2.1 INTRODUCTION

Enthalpy of mixing is defined as the change of enthalpy per mole of mixture when the pure components are mixed at definite temperature and pressure. For a given mixture it depends on the amounts of components 1 and 2 and also it is a function of temperature and pressure. The effect of pressure is insignificant in liquid systems while in gaseous systems the enthalpy of mixing itself is of minor effect except at high pressures, but there is no generalisation in case of temperature effect.

Systems depending on their nature may have low or high enthalpies of mixing and may or may not be sensitive to temperature changes. It is important to study the sign, magnitude, composition, temperature dependance of enthalpies of mixing. In general the
following observations can be made while reviewing the enthalpies of mixing behaviour of a variety of systems [67].

- Enthalpy of mixing can be either endothermic or exothermic.
- When a pair of non-polar or weakly polar components mix, $h^E$ decreases with temperature and it may become negative at high temperatures.
- A pair of paraffinic hydrocarbons normally mix giving rise to small positive values for $h^E$.
- When a pair involving at least one polar component mix, $h^E$ increase with temperature.
- Aromatic hydrocarbons mix with each other or with paraffins endothermally.
- Hydrocarbons mix endothermally with non-polar components.
- Other pairs of liquids usually mix endothermally unless:
  - there is compound formation through hydrogen bonding with a proton accepted as in the case of acetone-chloroform, benzene-chloroform etc.
  - there is an increase in the total number of hydrogen bonds as in the systems: mixtures of amines, alcohols-water, and in both cases mixing is exothermic.
  - a few mixtures may be exothermic over a part of the composition range and endothermic over the rest. Example is methanol-water.

The problem of accurate measurement of enthalpy of mixing and the development of suitable calorimeter methods are discussed in detail by Skinner [148].

Enthalpies of mixing data for binary solutions
are quite common in the literature. A comprehensive review of experimental enthalpies of mixing data are given by Wisniak, Tamir and Christensen [131,18]. The data for binary systems having isopropylbenzene as one of the components is scarce. In this work new experimental data are reported for binary systems made up of isopropylbenzene as one of the components.

A review of previous experimental enthalpy of mixing data for binary systems having isopropylbenzene as one of the components is given in Table 2.1.

2.2 CALORIMETRIC METHODS

There are two general procedures used in the calorimetric determination of enthalpies of mixing:

- **Adiabatic Method (Isoperibol)**

  Two or more components are mixed adiabatically and the final temperature is recorded. This change is used to calculate total heat produced or absorbed during the mixing process.

- **Isothermal Method**

  Two or more components are mixed and sufficient heat is added or removed during the mixing process so as to keep the temperature of the reaction vessel constant. This heat gives directly the enthalpy of mixing.

  The advantage of the first method is that it can be used for exothermic, endothermic or endo-exothermic systems. The environment of the calorimeter in the first
<table>
<thead>
<tr>
<th>System</th>
<th>Reference</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isopropylbenzene + Chloroform</td>
<td>[1,122]</td>
<td></td>
</tr>
<tr>
<td>Isopropylbenzene + 1,1,1-Trichloroethane</td>
<td>[1]</td>
<td></td>
</tr>
<tr>
<td>Isopropylbenzene + Isoamyl alcohol</td>
<td>[146]</td>
<td></td>
</tr>
<tr>
<td>Isopropylbenzene + Pentafluorobenzene</td>
<td>[147]</td>
<td>34.85 C and 54.85 C Exothermic</td>
</tr>
<tr>
<td>Isopropylbenzene + Bromobenzene</td>
<td>[100]</td>
<td></td>
</tr>
<tr>
<td>Isopropylbenzene + Benzene</td>
<td>[99, 146]</td>
<td>30 C Endothermic</td>
</tr>
<tr>
<td>Isopropylbenzene + Toluene</td>
<td>[127]</td>
<td></td>
</tr>
<tr>
<td>Isopropylbenzene + Heptane</td>
<td>[116]</td>
<td>25 C Endothermic</td>
</tr>
<tr>
<td>Isopropylbenzene + Ethylbenzene</td>
<td>[127]</td>
<td></td>
</tr>
<tr>
<td>Isopropylbenzene + Dimethyl aniline</td>
<td>[151]</td>
<td></td>
</tr>
<tr>
<td>Isopropylbenzene + Hexadecane</td>
<td>[116]</td>
<td></td>
</tr>
<tr>
<td>Isopropylbenzene + Dimethyl phthalate</td>
<td>[79]</td>
<td></td>
</tr>
<tr>
<td>Isopropylbenzene + 1,4-Dioxane</td>
<td>[41]</td>
<td>25 C Endothermic</td>
</tr>
<tr>
<td>Isopropylbenzene + Tetracloroethene</td>
<td>[149]</td>
<td>30 C Endothermic</td>
</tr>
</tbody>
</table>
method can be either a constant temperature or an adiabatic one, the former being the most commonly used.

The advantage of second method is that it yields a direct measurement of the enthalpy of mixing. The calorimeter surrounding is kept at a constant temperature.

These two methods are applicable for batch or flow calorimeters. The disadvantages of flow calorimeter is that large amounts of materials are necessary. The accurate measurement of flow rate are also a marked disadvantage. Generally, the precision of data obtained with this type of calorimeter will be of magnitude less than the one obtained in the batch type.

The components to be mixed can both be inside the calorimeter or one of the liquid to be mixed may be contained in some vessel outside the calorimeter. In the first case, one substance is trapped in glass bulbs or ampoules which can be broken by mechanical means. The disadvantage is that only few concentrations can be achieved in one run.

In the second case mercury has been used to separate the two liquids to be mixed. It has the disadvantage that some liquids might react with mercury.

Research pertaining to enthalpies of mixing was
started in about 1958 with the development of a working model of semicontinuous calorimeter by Robert V. M. Razek under the directions of van Ness. This was followed by major reconstruction of calorimeter by Savini [138]. This calorimeter was again modified by van Ness and Kovach [62]. After that the calorimeter used for finding enthalpies of mixing were modified by many researchers [77, 92, 136, 180].

The calorimeter used for this work is a modified form of previously described by Christensen [19, 20] and the details are given in chapter 3. Isoperibol mode has been used and the liquid is added with the help of precision buret at constant rate. Further improvements of calorimeter improved the precision of the apparatus and made it also feasible for the measurement of enthalpies of mixing for exothermic and endothermic systems. In this brief review of the calorimetric methods only salient points are considered.

