MEMORANDUM
RM-3935-1-PR
SEPTEMBER 1964

MASS ACTION LAWS AND
THE GIBBS FREE ENERGY FUNCTION
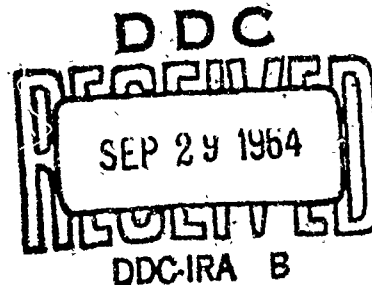
N. Z. Shapiro and L. S. Shapley

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N O T I C E

Enclosed is a revised version (RM-3935-1-PR) of RAND Memorandum RM-3935-PR,
Mass Action Laws And The Gibbs Free Energy Function, by N. Z. Shapiro and
L. S. Shapley. Please destroy your present version.

The two major changes in this revision are in Theorem 11.1 (p.45) and in
Corollary 12.3 (p.49). In the former, an omission in the statement of the
Theorem has been corrected (Theorem 11.1, line 3, addition of the phrase:
"and $N_k \neq 0$"). A restatement of the proof has been provided for Corollary
12.3.

Several less important typographical corrections have been made in various
parts of the Memorandum, and some additional, more recent references have
been added.

The RAND Corporation
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Santa Monica, California

PREFACE

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 in biology and physiology.

The Memorandum contributes to our ability to apply electronic computer techniques in the analysis of complex chemical systems, which, until recently, were far too complex for any quantitative analysis--e.g., models of complex physiological systems. But, as the capability to use computers in such applications becomes better understood, certain hitherto unresolved questions of mathematics and chemistry become apparent. This Memorandum considers the resolution of several of these problems, and should be of interest to both mathematicians and chemists.

The mathematical aspects should also be of interest in other fields where computational analyses of complex chemical systems are under consideration; e.g., in studies of rocket propulsion systems, planetary atmospheres, re-entry problems, etc.

[†]For example, see Refs. 4, 6-7, 9-12, and 14.

SUMMARY

Recent progress in computational techniques for the analysis of complex chemical systems has renewed interest in the relationship between the mass action laws, which have been traditionally employed for the computation of chemical equilibrium compositions, and the Gibbs free energy function, which until recently has generally been used only for theoretical purposes. Several attendant mathematical questions, hitherto unresolved, have now become important. These concern the existence and uniqueness of a solution to the equations arising from the mass action laws; the existence and uniqueness of a composition that minimizes the free energy; and the precise relationship between the two.

These questions become important because there is a greater probability of complex pathologies being exhibited when extremely large chemical systems are analyzed, and because the use of automatic digital computation demands a precise knowledge of these pathologies.

In Part I, the problems are formulated, both from the mathematical and chemical viewpoints. In Part II, mathematical tools unavailable in Gibbs' time are employed in

an attempt to answer the questions posed. Some applica-
tions of the results are given in the concluding section
for illustrative purposes.

ACKNOWLEDGMENTS

CONTENTS

INTRODUCTION

The problems discussed in this Memorandum are motivated by problems arising in the computation of chemical equilibrium. Classically, the composition of a single- or multi-phase chemical system in chemical equilibrium has been computationally determined by solving certain systems of simultaneous equations. These equations included linear equations (mass balance laws) as well as nonlinear equations (mass action laws). Gibbs [1] and others formulated the "free energy function" and showed that the mass action laws were closely related to a least-action principle with respect to that function. That is, he showed that under certain circumstances minimizing the free energy function is equivalent to satisfying the mass action laws.

Until recently, this relationship between the mass action laws and the Gibbs free energy function was ordinarily used only for theoretical purposes, while the actual computation of equilibrium compositions normally employed the mass action laws.[†] It has recently been shown [6-8] that chemical equilibrium compositions could be determined numerically by minimizing the Gibbs free

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[†]See, for example, Refs. 2-5.

energy function. Th , technique appears to offer extremely powerful and far reaching tools for the analysis of complex chemical systems. It has been employed in the analysis of extremely complex models of physiological systems which were formerly far beyond the reach of any quantitative analysis [9-12].

Due to the fact that it is now possible to analyze the equilibrium behavior of very complex chemical systems by means of automatic digital computation, certain questions which appear to have been left dormant since the time of Gibbs become important. We have in mind such questions as: Do the equations given by the mass balance laws and mass action laws possess a solution? Is this solution unique? If it is not unique, what is the nature of the set of all solutions? Does the Gibbs free energy function possess a minimum? Is this minimum attainable by a unique composition? If not, what is the nature of the set of all minimizing compositions? And finally, what are the relations between the solutions to the mass action laws and the minima of the Gibbs free energy function?

These questions now become important because, <u>first</u>, the extremely large chemical systems which are now

susceptible to analysis are more apt to exhibit pathologies, and are apt to exhibit more complex pathologies, than the simpler systems with which we have been able to deal in the past; and <u>secondly</u>, the use of automatic digital computation requires a much more precise knowledge of the nature of the pathologies which can occur.

In Part I (Sections 1-5) we will motivate formulations of these problems. In Part II (Sections 6-12) we will attempt to answer these questions, using mathematical tools which were unavailable to Gibbs.

An attempt has been made to write Part I so that it will be readable by the mathematically literate chemist, physiologist, etc. Part I also serves as a chemical introduction to the mathematician. Unfortunately, the chemist will find the chemical exposition of Part I quite elementary and belaboring of details. The mathematician will have an analogous complaint as to the mathematical exposition of Part I.

Part II will require some familiarity with mathematical analysis, linear algebra, and the theory of convex functions.

PART I

1. THE CHEMICAL SYSTEM

We will consider chemical systems composed of a finite

number of <u>homogeneous phases</u>. By a homogeneous phase we

mean one which is homogeneous in chemical composition,

pressure, and temperature. The question of under what

circumstances a phase is to be regarded as homogeneous is

one which is not considered here. It can only be answered

as part of the process by which we formulate a model of an

actual chemical system.

For example, a chemical system consisting of a liquid

solution in a vessel over which there is a vapor, might

be regarded as having two phases--a gas phase and a liquid

phase. A chemical system consisting of two solutions

separated by a semipermeable membrane might be regarded

as having two liquid phases.

It should be emphasized that all that is required of

a phase is that it be homogeneous. It <u>need not</u>, for example,

occupy contiguous portions of space. Thus, in Ref. 12, all

the interiors of the red cells of the body are usefully

regarded as forming a single phase. (Note that this phase

is not really homogeneous--but no phase is ever really

homogeneous. The only question is: Does the assumption of homogeneity hold to a sufficient degree for the analytical purposes which the designer of a model has in mind?) In what follows, the adjective "homogeneous" is generally omitted in referring to homogeneous phases. Note that the possibility of a chemical system consisting of exactly one phase has not been precluded.

It shall be assumed that each phase is at some specified pressure and temperature.

Let a chemical system have K phases, $P_1, P_2, \ldots, P_k, \ldots, P_K$. Let the chemical _species_ which can occur in the phase, P_k, be $A_{k1}, \ldots, A_{ki}, \ldots, A_{kI_k}$, where I_k is the number of species in phase k.

