A Class of Nonideal Solutions

I - Definition and Properties

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SUMMARY

A new class of nonideal solutions is defined by constructing a function to represent the composition dependence of thermodynamic properties for members of the class, and some properties of these solutions are studied. The constructed function has several useful features: (1) Its parameters occur linearly. (2) It contains a logarithmic singularity in the dilute solution region and contains ideal solutions and regular solutions as special cases. (3) It is applicable to N-ary systems and reduces to M-ary systems (M ≤ N) in a form-invariant manner. The ability of the function to describe data for a real system is tested in a companion report (NASA TP-1930).

INTRODUCTION

The effective application of classical thermodynamics to complex physical problems demands two things. First, it requires an understanding of the foundations of thermodynamics in order to appreciate both its capabilities and its inherent limitations. Second, it demands convenient and accurate mathematical representations of thermodynamic data in order to facilitate their use in computations. On the one hand, theoretical studies of thermodynamics are gradually and successfully exposing its foundations (ref. 1). On the other hand, theoretical thermodynamic studies have had little real success in guiding us to an accurate representation of thermodynamic data. The many different functions which have been, and are being, used to represent the composition dependence of thermodynamic properties are ample evidence of this. Each of these many functions, some wholly empirical and others with a theoretical base, has been used to give an adequate representation of data only for a limited number of systems or for a restricted composition range. None of them seems to have the flexibility to deal with a large variety of systems over their entire composition range. It would be a great computational convenience to have available a relatively simple "universal" function of composition variables which is capable of adequately representing the data for all systems over the complete range of compositions and which can be used for interpolation and extrapolation of the data. As nice as this would be, we have no assurances either that such a function exists or, if it exists, that we can find it. In fact, given the diversity of physical systems, it is more likely that such a universal function cannot be found. However, it does seem reasonable to expect that we can construct a function which is, in this respect, an improvement over those already being used.

In this report I shall first briefly survey some of the composition functions which have been used to represent thermodynamic data. Then I will construct a new function which I propose for the representation of data. Finally, I shall examine some of the properties of the class of solutions which can be represented by this function. The application of the new representation to the experimental data for a few different systems is discussed in a companion report (ref. 2).

In making a survey of the functions which have been used for the composition dependence of thermodynamic properties one quickly realizes two things. First, most of the functions tend to be expressed in terms of polynomials; second, by far the greatest variety of functions has been applied to binary systems, with ternary systems being in a distinct second place. This is a natural consequence of the need to deal with the idiosyncrasies of actual data for a particular system and the fact that experimental data have
been pretty much confined to binary systems with a small sprinkling of ternary systems. Marsh (ref. 3) has observed that many of the approximations to the thermodynamic excess functions of binary systems can be regarded as special cases of a rational function of two polynomials. Thus if $\Delta G$ is the excess Gibbs free energy per mole, $T$ the absolute temperature, $R$ the universal gas constant, and $x_1, x_2$ mole fractions, then he considered functions of the form

$$\frac{\Delta G}{x_1x_2RT} = \sum_{k=0}^{m} A_k(x_1 - x_2)^k - \sum_{j=0}^{n} B_j(x_1 - x_2)^j = [n,m], B_0 = 1$$  \hspace{1cm} (1)$$

Of course, for binary systems $x_1 + x_2 = 1$ and equation (1) could be written as a function of $x_1$ or $x_2$ alone. Approximations of the type (1) can clearly be regarded as Padé approximants (ref. 4) of numerator degree $m$ and denominator degree $n$ for $\Delta G/x_1x_2RT$, and this gives us a convenient classification scheme for discussing the many expressions used for binary systems. The approximants $[0,m]$ and $[n,0]$ have been discussed by Van Ness (ref. 5). Otterstedt and Missen (ref. 6) refer to the approximant $[0,m]$ as the general Margules representation and refer to approximants of the type $[n,0]$ as the general van Laar representation because $[1,0]$ corresponds to the original van Laar form (ref. 7). Myers and Scott (ref. 8) used the approximants $[1,m]$, $m < 4$, which might be regarded as modified Margules representations although they could equally well be viewed as generalizations of the van Laar form. Van Ness and coworkers suggested three equations which they regarded as modifications of the Margules form. Abbott and Van Ness (ref. 9) suggested the forms $[1,2]$ and $[2,3]$, while Shatas, Abbott, and Van Ness (ref. 10) proposed the form $[3,4]$ - all are of the type $[m - 1, m]$. The first of these is a special case of the functions used by Myers and Scott. Marsh expressed the second of these as a ratio of two quadratics but, from the Abbott and Van Ness version of the formula, it is clear that the numerator must be a cubic polynomial and therefore Marsh's formulas relating the coefficients in equation (1) to those used by Abbott and Van Ness may be incorrect. Not only can approximants of the type $[n,0]$ and $[1,m]$ be regarded as generalizations of the van Laar form $[1,0]$, but also there exists a third type which can be viewed logically in the same way. These are the approximants $[n, n - 1]$ since they too contain $[1,0]$ as a special case. These approximants also include as special cases the "q-equations" of Wohl (ref. 11) for binary systems. His $(n + 1)$-suffix q-equation corresponds to the approximant $[n, n - 1]$ if the coefficients of the denominator polynomial are of the form

$$B_j = B_j \left(\binom{n}{j}\right), \ j = 0, 1, \ldots, \text{where} \left(\binom{n}{j}\right) \text{is a binomial coefficient and the} \ B \text{on the right is a parameter expressible in terms of Wohl's parameters} \ q_1 \ \text{and} \ q_2. \ \text{Thus} \ B = (q_1 - q_2)/(q_1 + q_2). \ \text{Wohl actually considered only the cases} \ n = 1, 2, 3, 4. \ \text{There is still another approximation of binary properties which should be mentioned. It is the square root function of Otterstedt and Missen (ref. 6) and is not of Padé approximant type.}
Otterstedt and Missen use $n_1 = 1$ and Bandreth (ref. 12) uses $n_1 = 2$. The functions which have been mentioned to this point are only applicable to binary systems. If we wish to consider systems with $N$ constituents (N-ary systems), then we must use other forms which, of course, will apply to the binary forms for $N = 2$. The most obvious expression one could write would be an analog to a truncated Taylor expansion, and it could be thought of as a virial expansion.

$$\frac{\Delta G}{RT} = \sum_{k=n_1}^{n_2} A_k x_1^{(k-2)/2}$$  \hspace{1cm} (2)

Benedict, Johnson, Solomon, and Rubin (ref. 13) used an equation of this type; however, they restricted it to use only the quadratic, cubic, or quartic terms. Not all of the coefficients in equation (3) are independent since the coefficients must be symmetric in the indices. Also since $\Delta G$ is an excess function, then for all $i A + A_i + A_{ii} + A_{iii} + \ldots = 0$. Another form which can also be interpreted as a truncated Taylor series but with different term groupings is

$$\frac{\Delta G}{RT} = A + \sum_{i=1}^{N} A_i x_i + \sum_{i=1}^{N} \sum_{j=1}^{N} A_{ij} x_i x_j + \sum_{i=1}^{N} \sum_{j=1}^{N} \sum_{k=1}^{N} A_{ijk} x_i x_j x_k \ldots$$  \hspace{1cm} (3)

This form of representation was used by Pelton and Bale (ref. 14) for a ternary system ($N = 3$). The coefficients in equation (4) must satisfy

$$\sum_{n_1=0}^{M} A_{n_1} 00 \ldots 0 = \sum_{n_2=0}^{M} A_{0n_2} 0 \ldots 0 = \ldots = \sum_{n_N=0}^{M} A_{000 \ldots 0} = 0$$

for excess functions. A variant of equation (3) which has been given considerable attention is the approximation

$$\frac{\Delta G}{RT} = \frac{\sum_{i=1}^{N} A_i x_i}{\left( \sum_{k=1}^{N} B_k x_k \right)^0} + \frac{\sum_{i=1}^{N} \sum_{j=1}^{N} A_{ij} x_i x_j}{\left( \sum_{k=1}^{N} B_k x_k \right)^2} + \ldots$$  \hspace{1cm} (5)

For the choice $A_i = 0$ this becomes the N-ary version of Wohl's (ref. 11) q-equations for ternary systems, which he wrote through quartic terms. Another well-known special case can be obtained from equation (5) if we choose $A_{ij}, A_{ijk}$, and all higher-order coefficients as zero. Supplementing these conditions with $B_k = 1$ and $A_{kj} = w(1 - \delta_{kj})/2$, where $\delta_{kj} = \delta_{jk}$ is the Kronecker delta, gives the excess Gibbs free energy for
the regular solutions of Hildebrand (ref. 15). If instead we pick \( A_{ij} = w(1 - \delta_{ij})b_i b_j / 2 \), then we obtain an N-ary generalization of the binary van Laar solutions, that is, those characterized by the approximant [1,0]. Perhaps the most extensive use of equation (5) has been by Pitzer and coworkers (ref. 16), who applied it to aqueous electrolyte solutions. Their excess function can be obtained from equation (5) by selecting \( A_i = 0 \) for all \( i \), \( B_i = 0 \) for \( i \neq 1 \), and \( B_1 \) equal to the molecular weight of water. The form of the first term in equation (5) also suggests an N-ary analog of the Pade approximants for binary systems, that is, the ratio of two functions of the kind shown in equation (3), although I know of no instance where such an approximation has been attempted other than the two special cases just mentioned.

Each of the functions mentioned to this point has been firmly rooted in the polynomials. This is not true for the next example.

\[
\frac{\Delta G}{RT} = A \sum_{i=1}^{N} x_i \ln \left( \sum_{j=1}^{N} A_{ij} x_j \right) + B \sum_{i=1}^{N} x_i \left( \sum_{j=1}^{N} B_{ij} x_j / \sum_{k=1}^{N} C_{ik} x_k \right) \tag{6}
\]

This function was given by Renon and Prausnitz (ref. 17), who actually wrote it with \( C_{ik} = A_{ik} \). It contains a number of functions, proposed by others, as special cases. If \( B = 0 \), it becomes the Wilson equation (ref. 18). It becomes the equation of Heil and Prausnitz (ref. 19) for \( B = -A = 1 \) and \( C_{ik} = A_{ik} \) and the NRTL (nonrandom, two liquid) equation of Renon and Prausnitz (ref. 17) for \( A = 0 \) and \( B = 1 \).

A final illustration of the kinds of functions which have been used to represent the composition dependence of thermodynamic data is one which might be called the "bootstrap" representation. It is not as specific a functional form as those I have already mentioned, and it could utilize any one of them. Although this representation could be written for an N-ary system, the notation becomes complex and so I shall write it only for a ternary system.

\[
\Delta G(x_1, x_2, x_3) = \Delta G_{12}(x_1, x_2) + \Delta G_{13}(x_1, x_3) + \Delta G_{23}(x_2, x_3) + \Delta G_{123}(x_1, x_2, x_3) \tag{7}
\]

In this expression \( \Delta G_{ij}(x_i, x_j) \) are any suitable binary functions and \( \Delta G_{123}(x_1, x_2, x_3) \) is a ternary function. I call this a "bootstrap" representation because it is possible, but not necessary, to determine the coefficients in the binary functions from binary data alone and subsequently the coefficients in the ternary function only from those ternary data for which \( x_i = 0 \) for all \( i \). Shatas, Abbott, and Van Ness (ref. 10) used this kind of representation. For two of the binaries they chose a six-constant Margules representation from [0,5], and for the third binary they selected the [3,4] Pade approximant. The ternary function had the form of the cubic term in equation (3) multiplied by \( (x_1 x_2 x_3) \). For a quaternary system equation (7) would be replaced by the sum of a quaternary function and all possible binary and ternary combinations.

It would probably be helpful to point out, in general terms, some of the difficulties connected with the use of the functions I have been discussing before attempting to construct an alternative. I have already mentioned that many of the functions lack the flexibility to handle the wide diversity of behavior encountered in real systems. One is then continually faced with the prospect of constructing new functions tailored to the system of interest or else using available functions in a piecewise manner as was done for alcohol-
chloromethane binaries by Moelwyn-Hughes and Missen (ref. 20) and Paraskevopoulos and Missen (ref. 21). For most of these binary systems they found it necessary to use the approximant \([0,2]\) for \(\ln(\Delta G/x_1 x_2 RT)\) in the dilute alcohol region and a three-constant Margules form elsewhere. For the binary methanol–carbon tetrachloride they used \([0,2]\) in the dilute alcohol region and \([0,1]\) elsewhere as approximations for \(\ln(\Delta G/x_1 x_2 RT)\). Such piecewise fitting is a nuisance because one must ensure the continuity of the function and its first derivatives at the boundaries of the segments. The lack of a "universal" function is particularly disconcerting if one is attempting a Barker analysis (ref. 22) for the excess Gibbs free energy from vapor pressure data because one must make a commitment to a function in advance. The results are, to some extent, dependent on the function and its flexibility. A second source of difficulty is the fact that some of the functions I have mentioned are nonlinear in the parameters. This gives a person two options and neither is completely satisfactory. One can preselect some of the parameters as did Myers and Scott (ref. 8) and Pitzer (ref. 16) and so reduce the equations to linear form by limiting their flexibility. Alternatively, one can face the unpleasantness of nonlinear parameter estimation and the possibility of nonunique solutions. A third problem arises because accurate experimental data become increasingly difficult to obtain as one approaches the highly dilute solutions. But since the approximating equations are generally unconstrained, they supply no guidance on the shape of the function in this region. It would be better if the function could be so constructed that it supplied some help in dealing with the dilute solution. Pitzer (ref. 16), for example, has done this in his work with aqueous electrolyte solutions by relying on Debye–Huckel theory as a guide. The final problem which I wish to mention is the possibility of introducing undesirable singularities into \(\Delta G\) or its derivatives. This is built into the Otterstedt-Missen (ref. 6) formula and can arise in the functions with nonlinear parameters by an inappropriate choice of parameters. The Otterstedt-Missen function (2) with \(n_1 = 1\) produces an \(x_1^{-1/2}\) singularity in the excess chemical potential for species 1 which dominates the \(\ln x_1\) singularity from the ideal portion of the Gibbs free energy.