2.3 PREDICTION AND CORRELATIONS

Enthalpies of mixing data are available for a limited number of systems. The number is so insignificant relative to the number of systems of interest that it is very difficult to obtain experimental data for all such systems because the
experimental determination of data is very time consuming, tedious and require skill and patience. Therefore, it is essential that reliable methods of correlating and predicting enthalpies of mixing be developed.

Many attempts have been made for correlating and predicting enthalpies of mixing data. A brief review is given by Kumar and Raju [65]. A comprehensive review of the methods is given here. These methods may be classified as:

2.3.1 Semi Empirical Methods
- van Laar's Equation
- Scatchard Equation
- Wiehe and Bagley Model
- Wilson, Heil and NRTL Equations
- Associated solution theories

2.3.2 Statistical Methods

2.3.3 Empirical Methods
- Series Expansion
- Principle of Congruence
- Group Interaction Methods

Each of these methods is briefly described below:

2.3.1 Semi Empirical Methods:

- VAN LAAR'S EQUATION:

The first attempt to treat theoretically enthalpies of mixing was that of van Laar [165,166,167].
His equation is based on van der Waal's equation of state. According to his model enthalpies of mixing can be zero only if the critical pressure of the two pure components are alike and mixing could never be an exothermic process. Thus the inadequacy of the model is apparent. Based on many assumptions van Laar proposed the following equation:

$$h^E = \frac{x_1 x_2 b_1 b_2}{x_1 b_1 x_2 b_2} \left[ \frac{a_1^{\frac{1}{2}}}{b_1} - \frac{a_2^{\frac{1}{2}}}{b_2} \right]^2$$

Where a and b are characteristic constants for the pure component. van Laar and Lorenz [168] have modified the above equation by using molar volume instead of constant b, as:

$$h^E = \frac{x_1 x_2 v_1 v_2}{x_1 v_1 + x_2 v_2} \left[ \frac{a_1^{\frac{1}{2}}}{v_1} - \frac{a_2^{\frac{1}{2}}}{v_2} \right]^2$$

- SCATCHARD'S EQUATION

By making the following assumptions Scatchard [139] obtained an equation similar to the above equation.

- The mutual energy of two molecules is a function of the distance between them and of the relative orientation and it does not depend either on the nature of the other molecules between or around them or on the temperature.

- The volume change of mixing is zero at constant pressure.
The distribution of the molecules is random.

From these assumptions, Scatchard obtained the equation:

\[ \Delta e = \frac{x_1 x_2 V_1 V_2}{x_1 V_1 + x_2 V_2} \left[ \left( \frac{\Delta e_1 V}{V_1} \right)^{1/2} - \left( \frac{\Delta e_2 V}{V_2} \right)^{1/2} \right]^2 \]  \hspace{1cm} \text{(3)}

Where \( \Delta e_1 \) and \( \Delta e_2 \) are the molar internal energy changes of vaporization of pure components 1 and 2. The terms \( \Delta e / V \) are known as "cohesive energy densities" and represent a useful quantity for calculating deviations from ideal solutions. Scatchard's equation compare satisfactorily with experimental data for the mixtures for which the molecules are spherically symmetrical.

Energy of mixing \( \Delta e \) predicted by the above equation can be related to enthalpies of mixing \( h \) as:

\[ \Delta e = E T \left( \frac{\alpha}{\beta} \right) \Delta V + \frac{1}{2 \beta} \left[ \frac{\partial \ln \beta}{\partial \ln T} + \frac{\alpha T}{\beta} + \frac{\partial \ln \alpha}{\partial \ln \beta} \right] + \cdots \]

\hspace{1cm} \text{..............(4)}

where \( \alpha \) and \( \beta \) are coefficients of thermal expansion and the isothermal coefficients of compressibility. The term \( (\Delta V)^2 \) can usually be neglected. For very small volume changes in mixing the above equation reduces to:

\[ \Delta e \approx E h \]  \hspace{1cm} \text{........(5)}
- WIEHE AND BAGLEY MODEL

Wiehe and Bagley [175] proposed the alcohol-inert solvent solution model by assuming that volume change on mixing is zero and alcohol complexes form a Flory Huggins athermal solution with each other. Ratio and molar volumes and equilibrium constant for hydrogen bonding are needed for enthalpies of mixing data and are calculated from the vapour-liquid equilibrium data of the system. They tested the model on alcohol-aliphatic hydrocarbon mixtures and reported the average deviation between experimental and predicted values to be between 20 to 31 percent.

- WILSON HEIL AND NRTL EQUATIONS

Wilson [179] showed that the excess Gibbs free energy could be expressed by an algebraic function of local composition and in the final equation Wilson used the local volume fractions. In this semi empirical extension of the equation of Flory and Huggins for athermal mixtures, Wilson considered mixtures of molecules of different size and intermolecular forces. The equation given by Wilson has two disadvantages. First it is not suitable for mixtures of partially miscible liquids and second, it is not possible to evaluate Wilson parameters which produce maxima or
minima in activity coefficient. The essential contribution by Wilson was the introduction of the concept of local compositions.

Heil [46] proposed a modified form of Wilson equation for representing free energy of mixing for polymer solutions in single and mixed solvents. Two adjustable parameters are involved for each binary and the equation can be extended further for multicomponent systems. The equation is claimed to give good representation of properties of polymer solutions.

Renon and Prausnitz [132] developed the non random two liquid (NRTL) equation based on Scott's two liquid model and on assumption of non randomness similar to that used by Wilson. The NRTL equation, unlike Wilson, is applicable to both partially as well as completely miscible systems.