This last statement requires some elaboration. First, by a _species_ is meant a molecular species. Examples of species are H_2O, NaCl, Na^+. Note that when a species is specified, a molecular or ionic structure is implied as well as its composition in terms of the number of atoms of each element composing a molecule of the species. Thus, two distinct species might be identical when looked at in terms of their molecular formulas. Also, for reasons of technical mathematical convenience, a species which can occur in, say, two different phases will be regarded as representing two different species. Thus, if H_2O could

occur in both phase P_1 and phase P_2, we would regard H_2O in phase P_1, and H_2O in phase P_2, as representing two different species. Thus, if P_1 is a liquid phase and P_2 a gaseous phase, we might refer to H_2O-liquid, and to H_2O-vapor. When a molecule moves from one phase to another (for example, by evaporation, condensation, or migration across a semi-permeable membrane) we will regard a type of chemical reaction as having occurred--a reaction in which one species was transformed into another species.

Secondly, by saying that a species A_{ki} can occur in a phase P_k, it is not necessarily meant that at equilibrium any positive amount of A_{ki} will be found in P_k. It is merely that provision is to be made for the possibility that A_{ki} might occur in P_k. The question of what species will be provided for in what phases is a question which can only be answered by judgment and experience, and by some knowledge of the characteristics of the system under study. Theoretically, one might provide for the possible presence of each of the billions of chemical species in each phase. If this were done, and if the resulting numerical problem could be solved, almost all species would occur in negligibly small--less than trace--amounts. Thus, the problem of prescribing which species are to be

provided for in which compartments is a problem of predicting which species will occur in more than negligible amounts. Of course, in case of doubt, one can provide for a few species for which one is not certain.

It should be observed that if a phase P_k is a chemical solution, then the solvent itself is one of the species occurring in P_k.

Let N_{ki} be the number of <u>moles</u> of A_{ki} present in P_k. That is, the number of molecules of A_{ki} present is (by definition of a mole) equal to N_{ki} multiplied by Avagadro's number (approximately 10^{23}).

Let N_k be a vector whose components are $N_{k1}, \ldots, N_{kI_k}$. Let N be the vector whose components are

$$(N_{11}, N_{12}, \ldots, N_{1I_1}; N_{21}, N_{22}, \ldots, N_{2I_2}; \ldots; N_{K1}, N_{K2}, \ldots, N_{KI_K}) \ .$$

Thus, N_k is a vector with I_k components which specifies the <u>composition</u> of the phase P_k, and N is a vector with

$$I = \sum_{k=1}^{K} I_k$$

components which specifies the composition of the entire system.

Since the temperatures and pressures of the phases
are assumed specified, the vector N may be regarded as
a state vector. That is, N completely describes the state
of the system.

Let $\sigma_k(N)$ be the total number of moles in P_k when the
system is in state N; that is, let

$$(1.1) \qquad \sigma_k(N) = \sum_{i=1}^{I_k} N_{ki} \, , \qquad \text{for } 1 \le k \le K \, .$$

Also, let

$$(1.2) \qquad n_{ki}(N) = \frac{N_{ki}}{\sigma_k(N)} \, , \qquad \text{for } 1 \le k \le N \, , \quad 1 \le i \le I_k \, .$$

That is, $n_{ki}(N)$ is the <u>concentration</u> of A_{ki}, when the
system is in state N. Concentration can be measured in
a variety of scales. Our definition of n_{ki} amounts to
choosing the "mole fraction" scale.

2. THE MASS BALANCE LAWS

Following Ref. 10, we will express the mass balance
laws as linear conditions on N. Let $B_1, \ldots, B_\ell, \ldots, B_L$ be
a set of <u>fundamental building blocks</u>, such that each species
A_{ki} is composed of these building blocks.

For example, $B_1, \ldots, B_j, \ldots, B_L$ might be taken to be the atomic elements. However, it is often better to choose more complex structures as building blocks.[+] Let each molecule of A_{ki} contain $S_{k,i,j}$ units of B_j. Thus, the vector $(S_{k,i,1}, \ldots, S_{k,i,L})$ is essentially the molecular formula for A_{ki}. Note there is nothing to prevent two different species from having identical molecular formulas. Let S_j^0 be the total number of units of B_j in the system. We than have the conditions:

$$(2.1) \qquad \sum_{k=1}^{K} \sum_{i=1}^{I_k} S_{k,i,j} \, N_{ki} = S_j^0 \,, \qquad \text{for } 1 \le j \le L \,.$$

The description of those aspects of the system concerned with such questions as which species are permeable to interphase boundaries, can be implemented by an appropriate extension of the set of fundamental building blocks. This process has been more completely described elsewhere [10]; we will content ourselves here with a simple, brief example. Consider a system composed of two phases, separated by a semipermeable membrane. Suppose each phase contains the following species: H_2O, H^+, OH^-, a protein, R, and an ionized form of that protein, RH^+. Suppose the

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[+] See Refs. 10 and 11.

membrane is permeable to all species except R and RH^+.
This situation can be expressed by taking as <u>building</u>
<u>blocks</u>, H^+, OH^-, and two forms of R: R_1, representing
R in phase 1; and R_2, representing R in phase 2. Thus,
the following tableau gives the values of the $S_{k,i,\ell}$.
The columns represent building blocks; the rows represent
species; the body of the table gives the $S_{k,i,\ell}$.

Table I

	H^+	OH^-	R_1	R_2
$A_{1,1} = H^+$ in phase 1	1	0	0	0
$A_{1,2} = OH^-$ in phase 1	0	1	0	0
$A_{1,3} = H_2O$ in phase 1	1	1	0	0
$A_{1,4} = R$ in phase 1	0	0	1	0
$A_{1,5} = RH^+$ in phase 1	1	0	1	0
$A_{2,1} = H^+$ in phase 2	1	0	0	0
$A_{2,2} = OH^-$ in phase 2	0	1	0	0
$A_{2,3} = H_2O$ in phase 2	1	1	0	0
$A_{2,4} = R$ in phase 2	0	0	0	1
$A_{2,5} = RH^+$ in phase 2	1	0	0	1

We now leave the example and return to our discussion
of general chemical systems.

A chemical system may have one or more phases on which it is desirable to impose a condition of charge neutrality. To impose such a condition on, say, phase P_k, let $S_{i,k,L+1}$ be the charge per mole of A_{ik}. ($S_{i,k,L+1}$ will be zero unless A_{ik} is an ion.) Let $S_{i,k',L+1} = 0$ for $k' \neq k$. Let $S^0_{L+1} = 0$. Then, the charge neutrality condition for P_k has the same form as the equations of (2.1) and can be included among them.

Finally, from the definition of N_{ki}, it is clear that we must have

(2.2) $N_{ki} \geq 0$,   for $1 \leq k \leq K$, $1 \leq i \leq I_k$.

We are hence led to view the constraints on the system as a set of _simultaneous_ linear equations of the form (2.1) and a set of simultaneous inequalities of the form (2.2).

3. REACTION VECTORS AND THE STOICHIOMETRIC CONDITIONS

We consider chemical reactions involving the species of a system. In equilibrium chemistry, a reaction is described by writing two formal sums separated by a double arrow. Each of these formal sums consists of one or more

terms. Each of these terms consists formally of a positive
real number, called a stoichiometric coefficient, multi-
plied by the symbol for some chemical species of the system.
The species occurring in the left-hand formal sum are called
reactants; the species occurring in the right-hand formal
sum are called products. The two formal sums separated by
a double arrow form the stoichiometric equation of the
reaction. Note that mathematically speaking, the stoichi-
ometric equation is not an equation at all.

