CHAPTER II
LITERATURE REVIEW

2.1 General

The vast amount of literature available on different aspects of vapour-liquid equilibria makes the task of presenting a comprehensive review of all aspects in a thesis extremely difficult, necessitating confinement to the aspects that are of immediate relevance to the thesis.

The description of vapour-liquid equilibria would be the simplest if both the vapour and liquid phases are ideal. The vapour phase is ideal if it obeys the perfect gas laws. The liquid phase is ideal if, at constant temperature and pressure, the partial molar Gibbs free energy of each species in the mixture is dependent only on the mole fraction of the species. The partial molar enthalpy and the partial molar volume of any component in an ideal mixture are the same as the pure component molar enthalpy and molar volume respectively at the same temperature and pressure. That is, the excess thermodynamic functions are zero for an ideal mixture. This definition is a general one and is applicable to either vapour or liquid phases. Though mixtures of real fluids do not form near-ideal solutions, mixtures of similar compounds form near-ideal solutions. The excess thermodynamic functions relate the properties of real solutions to those of ideal solutions. For the consideration of vapour-liquid equilibria the excess free energy
of mixing is the most useful excess property because of its direct relationship to the activity coefficients, by the equation

$$g^E = RT \sum \frac{x_i}{\gamma_i} \ln \gamma_i$$

(2.1)

If $g^E$, for a solution, is greater than zero, the solution is said to be exhibiting positive deviations whereas if it is less than zero the solution is said to be exhibiting negative deviations.

For low pressures, the molecules in the vapour phase are far apart and their interactions become less frequent and often the vapour phase approaches ideality. The liquid phase is much denser and the molecular interactions are of much greater magnitude than those for the vapour phase and quite often the assumption that all the nonideality exists in the liquid phase is justified especially at low and moderate pressures. The vapour phase nonideality is described by means of an equation of state whereas activity coefficients are used to describe the liquid phase nonideality. Generally the vapour phase nonideality effects are combined with those of the liquid phase and described by the use of a single activity coefficient. Recently Ouyang and Othmer [307] used a 'nonideality coefficient' in place of the activity coefficient in a correlation developed by them. The 'nonideality coefficient' was obtained considering that for many liquid mixtures 'pure state' and 'mixed state' coexist.

The virial equation of state

$$\frac{PV}{RT} = 1 + \frac{B}{V} + \frac{C}{V^2} + \ldots$$

(2.2)

has received wide application in the determination of vapour phase
nonideality. The reason for its choice is that it is simple with a sound theoretical foundation. Each virial coefficient can be interpreted in terms of molecular properties. For moderate densities below the critical, the terms containing the third and higher order coefficients can be neglected.

The activity coefficients can be calculated by the following equation which combines the vapour phase nonidealities with those of the liquid. This equation is applicable at moderate to low pressures to normal systems with slight vapour phase imperfections:

$$\gamma_1 = \frac{\pi y_1}{\phi_1 x_1} \exp \left[ \frac{(B_1-V_1)(x-p_1^0)}{RT} + \frac{\pi \delta_{12} y_2^2}{RT} \right]$$  \hspace{1cm} (2.3)

where $$\delta_{12} = 2B_{12} - B_{11} - B_{22}$$  \hspace{1cm} (2.3a)

the interactions $$B_{11}$$, $$B_{12}$$, and $$B_{22}$$ are the second virial coefficients for pairs of molecules in collisions 1-1, 1-2, and 2-2, respectively. This equation is derived for binary mixtures [417]. A similar expression is obtained for component 2 by interchanging the subscripts. $$\delta_{12}$$ can be approximated to zero especially for mixtures of nonpolar molecules and Equation 2.3 simplifies to the following form proposed by Mertes and Colburn [260]:

$$\gamma_1 = \frac{\pi y_1}{\phi_1 x_1} \exp \left[ \frac{(x-p_1^0) (B_1-V_1)}{RT} \right]$$  \hspace{1cm} (2.4)

This equation results from the assumption that the vapour is not a perfect gas mixture but an ideal mixture of imperfect gases. This assumption is generally more nearly correct than that $$B_{11}$$, $$B_{12}$$, and $$B_{22}$$ are all zero. This equation is widely used for the inclusion of
slight imperfections in the vapour phase into the activity coefficients at atmospheric or below atmospheric pressures involving nonassociating compounds. This equation requires only pure component properties for the estimation of vapour phase imperfections and is applicable to binary or multicomponent systems.

Another familiar form uses fugacity coefficients \[ f_1^{\text{OL}} \]

\[ Y_1 = f_1^{\text{OL}} x_1 \]  

(2.5)

The fugacity coefficient \( f_1 \) is given by

\[ \ln f_1 = 2 / v \sum_{j=1}^{N} y_j B_{ij} - \ln Z \]  

(2.6)

The compressibility factor \( Z \) is evaluated from the virial equation truncated after the second term

\[ Z = P_v/RT = 1 + \sum_{i=1}^{N} \sum_{j=1}^{N} y_i y_j B_{ij} / v \]  

(2.7)

The liquid phase fugacity in the reference state \( f_1^{\text{OL}} \) is

\[ f_1^{\text{OL}} = f_1^{\circ} \exp \left[ \frac{v x_1}{RT} \right] \]  

(2.8)

The reference fugacities for pure components are calculated by

\[ f_1^{\circ} = \varphi_1^{\circ} \exp \left[ -V_1 P_1^{\circ} / RT \right] \]  

(2.9)

where \( \varphi_1^{\circ} \) is the fugacity coefficient of pure vapour \( i \) at temperature \( T \) and saturation pressure \( P_1^{\circ} \). \( \varphi_1^{\circ} \) can be calculated from the generalised three-parameter correlation of Lyckman et al. [234]

\[ \ln \varphi_1^{\circ} = (\ln \varphi_1^{\circ})^{(0)} + \omega_1 (\ln \varphi_1^{\circ})^{(1)} \]  

(2.10)

where \( (\ln \varphi_1^{\circ})^{(0)} \) and \( (\ln \varphi_1^{\circ})^{(1)} \) are generalised functions of the reduced temperature, given in tabular form [234].

This correlation is finding increasing use in the calculation of activity coefficients for moderately nonideal vapour phase.
Scheibel [367] presented a nomograph which combines in a single chart all the empirical equations for correcting the calculated activity coefficients for the vapour phase imperfection. This nomograph is applicable for normal fluids at moderate pressures.

Marek and Standart [247] and Marek [246] made a detailed theoretical study of systems where dimerisation of one of the components takes place, and developed equations for obtaining activity coefficients from vapour-liquid equilibrium data for associating substances and illustrated the method with some binary mixtures of acetic acid at atmospheric pressures. There is a growing interest for the study of vapour-liquid equilibria for reactive and associative systems. Prausnitz [318] presented a good review of the theories for the calculation of activity coefficients for associative and reactive systems. Engalbert [88] discussed a calculation method for associated binary systems and extended it to multicomponent systems.

2.2 Physical Properties

From the discussion in the preceding section, it can be seen that the calculation of activity coefficients requires vapour pressures, second virial coefficients, and liquid molar volumes for the pure components which are all functions of temperature. Of these, vapour pressure is the most important property requiring high accuracy in its estimation in order to obtain reliable activity coefficient data. In addition to these, some mixture properties are also required. For the vast number of commonly used organic compounds, to find experimental data would be rather inconceivable especially at the temperatures at which they are required. For mixtures the possibility
becomes still remote. It is, therefore, necessary to use some
generalised relationships that yield numerical values for the
desired properties.

