^{h(\theta,k,j)}$$

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

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).

<u>Lemma 10</u>. (A) If Eqs. (4) and (5) hold and if the x_θ are those associated with the equilibrium solution in the original problem; or (B) if Eqs. (7) and (8) hold, then:

$$\sum_{\theta \in \phi} x_\theta S_\theta = \sum_{i=1}^{I} y_i T_i + \sum_{k=1}^{K} \sum_{j=1}^{J_k} y_{kj} T_j \tag{25}$$

and

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

$$+ \sum_{k=1}^{K} \sum_{j=1}^{J_k} y_{kj} \left(\beta_{kj} + \log \frac{y_{kj}}{\sigma_k} \right) \tag{26}$$

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

$$\sum_{\theta \in \phi} x_\theta \log x_\theta = \sum_{i=1}^{I} y_i \log y_i$$

$$+ \sum_{k=1}^{K} \sum_{j=1}^{J_k} y_{kj} \log \frac{y_{kj}}{\sigma_k} . \qquad (27)$$

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 θ in $\emptyset_i$, and hence

$$
\sum_{\theta \in \emptyset} x_\theta \log x_\theta = \left(\sum_{i=1}^{I} \log y_i \sum_{\theta \in \emptyset_i} x_\theta \right)
$$

$$
+ \sum_{k=1}^{K} \sum_{j=1}^{J_k} \left(\log \frac{y_{kj}}{\sigma_k} \sum_{\theta \in \emptyset} h(\theta,k,j) x_\theta \right)
$$

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

which is Eq. (27). 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.

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