CHAPTER VIII

COMPARISON OF EXPERIMENTAL RESULTS WITH THEORETICAL CALCULATIONS
Comparison of Experimental Results
with Theoretical Calculations

Theoretical development of the liquid state has been very slow. It is only during the last one decade, that certain major break through in the field has been possible. Theoretical results for model liquids agree well with the quasi-experimental results obtained by Monte Carlo (107) and molecular dynamic methods (108). Satisfactory agreement between theory and experimental has been achieved for simple liquids like heavy noble gases. The extension of the theory (111) to solution of these simple liquids has also been made. However, for molecules of interest, rigorous theories of the liquids and their mixtures seem at present a distant goal. Attempts have been made from time to time to formulate empirical or semi-empirical theories. These theories are either based on radial distribution function or choice of suitable physical models from assumed or known values of the properties of molecules. However, when only excess properties of solutions are to be calculated the errors in the absolute values cancel and approximate agreement with experiment is obtained for the excess properties. In the theory based on radial distribution function the properties of the mixtures are expressed in terms of molecular distribution functions, which can be obtained in principle by solving certain integral equations but in practice these are very complicated and therefore few calculations have been made for the systems of interest (90 - 92).
A particularly simple version of this approach is due to Hildebrand and Scatchard (2) who make a number of assumptions. The second approach is based on the choice of a suitable model and thus calculating the partition function and other thermodynamic quantities. The difficulties in calculations depend upon how realistic is the model (e.g. lattice model, cell model etc.). Conformal solution theory which is based on the theorem of corresponding state is suitable only for a small number of molecules. Prigogine et al. (10, 93, 94) have incorporated in the cell model the main features of the conformal solution theory and from known critical constants of the pure components and a few other simplifying assumptions have obtained expressions for various thermodynamic excess functions. Prigogine et al. have extended it to the solutions formed by the components belonging to the same homologous series also. Although the theory is far from quantitative, it has to its credit, some measure of success and its scope and limitations have been recently discussed by Belleman (109).

A more general theory which incorporates some features of cell theory and empirical assumptions regarding the dependence of energy on volume (1/v) has been developed recently by Flory et al. (18-22). With the known P, V, T data for pure components and a disposable parameter the agreement between the theory and experiment is quite good on the whole.
In the following pages we discuss only the main features of some of the theories and give only the details of Flory's theory with which the results have been mostly compared.

**Interaction between Molecules:** The bulk properties of the liquids are mainly due to the interaction between its molecules. The problem of interactions between many body is extremely difficult and are simplified by assuming pairwise interactions. In principle the pairwise intermolecular potential can be calculated quantum mechanically. However, these calculations are tedious and limited to only very simple molecules. For the molecules of interest the expression for the intermolecular potential between simple molecules is retained with the introduction of two or more than two adjustable parameters.

The interaction potential contains an attraction term which usually depends upon the inverse 6th power of the distance between two molecules and a repulsive force which changes more steeply with distance. A commonly used form is the one first made popular by Lennard-Jones and may be written,

\[ \xi(r) = \frac{\lambda}{r^n} - \frac{\nu}{r^m} \quad (n > m) \quad \ldots \quad (8.1) \]

\( \xi(r) \) is spherically symmetrical. The value of \( m \) is taken as 6 and can be justified quantum-mechanically. The value of \( n \) is usually taken as 12 but it can vary between
Alternative form of the $(6,12)$ Lennard–Jones potential (Fig. 15) may be written as,

\[ \varepsilon(r) = \left( \frac{r^*/r}{r} \right)^{12} - 2 \left( \frac{r^*/r}{r} \right)^6 \] .... (8.2)

or

\[ 4 \varepsilon \left( \frac{\sigma^*/r}{r} \right)^{12} - \left( \frac{\sigma^*/r}{r} \right)^6 \] .... (8.3)

The meaning of the symbols $\varepsilon^*$, $r^*$, and $\sigma^*$ are clear from Fig. 15. For binary solutions of components 1 and 2 the following three interaction energies are required for theoretically calculating the excess functions.

\[ \varepsilon_{11}(r) = \varepsilon_{11}^* \left( \frac{r_{11}^*/r}{r} \right)^{12} - 2 \left( \frac{r_{11}^*/r}{r} \right)^6 \] .... (8.4)

\[ \varepsilon_{22}(r) = \varepsilon_{22}^* \left( \frac{r_{22}^*/r}{r} \right)^{12} - 2 \left( \frac{r_{22}^*/r}{r} \right)^6 \] .... (8.5)

\[ \varepsilon_{12}(r) = \varepsilon_{12}^* \left( \frac{r_{12}^*/r}{r} \right)^{12} - 2 \left( \frac{r_{12}^*/r}{r} \right)^6 \] .... (8.6)

