CHAPTER 1

INTRODUCTION TO SOLUTION THERMODYNAMICS
INTRODUCTION

The thermodynamic properties of binary mixtures of non-electrolytes have provided a valuable tool to understand the nature of molecular interactions that characterize these mixtures. A systematic attempt to study these properties was initiated by Young\textsuperscript{1} who calculated a large amount of experimental data on the thermodynamic properties of simple liquid mixtures. Since then, a number of workers\textsuperscript{2-9} have collected more data and tried to explain them in terms of the properties of pure liquids. The more complicated mixtures were attended to later on after the development of quantum mechanics, and various potential models were proposed. A systematic theoretical study of liquid mixtures has been made and various\textsuperscript{5,6,10} theories of liquids and liquid mixtures have been developed. These theories lead to the calculation of excess thermodynamic functions, and therefore a study of excess thermodynamic functions provides an important tool to check the conclusion of these theories. An understanding of these excess functions is, therefore, necessary before stating the theories.

Excess Thermodynamic Functions:

Excess thermodynamic functions represent a measure of departure from the ideal solution laws, and
are obtained by substituting from the thermodynamic function of mixing (denoted by super-script M) the value corresponding to an ideal solution at the same conditions of temperature, pressure and composition. The excess functions are denoted by a super-script E, i.e., $G^E$ (excess Gibbs's free energy), $S^E$ (excess entropy), $H^E$ (excess enthalpy), $V^E$ (excess volume) and $K^E$ (excess compressibility) etc. are expressed as

$$G^E = G^M - G^{\text{Ideal}} = RT \left( x_1 \ln \gamma_1 + x_2 \ln \gamma_2 \right) \quad (1.1)$$

$$S^E = - \frac{\partial G^E}{\partial T}$$
$$= -RT \left( x_1 \frac{\partial \ln \gamma_1}{\partial T} + x_2 \frac{\partial \ln \gamma_2}{\partial T} \right) - R \left( x_1 \ln \gamma_1 + x_2 \ln \gamma_2 \right) \quad (1.2)$$

$$H^E = - T^2 \frac{\partial (G^E/T)}{\partial T}$$
$$= -RT^2 \left( x_1 \frac{\partial \ln \gamma_1}{\partial T} + x_2 \frac{\partial \ln \gamma_2}{\partial T} \right) \quad (1.3)$$

$$V^E = \frac{\partial G^E}{\partial P} = RT \left( x_1 \frac{\partial \ln \gamma_1}{\partial P} + x_2 \frac{\partial \ln \gamma_2}{\partial P} \right) \quad (1.4)$$

$$U^E = H^E - PV^E$$
$$= -RT \left[ T \left( x_1 \frac{\partial \ln \gamma_1}{\partial T} + x_2 \frac{\partial \ln \gamma_2}{\partial T} \right) + P \left( x_1 \frac{\partial \ln \gamma_1}{\partial P} + x_2 \frac{\partial \ln \gamma_2}{\partial P} \right) \right] \quad (1.5)$$

$$C_P^E = \frac{\partial H^E}{\partial T} = - 2RT \left( x_1 \frac{\partial \ln \gamma_1}{\partial T} + x_2 \frac{\partial \ln \gamma_2}{\partial T} \right)$$
$$- RT^2 \left( x_1 \frac{\partial^2 \ln \gamma_1}{\partial T^2} + x_2 \frac{\partial^2 \ln \gamma_2}{\partial T^2} \right)$$
$$\ldots \quad (1.6)$$

$$K^E = (-1/V) \frac{\partial V^E}{\partial P}$$
$$= -RT/V \left( x_1 \frac{\partial^2 \ln \gamma_1}{\partial P^2} + x_2 \frac{\partial^2 \ln \gamma_2}{\partial P^2} \right) \quad (1.7)$$

where $x_1$, $x_2$ and $\gamma_1$, $\gamma_2$ represent the mole fractions and activity coefficients of components 1 and 2 respectively.
R is the universal gas constant and T is the absolute temperature. These functions are very helpful in understanding the deviations from ideality, as these are related to the nature of interactions (inter molecular) involved in a system. A brief review of the intermolecular forces is given and then the theories of non-electrolytic solutions are discussed.

**Intermolecular Forces:**

Intermolecular forces are defined as the forces existing between different molecules. Hirschfelder et al. have studied the various types of interactions between ions, atoms and molecules and reported them to be of two main types:

1) Short range forces.
2) Long range forces.

Short range forces are usually repulsive in character and are often highly directional. These are also known as valence or chemical forces and Longuet Huggins has attributed these forces (repulsive forces) to arise essentially due to the exclusion principle. Further, the energy of repulsion, $U_{\text{rep.}}$, is supposed to vary inversely as $r^n$, where $r$ is the intermolecular separation and "$n"$ is an index. However, these forces are not always repulsive, since this would render a chemical reaction impossible. Further even among "physical interactions," two types deserve special mention as being attractive rather than repulsive. One is the hydrogen bond...
and the other is the Mulliken force which contributes to the energy of the charge transfer complexes. According to perturbation theory, the binding energy of a charge transfer complex arises partly from a virtual transition to an excited state in which an electron has been transferred from donor to acceptor. An intense absorption in the region where neither partner absorbs on its own, indicates the existence of such a charge transfer complex.