For a large number of compounds experimental vapour pressure
data are available in normal literature sources [8, 74, 388, 408,
424]. Experimental data for second virial coefficients and liquid
molar volumes are available to a limited extent [8, 73, 77, 173,
215, 216, 408].

Reid and Sherwood [348] presented an excellent review of the
property estimation methods. Most of the methods require pure
component constants like molecular weight, normal boiling point,
critical properties, dipole moment, acentric factor, etc. These
constants might be available or sometimes need to be estimated.
The methods for the estimation of these constants are not discussed
in this review. They are available in the literature [348].

2.2.1 Vapour Pressures

A large number of correlations mostly based on the Clapeyron
equation

$$\frac{dP^0}{dT} = \frac{H_v}{TV_v}$$  \hspace{1cm} (2.11)

have been proposed from time to time relating temperature, vapour
pressure, and latent heat of vaporisation. In recent years some
attempts have been made to compare some of these correlations in
representing vapour pressure data of a wide variety of substances.

Detailed comparison of a number of vapour pressure correlations
covering a large number of compounds over a wide range of pressures
was made by Miller [261]. This study covers about a dozen general
types of equations with a large number of variants. The study covers
Figure 6. Equilibrium Diagram
System: Methanol-Benzene-1,2-Dichloroethane
SYSTEM: METHANOL - BENZENE - 1,2-DICHLOROETHANE

REFRACTIVE INDEX

E/G.6 6 ANALYTICAL DIAGRAM

SPECIFIC GRAVITY
FIG. 27  T-X-Y DIAGRAM
SYSTEM: ETHYLBENZENE--FURFURAL
FIG. 52 HIRATA'S A-Y DIAGRAM

SYSTEM: 1,2-DICHLOROETHANE-ETHYLFENE
FIG. 61 HINTAS X-Y DIAGRAM
SYSTEM: ETHYL BENZENE-ANISOLE
two pressure ranges, namely, \(10 - 1500\) mm of Hg and \(T_b - T_c\). The equations were divided into three classes, namely, reduced, semi-reduced, and nonreduced and for each class recommendations were made for their choice for the two pressure ranges. It was considered that the reduced equations are superior in the \(T_b - T_c\) region whereas semi-reduced or nonreduced equations in the \(10 - 1500\) mm of Hg pressure region. The MFA equation (Equation 2.14, Table 2.1) was found to be the most accurate in the low pressure region while the RPMH equation (Equation 2.17, Table 2.1) was found to be the best overall equation for the high pressure region. Othmer and Huang [297] made a thorough comparison of the reference substance equation first proposed by Othmer nearly 30 years back [292] with the equations studied by Miller [261 - 263] using the same compounds and the same statistical methods of analysis utilised by Miller. They found that the reference substance equation gives satisfactory results for each group of compounds over the entire pressure range and for better results in the high pressure region between \(T_b\) and \(T_c\) than the other equations. A number of extensions for the reference substance equation were published by Othmer and his coworkers in a series of articles [293, 294, 299, 303, 304].

Reid and Sherwood [348] presented a comprehensive review of vapour pressure equations with recommendations for their choice. Gold and Ogle [123] evaluated four variations of the Riedel correlation for accuracy and reliability over a wide range of vapour pressures and found that the choice of the correlation depends to a large extent on the range of vapour pressures and the nature of the substance.

Vapour pressure correlations with specific applications were reported from time to time. Thek and Stiel [404] developed a vapour
pressure relation which is quite accurate though rather complex algebraically. It is claimed that this equation accurately predicts vapour pressures for polar and polar hydrogen-bonding substances. Halm and Stiel [133] extended Pitzer's acentric factor [314] approach to the vapour pressures for polar compounds by the introduction of a polarity correction term which has improved the ability to correlate vapour pressures of highly polar compounds at low reduced temperatures. Ochley [285] derived an equation which is claimed to be accurate for the calculation of vapour pressures for associating as well as non-associating compounds. Nakanishi [274] proposed an Antoine-type equation which is claimed to be reproducing vapour pressure data accurately for different types of liquids including some cryogenic liquids at low and medium pressure ranges and discussed its applications to the prediction of the behaviour of binary azeotropes. Harlacher and Braun [136] used parachor as fourth parameter in the extension of the corresponding states principle for vapour pressures which is claimed to given an average deviation of 4.92 percent for 5952 data points representing 242 substances. The correlation gave substantial improvement for associating compounds over the correlations based on the three parameter corresponding states principle. For normal substances the results were of the same order of accuracy as with the three-parameter correlations. It was found that the use of parachor as the fourth parameter substantially improves vapour pressure correlations for the associating substances. No added advantage resulted for normal substances. Williamson [437] obtained a correlation for vapour pressures of homologous compounds which is claimed to be of the same accuracy as the Cox charts. Smialek and Thodos [379] gave a
vapour pressure relationship for normal paraffins which was tested on ten n-paraffins giving an average deviation of 1.81 percent for 72 experimental points extending up to the critical point.

In this work a comparison of data fit in the Antoine [12], Miller semi-reduced [262], Miller-Erpenbeck [261], \text{RFME} and \text{RFMH} versions of the Riedel-Plank-Miller [262, 263] correlations was made for ten different types of compounds which constituted the binary and ternary systems in this thesis. A total of 176 data points, extending over the temperature ranges for the systems, were used. Table B.4 (Appendix B) gives the average deviations for each compound in mm of Hg from the experimental data showing that the Antoine equation is better than the other equations in most of the cases. However, this comparison by itself does not lead to any general conclusions as it has been made with a limited objective. But it lends strength to the practice of using the Antoine equation to represent vapour pressure data in the calculation of activity coefficients to describe low pressure vapour-liquid equilibria.

Table 2.1 gives some of the important equations discussed in the preceding paragraphs.

2.2.2 Second Virial Coefficients

Reid and Sherwood [348] discussed the application of potential functions for the estimation of second virial coefficients and recommended that the Lennard-Jones potential be used for their estimation for nonpolar molecules and the Stockmayer potential for polar molecules. Hirschfelder, Curtiss, and Bird [157] and Prausnitz [318] discussed most of the potential functions and their applications for the estimation of second virial coefficients. Increasing attention
<table>
<thead>
<tr>
<th>Name</th>
<th>Equation</th>
<th>No.</th>
<th>Ref.</th>
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<tbody>
<tr>
<td>Antoine</td>
<td>( \log P^o = A - B/(C + t) )</td>
<td>2.12</td>
<td>[12]</td>
</tr>
<tr>
<td>Wrede</td>
<td>( \log P^o = A - B/T )</td>
<td>2.13</td>
<td>[442]</td>
</tr>
<tr>
<td>MRA</td>
<td>( \log P_{atm}^o = \frac{k}{T_R} \left( \frac{1}{T_R} \left( 0.60706 T_R - 1.44779 \right) - \frac{I_b}{T_R} - 0.98045 \right) )</td>
<td>2.14</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( I_b = -1.44779 \left( T_{rb} - 1 / T_{rb} \right) + 0.60706 \left( T_{rb} - 4/T_{rb} \right) )</td>
<td>2.14a</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( k = \log P_c/ \left( I_c - I_b \right) )</td>
<td>2.14b</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( I_c = -1.82118^p )</td>
<td>2.14c</td>
<td>[261]</td>
</tr>
<tr>
<td>EB2</td>
<td>( \log P_{atm}^o = A - B'/\vartheta + \log \left( 1 - C_b \vartheta \right) )</td>
<td>2.15</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( B' = 0.4343 \left[ 1.03 H_b/RT_b + C_b/(1 - C_b) \right] )</td>
<td>2.15a</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( A = B' - \log \left( 1 - C_b \right) )</td>
<td>2.15b</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( \vartheta = T/T_b )</td>
<td>2.15c</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( C_b = 0.512 + 4.3 \times 10^{-4} T_b ) (Organics)</td>
<td>2.15d</td>
<td></td>
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Table 2.1 (Continued)