There has been speculations regarding the relations between $\varepsilon_{12}^*$, $r_{12}^*$, $\varepsilon_{11}^*$, $\varepsilon_{22}^*$, $r_{11}^*$ and $r_{22}^*$. For simple molecules following approximations are usually made,

\[ \varepsilon_{12} = \left( \varepsilon_{11} \varepsilon_{22} \right)^{1/3} \] due to Lorentz(64) .... (8.7)

\[ r_{12}^* = \frac{1}{3} \left( r_{11}^* + r_{22}^* \right) \] due to Berthelot(110) .... (8.8)
FIG. 15. THE LENNARD-JONES (12,6) AS A FUNCTION OF $\frac{r}{r^*}$.
While Berthelot relation is valid for rigid spheres only, Lorentz relation is suitable when $\varepsilon_{11}$ and $\varepsilon_{22}$ are not very different. For such molecules the value of $\varepsilon_{12}$ can be obtained within 1% of $(\varepsilon_{11} \varepsilon_{22})^{1/2}$ but it must be stressed that even this 1% deviation from the geometrical rule may cause large errors in the calculated excess functions. It has been emphasized by a number of workers to treat $\varepsilon_{12}$ as a parameter instead of a calculable property.

It has been realised that Lennard-Jones potential is inadequate even for simple polyatomic molecules, e.g. $\text{CH}_4$ or $\text{CCl}_4$, due to eccentric distribution of polarizable electrons. This leads to drastic modification of this potential and both the attraction and the repulsion terms are rendered more steeply dependent on the distance between the molecular centres.

**Energy dependence of Liquids on Volume**: For a pure liquid the potential energy $E$ can be obtained by taking the sum over all the molecules of their potential energies of interaction with all the other molecules. For liquids whose molecules obey any spherically symmetrical interaction potential, one can write the potential energy for one molecule of the liquid:

$$E = 2\pi n^2/V \int_0^\infty g_{ii}(r) \varepsilon_{ii}(r) dr \quad \ldots \quad (8.9)$$

Right hand side of the above equation contains a definite integral. If $g_{ii}$ is independent of volume the integral will
be independent of volume whatever may be the form of interaction-potential $\xi_{ij}$. Hildebrand et al. have emphasized this point and for a number of liquids they have shown by equating the potential energy to the energy of evaporation that this inverse dependence on volume for energy is a good approximation for non-polar molecules. In general $E$ can be represented by the equation,

$$E = \frac{a}{V^n} \quad \text{.... (8.10)}$$

using the thermodynamic relation,

$$\left(\frac{\partial E}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V - P \quad \text{.... (8.11)}$$

and from the experimental data for a number of liquids with a wide range of molar volume they have found, that the value of $n$ is nearly one for many molecules. Table XLV gives the value of $n$ for some liquids.

<table>
<thead>
<tr>
<th>Table XLV*</th>
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</thead>
<tbody>
<tr>
<td>Values of $n$ for some liquids.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Liquid</th>
<th>$n$</th>
<th>Liquid</th>
<th>$n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_7F_{16}$</td>
<td>1.49</td>
<td>$n-C_4Cl_3F_7$</td>
<td>1.36</td>
</tr>
<tr>
<td>$c-C_6F_{11}CF_3$</td>
<td>1.44</td>
<td>$CCl_2F.CClF_2$</td>
<td>1.19</td>
</tr>
<tr>
<td>$n-C_6F_{14}$</td>
<td>1.39</td>
<td>$CCl_4$</td>
<td>1.09</td>
</tr>
<tr>
<td>$c-C_4Cl_2F_6$</td>
<td>1.35</td>
<td>$n-C_6H_{14}$</td>
<td>1.09</td>
</tr>
</tbody>
</table>

* Taken from reference (2), page 79.
Lattice Theory (95) :- The model for this theory is a rigid lattice with fixed number of sites occupied by molecules. It is further assumed that the configurational partition function can be resolved into two factors.