In my opinion a suitable function for the representation of the composition dependence of thermodynamic properties should exhibit six desirable features: (1) It should have a form directly applicable to \(N\)-ary systems. (2) It should reduce simply and obviously to lower order subsystems in a form-invariant manner. That is, the function for an \(M\)-ary system, \(M < N\), should have a form identical to that for an \(N\)-ary system. (3) It should contain ideal behavior as a special case because ideal behavior is often a good first approximation to real behavior. (4) Its behavior in very dilute solutions should be constrained to reflect the known behavior of these solutions. (5) Its parameters should appear linearly. Finally, (6) it should have sufficient flexibility to represent even difficult systems reasonably well.

DEFINITION OF A CLASS OF NONIDEAL SOLUTIONS

My desire to include ideal behavior as an integral part of the function rather than an add-on means that I must work with a thermodynamic potential rather than an excess function. Generally speaking, the most convenient experimental thermodynamic variables, other than composition variables, are
the intensive ones. These are the temperature and pressure in the case of a fluid. Consequently it is natural to work with the thermodynamic potential for which the moles of each constituent are the only extensive variables: the Gibbs free energy. In the following calculations only the composition variables will be written explicitly; the intensive variables will be suppressed. It should be kept in mind that all parameters are to be regarded as functions of the intensive variables. I shall begin by introducing notation and by obtaining some results which will be useful subsequently.

Consider a system of \( N \) constituents and let \( n_i, i = 1, 2, ..., N \) represent the moles of species \( i \) per unit mass. The Gibbs free energy per unit mass \( g \) is then a homogeneous function of degree 1 in the \( n_i \).

\[
g(\lambda n_i) = \lambda g(n_i) \tag{8}
\]

By definition the chemical potential for the \( i \)th species \( \mu_i \) is

\[
\mu_i = \mu_i(n_i) = \partial g / \partial n_i \tag{9}
\]

and by Euler's theorem for homogeneous functions it satisfies

\[
g = \sum_{i=1}^{N} \mu_i n_i \tag{10}
\]

It is a trivial consequence of equation (8) and the chain rule for differentiation that the chemical potential is a homogeneous function of degree zero in \( n_i \). For \( \lambda \) independent of \( n_i \)

\[
\lambda \mu_k(n_i) = \lambda \left[ \frac{\partial g(n_i)}{\partial n_i} \right] = \left[ \frac{\partial g(\lambda n_i)}{\partial \lambda n_i} \right]
\]

\[
= \sum_{j=1}^{N} \left[ \frac{\partial g(\lambda n_i)}{\partial \lambda n_j} \right] \delta_{jk}
\]

\[
= \lambda \sum_{j=1}^{N} \left[ \frac{\partial g(\lambda n_i)}{\partial \lambda n_j} \right] = \lambda \mu_k(\lambda n_i)
\]

Hence we conclude that

\[
\mu_k(n_i) = \mu_k(\lambda n_i) \tag{11}
\]

and then from Euler's theorem and \( \partial \mu_k / \partial n_j = \partial^2 g / \partial n_j \partial n_k = \partial \mu_j / \partial n_k \) we obtain

\[
\sum_{j=1}^{N} n_j \partial \mu_k / \partial n_j = \sum_{j=1}^{N} n_j \partial \mu_j / \partial n_k = 0 \tag{12}
\]
The second equality is known as the Gibbs-Duhem equation. We now define the total moles per unit mass \( n \) and the mole fractions \( x_i \).

\[
\begin{align*}
n &= \sum_{j=1}^{N} n_j \\
x_i &= n_i / n
\end{align*}
\]  

(13)

The choice \( \lambda = n^{-1} \) in equations (8) and (11) immediately shows that the chemical potential and the Gibbs free energy per mole \( G \) can be regarded as functions of the mole fractions.

\[
\begin{align*}
G &= n^{-1}g(n_i) = g(n_i / n) = g(x_i) = G(x_i) = \sum_{j=1}^{N} u_j x_j \\
\mu_k &= u_k(n_i) = u_k(n_i / n) = \mu_k(x_i)
\end{align*}
\]  

(14)

The last equality in the first member of equation (14) comes directly from equation (10). In principle, one can conclude from equation (14) that \( G(x_i) \) and \( \mu_k(x_i) \) are homogeneous of degree 1 and 0, respectively, in the mole fractions because \( g(n_i) \) and \( \mu_k(n_i) \) are such functions with respect to the moles. In practice these restrictions are both unnecessary and unwise because they would force us to write unnecessarily complex functions. This is a direct consequence of the fact that the mole fractions satisfy \( \sum_{j=1}^{N} x_j = 1 \). Consider as an example the simple function

\[
\frac{n_i}{\sum_{j=1}^{N} n_j} = \frac{x_i}{\sum_{j=1}^{N} x_j} = x_i
\]

Although the first two members are clearly homogeneous of degree 0, the last member is just as clearly homogeneous of degree 1. Over the domain of definition \( \sum_{k=1}^{N} x_k = 1, x_j \geq 0 \), the last two members have the same value, but the values differ if extended outside this domain. The identity \( \sum_{k=1}^{N} x_k = 1 \) can be used to interconvert mole fraction dependent functions which are homogeneous functions of any degree and nonhomogeneous functions within the domain of interest to thermodynamics, and so I shall disregard the homogeneous conditions. Because of equation (14) we can now express derivatives with respect to \( n_i \) in terms of derivatives with respect to \( x_i \). From equation (13) we find that

\[
\frac{ax_i}{an_j} = (\delta_{ij} - x_i) / n
\]

(15)

If we apply this and the chain rule for differentiation to equation (14), we obtain
where $\phi_i$ is a differentiation operator. The second member of equation (16), when combined with the second equality in equation (12), gives the Gibbs-Duhem equation written in mole fractions.

$$\mu_i = \frac{a g}{a n_i} = \left(1 - \sum_{k=1}^{N} x_k \frac{a}{a x_i} + \frac{a}{a x_i}\right) G(x_j) = (1 + \phi_i) G(x_j)$$

$$\frac{a \mu_k}{a n_j} = n^{-1} \left(\frac{a}{a x_j} - \sum_{k=1}^{N} x_k \frac{a}{a x_k}\right) \mu_k(x_i) = n^{-1} \phi_j \mu_k(x_i)$$

where $\phi_k$ is a differentiation operator. The second member of equation (16), when combined with the second equality in equation (12), gives the Gibbs-Duhem equation written in mole fractions.

$$\sum_{j=1}^{N} n_j \frac{a \mu_j}{a n_k} = \sum_{j=1}^{N} x_j \frac{a \mu_j}{a x_k} - \sum_{k=1}^{N} x_k \sum_{j=1}^{N} x_j \frac{a \mu_j}{a x_k}$$

$$= \sum_{k=1}^{N} (\delta_{k\ell} - x_k) \sum_{j=1}^{N} x_j \frac{a \mu_j}{a x_k} = 0 \quad (17)$$

We can now begin the actual construction of a function to represent the Gibbs free energy. Suppose we consider a system of $N$ nonreacting species labeled by Latin indices $i$, $j$, $k$, ..., $= 1, 2, ..., N$ which can form two or more coexisting phases labeled by Greek indices from the first portion of the alphabet $a, b, ... = 1, 2, ...$. The condition for phase equilibrium is simply the system of equations

$$\mu_i(x_i) = \mu_j(x_j) \quad (18)$$

Remember that we are suppressing the writing of the intensive thermodynamic variables which label the state. Let $k$ be a fixed index and examine the behavior of dilute solutions in the vicinity of the point $x_k = \delta_{ik}$, that is, solutions in which species $k$ is dominant and all species $j \neq k$ are trace species. Then it is an experimental fact, known as Raoult's law, that the mole fraction of a trace species in one phase is proportional to its mole fraction in some other phase, assuming that we are sufficiently close to $x_k = \delta_{ik}$. Of course, the proportionality depends on the choice of trace species, dominant species, and the pair of phases being considered.

$$x_j^\alpha = f_{jk} x_j \quad j \neq k, \text{ as } x_i = \delta_{ik}$$

A natural generalization of this is the equation
As the concentrations of the trace species increase, \( \alpha^\beta_{jk} \), \( q_j^\alpha \), and \( q_j^\beta \) will become concentration dependent. In the thermodynamics of multiphase systems, one usually assumes that the phases are noninteracting in the sense that the Gibbs free energy of the whole system is the sum of the Gibbs free energies for each phase. This implies that one can factor \( \alpha^\beta_{jk} \) into contributions from each phase. Thus we write the factorization

\[
\alpha^\beta_{jk} = \frac{K^\beta_{jk}}{K^\alpha_{jk}}
\]

(20)

This factorization is not unique because we can put a common factor in the numerator and denominator on the right side and not affect the left side of equation (20). Let \( e_{jk} \) be any quantity with dimensions of energy per mole which depends on the choice of dominant and trace species but not phase. Then by taking the logarithm of equation (19) and combining it with equations (18) and (20), we obtain

\[
u_j^\alpha - e_{jk} \left( q_j^\alpha \ln x_j^\alpha + \ln K_j^\alpha \right) = \nu_j^\beta - e_{jk} \left( q_j^\beta \ln x_j^\beta + \ln K_j^\beta \right)
\]

\[j \neq k, \text{ as } x_i + \delta_{ik} \]        (21)

From equation (21) it is clear that we will obtain the condition (19) from the solution to the equations (18) if we equate both sides of equation (21) to a quantity \( f_{jk} \) which depends only on the choice of dominant and trace species.

\[
u_j^\alpha = f_{jk} + e_{jk} \ln K_j^\alpha + e_{jk} q_j^\alpha \ln x_j^\alpha \quad j \neq k, \text{ as } x_i + \delta_{ik}
\]

(22)

This form for the chemical potential can also be extended to the dominant species because as \( x_i + \delta_{ik} \), \( \ln x_k + 0 \) and the \( \ln x_k^\alpha \) term does not contribute. Hence we tentatively write the chemical potential for all species in the form

\[
u_j = \nu_{jk} + e_{jk} \ln x_j \quad \text{as } x_i + \delta_{ik}
\]

(22)

where the phase index has now been suppressed and \( \nu_{jk} \) and \( e_{jk} \) may be composition dependent.

