CHAPTER 1
INTRODUCTION
Introduction

The equilibrium properties of liquid mixtures of non-electrolytes attracted the attention of scientists for a long time, since they provide valuable tools to understand the nature of molecular interactions among the constituents of the liquid mixtures. Young made a systematic attempt in this direction by collecting a large amount of data on the thermodynamic and mechanical properties of liquid mixtures. Since then, quite a systematic theoretical study have been made on liquid mixtures. All these theories of liquid mixtures concern themselves with the evaluation of excess thermodynamic functions. It is thus imperative that these excess thermodynamic functions be first understood before we can make a critical assessment of various theories of solutions of non-electrolytes.

Ideal and non ideal solutions

When a solute or a number of solutes are dissolved in a solvent, the resulting solution may be

(i) ideal or

(ii) non ideal

Ideal solutions are those which obey an idealized form of Kaoult's law over the entire range of composition at all temperatures and pressures i.e. for which
\[ p_i = x_i p_i^* \]  

where  
\( p_i \) = the partial pressure of \( i \)  
\( x_i \) = the mole fraction of \( i \)  
\( p_i^* \) = vapour pressure of pure \( i \)

However, equilibrium between the liquid and the vapour phases require that \( \mu_i(\text{liq}) = \mu_i(\text{vap}) \), but

(a) the vapour is not a perfect gas (otherwise it would not liquify) and contributes a term \( B_i(p_m - p_i^*) \) to the chemical potential (where \( B_i \) is the second virial coefficient, higher terms being neglected), for the non-ideal work of expansion from the pressure of the pure component, \( p_i^* \), to the pressure of the mixture, \( p_m \);  

(b) Again the liquid is not under the same pressure in the pure states and in the mixture, a compression term \( v_i^*(p_i^* - p_m) \) must, therefore, be added to the chemical potential. The requirement that \( \mu_i(\text{liq}) = \mu_i(\text{vap}) \) then leads to

\[ \ln p_i = \ln x_i p_i^* - \left[ B_i(p_m - p_i^*)/RT - v_i^*(p_i^* - p_m)RT \right] \]

... (2)

The validity of Raoult's law then requires that in equation (2) the last two terms on the right hand side exactly cancel each other, i.e. \( B_i = v_i^* \). Since \( v_i^* \) is positive if the vapours are perfect, the liquid mixtures can not be perfect
in terms of Raoult's law. Usually \(|B_1| \gg \nu_1^*\), so that a perfect mixture in terms of \(H^M = 0\) and \(V^M = 0\) will not obey Raoult's law (and vice versa), although the deviations are quite small.

Often the terms 'perfect mixture' and ideal mixture are used interchangeably. It is, however, convenient to apply the term ideal mixtures or ideal solutions in mixture in which the solvent A obeys Raoult's law

\[ p_A = x_A p_A^* \]

over a composition range, where for the solute B, Henry's law

\[ p_B = K_B(A) x_B \]

holds, where \(K_B(A)\) is a constant characteristic of both B and A and is different from \(p_B^*\). If the solute B is a gas, then \(K_B(A)\) is its Bunsen solubility coefficient. Solutions are usually not ideal over the whole composition range which may often not be realizable because of solubility limitations but approach ideality as they become dilute in B. The ideal dilute solution is thus the limiting case

\[ \lim_{x_B \to 0} \frac{dp_B}{dx_B} = K_B(A) = \text{Const.} \quad \ldots \quad (5) \]

\[ x_B \to 0 \]

\[ \lim_{x_A \to 1} \left( \frac{dp_A}{dx_A} \right) = p_A^* \quad \ldots \quad (6) \]

Non ideal solutions on the other hand are those
which do not obey Roult's law and hence for them we can write

\[ H^M \neq 0, \]
\[ V^M \neq 0, \]

When an ideal mixture is formed from its components, any extensive thermodynamic property \( Y \) (e.g., \( G, S, V \) etc) can be expressed as the sum

\[ Y_m = \sum_i n_i Y_i \]

where \( Y_m \) refers to the mixtures and \( Y_i \) is the partial molar thermodynamic property of \( i \) in the mixture. However, thermodynamic functions for a non-ideal mixture is the sum of three terms, one for the pure component in their standard state, one for ideal process of mixing, and one for the excess function for the real mixture, for example for Gibb's energy the expression

\[ G_m = \sum_i n_i g_i^0 + G^M = \sum_i n_i g_i^0 + G_{id}^M + G^E \]

**Excess thermodynamic functions**

Excess thermodynamic functions, \( X^E \), on the other hand, denote a measure of departure of any thermodynamic property of a real solution from ideality. These may be defined as the difference between the thermodynamic function of mixing, \( X_M \), for an actual system and the value corresponding to an ideal
solution at the same temperature, pressure and composition.
Since a solution is formed by the replacement of like contacts in the pure components by unlike contacts in the mixture, $x^E$ also reflects the difference between the intermolecular interactions in the mixture from those in the pure components.

If $x_1$, $x_2$,...,$x_n$ and $Y_1$, $Y_2$,...,$Y_n$ etc represent the mole fraction and activity coefficients respectively of components 1, 2,...,n for a single phase multi-component system, the excess Gibbs free energy at a given temperature, T, for such a system is given by

$$G^E = RT \left[ \sum_{i=1}^{n} (x_i \ln \ Y_i) - \sum_{i=1}^{n} x_i \ln x_i \right]$$

...(9)

For a binary mixture equation (9) yields

$$G^E = RT (x_i \ln \ Y_i + x_j \ln \ Y_j)$$

...(10)

and for a ternary mixture equation (9) reduces to

$$G^E = RT(x_i \ln \ Y_i + x_j \ln \ Y_j + x_k \ln \ Y_k)$$

...(11)

All other excess thermodynamic functions for binary and ternary mixtures can be derived from equation (9). Thus

1. Excess entropy

$$S^E = - (\partial G^E / \partial T)$$

so that $S^E$
(a) for a binary mixture

\[ S^E = -RT \left[ \sum_{i=1}^{2} x_i \frac{\partial \ln \gamma_i}{\partial T} \right] - R \left[ \sum_{i=1}^{2} x_i \ln \gamma_i \right] \] ... (12)

and

(b) for a ternary mixture

\[ S^E = -RT \left[ \sum_{i=1}^{3} x_i \frac{\partial \ln \gamma_i}{\partial T} \right] - R \left[ \sum_{i=1}^{3} x_i \ln \gamma_i \right] \] ... (13)

2. Excess volume

\[ V^E = \frac{\partial G^E}{\partial p} \] so that, \( V^E \)

(a) for a binary mixture

\[ V^E = kT \left[ \sum_{i=1}^{2} x_i \frac{\partial \ln \gamma_i}{\partial p} \right] \] ... (14)

and

(b) for a ternary mixture

\[ V^E = kT \left[ \sum_{i=1}^{3} x_i \frac{\partial \ln \gamma_i}{\partial p} \right] \] ... (15)
3. Excess enthalpy

\[ H^E = -RT^2 \left[ \frac{\partial}{\partial T} \left( \frac{G^E}{T} \right) \right] \], so that

(a) for a binary mixture

\[ H^E = -RT^2 \left[ \sum_{i=1}^{2} x_i \frac{\partial \ln \gamma_i}{\partial T} \right] \]  

... (16)

(b) for ternary mixture

\[ H^E = -RT^2 \left[ \sum_{i=1}^{3} x_i \frac{\partial \ln \gamma_i}{\partial T} \right] \]  

... (17)

4. Excess heat capacity

\[ C^E_p = \left( \frac{\partial H^E}{\partial T} \right) \]

(a) for a binary mixture

\[ C^E_p = -2RT \left[ \sum_{i=1}^{2} x_i \frac{\partial \ln \gamma_i}{\partial T} \right] -RT^2 \left[ \sum_{i=1}^{2} x_i \frac{\partial^2 \ln \gamma_i}{\partial T^2} \right] \]

... (18)

and for a ternary mixture

\[ C^E_p = -2RT \left[ \sum_{i=1}^{3} x_i \frac{\partial \ln \gamma_i}{\partial T} \right] -RT^2 \left[ \sum_{i=1}^{3} x_i \frac{\partial^2 \ln \gamma_i}{\partial T^2} \right] \]

... (19)

Since all these excess thermodynamic functions are a
useful measure of the non-ideality of solutions and as the non-ideality is directly linked with the intermolecular interactions, it is imperative that a brief review of the intermolecular forces be first made. A critical assessment of the various theories of solutions will then follow.

**Intermolecular forces**

Intermolecular forces are the forces that exist between different molecules. These forces are different in degree and kind from the forces that hold the atoms together - the so called intramolecular or valence forces. Intermolecular forces have been classified into four categories:

1. **Gravitational forces**
2. **Electromagnetic forces**
3. **Strong nuclear forces**
4. **Weak nuclear forces**

Since the gravitational force is extremely long range and as the molecular dimensions of such forces are of the order of \(5 \times 10^{-7}\) nm, the gravitational potential energy is much less than the intermolecular forces. Therefore intermolecular forces must have an electromagnetic origin and must be due to charged particles, electrons and protons that make up an atom or molecule. The strong nuclear forces are responsible for binding the neutrons and protons inside the nucleus and are significant over a distance of \(10^{-6}\) nm. On the other
hand the weak nuclear forces are of similar nature but are of short range. Further these intermolecular forces involve short range repulsion as well as long range attraction. Short range forces are repulsive in nature which prevent two molecules from coalescing. These forces arise when the molecules approach sufficiently close to each other so that their electron cloud may overlap. This, according to Pauli's exclusion principle (which prohibits some electrons from occupying the overlap region) produces a nodal plane in this region. Short range forces vary at large value of $R$ as $\exp(-kR)$, where $k$ is a constant.

Short range forces are not always repulsive in nature or else chemical combinations between atoms would have been impossible.

Long range forces on the other hand, vary at large $R$ as some inverse power of $R$, say $R^{-n}$. The coulombic force between charges fall in this category having $n = 2$, long range forces arise when the overlap of approaching molecules is small.