1. $Q_{\text{lattice}}$
2. $Q_{\text{oscillation}}$

$Q_{\text{lattice}}$ corresponds to lattice energy when the molecules are at rest (lattice energy) and $Q_{\text{oscillation}}$ is due to the oscillation of the molecules around the lattice point. It is assumed that the latter remains the same both in the pure liquid and the solution. For polymer solutions the polymer segments are supposed to occupy more than one lattice sites. Several variations of the theory are available. Although the model served some useful purpose and has been applied to polymer solutions but the model is too simple and assumes zero excess volume for all the solutions. Zero excess volume for most of the solutions is exception rather than the rule. Therefore, we shall not compare our results with the predictions of this model.

Conformal theory (10, 93, 94) :- This theory is based on the idea that there exists a universal form of intermolecular potential $\delta_{ij}$ and then applying first order perturbation theory, expressions are obtained for various excess functions. In simple form the theory predicts all the functions to have the same sign. The theory is limited to a very small class of mixtures. The
advanced version of this theory are quite involved and the results do not agree with experiment. The main features of this theory have been incorporated by Prigogine et al. in the cell model.

Cell Theory (3, 96, 97) :- In the cell model of the liquid the molecule is confined to a small region of space, formed by a sort of enclosure or a cell by the neighbour molecules. Within the cell the molecule moves in a potential field arising from its neighbours. The life time of the molecule in a particular cell is long enough as not to effect the equilibrium properties of the liquid. In the case of pure liquids the molecules forming the cell are identical whereas, in the binary mixture both type of molecules will be encountered. Thus the potential in the cell will depend upon the components of the mixture. The cell partition function can be evaluated on assuming the form of the potential both in the pure liquid and the mixture and hence the expression for the various excess functions can be obtained. The theory however, has been modified by incorporating the features of the conformal solution theory, that is making full use of the principle of corresponding states. The expressions for the excess functions can be obtained in terms of the configurational properties of the pure components and the parameters $f$, $\phi$ and $\delta$ which in their turn are related to the quantities $\epsilon_{11}^*$, $\epsilon_{22}^*$, $\epsilon_{12}^*$, $r_{11}^*$, $r_{22}^*$ and $r_{12}^*$ by the relations given overleaf,
\[
\delta = \frac{\varepsilon_{22}^* - \varepsilon_{11}^*}{\varepsilon_{11}^*}
\quad \ldots \quad (8.12)
\]
\[
\Theta = \frac{\varepsilon_{22}^* - \varepsilon_{12}^*}{\varepsilon_{11}^*}
\quad \ldots \quad (8.13)
\]
\[
\rho = \frac{r_{22}^* - r_{11}^*}{r_{11}^*}
\quad \ldots \quad (8.14)
\]

In actual calculations the values of \(\delta\) and \(\rho\) are obtained from the critical constants of the pure components and for evaluation of \(\Theta\), Lorentz relation is used. The details are discussed in the well known monograph by Prigogine et al. (3).

Calculations have already been reported for a few of the systems (23) and as apparent from Table XLVI the agreement is not good at all. In view of poor agreement the calculations have not been extended to other systems. Even by making \(\Theta\) as a disposable parameter by calculating its value from one of the experimental excess functions, does not give good agreement for the remaining excess functions. Reasons relating to the limitation of the cell model are due to severe departure from the universal form of the intermolecular potential \(\varepsilon_{ij}\) for component molecules which differ appreciably in size and shape. Besides the other shortcomings of the cell model have been pointed out by Flory (21) and in his words,

"The definition of the cell, consisting of neighbour molecules in fixed array about the central "wanderer" erroneously ascribes crystal like characteristics, to the liquid. Each
molecule is regarded to perform dual, mutually inconsistent roles. It must function both as a fixed neighbour and as the wanderer, within its own cell. Thus, not only does the cell model incorporates the acknowledged deficiencies of the Einstein model for a solid, but it also fails to take account of these features which set a liquid apart from a solid. These shortcomings of the cell model have been stressed by Hildebrand and Coworkers" (1,2).

