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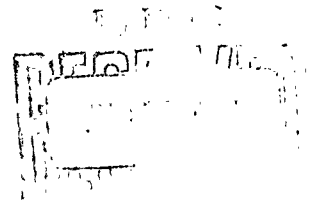
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CONDITIONS FOR  
A HOMOGENEOUS MIXTURE TO BE IDEAL

N. Z. Shapiro



PREPARED FOR:  
UNITED STATES AIR FORCE PROJECT RAND

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The **RAND** Corporation  
SANTA MONICA • CALIFORNIA

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PREFACE

The chemical equilibrium problem documented in this Memorandum stems from a continuing program of research at The RAND Corporation in the fields of biology and physiology. The work has application also to studies of rocket propulsion systems, upper atmosphere chemistry, re-entry phenomena, etc.

SUMMARY

This Memorandum considers homogeneous mixtures of three or more chemical species, obtaining conditions for such mixtures to be "ideal" over some range of chemical compositions. Temperature and pressure are assumed constant.

Ideality is shown to derive from the assumption that for each species, the activity of the species depends only on the concentration of that particular species, independently of the concentrations of the other species.

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CONDITIONS FOR A HOMOGENEOUS MIXTURE TO BE IDEAL

1. Introduction

Homogeneous mixtures of three or more chemical species at fixed temperature and pressure are considered. We obtain conditions for such a mixture to be "ideal" over some range of chemical compositions. Classically, ideality has been obtained as a consequence of various assumptions concerning the intermolecular forces operating in the mixture. (For example, see reference [1].) Our conditions are independent of any explicit assumptions concerning the mechanisms underlying the behavior of the mixture.

In particular, it is shown that ideality follows from the assumption that for each species the activity of that species depends only on the concentration of that species, and hence, is independent of the concentrations of the other species. This assumption is equivalent to the assumption that the activity coefficient of each species depends only on the concentration of that species. Similarly, it is equivalent to the assumption that the partial molar free energy of each species depends only on the concentration of that species.

2. Notation

We will consider a homogeneous mixture of  $m$  ( $m \geq 3$ ) species whose constituents are the chemical species,

$A_1, \dots, A_i, \dots, A_m$ . For each  $i$ ,  $1 \leq i \leq m$ , let  $N_i$  be the number of moles of  $A_i$  present in the mixture. Let  $N$  be an abbreviation for  $(N_1, \dots, N_i, \dots, N_m)$ . Thus,  $N$  is the composition of the mixture.

Let  $\bar{N}$  be the total number of moles in the mixture. That is, let:

$$\bar{N} = \sum_{i=1}^m N_i. \quad (1)$$

For each  $i$ ,  $1 \leq i \leq m$ , let  $n_i$  be the concentration of  $A_i$ , measured in mole fractions. That is, let

$$n_i = \frac{N_i}{\bar{N}}. \quad (2)$$

Let  $F(N)$  be the free energy of the mixture with composition  $N$ .

Let  $\mu_i(N)$  be the partial molar free energy of  $A_i$  when the mixture has composition  $N$ . We write  $\mu_i(N)$  instead of simply  $\mu_i$  to emphasize the functional dependence of  $\mu_i$  on  $N$ . Thus,

$$\mu_i(N) = \frac{\partial F(N)}{\partial N_i}. \quad (3)$$

Note that in this partial differentiation, we are assuming pressure and temperature constant, as we do throughout this Memorandum. It is well known that:

$$F(N) = \sum_{i=1}^m N_i \mu_i(N) . \quad (4)$$

Let  $a_i(N)$  be the absolute activity of  $A_i$ . Although we use absolute activities here as a mathematical convenience, we could just as well have used relative activities, which are proportional to absolute activities. Thus,  $a_i(N)$  satisfies the relation\*

$$\mu_i(N) = b \log a_i(N), \quad (5)$$

where  $b$  is a fixed constant. Normally  $b$  is taken equal to  $RT$ , but since we are dealing with a fixed constant temperature, this is of no matter to us.

Finally, let  $\lambda_i(N)$  be the absolute activity coefficient of  $A_i$ . Again we use absolute activity coefficients rather than relative activity coefficients just as a mathematical convenience. Thus the  $\lambda_i(N)$  satisfies the relation

$$a_i(N) = n_i \lambda_i(N) . \quad (6)$$

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\*All logarithms are natural logarithms.

### 3. Definition of Ideality

We now wish to define precisely what we mean by an ideal mixture. We will, in fact, give four completely equivalent definitions of ideality. The reader may choose any one of the four as the fundamental definition and regard the other three as consequences. In any case, we will show (in Sec. 5) that all four of these mutually equivalent definitions follow from the assumption which we stated briefly in Sec. 1, and which we will restate more completely in Sec. 4.

For all four definitions we will not require that an ideal mixture exhibit the specified behavior for all compositions, but only over some range\* of compositions,  $N$ .

Definition A. A mixture is ideal over some range of compositions if in that range the free energy takes the form:

$$F(N) = b \left( \sum_{i=1}^m N_i (c_i + \log n_i) \right), \quad (7)$$

where the  $c_i$  are constants, that is, are independent of  $N$ .