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<thead>
<tr>
<th>Name</th>
<th>Equation</th>
<th>No.</th>
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<tbody>
<tr>
<td>$C_b$</td>
<td>$= 0.59 \ (\text{Inorganics})$</td>
<td>2.15e</td>
<td>[261]</td>
</tr>
<tr>
<td>RPME</td>
<td>$\log P_r = -G/T_r \left[ 1 - T_r + k \left( 3 + T_r \right) \right] \left( 1 - T_r \right)^2$</td>
<td>2.16</td>
<td></td>
</tr>
<tr>
<td>$G$</td>
<td>$= 0.21 + 0.20a$</td>
<td>2.16a</td>
<td></td>
</tr>
<tr>
<td>$a$</td>
<td>$= T_{rb} \ln P_c/(1 - T_{rb})$</td>
<td>2.16b</td>
<td></td>
</tr>
<tr>
<td>$k$</td>
<td>$= \left[ (a/LG) - (1 + T_{rb}) \right]/(3 + T_{rb}) \left( 1 - T_{rb} \right)^2$</td>
<td>2.16c</td>
<td></td>
</tr>
<tr>
<td>$L$</td>
<td>$= 2.3026$</td>
<td>2.16d</td>
<td>[263]</td>
</tr>
<tr>
<td>RPMH</td>
<td>$\log P_r = -G/T_r \left[ 1 - T_r^2 + k \left( 1 - T_r \right)^3 \right]$</td>
<td>2.17</td>
<td></td>
</tr>
<tr>
<td>$G$</td>
<td>$= 0.2271 + 0.19654 \left[ T_{rb} \ln P_c/\left( 1 - T_{rb} \right) \right]$</td>
<td>2.17a</td>
<td></td>
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Table 2.1 (Continued)

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<th>Name</th>
<th>Equation</th>
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<th>Ref.</th>
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<tbody>
<tr>
<td>k</td>
<td>$k = \frac{T_{rb}}{(1 - T_{rb})^3} \log P + (-2.880814 +$</td>
<td></td>
<td>[261,263]</td>
</tr>
<tr>
<td></td>
<td>$\log P_c - [(1 - T_{rb}^2)/(1 - T_{rb})^3]^{2.17b}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Othmer</td>
<td>$\log P_R = m_r \log P - 0.76J$</td>
<td>2.18</td>
<td>[292]</td>
</tr>
<tr>
<td>Halm and Stiel</td>
<td>$\log P_R = (\log P_R)^{(0)} + (\log P_R)^{(1)} + \chi (\log P_R)^{(2)}$</td>
<td>2.19</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\omega = -\log P_R \bigg</td>
<td>_{T_R = 0.7 - 1.000}$</td>
<td>2.19a</td>
</tr>
<tr>
<td></td>
<td>$\chi = \log P_R \bigg</td>
<td>_{T_R = 0.6 + 1.70(\omega) + 1.552}$</td>
<td>2.19b</td>
</tr>
<tr>
<td></td>
<td>$(\log P_R)^{(0)}$, $(\log P_R)^{(1)}$, $(\log P_R)^{(2)}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>values are tabulated for $T_R = 0.44$ to $0.70$</td>
<td>2.19c</td>
<td>[133,134]</td>
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<th>Name</th>
<th>Equation</th>
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<tbody>
<tr>
<td>Thek and Stiel</td>
<td>( \ln P_r = A \left( 1.14893 - \frac{1}{T_r} - 0.11719 T_r \right) - 0.03174 T_r^2 - 0.375 \ln T_r + (1.042 , \alpha_c - 0.46284 , A) \left( T_r \left( 5.2691 + 2.0753 , A - 3.1738 \right) - 1 \right)/(5.2691 + 2.0753 , A - 3.1738) + 0.04 \left( \frac{1}{T_r} - 1 \right) )</td>
<td>2.20</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( A = \Delta H_b / [RT_c \left( 1 - T_{rb} \right)^{0.375}] )</td>
<td>2.20a</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( a = -T_{rb} \ln P_c / (T_{rb} - 1) )</td>
<td>2.20b</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( \alpha_c = \text{Slope, } (d \ln P_r / d \ln T_r) \text{ at } T_c \text{ and } P_c )</td>
<td>2.20c</td>
<td>[404]</td>
</tr>
<tr>
<td>Harlacher and Braun</td>
<td>( \ln P_r = B \left( 1 - \frac{1}{T_r} \right) - (E + B) \ln T_r + 0.4218 \left( P_r^* / T_r^2 - 1 \right) )</td>
<td>2.21</td>
<td></td>
</tr>
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</table>
Table 2.1 (Continued)

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<thead>
<tr>
<th>Name</th>
<th>Equation</th>
<th>No.</th>
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<tbody>
<tr>
<td>$B$</td>
<td>$= 6.545986 + 8.30918 \times 10^{-3}P +$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$8.87139\omega - 5.566785 \times 10^{-5}P^2 +$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$5.173538 \times 10^{-2}P\omega - 3.0657\omega^2$</td>
<td>2.21a</td>
<td></td>
</tr>
<tr>
<td>$E$</td>
<td>$= -4.14342 + 1.13843 \times 10^{-3}P -$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$4.0796\omega - 1.223881 \times 10^{-5}P^2 +$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$1.2214605 \times 10^{-2}P\omega - 1.348086\omega^2$</td>
<td>2.21b</td>
<td>[136]</td>
</tr>
</tbody>
</table>

* Obtained by putting $T_b = T_c$ in Equation 2.14a.

** $k$ is obtained from Equation 2.17 by substitution of $T_b$ for $T$ and rearrangement.
has been paid in recent years on the development of correlations based on potential functions [166, 202, 204, 403]. Prausnitz [318] is optimistic that although engineering applications of potential functions are at present limited, they will find increasing use in future.

Several correlations have been reported in literature for the estimation of second virial coefficients based on the corresponding states principle. The correlation of McGlashan and Potter [255] involving the reduced temperature and the critical volume, gives good representation of the second virial coefficients of small nonpolar molecules which has been extended to represent larger nonpolar molecules by introducing carbon number as the third parameter [255, 256]. Pitzer and Curl [315] used the acentric factor, \( \omega \), which is a macroscopic measure of the extent to which the force field around a molecule deviates from spherical symmetry, as the third parameter in their correlation for second virial coefficients which is excellent for normal fluids, that is, either for nonpolar or slightly polar molecules which do not associate strongly. Wohl's generalised correlation [441] involves the reduced temperature and the critical pressure and is satisfactory for simple nonpolar molecules.

The correlations discussed above are generally application to nonpolar gases and there is lack of a well developed correlation for polar gases. The difficulty in the development of such a correlation is mainly due to the reason that no simple parameter to characterise the effect of polarity on thermodynamic properties is available. The dipole moment is not considered sufficient to describe polarity because it is necessary to know whether the dipole moment is at the centre of the molecule or at its periphery. The magnitude and location of the dipole moment are not sufficient to describe the polar character of the
hydrogen-bonding molecules. The correlations of Black [24] and O'Connell and Prausnitz [286] are only approximations for the estimation of second virial coefficients for polar compounds. Black's correlation is based on a van der Waals-type equation developed for nonpolar and polar gases. In addition to the generalised constants, additional constant terms were used to account for polarity. The correlation of O'Connell and Prausnitz is an extension of the Pitzer-Curl correlation. In the place of the acentric factor for the polar compound, acentric factor of a homomorph, which is a nonpolar molecule having approximately the same size and shape, has been used. Two additional empirical functions, which depend on the reduced dipole moment (cf. Equation 2.26a, Table 2.2), reduced temperature, and the tendency of a compound to associate with itself to form dimers, were added to extend the Pitzer-Curl correlation to represent polar gases.