Given any such stoichiometric equation, we shall define
a vector θ, with components θ_{ki} ($1 \leq k \leq K$, $1 \leq i \leq I_k$),
as follows. To define θ, consider the reaction as written
out. If A_{ki} does not occur in the reaction, either as a
product or as a reactant, let $\theta_{ki} = 0$. If A_{ki} occurs as
a reactant, but not as a product, let θ_{ki} be its stoichi-
ometric coefficient. If A_{ki} occurs as a product, but not
as a reactant, let θ_{ki} be the negative of its stoichiometric
coefficient. Finally, if A_{ki} occurs both as a product and
as a reactant, let θ_{ki} be its coefficient as a reactant,
minus its coefficient as a product.

To understand the definition of θ, treat the stoichi-
ometric equation formally as a mathematical equation,
bringing all terms to the left-hand side (changing the

signs in the process) and collecting terms. The vector θ has been defined so that this manipulation yields the "equation"

$$(3.1) \qquad \sum_{k=1}^{K} \sum_{i=1}^{I_k} \theta_{ki} A_{ki} \rightleftharpoons 0 .$$

We shall call any vector θ so obtainable from a reaction a __reaction vector__. Observe that different reactions may have the same reaction vector.

We have, as a condition for a vector θ to be a reaction vector, that

$$(3.2) \qquad \sum_{k=1}^{K} \sum_{i=1}^{I_k} S_{k,i,\ell} \, \theta_{ki} = 0 , \qquad \text{for } 1 \le \ell \le L ,$$

where the $S_{k,i,\ell}$ are those of equations (2.1). The condition is sufficient as well as necessary; we shall regard any vector θ that satisfies (3.2) as a reaction vector.

Note that (2.1) and (3.2) are closely related. They differ, however, in two respects: 1) in that (2.1) is a condition on a vector N in order that it be a composition vector, while (3.2) is a condition on a vector θ in order that it be a reaction vector; and 2) in that the right-hand

sides of (3.2) are all zero, while those of (2.1) are not.

Unfortunately, the chemical literature refers to both sets of conditions as mass balance laws. We shall reserve the term "mass balance laws" for (2.1) and call (3.2) the stoichiometric conditions.

4. THE MASS ACTION LAWS

We shall confine our attention to systems which exhibit the simplest form of the mass action laws. Such systems are called "ideal" in Ref. 13.[†]

In our terminology, the mass action laws can be stated as follows: For any reaction having a reaction vector θ, there is an equilibrium constant $k(\theta)$, such that, for any composition vector N representing an equilibrium state of the system, we have

$$(4.1) \qquad \prod_{k=1}^{K} \prod_{i=1}^{I_k} (n_{ki}(N))^{\theta_{ki}} = k(\theta) \ .$$

We shall find it useful to perform certain manipulations on (4.1). Let us first take the logarithm of each side to get

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[†]The results of this paper also apply to certain types of non-ideal systems. However, we prefer to simplify the exposition by expressing our results in terms of ideal systems.

$$(4.2) \qquad \sum_{k=1}^{K} \sum_{i=1}^{I_k} \theta_{ki} \, \log n_{ki}(N) = \log k(\theta) \; .$$

Equation 4.2 is thus satisfied for all vectors θ which are reaction vectors; that is, for all vectors θ which satisfy the stoichiometric condition (3.2). It should be noted that the form of (3.2) implies that any scalar multiple of a reaction vector is a reaction vector, and that the sum of any two reaction vectors is a reaction vector. Furthermore, the form of equation (4.2) shows that if θ and φ are reaction vectors, then

$$\log k(\theta + \varphi) = \log k(\theta) + \log k(\varphi) \; ,$$

and that if r is a scalar, then

$$\log k(r\theta) = r \, \log k(\theta) \; .$$

These facts imply[†] the existence of constants C_{ki} such that

$$(4.3) \qquad \log k(\theta) = - \sum_{k=1}^{K} \sum_{i=1}^{I_k} C_{ki} \, \theta_{ki} \; .$$

[†]Because $\log k(\theta)$ is then a linear function of θ.

The substitution of the value of log $k(\theta)$ from (4.3)
into (4.2) allows us to restate the mass action laws as
follows: There are constants C_{ki} ($1 \le k \le K$, $1 \le i \le I_k$)
such that if θ is any reaction vector, and if N is any
equilibrium composition, then

$$(4.4) \qquad \sum_{k=1}^{K} \sum_{i=1}^{I_k} \theta_{ki} \, (C_{ki} + \log n_{ki}(N)) = 0 \, .$$

This form of the mass action law, which is quite equiv-
alent to the standard forms, is more convenient for our
purpose.

Another form is often quite useful for computational
purposes. Although there is no need for it in the present
paper, it is developed here for the sake of completeness;
the reader may omit the rest of this section without
destroying any continuity with what follows it.

Let us define

$$(4.5) \qquad y_{ki} = C_{ki} + \log n_{ki} \, .$$

Let us think of y as an I-dimensional vector where

$$I = \sum_{k=1}^{K} I_k \; .$$

If we do this, then the condition (4.4) states that y is
<u>orthogonal</u> to all vectors θ which satisfy the stoichio-
metric equations (3.2). If we think of the quantities
$S_{k,i,\ell}$ as forming L vectors $S_1, \ldots, S_\ell, \ldots, S_L$, each having
dimension I, then (3.2) becomes: θ is orthogonal to each
S. Thus, the mass action law may be restated as follows:
y is orthogonal to every vector which is orthogonal to each
S. But, it follows from elementary linear algebra that
the condition is satisfied if and only if y is representable
in the form

$$(4.6) \qquad y = \sum_{\ell=1}^{L} \pi_\ell \, S_\ell$$

or, equivalently,

$$(4.7) \qquad C_{ki} + \log n_{ki} = \sum_{\ell=1}^{L} \pi_\ell \, S_{k,i,\ell} \; .$$

Thus, the satisfaction of the mass action laws is
equivalent to the existence of quantities $\pi_1, \ldots, \pi_\ell, \ldots, \pi_L$
which satisfy (4.7).

5. THE GIBBS FREE ENERGY FUNCTION

We will have frequent occasion to refer to the free energy of a system. Since we are dealing with ideal systems and since pressure and temperature are constant for each phase, the free energy of a system is a function $F(N)$ of its composition N. It may be written as follows [13,14]

$$(5.1) \qquad F(N) = \sum_{k=1}^{K} \sum_{i=1}^{I_k} N_{ki} (C_{ki} + \log n_{ki}(N))$$

where C_{ki} (a constant) is called the free energy parameter of A_{ki}.

The least-action principle for the free energy states that the system is in equilibrium if and only if its free energy is a minimum, subject to the mass balance constraints (2.1) and to the constraint (2.2); that is to say, a composition vector N^0 represents an equilibrium state if and only if $F(N^0) \leq F(N)$ holds for all states N which satisfy the conditions (2.1) and (2.2) and which are sufficiently close to N^0.

Note that the least-action principle, as stated here, requires only that F have a local minimum at N^0. It will,

however, turn out that every local minimum of F is really
a global minimum, and hence that the underlined phrase
above can be eliminated.

