PREDICTION OF NON-IDEAL EQUILIBRIA
FOR SEPARATION OPERATIONS

by

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We accept this thesis as conforming to the
required standard.

THE UNIVERSITY OF BRITISH COLUMBIA

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Date December 20th, 1970
ABSTRACT

A rather general expression for the excess Gibbs free energy of a nonionic liquid mixture has been developed in this thesis, and the expression has been tested on nine binary mixtures exhibiting a considerable range of nonideal behavior in both vapor-liquid and liquid-liquid equilibria. The basis for the formulation is that of the constant coordination number quasichemical mixture theory of Guggenheim, suitably modified to account for the major effects arising from the nonconstant coordination number situation inherent in a mixture of unequally sized constituents. The development of the geometric aspects of the theory is considerably based on the ideas of Hogendijk for mixtures of random-packed spheres. The generalization of the theory to multicomponent systems is based on the work of Barker on associated mixtures.

Because the expression handles a nonconstant coordination number system, it has for brevity been termed the NCZ equation.

Although in many cases the proposed equation performed no better than those already available for certain systems, no existing theory was able to deal with all of the nine binaries on which the NCZ expression has been so far tested.

The proposed method of formulating the excess Gibbs function has brought to the fore the need for physical chemical measurement of data of a kind not presently available on a large scale, despite the fact that the required parameters are in
themselves standard thermodynamic quantities, such as the pure-component free energy of a liquid.

The present extension of quasichemical theory is seen as an indication of the basic viability of the quasichemical type of approach for the prediction of the excess properties of liquid mixtures.

Professor James S. Forsyth
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Dedication

to:-

rolus
arvid
barb
bev
dale
donna
freda
judy
johann
frind
&
friend

and to

peter

pat
david
bob
robin
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collection.
A Ph.D. thesis is read by individuals of very different background interests and detailed expertise in the field of the thesis. To avoid tedious and needless reading, three charts have been provided showing possible reading routes to meet the potential needs of three types of readers.

1) The expert who is familiar with the background and needs only to consider what is new in the thesis, both in the theory and in the results.

2) The reader who is only generally knowledgable in the field and who might therefore wish to be reminded of relevant background.

3) The reader who is only concerned in the results obtained and who is prepared to take derivations on trust.

Illustration 1 provides a routing guide for readers having one of the above purposes in mind.
Illustration 1. Reader Routing Guide.
CHAPTER 1

GENERAL ORIENTATION OF THE RESEARCH

1. THE EFFECT OF NON-IDEALITY ON MULTICOMPONENT DISTILLATION

2. FIVE POINT RESEARCH PROGRAM

   A. General
   B. Search for Presently Available Data
   C. Measurement of Vapor-Liquid Equilibrium
   D. Measurement of Heat of Vaporization
   E. Calculation Program
   F. Development of More Powerful Predictive Expressions

3. THE DESIGN IMPLICATIONS OF THERMAL AND EQUILIBRIUM DATA

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6. THE NEED FOR VERSATILE EXPRESSIONS FOR PROPERTY PREDICTION

7. THE NEED FOR A GENERAL CLASSIFICATORY SYSTEM FOR NON-IDEALITY

8. USEFUL ATTRIBUTES OF SUCH A CLASSIFICATION

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CHAPTER 1

GENERAL ORIENTATION OF THE RESEARCH

1. THE EFFECT OF NON-IDEALITY ON MULTICOMPONENT DISTILLATION

At the outset of the work reported herein, the author embarked on a study of the effect of non-ideality in the phases present in fractionating columns on such important parameters as the number of stages required, the minimum reflux ratio and the distribution of the various components between two or more outlet streams. The intended mode of attack was to consider 3-component systems for which extensive vapor liquid ternary equilibrium data as well as all the necessary thermal values were available. Knowing these data for several ternary systems, it would have been possible to examine the behavior of systems to see which features of their non-ideality were most important and, if these features affected the final performance of the column in different ways, to enumerate these effects for the guidance of future users.

It was hoped that among other things, the results might be amenable to summary in some way which would give a clear general understanding of the behavior of a column handling non-ideal mixtures in the way that the equations of Underwood\(^{1}\) and their extension and graphical interpretation by Forsyth and Franklin\(^{2}\) has done for the case of ideal

\(^{1}\) wherever possible, format of reference is according to reference (97).
mixtures. Even if this were not possible it was hoped that by doing a number of column calculations it would be possible to offer some generalizations of use to a designer.

It would not be possible to produce any graphical generalizations for systems with more than four components, but the illustrations referring to three and possibly four components together with an extension of the arguments by analogy might give some general guidance to the behavior of multicomponent systems.

2. **FIVE POINT RESEARCH PROGRAM**

   A. **General**

   A research program was set up comprising five constituent parts, all of which would be needed to achieve the final goal, yet, each being sufficiently independent of the others that some progress could hopefully be made in a given part, independent of difficulties which may have arisen in the meantime in the parallel studies. Some of these programs were carried out entirely by the author, but some formed work carried out by undergraduates as part of their graduating research projects and so, while being supervised by the author, were only to a limited extent carried out by him. In addition, part of the considerable literature search for experimental data, which will be mentioned later, was carried out under guidance by an undergraduate student working during the summer vacation.

   For clarity, it is convenient to list the five sub-
sections at this point.

**B. Search for Presently Available Data**

A considerable search of the literature was made in order to find as many systems as possible containing three or more components for which a 'complete' set of physical data was available. These data had to include binary vapor-liquid equilibrium for all possible binaries, and some multicomponent vapor-liquid equilibrium data. In addition was required the enthalpy of a sufficiently large number of multicomponent liquid and vapor mixtures, and liquid and vapor enthalpy of the pure components together with reliable heats-of-mixing.

**C. Measurement of Vapor-Liquid Equilibrium**

Before the search for data had been underway for very long it became obvious that it was unlikely that even a very limited amount of data meeting the specifications given would become available through a literature search, and, accordingly, a limited program was undertaken$^{(3)}$ for determining three component vapor-liquid equilibrium data for the system Benzene-Toluene-Xylene. This system had already been examined as far as the Benzene-Toluene- and Toluene-Xylene binaries, but the third binary had not been studied and no ternary data were available. Experimental and analytical technique available to hand proved inadequate, and the work must be regarded as unsatisfactory.
D. Measurement of Heat of Vaporization

Parallel with above undertakings, an attempt was made to measure the difference between the actual heat of vaporization of Benzene-Toluene-Xylene mixtures, and that which would have been predicted by ideal mixing rules\(^4,5\). 

E. Calculation Program

If the above three programs had come to fruition, or even if only the first had been successful, then data would have been available for use in fractionating column calculations, either as tabular data, or fitted to standard data-reduction expressions\(^6,7\). To this end computer programs were devised and tested to use the data when it became available. Certain assumptions had to be made about the form the data would take when it became available, but within these restrictions programs were written and tested\(^8\). It was hoped that these would be flexible enough to deal with a wide range of different situations.

One of the main concerns of the overall work was to examine the effect of non-ideality on the minimum reflux ratio in fractionating columns. Particular attention was given to this feature. Realizing that no plate-to-plate calculation could ever be done exactly at the minimum reflux ratio, provision was made for calculating at a reflux ratio slightly above and also slightly below the minimum value. The latter calculation gives results leading to compositions negative in one or more components, but these results, although unreal, can serve to evaluate the minimum reflux ratio more closely.
than would be possible if only ratios greater than the minimum could be used (9).

F. Development of More Powerful Predictive Expressions

The fifth prong of attack on the overall problem, and the one which, in the event, has been given the most attention and which forms the bulk of the matter in this thesis, was an attempt to predict, on theoretical grounds, consistent vapor-liquid equilibria and thermal data. Initially, this attempt (3) was made at what is now realized was an insufficiently profound level, and made use of the Clausius-Clapeyron equation to relate relative volatilities of pairs of components directly to the difference in their heats of vaporization, rather than deriving both thermal and volatility data from a free energy expression, as is more usual (10). This work initiated a train of thought which later led to a generalization of pre-existing theories to include, in a new way, the effects of unequally sized molecules. However, in due course, the use of the Clausius-Clapeyron approach itself had to be given up as lacking sufficient flexibility of application*, and a considerable study of solution theory was

* The unenforcibility of constant T and P over a range of compositions does not invalidate the Clausius-Clapeyron equation as a point transformation at a given composition, though it may make it inconvenient to apply in practice.
undertaken. It now appears that this fifth avenue of attack has produced useful results and that the author now has available to himself, consistent (if somewhat incomplete, in the case of the thermal data) estimates of thermal and equilibrium data which can be used in the programs already developed. This later step has not yet been taken.

3. **THE DESIGN IMPLICATIONS OF THERMAL AND EQUILIBRIUM DATA**

The relative sensitivity of column calculations to equilibrium data on the one hand, and to thermal data on the other, depends upon the intended operating conditions of the column. At high reflux ratios, the thermal properties of the liquid and vapor have very little effect on the column performance. Except inasmuch as the total throughput of the apparatus may be dependent on those thermal properties, the separation performance is minimally affected. However, near the minimum reflux ratio, the quantity of the liquid and vapor phases flowing at any one point in the column may have a decisive effect on the separation, and so under these conditions (and these are the conditions near which commercial columns operate) the thermal properties become important as well. Not only must such relevant data be available for calculation, but they must possess an adequate degree of reliability to avoid excessive contingency allowances in physical column design.

4. **THERMODYNAMIC CONSISTENCY TESTS**

Experimental data may have in it sources of errors
which might well be divided into two kinds. Firstly, there is
the random scatter about the true line which all experimental
results display, and secondly, the systematic error in y-versus-x
arising from experimental technique, or some other source of
constant error.

It is entirely possible that a set of data containing
a systematic error will, when the random errors are removed
by curve-fitting, produce a curve which shows consistency with
the Gibbs-Duhem equations method of testing\(^{(11)}\).

It is therefore pointed out that while meeting this
standard is a necessary condition it is by no means sufficient,
and it is entirely possible that some data is being accepted
as reliable because it has met this consistency test whereas
in fact it contains unrevealed discrepancies.

If, however, it were possible to evaluate the Gibbs
free energies of the mixtures involved, then equilibrium data
derived from this would, of necessity, satisfy the Gibbs Duhem
consistency tests, obviating them, and transferring the
question of uncertainty of data to a more fundamental level than
that which can be inspected by consistency tests. In this
thesis, predictive expressions are formulated in the excess
free energy form. These are conformal with the principle of
thermodynamic consistency as long as the transformations re-
sulting in the expressions derived from the mixture free energy
are correctly performed.
5. **CONSISTENCY BETWEEN EQUILIBRIUM AND THERMAL DATA**

Consistency between vapor-liquid equilibria and corresponding thermal data must also be considered. Of course in principle, if the vapor-liquid equilibria prove to be consistent, and if it can then be shown they conform with the heat of mixing or heat of vaporization by any valid thermodynamic relationship, under the pertinent conditions of temperature and pressure for a given mixture, then the given thermal data will perforce be consistent with the equilibrium data. Such a valid thermodynamic relationship is exemplified by a modified form of the Clausius-Clapeyron equation relating the vapor pressure ratio of a pair of components to the difference in their partial molal heats of vaporization in a given mixture. This method of producing equilibrium data from thermal data was in fact used for some time in the present work. Unfortunately, the apparent straightforwardness of such a means of securing consistency between thermal and equilibrium data encountered the following difficulty. There is an extreme difference in degree of sensitivity of vapor-pressure data and heat of vaporization data to volume changes in the liquid phase upon mixing: the former are most insensitive to volume change effects, and the latter extremely sensitive. Since the measurements useful for column design are the isobaric ones (in which liquid expansion effects are free to occur), the fact that no very reliable quantitative means exists for assessing the effect of liquid volume changes upon thermal properties effectively
undermines the usefulness of applying consistency tests between the two sets of properties - no matter how formally correct are the algebraic thermodynamic descriptions which are presently available\(^{(12)}\), nor how diligently these tests are applied.

6. **THE NEED FOR VERSATILE EXPRESSIONS FOR PROPERTY PREDICTION**

Even if one were to ignore the operational difficulties in transforming one set of data into another, and even allowing that such transformations are entirely valid, it is obvious that no demonstration of the internal consistency of an experimentally determined set of data is going to assist with the problem of predicting the behavior, even of the same system away from conditions under which it was tested. The above is true even with the same system to be used under different conditions of T and P, and of course becomes even more obviously true if the composition range is switched from one region to another. Indeed what is required more than a means of testing the consistency of measured data (and the worthwhileness of such testing has already been questioned by authors such as Van Ness\(^{(13)}\) and Chang and Lu\(^{(14)}\)) is rather the means to predict data away from the regions in which measurements have been made, even if these predictions are somewhat less than completely reliable. Specifically it would appear that from an engineering point of view, even rather poor data on a 5-component system which has to be processed is more valuable than extremely reliable data on any of the binaries.
In fact, in such a case the designer would probably be prepared to accept less certainty in his data, if, in return, he were able to increase the comprehensiveness of predictions about what might be expected to happen in the mixture he wishes to employ under various design conditions, even if this guidance were only rather qualitative.

It is obvious that a designer must have guidance as to what effects on the performance of his column will come from the particular kind of non-ideality which his system is liable to exhibit. For example, if a system had a non-ideality such that the ratio of liquid to vapor molal rates increased down the column from the top plate, then a different situation might arise with respect to the onset of a pinch than if the reverse were true. Equally, if the K-value of one component in a multicomponent system were reduced to a value near to unity because of a high concentration of some other component, then the normal expectation that the former component would diminish rapidly either as one proceeded down or up the column would not be met, and would quite seriously interfere with the column's separation performance. Such an example is included for purposes of perspective, to show that there can be real problems, and that these problems can arise either from the equilibria non-ideality or from the flow non-ideality.

7. THE NEED FOR A GENERAL CLASSIFICATORY SYSTEM FOR NON-IDEALITY

In the field of predictive theories of non-ideality, much recent work is concerned with the study of vapor-liquid
non-idealities. Various broad classifications of non-idealities have become recognized, investigated, and named. As long as a system is showing only one kind of non-ideality, the situation is not confusing. But it is in the nature of things that experiment and classification of this kind can usually only tell of the resulting overall effect, and cannot often distinguish whether or not there is only one kind of non-ideality present or whether there is more than one kind of non-ideality at work, with diverse effects reinforcing or cancelling to an unknown extent. In fact one might be thinking in terms of one type of non-ideality when the system actually exhibits another (or others), so that any attempt to predict parameters for a system under such circumstances would represent efforts made in the wrong context. Hence workers in this field have been striving for many years to produce mathematical expressions of the kind which attempt to incorporate some specific idea of the physical behavior of liquids into their mathematical expressions, and which it is hoped will describe quantitatively all the features of a system displaying more than one specific pattern of nonideality.

8. USEFUL ATTRIBUTES OF SUCH A CLASSIFICATION

So far results have been far from complete, and the situation is by no means resolved. It would be useful however to consider the form that such an expression might take. Some desired variable, and for reasons which will appear later let us choose the excess Gibbs free energy $G^E$, would be equated to
a number of terms, each of which would incorporate, together with the necessary mathematical operators, only 'recognizable' thermodynamic and physical parameters which would, hopefully, also be easily measurable. Each parameter could be distributed in various functional relationships through the thermodynamic classes of component terms present in a general expression. The parameter might appear in several of the component terms of the overall expression and be missing from several. It could appear in one guise in some terms and in another in other terms. Terms would be formulated so that the numerical extent of any kind of non-ideality would be reflected in the numerical magnitude of component terms of the overall expression. In this way, a statement of non-ideality would be unambiguous, inasmuch as it would take numerical cognizance of each kind of possible non-ideality, and while recognizing the contribution of these various kinds of non-ideality would, in total, give the overall non-ideality of the system however contributed. Implicit in the foregoing is the assumption that all the relevant physical parameters must be included in the expression, even if some of their effects were negligible in any one particular system. These parameters would constitute what is known mathematically as a spanning set of independent variables for the system. It would be understandable that a number of possible spanning sets could be specified but the existence of a minimum set is mandatory in the argument. It might be that the numerical magnitude of recognizable members of the spanning set for a given system would indicate
in some way the type of non-ideality which the system would exhibit, but it is much more probable that the same physical parameter will be involved in a number of different ways and the author feels it more probable that the terms of the overall expression, rather than the parameters which are used to construct them, would be the basic units for description of non-ideality.

The above observations have been written with some hindsight, because such an expression has indeed been developed and seems to have most of the properties described. In developing such an expression, which after all is rather an ambitious task, a reasonable place to start would be to see to what extent existing theories which, although fragmentary, are successful in the more limited contexts for which they were designed, might be brought together. It did seem most probable that the theories which can most easily be brought together would be those which had the common basis of a physical imagined picture of molecular behavior. This conclusion is strengthened by the fact that the seemingly most effective theories at the moment are those which do include such a physical picture in their formulations. The way in which the present work is based upon such existing theories will be illustrated in the chapters dealing with the derivation of formal results.

Also, an expression developed from well-established formulations has the double advantage of reducing the amount of new formulation necessary while at the same time preserving
structures in formulation which are at least partly familiar to the reader.

It is of course well recognized that other approaches are possible, including those of pure data reduction nature (7). Such procedures are not really thermodynamic in nature and therefore are rarely predictive - at least beyond a very limited range. Although they are useful manipulative devices, they provide a rather limited insight into the nature of the problem of recognizing specific non-idealities, and while undoubtedly of very considerable value in engineering design, are inevitably suspect when the predictions are extrapolated to any noticeable extent. It is also realized by those who have had to make use of them that empirical polynomial fits are notoriously sensitive to the data from which they have been derived, and it is this very sensitivity which makes the user cautious about using extrapolations.

The author therefore proposes not to devote more than cursory attention to highly empirical approaches except by way of illustration, and for comparison purposes later on in the discussion of results. While recognizing the power of highly empirical approaches to deal with known experimentally determined results, because of their lack of utility in predicting results, and above all in their incapacity to elucidate the problem of the existence of various kinds of non-ideality, such attention should suffice for the particular purposes of this thesis.
9. RESULTS OF THE PRESENT STUDY

The reader will find in due course that the expression developed is complex, a complexity which reflects the generality of the concepts embodied in it. Inherently the complexity of an expression is, nowadays, no barrier to its use provided its predictions are superior to those of alternatives available (52).

If, as the author hopes, the expression can, by the examination of a limited number of systems for which data is more or less available, prove to be a potentially useful and powerful one, then he believes that more data will be generated, this data being of a form most conveniently usable in the expression.
CHAPTER 2

INTRODUCTION TO THE THERMODYNAMIC PROBLEM

1. GENERAL

2. FRAMEWORK OF STANDARD THERMODYNAMIC AND STATISTICAL RELATIONSHIPS

3. KEY INDEPENDENT VARIABLES

4. THE QUASICHEMICAL THEORY OF SOLUTIONS

5. THE PRINCIPLE OF MINIMUM FREE ENERGY IN EQUILIBRIUM

6. THE PARTITION FUNCTION

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8. PRESENT EXTENSION OF THE THEORY
   A. General
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9. GEOMETRIC INTERPRETATION OF THE NCZ CASE

10. ENERGETIC RAMIFICATIONS OF NCZ PACKING GEOMETRY

11. ENTROPY EFFECTS OF NCZ PACKING GEOMETRY
    A. The Primary Configurational Entropy Effect
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12. CONCLUDING REMARKS
CHAPTER 2

INTRODUCTION TO THE THERMODYNAMIC PROBLEM

1. GENERAL

It has now been shown how the theoretical thermodynamics problem which became the topic of the thesis arose out of the original context of an engineering study of the effects of non-ideality in multicomponent distillation. It is now time to introduce, in the following section, the outlines of the thermodynamic research into mixture non-ideality which became the main work carried out by the author.

2. FRAMEWORK OF STANDARD THERMODYNAMIC AND STATISTICAL RELATIONSHIPS

A review of standard thermodynamic relations\(^\text{(15)}\) will now be given. These relate the mixture properties being sought to other, more fundamental though more easily calculable quantities.

The more detailed observations to be made in the present work will be then inserted into the standard relationships. The standard relationships used are those between the activity coefficient \((\gamma)\) of a component present in the mixture, molar heat of mixing \((\Delta H^E)\) (two properties sought for distillation purposes) and the excess Gibbs free energy of mixing \((\Delta G^E)\), and a fundamental quantity from statistical mechanics known as
Illustration 2. Thermodynamic Relationships.
the partition function (designated in this work as \( Q \)). For brevity, these are first introduced in elementary notation to indicate the general nature of the relationships and to introduce the set of independent variables chosen to be incorporated.

\[
\gamma, H^E = f_1(G^E) \tag{1}
\]

\[
G^E = f_2(Q) \tag{2}
\]

\[
Q = Q(x_i, R_i, n_i, r_1, \omega_{ij}, A_1, \Pi, T) \tag{3}
\]

The organization scheme to be followed is shown in Illustration 2.

By consolidation of the above relations, the overall plan was to establish a set of relations between \( G^E \) and \( H^E \) and the independent variable set entities, as summarized by

\[
\gamma, H^E = f_2(x_i, R_i, n_i, \mu_i, \omega_{ij}, A_1, \Pi, T) \tag{4}
\]

These relations indicate that \( \gamma \) and \( H^E \) are obtainable by thermodynamic methods from the Gibbs excess free energy of mixing \( G^E \), while in turn \( G^E \) is obtainable through a standard formalism from the partition function \( Q \) for the mixture. Other thermal properties needed for column calculations, namely enthalpy of the pure liquid and pure vapor and non-ideality of the vapor are taken for present purposes as being available from tables of data and are not given any further detailed con-
sideration in this part of the thesis. Customarily, the thermodynamic variable $G^E$ is that for which explicit expressions are written, and this practice will be maintained in the present work.

3. **KEY INDEPENDENT VARIABLES**

One set of independent variables which define $Q$ and hence $G^E$, is that bracketed in Equation 3. Note that the set explicitly contains the molecular radius variable $R$. This inclusion implies that all molecules in the mixture (more exactly monomer units) need not be considered as being of the same size. Specifically, the inclusion of the variable $R$ is to permit of formulating equations not necessarily presuming that all molecules are of the same size. This is one difference between the work now to be proposed and that described in existing theories, and will be the subject of very considerable attention later in the present work.

4. **THE QUASICHEMICAL THEORY OF SOLUTIONS**

One mainstream of existing theory, and the one which is also followed in this work may be called broadly the "quasichemical theory of solutions". The name 'quasichemical' designates one of the primary features of the theory, namely that the process of mixing two liquids which results in unlike molecules being juxtaposed (in contrast to the juxtaposition of molecules of the same species in the pure component state) is conceived of in the same terms as those describing a reversible
chemical reaction consistent with such a reorganization.

If attention is focused on the individual points of contact of molecules in nearest-neighbor relations, then the 'forward' reaction involves the reorganization of two 'like' pairs of such contacts, one pair for each of the two types of molecules being considered, and with the formation of two 'unlike' pairs representing the mixed situation. The 'reverse' reaction simply returns the two unlike pairs to the like-pairs found in respective pure component states.

Illustration 3 indicates the ideas of contacts, 'pairs', and the reorganization reaction just described. This reorganization is associated with the release or absorption of energy which is the heat of mixing. For example, the forward 'reaction' is exothermic if the cohesion of the unlike pair bond formed is stronger than the arithmetic average of the two original like-pair bonds. The equilibrium mixture of like and unlike pair associations, where a large number of like pairs of each substance was initially present, is the one for which the overall system has assumed its lowest free energy, subject to the additional system restraints which are the physical properties of the component substances and their relative abundance. The conception of the liquid as an assemblage of pairs of contacts is the basis of what was called the 'independent pairs liquid' by Guggenheim. It will be seen that this representation of the liquid is well suited for formal analysis of mixing phenomena, in that it leads to expressions formally identical with the mass law expressions in reaction
Illustration 3. The Pairs Reorganization Reaction.
chemistry used to relate equilibrium concentrations of products and reactants to standard free energy changes. In the independent pairs liquid, like pairs of the pure component states are the 'reactants' and the unlike pairs formed on mixing are the 'products' of the mixing 'reaction'. Hence the name quasichemical solution theory.

5. THE PRINCIPLE OF MINIMUM FREE ENERGY IN EQUILIBRIUM

Operationally what has to be done to minimize the free energy of the mixture can be summarized in step 1) to 3) following:

1) Evaluate $Q$ for the mixture
2) $A = -kT \ln Q$
3) $A \rightarrow \text{min.}$ for values of $X_i$ such that: $\left( \frac{\partial A}{\partial X_i} \right) X_j = 0$
   (Then to find $X_i$ consistent with $A_{\text{min.}}$)
4) Solve (3) for $X_i$, the independent variable 'minimized', whose equilibrium value is thus determined.

$A_{\text{min.}}$ is consistent with stage 3). Minimum free energy values of the independent variable set (the $X_i$) are obtained via step 4). The symbol $X_i$, here used in step 3) in the general sense, is consistent with the notation of variational calculus to describe any spatial variable. In particular, here, since $A = A(T,V,N_i)$, $A_{T,V} = A(N_i)$, so that if $Q$ is properly formulated, condition 3) results in a simple algebraic expression, which in the case of a binary mixture is soluble for the equilibrium population of unlike pairs,
designated in this thesis as $X_{ij}$, related to the unlike pairs concentration $X_{ij}$ by a simple normalization. (Incidentally, the difficulty of maintaining a notation scheme which is both faithful to conventions in the field of origin, suggestive of the physical situation and also compatible with notation of other areas of this work becomes apparent. To resolve it, unique symbols are employed whenever possible — where it was not, special meanings are always given in close conjunction with the expression in which they appear, as is the case here for $X_i$).

6. THE PARTITION FUNCTION

It is seen that $Q$, the partition function, (more precisely the Canonical Ensemble Partition Function) is the basic starting quantity upon which operations are performed. $Q$ is directly related to system parameters: a cursory definition of $Q$ is that it is the sum of the unnormalized statistical weightings of all the distinguishable subclasses of events existing in the system. The weightings take into account the relative populations of the subclasses, and energy and geometry effects. The most important single thing to notice at this point is that the weightings are directly expressible in terms of the independent variable set in conjunction with a set of specific rules governing the behavior of the liquid being modelled, and the general statistical rules governing the type of partition function being constructed.
7. **THE SCOPE OF THE QUASICHEMICAL THEORY**

The quasichemical theory presents a formulation which permits of the use of a very small number of behavioral observations to determine, through the appropriate mathematical structure, the partition functions required for calculation of thermodynamic properties. (See Chapter 4 for a discussion of these behavioral observations).

The quasichemical theory, as originally formulated, implied that all molecular species will be of the same size, and it must be obvious to the reader that the component molecular species of a real liquid mixture will not necessarily be of equal size. It was this limitation which resulted in quasichemical theory falling into disuse; and other theories, incompatible with it but which did incorporate molecular size parameters, have become prominent. In view of the resilience and generality of the basic principles of the quasichemical theory, this situation seemed unfortunate, and so a reassessment of the theory was undertaken. A brief investigation revealed that it might be usefully considered that the quasichemical solution theory comprises two recognizable parts. The first of these is the 'quasichemical reaction' part, namely that governing the formation of unlike pairs from like pairs, and the second is the group of concepts of liquid structure into which the quasichemical reaction idea had to be incorporated to produce an overall solution theory. It was this group of structural concepts which needed to be broadened beyond the case of equal sized molecules. The basic
attractiveness of the theory nonetheless remained: if it is legitimate to treat all nonionic liquids as an assemblage of pairs, then the concept of the quasichemical formulation of pairs is a powerful one, and capable of generalization into any type of molecular geometry which suitably describes the class of liquids to be analysed. The bulk of this work was to extend quasichemical theory to incorporate a more flexible structural basis, and thus extend the usefulness of the quasichemical theory as a means of predicting excess free energies of mixing.

8. PRESENT EXTENSION OF THE THEORY

A. General

Any theory which aspires to comprehensiveness must incorporate all the variables which influence the behavior of the system being examined. The argument of equation (3) is precisely such a set. In particular it should be noted that the molecular radius parameter $R$ has been included. In particular this extension and generalization of quasichemical theory to the case of unequally sized molecules involved elucidation of geometric considerations governing the nature of the effects of contacting unequally sized molecules, a feature missing from the original theory.

Starting from a picture of the model of a liquid as being analogous to that of a bed of spheres of unequal size, the ramifications of this concept have been pursued to produce new expressions predicting the behavior of such liquids. The
test of the expression developed has been in its ability to predict the behavior of a number of experimental systems.

B. Basic Nature of the Extension

The basic mathematical implications of the extension are followed through the whole body of the theory, resulting in a quite considerably changed formulation. Only the most general aspects of the extension need to be noted at this point. Basically, the conversion involves changing the geometric conceptual basis of the liquid model from that of an assemblage of molecules arranged on the points of intersection of a 3-dimensional regular lattice, to one which regards the assemblage as largely equivalent in organization to that of a close-random packed bed of unequally sized spheres. The result of this change in outlook is that the number of nearest neighbors per molecule is no longer regarded as a constant as in the 'lattice' case, but becomes a function of the relative size of the molecular species involved, and the proportions of these specified components, as well as of secondary modifications in local organization resulting from binding energy effects.

The terminology to be used distinguishing the two methods of geometric assignment, which also serves to designate the two types of quasichemical theories using the different geometric bases, is that of constant coordination number for the lattice case (or "CZ", for constant-z, where Z is the symbol for coordination number), and non-constant coordination number ("NCZ") to characterize the case of packing of unequally
sized molecules.

It will be realized even from this brief mention of the two situations, namely CZ and NCZ, that the CZ case effectively constitutes, at least in the context of quasi-chemical property estimates, a special case of NCZ which may be achieved in the limit where the constituent molecular species are of equal size. This statement is later shown to be quantitative, in that the expression for evaluating $G^E$ in the NCZ case reduces mathematically to that for the CZ case upon formally setting size ratio parameters to unity in the former.

9. GEOMETRIC INTERPRETATION OF THE NCZ CASE

Illustration 4 indicates schematically the geometry of NCZ packing for a mixture of unequal sized spheres, an effect previously studied by Hogendijk$^{(17)}$ and co-workers for packed beds. This diagram is only qualitative, in that the representation is two-dimensional rather than showing the three dimensional nature of the actual situation, but NCZ effects are nonetheless clearly manifested by the Illustration. Actual calculation of coordination number ($z$) is made on the basis of this bed of spheres model, with suitable modification for the energy effects that exist in the real liquid.

10. ENERGETIC RAMIFICATIONS OF NCZ PACKING GEOMETRY

From the general thermodynamic formula

$$G^E = H^E - TS^E$$ (5)
Illustration 4. Coordination Number Change due to Mixing of Unequal Sized Particles.
it is seen that the free energy of a mixture contains both heat ($H^E$) and entropy ($S^E$) of mixing effects. Both of these involve not only the nature but also the number of contacts per molecule. In the NCZ case, the act of mixing inevitably alters both the nature and number of pair contacts from their pure component values. The additional energetic ramifications of NCZ arise out of the cohesion changes due to changes in the population of like pairs, due to coordination number changes, as well as the more familiar heat of mixing effects due to the pairs reorganization reaction accounted for in the original CZ theory.

11. **Entropy Effects of NCZ Packing Geometry**

A. **The Primary Configurational Entropy Effect**

Particular entropy effects are more difficult to describe at the level of this introductory chapter, but suffice it to say, the main effect also arises out of a change in the number as well as in the kind of contacts per molecule upon mixing. The situation exists because of a change in the number of ways in which a new configuration of the system can be defined in the NCZ (versus the CZ) case and hence in the configurational term in the partition function, hence ultimately in $S^E$, the configurational contribution to $G^E$.

B. **Secondary Entropy Effects**

For certain other excess entropy contributions to be reckoned into the complete $G^E$ expression, it is easier to employ
an alternative formulation for entropy than that afforded in connection with the partition function. This alternative approach is that of the 'probability distribution' \( \left( \sum_i p_i \right) \) approach, coupled with the use of the "Boltzman" definition of entropy\(^{(18)}\) written as a function of probabilities. The basic formulation is given by equation (6)

\[
S = -k \sum p_i \ln p_i
\]

(6)

Because two of the entropy terms in the general expression are obtained in this way, the section of Chapter 9 in which these are discussed is set apart from the derivation of terms in which the usual partition function approach is used. Because of the relation of probabilities to concentrations, certain concentration terms used in the general expression are also obtained through this 'probability' approach. The development of this approach in its application to the quasichemical theory of multicomponent solutions was due first to Barker\(^{(19)}\).

Bare mention of the existence of this alternative approach has been made at this point, simply for purposes of introducing the idea, without attempting to elaborate further on it.

12. CONCLUDING REMARKS

Although no attempt to do more than mention the existence of the salient points of the thesis has been made so far, it is hoped that the reader is now sufficiently familiarized with the concepts included in it to facilitate reading the more detailed treatment to follow.
Of the following Chapters, Chapter 6 introduces the idea of packing fraction unit and explains the method of evaluating appropriate coordination numbers. In Chapter 7 the configurational effects of NCZ are introduced. In Chapter 8 an exposition of the extension of the variable coordination number concept to the simplest type of real liquid mixture is given. In Chapter 9, an extension of the expression is undertaken, resulting in the general form of the excess free energy expression. In Chapter 10 an extensive comparison of the theory to related ones is made. Chapter 11 illustrates the comparison of the theory to experimental results reported in the literature. Chapters 3 to 5 are of an introductory nature, included to make the Thesis relatively more self-contained.
CHAPTER 3

REVIEW OF CONSTANT COORDINATION NUMBER
QUASICHEMICAL AND RELATED THEORIES

1. EXTENSIONS OF THE CZ CASE
   A. General
   B. Triplets of Contacts
   C. Multifunctional Solutions - Pairs Concentration Matrix
   D. Quasicheoretical n-mer Theory

2. LESS CLOSELY RELATED THEORIES
   A. Regular Solutions
   B. The 2-Liquid Theory
   C. Local Composition Theories

3. THE PROBLEM OF THE CZ LATTICE

4. SUMMARY OF THE SOURCES OF EARLIER WORK USED
CHAPTER 3

REVIEW OF CONSTANT COORDINATION NUMBER

QUASICHEMICAL AND RELATED THEORIES

1. EXTENSIONS OF THE CZ CASE

A. General

The independent pairs liquid, the simple mechanical properties of which have been outlined in Chapter 2, invites examination of the energetics of the solution as a whole using analysis of changes in the pairwise linkage energetics as the tool. The contribution of Guggenheim in this area was, through operations on the 'independent pairs liquid', to include a correction for the effect of local clustering in the concentration portion of the heat of mixing term of the free energy. Specifically he corrected the heat of mixing term to include the stoichiometric effect of energetically induced local clustering. Guggenheim's approach, described in simple terms was to minimize the free energy of the system, subject to the restraints of constant temperature, volume, and overall composition, leaving as the single disposable degree of freedom the concentration of unlike pairs. He illustrated the procedure to be used for the case of a binary mixture of monofunctional* species. In such a system, the

* one type of surface functional group per molecule. Carbon tetrachloride and butane would be examples of monofunctional species.
effect of the energy-induced clustering upon the equilibrium concentration of unlike pair associations is evaluated through the solution of a mass-law expression explicitly involving the pure component concentrations, the coordination number, and the net reorganization energy change $\omega_{ij}$. The mass-law expression itself is obtained formally by the variational method, in which the free energy of the system is mathematically minimized. The internal consistency of approach indicated by the above comments accounts for the elegance of this part of his method. Schematically, the process is set forth by the operations numbered 1) to 4) in section 5 of Chapter 2.

Guggenheim's main objective in formulating the concept of the pairs liquid evidently was to be able to provide a rational basis for calculating the energetically induced local clustering in mixtures. However, the versatility and basic soundness of the approach has made possible various extensions of his initial theory, although there have also been certain problems, involving calculational difficulties in solving the algebra, which arise in cases less restricted than that considered by Guggenheim himself. This chapter will serve to introduce five lines of investigation related to quasi-chemical theory. In this chapter will be indicated some of the directions of extensions made by Guggenheim and other workers to the original theory, and some of the problems which have already been overcome by more or less related (but compatible) approaches, as well as by some seemingly incompatible ones.
This section should also serve as an introduction to certain problems which remain, and which form the main burden of later chapters of this work. The chapter concludes with a brief resumé of previous source work.

The numbered steps of section 5, Chapter 2, while fundamentally correct and leading to useful answers, may prove to be very difficult to handle numerically. So much so, that restrictions on the generality of the concept have been introduced at various stages to simplify the mathematical manipulation. It will now be considered how these restrictions have been removed or relaxed by other workers, and later in the work to draw attention to still other relaxations properly the work of the author. The first restriction to be investigated is the validity of assigning the properties of the pairs-liquid to pairs only, rather than considering triplets of contacts, or quadruplets of contacts.

Next, comes the question of removing the restriction of the method which confined the method to apply first only to binary and monofunctional cases; next, to monomer cases. Finally, the restriction imposed by requirements of a lattice configurational model concomitant with a formalization which implies that the mixture is made up of equally sized molecules is investigated at length.

B. Triplets of Contacts

The original theory applies to the case of constant-\(z\) monofunctional monomer binaries. The first extension, of the theory of Guggenheim, Chang et al, as discussed by Guggenheim\(^{(16)}\), was for the same
class of mixtures in which not only pairs of contacts were considered, but also the case of triplets of contacts (i.e. interactions between three contacting molecules), and the case of quadruplets of contacts. Theirs was principally a study of the magnitude of predicted quantum-mechanical deviations from the strictly additive pairwise nature of dispersion type interactions for groups of interacting molecules larger than two. However, the results of these studies mainly confirmed the original prediction that estimates of excess free energy obtained by accounting for pairwise interactions could be only slightly improved by these rather laborious, though interesting, considerations of higher order effects. While well worth the trouble from a research point of view, such considerations no longer are, from the pragmatic point of view of the results. Other, more serious problems first needed attention. However, such studies are important in another way. In the inverse direction, they indicated that quite accurate estimates of local 'structures' in liquids (the word 'structure' meaning simply statistically most probable associations of groups of contacts, hence of local associations of molecules in the solution) could be obtained if a means could be found to establish just the equilibrium pairwise association probabilities of contacting sites of various possible types in a solution containing more than two chemical site types.

C. Multifunctional Solutions - Pairs Concentration Matrix

A solution becomes multifunctional either when one component of a binary mixture contains more than one type of
functional group, or when more than two components are present in the mixture. In the general case both situations exist. The problem of how to calculate the pairwise probabilities in multifunctional solutions and thus the problem of the deduction of 'the statistically favored structures' of the type described above, was solved by Barker (19). Recognizing that the variational approach led to insoluble coupled sets of pseudo quadratic equations in the unknown pairwise concentrations when more than two species of functional groups (hence more than one unknown) were involved, Barker, in section 5 of Chapter 2, proposed an approximate solution for the multifunctional case based on symmetry arguments. This approach, while perhaps over symmetrizing the problem slightly, still resulted in equilibrium pairwise concentrations from which thermodynamic properties in close accord with experimental ones could be obtained. Since the formulation was not a variational one based on perturbations about the maximum randomness case, but was rather basically a 'probability' approach as mentioned in Chapter 2, even very large energy effects could be taken into account, rendering the method useful in describing effects in so-called 'associated solutions' of polar molecules. Because of the generality of Barker's approach, no problems are encountered in the case of multicomponent solutions of either monofunctional or multifunctional species.

D. Quasichemical n-mer Theory

Another extension of the original theory of Guggenheim, due to Chang (20), Flory (21) and Huggins (22) was to
develop a quasichemical theory of constant-\(z\) n-mers. (A n-mer is a chain of \(n\) monomer units strung together. A constant-\(z\) n-mer solution is one in which both the monomer species and the n-mer species are assumed to have equally sized monomer units. In this context a monomer is not to be considered as a total molecular species but rather as a single unit of a molecule, this unit being recognizable only by its configurational properties. Considerably amplified description of the physical situation represented by the contents of this parenthesis will be given in Chapter 6). The formal relation of quasichemical theory to the polymer theories of Flory-Huggins(23), etc., is thus indicated.

A result of the Flory-Huggins theory was that the concentration unit relevant to the calculation of standard heat of mixing and configurational effects of mixtures in a form comparable to that for monomers was considered to be the volume fraction, if one of the components of the mixture was an n-mer of asymptotic length.

2. LESS CLOSELY RELATED THEORIES

A. Regular Solutions

The connection between polymer theory and quasichemical theory had important consequences in another field of solution theory, namely that of 'regular solutions', pioneered by Hildebrand(24,25) and later also developed by Scott(26).

Hildebrand substituted volume fractions for mole fractions in the heat of mixing term in the expression for the
excess free energy of a liquid mixture. In fact this use of the volume fraction can be shown not to be a formal extension of quasichemical theory. Problems associated with the use of volume fraction concentration units are discussed in Chapter 10.

B. The 2-Liquid Theory

In various recent semiempirical theories related to quasichemical theory, renewed emphasis has been placed on the primary importance of local molecular configurations (on the nearest neighbor scale) in the determination of excess mixture properties. The evolution of this type of thought began with Scott's\(^{26}\) proposal of the two-liquid theory, wherein the local composition about one species was considered to be different both configurationally and energetically from the local environment of the other species. The liquid was thus visualized as an interpenetrating mixture of the two liquids, each of which had the composition of one of the two local environments, still subject of course, to the constraint of the overall material balance on the component species present.

C. Local Composition Theories

The underlying idea of 'local composition' was elaborated in various ways by Wilson\(^{27}\), Prausnitz et al.\(^{10}\), Heil\(^{28}\) and Renon\(^{29}\). The notable success of these theories has lent fresh impetus to investigations of local composition in liquids, begun by the analysis of energetically induced local clustering effects in the theory of Guggenheim.

Some of the aspects of the theories of these workers
will be discussed in Chapter 10, in comparison with the approach taken in this work.

3. THE PROBLEM OF THE CZ LATTICE

In this section the problem of the restriction of the original quasichemical formulation to the CZ case is introduced.

For a 'liquid' visualized as an assemblage of disembodied pairs of contacts between molecules, mixing energies and local clusterings arising therefrom have been obtained. Next, for purposes of calculation of configurational entropies, a change in visualization is requisite; namely, to revert attention to the liquid as an assemblage of molecules, and then to consider the interchange behavior of the assemblage so regarded.

In the quasichemical theory of solutions as originally stated, it was at this point assumed that each molecule was located at the intersection point of a regular lattice, a facet of the theory directly borrowed from the lattice theories of the solid state. In this model, the number of possible species assignments to the sites of a given configuration of the system is given by a combinatorial term enumerating possible interchanges of the two species (for the binary case) on an N-point 3-dimensional z-connected lattice. The problem is that this lattice configurational model is incapable of mathematically accommodating local packing effects (energetic or geometric).
These geometric effects arise out of changes in the number of nearest neighbors found about a molecule of a given species in a mixture of species of unequal sizes, relative to the number of nearest neighbor contacts the given species makes in the pure component state. The fact that the lattice model might also seem to over-order the system, in that both local and long range geometric ordering is implied, is not the problem, since the lattice is used only as a basis for counting possible interchanges without regard to the regularity, per se, of the large scale array. The real problem of the CZ lattice is that large scale consequences resulting from the local peculiarities induced by packing effects are not acknowledged by the method. While for mixtures of equal sized molecules, the CZ theory still produces the correct 'ideal' entropy of mixing term, for mixtures of unequal sized molecules it does not, and in such instances various problems arise in the application of the straightforward CZ approach.

Fortunately, the other assumptions and basic thermodynamic and statistical arguments of the quasichemical approach are in no way inherently dependent upon the above 'lattice' assumption, though formulations are thereby greatly simplified. Since liquids do have local configurational anomalies not explicitly includable in the constant-\(z\) lattice model, a major, and, it seems, an unnecessary, artificiality is introduced into the theory by rigorous adherence to the dictates of a lattice configurational model. How this restriction was removed by the author is the topic of subsequent chapters.
4. SUMMARY OF THE SOURCES OF EARLIER WORK USED

The foregoing introduction to constant-z approaches is sufficient to provide a context for the efforts of the present work outlined in subsequent chapters. It is seen that the CZ basis from which the present work is generalized is that of Guggenheim (S-regular* binary quasichemical model of the 'pairs' liquid) and that of Barker\(^{(19)}\) (extensions of quasichemical theory to the multicomponent case). The present work has also benefitted more indirectly from ideas of the following men: Langmuir\(^{(30)}\) (surface interactions); Scatchard\(^{(31)}\) (surface fractions); Flory-Huggins\(^{(23)}\) (volume fraction representation for polymers); Hildebrand\(^{(24)}\) (volume fractions for monomers); Scott\(^{(26)}\) (two-liquid theory); Bethe\(^{(32)}\) (energetic second neighbor correction factors), and from the recent work of Wilson\(^{(27)}\), Prausnitz et al\(^{(10)}\), Renon\(^{(29)}\), Heil\(^{(28)}\) and Derr and Deal\(^{(33)}\) (all concerned with the idea of 'local' composition, an idea resulting in expressions such as that of Wilson, or that of Heil, or the NRTL equation for \(G^E\)). In addition, recent work by Sams\(^{(34)}\), Bondi\(^{(35)}\), and Kreglewski\(^{(36)}\), on intermolecular forces, and that of Lielmezs and Bondi\(^{(37)}\), on Van der Waals radii, have been found to be useful.

* Note: S-regular is the term used by Guggenheim to describe a solution in which the configurational energy term was the same as in a Raoult's law solution. Regular solutions are those defined by Hildebrand as exhibiting a systematic departure from the ideal mixture due to size induced effects.
CHAPTER 4

REVIEW OF THE PHYSICAL BASIS OF CELL THEORIES

1. GENERAL

2. THE NATURE OF LOCAL ORDERING IN A LIQUID

3. CONSEQUENCES OF LOCAL ORDERING IN MODEL BUILDING

4. LIMITATIONS IMPLICIT IN A SINGLE-OCCUPANCY CELL MODEL

5. STATISTICAL AND CONFIGURATIONAL ASPECTS OF SINGLE-OCCUPANCY CELL MODEL

6. ENERGETIC ASPECTS OF THE PHYSICAL MODEL
   A. Nearest-Neighbor Allocation of Liquid Cohesion
   B. The Pairwise Nature of Intermolecular Cohesions
      1. Pairwise Additivity of Cohesions
      2. Pairwise Independence of Cohesions
      3. Axiomatic Applicability to the Multicomponent Case

7. CONSTANT-VOLUME PROPERTY ESTIMATES FROM A QUASICHEMICAL MODEL
   A. Effect on Estimate of $G^E$
   B. Effect on Estimate of $H^E$

8. A SPANNING SET OF INDEPENDENT VARIABLES
CHAPTER 4

REVIEW OF THE PHYSICAL BASIS OF CELL THEORIES

1. GENERAL

Before embarking on the details of the theories in this thesis, a review of certain physical principles and observations is provided for reference.

Two groups of phenomena are enumerated and discussed: one, configurational or geometric or structural, the other, energetic or cohesive. A description of the independent variable set employed is also provided, as well as a mention of certain important statistical and thermodynamic principles bearing on model construction. A brief resume of properties of types of partition function encountered is included as an extension of the discussion of underlying statistical principles.

2. THE NATURE OF LOCAL ORDERING IN A LIQUID

Configurationally the dense liquid state exhibits long range and long time chaos yet local, short-time ordering. It should be realized that these two sets of characteristics are not mutually contradictory, and in fact both characteristics must be exhibited by any realistic model of a liquid. By 'local' it is specifically meant that, if a given molecule is
chosen as the central one, then the number, nature, and position of the molecules in its nearest neighbor shell is influenced by certain properties of the central molecule. For example the coordination number, which is defined as the number of such nearest neighbors, is influenced by local geometric, and energetic considerations as well as by general statistical considerations. The ordering effect of a central molecule diminishes so rapidly beyond the first neighbors shell, however, that further-neighbor ordering with respect to a given central molecule may be ignored for purposes of the present theory. On the other hand, the influence of the central molecule is so strong upon its nearest neighbors that the coordination number can be thought of as a 'material property' attributable to each species of central molecule in a mixture. As will be seen in Chapter 6, the magnitude of this property can be calculated quantitatively.

3. CONSEQUENCES OF LOCAL ORDERING IN MODEL BUILDING

It will be seen from a model-building point of view that the dense liquid can often be viewed fairly successfully simply as a superposition of nearest neighbor structures. The fact that these structures interpenetrate needs to be accounted for only in second order adjustment to estimates of the liquid's properties (32). Moreover, it becomes obvious that average local composition of nearest neighbor cell structures need not necessarily conform exactly (or even closely) to the overall average composition of the mixture. Local and overall average
compositions only coincide if there are no local geometric or cohesive restraints imposed on the maximum-randomness homogeneity of the mixture. Whenever these local geometric and cohesive effects are not the same for all species present, both of these effects bias local compositions to some extent. Effective theories must account for such local effects with some accuracy, for, while the effects are local with respect to any one molecule, they are also general in the sense that they affect all the individual molecules of a given type in the system, hence they bias the partial molal properties of the overall system.

4. LIMITATIONS IMPLICIT IN A SINGLE-OCCUPANCY CELL MODEL

It is possible to make use of a conceptual "cell" framework in the description of a particle aggregate under dense-liquid conditions. Such a conceptual framework serves as a basis for calculating the cohesion of a molecule within a cell arising from its interactions with molecules forming the cell (which are therefore those in adjacent cells). The same concept also serves as a guide to indicate which statistical manipulations are applicable for the aggregate. The principal limitations on real behavior required to make valid the assumption of a single-occupancy cell model are twofold:

1) firstly, because the space occupied by the liquid is thought of as being divided up into individual cells of a size to hold one molecule each, the actual number of empty cells or multiply-occupied cells at any one moment must be small enough
to be insignificant for present purposes. This situation typically exists, at least to a good approximation, in the dense liquid state.

ii) secondly, the frequency of interchange of positions of molecules between neighboring cells must be much less than the frequency of random thermal buffeting motions within a given cell. This assumption, implicit in quasichemical theories, has been borne out by molecular dynamics studies\(^{38}\).

5. **STATISTICAL AND CONFIGURATIONAL ASPECTS OF SINGLE-OCCUPANCY CELL MODEL**

On the scale of nearest neighbors shells, adherence to single occupancy cell behavior means that a given central molecule is constrained configurationally to its cell or cage of nearest neighbors sufficiently permanently that various caging arrangements can be formulated, then averaged in some appropriate way to obtain information about the effects of a given species of molecule's average environment of nearest neighbors. The averaging procedure used incorporates a formal recognition of the fact that the frequency of any particular nearest neighbor configuration is also governed by the statistics of the mass as a whole. The result of making the assumptions of single cell occupancy, caging, and the meaningfulness of an average local environment for a given species of molecule is that the mathematical simplification of breaking up the 3-N space of an N-particle aggregate into N freely permutable 3-spaces becomes possible. This simplification results in the
avoidance of certain intractable 3-N space configurational integrals describing the potential energy of the liquid, and instead algebraically approximates these integrals by ordinary 3-space integrals for individual particles, plus a purely statistical generalization of the results for the individual particles to form a description of the whole aggregate. The mathematical end-product of these simplifications is called a partition function.* Particles of a given species are regarded as indistinguishable. As a matter of fact, the average cohesion per particle of a class of particles is used to characterize individual particle energies in the following treatment (39). For geometric purposes a particle is a monomer unit; for energetic purposes, it is a 'pair'.

6. **ENERGETIC ASPECTS OF THE PHYSICAL MODEL**

Energetically, two properties of dense liquids proved to be very useful in arriving at mathematically tractable formulations for $G^E$. They are the approximation of nearest neighbor allocation of liquid cohesion, and the approximation of pairwise independence (hence pairwise additivity) of the intermolecular cohesion, and the approximation of $G^E_{(π)} = A^E_{(v)}$

A. **Nearest-Neighbor Allocation of Liquid Cohesion**

Studies (40) of the cohesion energy binding a given molecule into the liquid state indicate that over two thirds of the cohesion arises from interactions with nearest neighbors.