Reid and Sherwood [348] presented a brief review of the application of the virial equation to mixtures and gave recommendations for the methods to be used to determine potential parameters for mixtures. In the correlations cited in the preceding paragraphs, mixing rules were discussed for the calculation of mixture virial coefficients. In the absence of well developed theories, these mixing rules might be employed to determine the cross coefficients. Blanks and Prausnitz [28] presented methods for the calculation of the cross coefficients for binary mixtures consisting of polar-nonpolar and polar-polar pairs. They showed that for polar-polar pairs the use of the Stockmayer potential alone is not satisfactory for accurate prediction of the cross coefficients and the use of a corrected collision diameter in the Stockmayer potential improved the accuracy of prediction. Kreglewski [203] discussed mixing
rules for the treatment of fluid mixtures and their application to second virial coefficients.

Some of the important correlations for the estimation of second virial coefficients are given in Table 2.2.

2.2.3 Liquid Molar Volumes

The development of prediction methods for pure component liquid molar volumes has received considerable attention and many relatively accurate correlations have been proposed which range from very simple correlations requiring no experimental data to more complex correlations and techniques for extending known data to other ranges of temperature and pressure.

Cailletet and Mathias [44] reported that a linear relationship exists between temperature and the mean of the isothermal saturated liquid and vapour densities. This relationship is useful to detect abnormalities in the observed data but not for prediction of accurate data. Othmer et al. [298] extended Othmer's reference substance correlation [292] to liquid densities and prepared a nomograph which permits direct determination of liquid densities at any temperature using experimental densities at two temperatures.

Francis [106, 107] developed empirical relationships for the determination of saturated liquid densities and tabulated constants in his equations for a number of liquids. Li et al. [222] developed an empirical equation for n-alkyl compounds. These equations are quite accurate for the calculation of liquid densities. Ritter et al. [353] gave nomographs for the estimation of saturated liquid densities for
### Table 2.2 Correlations for Second Virial Coefficients

<table>
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<tbody>
<tr>
<td>Wohl</td>
<td>[ B = \frac{R T_c}{P_c} \left[ 0.197 - 0.012 T_r - 0.4 / T_r - 0.146 / T_r^3 \right] ]</td>
<td>2.22</td>
<td>[441]</td>
</tr>
<tr>
<td>McGlashan and Potter</td>
<td>[ B = 0.430 - 0.886 / T_r - 0.694 / T_r^2 ]</td>
<td>2.23</td>
<td>[255]</td>
</tr>
<tr>
<td>McGlashan and Wormald</td>
<td>[ \frac{B}{V_c} = 0.430 - 0.886 / T_r - 0.694 / T_r^2 - 0.0375 (n - 1) / T_r^{4.5} ]</td>
<td>2.24</td>
<td>[256]</td>
</tr>
<tr>
<td>Pitzer and Curl</td>
<td>[ B \frac{P_c}{RT_c} = f_b^{(0)}(T_r) + \omega f_b^{(1)}(T_r) ]</td>
<td>2.25</td>
<td></td>
</tr>
<tr>
<td></td>
<td>[ f_b^{(0)}(T_r) = 0.1445 - 0.33 / T_r - 0.1385 / T_r^2 - 0.0121 / T_r^3 ]</td>
<td>2.25a</td>
<td></td>
</tr>
<tr>
<td></td>
<td>[ f_b^{(1)}(T_r) = 0.073 + 0.46 / T_r - 0.50 / T_r^2 - 0.097 / T_r^3 - 0.0073 / T_r^8 ]</td>
<td>2.25b</td>
<td>[315]</td>
</tr>
</tbody>
</table>
Table 2.2 (continued)

<table>
<thead>
<tr>
<th>Name</th>
<th>Equation</th>
<th>No.</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>O Connell and Prausnitz8</td>
<td>[ B \frac{P_0}{RT_c} = f_b^{(0)}(T_r) + \omega_H f_b^{(1)}(T_r) + ] f_\mu(\mu_r, T_r) + \eta_1 f_a(T_r) ]</td>
<td>2.26</td>
<td></td>
</tr>
<tr>
<td></td>
<td>\mu_r = 10^5 \mu^2 \frac{P_0}{T_c^2}</td>
<td>2.26a</td>
<td></td>
</tr>
<tr>
<td></td>
<td>f_\mu(\mu_r, T_r) = -5.23722 + 5.665807 ln \mu_r - ]</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.133816 (ln \mu_r)^2 + 0.2525373 ]</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(ln \mu_r)^3 + 1/T_r [ 5.76977 - 6.181427 ln \mu_r + 2.28327 (ln \mu_r)^2 - 0.2649074 (ln \mu_r)^3] ]</td>
<td>2.26b</td>
<td></td>
</tr>
<tr>
<td></td>
<td>f_a(T_r) = \exp [6.6 (0.7 - T_r)]</td>
<td>2.26c</td>
<td>[286]</td>
</tr>
<tr>
<td></td>
<td>\omega_H = acentric factor for homomorph</td>
<td>2.26d</td>
<td></td>
</tr>
<tr>
<td>Black</td>
<td>B = b - a \epsilon^0/RT</td>
<td>2.27</td>
<td></td>
</tr>
</tbody>
</table>

...
Table 2.2 (Continued)

<table>
<thead>
<tr>
<th>Name</th>
<th>Equation</th>
<th>No.</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>b</td>
<td>( \frac{RT_c}{8P_c} )</td>
<td>2.27a</td>
<td></td>
</tr>
<tr>
<td>a</td>
<td>( 27b \frac{RT_c}{8} )</td>
<td>2.27b</td>
<td></td>
</tr>
<tr>
<td>( \varepsilon^0 )</td>
<td>( A' + B' \frac{T_r}{C'} - C'/T_r^2 + D'/T_r^3 + 64E'/27T_r^m )</td>
<td>2.27c</td>
<td></td>
</tr>
<tr>
<td>A'</td>
<td>0.396</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B'</td>
<td>1.181</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C'</td>
<td>0.864</td>
<td></td>
<td></td>
</tr>
<tr>
<td>D'</td>
<td>0.384</td>
<td></td>
<td>2.27d</td>
</tr>
<tr>
<td>E'</td>
<td>0.000</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\( A', B', C' \) are same as in Equation 2.27d. 
\( D' = 0.384 \) for alcohols, water, nitriles, aldehydes, acetone, and ammonia.
\( E' \) is estimated from experimental vapour density or second virial coefficient data putting \( m = 4.75 \) in Equation 2.27c.
\( D' \) for chlorinated, fluorine, sulphur, and other compounds might be estimated using experimental vapour density or second virial coefficient data putting \( E' = 0.0 \) in Equation 2.27c. [24]

\( f_b^{(6)}(T_r) \) and \( f_b^{(1)}(T_r) \) are identical to Equations 2.25a and 2.25b.
a number of pure liquids. Meissner and Sefarian [259] proposed an extension of the corresponding states principle using the critical compressibility factor as the third parameter. Lydersen, Greenkorn, and Hougen [237] developed a generalised correlation for pure component liquid densities over a wide range of temperatures and pressures. This correlation was presented in the form of tables as well as graphs and is considered to be one of the best corresponding states correlations for the estimation of liquid densities. One of the drawbacks of this correlation is that it is not easily amenable for computer application. The Lydersen et al. tables were expressed in the form of an equation by Wicks [431] which is applicable for $Z_c$ from 0.25 to 0.29 up to $T_r = 0.99$.