PART II

6. NOTATION

Let E be the real line. For any integer J let E^J be the real Euclidean space of dimension J. For a point $N \in E^J$ we will say that $N \geq 0$ when all the components of N are non-negative. We will say that $N > 0$ when all the components of N are positive.

Let K be a positive integer representing the number of phases. Let $I_1, \ldots, I_k, \ldots, I_K$ be positive integers, I_k being the number of species in the kth phase. Let

$$I = \sum_{k=1}^{K} I_k .$$

We will find it convenient to designate the components of a point $N \in E^I$ by means of a doubly-indexed system of subscripts. Thus:

$$N = (N_{11}, \ldots, N_{1I_1}, \ldots, N_{k1}, \ldots, N_{kI_k}, \ldots, N_{K1}, \ldots, N_{KI_K}) .$$

For each k $(1 \leq k \leq K)$, let N_k denote the I_k-dimensional vector whose components are N_{ki} $(1 \leq i \leq I_k)$; thus,

$$N_k = (N_{k1}, \ldots, N_{kI_k}) \ .$$

N_k then represents the composition of the kth phase. We can then symbolically write

$$N = (N_1, \ldots, N_k, \ldots, N_K) \ .$$

7. QUASI-DEPENDENCE

DEFINITION 7.1. Two points M, N $\in$ E^I are <u>quasi-dependent</u> if for each phase, k, the vectors M_k and N_k are linearly dependent; that is, if for each k there exist scalars a_k and b_k, not both zero, such that $a_k M_k + b_k N_k = 0$. If M and N are quasi-dependent, we will write M ~ N.

The following properties of quasi-dependence are readily apparent from the definition.

THEOREM 7.2 Let M, N, N' $\in$ E^I.

A. M ~ M.

B. If M ~ N, then N ~ M.

C. If M and N are quasi-dependent, then any
    two linear combinations of M and N are quasi-dependent.

D. If M ~ N and M ~ N', then M ~ N $\div$ N'.

We note that "$\sim$" is not a transitive relation: $N \sim M$ and $M \sim N'$ do not necessarily entail $N \sim N'$-- for example, if $M = 0$.

THEOREM 7.3. Let M, $N \in E^I$. A necessary and sufficient condition for $M \sim N$ is that for every phase k and all i and j with $1 \le i$, $j \le I_k$, we have

$$(7.1) \qquad M_{ki} N_{kj} = M_{kj} N_{ki} \, .$$

Proof. First, to prove sufficiency, assume that (7.1) holds and let k be any phase. If $M_k = 0$, then M_k and N_k are clearly linearly dependent. Otherwise, there is a j with $M_{kj} \ne 0$. With j regarded as fixed and i as variable, (7.1) then says

$$N_{kj} M_k - M_{kj} N_k = 0 \, .$$

But since $M_{kj} \ne 0$, this shows that M_k and N_k are linearly dependent.

Second, to prove necessity, let M_k and N_k be linearly dependent. There are constants a_k and b_k, not both zero, with $a_k M_k + b_k N_k = 0$. We may assume without loss of generality that $a_k \ne 0$. We then have for all i

$$M_{ki} = - \frac{b_k}{a_k} N_{ki} \ .$$

Hence,

$$M_{ki} \ N_{kj} = - \frac{b_k}{a_k} N_{ki} \ N_{kj} = - \frac{b_k}{a_k} N_{kj} \ N_{ki} = M_{kj} \ N_{ki} \ . \quad \text{Q.E.D.}$$

DEFINITION 7.4. Let M, N $\in$ E^I. We will say

that M is quasi-dependent on N if, for each phase k,

the vector M_k is a scalar multiple of N_k. For any

N $\in$ I, let $\Lambda(N)$ denote the set of all M $\in$ E^I which

are quasi-dependent on N.

We thus see that:

THEOREM 7.5. $\Lambda(N)$ is the set of all points in

E^I which can be written in the form

$$(7.2) \qquad (\lambda_1 N_1, \ldots, \lambda_k N_k, \ldots, \lambda_K N_K) \ ,$$

where the λ_k are scalars. $\Lambda(N)$ is a linear subspace

of E^I. The dimension of $\Lambda(N)$ is the number of phases

k for which $N_k \neq 0$. If M, M' $\in$ $\Lambda(N)$, then M $\sim$ M'.

Finally, M $\in$ $\Lambda(N)$ if and only if M $\sim$ N, and $M_k = 0$

whenever $N_k = 0$.

Proof. Clear.

The following lemma will be used in a later proof.

LEMMA 7.6. Let $N \geq 0$, $M \in \Lambda(N)$, $M \geq 0$, and $M \neq N$. Then there exists $M' \in \Lambda(N)$ such that $M' \geq 0$ and $M' \neq N$, and such that N lies on the interior of the line segment joining M to M'.

Proof. Let $\lambda_1, \ldots, \lambda_k, \ldots, \lambda_K$ be the scalars in the representation (7.2) of $M \in \Lambda(N)$. Since $M \neq N$, not all the λ_k are 1. Hence, the number $c = \max_k |1 - \lambda_k|$ is positive. Define $\lambda'_k = 1 - (\lambda_k - 1)/c$, and define $M'_k = \lambda'_k N_k$, for each k. Then $M' \in \Lambda(N)$. Now, $(\lambda_k - 1)/c$ never exceeds 1, and is nonzero for at least one k. It follows that $M' \geq 0$ and $M' \neq N$. Moreover, we have

$$N = \frac{1}{1+c} M + \frac{c}{1+c} M' . \qquad Q.E.D.$$

Note. To understand the relevance of quasi-dependence, let us consider its meaning as applied to two points, M, $N \in E^I$ with $M > 0$ and $N > 0$. Then, by Theorem 7.5, M is quasi-dependent on N if and only if M and N are quasi-dependent. Furthermore, in the notation of Sec. 1, we have (by Theorem 7.3) that $M \sim N$ if and only if $n(M) = n(N)$; that is, $M \sim N$ if and only if M and N are composition vectors yielding identical concentrations.

8. PROPERTIES OF THE FREE ENERGY FUNCTION

The free energy function as given by (5.1) is defined only for those $N \in E^I$ for which $N > 0$. This is so because log t is undefined when $t \leq 0$. However, the definition can be extended to all $N \in E^I$ for which $N \geq 0$. To do this, first let us repeat the definition (1.1):

DEFINITION 8.1. Let $1 \leq k \leq K$ and let $N \in E^I$. Then

$$\sigma_k(N) = \sum_{i=1}^{I_k} N_{ki} .$$

If we expand (5.1), taking note of (1.2), and simplify the result, we arrive at the extended definition of F(N):

DEFINITION 8.2.

$$F(N) = C \cdot N + \sum_{k=1}^{K} \sum_{i=1}^{I_k} N_{ki} \log N_{ki} - \sum_{k=1}^{K} \sigma_k(N) \log \sigma_k(N) ,$$

where 0 log 0 is taken to be zero, and where

$$C \cdot N = \sum_{i,k} C_{ik} N_{ik} .$$

This then defines a function $F(N)$ for all $N > 0$,

because if $N \geq 0$, then $\sigma_k(N) \geq 0$, for all k. Also,

since $\lim_{t \to 0^+} t \log t = 0$, we have:

THEOREM 8.3. $F(N)$ is defined and continuous for

all $N \geq 0$.

We will wish to consider directional derivatives of F.