Table XLVI

Comparison between the experimental and theoretical values of $v^E$
at $x_1 = 0.5$

<table>
<thead>
<tr>
<th>System</th>
<th>$v_{exp.}^E$</th>
<th>$v_{calc.}^E$</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-hexane/benzene (23)</td>
<td>0.40</td>
<td>2.0</td>
</tr>
<tr>
<td>n-heptane/benzene (23)</td>
<td>0.65</td>
<td>5.8</td>
</tr>
<tr>
<td>n-heptane/carbon tetrachloride</td>
<td>0.23</td>
<td>7.3</td>
</tr>
<tr>
<td>n-octane/carbon tetrachloride</td>
<td>0.32</td>
<td>13.7</td>
</tr>
<tr>
<td>n-tetradecane/carbon tetrachloride</td>
<td>0.53</td>
<td>68.4</td>
</tr>
<tr>
<td>n-hexadecane/carbon tetrachloride</td>
<td>0.67</td>
<td>93.9</td>
</tr>
</tbody>
</table>
Hildebrand Scatchard Theory (98, 99) :- The total potential energy as mentioned previously (see page 100) is given by

\[ E = 2 \pi N_0^2 / V \int_0^\infty \xi_{ii}(r) g_{ii}(r) \, dr \] .... (8.10)

In a solution consisting of two components around the molecules of component one, the molecules of both the components (1 and 2) may be found with the radial distribution function \( g_{11} \) and \( g_{21} \). Similarly for the molecules of the component 2 as the central molecules, \( g_{22} \) and \( g_{12} \) are radial distribution functions. Then the energy for one molecule of the mixture with the mole fractions \( x_1 \) and \( x_2 \) and random mixing is given by the expression,

\[ E_{\text{mix.}} = \frac{2 \pi N_0^2}{V} \left( x_1 \int \xi_{11} g_{11} r^2 \, dr + x_2 \int \xi_{21} g_{21} r^2 \, dr \right) \]
\[ + x_2 \left( x_1 \int \xi_{12} g_{12} r^2 \, dr + x_2 \int \xi_{22} g_{22} r^2 \, dr \right) \] .... (8.16)

the energy for the pure components before mixing is

\[ E^0 = 2 N_0^2 \left( \frac{x_1}{V_1} \int g_{11}^0(r) \xi_{41}(r) \, dr \right) \]
\[ + \left( \frac{x_2}{V_2} \right) \int g_{22}^0(r) \xi_{22}(r) \, dr \] .... (8.17)

where, \( g_{11}^0(r) \) and \( g_{22}^0(r) \) are the radial functions for the
pure components. The energy of mixing is then given by the difference of equation (8.16) and (8.17).

Thus if we know $g_{11}, g_{ij}$ and $\xi_{ij}$ and $V_i$, it is possible to estimate the energy of mixing and also other thermodynamic functions from the known dependence of $g_{ij}, \xi_{ij}$ etc. on temperature. This at present seems to be possible only for very simple systems and very few calculations have been reported.

Hildebrand and Scatchard using equation (8.16) and (8.17) and introducing the following assumptions:

1. There is no change in volume on mixing i.e.,

$$V^m = x_1 V_1 + x_2 V_2$$

2. The potentials are spherically symmetric and can be expressed by,

$$\xi_{11} = \xi_{11} \phi \left( \frac{r}{r_{11}}^* \right),$$

$$\xi_{12} = \xi_{12} \phi \left( \frac{r}{r_{12}}^* \right),$$

and

$$\xi_{22} = \xi_{22} \phi \left( \frac{r}{r_{22}}^* \right)$$

.... (8.18)

3. The radial functions are independent of composition, i.e.,

$$g_{11}^0 (r) = g_{11}(r) = g \left( \frac{r}{r_{11}^*} \right),$$

$$g_{12} = g \left( \frac{r}{r_{12}^*} \right)$$

and

$$g_{22}^0 (r) = g_{22}(r) = g \left( \frac{r}{r_{22}^*} \right)$$

.... (8.19)
substituting equations (8.18) and (8.19) in equations (8.16) and (8.17) and taking their difference the following expression for the energy of mixing at constant volume is obtained.

\[
\Delta E^m = (x_1V_1 + x_2V_2) \phi_1 \phi_2 ((2 \xi_2 r_{12}^3 / V_1 V_2) - (\xi_{11}^* r_{11}^* / V_1) \\
- (\xi_{22}^* r_{22}^2 / V_2)) 2 \pi N_0 \int_\phi (\gamma V_2) (y^2 dy) ....(8.20)
\]

for pure liquids at ordinary temperature the quantities,

\[
\xi_{11}^* r_{11}^* / V = 2 N_0 \int_\phi \gamma V_2 (y^2 dy) \quad \text{(cohesive energy)}
\]

be approximated to the energy of vaporisation \(\Delta E^v\). Further if geometric mean rule is adopted so that,

\[
\xi_{12}^* = (\xi_{11}^* \xi_{22}^*)^{1/2}
\]

\[
\Delta E^m_v = (x_1V_1 + x_2V_2) \phi_1 \phi_2 (\delta_1 - \delta_2)^2 .... (8.21)
\]

where , \(\delta_i = (E_i / V_i)^{1/6}\) is called solubility parameter.