The various contributions to the long range forces may vary inversely as powers of intermolecular separation and include:

i) The electrostatic contribution

ii) The inductive contribution and

iii) The dispersion contribution.

The electrostatic contribution to the intermolecular potential energy results from the interaction of the various components in the molecules, such as charges, dipole moments, quadrupole moments etc.

The induction contribution to the potential energy arises when a charged particle interacts with a neutral molecule by including a dipole moment in the neutral molecule.

The dispersion contribution to the potential energy arises when the non-polar molecules having long range forces of attraction between them interact. At
any instant the electrons in the molecule "a" are in some configuration that they induce an instantaneous dipole moment in the molecule "b". The induced dipole in "b" then interacts with the instantaneous dipole in "a" to produce an energy of attraction between the two molecules regardless of the orientation of the dipole. London\textsuperscript{13} developed a quantum mechanical theory and expressed this interaction between "a" and "b" by

\[
U_{ab} \text{(dispersion)} = -\frac{3h}{4\pi} \left[ \frac{\hbar \nu_a \hbar \nu_b}{(\hbar \nu_a + \hbar \nu_b)} \right] \frac{\alpha_a \alpha_b}{r^6} \tag{1.8}
\]

where $\hbar \nu_a$ and $\hbar \nu_b$ are characteristic energies of the two molecules, approximately equal to their ionization potentials and $\alpha_a$ and $\alpha_b$ are corresponding polarizabilities, $r$ is the distance between the centres of the two molecules.

The perturbation of electronic motion by another molecule is related to its perturbation by light of varying frequencies as expressed by the formula for dispersion of light i.e. the variation of refractive index "n" with frequency

\[
n - 1 = \frac{C}{(\nu_0^2 - \nu^2)} \tag{1.9}
\]

where $C$ is the characteristic constant. It is this relationship which led London to designate this type of molecular interaction as "Dispersion Effect."
According to Howlinson\textsuperscript{9} dispersion forces are important in three ways:

i) They operate between all neighbouring atoms or molecules and so can account for the existence of attractive forces between spherically symmetrical systems such as inert gas molecules where the forces are beyond the scope of classical electrostatics.

ii) They are shown to be additive to a good approximation and so permit the separation of intermolecular energy of an assembly into the sum of pair potentials.

iii) They are usually the negative terms in the potential.

Again, little is known of the dependence of these forces on the orientation of non-spherical molecules. The only reliable calculations are for hydrogen molecule\textsuperscript{14-15}.

The various types of intermolecular forces with the range and intermolecular energy are given below:

<table>
<thead>
<tr>
<th>Name</th>
<th>Mechanism</th>
<th>Order of magnitude of interaction energy Kcal/mol.</th>
<th>Range of action Å \textsuperscript{°}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Homopolar</td>
<td>Electron sharing</td>
<td>60</td>
<td>1-2</td>
</tr>
</tbody>
</table>
Hydrogen bond: Action of incompletely screened hydrogen atom attached to one atom or other polarizable atoms.

Ionic: Coulomb attraction between ions or charged atoms of different signs.

Vander Waals: Mutual induction of moments from electrically polar molecules.

Diagrammatically the difference in various types of interactions can be expressed with the help of potential energy diagrams as shown in figure 1-I:

![Potential Energy Diagrams](image)

(a) Homopolar bond  
(b) Hydrogen bond  
(c) Vander Waals interactions

Fig. 1-I

Stronger interaction means a very deep and narrow trough.

Specific interactions also exist among molecules and arise due to:

1. Polar nature of components,
2. Hydrogen bonding,
3. and the differences in positive and negative character of the components which lead to the formation of associated complexes.
The information about the inter-molecular forces can be had from

i) the thermodynamic properties of gases at low densities;

ii) the transport processes in dilute gases;

iii) the thermodynamic properties of crystals.

However, accurate results are not expected from the theory of the above forces, but a detailed information can be derived from semi-emperical procedures which involve-

1) an intermolecular force law with one or more adjustable parameters on the grounds of physical plausibility and mathematical convenience;

2) a macroscopic property which can be accurately measured and accurately calculated from the force law assumed.

3) measurement over a wide range of experimental conditions to fix the values of the adjustable parameters in the force law.

Various intermolecular potential models have been suggested to fit the experimental data, some of which are-

(a) the hard sphere potential model
(b) Lennard Jones model
(c) Stock-Mayer model
(d) Square well model
(e) Buckingham model
(f) Sutherland model
(g) Guggenheim-McClashan potential model.

A knowledge of the 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 on the whole in a less systematic way. The reason is clear as there is no way of inverting the equation of statistical mechanics to give the potential as explicit functions of the physical properties. All attempts to follow the second method were bound to start by setting up a potential model with two or more adjustable parameters, and the physical properties in terms of these parameters were calculated.