Definition B. A mixture is ideal over some range of compositions, if in that range the partial free molar

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\*For those readers interested in more mathematical precision, a "range of compositions" is an open subset of the positive orthant of  $m$ -dimensional Euclidean space.

energies take the form:

$$\mu_i(N) = b(c_i + \log n_i), \quad (8)$$

where the c's are constants.

Definition C. A mixture is ideal over some range of compositions if, in that range, the activities take the form

$$a_i(N) = k_i n_i \quad (9)$$

where the k's are constants.

Definition D. A mixture is ideal over some range of compositions if the activity coefficients,  $\lambda_i(N)$ , are constants in that range.

We must now show that A, B, C, D are mutually equivalent. To do this we will show that A is equivalent to B, which is equivalent to C, which is equivalent to D.

That B follows from A may be seen by differentiating (7), with respect to  $N_i$ , taking account of (2) and (3). That A follows from B is an immediate consequence of (4).

The equivalence of B and C (with  $c_i = \log k_i$ ) is an immediate consequence of (5).

The equivalence of C and D is an immediate consequence of (6).

#### 4. Assumptions under Which Ideality Holds

We now state three mutually equivalent assumptions, which will be shown (in Sec. 5) to yield ideality.

Assumption B': Over some range of compositions each  $\mu_i(N)$  depends only on  $n_i$ .

Assumption C': Over some range of compositions each  $a_i(N)$  depends only on  $n_i$ .

Assumption D': Over some range of compositions each  $\lambda_i(N)$  depends only on  $n_i$ .

The mutual equivalence of the assumptions B', C', D', follows at once from (5) and (6).

Note that in showing that either B', C', or D' implies ideality (that is, that B', or C', or D' implies A and B and C and D) we will have, for example, proven the following results:

I. If, over some range of compositions, the  $\mu_i(N)$  depend only on  $n_i$  then they must take the form (8), the free energy must take the form (7), the activities must be proportional to concentrations, and the activity coefficients are constants.

II. If, over some range of compositions, each activity  $a_i(N)$  depends only on  $n_i$ , then each  $a_i(N)$  is proportional to  $n_i$ .

5. Proof of Result

In order to prove the results stated here, it will clearly be sufficient to prove that B' implies B. Thus we will assume that over some range of compositions each  $\mu_i(N)$  depends only on  $n_i$ . Thus, we will assume that there are  $m$  functions:  $g_1(t), \dots, g_m(t)$ , such that over the range in question:

$$\mu_i(N) = g_i(n_i) . \quad (10)$$

Let

$$g_i'(t) = \frac{dg_i(t)}{dt} .$$

Note that if  $i$  and  $j$  are any distinct indices between 1 and  $m$ , then using (2) and (1):

$$\frac{\partial(n_i)}{\partial N_j} = \frac{\partial\left(\frac{n_i}{N}\right)}{\partial N_j} = -\frac{n_i}{N^2} \frac{\partial N}{\partial n_j} = -\frac{n_i}{N^2} . \quad (11)$$

Hence, if we differentiate (10) with respect to  $N_j$ , we get

$$\frac{\partial \mu_i(N)}{\partial N_j} = g_i'(n_i) \frac{\partial n_i}{\partial N_j} = -\frac{g_i'(n_i)n_i}{N^2} . \quad (12)$$

But from (3) we obtain:

$$\frac{\partial \mu_i(N)}{\partial N_j} = \frac{\partial^2 F(N)}{\partial N_i \partial N_j} = \frac{\partial^2 F(N)}{\partial N_j \partial N_i} = \frac{\partial \mu_j(N)}{\partial N_i} . \quad (13)$$

Combining (12) and (13) we get:

$$g_i'(n_i)n_i = g_j'(n_j)n_j . \quad (14)$$

Let us define:

$$h_i(t) = t g_i'(t) ; \quad (15)$$

then (14) becomes:

$$h_i(n_i) = h_j(n_j) . \quad (16)$$

Let us now vary  $N$  by an increment,  $dN$ , so small that  $N + dN$  remains within the range of compositions under consideration. Let us do this in such a way that  $dn_j = 0$  but  $dn_i \neq 0$ . (We may do this despite the restriction that  $\sum dn_i = 0$ , because  $m \geq 3$ .) We see that since  $dn_j = 0$  the right side of (16) is not changed, and hence, the left hand side of (16) is not changed, but  $dn_i \neq 0$ ; thus, we have shown that each  $h_i(t)$  is a constant,  $b_i$ . But again by (16), we have  $b_i = b_j$ . We have thus proved



that each  $h_i(t)$  is a constant,  $b$ , independent of both  $i$  and  $t$ :

$$h_i(t) = b ; \quad (17)$$

or using (15):

$$t g_i'(t) = b \quad (18)$$

or

$$g_i(t) = b(\log t + c_i) . \quad (19)$$

If we combine (19) and (10) we obtain the desired

$$\mu_i(N) = b(c_i + \log n_i) .$$

REFERENCE

1. Guggenheim, E. A., "On the Statistical Mechanics of Dilute and of Perfect Solutions," Proc. Royal Soc. London, Vol. A135, 1932.