Equation (22) is a nice simple form for the chemical potential as \( x_i + \delta_{ik} \) and is consistent with the generalization (19) of Raoult's law. But this is not sufficient. The chemical potential must also be the gradient of the Gibbs free energy, that is, there must exist a function \( g \) which generates equation (22) by differentiation as shown in equation (9). But this can only happen if the chemical potential satisfies the integrability conditions \( \alpha_j \partial \alpha_k = \alpha_k \partial \alpha_j \) (see, e.g., theorem III.8, p. 1600, ref. 1a).
If we temporarily treat \( u_{jk} \) and \( \epsilon_{jk} \) as constants and apply the second member of equation (16) to (22), we obtain

\[
n(\Delta u_j/\Delta n_i) = \epsilon_{jk} \delta_{ji}/x_j - \epsilon_{jk}
\]

Thus we find that

\[
n\left(\frac{\partial u_j}{\partial n_i} - \frac{\partial u_i}{\partial n_j}\right) = \epsilon_{ik} - \epsilon_{jk}
\]

and the form (22) does not satisfy the integrability conditions even with \( u_{jk} \) and \( \epsilon_{jk} \) as constants because the trace species \( i \) and \( j \) could behave quite differently near the point \( x_k = \delta_{ik} \) and therefore we do not wish to assume that \( \epsilon_{ik} \) and \( \epsilon_{jk} \) are the same. This forces us to look for the simplest modification of equation (22) which does satisfy the integrability conditions when \( u_{jk} \) and \( \epsilon_{jk} \) are independent of composition. Observe that

\[
n \left(\frac{a}{\Delta n_i} - \frac{a}{\Delta n_j}\right) \sum_{k=1}^{N} x_k \epsilon_{ik} = \epsilon_{ik} - \sum_{k=1}^{N} x_k \epsilon_{ik}
\]

and thus

\[
n \left(\frac{a}{\Delta n_i} - \frac{a}{\Delta n_j}\right) \sum_{k=1}^{N} x_k \epsilon_{ik} = \epsilon_{ik} - \epsilon_{jk}
\]

Equations (23) and (24) show that if a linear combination of the \( \epsilon_{ik} \) is subtracted from the right side of equation (22), a function results which satisfies the integrability conditions. Any quantity independent of mole fractions could be added without affecting integrability and, since adding \( \epsilon_{jk} \) will give a simpler function for the Gibbs free energy, we write

\[
u_j = u_{jk} + \epsilon_{jk} \ln x_j - \sum_{k=1}^{N} x_k \epsilon_{ik}
\]

as \( x_i + \delta_{ik} \) \hspace{1cm} (25)

From this function the Gibbs free energy per mole in the vicinity of \( x_i = \delta_{ik} \), \( G(k) \), can be obtained by integrating the first member of equation (16) or more simply by using the last equality in the first member of equation (14). Its validity can be checked by differentiation.

\[
G(k) = \sum_{j=1}^{N} (u_{jk} + \epsilon_{jk} \ln x_j)x_j \hspace{1cm} \text{as } x_i + \delta_{ik}
\]

(26)

Finally, to obtain a function which is suitable away from \( x_i = \delta_{ik} \), I shall merely superpose the \( G(k) \) weighted by the mole fractions.

\[
G = \sum_{k=1}^{N} G(k)x_k = \sum_{j=1}^{N} \sum_{k=1}^{N} (u_{jk} + \epsilon_{jk} \ln x_j)x_j x_k
\]

(27)
The simple function (27), with \( \mu_{jk} \) and \( \epsilon_{jk} \) independent of composition but functions of the intensive variables, should represent the behavior of an N-ary system for the dilute solution regions in the vicinity of each of the N points \( x_i = \delta_{jk}, k = 1, 2, ..., N \). Consequently it is probable that it will also do quite well in other parts of the domain of the function. However, it is still possible to improve its flexibility and enhance its capability for dealing with concentrated solutions without diminishing its capabilities in the dilute solution regions of the domain. This can be accomplished by the simple expedient of returning the parameters \( \mu_{jk} \) and \( \epsilon_{jk} \) in equation (27) to composition dependent functions. We must then face the problem of making an explicit choice for the functions \( \mu_{jk} \) and \( \epsilon_{jk} \). Clearly, one might concoct many potentially suitable functions on the basis of some selected criteria or personal whim. One can, in a sense, avoid making an explicit choice and permit the thermodynamic system to make the selection by working with an expansion of \( \mu_{jk} \) and \( \epsilon_{jk} \) as a linear combination of a suitable finite basis set of composition dependent functions. The expansion parameters can then be determined from data. That is the approach I shall pursue here. I shall only demand that the character of the expansion permit the functions \( \mu_{jk} \) and \( \epsilon_{jk} \) to approach constant values in the dilute solution regions so that conventional Raoult's law behavior can be accommodated there. Probably a number of basis sets exist that one might wish to consider. But there is one which comes to mind first because it offers both simplicity and elegance and at the same time is consistent with the six criteria enunciated at the beginning of this section: the set of N elementary symmetric functions of the N variables \( x_i \). The elementary symmetric functions \( \varphi(z)(x_i; N) \) are most conveniently defined by their generating function \( \mathcal{G}(z; x_i, N) \).

\[
\mathcal{G}(z; x_i, N) \equiv \prod_{k=1}^{N} (1 + x_k z) = \sum_{k=0}^{N} \varphi^{(k)}(x_i; N) z^k
\]  

(28)

The functions \( \varphi(z) \) can be obtained from \( \mathcal{G} \) by differentiations with respect to \( z \).

\[
\varphi(z)(x_i; N) = \left. \frac{1}{z!} \frac{d^k}{dz^k} \mathcal{G}(z; x_i, N) \right|_{z=0}
\]

(29)

Clearly \( \varphi(0) = 1 \) is trivial and of no interest. For \( N = 3 \) the nontrivial functions are

\[
\begin{align*}
\varphi^{(1)}(x_i; 3) &= x_1 + x_2 + x_3 \\
\varphi^{(2)}(x_i; 3) &= x_1 x_2 + x_1 x_3 + x_2 x_3 \\
\varphi^{(3)}(x_i; 3) &= x_1 x_2 x_3
\end{align*}
\]

(30)

The elementary symmetric functions of the mole fractions have some convenient properties. Suppose we consider an M-ary subsystem of the N-ary
system. Then only \( M \) of the mole fractions are nonzero, and it is obvious from the definition of the generating function that \( \varphi^{(\xi)}(x_i; N) = 0 \)
for \( M < \xi < N \). Furthermore for \( 1 < \xi < M \) the \( \varphi^{(\xi)}(x_i; N) \) are identical with the corresponding elementary symmetric functions formed from the \( M \) nonzero mole fractions. This can easily be verified from equation (28) or from equation (30) for the special case \( N = 3 \) by setting \( x_3 \) to zero, for example. A generating function for the partial derivatives of \( \varphi^{(\xi)} \) can be obtained by differentiating the generating function (28) with respect to the mole fractions.

\[
\frac{\partial \mathcal{G}(z; x_i, N)}{\partial x_{\xi}} = \sum_{k=0}^{N} z^k \frac{\partial \varphi^{(k)}(x_i; N)}{\partial x_{\xi}} \tag{31}
\]

But

\[
\frac{\partial \ln \mathcal{G}(z; x_i, N)}{\partial x_{\xi}} = \frac{z}{(1 + x_{\xi} z)}
\]

and therefore we obtain a very simple result.

\[
\frac{\partial \mathcal{G}(z; x_i, N)}{\partial x_{\xi}} = \frac{z \mathcal{G}(z; x_i, N)}{(1 + x_{\xi} z)} = z \prod_{k \neq \xi} (1 + x_k z) = z \mathcal{G}(z; x_i, i \neq \xi, N - 1) \tag{32}
\]

If we apply the Liebnitz formula for the differentiation of a product \( uv \) in the form

\[
(uv)^{(n)} = \sum_{k=0}^{n} \binom{n}{k} u^{(k)} v^{(n-k)}
\]

to the function \( z \mathcal{G} \), we obtain

\[
(z \mathcal{G})^{(j)} = j \mathcal{G}^{(j-1)} + z \mathcal{G}^{(j)}
\]

But then

\[
\frac{\partial \varphi^{(j)}(x_i; N)}{\partial x_{\xi}} = \frac{1}{j!} \frac{d^j}{dz^j} \left[ z \mathcal{G}(z; x_i, i \neq \xi, N - 1) \right]_{z=0}
\]

\[
= \frac{1}{(j - 1)!} \frac{d^{j-1}}{dz^{j-1}} \mathcal{G}(z; x_i, i \neq \xi, N - 1)_{z=0}
\]

and so we have shown that
All higher derivatives can be obtained by further differentiation of equation (33). The validity of equation (33) can be verified for \( N = 3 \) by direct differentiation of equation (30).

Now that the properties of the basis set have been established, it is simple to write the final form for the function which will be used to represent the Gibbs free energy in an \( N \)-ary system. We write

\[
\begin{align*}
\mu_{jk} &= \mu_{jk}(x_i) = \sum_{\lambda=1}^{N} \mu^{(\lambda)}_{jk} b^{(\lambda)}(x_i; N) \\
\epsilon_{jk} &= \epsilon_{jk}(x_i) = \sum_{\lambda=1}^{N} \epsilon^{(\lambda)}_{jk} \varphi^{(\lambda)}(x_i; N)
\end{align*}
\]  

(34)

where \( \mu^{(\lambda)}_{jk} \) and \( \epsilon^{(\lambda)}_{jk} \) are independent of mole fractions. Substitution of this expansion into equation (27) gives the appropriate function for the Gibbs free energy in expanded form.

\[
G = \sum_{\lambda=1}^{N} \varphi^{(\lambda)}(x_i; N) \sum_{j=1}^{N} \sum_{k=1}^{N} \left( \mu^{(\lambda)}_{jk} + \epsilon^{(\lambda)}_{jk} \ln x_j \right) x_j x_k
\]

\[
= \sum_{\lambda=1}^{N} \varphi^{(\lambda)}(x_i; N) G^{(\lambda)}(x_i)
\]  

(35)

This representation for the Gibbs free energy defines a new class of non-ideal solutions whose properties will be studied for the balance of the report. The structure of equation (35) shows that only the symmetric part of \( \mu^{(\lambda)}_{jk} \) can contribute to \( G \), and so without loss in generality we take

\[
\mu^{(\lambda)}_{jk} = \mu^{(\lambda)}_{kj}
\]  

(36)

This property does not apply to \( \epsilon^{(\lambda)}_{jk} \) because the \( \ln x_j \) term introduces asymmetry. If the full expansion (35) is truncated after the first \( L \) elementary symmetric functions, then the expansion will be called an expansion of degree \( L \). The number of independent parameters for each \( \lambda \) is \( \frac{N(N+1)}{2} + N^2 = \frac{N(3N+1)}{2} \), and hence for an expansion of degree \( L \) there are \( L N(3N+1)/2 \) independent parameters.

The properties of the elementary symmetric functions allow a simple interpretation of the terms in the Gibbs free energy expansion (35), which correspond to different values of \( \lambda \). The functions \( \varphi^{(\lambda)} \) can be regarded as weighting functions for different regions of the domain of
definition $0 \leq x_i \leq 1$, $\sum_{k=1}^{N} x_k = 1$. Since $\varphi^{(1)} = \sum_{i=1}^{N} x_i \equiv 1$, the function $\varphi^{(1)}$ is a constant function over the domain and thus the $\lambda = 1$ term samples all points of an $N$-ary system with equal weight. The function $\varphi^{(2)} = \sum_{i<j} x_i x_j$ vanishes at the $N$ points $x_i(k) = \delta_{ik}$, $k = 1, 2, ..., N$, and so the $\lambda = 2$ term samples all points with the exception of those $N$ points corresponding to the unary subsystems. The function $\varphi^{(3)}$ vanishes for all unary and binary subsystems but samples all other points. Similarly $\varphi^{(4)}$ vanishes for all unary, binary, and ternary subsystems. In general, $\varphi^{(\ell)}(x_i; N)$ is zero for all $M$-ary subsystems for which $M < \ell$. This situation can be visualized by the description that, as $\lambda$ increases, the terms progressively sample more and more of the "interior" and less and less of the "boundary" of an $N$-ary system. This description is especially appropriate when applied to the graphic portrayal of ternary systems by equilateral triangular diagrams where the vertices are the unary subsystems, the sides are the binary subsystems, and the interior is the portion of the ternary system for which $(x_i \neq 0, i = 1, 2, 3)$.

There still remains the task of calculating the chemical potentials for the Gibbs free energy function (35) by using the last equality in the first member of equation (16). Suppose we define

$$\mu_i^{(\ell)} = (1 + \partial_i)G^{(\ell)}$$

were the differentiation operator $\partial_i$ is defined in equation (16). Then from the last equality in equation (35) we find

$$\mu_i = \sum_{\ell=1}^{N} \left\{ \varphi^{(\ell)}(x_j; N)\mu_i^{(\ell)} + G^{(\ell)}\left[ \varphi^{(\ell)}_i(x_j; N) - \sum_{k=1}^{N} x_k\varphi^{(\ell)}_k(x_j; N) \right] \right\}$$

But since $\varphi^{(\ell)}$ is homogeneous of degree $\lambda$, we know that

$$\sum_{k=1}^{N} x_k\varphi^{(\ell)}_k = \lambda\varphi^{(\ell)}$$

and thus

$$\mu_i = \sum_{\ell=1}^{N} \left[ (\mu_i^{(\ell)} - \lambda G^{(\ell)}) \varphi^{(\ell)}(x_j; N) + G^{(\ell)}\varphi^{(\ell)}_i(x_j; N) \right]$$

The $\lambda = 1$ term can be simplified because $\varphi^{(1)} = \sum_{j=1}^{N} x_j = 1$ and $\partial\varphi^{(1)}/\partial x_i = 1$.