After a general discussion of the excess functions and the intermolecular forces, it is feasible to give an account of the theories of liquids and liquid mixtures, which is given below:

A number of theories for liquids and their mixtures exist but the following appear more promising:

1. The Flory's Theory.
2. Sanchez and Lacombe's Theory.
Flory's Theory:

This theory is based on the assumption that a molecule is made up of segments (isomeric portions). The effective number of the segments is 'r' and each segment has 's' intermolecular contact sites. The volume per mole of segment is denoted by 'v' and the corresponding hard core or characteristic volume by 'v^*'. The molar volume of these are indicated by:

\[ V = rv \quad \text{(1.10)} \]
\[ V^* = rv^* \quad \text{(1.11)} \]

respectively. The reduced volume of a mole of a segment is

\[ V = v/v^* = V/V^* \quad \text{(1.12)} \]

and is calculated from the coefficient of thermal expansion \( \alpha \) by the expression

\[ \bar{V}^{\frac{1}{3}} = \left[ 1 + \frac{\alpha T/3}{1 + \alpha T} \right] \quad \text{(1.13)} \]

The reduced volume (\( \bar{V} \)) and the reduced temperature (\( \bar{T} \)) are related at zero pressure as

\[ \bar{T} = \left( \bar{V}^{\frac{1}{3}} - 1 \right)/V^{4/3} \quad \text{(1.14)} \]

This is the central equation of Flory's Theory. The characteristic temperature \( T^* \) and pressure \( P^* \) are obtained from the relations

\[ T^* = T/\bar{T} \quad \text{(1.15)} \]
\[ P^* = \sqrt{TV^2} \quad \text{(1.16)} \]
where $V = \gamma_p$ is the thermal pressure coefficient and $\beta$ is the isothermal compressibility. It has been shown that the reduced temperature of binary mixture having two types of molecules indicated by sub-scripts 1 and 2 at mole fraction $x_1$ is given by

$$T = \left( \phi_1 P_{11}^* + \phi_2 P_{22}^* \right) / \left( \phi_1 P_{11}^* - \phi_2 P_{22}^* - \phi_1 \theta_{2} \chi_{12} \right)$$ (1.17)

where the segment fractions $\phi_1$ and $\phi_2$ are defined by

$$\phi_2 = 1 - \phi_1 = N_2 V_2^*/(N_1 V_1^* + N_2 V_2^*) = x_2 / (x_2 + x_1 r_1 / r_2)$$ (1.18)

and site fraction $\theta_2$ by

$$\theta_2 = \phi_2 / (\phi_2 + \phi_1 s_1 / s_2)$$ (1.19)

The molar excess enthalpy, excess volume and residual free energy of mixture (Flory has employed the term residual to indicate the normal thermodynamic function of mixing exclusive of the combinatorial term which differs from that used by Rowlinson), are

$$H^E = x_1 P_{11}^* (\bar{V}_1^{1-1} - \bar{V}_1^{1-1}) + x_2 P_{22}^* (\bar{V}_2^{1-1} - \bar{V}_2^{1-1}) + x_1 V_1^* \theta_2 \chi_{12} \bar{V}_2^{1-1}$$ (1.20)

$$V^E = (x_1 V_1^* + x_2 V_2^*) (\bar{V} - \phi_1 \bar{V}_1 - \phi_2 \bar{V}_2)$$ (1.21)

$$G^E = 3T \left[ x_1 (P_{11}^* / T_{11}) \ln (\bar{V}_1^{1-1} / (\bar{V}_1^{1-1}) + x_2 (P_{22}^* / T_{22}) \ln (\bar{V}_2^{1-1} / (\bar{V}_2^{1-1})) \right] + H^E$$ (1.22)

$\chi_{12}$ is a constant characterizing the difference in the energy of interaction between sites of neighbouring molecules of species 1 and 2 from the average of the interaction
in pure component liquids.

The geometric parameters 'r' and 's' enter the equations for the excess properties of mixtures only as ratios \( r_1/r_2 \) and \( s_1/s_2 \). Since the same hard core volume is adopted for segments of both species, it follows:

\[
\frac{r_1}{r_2} = \frac{V_1^*}{V_2^*}
\]

(A.23)

Abe and Flory assumed that the number of contact sites on a number of molecules are proportional to the surface areas of spheres having the same core volumes and deduced that

\[
\frac{v_1^*/v_2^*}{s_1/s_2} = \frac{v_2^*/v_1^*}{s_1/s_2}
\]

(A.24)

The evaluation of the excess thermodynamic function, \( H^E \), \( V^E \), and \( G^E \) for binary mixtures requires a knowledge of interaction energy \( \chi_{12} \), in addition to the data for the pure component liquids. This quantity was treated by Abe and Flory as an adjustable parameter and its value was chosen to fit the equation (1.20) for an equimolar mixture by substituting the \( H^E \) value for the same in the equation.

Sanchez and Lacombe's Theory of Fluids and Fluid Mixtures:

Sanchez and Lacombe have proposed a molecular theory of classical fluids based on a well defined statistical mechanical model and have further extended it to fluid mixtures. All fluids according to this theory are regarded as Ising or lattice fluids and it is
further assumed that all the lattice sites are not occupied by the 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 $N_0$ vacant lattice sites (holes) were then obtained as suggested by Guggenheim. Consequently, the total number of sites of a binary mixture of $N$ $r$-mers and the $N_0$ empty sites is given by

$$N_r = N_0 + rN$$  \hspace{1cm} (1.25)$$

Sanchez and Lacombe assumed that the lattice is characterized by a coordination number $Z$, so that each interior mer of a linear chain is surrounded by $Z-2$ nearest non-bonded neighbours; mers at the chain ends have $Z-1$ nearest non-bonded and one bonded neighbour. Thus, each $r$-mer is surrounded by $qZ$ nearest non-bonded neighbours where

$$qZ = (r-2)(Z-2) + 2(Z-1) = r(Z-2) + 2$$  \hspace{1cm} (1.26)$$

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

$$N_q = N_0 + qN$$  \hspace{1cm} (1.27)$$

The numbers $N_r$, $N_q$, $N_0$ and $N$ are related by

$$(Z/2)N_q = (Z/2 - 1)N_r + N + N_0$$  \hspace{1cm} (1.28)$$

An $r$-mer is characterized by a symmetry number $\sigma$. For example, for a linear $r$-mer it is equal to two, if the chain ends are distinguishable. The exact value of $\sigma$ is found to be of inconsequential importance.
4. An r-mer is also characterized by a "flexibility parameter" $\delta$. It is a measure of the r-mer's internal degrees of freedom. For molecules occupying a single site i.e. for $r = 1$, $\delta = 1$; for $r = 2$, $\delta = Z$, for $r = 3$ there are three distinct cases:

i) If the trimer is linear and rigid $\delta = Z$.

ii) If the trimer is non-linear and rigid $\delta = ZZ'$, where $Z'$ is the number of allowable sites for the third mer after the first two mers have been placed ($Z' \leq Z-1$).

iii) If the trimer is flexible then $\delta = Z (Z-1)$. In general the maximum value for $\delta$ for a r-mer is $\delta_{\text{max}} = Z (Z-1)^{r-2}$

$$\frac{\delta_{\text{max}} = Z (Z-1)^{r-2}}{(1.29)}$$

The number of configurations available to a system of $N$ r-mer and $N_o$ empty sites according to Guggenheim, is after the assumption that when the two sites are not occupied by the same molecules the probability of being occupied or vacant are independent for the two sites, are

$$\Omega = \left(\frac{\delta}{\delta_{\text{max}}}\right)^N \frac{N_r!}{N_o!N^r!} \left(\frac{N_q!}{N^r!}\right)^{Z/2}$$

(1.30a)

Using Sterlign's approximation and equation (1.28) it was shown that (1.30a) takes the following limiting form for large $Z$.20-22
and where the empty site fraction \( f_0 \) and the fraction of occupied sites \( f \) are given by

\[
f_0 = \frac{N_0}{N_r}; \quad f = \frac{N}{N_r}
\]

Equation (1.30b) is the base of all calculations and was assumed to apply to all types of molecular geometries. In addition to the above treatment, two assumptions were made:

1. that the flexibility parameter is independent of temperature and pressure
2. and that the close packed volume \( v^* \) of a molecule is independent of temperature and pressure. The close packed volume of a mer is \( v^* \); it is also the volume of a lattice site. The close packed volume of the \( N \) r-mers (no holes) is then

\[
V^* = N(v^*)
\]

If \( \rho^* \) is the close packed mass density, then the close packed molecular volume is given by

\[
r v^* = \frac{M}{\rho}
\]

where \( M \) is the molecular weight. As a first approximation \( \rho^* \) is taken equal to the crystal density and equation (1.34) provides a useful means of estimating the close packed molecular volume \( v^* \).
The volume associated with an empty lattice with (a hole) is also equal to $v^*$. The volume of the system is therefore

$$ V = (N_v + vN)v^* = N_r v^* = v^* f $$ \hspace{1cm} (1.35) $$

In general, the lattice energy (attractive) can be written as

$$ E = - (\frac{Z}{2}) N_r \sum_i \sum_j P(i,j) \xi_{ij} $$ \hspace{1cm} (1.36) 

where $\xi_{ij}$ is the pair interaction energy between components $i$ and $j$ and $P(i,j)$ is the pair (joint) probability of an $(i,j)$ pair in the system. By making the same approximations as in the evaluation of $\Omega$, the pair probability of non-bonded mer-mer interaction is

$$ P(\text{mer-mer}) = \frac{(qN)^2}{N_q N_r} \hspace{1cm} (1.37a) $$

or in the large $Z$ limit becomes

$$ \lim_{Z \to \infty} P(\text{mer-mer}) = (\frac{rN}{N_r})^2 = f^2 $$ \hspace{1cm} (1.37b) 

Thus from equation (1.35) and equation (1.37a) the lattice potential energy is

$$ E = - N_r (Z \xi/2) f^2 $$ \hspace{1cm} (1.38a) 

or by using equation (1.33) and (1.35)

$$ \frac{E}{rN} = - \xi \frac{v^*}{V} = - \xi f $$ \hspace{1cm} (1.38b) 

where $\xi$ is the non-bonded, mer-mer interaction energy and

$$ \xi^* = \frac{Z \xi}{2} $$ \hspace{1cm} (1.39) 

is the total interaction energy per mer. $r\xi^*$ is the
characteristic interaction energy per molecule in the absence of holes and $\epsilon^*$ the energy required to create a lattice vacancy (hole). Since $E$ and $\Omega$ are functions of a single parameter the partition function is expressed by

$$Z(T,P) = \sum_{N=0}^{\infty} \frac{\Omega^N}{N!} \exp \left[ -\beta(E+PV) \right] \quad (1.40)$$