Yen and Woods [445] developed an analytical equation, mainly based on a modified corresponding states principle and the correlation of Lydersen et al., which was tested for 62 compounds with $Z_c$ ranging from 0.21 to 0.29. It was claimed that for 693 data points, the calculated liquid densities agreed with the literature values to within two percent. This correlation has been extended to compressed liquids and, with the aid of a pseudocritical method and a generalised vapour pressure equation, to mixtures with good accuracy.

Lyckman, Eckert, and Prausnitz [55, 235] improved Pitzer's generalised correlation [316] by calculating the generalised functions [Equation 2.34, Table 2.3] from reliable liquid density data for different types of selected compounds. The correlation was applied to 27 liquids including some highly polar liquids. For nonpolar liquids the accuracy was quite good. Although the theory of regular solutions, from which the correlation was developed, is not applicable to polar fluids, the deviations were not found to be large even for polar
liquids. The correlation is particularly useful for liquids with large acentric factors.

Halm and Stiel [134] developed a correlation by an extension of Pitzer's acentric factor approach using the polar factor [133] as the fourth parameter. The correlation gives about as good agreement for polar fluids, including large polar molecules, as do Pitzer's functions applied to normal fluids. Bondi and Simkin [30] developed a correlation based on a modified corresponding states principle in which they used new reduced property parameters. The method is particularly suitable for high molecular weight compounds which decompose before attaining critical state. The correlation makes use of a group contribution technique. Mustafaev [266] obtained a relationship from the corresponding states principle using carbon number as a parameter.

Barile and Thodos [16] correlated \( Z_T \) as a function of \( P_T \) for the prediction of pure component liquid densities. The correlation was tested for 23 polar and nonpolar compounds considering 54 experimental points for each compound. The average deviation claimed was 2.7 percent. Hobson and Weber [159] presented a graphical relationship of this type. Bradford and Thodos [35] developed a correlation for hydrocarbons which was claimed to be giving an average deviation of 1.1 percent over the entire temperature range up to the critical. The applicability of the correlation to nonhydrocarbon compounds requires further study as pointed out by the authors [35]. Goyal and Dorsaiswamy [125] presented a method for estimating liquid densities using Watson's expansion factor [422], reduced temperature, and the critical compressibility factor. The correlation is claimed to be applicable for reduced temperatures up to 0.8 and for \( Z_c \) between 0.2 and 0.3 with an average deviation of
<table>
<thead>
<tr>
<th>Name</th>
<th>Equation</th>
<th>No.</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Francis</td>
<td>( \rho_L = A - Bt - C/(E - t) )</td>
<td>2.28</td>
<td>[106,107]</td>
</tr>
<tr>
<td>Eykman</td>
<td>( \rho_L = (n^2 - 1) \left[ c (n^2 + 0.4) \right] )</td>
<td>2.29</td>
<td>[122]</td>
</tr>
<tr>
<td>Surface-tension</td>
<td></td>
<td>2.30</td>
<td></td>
</tr>
<tr>
<td>(Modified Goldhammer)</td>
<td>( \rho_L = \rho_v + \rho_1 \left[ 1 - T_r \right]^{0.3} )</td>
<td>2.30a</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( \log \rho_v/\rho_{vb} = 5 \left[ T/T_b - 1 \right] )</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>( \rho_{vb} = M / (82.06 T_b) )</td>
<td>2.30b</td>
<td>[124]</td>
</tr>
<tr>
<td>Lydersen, Greenkorn,</td>
<td>( V_1 \rho_{r_1} = V_2 \rho_{r_2} ) or ( V_1 = V / \rho_{r_1} )</td>
<td>2.31</td>
<td></td>
</tr>
<tr>
<td>and Hougen</td>
<td>( \rho_r = f \left( T_r, P_r, Z_c \right) ) from tables</td>
<td>2.31a</td>
<td>[237]</td>
</tr>
<tr>
<td>Yen and Woods</td>
<td>( \rho_{rs} = 1 + A \left( 1 - T_r \right)^{1/3} + B \left( 1 - T_r \right)^{2/3} + D \left( 1 - T_r \right)^{4/3} )</td>
<td>2.32</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( A = 17.4425 - 214.578 Z_c + 989.625 Z_c^2 - 1522.06 Z_c^3 )</td>
<td>2.32a</td>
<td></td>
</tr>
</tbody>
</table>
Table 2.3 (Continued)

<table>
<thead>
<tr>
<th>Name</th>
<th>Equation</th>
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<tbody>
<tr>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>If $Z_o \leq 0.26$,</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$B$</td>
<td>$-3.28257 + 13.6377 Z_o + 107.4844$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$Z_o^2 - 384.211 Z_o^3$</td>
<td>2.32b</td>
<td></td>
</tr>
<tr>
<td>If $Z_o &gt; 0.26$,</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$B$</td>
<td>$60.2091 - 402.063 Z_o + 501.0 Z_o^2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$+ 641.0 Z_o^3$</td>
<td>2.32c</td>
<td></td>
</tr>
<tr>
<td>$D$</td>
<td>$0.93 - B$</td>
<td>2.32d</td>
<td>[445]</td>
</tr>
<tr>
<td>Wicks</td>
<td>$\rho_r = 1.20 + (5.563 - 11.03 Z_o)$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$(1 - T_r)^0.8 Z_o + 0.31$</td>
<td>2.33</td>
<td></td>
</tr>
<tr>
<td>For $0.25 \leq Z_o \leq 0.29$ and $T_r = \text{upto } 0.99$</td>
<td></td>
<td>2.33</td>
<td></td>
</tr>
<tr>
<td>Lyckman, Eckert, and Fraunhitz</td>
<td>$V_r = V_r(0) + \omega V_r(1) + \omega^2 V_r(2)$</td>
<td>2.34</td>
<td>[234]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td></td>
<td></td>
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</tbody>
</table>
Table 2.3 (Continued)

<table>
<thead>
<tr>
<th>Name</th>
<th>Equation</th>
<th>No.</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>For $0.56 \leq T_r \leq 0.99$,</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\[
V_r^{(0)} = 0.11917 + 0.009513 T_r + 0.21091 T_r^2 \\
- 0.06922 T_r^3 + 0.0748 / T_r - 0.084476 \ln (1 - T_r) \\
2.34a
\]

\[
V_r^{(1)} = 6.98465 - 1.60378 T_r + 1.82484 T_r^2 \\
- 0.61432 T_r^3 - 0.34546/T_r + 0.087037 \\
\ln (1 - T_r) \\
2.34b
\]

\[
V_r^{(2)} = -0.55314 - 0.15793 T_r - 1.01601 T_r^2 \\
+ 0.34095 T_r^3 + 0.46795/T_r - 0.239938 \\
\ln (1 - T_r) \\
2.34c \hspace{1cm} [55]
\]

Halm and Stiel

\[
V^* = P_c V / RT_c = V^{* (0)} + \omega V^{* (1)} + \chi V^{* (2)} + \omega^2 V^{* (3)} + \chi^2 V^{* (4)} + \omega \chi V^{* (5)} \\
2.35
\]