The long range attractive component $^8$ can be divided into three types -

(i) Electrostatic

(ii) Induction and

(iii) Dispersion

The electrostatic contribution $^8$ to the potential energy
results from the interaction of various components in the molecule such as charges, dipole moments, quadrupole moments etc. Electrostatic energy can be either repulsive or attractive. The electrostatic energy is exactly pair additive for example the electrostatic energy for three point charges is the sum of three coulombic energies for the charges interacting in pairs.

Induction\(^9\) as well as dispersion\(^10\) contributions are due to the changes in the electron distribution within the molecules when they come within each other's influence. The electric fields arising from the permanent moments of one molecule will induce moment in the neighbouring neutral molecule and the interaction between the permanent and induced moments will lead to attraction between the two. This is the induction contribution to long range forces. The induction contribution can be large for interacting ions or molecules with large dipole moments but it is small for nearly spherical molecules like \(\text{CH}_4\) and \(\text{SF}_6\), because they have low order moments, electric field in their vicinity are small. It will be zero for inert gas atoms since they have no moments of any order. The induction contribution to the potential energy are attractive in nature and are not pair-additive.

The dispersion contribution to potential energy arises\(^11\) when non-polar molecules having long range forces of attraction between them interact. At any instant the electrons in molecule "a" are in such a configuration which results in the instan-
taneous development of dipole moment. This instantaneous dipole moment induces dipole in the molecule "b". The induced dipole in the "b" thus interacts with the inducing dipole to produce, regardless of the orientation of the dipole, an attractive force between the two molecules.

Although the instantaneous moments average over time to zero, the polarization energy that is associated with them does not average to zero. Dispersion forces are also known as "London" forces due to F. London. Dispersion forces are attractive in nature and are pairwise additive.

**Specific interactions**

Some of the other important types of interactions between the components of mixture are

(i) Polar nature of components

(ii) Hydrogen bonding

(iii) The difference in the positive and negative character of the components of mixture which results in the formation of associated complexes.

It has been proposed\(^1\) that all molecular species necessarily have an ionic structure of the type, \(B^+ A^-\) and that the low ionization energies of the base \(B^-\) and high electron affinity of \(A^-\) favours the formation of stable complex. But Brackmann\(^2\) has attributed molecular complex formation to quantum mechanical resonance between a
no bond structure and a structure having a bond between the
two species A and B.

None of these views are, however, correct. Mulliken has, however, developed a quantum mechanical theory which
assumes that charge transfer forces operate in more or less
localized fashion in much the same way as in solids and
that they are of the same order of magnitude as dispersion
forces. This theory has recently been reviewed.

Charge Transfer Interactions

Charge transfer complexes (CT) arise between an acceptor
molecule \(a\) and a donor molecule \(d\). The intermolecular complex
is stabilized by a net charge (electron) transfer from \(d\) to \(a\).

Excited states of such complexes often have as a main term an
excited state of the \(a^-d^+\) type. Example of CT complex format is the case of benzene & iodine.

Benzene is a "sacrificial" donor i.e. the electrons as
donated from a bonding MO. Iodine is a sacrificial acceptor.
Thus on entering into the CT complex the bond length of \(I_2\)
is expected to increase, indicating a weaker I-I bond. Although
both benzene and iodine are in the CT complex individually in
less stable states, there is a nevertheless, a net gain of
stability in the CT complex as a whole. "Inrevaalent" donors
and acceptors can also be present where a lone pair is donated
or obtained e.g., \(\text{NH}_3\) (donor) or \(\text{SnCl}_4\) (acceptor). A wide
variety of phenomena, from ion pairing to Lewis acid-base pairing, to even covalent compound formation, can be treated under this formalism. These types of interactions may exist between both like and unlike molecules. However, these interactions are generally weaker for like molecules. These forces may often share with dispersion forces in accounting for Vander Waals cohesive forces between molecules especially in systems containing more than one component. The charge transfer forces may often be of the same order as dispersion forces but the former predominate in solution and other systems in which molecules of different kind are present together. Dispersion forces predominate where interactions between like molecules occur. The dispersion force of attraction tends to be maximum in those orientations that bring maximum polarisabilities to play, while the orientational properties of charge transfer forces are governed by considerations of quantum mechanical symmetry of molecular wave-functions.

Contact Charge Transfer Interactions

These types of interactions can occur whenever the donor and acceptor molecules are in contact. According to Mulliken, the absorption bands corresponding to intermolecular charge transfer transition should occur when a donor-acceptor complex is formed, applied equally well to pairs of molecules when in contact or when sufficiently close to each other. It does not depend upon the ability of charge transfer forces that overcome exchange between the components but on repulsions, the existence of non-zero overlap integral
between donor and acceptor orbitals.

**Hydrogen bond**

Amongst those systems where the intermolecular energy is exceptionally large the hydrogen bond is the most important constituent of the liquid state. Hydrogen bond is a structure in which hydrogen atom is partly bonded to two electronegative atoms, most commonly nitrogen, oxygen or a halogen atom, the three atoms being usually colinear. In most cases the hydrogen bond is more strongly bound to one atom (A) than the other (B), the A-H bond being almost of the same length as in the uncomplexed system. A-H and the other bond B-H being longer than a normal chemical bond or a covalent bond. In a few strong complexes the hydrogen is symmetrically placed between A and B.

Recent calculations\(^7\) have shown that the main contribution to the binding energy comes from the electrostatic energy between the dipolar A-H bond and a partial negative charge on the electronegative atom B. For the stronger complexes, however, there is a significant contribution to the energy from a valence type interaction arising from the overlap of orbital of A-H with those of B. This interaction leads to a partial transfer of electrons from B to A-H bond.

Generally hydrogen bond\(^2^0\) formation is believed to involve three types of interactions viz., dipole-dipole,
charge transfer and $\pi$-electron interactions so that

\[ U_{\text{H-bond}} = U_{\text{dipole-dipole}} + U_{\text{charge transfer}} + U_{\pi} \]

(20)

Sources of information about intermolecular forces

Following are the various sources of information about the intermolecular forces:

(i) Thermodynamic properties of gases at low densities
(ii) Transport properties of dilute gases
(iii) Molecular beam study
(iv) Spectra and
(v) Solid state properties

Although, accurate results are not expected from the theory of the above forces, yet detailed information can be obtained from semiempirical procedures. It now remains to be seen as to how to represent the forces between two atoms.

When the molecules are very much far away from each other i.e. the intermolecular distances are very large, the molecules "i" and "j" do not interact at all, therefore the total energy of this two atom system is given by the sum of the energies of the individual atoms i.e.

\[ E_{\text{total}}(r=\infty) = E_i + E_j \]

(21)
However, at finite intermolecular distance, these two atoms interact so that the total energy is given by

$$E_{\text{total}}(r) = E_i + E_j + U(r) \quad \ldots \quad (22)$$

Consequently $U(r)$ is given by

$$U(r) = E_{\text{total}}(r) - E_i - E_j$$
$$= E_{\text{total}}(r) - E_{\text{total}}(r = \infty) \quad \ldots \quad (23)$$

$U(r)$ is called the intermolecular pair potential energy function\textsuperscript{23} and is numerically equal to the work done in bringing the two atoms from infinite separation ($r = \infty$) to a separation $r$.

Various intermolecular potentials have been suggested to fit the experimental data, some of the most important intermolecular potentials are as follows:

1. Hard sphere potential\textsuperscript{24}. This is the simplest model of molecular interaction and is expressed as

$$U(r) = \infty; \quad r < d$$
$$U(r) = 0; \quad r \geq d \quad \ldots \quad (24)$$

2. Square well potential\textsuperscript{24}

This model considers interactions between rigid spheres of certain diameters surrounded by an attractive core of strength, $\epsilon$, which extends to a separation of $R \sigma$ and expresses the interaction energy $U(r)$ by
3. Sutherland potential

This model visualizes that rigid spheres of diameters attract one another according to an inverse power law. The second virial co-efficients and the transport properties have been calculated for this potential from the relations

\[ U(r) = \infty; \quad r < \sigma \]  \quad \ldots (25)

\[ U(r) = -\varepsilon; \quad \sigma \leq r \leq R\sigma \]  \quad \ldots (26)

\[ U(r) = 0 \quad \quad r > R\sigma \]  \quad \ldots (27)

4. Lennard–Jones potential

According to this potential

\[ U(r) = U(r) /\varepsilon = 4 \left[ (\sigma/r)^{12} - (\sigma/r)^6 \right] \]  \quad \ldots (30)

where \( \varepsilon \) is the minimum potential energy and \( \sigma \) the collision diameter or the distance where \( U = 0 \). This potential is quite suitable for inert gases and for simple non-polar molecules.

5. Kihara spherical core potential

This potential has three adjustable parameters.

\[ U^*(r) = U(r) /\varepsilon = (n/n-m)(n/m)^{m/n-m} \left[ \left( \frac{\sigma-2a}{\lambda-2a} \right)^{\eta} - \left( \frac{\sigma-2a}{\lambda-2a} \right)^{\eta} \right] \quad \lambda > 2\sigma \]

\[ U^*(r) = U(r) /\varepsilon = \infty; \quad r < 2a \]  \quad \ldots (31)
6. Buckingham - Corner potential

This potential expresses the potential energy by

\[ U^*(r) = b e^{\frac{\beta r}{\alpha}} - C \left[ \frac{\alpha^{-6} \beta^{\frac{\alpha}{\beta}}}{\alpha^{\frac{\alpha}{\beta}} - \alpha^{\frac{\alpha}{\beta}}} \right] \cdot \frac{\alpha}{\beta} > 1 \]

\[ = b e^{\frac{\beta r}{\alpha}} - C \left[ \frac{\alpha^{-6} \beta^{\frac{\alpha}{\beta}}}{\alpha^{\frac{\alpha}{\beta}} - \alpha^{\frac{\alpha}{\beta}}} \right] e^{4 \left( 1 - \frac{\alpha}{\beta} \right)^3} \cdot \frac{\alpha}{\beta} < 1 \]

... (32)

where \( r = r/\hbar_m \)

\[ b = (6 + 8\alpha) e^{\frac{\alpha}{\beta}} \left[ (1 + \beta) - (6 + 8\beta) \right] \]

\[ c = \alpha \left[ (1 + \beta) - (6 + 8\beta) \right] \]

and \( \alpha \) is the parameter that measures the steepness of the repulsive energy. Thus it is a four parameter potential model involving the induced dipole - induced dipole interaction, induced dipole - induced quadrupole interaction and an experimental term as the repulsive contribution to the potential function.