Clearly, it does not make sense to speak of the derivative

of F at N in the direction $\hat{\ }$, unless $N + t\hat{\ }$ is in the

domain of F for all small positive t. This motivates the

following definition:

DEFINITION 8.4. Given $\hat{\ }$, $N \in E^I$, we will say

that θ is admissible at N if $N + t\theta \geq 0$ for all suf-

ficiently small, positive, real t.

The following facts about admissibility will be

useful:

LEMMA 8.5. Let θ, $N \in E^I$. A necessary and suf-

ficient condition for θ to be admissible at N is that

$N \geq 0$ and that $\theta_{kj} \geq 0$ whenever $N_{kj} = 0$.

Proof. Clear.

LEMMA 8.6. Let θ be admissible at N. For each

k ($1 \leq k \leq K$) let J_k be the set of all j for which

either $N_{kj} \neq 0$ or $\theta_{kj} \neq 0$. Let J be the set of all

k, for which either $\sigma_k(N) \neq 0$ or $\sigma_k(\theta) \neq 0$; then:

<u>8.6A</u>: J_k is empty for all k for which k $\notin$ J.

<u>8.6B</u>: $N_{kj} + t\, \theta_{kj} > 0$ for all k, j, with j $\in J_k$,

and for all sufficiently small, positive t.

<u>Proof of 8.6A</u>. Let k $\notin$ J. We have, by the definition

of J,

1) $\sigma_k(N) = 0$

2) $\sigma_k(\theta) = 0.$

By Lemma 8.5, N $\geq$ 0. Hence, using (1):

3) $N_k = 0.$

Hence, by Lemma 8.5, $\theta_k \geq 0$; but then, using (2):

4) $\theta_k = 0.$

But (3) and (4) imply that J_k is empty. Q.E.D.

<u>Proof of 8.6B</u>. If $N_{kj} > 0$, the result clearly holds.

Otherwise (since N $\geq$ 0 by Lemma 8.5), $N_{kj} = 0$, and by

Lemma 8.5, $\theta_{kj} \geq 0$; but by the definition of J_k, we see

that N_{kj} and θ_{kj} cannot both vanish. Hence, $\theta_{kj} > 0$, and

again the result holds.

LEMMA 8.7. Let θ be admissible at N. Let the

sets J_k, and the set J be defined as in Lemma 8.6.

Let $Z = N + t\theta$. Then, for all sufficiently small

t > 0, we have:

8.7A:

$$F(Z) = C \cdot Z + \sum_{k \in J} \sum_{j \in J_k} Z_{kj} \log Z_{kj} - \sum_{k \in J} \sigma_k(Z) \log \sigma_k(Z) \; ;$$

and,

8.7B: $F(N + t\theta)$ is differentiable with respect to t; in fact

$$\frac{d}{dt} F(Z) = C \cdot \theta + \sum_{k \in J} \sum_{j \in J_k} \theta_{kj} \log Z_{kj} - \sum_{k \in J} \sigma_k(\theta) \log \sigma_k(Z) \; ;$$

and,

8.7C:

$$\frac{d}{dt} F(Z) = \sum_{k \in J} \sum_{j \in J_k} \theta_{kj} \left(C_{kj} + \log \frac{Z_{kj}}{\sigma_k(Z)} \right) \; ;$$

and,

8.7D: $F(N + t\theta)$ is twice-differentiable with respect to t; in fact,[†]

[†]This formula, for the case $K = 1$ and $N > 0$, appeared in Ref. 6.

$$\frac{d^2}{dt^2} F(Z) = \frac{1}{2} \sum_{k \varepsilon J} \frac{1}{\sigma_k(Z)} \sum_{i,j \varepsilon J_k} \frac{(Z_{ki} \theta_{kj} - Z_{kj} \theta_{ki})^2}{Z_{ki} Z_{kj}}$$

Also, we have,

<u>8.7E</u>: If for some k and j we have $N_{kj} = 0$, $\sigma_k(N) > 0$, and $\theta_{kj} > 0$, then $\lim_{t \to 0^+} \frac{d}{dt} F(Z) = - \infty$. Finally,

<u>8.7F</u>: If for all k and j for which $N_{kj} = 0$ and $\sigma_k(N) > 0$, we have $\theta_{kj} = 0$ (i.e., if the hypothesis of 8.7E is not satisfied), then

$$\lim_{t \to 0^+} \frac{d}{dt} F(Z) = \sum_{\substack{k \varepsilon J \\ }} \sum_{\substack{j \varepsilon J_k \\ N_{kj} > 0}} \theta_{kj} \left(C_{kj} + \log \frac{N_{kj}}{\sigma_k(N)} \right)$$

$$+ \sum_{\substack{k \varepsilon J \\ }} \sum_{\substack{j \varepsilon J_k \\ N_{kj} = 0}} \theta_{kj} \left(C_{kj} + \log \frac{\theta_{kj}}{\sigma_k(\theta)} \right).$$

<u>Proof of 8.7A</u>. This formula follows from Definition 8.2 and the convention concerning 0 log 0.

<u>Proof of 8.7B</u>. If we differentiate both sides of 8.7A, we obtain

$$\frac{dF(Z)}{dt} =$$

$$C \cdot \dot{c} + \sum_{k \in J} \sum_{j \in J_k} (1 + \log Z_{kj}) \dot{c}_{kj} - \sum_{k \in J} (1 + \log \sigma_k(Z)) \dot{\sigma}_k(\dot{c}) \ .$$

This differs from the right side of 8.7B by

$$\sum_{k \in J} \sum_{j \in J_k} \theta_{kj} - \sum_{k \in J} \sigma_k(\dot{c}) \ .$$

But this is seen to be 0, using Definition 8.1 and the fact that $\theta_{kj} = 0$ when $j \notin J_k$.

Proof of 8.7C. Follows from 8.7B. The right-hand side is well defined, because of 8.6B.

Proof of 8.7D. If we differentiate both sides of 8.7B we get:

$$(1) \quad \frac{d^2 F(Z)}{dt} = \sum_{k \in J} \sum_{j \in J_k} \frac{\theta_{kj}^2}{Z_{kj}} - \sum_{k \in J} \frac{\sigma_k(\dot{c})^2}{\sigma_k(Z)} \ .$$

But if we expand the inner term of the right-hand side of 8.7D, we get

(right-hand side of 8.7D) =

$$\frac{1}{2} \sum_{k \in J} \frac{1}{\sigma_k(Z)} \sum_{i,j \in J_k} \left(\frac{z_{ki}}{z_{kj}} \theta^2_{kj} - 2\varepsilon_{ki} \cdot_{kj} + \frac{z_{ki}}{z_{ki}} \theta^2_{ki} \right) =$$

$$\frac{1}{2} \sum_{k \in J} \frac{1}{\sigma_k(Z)} \left[\left(\sigma_k(Z) \sum_{j \in J_k} \frac{\theta^2_{kj}}{z_{kj}} \right) - 2\sigma_k(\theta)^2 + \left(\sigma_k(Z) \sum_{i \in J_k} \frac{\theta^2_{ki}}{z_{ki}} \right) \right]$$

= (right-hand side of (1)). Q.E.D.

<u>Proof of 8.7E and 8.7F</u>. Both of these propositions
follow from 8.7C, as can be seen by separating the sum-
mation of 8.7C into three portions, depending on the
following conditions on k ϵ J and j ϵ J_k:

Portion 1: $N_{kj} > 0$.