...
<table>
<thead>
<tr>
<th>Name</th>
<th>Equation</th>
<th>No.</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( v' (0) , v' (1) , v' (2) , v' (3) , v' (4) , ) ( v' (5) )</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>are tabulated for ( 0.56 \leq T_R \leq 1.0 )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bradford and</td>
<td>( \ell_{rl} = 1 + \beta (1 - T_R) + \gamma (1 - T_R)^2 + ) ( \delta (1 - T_R)^n )</td>
<td>2.36</td>
<td></td>
</tr>
<tr>
<td>Thodos</td>
<td>( n = 0.16 + 0.586 \ Z_c )</td>
<td>2.36a</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( \delta = 2.785 - 3.544 \ Z_c )</td>
<td>2.36b</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( \beta = 2.924 - 7.34 \ Z_c )</td>
<td>2.36c</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( \gamma = \delta - \beta - 1 )</td>
<td>2.36d</td>
<td>[35]</td>
</tr>
<tr>
<td>Barile and</td>
<td>( \ell_1 = \frac{P_T \ \ell_C}{Z_{rl} \ T_R} )</td>
<td>2.37</td>
<td></td>
</tr>
<tr>
<td>Thodos</td>
<td>For ( 0.1 \leq P_T \leq 1.0 ), ( Z_{rl} = \alpha P_T + \beta P_T \gamma + \gamma \ P_T \gamma )</td>
<td>2.37a</td>
<td></td>
</tr>
<tr>
<td></td>
<td>At the critical point, ( \alpha + \beta + \gamma = 1.0 )</td>
<td>2.37b</td>
<td></td>
</tr>
</tbody>
</table>

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Table 2.3 (Continued)

<table>
<thead>
<tr>
<th>Name</th>
<th>Equation</th>
<th>No.</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>α</td>
<td>$= 0.2094 + 1.2375 \ Z_o$</td>
<td>2.37c</td>
<td></td>
</tr>
<tr>
<td>β</td>
<td>$= 0.269 - 0.298 \ Z_o$</td>
<td>2.37d</td>
<td></td>
</tr>
<tr>
<td>γ</td>
<td>$= 9.659 - 50.597 \ Z_o + 114.49 \ Z_o^2$</td>
<td>2.37e</td>
<td></td>
</tr>
<tr>
<td>τ</td>
<td>$= 34$</td>
<td>2.37f</td>
<td></td>
</tr>
</tbody>
</table>

For $P_r \leq 0.10$,

<table>
<thead>
<tr>
<th>Equation</th>
<th>No.</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Z_{xl} = \delta + \varepsilon \ P_r$</td>
<td>2.37g</td>
<td></td>
</tr>
<tr>
<td>$\delta = 0.011536 \ Z_o - 0.002071$</td>
<td>2.37h</td>
<td></td>
</tr>
<tr>
<td>$\varepsilon = 1.0715 - 5.5875 \ Z_o + 13.4886 \ Z_o^2$</td>
<td>2.37i [16]</td>
<td></td>
</tr>
</tbody>
</table>
about 1.5 percent for nonpolar and polar compounds. Narasimhan [278] proposed a correlation which is claimed to predict saturated liquid densities with an average error of about two percent.

Other correlations of importance include the surface-tension correlation (modified Goldhammer equation) [124] based on reduced temperature, and the Eykman correlation [122] based on refractive index. Reid and Sherwood [348] and Gold and Ogle [122] presented comprehensive reviews of different correlations with recommendations for their use. These reviews do not cover some of the recent correlations [35, 134, 136, 266]. Gold and Ogle considered the surface-tension method to be generally the most accurate with an overall reliability of ± two percent when tested on 136 organic compounds. The Eykman method was considered to be accurate for polar organics.

In the absence of a detailed comparison of the large number of correlations, it is rather difficult to sort out the correlations in the order of their accuracy. For nonpolar as well as polar compounds the well tested Lydersen, Greenkern, and Hougen correlation or the surface tension method can be expected to give good accuracy. The Lyckman, Eckert, and Prausnitz correlation gives good accuracy for nonpolar compounds. For polar compounds the correlations of Halm and Stiel and Eykman appear to be fairly accurate and reliable.

Some of the important correlations are given in Table 2.3.

2.3 The Gibbs - Duhem Equation and its Applications

One of the most useful and fundamental thermodynamic equations, relating the partial molar properties of the components to one another in a mixture, is the Gibbs - Duhem equation. At constant
pressure and temperature this equation can be written as

\[ \sum_{i} x_i \, d \bar{m}_i = 0 \]  

(2.38)

where \( \bar{m}_i \) is any partial molar property. Equation 2.38 holds for ideal and nonideal solutions and can be written in terms of partial molar excess free energy:

\[ \sum_{i} x_i \, d \bar{g}_i^E = 0 \]  

(2.38a)

The excess free energy is directly related to the activity coefficients (Equation 2.1) and in terms of activity coefficients Equation 2.38a can be written as

\[ \sum_{i} x_i \, d \ln \gamma_i = 0 \]  

(2.39)

Equation 2.39 is the most widely used form of the Gibbs—Duhem equation in vapour-liquid equilibrium thermodynamics.

The Gibbs—Duhem equation is used for either the estimation of additional properties in the absence of complete experimental data or, when experimental data are available, to verify the thermodynamic consistency of the data. Sometimes it is simpler to calculate the activity coefficients for one of the components in a binary system from the experimental data compared to the other component. Lodi and Scheller [228], in their work on binary vapour-liquid equilibria for mixtures consisting of an associating and a non-associating component, calculated the activity coefficients for the non-associating component using the conventional methods from the experimental data and the activity coefficients for the associating component from those of the non-associating component and the Gibbs—Duhem equation. Another situation where the Gibbs—Duhem equation is applied to calculate the activity coefficients of one of the components from those of the other, is when the two components differ widely in volatility as in such cases it
would not be practical to measure the extremely small partial pressure of the higher boiling component over the solution.

Another area of application for the Gibbs–Duhem equation is to convert isothermal total pressure–composition data or isoboric temperature–composition data for a binary system into \( y - x \) data. These applications are further considered in the later part of this section.

A number of papers appeared in the literature on the integration and usefulness of the Gibbs–Duhem equation. Ibl and Dodge [172] presented derivations of the exact forms of the Gibbs–Duhem equation in terms of fugacities and activity coefficients for binary systems for (i) isobaric and (ii) isothermal conditions. At constant temperature

\[
\frac{V^E}{RT} \left( \frac{\partial \ln y_1}{\partial x_1} \right)_T = \sum_{i=1}^{n} x_i \frac{\partial \ln y_i}{\partial x_1}
\]  

(2.40a)

At constant pressure

\[
-\frac{n^E}{RT^2} \left( \frac{\partial T}{\partial x_1} \right)_N = \sum_{i=1}^{n} x_i \frac{\partial \ln y_i}{\partial x_1}
\]  

(2.40b)

It has been shown that the left-hand term in Equation 2.40a is very close to zero because of the small change in volume on mixing and the larger divisor. The left-hand term in Equation 2.40b cannot be always assumed to be negligible. Sometimes it can be considerably large [172, 405]. Van Ness [415] has developed unrestricted exact forms of the Gibbs–Duhem equation, in terms of fugacities and activity coefficients, which are applicable to any phase and system with any
number of components. Francesconi and Trevissoi [105] derived an expression for the left-hand term in Equation 2.40b replacing the term \( \left( \frac{\partial T}{\partial x_i} \right)_n \) by terms involving activity coefficients and pure component vapour pressures. Ellis and Bourne [82] discussed the effect of the heat of mixing portion and the \( \left( \frac{\partial T}{\partial x_i} \right)_n \) portion of the left-hand term in Equation 2.40b and observed that the difference in the boiling points determine the magnitude of this term and for less than 10°C difference, the term is usually negligible.