On the basis of the concept of local composition, the excess Gibbs free energy, function of the Wilson, Heil, NRTL equations for expressing the non ideality of binary mixtures is given as:

\[
ge^{E/RT} = x \ln Y_1 + x \ln Y_2
\]

\[
= -q \left\{ x \ln \left( x + x G \right) \right\} + x \ln \left( x + x G \right)
\]

\[
+ p x \left[ \frac{T}{21} \frac{G}{21} + \frac{T}{12} \frac{G}{12} \right]
\]

\[
= \left[ \frac{T}{21} \frac{G}{21} + \frac{T}{12} \frac{G}{12} \right]
\]

\[
\text{...(6)}
\]
\[ \tau_{12} = \frac{(g_{12} - g_{22})}{RT} \quad \ldots (7) \]

\[ \tau_{21} = \frac{(g_{21} - g_{11})}{RT} \quad \ldots (8) \]

\[ G_{12} = \rho_{12} \exp (-\kappa_{12} \tau_{12}) \quad \ldots (9) \]

\[ G_{21} = \rho_{21} \exp (-\kappa_{21} \tau_{21}) \quad \ldots (10) \]

The Wilson, Heil and NRTL equations are obtained by substituting for \( p, q, \rho \), and \( \kappa \), the values listed in Table 2.2 as given by Renon and Prausnitz [132].

\( (g_{12} - g_{22}), (g_{21} - g_{11}) \) and \( \kappa \) are three adjustable parameters to be determined from experimental data. If these three parameters are assumed to be temperature independent, then the enthalpies of mixing for a binary solution \( h^E \) are obtained by differentiation of Equation (6) using the Gibbs-Helmholtz relation:

\[ \frac{-h^E}{RT} = \frac{\partial}{\partial T} \left( \frac{g^E}{RT} \right)_{p, x} \quad \ldots (11) \]

Thus \( h^E \) is,

\[ \frac{h^E}{R} = -q \left[ \frac{x_1 x_2 G^f_{12}}{x_1^+ x_2^G_{21}} + \frac{x_1 x_2 G^f_{12}}{x_2^+ x_1^G_{12}} + \rho x_1 x_2 \left[ \frac{\tau_{21} G_{21}}{x_1^+ x_2^G_{21}} \right] + \frac{x_1 \tau_{21} G_{21}}{(x_1^+ x_2^G_{21})^2} \right] \quad \ldots (12) \]
Where
\[ P_i j' = \frac{1}{P_{ij}} \frac{dP_{ij}}{d(1/T)} = -P_{ij}' \quad \ldots \ldots \ldots \ldots (13) \]

\[ P_{ij}' = 0, \text{ if } P_{ij} = 1 \]

\[ \tau_i j' = \frac{d\tau_{ij}}{d(1/T)} \quad \ldots \ldots \ldots \ldots (14) \]

\[ \alpha_i j' = \frac{d\alpha_{ij}}{d(1/T)} \quad \ldots \ldots \ldots \ldots (15) \]

\[ G_i j = \frac{dG_{ij}}{d(1/T)} = G_i j (P_{ij}' - \alpha_i j' \tau_i j' - \alpha_{ij} \tau_{ij}' ) \quad \ldots \ldots \ldots \ldots (16) \]

**TABLE - 2.3**

<table>
<thead>
<tr>
<th>Equation</th>
<th>( p )</th>
<th>( q )</th>
<th>( p_{ij} )</th>
<th>( \alpha_{ij} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wilson</td>
<td>C</td>
<td>1</td>
<td>( V/V_i j )</td>
<td>1</td>
</tr>
<tr>
<td>HEIL</td>
<td>1</td>
<td>1</td>
<td>( V/V_i j )</td>
<td>1</td>
</tr>
<tr>
<td>NRTL</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>( \alpha_{ij} )</td>
</tr>
</tbody>
</table>

The applicability of Wilson, Heil, NRTL equations for prediction of enthalpy of mixing has been investigated by many researchers. Orye and Prausnitz [110] found that Wilson equation gives a rough estimate of non-associated solutions. Asselineau and Renon [7]
extended NRTL equation to have three temperature dependent parameters to represent the properties of binary liquid mixtures over a certain range of temperature.

Hanks et al. [42] produced reliable x-y curves directly from the measured enthalpies of mixing data and pure component vapour pressure data for six non-ideal solutions using Wilson and NRTL equations. The parameters in this estimation of excess free energy function were assumed to be temperature independent. Duran and Kalliajine [28] gave representation of excess free energies and enthalpies of mixing for eleven completely miscible binary systems using Wilson equation. Hanks et al. [43] have shown that Wilson and NRTL equation break down for $h > 840$ J/mol.

Nagata et al. [96] tested the accuracy of the Wilson, Heil and NRTL equations for calculation of enthalpies of mixing for non-ideal liquid mixtures. It was assumed that the binary parameters of these equations vary linearly with temperature as:

$$g_{21} - g_{11} = C + D (T-273.15) \quad \ldots \ldots (17)$$

$$g_{12} - g_{22} = C + D (T-273.15) \quad \ldots \ldots (18)$$

$$\alpha_{12} = C + D (T-273.15) \quad \ldots \ldots (19)$$
The absolute arithmetic deviations in estimated enthalpy of mixing ranged from 50 to 830 J/mole for four binary systems reported. Nagata et al recommended that both Gibbs free energy and enthalpies of mixing data should be used from which binary parameters must be determined to interpolate or extrapolate these properties.

Nagata et al [97] showed that assumptions of a quadratic function of temperature for the energy parameter differences is suitable for simultaneous correlation of excess Gibbs free energy and enthalpy of mixing data over a moderate temperature range from alcohol-hydrocarbon and hydrocarbon-hydrocarbon mixtures showing the superiority of the Wilson equation over NRTL and Heil equations.

Tai et al [155] developed a calculation technique utilizing the Wilson equation and total pressure data of binary systems and predicted isothermal vapour-liquid equilibrium data and enthalpies of mixing for binary and ternary systems.

- ASSOCIATED SOLUTION THEORIES

When one or some kinds of polar components are present in a solution, association between molecules plays an important role.
The concept of continued association was introduced by Lassettre [70]. Equations for free energy of mixing with a non-associating solvent have been derived by Tobolsky and Blatz [158], Scatchard [140], Redlich and Kister [129] and Flory [31]. The treatment of Redlich and Kister is successful in representing the behaviour of methanol in mixtures of various hydrocarbons.

Kretschmer and Wiebe [63] explained the thermodynamic properties of alcohol-hydrocarbon mixtures on the basis of association of the alcohol to form polymers. Their treatment is different from Redlich and Kister [129] in using Flory Huggins expression for free energy and an equilibrium constant in terms of concentrations rather than mole fractions.