Portion 2: $N_{kj} = 0$ and $\sigma_k(N) = 0$.

Portion 3: $N_{kj} = 0$ and $\sigma_k(N) > 0$.

Portion 3 will be vacuous in the case hypothesized
by 8.7F and Portions 1 and 2 converge to the two sums of
8.7F. If Portion 3 is not vacuous, it converges to $-\infty$.
Q.E.D.

DEFINITION 8.8. Let ℓ be admissible at N. Define the directional derivative $F'_\ell(N)$ to be

$$\frac{d}{dt} F_\theta(N + t\,\theta)_{t=0}+ \overset{\text{def}}{=} \lim_{t\to 0^+} \frac{F(N + t\,\theta) - F(N)}{t} \; ,$$

in the event that this limit exists, accepting $+\infty$ and $-\infty$ as possible limits.

In order to evaluate $F'_\theta(N)$, we will need the following consequence of the mean value theorem of elementary calculus.

LEMMA 8.9. Let $t_o > 0$ and let $g(t)$ be a continuous real-valued function in the interval $0 \le t \le t_o$. Suppose that $\frac{dg(t)}{dt}$ exists in $0 < t < t_o$ and that

$$\alpha = \lim_{t\to 0^+} \frac{dg(t)}{dt}$$

exists (accepting $+\infty$ and $-\infty$ as values for α); then,

$$\left(\frac{dg(t)}{dt}\right)_{t=0^+}$$

exists and is equal to α.

THEOREM 8.10. Let θ be admissible at N. Suppose that for some k and j we have $N_{kj} = 0$, $\sigma_k(N) > 0$, and $\theta_{kj} > 0$. Then, $F_\theta'(N) = -\infty$.

Proof. Lemmas 8.7E and 8.9.

THEOREM 8.11. Let θ be admissible at N. Suppose that for all k and j for which $N_{kj} = 0$ but $\sigma_k(N) > 0$, we have $\theta_{kj} = 0$. Then

$$F_\theta'(N) = \sum_{k \in J} \sum_{N_{kj} > 0} \theta_{kj}\left(C_{kj} + \log \frac{N_{kj}}{\sigma_k(N)}\right)$$

$$+ \sum_{k \in J} \sum_{N_{kj} = 0} \theta_{kj}\left(C_{kj} + \log \frac{\theta_{kj}}{\sigma_k(\theta)}\right).$$

Proof. Lemmas 8.7F and 8.9.

The reader might ask why we have not dealt directly with the partial derivatives of F in order to calculate such quantities as $F_\theta'(N)$, or indeed in order to examine directly the behavior of F. The answer lies in an inspection of the formula of (8.11), which is nonlinear in θ, as long as any of the components of N vanish; that is, as long as the second summation of Theorem 8.11 is not vacuous.

The techniques for studying the extreme points of a function of several variables through their first-order partial derivatives depends on the fact that, for sufficiently well behaved functions, the directional derivative of a function $G(N)$ in the direction θ is a linear function of θ, and hence,

$$G'_\theta(N) = \sum_i \theta_i \frac{\partial G(N)}{\partial N_i} \; ,$$

where the summation index ranges over the components of θ. Many of the complications of this paper arise because this relation fails for $F(N)$.

LEMMA 8.12. Let θ and $-\theta$ be admissible at N. Then $F'_\theta(N) = -F'_{-\theta}(N)$.

Proof. We must have (because of Lemma 8.5) $\theta_{kj} = 0$ for all k and j for which $N_{kj} = 0$. Hence, the result follows from Theorem 8.11.

THEOREM 8.13. F is convex on its domain.

Proof. This follows immediately from the fact that F is continuous (Theorem 8.3), and from Lemma 8.7D, which guarantees that F is convex in the interior of all line segments contained in its domain [15].

LEMMA 8.14. Let $\theta \sim N$, let θ, $N \in E^I$, and let θ be admissible at N. Then, $F(N + t\theta)$ is a linear function of t, for all t (positive, zero, or negative) for which $N + t\theta \subset 0$.

Proof. Let $g(t) = F(N + t\theta)$. We will first consider only the $t > 0$ for which $N + t\theta \geq 0$. By Lemma 8.7D, Theorem 7.2C, and Theorem 7.3, we have

$$\frac{d^2 g(t)}{dt^2} = 0$$

for $t > 0$. Hence, $g(t)$ is linear for $t > 0$. Similarly, $g(t)$ is linear for $t < 0$, in the event that $-\theta$ is also admissible. That the two linear functions are the same is due to the fact that they coincide at $t = 0$ (Theorem 8.3), and to Lemma 8.12, which says that

$$\left(\frac{dg(t)}{dt} \right)_{t=0^-} = \left(\frac{dg(t)}{dt} \right)_{t=0^+}. \qquad \text{Q.E.D.}$$

Conversely:

LEMMA 8.15. Let t, $\bar{t}$ be real numbers different from zero. Let M, $N \in E^I$. Suppose that $M \geq 0$, $N \geq 0$, $tM + \bar{t}N \geq 0$ and that $F(tM + \bar{t}N) = tF(M) + \bar{t}F(N)$. Then, $M \sim N$.

Proof. By Theorem 7.2, and the fact that $F(tN) = tF(N)$ for all $t \geq 0$, $N \geq 0$, we may assume without loss of generality--by a change of notation--that $t > 0$, $\bar{t} > 0$, and $t + \bar{t} = 1$. Then we know, by the convexity of F (Theorem 8.13), that F is linear on the line segment joining M to N [15]. The result then follows from Lemma 8.7D and Theorem 7.3.

9. THE MINIMUM SET OF THE FREE ENERGY FUNCTION

The results of Sec. 8 will now enable us to specify the nature of the set on which F takes its minimum.

The mass balance laws of Sec. 2 have the effect of confining N to a certain linear manifold in E^I. Accordingly, we shall be interested in the minimum of F on a fixed linear manifold, H of E^I, subject to the additional constraint that $N \geq 0$.

DEFINITION 9.1. Let Q be the set of all $N \in E^I$ for which $N \geq 0$. Let H be a fixed linear manifold (the "mass balance" manifold) of E^I. Let D be the minimum set of F on $H \cap Q$. That is, let D be the set of all $N \in H \cap Q$ such that $F(N) \leq F(M)$ for all $M \in H \cap Q$.

Note. We have now introduced all the concepts necessary to define a chemical equilibrium problem. We might

thus define an <u>abstract chemical system</u> to be:

1) An integer, $K > 0$.

2) Integers $I_1, \ldots, I_k > 0$.

3) A linear manifold H of E^I, such that $H \cap Q$ is not empty, where

$$I = \sum_k I_k \ .$$

4) A point $C \in E^I$.

K specifies the number of phases. The I_k specify the number of species in the various phases. H determines the mass balance laws. C determines the parameters of the free energy function (or of the mass action laws).

THEOREM 9.2. If D is nonempty, there is a point $N \in D$ such that[+] $D = '(N) \cap H \cap Q$.

We shall obtain Theorem 9.2 as a consequence of several lemmas.

LEMMA 9.3. D is convex.

<u>Proof</u>. This follows from the fact that F is convex (Theorem 8.13) and the fact that at the minimum set of a convex function is convex.[±] Q.E.D.