Engalbert, Bugarel, and Gardy [89], Van Ness [414], and White and Lawson [428] discussed the integration of the Gibbs - Duhem equation and presented guidelines on the integration procedures for the isothermal Gibbs - Duhem equation for binary systems which form (i) no azeotropes, (ii) positive azeotropes, and (iii) negative azeotropes. Nord [281], Ibl and Dodge [172], and Othmer, Ricc.ardi, and Thacker [301] discussed the utility of the following isobaric form of the Gibbs - Duhem equation, applicable for ideal vapour phase:

\[
\frac{x - y}{y(1-y)} \left[ \frac{dy}{dt} \right] = \frac{h^E}{RT^2} \quad (2.41)
\]

Equation 2.41 may be used to verify the thermodynamic consistency of experimental isobaric vapour-liquid equilibrium data by computing and comparing both sides of the equation. It can also be applied to calculate the \( t - x \) curve from the \( t - y \) curve or the evaluation of heat of mixing from the \( t-x-y \) diagram and the heats of vapourisation of the pure components.

Since the left-hand term in Equation 2.40a is usually negligible in comparison to the left-hand term in equation 2.40b, it would be
instructive to measure the total pressure-liquid composition data experimentally at constant temperature and calculate the vapour compositions applying the Gibbs - Duhem equation. This reduces the experimental effort involved. This method is particularly advantageous for mixtures of high relative volatility and for mixtures difficult to analyse. A large number of papers appeared in the literature on this subject [17, 48, 54, 85, 90, 158, 194, 226, 239, 254, 265, 311, 323, 333, 362, 396, 399].

Scatchard [362] discussed the advantages of the total pressure measurements. Barker [17] has described a numerical procedure based on the method of least squares for the calculation of the activity coefficients from total pressure measurements. Although the method is complicated for manual calculation, it can easily be adopted for a digital computer. Kogan and Fridman [194] described a method based on the Margules solutions of the Gibbs - Duhem equation which requires the pure component vapour pressures and those of two mixtures containing 1/3rd and 2/3rd mole fractions of one of the components. A nomograph has been constructed to simplify its application. Hala et al. [132] described a method due to Erdős [90] which is applicable if the vapours obey ideal gas laws. The Runge-Kutta method of numerical integration was used for solving the differential equation obtained. Ho et al. [158] developed two digital computer methods, one based on the use of the Redlich-Kister [344, 345] equation for representing the activity coefficients and the other using a stepwise integration procedure. The second method is limited to nonazeotropic systems while the first one is applicable for both azeotropic and nonazeotropic systems. Tao [396] developed a rigorous numerical method applicable
to binary systems with nonideal vapour phase. This method can be applied to either $p$ - $x$ or $t$ - $x$ data and requires volume change on mixing or heat of mixing and the vapour phase nonideality factors for obtaining accurate and precise results. The method can be applied to testing the thermodynamic consistency of the data or to find the degree of attainment of equilibrium in the still and has been extended to multicomponent mixtures [399]. Ljunglin and Van Ness [226] discussed the advantages and disadvantages of the total pressure measurements for obtaining vapour-liquid equilibrium data and derived equations for the calculation of $t$ - $y$ data considering vapour phase imperfections. Mixon [265] presented a method for computing vapour-liquid equilibrium data from solution vapour pressure measurements for multicomponent systems using the excess free energy function. Ramalho and Delmas [333] developed a numerical method for binaries based on the series expansion of Redlich, Kister, and Turnquist [345] for the excess free energy function and compared it with other methods. The vapour phase non-idealities were considered and it was claimed that the method is fairly accurate to represent the data. Chang and Lu [48] presented a direct method for evaluating ternary vapour-liquid equilibrium compositions from total pressure-composition data along lines of constant liquid mole fraction ratio. The method is applicable to data at low pressures. MacKay and Wong [239] proposed a method for binary systems based on the solution of algebraic equations derived by writing the Gibbs - Duhem equation in terms of fugacity in finite difference form. The method compared well with those proposed by Van Ness [414] and Tao [396]. Davison, James, and Tromblee [62] recently proposed a method for calculating the vapour-liquid equilibria for multicomponent
systems based on experimental dew point pressure and vapour compositions at constant temperature, using the Gibbs - Duhem equation.

For systems with close-boiling components or negligible heats of mixing, measurement of boiling point-liquid composition data will be sufficient to describe complete vapour-liquid equilibria. The Gibbs - Duhem equation can be applied to \( t - x \) data to calculate vapour compositions for such isobaric systems, as the left-hand term in equation 2.40b can be neglected. Several references can be found in literature for this technique [42, 46, 130, 150, 176, 301]. Othmer, Ricciardi and Thacker [301] proposed a stepwise integration technique and an algebraic method using the \( X - Y \) plots technique proposed by Hirata [150]. Hirata [150] developed methods for prediction of binary and ternary vapour-liquid equilibria from \( t - x \) measurements. Bukala et al. [42] described a method which is applicable to both azeotropic and nonazeotropic mixtures. Hala et al. [132] described a method developed by Hala et al. [130] for binary systems using Milne’s numerical technique and illustrated its application by considering acetone-tetrachloromethane system. Recently Jasinski and Malanowski [176] proposed an iterative method for obtaining \( t - x - y \) data from \( t - x \) measurements for multicomponent systems which takes into account the vapour phase nonideality. The method is an indirect one assuming the Redlich-Kister [344] type series expansion for the excess free energy function.

Ellis and Jonah [84] have suggested that the boiling temperature, \( T \), for an isobaric binary system, be expressed in the form:

\[
T = T_1 x_1 + T_2 x_2 + \Delta T
\]  
(2.42)
where $\Delta T$ = the difference between the experimental and the calculated boiling temperature for the binary mixture using Equation 2.42.

The activity coefficient at infinite dilution is given by

$$\gamma_1^\infty = \frac{\pi}{(P_1^c)_T} [1 - \left( \frac{\Delta H_2}{RT_2^2} \right) $$

$$T_1 - T_2 - \left( \frac{\Delta T}{x_1 x_2} \right) x_1 = 0 ]$$ (2.43)

The equation for $\gamma_2$ is obtained by rotating the suffices. The value of $\Delta T / (x_1 x_2)$ at $x_1 = 0$ is evaluated by extrapolating a plot of $\Delta T / (x_1 x_2)$ vs. $x_1$. For isothermal conditions similar equations containing the slope $\Delta \pi / (x_1 x_2)$ at $x_1 = 0$ were derived. The method has been tested on a satisfactorily predicting infinite dilution activity coefficients.

Bowrey and Marek [34] recently proposed a graphical method for the calculation of the isothermal bubble point pressure-composition line for binary mixtures from measurements of the total pressure and vapour composition.

Danciu [61] has developed a method for the estimation of boiling point curve for binary systems by an empirical equation based on Clausius-Clapeyron equation in finite difference form. The method can be applied to homogeneous azeotropic and nonazeotropic systems and is relatively insensitive to small variations in the atmospheric pressure. Raju and Sawarkar [331] developed an equation for the boiling point curve using the expansion for $g^F$ based on Hildebrand's regular solution theory. The method is an approximate one and involves the use of entropies of vapourisation for pure components which are often not
available in the literature. The usefulness of the method lies in its dependence only on pure component properties. Nakanishi [276] gave an empirical relationship which permits extension of \( t - x \) or \( x - x \) data for binary azeotropic and nonazeotropic systems from one set of conditions to another.