7. Morse potential

According to this potential, potential energy is given by

\[ U^*(r) = e^{-2C/\sigma}(r-r_m)^{-2e}(-C/\sigma)(\hbar-\Lambda_m) \]

... (33)

where the parameter \( C \) is related to the curvature of \( U^*(r) \) at its minimum
\[ C^2 = \frac{1}{2} (\sigma^{-2}/\epsilon) (d^2 u/dr^2); \quad r = r_m \]

8. **Boys and Shavitt function**

This potential expresses the potential energy by the following equation

\[
U^*(r) = \frac{4}{[r/\sigma]^2 + \beta^2} \sum_{i=0}^{\infty} C_{2i} \left[ (r/\sigma)^{2i} \epsilon^{A(1-(r/\sigma)^2)} \right]^{-1}
\]

where \( A, \beta, C_0, C_2, C_4 \) etc. are adjustable parameters.

9. **Barker - Pompe potential**

According to this potential, potential energy is given by

\[
U^*(r) = \exp \left[ \alpha (1-r) \right] \sum_{i=0}^{n} A_i (r-1)^i + \sum_{j=0}^{2} (r^2 + 6r^2j^2 + 6r^2j^6)
\]

This potential played an important role in establishing the intermolecular potential for Ar.

10. **Barber - Bobetic - Maitland - Smith (BBMS) potential**

This is another important potential for Ar and is the modified version of the Barker - Pompe potential, to make it consistent with spectroscopic data.

\[
U^*(r) = U^*(\text{Barber-Pompe}) + \alpha' \exp \left[ -50(r-1.33)^2 \right]
\]
11. **Maitland-Smith potential**\(^\text{32}\)

This potential represents the potential energy by

\[
U^*(r) = \left[ \frac{6}{n-6} r^{-n} - \frac{n}{n-6} r^{-6} \right]
\]

\...(36)

where \(n\) is allowed to vary with \(\bar{r}\). This function gives a remarkably accurate representation of inert gas potential functions.

12. **Stockmayer potential**\(^\text{33}\)

This function combines a Lennard-Jones potential with a dipole-dipole contribution and \(\phi_1, \phi_2, \Theta\) and defines the relative orientation of the two dipoles.

\[
U(r, \phi_1, \phi_2, \Theta) = 4 \epsilon \left[ \left( \frac{\sigma}{\bar{r}} \right)^{12} - \left( \frac{\sigma}{\bar{r}} \right)^{6} \right] - \frac{\epsilon}{4\pi\epsilon_0} \frac{\phi_1 \phi_2}{r^2} \sqrt{\frac{\cos \Theta}{\cos \phi_1}}
\]

\...(37)

13. **Parson-Siska-Lee potential**\(^\text{34}\)

This potential is based on molecular beam data and gives a good representation of the Ar-Ar interactions. According to this potential, potential energy is given by

\[
U^*(r) = \exp \left[ -2\theta(\bar{r} - 1) \right] - 2 \exp \left[ -\theta(\bar{r} - 1) \right] ; 0 \leq \bar{r} \leq x_1
\]

\[
eq b_1 + (\bar{r} - x_1) \left[ b_2 + (\bar{r} - x_2) \left[ b_3 + (\bar{r} - x_1) b_4 \right] \right] ;
\]

\[
x_1 \leq \bar{r} \leq x_2
\]

\[
eq c_6^* \bar{r}^{-6} + c_8^* \bar{r}^{-8} + c_{10}^* \bar{r}^{-10} ; x_2 \leq \bar{r} \leq \infty \ldots (38)
\]
The potential energy between a pair of unlike molecules can be represented in the same way as that between a pair of molecules of the same kind with the help of combining rules\(^{35}\) such as

\[
\begin{align*}
 r_{ij}^* &= (r_{ii}^* + r_{jj}^*)/2 \quad \ldots \quad (39) \\
 \varepsilon_{ij}^* &= (\varepsilon_{ii}^* \cdot \varepsilon_{jj}^*)^{1/2} \quad \ldots \quad (40)
\end{align*}
\]

But none of the rules is exact though first one appears to be a useful approximation in many cases. The second rule tends to overestimate\(^{36}\) \(\varepsilon_{ij}^*\) and is now expressed as

\[
\begin{align*}
\varepsilon_{ij}^* &= (\varepsilon_{ii}^* \cdot \varepsilon_{jj}^*)^{1/2} (1 - k_{ij}) \quad \ldots \quad (41)
\end{align*}
\]

\(k_{ij}\) is the measure of departure from geometric mean rule for \(\varepsilon_{ii}^*\) and \(\varepsilon_{jj}^*\). Alternatively Hudson and McCoubrey\(^{37}\) and Fender and Halsey\(^{37}\) express \(\varepsilon_{ij}^*\) by

\[
\begin{align*}
\varepsilon_{ij}^* &= (\varepsilon_{ii}^* \cdot \varepsilon_{jj}^*)^{1/2} \frac{2(I_i I_j)^{1/2}}{I_i + I_j} \times \frac{2(\sigma_{ii} - \sigma_{jj})}{(\sigma_{ii} + \sigma_{jj})} \quad \ldots \quad (42)
\end{align*}
\]

where \(I_i\) is the ionization potential of \(i\) and

\[
\varepsilon_{ij}^* = \frac{2 \varepsilon_{ii}^* \varepsilon_{jj}^*}{(\varepsilon_{ii}^* + \varepsilon_{jj}^*)} \quad \ldots \quad (43)
\]

respectively, and while Hudson - McCoubrey rule is superior\(^{35}\) to the geometric mean rule, it still tends to over-estimate
\( \varepsilon_{ij} \). The Fender & Halsey rule\(^{38} \), on the other hand, suggests that \( \varepsilon_{ij} \) will be determined by the component with the weaker intermolecular forces.

Since the equilibrium properties of fluid mixtures depend on the forces between the molecules and as these forces change with composition, it follows that a knowledge of potential energy of a group of molecules as a function of their mutual separation and if necessary, orientation should suffice to determine the macroscopic properties of a substance. The inverse problem, that of determining the potential energy from the physical properties has also been widely studied\(^{39,40} \) on the whole in a less systematic way as there is no way of inverting the equation of statistical mechanics to give the potential as explicit function of the physical properties. Therefore almost all the recent attempts start by setting up a model potential with two or more adjustable parameters, calculate one or more physical properties in terms of these parameters and then compare them with the experimental results.

**Theories of solutions**

Formulation of a theory, which is adequate for calculating thermodynamic functions, can be attacked from two directions

(i) by extrapolating from the properties of gases or

(ii) by starting from the properties of crystals. But none
of them could lead to desired goal because the former involves the formidable transition from binary collisions to multiple interactions in liquids, while latter assumes the structures that are contrary to various evidences set forth by Barker. Following are, however, some more important theories of liquid mixtures which have been proposed in recent years in order to achieve the desired goal.

(i) Lattice model theory;

(ii) Conformal solution theory;

(iii) Cell model theory of Prigogine;

(iv) Flory's theory;

(v) Sanchez and Lacombe theory;

(vi) Distribution function theories of liquids;

(vii) Statistical mechanics of associated mixtures; and

(viii) Other theories of fluid mixtures.

1. **Lattice Model theory**\(^{42}\)

   This theory states that liquid is a solid melt and the molecular motions in a liquid are merely oscillations about some equilibrium positions. Lattice model further assumes that the lattice is rigid and each molecule occupies a single lattice site. Partition function can then be factorized into

   \[ \tilde{Q} = Q_{\text{latt}} \cdot Q_{\text{vib}}. \]
where $Q_{\text{latt}}$ is the lattice partition function which corresponds to the energy of the system when each molecule is at rest at a lattice point, while $Q_{\text{vib}}$ is the vib. partition function that corresponds to the oscillations of molecules about their lattice point.

The lattice energy, $E_{\text{latt}}$ for a binary solution, that contains $n_i$ molecules of $i$ and $n_j$ molecules of $j$ that are distributed on a lattice of $N = (N_i + N_j)$ sites with a coordination number $Z$, is then given by:

$$E_{\text{latt}} = E_{ii} + E_{jj} + N_{ij}W$$

where

$$W = U_{ij} - (U_{ii} + U_{jj}) / 2$$

and $E_{ii}$ etc denote the lattice energy of pure $i$, and $W$ is the energy gained for the creation of $N_{ij}$ pairs of neighbours. $Q_{\text{latt}}$ and the Helmholtz free energy of mixing, $F^m$ is then given by:

$$Q_{\text{latt}} = \sum_{N_{ij}} g(N_i, N_j, N_{ij}) \exp (-E_{\text{latt}}/kT)$$

and

$$F^m = -kT \ln Q_{\text{latt}} = -kT \ln \frac{N!}{N_i!N_j!} + ZWN_iN_j/(N_i + N_j)$$
\[ G^E = \sum W x_i x_j = H^E \] and \[ S^E = 0 \] ...(49)

Hence according to this model \( G^E = H^E \) for binary mixtures, which is not true\(^4\). And for a ternary \((i + j + k)\) mixture this model expresses \( G^E, H^E \) and \( S^E \) by\(^3\)

\[ G^E = \sum W_{ij} x_i x_j + \sum W_{jk} x_j x_k + \sum W_{ik} x_i x_k \] \ ...(50)

\[ = H^E \] \ ...(51)

and \[ S^E = 0 \] \ ...(52)

In deriving equation (50), it has been assumed that the distribution is completely random. This may not be completely true, since differences in the intermolecular interactions would tend to favour distributions which would lower the lattice energy\(^4\) so that

\[ N_{ij} > N_{ij}' \text{ or } N_{ij} < N_{ij}' \text{ and } W_{ij} \neq 0 \text{ etc.} \]

This would then introduce a certain amount of order in the distribution of molecules.