[+]Recall the definition of '(N) in Definition 7.4.
[±]See Ref. 15.

LEMMA 9.4. F is constant on D.

Proof. This follows from the definition of D. Q.E.D.

LEMMA 9.5. If M M' ~ D, then M ~ M'.

Proof. If $M = M'$, then the result holds because $M \sim M$ (Theorem 7.2A). If $M \neq M'$, then by the convexity of D (Lemma 9.3), D contains the interval joining M to M'. Hence, since F is constant on D (Lemma 9.4), F is constant on the interval, and hence linear on the interval. Under these circumstances, we must have (Lemma 8.15) $M \sim M'$. Q.E.D.

LEMMA 9.6. Let N ∈ D; then, '(N) ^ H ^ Q ⊂ D.

Proof. Choose any point M ∈ '(N) ^ H ^ Q and choose M' ∈ '(N) ^ Q according to Lemma 7.6, so that N is interior to the line segment L joining M and M'. We have $M \sim M'$ (Theorem 7.5); hence, $M \sim M' - M$ (Theorem 7.2C); hence, F is linear on L, by Theorem 8.14. But, $L \subset H \cap Q$, because M, N ∈ H and M, M' ∈ Q. If F were not constant on L, then either $F(M) < F(N)$ or $F(M') < F(N)$, contradicting N ∈ D. Hence, $F(M) = F(N)$, and M ∈ D. Q.E.D.

LEMMA 9.7. If D is nonempty, there is a point, N ∈ D, such that if for any k, $N_k = 0$, then for all M ∈ D we must have $M_k = 0$.

Proof. For each k $(1 \leq k \leq K)$, define a point $M^{(k)}$ as follows: If M ∈ D can be found with $M_k \neq 0$, take $M^{(k)} = M$;

if not, let $M^{(k)}$ be an arbitrary element of D. Then the point

$$N = \frac{1}{K} \sum M^{(k)}$$

has the required properties, by convexity (Lemma 9.3) and the fact that $D \subset Q$ by definition of D.

Proof of Theorem 9.2. Let N be the point given by Lemma 9.7. By Lemma 9.6, $\Lambda(N) \cap H \cap Q \subset D$. Let $M \in D$. By Lemma 9.5, $M \sim N$. By the way in which N was defined, for no k can N_k be zero unless M_k is also zero. Hence, by Theorem 7.5, $M \in \Lambda(N)$. We have proved that $D \subset \Lambda(N)$. But, by the definition of D, $D \subset H \cap Q$. Hence, $D \subset \Lambda(N) \cap H \cap Q$. Thus, $D = \Lambda(N) \cap H \cap Q$. Q.E.D.

THEOREM 9.8. Let $N \in D$. Suppose that for some k and j, we have $N_{kj} = 0$, but $N_k \neq 0$. Then, for all $M \in H \cap Q$, we must have $M_{kj} = 0$.

Proof. Suppose that for some $M \in H \cap Q$, we have $M_{kj} > 0$. Since $N \geq 0$ and $N_k \neq 0$, we have $\sigma_k(N) > 0$. Let $\theta = M - N$. Then, $N + t\theta \in H \cap Q$ for all real t for which $0 \leq t \leq 1$. Therefore, $F(N + t\theta) \geq F(N)$ for $0 \leq t \leq 1$. Furthermore, $\theta_{kj} = M_{kj} - N_{kj} = M_{kj} > 0$. But then by Theorem 8.10, $F(N + t\theta)$ is a strictly decreasing function

of t for all sufficiently small positive t--this con-
tradicting the assumption that $N \in D$.   Q.E.D.

Note.   The import of Theorem 9.8 is roughly that every
species (j) whose presence has been allowed for, must be
present in some positive amount in any equilibrium com-
position, unless the entire phase (k) containing that
species is not present.   More precisely, if no amount of
j is present at equilibrium, then either N_{kj} must be zero
by virtue of the mass balance laws alone, or no amount of
any j' in the same phase as j can be present for that
equilibrium composition.

Of course, nothing in this theorem forbids N_k being
0 for some equilibrium compositions and non-zero for
other equilibrium compositions.

Note.   Theorems 9.2 and 9.8 provide a complete de-
scription of the possible equilibrium sets, D.   As a
matter of fact, we will prove below (Theorem 11.1) that
any nonempty set D satisfying the conditions of these
theorems is capable of being the equilibrium set for some
chemical system.

It follows from the fact that F is a convex function,
that D is a convex set.   But, Theorem 9.2 asserts much
more than the convexity of D.   In fact, Theorem 9.2

represents D as the intersection of a linear manifold, $(\cdot(N) \cap H)$, with Q.

THEOREM 9.9. If $H \cap Q$ is bounded, then D is nonempty.

Proof. Since $H \cap Q$ is closed and F is continuous (Theorem 8.3), F must attain a minimum value on $H \cap Q$. Q.E.D.

Note. There are no results in this paper which deal with the question of under what conditions D is nonempty when $H \cap Q$ is unbounded. Although the question appears to be interesting mathematically,[†] it appears to be of little chemical interest, because in actual applications $H \cap Q$ is always bounded. Thus, we would have been content to assume, from the outset, that $H \cap Q$ is bounded. We have not done so, since all of our results (except, of course, Theorem 9.9) are valid without this assumption, and, in fact, the proofs would not be simpler were we to make this assumption.

10. RELATION TO THE MASS ACTION LAWS

We now wish to relate D to the mass action laws. Recall from Secs. 3 and 4 that the mass balance laws make

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[†] For a discussion of this problem for single-phase systems (that is, for the case K = 1) see [16].

assertions about certain points $\alpha \in E^I$ which satisfy the
stoichiometric conditions. Since the stoichiometric con-
ditions are obtainable from the mass balance laws by
setting the right-hand sides of the mass balance laws
to zero, the set, H_0, of solutions to the stoichio-
metric conditions is a linear space; and H, the mass
balance manifold is a translation of H_0. We accordingly
define:

DEFINITION 10.1. H_0 is the set of all points
of the form M - N where M ϵ H and N ϵ H. D_0 is the
set of all points N ϵ H, such that N > 0, and such
that for all $\theta \in H_0$, we have:

$$\sum_{k=1}^{K} \sum_{i=1}^{I_k} \epsilon_{ki} \left(C_{ki} + \log \frac{N_{ki}}{\sigma_k(N)} \right) = 0 \ .$$

Thus, D_0 is the set of points satisfying the mass
balance, as well as the mass action laws. We have in-
sisted that N > 0 for N ϵ D_0, because the mass action
laws as ordinarily stated are only applicable when N > 0.

We now present a theorem which generalizes the mass
action laws. That is, the condition of Theorem 10.2
reduces to the mass action laws when N > 0.

THEOREM 10.2. (Generalization of mass action laws.) $N \in H \cap Q$ is an element of D if and only if $F'_\theta(N) \geq 0$ for all $\theta \in H_0$ for which θ is admissible at N, where $F'_\theta(N)$ is given by Theorem 8.10 or Theorem 8.11.

Proof. The theorem follows from the definition of D and the convexity of F. Note that Theorems 8.10 and 8.11 assure the existence of $F'_\theta(N)$ for θ admissible at N.

THEOREM 10.3. D_0 is the set of all $N \in D$ with $N > 0$.