Thus we can write

$$\mu_i = \mu_i^{(1)} + \sum_{\ell=2}^{N} \left[ (\mu_i^{(\ell)} - \lambda G^{(\ell)}) \varphi^{(\ell)}(x_j; N) + G^{(\ell)}\varphi^{(\ell)}_i(x_j; N) \right]$$
By using the definition of $\mu_i^{(j)}$ (eq. (37)) and the symmetry property (eq. (36)) of the parameters $\mu_{jk}^{(j)}$, it is a simple calculation to establish an explicit formula for $\mu_i^{(j)}$.

$$
\mu_i^{(j)} = \sum_{k=1}^{N} \left[ 2\mu_{ik}^{(j)} + \epsilon_{ij}^{(j)} (1 + \ln x_i) + \epsilon_{kj}^{(j)} \ln x_k \right] x_k
$$

$$
- \sum_{j=1}^{N} \sum_{k=1}^{N} \left[ \mu_{jk}^{(j)} + \epsilon_{jk}^{(j)} (1 + \ln x_j) \right] x_j x_k
$$

$$
= \sum_{k=1}^{N} \left[ 2\mu_{ik}^{(j)} + \epsilon_{ij}^{(j)} (1 + \ln x_i) + \epsilon_{kj}^{(j)} \ln x_k \right] x_k
$$

$$
- G^{(j)} - \sum_{j=1}^{N} \sum_{k=1}^{N} \epsilon_{jk}^{(j)} x_j x_k
$$

(40)

It is sometimes convenient to have an expression for $\mu_i^{(j)}$ in which terms are grouped by parameter.

$$
\mu_i^{(j)} = \sum_{j=1}^{N} \sum_{k=1}^{N} \left\{ x_j (2\delta_{ik} - x_k) \mu_{jk}^{(j)} + \left[ (x_j \delta_{ik} + x_k \delta_{ij} - x_j x_k) \ln x_j + x_k (\delta_{ij} - x_j) \epsilon_{jk}^{(j)} \right] \right\}
$$

(41)

At first glance the result given by equations (39) and (41) is a bit disconcerting for it seems to imply that we can extract all parameters in the Gibbs free energy by fitting one of the $\mu_i$ alone. This seems to contradict the fact that differentiation of a function results in a loss of information about the function because in the differentiation we discard the constant of integration. That, in fact, is also the case here. To see this most simply, we need only define functions $\bar{\mu}_{ij}(x_k)$ by

$$
\mu_{ij}(x_k) = \bar{\mu}_{ij}(x_k) + (n_i + n_j)/2
$$

and the $n_k$ are arbitrary and independent of composition. If this is substituted into the expression for the Gibbs free energy (eq. (27)), we find

$$
\sum_{j=1}^{N} \sum_{k=1}^{N} (\mu_{jk} + \epsilon_{jk} \ln x_j) x_j x_k = \sum_{j=1}^{N} \sum_{k=1}^{N} (\bar{\mu}_{jk} + \epsilon_{jk} \ln x_j) x_j x_k + \sum_{j=1}^{N} n_j x_j
$$

If $\mu_i$ is the chemical potential calculated from the $\mu_{jk}$ and $\bar{\mu}_i$ is the chemical potential calculated from the $\bar{\mu}_{jk}$, then the two are obviously related by the expression
μ_i = \bar{μ}_i + n_i

From this it follows that there are \( N - m \) arbitrary parameters in the Gibbs free energy function (eq. (27) or (35)) if we have data on only \( m \) chemical potentials.

It is occasionally of some interest to have an expression for the second derivatives of the Gibbs free energy. An appropriate formula for the calculation of the second derivatives from \( G \) can be obtained easily from equation (16).

\[
n \frac{\partial^2 G}{\partial n_k \partial n_i} = \partial_i \mu = \partial_k(1 + \partial_i)G
\] (42)

The left side is manifestly symmetric, but the symmetry of the right side is not obvious. To demonstrate the symmetry in a simple way, it is convenient to use the commutation properties of the operators \( \partial_k \). One can evaluate the commutators of the operators from the definition of the operators by a straightforward computation.

\[
[\partial_k, \partial_i] = \partial_k \partial_i - \partial_i \partial_k = \frac{\partial}{\partial x_i} - \frac{\partial}{\partial x_k} = \partial_i - \partial_k
\] (43)

Symmetry can now be simply demonstrated by combining equations (42) and (43).

\[
n \left( \frac{\partial^2 G}{\partial n_k \partial n_i} - \frac{\partial^2 G}{\partial n_i \partial n_k} \right) = \left[ \partial_k(1 + \partial_i) - \partial_i(1 + \partial_k) \right]G
\]

\[= (\partial_k - \partial_i + [\partial_k, \partial_i])G \equiv 0
\]

The actual calculation of the second derivative by means of the first equality in equation (42) can be somewhat simplified by taking advantage of some properties of the operators \( \partial_k \). When \( \partial_k \) is applied to a product of functions, it has a simple behavior.

\[\partial_k(uv) = u \partial_k v + v \partial_k u \] (44)

When it acts on the functions \( G^k(\lambda) \), \( \varphi^k(\lambda) \), and \( \varphi_i^k(\lambda) \), we obtain

\[
\begin{align*}
\partial_k G(\lambda) &= \mu_k^k(\lambda) - G(\lambda) \\
\partial_k \varphi(\lambda) &= \varphi_k^k(\lambda) - \lambda \varphi(\lambda) \\
\partial_k \varphi_i(\lambda) &= \frac{\partial^2 \varphi(\lambda)}{\partial x_k \partial x_i} - (\lambda - 1) \varphi_i(\lambda)
\end{align*}
\] (45)
The first of these three results is an immediate consequence of equation (37), and the remaining two follow from the definition of the operator and the fact that $\phi^{(z)}$ is homogeneous of degree $z$. The effect of $\mathcal{O}_k$ on $\mu_i^{(z)}$ can be calculated by expressing $\mathcal{O}_k^{(z)} \mu_i^{(z)}$ in terms of derivatives of $G^{(z)}$.

$$
\mathcal{O}_k^{(z)} \mu_i^{(z)} = \mathcal{O}_k(1 + \mathcal{O}_1)G^{(z)} = \frac{\partial^2 G^{(z)}}{\partial x_k \partial x_i} - \sum_{j=1}^{N} x_j \left( \frac{\partial^2 G^{(z)}}{\partial x_k \partial x_j} - \frac{\partial^2 G^{(z)}}{\partial x_i \partial x_j} \right) + \sum_{j=1}^{N} \sum_{m=1}^{N} x_j x_m \frac{\partial^2 G^{(z)}}{\partial x_j \partial x_m}
$$

The evaluation of the right side of this expression gives the final formula which is required for the evaluation of the second derivatives of $g$.

$$
\mathcal{O}_k^{(z)} \mu_i^{(z)} = 2 \mu_k^{(z)} + \epsilon_k^{(z)} (1 + \ln x_k) + \epsilon_i^{(z)} (1 + \ln x_i) + x_i^{-1} \delta_{ik} \sum_{j=1}^{N} \epsilon_{ij} x_j
$$

$$
- \sum_{j=1}^{N} x_j \left[ 2 \left( \mu_k^{(z)} + \mu_i^{(z)} \right) + \epsilon_k^{(z)} (1 + \ln x_k) + \epsilon_i^{(z)} (1 + \ln x_i) \right]
$$

$$
+ \left( \epsilon_{jk}^{(z)} + \epsilon_{ji}^{(z)} \right) (1 + \ln x_j) \right] + 2 \sum_{j=1}^{N} \sum_{m=1}^{N} \left[ \mu_{mj}^{(z)} + \epsilon_{mj}^{(z)} (1 + \ln x_m) \right] x_j x_m
$$

(46)

The second derivatives are obtained by combining equations (42), (44), and (45) with the expression for $\mu_i^{(z)}$ given in equation (39).

$$
\frac{n}{\partial^2 q}{\partial x_k \partial x_i} = \mathcal{O}_k^{(z)} \mu_i^{(z)} + \sum_{z=2}^{N} \left\{ \phi^{(z)} \mathcal{O}_k^{(z)} - \left( \mu_k^{(z)} + \mu_i^{(z)} \right) \left( \epsilon q^{(z)} - \phi^{(z)} \right) \right. + \left. \frac{\partial^2 \phi^{(z)}}{\partial x_k \partial x_i} - (\epsilon + 1) \phi^{(z)} - (\epsilon - 1) \phi^{(z)} + \epsilon (\epsilon + 1) \phi^{(z)} \right\} G^{(z)}
$$

(47)

The function I have constructed to describe the composition dependence of the Gibbs free energy for a class of nonideal solutions contains an important special case. Suppose that we make a special choice for the functions $\mu_{jk}$ and $\epsilon_{jk}$, which appear in equation (27).

$$
\mu_{jk} = \tilde{\mu}_{jk} = \frac{\bar{\mu}_j + \bar{\mu}_k}{2}
$$

$$
\epsilon_{jk} = \tilde{\epsilon}_{jk} = \tilde{\epsilon}
$$

(48)

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Then

\[
\tilde{G} = \sum_{j=1}^{N} \sum_{k=1}^{N} (\tilde{\mu}_{jk} + \tilde{\epsilon}_{jk} \ln x_j)x_j x_k = \sum_{j=1}^{N} (\tilde{\mu}_{j} + \tilde{\epsilon} \ln x_j)x_j
\]

(49)

and if \( \tilde{\epsilon} \) and the \( \tilde{\mu}_j \) are taken to be independent of composition, then \( \tilde{G} \) becomes the ideal Gibbs free energy if \( \tilde{\epsilon} = RT \). The function \( \tilde{G} \) is useful for defining a relative Gibbs free energy function which has the same form as \( G \) itself.

\[
\Delta \tilde{G} = G - \tilde{G} = \sum_{j=1}^{N} \sum_{k=1}^{N} (\Delta \tilde{\mu}_{jk} + \Delta \tilde{\epsilon}_{jk} \ln x_j)x_j x_k
\]

\[
\Delta \tilde{\mu}_{jk} = \mu_{jk} - \tilde{\mu}_{jk} = \mu_{jk} - (\tilde{\mu}_j + \tilde{\mu}_k)/2 = \sum_{i=1}^{N} \Delta \tilde{\mu}_{jk} \varphi(i)(x_i; N)
\]

\[
\Delta \tilde{\epsilon}_{jk} = \epsilon_{jk} - \tilde{\epsilon} = \sum_{i=1}^{N} \Delta \tilde{\epsilon}_{jk} \varphi(i)(x_i; N)
\]

(50)

Naturally \( \Delta \tilde{G} \) becomes identical to the excess Gibbs free energy \( \Delta G \) if \( \tilde{\epsilon} = RT \) and \( \tilde{\mu}_j = \mu_j^* \), where \( \mu_j^* \) are the chemical potentials of the pure constituents, that is, the Gibbs free energies per mole. This means that the expression for the derivatives of the Gibbs free energy are immediately applicable to the excess Gibbs free energy merely by replacing \( \mu_{jk} \) and \( \epsilon_{jk} \) with \( \Delta \mu_{jk} \) and \( \Delta \epsilon_{jk} \) with the understanding that

\[
\Delta \mu_{jk} = \mu_{jk} - (\mu_j^* + \mu_k^*)/2 \quad \text{if } \varepsilon = 1
\]

\[
\Delta \epsilon_{jk} = \epsilon_{jk} - RT \quad \text{if } \varepsilon \neq 1
\]

The special choice \( \Delta \mu_{jk} = 0 \) for \( \varepsilon \neq 1 \) and \( \Delta \epsilon_{jk} = 0 \) shows that Hildebrand's regular solutions are special cases of the class of solutions considered here.

**GIBBS FREE ENERGY IN A SUBSPACE**

I have already briefly mentioned M-ary subsystems of an N-ary system (M < N) in the preceding section. This is nothing more than a special case of another more general notion, that of a subspace, which also is relevant to
thermodynamics. The simplest example is an aqueous sodium chloride solution, which is a ternary system with constituents $\text{H}_2\text{O}$, $\text{Na}^+$, and $\text{Cl}^-$. The solution is formed by dissolving NaCl in water and therefore the moles of $\text{Na}^+$ and $\text{Cl}^-$ are always equal. This implies that there are not three, but only two independent composition variables despite the fact that we have a ternary system. The independent variables are clearly the moles of water and the moles of sodium chloride. The form of the Gibbs free energy written in terms of the independent variables will differ from the form written in terms of variables which are not all independent. In this section I shall examine the form of the Gibbs free energy in a subspace of an $N$-ary system.