Hagemark\(^4\) recently employed a quassi-chemical approximation to derive an expression for the energy of mixing, \( \Delta E \), excess Gibbs free energy of mixing, \( \tilde{G}^E \), and the partial excess Gibbs free energy of mixing, \( \tilde{G}_{ij}^E \), of a solution containing \( r \) components which for a ternary solution suggests\(^4\)

that the excess \( \tilde{E}^1 \), of \( \Delta E \) of a ternary solution over the \( \Delta E \)
of binary solutions should be given by

\[
\mathbf{E}^1 = -\frac{2}{4} RT x_i x_j x_k \left[ (1-2x_i x_k) \frac{2 - x_j}{(1-x_j)^2} \right] \epsilon_{ik}^2 + \\
\left[ (1 - 2x_j x_k) \frac{2 - x_i}{(1-x_i)^2} \right] \epsilon_{jk}^2 + \left[ (1-2x_i x_j) \frac{2 - x_k}{(1-x_k)^2} \right] \epsilon_{ij}^2
\]

\[
2(1 - 2x_j) \epsilon_{ik} \epsilon_{jk} - 2(1 - 2x_i) \epsilon_{ik} \epsilon_{ij} - 2(1 - 2x_j) \epsilon_{jk} \epsilon_{ij}
\] ...

(53)

Meschel and Kleppa\textsuperscript{47} have measured the enthalpy of mixing for ternary alkali and silver nitrate mixtures. Their results show that the ternary excess term, \( E^1 \), should be of the form

\[
E^1 \propto (x_i x_j x_k) \Theta
\] ...

(54)

where \( \Theta \) varies with composition. But according to Hagemark\textsuperscript{46} \( E^1 \) should vary with \( x_i x_j x_k \) as

\[
E^1 \propto x_i x_j x_k f(\epsilon, x)
\] ...

(55)

Major weakness of all these approaches\textsuperscript{42-46} is that they require \( \mathbf{V}^E = 0 \), which is not true.

2. Conformal Solution Theory:

This theory provides a simple means to evaluate therm...
dynamic excess functions for a ternary \((i + j + k)\) mixture of non-electrolytes.

Potential energy of a ternary mixture which is composed of \(i, j\) and \(k\) molecular species, having intermolecular distances \(r_{ij}, r_{jk}\) and \(r_{ik}\) between \(i\) and \(j\), \(j\) and \(k\), \(i\) and \(k\) respectively is given by

\[
U = \sum_{i<j} \varepsilon_{ij}(r_{ij}) + \sum_{j<k} \varepsilon_{jk}(r_{jk}) + \sum_{i<k} \varepsilon_{ik}(r_{ik})
\]

Further interaction between \(i\) and \(j\), \(j\) and \(k\) and \(i\) and \(k\) molecular species are expressed by

\[
\varepsilon_{ij}(r_{ij}) = f_{ij} \varepsilon(g_{ij}, r_{ij}) \quad \ldots (57)
\]

\[
\varepsilon_{jk}(r_{jk}) = f_{jk} \varepsilon(g_{jk}, r_{jk}) \quad \ldots (58)
\]

\[
\varepsilon_{ik}(r_{ik}) = f_{ik} \varepsilon(g_{ik}, r_{ik}) \quad \ldots (59)
\]

where \(f_{ij}\) and \(g_{ij}\) etc. are constants depending only on the chemical nature of \(i\) and \(j\) etc. molecular species. If the intermolecular forces are of the same order of magnitude for all pairs of molecules, then it is possible to find a reference species such that

\[
f_{ij} = f_{jk} = f_{ik} = g_{ik} = g_{jk} = g_{ik} = 1 \quad \ldots (60)
\]

It is further assumed that
Multicomponent systems that satisfy these assumptions have been described as conformal solutions. If \( U \) and \( U^0 \) denote the potential energy of the solution and that of the components in the reference state, then the difference between the Helmholtz free energy of the mixture and that of the reference state is given by:

\[
F(V,T) - F^0(V,T) = \int (U - U^0) \exp(-U^0/kT) dr_1 \ldots dr_n
\]

\[\int \exp(-U^0/kt) dr_1 \ldots dr_n \]

But the energy of the mixture in the perturbed state, \( U \), and in the unperturbed state, \( U^0 \), is given by:

\[
U = \sum_{i<j} \sum_{i,j} x_i x_j f_{ij} (r_{ij}, g_{ij}) + \sum_{j<k} \sum_{j,k} x_j x_k f_{jk} (r_{jk}, g_{jk}) + \sum_{k<i} \sum_{i,k} x_i x_k f_{ik} (r_{ik}, g_{ik})
\]

... (65)

and

\[
U^0 = \varepsilon_{ij} + \varepsilon_{jk} + \varepsilon_{ik}
\]

... (66)

respectively so that equation (64), reduces to

\[
F(V,T) - F^0(V,T) = \sum_{i,j} x_i x_j I(f_{ij}, g_{ij}) + \]
and since \( I(f_{ij}, g_{ij}) \) etc are given by

\[
I(f_{ij}, g_{ij}) = E_{\text{conf r}}^{\circ} (f_{ij} - 1) + 3(NkT - PV^0)(g_{ij} - 1) \text{ etc.}
\]

Consequently \( F(V, T) - F_0(V, T) \) is given by

\[
F(V, T) - F_0(V, T) = \sum_{i,j} x_{ij} \left[ E_{\text{conf r}}^{\circ} (f_{ij} - 1) + 3(NkT - PV^0)(g_{ij} - 1) \right] + \\
\sum_{j,k} x_{jk} \left[ E_{\text{conf r}}^{\circ} (f_{jk} - 1) + 3(NkT - PV^0)(g_{jk} - 1) \right] + \\
\sum_{i,k} x_{ik} \left[ E_{\text{conf r}}^{\circ} (f_{ik} - 1) + 3(NkT - PV^0)(g_{ik} - 1) \right]
\]

where \( E_{\text{conf r}}^{\circ} \) is the configurational energy of the solution in the reference state.  

Now at constant temperature and pressure, the change in Gibbs free energy is expressed by

\[
(dG)_{\lambda, j,k} = -SdT - VdP + \sum_{i,j} x_{ij} \left[ E_{\text{conf r}} df_{ij} + 3(NkT - PV^0)dg_{ij} \right] + \\
\sum_{j,k} x_{jk} \left[ E_{\text{conf r}} df_{jk} + 3(NkT - PV^0)dg_{jk} \right] + \\
\sum_{i,k} x_{ik} \left[ E_{\text{conf r}} df_{ik} + 3(NkT - PV^0)dg_{ik} \right]
\]
\[ G-G^0 = \sum_{i,j} x_i x_j \left[ \mathcal{E}^0_{\text{confr}}(f_{ij} - 1) + 3(NkT-PV^0)(g_{ij} - 1) \right] + \]
\[ \sum_{j,k} x_j x_k \left[ \mathcal{E}^0_{\text{confr}}(f_{jk} - 1) + 3(NkT-PV^0)(g_{jk} - 1) \right] + \]
\[ \sum_{i,k} x_i x_k \left[ \mathcal{E}^0_{\text{confr}}(f_{ik} - 1) + 3(NkT-PV^0)(g_{ik} - 1) \right] \]

... (71)

But \( G_i \) for pure \( i \) etc. is expressed by

\[ G_i = G^0_i + \mathcal{E}^0_{\text{confr}}(f_{ii} - 1) + 3(RT-PV^0)(g_{ii} - 1) \]

... (72)

So that excess Gibbs free energy per mole, \( g^E \), of a ternary \((i + j + k)\) solution is given by

\[ g^E = \sum_{i,j} x_i x_j \left[ \mathcal{E}^0_{\text{confr}}(2f_{ij} - f_{ii} - f_{jj}) + (3NkT-PV^0) \right] + \text{similar terms for } jk \text{ and } ik \text{ pairs} \]

... (73)

Equation (71) in view of equations (69) and (70) reduces to

\[ g^E = \mathcal{E}^0_{\text{confr}} \left[ \sum_{i,j} x_i x_j \delta_{ij} + \sum_{j<k} x_j x_k \delta_{jk} + \sum_{i<k} x_i x_k \delta_{ik} \right] \]

... (74)

where

\[ \delta_{ij} = 2f_{ij} - f_{ii} - f_{jj} \]

... (75)

\[ \delta_{jk} = 2f_{jk} - f_{jj} - f_{kk} \]

... (76)

\[ \delta_{ik} = 2f_{ik} - f_{ii} - f_{kk} \]

... (77)
It can readily be shown that

$$H_{ijk} = H_{ij}^E + H_{jk}^E + H_{ik}^E \quad \ldots \ (78)$$

$$V_{ijk} = V_{ij}^E + V_{jk}^E + V_{ik}^E \quad \text{etc.} \quad \ldots \ (79)$$

This theory thus shows that the excess functions for ternary solutions are the sum of the excess functions of the three binary solutions of the three components.

3. Cell model theory for liquid mixtures

This model provides a reasonable physical description of liquid properties. According to this model each molecule in a liquid passes much of its time in a small cage or cell formed by the surrounding molecules, and molecules move entirely independent of one another. It is further assumed that all cages are identical and that each contains just one molecule. The latter assumption imposes severe restrictions on fluctuations of density and does not permit the molecules to share the volume fully. The calculated entropy at low densities is thus too low. The additional entropy that would arise if the molecules were given access to the whole configuration space is called the communal entropy, and physically, it is interpreted as the entropy due to disorder which arises when the molecules become sufficiently free to exchange places with each other. Thus it is natural to suppose that communal entropy appears at the melting point, i.e. at the point, at which the molecules become free to move.
The cell model further assumes that cell sizes are only slightly larger than the molecular diameters, such that it is very rare that molecules exchange their cells. Moreover, due to this infrequent interchange of cells the total energy contribution is negligible, relative to the energy that is associated with the motion of molecules within the cells. The cell theory is thus not valid in the expanded liquid region. This theory provides only a qualitative estimate\textsuperscript{55, 56} of the equilibrium properties of binary mixtures of non-electrolytes. Moreover it cannot be easily extended to multicomponent systems.

The greatest success of this theory lies in its qualitative predictions that mixtures of spherical molecules of the same size may simultaneously show a positive excess free energy and a negative excess volume\textsuperscript{55}. An example of this behaviour was reported for the first time by Mathor and Desmyter\textsuperscript{56}.