The Gibb's free energy for the system is given by

$$G = E + PV - RT \ln \Omega \quad (1.41a)$$

Using equation (1.30b), (1.35) and (1.38), equation (1.41) becomes

$$G/N_T^* \varepsilon^* = -\varepsilon + \tilde{P}\tilde{V} + \tilde{T} \left[ (\nu-1)\ln(1-\tilde{\varepsilon}) + \frac{1}{T} \ln \frac{\tilde{\varepsilon}}{\varepsilon} \right] \quad (1.41b)$$

where $\tilde{T}$, $\tilde{P}$, $\tilde{V}$ and $\tilde{\varepsilon}$ the reduced temperature, pressure, volume and density

$$\tilde{T} = \frac{T}{T^*}, \quad \tilde{T} = \frac{\epsilon}{kT} \quad (1.42)$$

$$\tilde{P} = \frac{P}{P^*}, \quad \tilde{P}^* = \frac{\epsilon}{\nu^*} \quad (1.43)$$

$$\tilde{V} = \frac{V}{V^*}, \quad \tilde{V}^* = \frac{N}{N^*(r^*)} \quad (1.44)$$

The minimum values of the free energy is found in the usual way

$$\frac{\partial G}{\partial \tilde{V}} \bigg/ \frac{\partial \tilde{V}}{\partial \tilde{T}, \tilde{P}} = 0 \quad (1.45a)$$

which yields

$$\tilde{\varepsilon}^2 + \tilde{P} + \tilde{T} \left[ \ln(1-\tilde{\varepsilon}) + (1-1/r)\tilde{\varepsilon} \right] = 0 \quad (1.45b)$$

Equation (1.45b) is the equation of state for the system.

The extension of the Sanchez and Lacombe's fluid theory to fluid mixtures is very similar to the theory of Flory and Huggins, the important difference being the allowance made for empty sites on the lattice used to
enumerate the number of configurations available to a system of $N_1 r_1$-mers $\ldots$ $N_k r_k$-mers and $N_0$ empty sites (holes) $\Omega$ is approximately given by

$$\Omega = \left(\frac{\delta_1}{\sigma_1}\right)^{N_1} \left(\frac{\delta_2}{\sigma_2}\right)^{N_2} \ldots \left(\frac{\delta_k}{\sigma_k}\right)^{N_k}$$

$$\times \frac{N_r! \times \left(\frac{N_0!}{N_r!}\right)^{2/2}}{N_0! N_1! N_2! \ldots N_k!}$$

(1.46)

where

$$N_r = N_0 + \sum r_i N_i$$

(1.47)

$$N_q = N_0 + \sum q_i N_i$$

(1.48)

$$q_i z = r_i(z-2) + 2$$

(1.49)

$$(z/2)N_q = (z/2 - 1)N_r + N_0 + \sum N_i$$

(1.50)

A treatment similar to that of simple fluids leads to the equation of Gibb's free energy analogous to (1.41)

$$\tilde{G} = -\tilde{e} + \tilde{P} \tilde{v} + \tilde{T} (\tilde{v} - 1) \ln (1-\tilde{e}) + 1/r \ln \tilde{e}$$

$$+ \sum \frac{\phi_i}{r_i} \ln \left(\frac{\phi_i}{\omega_i}\right)$$

(1.51)

and the equation of state for mixture is found to be

$$\tilde{e}^2 + \tilde{P} + \tilde{T} \left[ \ln (1-\tilde{e}) + (1 - 1/r) \right] = 0$$

(1.52)

which is formally identical with the equation of state of pure fluids. The excess functions for the mixtures are expressed by

$$\frac{\Delta V_m}{N} = r v^* \left[ \tilde{v} - \sum \phi_i v_i \right]$$

(1.53)
\[ \frac{\Delta H_m}{N} = \text{rkt} \left[ \bar{\chi} \sum_i \sum_j \phi_i \phi_j \chi_{ij} + \sum_i (\bar{e}_i \phi_i^* - \bar{e}_i^* \phi_i) \right] \\
\quad + P(\Delta V_m/N) \quad (1.54) \]

\[ \frac{\Delta S_m}{N} = -k \left\{ \sum_i x_i \ln \phi_i + \bar{r} (v_i - 1) \ln (1 - \bar{r}) + \ln \bar{r} \\
\quad - \sum_i x_i \left[ r_i^0 (v_i - 1) \ln (1 - r_i) + \ln r_i \right] \right\} \quad (1.55) \]

Klura et al. have tested the conclusion of this theory by comparing the theoretical results with the corresponding experimental data with reasonable success. Thus one of the plus points of this theory is its predictive potential. It is also capable of defining thermodynamic properties of ternary and higher order mixtures in terms of the pure fluid parameters and the binary interaction energies.