However, most of the measurements are made at constant pressure and we can obtain

\[
\Delta h_p^m = E_v^m + T (\partial P / \partial T)_v \Delta V^m_p ......(8.22)
\]

or

\[
h_p^m = E_v + T (\partial P / \partial T)_v V_p^E ......(8.23)
\]

Still for making a comparison with experimental \(h_p^m\) excess volume \(V_p^E\) and \(\partial P / \partial T\) are needed. The latter may be calculated from thermal pressure coefficient for the mixture. Another
experimental quantity of interest is $g^E_p$ which is nearly equal to $f_V^E$. For regular solutions where $v^E = 0$ and $s_V^E = 0$, $g^E_p$ becomes,

$$g^E_p = f_V^E = (x_1 V_1 + x_2 V_2) \left( \delta_1 - \delta_2 \right)^2 \phi_1 \phi_2 \quad \ldots \quad (8.24)$$

We shall compare our results for only $g^E$ at $25^\circ C$. The values $\delta_i$, $\varphi_i$ etc. used in these calculations are given in Table XLVII. The experimental data for $g^E$ for each system are compared with those calculated from equation (8.24) and are illustrated in figures 16-19.

**Table XLVII**

Values of constants in equation (3.24) at $25^\circ C.$

<table>
<thead>
<tr>
<th>Substance</th>
<th>Molar volume (ml/mole)</th>
<th>$\delta_i$ (J cm.$^{-\frac{1}{2}}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-octane</td>
<td>163.63</td>
<td>31.56</td>
</tr>
<tr>
<td>n-hexadecane</td>
<td>294.03</td>
<td>33.44</td>
</tr>
<tr>
<td>Benzene</td>
<td>89.40</td>
<td>38.25</td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>97.09</td>
<td>35.95</td>
</tr>
</tbody>
</table>
FIG. 16 FIG. 17
COMPARISON BETWEEN EXPERIMENTAL $g_\theta$ & CALCULATED BY HILDEBRAND SCATCHARD THEORY

THEORETICAL

n-Hexadecane/Benzene 25°C

n-Octane/Benzene 25°C

Joules

$g_\theta$
COMPARISON BETWEEN EXPERIMENTAL \( \delta^0 \) AND CALCULATED BY HILDEBRAND SCATCHARD THEORY.
Flory's Theory:- Recently Flory (16-20) has developed a general theory for thermodynamic properties for mixtures of non-polar molecules having different size and shape. He has used one disposable parameter and the agreement obtained between the experimental and calculated quantities is quite satisfactory for a large number of mixtures.

This theory considers a linear chain molecules to be consisting of \( r \) isometric segments each possessing \( 3c \) external degrees of freedom. The configurational partition function of the liquid containing \( N \) such molecules is given by,

\[
Z = Z_{\text{comb}} \cdot \left[ \gamma \left( v - v^* \right)^3 \right]^{\frac{Nc}{2}} \exp \left( - \frac{E_0}{kT} \right) \quad \text{...(8.25)}
\]

where \( Z_{\text{comb}} \) is a combinatorial factor and the communal entropy factor \( e^{3N} \) may also be considered to be absorbed in \( Z_{\text{comb}} \); and \( E_0 \) is the intermolecular energy. When considering the excess functions \( Z_{\text{comb}} \) and \( r^N \) will cancel out.

Intermolecular energy \( E_0 \) may be written in the form,

\[
E_0 = - \text{constant} / v^m \quad \text{...(8.26)}
\]

where \( m \) is very near unity (1,2 and 100) which in terms of \( r \) (number of segments), \( s \) (number of intermolecular contact sites per segment), \( \gamma \) (constant characteristic of the energy of interaction for a pair of neighbouring sites) and \( v \) the volume per segment can be written as,

\[
E_0 = - \frac{Nrs\gamma}{2v} \quad \text{...(8.27)}
\]
and the reduced partition function becomes,