While the cell model of Prigogine\textsuperscript{55} derives its conceptual basis from the cell model of liquids, the conformal solution theory including the corresponding states approach, proceed by expressing the intermolecular potential in the form of $\varepsilon_{ij} = \varepsilon_{ij}^{*} \phi\left(\frac{r_{ij}}{r_{ij}^{*}}\right)$ where $r_{ij}$ is the distance between centres of $i$ and $j$ molecules, $\varepsilon_{ij}^{*}$ and $r_{ij}^{*}$ are characteristic parameters for the $ij$ pair and $\phi\left(\frac{r_{ij}}{r_{ij}^{*}}\right)$ is
a universal function. One is thus not able to establish any decisive advantage of these approaches over the lattice model theory. Therefore it points out to the limitations of the cell model and also of expressing intermolecular potential in the form

\[ \varepsilon_{ij} = \varepsilon^*_i \phi \left( \frac{r_{ij}}{r^*_i} \right) \]

for molecules that differ appreciably in size, shape or composition. Moreover this theory confers a crystal like structure to the liquids and incorporates the known differences of Einstein model for a liquid. The theory also fails to account for those features that differentiates a liquid from a solid. These and some other arguments\textsuperscript{57,58} led Flory to put forward his own theory\textsuperscript{59}.

4. Statistical theory of Flory

According to this theory\textsuperscript{59} the configurational space, \( \Omega \), available to a one dimensional system of \( N \) particles each of length 1 is given by

\[ \Omega = (L - Nl^*)N!^N \]
\[ \Omega = (f - f^*)e^N \]

...(80)

...(81)

The partition function of this assembly would then be expressed by

\[ Z = \Omega \exp(-E_0/kT) \]

...(82)
where $E_o$ is the "mean" intermolecular energy.

Flory next regarded a three dimensional molecule to be made up of a number of isomeric segments (each molecule was regarded to be an $r$-mer) and expressed its partition function by

$$Z = Z_{comb} \left[ r(V^{1/3} - V^*/3)^{3rNC} \exp(-E_o/kT) \right] \quad \ldots (83)$$

Further as $E_o$ is expressed by

$$E_o = -N\sigma/2V = \text{const}/V^m \quad \ldots (84)$$

the reduced equation of state of the assembly would be given by

$$P V / T = \frac{1}{V^3} / \left( \frac{1}{V^3} - 1 \right) - 1 / V T \quad \ldots (85)$$

where all the terms have the same significance as given by Flory. 59

For a binary mixture of components $i$ and $j$ Flory regarded each segment to have a "hard core" volume, $V^*$, occupying an effective volume, $V$, in the mixture and expressed $E_o$ as

$$-E_o = (A_{ii} \sigma_{ii}^* + A_{jj} \sigma_{jj}^* + A_{ij} \sigma_{ij}^*) / V \quad \ldots (86)$$

where

$$2A_{ii} + A_{ij} = r_i s_{ii} \quad \ldots (87)$$

$$2A_{jj} + A_{ij} = s_j r_{jj} \quad \ldots (88)$$
and $A_{ii}$, $A_{ij}$, $\xi_{ii}/V$ and $\xi_{ij}/V$ denote respectively, the number of contacts and energies associated with each of them. If $\Theta_i$ and $\Theta_j$ are the site fractions of i and j in the mixture, then

$$\Theta_j = 1 - \Theta_i = \frac{S_j r_j N_j}{S r N} \quad \ldots (89)$$

$$A_{ij} = S_i r_i N_{ij} = S_j r_j N_j \Theta_j \quad \ldots (90)$$

where $\bar{r} = \frac{(r_{in_i} + r_{jn_j})}{N}$ \ldots (91)

$$S = \sum_{i=1}^{2} S_i r_i N_i / r N \quad \ldots (92)$$

$$N = \sum_{i=1}^{2} N_i \quad \ldots (93)$$

so that

$$-E_o / \bar{r} N = \left(\frac{S}{2V}\right) \left[ \frac{2 \Theta_i \xi_{ii}^* + \Theta_j \xi_{jj}^* + 2 \Theta_i \Theta_j \xi_{ij}^*}{S} \right] \quad \ldots (94)$$

If the segment fraction $\Phi_i$, is defined by

$$\Phi_j = 1 - \Phi_i = \frac{r_j N_j}{S N} \quad \ldots (95)$$

and the characteristic pressure of the pure components is expressed by

$$P_i^* = S_i \xi_{ii}^* / 2V^*; P_j^* = S_j \xi_{jj}^* / 2V^* \quad \ldots (96)$$
then

\[-E_0/rN = P^* V^*/\bar{V}\]

and the characteristic temperature of the mixture is given by

\[(T^*)^{-1} = \left( \sum_{i=1}^{2} \phi_i P_i^*/T_i^* \right) \left( \sum_{i=1}^{2} \phi_i P_i - \phi_i \phi_j \chi_{ij} \right)^{-1}\]

...(97)

where

\[\chi_{ij} = s_i (\varepsilon_{ii}^* + \varepsilon_{jj}^* - 2 \varepsilon_{ij}^*) 2v^*\]

...(98)

According to this theory molar excess enthalpy, excess volume, and excess free energy are expressed by

\[E^E = \sum_{i=1}^{2} x_i P_i^* V_i^* (V_i^{-1} - \bar{V}_{\text{calc}}^{-1}) + x_i v_i^* \Theta_j \chi_{ij} \bar{V}_{\text{calc}}^{-1}\]

...(99)

\[V^E = \sum_{i=1}^{2} (x_i v_i^*) (\bar{V}_{\text{calc}} - \sum_{i=1}^{2} \phi_i v_i)\]

...(100)

\[G^E = 3T \left[ \sum_{i=1}^{2} x_i (P_i^* V_i^*/T_i^*) \ln x \left\{ \frac{(v_i^3 - 1)}{(v_{\text{calc}} - 1)} \right\} + H^E \right]\]

(Flory theory)

...(101)

where \(\chi_{ij}\) is a constant characterizing the difference in the energy of interaction between sites of neighbouring molecules if species \(i\) and \(j\) form the average of interaction
in the pure components. This quantity was treated by Abe and Flory as an adjustable parameter and its value was chosen to fit $H^E$ for an equimolar solution.

Singh et al. have observed that in general different values of $\chi_{ij}$ are required to fit $H^E$ at each concentration. Siddiqi, Gotze and Kohler have further brought to light the inability of this theory to fully account for the packing effects due to molecular structure.

5. Sanchez and Lacombe theory

The molecular theory of classical fluids proposed by Sanchez and Lacombe is similar to the lattice theory of Flory and Huggins yet it differs from it in a very important aspect. All fluids according to this theory are regarded as lattice fluids but all the lattice sites are not occupied by molecules; some of these sites are vacant. The number of configurations, available to a system of $N$ molecules each of which occupies $r$ sites ($r$-mer) and the number of vacant lattice sites (holes), have been obtained as suggested by Guggenheim. Consequently, the total number of sites of a binary mixture of $N$ $r$-mers and $N_0$ empty sites is given by $N_k = N_0 + rN$ sites. It is further assumed that lattice has a coordination number $Z$, that each $r$-mer is characterized by a symmetry number $\sigma$ (which is one if the chain ends are indistinguishable) and a flexible parameter $\delta$ (which is
equal to the number of ways in which the r-mer can be
arranged on the lattice after one of its mers has been
fixed on a lattice site) and that the maximum value of $\delta$ is
$\delta_{\text{max}} = Z(Z-1)r^{-2}$.

Each interior mer of a linear chain is thus surrounded
by $Z-2$ nearest non-bonded neighbours and two bonded neigh­
bours, mers at the chain ends have $Z-1$ nearest non-bonded
neighbours and one bonded neighbour. Thus each r-mer is
surrounded by $qZ$ nearest non-bonded neighbours where

$$qZ = (r-2)(Z-2) + 2(Z-1) = r(Z-2) + 2 \quad \ldots \quad (102)$$

The total number of nearest neighbour pairs in the system
is $(Z/2)N_2$ and only $(Z/2)N_q$ are non-bonded.

Thus

$$N_q = N_0 + qN \quad \ldots \quad (103)$$

Further $N_h$, $N_q$, $N_0$ and $N$ are related by

$$(Z/2)N_q = (Z/2-1)N_h + N + N_0 \quad \ldots \quad (104)$$

so that the number of configurations $\Omega$, available to a system
of $N$ r-mer and $N_0$ empty sites is expressed by

$$\Omega \quad = \quad (\frac{\delta}{\delta_{\text{max}}})^N \quad \frac{N_h!}{N_0!} \quad \frac{N!}{N!} \quad (\frac{N_q}{N})^{Z/2} \quad \ldots \quad (105)$$

The theory next assumes that

(i) $\delta$ is independent of temperature and pressure, and that
(ii) close packed volume $rV^*$ of a molecule is independent of temperature and pressure; and the closed packed volume of a mer is $V^*$ which is also the volume of a lattice site as well as that of the hole.