* The term 'partition function' is thus used in a restricted sense in this thesis to apply only to the potential energy part of the Hamiltonian.
A major simplifying assumption allocating the entire cohesion to nearest neighbor interactions is thus found to be practicable, at least for purposes of calculating net cohesion changes produced by mixing in nonionic solutions. The evaluation of mixture cohesion changes for a nearest-neighbor liquid model is thus, to a first approximation, physically meaningful.

B. The Pairwise Nature of Intermolecular Cohesions

1. Pairwise Additivity of Cohesions

The second property of cohesion, that of its approximate pairwise additivity, was first revealed by the quantum mechanical studies of London(41), who demonstrated that the principle holds closely for dispersion-force systems (involving attractions between nonpolar molecules). Adoption of the assumption in general, while not strictly correct, proves to be a useful simplifying assumption when used with sufficient caution.

The concept of pairwise additivity of cohesion, reduced to mechanical terms, is that the cohesion between any two molecules is not affected by the presence or absence of other molecules. Of particular interest is the pairwise additivity of cohesions of neighboring ("contacting") molecules.

2. Pairwise Independence of Cohesions

In addition, the concept of pairwise additivity of cohesions contains in it the assumption of pairwise independence of cohesions. This assumption of independence is important in the present work, since it entails the idea, that
in a nearest neighbors shell of molecules about a 'central' one, the total cohesion of the central molecule is changed when the number of neighbors changes as well as when the kind of neighbors changes. If the process of mixing causes a modification of packing effects due to the size difference of the various components in the nearest-neighbors shell, then the cohesion attributable to the central molecule will change because of both these effects. A much fuller development of this theme of modification of packing effects due to mixing of unequal sized molecules is given in Chapter 6.

3. Axiomatic Applicability to the Multicomponent Case

Another facet of the pairwise additivity assumption is that if the nature of a given type of 'unlike' pairwise attraction is determined in the simplest case of a binary mixture, then the same value will closely apply for that interaction in the multicomponent mixture case, under the assumption that a given pair interaction is independent both of the number and nature of other pair contacts into which the two molecules enter. In a correctly formulated expression, the generalizability of binary energy parameters into multicomponent situations is thus a test of the degree to which nearest neighbor cohesions are of a pairwise additive nature.

7. CONSTANT-VOLUME PROPERTY ESTIMATES FROM A QUASICHEMICAL MODEL

A useful attribute of liquid mixtures from the point of view of formulating $G^E$ is the close approximation of the Gibbs to the Helmholtz free energy for a dense liquid. Since
$G = A + \Pi v$, and since $\Pi v$ for the liquid state is only a few percent of the magnitude of $A$, $G^E \approx A^E$.

A. Effect on Estimate of $G^E$

Since $A = A(T, V, N_1)$, then for an equilibrium mixture $\frac{\partial A}{\partial V} N_1, T = 0$. Thus, at least to a first approximation, volume changes due to mixing do not enter into estimates of $G^E \approx A^E$, although various second-order effects are of course non-zero. Still, in this work, such terms will not be included as being of small magnitude, and not easy to calculate. Hence in this work the standard approximation $G^E \approx A^E$ will be made.

B. Effect on Estimate of $H^E$

If in expressions for

\[ G^E = H^E - TS^E \]  \hspace{1cm} (5)

the $H^E$ terms are separated out and used as the basis for heat of mixing estimates, $H^E(v,T)$ is an incomplete estimate of heat of mixing, and may be in serious discrepancy with $H^E(\Pi,T)$ which is the property relevant to distillation calculations. If $\frac{\partial H}{\partial V} \Pi, T$ differs significantly from zero, the volume change term may even in some cases overshadow the constant volume term in equation (5) just stated \hspace{1cm} (12). The heat of mixing behaviour of ethanol-water solutions is a case in point.

8. A SPANNING SET OF INDEPENDENT VARIABLES

Now that the set of general geometric and energetic observations about the dense liquid state relevant to model building have been noted, the set of independent variables
found to be sufficient to describe a general liquid mixture needs to be introduced. These variables have already been enumerated in the function bracket of equation (3) of Chapter 2, namely the set \( (R_i, n_i, \eta_i, x_i, \omega_{ij}, A_i, \Pi, T) \). They are now to be briefly described. \( R_i \) is the effective dimensionless* diameter of a molecule (or molecular segment, in the case of a long molecule) occupying one unit of the packing arrangement. The chain length parameter \( n_i \) is the number of units of the packing arrangement occupied by species \( i \) when the species is a long molecule. The \( \eta_i \) stands for the proportion of a molecule of a given species devoted to the \( i \)th type of functional group for a multifunctional molecule. If only one type of functional group exists, the species is monofunctional and \( \eta_i \) assumes the trivial value of 1. The relevant energy variable is \( \omega_{ij} \), namely the net pairwise reorganization energy, representing the coefficient of the heat of mixing effect. It is responsible for energetically caused local clustering effects in the liquid. \( A_i \) is the pure component Helmholtz free energy of the \( i \)th species. The population fraction or mole fraction of a given species is given by the usual symbol \( x_i \). \( T \) and \( \Pi \) have their usual thermodynamic meanings of system temperature and pressure. For monofunctional mixtures, \( i \) refers to a molecular species. For multifunctional ones, \( i \) refers to a particular

* with respect to an arbitrarily chosen reference radius to reduce \( R \) to a radius ratio, hence dimensionlessness.
type of chemical site, and the molecular species index is replaced by the index "a". Retention of \( i \) and \( j \) for a molecular species as well as functional group index for mono-functional liquids is to maintain consistency with the notation of Guggenheim: subsequent adoption of 'a' as a molecular species index, retaining \( i \) as the functional group index arises out of the necessity to distinguish 'chemical' and 'geometric' aspects of the molecule in the later treatment of multifunctional substances. All variables are further defined both in nomenclature and operationally in subsequent chapters.
CHAPTER 5

RELATIONSHIPS INVOLVING THE PARTITION FUNCTION

1. THERMODYNAMIC BASIS
   A. The Nature of \( A \) and \( Q \)
   B. \( A \) and \( Q \) as Functions of Volume
   C. \( A \) and \( Q \) as Functions of Concentration
   D. Relation of \( A \) to \( E \) and \( S \)
   E. Difference of the Temperature Response of \( A \) from that of \( E \) and \( S \)
   F. The Gibbs Helmholtz Equation for Free Energy
   H. Summary

2. FORMS OF THE PARTITION FUNCTION
   A. The Canonical Partition Function
   B. The Grand Canonical Partition Function
   C. The G.C.P. in Descriptions of Local (Nearest-Neighbor Shell) Behavior

3. APPROXIMATION OF THE G.C.P. BY A MULTINOMIAL SERIES

4. PROBLEMS IN THE DIRECT USE OF THE G.C.P.

5. USE OF THE G.C.P. TO ILLUSTRATE LOCAL PHENOMENA IN SOLUTIONS

6. DEVIATION OF LOCAL FROM AVERAGE COMPOSITION

7. PARTIAL MOLAL PROPERTIES

8. MACROSCOPIC SYSTEM PROPERTIES DERIVED FROM MOLECULAR SCALE PARAMETERS
9. USE OF DIFFERENT SCALES IN THE $\Omega$ AND $\frac{1}{f_1}$ FACTORS OF THE CANONICAL PARTITION FUNCTION $Q(N)$
CHAPTER 5

RELATIONSHIPS INVOLVING THE PARTITION FUNCTION

1. THERMODYNAMIC BASIS
   
   A. The Nature of A and Q

   As indicated in a very cursory way in Chapter 2, the chief interest in Q (the Canonical Ensemble Partition Function or C.P.F.) for the purposes of this thesis arises from the fact that the usual route followed to obtain thermodynamic property predictions (such as those for γ and H^E) from a given molecular model of a liquid involves the incorporation of modelling assumptions into a formulation for the partition function (Q - for one mole of the mixture in this case), and then subsequently obtaining γ and H^E by carrying out certain standard mathematical operations on Q, as shown schematically in Illustration 2.

   The relation

   \[ A = -kT \ln(Q) \]  \hspace{1cm} (7)

   can be rearranged as follows. An initial trivial transposition yields:

   \[-A/kT = \ln(Q)\]  \hspace{1cm} (8)

   In this form, the equation is dimensionless.

   If the operational definition of Q, that Q is the sum
of Boltzman-factor weightings for the n particles comprising
the system is written out formally, one obtains:* 

\[-\frac{A}{kT} = \ln \left( \frac{\sum e^{-\varepsilon_i/kT}}{n} \right) \]  
\[e^{-\frac{A}{kT}} = \sum_i^n e^{-\varepsilon_i/kT} \]  

The dimensionless Boltzman factor argument, \(-\frac{A}{kT}\) is thus defined as being the equivalent to the sum of the arguments of the Boltzman factors of the R.H.S. series. This is the basic operational definition of Helmholtz Free Energy A, or rather of the dimensionless quantity \(-\frac{A}{kT}\). To convert the sum A to a mean value of A per particle, the relations 

\[n(e^{-a/kT}) = e^{-\frac{A}{kT}} = \sum_i^n e^{-\varepsilon_i/kT} \]  

may be solved for a.

A is thus the single energy factor which characterizes the energy exponents of the series represented by the C.P.F. It is seen that the compact form of the L.H.S. of equation (10) permits of mathematical manipulations which would be extremely awkward with a sum of exponentials as is the R.H.S.

The relative compactness of the L.H.S. of equation (10) compared to its R.H.S. is most important, when not just one but

* if \(Q\), the molar scale partition function is being discussed, \(n = N\).
a sequence of transformations must be made on \( \varphi \). Consider, for example the series of operations by means of which \( \gamma_i \) (the activity coefficient of component \( i \)), is derived from the expression for \( \varphi \).

B. \( A \) and \( \varphi \) as Functions of Volume

In the case where \( \tilde{\epsilon}_j \) is the average value of the point potential over a small volume domain \( v_j \) (the domain volumes need not be of equal size), and \( V \) is the total volume (i.e. \( V = \sum v_j \)), one can write

\[
e^{-A/\kappa T} = \sum_j e^{-\tilde{\epsilon}_j/\kappa T} \left( v_j/V \right)
\]

where \( (v_j/V) \) is a volumetric weighting factor or spatial probability of the \( j \)th domain.

By transposing the common denominator \( V \) to the L.H.S. the expression is rearranged to

\[
e^{-A/\kappa T[V]} = \sum_j e^{-\tilde{\epsilon}_j/\kappa T} v_j
\]

In the latter form, which is most applicable to a cell model of a liquid, it is self-evident that \( (-A/\kappa T) \) is the Mean-Value – Theorem Boltzmann factor argument which, when applied to the whole volume \( V \), make the L.H.S. of equation (13) equivalent to the sum of the R.H.S. series of local weighting factors and domain volumes. Note now that in equation (13) \( A \) bears the same relation to the individual \( \tilde{\epsilon}_j \) as \( \tilde{\epsilon}_j \) bears to the \( \epsilon_j \) within the \( j \)th domain. Two points should be raised in
In this regard.

Firstly, the $v_j$ are formally volumes of integration over which $\bar{\varepsilon}_j$ is the appropriate average energy. In the general case, these volumes of integration can overlap, or interpenetrate, or be as large as the total physical volume of the system. Thus, implicit in the relation $\sum_j v_j = V$ is the additional assumption that domain volumes correspond to real volumes of the order of $V/n$ (for an $n$-particle system), so that, in consequence the $v_j$ do not seriously overlap. This is one of the special suppositions required of a cell theory.

Secondly, that the "appropriate form of average" is the average exponent in this case. The level of subdivision into domains defines the level at which one begins to call the exponential average energy of a domain (which is really thus a free energy) simply "the energy". This degree of subdivision corresponds to the degree of "fine-graining" adopted in regarding the system.

$A$ is seen to vary not only with the $\bar{\varepsilon}_j$, but also with their disposition in space, and with the relative abundance of the particular species present, if these species have different characteristic values of $\bar{\varepsilon}_j$ and $v_j$.

C. $A$ and $Q$ as Functions of Concentration*

If the $k^{th}$ species has characteristic values of energy and domain size $\bar{\varepsilon}_k$ and $v_k$ respectively, and is present in concentration $x_k$ then for an $N$-particle assemblage

* really, most directly, of $N_1$ not of $x_1$
$$e^{-A/kT} = N \sum_k x_k e^{\epsilon_k/kT}$$  \hspace{1cm} (14)

D. Relation of $A$ to $U$ and $S$

The difference in nature between $A$ (the Free Energy) and $U$ (the Total Energy), and their relation to $S$ (the system's Entropy) are clearly borne out through definitions of each as related to $Q$. In particular, it is of interest to relate $A$ to $U$, because $U$, as a total energy, is an inherently more understandable quantity than $A$, hence serves as a point of reference for the understanding of $A$.

The difference between the natures of $A$ and $U$ is shown by expanding the axiomatic definition of $E$, namely

$$U = \sum_i \epsilon_i p_i$$  \hspace{1cm} (15)

$$p_i = e^{-\epsilon_i/kT}/Q$$  \hspace{1cm} (16)

Equation (15) is simply a formal expression of the fact that the overall energy is the average of the individual component energies of the system. (It is an average, not an average exponent, regardless of the fact that Boltzmann factors may have been used to weight this average).
By simple operations on $Q$, it can be shown that equation (15) is equivalent to

$$ U = kT^2 \frac{\partial \ln Q}{\partial T} $$

(as compared to the definition of $A$ in terms of $Q$, namely $A = -kT \ln Q$)

The relation between $U$ and $A$, involving $S$, is obtained straightforwardly by expanding the "probability" definition of $S$, and, after inserting the explicit form of $P_\pm$ given by equation (16)

$$ S = -k \sum_i \left( \frac{e^{-\epsilon_i/kT}}{Q} \right) \left[ -\frac{\epsilon_i}{kT} - \ln Q \right] $$

$$ S = -k \sum_i \frac{\epsilon_i}{kT} P_\pm + k \ln Q $$

$$ S = \frac{U}{T} + k \ln Q $$

whence is obtained, by a trivial rearrangement,

$$ -kT \ln Q = U - TS $$

Finally, by substituting the definition of $A$ for the L.H.S.,

* leaving aside, for the moment, the necessity for the $P_\pm$ to be the probabilities of independent events (See Chapter 9)
is obtained

\[ A = U - TS \]  \tag{22}  

The reason for the term 'free' energy for \( A \) is that \( A \) is the difference between the total energy \( U \), and the product of temperature times the system Entropy \( S \).

E. Difference of the Temperature Response of \( A \) from that of \( U \) and \( S \)

\( A \) and \( U \), apart from having quite different definitions in terms of \( Q \) (and hence responding differently to \( \varepsilon_k, x_k, v_k \)) are shown by equation (22) to have basically different temperature-characteristics. \( A \) is always an explicit function of \( T \) (because of the TS product in equation (22)), whereas \( S \) and \( U \) are only implicit functions of \( T \) in this regard. Also, because in equation (16), \( p_k \) for a species \( k \) involves its mole fraction \( x_k \), equation (22) implies that \( A \) is a much more active function of concentration than \( U \), again because of \( A \)'s dependence on \( S \), hence on \( \varepsilon \), through the entropy of mixing effect.

F. The Gibbs Helmholtz Equation for Free Energy

\( S \) can be eliminated from equation (22) by making the substitution

\[ S = - \frac{\partial(A)}{\partial T} \]  \tag{23}  

(which can also be arrived at from the above definitions of A and S).

The substitution gives rise to the Gibbs-Helmholtz equation

$$\frac{\partial (A/T)}{\partial (1/T)} = U \quad (24)$$

or

$$\frac{\partial (A/T)}{\partial T} = -\frac{U}{T^2} \quad (25)$$

The Gibbs-Helmholtz relation holds equally for partial molal excess quantities $A^E_1$ and $U^E_1$ in place of A and U in equation (25).

Since

$$\ln \gamma_1 = \frac{A^E_1}{RT} \quad (26)$$

the partial molal version of equation (25) serves to predict the primary temperature dependence of activity coefficients as an integrable differential equation in T:

$$\frac{\partial \ln \gamma_1}{\partial T} = -\frac{U^E_1}{RT^2} \quad (27)$$

Finally, because $A = G$ in systems considered, $\overline{H^E_1}$ can be used in place of $U^E_1$ in equation (27).
H. Summary

Though some of the foregoing definitions are unavoidably being drawn on out of order in terms of the logical development of the arguments of the thesis, the compactness of the framework of thermodynamic and statistical mechanical relations among the primary quantities $Q$, $A$, $U$, $S$, $T$, and also among $V$, $x$ and $y$, alluded to in Chapter 2, is revealed, and the 'operational' nature of relations between $A$ and $Q$ in particular is also suitably illustrated for use in later discussion.

2. FORMS OF THE PARTITION FUNCTION

At this point it will be useful to make some general comments about the technique of applying partition functions to the present study, about the realm of applicability of certain types of partition functions, and about relations between types of partition functions and the scales of assemblage which must be considered in order to develop various aspects of the theory.

A. The Canonical Partition Function

One convenient type of partition function used is the Canonical Ensemble Partition Function (C.P.F.) designated by the symbol $Q$. This obtains for a fixed population imposed by the assumption of a closed system, for example for one mole of a mixture of a specified composition. A mathematical feature of the C.P.F. important to this work is that it can be represented as a mathematical product of two types of factors. This is shown by the formalism;
\[ Q = (\Omega) \times (\prod f_i) \]  

(28)

where the individual particle weight \( f_i \) is given by:

\[ f_i = g_i e^{-\epsilon_i/kT} \]  

(29)

where \( \epsilon_i \) is a generalized energy of a molecule, and \( g_i \) is a generalized geometry factor per molecule depending on its domain volume.

The portion \( (\prod f_i) \) is the weight of a given permutation of the particles in a given configuration of the system, hence itself is a product of the weights (the \( f_i \)) of the individual particles of the assemblage, and \( \Omega \) is a combinatorial term, enumerating the number of distinguishable species assignments possible for the chosen system configuration.

If the C.P.F. for an idealized binary n-particle system, consisting of \( n_1 \) particles of species 1 and \( n_2 \) particles of species 2 is designated \( Q(n_1, n_2) \), then

\[ Q(n_1, n_2) = [n!/(n_1!n_2!)] \times \left[ g_1 e^{-\epsilon_1/kT} \right]^{n_1} \times \left[ g_2 e^{-\epsilon_2/kT} \right]^{n_2} \]  

(30)

Factors \( g_1 \) and \( g_2 \) are again generalized geometry factors, and \( \epsilon_1 \) and \( \epsilon_2 \) are energy factors per molecule, but now specifically applying to the average cohesion per molecule of 1 and 2, respectively, in the mixture.
B. The Grand Canonical Partition Function

A second type of partition function used in arguments in this work is the Grand Canonical Ensemble Partition Function (G.C.P.)*, designated by the symbol \( \overline{Z} \). The G.C.P. applies to an open system, in which the molecules are free to enter and leave, although it is usually written for the case where the net balance of entrance and egress rates maintains a constant total population within the system. While the choice between regarding the system as being "open" or "closed" is often a matter of convenience, the thermodynamic quantities eventually extracted from the resulting partition functions will depend on the choice of basis which was made. Whereas the "characteristic" function of \( A = -kT \ln Q \), the characteristic function corresponding to \( \overline{Z} \) for an open system is

\[
\Pi V = RT \ln \overline{Z}
\]  

(31)

From the point of view of estimating Free Energies, this characteristic function for \( \overline{Z} \) means that \( A \) can only be obtained from \( \overline{Z} \) by a rather roundabout thermodynamic route, which in fact proves to be rather unsatisfactory. The concept of the G.C.P. is most useful however, in illustrating the role of local-scale behavior in solutions, and for this it is introduced here.

* These abbreviations; namely G.C.P. and C.P.F. are those employed by Hill(23).
The G.C.P. for \( n \) particles in a 2-species system is given by the general formalism

\[
\mathcal{Z}(n) = \sum_{n_1, n_2} \mathcal{Q}(n_1, n_2) \lambda_1^{n_1} \lambda_2^{n_2}
\]

where \( \lambda_1 \) is the independent probability of the presence of a single particle of species 1, within the bounds of the system and \( \lambda_2 \) is that for species 2. The symbol \( \lambda \) is also called the absolute activity of a single particle(16). Thus the G.C.P. for \( n \) particles is seen to be the sum (over all possible \( n_1 + n_2 = n \)) of C.P.F. s for each given value of \( n_1 \) and \( n_2 \), times the individual species probabilities to powers \( n_1 \) and \( n_2 \). In form

\[
\lambda_i = x_i e^{-\delta_i/kT} g_i
\]

where \( \delta_i/kT \) and \( g_i \) are energy and geometry factors respectively, depending on the system, not exactly identical to the energy and geometry factors of the C.P.F.

C. The G.C.P. in Descriptions of Local (Nearest-Neighbor Shell) Behavior

In an open system, the system boundary can usually be designated in any way that proves to be convenient. In one particular application of the general formalism for \( \mathcal{Z} \) (equation (32)), \( n \) is set equal to \( z \), the nearest neighbor coordination number. So doing enables one to investigate the
form of the G.C.P. applicable to a set of \( z \) nearest neighbors of some designated central molecule.

For the case of a binary species mixture, a particular shell might contain \( n_1 \) molecules of 1, and \( n_2 \) of 2, so that \( (n_1 + n_2 = z) \). Hence

\[
\mathcal{F}(z) = \sum_{n_1, n_2} Q(n_1, n_2) \lambda_1^{n_1} \lambda_2^{n_2} \quad \text{for } (n_1 + n_2 = z)
\]

where the summation is over all possible numbers \( n_1 \) and \( n_2 \) from 0 and \( z \), to \( z \) and 0, respectively.

In order to evaluate equation (34) in the presence of local effects (i.e. those produced by the central molecule species about which the shell is gathered), one would have to start by specifying about which species of central molecule the \( z \) nearest neighbors were being considered. Alternatively, and more generally, one could write the G.C.P. representative of all the arrangements of \( (z+1) \) molecules, for all possibilities of \( z \) neighbors plus one central molecule, namely the extra 1 shown in the \( (z+1) \) bracket, for all central species. If now \( z_1 \) is specified as being the coordination number around the \( \frac{1}{3} \) th central molecule species, (with centrality indicated here by an index-circling convention) the G.C.P. would be

\[
\mathcal{F}(z+1) = \sum_{\frac{1}{3}} \lambda_{\frac{1}{3}} \mathcal{F}(z_{\frac{1}{3}}) \quad \text{for } \frac{1}{3}
\]

(35)
Circling of the subscript $i$ of each of the G.C.P. s on the R.H.S. of equation (35) designates that each of the $m$ (for $m$ species present in the mixture G.C.P. s (i.e. each $\mathcal{Z}(z_i)$) pertains to the local environment of the $i_{th}$ species of central molecule. By this means it is possible formally to incorporate local effects into each of the $\mathcal{Z}(z_i)$ which are otherwise, in form, as indicated by equation (32).

3. APPROXIMATION OF THE G.C.P. BY A MULTINOMIAL SERIES

If the independent probabilities $\lambda_1$ and $\lambda_2$ are approximated by $x_1$ and $x_2^*$, the mole fractions of species 1 and 2, respectively, in the overall mixture, equation (32) may be approximated by

$$\mathcal{Z}(z) = \sum_{\text{all } n_1, n_2} \frac{Q(n_1, n_2)}{\gamma(n_1 + n_2 = n)} x_1^{n_1} x_2^{n_2}$$

(36)

Thus

$$\mathcal{Z}(z) = \sum_{\text{all } n_1, n_2} [\Omega(n_1, n_2) (g_1 e^{-\epsilon_1/kT} x_1)^{n_1} \times (g_2 e^{-\epsilon_2/kT} x_2)^{n_2}]$$

(37)

The terms of equation (37) are recognizable as being those of a binomial expansion, whose sum is therefore given by

$$\lambda_i = g_i e^{-\delta_i/kT} x_i$$. While for an ideal solution of equal sized molecules $g_i \rightarrow 1$ and $\delta \rightarrow 0$, for real solutions the approximation of $\lambda$ by $x$ is more or less inaccurate.
\[ \bar{Z}(z) = \left[ g_1 e^{-\varepsilon_1/\kappa T} x_1 + g_2 e^{-\varepsilon_2/\kappa T} x_2 \right]^z \]  

(38)

In the case of more than two components, the terms of the corresponding G.C.P. correspond to those of a multinomial distribution.

4. PROBLEMS IN THE DIRECT USE OF THE G.C.P.

Of course, it is possible to make thermodynamic property estimates in ways other than using the characteristic relations \( A = -kT \ln Q \) or \( PV = kT \ln \bar{Z} \) in the G.C.P. case. In one early attempt to evaluate solution properties, weights (as given by individual terms of equation \((37)\)), normalized by their sum (as given by equation \((38)\)), were used simply as weighting factors in a computation of the partial molal energy of vaporization of a given species of central molecule \((3)\). The method consisted of summing the product of each weight times the cohesion due to the corresponding nearest neighbor assemblage about the given central molecule. The resulting energy was then related to the partial molal Helmholtz Free Energy through a suitable form of the Gibbs-Helmholtz equation. By this means, quite good estimates of \( \gamma_1 \) (as related to the partial molal excess free energy of mixing, obtained by subtracting the pure component free energy from the above) would result from even a very crude form of the G.C.P. for each central molecule's spectrum of nearest-neighbor arrangements. However, apart from
its inherent lack of formal elegance, this route proved to involve other difficulties. These will be briefly mentioned to illustrate how easily one can become trapped by the use of an inappropriate formulation, even if the formulation is sound in principle.

Because the Gibbs-Helmholtz relations (or Clausius Clapeyron type integrations of the Gibbs-Helmholtz equation), do not explicitly contain S (see equation 25), expressions for $A^E$ developed through the above route are not amenable to inclusion of $S^E$ terms (see Chapter 9, for such a general expression for $A^E = g^E$). Also, the method does not provide a mechanism for calculating local concentrations or net mixing energies, which are consistent with the principle of minimum free energy, as does the quasichemical method. Eventually then, the above-described 'direct' method of estimating free energy was abandoned in favor of the quasichemical approach.

5. USE OF THE G.C.P. TO ILLUSTRATE LOCAL PHENOMENA IN SOLUTIONS

Semi-quantitative arguments involving the G.C.P. are most useful in illustrating local effects in solutions. One begins by considering a local assemblage, consisting of an open system of the $z$ nearest neighbor positions about a chosen central molecule. This open system exists in equilibrium with "the environment". The environment consists of an infinite reservoir of the mixture, whose overall species mix is characterized by the mole fractions of the various species.

It is possible for a $z$-particle assemblage to be con-
stituted in any proportions from the species present in the environment, as long as the total number present in the system remain equal to \( z \). In fact, the relative frequencies of occurrence of each of the variously composed nearest neighbor shells is given by an individual term of \( \overline{f}^{(z)}_{\overline{z}} \) (the G.C.P. about the \( i \)th central molecule). The energetic and geometric variations between individual terms of \( \overline{f}^{(z)}_{\overline{z}} \) serve to skew the distributions, so that each \( \overline{f}^{(z)}_{\overline{z}} \) will depart more or less from \( \overline{f} \). It must also be remembered that a different average coordination number will exist for each central species; hence each of the \( \overline{f}^{(z)}_{\overline{z}} \) will depart more or less from \( z \). Differences in size of the various molecular species present will exert the largest influence on \( \overline{f}^{(z)}_{\overline{z}} \). Energetically induced clustering tendencies result in enrichment of nearest neighbor assemblages in the species which interact most strongly with the \( i \)th central molecule. This also contributes to skews in \( \overline{f}^{(z)}_{\overline{z}} \). The relation between the local behavior incorporated in \( \overline{f}(z) \) and that on the molar scale is illustrated by considering the overall \( N \)-molecule assemblage as being comprised of \( N \) overlapping assemblages, each consisting of \( z \) nearest neighbors and a central molecule (momentarily ignoring the secondary accounting problems arising from variations in the \( \overline{z} \)). For each of the \( \overline{z} \) species present, the G.C.P. will be given by the corresponding \( \overline{f}^{(z)}_{\overline{z}} \).

6. **DEVIATION OF LOCAL FROM AVERAGE COMPOSTION**

Because each of the \( \overline{f}^{(z)}_{\overline{z}} \) contains local compositions,
energy effects and geometry effects, the modal (most probable) compositions of such local distributions need no longer correspond to the overall composition. Rather, each average local composition may depart from the overall — sometimes markedly — but the departures of local compositions with respect to the various species present from the overall composition must be in compensating amounts and directions, so that the overall material balance on each species present in the mixture is conserved. The magnitude of such local clustering effects is also tempered by the tendency of the solution as a whole to remain as near to maximum-randomness (complete homogeneity) as is possible under the restraints imposed by the local energy-induced clustering effects and local geometry effects. The average configuration of the mixture thus represents the equilibrium balance between the local clustering and overall randomizing tendencies above described.

7. PARTIAL MOLAL PROPERTIES

In particular, the modal compositions of each of the \( \frac{L_3}{z_3} \) will differ, if differential energy and geometry effects exist. Thus, the properties of each species of central molecule which depend on the composition of the nearest neighbor shell, such as cohesion, will also differ on account of local composition differences.
On the macro-scale, the, partial molal properties will reflect the local properties corresponding to the most probable local compositions about each species of central molecule rather than upon the overall average composition, where these are not the same.

8. MACROSCOPIC SYSTEM PROPERTIES DERIVED FROM MOLECULAR SCALE PARAMETERS

It is obviously always possible to take, as an approximation of the average value of a property of a z-scale assemblage, the value of that property calculated for the composition corresponding to the modal term of its \( \bar{E}_1(z_1) \). One might also reasonably suppose that this estimate could be improved by also including in it appropriately weighted contributions from compositions corresponding to off-modal terms of the distribution. This might be so on the z-scale, but one is in fact primarily concerned with estimating, instead, the partial molal property, on the N-scale. If the G.C.P. on the N-scale, namely \( \bar{E}(N) \) can be thought of as being made up of a large number of replicated subsystems on the z-scale, then it can be shown that due to a combinatorial effect involved in the 'scale-up' from the z-scale to the N-scale in such a situation, that there is an enormous increase in sharpness of the distribution of a property in the N-scale composite system with respect to that for any one of the z-scale replicates. It can also be shown that the compositions corresponding to the modal terms of N-scale and z-scale distributions coincide. Thus, while characterization of the z-scale system's properties by the z-scale modal term estimate may be a rather poor approximation, the approximation of the
average properties of the N-scale system by the modal properties of any one of the z-scale systems is very good indeed. The consequences are 3-fold: 1) Modal z-scale properties - the most obvious example being z itself - are compatible with N-scale partition functions. 2) Modal z-scale estimates form extremely good estimates of N-scale properties. 3) Because of the above-mentioned modal-term dominance, the z-scale canonical partition function $Q(z)$ can be used in place of $\overline{Z}(z)$, and $Q(N)$ can be used in place of $\overline{Z}(N)$ even for an open system. The combined result of 1), 2), and 3), is that modal z-scale properties, particularly $z_i$, can be included in the detailed formulation of $Q(N)$, which is the partition function most directly related to $A$ for a mole of the liquid mixture being 'modelled' by $Q(N)$.

The above arguments on the compatibility of modal properties of replicated small (closed or open) ("local") ensembles used in the large scale ensemble composed of all the replicates, also extends quite generally to such other instances as the use of most-probable pairs properties in N-scale thermodynamic estimates. As a first point in summary of the above, it is hoped that the above comments should help the reader understand the permissibility of working at various scales to obtain various terms in the overall expression, such as the expression for excess free energy of mixing obtained as the end product of the formulations undertaken in the theoretical section of this thesis.

As a second point, the relation of partial molal pro-
Property estimates to local compositions should have been established.

Having used the G.C.P. to make the above points, the discussion may now be redirected to further consideration of applications of the C.P.F. to the present work.

9. USE OF DIFFERENT SCALES IN THE Ω AND \( \prod_i f_i \) FACTORS OF THE Q(N) CANONICAL PARTITION FUNCTION

It is now apparent that for a monofunctional monomer binary system displaying only moderate energetically induced local clustering, the free energy of mixing can be obtained directly from Q(N), the C.P.F. for the entire N-particle system. However, for systems which are multifunctional, or contain more than two components, or contain very strong energy effects, the properties of z-particle systems must again be considered as well. This is because in certain cases, the method of partition functions becomes unmanageable, and another method altogether (the probability distribution method) must be resorted to. The probability distribution method of property formulation is discussed in Chapter 9.

The configuration normally chosen in which to evaluate the \( \prod_i f_i \) term of Q(N) of equation (28) is that corresponding to the most probable single configuration of the system. The factor Ω is seen to be a combinatorial expression specifying the number of distinguishable assignments by species of the particles of the system that can be made in the chosen system configuration. Since computing A from Q(N)(via the formula
A = -kT \ln Q(N) entails taking the logarithm of $Q(N)$, the product of the two portions of $Q(N)$ is transformed into a sum of the logarithms of the two factors in the resulting free energy expression. Such separation of terms will shortly be seen to be a powerful technique and is made use of in this thesis, and in anticipation of such use the reader might note that: as long as care is taken that the bases of formulation of $(\Omega)$ and $(\prod i f_i)$ portions of the partition function are not incompatible, the basis of formulation for each portion need not be identical. Indeed, the form of $Q(N)$ most convenient for this work is one in which the two portions of $Q$ are formulated by consideration of assemblages of different scale. Factor $\Omega$ is formulated on a molecular scale, in which the individual "particle" is regarded to be a molecule, and the $(\prod i f_i)$ factor is formulated on a "pairs" scale, where the individual "particle" is a "pair", an entity consisting of a contacting pair of sites on neighboring molecules. (See Chapter 8). The $(\Omega)$ term gives rise to the configurational entropy of mixing effects, while the $(\prod i f_i)$ product gives rise, in simple cases, to heat of mixing effects.

In the following discussion of the quasichemical expression of Guggenheim for monofunctional monomer binary mixtures, and the extension of this theory to more complex types of solutions, by himself and other workers, specific note should be taken by the reader of the forms of the $\Omega$ and $(\prod i f_i)$ portions of the C.P.F. employed.
CHAPTER 6

NONCONSTANT-COORDINATION NUMBER MECHANICS

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CHAPTER 6

NONCONSTANT-COORDINATION NUMBER MECHANICS

1. GENERAL

In this chapter a quantity called the contact fraction \( \xi_i \) is introduced as a measure of the number of contacting sites associated with the \( i^{th} \) molecular species in the mixture. The usefulness of the contact fraction arises from its ability to characterize the pair-forming capacity of different constituent species of molecule in the case of mixtures containing different sizes. A calculation scheme relating \( \xi_i, z_i \) and \( x_i \), the contact fraction, coordination number, and mole fraction of the \( i^{th} \) species present in the mixture respectively, is then illustrated. The treatment is restricted initially to monofunctional binary mixtures, which permits closed mathematical solutions to certain aspects of the theory which are not available in the multicomponent case. Additional methods which must be involved in the multifunctional and multicomponent cases are treated in Chapter 9, although toward the end of this chapter certain configurational aspects of n-mer solutions are discussed (without regard as to whether they are monofunctional or multifunctional), in order to generalize the calculation scheme for contact fraction into the n-mer case.
The question of the modification of nearest neighbor coordination number and of the composition of the average nearest neighbors shell by geometry and energy effects might be approached either in terms of the effects produced in "most-probable" nearest neighbor structures, or more generally in the context of the partition functions discussed in the previous chapter. In fact - it is convenient to make use of both levels of analysis, and this procedure is used in subsequent formulations in this work.

The effects of geometry and energy on the average nearest neighbor shell composition are easy to understand qualitatively. First, consider the energy effect. About a given central species, the neighbor species whose net heat of mixing with the central molecule is most exothermic is relatively favored, as most lowering the overall mixture free energy. Secondly, consider the geometry effect. A larger central molecule tends to be able to accommodate a larger number of nearest neighbors of the average size than would a smaller one. Thus such a larger species is exposed to more nearest neighbors and hence tends to participate as a nearest neighbor in more arrangements, than would a smaller species. A large species would thus tend to exert an influence in nearest neighbor arrangements disproportionately above its simple concentration effect. In thinking about nearest neighbor arrangements an important symmetry axiom must be observed, concerning 'neighbor' and 'central' positions, namely:
In relation (39), $p_{ij}$ is the probability of a given type of pairwise interaction. Subscripts $i$ and $j$ stand for two types of molecules which can form contacts in the solution, and the circled index designates the arbitrarily chosen central molecule of a nearest neighbors arrangement. The symmetry axiom, together with the statement preceding it, forms the basis of quantitative calculation of the species coordination numbers in a mixture of unequal sized molecules by a method originated by Hogendijk. In the present work, the method has been generalized to include, in addition, a correction for energetically induced clustering and for the effects of long molecules.

2. THE ANALOGY OF A PACKED BED OF SPHERES

Hogendijk's method was originally developed for calculating the average number of contacts per sphere of a given species in a close-random-packed bed of spheres of discrete sizes, each 'species' being identified by its discrete size.

In order to adapt the method for coordination number calculation to a real liquid, the analogy of a real liquid to a packed bed of spheres is drawn.

The analogy between a packed bed of spheres and the organization of a dense liquid does not imply a hard sphere liquid model in the usual full sense of the word, since the
molecules do not need to be 'hard' to permit such a method of calculation of coordination number, but need only be associable with a characteristic domain size, from which they statistically tend to 'displace' or 'exclude' their nearest neighbors. Thus, the pertinent size of a molecule is measurable by means of the effective diameter which can be associated with the sum of its equivalent hard sphere volume surrounded by a shell of size equivalent to its average free volume. The assignment of 'packing-based' coordination numbers to molecular species in liquids, especially in mixtures with large and anisotropic cohesion effects, may seem at first to be a crude proposition, since at some point or other the 'packing' mechanism of determining of the number of neighbors is overwhelmed by other factors. It is thus important to know what some of these factors are, and how and at what point they impose effective limitations upon the applicability of the free energy expression.

3. EXPECTED RANGE OF APPLICABILITY OF THE GEOMETRIC MODEL

One bound on the region of applicability of the analogy is imposed by the 'stereo-specific' 'fixing' effect of very strong specific interaction energies. At some point these energies seriously disrupt the 'packing-dominated' mode of liquid organization. In still other cases, the onset of lock-and key 'fit' effects characterizing chelates, or concerted nearest-neighbor actions, as in the case of coordination complexes, should by definition cause any pairwise theory to break down.
The very rapid expansion of the liquid phase as conditions approach the mixture's vapor-liquid critical point sets another limit on the range of applicability of a liquid model incorporating a packing method of assigning coordination numbers. Failure of a packing configurational model is bound to occur with the breakdown of the effectiveness of the 'caging' phenomenon when the liquid becomes sufficiently expanded. Nevertheless, one experimental system (system 7)* was found to be amenable to the expression developed, under pressures up to 0.4 of the critical pressure.

In fact, one of the main points illustrated by the examples of real systems chosen for the experimental part of the thesis is that the quasichemical model works to a useful degree in nonionic solutions as long as interactions between geometry and energy effects are properly accounted for, even in the case of some highly polar mixtures and relatively high pressure.

4. THE COORDINATION (OR CONTACT) FRACTION

It is convenient to refer to a molecule or sphere which contacts z nearest neighbors as being z-coordinated. Similarly a lattice, or packing arrangement in which each molecule or sphere is z-coordinated is called a z-coordinated 'lattice' or packing. (It is remembered that a system in which z is constant has been termed a CZ system and one in which coordination numbers of species vary with composition a nonconstant-z system, or NCZ system).

In a bed of random-packed spheres of unequal size, the

* Using the numbering system of Table 4, Chapter 10.
numerical values of the coordination numbers of the species are not the same as would be found in a bed of spheres all of equal size. Mutual distortion of coordination number occurs, augmenting the coordination number of the larger species and decreasing that of the smaller from the self-packing coordination number. To this extent, in a mixture, the coordination number could be regarded as being changed or distorted by the mere act of mixing. It is still quite possible however, though not necessarily so, for the total number of contacts in the mixture to remain the same as that of the sum of the subtotals of the two species populations as pure components, in spite of the distortions just described.

If species i is $z_i$ coordinated and species j is $z_j$ coordinated, the total number of contacts in the assemblage is $\frac{z_i}{2}N_i + \frac{z_j}{2}N_j$. For a mixture of $N_i$ spheres of species i and $N_j$ spheres of species j, the fraction of the total number of contacts due to species i, namely $\xi_i$ is given by

$$\xi_i = \frac{z_i/2 \frac{N_i}{z_i/2 N_i + z_j/2 N_j}}{40}$$

Upon dividing numerator and denominator by $(N_i + N_j)$ and also by the overall average coordination number $z_{ave}$, and noting that

$$\frac{N_i}{(N_i + N_j)} = x_i$$

and that $z_{ij} = z_{ave}$, the final form of $\xi_i$ obtained is
\[ \xi_i = \frac{z_i/z_{ij} \times x_i}{(z_i/z_{ij} \times x_i + z_j/z_{ij} \times x_j)} \] (42)

5. CONSIDERATION OF \( z_i \) AS A PARTIAL MOLAL PROPERTY

While \( z_i \) is a function of the mixture composition and species size, it is more strongly a property of the size and configuration of the chosen central molecule than of the environment, though obviously it depends on both. Thus it is meaningful to associate a characteristic \( z_i \) with each component of the mixture. To a first approximation, \( z_i \) can thus be regarded as a material property of the central species. It should more precisely be regarded as a partial molal quantity, dependent both on the species present, and on their concentrations.

6. ROLE OF \( \xi \) IN LOCAL CONTACT FRACTIONS IN A REAL LIQUID

For a given mixture of composition \( x_i \) and \( x_j \) in which energy effects are negligible, the proportion of i-i and j-i 'pairs' contacts around an i-type sphere due to its nearest neighbors is given by \( \xi_i \) and \( \xi_j \), not by \( x_i \) and \( x_j \). The overall probability of a given type of 'pair' contact in a bed of spheres, say of type i-j, is the product of the proportion of the total population coordinated by j, \((\xi_j)\) times the nearest-neighbor probability of the i-th species (namely \( \xi_i \)) so that
where $p(i-j)$ is the normalized probability of the given pair event. This probability is more simply written as $p_{ij}$. Similar expressions for $p(i-i)$ and $p(j-j)$ can be obtained by setting $i=j$.

7. LOCAL CLUSTERING EFFECT

In a binary mixture of highly spherical molecules, as for example Argon-Krypton well below its critical point, one would expect to encounter 'local organizations' analogous to those which would occur in a bed of unequally sized spheres which had been randomly packed, namely an organization heavily dominated by the packing considerations brought about by the difference in the size of the spheres. In the usual molecule-packings, however, these simple ideas of coordination number derived from the non-interacting spheres model will be modified by the fact that the molecules attract each other in a way that the solid spheres do not, and that these attractions will be species-dependent. A better representation of the proportions of $i$ and $j$ contacts around a molecule of $i$ is given by

$$
\xi'_{i} = \xi_{i}e^{-\omega_{ii}/kT}
$$

(44)
respectively, where $\omega_{ij}$ is the net reorganization energy of the quasichemical pairs reaction mentioned in Chapter 3.

Since by definition $\omega_{ii} = 0$, the Boltzman factor multiplying the first term is unity, so that the first term degenerates simply to $\xi_i$. It is obvious that any preferential clustering of one species around another must produce an oppositely compensating effect somewhere else in the overall mixture and that such secondary redistributive effects cannot be zero as long as any value of $\omega_{ij}$ is nonzero. This secondary redistributive effect is illustrated by the statement that the more interactive species tends to exclude the less interactive from the nearest neighbor shell of any chosen species of central molecule, which thus tends to residually concentrate the less interactive species about some other 'central' species. The species about which residual concentration chiefly occurs is the most weekly interactive species in the mixture. Ultimately, of course, the rejected material may form a second liquid phase, if differential attractions are large enough, and indeed, liquid-liquid equilibria have been predicted on precisely this basis. The indirect effects of energetically induced clustering tendencies are more fully accounted for by the quasichemical model of Chapter 8, so that further discussion is unnecessary at this point.
8. THE CONCENTRATION MEASURES OF SCATCHARD AND HILDEBRAND

The contact fraction \( \xi_1 \) (as distinct from the mole fraction \( x_1 \)) is the appropriate concentration measure for a liquid model in which the behavior of the contact points between molecules is to be emphasized. The contact fraction has connotations more similar to Scatchard's surface fraction* as given by the symbol \( S \):

\[
S = \frac{x_i \rho_{ij}^{2/3}}{x_i \rho_{ij}^{2/3} + x_j}.
\]  

(46)

than to Hildebrand's volume fraction

\[
\phi_i = \sum_{i} v_i x_i / \sum_{i} v_i \rho_{ij}
\]

(47)

where \( v_i \) is the molar volume of component \( i \).

9. CALCULATION OF COORDINATION NUMBER \( z_a \) AND \( z_{ave} \)

The scheme used in calculations of coordination numbers, whence contact fractions, is now presented. Subscript 'a' is now used in place of 'i' to denote species. Subscript 'a' has the specific connotation of molecular species and it is now intended that 'i' will subsequently be reserved for use in re-

* The notation of equation (46) is adopted from Scatchard\(^{(12)}\) and no attempt has been made to translate the notation into that of this thesis since the equation will not subsequently be used and is included here for comparison purposes only.

\[
\rho_{ij} = \frac{v_i}{v_j} = \text{volume ratio of two components. See p. 19 of ref.}(12)
\]
ferring to a particular type of contact. Since a molecule may have a number of different chemical function groups several energetically distinguishable kinds of pairs may be formed from the same molecule 'a'.

The value given to \( z_a \) is the number of molecules contacting a molecule of species 'a' for the average local composition of the nearest neighbor shell about that species. Also it is usually assumed that all self-packed species, i.e., those in pure component form, have the same pure component monomer packing number, \( z_s \).

In the pure component state, all 'central' molecules are surrounded by \( z_s \) identical molecules. By simple geometry (and referring by way of example to species 'a') the view factor of a nearest neighbor (and here 'hard sphere' geometry is being employed) as seen from the centre of the central molecule is

\[
\alpha_{a_a} = R_a^2/((4\times (R_a + R_a)^2)
\]

To correct this estimate for the non-rigid properties of molecules, in order to conform with the real experimental situation, the proportionality constant \( k \) is introduced, thus

\[
1/z_s = \alpha_{a_a}/k
\]

Because the self-coordination number of all molecules is taken to have the same numerical value in this work, \( k \) is assumed
constant and identical for all species, and is also assumed to apply to the mixed as well as pure component states.

It is now convenient for purposes of notation, to introduce index 'c' to denote the nearest-neighbors position. The 'blanking effect' inherent in the 'pairwise' contact between a 'c' species nearest neighbor and a central is written \( \alpha_c \). Also with a mixture of species present, the radius of the ring of centres of neighbors is no longer simply \( 2R \) but is designated as \( \bar{R}_{ave} \). Thus, after establishing the initial conditions

\[
\xi_a = x_a, \quad \xi_b = x_b
\]

\[
R_{ave} = 2R, \quad z = z_s
\]

it is possible to follow the iteration:

\[
\bar{R}_{ave} = R + \sum_c \xi_c R_c / \sum_c \xi_c
\]

\[
\alpha_c = R^2_c/(4 \times (\bar{R}_{ave} \bar{R}^2))
\]

\[
z = k/(\sum_c \xi_c \alpha_c) / \sum_c \xi_c
\]
\[ \xi_a = z_a \sum_a x_a / \sum_a z_a x_a \]  

(55)

and so, by using all the species present in turn, obtain new values of \( \xi_a, \xi_b, R_{\text{ave}}^a, z_a, \) and \( z_b \), and to reinsert these in the next iteration beginning at the first step (equation (52)). Convergence is rapid.

Of course, it is realized that all molecules are equally 'central', and therefore that the device of assuming the centrality of 3 has been only a calculation artifice. Thus use of the subscript 'c' to denote generic neighbor species is now superfluous and, over the solution as a whole, \( z_a \) (i.e., with no connotation of centrality) can be regarded as being a material property associated with species 'a' whose value is equal to \( z_a \). \( z_{\text{ave}} \) is defined by

\[ z_{\text{ave}} = \sum_a \xi_a z_a / \sum_a \xi_a \]  

(56)

The effect of energy-induced local clustering is included in the iterative scheme for calculating \( z_a \), as outlined by equation (52) to (55), through the use of local species concentrations of c around central a. Specifically, Barker's local concentration functions* which are functions of \( \xi \) and

* Barker functions \( X_j \) are defined in Chapter 9 under notes on the general equation - see program listing for exact algorithm in Appendix 4(c).
reduce to $\xi$ in the monofunctional zero-energy interaction case, are used as weighting factors in place of $\xi_1$, for mixtures containing multifunctional molecules. The computation still results in convergent values of $z_a$ for all systems so far studied.

In the case of large net energies of pairs reorganization, $z_a$ becomes a fairly strong function of energy as well as of relative molecular size. If unlike species attract, $z_a/z_b$ will be larger than for the case of $\omega_{ij} = 0$. If the self interaction of a species is very strong, molecularly unlike pairs are discouraged, hence $z_a/z_b$ ratios will be closer to unity than for the nonenergetic case, because $z_a$ and $z_b$ both separately tend toward $z_s$ as the molecular species tend to segregate.

This crude geometry can be justified only in that, in the expressions developed to calculate $G^E$, relative changes in coordination numbers are often more important than the absolute value of these numbers.

10. CLOSED FORMULA FOR COORDINATION NUMBER IN A SIMPLE BINARY

For a binary mixture, and when the $\omega_{ij}$ factors are not too large, it can be considered that

$$z_{\text{ave}} = z_s : z_a/z_b = R_a/R_b = R_{ab}$$  \hspace{1cm} (57)

so that the approximations
\[ z_b = z_s \times \left( R_{ab} x_a + x_b \right) / \left( R_{ab}^2 x_a + x_b \right) \]  

(58)

and

\[ z_a = R_{ab} \times z_b \]  

(59)

are obtained. Here 'a' specifically applies to the larger molecule. The just-mentioned approximations are very useful is visualizing the concentration dependence of \( z_a \) and \( z_b \) in simply binary mixtures.

11. TERMINOLOGY FOR A SOLUTION CONTAINING n-MERS

If at least one of the molecular species in a mixture is sufficiently elongated to behave as a rod or concatenated structure rather than as a single compact entity in the packing arrangement, this additional complexity must be taken into account in packing calculations. Before specifying the method of doing this, a brief note is needed as to how the degree of concatenation of a molecule is to be defined.

From the organic chemist's viewpoint, the word polymer implies a species of long chain molecule made up of repeating
chemical units, described in notation as $R_1 - (R_2)_m - R_3$, where $R_1$ and $R_3$ are terminal groups between which are $m$ repeating units of the group $R_2$. The word 'n-mer' was coined by physical chemists (16) to characterize a molecule of $n$ units linked together into a physical chain structure without any distinction being made between end and internal units. The analogy between chemical and physical chemical terminology for concatenated species is evident, but it is in another sense unfortunate that polymer chemists and physical chemists chose such similar terminology for uses which were basically different: a succinct description of chemical composition on the one hand and an indication of a physical chain-like structure on the other. Nevertheless since both usages are current, the most that can be done is to point out that in this thesis the physical chemist's definition emphasizing morphology rather than chemistry is used.

In this work the structural chain connotations of the word n-mer are retained without including the restriction that the $n$ units be identical or even similar chemically to each other, nor need they be chemically similar to other species present in the mixture. In the context of this thesis, an n-mer is any molecular species which occupies $n$ unit cells in the packing arrangement. If $n$ assumes the trivial value of one, the species is a monomer species. It follows that a monomer unit is operationally defined as that portion of a molecule which occupies one unit of the packing arrangement. The pack-
ing arrangement is determined in concert by all the species present. When these species are of different monomer sizes, there is no exact one-to-one relationship necessarily to be expected between the chain length of a molecule in terms of the number of chemical units, and the molecule's effective configurational n-mer chain length in a particular type of mixture.