\[ Z = Z_{\text{comb.}} (\mathbf{v}^*)^x \mathbf{Nc} (\mathbf{v} - 1)^{3\gamma Nc} \exp \frac{xNc}{\mathbf{v}T} \quad \ldots \ldots (8.28) \]

where \( \mathbf{v}, \mathbf{T} \) and \( \mathbf{p} \) are the reduced quantities corresponding to per mole of the segments (i.e., \( L \) segments where \( L \) is the Avogadro's number) and are defined as follows:

\[ \mathbf{v} = \frac{v}{v^*} \quad \ldots \ldots (8.29) \]
\[ \mathbf{T} = \frac{T}{T^*} = 2v_c^* \frac{RT}{} \quad \ldots \ldots (8.30) \]
\[ \mathbf{p} = \frac{p}{p^*} = 2pv^*2/s_\gamma \quad \ldots \ldots (8.31) \]
\[ p^* = cRT^*/v^* \quad \ldots \ldots (8.32) \]

which in terms of per molecule of the substance is,

\[ p^* = cRT^*/V^* \quad \ldots \ldots (8.33) \]

where \( C = rc \) and \( V^* = rv^* \)

The reduced equation of the state at \( P = 0 \) becomes,

\[ \left( \mathbf{v}^* - 1 \right) / \mathbf{v}^{4/3} = \mathbf{T} \quad \ldots \ldots (8.34) \]

With the help of equation (8.34) and the properties of the pure components such as volume \( v \) and thermal expansion coefficient \( \alpha \), the compressibility \( \beta \) (or the thermal pressure coefficient \( \gamma \)) the quantities \( v^*, T^* \) and \( p^* \) can be calculated. These quantities for the substances comprising the mixtures studied, are given in Table XLVIII.
For a binary mixture consisting of $N_1$ molecules of component 1 and $N_2$ molecules of component 2, the energy $E_0$ may be written as,

$$-E_0 = (A_{11} \eta_{11} + A_{22} \eta_{22} + A_{12} \eta_{12})/v \quad \ldots \quad (8.35)$$

where $A_{11}$, $A_{22}$, and $A_{12}$ represent the number of contacts between the segments. Then we have,

$$2A_{11} + A_{12} = s_1 r_1 N_1 \quad \ldots \quad (8.36)$$
$$2A_{22} + A_{12} = s_2 r_2 N_2 \quad \ldots \quad (8.37)$$

and

$$-E_0 = (s_1 r_1 N_1 \eta_{11} + s_2 r_2 N_2 \eta_{22} - A_{12} \Delta \eta)/2 \quad \ldots \quad (8.38)$$

where $\Delta \eta = \eta_{11} + \eta_{22} - 2 \eta_{12} \quad \ldots \quad (8.39)$

Let us define here the quantities site and segment fractions,

Site fraction = $r_1 s_1 N_1 / (r_1 s_1 N_1 + r_2 s_2 N_2) \quad \ldots \quad (8.40)$

Segment fraction = $r_1 N_1 / (r_1 N_1 + r_2 N_2) \quad \ldots \quad (8.41)$

$N = N_1 + N_2 \quad \ldots \quad (8.42)$

$$\bar{r} = (r_1 N_1 + r_2 N_2 / (N_1 + N_2)) = \Sigma r_1 N_1 / \Sigma N_1 \quad \ldots \quad (8.43)$$

Assuming the mixing to be random, and substituting the equations (8.40 - 8.43) in equation (8.38) we get,
In equation (8.45) substituting \( p_1^* = s_1 \gamma_{11}/2 v^* \)
and defining the parameter \( \gamma_{12} \) as,
\[
\gamma_{12} = s_1 \Delta \eta / 2 v^* \quad \text{... (8.46)}
\]
we get,
\[
- \frac{E_0}{\overline{r}N} = \left( \frac{v^*/v}{v^*} \right) \left( \phi_1 p_1^* + \phi_2 p_2^* - \phi_1 \phi_2 \gamma_{12} \right) \quad \text{... (8.47)}
\]
where,
\[
\phi_1 p_1^* + \phi_2 p_2^* - \phi_1 \phi_2 \gamma_{12} = p^* \quad \text{... (8.48)}
\]
From the generalisations obtained above it is possible to write the expressions for various excess functions.
\[
\overline{h}^E = \overline{r}N v^* \left( \phi_1 p_1^* \left( \frac{1}{v_1} - \frac{1}{\overline{v}} \right) + \phi_2 p_2^* \left( \frac{1}{v_2} - \frac{1}{\overline{v}} \right) \right)
+ \phi_1 \phi_2 \gamma_{12} / \overline{v} \quad \text{... (8.49)}
\]
or
\[
= N_1 p_1^* v_1^* \left( \frac{1}{v_1} - \frac{1}{\overline{v}} \right) + N_2 p_2^* v_2^* \left( \frac{1}{v_2} - \frac{1}{\overline{v}} \right)
+ N_1 v_1^* \phi_2 \gamma_{12} / \overline{v} \quad \text{... (8.50)}
\]
which for one mole of the mixture is written as,
\[
\overline{h}^E = x_1 p_1^* v_1^* \left( \frac{1}{v_1} - \frac{1}{\overline{v}} \right) + x_2 p_2^* v_2^* \left( \frac{1}{v_2} - \frac{1}{\overline{v}} \right)
+ x_1 v_1^* \phi_2 \gamma_{12} / \overline{v} \quad \text{... (8.51)}
\]
\[ v^E = \frac{7/3}{\nu_0} / (4/3 - \frac{1}{3}) \cdot \frac{T_0}{(x_1 v_1^* + x_2 v_2^*)} \cdot \]