The closed packed volume of the $N$ r-mer would then be

$$V^* = N (rV^*) \quad \ldots \quad (106)$$

if there are no holes. If $\rho^*$ is the close pack mass density then

$$rV^* = M/\rho^* \quad \ldots \quad (107)$$

where $M$ is the molecular weight. The total volume of $N^r$-mers and $N^o$ holes would then be

$$V = (N^o + N^r) V^* = N^r V^* = V^*/f \quad \ldots \quad (108)$$

where $f$ is the fraction of occupied sites. Since the energy of the lattice depends on the nearest neighbour interactions, the lattice energy (attractive) is given by

$$E = -(Z/2)N \sum_i \sum_j P(i,j) \epsilon_{ij} \quad \ldots \quad (109)$$

where $\epsilon_{ij}$ is the pair interaction energy between $i$ and $j$, $P(i,j)$ is the probability of $(i, j)$ pair in the system and for random mixing of holes and molecules is given by

$$P(\text{mer, mer}) = \frac{(qN)^2}{N^q \cdot N^r} \quad \ldots \quad (110)$$
or \( \text{Lt} \ P \ (\text{mer, mer}) = N \left( \frac{r N/N_r}{r} \right)^2 = f^2 \) \( \ldots \) (111)

The lattice energy is thus given by

\[ E = -N \left( \frac{Z \varepsilon}{2} \right) r^2 \] \( \ldots \) (112)

and the partition function is expressed by

\[ Z(T, P) = \sum_{N_0=0}^{\infty} \Omega \exp \left( \frac{-E + PV}{kT} \right) \] \( \ldots \) (113)

Gibbs free energy (in dimensionless variables) is then given by

\[ \frac{G}{(N_r \varepsilon^*)} = \bar{G} = -\bar{P} + \bar{P} \bar{V} + \bar{T} \left[ (V-1)\ln(1-\bar{P}) + \frac{1}{r} \right] \] \( \ldots \) (114)

\[ \ln \left( \frac{\rho}{\rho_0} \right) \]

where

\[ \bar{T} = \frac{T}{T^*} \]
\[ T^* = \frac{\varepsilon}{k} \] \( \ldots \) (115)

\[ \bar{P} = \frac{P}{P^*} \]
\[ P^* = \frac{\varepsilon}{V^*} \] \( \ldots \) (116)

\[ \bar{V} = \frac{1}{V^*} = \frac{V}{V^*} \]
\[ V^* = N(rV^*) \] \( \ldots \) (117)

and from \( \frac{\partial G}{\partial V} = 0 \), the equation of state for the system is given by

\[ \bar{P}^2 + \bar{P} + \bar{T} \ln (1-\bar{P}) + \bar{P}(1-\frac{1}{r}) = 0 \] \( \ldots \) (118)

This equation of state has been shown to be better than the available equations of state for fluids.
Lacombe and Sanchez later extended this theory to liquid mixtures. According to this theory the number of configurations, \( \Omega \), available to a system of \( N_i \) \( r_i \)-mers, \( N_j \) \( j \)-mers, \( N_k \) \( k \)-mers and \( N_q \) empty sites on a lattice of coordination number \( Z \) where an \( r \)-mer occupies \( r \) sites is given by

\[
\Omega = \left( \frac{\delta}{\delta_j} \right)^{N_1} \left( \frac{\delta}{\delta_2} \right)^{N_2} \cdots \left( \frac{\delta}{\delta_k} \right)^{N_k} \prod_{r=1}^{R} \frac{N_r!}{N_0! N_1! N_2! \cdots N_k!} \left( \frac{N_q!}{N_r!} \right)^{z/2} \]

where

\[
N_r = N_q + \sum_i r_i N_i 
\]

\[
N_q = N_q + \sum_i q_i N_i 
\]

\[
q_i Z = r_i (Z-2) + 2 \]

\[
(Z/2) N_q = (Z/2-1) N + N_0 + \sum N_i 
\]

If the hole-mer and hole-hole interactions have a zero energy and if the mixing of components is assumed to be random then the lattice energy as \( Z \to \infty \) is given by

\[
E = -N \sum_r \sum_i (f_i - f_j) \epsilon_{ij}^* \]

\[
\epsilon_{ij}^* = (Z/2) \epsilon_{ij} 
\]
where $\mathcal{E}^*$ is the interaction energy of a mer belonging to component $i$ when it is surrounded by $Z$ mers of the $j$th component. The volume of the mixture is then given by

$$V = N_r V^* = (N_0 + rN)V^*$$  \hspace{1cm} \ldots (126)$$

where $r = \sum x_i r_i$ and $V^*$ is the average close packed volume of a mer in the mixture. The close-packed volume of the mixture on the other hand is given by

$$V^* = v^* \sum r_i N_i = r N v^*$$  \hspace{1cm} \ldots (127)$$

If now an $i$th molecule occupies $r_i^0$ sites in the pure state and has a close-packed molecular volume of $r_i^0$ then it will occupy $r_i$ sites in the mixture

where $r_i = x_i r_i^0 (V_i^*/v^*)$  \hspace{1cm} \ldots (128)$$

Further the total number of pair interactions in the closed packed mixture is equal to the sum of the pair interactions of the components in their close packed pure state i.e.

$$(Z/2) \sum r_i^0 N_i = (Z/2) \sum r_i N_i = (Z/2) r N$$  \hspace{1cm} \ldots (129)$$

so that

$$V^* = \sum \phi_i r_i^0 V_i^*$$  \hspace{1cm} \ldots (130)$$

where \( \phi_i^0 = r_i^0 N_i/rN \)  \hspace{1cm} \ldots (131)$$
Gibbs free energy of the mixture is then given by (in dimensional variables)

\[
\bar{G} = (G/rN^*) = \bar{\rho} + \bar{P} \bar{V} + \bar{T} \left[ (\bar{V} - 1) \ln (1 - \bar{\rho}) \right] + \frac{1}{r} \ln \bar{\rho} + \sum \frac{\Phi_i}{r_i} \ln \left( \frac{\Phi_i}{\omega_i} \right)
\] ...

(132)

where

\[
\varepsilon^* = \sum \sum \Phi_i \Phi_j \varepsilon_{ij}^* \quad \ldots \quad (133)
\]

\[
\chi_{ij} = (\varepsilon_{ii}^* + \varepsilon_{jj}^* - 2 \varepsilon_{ij}^*) / kT \quad \ldots \quad (134)
\]

and all the terms have the same significance as given by Lacombe and Sanchez. The equation of state for the mixture is then given by

\[
\bar{\rho}_{\text{mix}}^2 + \bar{P} + \bar{T} \left[ \ln (1 - \bar{\rho}) + \bar{\rho}_{\text{mix}} \left( 1 - \frac{1}{r} \right) \right] = 0 \quad \ldots \quad (135)
\]

Molar excess enthalpy and molar excess volumes according to this theory are given by

\[
V^E = rV \left[ V - \sum \Phi_i V_i \right] \quad \ldots \quad (136)
\]

\[
H^E = rRT \left[ \bar{\rho} \sum \sum \Phi_i \Phi_j \chi_{ij} + \sum \left( \bar{\rho} \Phi_i^0 - \bar{\rho} \Phi_i^0/T_1 \right) \right] + P V^E \quad \ldots \quad (137)
\]

This theory has been quite successful to explain equilibrium properties of binary as well as ternary mixtures of non-electrolytes.
Ideal associated model approach:

This approach postulates the existence of chemically distinct species in solution which are assumed to be in chemical equilibrium. The approach further assumes that these chemically distinct substances form an ideal solution. Thus the observed non-ideality of the solution according to the approach is merely in apparent one because it is based on an apparent rather than a true account of the solution composition. Here we consider these cases.

(i) Self association of component takes place to form dimers, so that the species $j$ and $j_2$ are in equilibrium with each other and species $i$, $j$ and $j_2$ form an ideal solution.

(ii) Mutual interactions of $i$ and $j$ to form $ij$ so that the mixture involves $i$, $ij$ and $j$.

(iii) Mutual interaction of $i$ and $j$ to form $ij$ and $ij_2$ species so that $i$, $j$, $ij$ and $ij_2$ form an ideal solution.

Case (i)

Dimerisation process may be represented by

\[ 2j \rightleftharpoons j_2 \] ...

(138)

the equilibrium constant for this dimerization process is given by

\[ K = \frac{a_{j_2}}{a_j^2} \] ...

(139)
where \( a_j \) is the activity of monomer \( j \) molecule and \( a_{j_2} \) is the activity of dimer \( j_2 \) molecules. Since \( i, j \) and \( j_2 \) form an ideal solution activity may be replaced by mole fraction, so that equation (139) reduces to

\[
K = \frac{\xi_j \xi_{j_2}}{\xi_{j_2}} \quad \ldots (140)
\]

where \( \xi \) stands for true mole fraction.

If there are \( n_1 \) moles of 1 and \( n_2 \) moles of 2 then

\[
n_1 = n_i \quad \ldots (141)
\]

\[
n_2 = n_j + 2n_{j_2} \quad \ldots (142)
\]

the true total number of moles is \( n_1 + n_j + n_{j_2} \) which is equal to \( n_1 + n_2 - n_{j_2} \). Thus three true mole fractions are

\[
\xi_i = \frac{n_1}{n_1 + n_2 - n_{j_2}} \quad \ldots (143)
\]

\[
\xi_j = \frac{n_j}{n_1 + n_2 - n_{j_2}} = \frac{n_2 - 2n_{j_2}}{n_1 + n_2 - n_{j_2}} \quad \ldots (144)
\]

\[
\xi_{j_2} = \frac{n_{j_2}}{n_1 + n_2 - n_{j_2}} \quad \ldots (145)
\]

equation (143), (144) and (145) can then be solved for \( \xi_1 \).
since \( x_1 = \frac{n_1}{n_1 + n_2} \) and \( x_2 = \frac{n_2}{n_1 + n_2} \)

\[
Y_1 = \frac{a_1}{x_1}
\]

is then ultimately given by

\[
Y_1 = \frac{2k}{(2k-1)x_1 + kx_2 + (x_1^2 + 2kx_1x_2 + kx_2^2)^{1/2}}
\]

where \( k = 4k + 1 \)

similarly the activity coefficient for the dimerized component is

\[
Y_2 = \frac{a_2}{x_2} = \left( \frac{K^{0.5} + 1}{x_2} \right)
\]

\[
\left[ \frac{-x_1^2 + 2kx_1x_2 + kx_2^2}{(2k-1)x_1 + kx_2 + (x_1^2 + 2kx_1x_2 + kx_2^2)^{0.5}} \right]
\]

\[
\left[ \frac{x_1(2k-1)x_1 + kx_2 + (x_1^2 + 2kx_1x_2 + kx_2^2)^{0.5}}{2k-1} \right]
\]

\[
\left[ \frac{x_1^2 + 2kx_1x_2 + kx_2^2}{(2k-1)x_1 + kx_2 + (x_1^2 + 2kx_1x_2 + kx_2^2)^{0.5}} \right]
\]

\[
\left[ \frac{2k}{(2k-1)x_1 + kx_2 + (x_1^2 + 2kx_1x_2 + kx_2^2)^{0.5}} \right]
\]

Now for (146) and (147) as \( K > 0 \), +ve deviations from haoult's law results i.e. \( Y_1 \gg 1 \) and \( Y_2 \gg 1 \); for \( K = \infty \), all molecules of component 2 are dimerized. In this limiting case

\[
\lim_{K \to \infty} Y_1 = \frac{1}{x_1 + 0.5x_2} \quad \text{and} \quad \lim_{K \to \infty} Y_2 = \frac{1}{(2x_1x_2 + x_2^2)^{0.5}}
\]

At infinite dilution

\[
\lim_{K \to \infty} Y_1 = 2 \quad \text{and} \quad \lim_{K \to \infty} Y_2 = \infty
\]

\[
\lim_{x_1 \to 0} x_1 = 0 \quad \text{and} \quad \lim_{x_2 \to 0} x_2 = 0
\]

for the non-dimerizing component the large possible value of \( Y_1 \) is 2.
Further as $K$ becomes large, $G^E$, also increases and reaches the limits

$$\lim_{K \to \infty} \frac{G^E}{RT} = 0.5 \left[ 2(1-x_1) \ln 2-x_1 \ln x_1 - (2-x_1) \ln (2-x_1) \right]$$

which is asymmetric with respect to composition with a maximum value of 0.224 at $x_1 = 0.4$.