12. PACKINGS INVOLVING ELONGATE MOLECULES

The difficulties, which have just been outlined, arising largely because of nomenclature problems, may to some extent be resolved by considering the illustration series 5, showing various examples of possible relationships between effective cell size in the packing arrangement and the effective n-mer chain length of concatenated species present in the mixture. In each illustration, the unit cell boundaries about 'monomer' segments of the central molecule are shown in heavy dashed lines. Cell centres are shown by crosses, and nearest neighbor rings are indicated by a light dashed line through the centres of the neighbors. The actual form of the central molecule is shaded. Values or ranges of values for n, z_{ext}, and \( v \) indicated, corresponding to effective chain length, exterior* coordination number and the proportion of nearest neighbors which are proximal chain units. Because the packing arrangements shown are

* The significance of the word "exterior" in association with coordination number indicates the number of external neighbors (as distinct from proximal chain units) a given monomer unit can coordinate.
two-dimensional rather than corresponding to the actual three-
dimensional situation in the liquid, parameter values are not
physically meaningful, but rather serve only to indicate the
concepts being used.

Let us first consider Illustration 5(a). The central
molecule (shaded) is, for the present Illustration regarded as
comprising two parts, A and B, each of which can be considered
as occupying a single cell. However, note that unit B re-
presents one of the nearest neighbor ring properly belonging to
unit A and similarly unit A is part of the nearest neighbor ring
of B. It will be seen that regardless of how flexible the
bond between the portions A and B may be, there are two adjacent
cells of the packing arrangement occupied by segments of the
central molecule. The number for \( z_{\text{ext}} \), which represents the
overall exterior coordination number per monomer unit, must
take into consideration that one nearest neighbor for both A
and B is a proximal chain unit. Since the central molecule is
being treated as filling two adjacent cells, \( n \) equals 2. These
numbers are attached to Illustration 5(a) although they have
been explained in this text so that the corresponding Illustra-
tions in slightly more complex cases can be compared.

Illustration 5(b) depicts a similar but more complicated
case. In this situation the central molecule, although of
roughly the same size as in Illustration 5(a), is considered
to be of such a chemical structure that no free rotation around
A's chemical bond is possible, and so configurationally the
central molecule behaves as a rigid blob as shown again by
Illustration 5(a). Representative Packing Arrangements.

Dimer.
Illustration 5(b). Representative Packing Arrangements.
Short Rod like Molecule.
shading. Nevertheless it can be seen that it is still legitimate to treat the A and B fractions as occupying adjacent cells, and once again A fraction has B as its proximal chain units neighbor. A has 7 external neighbors, giving $z = 8$. The B portion, on the other hand, has a proximal chain nearest neighbor and 5 external neighbors, giving $z = 6$. This drawing has been deliberately adjusted so that the A end is rather larger than the B end to show that one need not have the same coordination number around each part of the dimer. The statistical average of the number of external nearest neighbors around the complete molecule, divided by the number of monomer units will represent the average coordination number per monomer unit of that central molecule. In this case, the external coordination number of the average monomer unit will lie between 5 and 7.

Now consider the situation represented by the pair of Illustrations 5(c)i and 5(c)ii. These have been drawn to illustrate a point about the effect of the size of surrounding molecules acting as neighbors to n-mer units. Illustration 5(c)i has been drawn so that each monomer unit of a 4-mer molecule has been considered to be occupying one cell and the neighbor molecules have been drawn to surround it as comfortably as possible. However, in Illustration 5(c)ii, where an n-mer of small monomer unit size is surrounded by large neighbors, operationally, the central molecule behaves as a 3-mer. In this case the central 2 monomer units of the central molecule are allocated to one cell. It will be seen that this last arrange-
Illustration 5(c)i. Representative Packing Arrangements.
Short Flexible Chain like Molecule.
CENTRAL MOLECULE BEHAVES AS 3-MER

Illustration 5(c)ii. Representative Packing Arrangements.
Small n-mer Surrounded by Large Neighbors.
ment is a more comfortable one than an attempt to find a packing in which the molecule could act as a 4-mer under the given circumstances.

In Illustration 5(c)i a four monomer unit central molecule has been illustrated as being surrounded by nearest neighbors of sizes approximately equal to the monomer unit, and no great difficulty is encountered in recognizing the nesting process, in identifying the interior neighbor and external neighbors. It can be seen from Illustration 5(c)i no difficulty arises in defining the order of the polymer in such a case. Case 5(c)i is handled by classical methods in which the size of the molecules, or rather, here, the surrounding molecules and monomer unit, are approximately the same. Difficulties only begin to occur when real size differences exist between nearest neighbors and monomer units as seen in Illustrations 5(b) and 5(c)ii.

Further complications can exist. In Illustration 5(d) is shown a central molecule of 5 flexibly connected units. It probably can most comfortably be represented as a dimer, the coordination number of the two units A and B of the dimer being unequal. Appropriate data is attached to the Illustration. The ramifications of case 5(d) are more fully discussed later in the chapter.

13. DIFFICULTIES IN THE DEFINITION OF A MONOMER UNIT

The definition of a monomer unit as the amount of a molecule which occupies one unit of the packing arrangement, with the
Illustration 5(d). Representative Packing Arrangements.
Partly Rolled-up Central Molecule.
'packing arrangement' in turn being cooperatively determined by all the species present, may seem a rather noncommittal set of statements in view of the obvious interdependence of monomer unit and cell size in the packing arrangement. However, one must really not ask whether the above definitions are circular (indeed, they are), but rather whether they can form the basis of a set of mathematical statements by means of which effectively convergent values of chain length could be obtained by an appropriate iterative procedure (this in fact also is so). Hence, in the operative sense, the above definitions are adequate.

14. IDEALIZATION OF POLYMER GEOMETRY IN CLASSICAL TREATMENTS

The precision of the definition of monomer unit to be found in classical treatments of the properties of n-mer solutions (23) is achieved by idealizing the properties of n-mers to the point where they become compatible with a regular lattice structure, so that thermodynamic estimates of n-mer mixtures may be obtained through the use of lattice statistics. In such idealized solutions, all monomer units are assumed to be identical in size, and also identical in size to the monomer units of other species present in the mixture (see Illustration 5(c)i. Intra- and inter-molecular distances are considered to be identical. The n-mers are considered to be of a specified degree of rigidity - usually specified as being perfectly flexible, so that any proximal link on a chain is able to occupy any nearest neighbor site in the lattice not already occupied.
Packing in the lattice model, hence the nearest-neighbor packing number, is a strictly predetermined and invariant phenomenon dictated by the assumed coordination number of the lattice. The problem of interdependency of assigned cell size and effective chain length is circumvented under such stringent idealization. By definition, (in the lattice model), an interior monomer unit has \( z - 2 \) chain connections, hence \( (z-2) \) external neighbors, a terminal has one chain connection, hence \( (z-1) \) external neighbors, and a monomer species has no chain connections, and \( z \) exterior nearest neighbors, with \( z \) being in all cases the same constant.

15. **CONTRAST BETWEEN IDEALIZED AND ACTUAL POLYMER GEOMETRY**

If one 'liberalizes' the above regime to the case of a real solution of molecules of different sizes, shapes, lengths, and energetically induced clustering tendencies, and where some of the molecules may be in partly rolled up configurations, one has to return to the kind of operative definitions of chain length estimate based on the amount of effective cell occupancy as given in the present work. In fact, one can adopt either of two viewpoints on the matter. The first is that chain length in the circumstances just described is indeterminate. Such a situation is contrary to the physical intuition that solutions almost always settle to an unique lowest free energy configuration. For such a minimum to exist, the mixture must respond to a unique set of physical parameters, one of which obviously is chain length. One is thus heartened to take the more positive viewpoint, that there is an effective chain length, even if it is not readily measurable. One can then either try to calculate an effective
chain length, or failing that, simply to include effective chain length as an empirical constant in the equations. A completely internally consistent treatment of the general case above would obtain the effective value of $n$ from additional fundamental information about all the species present in the mixture through an iterative calculation; but in this thesis, $n$ is treated as a parameter to be varied, or set according to the best estimate available from external physical observations, or assigned the value which gives the best thermodynamic results. This thesis was not primarily intended to be a study of chain effects in mixtures, though $n$ had to be included for completeness in all the formulations. This accounts for the lack of rigor in evaluating $n$, despite its inclusion in the algebra. The reader might wish to refer back to Illustration 5(d) at this point.

16. NOMENCLATURE FOR CHAINS OF NONUNIFORM MONOMER UNITS

Consistent with the above level of rigor with regard to $n$, the case of a molecule composed of monomer units of different sizes has not been included in the formulation. If the parameter $n$ is a species effective chain length, then the parameter $R$ becomes its effective monomer radius, which in the case of a heterogeneous $n$-mer is an average of its constituent monomer-unit radii. Furthermore, it is hoped that defining $n$ as a chain length for packing considerations, while employing $n_i$ to differentiate fractions of the surface of a monomer unit on chemical grounds, is not felt to be a problem. Excessive concern over such second order level refinements in definitions of what is, operatively, a first order theory, would tend to imply
a non-existent corresponding degree of refinement to be ex-
pected in the thermodynamic estimates arising from the calcula-
tions.

17. CALCULATION OF PACKING NUMBERS WITH n-MERS PRESENT

The calculation of packing number per monomer unit has
been extended in this work to the case where n-mer species are
present, without modification to the basic calculation method
employed (equations (52) to (55)) in the 'all-monomers' case.
The fact of concatenation was accounted for by incorporating
a correction factor, $E_a$, such that:

$$z_a(\text{exterior}) = E_a z_a(\text{isolated monomer})$$  \hspace{1cm} (60)

when the unit 'a' belongs to an n-mer molecule.

For the $a^{th}$ species of n-mer length $n_a$, (see Illustration
5(c)i)

$$E_a = \frac{1 - (1 - 2 \psi_a)(n_a - 1)}{n_a}$$  \hspace{1cm} (61)

where

$$\psi_a > \frac{1}{z}$$  \hspace{1cm} (62)

For long chain species

$$E_a \approx (z_s - 2)/z_s$$  \hspace{1cm} (63)

For a dimer

$$E_a \approx (z_s - 1)/z_s$$  \hspace{1cm} (64)
and for monomer molecules,

\[ E_a = 1 \]  \hspace{1cm} \text{(65)}

The symbol \( z_a \) appearing in equations (52) to (55) is in the general case taken to be the exterior coordination number per monomer unit of species 'a'. It is obtained from the value of the coordination number obtained from purely packing-geometry considerations, namely \( z_a \) (isolated monomer) by equation (60) and (61). Because coordination numbers per monomer unit in mixtures are understood to be exterior ones, \( E_a \) only explicitly appears as applied to \( z_a \) in the formulations of this work.

Since packing number calculations include only nearest neighbors, the presence or absence of remote units of long chains in the nearest neighbor shell is immaterial to the calculation of packing numbers*. Whether a nearest neighbor is a remote unit of the same chain, or whether it belongs to a different chain, does not change the considerations which determine the average packing number for a species of monomer unit - namely the sizes and overall proportions of various kinds of monomer units present in the mixture. The permanence of proximal chain units in the nearest neighbor shell of the \( m \)th monomer unit of concatenated species simply requires that in the calculation of packing numbers such proximal units be accounted for in the weighted average of nearest neighbors. However, in

* This is of course the case for 'lattice' calculations of configurational entropy, where dispositions of whole n-mer chains distinguish system permutations of the N-particle system.
the calculation of the exterior packing number (the number of nearest neighbors which are constantly being interchanged by the random thermal motion of the liquid, hence are available for participation in mixing effects) the number of proximal units for the average monomer unit of a given species must be subtracted from the total packing number to obtain the average exterior packing number per monomer unit of the given n-mer species for a particular mixture.

18. THE EFFECT OF ROLLED-UP CONFIGURATIONS ON THE EFFECTIVE PACKING NUMBER

In connection with packing number calculations involving concatenated species, it should be borne in mind that while the disposition of remote monomer units poses no problem, a further complication can arise - due to local molecular configurations. For example the sigma bonds of proximal methylene groups of paraffin hydrocarbons permit the skeleton of the molecule to rotate in such a way that the molecule can assume a much more compact form in some configurations that in those of maximum extension. (See again Illustration 5(d)). Normal butane, for example, may tend to exist in a compact form which acts, as far as its packing number goes, like a large monomer species with a large packing number, rather than as an n-mer (with n > 1), whose packing number per monomer unit is lower. The effective chain length of a relatively long flexible molecule, namely \( n_a \), is not immediately deducible from its chemical formula, though the relation
\[
\bar{v} = K n_a \times R_a^2
\]  
(66)

must hold, where \( K \) is a proportionality constant. Since the roles of \( R \) and \( n \) are not interchangeable in their effect on \( G_E \), departure of \( n_a \) from the value of \( n_a \) for the molecule's configuration of maximum extension alters the effective value of \( R \). Nevertheless, the above complication due to the existence of partly "rolled up" configurations for certain flexible \( n \)-mers still does not change the mechanics of the calculation of \( z \), given \( n \) and \( R \). Thus the problem was not given extensive attention; even though it does bear on the a priori values assigned \( n \) and \( R \) for a given species of long molecule, and thereby affects the value of \( z \) which is effective in the mixture.

19. \( \xi_a \) FOR AN \( n \)-MER CONTAINING SOLUTION

The only modification of the packing calculations scheme necessitated to accommodate the presence of an \( n \)-mer species is the appropriate inclusion of factor \( E_a \) into the algebra to modify the value of the packing number per monomer unit, remembering that for monomer species, \( E_a \) assumes the trivial value of 1.0. Thus when \( n \)-mer species are present, the contact fraction of species \( a \) is generalized to

\[
\xi_a = \frac{z_a \times n_a \times x_a}{\sum_a z_a n_a x_a}
\]  
(67)
where $z_a$ is understood to be the exterior coordination number per monomer unit as discussed above.

20. **EFFECTIVE MONOMER RADIUS**

A note on the calculation of $R_a$, the monomer-unit radius, is appropriate at this point. For a binary mixture,

$$\frac{R_a}{R_b} = R_{ab} = \left(\frac{v_a}{v_b}\right)^3$$

where $v_a$ and $v_b$ are the pure component molal liquid volumes. This estimate is a very approximate one, particularly in the case of dilute solutions, but, it can be somewhat improved if the partial molal volumes are used. In such a case the better estimate is provided by

$$\frac{R_a}{R_b} = \left(\frac{\overline{v_a}}{\overline{v_b}}\right)^3$$

The more sophisticated methods described by Reid and Sherwood (43), and also that of Lielmezs and Bondi (37) were used in the actual calculations, the results of which appear in Chapter 11.
CHAPTER 7

CONFIGURATIONAL ENTROPY EFFECT

1. THE IRREGULAR MULTIPARTICLE ARRAY
2. INCORPORATION OF z IN N-SCALE ENTROPY FORMULATIONS
3. COMPATIBILITY WITH LATTICE STATISTICS
4. PAIRS-PERMUTATIONS IN THE NCZ CASE
5. ENTROPY OF MIXING EXPRESSION IN TERMS OF CONTACT FRACTIONS
6. SUMMARY
CHAPTER 7

CONFIGURATIONAL ENTROPY EFFECT

1. THE IRREGULAR MULTIPARTICLE ARRAY

Close examination of Guggenheim's theory of CZ binary mixtures suggested to the author (following the example of cell theories, of which lattice theories are one limiting case) that the idea of a three-dimensional network of instantaneous molecular locations would be equally well served by considering a 'snapshot' of the liquid as an adequate basis on which to define N instantaneous molecular positions. Permutation interchanges could equally well be counted in such a framework, whether or not the lattice obtained by connecting centres had any long range regularity. The useful idea of permutation interchanges could thus be separated from the complete lattice structural idea and would permit the incorporation of the effect of different coordination numbers for the various species present in the mixture into the permutation interchange formulas for the system. A study of the consequences of abandoning the restriction of a constant coordination number, as required in classical quasichemical expressions, became one of the main areas of formal investigation of the present work, and resulted in a generalization of quasichemical theory to the non-constant coordination number case. In developing this
idea in detail it will be revealed that the lattice concept is
simply a conceptual device permitting the reduction of the 3-N
space of the configurational integral for the system of N
particles into N independent integrals, each in its own 3-space
of point dimensions. The interchange of any two molecules on
their respective lattice sites defines a new configuration for
the whole system.

The basic simplification involved in the approxi-
mation of 3-N space by N independent 3-spaces is also possible
for any 'cell' model as long as the approximation of single-
occupancy of the cells by the molecules is imposed. For per-
mutation purposes, a 'location' is now designated as "anywhere
within a specified cell" (that is, rather than in some other
cell). In a dense liquid far from its critical range, the
molecular dynamics studies of Wainwright and Alder (38) show
that a molecule tends to rebound within the confines of the
'cage' or 'cell' formed by its nearest neighbors, and only
rather infrequently breaks out of the cage to penetrate an ad-
jacent cell. On a time scale established by the period of
thermal randomness motions, then, N distinct spatial domains
are defined by the N cages confining the N molecules of the
system. At least in theory, a given configuration of the
whole system could be defined by means of a 3-dimensional
photograph of the system to 'stop the action' hence define the
position of the N cage volumes in the given system configuration.
The number of distinct permutations of molecules with respect
to the N cages defined by such a photograph is given by:
\[ \Omega = \frac{N!}{(N_i!N_j!)} \]  

for \( N_i \) molecules of \( i \) and \( N_j \) of \( j \), where \( N_i + N_j = N \). This is the same result which would have been obtained for the number of distinct permutations of molecules about the position points of a lattice. If a molecule breaks out of its cage, it in effect interchanges positions with a nearest neighbor. This defines a new permutation of the whole system.

2. INCORPORATION OF \( z \) IN N-SCALE ENTROPY FORMULATIONS

In order to derive the thermodynamic properties of the N-scale system (and it is of course at this scale that the figures are ultimately required) it is most convenient to accept the conclusions of Chapter 6, and formulate the N-scale properties incorporating necessary \( z \)-scale variables. In other words an inverted viewpoint is being used: now taking the compatibility of local properties with those of the N-scale for granted, the ways in which N-scale configurational formulas are dependent on the \( z_1 \) in the NCZ case are described, and the modified N-scale configuration expressions are then written.

3. COMPATIBILITY WITH LATTICE STATISTICS

While the concept of the snapshot has been used to illustrate an idea (that of the geometric basis of the present
model) and while in principle a counting process on the snapshot would enable the evaluation of $z_1$ to be carried out, in reality such unsophisticated procedures would have to be replaced by a more formal calculation method. This is accomplished by realizing that the idea of NCZ, both on the $z$-scale and on the $N$-scale, does not require an irrevocable mathematical departure from the $N$-scale CZ lattice viewpoint of the original quasichemical theory. What was done was to reframe the mathematics of particle interchange computations by combinatorial methods in a more flexible conceptual context. In such a context, the interchange computations become amenable to the incorporation of the effects of local properties of the liquid (specifically the variable $z$), as well as to pairwise energy attractions.

4. PAIRS-PERMUTATIONS IN THE NCZ CASE

The constancy of coordination number of a regular $z$-coordinated packing conveniently ensures that the permutation operation involving the interchange of two molecules affects only $z$ sites or contacts in each case. The number of physically permitted interchanges of pairs of contacts or 'pairs' is constrained by the fact that in any given permutation operation, each molecule must be moved as a whole, thus $z/2$ pairs must be interchanged as a group. The factor of 2 arises from the fact that each pair is associated with 2 molecules rather than 1, and so the number of pairs attributed to any specific molecule is $(z/2)$, to avoid duplicating the count.
While a permutation operation interchanging two molecules affects just \( z/2 \) pairs in each case, if the two molecules are \( z \)-coordinated, in creating new molecular configurations one is not restricted to permuting only two molecules at a time. If species \( i \) is \( z_i \) coordinated and species \( j \) is \( z_j \) coordinated and \( z_{\text{ave}} \) is the overall average coordination number, an interchange involving \( A_i \) molecules of \( i \) and \( B_j \) molecules of \( j \) affects the \( z_i \times A_i \) pairs anchored by the \( A_i \) and the \( z_j \times B_j \) pairs anchored by the \( B_j \), with only second order accommodating movements required on the part of the other (unpermuted) molecules of the system. A slight notational simplification exists for a binary where we can refer to \( z_{\text{ave}} \) simply as \( z_{ij} \). Thus it may be seen that if \( i \) is the larger molecule, then the relative number of pairs per molecule directly affected by its movement is \( (z_i/z_{ij}) \), and for the smaller \( j \) only \( (z_j/z_{ij}) \). These two ratios represent the relative importance per individual molecule of the two species for pairs permutation purposes.

If a larger number, \( N \), of molecules (\( N_i \) of coordination number \( z_i \) and \( N_j \) of coordination number \( z_j \)) are permuted, the total number of distinguishable and permitted pairs permutations represented by the symbol, \( \Omega' \), is given not by

\[
\Omega = \frac{(N_i + N_j)!}{(N_i!N_j!)}
\]

but more closely by

\[
\Omega = \frac{(N_i + N_j)!}{(N_i!N_j!)}
\]
\[ \Omega' = \frac{(z_i/z_{ij} N_1 + z_j/z_{ij} N_j)!}{(z_i/z_{ij} N_1)! (z_j/z_{ij} N_j)!} \]  \hspace{1cm} (72)

Where \( z_i \) and \( z_j \) are not too different, equation (72) will be substantially correct. The form of \( \Omega' \) is consistent with a transformation from a real population of \( N_1 \) groupings of pairs of group size \( z_i/2 \) and \( N_j \) groupings of pairs of group size \( z_j/2 \) to pseudopopulations of \( z_i/z_{ij} N_1 \) groupings of type \( i \) and \( z_j/z_{ij} N_j \) groupings of type \( j \) of the same grouping size, namely of the overall average size \( z_{ij}/2 \). The term \( \Omega' \) is then in the form which equalizes the size of pairs bundles for interchange purpose, hence conserves the number of pairs interchanged in a given permutation of spheres. This same transformation will be found useful in Chapter 8.

5. ENTROPY OF MIXING EXPRESSION IN TERMS OF CONTACT FRACTIONS

It should be noted in passing that the expansion of the negative logarithm of \( \Omega' \) by Sterling's approximation for the logarithms of factorials, after normalizing, yields an expression in \( \xi_i \) and \( \xi_j \), namely,

\[ -\frac{\ln \Omega'}{(z_i/z_{ij} N_1 + z_j/z_{ij} N_j)} = \xi_i \ln \xi_i + \xi_j \ln \xi_j \]  \hspace{1cm} (73)

In the limit of equal sized spheres (the constant-\( z \) case) \( \Omega' \) reduces to \( \Omega \) and we obtain simply
6. SUMMARY

It has been shown that counting the nearest neighbor contacts of a given central molecule establishes its nearest neighbor coordination number. In a mixture of unequal sized spheres, each species assumes a different value of $z$, and thus the $z_i$ may be considered as a mixture-dependent material property of the given species. Consideration of the possible interchanges of contacts for the NCZ case has provided the form of the configurational mixing term, to be incorporated into the formulation of the expression for the excess free energy of a real liquid in the next chapter.
CHAPTER 8

CALCULATION OF EXCESS FREE ENERGY FOR THE
SIMPLEST NCZ CASE

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12. SUMMARY
CHAPTER 8

CALCULATION OF EXCESS FREE ENERGY FOR

THE SIMPLEST NCZ CASE

1. OBJECTIVE

In this chapter, the quasichemical expression for $g^E$ for a monofunctional monomer binary mixture of unequally sized molecules is developed.

First the basis of the CZ quasichemical theory is set out in a form suitable for extension into the NCZ case, and then the formal extensions to the present work are shown, and their consequences discussed for this simplest possible case in which NCZ effects contribute to the expression for $g^E$.

2. REFORMULATION OF CONSTANT COORDINATION NUMBER THEORY FOR

THE NCZ CASE

A. Review of Pairs-Liquid

The treatment begins with a detailed inspection of the energetic aspect of the liquid model, in which the liquid is regarded as an assemblage of independent 'pairs'. A pair is an entity with both a geometric and energetic identity.

B. Review of the Mixing Process Seen as a Reaction

Energetically, the mixing process is regarded in the light of a 'quasichemical' reorganization reaction of pairs, wherein
the like pair species \((i-i)\) and \((j-j)\) found in the pure component state reorganize to form unlike pairs \((i-j)\). The reaction is written

\[
(i-i) + (j-j) \rightleftharpoons (i-j) + (j-i)
\]

(75)

and is associated with the pairs cohesion energies

\[
\epsilon_{ii} + \epsilon_{jj} \rightarrow 2\epsilon_{ij}
\]

(76)

Terms \(\epsilon_{ii}\) and \(\epsilon_{jj}\) are the like-pairs cohesion energies, and \(\epsilon_{ij}\) is that of the unlike pairs. Like-pair cohesions are obtained from the pure component energy of vaporization \(E_{vap_i}\) at the given temperature, by the relation

\[
\epsilon_{ii} = \frac{E_{vap_i}}{(z_s/2)}
\]

(77)

\(\epsilon\) values carry a negative sign, since they are cohesive (binding) energies. The net reorganization energy, which, because of its origin is usually an insensitive function of temperature, is defined as *

\[
\omega_{ij} = [\epsilon_{ij} - \frac{1}{2}(\epsilon_{ii} + \epsilon_{jj})]
\]

(78)

* It should be emphasized that the arithmetic average reference unlike pair cohesion energy, given by \(\frac{1}{2}(\epsilon_{ii} + \epsilon_{jj})\) in equation (78), simply represents the ideal mixing case for the process described by relation (75). Physically it is rare to encounter a value of \(\epsilon_{ij}\) such that \(\epsilon_{ij} = \frac{1}{2}(\epsilon_{ii} + \epsilon_{jj})\) so that \(\omega_{ij} = 0\). In dispersion-force type systems (non-polar interactions) appropriate values for \(\epsilon_{ij}\) are of the type

Continued
If unlike pair cohesion is more binding than the arithmetic average of like-pair cohesions, $\omega_{ij}$ is negative and unlike pairing is thus energetically favored. Note that $\omega_{ij}$ is independent of the difference in the pair cohesions per se. Since no general method of evaluating $\epsilon_{ij}$, hence of $\omega_{ij}$, by direct calculation has yet been developed, $\omega_{ij}$ must usually be experimentally determined by at least one measurement per binary involved in the mixture. The assumption of the present theory is that $\omega_{ij}$ is independent of composition, and also that it is the same in a multicomponent mixture as it is in the binary mixture.

The calculation for $\omega_{ij}$ does not contain any assumption as to where or how the rearrangement of 2 like pairs takes place. Hence it simply and completely accounts for the

\[ \frac{\epsilon_{ij}}{\epsilon_{ij} + \epsilon_{jj}} \]

Continued

or

\[ \epsilon_{ij} \leq (\epsilon_{ii} \epsilon_{jj})^{\frac{1}{2}} \]

which may tend toward $\epsilon_{ij} = \epsilon_{ii}$, where $i$ is the less cohesive species, so that $\omega_{ij}$ is normally positive (36). When specific interactions of a polar nature are involved, the magnitude of $\epsilon_{ij}$ is usually much larger than the arithmetic mean of the unlike pair cohesions, so that $\omega_{ij}$ becomes large and negative, and is associated with an 'exothermic' heat of mixing effect. See for example reference (34).
lowering of the overall assemblage's energy as a result of one such additional 4-molecule rearrangement resulting in the juxta-position of unlike species. Thus, while not incompatible with consideration of the binding energy of a central molecule by its nearest neighbors, the quasichemical rearrangement energy \( \omega_{ij} \) formulation in no way 'isolates' or 'decouples' the nearest neighbors assemblage from the liquid as a whole. This is the key conceptual difference between quasichemical energy considerations and those involved in the 2-liquid theories discussed in Chapter 10, which do regard each nearest neighbor assemblage as being (energetically) isolated from the rest of particle assemblage.

3. STOICHIOMETRIC ADAPTATION TO THE NCZ CASE

The stoichiometry of equation (75) (i.e. the numbers of pairs of 'reactants' and 'products' involved in pairs reorganization) is only strictly correct for the constant-z case. In the NCZ case, where coordination numbers become dependent on composition, in order to ensure consistency with an overall stoichiometric balance, one would first write the overall reorganization reaction, namely that starting with like-pairs in the pure component state, for the number of pairs coordinated per molecule.

\[
\frac{z_i}{2} (i-i) + \frac{z_j}{2} (j-j) \rightarrow \frac{z_{ij}}{2} (i-j) + \frac{z_{ij}}{2} (j-i) \quad (81)
\]

(The reader may find it helpful to look again at Illustration 4,
Dividing by $z_s$ results in the desired pairs-scale reaction:

$$(i-i) + (j-j) \xrightarrow{z_s} 2\left(\frac{z_{ij}}{z_s}\right)(i-j)$$

Hence the effective reorganization energy per unlike pair formed, $\omega'_{ij}$ is given by

$$\omega'_{ij} = \left[\varepsilon_{ij} - \frac{1}{2}\left(\frac{z_s}{z_{ij}}\times (\varepsilon_{ii} + \varepsilon_{jj})\right)\right]$$

If $(z_s/z_{ij})$ seriously departed from unity, the stoichiometry of the pairs reorganization reaction would depart correspondingly from the integer form and, for one thing $\omega'_{ij}$ would become appreciably dependent on $z$, hence on composition, in the NCZ case.

However

$$z_{ij} \approx z_s$$

for solutions encountered, so that $\omega_{ij}$ may be used as an adequate approximation to $\omega'_{ij}$ without appreciable loss of accuracy. The fact that $\omega'_{ij}$ characterizes the overall mixing process, starting from the pure component state, prevents $\omega'_{ij}$ from being a highly concentration-dependent relation depending on $z_i$ and $z_j$ applied to self-pair cohesions, in a form such as

$$\omega''_{ij} = \left[\varepsilon_{ij} - \frac{1}{2}\left((z_i/z_{ij}) \times \varepsilon_{ii} + (z_j/z_{ij}) \times \varepsilon_{jj}\right)\right]$$
as well as $z_{ij}$ being applied to the unlike pair cohesion.

4. ENERGETIC INTERPRETATION OF THE INDEPENDENT PAIRS ASSUMPTION

Implicitly included in equation (81) is another major energetic assumption of quasichemical theory, which is even more important in the NCZ case than for constant-$z$ solutions: namely that the pairwise cohesion is regarded as independent of coordination number. The assumption is merely an emphasis on one aspect of the meaning of independent pairs' interactions. Solutions in which cohesion is dominated by London-force or dispersion-force interactions conform with this assumption, because the dispersion attraction between any two molecules is a quantum mechanical effect, shown by London not to be seriously perturbed by the presence or absence of other molecules. The pairwise independence of interaction of any arbitrarily chosen "central" molecule and a 'nearest neighbor', would be a case in point. Hence, in dispersion-force systems the cohesion of the central molecule to one nearest neighbor is not seriously perturbed by the presence of a second, third ...$z_1$ th nearest neighbor, where packing relations are such that the central one is $z_1$ coordinated. The assumption of pairwise independence has been used as an approximation for all systems in this work, even those in which interactions are far from purely 'dispersion'in nature.

A direct corollary of the assumption of pairwise independence of energy interactions is that packing-induced
changes of a species' coordination number, as demonstrated in Chapter 6 for a packed bed, and here extended by analogy to the case of a real liquid, cause directly calculable changes in the total cohesion per molecule, and hence in the solution as a whole.

Whereas the constant-z treatment focuses on the effects of cohesion changes in a mixture due to non-zero $\omega_{ij}$, the NCZ treatment also accounts for the cohesion changes which could arise directly from packing-induced $z$ changes*. Packing induced changes thus result in terms in the NCZ form of the excess free energy of mixing expression which are not present in constant-z formulations. These effects can occur even in the case where the $\omega_{ij}$ terms are all zero.

In fact, because of the phenomenon of the near equality of $z_{ij}$ and $z_s$ in equation (83), it may be seen that the additional cohesion effects of the NCZ case are nearly independent of the classical ones of constant-z quasichemical theory. Formulation and subsequent assessment of the 'new' terms thus became a matter of considerable practical interest.

5. BUNDLE-SPECIES MOLECULAR-SCALE QUANTITIES

In Chapter 7 was derived an expression for $\omega^*$, the

* The use of $\omega_{ij}$ (as an adequate approximation to $\omega_{ij}^*$) rather than that of $\omega_{ij}^{**}$ in the NCZ case represents an important choice. Hence this note.
appropriate combinatorial term describing the number of possible interchanges of contacts in the NCZ case, which was obtained from a transformation of \( \Omega \), the number of possible and distinguishable interchanges of molecules in a binary mixture. The main configurational restraint upon a real liquid regarded as an assemblage of pairs of contacts is the same: namely that for configurational purposes, pairs must be regarded as reassembled into molecular-scale entities.

The molecular-scale entity formed from the pairs assembly is hereafter designated a 'pairs-bundle', or group of \( z/2 \) pairs. Unlike an actual molecule, which in a mixed environment forms various species of pairs, a pairs-bundle is composed exclusively of only one pairs-species. In a simple binary mixture of i and j type sites, the actual pairs populations can be reformed by an imaginary segregation process into four possible types of bundles with bundle populations made consistent with an overall balance of types of pairs. The four bundle-species would thus be those of i surrounded by i, j surrounded by j, i surrounded by j and j surrounded by i. The reformation of a mixture into four kinds of bundle species is shown in Illustration 6. The point of doing this is so that each type of pair can be associated with a coordination number. It is convenient to amalgamate the two unlike-pair bundle-species into one undifferentiated unlike-pair bundle species. For calculation purposes, thus, three bundle-species exist: i-i type bundles of bundle size \( z_i/2 \), j-j type bundles of size \( z_j/2 \), and i-j type bundles of size \( z_{ij}/2 \). Dividing
Illustration 6. Bundle-Species.

ACTUAL CONFIGURATION

<table>
<thead>
<tr>
<th>2-2 PAIRS</th>
<th>1-1 PAIRS</th>
<th>2-1 PAIRS</th>
<th>1-2 PAIRS</th>
</tr>
</thead>
<tbody>
<tr>
<td>BUNDLE</td>
<td>BUNDLE</td>
<td>BUNDLE</td>
<td>BUNDLE</td>
</tr>
</tbody>
</table>

IDEALIZATION AS BUNDLE-SPECIES MOLECULAR SCALE GROUPINGS (NOTE: IN OVERALL MIXTURE, 1-1 BUNDLE POPULATION = Z_j/2x (1-1) ACTUAL PAIRS POPULATION)
by 2 reduces the number of contacts per bundle to the number of contacts associated with one molecule. Since \( z_i, z_j \) and \( z_{ij} \) all have different values in the NCZ case, reformulation of the configurational behaviour of the pairs assemblage into that of 'bundles' differs from direct consideration of real-molecule behavior in a non-trivial way. The concept of 'bundling' together with a method for evaluating the equilibrium populations of the bundle species* in a mixture forms the basis for defining mixture behaviour in the quasichemical model.

6. FORMULATION OF THE PARTITION FUNCTION

The basic mechanical and energetic postulates of the quasichemical model are now defined in a way compatible with an NCZ mixture. It is now necessary to construct a molar scale partition function for the mixture and pure component \( i \), namely, \( Q_{\text{mix}} \) and \( Q_i^0 \) respectively, from which to obtain the excess free energy of mixing from the standard relation:

\[
A_{\text{mixing}} = -kT[\ln Q_{\text{mix}} - \sum_i \ln Q_i^0]
\]

(86)

Since the mechanical model is formulated on the 'pairs'

* This must be done consistent with energetically induced local clustering tendencies, stoichiometric restrictions, and conformity with the principle of maximum randomness.
and 'bundle' levels, it is first necessary to define partition functions at these levels, and relate these to the molar scale ones. The partition function for an i-j pair is defined as

\[ q_{ij} = (e^{-\frac{\varepsilon_{ij}}{kT}} v_{f_{ij}}) \]  

(87)

Term \( \varepsilon_{ij} \) is the pairwise cohesion of the i-j pair and \( v_{ij} \) is a volume-of-integration factor defining the 3-space region over which the value of \( \varepsilon_{ij} \) is the average value of the cohesion.

\[ v_{f_{ij}} = \frac{(v/N)/(z_{ij}/2)} {z_{ij}/2} \]  

(88)

where \( v \) = molar void volume of the liquid, \( N \) is Avogadro's number and \( z_{ij} \) is the coordination number appropriate to the i-j bundle species. \( v_{f_{ij}} \) is not an easily evaluable number, and whenever possible formulations requiring direct assignment of a number to it are avoided.

The molecular scale partition function (of the i-j bundle species) is designated by

\[ Q_{ij} = (q_{ij})^{z_{ij}/2} \]  

(89)

If \( q_{ij} \) is taken to be independent of concentration (assumed in this formulation) then \( Q_{ij} \) is explicitly a function only of relative bundle size \( z_{ij}/2 \), so that in particular.
or more specifically

$$Q_{ii} = (q_{ii}^0)^{z_i/z_s}$$  \hspace{1cm} (90)

For $N_i$ molecules of pure component $i$

$$Q_i^0 = (q_{ii}^0)^{N_i}$$  \hspace{1cm} (92)

For a binary mixture *

$$Q_{mix} = \Omega' (Q_{ii})^{N_i-X_{ij}} \times (Q_{jj})^{N_j-X_{ij}} (Q_{ij})^{X_{ij}} (Q_{ji})^{X_{ji}}$$  \hspace{1cm} (93)

* In equation (93) transformed bundle populations are used in $\Omega'$. The actual populations, which are the only populations consistent with stoichiometry, are used as the indices of the $q$ terms. The reason is that $\Omega'$ is reducible into terms of ratios of populations, whereas the powers of the $q$ terms represent populations so that numbers of bundle populations rather than a balance on number of contacts must be maintained. For the meaning of 'transformed', refer back to Chapter 7, equations (71) and (72).
where \( N_i \) and \( N_j \) are the molecular populations of components \( i \) and \( j \) and \( X_{ij} \) is the equilibrium unlike-pair bundle-population in the mixture.

### 7. REVIEW OF FORMULATION OF THE \( g^E \) EXPRESSION FOR THE CZ CASE

The Helmholtz free energy change due to mixing is obtained by substituting equations (89) and (90) into (92), and (92) into (86), then (91), (89) and (93) into (86), then writing out the bundle species partition functions in terms of their pairs partition functions via (87).

This results in:

\[
-\frac{A^{\text{mixing}}}{kT} = \ln \left\{ \frac{(z_i/z_{ij}N_i + z_j/z_{ij}N_j)!}{(z_i/z_{ij}N_i)! (z_j/z_{ij}N_j)!} \times \left[ q_{ii}^{z_i/2} \right]^{N_i-X_{ij}} \times \left[ q_{jj}^{z_j/2} \right]^{N_j-X_{ij}} \times \left[ q_{ij}^{z_{ij}/2} \right]^{X_{ij}} \right\} \tag{94}
\]

In the constant-\( z \) case,

\[
z_i = z_j = z_{ij} = z_s = z \tag{95}
\]

A summary of the reduction of equation (94) in the constant-\( z \) case is set out below for purposes of comparison to corresponding operations for the NCZ case next to be con-
mixed.

\[
\frac{A_{\text{mixing}}}{kT} = \ln \left[ \frac{(N_i+N_j)!}{N_i!N_j!} \right] + \ln \left[ \frac{q_{ij}q_{ji}}{q_{ii}q_{jj}} \right] z/2 \chi_{ij}
+ \ln \left[ \frac{q_{ii}^0}{q_{ii}^0} \right] z/2 N_i + \ln \left[ \frac{q_{jj}^0}{q_{jj}^0} \right] z/2 N_j
\]

(96)

The last two terms are zero through the assumptions of equation (91). In the second term of equation (96)

\[
\ln \left[ \frac{q_{ij}q_{ji}}{q_{ii}q_{jj}} \right] = \ln \left[ \frac{-\varepsilon_{ij}/kT}{-\varepsilon_{ii}/kT} \right] \times \ln \left[ \frac{-\varepsilon_{ij}/kT}{-\varepsilon_{jj}/kT} \right] \times \ln \left[ \frac{v_{f_{ij}}v_{f_{ji}}}{v_{f_{ii}}v_{f_{jj}}} \right]
\]

(97)

\[
= -2 \frac{kT}{\varepsilon_{ij}} \left( \varepsilon_{ij} - \frac{1}{2}(\varepsilon_{ii} + \varepsilon_{jj}) \right) = \ln \left[ \frac{v_{f_{ij}}v_{f_{ji}}}{v_{f_{ii}}v_{f_{jj}}} \right]
\]

(98)

\[
= -2\omega_{ij}/kT
\]

(99)

The extensive cancellations result from the assumption that the ratio of volume factors is essentially unity, and from the identification of the term in square brackets as the net reorganization energy, \( \omega_{ij} \). By substituting the result of (99) back into (96), and evaluating the \( \Omega \) term in (96), the final expression is obtained for one mole of mixture:
\[
\frac{A_{\text{mixing}}}{RT} = (x_i \ln x_i + x_j \ln x_j) + x_{ij} \frac{\omega_{ij}}{RT} \quad (100)
\]

where

\[
X_{ij} = \frac{X_{ij}}{(N_i + N_j)} \quad (101)
\]

\(X_{ij}\) is the equilibrium unlike-pairs concentration, evaluated from mass law considerations as

\[
X_{ij} = x_i x_j \times \frac{2}{(\beta_{ij} + 1)} \quad (102)
\]

where \(\beta_{ij}\) is a correction factor for energetically induced clustering, given by

\[
\beta_{ij} = (1 + 4x_i x_j \times [e^{\omega_{ij} / kT} - 1])^{\frac{1}{2}} \quad (103)
\]

Subtracting from equation (100) the ideal mixture configurational extropy mixing term, namely \(x_i \ln x_i + x_j \ln x_j\) results in the extremely simple Guggenheim form for the excess free energy of mixing, \(A^E = G^E\),

\[
G^E/RT = X_{ij} \frac{\omega_{ij}}{RT} \quad (t_{4''}) \quad (104)
\]

In the present work, the name \(t_{4''}\) is assigned this expression, as it will prove to be term \(t_{4''}\) in the general form of the NCZ equation obtained by the end of Chapter 9, although the
formula for $X_{ij}$ will be modified by NCZ effects in that case. Six other "t" terms will be similarly identified as they arise in the two chapters to follow.

8. THE $G^E$ EXPRESSION FOR THE CORRESPONDING NCZ CASE

A. General

Leaving aside for the moment the question of mass-law expressions* for $X_{ij}$, the reduction of equation (94) in the NCZ case is now undertaken. In this case the neat cancellations which were possible in the constant-$z$ case above can no longer be made.

The spirit of the investigation at this point was one of developing the algebraic consequences of the NCZ idea, insofar as possible, as an exercise in dead-reckoning, and not to discard terms for the sake of conformity with any preconceived ideas as to what the results should look like. Next, terms were reduced to as elegant a form as possible to aid in physical and thermodynamic identification; in some cases certain formal simplifications had to be forced through simplifying approximations. Care was exercised not to introduce too many of these approximations too early, and thereby lose track of the underlying formal method, since the basic approach was

* A section on mass law considerations in included at the end of this chapter.
felt to be both powerful enough and well enough verified on real "constant-z" systems to bear the pressure put on it by the extension. The only point at which the extension appears to be somewhat unclear concerns the coefficient of one of the new terms, which experimental results indicate should differ from the derived value by a factor of \( z/2 \).

B. Primitive Form of the \( G^E \) Expression

By straightforward algebraic manipulation, the NCZ equivalent of equation (104) is obtained, as indicated below.

\[
\frac{G_{\text{mixing}}}{RT} = N \times (\xi_i \ln \xi_i + \xi_j \ln \xi_j) + X_{ij} z_{ij} \frac{\omega_{ij}}{RT} \\
+ (N_i - X_{ij}) \times (1 - z_i/z_s) \frac{z_s \ln q_{i1}^0}{RT} \\
+ (N_j - X_{ij}) \times (1 - z_j/z_s) \frac{z_s \ln q_{j1}^0}{RT} \\
+ X_{ij} (1 - z_i/z_s) \times \left( \frac{z_s \ln q_{i1}^0}{RT} \right)
\]

(105)

Substituting in:

\[
X_{m_{i1}} = (N_i - X_{ij})/N
\]

(106)

* substitutions are leftward conformal with FORTRAN practice. The subscript \( m \) indicates that the proportions are properties of the total molecular population. The significance of this detail emerges in equations (117) to (121) later in the chapter. Note that equation (105) contains approximations. \( N' = N \).
\[ X_{m_{ij}} = (N_j - X_{ij}) / N \] (107)

\[ X_{m_{ij}} = X_{ij} / N \] (108)

and realizing that formally,

\[ \frac{z_s}{2} \ln q_{jj}^o = \ln q_{jj}^o z_s / 2 = \ln Q_{jj}^o = -A_j^o / N kT \] (109)

where \( A_j^o \) = the molal Helmholtz free energy of species in the pure component state, one would expect the NCZ equivalent of (104) to be given by

\[
\frac{G_{\text{mixing}}}{RT} = \xi_i \ln \xi_i + \xi_j \ln \xi_j + X_{m_{ij}} z_{ij} \frac{\omega_{ij}}{RT} \\
-\{X_{m_{ij}} (1 - z_i / z_s) \frac{A_i^o}{RT} \} \\
+ X_{m_{ij}} (1 - z_j / z_s) \frac{A_j^o}{RT} \\
+ X_{m_{ij}} (1 - z_{ij} / z_s) \times (A_i^o + A_j^o) / RT \}
\]

(110)

C. The Problem of the Free Energy Constant

1. Quantitive Difficulty

However it is found that (110) overstates each of the terms included in the braces \{ \} by a factor of very approximately
The reason evidently lies in the assumption that the like-pairs bundle partition functions are functions strictly as simple as is implied by equation (90). In fact, it is found that (110) gives better results upon replacing $A_i^0$ by

$$a_i^0 = \frac{|A_i^0|}{(z_{s/2})}$$

(111)

a substitution which however has apparent mass law implications not yet fully understood by the author.

2. Qualitative Justification

However, a justification of the basic free energy nature of the $a_i^0$ coefficient is given experimentally by the markedly different temperature dependence of the heat of mixing and NCZ free energy terms. Whereas $\omega_{ij}$ is either constant with increasing temperature (dispersion energy case), or rapidly attenuating with increasing temperature (dipole energy case), $|a_i^0|$ and $|a_j^0|$ increase at increased temperature, such that $|a_i^0|_{RT}$ has a much slighter rate of temperature attenuation than would a heat of mixing effect.

D. Other Considerations Involved in the Coefficient a

As a brief aside on the question of the "a" coefficient at this point, a thermodynamic condition for equilibrium is given by

$$\left(\frac{\partial A}{\partial v}\right)_{T, N_1} = 0$$

(112)
That the form of $a_{1}^{\circ}$ and $a_{2}^{\circ}$ also represents an oversimplification will be evident if a Taylor's series in $A(z_{i} z_{j})$ is related to one in $A(\bar{v}_{i}, \bar{v}_{j})$ through the approximate relations between $z_{i}$ and $\bar{v}_{i}$. (See equations (58), (59) and (69)). Equation (110) would be 'exact' if there were no thermodynamic difference between total energies and free energies. Remembering that the form of $q_{ii}$ is given by

$$q_{ii} = (e^{-\varepsilon_{ii}/kT})^{v_{f_{i-1}}^{1}}$$ (113)

In equation (113) where $v_{f_{i-1}}$ is the volume-of-integration appropriate to a pair, the assumption that the ratio of volume fractions in the mixing term, i.e., in the ratio

$$\frac{v_{f_{i-1}} v_{f_{i-j}}}{v_{f_{i-j}} v_{f_{i-j}}} = 1$$ (114)

is a good approximation. However, there is no such approximation to help dispose of the $v_{f_{i-1}}$ factors present in the terms in braces in (110), so that, in order to avoid evaluating the $v_{f_{i-1}}$ factors explicitly, they are left combined with their Boltzmann factors, and the whole term containing them is evaluated as a free energy. The total cohesion per mole of the solution is changed on mixing by changes in the strength of pair bonds, as reflected by
\[
X_{mi} (1 - z_i/z_s) \times (-\varepsilon_{ii} \times z_i/2) + X_{mj} (1 - z_j/z_s) \times (-\varepsilon_{jj} \times z_j/2)
\]

\[+
X_{mj} (1 - z_{ij}/z_s) \times (-[\varepsilon_{ii} + \varepsilon_{jj}] \times z_{ij}/2)
\]

(115)

However, the change in the total pairs populations' free energy also depends on a similar function in \(\frac{z_{ij}}{2} \ln \nu_{ij} \), which partly compensates the NCZ cohesion change shown.

### E. \(G^E\) in Terms of Pairs Concentrations

Finally, it is required to express the molecular pairs concentration terms in equation (110) by \(X_{ij}, X_{ii}\) and \(X_{jj}\), noting that

\[
X_{ii} = \xi_i - X_{ij}
\]

(116)

and

\[
X_{jj} = \xi_j - X_{ij}
\]

(117)

by their relation to the population pairs functions

\[
X_{mj} = X_{ij} \times z_{ave}/z_{ij}
\]

(118)

\[
X_{mi} = X_{ii} \times z_{ave}/z_i
\]

(119)

\[
X_{jj} = X_{ij} \times z_{ave}/z_j
\]

(120)
The $X_{ij}$ pairs concentrations are proportions of a population of pairs treated as being $z_{\text{ave}}$-coordinated. The $X_{ij}$ form is more convenient to calculate in the multicomponent case, so is introduced here in the interest of consistency. The coordination number ratios relate the $X_{ij}$ to the $X_{m_{jj}}$ pairs concentrations actually arising in the derivation.

F. The Final NCZ Expression for a Monofunctional Monomer

Binary

Making the approximation

$$\frac{G^E(\Pi)}{RT} \approx \frac{A^E(V)}{RT}$$

(121)

one obtains:

$$\frac{G^E(\Pi)}{RT} = \{c_1 \ln c_1 + c_j \ln c_j - (x_i \ln x_i + x_j \ln x_j)\}$$

(t)

$$+ X_{ij} \frac{z_{ij} \omega_{ij}}{RT}$$

(t''')

$$+ \{x_{ii} (1 - z_i/z_{ij})(z_{ij}^i z_i^o a_i^o)/RT + x_{jj} (1-z_j/z_{ij})(z_{ij}^j z_j^o a_j^o)/RT\}$$

(122)

Equation (122) is the form of the NCZ equation for a monofunctional monomer binary mixture.

In equation (122), two more terms of the general expression for $G^E$ have arisen, namely $t_1$ and $t_5$, and the form of $t_4''$ has been altered. Note that the approximation
\[ z_{\text{ave}} = z_{ij} \] (123)

has been made, and that the ideal entropy of mixing term 
\((x_i \ln x_i + x_j \ln x_j)\) has been subtracted in term \(t_1\) of equation (122) to arrive at the usual definition of excess energy, \(G^E\). Equation (122) is the form usable for many mixtures of fairly round monomers of unequal size, and of rather low \(\omega_{ij}\), in which there is only one kind of functional group on each molecular species.

9. MASS LAW CONSIDERATIONS

A. The Simplest NCZ Form

Although investigations of the forms of the mass law, and the problems associated with the constant-volume nature of the formulations of quasichemical theory, really do not fit very concordantly into the development of the mainstream of development of thought at this particular point; still they constitute considerations which must be borne in mind (and will have to be referred back to from the next chapter) before the NCZ equation can be generalized, as at least the former causes serious problems when attempts are made to apply quasichemical theory to mixtures of more than two components. The latter is another limitation of quasichemical theories, but can be shown to be of a much less serious nature than the former. It is therefore proposed to conclude the more formal discussion.
of this chapter with these two somewhat apocryphal topics, hoping not to try the reader's patience too far in the process.

It was mentioned, apropos equation (122), that the formula for $X_{ij}$ resulted from mass-law considerations. Since these are modified in the NCZ case, a brief account of the relations should be included for the case of a binary mixture.