To carry out this task expeditiously, I must introduce some helpful notation. Latin indices will continue to use the range $1, 2, \ldots, N$, while Greek indices from the last part of the alphabet ($\mu, \nu, \sigma, \tau, \ldots$) will use the range $1, 2, \ldots, M < N$. For thermodynamic purposes an $M$-dimensional subspace can be defined by the equations

$$
\begin{align*}
\mathbf{n}_i &= n_i(n_\sigma) \\
\mathbf{n}_i(\lambda n_\sigma) &= \lambda n_i(n_\sigma)
\end{align*}
$$

(51)

where, of course, $n_\sigma$ represents the independent composition variables of the subspace in moles per unit mass and the second member of equation (51) is the requirement that the functions $n_i(n_\sigma)$ be homogeneous of degree 1. The functions $n_i(n_\sigma)$ always turn out to be linear functions in actual situations, but this specialization does not lead to any mathematical simplification, and so I shall use the more general case. Suppose we define "stoichiometric coefficients" $v_{i\sigma}$ by

$$
v_{i\sigma} = v_{i\sigma}(n_\tau) = \frac{\partial n_i}{\partial n_\sigma} \geq 0
$$

(52)

where $v_{i\sigma}$ would be a constant in the usual case of linear functions. We can now apply Euler's theorem to equation (51), as we did before in the case of the Gibbs free energy, to obtain

$$
\begin{align*}
\mathbf{n}_i &= \sum_{\sigma=1}^{M} v_{i\sigma} n_\sigma \\
v_{i\sigma}(\lambda n_\sigma) &= v_{i\sigma}(n_\tau)
\end{align*}
$$

(53)

The total moles $\mathbf{n}$ and mole fractions $x_\sigma$ of the independent variables are defined analogously to equation (13).

$$
\mathbf{n} = \sum_{\sigma=1}^{M} n_\sigma
$$

$$
x_\tau = n_\tau/\mathbf{n}
$$

(54)
If we define

\[ v_\sigma \equiv \sum_{i=1}^{N} v_{i\sigma} > 0 \]  

(55)

then we have simple relationships between the two kinds of total moles and mole fractions.

\[
\begin{align*}
x_i &= \frac{\hat{n}}{n}^{-1} \sum_{\sigma=1}^{M} v_{i\sigma} x_\sigma \\
\hat{n}^{-1} &= \sum_{\tau=1}^{M} v_\tau x_\tau
\end{align*}
\]

(56)

We are now in a position to define the Gibbs free energy functions and the chemical potentials in the subspace.

\[
\begin{align*}
g &= \hat{g}(n_\sigma) = g[n_i(n_\sigma)] \\
\hat{G} &= \hat{n}^{-1} \hat{g}(n_\sigma) \\
\mu_\sigma &= \frac{\partial \hat{g}}{\partial n_\sigma}
\end{align*}
\]

(57)

The function \( \hat{g} \) is homogeneous of degree 1 in the \( n_\sigma \) because \( g \) is homogeneous of degree 1 in the \( n_i \) and the \( n_i \) are homogeneous of degree 1 in the \( n_\sigma \). It is simple to establish the relationship between \( \hat{G} \) and \( G \) and between \( \mu_\sigma \) and \( \mu_i \).

\[
\hat{G} = n^{-1} g[n_i(n_\sigma)](n/\hat{n}) = G n/\hat{n}
\]

(58)

\[
\mu_\sigma = \sum_{i=1}^{N} \left( \frac{\partial g}{\partial n_i} \right) \left( \frac{\partial n_i}{\partial n_\sigma} \right) = \sum_{i=1}^{N} \mu_i v_{i\sigma}
\]

A complete parallel exists between the \( N \)-ary equations and those of the subspace. The counterparts of equations (14), (16), (43), and (44) are
\[ \hat{G}(x_\rho) = \sum_{\sigma=1}^{M} \mu_\sigma x_\sigma \]

\[ \mu_\sigma = \left( 1 - \sum_{\tau=1}^{M} x_\tau \frac{a}{\partial x_\tau} + \frac{a}{\partial x_\sigma} \right) \hat{G}(x_\rho) = (1 + \theta_\sigma) \hat{G}(x_\rho) \]

\[ \hat{n} \frac{\partial u_\sigma}{\partial n_\nu} = \left( \frac{a}{\partial x_\nu} - \sum_{\tau=1}^{M} x_\tau \frac{3}{\partial x_\tau} \right) u_\sigma(x_\rho) = \theta_\nu u_\sigma(x_\rho) = \theta_\nu (1 + \theta_\sigma) \hat{G}(x_\rho) \]

\[ [\theta_\sigma, \theta_\tau] = \theta_\tau - \theta_\sigma \]

\[ \theta_\sigma(uv) = u \theta_\sigma v + v \theta_\sigma u \]

While the expressions given in equation (59) for \( \mu_\sigma \) and \( \frac{\partial u_\sigma}{\partial n_\nu} \) are correct, they are not necessarily the simplest ways to calculate these quantities. It might be simpler to calculate \( \mu_\sigma \) from the second equation in (58) if one already has expressions for \( u_\tau \). A similar formula can easily be found to relate the derivatives \( \frac{\partial u_\sigma}{\partial n_\tau} \) to \( \frac{\partial u_\tau}{\partial n_j} \) merely by differentiating the second equation in (58).

\[ \frac{\partial u_\sigma}{\partial n_\tau} = \sum_{j=1}^{N} \sum_{i=1}^{N} v_{j \tau} v_{i \sigma} \frac{\partial u_j}{\partial n_j} + \sum_{i=1}^{N} u_i \frac{\partial v_{i \sigma}}{\partial n_\tau} \]

Only the first part of equation (60) will contribute in actual problems because, as I pointed out before, \( \frac{\partial v_{i \sigma}}{\partial n_\tau} = 0 \) in the usual case. The Gibbs-Duhem equation for the subspace, \( \sum_{\sigma=1}^{M} n_\sigma \frac{\partial u_\sigma}{\partial n_\tau} = 0 \), follows from equations (60) and (53) and the Gibbs-Duhem equation (12).

From equations (35) and (58) it may be seen that \( G \) can be written as

\[ \hat{G} = \sum_{i=1}^{N} \theta_i [x_i(x_\sigma); N] \hat{G}^{(i)} \]

where
Similarly the combination of equations (39) and (58) gives an expression for $\mu_\sigma$.

$$\mu_\sigma = \mu_\sigma^{(1)} + \sum_{k=2}^{N} \left\{ \left[ \mu_\sigma^{(k)} - \nu_\sigma \hat{n}_n^{-1} \Gamma(k) \right] \phi_\sigma(x_i(x_\sigma); N) + \hat{n}_n^{-1} \Gamma(k) \phi_\sigma \right\}$$

$$\mu_\sigma^{(k)} = \sum_{i=1}^{N} \mu_1^{(k)} \nu_i \sigma$$

$$\phi_\sigma = \sum_{i=1}^{N} \phi_i^{(k)} \nu_i \sigma$$

To obtain an explicit expression for $\mu_\sigma^{(k)}$, we can use equation (58) with either the first equality in (40) or (41). I shall only give the one which comes from equation (41) since it gives the most compact form directly.

$$\mu_\sigma^{(k)} = \sum_{\rho=1}^{M} \sum_{\tau=1}^{M} \hat{n}_n^{-1} x_\rho \left( 2 \delta_{\sigma \tau} - \hat{n}_n^{-1} \nu_\tau x_\tau \right) \mu_\rho^{(k)}$$

$$+ \sum_{i=1}^{N} \sum_{\tau=1}^{M} \left[ \delta_{\sigma \tau} x_i \ln x_i + \hat{n}_n^{-1} x_\tau (\nu_i \sigma - x_i \nu_\sigma)(1 + \ln x_i) \right] \phi_i^{(k)}$$

$$= \sum_{\rho=1}^{M} \sum_{\tau=1}^{M} \hat{n}_n^{-1} \left( x_\rho \delta_{\sigma \tau} + x_\tau \delta_{\sigma \rho} - \hat{n}_n^{-1} \nu_\tau x_\tau \right) \mu_\rho^{(k)}$$

$$+ \sum_{i=1}^{N} \sum_{\tau=1}^{M} \left[ \delta_{\sigma \tau} x_i \ln x_i + \hat{n}_n^{-1} x_\tau (\nu_i \sigma - x_i \nu_\sigma)(1 + \ln x_i) \right] \phi_i^{(k)}$$

The second equality is obtained from the first by using the symmetry of the $\mu_\rho^{(k)}$ (eq. (62)). The number of independent parameters in $G$ is easily calculated since for each $k$ we have $M(M + 1)/2$ independent $\mu_\rho^{(k)}$ and at most
independent \( \varepsilon_{1\tau}^{(x)} \) and hence for \( L \) terms the total is \( LM(M+1+2N)/2 \). The number of independent \( \varepsilon_{1\tau}^{(x)} \) parameters might be less than \( MN \) for each \( x \) for special choices of the stoichiometric coefficients. Suppose that for a given \( i \) and \( j \) we have \( \nu_{i\sigma} = \nu_{j\sigma} \) for all \( \sigma \). Then \( x_i = x_j \) and therefore for all \( \tau \)

\[
x_{\tau} \sum_{\sigma=1}^{M} \nu_{i\sigma} x_{\sigma} \ln x_{i} = x_{\tau} \sum_{\sigma=1}^{M} \nu_{j\sigma} x_{\sigma} \ln x_{j}
\]

and therefore the functions multiplying \( \varepsilon_{1\tau}^{(x)} \) and \( \varepsilon_{j\tau}^{(x)} \) in \( \hat{G} \) are equal, which precludes the separate determination of \( \varepsilon_{1\tau}^{(x)} \) and \( \varepsilon_{j\tau}^{(x)} \). In such a case, for all \( \tau \) and \( x \), only the combination \( \varepsilon_{1\tau}^{(x)} + \varepsilon_{j\tau}^{(x)} \) can be determined by fitting data, and one may impose arbitrary subsidiary conditions to determine separately the individual coefficients.

One can introduce a relative Gibbs free energy in the subspace in much the same way as was done for an N-ary system by equation (50).

\[
\Delta \hat{G} = \hat{n} n^{-1} \sum_{\tau=1}^{M} \sum_{\sigma=1}^{N} \left( \Delta \hat{\mu}_{\sigma \tau} + \sum_{j=1}^{N} \Delta \hat{\varepsilon}_{j\tau} \nu_{j\sigma} \ln x_{j} \right) x_{\sigma} x_{\tau}
\]

\[
\Delta \hat{\mu}_{\sigma \tau} = \mu_{\sigma \tau} - (\hat{\mu}_{\sigma} + \hat{\mu}_{\tau})/2 = \sum_{k=1}^{N} \Delta \hat{\mu}_{\sigma \tau}^{(x)}(x) [x_{i}(x_{j}; N)]
\]

\[
\Delta \hat{\varepsilon}_{j\tau} = \varepsilon_{j\tau} - \hat{\varepsilon} = \sum_{k=1}^{N} \Delta \hat{\varepsilon}_{j\tau}^{(x)}(x) [x_{i}(x_{j}; N)]
\]

The relative Gibbs free energy \( \Delta \hat{G} \) becomes an excess Gibbs free energy if \( \hat{e} = RT \) and \( \hat{\mu}_{\sigma} = u_{\sigma}^{*} \), where \( u_{\sigma}^{*} \) are the Gibbs free energies per mole for the independent species. I should point out that \( \Delta \hat{\mu}_{\sigma \tau} \) and \( \Delta \hat{\varepsilon}_{j\tau} \) are not the same as the transformed versions of \( \tilde{\Delta} \mu_{jk} \) and \( \tilde{\Delta} \varepsilon_{jk} \), which are given in equation (66).

\[
\tilde{\Delta} \mu_{\sigma \tau} = \sum_{j=1}^{N} \sum_{k=1}^{N} \nu_{j\sigma} \nu_{k\tau} \Delta \hat{\mu}_{jk} = \mu_{\sigma \tau} - (\mu_{\sigma} \nu_{\tau} + \mu_{\tau} \nu_{\sigma})/2
\]

\[
\tilde{\Delta} \varepsilon_{j\tau} = \sum_{k=1}^{N} \nu_{k\tau} \Delta \hat{\varepsilon}_{jk} = \varepsilon_{j\tau} - \hat{\varepsilon}_{\tau}
\]

\[
\tilde{\mu}_{\sigma} = \sum_{j=1}^{N} \nu_{j\sigma} \mu_{j}
\]

\[
\tilde{\varepsilon}_{j\tau} = \sum_{k=1}^{N} \nu_{k\tau} \Delta \hat{\varepsilon}_{jk} = \varepsilon_{j\tau} - \hat{\varepsilon}_{\tau}
\]

(66)
The differences between $\Delta \mu_{\sigma \tau}, \Delta \xi_{j\tau}$ and $\Delta \tilde{\mu}_{\sigma \tau}, \Delta \tilde{\xi}_{j\tau}$ can be seen by comparing the last two members of equation (65) with the first two members of equation (66).

The choice of independent composition variables is not unique and often-times one choice might be more convenient than another. Suppose we wished to use the variables $n_\sigma \bar{\rho}$ in place of $n_\sigma$. Then for thermodynamic purposes the transformation between the two sets of variables must satisfy

$$n_\sigma = n_\sigma (\bar{n}_\rho)$$

$$n_\sigma (\lambda \bar{n}_\rho) = \lambda n_\sigma (\bar{n}_\rho)$$

$$J = \left| \frac{an_\sigma}{an_\bar{\rho}} \right| = \left| T_{\sigma \rho} \right| \neq 0$$

where $J$ is the Jacobian of the transformation. It is an immediate consequence of the chain rule for differentiation that

$$\frac{an_j}{an_\sigma} = \bar{\nu}_{i\sigma} = \sum_{\rho=1}^{M} \nu_{i\rho} T_{\rho \sigma}$$

$$\frac{\bar{\alpha}_{j}}{an_\sigma} = \bar{\nu}_{\sigma} = \sum_{\rho=1}^{M} \nu_{\rho} T_{\rho \sigma}$$

and obviously

$$\bar{\nu}(x) = \sum_{\rho=1}^{M} \sum_{\lambda=1}^{M} \nu_{\rho \lambda} T_{\rho \sigma} T_{\lambda \tau}$$

with similar transformation rules for other quantities. I shall not pursue this farther except to mention that the $T_{\rho \sigma}$ will generally be constants.