\[ (\phi_1 \phi_2 x_{12}) / (\phi_1 p_1^* + \phi_2 p_2^*) \quad \ldots (8.52)** \]

\[ T_s^E = -3 \left( x_1 p_1^* v_1^* T_1 \right) \ln \left( \frac{v_1^3}{v_1 - 1} \right) - 3 \left( x_2 p_2^* v_2^* T_2 \right) \ln \left( \frac{v_2^3}{v_2 - 1} \right) \]

\[ \ldots (8.53) \]

and

\[ g^E = h^E - T_s^E \]

\[ \ldots (8.54) \]

The value of the parameter \( X_{12} \) can be guessed from Berthelot relationship, but as pointed out by Flory that it is more realistic to consider it as a disposable parameter and determine its value from equation (8.49) by using the experimental value of \( h^E \). In case of the systems with known heats of mixing, we have determined the values of \( X_{12} \) by using \( h^E \) values at \( x = 0.5 \). These are presented in Table IL.

Once this parameter is estimated other functions can be calculated over the whole range of mole fraction. The calculated values of the excess volumes and entropies have been compared with the experimental values.

Flory et al. have compared the experimental results for a large number of binary mixtures with the calculated values (22). They find the agreement for the excess volume is generally good.

For \( T_s^E \) the agreement is not always good.

** In this equation it is assumed that \( \phi_1 \phi_2 X_{12} / (\phi_1 p_1^* + \phi_2 p_2^*) \lesssim 1 \) so that its powers have been neglected.
### Table XLVIII

Values of some parameters for the pure components at 25°C

<table>
<thead>
<tr>
<th>Substance</th>
<th>$\bar{v}$</th>
<th>$v^*$</th>
<th>$T^*$</th>
<th>$P^*$</th>
<th>$V^0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-hexane</td>
<td>1.3215</td>
<td>99.65</td>
<td>4437</td>
<td>101.2</td>
<td>131.57</td>
</tr>
<tr>
<td>n-heptane</td>
<td>1.2973</td>
<td>113.79</td>
<td>4652</td>
<td>102.5</td>
<td>147.51</td>
</tr>
<tr>
<td>n-octane</td>
<td>1.2793</td>
<td>127.37</td>
<td>4836</td>
<td>103.5</td>
<td>163.63</td>
</tr>
<tr>
<td>n-hexadecane</td>
<td>1.2270</td>
<td>241.09</td>
<td>5548</td>
<td>110.7</td>
<td>294.03</td>
</tr>
<tr>
<td>Benzene</td>
<td>1.2916</td>
<td>69.21</td>
<td>4708</td>
<td>150.0</td>
<td>89.40</td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>1.2927</td>
<td>75.10</td>
<td>4697</td>
<td>136.0</td>
<td>97.08</td>
</tr>
</tbody>
</table>
Table II

Values of some parameters and excess functions for equimolar mixtures at 25°C.