The mass law expression for $X_{ij}$ is one consistent with the constraint of lowest system free energy, characterized as

$$A_{\text{mix}} \rightarrow \text{minimum.} \quad (124)$$

Because

$$A_{\text{mix}} = -kT \ln Q_{\text{mix}} \quad (125)$$

and since $Q_{\text{mix}}$ can be formulated in terms of $X_{ij}$, the unknown equilibrium pairs population, it is possible to solve for $X_{ij}$ through solution of the extremum condition

$$\frac{\partial \ln Q_{\text{mix}}}{\partial X_{ij}} = 0 \quad (126)$$

operating upon a suitable formulation for the molar scale mixture partition function, then relating $X_{ij}$ to $X_{ij}$ through equation (101).

The NCZ case mass-law expression is computed from the perturbed mixture partition function shown by equation (127).
\[ Q'(N) = \frac{(z_i/z_{ij}^N_1 + z_j/z_{ij}^N_1)!(z_i/z_{ij}^N_2 + z_j/z_{ij}^N_2)!}{(z_i/z_{ij}^N_1)!(z_j/z_{ij}^N_2)!} \]

\[ \times \left\{ \frac{z_{ij}^*(z_i/z_{ij}^N_1 - X_{ij}^*)! [z_{ij}^*(z_j/z_{ij}^N_1 - X_{ij}^*)!] [z_{ij}^*(z_i/z_{ij}^N_2 - X_{ij}^*)!] [z_{ij}^*(z_j/z_{ij}^N_2 - X_{ij}^*)]!}{[z_{ij}^*(z_i/z_{ij}^N_1 - X_{ij}^*)!] [z_{ij}^*(z_j/z_{ij}^N_1 - X_{ij}^*)!] [z_{ij}^*(z_i/z_{ij}^N_2 - X_{ij}^*)!] [z_{ij}^*(z_j/z_{ij}^N_2 - X_{ij}^*)]!} \right\} \]

\[ \left[ \frac{q_{ii}^{z/2}(N_i - X_{ij}^*)}{q_{ij}^{z/2}} \right] \left[ \frac{q_{jj}^{z/2}(N_j - X_{ij}^*)}{q_{ij}^{z/2}} \right] \left[ \frac{q_{ij}^{z_{ij}^*/2}X_{ij}}{q_{ij}^{z_{ij}^*/2}} \right] \left[ \frac{q_{ij}^{z_{ij}^*/2}X_{ij}}{q_{ij}^{z_{ij}^*/2}} \right] \]

This is the same form as the mixture partition function of equation (93'), except for the inclusion of the term in braces above.

The term in braces is the ratio of the combinatorial degeneracy of the pairs assemblage in the maximum randomness case, in which \( \omega_{ij} \) is zero, where the equilibrium unlike pairs population is given by \( z_{ij}^*/2X_{ij}^* \), to that of the pairs assemblage in the actual case in which \( \omega_{ij} \) is nonzero, resulting in an equilibrium unlike pairs population \( z_{ij}^*/2X_{ij} \). Note that in carrying out the operations indicated by equation (126), \( X_{ij}^* \) is not a function of \( X_{ij} \), nor is \( \Omega' \) (the first term of \( Q''(N) \), as expanded in equation (127)).

Substituting equation (127) into equation (126), and computing the expression for the partial derivative with respect to \( X_{ij} \), and rearranging, yields the mass law expression.
\[
\frac{X_{ij}}{X_{ij}^2} = e^{\frac{-2\omega_{ij}}{RT}}
\] (128)

whence

\[
X_{ij} = \frac{[z_i/z_{ij}N_i] \times [z_j/z_{ij}N_j]}{[z_i/z_{ij}N_i + z_j/z_{ij}N_j]} \times \frac{2}{(\beta_{ij}' + 1)}
\] (129)

\(X_{ij}\) (is the proportion of the total pairs population which are \(i-j\)'s) is given by

\[
X_{ij} = \frac{X_{ij}}{[z_i/z_{ij}N_i + z_j/z_{ij}N_j]}
\] (130)

\[
= [(z_i/z_{ij})x_i + (z_j/z_{ij})x_j] \times \xi_i \xi_j \times \frac{2}{(\beta_{ij}' + 1)}
\] (131)

where now

\[
\beta_{ij}' = (1 + 4 \xi_i \xi_j [e^{\frac{2\omega_{ij}}{RT}} - 1])^{1/2}
\] (132)
If all values of $z$ are made equal, the above relations reduce to those resulting in the constant-$z$ mass law expression for a binary.

B. Approximations Involved in Using Mass-Law-Average Concentrations

Rushbrooke\(^{(45)}\) showed that the use of mass-law average pairs concentration in a free energy expression is not strictly correct, though is within a few percent for moderate values of $\omega_{ij}$. This approximation is incorporated in the present work.

C. More Formally Correct Form of the Mass Law Expression

The more strictly correct form for the mass-law expression than equation (128) is obtained by leaving terms of the perturbation term of the expression in $[z_i/2(N_i - X_{ij})]$! form, which results in

$$X_{ij} = \frac{X_{ij} X_{ij}}{(N_i - X_{ij}) z_i/z_{ij} x (N_j - X_{ij}) z_j/z_{ij}} e^{-2\omega_{ij}/RT} \tag{133}$$

which may be (only approximately) solved for $X_{ij}$

$$X_{mij} = X_{ij}/N = [(x_i)_{z_i/z_{ij}}] \cdot [(x_j)_{z_j/z_{ij}}] \cdot 2/(\beta_{ij+1}) \tag{134}$$

where the concentration function in $\beta_{ij}$ are also $[(x_i)_{z_i/z_{ij}}]$ and $[(x_j)_{z_j/z_{ij}}]$. Hence while the concentration function $[\xi_a]$ is more tractable than $[x_a] z_{ave}$, especially for later generalization into the multicomponent case, it somewhat understates the NCZ effect at higher ratios, i.e. is seen to provide a conservative estimate of NCZ effects. Note also in both forms of
the mass law expression the value of $\omega_{ij}$ arising from straightforward substitution of equation (127) into equation (126) is

$$\omega''_{ij} = [\varepsilon_{ij} - \frac{1}{2}(z_i/z_{ij})\varepsilon_{ii} + (z_j/z_{ij})\varepsilon_{jj}]$$

while the form shown in equation (128) is the same form as in CZ quasichemical theory, namely

$$\omega_{ij} = [\varepsilon_{ij} - \frac{1}{2}(\varepsilon_{ii} + \varepsilon_{jj})]$$

The reason for using $\omega_{ij}$ is that $\omega_{ij}$ corresponds closely to $\omega'_{ij}$, the net energy of the unlike pairs 'reaction' of the overall mixing process (i.e., where the components start in pure component form, $z_s$ coordinated, and end up in the mixture, with unlike-pairs pair-bundles being $z_{ij}$ coordinated). While, where bundle size is

$$(z_i/2) \neq (z_{ij}/2)$$

$\omega''_{ij}$ is compositionally dependent through a dependence* of $z_a$ on $z_a$, $\omega'_{ij}$ is very insensitive to composition since in equation (82), $z_{ij} = z_s$. Since little is gained using $\omega'_{ij}$ in place of $\omega_{ij}$, it was decided to use $\omega_{ij}$, the constant-$z$ case value, for the sake of simplicity.

* remember that $z_i$ and $z_a$ are interchangeable for a mono-functional species $a$ containing only i-type functional groups.
10. **EFFECT OF VOLUME CHANGES UPON ESTIMATES OF G^E AND H^E**

The problem of the effect of volume of mixing changes upon estimates of G^E and H^E was introduced in Chapter 4, where it was indicated that G^E is insensitive to V^E (the excess volume, or volume change due to mixing), whereas H^E was sensitive to V^E. How these conclusions are reached is illustrated by considering the difference in the response of H and G to V in an equilibrium mixture. At low pressure (in the atmospheric pressure range) for a liquid,

\[ G(T,\Pi) = A(T,V) \]  \hspace{1cm} (137)

The condition of equilibrium in a mixture is a condition on the free energy, and not on the total energy, of the system.

Thus, to a close approximation, because of equation (137) the equilibrium condition is that

\[ \delta A(T,V) = 0 \]  \hspace{1cm} (138)

which ensures that

\[ \frac{\partial^2 A}{\partial V^2} T, \text{ equilibrium} = 0 \]  \hspace{1cm} (139)

Hence it will be realized that the variation of the free energy with respect to volume changes due to mixing (namely due to V^E) must be of no lower order than 2 mathematically in the mixture at equilibrium. However, since the equilibrium condition is not a restriction on H, per se, \( \frac{\partial H}{\partial V} T,\Pi \)
would not be expected to be zero in the equilibrium mixture, nor is it in practice. Thus the integral of this quantity with respect to V over limits zero to $V^E$, representing the effect of $V^E$ upon $H^E$, could also not be expected to be negligible.

A correction for the second order $V^E$ dependency of $G^E$ can of course be added to the constant volume $G^E$ result, although the difficulties in calculating the correction are such that it may well have to be ignored. This correction term cannot be calculated directly by the methods of this thesis, but Scatchard \(^{(12)}\) gives a detailed analysis of the errors likely to be incurred by its omission.

Problems arising out of ignoring the effects of volume changes only become serious when heat of mixing estimates made from quasichemical $G^E$ expressions are being considered. $H^E$ expressions obtained by abstracting the $H$ terms out of the $G^E$ expression are not themselves complete estimates of $H^E$ (nor are they, in consequence, accurate), though such $H^E$ expressions are compatible with the $G^E$ expression from which they came.

If $G^E_V$ is expressed as a group of constant-volume terms (grouped as $G^E$), and a second group of terms explicit in $V^E_P$ (the excess volume at constant pressure) is appended, one obtains the formalism

$$G^E_V = H^E_V - TS^E_V - \sum x_i \ln x_i$$

\(^{(140)}\)
But

\[ A_V^E = G_P^E = \{H_V^E + TS_V^E - \sum x_i \ln x_i \} + \{H(V_p^E) - TS(V_p^E)\} \]  

(141)

The foregoing expressions employ Scatchard's scheme of notation. The second group of terms in braces in equation (141) represents the effects of \( V^E \) upon \( G^E \) under the isobaric conditions which exist in distillation columns.

If

\[ \frac{\partial A}{\partial V} \to 0 \]  

(142)

as a condition of equilibrium, then

\[ H(V_p^E) = TS(V_p^E) . \]  

(143)

This would be true even though the \( H(V^E) \) component of the heat of mixing terms may in fact be large, and in some cases of opposite sign to \( H_V^E \).

The value of \( H^E \) determined from the temperature dependence of \( G^E \) via the Gibbs Helmholtz relation, namely

\[ H^E = -RT^2 \frac{\partial (G^E/RT)}{\partial T} \]  

(144)

is \( H_V^E \), not
Similarly, if the temperature dependence of an activity coefficient is to be predicted from the partial molal form of equation (144), namely

\[ \frac{\partial \ln y_i}{\partial T} = \frac{(G_i^E/RT)}{\partial T} = - \frac{H_i^E}{RT} \]  

(146)

the partial molal heat of mixing at constant volume \( H_i^V \) is the quantity involved. Thus, values of \( H_i^E \) obtained via the Gibbs Helmholtz equation starting from quasichemical estimates of \( G_i^E \) are estimates of \( H_i^E \) obtained by summing directly the explicit \( H_i^E \) terms of the \( G_i^E \) expression and are thus estimates of heat of mixing at constant volume.

If isobaric \( H_i^E \) values are desired, as is the case for distillation column plate heat balances, the prediction of \( H_i^E \) by the quasichemical method is incomplete. This problem is common to all cell-theory approaches to \( G_i^E \) and \( H_i^E \).

It should be noted that vapor pressure responds exponentially to \( G_i^E \) changes, whereas the heat balance responds only linearly to heat of mixing changes (or to the degree of mis-estimate in heat of mixing resulting from using \( H_i^V \)).

In placing the above observation into the context of distillation column calculations, the conclusion is that vapor pressures and activity coefficients are sensitive functions of
G^E, but not of V^E, whereas though phase flows are not usually sensitive to H^E, H^E is sensitive to V^E. In practice, as was mentioned in Chapter 1, one is somewhat saved in this respect by the usually greater importance of partial vapor pressure changes (induced by \( \gamma \) effects) in column calculations than of operating line curvature effects due to changes in partial molal enthalpies with change in composition of the distilling mixture, except at close to minimum reflux ratios.

11. EXPERIMENTAL EVIDENCE FOR NCZ EFFECTS IN REAL SOLUTIONS

A. General

The chapter is concluded with a discussion of two examples of the predictive use of equation (122) which have been chosen to provide evidence for the existence of NCZ effects in real solutions.

For the purpose of examining the equation (122), a search was made for experimental data for monofunctional 'monomer' binaries which would pre-eminently display effects of disparity of molecular size. Later in this work additional terms will be added to equation (122), and the significance of these will be tested in due course. Now it is the intention to examine systems which can be described satisfactorily by the three terms, \( t_1 \), \( t_4'' \), and \( t_5 \), so far obtained.

The search for monofunctional molecules of very unequal size in binary mixtures led to systems which had been used by Hildebrand\(^{(24)}\) as a test for his Solubility Parameter theory, and were regarded by him as extreme examples of such
systems. The first system to be examined will be perfluoro-n-heptane carbon tetrachloride (a liquid-liquid equilibrium system). The choice of a liquid-liquid system arises because extreme molecular size disparity will (normally) result in extreme liquid non-ideality and, in the limit, liquid immiscibility.

Figure 1 shows the excess free energy of such a mixture (curve a) and the ideal free energy of mixing (k). Forming the algebraic sum of a and k gives the free energy of the mixture (curve η). Common tangent PQ drawn to curve η locates the composition of the coexisting liquid phases.

This is true because of the requirement that the chemical potential of a given species be the same in two phases at equilibrium. Because the chemical potential of a component i, is defined* by

\[ \mu_i = \mu_i^0 + RT \ln a_i \]  \hspace{1cm} (147)

where

\[ \mu_i = \frac{\partial G}{\partial n_i} n_j = \text{const} \]  \hspace{1cm} (148)

* In equation (146), in notation consistent with standard texts, such as Hougen, Watson and Ragatz, \( a_i \) stands for the activity of component i. Thus in equation (147), \( a_i = \gamma_i x_i \). Here also, \( n_i \) stands for the population of molecules of the \( i^{\text{th}} \) species.
Figure 1. Location of Consolute Compositions.
Then for a two component system, equation (147) is represented by the tangent to the $G_{\text{mix}}$ versus composition curve at any point. If the $G_{\text{mix}}$ versus composition curve is inflected such that it admits of two tangents of the same slope (a "common tangent"), the two points of tangency mark the compositions of the two liquid phases in equilibrium (47).

Figure 1 is drawn for a given constant value of temperature. For systems in which the variation of free energy with temperature is to be examined, the constructions of Figure 1 must be repeated at the various temperatures required. In constructing a consolute envelope from data such as Figure 1, a series of curves such as $n$ must be determined at different temperatures. From the curves, sets of points PQ are obtained, and the phase compositions plotted against temperature. In using such a method it should be noted that in many cases, $h$ is small, and drawing tangents accurately is therefore difficult. In extreme cases, careful plotting and closely spaced points on the $G_{\text{mix}}/RT$ versus $x$, curve are required for accurate location of the phase compositions.

If $h$ is small it is because the phases change little in $u_i$ with $x_i$. Thus, for such a system, phases separate with difficulty. This is consistent with the observation of Hildebrand and co-workers that certain binary mixtures containing large fluorocarbon compounds took a very long time to come to phase equilibrium from an initially turbid state (particularly in the region just below the upper critical solution temperature (48)). In other words
when the "energy preference" of the system for two phases instead of one was very slight, achievement of two phase equilibrium was correspondingly slow.

B. Perfluoro-n-Heptane Carbon Tetrachloride

Figure 2(a) plots the values of \( t_1 \), \( t_5 \), and \( t_4'' \) against \( x_1 \) at 40° C. Because it is frequently desired to separate the effects of those terms in the NCZ equation which arise only in the case of nonconstant coordination number, from others (such as the simple heat of mixing effect given by \( t_4'' \)), the combined curve \( (t_1 + t_5) \) is usually drawn. This is the case in Figure 2(b). The values for \( t_4'' \), \( (t_1 + t_5) \), and \( k \), the ideal free energy of mixing curve are added to give curve \( n \) of Figure 2(c) upon which the constructions of Figure 1(b) can be performed.

The operations used to produce Figure 2 (at 40° C) have been repeated at 50° C, 60° C, and 70° C, and are shown as the series Figures 2(d). The resulting pairs of consolute points PQ are plotted against temperature in Figure 2(e)**

Also shown in Figure 2(e) is the experimentally determined curve (46).

* System (5) in the classification system of Chapter 10.

** The calculation program used was for a general form of the NCZ equation (equation (212)), which reduces to equation (122) to within terms of a trivial size for the given system. These additional terms are included in \( n \) but are not displayed individually in the above Figures.
Figure 2(a). Perfluoro-n-heptane Carbon tetrachloride.

NCZ Component Curves at 40°C.
Figure 2(b) and 2(c). Perfluoro-n-heptane Carbon tetrachloride.
Component and Sum Curves for Free Energy
at 40°C.
Figure 2(d). Perfluoro-n-heptane. Carbon tetrachloride. As above, at 40, 50, 60 and 70°C.
Figure 2(e). Perfluoro-n-heptane Carbon tetrachloride. Consolute Envelope. Calculated and Experimental.
The basic shapes of the curves produced by $t_{1''}$, $t_1$ and $t_5$ remain substantially unchanged over the temperature range considered, but their respective amplitudes do change (see Figure 2(d)). The overall result is to force the critical solution composition of the system well away from the eqimolecular, towards mixtures rich in the smaller component. The prediction of critical solution compositions in this region, using a physical argument basically different from that of Hildebrand is one feature making an equation based on NCZ of real interest.

For comparison, also shown on Figure 2(e) is a curve calculated from the Solubility Parameter expression for excess free energy. For this expression, the difference between actual literature values of the solubility parameter for Perfluoro-n-Heptane ($\delta_1 = 6.0$) and Carbon Tetrachloride ($\delta_2 = 8.6$) was not great enough to produce two liquid phases. The solubility parameter curve for comparison in Figure 2(e) involves an assumed value of $\delta_1 = 5.6$. A somewhat better fit might have been obtained by attenuating the difference $(\delta_1 - \delta_2)^2$ with increasing temperature, as has been suggested by Hildebrand, but this line of refinement was not pursued.

As in the case of the NCZ equation, the free energy of mixing curve resulting from the Solubility Parameter expression inflects only just sufficiently to permit the drawing of the common tangent indicative of the existence of two liquid phases. This is particularly true near the upper critical solution temperature. This is the phenomenon associable with vanishingly
small values of $h$ in Figure 1, discussed earlier. The fit of the two curves (namely those obtained from NCZ and Solubility Parameter expressions) in this system should be regarded as equally good, though the assumptions about the liquid behaviour underlying the two models are significantly different.

C. Pentaerythritol Tetraperfluorobutrate Chloroform*

This system is very similar in general character to the Perfluoro-n-Heptane-Carbon Tetrachloride system. The difference is quantitative rather than qualitative inasmuch as the amplitude of the curve generated by $(t_1 + t_5)$ is much greater than in the previous system. In this latter case $(t_1 + t_5)$ dominates in locating the two-phase region rather than operating in concert with the $t_{4''}$ term as was the case in the previous system. The curves for the present system are shown in Figure 3(a) all drawn on the same scale; whereas in the previous system curve $(t_1 + t_5)$ was drawn on a greatly expanded scale. For the present system, the sum (curve 3(b)), has therefore the leftward minimum at a much lower concentration of the larger molecule than is the case in the previous system. Repeating these calculations at a series of temperatures, and plotting the appropriate PQ pairs, results in the pairs of circles on Figure 3(c). It is seen that the envelope is narrower, sharper, and closer into the side represented by the smaller molecule.

* System (6) in the general classification system of Chapter 10.
Figure 3(a) and 3(b). Pentaerythritol tetramerperfluorobutyrate Chloroform.

Component and Sum Curves for Free Energy at 20°C.
Figure 3(c). Pentaerythritol tetrafluorobutyrate. Chloroform. Consolute Envelope. Calculated and Experimental.
than is the case in the previous system. Figure 3(c), also includes for comparison purposes the Solubility Parameter prediction for the system, as well as the experimentally determined envelope (24). The relative persistence of the envelope to higher temperatures is due to the positive temperature dependence of \( \frac{a_2^0}{RT} \) and could not have been achieved without it. The Solubility Parameter expression gives a fit (see Figure 3(c)) which is as good as that predicted by the NCZ equation, although the envelope shown results from variation of the Solubility Parameter (\( \delta \)) values by the author to give a best-fit line.

12. SUMMARY

Having demonstrated in these two examples very strong indications that NCZ effects do exist in real solutions, it is now reasonable to proceed to introduce this concept into a general expression for multifunctional multicomponent solutions. This will be the burden of the next chapter, after which more extensive comparisons with experimental data can fruitfully be made.
CHAPTER 9

EXTENSION OF THE NCZ EQUATION TO THE GENERAL CASE OF MULTICOMPONENT MIXTURES

1. GENERAL

2. PAIRS CONCENTRATION FUNCTIONS FOR MORE THAN TWO TYPES OF FUNCTIONAL GROUPS
   A. Insolubility of the Mass-Law Expression for a More Than Bifunctional Mixture
   B. The Pairs Concentration Matrix
   C. Extension of the Pairs-Concentration Matrix to the NCZ Case
   D. Generalization of the Method to Include Multifunctional Species
   E. Calculation of the Energetic Component of Pairs-Concentrations Non-Randomness
   F. Summary of Remarks on the Pairs-Concentration Matrix

3. MODIFICATION OF THE HEAT OF MIXING TERM FOR A MULTIFUNCTIONAL SPECIES

4. HEAT OF MIXING TERMS FOR THE CASE OF n-MER SPECIES

5. ADAPTATION OF TERM $t_5$ (THE PURE COMPONENT FREE ENERGY TERM) TO THE GENERAL CASE

6. ORIGIN OF THE MINOR TERM $t'_5$

7. ADDITIONAL ENTROPY TERMS
A. Configurational Terms (Due to Non-Unit $n_a$ and $n_{ia}$ - Distribution Function Approach

1) Distinction between Partition Function and Distribution Function (Probability) Approaches
2) Application of the Distribution Function Approach
3) Additional Configurational Terms - The Problem of the Correct Scale
4) Additional Scale Considerations in the Presence of n-mer Species
5) The Meaning of $\xi_a$ in an n-mer Containing System
6) Necessity for Separate Methods of Approach for Configurational and Hindered Rotation Entropy Effects
7) Derivation of Additional Configurational Entropy Terms

B. Energetically Hindered Rotational Entropy Term

1) General
2) Description of the Concept of Hindered Rotation
3) Formulation of the Hindered Rotation Effect.
4) Hindered Rotation Terms in Partial Molal Form
5) Derivation of the Hindered Rotation Term
6) Conversion of Results into Desired 'Excess' Form

8. THE GENERAL NCZ EXPRESSION FOR $G^E/RT$
1. GENERAL

In this chapter, the additional complexities of calculating equilibrium pairs concentrations in multifunctional and/or multicomponent mixtures of monomers are first introduced. Then the configurational effects of n-mer components in the NCZ solution are set forth. Next the additional terms for excess free energy arising in the case of strongly associated multifunctional systems are derived. Finally, the terms which have been developed separately in Chapters 6, 7 and 8 are gathered into a final general NCZ equation in which the various effects described appear individually as terms $t_1$ through $t_5$. It will then appear that the goal of deriving an expression the terms of which indicated in one way or another the nonideality of the system, as was described in Chapter 1, has now in fact been achieved.

2. PAIRS CONCENTRATION FUNCTIONS FOR MORE THAN TWO TYPES OF FUNCTIONAL GROUPS

A. Insolubility of the Mass-Law Expression for a More Than Bifunctional Mixture

When three types of like pair species are present in the
mixture instead of two, \( Q''_\text{N} \) (in equation (125) Chapter 8), becomes a function of 3 unlike pairs equilibrium populations, say \( \chi_{ij}, \chi_{jk}, \) and \( \chi_{ik}, \) and in place of a single equation like equation (128) of Chapter 8, a set of 3 coupled pseudoquadratic equations (of order close to 2) arise which are not directly soluble for the three unknowns. Consequently an alternate route must be employed to obtain equilibrium pairs concentrations in the multifunctional case rather than attempting to argue through mass-law type formulations.

**B. The Pairs Concentration Matrix**

A successful alternative approach to this problem was originated by Barker\(^{(19)}\), and with slight modification is adapted herein to the NCZ case. His approach will be reviewed in a form as brief as possible to show the method of incorporating NCZ effects. Development of the method is most easily shown by example. In a binary mixture of equal sized molecules for which \( \omega_{ij} = 0, \) concentration of the \( i-j \) pairs is given by

\[
\chi_{ij} = x_i x_j
\]

(149)

This result can be obtained either formally, by operating on a suitable partition function as in equation (127) in Chapter 8, or intuitively, considering \( x_i \) and \( x_j \) to be the probabilities of two kinds of independent events \( i \) and \( j \) respectively. The concentration of the \( j-i \) pairs is given by their product, again by equation (149). The total concentration of \( i-j \) pairs, when
orientation is not considered, is $2x_i x_j$. The subject of ordering of the unlike pairs of any given configuration of the assemblage did not enter explicitly into discussion of the derivation of the excess free energy expression (in its simplest form in equation (104) for the constant-$z$ case). No distinction was needed between the two possible orientations of unlike pairs ($i$-leftward $i$-$j$ pairs, and $j$-leftward $i$-$j$ pairs, to demonstrate the method of distinction between the two) for energetic purposes. However, equation (104) is equivalent to

$$G^E/RT = (x_{ij} + x_{ji}) \frac{z_{ii} \omega_{ij}}{2 RT}$$  \hspace{1cm} (150)$$

where $\frac{z_{ii} \omega_{ij}}{2}$ is now the reorganization energy per unlike pair bundle. If the possible pairs concentrations are written in a matrix array, the role of orientation becomes both more useful and more apparent. Hence,

$$\begin{pmatrix} x_{ij} & x_{ji} \\ x_{ji} & x_{jj} \end{pmatrix} = \begin{pmatrix} x_i x_i & x_i x_j & x_{ii} & x_{ij} \\ x_i x_j & x_j x_j & x_{ji} & x_{jj} \end{pmatrix}$$  \hspace{1cm} (151)$$

The representation of (151) is used to imply that terms in corresponding matrix locations are equal. For example,

$$x_{ij} x_{ij} = x_{ij}$$  \hspace{1cm} (152)$$

In relation (151), various self-evident regularities may be formalized which may then be extended into cases of more interest. These are as follows:
\[ X_{ij} = X_{ji} \]  

(153)

The concentration pairs matrix is symmetric across the main diagonal.

\[ \sum_j x_i x_j = x_i \sum_j x_j = x_i \]  

(154)

Because

\[ \sum_j x_j = 1 \]  

(155)

Summing over one index "removes" one set of concentrations.

C. Extension of the Pairs-Concentration Matrix to the NCZ Case

In a binary mixture of unequal-sized molecules, relation (151) may be rewritten for relations in terms of contact fractions.

\[ \xi_i \xi_j X_{ii} X_{jj} \]

(156)

\[ \xi_i \xi_j X_{ij} X_{ji} \]
Symmetry relation (153) remains unchanged. The row normalization relation (154) becomes

$$\sum_j \xi_j = \xi \sum_j \xi_j = \xi$$

(157)

because by definition

$$\sum_j \xi_j = 1$$

(158)

If the complications of local energy-induced clustering effects are introduced into relation (158) one could write

$$\xi_i \theta_{ii} \xi_j e^{-\omega_{ij}/RT} \theta_{ij} x_{ii} x_{ij} =$$

$$\xi_i \xi_j e^{-\omega_{ij}/RT} \theta_{ji} \xi_j \theta_{jj} x_{ji} x_{jj}$$

(159)

Auxiliary functions $\theta_{ij}$ are introduced to account for secondary reorganization effects of the primary (Boltzman factor) energetically induced clustering factors in the interacting solution. Obviously, also, since $\omega_{ij} = \omega_{ji}$, the Boltzman factors are equal and symmetric across the main diagonal.
Barker introduced the postulate that the $\theta_{ij}$ were symmetric product functions such that

$$\theta_{ij} = \theta_i \theta_j \quad (160)$$

Array (159) becomes

$$\xi_i \theta_i \theta_i \quad \xi_j \theta_j e^{-\omega_{ij}/RT} \quad \xi_i \theta_i \theta_j \quad x_{ii} \quad x_{ij}$$

$$= \quad \xi_j \theta_j e^{-\omega_{ij}/RT} \quad \xi_i \theta_i \theta_j \quad \xi_j \theta_j \theta_j \quad x_{ji} \quad x_{jj} \quad (161)$$

The real contact fraction concentration variables, $\xi_i$ and $\theta_i$ functions are now replaced by a set of single-indexed pseudo-concentration $X_1$ such that

$$X_1 = \xi_i \theta_i \quad (162)$$

Thus the lefthand array becomes

$$X_i X_1 \quad X_i X_j e^{-\omega_{ij}/RT} \quad x_{ii} \quad x_{ij}$$

$$= \quad X_j e^{-\omega_{ji}/RT} \quad X_j X_j \quad x_{ji} \quad x_{jj} \quad (163)$$

Because assignment of centrality (designated by circling) is arbitrary

$$X_3 = X_1 \quad (164)$$
The set of row normalization restrictions are exemplified by

\[ x^{(i)} \sum_{j} x_{j} e^{-\omega^{(i)}/RT} = \xi_{i} \]  \hspace{1cm} (165)

This may be transposed into an equation set of the form

\[ x^{(i)} = \xi^{(i)}/\sum_{j} x_{j} e^{-\omega^{(i)}/RT} \]  \hspace{1cm} (166)

The equation set (166) is soluble by iterative substitutions of a set of \( x_{j} \) into the right hand side, recalculating a set of \( x^{(i)} \) then resetting \( x^{(i)} = x_{i} \). Convergence occurs within a few iterations. For an initial approximation, the value of \( x_{j} \) is set = \( \xi_{i} \). The circling convention denotes arbitrary 'central-ity' of the row indexed species.

D. Generalization of the Method to Include Multifunctional Species

Relations (163) are in no way restricted to a binary mixture in order to be soluble, as opposed to the method of establishing the \( x_{ij} \) pairs concentrations by means of the mass-law. For multifunctional liquids, if the contact fraction of the \( i^{th} \) type of contact on the \( a^{th} \) molecular species is designated by
and dropping the "a" index (each type of contact species is considered to be a separate species in the matrix) equation set (166) becomes

\[ X_j = \frac{\xi_j}{\xi} \sum_i \frac{\xi_i}{\xi} e^{-\frac{\omega}{RT}} \]  

(168)

where the summation on \( j \) is now over all functional group species on all molecules. That the row-sum normalization condition incorporated in equation set (168) is valid is shown by the true relation

\[ \sum_{i \in a} \xi_i = \xi_a \sum_{i \in a} \eta_i = \xi_a \]  

(169)

E. Calculation of the Energetic Component of Pairs-Concentrations Non-Randomness

If another symmetric matrix whose representative element is given by

\[ u_{ji} = u_{ij} \]  

(170)

is defined by

\[ u_{ji} = \frac{X_{ji}}{(\xi_j \times \xi_i)} - \frac{X_{ij}}{(\xi_j \times \xi_i)} \]  

(171)
then the elements $u_{ij}$ represent the proportionate energy skew effect, or the energetic component of non-randomness pairs association of given j-j pairs interactions. The $u_{ij}$ are used in obtaining the 'hindrance of rotation' entropy term later in the chapter.

F. Summary of Remarks on the Pairs-Concentration Matrix

In summary it is noted that NCZ effects are incorporated in the Barker relations for the equilibrium pairs concentration in the mixture, namely the $X_{ij}$, simply by forcing row sums to equal $\xi_a$, or in the case of multifunctional systems $S_{ia}$. Barker's postulation of the symmetric decomposition of the $\theta_{ij}$ factors into $\theta_i \times \theta_j$ is unproven, and probably overstates the symmetry of the solution. Nevertheless, the method is again justified on the basis of its practical success.

3. MODIFICATION OF THE HEAT OF MIXING TERM FOR A MULTIFUNCTIONAL SPECIES

While the heat of mixing term resulting from unlike pair formation between molecular species for which $\eta_{ia} = 1$ (monofunctional species) remains as shown in (104), namely $X_{ij} \omega_{ij} / RT$, a modification must be made in the form of the heat of mixing terms in the case of multifunctional molecular species (for which $\eta_{ia} < 1$). The correction is again due to the existence of unlike functional group pairing in multifunctional liquids in the pure component state. The reference state for the pairs reorganization reaction is an assemblage in which only like-pairs are present. Hence, when
multifunctional components are present in the mixture, the net change in the amount of a given type of unlike pairing resulting from the mixing process is not simply $X_{i\text{aja}}$ but rather

$$\left(X_{i\text{aja}} - x_a \times \frac{z_s E_a}{z_{\text{ave}}} X_{i\text{aja}}^o\right)$$

(172)

$x_{i\text{aja}}^o$ is the equilibrium concentration of the i-j pair per mole of species "a" in the pure component state. The factor $\frac{z_s E_a}{z_{\text{ave}}}$ corrects for the fact that $X_{i\text{aja}}$ is a proportion of a pairs population whose overall average external coordination number is $z_{\text{ave}}$, whereas the coordination number for the pure component assemblage is $z_s E_a$. The factor $x_a$ accounts for the simple dilution by other components which would be present in an ideal mixture. In an ideal (Raoult's Law) mixture the term given by (172) caused by dilution by $(1 - x_a)$ moles of the other ideal liquids would be zero for all values of $x_a$. While $X_{i\text{aja}}$ by itself is always positive, the net pairs concentration change term may be either positive or negative, depending on the relative strengths of $\omega_{ij}$ factors for possible pairs associations in the mixed and pure component states. For certain highly associated mixtures, the value of

$$\left(X_{i\text{aja}} - x_a \times \frac{z_s E_a}{z_{\text{ave}}} X_{i\text{aja}}^o\right)$$

for the most strongly associating pair species may be positive for part of the concentration range and negative for others.
This behavior contributes to the unusual heat of mixing phenomena often observable in such mixtures.

The final form for the heat of mixing contribution to the excess free energy of mixing for such a general mixture may be written as the sum of two sets of terms, one describing the simple heat of mixing, the other the net heat of mixing of unlike pairs from multifunctional components just discussed. This sum is thus represented as

\[
\sum \sum (n_{ave} x_{i} a_{j} - n_{ave} x_{i} a_{j} x_{ave}^{E} \frac{z_{ave}^{E}}{z_{ave}} \times \frac{z_{ave}^{w_{ij}}}{RT})
\]

\[
+ \sum \sum n_{ave} x_{i} a_{j} b_{j} z_{ave}^{w_{ij}} / RT
\]

(173)

4. HEAT OF MIXING TERMS FOR THE CASE OF n-MER SPECIES

In the final form of the NCZ equation for \( G^{E} / RT \) the effect of concatenation is also taken into consideration by the inclusion of factors \( n_{ave} \) and \( n_{a} \). These factors account for the fact that the final NCZ expression is written for one mole of molecules, which in the case of a mixture whose average chain length is \( n_{ave} \), is \( n_{ave} \) moles of monomer segments. The total population of pairs interactions, hence the total heat of mixing effect, must thus be modified by the appropriate chain-length correction factors. These will be shown included in the final formulation of the heat of mixing terms.
5. ADAPTION OF TERM $t_5$ (THE PURE COMPONENT FREE ENERGY TERM) TO THE GENERAL CASE

For the simplest binary case (equation (122) Chapter 8)

$$
t_5 = x_{ii} \times (1 - z_i/z_{ij}) \times (z_{ij}/z_i) \frac{a_i^o}{RT}
$$

$$
+ x_{jj} \times (1 - z_j/z_{ij}) \times (z_{ij}/z_j) \frac{a_j^o}{RT}
$$

(174)

In the case of a multifunctional molecule, the total amount of self-association of the molecular species is found by adding all the pairs concentration terms for all the types of pairs possible between various functional groups of that type of molecule. This sum is represented by the term

$$
\sum_{i \text{on}^a} \sum_{j \text{on}^a} X_{iaja}^a
$$

(175)

For example, if the molecule were bifunctional, of group types 1 and 2, the sum would then be

$$
x_{1a1a} + x_{1a2a} + x_{2a1a} + x_{2a2a}
$$

(176)

showing that functionally unlike pair types of terms of the Barker $X_{ij}$ matrix are counted twice (once for each ordering) in the sum.

The term $(1 - z_i/z_{ij})$ of the simple binary case (equation (174)) is rewritten for the general case as $1 - (z^a/z^s E^a)$. The term accounting for the transformation from $X$ to $X_m$ form is no longer written as
(z_{ij}/z_i), but as (z_{ave}/z_a), where molecular subscripting must replace the site subscripting appropriate to the monofunctional binary mixture case. The approximation \( z_{ave} \approx z_{ij} \) is also made, where \( z_{ave} \) is the overall mixture average external monomer coordination number.

Finally, because \( a_i^o \) is calculated as a molecular scale quantity, the term \( t_5 \) is multiplied by \( n_{ave} \), the mixture average chain length, to convert to the monomer population of a mole of molecules, then divided by \( n_a \) to reduce this monomer population to the number of \( n_a \) length molecules. The generalized form of \( t_5 \) is thus

\[
t_5 = \sum_a \left( \sum_i \sum_j X_{iaj} \right) \times \left( 1 - \frac{z_a}{z_s} \right) \times \left( \frac{z_{ave \ ave}}{z_{ave \ ave}} \right) \times \frac{a_i^o}{RT}
\]

6. **ORIGIN OF THE MINOR TERM \( t'_5 \)**

In multifunctional and/or multicomponent mixtures, another term of the same nature as \( t_5 \) arises, formally due to slight departures of the coordination numbers \( z_{ab} \) (the coordination number analogous to \( z_{ij} \), but for multicomponent multifunctional mixtures) from the self-coordination numbers, namely \( z_s E_a \) and \( z_s E_b \). This term, called \( t'_5 \) was included in the general expression for the sake of completeness, mainly to see whether it ever assumed significant proportions compared with other terms. It did not; so, beyond showing its form, no
further mention will be made of it.

$$t'_3 = \sum_{ab \text{ pairs on } a \neq b} \left( \sum_i x_{iaj}b \cdot \left[ (1 - \frac{z_{ab}}{z_{s \text{ a}}}) \left( \frac{z_{s \text{ b ave}}}{z_{ab \text{ a}}} \right) \frac{a^o}{RT} \right] \right)$$

$$+ (1 - \frac{z_{ab}}{z_{s \text{ b}}} \times \left( \frac{z_{s \text{ b ave}}}{z_{ab \text{ a}}} \right) \frac{a^o}{RT})$$

(178)

7. ADDITIONAL ENTROPY TERMS

A. Configurational Terms (Due to Non-Unit $n_a$ and $n_{1a}$)

Distribution Function Approach

1) Distinction between Partition Function and Distribution Function (Probability) Approaches

The configurational contribution to the value of $\frac{g_{mix}}{RT}$ (the reduced form of the free energy of mixing) for round monomer systems, namely $\sum_a \xi_a \ln \xi_a$ is obtainable by two methods. The one already presented in equation (73), Chapter 7, was to formulate $\Omega'$ which is the combinatorial degeneracy term in the canonical partition function for the mixture, then obtain the free energy terms through the operations on $\Omega'$ indicated by $-kT \ln(\Omega')$. This method is called "the partition function" approach. The second method, called "the distribution function" approach, which has certain formal advantages for the purposes of this section, is now introduced. The term $\sum_a \xi_a \ln \xi_a$ can be obtained directly by expanding the definition of the Boltzmann entropy (78) of the normalized probability distribution representing the classes of 'independent' events present in the system.
2) Application of the Distribution Function Approach

If \( \xi_a \) is the probability of a site type on the \( \text{a}^{\text{th}} \) molecular species, then for a mixture, the normalized probability distribution of events \( \xi_a \) is simply

\[
\sum_a \xi_a = 1
\]  
(179)

and the negative of the Boltzmann entropy is given by

\[
-\frac{S}{k} = \sum_a \xi_a \ln \xi_a
\]  
(180)

where \( k \) is a proportionality constant, in this case equal to \( R \) for a mole of mixture. In the limiting case of constant-\( z \), equation (180) reduces to \( \sum_a x_a \ln x_a \), the ideal mixing term.

The normalized probability distribution for a 'general' liquid can also be formulated in a form explicit in \( \xi_a \) as well as in the additional configurational variables \( n_a \) and \( \eta_{ia} \) to describe \( n \)-mer and multiple functional group type characteristics of the system respectively. The configurational mixing term obtained by expansion of the Boltzmann entropy of its probability distribution can be written in a form in which the \( \sum_a \xi_a \ln \xi_a \) term already obtained, which incorporates the coordination number distortion effect, is a separate term from those in which additional configurational variables \( n_a \) and \( \eta_{ia} \) appear. Since such a separation is desirable for solution-categorization purposes, the probability distribution route is
the one now employed.

3) Additional Configurational Terms – The Problem of the Correct Scale

In the 'partition function' approach to the formulation of excess free energy terms of Chapter 8, the molecular-scale restraint on configurational behavior was built into the partition function by means of bundling of pairs into molecular scale entities. By contrast, in the present 'probability-distribution' approach, instead of 'building-in' such configurational molecular scale constraints into the pairs model a priori, the entropy of the assemblage is first formulated on the "sites" level, though the formalism is written to include the molecular scale probabilities by expressing the sites probabilities as dependent probabilities of the molecular scale ones. Then the molecular scale is established, ex-post, by forcing the final result into a form in which the familiar molecular scale term \( \xi_a \ln \xi_a \) appears as a separate term. Since the latter is the expression to which the general expression must reduce in the special case where \( n_a \) and \( n_{ia} \) become unity, and since \( \xi_a \ln \xi_a \) has already been shown to be consistent with a 'molecular scale' liquid, other terms present in the general expression will also forcibly be consistent with the same correct scale, in an expression which so reduces.

4) Additional Scale Considerations in the Presence of n-mer Species

In the matter of scale it must further be established whether, in the case of a species which behaves as an n-mer,
the proper configurational scale is that of the whole molecule, or whether it is that of a monomer segment. The latter choice is consistent with the Flory-Huggins theory of n-mer solutions. The implication involved is that the entropy based on such an n-mer chain is an upper limit for real (that is less than completely flexible) polymers. However, in the Flory-Huggins treatment, a rigid n-mer has the same entropy as a dimer, since third and higher numbered segments must lie in the line defined by the first two segments placed in the lattice. Also, no distinction exists between the cases of rigid or flexible dimers. The indistinguishableness of rigid and flexible dimer behavior in such a treatment indicates the insensitivity of the entropy of mixing term to assumptions of degree of rigidity for sufficiently short molecules, which are the class of substances most commonly encountered in systems of particular interest in this work. In the approach below, monomer scale is to be taken as the scale corresponding to actual configurational behavior of the liquid, and little further formal attention will be devoted to the question of the rigidity of the short-chain species.

5) The Meaning of $\xi_a$ in an n-mer Containing System

In the general definition of $\xi_a$ for n-mer solutions as used in this work

$$\xi_a = \frac{n \sum a_a a_a a_a}{\Sigma n \sum a_a a_a a_a}$$

(181)

$\xi_a$ is thus the probability of encountering the exterior portion
of a monomer segment of the $a^{th}$ molecular species. $\xi_a$ is thus a monomer-scale quantity in the n-mer solution case, just as it is in the monomer case, obtainable from (181) by reducing all $n_a$ to 1, so that the $E_a$ also become 1 by definition of $E_a$. (See equation (65)).

6) Necessity for Separate Methods of Approach for Configurational and Hindered Rotation Entropy Effects

In a liquid where nonzero $\omega_{ij}$ exist, equilibrium pairs concentrations are no longer exactly given by binary products of appropriate contact fractions, but deviate more or less from such binary products due to energetically induced local clustering. Mathematically, while the pairs probabilities are independent probabilities, because they have been forced to be so by the pairs concentration matrix method as described, they differ from those of an ideal solution. Specifically, they are differently distributed, and thus the entropies of energetically unhindered and energetically hindered distributions will not be the same. In contrast to the treatment of Barker, the net excess free energy component due to energetically induced clustering is, in this work, separated from the purely configurational effects described above. To a first order, these two effects should be separable: the configurational variables $n$ and $R$ describe molecular properties, hence probabilities, and $\omega_{ij}$ describe intra-

*At this point the reader may wish to refer back to the discussion of contact fractions in Chapter 6.
molecular properties and probabilities. The method of estimating the two types of effects thus need not be the same, which considerably simplifies the method of formulation. In the next section it is proposed to deal with the additional configurational effects due to non-unit $n_a$ and $n_{ia}$, and to leave formulation of the effects of the $\omega_{ij}$ to a later section.

7) Derivation of Additional Configurational Entropy Terms

The most detailed possible description of a particular site would be to specify it as a particular type of functional group on a particular segment of a molecule of a particular molecular species. Only a slight loss of specificity (insignificant for purposes of calculation of net mixture properties) would result from counting the total number of contacts of each functional group type, for example those on the $a^{th}$ molecular species, letting $n_{ia}$ be the fraction of the total due to the $i^{th}$ type of functional group, and then to apply $n_{ia}$ equally to each segment. The various segments of the $n$-mer could then be regarded as energetically identical, distinguishable only by relative position on the chain.

Letting $\eta_{ia}$ be the normalized probability of the $i^{th}$ functional group type on the given $A$ segment of the $a^{th}$ molecular species, the probability of its occurrence in the solution would be given by

$$p_{iAa} = \eta_{ia} \times \frac{1}{n_a} \times \xi_a$$  \hspace{1cm} (182)
so that the distribution of all such probabilities, namely

\[ \sum_{\text{all } i,A,a} p_{iAa} = 1 \quad (183) \]

Equation (182) involves the use of dependent probabilities; \( \eta_{ia} \) is mathematically dependent on \( \frac{1}{n_a} \) and \( \frac{1}{\eta_{a}} \) is mathematically dependent on \( \xi_{a} \). The negative of the Boltzmann entropy of the probability distribution would then be given by

\[ - \frac{S}{k} = \sum_{\text{all } i,A,a} p_{iAa} \ln p_{iAa} \quad (184) \]

Purely mechanical expansion of this definition yields the expression

\[ - \frac{S}{k} = \sum_{a} \xi_{a} \ln \xi_{a} + \sum_{a} \xi_{a} (\sum_{A \text{ on } a} W_{Aa} \ln W_{Aa}) \]

\[ + \sum_{a} \xi_{a} \times \left[ \sum_{A \text{ on } a} (\sum_{i \text{ on } A} \eta_{iAa} \ln \eta_{iAa}) \right] \quad (185) \]

Here \( W_{A} \) is the probability of the \( A^{th} \) segment on the \( a^{th} \) molecular species. Allowing \( \eta_{ia} \) to be the site fraction of site type \( i \) on an average segment of molecule 'a', and also now dropping the distinction between segments on a given molecular species so that

\[ W_{Aa} = W_{Ba} = \frac{1}{n_{a}} \quad (186) \]
equation (185) is reduced to

\[- \frac{S}{k} \text{ (configurational)} = \sum \xi_a \ln \xi_a + \sum \xi_a \times [-\ln \eta_a + \left( \sum \eta_{ia} \ln \eta_{ia} \right)]\]

(187)

The additional configuration terms are grouped by the second summation of the expression.

**B. Energetically Hindered Rotational Entropy Term**

1) General

In the section on calculation of pairs concentrations in the general case (see section 2D.) the elements of the \(u_{ij}\) matrix were defined as the ratio of actual equilibrium pairs concentrations (the \(X_{ij}\)) to those (the \(\times \) products) in a solution in which all \(w_{ij}\) were zero. When at least one of the energies of net pairs rearrangement (one of the \(w_{ij}\) terms) is nonzero in the mixture, energetically induced clustering effects are reflected in non-unit values of the \(u_{ij}\) terms. Explicitly, for such a solution:

\[u_{ij} \neq 1\]

(188)

When such local clustering effects become significant, they give rise to an excess free energy of mixing effect characterized by Barker as the 'hindrance of rotation entropy effect'.
2) Description of the Concept of Hindered Rotation

Consideration of the rotational behavior of an arbitrarily chosen 'central' molecule within its nearest neighbor 'cage' serves to illustrate the aptness of the hindrance of rotation description attributed to the effect in question. If sites on the 'central' molecule can give rise to values of $\omega_{ij}$ of various magnitudes with the contacts of various members of its nearest neighbor shell, the central molecule will tend to spend a disproportionately large amount of its time in orientations for which $\omega$ is strongly negative ("binding") and correspondingly less in orientations where $\omega$ is zero or positive ("unbinding"). This partial alignment tendency will be reflected as a partial decrease in the central molecule's full 3-dimensional rotational freedom within the neighbor case above and beyond the restrictions imposed by the geometry of the molecule. The central molecule's rotational degrees of freedom will thus be fractionally decreased hence the central molecule's contribution to the rotational entropy of the system will be correspondingly decreased. The overall result of the hindrance of the rotation of a species is an increase in the partial molar free energy of that species.

3) Formulation of the Hindered Rotation Effect.

Since any arbitrarily chosen central monamer unit is bound by $z_1/2$ pairs cohesions simultaneously, it is necessary to formulate first the energetically induced nonrandomness component of the Boltzman entropy of the actual pairs distribution in terms of the $u_{ij}$ component matrix and then to transform this result to apply to a distribution of $z/2$ grouped simultaneous events.
4) Hindered Rotation Terms in Partial Molal Form

When one realizes, however, that each molecular species is associated with its own specific coordination number, the actual transformation to an expression involving the appropriate coordination number effects becomes somewhat more intricate than the general procedure just outlined would indicate. In fact, the nonrandomness component of the entropy of the pairs distribution must be rewritten in partial molal form so that each partial molal entropy component may be multiplied separately by its own appropriate coordination number effect, and the individual results combined into a mole fraction weighted average which constitutes the final result.