Tompa [162] and Barker [8,9] derived an equation by constructing the partition function for the arrangement of molecules on lattice, when the energy of interaction depends on the relative orientation of the molecules concerned. They predicted correct shapes of curves for alcohol-hydrocarbon solutions. Barker [9] obtained good agreement with the experimental data for methanol-carbon tetrachloride and methanol-benzene solutions. The mathematical complexity of these theories is considerable.
Renon and Prausnitz [131] developed an association model based on the work of Flory [30] and Scatchard [140]. This model gives excellent representation of the enthalpies of mixing for alcohol-hydrocarbon mixtures. However, the model fails where degree of association is small or for dilute solutions.

Nitta and Katayama [107] have discussed the thermodynamic properties of associated solutions using two associated models. The first model deals with self associated systems. The second model deals with systems having species associated with like and unlike molecules. These models have been shown to give good representation of excess free energies and enthalpies of mixing for a variety of systems. Using Kretschmer-Wiebe type equation Nitta and Katayama [108] generated association parameters for alcohols which were correlated using the concept of solubility parameter for alcohols and branching parameters. These gives better correlation for vapour-liquid equilibria for alcohol-nonpolar systems and estimates for enthalpies of mixing were not encouraging.

2.3.2 Statistical Methods

Large amount of the work concerned with the theory of liquids involves the use of statistical methods. An
introduction to these theoretical methods was discussed by London [72]. Scott [144] has compared the theories based on "Regular solution" concept of Hildebrand [49,51] and Guggenheim [37], the conformal solution of Longuet-Higgins [73] and the "Cell Model" of Prigogine and Mathot [120]. He has shown that to the first approximation, thermodynamic functions obtained from these models are all equivalent. Barker [9] extended Gugenheim's method to solutions of polar molecules by determining three interaction energies in a binary system having one polar component. This requires experimental data to determine interaction energies and also the values of excess enthalpies are essential for practical solution of this method. Hence it is of little use.

Schnaible [142] has applied all these theories to ten binaries, six hydrocarbons and four alcohol-hydrocarbon systems. He concluded that no satisfactory method was available for predicting enthalpies of mixing from pure component data. He also pointed out the difficulty in dealing with polar systems to the assumption that molecular interaction is due to dispersion forces. Such assumption cannot be expected for polar substances where hydrogen bonds exist.

Boer [10] and Munster [87] have given excellent reviews of statistical methods. They concluded that from
the knowledge of molecular theory enthalpies of mixing cannot be predicted accurately from data of pure components alone. All improvements of existing theories remain guess work.

Many modifications to these theories have been proposed and new models have been developed. All of them, however, fail to predict good results for systems with complicated chemical formulae. For these reasons it has been customary to employ empirical or semi-empirical correlations for relating the thermodynamic properties.

2.3.3 Empirical Methods

- SERIES EXPANSION

Most of the empirical correlations used are based on series expansion, and are of two types, - ascending power series and descending power series.

The choice of the series generally depend on the nature of the data [5]. An ascending power series is recommended with the absolute value of the slope $\frac{dy}{dx}$ increases as $x$ increases; a descending power series when the value of the slope decrease as $x$ increases.

It two components 1 and 2 have comparable liquid molar volumes, are chemically not too different, it is observed that the ratio $h_{12}/x_{1}x_{2}$ is independent of composition at constant temperature and pressure. This means
\[
\frac{E}{x_1 x_2} = A \quad (20)
\]

Where \( A \) is only a function of temperature and pressure and not of composition.

For the general description of \( h \) data the above equation is not satisfactory and it has become a common practice to expand \( \frac{h}{x_1 x_2} \) as power series in mole fractions.

Hildebrand [50] proposed that any set of equations used to correlate enthalpies of mixing data should be symmetrical with respect to the two components. This conclusion was made in considering the shape of \( h \) vs \( x_1 \) curves for non-polar mixtures and was used by Scatchard [140] who proposed the following equation to fit the experimental enthalpies of mixing data.

\[
\frac{E}{x_1 x_2} = \sum_{n=0}^{\infty} A_n (x_1 - x_2)^n \quad (21)
\]

For polar-nonpolar systems, the deviation from linearity is appreciable. Plots of \( \frac{h}{x_1 x_2} \) for these two types of systems are shown in Figure 2.1 (a) and (b).

Due to large deviations for polar-nonpolar systems it is difficult to fit the data with the equation proposed by Scatchard. The reciprocal function \( x_1 x_2 / h \) presents a much more linear curve and can be fitted with fewer constants [169]. The proposed correlation was:
FIG. 2-1

(a) \( \frac{h^E}{x_1 x_2} \)

(b) \( \frac{h^E}{x_1 x_2} \)

(c) \( \frac{h^E}{x_1 x_2} \)

(d) \( \frac{x_1 x_2}{h^E} \)

FIG. 2-1
\[ E^{x_1 x_2/n} = \sum_{n=0}^{\infty} B_{n} (x-x_1)^{n} \quad \ldots \quad (22) \]

The curve \( E^{x_1 x_2} \) vs \( x_1 x_2 \) has decreasing slope and is represented by decreasing power function, whereas in the reciprocal function the slope is changed from a decreasing to an increasing power expansion. Figures 2.1 (c) and (d) show this phenomenon.

If sufficient number of terms are taken in the above Equation (21) it can be made to represent any set of data exactly. It is not wise to fit in this way since determination of constants is very laborious and the equation has numerous maxima and minima and does not represent the shape of the data as pointed out by Schnaible [142].

Van Ness and Klaus have proposed two numerical procedures for the representation of thermodynamic excess functions. First is the representation by orthogonal polynomials. The order of polynomial can be determined by an error analysis and by statistical tests. The excess properties have been well represented by these polynomials. Data for few exceedingly non-ideal systems were not correlated satisfactorily. For such cases, extension of the spline fit technique was proposed by Klaus and van Ness [60]. Enthalpies of mixing data of alcohol-alkane, water systems have been excellently fitted by this technique.
One successful series expansion was introduced by Redlich and Kister [130].

\[
\begin{align*}
\frac{E}{h} \times x^{1/2} = \sum_{i=0}^{n=1} A_i (2x \ 1) \quad \ldots \ldots (23)
\end{align*}
\]

Where \( A \) represents constants and \( n \) is the number of parameters.

The number of parameters which are needed to represent the experimental data depends on the complexity of the \( h/x_x \) curve, on the quality of the data and on the number of experimental points.