LIMITING BEHAVIOR

Thermodynamicists are often preoccupied with the limiting behavior of thermodynamic properties in dilute solutions where the concentration of one species dominates that of all other species. This naturally raises the question of the limiting behavior of the Gibbs free energy function and its derivatives for the class of solutions discussed in the preceding section. For this reason I shall examine the dilute solution behavior of these solutions and shall obtain an interpretation of some of the parameters as a byproduct of the analysis. The limiting process will be carried out for constant values of all intensive parameters, such as temperature and pressure for fluids, which characterize the thermodynamic state. It should be kept in mind that although this limiting process always makes mathematical
sense, it might not always be physically meaningful. For example, suppose that we ask for the limiting behavior of an aqueous sodium chloride solution as the concentration of NaCl goes to zero at some given temperature and a pressure less than the vapor pressure of pure liquid water at that temperature. But pure liquid water is inaccessible from the aqueous solution phase under the specified conditions, and the limiting process is not physically meaningful. Similarly, the limiting process is not physically meaningful in the pure sodium chloride limit at ordinary temperatures and pressures because NaCl has a limited solubility in water. The formulas which follow all presuppose that the pure state $x_i = x_i(p) = \delta_{ip}$, where $p$ is a fixed index, is physically accessible from the phase under consideration and, strictly speaking, they are physically meaningless if it is not.

To simplify the calculation of the limiting values of the Gibbs free energy and its derivatives, it will be helpful to know some auxiliary limiting values.

\[
\begin{align*}
\lim_{x \to 1} x^a \ln x & = 0 \quad \text{for all } a \\
\lim_{x \to 0} x^a \ln x & = 0 \quad a > 0
\end{align*}
\]

\[
\left\{ \begin{array}{l}
x_j = \delta_{jp} \\
\lim_{x_i \to \delta_{ip}} \phi^{(k)}(x_i; N) = \delta_{1k} \\
\frac{\partial \phi^{(k)}}{\partial x_k} = \delta_{1k} + (1 - \delta_{kp})\delta_{2k}
\end{array} \right. \tag{67}
\]

The second of these five limiting values comes from a simple application of L'Hopital's rule and shows that $\ln x$ has a weak singularity indeed in the limit $x \to 0$. The fourth and fifth values make explicit use of specific properties of $\phi^{(1)}$ and $\phi^{(2)}$, namely,

\[
\begin{align*}
\phi^{(1)} & = \sum_{i=1}^N x_i = 1 \\
\phi^{(2)} & = \sum_{i<j} x_i x_j \\
\frac{\partial \phi^{(1)}}{\partial x_k} & = 1 \\
\frac{\partial \phi^{(2)}}{\partial x_k} & = \sum_{j \neq k} x_j = 1 - x_k
\end{align*}
\tag{68}
\]
and that $\varphi^{(x)}$ is of degree $x$ in the mole fractions. We now use the limiting behavior given in equation (67) in evaluating the limiting behavior of $G$ as given in equation (35).

$$
\mu^* = \lim_{x_i \to \delta_{ip}} G = \lim_{x_i \to \delta_{ip}} G^{(1)} = \mu^{pp}
$$

(69)

Hence we have the important conclusion that when a pure species is accessible from a phase, the corresponding diagonal parameter must be chosen as the Gibbs free energy of the pure species. From the expression (41) for $\mu^{(x)}_i$ it is easy to see that

$$
\lim_{x_m \to \delta_{mp}} \left[ \mu^{(x)}_i - \sum_{k=1}^{N} \epsilon^{(x)}_{ik} x_k \ln x_i \right]
= \lim_{x_m \to \delta_{mp}} \left[ \mu^{(x)}_i - \sum_{j=1}^{N} \sum_{k=1}^{N} \epsilon^{(x)}_{jk} x_k \delta_{ij} \ln x_j \right]
= \sum_{j=1}^{N} \sum_{k=1}^{N} \left[ \delta_{jp} (2 \delta_{ik} - \delta_{kp}) \mu^{(x)}_{jk} + \delta_{kp} (\delta_{ij} - \delta_{jp}) \epsilon^{(x)}_{jk} \right]
= \mu^{(x)}_{ip} + \mu^{(x)}_{pi} - \mu^{(x)}_{pp} + \epsilon^{(x)}_{ip} - \epsilon^{(x)}_{pp}
$$

(70)

where, of course, in $\sum_{k=1}^{N} \epsilon^{(x)}_{ik} x_k \ln x_i$ the term $k = i$ vanishes in the limit as does the complete sum for $i = p$. Suppose we define

$$
\mu^{\infty}_i(p) \equiv \lim_{x_m \to \delta_{mp}} \left[ \mu^{(x)}_i - \sum_{k=1}^{N} \varphi^{(x)} \sum_{k=1}^{N} \epsilon^{(x)}_{ik} x_k \ln x_i \right]
$$

(71)

then it follows from equation (39) that

$$
\mu^{\infty}_i(p) = \lim_{x_m \to \delta_{mp}} \left[ \mu^{(1)}_i - \sum_{k=1}^{N} \epsilon^{(1)}_{ik} x_k \ln x_i + G^{(2)} \varphi^{(2)}_i \right]
= \mu^{(1)}_{ip} + \mu^{(1)}_{pi} - \mu^{(1)}_{pp} + \epsilon^{(1)}_{ip} - \epsilon^{(1)}_{pp} + (1 - \delta_{ip}) \mu^{(2)}_{pp}
$$

(72)

and from this we see that for $i = p$

$$
\mu^{\infty}_p(p) = \mu^{(1)}_{pp} = \mu^*
$$

(73)
The chemical potentials in a dilute solution have a simple form as can be seen from equations (71) and (34).

\[ \mu_i = \mu_i^\omega(p) + \sum_{k=1}^{N} \epsilon_{ik} x_k \ln x_i \quad \text{as} \quad x_j + \delta_{jp} \]  

(74)

If we compare this to the defining equation for the rational osmotic coefficient (Kirkwood and Oppenheim, ref. 23, p. 164, eq. (11-31), and Pitzer and Brewer, ref. 24, p. 321, eq. (22-22)), we see that the similarity of form permits us to interpret the functions \( \epsilon_{ij} \) as generalizations of the rational osmotic coefficients.

The limiting behavior in a subspace is a bit more difficult to discuss because we must now take into account the stoichiometric coefficients \( \nu_{i\sigma} \) and because we are now concerned with the behavior as \( x_\alpha + x_\rho(\omega) = \delta_{\rho\omega} \), where \( \omega \) is a fixed index, and not as \( x_i + \delta_{i\rho} \). Instead of the relatively simple limiting values shown in equation (67) we have

\[
\begin{align*}
  \lim_{x_\rho + \delta_{\rho\omega}} \left\{ \begin{array}{l}
    x_\tau = \delta_{\tau\omega} \\
    n_n-1 = \nu_\omega \\
    x_i = \nu_{i\omega}/\nu_\omega \\
    \varphi(\xi)(x_i; N) = \nu_\omega^{-1} \varphi(\xi)(\nu_{i\omega}; N)
  \end{array} \right.
  \\
  \varphi(\xi)(x_i; N) = \nu_\omega^{-(\xi-1)} \varphi(\xi)(\nu_{i\omega}, i \neq k; N - 1)
\end{align*}
\]

(75)

where in equation (75) and for the remainder of this section the symbols \( \nu_{i\sigma} \) are to be interpreted as \( \lim x_\rho + \delta_{\rho\omega} \nu_{i\sigma} \). The second and third parts of equation (75) are a direct consequence of equation (56). The fourth part can be obtained simply by looking at the limiting behavior of the generating function \( \varphi(\xi) \) (eq. (28)) and recalling that the \( \varphi(\xi) \) are homogeneous of degree \( \xi \), while the fifth part comes from equation (33). The last part of equation (75) is a
consequence of Euler's theorem applied to $\phi^{(\lambda)}$. From the definition of $\hat{G}^{(\lambda)}$ given in the first member of equation (62) we see that

$$\lim_{\rho \to \rho_0} \hat{G}^{(\lambda)} = \lim_{\rho \to \rho_0} G^{(\lambda)} = \lim_{\rho \to \rho_0} \sum_{i=1}^{N} \phi^{(\lambda)}(i) G^{(\lambda)}$$

and so from equation (61)

$$\mu^* = \lim_{\rho \to \rho_0} G = \lim_{\rho \to \rho_0} \sum_{i=1}^{N} \phi^{(\lambda)}(i) G^{(\lambda)}$$

$$= \lim_{\rho \to \rho_0} \sum_{i=1}^{N} \phi^{(\lambda)}(i) G^{(\lambda)}$$

$$= \lim_{\rho \to \rho_0} \sum_{i=1}^{N} \phi^{(\lambda)}(i) G^{(\lambda)}$$

$$= \lim_{\rho \to \rho_0} \sum_{i=1}^{N} \phi^{(\lambda)}(i) G^{(\lambda)}$$

and as a general rule $\mu^* = \mu^{(1)}$ although it could still be true in some particular case. One very important special case for which it is true is the one corresponding to an aqueous electrolyte solution in water assumed to be nonionized and the index $\omega$ labels water. Under these conditions the stoichiometric coefficients for water satisfy $v_{j\omega} = 0$ or $v_{j\omega} = 1$ and $v_{\omega} = 1$. For these stoichiometric coefficients only $\mu^{(1)}$ survives on the right side of equation (76). In general, from the nonnegativity conditions (52) and (55), it is sufficient to require only that $v_{\omega} = 1$.

$$\mu^* = \mu^{(1)} \quad \text{if} \quad v_{\omega} = 1$$

(77)

The condition in equation (77) would not be satisfied if we took the ionization of water into account.

Next I shall establish the limiting form of the chemical potential $\mu^*$ in the vicinity of the point $x_\rho(\omega)$. The chemical potential $\mu^*$ only had the logarithmic singularity $\ln x_i$; however, $\mu_{\omega}^*$ can have a logarithmic singularity for each $i$ for which $v_{i\sigma} = 0$. Therefore, in contrast to equation (71), I shall define

$$\mu_{\omega}^*(\omega) = \lim_{\rho \to \rho_0} \left[ \mu_{\omega} - \sum_{i=1}^{N} v_{i\omega} \sum_{k=1}^{N} e_{ik} x_k \ln x_i \right]$$

$$= \lim_{\rho \to \rho_0} \left[ \mu_{\omega} - \sum_{i=1}^{N} v_{i\omega} \sum_{k=1}^{N} e_{ik} x_k \ln x_i \right]$$

(78)

From the first expression in equation (64) for $\mu_{\omega}^{(\lambda)}$ we have
\[
\lim_{\rho \to \rho_0} \left[ \mu_\sigma (\ell) - \hat{\mu}_\omega \sum_{i=1}^{N} \sum_{\tau=1}^{M} \nu_{i\sigma} e_{i\tau} (\ell) x_\tau \ln x_i \right]
\]

\[
= \nu_{\omega}^{-2} \left[ \nu_{\omega} \left( 2\mu_{\sigma\omega} + \epsilon_{\sigma\omega} \right) - \nu_{\sigma} \left( \mu_{\omega\omega} + \epsilon_{\omega\omega} \right) + \sum_{i=1}^{N} \left( \nu_{\omega} e_{i\sigma} (\ell) - \nu_{\sigma} e_{i\omega} (\ell) \nu_{i\omega} \ln (\nu_{i\omega}/\nu_{\omega}) \right) \right] \tag{79}
\]

where I have used notation analogous to that in equation (62).

\[
e_{\sigma\omega} (\ell) = \sum_{i=1}^{N} \nu_{i\sigma} e_{i\omega} (\ell)
\]

If we use the expression for \( \mu_{\sigma} \) given in equation (63) and take advantage of the fact that \( \phi^{(1)} = 1 \), then

\[
\mu_{\sigma} - \hat{\mu}_{\omega}^{-1} \sum_{\ell=1}^{N} \sum_{i=1}^{N} \sum_{\tau=1}^{M} \varphi (\ell) e_{i\sigma} (\ell) x_\tau \ln x_i
\]

\[
= \sum_{\ell=1}^{N} \left( \mu_{\sigma} - \hat{\mu}_{\omega}^{-1} \sum_{i=1}^{N} \sum_{\tau=1}^{M} \nu_{i\sigma} e_{i\tau} (\ell) x_\tau \ln x_i \right) \varphi (\ell)
\]

\[
+ \sum_{\ell=2}^{N} \hat{\mu}_{\omega}^{-1} \sum_{i=1}^{N} \left[ \nu_{i\sigma} e_{i\omega} (\ell) - \nu_{i\omega} e_{i\sigma} (\ell) \right] \left[ \varphi (\ell) - \varphi (\ell) \right]
\]

From this equation and (79) it immediately follows that

\[
\mu_{\omega} (\omega) = \sum_{\ell=1}^{N} \nu_{\omega}^{-2} \varphi (\ell) (\nu_{i\omega}; N) \left[ \nu_{\omega} \left( 2\mu_{\sigma\omega} + \epsilon_{\sigma\omega} \right) - \nu_{\sigma} \left( \mu_{\omega\omega} + \epsilon_{\omega\omega} \right) + \sum_{i=1}^{N} \left( \nu_{\omega} e_{i\sigma} (\ell) - \nu_{\sigma} e_{i\omega} (\ell) \nu_{i\omega} \ln (\nu_{i\omega}/\nu_{\omega}) \right) \right]
\]

\[
+ \sum_{\ell=2}^{N} \nu_{\omega}^{-2} \nu_{k\sigma} e_{k\omega} (\ell) (\nu_{j\omega}, j \neq k; N - 1) - \nu_{\sigma} \varphi (\ell) (\nu_{i\omega}; N) \left[ \mu_{\omega\omega} (\ell) + \sum_{i=1}^{N} \nu_{i\omega} e_{i\sigma} (\ell) \ln (\nu_{i\omega}/\nu_{\omega}) \right] \right]
\]

\[
x \left[ \mu_{\omega\omega} (\ell) + \sum_{i=1}^{N} \nu_{i\omega} e_{i\sigma} (\ell) \ln (\nu_{i\omega}/\nu_{\omega}) \right] \tag{80}
\]
and this result is considerably more complex than the corresponding formula for \( \mu_1(p) \) given in equation (72). From equation (78) it follows that

\[
\mu_\sigma = \mu_\sigma^\omega(\omega) + \hat{n}\ln \sum_{i=1}^{N} \sum_{\tau=1}^{M} \nu_{i\sigma}^{\tau} x_{\tau} \ln x_i \quad \text{as} \quad x_\rho + \delta_{\rho \omega}
\]  

(81)

represents the limiting behavior of \( \mu_\sigma^\omega \).