If $\Delta H^o_{J_2}$ is the standard molar enthalpy change for the dimerization reaction, then $H^E$ for this mixture has been given by

$$H^E = \left[ \frac{\delta_j}{x_j} \left( 1 - \frac{\delta_j}{x_j} \right)^{-1} - x_1 \frac{\delta_{J_2}}{x_{J_2}} \left( 1 + \frac{\delta_{J_2}}{x_{J_2}} \right)^{-1} \right] \Delta H^o_{J_2}$$

where the term in the brackets can be shown to be negative. Hence $H^E$ and $\Delta H^o_{J_2}$ have always opposite signs, and since the latter can be expected to be negative the former would be positive.

Case (ii)

Here $i + j \rightarrow ij$ is symmetric in composition, hence it is expected that all the excess functions will also be symmetrical. The equilibrium constant of this reaction would be given by

$$K = \frac{a_{ij}}{a_i \cdot a_j} \quad \ldots \ (148)$$

If the solution is formed from $n_1$ moles of $i$, $n_2$ moles of $j$ and if at equilibrium $n_{ij}$ moles of $ij$ are formed, then the true mole fractions of $i$, $j$ and $ij$ are
Following Dolezalek, it is now assumed that the true species form ideal solution and so activity of each species is equal to its true mole fraction. Equation (148) - (151) may then be used to eliminate \( n_{ij} \). Algebraic manipulation then gives

\[
Y_1 = \frac{a_i}{x_1} = \frac{kx_1-2+2(1-kx_1x_2)^{0.5}}{kx_1^2} \quad \ldots \ (152)
\]

\[
Y_2 = \frac{a_i}{x_2} = \frac{kx_2-2+2(1-kx_1x_2)^{0.5}}{kx_2^2} \quad \ldots \ (153)
\]

where \( k = \frac{4K}{(K+1)} \) and \( x_1 = \frac{n_i}{n_1+n_2} = 1-x_2 \).

Now when \( K = 0 \), \( Y_1 = 1 \) for all \( x_1 \) as expected, since no complex is formed. When \( K = \infty \), \( Y_1 \to 0 \to Y_2 \) at \( x_1 = x_2 = 0.5 \), since at this particular composition all the molecules are complexed and no uncomplexed molecules of \( i \) or \( j \) remain. Equations (152) and (153) predict negative deviations from Raoult's law for \( K > 0 \) and as a result it has unfortunately
become all too common to ascribe negative deviations from Haoult's law to complexation reaction. It is true that strong negative deviations usually result from complex formation but in systems where complexation is weak, physical effects are by no means negligible and such solutions sometimes show positive deviations from Raoult's law. The same is also true of small negative deviations from Raoult's law observed in mixtures of normal paraffins (size effect). \( G^E \) for such a solution is given by

\[
\frac{G^E}{RT} = x_1 \ln \left( \frac{\delta_i}{\delta_1} \right) + x_2 \ln \left( \frac{\delta_j}{\delta_2} \right)
\]

since \( \delta_i < \delta_1 \) and \( \delta_j < \delta_2 \), \( G^E \) is always negative

\[
H^E = -RT^2 \left[ \frac{\partial}{\partial T} \frac{G^E}{RT} \right] p_x
\]

Case (iii)

\[
i + j \xrightarrow{K} ij
\]

\[
i + 2j \xrightarrow{K} ij_2
\]

Where \( K_1 \) and \( K_2 \) are given by

\[
K_1 = a_{ij} / a_{i}a_{j}
\]

\[
K_2 = a_{ij_2} / a_{i}a_{j}^2
\]

Now \( i, j \) and \( ij_2 \) form ideal solution so that

\[
a_{ij} = \xi_{ij} \text{ etc. and}
\]

\[
K_1 = \xi_{ij} / \xi_i \cdot \xi_j
\]

\[
K_2 = \xi_{ij_2} / \xi_i \cdot \xi_j^2
\]
By material balance
\[
\delta_i + \delta_j + \delta_{ij} + \delta_{i2j} = 1 \quad \ldots (160)
\]
Eliminating \( \delta_{ij} \) and \( \delta_{i2j} \) with (158) and (159), equation (160) gives
\[
1 - \frac{\delta_i}{\delta_i} - \frac{\delta_j}{\delta_j} = K_1 + K_2 \delta_j \quad \ldots (161)
\]
or
\[
\frac{1 - a_i - a_j}{a_i a_j} = K_1 K_2 a_j \quad \ldots (162)
\]
The activities \( a_i \) etc are obtained from vapour liquid equilibrium data. From 'a', \( K_1 \) and \( K_2 \) can be readily determined.

7. Distribution function theories of liquids

These theories of fluids calculate distribution function after assuming a suitable form for the intermolecular potential\(^77,78\). For spherical molecules the structure can be conveniently described by using the radial distribution function \( g(r) \).

In fact, \( g(r) \) describes the probability of finding another molecule at a distance \( r \) from a central reference molecule\(^77,79\). If \( N \) is the number of molecules in a volume \( V \), then the number of molecules, \( n(r) \), at a distance \( r \) from a central molecule is given by
\[
n(r) = \left( \frac{n}{V} \right) g(r) \cdot \pi r^2 \, dr \quad \ldots (163)
\]
The total number of pairs of molecules which lie in the range \( r \) and \( r + dr \) from the central molecule is given by
\[
n'(r) = N^2/2V g(r) \cdot \pi r^2 \, dr \quad \ldots (164)
\]
If the molecules interact through pairwise additive intermolecular potential \( u(r) \), then total intermolecular potential energy is given by\(^79\).
The total energy $U$, including kinetic energy of the molecules is given by

$$U = \frac{3}{2} N k T + \frac{2\pi N^2}{V} \int_0^\infty u(r) g(r) r^2 dr \quad \ldots \quad (165)$$

then the pressure $P$ is given by

$$\frac{PV}{NkT} = 1 - \frac{2N}{3kTV} \int_0^\infty g(r) \frac{du(r)}{dr} r^3 dr \quad \ldots \quad (167)$$

and the configurational partition function $Q_N$ is given by

$$Q_N = \left( \frac{1}{N!} \right) \int \ldots \int \exp(-U/kT) dr_1 \ldots dn_N \quad \ldots \quad (168)$$

All other thermodynamic functions can be easily determined.

The success of this approach depends upon the uncertainties in $g(r)$. Born and Green, Yvon, and Kirkwood and co-workers have done some really commendable work in this direction.

Nevertheless this approach has not developed to a stage where it could be readily used to describe excess thermodynamic functions of binary solutions of polyatomic molecules. Again because of many body problems, serious problems crop up in the case of ternary mixtures.
Graph Theoretical Approach

A graph $G$ is a pair $(V(G), E(G))$ where $V(G)$ is a finite nonempty set of elements called vertices and $E(G)$ is a finite family of (not necessarily distinct) unordered pairs of elements of $V(G)$ called edges (Fig. 1.1). $V(G)$ is called the vertex set of $G$ and the number of vertices of $G$ is called the order of $G$. On the other hand $E(G)$ is called the edge set of $G$.

If $e = AB$ is an edge of $G$, then $e$ is said to join the adjacent vertices $A$ and $B$. Two or more edges joining the same pair of vertices is called the multiple edge. An edge joining a vertex to itself is called a loop. Two graphs $G$ and $H$ are said to be isomorphic if there is one to one correspondence between their vertex sets which preserves the adjacency of vertices. A graph $H$ is a subgraph of $G$ when its vertex set $V(H)$ is contained in $V(G)$ and all the edges of $H$ are edges of $G$. A section graph $G(A)$ of $G$ is defined as the subgraph of $G$ whose vertex set is $A$ and whose edges are all those edges of $G$ which connect two vertices in $A$.

For each vertex $A$ in a graph $G$, the number of edges incident to $A$ is called the valency or order of $A$. Thus in fig. 1.1, the valency of $A = 2$. 