**Statistical Mechanics of Associated Mixtures**

**The Ideal Associated Model:**

The thermodynamics of associated solutions consisting of pure phases A and B present in the form of monomers only, and their associated complexes, has been successfully explained by Sarolea-Mathot. According to this theory, a solution of A and B and the complex AB, behaves as an ideal solution so that the difference in sizes can be neglected and the heat of mixing can be supposed to be equal to heat of reaction. Partogi and Girdhar have also developed a statistical mechanical treatment of associated mixtures where the individual components do not associate but form one or more associated complexes. This is
primarily a lattice model and takes into account the influence of orientation of the molecules. Its greatest weakness is the assumption that molecules occupy rigid lattice points and that the only degree of freedom that molecule can have is the vibrational motion about a fixed lattice point as the mean position. This lead them to formulate the theory on the basis of cell model. They abandoned the idea of lattice but assumed that the molecules are not rigidly attached to the sites but have the freedom to move in the cell volume of each molecule. This theory has been applied to the mixtures of acetone + chloroform and dioxane + chloroform, and has given a correct order of magnitude for the various excess functions although the quantitative agreement is not very impressive. McGlashan and Rastogi while treating the thermodynamics of associated mixtures based on ideal associated model assumed that in a mixture of A and B there are four species A, AB, AB\textsubscript{2} and B in mutual equilibrium according to the equation

\[ \lambda_{AB} = \lambda_A \lambda_B \quad AB_2 = \lambda_A \lambda_B^2 \] (1.56)

They denoted stoichiometric molefraction of B by \( x \) and the actual molefractions of the species A, AB, AB\textsubscript{2} and B by \( \xi_A, \xi_{AB}, \xi_{AB_2} \) and \( \xi_B \) respectively. These quantities were then inter-related by the formulae

\[ x = \frac{\xi_{AB} + 2\xi_{AB_2} + \xi_B}{\xi_A + 2\xi_{AB} + 3\xi_{AB_2} + \xi_B} \] (1.57)

where \( \xi_A + \xi_{AB} + \xi_{AB_2} + \xi_B = 1 \) (1.58)
They further assumed that the four species form an ideal mixture so that

\[ \lambda_A = \xi_A \lambda_A \quad (1.59a) \]
\[ \lambda_{AB} = \xi_{AB} \quad (1.59b) \]
\[ \lambda_{AB_2} = \xi_{AB_2} \quad (1.59c) \]
\[ \lambda_B = \xi_B \lambda_B \quad (1.59d) \]

where \( \lambda_A^0, \lambda_B^0 \) are the absolute activity of pure A and B, substituting the values of various \( \lambda \) in equation (1.56) from equation (1.59) we have

\[ \xi_{AB} = K_1 \xi_A \xi_B \quad (1.60a) \]
\[ \xi_{AB_2}^2 = K_2 \xi_A \xi_B^2 \quad (1.60b) \]

where \( K_1 \) and \( K_2 \) are equilibrium constants for the chemical reactions

i) \( A + B \rightleftharpoons AB \)

ii) \( A + 2B \rightleftharpoons AB_2 \)

Using the equation (1.58) and equations (1.60) in (1.59a) and (1.59d) and writing \( \xi_B = \xi \) they obtained

\[ a_A = \lambda_A / \lambda_A = \xi_A = (1 - \xi)/(1 + K_1 \xi + K_2 \xi^2) \quad (1.61a) \]
\[ a_B = \lambda_B / \lambda_B = \xi_B = \xi \quad (1.61b) \]

Further on substituting values from equation (1.58 and 1.60) in (1.57) they obtained

\[ x = \frac{(1 + K_1 \xi + K_2 \xi^2 (2 - \xi))}{1 + K_1 \xi (2 - \xi) + K \xi^2 (3 - 2 \xi)} \quad (1.62) \]
equations (1.61a) and (1.61b) can be expressed in the alternative form

$$1 - \frac{a_A - a_B}{a_A a_B} = K_1 + K_2 a_B$$

(1.63)

The above equations can be used as a sensitive test of the theory by plotting experimental values of the left hand side of the equation (1.63) against the corresponding values of $a_B$. If the theory is valid, the points should lie on a straight line and, in this case, the equilibrium constants $K_1$ and $K_2$ can be determined from its intercept and slope. This approach, when applied to dioxane (A) + chloroform (B) mixture, gave the equilibrium constants

$$K_1 = 1.11, \quad K_2 = 1.24$$

(1.64)

The study was further extended to find out the heat of formations of $AB$ and $AB_2$ molecular species by using the $G^E$ and $H^E$ data. The excess Gibb's function, $G^E$, of mixing per mole of mixture is given for any mixture $\Lambda$ and $B$ whether or not any association occurs by the formula

$$G^E/RT = (1-x)\ln(a_A/1-x) + x\ln(a_B/x)$$

(1.65)

which in view of (1.61a) and (1.61b) reduces to

$$G^E/RT = (1-x)\ln \left[ \frac{1 - \xi}{(1+K_1 \xi + K_2 \xi^2)(1-x)} \right] + x\ln(\xi/\xi^x)$$

(1.66)
where $\xi$ is again determined by a given $x$ by (1.57). The excess heat of mixing $A\Delta H$ is related to $G^E$ by the formula

$$H^E = -RT^2d(G^E/RT)dt$$

which can be expressed as

$$H^E = \sqrt{(1-x)\xi \over 1+K_1^2 + K_2^2} (K_1h_1 + K_2h_2)$$

where $h_1$ and $h_2$ defined by the relations

$$h_1 = RT^2d\ln K_1/dT, \quad h_2 = RT^2d\ln K_2/dT$$

are the heats of the chemical reactions

$$A + B \rightarrow AB$$
$$A + 2B \rightarrow AB_2$$

This approach gave

$$h_1 = -8.4 \text{ KJ mol}^{-1}, \quad h_2 = -15.1 \text{ KJ mol}^{-1}$$

whereas 8.4 KJ is evolved during the formation of the first hydrogen bond, slightly less, 6.7 KJ is evolved during the formation of the second hydrogen bond. This is what one would expect if some of the effects of the approach of the hydrogen of the first chloroform to one of the oxygens of the dioxane is transmitted as far as the other oxygen.