5) Derivation of the Hindered Rotation Term

The procedure may be made explicit as follows:

If a (new) general probability $p_i$ of an individual event $i$, is now considered and normalized so that

$$\sum_i p_i = 1 \quad \text{(189)}$$

then the entropy of such a distribution of 'one-grouped' events is

$$- \frac{S(1)}{k} = \sum_i p_i \ln p_i \quad \text{(190)}$$

If $\eta_{ij}$ is the simultaneous probability of a pair of such independent events, then
\[ p_{ij} = p_i \times p_j \]  \hspace{1cm} (191)

and the entropy of the independent pairs probability distribution can be shown by simple expansion to be

\[ -\frac{S(2)}{k} = \sum_{i,j} p_{ij} \ln p_{ij} = 2 \times (-\frac{S(1)}{k}) \]  \hspace{1cm} (192)

In general, for grouping independent events:

\[ S(\text{m-grouped}) = \frac{m}{n} \times S(\text{n-grouped}) \]  \hspace{1cm} (193)

In an energetically random solution of monomers

\[ x_{ij} = \xi_i \times \xi_j \]  \hspace{1cm} (194)

The pair probability \( x_{ij} \) is 2-grouped. The probability of a given set of \( z \) nearest neighbors is that of a \( z \)-group, so that by equation (193),

\[ -\frac{S}{k \text{ const } z} = \frac{z}{2} \times (-\frac{S(\text{pairs})}{k}) \]  \hspace{1cm} (195)

From the definition of partial molal entropy, \( \overline{S}_a \)
is defined operationally by

\[ S = \sum_a x_a \overline{S}_a \]  \hspace{1cm} (196)
Then

\[- \frac{S}{k} (\text{mixture, monomers})^{\text{NCZ effects}} = \sum_{a} \frac{z_{a}}{2} \times a_{a} \times (- \frac{S_{a} (\text{pairs})}{k}) \]  

(197)

This would also apply to perfectly flexible polymers. For perfectly rigid polymers (or very short stiff groups of n-segments)

\[- S (\text{mixture, n-mers})^{\text{NCZ effects}} = \sum_{a} \frac{n_{a} z_{a}}{2} \times a_{a} \times (- \frac{S_{a} (\text{pairs})}{k}) \]  

(198)

In general, one could think of \( n'_{a} \) as the equivalent 'stiff-polymer' chain length, not necessarily simply related to structural chain length. This stiff polymer chain length is usually in the order of 1 to 5.

\[ n'_{a} < n_{a} \]  

(199)

For an infinitely flexible polymer \( n'_{a} \) is always equal to 1. The pairs entropy of the unhindered solution can now be designated* as \( S^{R}(ij) \) such that

\[- \frac{S^{R}(ij)}{k} = \sum_{i,j} x^{R}_{ij} \ln x^{R}_{ij} = \sum_{i,j} \frac{S_{i} S_{j}}{i} \ln (\frac{S_{i} S_{j}}{i}) \]  

(200)

* Superscript R, stands for "random", superscript NR stands for "non-random", and superscript NR-R stands for the net non-randomness component (non-random minus random), as in the ex-

Continued
The actual (energetically clustered) pairs entropy is given by $S^{NR}_{ij}$

$$-\frac{S^{NR}_{ij}}{k} = \sum_{i,j} x^{NR}_{ij} \ln x^{NR}_{ij} = \sum_{i,j} s_i s_j u_{ij} \ln(s_i s_j u_{ij})$$  \hspace{1cm} (201)

where $u_{ij}$ is defined by equation (171). If we can expand the difference symbolically as

$$\frac{\Delta G^{NR-R}}{RT} = (-\frac{\Delta S^{NR-R}}{R})_{ij} = (-\frac{S^{NR}}{R}) - (-\frac{S^{N}}{R})$$  \hspace{1cm} (202)

Continued

pression $(-\Delta S^{NR-R})$. The bulkiness of the explicit form for the term in the bracket make it difficult to write in full and is not particularly informative in detail. Thus, after having shown the explicit form of the term, the abbreviation ($\Delta S^{NR-R}$) is retained in the general expression in the above symbolic form for succinctness. The explicit expression by means of which the term is computed is given on p. 200, and also as a footnote under the general excess free energy expression in its final form on p. 205.
into terms of the form $x_a \overline{\theta}_a$, then each of the "$\overline{\theta}_a$" are identified. This is done through the simple mechanism of isolating the coefficient of $x_a$ and identifying it with "$\overline{\theta}_a$" for each component. The $\theta_a$ are then the required partial molal mixture non-randomness terms required for use in equation (196). By expanding the right hand side of equation (201) and that of (200), and subtracting, equation (203) is obtained.

$$-\frac{\Delta S_{NR-R}}{R} = \sum_a \xi_a \times \left\{ \sum_i \eta_i \sum_a x_{ia} \ln \frac{Z_a n_a}{z_{ave} n_{ave}} x_{ia} \left( u_{ij} (1 + 1) - 1 \right) \right\} \ln u_{ij}$$

(203)

Since

$$\xi_a = \frac{Z_a n_a}{z_{ave} n_{ave}} x_a$$

(204)

The term in braces of equation (203), times $\frac{Z_a n_a}{z_{ave} n_{ave}}$, is the $\overline{\theta}_a$ sought. Defining, for the present the term within braces in equation (203) as being represented by $\left\{ \frac{NR-R}{a} \right\}$, then $\left\{ \frac{NR-R}{a} \right\}$ multiplied by $\frac{Z_a n_a}{z_{ave} n_{ave}}$ is equal to $\overline{\theta}_a$.

* $\theta$ is used here simply as a generalized unknown.
\[
- \frac{\Delta S_{NR-R}}{R}^{(mixture, n-mers)} = \sum_a \frac{n'^z a}{2} \frac{z a}{z_{ave}} \frac{n a}{n_{ave}} \times \left\{ \text{NR-R} \right\}_{a} (205)
\]

\[
- \frac{\Delta S_{NR-R}}{R}^{(mixture, n-mers)} = \sum_a \frac{n'^z a}{2} \xi \left\{ \text{NR-R} \right\}_{a} (206)
\]

6) Conversion of Results into Desired 'Excess' Form

Equation (206) now incorporates the new terms present in the free energy of the mixture due to the effects of non-unit \( n_a, n_{ia} \) and \( u_{ij} \) variables.

Because hindrance of rotation can obviously occur in pure multifunctional liquids (such as ethanol or water, for example), the pure component effect must then be subtracted from that for the mixture in order to obtain the net change due to mixing. For \( x_a \) moles of pure component 'a', the new terms in \( n_{ia} \) and \( n_a \) of the second line of equation (187) become of the form

\[
x_a \left\{ -\Delta n_a + \left( \Sigma \eta_{ia} \Delta n_{ia} \right) \right\} (207)
\]

so that the new mixture excess term due to \( n_a \) and \( n_{ia} \) effects is
The form of (206) for \( x_a \) moles of pure component "a" is given by

\[
\Sigma (\xi_i - x_a) \times [-\ln n_a + (\Sigma \eta_i a \ln n_i a)]
\]

(208)

where

\[
\left\{ \eta_i \right\}_{a} = \left\{ \eta_i \right\}_{a}^{NR-R} \times \left[ \sum_{ja} \eta_{ja} (u_{ij}^{o} - 1) \ln \eta_{ja} + u_{ij}^{o} \ln u_{ij}^{o} \right]
\]

(210)

which is the form of \( \left\{ \eta_i \right\}_{a}^{NR-R} \) for pure component a. A term such as \( u_{ij}^{o} \) is the value of \( u_{ij}^{o} \) for pure component "a". For multifunctional molecular species, particularly in the case where functionally unlike groups tend to interact strongly (for example "O" and "H" groups in a pure alcohol) elements of the \( u_{ij}^{o} \) matrix depart strongly from unity. The excess mixing effect corresponding to equation (206) is thus
which is term $t_3$ in the NCZ expression. This term becomes important when liquids of differing polarity are mixed.

8. THE GENERAL NCZ EXPRESSION FOR $\frac{G^E}{RT}$

Since each of the terms of the NCZ equation has been individually set forth by this point, it is now possible to write the NCZ equation for $(G^E/RT)$ for the general case of a multifunctional and/or multicomponent n-mer solution. These terms are assembled in equation (212). (See also reference (49)).
\[ G^E_{\text{RT}} = \sum_{a} \xi_{a} \ln \xi_{a} - x_{a} \ln x_{a} \]

\[ + \Sigma (\xi_{a} - x_{a}) \times [-\ln n_{a} + \left( \sum_{ia} \eta_{ia} \ln \eta_{ia} \right)] \]

\[ + \Sigma n_{ave}^{i} \frac{z}{2} \xi_{a} \times \left\{ \frac{1}{2} - \frac{E^a}{RT} \right\} - \frac{E^a}{RT} \]

\[ + \sum_{a} \frac{z_{ave}}{2} \xi_{a} \times \left\{ \frac{1}{2} - \frac{E^a}{RT} \right\} \]

\[ + \sum_{i a j a} \left[ n_{ave}^{i a j a} - n_{a}^{i a j a} x_{a}^{i a j a} \left( z E_{ave}^{i a j a} \right) \right] \frac{z_{ave}^{i a j a}}{RT} \]

\[ + \sum_{i a j b} \left[ n_{ave}^{i a j a} z_{ave}^{i a j a} \omega_{ij} \right] / RT \]

\[ + \sum_{a} \left( \sum_{i on a, j on b} \xi_{ia j a} \right) \times (1 - z_{ave}^{i a j a} / z_{ave}^{a}) \left( z_{ave}^{n ake} / z_{ave}^{n ake} \right) / \]

\[ + \sum_{a \neq b} \left( \sum_{a \neq b} \xi_{ia j b} \right) \times (1 - z_{ave}^{a b} / z_{ave}^{a b}) \left( z_{ave}^{n ake} / z_{ave}^{n ake} \right) / \]

\[ + (1 - z_{ave}^{a b} / z_{ave}^{a b}) \left( z_{ave}^{n ake} / z_{ave}^{n ake} \right) / \]

\[ (212) \]
1. Notes on General NCZ Equation:

a) $t_i'$ is carried in $G^E/RT$ in calculations but not elsewhere discussed.

b) $\{NR-R\}_{\alpha} = \sum_{j} \eta_{i\alpha} a \times \left[ \sum_{j} \eta_{ja} \left[ u_{ij} n_{ija} - 1 \right] \ln n_{ija} + n_{ija} \ln n_{ija} \right]$.

c) = pure component form of b)

$$\{NR-R\}_{\alpha}^o = \sum_{i\alpha} \eta_{i\alpha} \sum_{ja} \eta_{ja} \left[ u_{ij}^o \ln n_{ija} + n_{ija} \ln n_{ija} \right].$$

d) For simple binary

$$X_{ij} = X_{ab} = \frac{z_a n_a x_a + z_b n_b x_b}{(n_a x_a)} \left( n_b x_b \right) \left( X_{ab} \right) \left( 1 - \frac{2 \omega_{ij}}{kT} \right)$$

$$\beta_{ab}' = (1 - 4 \eta_{a} \xi_{b} \left( 1 - \frac{2 \omega_{ij}}{kT} \right))^{\frac{1}{2}}.$$
2. **Multifunctional and/or Multicomponent System**

\[ x_{ij} = x_i x_j e^{-\omega_{ij}/kT} \]

\[ x_i = \text{Barker type pseudocomposition} \]

\[ x_i = \sum_j x_j e^{-\omega_{ij}/RT} \]

obtained by iterating from initial estimate

\[ x_j = s_j \]

on RHS of above equation.

e) \[ \bar{E}_a = [1 - (1 - 2 \psi_a)(n_a - 1)/n_a] \]

\[ \psi_a > 1/z_s \]

\[ \bar{E}_a = \text{exterior fraction of a monomer} \]

\[ \bar{E}_a \to 1 \text{ as } n_a \to 1, \text{ otherwise } \bar{E}_a < 1 \]

\[ n_{a}^{\text{eff}} = \text{effective stiff-polymer chain length} \leq n_a \]

\[ n_{a\text{ave}} = \sum_n n_{a\text{ave}} / \sum x_{a\text{ave}} \]
CHAPTER 10

RELATION OF 2-LIQUID THEORIES TO QUASICHEMICAL THEORIES

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CHAPTER 10

RELATION OF 2-LIQUID THEORIES
TO QUASICHEMICAL THEORIES

1. GENERAL

At this point, two equally important considerations must be attended to:

1) To show the relation of the NCZ equation to more or less related approaches, and
2) To test equation (212) against a wide range of experimental data.

Neither consideration has clear precedence, but the results of one to some extent influence the arguments of the other. The course taken has been rather arbitrarily, to follow through 1), then 2) in this and the succeeding chapter. The discussion of Related Theories in this chapter has been conducted on a relatively fundamental level involving, in particular, point by point comparison of major theoretical precepts of quasichemical theories and 2-liquid theories; whereas in Chapter 11, the comparison with Related Theories is made on the purely practical level. In Chapter 11 the relative performance of various excess free energy prediction theories is compared with the excess free energy versus composition curve derived from experimental results. While each chapter provides insight into the other,
still the reader who is more practically oriented is urged to read Chapter 11 first (or only): the reader who is more theoretically inclined is urged to read both chapters in the order presented.

2. INTRODUCTION

The prediction of liquid mixture excess free energies is but one aspect of the investigation of the liquid state and the predictions of mixture properties for dense liquids which are also nonionic* is but a small part of this. Notwithstanding, the number of nonionic mixture excess free energy predictive expressions is considerable and their detailed formulations not only diverse, but also not in all cases entirely compatible (50). A somewhat detailed examination of the situation is thus required.

The organizing idea of the first section of this chapter is to argue the formal development of Solubility Parameter, Wilson and NRTL (nonrandom 2-liquid) expressions on the one hand, and quasichemical theories on the other from fundamentals, in order to show inherent differences in the partition functions from which the two groups of theories can be shown to result, and then to show points of parallelism and difference in the subsequent steps of the derivations of the two sets of theories.

* See Appendix 1
This is followed by a description of the A.S.O.G. (Associated Solution of Groups) theory, which is a generalization of the Wilson Equation to the groups or 'pairs' level, thus which is also formulated on the energy scale used in quasichemical theories.

To summarize the foregoing arguments in graphic form, some of the chief structural assumptions of quasichemical and 'related' theories discussed are then displayed in Table 1 on p. 248. This is followed by Table 2 which footnotes the brief headings of Table 1 and 'indexes' these with references to specific locations elsewhere in the thesis where the points in question have been dealt with in detail. Thus Table 2 is also useful as a 'point of access' to the thesis for those who wish first to look at the results, and then refer these back to earlier discussions.

Next, the question of 'thermodynamic' criteria of applicability of expressions (as distinct from their wider engineering use as empirical curve-fitting expressions) is briefly discussed in terms of degree of correspondence between 'best fit' and independently measured constants for a given system. Some of these comparisons for NCZ and Wilson theories are set out in Table 3 on p. 252.

For the further assistance of the reader, specific examples of real systems, their commonly understood type names, and theories which are useful for the prediction of their phase equilibria are given in Table 4. Also in Table 4 are set out the parameters which are prominent in determining the behavior
of these systems, hence those which applicable predictive expressions should include in their formulations.

Also included is a section on functional response of component terms of the NCZ equation (shown graphically as $G^E/RT$ vs $\alpha$ curves) to encourage the reader to see the excess free energy behavior of systems chosen for analysis in the frame of reference of this work.

3. REDUCTION OF THE CONFIGURATIONAL INTEGRAL TO PARTITION FUNCTIONS

It is convenient to begin arguing from fundamentals at the stage of considering the form of the configuration integral applicable to cell theories. The steps by which the reduction of the configuration integral to partition functions takes place have far-reaching consequences on all subsequent formulation steps, although the actual assumptions themselves are quite straightforward. The formally correct N-particle configuration integral in 3-N space may be written:

$$Q(N) = \int_{i=1}^{3N} ... \int_{i=1}^{3N} e^{-U(all-all)/kT} \, dx_1 \ldots dx_{3N} \quad (213)$$

Upon making the standard cell theory simplification that particle movements are localized to within definable "cells", (and assuming single occupancy of each cell) the equivalent partition function for the N-particle assemblage is obtained.
Comparing equation (214) to (213), it is seen that the potential $U\ (\text{all-all})$ of all molecules-bound-by-all-molecules in equation (213), is decoupled in (214) into $N_1$ contributions of $\varepsilon(1\text{-all})$ (the potential of one molecule of 1 bound by all) and $N_2$ contributions of $\varepsilon(2\text{-all})$ (the potential of one molecule of 2 bound by all) such that

$$U(\text{all-all}) = N_1 \varepsilon(1\text{-all}) + N_2 \varepsilon(2\text{-all})$$  \hspace{1cm} (215)$$

The actual process of evaluation of one of the single molecule partition functions (the terms in the square brackets in equation (214)) such as

$$\left[ \int_{V_{f_1}} e^{-\varepsilon(1\text{-all})/kT} \, dx_1 \, dy_1 \, dz_1 \right]^{N_1}$$

is visualized as follows. The whole $N$-molecule system representing the mixture is first imagined as being arranged into its most probable configuration. (This configuration gives
the best single estimate of the properties of the system).
Indeed, because of the large size of the whole system, (a mole of molecules is usually chosen) the most probable configuration is enormously dominant over less probable configurations, due to the sharpness of the probability distributions for systems of such a size about their largest term. From here on therefore \( \Omega' \) will be considered to be simply the degeneracy of the most probable configuration.

The limits of integration are defined for any individual molecule as the volume of permitted movement within the cage of its nearest neighbors. This domain of integration is \( v_{f_i} \) for a molecule of species \( i \). For each point in this small volume \( v_{f_i} \), the point value of \( \varepsilon(1-all) \) is evaluable (or would be if the exact form of the intermolecular potential function were known).

The integrals in equation (214) could normally be evaluated by a summation of these point values of \( e^{-\varepsilon(1-all)/kT} \) such that

\[
e^{-\varepsilon_1/kT} = \sum_{i} e^{-\varepsilon(1-all)/kT} \frac{d\tau_i}{v_{f_i}}
\]

where now \( \frac{d\tau_i}{v_{f_i}} \) is the volumetric weighting factor for each point value of the exponent. \( \frac{d\tau_i}{v_{f_i}} \) is thus a configurational (spatial) type of probability.

From the form of equation (217) it is realized that the appropriate average value of the exponent of \( \varepsilon(1-all) \) over the...
volume, i.e., \( \tilde{\varepsilon} \) is a free energy average*, since equation (217) can be rearranged such that \( -\frac{\varepsilon_1}{kT} \) is a single exponent representing the right hand side partition function. Thus

\[
(q_1) = \left(\tilde{\varepsilon}_1 e^{-\varepsilon_1/kT}\right) = \sum_i e^{-\varepsilon(1-\alpha_i)kT} \text{all volume elements in } v_f^1
\]

(218)

If the smooth integration over the region is replaced by summation as shown, the number of volume increments summed over represents the degree of "fine-graining" of the approximation of this sum of the RHS of equation (218) to the integral on the LHS. Now if all the energy binding \( l \) is attributed to its \( z_1 \) nearest neighbors, as is the formal assumption of the quasichemical method, the operation on the right hand side of equation (218) becomes, instead of the volumetrically weighted sum over point energies, the product of the (assumed) independent partition functions for each of the \( z/2 \) pairs interactions given as \( q_{i-j} \times z/2 \).

\[
(q_1) = \prod_{i=1}^{(z/2)} q_{i-j} = (e^{-\varepsilon_{ij}/kT} v_f^{i-j} \text{pairs})^{(z/2)}
\]

(219)

* In fact, the free-energy average may be approximated by a measured mass-law average quantity in most cases(16).
Thus the pairs-liquid assumption corresponds to a coarseness of graining corresponding to dividing up the total volume of integration per molecule into $z/2$ regions. In a further assumption, it is now considered that each pairs interaction need be integrated only over a domain of size $v_f/(z/2)$. It is seen from equation (219) that the free volume per pair is of the form

$$v_{f_{i\rightarrow i}} = (v_f)^{(2/z_i)}$$

(220)

If it is argued from the pairs partition function point of view, whereas it is

$$v_{f_{i\rightarrow i}} = v_f/(z/2)$$

(221)

from the consideration of additive volumes. This discrepancy is one of the drawbacks of the 'pairs-liquid', and in fact deters one from directly considering free volume per pair terms explicitly, if there is any way of avoiding it. Nevertheless, disregarding this difficulty, the development is pursued by inserting the additional assumption whereby the final form of the pairs liquid used in the quasichemical model is obtained.

Rather than actually evaluating equation (219), it is more profitable to evaluate four 'molecular-scale bundle species', i-surrounded by i's, 1-surrounded by 2's, 2-surrounded by 1's and 2-surrounded by 2's, and to regard $q_1$ and $q_2$ as composed of appropriate averages of these four. Thus:
The 4 bundle-species partition functions are the ultimate building blocks from which free energy of mixing estimates can be assembled.

Alternately, however, (as is the case in 2-liquid theories) it is also possible to re-compose the single molecule scale partition functions for species 1 and 2 in the average environment of the mixture by making use of what are considered to be appropriately weighted averages of the bundle species partition function. Thus

\[
\tilde{q}_1 = \zeta_{11} q_{11} + \zeta_{12} q_{12} + \zeta_{21} q_{21} + \zeta_{22} q_{22}
\]  

(221)
\[ q_2 = \zeta_{1(2)} q_{1(2)} + \zeta_{2(2)} q_{2(2)} \]  (222)

The weighting factors, namely the \( \zeta_{ij} \) may be volume fractions, local volume fractions, mole fractions, contact fractions, local contact fractions, etc., depending on the interpretation of the local configuration of the liquid being used. Equation (214) then becomes

\[ Q_w = \Omega'(N'_1, N'_2, N')(q_1^{N_1} q_2^{N_2}) \]  (223)

This is the form of the partition function from which amalgamated \((t_1 + t_4'')\) type excess free energy expressions of the Wilson type are derived (hence the subscript \( w \)). The primes on \( N_1' \) and \( N_2' \) indicate adjustment of populations to the primed ones of equal coordination number if the treatment requires it.

If the four molecular scale bundle species partition functions are used instead, the result is obtained:

\[ Q_H = \Omega'(N'_1, N'_2, N')(q_1_{\overline{1}}^{n_{11}} q_1_{\overline{2}}^{n_{12}}) \]
\[ \times (q_2_{\overline{1}}^{n_{21}} q_2_{\overline{2}}^{n_{22}}) \]  (224)

This form of the configurational partition function may be used to obtain separate \( t_1 \) athermal (Flory type) and \( t_4'' \) thermal (Guggenheim type) terms in the excess free energy expression as
used by Heil (hence the subscript \( H \)). The symbols \( n_{11} \), \( n_{12} \), \( n_{21} \), and \( n_{22} \) represent the populations of the four molecular scale bundle species at equilibrium. Athermal and thermal terms must be expressed separately in this case, since the Flory terms involve concentrations of the two actual molecular species \( N_1 \) and \( N_2 \), whereas the thermal terms involve concentration functions involving the four bundle species populations, which are quadratic functions of \( N_1 \) and \( N_2 \) through mass-law relations.

The combinatorial term \( \Omega'(N_1', N_2', N') \) is the same function in both (223) and (224). Whatever assumptions are made about the number or nature of bundle species, these combinatorial terms must be the same in \( Q_w \) as in \( Q_H \), and also must be, within the limits of allowing for equalizing the size of the pairs bundles, consistent with the number of actual molecular configurations defined by \( \Omega(N_1, N_2, N) \) for molecules, and

\[
\Omega'(\frac{z_1}{z_{12}} N_1, \frac{z_2}{z_{12}} N_2, \frac{z_1}{z_{12}} N_1 + \frac{z_2}{z_{12}} N_2)
\]

(225)

for permitted pairs permutations.

In brief summary up to this point:

(1) A presentation has been made of the usual treatment of volume-of-integration factors, which in turn lays the stage for the three main ways of dealing with the volume-of-integration effects more quantitatively. The three ways are:

(a) by substitution, through the somewhat tenuous connection between volume-of-integration and the molecular displacement.
volume per cell (V/N), or with the molal or partial molal volume of the components in solution, or with the free or void volume (used in evaluation of \( \Omega_W \));

(b) by writing formulations from which the volume-of-integration factors tend to cancel (the method used in evaluation of \( \Omega_H \)), or

(c) by leaving non-cancelling portions in \( v_f \) together with their energy exponents (thus in free energy form) and thus trying directly to evaluate the resulting free energies (the method used in evaluating \( t_5 \) terms in the NCZ equation).

Classical methods involve (a) and (b) only.

(2) Probably more important, the first basic bifurcation in approach to \( G^E \) expressions has been revealed, that of the choice between \( \Omega_W \) or \( \Omega_H \) as a starting point for detailed formulation of mixture property predictions. Historically, Van Laar and Hildebrand began with the \( \Omega_W \) form, and Guggenheim initiated use of \( \Omega_H \). Since the basic form of \( \Omega_H \) expressions has been outlined in the first part of Chapter 8, Heil's equation which starts from \( \Omega_H \) will not be discussed in detail, since it is of this type. Instead, a brief resume of \( \Omega_W \) results leading up to the Solubility Parameter and Wilson expressions will now be given.

4. THEORIES FOR \( \Omega_W \)

Naturally the original presentations of the related theories were not made in as unified a form as it is now hoped to employ, and in particular these were not necessarily brought
about explicitly through the consideration of operations on the $Q_w$ partition function per se. Nevertheless, in the interests of consistency, in the present work steps leading to formulation of expressions for the excess free energy for non-ionic solutions proposed by particular workers in the field of quasichemical and related solution theories will be argued from the partition functions from which their expressions can be shown to result.

If we write the mixture partition function in the most general way possible, namely

$$Q_{\text{mixture}} = n'(N'_1, N'_2, N') \prod_{\text{all } i} q_i$$  \hspace{1cm} (226)

where

$$q_i = (e^{-\epsilon_i/RT} \nu_{f_i})$$ \hspace{1cm} (227)

It is seen that the partition function (226) responds to three quite different types of independent variables:

1) Numbers $N_i$ of various molecular species present, which appear in overall configurational terms in the mixture free energy expression. When the log of the $\Omega'$ combinatorial term is expanded via Sterling's approximation these $N_i$ generate terms of the form

$$N' \ln \left( \frac{N'_1}{N'_1 + N'_2} \right)$$ \hspace{1cm} (228)
(2) The appropriate cohesive energy per molecule, $\tilde{\varepsilon}_i$, and

(3) the volume of integration $v_{f_i}$.

Parts (2) and (3) make up the constituents of the single-molecular-scale partition functions, $q_i$ (equation (227)).

In attempting to evaluate $Q_{\text{mixture}}$ (equation (226)) the part of the overall operation represented by $\Omega'$ presents no particular formal difficulties as was seen in Chapter 7. The evaluation of $\tilde{\varepsilon}$ in (227) again presents no formal difficulties inasmuch as it can in principle be evaluated from the latent heat of evaporation of the two pure components, and the measurement of one heat of mixing. The real difficulty arises in the evaluation of $v_{f_i}$, or more precisely, in the relations between this variable on the pairs and molecular scales, leading to the paradox (see again in equations (220) and (221))

$$v_{f_i} = (v_{f_i} \star 2/z)^{z/2}$$  \hspace{1cm} (229)

which occurs when the operations which transform pairs-scale energies to molecular scale energies are applied to the corresponding free volume factors. Relation (229) indicates that the problem of manipulating and evaluating volume factors must be less straightforward than that of the interaction energies, in the production of excess free energy expressions through operations on partition functions.

Nevertheless volume-of-integration factors do appear in the partition function, and to some extent the formulations made in related theories have been dependent on how to get rid
of the difficulties introduced by this factor. (Note: the paradox of equations (220) and (221) is avoided (at least ostensibly) if molecular scale formulations, not pairs scale formulations, are employed.) It is remembered that in 2-liquid theories, the difficulty has been circumvented by incorporating the \( v_i \) in some way in the \( \eta' \) configurational aspect of the overall expression. It is avoided in Guggenheim's formulation, by making the assumption that

\[
\frac{v_{i-j}}{v_{i-j}} \approx 1
\]

(230)

an assumption which was legitimate in CZ formulations and also holds quite closely for the NCZ solution. In the present work the problem of evaluation or operating on \( v_{i-j} \) in the \( t_5 \) term has been again circumvented by including this term in expressions involving "a" and thus being able to regard it as a component of the free energy.

In the following exposition of individual related theories, particular care has been taken to differentiate between various approaches taken toward \( N_i, \epsilon_{ij} \), and \( v_{fi} \) effects, with special attention given to the latter.

5. **INDIVIDUAL APPROACHES BASED ON** \( \text{Q}_w \)

A. **The Solubility Parameter Expression**

The first approach of this type was that due to Hildebrand. The mixture partition function was regarded as being:
\[ Q_{\text{mixture}} = \Omega(N_1, N_2, N) \times (q_1)^{1/2} (q_2)^{1/2} \]  

(231)

yielding

\[ \frac{G_{\text{mixture}}}{RT} = x_1 \ln x_1 + x_2 \ln x_2 - \ln q_1 - \ln q_2 \]  

(232)

Since the real mixtures selected for testing the theory happened to have unlike pair cohesions close to the arithmetic average of like pair cohesions, energy effects were disregarded. Average values of the molecular partition function were thus considered to be

\[ q_1 = q_2 = x_1 q_1^0 + x_2 q_2^0 = x_1 \varphi_1^0 + x_2 \varphi_2^0 \]  

(233)

(Superscript \(^o\) indicating pure component state quantities). Whence, by substitution of (233) into (232)

\[ \frac{G_{\text{mixing}}}{RT} = x_1 \ln x_1 + x_2 \ln x_2 - (x_1 + x_2) \ln (x_1 \varphi_1^0 + x_2 \varphi_2^0) \]  

(234)

\[ + x_1 \ln \varphi_1^0 + x_2 \ln \varphi_2^0 \]

The ensuing amalgamation of pure component and mixture effects yields, after subtraction of the ideal mixing term:

\[ \frac{G^E}{RT} = x_1 \ln (\phi_1/x_1) + x_2 \ln (\phi_2/x_2) \]  

(235)
where the volume fraction $\phi$ is defined:

$$\phi = \frac{x v^0}{\frac{1}{f_1}}$$

(236)

The form of the excess free energy expression (equation (235)) is the same as Flory's for an athermal mixture, though Hildebrand's method of derivation relies upon amalgamation of (what are ultimately) local volume-of-integration factors into the overall configurational term to produce the volume fraction effect (though simultaneously assuming a purely random form of $\Omega$), rather than using the purely configurational arguments employed by Flory in the derivation of the polymer theory. The result is a function of volume fraction $\phi$, defined in terms of molar volumes rather than chain lengths. Trivial cancellation of $x$ and division of each term by its numerator $v_{f1}$ in equation (235) yields the expression:

$$\frac{G^E}{RT} = -x_1 \ln(x_1 + (v_{f2}^o/v_{f1}^o)x_2) - x_2 \ln (v_{f1}^o/v_{f2}^o)x_1 + x_2$$

(237)

B. The Wilson Expression

Wilson pursued the "\(q_{W}\)" theme further by including the energy of the $q$ terms in the resulting relation for $G^E$, which would have the effect of further modifying equation (237). The expression for the free energy of mixing then becomes:

$$G_{\text{mixing}}^{E}/RT = x_1 \ln x_1 + x_2 \ln x_2 - (x_1 + x_2)\ln(x_1 e^{\frac{-\varepsilon_1}{kT}} v_{f1}^o + x_2 e^{\frac{-\varepsilon_2}{kT}} v_{f2}^o)$$

$$+ x_1 \ln (e^{\frac{-\varepsilon_1}{kT}} v_{f1}^o) + x_2 \ln (e^{\frac{-\varepsilon_2}{kT}} v_{f2}^o)$$

(238)
Amalgamating, then dividing throughout by the numerator terms 
\(-\varepsilon_1/kT\) \((e^{f_1}/v_{f_1})\) in each amalgamated term, and subtracting the ideal mixing terms, yields the result

\[
G^E/RT = -x_1 \ln (x_1 + e^{-\varepsilon_{11}/kT} (v_{f_1}^{o}/v_{f_1}^{o}) x_2) \]

\[-x_2 \ln (e^{-\varepsilon_{22}/kT} (v_{f_2}^{o}/v_{f_2}^{o}) x_1 + x_2)\]

In Wilson's "\(\Lambda\)" notation

\[
G^E/RT = -x_1 \ln (x_1 + \Lambda_{22} x_2) - x_2 \ln (\Lambda_{22} x_1 + x_2) \]

(239)

A more succinct representation of equation (239) is

\[
G^E/RT = x_1 \ln (\phi_1/x_1) + x_2 \ln (\phi_2/x_2) \]

(240)

The \(\phi\)'s are 'volume fractions' (see the form of (235)), now also containing energy weighting factors of the form shown in (239).

C. Difference Between Quasichemical and 2-Liquid Theory

Energy Weighting Factors

Except in the case where

\[
|\omega_{12}| = |\varepsilon_{11} - \varepsilon_{22}| \]

(241)

(which conforms to Kreglewski's (36) observation that, for light hydrocarbon systems for example, \(\varepsilon_{12} = \varepsilon_{22}\) where \(\varepsilon_{22}\) is the self cohesion of the more weakly bound species), the algebraic form of the energy exponents in expression (239) violates the principal assumption of the quasichemical approach as outlined in
Chapter 8. This problem exists because relative probabilities of configuration (local configuration included) exhibiting like versus unlike pairing depend not on $\epsilon_{21}$ versus $\epsilon_{11}$ or $\epsilon_{12}$ versus $\epsilon_{22}$ but upon $\omega_{12}$, the net pairwise reorganization energy, which is the actual measure of the amount by which the configuration richer in unlike pairs will lower the energy (and in this case the free energy) of the system as a whole. The use of actual values of $(\epsilon_{ij} - \epsilon_{ii})$ type energy factors instead of $\omega_{ij}$ factors can be expected sometimes to exaggerate, or in some cases to reverse the estimates of the energy induced local clustering effects caused by the same species of molecule. Also, the unequal split of energy weightings into $(\epsilon_{12} - \epsilon_{11})$ and $(\epsilon_{21} - \epsilon_{22})$, rather than into two identical factors (both $\omega_{12}$), further deviates from the prescriptions of the mass law. However, the situation in practice is not as grave as it seems, since differences are actually assigned by empirical curve fitting; and since energies, (hence $\omega_{12}$) may well be somewhat concentration-dependent in real solutions. Because the regions of maximum sensitivity of the activity coefficients to their particular energy factors are at the opposite ends of the binary region, the postulation of two energy fit-factors unconstrained by mass law symmetry restrictions may be useful as it is then possible to fit each activity coefficient of a given binary individually in its dilute region. In the final form of the Wilson expression, substitution of partial molal volume ratio for volume of integration factor ratios is made before the energies are fitted. Thus in the Wilson equation there are three disposable
parameters, \((v_1/v_2)\) and the two energy factors, \((\epsilon_{12} - \epsilon_{11})\) and \((\epsilon_{21} - \epsilon_{22})\). As an empirical equation, the Wilson expression has had notable success for the prediction of vapor liquid equilibria because of its remarkable brevity and flexibility of form. It has however the inherent structural problems which are seen to be inevitable consequences of the contracted \(Q_W\) type of partition function used as the starting point in its derivation. Unfortunately, these same features contribute to its inability to deal very successfully with 2 liquid phases, resulting in systems exhibiting very large excess free energies of mixing.

6. LOCAL COMPOSITION IN MASS LAW TERMS

Designation of \(z\) rather than \(v\) as the explicit geometry factor in the NCZ equation is a main point of distinction between the viewpoint on geometric effects upon local concentrations taken in the present work, and that taken by Hildebrand and Wilson. In addition to the problems with the pairwise energy interaction terms mentioned above, amalgamation of the \(t_4\) "simple heat of mixing term into the overall configurational term \(t_1\), engenders the difficulty that the term \(t_4\) involves inherently quadratic concentration functions whereas the configurational term involves linear functions of concentration applied to logarithmic terms. Renon\(^{29}\) recently studied means of formally 'uncoupling' the mass law expression for the equilibrium unlike pairs concentration in an attempt to reduce the quadratic concentration functions into a product of
first order factors, the sum of whose logarithms would thus be more suitable for amalgamation with those of the $t_1$ term.

It will now be shown that Renon's method of investigation admits of various answers, depending upon how one choses to make a key substitution. If the mass law expression is written in a form including free volume factors per pair, its form can be represented as

$$\frac{X_{21}X_{12}}{X_{11}X_{22}} e^{\frac{2\omega_{12}}{kT}} \times \begin{bmatrix} \nu_{f_1-2} & \nu_{f_2-1} \\ \nu_{f_1-1} & \nu_{f_2-2} \end{bmatrix} \quad (242)$$

or

$$\frac{X_{21}X_{12}}{X_{11}X_{22}} e^{-\frac{2\omega_{12}}{kT}} \times \begin{bmatrix} \nu_{f_1-1} & \nu_{f_2-2} \\ \nu_{f_2-1} & \nu_{f_1-2} \end{bmatrix} = 1 \quad (243)$$

If the product of any other four factors $K_{12}$ arbitrarily chosen is such that

$$\frac{K_{21}K_{12}}{K_{11}K_{22}} = 1 \quad (244)$$

The equation (243) and (244) can be equated through their RHSs. Then by equating appropriate parts of $K_{12}$ ratios to selected factors of the LHS of (243), Renon obtained two expressions of first order:

$$\frac{K_{21}}{K_{11}} = \frac{X_{21}}{X_{11}} e^{\frac{\omega_{12}}{kT}} \frac{\nu_{f_2-1}}{\nu_{f_1-1}} \quad (245)$$
and

\[
\frac{K_{12}}{K_{22}} = \frac{X_{12}}{X_{22}} e^{\frac{-\omega_{12}/kT}{v_{f_{2-1}}/v_{f_{2-2}}}} \tag{246}
\]

Equations (245) and (246) can each be rearranged into a form, as typified by the rearrangement of (245), such as equation (247).

\[
\frac{X_{21}}{X_{11}} = \frac{K_{21}}{K_{11}} e^{\frac{-\omega_{12}/kT}{v_{f_{2-1}}/v_{f_{1-1}}}} \tag{247}
\]

The only restriction that has been arrived at in obtaining equation (247) is the very weak one (a normalizing assumption) imposed by equation (244). Since the exact nature of \(X_{21}/X_{11}\) is not known, a priori, no new light is shed on the exact nature of \(K_{21}/K_{11}\) by the development, although its form is suggestive. If the factor \(K_{21}/K_{11}\) is regarded as a local concentration ratio of 2 about 1 over 1 about 1 for the example shown, one may substitute for it the local concentration ratio of one's choice. The nature of such local compositions is thus left to be decided by other physical arguments. For reasons outlined in Chapter 7, \(\xi_1\) (rather than \(x_1\) as is used by Renon) seems to be suggested in this work as the most relevant local concentration variable. The local situation around a molecule of 2 for a binary, may thus be represented by the ratio

\[
\frac{\xi_1}{\xi_2} = e^{\frac{-\omega_{12}/kT}{v_{f_{1-2}}/v_{f_{2-2}}}} \left[\frac{v_{f_{1-2}}^{(2/z_{12})}}{v_{f_{2-2}}^{(2/z_{2})}}\right] \tag{248}
\]
Since

\[ \frac{\xi_1}{\xi_2} = \frac{z_1 x_1}{z_2 x_2} \quad (240) \]

then

\[ \frac{x_{12}}{x_{22}} = \frac{x_1}{x_2} \frac{z_1}{z_2} \left( \frac{v_{f_{1-2}}}{v_{f_{2-2}}} \right) 2^{2/z_{12}} e^{-\omega_{12}/kT} \quad (250) \]

Equation (250) accentuates the need for careful evaluation of 'local geometry effects' which evidently combine packing (z) and displacement volume (v) effects. Note that in equation (250) the volume ratio is present in a local concentration ratio only to the \( \frac{2}{z} \)th power, whereas it will be seen that the volume ratio present in the Wilson formulation of the same effect is to the power one. On the other hand, the z ratio occurs in equation (250) to the first power.

While characterizing local geometry factors by the z ratio (which involves \( R_{12} \) to the first power) alone perhaps somewhat understates them, use of the volume ratio (which varies as \( R_{12} \) to the third power) alone is bound to overstate them. In addition to this, the z ratio, while not a very sensitive function of composition, certainly responds differently to composition than does the volume ratio. It is the opinion of the author that in equation (250), the effects of the z ratio overshadow those of the volume ratio, and consequently, NCZ formulations retain the z ratio. As a matter of fact, in some future work it would be interesting to see how well the z ratio to an
immediate power, say two, would represent local geometry effects.

7. THE NRTL EQUATION

The NRTL equation is best attributable to $Q_H$, though it has elements of both approaches. Renon's investigations into 'decoupling' the mass law eventually lead to the NRTL expression. If one were to begin with the simplest form of the $t_1^2$ term from equation (104) in Chapter 8 for a CZ binary mixture, namely

$$G^E = x_1 x_2 w_{12}$$

and were to expand the expression for $w_{12}$, one would obtain

$$G^E = 2x_1 x_2 z/2[\varepsilon_{12} - \frac{1}{2}(\varepsilon_{11} + \varepsilon_{22})]$$

$$= x_1 x_2 z/2(\varepsilon_{12} - \varepsilon_{11}) + x_2 x_1 z/2(\varepsilon_{12} - \varepsilon_{22})$$

If now, as indicated by the usual convention of circling the index on the 'central' molecule, the connotation of local composition were given to the now-separated pair of terms of the RHS of equation (252), one could write

$$G^E = x_1 x_2 z/(2(\varepsilon_{21} - \varepsilon_{11})) + x_2 x_1 z/(2(\varepsilon_{12} - \varepsilon_{22}))$$

If the Wilson form of energetically induced local clustering weighting factor were used to relate $x_2 1$ to $x_2$, and $x_1 2$ to $x_1$, one would make the substitutions
\[ x_2 \frac{1}{1} = x_2 x_2 \frac{e^{-\left(\varepsilon_{21} - \varepsilon_{11}\right)/RT}}{x_1 + x_2 e^{-\left(\varepsilon_{21} - \varepsilon_{11}\right)/RT}} \frac{-(\varepsilon_{21} - \varepsilon_{11})}{RT} \]  

(254)

and

\[ x_1 \frac{1}{2} = x_1 \frac{e^{-\left(\varepsilon_{12} - \varepsilon_{22}\right)/RT}}{x_1 e^{-\left(\varepsilon_{12} - \varepsilon_{22}\right)/RT}} + x_2 \frac{-\left(\varepsilon_{12} - \varepsilon_{22}\right)}{RT} \]  

(255)

Substituting (254) into (253) for \( x_2 \frac{1}{1} \) and (255) into (253) for \( x_1 \frac{1}{2} \) would give rise to the NRTL form of expression for a binary mixture. It should be noted however, that in its generally accepted form, the NRTL expression is written containing energy parameter on a molecular scale.

If \( \varepsilon'_{21} \) is substituted for \( z/2 \times \varepsilon_{12} \) and the parameter \( a \) for \( 2/z \), and the circling convention is not explicitly used, one arrives at the NRTL expression in notation compatible with that of Renon. The result of these transformations of variables is given by

\[ G = x_1 x_2 \frac{e^{-\alpha(\varepsilon'_{21} - \varepsilon'_{11})/RT}}{\left[ x_1 + x_2 e^{-\alpha(\varepsilon'_{21} - \varepsilon'_{11})/RT}\right]} \frac{-\alpha(\varepsilon'_{21} - \varepsilon'_{11})}{RT} \frac{(\varepsilon'_{21} - \varepsilon'_{11})}{x_1 e^{-\alpha(\varepsilon'_{12} - \varepsilon'_{22})/RT} + x_2} \left[ x_1 e^{-\alpha(\varepsilon'_{12} - \varepsilon'_{22})/RT} + x_2 \right] \frac{-\alpha(\varepsilon'_{12} - \varepsilon'_{22})}{RT} \frac{(\varepsilon'_{12} - \varepsilon'_{22})}{x_2} \]  

(256)

Finally, the molecular scale energies are invested with the properties of free energies by the formal replacement of
and the substitutions $\Delta G_{12} = G_{12} - G_{11}$ and $\Delta G_{21} = G_{12} - G_{22}$ are made, leading to the final form of the expression for a binary mixture

$$
G^E = x_1x_2 \times \frac{-\alpha(\Delta G_{21})/RT}{(x_1 + x_2 e^{-\alpha(\Delta G_{21})/RT})} \times \Delta G_{21} \\
+ x_2x_1 \times \frac{-\alpha(\Delta G_{12})/RT}{(x_1 e^{-\alpha(\Delta G_{12})/RT} + x_2)} \times \Delta G_{12}
$$

This is now clearly the form of the NRTL expression as originally reported\(^{(29)}\). The expression is regarded as containing three freely variable fit parameters, namely $\alpha$, $\Delta G_{12}$ and $\Delta G_{21}$. Parameter $\alpha$ is usually assigned a value close to 0.3. $G^E$ is then empirically represented as the sum of two skewed parabolic component curves, either or both of which can be positive or negative depending on the sign given $\Delta G_{12}$ and $\Delta G_{21}$. The form of the sum curve is thus quite flexible, ranging from unimodal symmetrical (either positive or negative) to increasingly assymmetrical unimodal, or even to righthand or lefthand positive sigmoid, in the extreme case of energies of large magnitude and different signs.
Operationally, the NRTL Expression could be defined as another interesting type of hybrid expression. Instead of amalgamating the heat of mixing term into the configurational term, and obtaining a logarithmic expression as was the case with the Wilson equation; the NRTL expression is an example of amalgamating Wilson-type local clustering factors into an expanded form of the heat of mixing term. While the operations transforming equation (251) into equation (252) are not inconsistent with the mass law, the use of the $\Delta G_{ij}$ factors in the exponent terms is still subject to the same problems experienced with this form in the Wilson equation. Note also that no explicit volume weighting factors appear in the final expression for $G^E$, although the $\alpha$ factor, if given a different value in each exponent, has the effect of a geometry factor.

8. THE ASOG EQUATION

The ASOG (Associated Solution of Groups) model of a liquid, is composed of a Flory-Huggins configurational term regarding the solution on a molecular scale for configuration purposes, and a Wilson type treatment of the pairwise interaction effects which are considered on a groups scale. The concentration variable employed in the Flory-Huggins term is the mole-fraction, and that in the Wilson term is the "group fraction". The group fraction is the proportion of the total population of groups (consisting of all groups on all molecules) which are of a given functional group species. In the treatment of Derr and Deal, for example, in a solution of
butanol, methanol and water, the group fraction of OH would derive from all three molecular species present. Only two group species are considered to be present; namely OH and methyl.

The proportion of molecular surface represented by a given functional group, and volumetric displacement effects are represented by different (and independently evaluated) sets of parameters in the ASOG theory. 'Group numbers' designating number per molecule of a given type of group for pairwise contributions to the heat of mixing are denoted by $v_{ki}$ (for group $k$ on molecule $i$). The displacement volume and/or chain length parameter used in the volume fraction factors in the Flory-Huggins term of the ASOG expression is designated by $v_{FH}^i$ for species $i$. The effects of energetically induced local clustering are not included in the ASOG formulation. Geometry determining parameters $v_{ki}$ and $v_{FH}^i$ are not concentration dependent. Each group pairwise interaction is characterized by two pairwise interaction Wilson type constants. Measurements are made of the activity coefficients of real solutions containing the two interacting groups. Then, by mathematical analysis, 'group' effects are allocated. The desired final parameters characterizing the (sometimes hypothetical) solutions of 1) groups A in infinite dilution in a solution of group B, and 2) group B in infinite dilution in a solution of group A.

Adjustment of these two energies per pair of groups thus adds useful degrees of freedom to the expression to help accommodate not only compositional dependence of unlike pair interaction
energy, but also that of coordination number and energetically induced local clustering tendency, which are not directly calculated. In a recent paper\(^{(33)}\), the success of the ASOG Equation in fitting numerous systems has been demonstrated.

One of the equation's features is that, like any solution-of-groups approach, an economy of parameters is effected, relative to a molecular-level treatment, in that many molecular species can be formed from a given set of group types.

The ASOG equation embodies the characteristics of the Wilson equation on the pairs level. A 'group' would be the close equivalent of a 'site' of a given species in the terminology of this thesis. The form of the excess free energy expression according to the ASOG theory is written:

\[
\frac{G^E}{RT} = \sum_i x_i \ln \phi''_i/x_i + \sum_k -x'_k \ln \left(\sum_{l} x'_l a_{kl}\right)
\]  

(259)

where the first summation over all molecular species is the Flory-Huggins term, and the second summation over all group species is the Wilson type of expression for the energy interaction part of \(G^E/RT\) written on a groups-scale. Concentration variable \(x_i\) is the mole fraction of molecular species \(i\), and \(x'_k\) is the group fraction of the \(k\)th species of functional group. \(\phi''\) is the form of the volume fraction used in the ASOG equation.

9. AN NCZ ANALOGUE TO THE WILSON EQUATION

A. \(G^E/RT\) Expression

Since the Wilson equation has probably been the most
widely successful of the \( (G^E/RT) \) expressions derived from \( Q_w \), it was felt to be useful to force algebraic parallelism between the activity coefficient expressions obtained from the Wilson equation and the expressions resulting from incorporating the NCZ effects of terms \( t_1 \) and \( t_4' \) into the \( Q_w \) form of the partition function. The object was to demonstrate under what conditions the two sets of activity coefficient expressions become identical, at least in algebraic form. One begins with \( Q_w \) in the usual way

\[
Q_w = N(N_1', N_1')(q_1) / (q_2)
\]

But now

\[
N_1' = z_1 / z_{12} N_1
\]

and

\[
N_2' = z_2 / z_{12} N_2
\]

Substituting into a general statement of the free energy of mixing, namely equation (262)

\[
G_{\text{mixing}}^{\text{RT}} = -\ln Q_w^{\text{mixture}} + \ln Q_1^o + \ln Q_2^o
\]

results in

\[
G_{\text{mixing}}^{\text{RT}} = \ln \left( \frac{z_1}{z_{12}} N_1 + \frac{z_2}{z_{12}} N_2 \right)! \times \frac{z_1}{z_{12}} N_1 \times \frac{z_2}{z_{12}} N_2
\]

\[
\ln \frac{z_1}{z_{12}} N_1 + \ln \frac{z_2}{z_{12}} N_2
\]
At this point the \( q \) terms are on a molecular scale, with populations adjusted to equalize the size of the pairs bundles for each species. The reference populations of 1 and 2 have also been correspondingly adjusted, so that only the mixing effect is felt by the molecular partition functions, rather than a combination of population and mixing effects. (This amounts to ignoring term \( t_5 \) in the general expression (122) of Chapter 8. Expansion of equation (263) leads to:

\[
\frac{G_{\text{mixing}}}{kT} = N_1' \ln \frac{N_1'}{N_1' + N_2'} + N_2' \ln \frac{N_2'}{N_1' + N_2'} \\
+ N_1' \ln \left( \frac{q_1^o}{q_1} \right) + N_2' \ln \left( \frac{q_2^o}{q_2} \right)
\]

Since, for a monofunctional monomer binary when heat effects are low,

\[
\frac{N_2'}{N_1' + N_2'} = \xi_1
\]

and

\[
\frac{N_2'}{N_1' + N_2'} = \xi_2
\]

\[
\frac{G_{\text{mixing}}}{kT} = N_1' \ln \xi_1 + N_2' \ln \xi_2 + N_1 \ln \left( \frac{q_1^o}{q_1} \right) + N_2' \ln \left( \frac{q_2^o}{q_2} \right)
\]

Realizing that the 'molecular' partition function ratios represent 'pairs' bundles, and following the example of Hildebrand, one may substitute for the molecular partition function appropriately weighted averages of these for the molecular
partition functions obtaining in the mixture. Thus substituting one obtains

\[ q_1 = \xi_1 q_1^o + \xi_2 q_2^o \]  
\[ q_2 = \xi_1 q_1^o + \xi_2 q_2^o \]  

After substituting and multiplying through, the result is obtained:

\[ \frac{G_{\text{mixing}}}{kT} = N_1' \ln \xi_1 + N_2' \ln \xi_2 + N_1' \ln \left( \frac{q_1^o}{\xi_1 q_1^o + \xi_2 q_2^o} \right) + N_2' \ln \left( \frac{q_2^o}{\xi_1 q_1^o + \xi_2 q_2^o} \right) \]  

Although the next step is not formally defensible, one suspects from the mass law expression that the pertinent local ratios of \( q_i' \) are really those of the pairs partition functions designated \( q_1 (1) q_2 (1) \) and \( q_2 (2) \) where the second circled index now indicates the central molecule. Amalgamation of configurational and energy terms as usual, results in:

\[ \frac{G_{\text{mixing}}}{kT} = N_1' \ln \left( \frac{\xi_1 q_1 (1)}{\xi_1 q_1 (1) + \xi_2 q_2 (1)} \right) + N_2' \ln \left( \frac{\xi_2 q_2 (2)}{\xi_1 q_1 (2) + \xi_2 q_2 (2)} \right) \]
The excess free energy expression is obtained by subtracting the ideal mixing term $x_1 \ln x_1 + x_2 \ln x_2$.

Doing so, with a slight rearrangement into denominator form, the following result is obtained:

$$
\frac{G_{\text{mixing}}}{RT} = x_1 \ln \left( \frac{\epsilon_1 q_1 1}{\epsilon_1 q_1 1 + \epsilon_2 q_2 2} + x_2 \ln \frac{\epsilon_2 q_2 2}{\epsilon_1 q_1 1 + \epsilon_2 q_2 2} \right)
$$

(272)

B. Activity Coefficients

Wilson shows that the $x$-explicit form for two components can be obtained by following through the operations indicated by Equation (26)*, whereby $\ln \gamma_i$ is obtained from $G^E$.