The number of parameters, \( n \), needed for a particular data set is determined on the basis of rather empirical analysis of the goodness of the fit. Plots of experimental and calculated values of \( h \) and \( h/x_x \) have been of great help for the choice of the 'best' number of parameters.

If experimental \( h \ vs \ x \) curve is highly skewed then the Redlich-Kister expansion will not always be appropriate. On the other hand, for systems which exhibit more simple composition dependence of \( h \), this equation is to be the best.

The modifications of Redlich-Kister equation have been proposed to overcome this difficulty. One of the well known is Myers-Scott [91] equation. Other equations, 'tailor-made' to certain classes of mixtures,
Another equation called the SSF (Sum of Symmetrical Functions) equation was proposed by Rogalski and Malanowski in 1977 [134]. This equation is far superior to Redlich-Kister equation for systems where $h vs x$ curve is highly skewed. In the SSF equation it is assumed that an excess function of a binary mixture can be represented as a sum of $m$ curves, each of which can be characterized by two parameters: one expressing the mole fraction corresponding to the extremum, and the other, determining the maximum value. The resulting equation is

$$h^E = \sum_{L=1}^{m} \frac{A_L x_1 x_2}{(\frac{x_1}{a_L} + \frac{x_2 a_L}{a_L})^2} \ldots\ldots(24)$$

Where $A_L$ and $a_L$ are parameters in the $L$th term, such that the number of parameters equals $2m$. The general form of this equation represents well asymmetrical curves and its parameters may be given a geometrical interpretation as explained by Rogalski and Malanowski [134].

Both the Redlich-Kister and the SFF equations may be extended to Multicomponent systems. The parameters have no physical meaning and it is not possible to
predict excess enthalpies for multicomponent mixtures from parameters estimated from data for binary systems.

- PRINCIPLE OF CONGRUENCE

A mathematical development which has been formulated to calculate the properties of a mixture from those of the pure components is called principle of congruence.

This principle states that the thermodynamic properties of a mixture of chain molecules from a homologous series, at a given temperature and pressure depends only on the average chain length $\bar{n}$ defined as:

$$\bar{n} = n_i x_i + n_j x_j$$

Where $n_i$ and $n_j$ are the number of carbon atoms of the molecules of species $i$ and $j$ respectively and $x_i$ and $x_j$ are their mole fractions. Mixtures of molecules with same chain length are called congruent.

Brönsted and Koefoed [12] used this principle to explain the thermodynamic properties of n-alkane mixtures. As the experimental results obtained were symmetrical with respect to mole fraction $x = 0.5$, the analytical form of the principle was a simple parabolic function with a maxima at $x = 0.5$.

$$\Delta G = - B (n - n_m)^2 x_i x_j$$

.....(26)
35

f(n) and f(n) in a series of descending powers of
• •
i J(n-2). This has not a validity because at n=2, the
excess function will become infinite.

Pena and Martin [25] expanded f(n), f(n) and
j
f(n) in a series of descending powers of n instead
of n-2, i.e.

\[ f(n) = \sum_{r=0}^{1-r} B_r n^{1-r} \]  
\[ \text{.....(30)} \]

They also tested the principle of congruence for
n-alcohols and found that it was corroborated by
following methods.

- Graphical (According to Hijmans [47])
  - equation of type
  \[ h^{E}_{ni/nj} = x_i x_j \sum_r A_r (x_i-x_j)^r \]  
  \[ \text{.....(31)} \]

- equation of type 28
- equation of type 30

In the further study of limitations of principle
of congruence Holleman and Hijmans [52] modified their
graphical principle as a function of the principle of
congruence and enthalpies of mixing of four mixtures:

\[ h^{E}(n_i, n_j, n, T) = h^{E}(n_1, n_2, n, T) - \frac{n_j - \bar{n}}{n_j - n_i} h^{E}(n_1, n_2, \bar{n}, T) \]
\[ - \frac{n - \bar{n}}{n_j - n_i} h^{E}(n_1, n_2, n, T) \]  
\[ \text{.....(32)} \]
Where $n_1$ and $n_2$ are the number of carbon atoms in the reference system made up of components 1 and 2. Four mixtures considered in above equation are:

- $(n_1, n_j, \bar{n})$ is the mixture for which it is desired to predict the value of the enthalpies of mixing. $n_1$ and $n_j$ are the number of carbon atoms in pure components 1 and j;

- $(n_2, n_j, \bar{n})$ is the mixture corresponding to the reference system having the same average number of carbon atoms as per mixture above;

- $(n_1, n_2, \bar{n})$ is the mixture corresponding to the reference system having an average number of carbon atoms equal to $n_1$;

- $(n_1, n_2, n_j)$ is the mixture corresponding to the reference system having an average number of carbon atoms equal to $n_j$.

From the study of the above principle applied to n-alkane mixtures, following conclusions were made:

- The principle can be used as a first approximation at one temperature.

- For mixtures near room temperature the principle is quantitatively correct.

- This is also the case at higher temperature for mixtures having the same volatile component as that of the reference system.

Because of these limitations, data for systems having a different less volatile component are necessary to predict enthalpies of mixing at a given temperature and pressure.

Ramalho and Ruel [121] developed extension of the principle of congruence. This model uses enthalpies of mixing data for two reference systems having the same less volatile component. With same model and two
reference systems these authors proposed enthalpies of mixing for all binary systems formed of n-alkanes at the reference temperature where \( n > 7 \). They also showed the applicability of their model to n-alcohol and n-alcohol - n-alkane systems. The calculated values for ketone mixtures were claimed to be within 10% of the experimental values.

- GROUP INTERACTIONS

The basic idea of Group Interaction theories is that the total interaction energy of two molecules in contact can be represented as the sum of contribution of pairs of interaction group (CH\(_3\), CO, OH, C=C, etc.). The contribution of each pair of group is assumed to be independent of the nature of the molecules involved and dependent on group concentrations and energy parameters which describe the group interactions in solution.

Homologous series of components are made up of few groups. Once the group parameters are evaluated, mixture properties can be predicted for all mixtures containing these groups.