If the dioxane was replaced by a diether or dioxane in which the two oxygens were separated by a longer chain then $h_2$ should be more nearly equal to $2h_1$.

Such a study requires that both $G^E$ and $H^E$ of the mixture must be known. In an interesting alternate
approach, based on ideal associated model. Hepler and Fenby have shown that it is possible to evaluate both $K_1$ and $\Delta H^0_1$ for a mixture $(A+B)$ in which $A$, $B$ and $AB$ molecular species exist from measurement of $H^E$ at one temperature only. They have applied their approach to dimethyl sulfoxide + chloroform mixtures with remarkable success. These workers have, however, further extended this approach to include solutions containing $A$, $B$ and $AB$ and $AB_2$ molecular species in solution.

Alexander investigated in detail the theory of ideal associated solution of the type $A + B + AB_2$ in a solution of the molecular species $A$ and $B$. The solution contains the complex $AB_2$ resulting from the association reaction $A + 2B \rightarrow AB_2$. The molefractions actually present in the mixture of $A$, $B$ and $AB_2$ ($x_A$, $x_B$ and $x_{AB_2}$) are related to the stoichiometric molefraction $x$ of the normal components $A$ in the following way

\[
x_A = x(1 + 2\xi) - \xi \quad x_B = 1-x(1 + 2\xi)
\]

(1.71)

The equilibrium constant of the association reaction is given by

\[
K = \frac{x_{AB_2}}{x_A x_B^2}
\]

(1.72)

This, in view of (1.71) is reduced to

\[
4x^2(1-2x)\xi^3 + 4x(-1 + 3x - 3x^2)\xi^2 + \frac{1}{Kx}(1-x)(1-3x + 6x^2)\xi - x(1-x)^2 = 0
\]

(1.73)

The third order equation (1.73) for $\xi$ is solved treating $K$ as parameter $\xi = F(K/x)$. Equation (1.73) is reduced to
the equation of the second order which has the solution

$$\xi = \frac{1}{2} + \frac{1}{K} (1 - \sqrt{1+K})$$  \hspace{1cm} (1.74)

The differential of $\xi$ with respect to $x$ is

$$\frac{\partial \xi}{\partial x} = \frac{2(3x-1)[4x^3 + 2(3x-1)x^2 + (3x-2)x] + 1 - 4x + 3x^2}{12x^2(1-2x)x^2 + 8x(-1+3x-3x^2)x + 1/K + (1-x)(1-3x+6x^2)}$$

... (1.75)

In the limit

$$\lim_{x \to 0} \frac{\partial \xi}{\partial x} = \lim_{x \to 0} (\frac{\xi}{x}) = \frac{K}{1+K}$$

$$\xi \to 0 \quad \xi \to 0$$

$$\lim_{x \to 1} \frac{\partial \xi}{\partial x} = 0$$

$$\xi \to 1$$

Denoting \(\frac{\partial \xi}{\partial x}\) to zero, one obtains that the maximum concentration of $AB_2$ appears for $x = 1/3$, i.e., for any $K$, the value of $\xi_{\text{max}}$ is given by the solution of the equation

$$\xi_{\text{max}}^3 - 3\xi_{\text{max}}^2 + 3(9/K + 1)\xi_{\text{max}} - 1 = 0$$  \hspace{1cm} (1.77)

and of equation (1.78)

$$\xi_{\text{max}} = 1 + 3/2 \left[ - \frac{(1+D)^{1/2}}{K} + \left( - \frac{1-D}{K} \right)^{1/2} \right]$$  \hspace{1cm} (1.78)

where \(D = (\frac{1+K}{K})^{1/2}\)  \hspace{1cm} (1.79)

As expected $\xi_{\text{max}}$ tends to unity for $K \to \infty$. From the fact that the chemical potentials of the nominal components in an associated mixture are equal to the chemical potentials of the monomer molecules, the excess Gibb's free energy
of mixing can be written in the form

$$G^E = RT \left[ x \ln \left( \frac{x}{x_A} \right) + (1-x) \ln \left( \frac{x_B}{1-x} \right) \right]$$  \hspace{1cm} (1.80)

This is a particular case of Prigogine's equation.\textsuperscript{31} Using equation (1.81), the activity coefficients of the normal components A and B are given by

$$\gamma_1 = \frac{x_A}{x} \hspace{1cm} (1.81)$$
$$\gamma_2 = \frac{x_A}{1-x}$$

$$\gamma_1 = \left( 1 + 2 \frac{\gamma_A - \gamma_B}{x} \right) \gamma$$
$$\gamma_2 = \left( 1 - 2 \frac{\gamma_A - \gamma_B}{1-x} \right) \gamma$$ \hspace{1cm} (1.82)