<table>
<thead>
<tr>
<th>Mixture</th>
<th>$r_1s_1/r_2s_2^*$</th>
<th>$E^*$</th>
<th>$h$</th>
<th>$X_{12}$</th>
<th>$V_{exp.}$</th>
<th>$V_{calc.}$</th>
<th>$T_{s exp.}$</th>
<th>$T_{s calc.}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td><em>(J/mole)</em></td>
<td><em>(J/mL)</em></td>
<td><em>(ml./mole)</em></td>
<td><em>(ml./mole)</em></td>
<td><em>(J/mole)</em></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-hexane/benzene</td>
<td>0.6602</td>
<td>880.0(a)</td>
<td>36.57</td>
<td>0.40</td>
<td>0.76</td>
<td>498.1</td>
<td>339.5</td>
<td></td>
</tr>
<tr>
<td>n-heptane/benzene</td>
<td>0.5958</td>
<td>937.0(b)</td>
<td>40.25</td>
<td>0.65</td>
<td>0.83</td>
<td>506.6</td>
<td>337.9</td>
<td></td>
</tr>
<tr>
<td>n-octane/benzene</td>
<td>0.5349</td>
<td>996.1(c)</td>
<td>43.60</td>
<td>0.73</td>
<td>0.88</td>
<td>664.8</td>
<td>344.9</td>
<td></td>
</tr>
<tr>
<td>n-hexadecane/benzene</td>
<td>0.3040</td>
<td>1225.0(d)</td>
<td>50.17</td>
<td>0.36</td>
<td>0.96</td>
<td>1133.7</td>
<td>520.8</td>
<td></td>
</tr>
<tr>
<td>n-hexane/carbon tetrachloride</td>
<td>0.6952</td>
<td>285.9(e)</td>
<td>10.21</td>
<td>0.18*</td>
<td>0.23</td>
<td>147.1</td>
<td>146.4</td>
<td></td>
</tr>
<tr>
<td>n-heptane/carbon tetrachloride</td>
<td>0.6223</td>
<td>301.3(e)</td>
<td>11.97</td>
<td>0.23</td>
<td>0.27</td>
<td>171.2</td>
<td>141.2</td>
<td></td>
</tr>
<tr>
<td>n-octane/carbon tetrachloride</td>
<td>0.5632</td>
<td>354.9(e)</td>
<td>15.02</td>
<td>0.32</td>
<td>0.33</td>
<td>259.5</td>
<td>156.0</td>
<td></td>
</tr>
<tr>
<td>n-hexadecane/carbon tetrachloride</td>
<td>0.3201</td>
<td>394.1(e)</td>
<td>16.57</td>
<td>0.67</td>
<td>0.35</td>
<td>512.1</td>
<td>324.5</td>
<td></td>
</tr>
</tbody>
</table>

*Extrapolated from the excess volume data of n-heptane and n-octane in carbon tetrachloride.
†These values have been taken from the references 64(a), 39(b & d), 112(c) & 86(e).
Figures 24 - 27 give a comparison between the experimental quantities for n-octane and n-hexadecane solutions. Although the main features are reproduced by the theory yet the quantitative agreement is lacking. It would be of interest to compare the results of other such systems as given in chapter III, but unfortunately all the data required for the pure components are not available.

It may be mentioned that strictly speaking equations (8.53) and (8.54) give only the residual property and not excess property (not very different for molecules of about the same size). Therefore, corrections have to be made for this effect and \( T \Delta s^E \) is then given by,

\[
T \Delta s^E = T \Delta s^R + T \Delta s^f - T \Delta s_1^m \quad \ldots \quad (8.55)
\]

we have compared the results for eight systems. The calculated values of the important excess functions at 25°C and \( x = 0.5 \) are given in Table II. Results over entire concentration range of mole fractions are given in figures 20 - 23.

Once again it can be seen that the agreement for \( \nu \) is quite good, and for \( T s^E \) the agreement is poor and becomes worse as the chain length increases.

***************
FIG. 20 & FIG. 21
COMPARISON BETWEEN EXPERIMENTAL $T_S$ & THEORETICAL $T_S$ CALCULATED BY FLORY'S METHOD

n-OCTANE/BENZENE AT 25°C
n-HEXADECANE/BENZENE AT 25°C
Comparison between experimental $V^E_0$ and theoretical $V^E$ calculated by F Kokys method.

**n-OCTANE/BENZENE 25°C**

**n-HEXADECANE/BENZENE 25°C**
FIG. 26 COMPARISON BETWEEN EXPERIMENTAL $v^E_0$ & THEORETICAL $v^E$ AS CALCULATED BY FLORY'S METHOD

n-OCTANE/CARBONTETRA CHLORIDE

n-HEXADECANE/CARBONTETRA CHLORIDE 25°C