Group interaction theories have been proposed in various forms [13, 140, 161] after the original work of Langmuir [69]. A group interaction theory for enthalpies of mixing was developed by Redlich et al [128] and was
tested by Papadopoulos and Derr [114] on hydrocarbon mixtures. The main features of this were:

- The interaction energy of molecules is considered to be the sum of the individual contributions due to contacts between the groups and radicals in the molecules. The contribution of each contact is dependent of the two groups concerned and is independent of other groups of the same molecules or of other molecules in the mixture.

- The relative frequency of interactions along the groups is assumed to be dependent on the cross section of groups.

For groups which have interaction energy of comparable magnitude, it is reasonable to expect that relative frequencies of interactions are governed by geometrical property - group cross section or group free surface area. For solutions containing polar components interaction energies can be of different order of magnitude and strongly attracted pairs such as OH radicals, will interact preferentially. Hence the relative frequency of interaction is governed by energy properties of the groups and their geometrical properties.

From the above consideration Chao et al [17] developed a group interaction theory. The probability of group interaction with a group depends on free surface area of the groups and the ratio of interaction energy between the two groups to its associated thermal energy. Taking these assumptions into consideration
Chao et al obtained the following equations for the energy of vapourization into vacuum for pure liquids ($\Delta U^v$) and for the molar energy of vapourization into vacuum of mixtures containing polar substances ($\Delta U^M$)

$$-\Delta U^v = \frac{1}{2} \sum_{u<v} \left( \frac{A_u A_v}{A_w} \exp \left( -\frac{S_{uv} \lambda_{uv}}{kt} \right) \right) \lambda_{uv} \cdots (33)$$

$$-\Delta U^M = \frac{1}{2} \sum_{u<v} \sum_{j<k \in u<v} x_j x_k A_{uj} A_{vk} \exp \left( -\frac{S_{uv} \lambda_{uv}}{kt} \right) \lambda_{uv} \cdots (34)$$

The enthalpy of mixing is related to the energy of vapourization into vacuum by the following equation.

$$h = \sum_i x_i (\Delta U^v_i) - \Delta U^M \cdots (35)$$

Chao et al [17] on testing their group interaction theory, on binary mixtures of n-alcohol-n-alkane, found that best agreement between experimental and predicted values of $h$ was at high alcohol concentration for mixtures of high molecular weight components. Least satisfactory agreement occurred at low alcohol concentrations for all systems studied.

Kuo et al [66] reexpressed the quasi lattice theory advanced by Guggenheim [38] and Barker [9]. They have tested their theory on nine n-alcohol-n-paraffin mixtures and found that best agreement between experimental and predicted values of $h$ was reached at
high alcohol concentrations, similar to that concluded by Chao et al [17].

Nitta et al [109] developed a group interaction molecular model for quantitative description of the thermodynamic properties of liquids of polar and non-polar substances and their solutions. This model is based on cell theory and gives reliable estimates of energies of vapourisation and densities of pure components, activity coefficients and enthalpies of mixing for a variety of mixtures made up of methyl, methylene, hydroxyl and carbonyl groups.

Another development in group interaction technique is the concept of solution of functional groups. This has been used to predict thermodynamic as well as transport properties [32, 75, 76, 94, 101-104, 123, 124, 135, 178].

- AGSM MODEL -

The analytical group solution model (AGSM) of Nguyen and Ratcliff [101-104] is based on the following assumptions:

- The non-ideal behaviour of a molecule in solution may be broken down into two independent parts. One is associated with overall skeleton of the molecule and reflects the number of groups. This term does not appear, however, in the expression for enthalpy of mixing since it drops out in the differentiation with respect to
temperature. The second term reflects interactions between the groups in solution and it is evaluated for AGSM/ASOG model from Wilson's equation.

- The groups are assumed to act independently.
- The standard state chosen for groups is that of the pure molecular species under consideration.
- The group excess enthalpies are functions only of the group composition, temperature and pressure.

The model is summarized by the following equations:

\[
E = \sum_i x_i h_i \quad \cdots (36)
\]

\[
h = \sum_i N_{ki} (h - h_i) \quad \cdots (37)
\]

\[
\frac{h_k}{RT^2} = \sum_i x_i \frac{b_{kj}}{k_j} + \sum_j x_j \frac{c_{kj}}{k_j} - \sum_m x_m \frac{b_{jm}}{m_j} \quad \cdots (38)
\]

Where

\[
x_k = \text{mole fraction of group } k \text{ in the mixture.}
\]

\[
x_k = \frac{\sum_i x_i N_{ki}}{\sum_k \sum_i x_i N_{ki}} \quad \cdots (39)
\]

\[
h \text{ is calculated from Equation 38 using the group fraction of group } k \text{ in pure component } i. \text{ The group interaction parameters } b_{kj}, c_{kj} \text{ are related as}
\]

\[
b_{kj} = \frac{\Delta}{RT} (c_{kj}) \quad \cdots (40)
\]
Nguyen and Ratcliff used the experimental enthalpies of mixing for computing group excess enthalpies \( h_k \) as a function of \( X \) for mixtures of methylene and hydroxyl groups. The principle of congruence formulated by Holleman and Hijmans [52] was used for computing skeletal contributions. The model was tested on 14 binary and two ternary systems. Root-mean-square deviation of about ten percent was recorded for alcohol-alkane mixtures. Later on Nguyen and Ratcliff [102] extended the model to mixtures containing aliphatic hydrocarbons and ketones.

Nguyen and Ratcliff [103] used the Wilson equation in the analytical representation of group excess enthalpies. The group excess enthalpies are related to the group activity coefficients through the well known Gibbs - Helmholtz relation,

\[
\frac{\partial}{\partial T} \left( \ln \gamma_k \right)_{p,x} = - \frac{1}{RT} \frac{\partial}{\partial T} h_k \quad \text{ ....(41)}
\]

The form of the Wilson equation in representing group activity coefficients is [22]:

\[
\log \gamma_k = \log \gamma_1 + a_{k1} + 0.434 \left[ 1 - \sum_{\substack{1 \leq i \leq X \leq m \geq m \geq 1 \geq m}} a_k \right] \quad \text{ ....(42)}
\]

The model parameters were generated using the experimental enthalpies of mixing of alcohol mixtures. The model was then tested on the reference systems with
an average root mean square deviation of five percent.