For the sake of parallelism constants ratios are shown in Wilson's notation of $a$ and $b$:

* more explicit forms for computation are:

$$
\ln \gamma_i = \frac{\partial}{\partial N_i} \left( \prod_{k} N_k \right) \times \frac{G^E(N_i)}{RT}
$$

(274)

$$
\frac{\partial}{\partial x_j} \ln \gamma_i = \frac{G^E(x_k)}{RT} - \sum_{j \neq i} \frac{\partial G^E(x_k)}{\partial x_j}
$$

(275)
Here

\[ a' = \frac{z_2}{z_1} e^{-\omega_{12}/RT} \]  

(276)

[Image 0x0]

\[ b' = \frac{z_1}{z_2} e^{-\omega_{12}/RT} \]  

(277)

whereas in Wilson's expression

\[ a = \frac{v_1}{v_2} e^{-(\epsilon_{21} - \epsilon_{11})/RT} \]  

(278)

\[ b = \frac{v_1}{v_2} e^{-(\epsilon_{12} - \epsilon_{22})/RT} \]  

(279)

By straightforward operation indicated by the first relation mentioned in the footnote and re-expressing the results in terms of \( x_i = \frac{N_i}{N_1} \), the expression:

\[ \ln \gamma_1 = (z_1/z_{12}) \times [-\ln (x_1 + a'x_2) + x_2 \left\{ \frac{x_1(1 - a')}{(x_1 + a'x_2)} + \frac{z_2}{z_1} \frac{x_1(1 - b')}{(b'x_1 + x_2)} \right\}] \]

(280)

\[ + \left[ \frac{z_2}{2} (1 - z_1/z_{12}) \left( \frac{\epsilon_{11}}{RT} \right) \right] + \left[ \frac{z_1}{z_{12}} - 1 \right] \ln x_1 + x_2 \left( \frac{z_1-z_2}{z_{12}} \right) \]

is obtained. Whence

\[ \ln \gamma_1 = (z_1/z_{12}) \times [-\ln a' + (z_2/z_1)(1 - b')] \]

\[ x_1 \to 0 \]

(281)

and

\[ \ln \gamma_2 = \left( \frac{z_2}{z_{12}} \right) \times [-\ln (b'x_1 + x_2) - x_1 \left( \frac{x_2(1 - b')}{b'x_1 + x_2} + \frac{z_2}{z_1} \frac{x_2(1 - b')}{b'x_1 + x_2} \right)] \]

(282)
\[
\ln \gamma_2(\infty) = \left(\frac{z_2}{z_{12}}\right) \times \left[-\ln b' + \left(\frac{z_1}{z_2}\right) \times (1 - a')\right] \\
\text{as } z_2 \to 0 \\
+ \frac{z_2}{2} \left(1 - \frac{z_2}{z_{12}}\right) \left(-\frac{\epsilon_{22}}{RT}\right) \left(\frac{z_2 - z_1}{z_{12}}\right)
\]  

(283)

Equations (280) and (281) correspond to the activity coefficients in logarithmic form for a monofunctional binary liquid mixture embodying the assumptions and approximations detailed above. These reduce to the exact algebraic form of Wilson's logarithmic activity coefficients \(\ln \gamma_1\), and \(\ln \gamma_2\) (as given in his thesis (51)) upon setting

\[z_1 = z_2 = z_{12}\]  

(284)

and replacing \(a'\) and \(b'\) by \(a\) and \(b\) as defined above. Thus, though the activity coefficient expressions of Wilson and that obtained by forcing the NCZ equation into a 'Wilson' form are algebraically similar, the two types of activity coefficient expression will not behave identically in practice, because of the different \(z\)-ratio exponents, the fact that \(a'\) and \(b'\) are usually somewhat different as well as stronger functions of composition than \(a\) and \(b\), and finally because of the extra terms in the NCZ case.

While the experimental part of this thesis is restricted to investigating the main features of the NCZ equation's ability to match \(G^E/RT\) behavior with experimentally derived results, the clearly different response behavior of NCZ and Wilson activity
coefficient predictions is of some interest, particularly in the
dilute solution region, in that it is in dilute solution that the
activity coefficient of the dilute species is both largest and
also most sensitive to composition, whereas $G^E/RT$ in the same
region tends toward zero. The study of dilute solution activity
coefficient behavior is also important in that the removal of
minor components is a most important aspect of commercial
product separations by distillation.

10. SUMMARY OF RELATIONS BETWEEN QUASICHEMICAL AND RELATED
THEORIES

Energetically, the principal difference that emerges be­
tween the NRTL, Wilson and ASOG expressions on the one hand and
those of Guggenheim, Barker, and the NCZ expressions on the
other is the number of energy interaction constants per unlike
pair. In the case of the former, there are two, namely

$$\lambda_{ij} = (g_{ij} - g_{ii})$$  \hspace{1cm} (285)

and

$$\lambda_{ji} = (g_{ji} - g_{jj})$$  \hspace{1cm} (286)

whereas in the latter there is only one, namely

$$\omega_{ij} = [g_{ij} - (g_{ii} + g_{jj})]$$  \hspace{1cm} (287)

In equations (285) and (286), the symbol $g_{ij}$ is intro­
duced as a generalized free energy per molecule without the de­
tailed further connotations discussed earlier. Its form is
consistent with the notation of Prausnitz and Cukor*. Also note that in the above equations, the same value of $\omega_{ij}$ is used both for the $ij$ and $ji$ senses of interaction. The second group of theories are consistent with the mass law, whereas the first do not appear to be. Prausnitz* has indicated that the reason NRTL and Wilson expressions depart from apparent conformity with the mass law is explained by the fact that they derive from the 2-liquid theory of Scott (26). In the 2-liquid theory, two interpenetrating liquids consisting of '2 around 1' and '1 around 2' are combined by linear superposition to make up the overall mixture, with no energy interactions between the two 'liquids'. It seems to the author that energetically, such a model would most accurately describe two mutually isolated liquid films (of termolecular thickness) of molecules in a vacuum. This is in view of the assumption of no competition for nearest neighbor species by central molecules sharing such neighbors, implicit in the 2-liquid theory. On the purely empirical level, the use of two disposable energy constants per pair interaction (which are, in practice, fitted independently) is most convenient in that compensation of these values to help account for the concentration dependence of local clustering effects, etc., can be accommodated in the two constants. This is particularly true when the two constants are evaluated, as in the case of the ASOG equation, at opposite infinite dilution.

* Private communication.
regions of the appropriate binary; but on the other hand, the practice leads to twice as many energy constants per binary as do the Barker, Guggenheim and NCZ models. It is admitted that this gain is at the cost of more computing to obtain local compositions \( (52,53) \).

When computing facilities are available, the less data-rich model may be preferable, especially with regard to the thermodynamic interpretation of the empirically determined energy constants found to produce a best-fit.

Configurationally, the most pronounced difference between the "2-liquid" and "quasichemical" sets of theories is that the volume-of-integration factors of the single-molecule partition function (see equations \( (226) \) and \( (227) \)) are manifested as molar volume ratio geometry factors in the Wilson and ASOG theories, whereas, in the NCZ theory, packing numbers calculated from monomer unit diameters are considered to exert the primary purely configurational effect (incorporated in the term \( t_1 \)) manifested as ratios of compositionally variable coordination numbers. The volume-of-integration terms are seen to "cancel out" in the heat of mixing term of quasichemical theories, though in the NCZ equation volume-of-integration factors are incorporated in the free energy "a" constants of the \( t_5 \) term. The fundamental difference of choice of configurational variable is that between a "v" effect from the "q" term in 2-liquid theories, and an "\( \Omega \)" effect in quasichemical theories (refer back to equation \( (226) \)). While the numerical values assigned the two effects may not, in practice, be very different, the formal difference between the two types
of configurational variable, at least, is fundamental, and adoption of the approach involving the latter gives rise to two additional and distinctive terms in the NCZ equation not arising in 2-liquid theories.

11. TABULAR COMPARISONS BETWEEN $g^E$ EXPRESSIONS

As a means of summarizing the discussion of the foregoing chapter, and relating it to the account of the various quasichemical theories outlined in previous chapters, some of the principal assumptions and structural attributes of various workers' expressions are set out in tabular form in Table 1. As was mentioned in the introduction to this chapter, Table 2 immediately following Table 1 amplifies and references entries in Table 1 to appropriate passages in the text of this thesis. For maximum utility, the two Tables should be considered by the reader in concert.

Table 1 shows in summary form the diversity of approaches existing in excess free energy expressions for non-ionic liquid mixtures, as well as differences in extensiveness of treatment of the problem. A dashed entry in Table 1 indicates that the given equation is not directly concerned with the given facet of solution behavior. One would thus not normally expect an expression for which certain columns of Table 1 were dashed to conform very closely with the experimentally derived excess free energy for the class of mixtures in which the given effects were prominent. Equally, one would not expect to find a particularly high correlation between best-
<table>
<thead>
<tr>
<th>Electrolytes</th>
<th>Expressed only</th>
<th>Separates</th>
<th>Monomer</th>
<th>Energy constants</th>
<th>Obey mass law</th>
<th>Hindered rotation</th>
<th>Polarizability</th>
<th>Prime geometry</th>
<th>Clustering</th>
<th>Scale of system</th>
<th>Expression</th>
</tr>
</thead>
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<td>-</td>
<td>-</td>
<td>yes</td>
<td>no</td>
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<td>yes</td>
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<td>yes</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>yes</td>
<td>-</td>
<td>yes</td>
<td>no</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>-</td>
<td>yes</td>
<td>yes</td>
<td>no</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>yes</td>
<td>no</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
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<td>yes</td>
</tr>
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<td></td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>yes</td>
<td>no</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
</tr>
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</table>

Structural assumptions of guest chemical and related theories

**Table 1**
<table>
<thead>
<tr>
<th>Key to Col. of Table 1</th>
<th>Notes</th>
<th>Ref. in Text</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>'Scale' defined by packing unit employed: molecule, or monomer unit.</td>
<td>CH9: 7A(2) and (4)</td>
</tr>
<tr>
<td>2</td>
<td>Cohesion reckoned per: molecule, monomer unit, or pair of contacts.</td>
<td>CH8: , CH10:5 to 10:9</td>
</tr>
<tr>
<td>3</td>
<td>Energetically-induced local clustering accounted for explicitly.</td>
<td>Eqns. 102 and 103, CH8:9A, CH9:2B.</td>
</tr>
<tr>
<td>4</td>
<td>Is argument of ( z ) ( x )-explicit?</td>
<td>CH6:9 and 6:10</td>
</tr>
<tr>
<td>5</td>
<td>Dominant effect of unequal molecule size: packing (( z )) effects arising in ( Q^a ), or displacement - volume (( v )) effects arising in the ( \Pi(f) ) part of ( Q^a ).</td>
<td>CH10:6, App.3, CH6:8</td>
</tr>
<tr>
<td>6</td>
<td>Consideration of configurational and/or energetic effects of NCZ packing.</td>
<td>CH7:5, term ( t_5 ) eq.122</td>
</tr>
<tr>
<td>7</td>
<td>Energy constants (normalised by ( \gamma T )) increase (+), decrease (-), with ( T ), or are of both types (+,-).</td>
<td>CH8: C:2</td>
</tr>
<tr>
<td>8</td>
<td>Local energy-clustering factor is same as in mass-law expression.</td>
<td>p.244,245</td>
</tr>
<tr>
<td>9</td>
<td>No. of energy constants assigned per unlike species binary interaction.</td>
<td>p.235,236 and pp.244-246</td>
</tr>
<tr>
<td>10</td>
<td>Explicit ( g^E ) term for rotational hindrance effect.</td>
<td>CH9:7B</td>
</tr>
<tr>
<td>11</td>
<td>Same properties attributed to large monomer as to polymer chain of same displacement volume.</td>
<td>CH10:5A. Contrast this to App.3</td>
</tr>
<tr>
<td>12</td>
<td>( H^E ) and ( Tg^E ) contributions to ( g^E ) shown separately or not? Various possibilities coded: ( s = ) separate terms. ( A = ) amalgamated. ( 1 = H^E ) only. ( 2 = Tg^E ) only.</td>
<td>CH10: Eqns (223),(224) More generally 10:3 to 10:8 inclusive</td>
</tr>
<tr>
<td>13</td>
<td>Contains only Flory-Huggins form of ( S^E ) term.</td>
<td>App 3, p.350, CH10:5 A and B</td>
</tr>
<tr>
<td>14</td>
<td>Expression applies to electrolyte components in mixtures.</td>
<td>App.1</td>
</tr>
</tbody>
</table>
fit values of constants of the expression in question to the values of the same constants obtained from independent thermodynamic property estimates. Apart from the ability of a given expression to produce a "fit", a test of the expression's 'thermodynamic' applicability in the given situation is afforded by the correspondence of 'best-fit' constants with those estimated by independent means. In actuality, most situations are far from clear-cut: lack of experimental data, basic similarity in the functional form of component curves representing quite dissimilar thermodynamic effects, formal obscurity, the existence of several compensating effects, and the predominence of intermediate cases all contribute to the difficulty of differentiating effects as clearly as might be desired from the viewpoint of thermodynamic analysis.

12. THERMODYNAMIC VALIDITY OF PARAMETERS

However, certain rudimentary tests are often possible. For example, in the Wilson equation if best-fit values of $\Lambda_{ij}$ are obtained from fitting a system, then the pure component volume ratio of the two pure components of the given binary may be estimated by the expressions *

$$\left(\frac{v_1}{v_2}\right) = \left[\left(\frac{\Lambda_{12}/\Lambda_{21}}{2}\right) \exp\left(+\left(\frac{E_{\text{vap}_2} - E_{\text{vap}_1}}{RT}\right) \times \frac{1}{2}\right)\right]^{\frac{1}{2}}$$

(228)

where

$$g_{iJ} = g_{jI}$$

(229)

* Here one takes $E_{\text{vap}}$ as a magnitude (a positive quantity)
and

\[ g_i \frac{1}{\lambda} = E_{vap_i} \times \frac{2}{z} \]  \hspace{1cm} (290)

where these symbols have been defined earlier in this work. From the heats of vaporization of the two components, at the given temperature, measurements of Wilson constants \( A_{ij} \) and an estimate of \( z \), values of pure component volume ratio from the equation can be compared with volume ratio resulting from direct property measurement. This comparison is shown in Table 3 along with the \((l/3)\) and first power of pure component radius ratios from the NCZ equation for the corresponding system.

A general conclusion to be drawn from the above discussion is that the region of thermodynamic applicability (indicated by a close correlation between best fit and independently determined constants), should probably be expected to be somewhat more restricted than the region in which a fit is obtainable by unrestricted variation of constants. Thus, two criteria for the appropriateness of a given expression must be considered: goodness of fit of the predicted to the experimental \( G^E/RT \) curve, and also the thermodynamic validity of the constants used to produce this fit. The latter consideration is of particular importance when the data obtained for one component in one systems is used to predict its behavior in another.
TABLE 3
Values of some Best-Fit Thermodynamic Constants from Wilson and NCZ Expressions.

<table>
<thead>
<tr>
<th>System No.***</th>
<th>System</th>
<th>$\Delta T_2$</th>
<th>$\Delta T_2$</th>
<th>$\frac{v_1}{v_2}$</th>
<th>$\frac{v_1}{v_2}$</th>
<th>$z_s$</th>
<th>Cals./QM.mol.</th>
<th>$\frac{R_{12}}{T}$</th>
<th>$T^\circ C$</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>n-C₄H₁₀-H₂S</td>
<td>(.525)</td>
<td>(.525)</td>
<td>.95</td>
<td>1.30</td>
<td>6</td>
<td></td>
<td>1.55</td>
<td>50°C</td>
</tr>
<tr>
<td>8</td>
<td>2-PROP-H₂O</td>
<td>(.25)</td>
<td>(1.30)</td>
<td>.750</td>
<td>1.58</td>
<td>8</td>
<td></td>
<td>1.3</td>
<td>80°C</td>
</tr>
<tr>
<td>9</td>
<td>CH₃OH-CCl₄</td>
<td>(.470)</td>
<td>(.010)</td>
<td>1.57</td>
<td>1.59</td>
<td>8</td>
<td></td>
<td>1.3</td>
<td>30°C</td>
</tr>
</tbody>
</table>

* $\frac{v_1}{v_2}$ calculated from equation (288) in text.

** From (Ref. 74) ( ) contain estimated temperature corrections.

*** Numbering is consistent with Table 4: 1 = the larger component.
13. CLASSIFICATION OF $G^E$ EXPRESSIONS WITH RESPECT TO STANDARD TYPES OF SOLUTIONS

In Table 4, another method of indicating regions of applicability of various expressions for excess free energy is shown. These expressions are the Wilson, ASOG, NRTL, Hala*, Barker, Hildebrand Solubility Parameter, Van Laar, Guggenheim, Flory-Huggins and NCZ expressions.

The purpose of Table 4 is both classificatory and analytic. The two sections of the Table are separated by a heavy black vertical line. The two halves of the Table have been set in juxtaposition to illustrate its classificatory and analytic aspects in relation to the same set of physical systems. The classificatory section will be dealt with first.

To the left of the heavy black line is indicated a number of systems, a generic physical and chemical description of these systems, and a typical example. Also indicated are those systems for which the NCZ equation is useful or applicable, as well as other equations which have been found to be useful or applicable. It is not attempted to define the bounds of the usefulness of the other solution theories mentioned, but simply to indicate those systems for which they are most popular or easily applied. Also indicated in a separate column is the maximum number of components which the theories can accommodate. It is not unreasonable to comment that some of the solution theories quoted as being able to handle only two components have in the nature of their formalism no such limitation, although the practical difficulties of handling more than two components by the given expression have proved insurmountable.

* See Appendix 1
While the NCZ expression is deliberately formulated in a form not restricted to binary mixtures, it is true that up to now, only two-component systems have been tested in detail against experimental results. The calculation program has been run on an n-mer containing ternary system comprising five functional group types, and no operational difficulties were experienced. The calculated results have not yet been tested in detail against experiment and so are not quoted here.

In Table 4 the procedure followed has been to show the kind of systems for which various solutions theories can apply but what does not appear, and what is well-known to anyone versed in the field, is that for any one of these theories there is a considerable range of the systems quoted for which it is not applicable. There may be very real difficulty in knowing where the boundaries exist between the regions of applicability and non-applicability of any one system, and this perforce engenders a feeling of disquiet when a theory is to be used in an area in which it has not been tested. The situation is even more disturbing when working in a region where two theories give conflicting results. Less serious from the point of view of obtaining numbers, but at least as disquieting from a satisfactory theoretical point of view, is the case when two theories which are fundamentally incompatible give essentially the same numerical answers from different input parameters. A situation of this kind is disquieting because, towards the boundary of applicability of any one theory, in the absence of any theoretical background one is unable to judge whether unknown factors are
**TABLE 4. Classification of Solution Types in Relation to the NCZ Equation.**

| Type of System | Typical example | Physical description | Classical description | NCE equation applicable? | Reaches steady state expression of? | Number of components which can be treated by expression of eqn. 9 or 10 | Terms of the NCE, either 
term are not negligible | Order of magnitude of input parameter | Number of self-interacting components |
<table>
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<th></th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>Carbon tetra-</td>
<td>Emulsified liquid</td>
<td>S-regular binomials</td>
<td>yes</td>
<td>van Leer</td>
<td>$f_1^1$ moderate</td>
<td>0 0 10 0 0</td>
<td>0 0 0 0 0 0</td>
<td></td>
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<tr>
<td></td>
<td>chloroform,</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>2</td>
<td>Carbon tetra-</td>
<td>Emulsified liquid</td>
<td>S-regular binomials</td>
<td>yes</td>
<td>Barkat</td>
<td>$f_1^1$ moderate</td>
<td>0 0 10 0 0</td>
<td>0 0 0 0 0 0</td>
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</tr>
<tr>
<td></td>
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<tr>
<td>3</td>
<td>Alcohol polymer</td>
<td>Homopolymer</td>
<td>Homopolymer</td>
<td>yes</td>
<td>Flory</td>
<td>$f_2^2$ large</td>
<td>0 10 10 0 0</td>
<td>0 0 0 0 0 0</td>
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<td></td>
<td>monomer solutions</td>
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<tr>
<td>4</td>
<td>Water-organic</td>
<td>Mixture of organic</td>
<td>S-regular binomials</td>
<td>yes</td>
<td>Wilson, Park, Barkat, ADG</td>
<td>$f_3^3$ small</td>
<td>10 10 10 0 0</td>
<td>10 0 0 0 0 0</td>
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<tr>
<td></td>
<td>compound</td>
<td>compounds</td>
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<tr>
<td>5</td>
<td>Perfluoro a-</td>
<td>Non-polar molecules</td>
<td>Regular</td>
<td>yes</td>
<td>Hildebrand</td>
<td>$f_2^2$ large</td>
<td>10 10 10 0 0</td>
<td>0 0 0 0 0 0</td>
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<tr>
<td></td>
<td>chloroform</td>
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<tr>
<td>6</td>
<td>Penicillin-chain</td>
<td>Non-polar molecules</td>
<td>Regular</td>
<td>yes</td>
<td>Hildebrand</td>
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<td>10 10 10 0 0</td>
<td>0 0 0 0 0 0</td>
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<tr>
<td>7</td>
<td>a-Arene</td>
<td>Tightly packed</td>
<td>Regular</td>
<td>yes</td>
<td>van Leer, Silva</td>
<td>$f_2^2$ small</td>
<td>10 10 10 0 0</td>
<td>0 0 0 0 0 0</td>
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<tr>
<td></td>
<td>Hydrogen sulfide</td>
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<tr>
<td>8</td>
<td>5-Propenoate</td>
<td>Highly polar</td>
<td>S-bonded</td>
<td>yes</td>
<td>Hildebrand</td>
<td>$f_3^3$ small</td>
<td>10 10 10 0 0</td>
<td>0 0 0 0 0 0</td>
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</tr>
<tr>
<td></td>
<td>Water</td>
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</tr>
<tr>
<td>9</td>
<td>Carbon tetra-</td>
<td>Non-polar</td>
<td>Regular</td>
<td>yes</td>
<td>S-regular binomials</td>
<td>$f_1^1$ moderate</td>
<td>0 0 10 0 0</td>
<td>0 0 0 0 0 0</td>
<td></td>
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<tr>
<td></td>
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<tr>
<td>10</td>
<td>Nitrogen</td>
<td>Semi-polar</td>
<td>S-regular binomials</td>
<td>yes</td>
<td>S-regular binomials</td>
<td>$f_1^1$ moderate</td>
<td>0 0 10 0 0</td>
<td>0 0 0 0 0 0</td>
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<tr>
<td></td>
<td>Water</td>
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<td>11</td>
<td>Sulfur</td>
<td>As (5), except</td>
<td>Regular</td>
<td>yes</td>
<td>Non-existant, Barkat, ADG</td>
<td>$f_2^2$ large</td>
<td>10 10 10 0 0</td>
<td>0 0 0 0 0 0</td>
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<tr>
<td></td>
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<td>insolubility</td>
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<td>12</td>
<td>Hydrogen sulfide</td>
<td>Converted near-</td>
<td>Electrally,</td>
<td>no</td>
<td>NCE eqn. fails by its own</td>
<td>$f_1^1$ moderate</td>
<td>0 0 10 0 0</td>
<td>0 0 0 0 0 0</td>
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<td>neighbor effects</td>
<td>hydrate forming</td>
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<td>term under certain conditions</td>
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<td>13</td>
<td>Hydrogen</td>
<td>Strongly basic</td>
<td>Electrally</td>
<td>no</td>
<td>NCE eqn. fails by its own</td>
<td>$f_1^1$ moderate</td>
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<td>0 0 0 0 0 0</td>
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<td></td>
<td>term under certain conditions</td>
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255
beginning to obtrude and make the expression inapplicable. It is precisely this lack of knowledge of the causes for equation failures which forces the cautious designer to use equations only well within the realms for which they have been proved to be useful. It is this atmosphere of indefinable doubt which prevents specialized theories being used predictively, even in those cases for which they would, in fact, have given reliable information.

It will be well realized that if a theory has been stated in a form which implied the inclusion of less than all the material contained in terms $t_1$ through $t_5'$ of the NCZ equation, yet the omitted terms were, in the event, zero for the system chosen, then a prediction made using only terms which were non-zero would still be valid. A change in the system might, however, render this simplification invalid because one of the terms which had been omitted might also now prove to be non-zero. Classical theory arose within a number of compartments, within each of which reasonable success has resulted in the study of systems with particular properties. Conversely, the compartmentalization of classical solution theory could be regarded as a result of considering only some of the terms $t_1$ through $t_5'$ at a time. Historically this practice made very good sense because of the complexity of the subject, but it now appears possible to decompartmentalize the subject and consider all seven terms simultaneously, recognizing of course, that for many cases some terms in the NCZ equation may well be negligibly small.
The fact that some of the terms of the NCZ equation can be reduced in special cases to classical equations is indeed not surprising since the present overall equation has been developed as a generalization of these special cases.

If, in the NCZ equation, coordination numbers are made constant some terms vanish and some do not. The non-vanishing terms are, for this special case, recognizable as the classical ones. The terms which do vanish are those which, hitherto, have been concealed by a formulation which demands constant coordination number. Even the non-vanishing terms, however, have been distorted in their classical forms by this imposition and difficulties encountered in describing experimental results unnecessarily engendered.

Table 4 sets out, for a number of chemical systems, a statement of which terms of the NCZ equation are not negligible. The chemical systems listed include some which have proved amenable to classical methods but also systems intractable to such analysis are named. Observation of Table 4 shows that over a range of system types much greater than that for any alternative theory, the general NCZ expression holds, and therefore it is with some hope of success that the author sets about using the NCZ equation not now primarily as a device for obtaining numerical values for \((G^E/RT)\), but as a device for classifying systems with respect to their behaviour, as revealed by the functional response of the various terms of equation (212) to their constituent independent variables.
14. FUNCTIONAL RESPONSE BEHAVIOR OF THE NCZ EXPRESSION

It has now been seen that the NCZ equation has considerable generality, so offers at least the possibility of being classificatory. To see whether it could classify effectively, the equation must be shown to have:

1) Selectivity of response to single independent variables (or small groups of these), and

2) Characteristic, or identifiable (hence "analytic") responses of the individual terms $t_1$ to $t_5$ to these parameters.

It is now proposed to examine the analytic properties of the NCZ equation under considerations 1) and 2). An example of a very severe and specific response to terms $t_1$ and $t_5$ has already been given and described in Chapter 8. It is now proposed to delineate the functional response of all the terms in a more comprehensive way, and to this end Figure 4 is introduced.

In Figure 4 are listed the six significant terms of the NCZ equation (it will be remembered that $t'_5$ was mentioned on page 187, and discarded as negligible). The first three of these terms correspond to the thermodynamic function $S$, used in the graphs presented as $TS$ to convert to energy units, the next two terms to $H$, and the last to $G$.

At this point the reason for the numbering system of the terms $t_1$ through $t_5$ appears, whereas looking at them as they arose throughout the text, the numbering system of the terms was not apparent. It will be seen that the parameters to which the individual terms respond sensitively are few - never more than
<table>
<thead>
<tr>
<th>Term Number</th>
<th>Term Description</th>
<th>Term Responds Sensitive to:</th>
<th>Thermo-dynamic Nature</th>
<th>Principal Mode shown Possible alternative model(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>t_1</td>
<td>N.C.Z. Configurational term</td>
<td>$R_{ab}$</td>
<td>S</td>
<td>(i)</td>
</tr>
<tr>
<td>t_2</td>
<td>&quot;Flory&quot; term</td>
<td>$n_a, n_{ia}$</td>
<td></td>
<td>(ii)</td>
</tr>
<tr>
<td>t_3</td>
<td>Hindered rotation term</td>
<td>$n_{ij}, n_{ia}$</td>
<td></td>
<td>(iii)</td>
</tr>
<tr>
<td>t_4</td>
<td>Net heat of mixing term</td>
<td>$n_{ij}, n_{ia}$</td>
<td>H</td>
<td>(iv)</td>
</tr>
<tr>
<td>t_4&quot;</td>
<td>Heat of mixing term</td>
<td>$n_{ij}, n_{ia}$</td>
<td></td>
<td>(v)</td>
</tr>
<tr>
<td>t_5</td>
<td>N.C.Z. Free energy term</td>
<td>$R_{ab}, A_{a}$</td>
<td>G</td>
<td>(vi)</td>
</tr>
</tbody>
</table>

Figure 4. Typical Relationship Between the Terms of the NCZ Expression and the Mole Fraction of the Larger Species.
two, and the total number of parameters for all terms is precisely that of the spanning set on page 22, remembering that \( x, n \) and \( T \) are the variables subject to external manipulation and which are not properties of the materials being examined. The potentiality of the NCZ expression as an analytical tool stems to no small extent from the fact that, as will be seen in Figure 4, terms \( t_1 \), and \( t_5 \) respond to molecular geometry and in the case of \( t_5 \) to free energy also, but not to site fraction \( (n_1) \), heat of mixing \( (\omega_{ij}) \) or polymer length \( (n_1) \). Terms \( t_3, t_4' \) and \( t_4'' \) on the other hand do not respond explicitly to molecular geometry (i.e. not to \( R_{ab} \) or \( n_1 \)). While terms \( t_2 \), \( t_4' \) and \( t_4'' \) all respond both to heat of mixing \( (\omega_{ij}) \) and site fraction \( (n_1) \), the approximate magnitude of term \( t_3 \) is frequently estimable a priori through external evidence (such as difference of polarity between corresponding species). Terms \( t_4'' \) and \( t_4' \) are basically similar and simply appear as two separate terms to differentiate between the simple heat of mixing effect between monofunctional species, and the more complex relationship between multifunctional ones.

Further comments on the behavior of these individual terms is probably more conveniently left until after the response of terms \( t_1 \) to \( t_5 \) to composition, as characterized by the sketches on the right hand side of Figure 4, have been expanded in Figure 5(a) to 5(f).

The conventions of Figures 5(a) to 5(f) must first be explained. The coordinates are normalized energy \((G^E/RT)\) plotted against the mole fraction of the larger molecule, and the
Figure 5(a). Response of NCZ t-Terms to $x_{\text{LARGER}}$. Term $t_1$.

\[ \theta_1 \neq \theta_2, \text{ large} \]
\[ ab < bc \]
\[ J_1 \leq J_2 \]
Figure 5(b). Response of NCZ t-Terms to $x_{\text{LARGER}}$ Term $t_2$.

$\theta_1 \geq \theta_2$, both quite large

$ab < bc$
\[ \left[ \frac{\omega_{ij}}{\omega_{ave}} - 1 \right], \eta_{ia} \]

\[ \theta_1 \approx \theta_2 = \text{small} \]

\[ ab \leq bc \]

Figure 5(c). Response of NCZ t-Terms to $X_{LARGER}$. Term $t_3$. 

---

POSSIBLE ALTERNATE FORM
Figure 5(d). Response of NCZ t-Terms to \( x_{LARGER} \). Term \( t_4 \).
Figure 5(e). Response of NCZ t-Terms to $x_{\text{LARGER}}$. Term $t_4$.
Figure 5(f). Response of NCZ t-Terms to $x_{Larger}$ Term $t_5$. 

$\theta_1 \neq \theta_2$, large $R_{ab}$

$ab < bc$

$J_1 \neq J_2$
examples cited are for binary mixtures.

In the trivial case of a Raoult's law solution, all the curves are horizontal straight lines (i.e. of zero amplitude). The Figures drawn therefore all characterize attributes of mixtures which are, in one way or another nonideal.

Features of a typical curve of the series 5(a) to 5(f) are constructed as follows:-

1) The amplitude (s) are marked as J (or J₁ and J₂).

2) All the curves have zeroes for the pure component states (designated as a and c), but some also have one additional zero in the mixture range, (designated as b). Some of the curves (t₄, for example) are of unimodal central maximum type. The composition corresponding to the maximum is also labelled b.

3) Also shown on all the curves of Figures 5(a) to 5(f), is the general direction of movement of the composition of some point of interest in the mixture range (such as a zero value of $G^{E}/RT$ for a sigmoid curve, as at b), or an extremum in a unimodal curve, such as a curve maximum (again indicated by b). Also shown is the amplitude response to input parameters. The convention used is that the point of interest will move in the direction of the arrow shown as the stated parameter increases.

4) Also indicated are $\theta_1$ and $\theta_2$, the angles of approach of the $(G^{E}/RT)$ curves to the abscissa in the infinite dilution regions.

5) In some cases, alternative forms of the curves being discussed arise in special cases, which are described in con-
Figures 5(a) to 5(f) have illustrated the analytic features of the terms of equation (212). Table 4 demonstrated the generality of this equation, and the subsequent Figures demonstrate, in conjunction with equation (212) and the parameter groupings on the right hand side of Table 4, the specificity of response of the terms of equation (212) to the various subgroups of independent variables of Figure 4. It is therefore apparent that a t-term classification corresponds to, but extends and unifies, the classical classification scheme provided by standard categories of solutions, as included in Table 4.

In the immediately following Chapter, a number of real systems will be examined with respect to capacity of the NCZ equation to predict results, and on the way opportunity will be taken to discuss and contrast it with other solution theories.

15. INTERCOMPARISON OF FUNCTIONAL RESPONSES OF VARIOUS EXPRESSIONS

It is apparent from Figure 4 that terms $t_2$, $t_3$, $t_4'$ and $t_4''$ are all capable of giving rise to what might be termed unimodal central (central maximum or minimum) excess free energy component curves, of roughly the same shape, whereas $t_1$ and $t_5$ component curves are individually distinguishable and not even approximately similar in shape to the above unimodal central group, being instead 'leftward minimum' and 'leftward maximum' sigmoid in shape (with respect to rightward increase in mole fraction of the larger molecular species). The $t_1$ and $t_5$ curves are shown by calculation to be not sinuosoidal, and are only partly compensating.
The algebraic form of term $t_2$ has a modified logarithmic argument, that of $t_3$, while complex, usually exhibits a 'central maximum' response, and curve $t_4$ is roughly parabolic. Nevertheless, the gross interresemblance of these three types of $t$ versus $x$ curves would allow the fitting of experimentally derived excess free energy curves which are of a general 'central maximum' type with quite good success by means of an expression containing any one of the above-described functions provided the excess free energy of the system is not too large. Thus, for example, the Wilson equation, whose form give rise to a modified logarithmic 'central maximum' shape, achieves quite good success in fitting systems exhibiting any or all of the three NCZ effects mentioned, as does that of Hildebrand, Barker, the NRTL equation and the ASOG equation, although thermodynamic interpretation of the best-fit parameters will vary considerably depending on which theory is being applied. A general comment which will prove to be useful in the present discussion should be introduced at this point.

It will be seen from the NCZ equation that attention is being focussed on what might be called an "$\xi$" liquid rather than on an "$x$" liquid. That is, the emphasis is being put on the proportion of distinguishable pair-species of various kinds existing within the overall mixture, rather than simply on the proportion of molecules of various kinds within the same mixture. When entropy effects are of prime concern the parameter $\xi$ is singly involved; when interaction effects are of concern the product $\xi_a \times \xi_b$ is inevitably involved.
Noting that

\[ \frac{\xi_a}{\xi_b} = \frac{z_a x_a n_a}{z_b x_b n_b} \]  \hspace{1cm} (219)

and adopting the convention that \( z_a > z_b \), then \( \frac{\xi_a}{\xi_b} \) for monomers will always be greater than \( \frac{x_a}{x_b} \). Specifically since the product \( \xi_a \times \xi_b \) will have a maximum where \( \xi_a = \xi_b \), this will occur where \( x_a < x_b \). It will be seen that terms \( t_{4}' \) and \( t_{4}'' \) contain the product \( \xi_a \times \xi_b \) explicitly (see equation (212)), and term \( t_3 \) contains this product in a more obscure way, and therefore all three of these terms must show skewing when the coordination numbers are not equal. By way of illustration of the just-mentioned skewing effect, the maximum in the heat of mixing term \( \left( t_{4}'' \right) \), which involves pair products \( (\xi_a \times \xi_b) \), is somewhat shifted toward compositions dilute in the larger component for mixtures of unequal sized molecules in the NCZ treatment.

However, it is possible to skew central-maximum curves (notably the equivalent of \( t_{4}'' \)) in various other ways, and thereby use terms derived to represent 'central maximum' effects to produce single-maximum curves, the composition of the maximum being in the region where the \( t_5 \) curve of the NCZ equation has its positive maximum. For example, this effect is accomplished, in the relation of Hildebrand, by using the volume fraction product in the parabolic heat of mixing term. In the case of mixtures of sufficiently large globular fluorcarbons and small globular solvents, maxima in the heat of mixing formulation characterized in the Solubility Parameter expression are thereby highly displaced into the region dilute in the larger species, where maxima in the experimentally observed excess free energies are seen to occur.
The problem with using the heat of mixing term to explain excess free energy maxima in a region so far removed from the equimolar, emerges in systems in which there is evidence of a superposition of both a leftward maximum, and a relatively centrally positioned effect, both of comparable importance. While the NCZ analysis of both systems 5 and 6 is based on the existence of both effects, the situation really becomes analytic for both when the heat of mixing starts to become large. Such is the case in the system Pentaerythritol tetramerfluoro-buturate c-Octamethyl siloxane studied by Shinoda and Hildebrand(54). The uncomfortable question then arises as to how to fit both effects with a single term in such a system. Empirically, this is accomplished in the case of the NRTL equation, by creating two parts to the heat of mixing term, the parts of which can now be made to maximize at fairly widely differing compositions, provided sufficiently different parameters are inserted into the two heat of mixing constants appearing in the expression (see equation (258)). Solubility Parameter Theory, however, has no such provision.

Where both a 'central maximum' and a far leftward and/or rightward effect are exhibited in the excess free energy curve at the same time for a system, the particular usefulness of the NCZ equation at the purely empirical level is shown. For a system of unequally sized molecules, both \( t_1 + t_5 \) and \( t_4'' \) curves exhibit maxima, which are considerably displaced from each other. An example of the latter behavior encountered in the systems studied in this work is n-Butane-Hydrogen sulfide (system 7).
In the comparison of functional responses of various expressions, the temperature characteristics of the various types of terms employed need also to be considered.

A significant property of the $t_5$ term of the NCZ expression is that its energy constants are free energies, not heats of mixing (i.e. not enthalpy differences). While the function $(H^E/RT)$ diminishes with $T$, the function $(A^E/RT)$ is capable of either decreasing or increasing somewhat, and at least in general 'attenuates' with increased temperature much more slowly, if indeed it attenuates at all. This accounts for the basically different temperature characteristic of the $t_5$ curve compared with the heat of mixing type of term. The $t_5$ effect persists to much higher temperatures than does a heat of mixing effect. It is this behavior which is thought to explain the extremely narrow (and leftward) two-phase envelope of the more extremely unequal sized fluorocarbon-solvent mixture of Hildebrand and coworkers. In another system included in this work, the sulfur-benzene system, also fitted by the NCZ expression, increase of the free energy constant of sulfur at high temperatures accounts in part for the system's unusual high temperature phase behavior. This increase is thought to explain the reappearance at a high temperature of a two-phase region, with a lower critical solution temperature, in the composition range dilute in the larger component (i.e. dilute in Benzene).

The advantages and disadvantages of displacing central maximum curves by various means, the benefits and drawbacks of the existence of at least three identifiably different types of 'central maximum' effect in solutions, and the varieties of
temperature response exhibited in various formulations for mixture effects in solutions are considerations which have relevance to most of the theories discussed in this Chapter. Some further effects of large pairs energy interactions on pairs-concentrations theories (that of Barker and the NCZ expression) need to be added to the discussion before concluding the formal side of the explanations of the behavior of excess free energy expressions' responses to input parameters.

The possibility of a sigmoid response of \( t_4' \) (the net heat of mixing term of a multifunctional solution) has been indicated in Figure 5(d), as has that for the \( t_3 \) term in Figure 5(c). Any verbal observation on the behavior of these two terms for solutions of groups of widely differing affinity (such as solutions containing OH and alkane groups) is likely to be an oversimplification. As is evident from Chapter 9, the existence of any one unusually large value of \( \omega_{ij} \) redistributes the pairwise associations of the entire \( x_{ij} \) matrix. Hence, effects either directly dependent on the behavior of individual pairwise concentrations with composition (as is the case with \( t_4' \)), or upon all of them at once (as is the case with \( t_3 \), which estimates the entropy decrease due to the reorganization of the \( x_{ij} \) matrix from the energetically random ideal value corresponding to maximum entropy), may respond in very complex ways to such energy disturbances in the solution. In the case of \( t_4' \), if \( \omega_{ij} \) for a given interaction is more negative than about \(-4000\) cal/s/mole of pairs at ordinary temperatures, and is also much larger than other attractions, a rather unexpected result can
occur. Very energetic pairs of interacting groups present in a multifunctional liquid may cluster more highly when 'inert diluent' is present than when the liquid involved is in the pure component state. This occurs when the increase in mutual orientation made possible by the presence of 'inert diluent' molecules more than offsets the straightforward diluent effect, so that the population of preferred interactions actually indicated increases rather than decreases as a result of dilution. This behavior then gives rise to a negative region in that pair's contribution to $t_4'$, contrary to what one would suppose from the sign of $\omega_{ij}$ alone. Finally, of course, the dilution effect overcomes that of increased specificity of orientation, and the component of the $t_4'$ term due to that pair then becomes positive. When various very strong (but not equally strong) pairwise interactions effects between multifunctional molecules exist, the rearrangements of the $X_{ij}$ matrix, hence the sign of the various pairwise contributions to $t_4'$ become difficult to predict short of doing calculations.

The term $t_3$ can also become sigmoid, but usually under rather different energy conditions: in a weakly energetic solution, large geometry effects and small energy effects may dominate in different composition ranges and cause a small amplitude sigmoid curve. In highly energetic solutions, particularly those exhibiting large differences in interaction energy, $t_3$ is almost always positive, relatively large and unimodal. Particularly when the strong interactions are polar, $t_3$ tends to attenuate more rapidly with temperature than does $t_4'$ or $t_4''$. 
A final comment on the effect of large pairwise energy interactions on the behavior of various terms involves the presence of very large positive ('unmixing') pairwise interactions. In the case of dilute solutions of very large molecules in small ones, between which a large positive interaction energy also exists, NCZ effects are first severe (in very dilute solution), then rapidly attenuate in more concentrated solutions, as the large positive interaction energy forces the species to segregate (even if no phase break results), hence forces the coordination number ratio toward unity. This effect appears to operate in the nicotine water system reported in this work, and also in certain sour-gas-light hydrocarbon systems currently under investigation (though not included in the detailed results of this work).

In discussions of the next chapter, the foregoing general considerations and comparisons will be detailed with specific systems, although it should be by now realized that programming the NCZ equation with appropriate parameter values does not rely on the observers' judgement of what, a priori, should happen in very complex cases, but simply exhibits the results in response to the given inputs. In simple cases, like most of those described above, the consequences are predictable in advance; in very complex cases, some very unusual behavior may result which is far from being obvious. If the equation is analytic in simple cases, and formally applicable in the complex cases, its performance in the latter cases can be hoped to give insight into some of the more sophisticated effects
exhibited by such solutions.
CHAPTER 11

ILLUSTRATION OF THE PREDICTIVE EQUATION

1. NATURE AND METHODS OF COMPARISONS

2. BASIS OF DETAILED GRAPHICS

3. VAPOR-LIQUID SYSTEMS
   A. n-Butane Hydrogen Sulfide
   B. 2-Propanol Water
   C. Methanol Carbon Tetrachloride

4. LIQUID-LIQUID SYSTEMS
   A. Systems with an Upper Critical Solutions Temperature Only
   B. The System Nicotine Water
   C. The Systems Benzene Sulfur, Toluene Sulfur and m-Xylene Sulfur
1. **NATURE AND METHODS OF COMPARISONS**

In this chapter, quantitative comparisons in graphical and numerical form are made between the experimentally derived excess free energy of mixing versus composition curves for seven binary systems and those resulting from various predictive expressions. The systems have been chosen as representative examples of the classes of systems discussed in Chapter 9, and are among those listed in column 1 of Table 4.

Table 5 indicates which expressions have been considered in conjunction with which system. Emphasis is placed on examining a broad range of rather highly nonideal system types rather than on exhaustively testing any one group. The total number of systems tested was not large, because each one represented a new set of particular problems. Not all systems are compared by all methods, but the comparisons made are felt to be illustrative.

As is discussed in Appendix 2, there are a number of ways in which the values of \(G^E/RT\) versus composition expressions can be compared with the corresponding experimentally derived values. However, for reasons given in that appendix, it was decided to produce liquid mixture excess free energy
**TABLE 5**
Comparisons Made Between Theories and Experimental Results.

<table>
<thead>
<tr>
<th>System no.</th>
<th>System*</th>
<th>Phase</th>
<th>Expt.</th>
<th>NCZ</th>
<th>NRTL (8(a)^* )</th>
<th>Wilson (8(b))</th>
<th>ASOG</th>
<th>Solan</th>
<th>Barke (8(e))</th>
<th>Key</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>PFH-CCl(_2)</td>
<td>L/L</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>PFH-CCl(_3)</td>
<td>L/L</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>(\text{C}<em>9\text{H}</em>{11}\text{O}) - (\text{H}_2\text{O})</td>
<td>L/V</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>(\text{p-PROP-H}_2\text{O})</td>
<td>L/V</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>(\text{CH}_3\text{OH-Cl})</td>
<td>L/V</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>NIC-H(_2\text{O})</td>
<td>L/L</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11(a)</td>
<td>BZ-S</td>
<td>L/L</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td></td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>11(b)</td>
<td>TOL-S</td>
<td>L/L</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td></td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>11(c)</td>
<td>(\text{n-XY-S})</td>
<td>L/L</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td></td>
<td>✓</td>
<td>✓</td>
</tr>
</tbody>
</table>

- Numbering consistent with Table 4.
- ** Keys to Tables 8(a) to 8(e) for parameter settings.

Key:
1. Good fit
2. Poor fit
3. Not applicable

Published parameters had to be modified to get good fit.

Good fit expected but not tried out.

Probably inapplicable.
\( \frac{G^E}{RT} \) versus composition curves from vapor liquid equilibrium data for comparison with the calculated expressions. For those systems exhibiting liquid-liquid equilibria, experimental versus theoretically derived consolute envelopes were compared.

The numbering system was established by Table 4 in Chapter 10. The systems to be discussed in the chapter are included in Table 5, using the same numbering plan. Systems 1, 2 and 3 which are not to be discussed in detail, are representative of mixtures for which the classical prediction equations were derived, although not all of them apply to all three classes. System 4 is one of intermediate difficulty, which has recently yielded to the work of Wilson, Prausnitz and Renon, Derr and Deal. Phase equilibrium properties of System 5 have been predicted by Hildebrand's method, as are those for System 6, regarded by Hildebrand as an extreme example of the class typified by System 5. Systems 7 to 9 have been found by various workers to present real difficulties in prediction, and no single equation in present use works for the whole group. The behavior of System 10 and System 11 has not, to the author's knowledge yet been predicted. All of the systems, with the exception of Systems 12 and 13, which by definition are ultra vires, were found to yield quite well to the equation proposed. (In regard to the inapplicability of the NCZ equation to fit systems 12 and 13, the word 'clathrate' implies highly concerted interactions between nearest neighbors, thus completely invalidating the independent pairs assumption. The inherent inappropriateness of the NCZ Equation for type 13 (ionic) systems will be apparent
from the comments made in Appendix 1. In this chapter a closer look will now be taken at Systems 5 to 11 inclusive. It will be convenient to begin by discussing systems in which vapor-liquid equilibrium is investigated.

In order that the argument will be as little encumbered as possible, the numerical data from which the NCZ curves for these systems have been calculated is given in Table 6, rather than being listed here. Reference to other workers' experimental data and particular methods of estimating physical properties is shown in Table 7. Tables 8 list the parameters used in the present work when an expression of some other worker had to be shown in connection with the experimentally derived \( \frac{G^E}{RT} \) results. In some cases the parameters given by the earlier workers had been those most appropriate to the correlation of many systems and thus did not give the best possible fit for a specific system. In order that these alternate expressions might be seen in their best light, such parameters were refitted to suit the specific system under examination, and these values are the ones reported in Table 8. The same procedure was followed where values of certain parameters did not exist, or at least could not be found in the literature to hand.

2. BASIS OF DETAILED GRAPHICS

The basis for the detailed graphics is now shown in the Figures of this Chapter.

The numerical contribution of each of terms \( t_1 \) through \( t_5 \) of the NCZ equation to the overall excess free energy of the
<table>
<thead>
<tr>
<th>TABLE 6</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>NCZ PARAMETERS FOR SYSTEMS TESTED</strong></td>
</tr>
</tbody>
</table>

**VALUES USED IN THE NCZ EQUATION**

<table>
<thead>
<tr>
<th>COMPOSITIONS</th>
<th>T°C</th>
<th>( R_k )</th>
<th>( k_0 )</th>
<th>( k_1 )</th>
<th>( k_2 )</th>
<th>( k_3 )</th>
<th>( k_4 )</th>
<th>( k_5 )</th>
<th>( k_6 )</th>
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<td>( F_2C_2H_5 - CHCl_3 )</td>
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<td>( CI - CCI_2 - CHCI_3 )</td>
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<td>( CI - COCl )</td>
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<td></td>
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<tr>
<td>( CI - CI(12) )</td>
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<td>-5000</td>
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<td>( CI - CI(12 - H_2) )</td>
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<td>1.</td>
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<td>65</td>
<td>-2800</td>
<td>0.30</td>
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<td>1.</td>
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<td>0.12</td>
<td>-3000</td>
<td>0.73</td>
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<td>65</td>
<td>-2800</td>
<td>0.30</td>
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<td></td>
</tr>
<tr>
<td>( Cl - Cl(12 - H_2) )</td>
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<td></td>
<td></td>
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<td></td>
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<td>-2500</td>
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<tr>
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<td>1.75</td>
<td>0.4</td>
<td>-6000</td>
<td>0.3</td>
<td>-2500</td>
<td>0.3</td>
<td>-2000</td>
<td>0.7</td>
<td>-2200</td>
<td>0.30</td>
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<tr>
<td><strong>SYSTEM 11</strong></td>
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<td></td>
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</tr>
<tr>
<td>( Cl - Cl(12) )</td>
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<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>25</td>
<td>1.57</td>
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<td>-2100</td>
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<td>-6500</td>
<td>0.3</td>
<td>-2200</td>
<td>0.3</td>
<td>-2000</td>
<td>0.7</td>
<td>-2100</td>
<td>0.30</td>
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<td><strong>SYSTEM 12</strong></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( Cl - Cl(12 - H_2) )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>1.58</td>
<td>0.4</td>
<td>-1500</td>
<td>0.3</td>
<td>-1500</td>
<td>0.3</td>
<td>-2000</td>
<td>0.7</td>
<td>-1400</td>
<td>0.30</td>
</tr>
<tr>
<td>30</td>
<td>1.58</td>
<td>0.4</td>
<td>-1500</td>
<td>0.3</td>
<td>-1500</td>
<td>0.3</td>
<td>-2000</td>
<td>0.7</td>
<td>-1400</td>
<td>0.30</td>
</tr>
</tbody>
</table>

**KEY TO TABLE 6**

- F • FLUORINE
- CI • CHLORINE
- A • UNDIFFERENTIATED TYPE
- S • SULPHUR
- H • ACTIVE HYDROGEN
- I • ALKANE
- O • OXYGEN
- N • NITROGEN
- *Aromatic

**Notes:**
- * • SITE FRACTION / ON SPECIES A
- # • PAIRWISE INTERACTION ENERGY IN CALS/MOLE OF PAIRS.
- *SITE FRACTION / ON SPECIES A
- #SITE FRACTION / ON SPECIES A
- **SITE FRACTION / ON SPECIES A

<table>
<thead>
<tr>
<th><strong>DIRECT ESTIMATE</strong></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>( V_{z} / \nu )</td>
<td>( V_{z + 1} / \nu )</td>
<td>( V_{z + 2} / \nu )</td>
<td>( V_{z + 3} / \nu )</td>
<td></td>
</tr>
</tbody>
</table>

**Notes:**
- *MEASURED AT 121°C (REF 60)
- *E MEANS ESTIMATED FROM RELATED COMPOUNDS
- *ESTIMATED FROM SUMMING ATOMIC VOLUMES
- #SITE FRACTION / ON SPECIES A
- **SITE FRACTION / ON SPECIES A

**Bracketing Convention:** Example: 5(1) means 5 on component 1. Unbracketed site types are either unambiguous or same on either component.
<table>
<thead>
<tr>
<th>System No.</th>
<th>System</th>
<th>Quantity in NCZ Equation</th>
<th>Exp. Data</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>A (1) (\omega_{ij})</td>
<td>(\eta_j) (1)</td>
</tr>
<tr>
<td>5</td>
<td>(C_7F_{16}(1) - CCl_4(2))</td>
<td>67</td>
<td>80</td>
</tr>
<tr>
<td>6</td>
<td>((C_3F_7COOCH_2)_4 - HCCl_3(2))</td>
<td>(68)</td>
<td>55</td>
</tr>
<tr>
<td>7</td>
<td>(n-C_4H_{10}(1) - H_2O(2))</td>
<td>60</td>
<td>-</td>
</tr>
<tr>
<td>9</td>
<td>(2-C_3H_7OH(1) - H_2O(2))</td>
<td>65 (64)</td>
<td>35</td>
</tr>
<tr>
<td>8</td>
<td>(CCl_4(1) - CH_3OH(2))</td>
<td>62</td>
<td>75</td>
</tr>
<tr>
<td>10</td>
<td>(C_{10}N_2H_{14}(1) - H_2O(2))</td>
<td>(66) (71)</td>
<td>35</td>
</tr>
<tr>
<td>11a)</td>
<td>(C_6H_6 - S)</td>
<td>(88), 82</td>
<td>(83)</td>
</tr>
<tr>
<td>11b)</td>
<td>Tol-S</td>
<td>(88), 81, 86</td>
<td>(82)</td>
</tr>
<tr>
<td>11c)</td>
<td>mXylene-S</td>
<td>(88), 81, 86</td>
<td>(82)</td>
</tr>
</tbody>
</table>

\(\omega\) indicates related compound
### TABLE 8(a)

**NRTL Parameters**

<table>
<thead>
<tr>
<th>System No.</th>
<th>System</th>
<th>$\Delta G_{21}/RT^*$</th>
<th>$\Delta G_{12}/RT$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>$n\text{-C}<em>4\text{H}</em>{10}(1)$-$H_2S(2)$</td>
<td>(0.4)$^*$</td>
<td>(0.4)</td>
<td>-</td>
</tr>
</tbody>
</table>

$T = 50.\,^\circ$C

* See Equation (258) of this thesis.