Proof. Let $N \in H$, $N > 0$. We need to show that $N \in D$ if and only if $N \in D^0$. Since $N > 0$, all $\theta \in E^I$ are admissible at N. Since (by Theorem 8.12) $F'_\theta(N) = -F'_\theta(N)$, Theorem 10.2 says that $N \in D$ if and only if $F'_\theta(N) = 0$ for all $\theta \in H_0$. But, $N > 0$ means that the hypotheses of Theorem 8.11 are satisfied and that the second sum of Theorem 8.11 is zero. Hence,

$$F'_\theta(N) = \sum_{k=1}^{K} \sum_{j=1}^{I_k} \theta_{kj}\left(C_{kj} + \log \frac{N_{kj}}{\gamma_k(N)}\right). \quad \text{Q.E.D.}$$

THEOREM 10.4. If D contains at least one point with $N > 0$, then D is the topological closure of D_0.

Proof.   Apparent from Theorem 10.3 and the convexity
cf D.   Q.E.D.

11.   THE POSSIBLE MINIMUM SETS

Thus far, I, K, and $I_1, \ldots, I_K$ have been fixed positive
integers, H has been a fixed linear manifold of E^I,   C
has been a fixed point in E^I, and hence D has been a
fixed subset of E^I.   For the purpose of this section and
this section only, we will abandon the convention as to
C.   That is, we will allow C to vary and ask what possible
sets D may result.   Our answer (Theorem 11.1) is that D
may be any set which is consistent with Theorem 9.2 and
Theorem 9.8.

THEOREM 11.1.   Let N be a fixed element of
H ∩ Q.   Suppose that N satisfies the condition of
Theorem 9.8; that is, suppose that for any k,j for which
$N_{kj} = 0$ and $N_k \neq 0$ we must also have $M_{kj} = 0$ for all
M ∈ H ∩ Q.   Then, it follows that there exists
$C \in E^I$ such that the resulting minimum set, D, is
given by:

$$D = \Lambda(N) \cap H \cap Q .$$

Proof. Let A be the set of all $M \in Q$ such that $M_{kj} = 0$ for all k,j for which $N_{kj} \neq 0$. Let B be the set of all $M \in A$ such that

$$\sum_{k,j} M_{kj} = 1 .$$

Then B is a bounded set. (Note that if $N > 0$, then B is empty and hence certainly bounded.)

Define

$$G(M) = \sum_{k,j} M_{kj} \log M_{kj} - \sum_{k} \sigma_k(M) \log \sigma_k(M) .$$

By Theorem 8.3 (with $C = 0$), G is defined and continuous for $M \in Q$.

Since $B \subseteq A \subseteq Q$ and B is a bounded closed set, $G(M)$ is bounded on B. Hence, there exists a p such that $G(M) > p$ for all $M \in B$.

Let $M \in A$ and suppose that $M \neq 0$. Let

$$|M| = \sum_{k,j} M_{kj} ;$$

then $|M| > 0$. Let $M^* = \dfrac{M}{|M|}$; then $M^* \in B$ and hence

$G(M^*) > p$. A direct calculation shows that for any

$t > 0$, $G(Mt) = tG(M)$. Taking $t = \frac{1}{|M|}$, this yields

$G(M^*) = \frac{1}{|M|} G(M)$. Hence, $G(M) = |M| \, G(M^*) > p|M|$.

If $M = 0$, then $G(M) = 0$. We have thus proved that

$G(M) \geq p|M|$ for any $M \in A$ and that $G(M) = p|M|$ only when

$M = 0$.

Let us now define

$$C_{kj} = - \log \frac{N_{kj}}{\jmath_k(N)} \quad \text{if} \quad N_{kj} > 0 \, ,$$

$$C_{kj} = - p \quad \text{if} \quad N_{kj} = 0 \, .$$

Let $\theta \in E^I$ be admissible at N and let $\varepsilon \in H_0$. The

hypotheses of our theorem guarantee that the hypotheses

of Theorem 8.11 are satisfied. Hence, defining M by

letting $M_{kj} = \rho_{kj}$ if $N_{kj} = 0$ and $M_{kj} = 0$ if $N_{kj} \neq 0$, and

using the definition of C, we get

$$F'_{\varepsilon}(N) = - p|M| + G(M) \, .$$

Since $M \in A$, we have that $G(M) \geq p|M|$, and hence

$F'_{\varepsilon}(N) \cdot 0$. Furthermore, $F'_{\varepsilon}(N) \neq 0$ unless $M = 0$; that is,

unless $\varepsilon_{kj} = 0$ whenever $N_{kj} = 0$. This shows that $N \in D$

(by Theorem 10.2).

Let M' $\in$ D. Then, M' $\sim$ N (by Lemma 9.5). Also, we must have F constant on the line segment joining N and M'. Hence, $F'_{M'-N}(N) = 0$. Thus, $(M' - N)_{kj}$ must be zero whenever $N_{kj} = 0$. This means that M'_{kj} must vanish whenever N_{kj} vanishes. This fact and the fact that M' $\sim$ N imply (Theorem 7.5) that M' $\in$ ℓ(N).

Thus, D $\subset$ Λ(N). Since D $\subset$ H $\cap$ Q, we have D $\subset$ Λ(N) $\cap$ H $\cap$ Q. But, since N $\in$ D, we must have (Lemma 9.6) Λ(N) $\cap$ H $\cap$ Q $\subset$ D. Q.E.D.

12. EXAMPLES OF SPECIAL CASES OF INTEREST

In this section we give some applications of our results to special cases. We give them more for their illustrative value than for their importance.

THEOREM 12.1. Suppose that N > 0 for all N $\in$ D; then D contains at most one point.

Proof. We have already shown that D is the intersection of some linear manifold, D^*, with Q. If D contains two distinct points, then D^* must contain the line L through these points. But Q contains no complete line; hence, L will contain both points in Q and points outside of Q. Therefore, L contains a boundary point of Q; that is, a point N with N $\geq$ 0, but not N > 0, a contradiction. Q.E.D.

COROLLARY 12.2. Suppose that H is such that $N_k \neq 0$ for all k and all N ϵ H $\frown$ Q, and suppose that H $\frown$ Q contains at least one element, M, with M > 0. Then D contains at most one point, and, furthermore, if N ϵ D, then N > 0.

Proof. Theorems 12.1 and 9.8.

COROLLARY 12.3. Let K = 1 (that is, assume the system consists of only one phase). Suppose that H does not contain the origin (that is, suppose the right-hand sides of the mass balance equations do not all vanish). Then, D cannot contain more than one point.

Proof. By Theorem 9.2, if D is non-empty, it is given by D = $\Lambda(N)$ $\frown$ H $\frown$ Q. But, according to the definition, 7.4 of $'(N)$, and because K = 1, the set $'(N)$ is the set of scalar multiples of N. If H were to contain two distinct elements of the line $'(N)$, H would have to contain $\prime(N)$ which contains the origin. Q.E.D.

THEOREM 12.4. Let N, N' ϵ D and suppose that for some k neither $N_k = 0$ nor $N_k' = 0$. Then,

$$\frac{N_k}{\sigma_k(N)} = \frac{N_k'}{\sigma_k(N')} \cdot$$

That is, the mole fractions yielded by any two points in D are the same as long as it is possible to define the mole fraction.

Proof.   We have $N \sim N'$, by Theorem 9.2 (or directly from Lemma 9.5).   Q.E.D.

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