The overall performance of ASOG method for the calculation of vapour-liquid equilibria and enthalpies of mixing for hydrocarbon-hydrocarbon systems have been improved by Vera and Vidal [171]. The following modifications have been made:

- a new combinatorial (athermal) contribution has been used.
- distinction has been made between methyl and methylene groups bonded to an aromatic ring and same group in an aliphatic chain. A CH$_3$ group bonded to an aromatic ring is equivalent to 0.8 CH$_2$ group and CH$_2$ group bonded to an aromatic ring is equivalent to 0.5 CH$_2$ groups.
- data of total pressure liquid composition and of enthalpies of mixing have been directly used for evaluation of group parameters.

Chao, Greenkorn, Nitta, [34, 109], developed an interaction model for liquids and their solutions. This give reliable estimates of enthalpies of mixing for binary mixtures composed of methyl, methylene, hydroxyl and carbonyl and other groups.

Many other developments involving group interaction theory have come up during recent years [33, 35].

-ZETA EQUATION-

The Zeta equation [54] is based on an extension of regular solution theory to include the concept of "Free coordinates" where the number of independently
determinable neighbours for a given molecule lies closer to unity than the actual coordination number depending on structure. The equation is:

\[
\frac{E_g}{RT} = -\lambda \left( x_1 v_1 + x_2 v_2 \right) \left[ \phi_1 \ln \left( \phi + \Delta_{12} \phi \right) + \phi_2 \ln \left( \phi + \Delta_{21} \phi \right) \right] + x_1 \ln \left( \phi / x_2 \right) + x_2 \ln \left( \phi / x_1 \right)
\]

Where:

\[
\phi_1 = \frac{x_1 v_1}{x_1 v_1 + x_2 v_2}
\]

\[
\phi_2 = \frac{x_2 v_2}{x_1 v_1 + x_2 v_2}
\]

\[
\Delta_{12} = \exp \left( -\frac{C_1 - C_{12}}{\lambda RT} \right)
\]

\[
\Delta_{21} = \exp \left( -\frac{C_2 - C_{21}}{\lambda RT} \right)
\]

\[
\lambda = \frac{s}{v_1 v_2}
\]

The Zeta equation has two parameters \( C_{ii} \) and \( C_{ij} \) assumed to be independent of temperature and in addition a third parameter \( s \). Nicolaides and Eckert [106] have tested these equations along with Wilson and NRTL equations over 20 binary systems.
The UNIQUAC model is discussed in detail by Abramas and Prausnitz \[2\] and UNIFAC by Fredenslund \[32\]. In the Uniquac equation the local area function is used as the primary concentration variable in connection with Guggenheim's quasichemical analysis \[39\]. The equation is:

\[
\begin{align*}
E_{\text{UNIQUAC}} = & \frac{RT}{1} \ln \left( \frac{\phi_1}{x_1} \right) + \frac{RT}{2} \ln \left( \frac{\phi_2}{x_2} \right) \\
& + \frac{Z}{2} \left[ \phi_1 \ln \left( \frac{\theta_1}{\phi_1} \right) + \phi_2 \ln \left( \frac{\theta_2}{\phi_2} \right) \right] \\
& - q_x \ln \left( \frac{\theta + \theta v}{\phi} \right) - q_x \ln \left( \frac{\theta + \theta v}{\phi} \right) \\
\end{align*}
\]

\[v = \exp \left[ - \frac{u - u}{RT} \right] \quad \ldots (49)\]

\[v_{12} = \exp \left[ - \frac{u_{12} - u_{22}}{RT} \right] \quad \ldots (50)\]

\[v_{21} = \exp \left[ - \frac{u_{21} - u_{11}}{RT} \right] \quad \ldots (51)\]

\[\theta = \frac{q_x}{(q_x + q_x)} \quad \ldots (52)\]

\[\theta = \frac{q_x}{(q_x + q_x)} \quad \ldots (53)\]

\[
\begin{align*}
E_{\text{UNIQUAC}} = & - \frac{RT}{1} \ln \left( \frac{\theta_1}{x_1} \right) - \frac{RT}{2} \ln \left( \frac{\theta_2}{x_2} \right) \\
& - q_x \ln \left( \frac{\theta + \theta v}{\phi} \right) - q_x \ln \left( \frac{\theta + \theta v}{\phi} \right) \\
\end{align*}
\]

\[h = - \frac{RT}{1} \ln \left( \frac{\theta_1}{x_1} \right) - \frac{RT}{2} \ln \left( \frac{\theta_2}{x_2} \right) \quad \ldots (54)\]
\[ v' = \frac{\delta v}{\gamma (1/T)} \] 

(55)

Nagata [95] tested the Wilson, NRTL and UNIQUAC equations over three alcohol-methyl ethyl ketone and methyl acetate systems. They concluded that Wilson and NRTL gave better fit of excess enthalpies than UNIQUAC equation.

The introduction of a general temperature function for the coordination numbers in the UNIQUAC and UNIFAC models have led to substantial improvements. A detailed review of this parameter is given by Jorgensen et al [57] and the temperature function was optimized for systems containing non-associating components. The modified models are able to fit \( h \) and vapour-liquid equilibrium data almost as accurately as the original models. Jorgensen et al indicated that UNIQUAC equation \( E \) is good for \( h \) up to about 1000 J/mol.

The UNIFAC group contribution model which is frequently used to predict activity coefficients in cases where limited or no data are available was considered for the prediction of enthalpies of mixing by Fredenslund and his co-workers [32] using the temperature independent parameters obtained from vapour-liquid equilibrium data. They concluded that predictions of enthalpies of mixing were poor. Several investigators
[27,82,94] have introduced temperature dependent parameters in local composition models leading to considerable improvements.

Nagata and Ohta [94] used temperature dependent parameters to successfully predict enthalpies of mixing for mixtures of alkanes with alcohols, ketones, esters and ethers.

Rupp et al [137] compared the UNIFAC and ASOG models with temperature dependent interaction parameters and the modified UNIFAC model by Jorgensen et al [57] in the prediction of enthalpies of mixing. Of the three group contribution models, they concluded that the latter which involves temperature independent interaction parameters with a universal temperature dependency for the coordination number $z$, is simpler and gives best results. Primary parameters are given for CH$_2$O$_2$ with 19 groups. In the temperature range 0 to 100°C results are reasonably good except for systems - where strong association is present (alcohols and acids).

The enthalpy of mixing $h$ can be calculated from the excess Gibbs free energy $g$ using the relation 11.