### TABLE 8(b)

**Wilson Parameters**

<table>
<thead>
<tr>
<th>System No.</th>
<th>System</th>
<th>$\Lambda_{22}^{**}$</th>
<th>$\Lambda_{21}$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>$n\text{-C}<em>4\text{H}</em>{10}(1)$-$H_2S(2)$</td>
<td>(0.625)$^+$</td>
<td>(0.625)</td>
<td>-</td>
</tr>
<tr>
<td>8</td>
<td>2-PROP(1)-$H_2O(2)$</td>
<td>(0.25)</td>
<td>(1.30)</td>
<td>-</td>
</tr>
<tr>
<td>9</td>
<td>CH$_3$OH(1)-$CCl_4(2)$</td>
<td>(0.470)</td>
<td>(0.010)</td>
<td>-</td>
</tr>
</tbody>
</table>

$^*$ See Equation (239A) of this thesis.  $^+$ own fit.
### TABLE 8(c) i

**ASOG Parameters**

**SYSTEM**: 9

2-PROP(1) - H₂O(2)

**D & D Parameters**

<table>
<thead>
<tr>
<th>COMPOUND</th>
<th>Group Counts (v_{ki})</th>
<th>Flory-Huggins Counts (v_{FH}^{i})</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-PROP (1)</td>
<td>(3)*</td>
<td>1.</td>
</tr>
<tr>
<td>H₂O(2)</td>
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<td>1.4</td>
</tr>
</tbody>
</table>

**Pair-interaction Wilson Parameter Array**

<table>
<thead>
<tr>
<th>Neighbor Group</th>
<th>CH₂</th>
<th>OH</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>2</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Central Group</th>
<th>CH₂</th>
<th>OH</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.0</td>
<td>0.305**</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>0.0147</th>
<th>1.0</th>
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<tbody>
<tr>
<td>OH</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Bracketed values due to the author. Note that D. & D assign CH₂ group counts to alkane alcohols equal to the number of carbons.

**i.e. in D. & D's notation, a OH/CH₂ = 0.0147 = a₂₁ when "central" group is circled:

\[
a \text{OH/CH}_₂ = 0.0147 = a_{21}
\]

\[
a \text{CH}_₂/\text{OH} = 0.305 = a_{12}
\]

These parameter values are from Figure iv, p. 41 of D. & D's paper (Ref. 33). They are the 'best-fit' values for a set of alkane alcohol, ether and water systems. See Fig. 8(c).
TABLE 8(c) ii

ASOG Parameters

Best-fit values, this work, for the specific system 2-PROP- H₂O only.

SYSTEM: 9
2-PROP(1) H₂O(2)

<table>
<thead>
<tr>
<th>COMPOUND</th>
<th>Assignment of Geom. Factors</th>
<th>(v_{ki})</th>
<th>(v_{FH}^{i})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Group Counts ((v_{ki}))</td>
<td>CH₂</td>
<td>OH</td>
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<tr>
<td>2-PROP(1)</td>
<td>(3.)</td>
<td>1.</td>
<td>(4.5)</td>
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<tr>
<td>H₂O(2)</td>
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<td>1.4</td>
<td>1.</td>
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</table>

Pair-interaction Wilson Parameter Array

<table>
<thead>
<tr>
<th>Neighbor Groups</th>
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<tbody>
<tr>
<td>CH₂</td>
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<tr>
<td>OH</td>
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</tbody>
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<table>
<thead>
<tr>
<th>Central Group</th>
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<tbody>
<tr>
<td>CH₂</td>
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<table>
<thead>
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<th>OH</th>
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<tr>
<td>(0.001)*</td>
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*Bracketed values due to the author.
### TABLE 8(d)
Solubility Parameters

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<th>Syst. No.</th>
<th>System</th>
<th>$(\text{cals/cm}^3)^{1/2}$</th>
<th>$(\text{cals/cm}^3)^{1/2}$</th>
<th>$(\text{cm}^3/\text{mole})$</th>
<th>Ref.</th>
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</thead>
<tbody>
<tr>
<td>5</td>
<td>PFH(l)</td>
<td>(5.6)**</td>
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<td>226. 97.</td>
<td>(80)</td>
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<tr>
<td>5</td>
<td>CCl₄(2)</td>
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<td>8.6</td>
<td>80</td>
<td>(15)</td>
</tr>
<tr>
<td>6</td>
<td>PFH(l)-HCl₃(2)</td>
<td>(7.1) [7.7]</td>
<td>(9.0) [9.3]</td>
<td>553. 82.6</td>
<td>(55)</td>
</tr>
<tr>
<td>10</td>
<td>NIC(l)-H₂O(2)</td>
<td>(18.2)</td>
<td>23.5</td>
<td>151. 18.</td>
<td>(69)</td>
</tr>
</tbody>
</table>

* [ ] denote literature values which did not work.

** values calculated in this work

### TABLE 8(e)
Barker Parameters

See references (19, 75).
system is calculated for a series of compositions. These individual values, together with their sum are plotted against composition. The resulting sum curve is that of the excess free energy for the system and can be used directly to compute vapor-liquid equilibria via relations given between $G^E$ and $\gamma_i$. Where the contribution of any term of the NCZ equation is small and not of interest, that term is not plotted although its contribution is always included in the sum curve.

In the three examples related to vapor-liquid equilibrium about to be discussed, the data is presented in the form of a comparison between the net excess free energy as calculated by the NCZ equation and that derived from experimental vapor-liquid equilibrium data. The experimentally derived value of $G^E/RT$ is back-calculated by means of the equation:

$$
G^E/RT = \sum_i x_i \ln \gamma_i
$$

(292)

where $\gamma_i$ has first been obtained by solving the single component phase equilibrium relation

$$
y_i \phi_i^\pi = \gamma_i x_i p_i^o \phi_i^s \exp \left(v_i \frac{(\pi - p_i^o)}{RT}\right)
$$

(293)

where the $\phi_i^\pi$ and $\phi_i^s$ are fugacity coefficients determined as in reference(10).

The method of presentation of the systems to be examined is essentially that presented for the perflouro-n heptane carbon tetrachloride system on page 162 . The interesting and
numerically significant curves out of the group of $t_1$ through $t_5$ will be displayed. Some terms will not be shown individually, but in all cases all terms were included in the computation of the final sum of terms constituting $(G^E/RT)$.

3. **VAPOR-LIQUID SYSTEMS**

   A. **Butane Hydrogen Sulfide**

   For this system these curves are displayed in Figures 6. Complicating factors in the analysis of this systems were:

1) The relatively high pressure (ranging from about 0.1 to 0.4 of the critical pressure) and

2) The low liquid cohesions, resulting in a rather expanded liquid phase.

In reducing vapor pressure data for purposes of obtaining the experimentally derived $(G^E/RT)$ curve, appreciable vapor phase fugacity coefficients are involved. $H_2S$ is a weakly self-interacting molecule which is slightly polar. The size difference between the two species is moderately large. Under such circumstances significant contributions to the overall net free energy arise from $t_1$, $t_2$, $(t_4' + t_4'')$ and $t_5$ of the NCZ equation, (see Figure 6(a)). The value of term $t_2$ shown results from two assumptions. These are that the $H_2S$ molecule has two types of sites, and that the effective chain length of butane in its most probable configuration can be considered as unity. The approximately symmetrical shape of $t_2$ taken also with the rather similar shape of $(t_4' + t_4'')$ makes it difficult, analytically, to apportion the contribution of the individual curves. Nevertheless, in this case, $t_2$ has been included, in order to illustrate its form in an actual
Figure 6(a). n-Butane Hydrogen sulfide. NCZ Component Curves at 50°C.
system. In Figure 6(b) the sum curve for the NCZ expression is plotted, along with the (suitably reduced) data of Hughes.

It will be seen that the agreement is good especially allowing for the unusual shape of the curve, but it must be admitted that this is one of the cases where a predictive method for determining the unlike pair vapor second virial coefficient had to be relied upon. Because in the system vapor nonideality is of the same order of magnitude as liquid phase nonideality, the shape of the experimentally derived $G^E/RT$ versus composition curve is fairly sensitive to the magnitude of the predicted value of the unlike virial coefficient.

Figure 6(b) shows the closest fitting of the NRTL and Wilson curves as well as the already mentioned NCZ curve and that experimentally derived for excess free energy of mixing of the system.

It is apparent from inspection of Figure 6(b) that both Wilson and NRTL expressions tend to produce $(G^E/RT)$ curves which are too "rounded" in this case, so that a good fit in the dilute regions produces a curve which is too high in the equimolar region, and a good fit in the equimolar region gives rise to a curve which is too low in the dilute regions. In the case of the Wilson equation, these problems may have contributed to the rather large deviations between the Wilson fit and the experimental values for the Butane - $H_2S$ System, reported by Robinson and Saxena (89). It is evident that the good fit produced by the NCZ expression arises from the existence of the
Figure 6(b). n-Butane Hydrogen Sulfide. Excess Free Energy - Calculated and Experimental.
t_1, and t_5 components of the overall excess free energy.

B. 2-Propanol-Water

This system represents an example of hydrogen bonding. The pairwise attractions are very large, but to some considerable degree, are compensating because the attraction between unlike molecules is comparable in magnitude to that between like molecules. There is, however, a significant residual heat of mixing. The hindered rotation term is larger than any of the others and relatively symmetrical. Although the system has a fairly large radius ratio, the magnitude of pairwise interactions tends to reduce the significance of this effect, as discussed in Chapter 10.

For this case two sets of input parameters have been used to illustrate the changes which can result in the excess free energy from changing the interaction energies assumed. The results from both these sets are plotted in Figure 7(a) and in Figure 7(a)' showing in both cases the curves for t_3, (t_1 + t_5) and (t_4' + t_4''). A point of interest is that the (t_1 + t_5) curve is in this case negative for all compositions, whereas, in some other discussed it shows a positive portion in mixtures rich in the smaller molecule. Figure 7(b) shows the experimental results for excess free energy and points calculated from the data used in producing Figure 7(a) and 7(a)'. 
Figure 7(a) and 7(a)'. 2-Propanol Water. NCZ Component Curves at 80°C. Two Sets of Parameters.
Figure 7(b). 2-Propanol Water. Excess Free Energy - Calculated and Experimental.
Excess free energy of mixing predictions given by the ASOG and Wilson expressions are included for purposes of comparison in this system in Figure 7(b). The best fit was obtained for the ASOG expression though the parameter settings giving this fit were not* the "best fit" for Alkyl plus OH group systems reported by Derr and Deal(33). The excess free energy curve for the Derr and Deal parameters is shown ("D & D"). An excellent fit of the propanol-rich portion of the range is afforded by the Wilson equation, which, however, results in excessive values in the water-rich region. Parameter values for the two ASOG curves and the Wilson curve are given in Tables 8. Results for this system indicate that the NCZ expression is able to predict results for hydroxyl-containing systems, though perhaps not as well as the ASOG equation, in this particular instance. While Barker's equation would have been of interest in this case, fitting it is difficult because of the large number of disposable parameters. It is discussed with reference to the next system, which also is strongly polar.

C. Methanol-Carbon Tetrachloride

The particular feature of significance in this system, and the reason why Barker studied it, is the extreme effect of hindrance of rotation reported. In this case the primary term is $t_3$ (the term related to hindrance of rotation). Terms * for reasons discussed at the beginning of this Chapter.
(t_{4}^{'} + t_{4}^{''}) and (t_{1} + t_{5}) are also plotted in Figure 8(a).

Figure 8(b) shows the experimental curve together with the calculated points. Because of its exceptional shape, the calculated points for the heat of mixing (given by (t_{4}^{'} + t_{4}^{''})) are also given in Figure 8(b), compared with experimental data.

It will be noted that in this case the fit is not noticeably better than that of Barker.

Reference curves selected for this system are those of Barker and Wilson, both of which are shown on Figure 8(b), along with the experimental curve and that derived from the NCZ expression. In this case the Wilson equation is regarded as giving marginally the best fit. However, again, the fit produced by the NCZ equation is comparable, indicating that it is capable of use in systems exhibiting extreme hindrance of rotation effects. Again, parameter values for the Wilson and Barker equations are given in Tables 8.

4. LIQUID-LIQUID SYSTEM

A. Systems with an Upper Critical Solution Temperature Only

Results for the two systems exhibiting this behavior (systems 5 and 6 in the current numbering scheme) have already been displayed in Figures 2(e) and 3(c) of Chapter 8, where their phase behavior was cited as providing especially strong evidence for the presence of the terms most analytic of NCZ effects, namely terms t_{1} and t_{5}, along with a small simple heat of mixing term t_{4}^{''}. Since both systems yielded to treatment as nonpolar monofunctional monomer binaries, the other terms of the general NCZ
Figure 8(a). Methanol Carbon tetrachloride. NCZ Component Curves at 30° C.
Figure 8(b). Methanol Carbon tetrachloride. Excess Free Energy -
Calculated and Experimental.
expression introduced subsequent to that point, namely terms \( t_2, t_3, \) and \( t_4' \), would either be zero ( \( t_2 \) and \( t_4' \)) or insignificant ( \( t_3 \)) for the two systems. Rapid attenuation of the simple heat of mixing effect was indicative that their unlike pair interaction was basically of "dispersion" type as expected for such relatively chemically insert species.

From the point of view of comparison of the experimentally measured consolute envelope with that derived from excess free energy expressions, other than NCZ and Solubility Parameter, the choice is somewhat limited. The Wilson equation is not to be used in cases where two liquid phases are involved (90). Since the constituents are both monofunctional molecules the group fraction of a given type of group is the same as its volume fraction, so that the Wilson term of the ASOG equation reduces to the Wilson equation. The separate molecular-scale Flory term of the ASOG expression, is, in any case, smoothly unimodal and approximately symmetrical, hence could not contribute to the change of curvature of the free energy of mixing curve required to produce a two phase region. The author was unable to find a set of parameters for the NRTL equation which could produce such an asymmetrical two phase region. Also, in view of the monofunctional nature of the species, Barker's expression, particularly useful where a strong hindrance of rotation effect results from unlike polar interactions, could not be expected to be particularly helpful.

In addition to reading the foregoing brief comments, the reader may wish at this point to review the Figures series 2 and 3 to refresh his mind on the salient aspects of the two
systems before passing on to the next system.

B. The System Nicotine-Water

An example for system whose liquid-liquid equilibrium phase behavior is relatively complex is the system Nicotine-Water. This system has always been one of very considerable interest to physical chemists because it displays both an upper and a lower critical solution temperature. From the viewpoint of the present work, the factors which are of importance and which lead to this remarkable solubility relationship, are an extraordinarily large radius ratio, the abnormal relationship between free energy and temperature for water, the partial compensation of the large nitrogen-water binding interaction by large H-OH binding of the water, and the rapid decrease of these (dipole type) interactions with temperature.

Curves generated by \((t_4' + t_4'\prime), t_3\) and \((t_1 + t_5)\) NCZ equation are shown for a series of temperatures in Figure 9(a). The heat of mixing given by term \((t_4' + t_4')\) is at first large and negative. It becomes positive and finally attenuates as pairwise interactions diminish as temperature is increased. The change of sign is primarily due to change in sign of the term \(t_4'\), which is negative for high magnitudes of O-H interaction, and positive for lower ones. The term \(t_4''\) is always a negative component and is mainly due to the strong interaction between the nitrogen atoms of the nicotine molecule and the hydrogen of water. It is this change of sign in the term \(t_4'\) which primarily causes the onset of the two phases at about 60°C.
Figure 9(a) and 9(b). Nicotine Water. Component and Sum Curves at a Series of Temperatures.
Term $t_3$ is very large and positive at low temperature and indicates the extreme hindrance of rotation caused by the attraction between the nitrogens of the nicotine and the hydrogen of water. The effect of increasing temperature in reducing polar interaction energies and in introducing randomizing effects, causes $t_3$ to attenuate rapidly. The maximum of the curve for $t_3$ is strongly towards the left and this determines the considerable leftward location of the consolute envelope at the lower temperature. Examination of the series 9(a) will now reveal that at the intermediate temperatures the decrease of the magnitude of the $t_3$ curve is more than offset by the increase in magnitude of the curve for $(t_{4'} + t_{4''})$ (now positive), and the two phase region is maintained. At the highest temperatures the only curve of significant magnitude is that for the heat of mixing $(t_{4'} + t_{4''})$. Were it not for the somewhat sigmoid shape of the $(t_1 + t_5)$ curve, the necessary inflection in the sum of all these curves, including of course that for the ideal heat of mixing, would either not be able to display the minimum free energy which is essential, or, alternatively, this minimum would occur much more towards the equimolar composition. The series 9(b) shows the overall net free energy for the series of temperatures and indicates the two-phase regions. Figure 9(c) displays this data along with the experimental consolute curve for the system.

The choice of reference curves for comparison for this system is also somewhat limited. The Wilson equation is ruled out because of two liquid phases being present. It is doubtful
Figure 9(c). Nicotine Water. Consolute Envelope - Calculated and Experimental.
if a set of NRTL parameters could be found to produce the observed degree of asymmetry or closure of the two-phase region. In any case, the equivalent of both an energy-induced local clustering effect in order to exhibit the equivalent of the sigmoid ($t_4'$) curve, and the equivalent of a hindered rotation ($t_3$) curve would probably have to be invoked to generate the lower critical solution point of a closed two phase envelope.

The ASOG equation which does not include either feature was not tried. The solubility parameter expression of Hildebrand, using the given molecular volumes, the Solubility Parameter for water, and a best-fit value for that of nicotine, provides a curve as shown on Figure 9(c). (The parameter settings used are recorded in Table 8(d)). The Solubility Parameter relation provides no mechanism for a lower critical solution temperature; so, despite the ability of the expression to be fitted to the correct concentration range for the upper critical solution temperature, it does not provide a very complete representation of the actual behavior of the system in this case, in contrast to its usefulness in Systems 5 and 6.

The expression which most closely resembles the NCZ expression for this system is that of Barker. Due to its large number of disposable parameters (when all its geometric factors are varied as well as its energy parameters), the author has not, to this point, attempted to fit it to the system nicotine-water, but believes that it might be capable of producing a closed two phase envelope. Whether it would be able to predict the correct concentration range for the upper critical solution temperature is far from certain, in view of the fact that this
range is fixed in the NCZ fit by the emergence of a slight positive leftward maximum in the \((t_1 + t_5)\) curve of the NCZ equation, due to the temperature increase of \((a_2/RT)\) for water at high temperature. Consequently this question must be left open for the moment, while regret is expressed for having not had the time so far to make an exhaustive attempt to fit Barker's expression to Nicotine-Water. Although Barker's expression does not take NCZ effects into account, these, in the case of Nicotine-Water at low temperatures, are almost completely suppressed by the very high pairwise interaction energies. (See values of these parameters in Table 6).

C. The Systems Benzene Sulfur, Toluene Sulfur and m-Xylene Sulfur

Figures 10(a) and 10(b) show NCZ equation prediction and 'experimental' consolute behavior of three Aromatic Sulfur systems. In all respects but one, the systems behave operationally as simply as do systems 5 and 6: all three systems are also analysable as monofunctional monomer binaries, in which the terms of equation (122) are the dominant ones. What accounts for the striking departure from systems 5 and 6 (namely, the appearance of an upper consolute region) is the fairly high positive temperature rate of increase of the magnitude of the 'a_2' constants in the term \(t_5\). This temperature characteristic of the \(t_5\) terms is primarily responsible for the appearance of the upper disjoint consolute envelope for Benzene-Sulfur shown on Figure 10(a). Also shown are those calculated for Toluene Sulfur and m-Xylene Sulfur for comparison purposes. Note that m-Xylene Sulfur, whose NCZ effects are rather more severe than those of Benzene Sulfur, does not have a miscible
Figure 10(a). Benzene Sulfur, Toluene Sulfur; m-Xylene Sulfur. Calculated Consolute Envelopes.
Figure 10(b). Benzene Sulfur, Toluene Sulfur, m-Xylene Sulfur. Experimental Consolute Envelopes.
region in the 160 - 190°C temperature range.

Other workers\(^{(91)}\) have cited as the basis for the appearance of the upper consolute region in Benzene Sulfur the resurgence of a large endothermic heat of mixing effect due to the solvation-induced opening of \(s_8\) sulfur rings in the mixture region at high temperatures. The explanation offered in this work does not require the postulate, although the operation of such an effect would tend to widen (rightwards) the upper consolute region with respect to the curve shown corresponding to the NCZ calculation. It is interesting in this connection that the right hand limb of the upper consolute region (previously appearing on p. 308) appears to be somewhat too leftward. Nevertheless, the basic NCZ nature of the phase behaviour is indicated by the more leftward location of the left hand side of the upper consolute curve than of the lower, and by the displacement of both envelopes toward the left hand side of the composition region. When the Benzene-Sulfur system was studied by Hildebrand, only the lower consolute region was reported. However, the existence of the upper one had been reported by other workers\(^{(92)}\).

Except for the high-temperature behavior of the Benzene-Sulfur system, its other similarities to systems 5 and 6 are sufficiently great that comments on the applicability of expressions other than the Solubility Parameter and NCZ ones would largely be a duplication of what has already been said about systems 5 and 6 in this regard, so further comment on the subject
is omitted here. It is possible that the phenomenon of an upper disjoint consolute region might well be revealed for systems other than Benzene-Sulfur and Toluene-Sulfur as phase measurements were extended to temperatures well above the normal boiling points of the given mixtures in suitable apparatus. The eventual rapid increase in the 'a' constants for many substances would seem to indicate that this behavior might not be as rare as is presently reported. While for no member of the series Benzene Sulfur, Toluene Sulfur or m-Xylene Sulfur, predicted and experimentally derived consolute behavior matches perfectly; still the ability of the NCZ equation to depict a systematic progression of phase relations for members of a homologous series is clearly demonstrated, as reference to the parameter values in Table 6 will indicate. Figure 10(d), which displays the energy parameter values for the three systems as functions of temperature further bears out the regularity noted above. The dominant role of radius ratios in determining the degree of miscibility of a given aromatic -sulfur binary is borne out, in Figure 10(c), where the interchange of radius ratios in the m-Xylene Sulfur and Benzene-Sulfur systems respectively results in calculated equilibria more closely resembling the system whose radius ratio is employed rather than retaining the aspect of the system whose energies are being used.

At this point, it is hoped that the reader will realize that the NCZ equation has been tested both against data, and the expressions of five other workers, indicating its scope of applicability and ability to fit a large range, if not so far a
Figure 10(c). Benzene Sulfur, m-Xylene Sulfur. Calculated Consolute Envelopes with Radius Ratios Interchanged.
Figure 10(d). Benzene Sulfur, Toluene Sulfur, m-Xylene Sulfur.

Energy Parameter Plotted against Temperature.
large number of physical systems. Whether the tests shown have legitimized the expression and illustrated its usefulness sufficiently in the reader's mind, at this point must be left up to the reader. It must be remembered that in a theoretical endeavor, just obtaining the expression to be tested in a usable form accounts for a large portion of the efforts invested in the project. Also the testing of extreme systems is a slow business, but was felt by the author to be a more useful route to follow than to mass-produce intermediate cases which are always rather easy to fit but correspondingly less convincing, if not only the utility of the expression, but also its validity is in question, as is bound to be the case when a new result is produced. In the way of utility, though, it is hoped that what has been demonstrated is the ability of the NCZ equation to operate effectively in the extremely nonideal region of liquid-liquid equilibria, an area becoming more important with the present trend towards renewed interest in liquid extraction, as well as in the less extreme region of nonideality characterizing liquid-vapor equilibrium property calculation germane to industrial distillation.
CHAPTER 12

CONCLUDING REMARKS

1. JUSTIFICATION OF THE NCZ ASSUMPTION
2. NOTE ON NCZ POLYMER SOLUTIONS
3. JUSTIFICATION OF THE NCZ FREE ENERGY TERM
4. CONSISTENCY OF THE NCZ EXPRESSION WITH THE MASS LAW
5. MULTICOMPONENT SYSTEMS
6. DIRECTIONS OF FUTURE INTEREST
1. **JUSTIFICATION OF THE NCZ ASSUMPTION**

   This work has had several main preoccupations, but all have been facets of the major premise that the concept of the pairs-liquid of quasichemical mixture theory could be considerably extended in its range of applicability by a suitable formal incorporation of the effects of compositional variation of nearest neighbor coordination number for the usually encountered case of mixtures of unequal sized molecules.

   Problems inherent in CZ binary quasichemical theory and auxiliary problems involved in arriving at an NCZ multi-component formulation for $G^E/RT$, and means by which these have been satisfactorily overcome are summarized in Table 9.

   There seemed no really inherent reason to abandon the quasichemical approach in favour of volume fraction theories (solubility parameter, Wilson and NRTL theories for example) if the formal restriction of a constant - $z$ formulation could be lifted. By dint of several assumptions and considerable
<table>
<thead>
<tr>
<th>Limitation of CZ Theory</th>
<th>Approach to Obtain NCZ Multi-Component Formulation</th>
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<tbody>
<tr>
<td>1) Geometric: CZ lattice</td>
<td>Place lattice 'mechanics' in 'bed of spheres' conceptual framework. (This work).</td>
</tr>
<tr>
<td>2) Numerical: no means of calculating mixing coordination-number changes</td>
<td>Evaluate 'bed of spheres' coordination number. (Adapted from Hogendijk).</td>
</tr>
<tr>
<td>3) Formal: limitation to binary mixtures</td>
<td>Adopt 'probability' approach (Barker), rather than 'partition function' approach (Guggenheim).</td>
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algebra, the author feels that he has managed to do just this, or at least make a start at it, and feels that the success of the NCZ expression in coping with the wide range of systems such as Butane - H₂S, Perfluoro-n-Heptane-Carbon Tetrachloride, Pentaerythritol-tetraperoxfluorobutyrate Chloroform, and Xylene-Sulfur, all of which seem to exhibit quite noticeable NCZ packing effects in their excess free energy behavior, justifies the work so far undertaken in this direction.
Another necessary preoccupation of the work has been the attempt to demonstrate, insofar as possible, the formal compatibility of the NCZ formulation with that of other quasi-chemical theories, notably that of Barker, who lifted the other major formal restriction of the original quasichemical theory of Guggenheim, namely its restriction to monofunctional binary systems, a restriction imposed simply because a rigorous mass law approach to local compositions leads to insoluble coupled sets of equations when more than one unlike-pair species is present. The comparable performance of the NCZ expression with respect to that of Barker for the system Carbon Tetrachloride-Methanol indicates that for this multifunctional system (3 group species: Cl, CH₂ and OH), which also exhibits a severe hindrance-of-rotation entropy effect, is indicative that the two expressions are, at least in principle compatible. The inclusion of NCZ effects in Barker's multifunctional pairs concentration matrix is the contribution of the author in this area.

2. NOTE ON NCZ POLYMER SOLUTIONS

While the Flory-Huggins theory gives rise to an athermal excess free energy term which is always negative, the NCZ athermal term is usually negative in mixtures dilute in the larger compound, and positive in mixtures rich in it.

Constant- \( z \) quasichemical theories are (configurationally) compatible with that of Flory-Huggins for solutions of polymer chains of equally sized monomer units mixed with monomer solvent
molecules of the same monomer size, in that both use lattice permutation statistics to calculate their configurational entropy of mixing. The NCZ expression is also compatible with the Flory-Huggins polymer theory in this way. In the classical Flory-Huggins case (for flexibly-linked constant-z n-mer chains), there is a decrease in the total permutations of the system due to the fact that locating the terminal unit of an n-mer molecule restricts the radius of placement of its successive units to within a spherical domain of radius of n-lattice sites*, rather than "anywhere on the lattice". However, in the Flory-Huggins case, this is always more than compensated for by the increase in the total number of distinguishable methods of positioning the n units of the n-mer chain, with regard to an equal number of monomer units. Thus by this theory the presence of n-mers in a mixture always increases the number of combinations for lattice site occupancy, hence gives rise to a positive excess entropy of mixing term. This results in a negative Flory-Huggins athermal free energy term.

It has been shown that in NCZ solutions, even those of unequal sized monomers, athermal free energy of mixing terms may be of either sign, depending on the composition of the mixture. Term $t_1$, in fact, assumes negative value for solutions dilute in the larger component, and positive ones for solutions concentrated in the larger component, representing an increase in the number of distinguishable systems permutations in solutions

* less the proportion of these sites already filled by previously placed n-mer molecules
dilute in the larger species, in the region of maximum packing distortion by the larger species, and a decrease in distinguishable system permutations in solutions concentrated in the larger species. Term \( t_1 \) is therefore not a Flory-type of athermal term.

The explicit NCZ n-mer entropy effect occurs in term \( t_2 \). This term was not obtained by direct generalization of Flory's expression to the NCZ case. Barker had been successful in obtaining an expression for the hindered rotation entropy effect in a polar mixture through incorporation of the definition of the probability of groups of simultaneous independent events into the Boltzmann definition of entropy*, using as 'independent probabilities' the 'independentized' pairs probability array from his pairs probability matrix. The author was thus prompted to incorporate the definition of the dependent probabilities of grouped events into the same definition of entropy to obtain the NCZ polymer entropy term appearing in term \( t_2 \) in the NCZ expression. Both the term obtained and the Flory-Huggins expression are negative for all mixtures: but the algebraic forms are not identical although the two functions behave in a

* The assumption of independent events, requisite to the use of Boltzmann entropy, is allowable if the system considered is that of the pairs whose effective pairwise concentrations (probabilities) have indeed been rendered independent by iteration of the pairs probability matrix to convergence.
rather similar way.

While it is not difficult to incorporate a compositionally dependent coordination number into the Flory-Huggins derivation (see Appendix 3) the compatibility of the expression so obtained with the n-mer entropy effect in term $t_2$ has not yet been formally shown. This would come about by attempting to demonstrate the formal equivalence of the two expressions. Thus the question of the extension of the NCZ equation into polymer solutions has not yet reached the systems-measurement stage. In the systems studied in detail in the thesis, none of the compounds are of long enough chain length to involve sufficiently large values of the term $t_2$ to exhibit large configuration polymer entropy effects compared to the magnitude of other effects exhibited in the systems chosen. This aspect of the work then must still be considered an open line of pursuit at this stage. Under the heading of related theories, the comparison of Flory-Huggins and Heil expression with the proposed extension should be undertaken.

3. JUSTIFICATION OF THE NCZ FREE ENERGY TERM

In the matter of the energetics of pairwise interactions, the author feels that he has discovered the existence of an 'NCZ' free energy effect, as incorporated in the term $t_5$ of the general expression. The implications of this term are that the Gibbs free energy of mixing is not insensitive to packing changes, though, at least in principle, it is insensitive to volume changes as long as the mixture is free to assume its minimum-free-energy volume during the mixing process. The second fact of interest regarding this term is that it pro-
vides an explanation of the persistence of far-leftward, narrow two-phase envelopes to higher temperature than the usual temperature attenuation of \( \omega_{ij}/RT \) parameters would permit. This is due to the very different temperature characteristic expected of the \((a/RT)\) term, when \(a\) is a free energy rather than a heat of mixing enthalpy difference.

There are strong indications, provided by systems 5), 6) and 7) that the basic NCZ effect — namely, a distortion of packing numbers in mixtures of unequal sized molecules, — does operate in solutions, even up to pressures that are appreciable fractions of the critical pressure. Thus the author feels that one innovation of his thesis, which was to incorporate a purely mechanistic postulate of packing behavior analogous to that of a bed of random packed unequal sized spheres, with suitable modifications for energetically induced clustering effects into the model for a real liquid mixture, is vindicated by experimental results so far. No formal proof has been supplied for the validity of the packing model analogy in real solutions.

4. CONSISTENCY OF THE NCZ EXPRESSION WITH THE MASS LAW

The author wishes to point out that the NCZ expression — as a quasichemical expression, remains consistent with the mass law expression for the minimum free energy of the mixture. This statement applies specifically to the form of the energetically induced local clustering effect, which is dependent on \(\omega_{ij}\), rather than on the \((\varepsilon_{ij} - \varepsilon_{ii})\) type of energy differences characteristic of clustering effects of 2-liquid theories.
5. MULTICOMPONENT SYSTEMS

Though no ternary or higher order systems have been run yet, it is felt that multifunctional two-component systems (such as Carbon Tetrachloride-Methanol and Nicotine-Water) have been fitted with adequate success to indicate that the expected property of quasichemical solution theories, namely that of generalization to the multicomponent case without the addition of ternary interaction parameters, is at least to be reasonably expected to hold for the NCZ expression. Because of the essential reasonableness of this supposition, the author has used the limited time available to investigate some examples of a very broad range of binary system types, rather than a larger number of more closely related or relatively well behaved ones (which would have been faster to analyse), or to investigate relatively well behaved ternary or higher systems. From the point of view of generalization to the multicomponent case, it can be said at this point that there are no formal difficulties to be expected in this regard. On the purely pragmatic level, the examination of goodness-of-fit criteria by other methods enumerated in Appendix 2 needs to be undertaken. A study of several sets of binaries involving common species is also needed followed by multicomponent studies of groups or all of these, to test the internal compatibility of NCZ parameters in a network of related systems.

6. DIRECTIONS OF FUTURE INTEREST

Finally, a few general directions of future interest might be briefly considered. In the preceding chapter, pre-
diction of phase equilibria has been made using the NCZ equation and the results compared for systems for which some experimental data were available, and others had to be estimated. Further validation of the NCZ equation will partly depend on it being tested against a considerably larger number of systems for which more complete sets of the appropriate properties will have to be measured. Some of these measurements may be uncommon; for example, data for heat of mixing at constant volume rather than at constant pressure is required, or for the free energies of the pure component liquids at high temperature. It is hoped however, that the success claimed for the wide range of system types indicated along with the reasonably acceptable accuracy obtained, will encourage such testing.

Classical methods most easily deal with liquid-liquid equilibria for which the critical solution composition is but little removed from the equimolecular. The NCZ equation will equally well deal with this situation but also can account for the case of extreme deviations from equimolecular conditions towards mixtures dilute in the larger molecular species. A useful test of the proposed equation in a region not examined in this thesis would be to find conditions which would predict critical solution compositions rich in the larger molecular species (this would imply a dominance of $\mathbf{t}_1$ in that region, and therefore, systems might be sought in which this particular feature was emphasized). Traditionally systems of interest have been those centred on compositions lean in the larger molecule,
but perhaps mixtures rich in the larger molecule could prove to be equally interesting. A very severe test might be the prediction of systems with two two-phase envelopes, either "side by side" (in two composition ranges at the same temperature, or in two temperature ranges in different composition ranges.

The examples worked out in this thesis are all of binary systems, and clearly, real interest lies in multicomponent phase equilibria rather than in binary, no matter how non-ideal the behavior of the latter may be. Predicting the behavior of mixed solvent systems in liquid extraction, and estimation of vapor-liquid equilibria for multicomponent distillations are examples of such uses. It is in this field, now, that the major effort must be made.

However, the time and resources of a graduate student are somewhat limited, and at some point he is expected to write up the work and hand in his thesis. In this light, the author now proposes to do so, although obviously the job is not finished. He hopes that the project is not finished, even if the thesis is, on the grounds that the only lines of research that ever really finish are those which represent dead ends.
NOMENCLATURE

SUBSCRIPTS AND SUPERSCRIPTS

A Subscript. Refers to a specific segment on a given n-mer molecule.

a Subscript. Specifically designates molecular species a. (b = another molecular species.) When molecular species are multifunctional, double subscript ia designates the ith chemical functional group on molecular species a.

ave Subscript. Denotes an overall average quantity. See for example the definition of zave.

c Subscript. Used in Chapter 5 to designate a generic nearest-neighbor molecule.

E Superscript. Denotes an excess thermodynamic property.

f Subscript. Stands for 'free'. See for example the definition of free volume. The thermodynamic variable Free Energy is not given this subscript.

H Subscript. Stands for "Heil". See definition of $Q_H$.

i Subscript. Specifically designates the i type of chemical functional group. (j = another species.) On a monofunctional species, however, i therefore also unambiguously designates molecular species. Subscript i is used this way in Guggenheim's treatment of monofunctional binaries. The same applies to other standard texts.

mix. Subscript. Designates the property so subscripted as being that of a mixture.

mixing. Subscript. Denotes the net effect due to mixing. This effect is the same as the "excess" effect, except in the case of free energy.

s Superscript. Denotes the saturated state. See the definition of $\phi_i^s$.

s Subscript. Designates the self-interacting (pure-component) state. See definition of $z_s$.

v Subscript. Used in the sense of an operator, indicating that the property so subscripted was the constant-volume property. For example, $H_{v,\Pi}$ means H at constant v and $\Pi$. 
W Subscript. Stands for "Wilson". See definition of $Q_W$.

FUNCTIONS, OPERATORS

° Superscript. Designates the pure-component state. See definition of $q^\circ_i$ for example. If it is used to indicate degrees of temperature, as in 50°C, this will be clear from context.

□ Subscript. ("circle"). Circling an index specifically designates it as being regarded as the central species in a central-molecule-plus-nearest-neighbors-shell arrangement. $i\, j$ means neighbor $j$ around central $i$: $i\, j\, i$ means neighbor $j$ around central $j$. Circling takes precedence over subscript ordering conventions, which vary from author to author in the literature. In fact, centrality is a physical artificiality, though formally very useful.

~ Superscript. (Tilda). Denotes that a quantity is an average value over a specified domain.

— Superscript. Designates the quantity it applies to as being explicitly molal. Bar plus subscript $i$ or $a$ designates the quantity as being partial molal. $\bar{V}_i$ is the partial molal liquid volume of species $i$, for example.

∞ Subscript. ("infinity"). Denotes the infinite dilution state. See for example the definition of $\gamma_\infty$.

e Base of the natural logarithm.

$f_i$ When used in the context $(\Pi f_i)$ indicates a product of each of the $i$th single molecule generalized partition functions $f_i$.

$f_1, f_2, f_3$ Generalized functions used in Chapter 2.

$f_1(y, x)$ Bracketing is, "function-bracketing". $y$ and $x$ are thus denoted as independent variables in the argument of the function $f$. $A(z_i, z_j)$ means that $A$ depends upon $z_i$ and $z_j$.

k Proportionality constant

ln Natural logarithm.

$\mathbb{J}$ Means "such that". $\mathbb{J}(n_1 + n_2 = n)$ means that "such that" $n_1 + n_2 = n$.

δ Variational operator.

(i-j) The i-j pair as an entity.
Multiplication symbol, as distinct from mole fraction $x$ for example. The symbol is used explicitly to denote a multiplication operation where ambiguity or confusion with other operations might arise.

Division symbol. Consistent with FORTRAN practice, $A/B \times C$ means $(A/B) \times (C)$. The / operator designates only the symbol immediately following it as being a divisor, unless bracketing indicates otherwise. i.e. $A/(B \times C)$ or $A/(BC)$ indicate division by the product $B \times C$. For example, $z_i/z_{ij}N_i = (z_i/z_{ij}) \times (N_i)$.

Have their usual meanings.

$$\sum_{i=1}^{n} x_i$$
Denotes summation of the elements $x_i$ to $x_n$ inclusive.

$$\frac{\partial x_i}{\partial x_j}$$ Partial derivative of $X_i$ with respect to $x_j$. $\frac{\partial x_i}{\partial x_j} \vert_{x_k}$ means $\frac{\partial x_i}{\partial x_j}$ with other variables $x_k$ held constant.

$$\prod$$
Product operator. $\prod$ denotes a product of each of a number of individuals, each of which is designated by a value of $i$. $\prod_{i=1}^{n} x_i$ is a more explicit operation, specifying a product to be taken of each $x_i$ from $x_1$ to $x_n$ inclusive.

$$| |$$
Absolute values operator. Takes the magnitude of a quantity.

$$!$$
Factorial operator.

**VARIABLES**

A
Helmholtz Free Energy

$A_j$
Pure component Helmholtz free energy of species $j$ at the temperature of the system.

a
Generalized Helmholtz free energy per molecule, used in Chapter 2.

$a_i, a_a$
"$a$" constant of the $t_5$ NCZ terms for species $a$ or $i$.

$a_{ij}$
The Group Wilson Parameter for the $ij$ group interaction in the ASOG equation.

$a, b$
Wilson constants in the form used in Wilson's thesis. (See equations 276-279.)

$E_a$
Average proportion of the nearest-neighbor shell which is "exterior". i.e. not proximal chain units, for molecular species $a$. 
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{vap_i}$</td>
<td>The molal energy of vaporization of component i.</td>
</tr>
<tr>
<td>$g_{ij}$</td>
<td>Molecular-scale geometry factor for i about central j.</td>
</tr>
<tr>
<td>$g_i$</td>
<td>Generalized single-molecule geometry factor of species i.</td>
</tr>
<tr>
<td>$g_i$ or $g_{i-j}$, Generalized free energy per molecule factor used in Related theories in Chapter 10. Circled second index denotes species i is in the nearest neighbor shell of the jth species. Dash specifies pairs.</td>
<td></td>
</tr>
<tr>
<td>$G$</td>
<td>Gibbs Free Energy</td>
</tr>
<tr>
<td>$G_{mix}$</td>
<td>Gibbs Free Energy of the mixture</td>
</tr>
<tr>
<td>$G_{mixing}$</td>
<td>The Gibbs Free Energy change due to mixing.</td>
</tr>
<tr>
<td>$G^E$</td>
<td>The excess Gibbs Free Energy of mixing.</td>
</tr>
<tr>
<td>$\bar{G}^E$</td>
<td>The partial molal Gibbs excess free energy of mixing.</td>
</tr>
<tr>
<td>$H$</td>
<td>Enthalpy</td>
</tr>
<tr>
<td>$H^E$</td>
<td>The excess enthalpy of mixing (same as heat of mixing).</td>
</tr>
<tr>
<td>$K_{ij}$</td>
<td>Generalized local composition parameter used in discussion of the NRTL theory in Chapter 10.</td>
</tr>
<tr>
<td>$k$</td>
<td>Boltzman constant.</td>
</tr>
<tr>
<td>$m$</td>
<td>Number of species present in a mixture.</td>
</tr>
<tr>
<td>$N$</td>
<td>Avagardro's number.</td>
</tr>
<tr>
<td>$N_i$</td>
<td>Number of molecules of species i, $\mathcal{J} \sum_{i=1}^{m} N_i = N$.</td>
</tr>
<tr>
<td>$N'_i$</td>
<td>Hypothetical population of molecular species i, transformed via $N'<em>i = z_i / z</em>{ave}$ to compensate for equalization of coordination number $z_i$ to $z_{ave}$.</td>
</tr>
<tr>
<td>$n_i$</td>
<td>Number of particles of species i, defined by context.</td>
</tr>
<tr>
<td>$n_{ij}$</td>
<td>Number of ij pairs-bundles in a mole of mixture as used in equation (224).</td>
</tr>
<tr>
<td>$n_a$</td>
<td>Effective n-mer chain length of species a in a mixture.</td>
</tr>
<tr>
<td>$n_{ave}$</td>
<td>Overall average n-mer chain length in a mixture.</td>
</tr>
<tr>
<td>$P$</td>
<td>Symbol used for the pressure of a given component.</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
</tr>
<tr>
<td>$P_i^o$</td>
<td>Vapor pressure of pure component $i$.</td>
</tr>
<tr>
<td>$p_i$</td>
<td>The independent probability of event $i$.</td>
</tr>
<tr>
<td>$p_{i-j}$ or $p_{ij}$</td>
<td>The independent of the binary event $ij$.</td>
</tr>
<tr>
<td>$p_{iAa}$</td>
<td>The probability of the $i^{th}$ functional group on the $A^{th}$ segment of the $a^{th}$ molecular species.</td>
</tr>
<tr>
<td>$Q$</td>
<td>Generalized form of the C.P.F. whose scale is defined by context.</td>
</tr>
<tr>
<td>$Q_{ij}$</td>
<td>Molecular-scale C.P.F. of the $(i-j)$ bundle species.</td>
</tr>
<tr>
<td>$Q_{i,j}$</td>
<td>As above, but specifically designating the centrality of species $j$.</td>
</tr>
<tr>
<td>$q$</td>
<td>Pair-scale C.P.F.</td>
</tr>
<tr>
<td>$q_{ij}$</td>
<td>Pair-scale C.P.F. for the $i-j$ pair species.</td>
</tr>
<tr>
<td>$q_{i,j}$</td>
<td>As above, but specifically indicating the centrality of species $j$.</td>
</tr>
<tr>
<td>$q_{ii}^*$</td>
<td>C.P.F. for the $i-i$ pair in the pure-component state.</td>
</tr>
<tr>
<td>$Q$</td>
<td>Canonical Ensemble Partition Function (C.P.F.) on a molar scale.</td>
</tr>
<tr>
<td>$Q(n_1, n_2)$</td>
<td>C.P.F. for $n_1$ particles of species 1 and $n_2$ particles of species 2.</td>
</tr>
<tr>
<td>$Q_a^o$</td>
<td>Molar scale C.P.F. for species $a$ in the pure component state.</td>
</tr>
<tr>
<td>$Q_w$</td>
<td>The Wilson form of the molar C.P.F.</td>
</tr>
<tr>
<td>$Q_H$</td>
<td>The Heil form of the C.P.F.</td>
</tr>
<tr>
<td>$R$</td>
<td>The gas constant per mole.</td>
</tr>
<tr>
<td>$R_a$</td>
<td>Monomer radius of molecular component $a$.</td>
</tr>
<tr>
<td>$R_{ab}$</td>
<td>Radius ratio of monomer unit of species $a$ to that of a reference monomer unit of species $b$. Convention: $R_{ab} = R_a / R_b$.</td>
</tr>
<tr>
<td>$S$</td>
<td>Molar entropy.</td>
</tr>
<tr>
<td>$\Delta_{NR-R}$</td>
<td>Excess entropy due to energetic non randomness</td>
</tr>
<tr>
<td>$\xi_{ia}$</td>
<td>Partial site fraction of group $i$ on molecular species $a$.</td>
</tr>
</tbody>
</table>
Temperature

'Total' or 'internal' energy.

$\bar{U}_i$

Partial Molal Excess Internal energy of component $i$.

$u_{ij}$

Element in the matrix representing proportionate energetically induced skew in the $i \cdot j$ pair concentration from that in an energetically uniform mixture.

$E$

Excess volume (volume change due to mixing) of a liquid.

$V$

Molar gas phase volume, or general thermodynamic volume per mole.

$\bar{v}_i$

Molar scale partial molal volume of molecular species $i$.

$v$

Molar scale liquid volume.

$v_{ki}$

Number of counts of the $k$th functional group type on the $i$th molecular species in the ASOG equation.

$v_{PH}$

Flory-Huggins group count in the ASOG equation. Corresponds approximately to the effective n-mer chain length of the $i$th molecular species.

$v$

Molal scale free volume for a liquid.

$v_i$

Approximate physical displacement volume per molecule of $i$.

$v_{fi}$

Single molecule free volume of species $i$.

$v_{fij}$

Single molecule scale free volume of the $ij$ bundle species.

$v_{f_{i-j}}$

Pairs-scale free volume per pair for the $i-j$ pair.

$W_A$

The probability of the $A$th segment on a single n-mer molecule.

$X_i$

Barker pseudo-composition. Reduces to mole fraction in absence of NCZ, energy or n-mer effects.

$X_{ij}$

Effective concentration of the $i \cdot j$ pair species, based on a population of pairs bundles having the overall average coordination number.

$X_{m_{ij}}$

Effective concentration of the $i \cdot j$ pair species, based on a population of pair bundles whose $z$ is that of the $i \cdot j$th bundle species.

$X_{iajb}$

Pairs concentration of site type $i$ on molecule a contracting site type $j$ on molecular species $b$. 
Liquid phase mole fraction of molecular species i or a.

Vapor-phase mole fraction of molecular species i or a.

Nearest-neighbor coordination number.

Self-packed nearest neighbor coordination number for a species. Usually assumed to be the same for each pure component species in a given system.

Coordination number of a\( ^{\text{th}} \) or i\( ^{\text{th}} \) molecular species.

Effective coordination number associated with the i j bundle species.

View factor of monomer unit around monomer unit b.

Parameter correcting the concentration of unlike pairs to account for the energetically induced clustering effect due to \( \omega_{ij} \), found in the Guggenheim form of unlike pairs concentration \( X_{ij} \).

As above, but with argument modified to incorporate NCZ effects.

Activity coefficient of the a\( ^{\text{th}} \) molecular species.

Activity coefficient of species a at infinite dilution in a specified solvent.

Generalized energy parameter in the Boltzman factor argument of the individual particle activity. Context distinguishes this usage from that for the Solubility Parameter (\( \delta_{i} \)) of molecular species i, and also from the Variational operator \( \delta \).

Mean-value theorem average energy of the i-j pair cohesion within a specified domain.

Cohesion of the (i-j) pair. Strictly speaking this is a point value, but where no ambiguity exists, \( \varepsilon_{ij} \) may be used to represent \( \tilde{\varepsilon}_{ij} \) within a specified domain.

Molecular scale cohesion of species a.

As above, but emphasizing that the energy is an average quantity.

Grand Canonical Partition Function (G.C.P.).
The G.C.P. for \( n \) particles.

The G.C.P. for the \( z \) nearest neighbor positions about the \( i \)th species of central molecule.

Generalized local concentration variable of species \( i \) about species \( j \) in equation (222).

The proportion of a molecule's contacts which are of the \( i \)th type of chemical functional group.

As above, but further specifies that group type \( i \) is on molecular species \( a \).