Fig. 1.1
Every skeletal structure can be formulated into a topological matrix to a HMO matrix. For hydrogen suppressed graph of a non-electrolyte if \( \delta_i, \delta_j, \delta_k \) etc denote the degree of \( i, j, k \) etc. vertices of the graph of a molecule, then the connectivity parameters, \( \alpha \), of the first, second, third etc. degrees are defined by:

\[
\begin{align*}
1_\alpha &= \sum_{i<j} (\delta_i \delta_j)^{-\frac{1}{2}} \\
2_\alpha &= \sum_{i<j} \sum_{j<k} (\delta_i \delta_j \delta_k)^{-\frac{1}{2}} \\
3_\alpha &= \sum_{i<j} \sum_{j<k} \sum_{k<l} (\delta_i \delta_j \delta_k \delta_l)^{-\frac{1}{2}}
\end{align*}
\]  

(169) \quad \ldots (170) \quad \ldots (171)

Since \( 1_\alpha \) depends on the degree of its closest vertices taken two at a time, it has been assumed to represent a measure of the oscillations of its bond lengths. Further \( 1_\alpha \) is expected to be independent of concentration and temperature in a binary mixture. Since the bond length remains practically constant with temperature and concentration, the connectivity parameters of the second degree, \( 2_\alpha \), appears at first glance to encode some information about the effect of branching on the structural information of molecule but according to Kier considerable structural information about the effect of branching in a molecule could be obtained by evaluating its \( 3_\alpha \) parameters.
It was actually observed that $^{3/4}$ values for the various isomeric compounds vary in the order $n$-pentane $\prec$ isopentane; $2$-methylpentane $\prec$ $n$-hexane $\prec$ $3$-methylpentane $\prec$ $2,3$-dimethylbutane; $n$-heptane $\prec$ $3$-methylhexane $\prec$ $2,3$-dimethylpentane; $2,2,4$-trimethylpentane $\prec$ $2,5$-dimethylhexane $\prec$ $n$-octane; $n$-nonane $\prec$ $2,3,5$-trimethylhexane $\prec$ $3,3$-dimethylpentane; and $m$-xylene $\prec$ $p$-xylene $\prec$ o-xylene. The molar volume at $298.15$ K of these compounds were found to vary in the following manner, isopentane $\prec$ $n$-pentane; $3$-methylpentane $\prec$ $n$-hexane $\prec$ $2,3$-dimethylbutane $\prec$ $2$-methylpentane; $3$-methylhexane $\prec$ $n$-heptane $\prec$ $2$-methylhexane $\prec$ $2,3$-dimethylpentane; $n$-octane $\prec$ $2,5$-dimethylhexane $\prec$ $2,2,4$-trimethylpentane; $3,3$-dimethylpentane $\prec$ $2,3,5$-trimethylhexane $\prec$ $n$-nonane, and o-xylene $\prec$ m-xylene $\prec$ p-xylene.

The molar volume of a molecule within the same isomeric species were thus found to vary inversely as its $^{3/4}$ parameter. Again $^{1/3}_{^{3/4}}$ value for most of the molecules was found to be less than unity. Since the branching in a molecule of the same isomeric species would allow only a part of its surface area to interact effectively with the corresponding surface areas of other molecules, $^{1/3}_{^{3/4}}$ was also taken to represent a measure of the probability that its surface area interacts effectively with the corresponding surface areas of other molecules.

Further since the $(i+j)$ mixture formation involves the replacement of the $i$-$i$ and $j$-$j$ contacts in pure components by
i-j contacts in the binary mixture, the change in energy when i and j are mixed was assumed to be due to the change in the interaction energies of the close neighbouring molecules. As the i-j contacts in turn depended on the surface areas of i and j that come into effective contact, and as 1/3 $\xi_i$ of a molecule had been taken to represent a measure of probability that its surface area interacts effectively, then following Huggins\textsuperscript{7,93} it was assumed that if $X_{ij}$ denotes the interaction energy per (i-j) contact and if mixing was regarded as perfectly random, then $H_{ij}^E$ according to this approach was expressed\textsuperscript{7,93} as
\begin{equation}
H_{ij}^E(T, x_i) = x_i X_{ij} S_j
\end{equation}
where $x_i$ is the mole fraction of component (i) in the mixture and $S_j$ is the effective contacting surface fractions of j defined by
\begin{equation}
S_j = (1-x_i) V_j / \left[ x_i V_i + (1-x_i) V_j \right]
\end{equation}
Since 1/3 $\xi_i$ of a molecule had been identified with a measure of the probability that its surface area interacts effectively, and as $V_j$ varied inversely with $\xi_j$, then,
\begin{equation}
\frac{V_j}{V_i} = \frac{3 \xi_i}{3 \xi_j}
\end{equation}
therefore
\begin{equation}
S_j = (1-x_i) \left( \frac{3 \xi_i}{3 \xi_j} \right) / \left[ x_i + (1-x_i) \left( \frac{3 \xi_i}{3 \xi_j} \right) \right]
\end{equation}
and hence
In deriving equation (176) it has been assumed that the $i$th and the $j$th components of the $(i+j)$ mixtures have almost identical abilities to form $i$-$j$ contacts. To overcome this limitation it was further assumed if $i$ and $j$ molecules of the binary solution had different $i$-$j$ contacts formation abilities, then $(V_j / V_i)$ should be expressed by

$$ (V_j / V_i) = k_{ij} \left( \frac{3 \sigma_i}{3 \sigma_j} \right) \quad ... (177) $$

where $k_{ij}$ is a constant characteristic of the $(i+j)$ mixture and was taken to represent a measure of the relative abilities of the $i$ and $j$ molecules to form $i$-$j$ contacts. $H^E_{ij}(T, x_i)$ was consequently expressed as

$$ H^E_{ij}(T, x_i) = x_i(1-x_i) \chi_{ij} k_{ij} \left( \frac{3 \sigma_i}{3 \sigma_j} \right) / x_i + k_{ij} x_j \left( \frac{3 \sigma_i}{3 \sigma_j} \right) \quad ... (178) $$

This approach was further applied to evaluate molar excess volume $V^E_{ij}(T, x_i)$ data of binary mixtures of non-electrolytes. $V^E_{ij}$ according to this approach was given by

$$ V^E_{ij}(T, x_i) = \alpha \left[ \sum x_i \frac{1}{3 \sigma_i} - \sum \frac{x_i}{3 \sigma_i} \right] $$
and is based on the assumption (Kier) that the molar volume of a molecule can be expressed as a function of $3\xi$ and $1\xi$ as

$$V = \frac{\kappa}{3\xi} + \beta \cdot 1\xi + \gamma \quad \ldots (179)$$

The ideal molar volume of the ($i+j$) mixture containing $x_i$ mole fractions of $i$ would then be

$$V_{\text{ideal}} = \sum x_i V_i = x_i \kappa_i / 3\xi_i + x_i \beta_i 1\xi_i + x_i \gamma_i$$

$$+ x_j \kappa_j / 3\xi_j + x_j \beta_j 1\xi_j + x_j \gamma_j \quad \ldots (180)$$

since the volume of the mixture would also be expressible by an expression analogous to equation (179) i.e.

$$V_m = \frac{\kappa_m}{3\xi_m} + \frac{\beta_m}{1\xi_m} + \gamma_m \quad \ldots (181)$$

Further $\beta_m(1\xi_m)$ was assumed to be given by

$$\beta_m(1\xi_m) = \sum_i x_i 1\xi_i \beta_i \quad \ldots (182)$$

As connectivity parameter of 3rd degree $(3\xi_i)^{-1}$ of the $i$th component was assumed to represent a measure of the probability that its surface area interacts effectively with other molecules, $(3\xi_m)^{-1}$ of a binary mixture containing $x_i$ and $x_j$ mole fractions of $i$ and $j$ was expressed as

$$(3\xi_m)^{-1} = \left[ \sum x_i (3\xi_i)^{-1} \right] \quad \ldots (183)$$

where summation is over all the components. Again $\gamma_m$ and $\kappa_m$ were expressed as
so that the molar excess volume of a binary mixture (i+j) at $T$ given by

$$V_{ij}^E(T,x_i) = V_m - \left[ \sum_{1}^{2} x_i V_i \right]$$

yielded

$$V_{ij}^E(T,x_i) = \kappa_{ij} \left[ \frac{1}{\sum x_i ^3 \delta_i} - \sum \frac{x_i}{3 \delta_i} \right]$$

Evaluation of $V_{ij}^E(T,x_i)$ and $H_{ij}^E(T,x_i)$ values from equation (188) and (178) required a knowledge of $\kappa_{ij}$, $\chi_{ij}$ and $3^\delta$ values. In principle $\kappa_{ij}$, $\chi_{ij}$ could be evaluated from the $V_{ij}^E(T,x_i)$ and $H_{ij}^E(T,x_i)$ values at any composition. But this approach would fail to differentiate $H_{ij}^E(T,x_i)$ and $V_{ij}^E(T,x_i)$ of say benzene(i) + toluene(j) from cyclohexane (i) + toluene(j) mixtures. Moreover it would also be not conducive to calculate $3^\delta$ parameters of such molecules as alkanols, ethers etc. In order to overcome this problem Singh has recently advocated the use of $\delta^\nu$ (valence $\delta$), which reflects explicitly the valency of the atoms forming the bonds, rather than $\delta$ to evaluate $3^\delta$ index of a molecule to calculate $V_{ij}^E$ and $H_{ij}^E$ data of a binary mixture of non-electrolytes.
According to Singh $\delta^v$ of carbon in any C-H linkage should be evaluated from

$$\delta^v(C) = Z - h \quad \ldots \quad (189)$$

where $Z$ is the maximum valency of C (i.e. 4), and $h$ is the number of hydrogen atoms linked to carbon atoms. Thus $\delta^v$ of C in $-\text{CH}_2$, $-\text{CH}_3$, or $-\text{CH}$ would be

$$\delta^v(C) \text{ in } -\text{CH}_2 = 4 - 2 = 2$$
$$\text{ in } -\text{CH}_3 = 4 - 3 = 1$$
$$\text{ in } -\text{CH} = 4 - 1 = 3$$

and so the $1^\alpha$, $2^\alpha$ and $3^\alpha$ indices of n-pentane, pent-1-ene would be

\[
\begin{align*}
1^\alpha &= 2.414 \\
2^\alpha &= 1.354 \\
3^\alpha &= 0.707
\end{align*}
\]

\[
\begin{align*}
1^\alpha &= 2.024 \\
2^\alpha &= 1.077 \\
3^\alpha &= 0.493
\end{align*}
\]

which clearly differentiated them. For bigger molecules $3^\alpha$ could be calculated as explained above. But the same could not be said of small molecules. These small molecules could not fold themselves and the whole of their
surface area could come into effective (i-j) contact so that for these small molecules $3\xi$ was taken to be unity.

$3\xi$ values evaluated from $\delta$ consideration coupled with $\alpha_{ij}$ and $\chi_{ij}$ values were found to give best representation of the $v_{ij}^E(T, x_i)$ and $H_{ij}^E(T, x_i)$ data of even those binary mixtures of non-electrolytes that are characterized by specific interactions between their components.
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