The $g$ expression for all models contain two terms: the combinatorial and residual.

Use of these two models in conjunction with Equations 11, 36, 37, yields:
\[
\frac{h}{k} = \frac{Q}{RT} \left[ \sum_{m} \theta_{m} \psi_{m}^{'} \left( \frac{\theta_{m}}{\sum_{n} \theta_{n} \psi_{nm}} \right) - \frac{1}{\sum_{n} \theta_{n} \psi_{nm}} \left( \sum_{n} \theta_{n} \psi_{nm} \psi_{nm}^{'} \right) \right] \quad \ldots(56)
\]

\[\theta_{m} = \text{area fraction of group } m\]
\[Q = \frac{\sum_{m} \theta_{m} \psi_{m}}{\sum_{n} \theta_{n} \psi_{nm}} \quad \ldots(57)\]
\[X = \frac{\sum_{m} \theta_{m} \psi_{m}^{'} \psi_{nm} \theta_{m}}{\sum_{m} \theta_{m} \psi_{m}^{'} \psi_{nm}} \quad \ldots(58)\]

\[\psi_{mn} = \exp \left( - \frac{Z_{mn} \cdot a}{2T} \right) \quad \ldots(59)\]

\[\psi_{mn}^{'} = \frac{\partial \psi_{mn}}{\partial T} \quad \ldots(60)\]

\[Z = Z(T) = 35.2 - 0.1272 \cdot T + 0.00014 \cdot T^{2} \quad \ldots(61)\]

\[Z = \text{temperature dependent coordination number}\]
\[a = \text{temperature independent interaction parameter between groups } m \text{ and } n.\]

The UNIFAC model used by Jorgensen [57], Rupp et al [137] for prediction and correlation of enthalpies of
mixing is further developed by Stathis and Tassios [152]. The approach of Rupp et al is modified to account for the presence of association. It has been suggested [129, 131] that the enthalpy of mixing of an associated solution can be separated into two additive contributions: one physical and the other chemical.

\[ E = h_p + h_c \] ......(62)

The chemical contribution results from the chemical equilibria of hydrogen bonding polymerization reactions and the physical part from the physical (van der Waals) forces. The physical part reflects the interaction among groups and is described by the UNIFAC model. The \( h_p \) is calculated using the Equations 36, 37, 56-61.

For the chemical part, the procedure given by Prausnitz [117] based on Flory's [30] lattice model is followed. The following assumptions are made:

- In a non-alcohol (A) - alcohol (B) solution, the alcohol exists in the form of hydrogen bonded polymers formed by successive reactions of type

\[ B + B = B_n \]

The association constant for such reactions is independent of \( n \).

- The molar volume of \( n \)-mer is given by the molar volume of the monomer multiplied by \( n \).

- There are physical interactions between all the molecules which can be accounted for by the UNIFAC model.
The temperature dependency of the association constant, $K$ is such that the heat of formation of hydrogen bond, $h_{f}^{o}$ is independent of the temperature and degree of association.

The expression for $h$ as obtained from Flory's theory is:

$$h = -K h_{f}^{o} [ \ln \left( \frac{\phi_{B1}}{\phi_{B1}^{*}} \right) ]_{B} + x \left( \frac{\phi_{B1}}{\phi_{B1}^{*}} \right)_{B} + K x \left( \frac{\phi_{B1}}{\phi_{B1}^{*}} \right)_{K} $$

$$+ K x \left( \frac{\phi_{B1}}{\phi_{B1}^{*}} \right)_{B} \left( \frac{\phi_{B1}^{*}}{\phi_{B1}^{*} - \phi_{B1}} \right) $$

... (63)

where

$$\phi_{B1}^{*} = \frac{1 + 2K}{2K^2} \left( \phi_{B1} - \frac{1}{Y} \right) $$

$$\phi_{B1} = \lim_{x \to 0} \phi_{B1}^{*} = \frac{1 + 2K - 1/Y}{2K^2} $$

$$Y = (1 + 4K)^{-1/2} $$

$$Y^{*} = (1 + 4K)_{B}^{-1/2} $$

The association constant $K$ can be obtained from its value $K_{o}$ at some reference temperature $T_{o}$ by the equation:

$$\ln K = \ln K_{o} - h_{f}^{o} \left( \frac{1}{T_{o}} - \frac{1}{T} \right) $$

... (68)
From above equation $h$ is given by

$$h = h_c \left[ x \left\{ \frac{1-Y}{B_1 K B} - \frac{1-Y^*}{K B_1} \right\} + K x \right]$$

Equation $(69)$

Stathis and Tassios [152] developed the following expression for the association constant $K$ of alcohols at $T = 50^\circ C$.

$$K = a (N^b) \quad \ldots(70)$$

$N$ is the number of carbon atoms in alcohol ($>2$), and $b = -0.435$ for all alcohols. $a = 145.0$ for primary alcohols. For methanol $K = 450$ and for ethanol $K = 190$ respectively. They also recommended a value of $h = -7.0$ kcal/mol for all alcohols.

With the introduction of a "Chemical Term" to account for association effects, Stathis and Tassios improved significantly the correlation and prediction results for systems containing alcoholic compounds. The model can be reliably used in the range $0$ to $100^\circ C$ and has also been successfully applied to cyclic alcohols. Errors are claimed to be in the range of $5-15\%$. 
In another recent study by Dang and Tassios [21] using the modified UNIFAC model of Skjold-Jorgensen et al and Stathis, Tassios [57, 152] it is concluded that this model provides a reliable method to estimate the enthalpies of mixing for a large variety of organic mixtures. A total of 172 pairs of interaction parameters are given by Dang et al. Prediction results are in a temperature range of 1-100°C and the error is claimed below 15%. It is also predicted that for systems containing cyclic compounds poorer results may be encountered in spite of the improvement realized by including the interaction parameters for cyclic and non-cyclic pair.

In this chapter predictive methods for enthalpies of mixing based on different theories have been discussed. Though a number of methods have been proposed, methods based on group contribution techniques enable systematic prediction of thermodynamic properties for a number of mixtures. The most important advantage of group interaction models is that mixture properties can be predicted by knowing the molecular structure only, even if no mixture data are available.

The experimental results of present work have been compared with the predictive values of enthalpies of mixing by using UNIFAC and ASOG models.