The expression (80) for \( \mu_\omega(\omega) \) simplifies considerably for \( \sigma = \omega \). For this case the second summation over \( \tau \) vanishes identically by virtue of the last member of equation (75) and only the first summation over \( \tau \) survives. From this we see immediately that

\[
\mu_\omega^\omega(\omega) = \nu_{\omega}^{-1} \sum_{k=1}^{N} \nu_{\omega}^{-k} \varphi(k)(v_{i\omega}; N) \mu_{\omega}(k)
\]  

(82)

Thus, in general, \( \mu_\omega^\omega(\omega) \neq \mu_\omega^* \) and from equations (82) and (76) we can obtain an explicit expression for the difference

\[
\mu_\omega^* - \mu_\omega^\omega(\omega) = \sum_{j=1}^{N} \sum_{k=1}^{N} \nu_{\omega}^{-k} \varphi(k)(v_{i\omega}; N) \varepsilon_{j\omega}(v_{j\omega}/v_{\omega}) \ln(v_{j\omega}/v_{\omega})
\]  

(83)

This formula can also be obtained directly from equation (81) with \( \sigma = \omega \) and \( \mu_\omega^* = \lim_{x_\rho + \delta_{\rho \omega}} \mu_\omega \). It is clear from equation (83) that \( \mu_\omega^\omega(\omega) \) and \( \mu_\omega^* \) will be equal only under special circumstances. One such special case is the condition \( v_{\omega} = 1 \), which implies that \( v_{j\omega}/v_{\omega} = 0 \) or 1 for all \( j \) values, but it could also be true under other circumstances since the \( \varepsilon_{j\omega}(k) \) may be positive or negative. The assumption \( v_{\omega} = 1 \) also engenders a considerable simplification in the expression for \( \mu_\omega^\omega(\omega), \sigma \neq \omega \). Under these circumstances

\[
\varphi(k)(v_{i\omega}; N) = \delta_{1\omega} \varphi(1)(v_{i\omega}; N) = \nu_{\omega} \delta_{1\omega} \quad \kappa \geq 1
\]

\[
\varphi(k)(v_{j\omega}, j \neq k; N - 1) = \delta_{2\omega} \varphi(1)(v_{j\omega}, j \neq k; N - 1)
\]

\[
= \delta_{2\omega} \sum_{j \neq k} v_{j\omega} = \delta_{2\omega} (v_{\omega} - v_{k\omega}) \quad \kappa \geq 2
\]
These results, when substituted into the formula (80) for \( \mu_\sigma^\omega \), produce the expression

\[
\mu_\sigma^\omega = 2\mu_\sigma^{(1)} + \varepsilon_\sigma^{(1)} - \nu_\sigma \left( \mu_\omega^{(1)} + \varepsilon_\omega^{(1)} - 1 \right) - \sum_{k=1}^{N} \nu_{k\sigma} \nu_{k\omega} \quad \sigma \neq \omega, \quad \nu_\omega = 1
\]  

(84)

where the sum over \( k \) contains only one nonzero term because \( \nu = 1 \). Of course, if the stoichiometric coefficients \( \nu_{k\omega} \) and \( \nu_{k\sigma}, \sigma \neq \omega \), are orthogonal, as is generally the case, then the sum over \( k \) vanishes.

Thermodynamic properties of solutions are always reported relative to reference values which, of course, may be chosen arbitrarily. Thus one would express the chemical potentials for an N-ary system as \( (\mu_i - \bar{\mu}_i) \) or as \( (\mu_\sigma - \bar{\mu}_\sigma) \) in a subspace, where \( \bar{\mu}_i \) and \( \bar{\mu}_\sigma \) are independent of composition.

For the class of solutions described by the equations of this report one might reasonably select \( \bar{\mu}_i = \mu_i^0(p) \) and \( \bar{\mu}_\sigma = \mu_\sigma^0(\omega) \). Perhaps the most commonly used reference values, especially for electrolyte solutions, are the so-called infinite dilution standard states. These standard states are described, for example, by Kirkwood and Oppenheim (ref. 23). The use of such standard states is predicated on the existence of certain limits involving the chemical potentials themselves. The particular values of these limits are of no practical consequence, but their existence certainly is. The limits in question are defined by

\[
\mu_i^0(p) \equiv \lim_{m_i \to 0} [\mu_i - RT \ln x_i] \quad (85)
\]

\[
\mu_\sigma^0(\omega) \equiv \lim_{\rho_i \to 0} \left[ \mu_\sigma - RT \sum_{i=1}^{N} \nu_{i\sigma} \ln \left( \sum_{\tau \neq \omega} \nu_{i\tau} m_{\tau} \right) \right] \quad (86)
\]

where \( m_\tau \) are molalities relative to species \( \omega \). The first of these is Kirkwood and Oppenheim's equation (11-8), while the second is a combination of their equations (12-3) and (12-7). The infinite dilution reference values are \( \mu_i^0(p) \) for an N-ary system and \( \mu_\sigma^0(\omega) \) for \( \sigma \neq \omega \) in a subspace. Are the infinite dilution values suitable as reference values? Only if the limits (85) and (86) exist. These limits, like all limits, are experimentally unobservable and their existence for real solutions must be taken as an article of faith when one makes a decision to use them. Because the limits are not experimentally measurable, their values for real solutions can only be obtained by an extrapolation of data. But this makes the resulting values an artifact of the extrapolation technique and hence they can be of no intrinsic significance. Nonetheless, for the class of solutions defined by the equations of this report and for those real solutions which can be adequately represented by these equations, it is possible to evaluate these limits exactly with the aid of the limiting behavior expressed by equations (74) and (81).
From equations (85), (74), and (67) we find that

\[
\nu_i^0(p) - \nu_i^\infty(p) = \lim_{x_m + \delta_m \to 0} \left[ \nu_i - \nu_i^\infty(p) - RT \ln x_i \right]
\]

\[
= \lim_{x_m + \delta_m \to 0} \left[ \left( \sum_{k=1}^{N} \sum_{k=1}^{N} \phi(z) \epsilon_{ik} x_k - RT \right) \ln x_i \right]
\]

\[
= \lim_{x_m + \delta_m \to 0} \left[ \left( \epsilon_i^1 - RT \right) \ln x_i \right]
\]

This then permits the enunciation of a simple theorem:

The limit \( \nu_i^0(p) \) exists and \( \nu_i^0(p) = \nu_i^\infty(p) \) if and only if \( i = p \) or \( \epsilon_i^1 / RT = 1 \).

The calculation of \( \nu_i^0(\omega) \) is a bit more involved. If we use \( m_{\tau} = x_{\tau} m_{\omega} / x_{\omega} \), then from equations (86), (81), and (75) it can be shown that

\[
\nu_i^0(\omega) - \nu_i^\infty(\omega) + RT \ln \left[ \left( \sum_{i=1}^{M} \nu_i^\sigma_{\omega} \epsilon_i^\omega_{\sigma_{\omega}} / \nu_i^\omega \right) \right]
\]

\[
= RT \sum_{i=1}^{N} \nu_i^\sigma \lim_{x_{\rho} + \delta_{\rho} \to 0} \ln \left[ \left( \sum_{\lambda=1}^{M} \nu_{i\lambda}^\omega x_{\lambda} \epsilon_i^\omega / RT \right) \right] / \sum_{\tau \neq \omega} \nu_{i\tau}^\tau x_{\tau}
\]

\[
= RT \sum_{i=1}^{N} \nu_i^\sigma \lim_{x_{\rho} + \delta_{\rho} \to 0} \ln \left[ \left( \nu_i^\omega x_{\omega} + \sum_{\lambda \neq \omega} \nu_{i\lambda}^\omega x_{\lambda} \epsilon_i^\omega / RT \right) \right] / \sum_{\tau \neq \omega} \nu_{i\tau}^\tau x_{\tau}
\]

where \( \epsilon_i^\omega \) and \( \epsilon_{\sigma_{\omega}} \) are defined by

\[
\epsilon_i^\omega = \lim_{x_{\rho} + \delta_{\rho} \to 0} \sum_{\lambda=1}^{M} \epsilon_i^\omega x_{\lambda} = \sum_{k=1}^{N} \nu_i^\omega \phi(z) (\nu_{j\omega}; N) \epsilon_j^\omega
\]

\[
\epsilon_{\sigma_{\omega}} = \sum_{i=1}^{N} \nu_i^\sigma \epsilon_i^\omega
\]

(87)
From this formula there results a second theorem:

\[
\begin{align*}
\text{The limit } \mu^0_\sigma(\omega) \text{ exists and } & \quad \mu^0_\sigma(\omega) = \mu^\infty_\sigma(\omega) - RT \ln \left[ \left( \prod_{\omega} \nu_\omega \right) \nu^\infty_\omega / \nu^\infty_\omega \right] \\
\text{if and only if } & \quad \nu_{i\sigma} = 0 \text{ or } (\nu_{i\omega} = 0 \text{ and } \epsilon^\infty_{i\omega} / \nu^\infty_\omega = 1) \text{ for all } i.
\end{align*}
\]

For \( \sigma = \omega \) we see that \( \mu^0_\omega(\omega) \) can exist only if \( \nu_{i\omega} = 0 \) for all \( i \), which clearly is not possible for it violates the condition (55) that \( \nu^\infty_\omega > 0 \). Thus \( \mu^0_\omega(\omega) \) never exists and \( \mu^0_\sigma(\omega), \sigma \neq \omega \), only exists under special circumstances. The nonexistence of \( \mu^0_\omega(\omega) \) is a consequence of the composition dependence used in the second term of the defining equation (86) and not because of the behavior of \( \mu^0_\omega \). The limits \( \mu^0_1(p) \) and \( \mu^0_\sigma(\omega) \) generally do not exist simply because the parameters \( \epsilon^\infty_{ij} \) are permitted to differ from \( RT \) for the class of solutions under discussion.

Thermodynamicists are not always content with giving thermodynamic properties relative to reference values. They often insist on expressing properties relative to a reference function with the expectation that properties relative to a suitably chosen function will exhibit simpler behavior than the property itself. This practice leads to the definition of activity coefficients both for N-ary solutions and for subspaces of these solutions. A common definition for the activity coefficient \( \gamma_i \) in an N-ary solution, relative to \( \tilde{\nu}_i \), is

\[
\gamma_i \equiv \tilde{\nu}_i + RT \ln (\gamma_i x_i) \quad (88)
\]

while for solutes in a subspace of an N-ary solution the activity coefficient \( \gamma_\sigma, \sigma \neq \omega \), relative to \( \hat{\nu}_\sigma \) is conventionally defined as

\[
\nu_\sigma \equiv \hat{\nu}_\sigma + \nu_\sigma RT \left[ \ln \gamma_\sigma + \sum_{i=1}^{N} \left( \nu_{i\sigma} / \nu_\sigma \right) \ln \left( \sum_{\tau \neq \omega} \nu_{i\tau} \right) \right] \quad (89)
\]

The following theorem is a trivial consequence of the definitions of the activity coefficients and the values \( \mu^0_1(p), \mu^0_\sigma(\omega) \):

The limit \( \lim_{x_1 \to \delta_{m\rho}} \ln \gamma_i \) exists and equals \( \left[ \mu^0_1(p) - \tilde{\nu}_i \right] / RT \) if and only if \( \mu^0_1(p) \) exists. The limit \( \lim_{x_\rho \to \delta_{\rho\omega}} \ln \gamma_\sigma, \sigma \neq \omega \), exists and equals \( \left( \mu^0_\sigma(\omega) - \hat{\nu}_\sigma \right) / \nu_\sigma RT \) if and only if \( \mu^0_\sigma(\omega) \) exists.