Since \( x_B \leq 1-x \), it follows that \( \gamma_2 \) is lower than unity. This is also true for \( \gamma_1 \) when \( x < 1/2 \). In the limit

$$\lim_{x \to 0} \gamma_1 = \frac{1}{(K+1)} = \gamma_1 \lim_{x \to 1} = 1$$
$$\lim_{x \to 0} \gamma_2 = 1 \lim_{x \to 1} \gamma_2 = 1$$ \hspace{1cm} (1.83)

Calculating the derivative of \( G^E \) with respect to \( x \) (for constant \( T, P \)) and using the Gibb's Duhem relationship, one obtains

$$\frac{\partial G^E}{\partial x} = RT \ln \left[ \frac{\gamma_1}{\gamma_2} \right]$$ \hspace{1cm} (1.84)

$$\lim_{x \to 0} \left( \frac{\partial G^E}{\partial x} \right) = RT \ln \gamma_1$$ \hspace{1cm} (1.85)

\( \left( \frac{\partial G^E}{\partial x} \right) \) equals zero when \( \gamma_1 = \gamma_2 \), i.e., for \( x = 1/3 \), the excess free energy of mixing \( G^E \) (which is always
negative) has a minimum value. The excess enthalpy of mixing for the associated mixture of the type \( A + B + AB_2 \) is given by

\[
H^E = \Delta H^0 \frac{\xi}{1 + 2\xi}
\]

(1.86)

where the standard reaction enthalpy

\[
\Delta H^0 = h_{AB_2} - h_A - 2h_{B_2}
\]

(1.87)

contains the molar enthalpies of the molecular species \( AB_2 \), \( A \) and \( B \) respectively since

\[
\frac{\partial H^E}{\partial x} = \Delta H^0 \left( \frac{\partial \xi}{\partial x} \right)
\]

(1.88)

It follows from equation (1.75) that the extreme of \( H^E \) appears for \( x = 1/3 \). The enthalpy of mixing \( H^E \) always has the same sign as \( \Delta H^0 \), because usually \( \Delta H^0 < 0 \), so \( H^E \) is also negative. The enthalpy of mixing at infinite dilution is

\[
h_1^E = \lim_{x \to 0} \left( \frac{\partial H^E}{\partial x} \right) = (\Delta H^0 K)/(1+K)
\]

(1.89)

\[
h_1^E = -RT^2 \left( \frac{\partial \ln V}{\partial T} \right)
\]

when \( \xi \to 1 \), \( (K \to \infty) \), then \( H^E \to 0 \) i.e. as expected the heat of mixing of undissociated \( AB_2 \) is zero. Using equations (1.80), (1.82) and (1.86) the excess entropy of mixing is

\[
S^E = \frac{\Delta H^0 \xi}{T(1+2\xi)} - R \left[ x \ln (1+2\xi) - \xi/x \right] + (1-x) \ln (1- \frac{2x\xi}{1-x})
\]

(1.90)

and taking into account that \( \Delta G^0 = -RT \ln K \), the standard entropy of the association reaction can be calculated from

\[
\Delta S^0 = R \left[ \ln K + T \left( \frac{\partial \ln K}{\partial T} \right) \right]
\]

(1.91)
The standard reaction entropy $\Delta S^o$, has been related to the loss of orientation of the molecules $A$ and $B$ when the complex is formed. Each molecule $A$ or $B$ can be oriented in $\eta$ ways with respect to the neighbouring molecules while in the complex one orientation of $A$ and $B$ is so favourable that it always occurred. The value of $\eta$ should then be of the same order of magnitude as the number of the nearest neighbours $Z$. 

These conclusions are based on Sarolea-Mathot investigations for $AB$ complexes and Rastogi and Girdhar for $AB + AB_2$ mixtures. Similarly, from the lattice model of associated solution

$$\Delta S^o = -3R \ln \eta$$

(1.92)

i.e. $\Delta S^o$ is always negative. Since $\eta$ is always related to $\Delta H^o$ by

$$K = \eta^{-3} \exp (-\Delta H^o/RT)$$

(1.93)

Therefore, $S^E$ in equation (1.90) is the difference between the two terms which are always negative. Their absolute value determines the sign of $S^E$ i.e. $S^E$ can acquire any positive or negative value for small values of $K$ (in this case $Y_1 << 1$ and $Y_2 - 1 << 1$) one obtains by expanding the logarithms in equation (1.90) so that

$$S^E/R = (\Delta H^o/RT +1)$$

(1.94)

The excess entropy is then positive for

$$K \eta^3 < 1$$

The excess volume is given by

$$V^E = \Delta V^o \frac{\xi}{1+2\xi}$$

(1.95)
\[ \Delta V^o = (V_{AB2}^o - V_\Lambda^o - 2V_B^o) \]  

(1.96)

and the excess heat capacity \( G^E \) is

\[ G^E_p = \frac{\Delta C_p^o \xi}{1+2\xi} + R \left( \frac{\Delta H^o \xi^2}{1+2\xi} \right) \left[ \frac{1-x(1+2\xi)}{x[K(1-x(1+2\xi))]^\frac{1}{2}\xi^2} \right] \]  

(1.97)

\[ \Delta C_p^o = (C_{AB2}^o - C_\Lambda^o - 2C_B^o) \]
REFERENCES

1. S. T. Young, Phil. Mag., 33, 153 (1892).