Element of the Barker pairs concentration array relating actual pairs concentrations to products of pairs of contact fractions.

The \( \Theta \)'s are considered to be a product of two first order factors, \( \Theta_1 \times \Theta_2 \). Also, in quite a different context, \( \Theta \) is used as a generalized unknown in Chapter 9.

Wilson Parameter for species \( j \) about species \( i \).

The absolute activity of an individual molecule, as defined by Guggenheim. It has the same meaning as the symbol \( a \) employed by Hougen, Watson and Ragatz, except that \( \lambda \) applies to one molecule, not one mole of molecules as does \( a \).

Site fraction of the \( a \)th type of molecule.

Site fraction of the \( i \)th type of chemical functional group.

\( \xi_i' = \xi_i \) but specifically including an estimate of energetically induced skew. In general the symbol \( \xi_i \) is used to represent the site fraction with geometry and energy skews incorporated.

Chemical potential of molecular species \( a \).

Total pressure.

\( \rho \) in Scatchard's surface fraction (equation 46).

Generalized mathematical 'volume-of-integration' element in a mathematical 3-space, which need not have any specific physical context in terms of real volume.

Volume fraction of molecular species \( i \) or \( a \).

Modified form of volume fraction obtained by contracting the Wilson equation into Flory-Huggins form (equation 240).

Wilson form of modified volume-fraction.
\( \phi_i'' \) Vapor-phase fugacity coefficient for the \( i^{th} \) molecular species.

\( \phi_i''s \) As above, except for the pure component vapor under its own pressure.

\( \chi_{ij} \) Population of the \( i \) \( j \) bundle species.

\( \psi_i \) Proportion of the total number of nearest neighbors of a monomer unit which are proximal chain units.

\( \Omega \) Combinatorial degeneracy operator. The number of distinguishable combinations.

\( \Omega(N_1, N_2, N) \) Number of distinguishable molecule interchanges possible for \( N_1 \) particles of 1 and \( N_2 \) particles of species 2, where \( N_1 + N_2 = N \).

\( \Omega' \) Combinatorial degeneracy of pairs-bundles whose populations have been adjusted to compensate for equalization of bundle size.

\( \Omega'(N'_1, N'_2, N') \) As above, for 'adjusted' populations bundle species \( N'_1 \) and \( N'_2 \).

\( \omega \) Free energy of reorganization to form unlike pairs. Approximately equal to the heat of mixing per unlike pair.

\( \omega_{ij} \) Pairwise heat of mixing for the \( i \) \( j \) pair. This is the value which would be obtained in the constant-\( z \) case.

\( \omega'_{ij} \) Pairwise heat of mixing specifically for the NCZ case, but not used except in equation (83) in Chapter 8.

\( \omega''_{ij} \) Form of the pairwise heating of mixing used in equation (85) in Chapter 8.

**ABBREVIATED CHEMICAL NAMES**

- **BZ** Benzene
- **BUT** Butane
- **NIC** Nicotine
- **PFB** Pentaerythritol tetraperfluorobutyrate
- **PFH** Perfluoro n-heptane
- **PROP** Propanol
- **TOL** Toluene
- **XY** Xylene
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APPENDIX 1

IONIC SOLUTIONS

Ideal non-electrolytes in solution exhibit linear partial-pressure versus concentration plots, whereas the more general case, involving fragmentation of the vapor-phase molecule into \( n \) fragments in solution, is marked by a \( P \) versus (concentration)\(^n\) power-law type of partial pressure versus concentration curve, where \( n \) is greater than one.

Also in regard to mixture nonideality, electrolyte solutions, with large coulombic components in their binding energies, for example are not amenable to a nearest-neighbor assignment of cohesion, and are in fact generally not even analysable by means of ordinary particle-mechanics models. (See for example: Hill\(^{23}\), Dienbigh\(^{93}\), Hala\(^{94,95}\), or Moore\(^{96}\) for succinct reviews of these topics).

Indeed, since the 'average' range of ionic interaction as characterized by the ion atmosphere 'radius' is almost always much larger than that of the nearest-neighbors shell about the ion, one would specifically not expect to witness, in ionic solutions, the peculiar 2-phase envelopes exhibited by certain nonionic mixtures of very unequal sized molecules. Thus, while NCZ nearest neighbor shell packing effects undoubtedly do occur about ions, there is now little interaction between the nearest neighbor shell distortion effect due to unequal particle size and the principle energy terms of \( G^E \) for the system, (which usually dominate in magnitude over
straight entropy effects) when the principle energy effects are of the ionic kind.
Methods of Comparison of Experimental and Predicted Phase Equilibrium Expressions.

In comparing the efficacy of various expressions to predict phase equilibrium, it must be realized that a considerable choice of comparison methods present itself. This choice includes:

1) Comparison of excess free energy versus composition curves.

2) Comparison of activity coefficient (or log activity coefficient) versus composition curves with those derived from measurement.

3) Comparison of plots of predicted versus measured vapor phase mole fraction of one or all components present through some or all of their composition ranges.

4) Comparison of K-ratio (equilibrium $y/x$ ratio) versus composition plots with those obtained by direct measurement.

5) Comparison of predicted versus experimentally measured total vapor pressures for a series of compositions.

6) In the case of mixtures sufficiently nonideal to form two liquid phases, comparison of experimentally determined versus predicted consolute envelopes.

7) Tests of internal consistency of formal activity coefficient expressions, either predicted or those derived from phase equilibrium measurements, involving the Gibbs Duhem
equations in differential or integral form.

Except in the case where a perfect coincidence between predicted and experimentally derived excess free energy expression could be produced for the entire composition range, the use of methods 1) to 6) would each result in a different set of 'best-fit' constants for any given predictive expression, as each method involves comparison of a different functional form embodying the constants. More specifically each form has a different and unique compositional response sensitivity to the constants: hence a 'least mean squares' fit of the constants to give the minimum discrepancy between experimentally derived and predicted expressions 'weights' different constants by differing amounts, because of the differential response behavior of the various functions throughout the mixture composition region.

In terms of the evaluation of the constants in the basic thermodynamic function \((\frac{G^E}{RT})\), from which each of 1) to 6) can be derived (see Table 10), it is apparent that each method would, for an imperfect fit between experimentally derived and predicted curves, produce a different set of best-fit constants for \(\frac{G^E}{RT}\), as influenced in diverse ways by the operations on \(\frac{G^E}{RT}\) required to produce the given final expression used as the basis of the predictive curve. Errors in the experimental observations would also be variously weighted by the operations required to produce the 'experimental' comparison curve for each method of comparison.

Since the actual solution's behaviour is always more complex than the approximate behavioral model reflected by
the explicit form of the $G^E/RT$ function being fitted an exact coincidence of experimental and predictive $G^E/RT$ functions is correspondingly unlikely, even if the experimental observations from which the 'experimental' comparison curve arose were completely free of both 'scatter' and systematic errors. (Method 7) for example, tends to point out the former, but not the latter. Thus, any degree of inherent incongruence between model and actual behaviour, and existence of systematic and random error in data in the 'experimental' comparison expression will result in a different best-fit value for a given constant of the $G^E/RT$ expression being evaluated for each of the six methods of Table 10. This fact is emphasized by a little reflection on the various functional forms in the Table, which are manifestly different in response sensitivity to both constants and data in different composition ranges.

Method 1) is often preferred on the grounds of straightforwardness of representation of the fundamental thermodynamic entity, namely $G^E/RT$, though 'experimental' values of $G^E/RT$ are not directly measurable, but must be calculated.

Method 2) is often preferred for distillation purposes, since the method emphasizes the fit of the dilute region, corresponding to the end zones in a distillation which determine final product specifications.

Method 4) is often preferred by petroleum reservoir engineers, since they are concerned with reservoir pressures.

Method 5) while it is perhaps inordinately sensitive to all the parameters in the $G^E/RT$ expression, both as functions of
and also of $T$, is of obvious practical importance in the liquid extraction field.

Method 7) is a popular method of evaluating the internal consistency of a set of activity coefficient expressions derived from experimental vapor pressures versus composition measurements. Formally, it tests the internal relationships between vapor pressure versus composition characteristics for various components, (or of one component in various composition regions) necessitated by the fact that all the activity coefficients for a given mixture originate, perforce, from the same $G^{E}/RT$ function, in ways prescribed by the $k$ relations:

$$\ln \gamma_k = (G^{E}/RT) - \sum_{j \neq k} \frac{\partial (G^{E}/RT)}{\partial x_j} x_j$$

for a $k$-component system.

From the point of view of constructing $G^{E}/RT$ functions, it is not possible for a $G^{E}/RT$ function to produce activity-coefficient expressions which do not satisfy the Gibbs Duhem equations, as long as these are derived from $G^{E}/RT$ in the formally prescribed way, unless a mistake is made in the algebraic operations involved in the transformation. Mathematically, as long as $G^{E}/RT$ becomes zero for pure components, and is a mathematically continuous function throughout the composition range, no new information can be obtained by performing Gibbs-Duhem tests on various 'derivative curves' (i.e. those involving tangents to the $G^{E}/RT$ curve, as do $\ln \gamma$ expressions) of a given $G^{E}/RT$ expression except to check the
algebra of the various derivative operations. This thesis does not contain type 7) test results, in view of its primary concern with rather broad comparisons between the various $G^E/RT$ formulations themselves.

As means of assessing $G^E/RT$ expressions, methods 3) and 4) are dependent on vapor phase nonideality estimates, as well as upon the form of $G^E/RT$, although the same may always be said for the estimate of $G^E/RT$ from vapor pressure data.

Comparison methods which involve a comparison of individual components partial vapor pressure or activity coefficients in some way, as do 2), 3), or 4), tend to emphasize the fit of the 'slope' of the $G^E/RT$ function in the dilute regions, whereas methods 1) and 5), by virtue of summing all the partial pressures, tends to respond rather less sensitively to $G^E/RT$ away from the equimolal compositions region.

The methods of evaluation of the relative merits of $G^E/RT$ formulations versus experimentally derived curves employed in this work are: Method 1) for vapor-liquid equilibria, and Method 6) for systems exhibiting liquid-liquid equilibria. In view of the possible use of the $G^E/RT$ expression for either phase equilibria or for total pressure prediction, Method 1) is also recommended as a reasonable compromise between the extreme values of fit parameters which would result from Method 2) and Method 5), for example.

In studying the performance of $G^E/RT$ formulations to fit real systems, one is not only interested in overall fit estimates, but rather, also, in a study such as this, in the nature of the fit. For example, instead of distributing the misfit be-
tween actual and predictive expressions as uniformly as possible over the entire composition range, a given expression may be fitted as exactly as possible for as much of the region as possible, at the expense of a fairly bad misfit in some local range of composition. This is a good way of studying differences in qualitative 'shapes' of curves produced by various predictive expressions, as distinct from the purely 'statistical' correlation obtained by computer optimization techniques.

In excess free energy work, the former method is felt by the author to be as valuable, if not more so, than the latter, and it is the former technique which has been employed in this work.
### Table 10

Relations Between \( \gamma_i \) and \( G^E/RT \) and Experimental Comparison Methods.

<table>
<thead>
<tr>
<th>METHOD</th>
<th>PREDICTED OR CALCULATED ORDINATE</th>
<th>FORMALISM IN TERMS OF ( G^E/RT )</th>
<th>FORMALISM IN TERMS OF ( \gamma_i )</th>
<th>ABISCISSA</th>
<th>EXPERIMENTAL MEASUREMENTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( G^E/RT )</td>
<td>( f_1 = G^E/RT )</td>
<td>( \xi \frac{x_k}{y_k} )</td>
<td>( x_k )</td>
<td>( y_k ), ( x_k )</td>
</tr>
<tr>
<td>2</td>
<td>( \ln \gamma_k )</td>
<td>( f_2 = (f_1 - \sum_{j=1}^{m} \frac{1}{x_k})x_k )</td>
<td>( \ln \gamma_k )</td>
<td>( z_k )</td>
<td>( y_k ), ( x_k )</td>
</tr>
<tr>
<td>3</td>
<td>( \gamma_k )</td>
<td>( f_3 = \frac{(\exp(f_2))^{\xi}}{\xi_k} )</td>
<td>( \frac{y_k}{\xi_k} )</td>
<td>( y_k )</td>
<td>( y_k ), ( z_k )</td>
</tr>
<tr>
<td>4</td>
<td>( \xi_k = \gamma_k )</td>
<td>( f_4 = \frac{\exp(f_2)}{\xi_k} )</td>
<td>( \frac{y_k}{\xi_k} )</td>
<td>( z_k )</td>
<td>( y_k ), ( x_k )</td>
</tr>
<tr>
<td>5</td>
<td>( \pi )</td>
<td>( f_5 = \frac{\exp(f_2)}{\xi_k} )</td>
<td>( \frac{y_k}{\xi_k} )</td>
<td>( z_k )</td>
<td>( y_k ), ( x_k )</td>
</tr>
<tr>
<td>6</td>
<td>( (\xi_k)_P, (\xi_k)_Q )</td>
<td>a) ( \frac{y_k}{\xi_k} )</td>
<td>( \frac{y_k}{\xi_k} )</td>
<td>( y_k ), ( x_k )</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>b) ( \frac{y_k}{\xi_k} )</td>
<td>( \frac{y_k}{\xi_k} )</td>
<td>( y_k ), ( x_k )</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>( \frac{y_k}{\xi_k} )</td>
<td>( f_7 = \frac{\exp(f_2)}{\xi_k} )</td>
<td>( \frac{y_k}{\xi_k} )</td>
<td>( y_k ), ( x_k )</td>
<td></td>
</tr>
</tbody>
</table>

* \( P \) and \( Q \) denote points of equal activity. Method (b) is used in this work.

** Integrated Gibbs-Duhem equations. More generally terms in \( V^E \) and \( H^E \) are also involved (ref: 52).
APPENDIX 3

INTRODUCTION OF NCZ EFFECTS INTO FLORY'S DERIVATION

With reference to the simplified derivation of the Flory-Huggins athermal mixing term $\sum x_i \ln \phi_i$, as presented in Hill (p. 401 of ref. 23), NCZ effects may be introduced by either of two methods. (Note in the following, component 2 is the chain species.)

1) By introducing $z_2$ and $z_s$ for the coordination number of component 2's monomer segments in the mixture and in the pure component states respectively. Chain length is designated by the symbol $n$.

The result is:

$$\frac{G^E}{RT} = [x_1 \ln \phi_1/x_1 + x_2 \ln \phi_2/x_2] - x_2(n-1)\ln \frac{z_2-1}{z_s-1}$$

(294)

where, as usual,

$$\phi_1 = \frac{x_1}{x_1 + nx_2}$$

and

$$\phi_2 = \frac{nx_2}{x_1 + nx_2}$$

The second term in equation (294) exhibits the NCZ effect.

If the solvent monomer species (component 1), is larger than that of the polymer chain unit, $z_2 < z_s$, and if the solvent monomer unit is smaller, $z_2 > z_s$, as would be expected. The larger is $z_2$ in the mixture, the
more nearest-neighbor position choices are available for the positioning of proximal chain units of a flexible polymer chain, increasing the entropy of mixing and correspondingly decreasing the mixture free energy.

2) Use is made of the NCZ transformations to equalize z values to \( z_{ave} \), and adjust monomer populations to maintain the same total number of pair contacts in the mixture. This results from the substitutions (leftward): \( N'_1 = N'_2 - N_2 \), z values in the mixture set equal to \( z_{ave} \), and \( z_{ave} = z_s \), resulting in:

\[
\frac{G_{mix}}{RT} = \frac{z_1}{z_{12}} x_1 \ln \left( \frac{z_1}{z_{12}} \frac{x_1}{x_1 + z_2/z_{12} n x_2} \right) + \frac{z_2}{z_{12}} x_2 \ln \left( \frac{z_2}{z_{12}} \frac{x_2}{x_1 + z_2/z_{12} n x_2} \right)
\]

Making the approximation \( z_{12}/z_2 = n \), and making the substitutions

\[
\xi'_1 = \frac{z_1/z_{12} x_1}{(z_1/z_{12} x_1 + z_2/z_{12} n x_2)}
\]

\[
\xi'_2 = \frac{z_2/z_{12} n x_2}{(z_1/z_{12} x_1 + z_2/z_{12} n x_2)}
\]

one obtains

\[
\frac{G^E}{RT} = \left( \frac{z_1}{z_{12}} x_1 + \frac{z_2}{z_{12}} n x_2 \right) [\xi'_1 \ln \xi'_1 + \xi'_2 \ln \xi'_2]
\]

\[
\quad - (x_1 \ln x_1 + x_2 \ln x_2) - (n-1) \frac{z_2}{z_{12}} x_2 \ln \xi'_2
\]

(295)
Equations (294) and (295) may be compared to terms $t_1$ and $t_2$ for a monofunctional athermal polymer mixture;

$$\frac{G^E}{RT} = \sum_i (\xi_i \ln \xi_i - x_i \ln x_i)$$

$$- \sum_i (\xi_i - x_i) \ln n_i$$

(296)

The formal differences between these three results (294, 295, 296) are still under study, and was the reason for the comment to that effect in Chapter 12.

Note that all coordination numbers appearing in this Appendix are values for the isolated monomer, rather than being "exterior" monomer segment ones used in the main body of the thesis. They can be converted to "exterior" monomer coordination numbers by means of equation (61) if desired, but were left in this form here to conform more closely with those employed in reference (23).
APPENDIX 4

(a) Logic Diagram for NCZ $G^E/RT$ Calculation Program (b)
SIGNON WOOG
USER "WOOG" SIGNED ON AT 10:37:32 ON 09-12-70

JLIST *SOURCE*
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NC1 GE/ RT FOR GUGGENHEIM BINARY
DIMENSIONED VARIABLES
READ-IN OF DATA
CALC. OF INTERIOR EXTERIOR COORD. NO. CONV. FACTOR
PROGRAM LOOPED TO RUN REPEATED TRIALS OF R1Z, W1Z, A1 AND A2
DO 17 NNR=1,1
SETS: R1Z, R(11), R(2)
DO 17 NG=1,6
SCANS 7 TEMPS AS PROGRAMMED
W1Z CALCULATION
CALCULATION OF A(1) AND A(2)
MAIN COMPOSITION LOOP
SETS X
DO 16 IPS = 1,10
INITIALIZE Z
LOOP IT TURNS OVER 20 TIMES TO INTERNAL CONSISTENCY OF X, S, Z.
DO 14 IT = 1, 20
CALCULATION OF SOLID ANGLES ABOUT 1 AND 2
CALC S I BY INVERTING SOLID ANGLE
CALC OF S FROM Z, X, AND EN
CALC OF RANDOM-PAIRS ARRAY
CALC OF Z12 AND BET12
EVALUATION OF XIJ ARRAY ELEMENTS FOR A GUGGENHEIM BINARY
53 C CALC OF THE UIIIJI NET ENERGETIC PAIRS SKEWS FOR T3
54 C CONTINUE,
55 C
56 C CALC OF ENTROPY HINDERANCE TERMS FOR T3
57 C CALCULATION OF GE/RT
58 C CALC OF COMPONENT CONTRIBUTIONS TO T-TERMS
59 C CALC. OF IDEAL MIXING TERM
60 C SUMMING TO GET T-TERMS
61 C SUMMING T-TERMS TO GERT
62 C SUM GERT * FIDL TO GET GMIX IF DESIRED
63 C STORAGE OF ENERGIES IN OUTPUT BUFFER
64 C CONTINUE
65 C RESULTS PRINTOUT
66 C CONTINUE
67 C END
68 C DATA
END OF FILE
APPENDIX 4

(b) FORTRAN-4 Listing for $G^E_{RT}$ Program
(Monofunctional Monomer Binary Case)
C DIMENSIONED VARIABLES
1 DIMENSION P(2,2),PA(2,2),UI(2,2),COMPl(20),ENERGY(20),PHI(2,2),
  1 RRR(lO),PHIG(lO),S(2),ALF(lO),FET(lO),FREE(10),F(2),FAL(7,6,12),
  2 POL(12),AST(3,7),SHP(2,10),CPM(2,10),EN(21),FMD(12),ADPM(12),
  3 ZS(2),Z(2),RAV(2),A(2),CST(2),GET(7,2),GW(2,R(2),X(2),
  4 XR(10),X(2,2),ROUT(2),AV(2)
C FORMATS
2 50 FORMAT(4F10.4)
3 51 FORMAT(4F10.4)
4 52 FORMAT(F10.4)
5 53 FORMAT(6F10.4)
6 54 FORMAT(2F10.4)
7 55 FORMAT(2F10,4)
8 56 FORMAT(3F10.3)
9 57 FORMAT(3F10.4)
10 58 FORMAT(2F10.4)
11 60 FORMAT(12F9.3)
12 61 FORMAT(7F12.4)
13 62 FORMAT(12F9.4)
C READ-IN OF DATA
14 READ(5,50) RR,TB,TNIT
15 WRITE(6,51) EN,NTOT
16 WRITE(6,51) EN,NTOT
17 READ(5,52) (F(I),I=1,NTOT)
18 WRITE(6,52) (F(I),I=1,NTOT)
19 WRITE(6,53) (COMPl,K=1,12)
20 WRITE(6,53) (COMPl,K=1,12)
21 READ(5,54) (RRR(K),K=1,12)
22 WRITE(6,54) (RRR(K),K=1,12)
23 READ(5,55) (ENERGY(K),ALF(K),K=1,2)
24 WRITE(6,55) (ENERGY(K),ALF(K),K=1,2)
25 READ(5,56) (FREEl,K),SNCP(J,K),CPM(J,K),K=1,2,J=1,12
26 WRITE(6,56) (FREEl,K),SNCP(J,K),CPM(J,K),K=1,2,J=1,12
27 READ(5,57) (EN(I),ZS(I)),ADPM(1),I=1,12
28 WRITE(6,57) (EN(I),ZS(I)),ADPM(1),I=1,12
29 C CALC. OF INTERIOR EXTERIOR COORD. NC. CONV. FACTOR
30 DO 30 I=1,NTOT
31 CST(I) = ZS(I)/RR
32 EMOD(I) = I*(I+2)*ADPM(I)*((EN(I)-1.)/EN(I))
PROGRAM LOOPED TO RUN REPEATED TRIALS OF R12,W12,A1 AND A2

33 DO 17 NMR= 1,2
34 SETS R12,R(1),R(2)
35 R12= R(NX)
36 P(1)= R12
37 R(2)= 1.
38 NC3 GE/ RT FCW GUGGENHEIM BINARY
39 GERT = GE/RT = EXCESS FREE ENERGY OF MIXING
40 FNET = FREE ENERGY OF MIXING
41 DO 17 NG= 1,2
42 T= TINIT
43 SCANS 7 TEMPS AS PROGRAMMED
44 DO 10 NT=1,7
45 TBASE= TB + 273.
46 T= T + DT
47 RT= T*TR
48 W12 CALCULATION
49 W12= ENERGYING1*EXP(-ALF(NG)*TT)
50 Q12= EXP(-W12/RT)
51 CALCULATION OF A(1) AND A(2)
52 DO 31 I=1,12
53 AI(I)=RT*ZS(I)*FREF(I,NG)/RT + (T-TB)*SBCP(I,NG)/RT
54 + CPM(I,NG)/PR)*ALOG(T/TBASE)
55 MAIN COMPOSITION LOOP
56 DO 16 IPS= 1,12
57 SETS X
58 X(I)= CCP(I)
59 X(2)= 1-X(1)
60 INITIALIZE Z
61 Z(1)= ZS(I)*(R12*EN(I)*X(1)+EN(2)*X(2))/((R12**2)*X(1)*EN(I) +
62 EN(2)*X(2))*FMOD(1)
63 Z(1)= R12*Z(1)**FMOD(1)/FMOD(2)
64 LOOP IT TURNS OVER 20 TIMES TO INTERNAL CONSISTENCY OF X,S,Z
65 DO 314 I=1,12
66 LOOP IT TURNS OVER 20 TIMES TO INTERNAL CONSISTENCY OF X,S,Z
67 DO 14 IT= 1,20
CALCULATION OF SOLID ANGLES ABOUT 1 AND 2

```
56 DO 32 J=1,NTOT
57 DO 32 K=1,NTOT
58 32 P(K,J)=S(K)*S(J)
59 DO 33 I=1,NTOT
60 33 XRISO(I)= (FMOD(I)/FMUD(1))*P(I,1)/P(I,2)
61 DO 33 I=1,NTOT
62 XRISO(2)=1./1.*XRISO(1)
63 33 XR(1,I)= XRISO(I)
64 DO 34 I=1,NTOT
65 RQUT(I)= R(I,1)*XR(1,1)+R(I,2)*XR(2,1) / (XR(1,1)+XR(2,1))
66 AAV(I)= (1./4.*RQUT(I)**2) * (XR(1,1)**2+XR(2,1)**2)
67 34 Z(I)= P(I,1)/AAV(I)
68 DO 34 I=1,NTOT
69 34 S(I)= Z(I)*EN(I)*X(I) / [Z(I)*EN(I)*X(I)+Z(2)*EN(2)*X(2)]
70 DO 39 K=1,NTOT
71 DO 39 J=1,NTOT
72 39 RA(J,K)= S(K)*S(J)
73 39 RAS= RA(J,K)
74 DO 39 K=1,NTOT
75 39 RA(J,K)= S(K)*S(J)
76 39 RA(J,K)= S(K)*S(J)
77 DO 39 K=1,NTOT
78 DO 39 J=1,NTOT
79 39 P(K,J)= S(K)*S(J)
80 39 P(K,J)= S(K)*S(J)
81 39 P(K,J)= S(K)*S(J)
82 39 SPCR= P(K,J) / P(K,J)
83 DO 39 K=1,NTOT
84 DO 39 J=1,NTOT
85 U(K,J)= P(K,J) / SPCR
86 RA(K,J)= RA(K,J) / RAS
87 39 U(K,J)= P(K,J) / RAS
88 CONTINUE
89 DO 40 I=1,NTOT
90 PHIG(I)=0.
```
91 DO 40 J=1,NTOT
92 IF(U(J,1).LT.ELH) GO TO 42
93 UFAC= U(J,1)*ALOG(U(J,1))
94 GO TO 41
95 42 UFAC= 0.
96 41 PHI(J,1)= F(I)*S(I)*U(J,1)*ALOG(S(I))
97 40 PHIG(J)= PHI(J,1) + PHI(J,2)
98 CALCULATION OF GE/RT
99 CALC. OF COMPONENT CONTRIBUTIONS TO T-TERMS
100 DO 35 I=1,NTOT
101 GET(I,1)= (1.0 - Z(1)/FMOD(1,1)*Z(2)/FMOD(2,2)*P(1,1)*X(1))/Z(1)/Z(2)/FMOD(1,1)*FMOD(2,2)*X(2)/EN(1)/RT
102 35 GET(I,2)= (S(I)*ALOG(S(I))-X(I))*ALOG(X(I))
103 GT(6,1)= 0.
104 GT(5)= Z(1)*P(1,2)*X(2)/RT
105 GT(7)= (1.0 - Z(2)*EN(2)*FMOD(1,1)*EN(1)*EN(2)*FMOD(2,2)*X(1))/Z(1)*EN(2)*FMOD(2,2)*X(2)/EN(1)*EN(2)*FMOD(1,1)*A(1,1)
106 FIDL= X(1)*ALOG(X(1))*(1.0 + Z(1)*EN(1)*FMOD(1,1)*X(1))/FMOD(1,1)*X(1)
107 GERT= 0.
108 DO 36 K=1,7
109 IF(K.EQ.4 .OR. K.EQ.5 .OR. K.EQ.7 ) GO TO 36
110 GT(K)= GET(K,1) + GET(K,2)
111 36 CONTINUE
112 GERT= 0.
113 DO 37 K=1,7
114 37 GERT= GERT + GT(K)
115 FNET= GERT + FIDL
116 STORAGE OF ENERGIES IN OUTPUT BUFFER
117 FET(I,PS)= FNET
118 FOL(I,PS)= FIDL
119 FAINT,1,1,PS)= GT(1,1)
120 FAINT,2,1,PS)= GT(2,1)
121 FAINT,3,1,PS)= GT(3,1)
122 FAINT,4,1,PS)= GT(4,1)
123 CONTINUE
124   AST(1,NT) = W12
125   AST(2,NT) = A11
126   AST(3,NT) = A12

C     RESULTS PRINTOUT
C
127   WRITE(6,50) (FET(L),L=1,12)
128   CONTINUE
129   WRITE(6,60) (FDL(K),K=1,12)
130   WRITE(6,61) ((AST(JK,JNT),JNT=1,7),JK=1,3)
131   WRITE(6,62) ((FAP(JOT,JK,JX),JX=1,12),JK=1,5),JNT=1,7)

C
132 IF(INNR.GE.1) GO TO 19
133   CONTINUE
134   CONTINUE
C
135   STOP
C
C     DATA
C
136   END
APPENDIX 4

(c) Table of Correspondences Between FORTRAN and Algebraic Variables
AAV(I) = \( a_{i}^{\text{ave}} \)

\( A(I) = a_{i} \), where \( a_{i} = A_{\text{ref}} + b/T + c_{i} \ln(T/T_{\text{ref}}) \)

ALF(I) = storage for \( a_{i} \). See W12.

AOBP(I) = \( \psi_{i} \).

AST(1, NT) = storage for \( \omega_{12} \) for a given temperature.

AST(2, NT) = storage for \( a_{1} \) for a given temperature.

AST(3, NT) = storage for \( a_{2} \) for a given temperature.

BET12 = \( \beta_{12} \)

COMP(20) = storage for \( x_{1} \) values.

CPM(I) = \( c_{i} \) (see A(I)).

CST(I) = proportionality constant \( k \) in equation (49).

ELN = tolerance for \( u_{i1} \).

EN(I) = \( n_{i} \).

ENERGY(10) = storage for \( \omega_{12}^{o} \). See W12.

F(I) = \( n_{i} \).

FA(NT, 1, IPS) = storage for term \( t_{1} \).

FA(NT, 2, IPS) = storage for term \( t_{5} \).

FA(NT, 3, IPS) = storage for term \( t_{4}'' \).

FA(NT, 4, IPS) = storage for \( (t_{1} + t_{5}) \).

FDL(IPS) = storage for FIDL.

FEN(10) = \( n_{1} \) storage.

FET(IPS) = storage for FNET.

FIDL = \( \frac{G_{\text{mix}}^{\text{(IDEAL)}}}{RT} \).

FMOD(I) = \( E_{i} \).

FNET = \( \frac{G_{\text{mix}}^{\text{(ACTUAL)}}}{RT} \).
FREE(I) = $A_i/z_s(i)$ . See A(I) .

GERT = $G^E/RT$

GET(M,I) = The $i^{th}$ component's contribution to GT(M) .

GT(1) = $t_1$

GT(2) = $t_2$

GT(3) = $t_3$

GT(4) = $t'_4$

GT(5) = $t''_4$

GT(6) = $t_5$

GT(7) = $t'_5$

IPS = composition index.

NNR = loop index controlling radius ratio.

NT = temperature index.

P(I,J) = $\chi_{ij}$

PHI(I,I) = component of $\Delta S_{NR-R}$ due to the $i-i$ pair species.

PHIG(I) = $\Delta S_{NR-R}^i$, Partial molal entropy of nonrandomness for species $i$.

PIE = $\Pi$

Q12 = $\exp(2. * \omega_{12}/RT)$, energy effect modifying unlike pairs concentration term.

RR = gas constant $R$.

R(I) = "dimensionless" $R$ ratio of component $i$.

R12 = Radius ratio of large species $R_1$ over reference species $R_2$

RA(I,J) = $\xi_i \cdot \xi_j$

RAS = sum of the RA(I,J).

RAV(I) = $R_1$ ave.

RRR(10) = storage for $R_{12}$.

ROUT(I) = average radius of nearest neighbor shell about species $i$. 
RT = RR* TT .

S(I) = \xi_i

SBCP(I) = (S_b - C_p) for component i . See definition of A_i

SPROB = summation of the X_{ij}

T = temperature in °K

TBASE = T_{ref} . See A(I)

TINIT = initial temperature for a run.

TT = temperature in °K

UU = working location for u_{ij}

UFAC = u_{ij} \ln u_{ij}

U(I,J) = X_{ij}/S_i * S_j

W12 = \omega_{12} . \omega_{ij} = \omega^o_{ij} * \exp(-\alpha_i T)

X(I) = x_i

XB(I,J) = local concentration of component i around central species j , treating both as isolated monomer species.

XRISO(I) = ratio of XB(1,I)/XB(2,I) . I is the central molecule.

ZS(I) = z_s(i)

Z(I) = z_i

Z12 = z_{12}
APPENDIX 4

(d) Logic Diagram for NCZ G_E^E/RT Calculation Program (e)
USER "WOOG" SIGNED ON AT 10:52:22 ON 09-12-70

%LIST +SOURCE#
1 C
2 C
3 C
4 C
5 C
6 C
7 C
8 C
9 C
10 C
11 C
12 C
13 C
14 C
15 C
16 C
17 C
18 C
19 C
20 C
21 C
22 C
23 C
24 C
25 C
26 C
27 C
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44 C
45 C
46 C
47 C
48 C
49 C
50 C
51 C
52 C

%SIGNON WOOG
**LAST SIGNON WAS: 10:38:44 09-12-70

**USER "WOOG" SIGNED ON AT 10:52:22 ON 09-12-70

1 C
2 C
3 C
4 C
5 C
6 C
7 C
8 C
9 C
10 C
11 C
12 C
13 C
14 C
15 C
16 C
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DIMENSIONED VARIABLES

GROUP MOLECULAR ASSIGNMENT LIMITS

FORMATS

READ-IN OF DATA

NOTE: R12 IS SIMPLY SET, AND NL AND N2 ARE ALSO SET IN THIS

VERSION OF THE PROGRAM.

CALC. OF INTERIOR EXTERIOR COORD. NO. CONV. FACTOR

PROGRAM SET TO SCAN T FOR GIVEN SET OF M, N, R12;

LOOPING DESIGN CAN SET ALTERNATE TYPES OF SCAN OF BASIC PROGRAM

T LOOP
SCANS 7 TEMPERATURES AS PROGRAMMED

DO 17 NT = 1, T

ASSIGN M AND A

MAIN COMPOSITION LOOP

DO 16 IPS = 1, T

SETS X

INITIALIZE Z, S

F(1) IS ETAJI, AI IN EQN 212

THE XXII ARE BARKER PSEUDOCOMPOSITIONS
THEY ARE INITIALLY SET EQUAL TO THE FS(I)

LOOP IT TURNS OVER 20 TIMES TO INTERNAL CONSISTENCY OF X,S,Z

DO IT = 1,20

THE DENOM(J) ARE FOR ROW NORMALIZATION OF THE BARKER PAIRS

ARRAY

CONVERT LOCAL BARKER CONCS TO LOCAL MONOMER CONCS (THE XB(I,J))

THE XB(I,J) NORMALIZE W.R.T. J, XB(I,J) .NE. XB(I,J)

CALCULATION OF SOLID ANGLES ABOUT 1 AND 2

CALCS Z BY INVERTING SOLID ANGLE

CALC OF S FROM Z,X, AND EN

CALCS Z BY INVERTING SOLID ANGLE

RESET THE FS(I)

RESET OF FS(I) FROM F(I) AND NEWEST S(I) VALUES

CALC OF SELF INTERACTING QUANTITIES

CALC OF RANDOM PAIRS OF PARTIAL SITE FRACTIONS

CALC OF THE P(I,J) FROM GUG(I,J) WTS ABOUND BARKER

PSEUOCOMPOSITIONS

CALC OF THE UI(I,J) NET ENERGETIC NONRANDOMNESS ARRAY ELEMENTS

CONTINUE

CALC OF SELF-INTERACTION QUANTITIES

CALC OF LI2

CALC OF ENTROPY HINDRANCE TERMS FOR T3

CALCULATION OF GE/RT

CALC. OF COMPONENT CONTRIBUTIONS TO T-TERMS

SUMMING T-TERMS TO GERT

CALC. OF IDEAL MIXING TERM

SUM GERT + FIDL TO GET GMIX IF DESIRED

STORAGE OF ENERGIES IN OUTPUT BUFFER

CONTINUE
APPENDIX 4

(e) FORTRAN-4 Listing for NCZ $G^E/RT$ versus Composition. (General Case)
$SIGNON WONG
$LAST SIGNON WAS: 10:52:22  09-12-70

USER "WONG" SIGNED ON AT 10:59:03 ON 09-12-70

$LIST $SOURCE

1 C
2 C  NCL GE/RT FOR A MULTIFUNCTIONAL BINARY (NIC-WATER)
3 C  1 = NICOTINE, 2 = WATER (MOLECULAR SPECIES NUMBERING)
4 C  1 = NIC(1), 2 = ARY(2), 3 = NIC(1), 4 = H2O(2), 5 = H2O(2) (GROUP NOS.)
7 C  2nd INDEX CONSIDERED TO BE CENTRAL
8 C
9 C  FOR SETTING OF SELF INTERACTING QUANTITIES:
10 C  IPS=1, XI=.9991 "PURE NIC", IPS=2, XI=.0011 "PURE" WATER.
11 C
12 C  DIMENSIONED VARIABLES
13 C
14 C  DIMENSION GUG(5,5), P(5,5), P0(5,5), XX(5), XI(5), DENOM(5),
15 C  1 = FLSI, ELSI, RA(5,5), UL(5,5), COMP(25), PHIL(5), PHI0L(5),
16 C  2 = FX(5), PHIG(5), PHIG0L(5), RAL(5), FAL(5,5), DAT(4,7,7),
17 C  3 = ATIT7, FET7(20), FREE7(2), FOLD7(12), EN7(2), FMD7(2), AD7(2),
18 C  4 = 5Z(2), 7Z(2), RAVZ(2), AIZV(2), CSTV7, GET7(2), GT7(7), R7(2), X7(2),
19 C  5 = 5X7S(2), 7X7S(2), ROTS7S(2), ROUT7S(2), AAX7S(2), EW7S(7), EN7S(2),
20 C  DIMENSION NL(2), NH(2), XB7S(2), PSEL7S(2), GL7S(2), FMD7S(2), AST7(3,7),
21 C
22 C
23 C  GROUP MOLECULAR ASSIGNMENT LIMITS
24 C
25 C  NTOI= 2
26 C  NGP= 5
27 C  NL(1)= 1
28 C
29 C  NH(1)= 1
30 C  NL(2)= 4
31 C  NH(2)= 5
32 C  FORMATS
33 C  50 FORMAT(F10.4)
34 C  51 FORMAT(F10.4)
35 C  52 FORMAT(F5.1)
36 C  53 FORMAT(F10.4)
37 C  54 FORMAT(F10.4)
38 C  55 FORMAT(F10.4)
39 C  56 FORMAT(F10.4)
40 C  57 FORMAT(F10.4)
41 C  58 FORMAT(F10.4)
42 C  59 FORMAT(F10.4)
43 C  60 FORMAT(F10.4)
44 C  61 FORMAT(F10.4)
45 C  62 FORMAT(F10.4)
46 C
47 C  READ-IN OF DATA
48 C  DATAL, A2, NH2, DHI, TEMP, INDIV )
49 C
50 C  READ(S,50) RR, TB, TINIT
51 C  WRITE(6,50) RR, TB, TINIT
52 C  READ(5,51) FLN, NTOI, NGP
53 READ(5,52) (F(I),I=1,NGP)
54 WRITE(6,52) (F(I),I=1,NGP)
55 READ(5,53) (CMP(I),I=1,12)
56 WRITE(6,53) (CMP(I),I=1,12)
57 READ(5,54) (RRR(K),K=1,2)
58 WRITE(6,54) (RRR(K),K=1,2)
59 READ(5,55) ((FREE(NSPEC,NT),NT=1,7),NSPEC=1,NTOT)
60 WRITE(6,55) ((FREE(NSPEC,NT),NT=1,7),NSPEC=1,NTOT)
61 READ(5,56) (EW(1,2),NT=1,7)
62 WRITE(6,56) (EW(1,2),NT=1,7)
63 READ(5,57) (EW(2,1),NT=1,7)
64 WRITE(6,57) (EW(2,1),NT=1,7)
65 READ(5,58) (EW(3,4),NT=1,7)
66 WRITE(6,58) (EW(3,4),NT=1,7)
67 READ(5,59) (EW(4,5),NT=1,7)
68 WRITE(6,59) (EW(4,5),NT=1,7)
69 READ(5,60) (EW(5,6),NT=1,7)
70 WRITE(6,60) (EW(5,6),NT=1,7)
71 READ(5,61) (EW(6,3),NT=1,7)
72 WRITE(6,61) (EW(6,3),NT=1,7)
73 READ(5,62) (EW(7,2),NT=1,7)
74 WRITE(6,62) (EW(7,2),NT=1,7)
75 READ(5,63) (EW(8,1),NT=1,7)
76 WRITE(6,63) (EW(8,1),NT=1,7)
77 READ(5,64) (EW(9,4),NT=1,7)
78 WRITE(6,64) (EW(9,4),NT=1,7)
79 READ(5,65) (EW(10,5),NT=1,7)
80 WRITE(6,65) (EW(10,5),NT=1,7)
81 READ(5,66) (EW(11,6),NT=1,7)
82 WRITE(6,66) (EW(11,6),NT=1,7)
83 READ(5,67) (EW(12,7),NT=1,7)
84 WRITE(6,67) (EW(12,7),NT=1,7)
85 READ(5,68) R12
86 WRITE(6,68) R12
87 C
88 C
89 C
90 C
91 C
92 C
93 C
94 C
95 C
96 C
97 C
98 C
99 C
100 C
101 C
102 C
103 C
104 C
105 C
106 C
107 C
108 C
109 C
110 C
111 C
112 C

NOTE: R12 IS SIMPLY SET, AND N1 AND N2 ARE ALSO SET IN THIS VERSION OF THE PROGRAM. METHOD OF SCANNING THESE IS AS SHOWN.

FOR THE ENERGY VARIABLES.

R(I) = R12
R(2) = 1.

C

CALC. OF INTERIOR EXTERIOR COORD. NO. CONV. FACTOR

DO 30 I=1,NTOT
30 CST(I) = ZS(I)/16.

FMOD(I) = 1*(I-2.5)*ABP(I)*(EN(I-1)/EN(I))

C

PROGRAM SET TO SCAN T FOR GIVEN SET OF M,A,N,R12.

LOOPING DESIGN CAN SET ALTERNATE TYPES OF SCAN OF BASIC PROGRAM.

T LOOP SCANS T TEMPERATURES AS PROGRAMMED.
DO 13 J=1,NGP
GUGIJ,JJ = 0.
JP = J+1
DO 13 K = JP,NGP
WI(J,K) = EMJ,J,K,NTI
WIX(J,J) = WIJ(J)
119 GUG(I,K) = EXP(-WIJ*(K)/RT)
GUG(K,J) = GUG(I,K)
121 CONTINUE
DO 100 I=1,NTOT
AI(I) = FREE(I,NTI)
124 100 CONTINUE
125 C
126 C MAIN COMPOSITION LOOP
127 DO 16 IPS= 1,10
129 C
130 C SETS X
131 X(1) = COMPS(IP)
X(2) = 1.-X(1)
133 C
134 C INITLIZE Z + S
136 Z(2) = Z(1)+((RIZ*EN(11)*X(1)+EN(21)*X(2))/(Z(1)*EN(11)+Z(2)*EN(21))
EN(11)*X(2))
137 1 EN(21)*X(2))*PMOD(2)
138 Z(1) = (RIZ*EN(11)+PMOD(1))/PMOD(2)
139 DO 314 I=1,NTOT
140 314 S(I) = Z(I)+EN(11)*X(1)/(Z(1)*EN(11)+Z(2)*EN(21)+X(2))
141 C
142 C F(I) IS ETA(I,A) IN EQN 212
143 C THE XX(I) ARE BARKER PSEU COMPOSITIONS
144 C THEY ARE INITIALLY SET EQUAL TO THE FS(I)
145 C LIMIT, 3 = NH(1)
146 C
149 C DO 29 K=1,NGP
150 C IF(K.GT.3) GO TO 601
151 C FS(K) = FK)*S(I)
152 C GO TO 29
153 601 FS(K) = FK)*S(I)
154 C CONTINUE
155 C LOOP IT TURNS OVER 20 TIMES TO INTERNAL CONSISTENCY OF X,S,Z
156 C
159 C DO 7 K=1,NGP
160 C XX(K) = FS(K)
161 C
164 C THE DENOM(I,J) ARE FOR ROW NORMALIZATION OF THE BARKER PAIRS
165 C ARRAY
169 C CONTINUE
170 781 CONTINUE
171 C
172 C DO 49 K=1,NGP
171  IF(K.GT.3) GO TO 701
174  F(K) = F(K)*S(1)
177  CONTINUE
178  C
179  C
180  IF(K.GT.3) GO TO 701
183  C
184  C
187  CONTINUE
188  C
189  C
191  C
194  C
197  C
198  C
199  C
202  C
203  C
206  C
207  CONTINUE
208  CONTINUE
211  C
214  CONTINUE
215  C
218  C
221  C
224  C
227  C
230  C
233  C
236  C
239  C
242  C
245  C
248  C
251  C
254  C
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623  C
626  C
629  C
632  C
635  C
638  C
641  C
644  C
647  C
650  C
653  C
656  C
659  C
662  C
665  C
668  C
671  C
674  C
677  C
680  C
683  C
686  C
689  C
692  C
695  C
698  C
701  F(K) = F(K)*S(2)
704  CONTINUE
707  F(K) = F(K)*S(2)
710  CONTINUE
713  CONTINUE
716  CONTINUE
719  CONTINUE
722  CONTINUE
725  CONTINUE
728  CONTINUE
731  CONTINUE
734  S(1) = (S(1)*EN(1)*X(1)/Z(1)*EN(1)+X(1)+Z(2)*EN(2)*X(2))
RESET OF FS(I) FROM F(I) AND NEWEST S(I) VALUES

CALC OF SELF INTERACTING QUANTITIES

IF(K,GT,3) GO TO 901
FS(K)= F(K)*S(I)
GO TO 90
FS(K)= F(K)*S(2)
CONTINUE

CALC OF RANDOM PAIRS OF PARTIAL SITE FRACTIONS

CALC OF THE P(I,J) FROM GUG(I,J) AND BARKER PSUEDOCOMPOSITIONS

CALC OF THE T(I,J) NET ENERGETIC NONRANDOMNESS ARRAY ELEMENTS

SPROB= 0.
DO 90 K=1,NGP
RA(K,J)= FS(K)*FS(J)
RA= RAS*RAK,K,J)
PIK,J)= XX(K)*XX(J)*GUG(K,J)
CONTINUE

DO 90 K=1,NGP
PIK,J)= P(K,J)/SPROB
RAIK...I> = RAIK,J)/RAS
UIK,J)= PIK,J)/RAIK,J)
CONTINUE

DO 915 J=1,NGP
DO 915 K=1,NGP
PIO1,N)= 0.
PHI01N.l)= F(L)*U(N,L)*U(N,L)-1)
GLI1(N)= GL11(N)+ PHI01N,L)
GO TO 16
CALC OF Z12

Z12 = Z(I)*S(I) + Z(2)*S(2)
CALC OF ENTROPY HINDRANCE TERMS FOR T3

T= CENTRAL MOLECULE(2ND INDEX), GLOG IS THE NEGATIVE OF INC S
CALCULATION OF \( \text{GE/RT} \)

CALC. OF COMPONENT CONTRIBUTIONS TO T-TERMS

\[
\begin{align*}
XX & = X1 \times EN1/EN1 \times X2 \times EN2 \\
DO & 122 J = 1, NT0T \\
PSLF(IJ) & = 0 \\
L1 & = NLIJ \\
L2 & = NHIJ \\
DO & 414 M = L1, L2 \\
PSLF(IJ) & = PSELF(IJ) \times PIM.LI \\
IF(PD.OIL.M.L.LT.0.0001) & \text{GO TO 414} \\
GT(4) & = GT(4) \times IPIM,L) \times XXBJI \times P0IM,L) \times M(M,L)/RT \times ZSIJ/Z12 \\
\text{CONTINUE} & \\
\end{align*}
\]

\[
\begin{align*}
PUNL & = 1. - (PSELF(I1) + PSELF(2)) \\
DO & 461 J = 1, NGP \\
DO & 461 I = 1, NGP \\
IFPD(OJ.I.L.LT.0.0001) & \text{GO TO 5932} \\
\text{GO TO 161} & \\
\end{align*}
\]

\[
\begin{align*}
GT(I1) & = GT(I5) \times P(I,J) \times W(I,J) \times RT/ES(I1)/Z12 \\
\text{CONTINUE} & \\
\end{align*}
\]

\[
\begin{align*}
GERT & = 0. \\
DO & 35 I = 1, NT0T \\
GET(3) & = (1. - ZI2 \times EN1) \times X1 \times EN2 \times X2 / ZS(I1) \times EN1 \times FMOD(I) \times X1 \\
GERT & = 0. \\
DO & 36 K = 1, 7 \\
\text{CONTINUE} & \\
\end{align*}
\]

SUMMING T-TERMS TO GERT

GERT = 0.

DO 37 K = 1, 7
37 GERT = GERT + GT(I)
38 C CALC. OF IDEAL MIXING TERM
39 C FIDL = X(I)*ALOG(X(I)) + X(2)*ALOG(X(2))
40 C SUM GERT + FIDL TO GET GMIX IF DESIRED
41 C FNET = GERT + FIDL
42 C STORAGE OF ENERGIES IN OUTPUT BUFFER
43 C
44 C FET(IPS)= FNET
45 C FDIL(IPS)= FIDL
46 C FAINT,1,IPS = GT(1)
47 C FAINT,2,IPS = GT(6)
48 C FAINT,3,IPS = GT(3)
49 C FAINT,4,IPS = GT(9)
50 C FAINT,5,IPS = GT(1) + GT(5)
51 C CONTINUE
52 C AST(1,NT)= W(4,5)
53 C AST(2,NT)= A(1)
54 C AST(3,NT)= A(2)
55 C RESULTS PRINTOUT
56 C WRITE(6,581) (FET(L),L=1,12)
57 C WRITE(6,601) (FDIL(K),K=1,12)
58 C WRITE(6,611) (FAINT(JK,JNT,JX),JX=1,12),JK=1,5,JNT=1,7)
59 C WRITE(6,621) (AST(IJK,JNT),IJK=1,5),JNT=1,7)
60 C IF(NNR.GE.1) GO TO 19
61 C CONTINUE
62 C STOP
63 C END
64 END OF FILE
APPENDIX 4

(f) Additional Table of Correspondence Between FORTRAN and Algebraic Variables for Program (e)
ADDITIONAL FORTRAN NAMES USED IN
MULTIFUNCTIONAL BINARY CASE

Note: FORTRAN variables not in this list have already been
defined in Appendix 4(c).

ATT(7) = storage for TT.
DAT(4,7,7) = input buffer for A(I) and W(I,J).
DENOM(I) = row normalizations for XX(I).
EW(I,J,NT) = storage for W(I,J) for a given setting of NT
FNOMO(I) = pure component contribution to $t_3$. See program.
FS(I) = $\xi_{ia} = \eta_{ia} x_a$ 
FX(I) = $\eta_{ia} \frac{x_a \eta_a}{\Sigma x_a \eta_a}$
GLIZ(2) = pure component contribution to $t_3$, See program.
GUG(I,S) = exp ($-\omega_{ij}/RT$).

NGP = total number of groups present.
NH(I) = upper counter for group numbers on molecular species $i$
NL(I) = lower counter for group numbers on molecular species $i$
NTOT = total number of molecular components

PHIGO(I) = PHIG(I) for pure component.
PHIO(I,J) = PHI(I,J) for pure component.
PO(I,J) = P(I,J) for pure component.

PSELF(I) = $\Sigma x_{ija}$ for molecular component $I$.
PUNL = $\Sigma x_{iajb} (\frac{a+b}{3})$
W(I,J) = $\omega_{ij}$ in multicomponent case.

XX(J) = $x_a \eta_a$ (Barker pseudo compositions).
XXB(2) = $x_a \eta_a / \Sigma x_a \eta_a$