Clearly, since \( \mu^0_1(p) \) and \( \mu^0_\sigma(\omega) \) do not generally exist, \( \gamma_i \) and \( \gamma_\sigma \) will
generally not have finite limiting values for members of the class of solutions under discussion. Nonetheless it is possible to define activity coefficients $\gamma_i$ and $\gamma_\sigma$, which will have finite limiting values for all members of the class. An obvious choice would be the definitions

$$
\begin{align*}
\mu_i &= \mu_i^\infty(p) + \sum_{k=1}^{N} \epsilon_{ik} x_k \ln x_i + RT \ln \gamma_i \\
\mu_\sigma &= \mu_\sigma^\infty(w) + nn^{-1} \sum_{i=1}^{N} v_i \sum_{t=1}^{M} \epsilon_{it} x_t \ln x_i + v_\sigma RT \ln \gamma_\sigma
\end{align*}
$$

(90)

and it is clear from equations (74) and (81) that $\gamma_i$ and $\gamma_\sigma$ both approach unity for the infinitely dilute solution.

The result that $\gamma_i$ and $\gamma_\sigma$ may not have finite limiting values is of considerable importance because they are sometimes used to calculate practical osmotic coefficients for the solvent in dilute binary solutions by quadrature. The integration extends from zero solute molality to some finite value and requires the extrapolation of the solute activity coefficient to zero molality. Consequently the value of the osmotic coefficient calculated in this manner is dependent not only on the activity coefficient data, but also on the chosen method of extrapolation. The extrapolation methods chosen always assume that the solute activity coefficient (89) is finite, actually unity, at zero molality. The resulting formula for the osmotic coefficient (ref. 25) (also see, e.g., Pitzer and Brewer, ref. 24, eq. (23-22), p. 339) implies that its value is also unity at zero molality. But since the assumption on which it is based is not generally valid for the class of solutions under discussion, it is necessary to look directly at the limiting behavior of the practical osmotic coefficient for these solutions.

Practical osmotic coefficients are defined in terms of the solvent chemical potential. For an $N$-ary solution we have the definition

$$
\phi_p = -x_p (\mu_p - \mu_p^*)/RT \sum_{i \neq p} x_i
$$

(91)

while for a subspace it is

$$
\phi_\omega = -x_\omega (\mu_\omega - \mu_\omega^*)/RT \sum_{\tau \neq \omega} v_\tau x_\tau
$$

(92)

(see Pitzer and Brewer (ref. 24), eq. 20-28), p. 263, and eq. (34-33), p. 570). If we use equations (91), (73), (74), and (67), we see that

$$
\lim_{x_m^+ \delta_{mp}} \phi_p = \lim_{x_m^+ \delta_{mp}} \phi_p/x_p
$$

$$
= -\lim_{x_m^+ \delta_{mp}} \sum_{k=1}^{N} \epsilon_{pk} x_k \left( \sum_{i \neq p} x_i \right)^{-1} \ln \left( 1 - \sum_{j \neq p} x_j \right)
$$
If we use the expansion \( \ln(1 + \alpha) \equiv \alpha \), it follows that

\[
\phi_p \propto \lim_{x \to \delta \rho} \phi_p = \frac{(1)}{RT}
\]  

(93)

To calculate the limiting value of \( \phi_w \), we first observe that

\[
\lim_{x \to \delta \rho} \phi_w = \lim_{x \to \delta \rho} \frac{\phi}{x} = \lim_{x \to \delta \rho} \left( RT \sum_{\tau \neq \omega} v_{\tau} x_{\tau} \right)^{-1} \left\{ \left[ u_{\omega}^* - u_{\omega}^\infty(\omega) \right] - \left[ u_{\omega} - u_{\omega}^\infty(\omega) \right] \right\}
\]

But if equations (83) and (87) are used for \( u_{\omega}^* - u_{\omega}^\infty(\omega) \) and equation (81) and the first member of (56) are used for \( u_{\omega} - u_{\omega}^\infty(\omega) \), then we may write

\[
\left[ u_{\omega}^* - u_{\omega}^\infty(\omega) \right] - \left[ u_{\omega} - u_{\omega}^\infty(\omega) \right] = -\epsilon_{\omega} \nu_{\omega}^{-1} \ln \left[ \nu_{\omega} \left( \hat{\nu}_{\omega} \right)^{-1} \right]
\]

\[
- \sum_{j=1}^{N} \epsilon_{j} \nu_{j} \nu_{j}^{-1} \ln \left[ \nu_{j}^{-1} \left( \sum_{\sigma=1}^{M} v_{j} x_{\sigma} \right)^{A_{j}} \right]
\]

where

\[
A_{\omega} \equiv \nu_{\omega} \hat{\nu}_{\omega}^{-1} \sum_{\tau=1}^{M} \epsilon_{\omega} x_{\tau} / \nu_{\omega}
\]

\[
A_{j} \equiv \nu_{j} \hat{\nu}_{j}^{-1} \sum_{\tau=1}^{M} \epsilon_{j} x_{\tau} / \nu_{j}
\]

But it is easy to see that

\[
\lim_{x \to \delta \rho} A_{\omega} = 1 = \lim_{x \to \delta \rho} A_{j}
\]

and consequently

\[
\lim_{x \to \delta \rho} \phi_w = -(v_{\omega} RT)^{-1} \sum_{j=1}^{N} \epsilon_{j} \nu_{j} \nu_{j}^{-1} \ln \left( \nu_{j}^{-1} \left( \sum_{\sigma=1}^{M} v_{j} x_{\sigma} \right) \right)
\]

If, for a given value of \( j, \epsilon_{j} \nu_{j} \nu_{j} = 0 \), then we get no contribution to the limit from this term. If, on the other hand, \( \nu_{j} \epsilon_{j} \nu_{j} \neq 0 \), then this implies that the term will contribute and also that \( \nu_{j} \neq 0 \). For such a value of \( j \) we see, by using \( x_{\omega} = 1 - \sum_{\sigma \neq \omega} x_{\sigma} \), that
where in the last step I used \( \ln(1 + a) \approx a \). From this it is clear that the contribution of a particular term is dependent on the direction in which one approaches the infinitely dilute solution and consequently so too is the limiting value of \( \phi_\omega \). Suppose we approach the infinitely dilute solution along a line of fixed solute proportions, that is, along a curve whose parametric representation in the vicinity of the infinitely dilute state is given, to first order in \( t \), by

\[ x_\lambda = a_\lambda t, \quad \lambda \neq \omega, \quad a_\lambda > 0, \quad \sum_\lambda a_\lambda \neq 0 \]

where \( a_\lambda \) are constants and \( t \) is a marking parameter for the curve.

Clearly, we then have

\[
\lim_{x_\rho + \delta \rho_\omega} \left( \sum_{\tau \neq \omega} v_\tau x_\tau \right)^{-1} \ln \left[ \sum_{\sigma}^M v_{j\sigma} x_\sigma \right] = \lim_{x_\rho + \delta \rho_\omega} \left( \sum_{\tau \neq \omega} v_\tau x_\tau \right)^{-1} \ln \left[ 1 + \sum_{\sigma}^M (v_{j\sigma} - v_{j\omega}) x_\sigma \right]
\]

\[
= \lim_{x_\rho + \delta \rho_\omega} \left( \sum_{\tau \neq \omega} v_\tau x_\tau \right)^{-1} \ln \left[ 1 + v_{j\omega} \sum_{\sigma}^M (v_{j\sigma} - v_{j\omega}) x_\sigma \right]
\]

\[
= \lim_{x_\rho + \delta \rho_\omega} \left( \sum_{\tau \neq \omega} v_\tau x_\tau \right)^{-1} \sum_{\sigma \neq \omega} (v_{j\sigma} - v_{j\omega}) x_\sigma
\]

where in the last step I used \( \ln(1 + a) \approx a \). From this it is clear that the contribution of a particular term is dependent on the direction in which one approaches the infinitely dilute solution and consequently so too is the limiting value of \( \phi_\omega \). Suppose we approach the infinitely dilute solution along a line of fixed solute proportions, that is, along a curve whose parametric representation in the vicinity of the infinitely dilute state is given, to first order in \( t \), by

\[ x_\lambda = a_\lambda t, \quad \lambda \neq \omega, \quad a_\lambda > 0, \quad \sum_\lambda a_\lambda \neq 0 \]

where \( a_\lambda \) are constants and \( t \) is a marking parameter for the curve.

If we designate the limiting value of \( \phi_\omega \) along this direction by \( \phi_\omega(a_\lambda) \), then

\[
\phi_\omega(a_\lambda) = (v_\omega RT)^{-1} \sum_{j : v_{j\omega} \neq 0} \varepsilon_j \left[ \sum_{\lambda \neq \omega}^M (v_{j\omega} - v_{j\lambda}) a_\lambda \right] / \sum_{\tau \neq \omega} v_\tau a_\tau 
\]

(94)

where the summation over \( j \) is to be read as the sum over all \( j \) values such that \( v_{j\omega} \neq 0 \). For the special case of a path along which only one solute is present we have \( a_3 = 0 \) and \( a_\sigma \neq 0 \) if \( \sigma \) is the label for that solute. Under these conditions the result (94) specializes to

\[
\phi_\omega(a_\lambda \neq 0) = \phi_\omega(\sigma) = (v_\sigma v_\omega RT)^{-1} \left( \varepsilon_\omega \sum_{j : v_{j\omega} \neq 0} \varepsilon_j v_{j\sigma} \right)
\]

(95)

If \( v_\omega = 1 \), then only one term in the sum over \( j \) in equations (94) and (95) survives and also \( \varepsilon_j = \varepsilon_j^1 \) and \( \varepsilon_\omega = \varepsilon_\omega^1 \). From equation (95) we can conclude that \( \phi_\omega(\sigma) \) will depend on the solute only through \( v_\sigma \) if and only if the sum over \( j \) vanishes. This will occur, for example, if \( v_{i\sigma} v_{i\omega} = 0 \)
or $\epsilon^{\infty}_{i\omega} = 0$ for all $i$. Similarly it is true that $\nu_{\sigma} \phi_{\omega}(\sigma) = \nu_{\tau} \phi_{\omega}(\tau)$ if and only if $\sum_{j: \nu_{j} \neq 0} \epsilon^{\infty}_{j\omega}(\nu_{j\sigma} - \nu_{j\tau}) = 0$, and this will happen if $(\nu_{i\sigma} - \nu_{i\tau}) \nu_{i\omega} = 0$ or $\epsilon^{\infty}_{i\omega} = 0$ for all $i$.

CONCLUDING REMARKS

In this report I have constructed a function to represent the composition dependence of the Gibbs free energy for a class of nonideal solutions and studied some of its properties. The function has several useful characteristics: (1) Its parameters, which depend on the intensive thermodynamic variables which specify the state, appear linearly. (2) It contains a logarithmic singularity in the region of dilute solutions and contains ideal solutions and regular solutions as special cases. (3) It is applicable to $N$-ary systems and reduces to $M$-ary systems ($M \leq N$) in a form invariant manner. Because the parameters in the function occur linearly, all discussions of the Gibbs free energy can be translated immediately to other thermodynamic functions. For example, in the case of a fluid, the intensive thermodynamic variables are the temperature $T$ and pressure $P$, and the Gibbs free energy (eq. (50)) can be converted into equations for enthalpy and volume by differentiation.

$$- \frac{\Delta H}{RT} = \frac{a(\Delta G/RT)}{a \ln T} = \sum_{x=1}^{N} \phi(z)(x_1; N)$$

$$x \sum_{j=1}^{N} \sum_{k=1}^{N} \left[ \frac{a(\Delta \mu_{jk}/RT)}{a \ln T} + \frac{a(\Delta \epsilon_{jk}/RT)}{a \ln T} \ln x_j \right] x_j x_k$$

$$\frac{P \Delta V}{RT} = \frac{a(\Delta G/RT)}{a \ln T} = \sum_{x=1}^{N} \phi(z)(x_1; N)$$

$$x \sum_{j=1}^{N} \sum_{k=1}^{N} \left[ \frac{a(\Delta \mu_{jk}/RT)}{a \ln T} + \frac{a(\Delta \epsilon_{jk}/RT)}{a \ln T} \ln x_j \right] x_j x_k$$

The utility of the function I have constructed must be judged not only by its convenient analytical properties, but also by its ability to reproduce the data for difficult real systems. This aspect of the problem is examined in a companion report (NASA TP-1930), where we determine the parameters from experimental data for several systems by the method of least squares.

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Cleveland, Ohio, December 15, 1981
REFERENCES


A new class of nonideal solutions is defined by constructing a function to represent the composition dependence of thermodynamic properties for members of the class, and some properties of these solutions are studied. The constructed function has several useful features: (1) Its parameters occur linearly. (2) It contains a logarithmic singularity in the dilute solution region and contains ideal solutions and regular solutions as special cases. (3) It is applicable to N-ary systems and reduces to M-ary systems (M ≤ N) in a form-invariant manner. The ability of the function to describe data for a real system is tested in a companion report (NASA TP-1930).