These methods considerably reduce the amount of experimental effort needed for obtaining the vapour-liquid equilibrium data. One of the major problems in obtaining experimental vapour-liquid equilibrium data is the analysis of the samples. The analysis of binary mixtures is relatively simpler but for multicomponent systems this becomes a complex problem and the precision is often limited. These methods eliminate these problems as no sampling and analysis are required especially when an apparatus, with a very small volume of the vapour space compared to that of the liquid, is used. But the methods suffer from the disadvantage that the data cannot be subjected to thermodynamic consistency tests because the Gibbs - Duhem equation, which is used for testing the thermodynamic consistency, is employed in the computations.

2.4 Thermodynamic Consistency of Vapour-Liquid Equilibrium Data

Reliability of experimental data is often tested for internal consistency because experimental errors might arise out of fractionation taking place in an equilibrium still, incorrect sampling, entrainment in the still, attainment of nonequilibrium steady state or measurements and analyses.

Errors are generally classified as random and systematic. The random errors which are quite irregular, are usually due to the observer and are often revealed by inspection of the results obtained
by repeated experiments and graphical techniques. Systematic errors are of constant character and may arise from the observer or the experimental method through lack of precision in some instrument or its incorrect usage. These errors are usually the more troublesome as repeated observations do not necessarily reveal them. They may be constant or may vary in some regular way. Frequently it is possible to establish the cause of a systematic error and remove it by modifying the procedure or replacing part of the apparatus. Thermodynamic consistency tests are applied to detect systematic errors.

As the Gibbs–Duhem equation interrelates activity coefficients of all components in a mixture, if data are available for all the activity coefficients, these data should satisfy the Gibbs–Duhem equation; if they do not, then the data cannot be correct. If they do obey the Gibbs–Duhem equation, then the data are probably correct, although not necessarily, correct. Testing of vapour–liquid equilibria for thermodynamic consistency has received very close attention because the experimental determination of vapour–liquid equilibria is a difficult problem highly susceptible to errors.

A. Binary Systems

A.1 Area or Integral Tests

It can be shown that at constant temperature and pressure \([60, 142, 344, 345]\)

\[
\frac{1}{0} \ln \gamma_1 / \gamma_2 \, dx_1 = 0
\]  

(2.44)

Equation 2.44 can readily be derived from the direct relationship between the excess free energy function and the activity coefficients (Equation 2.1) using the Gibbs–Duhem equation, at constant temperature and pressure (Equation 2.39). Equation 2.44 provides what is commonly
known as the area test of vapour-liquid equilibrium data [142, 344, 346]. This test is easy to apply and involves plotting of \( \ln \frac{y_1}{y_2} \) vs. \( x_1 \) and measuring the area under the curve. If the experimental data are correct, the algebraic sum of the areas enclosed by this curve and the ordinates at \( x_1 = 0 \) and \( x_1 = 1 \) must be zero. Equation 2.44 is strictly valid thermodynamically at constant temperature under conditions far from critical when the molar volume of the liquid phase may be neglected by comparison with the molar volume of the vapour (Equation 2.40a). It is considered [82] that in cases where the end values of \( \log \frac{y_1}{y_2} \) vs. \( x_1 \) curves are greater than approximately 0.3, an error of up to 0.03 in the ratio of the areas above and below the line \( \log \frac{y_1}{y_2} = 0 \) can arise from the scatter of the data points and consequent uncertainty in drawing a smooth curve through them. In such cases if the ratio of areas exceeds 1.05 to 1.06, significant departure from equilibrium is confirmed. For near-ideal systems the effect of scatter on the ratio of the areas is much more pronounced. At constant pressure the areas differ by an amount depending on the integral heat of mixing and the temperature range [71, 141, 181, 341, 405]. Ellis and Bourne [82] showed that in cases where the end values of the \( \log \frac{y_1}{y_2} \) vs. \( x_1 \) curves for isobaric systems are approximately 0.6 the areas above and below the line \( \log \frac{y_1}{y_2} = 0 \) are approximately 0.16 and must differ by 0.008 to give a ratio of areas of 0.95 because of nonisothermal conditions. The ratio of the areas for some systems may be as low as 0.9 and yet the data pass the test.

The area test is not very stringent even under the conditions of its applicability as departures from equilibrium in one part of the composition range may compensate deviations in another part. This is a consequence of integrating across the whole concentration range. Bourne [33] discussed in detail the possible errors that might crop up in the
application of this test. The discussion covers the effects of fractionation, entrainment and flash vapourisation during the operation of the still. He illustrated how the test fails to recognise the inaccuracies resulting from these malfunctions of the equilibrium stills which are frequent in the determination of the equilibrium data. Zharov and Morachevskii [450] studied the relation between the value of the integral and the magnitude of systematic errors in experimental data. They described methods for establishing the type of the resultant systematic error from the value of the integral and gave an equation relating the error in y to \( \ln \gamma_1 / \gamma_2 \).

Komarova and Kogan [201] studied the estimation of the deviations of the integral from zero and arrived at the following conclusions:

i) If the absolute magnitude of the deviations is not more than 0.01, the deviations might be either due to systematic errors in the determination of the vapour compositions or due to nonideal behaviour of the vapours.

ii) If the absolute magnitude of the deviations exceed 0.01, a systematic error in the determination of the equilibrium phase compositions is more likely.

Prausnitz [318] gave the following guideline to decide whether a set of experimental data satisfied the test or not:

\[
0.02 > \frac{(\text{Area above x-axis}) - (\text{Area below x-axis})}{(\text{Area above x-axis}) + (\text{Area below x-axis})} \tag{2.45}
\]

For near ideal systems with \( \frac{g_{\text{max}}^E}{g_{\text{mole}}} < 50 \text{ cal/g mole} \), Prausnitz [318] observed that 0.02 is too low as the limit.

The area test represented by Equation 2.44, strictly speaking, is an approximation because vapour-liquid equilibrium data for a binary
system cannot be both isothermal and isobaric. The unrestricted forms of the area test for isothermal and isobaric conditions for a binary system can be obtained from Equations 2.40a and 2.40b (Section 2.3):

Isothermal

\[
\int_{x_1=0}^{x_1=1} \left( \ln \frac{\gamma_1}{\gamma_2} \right) \, dx_1 = \int_{x_1=0}^{x_1=1} \left( \frac{\gamma^E}{RT} \right) \, dx \quad (2.46)
\]

Isobaric

\[
\int_{x_1=0}^{x_1=1} \left( \ln \frac{\gamma_1}{\gamma_2} \right) \, dx_1 = -\int_{x_1=0}^{x_1=1} \left( \frac{h^E}{RT^2} \right) \, dT \quad (2.47)
\]

One of the major difficulties in applying the area test according to Equations 2.46 and 2.47 is the lack of data required to evaluate the right-hand terms in these equations. This situation calls for approximations or indirect estimations to be made for these terms. In the case of Equation 2.46 setting the right-hand term to zero is usually a good approximation but for Equation 2.47, often the right-hand term cannot be neglected. Ellis and Bourne [82] discussed the effect of these terms and pointed out that the right-hand term of Equation 2.46 is frequently less than 0.001, because the integral volume change of mixing is often less than 0.5 ml/g mole. If the boiling range is 25°C, the system is nonazeotropic, and the maximum heat of mixing is 300 cal/g mole, the value of the right-hand term of Equation 2.47 is 0.008. If the boiling range does not exceed 10°C, the right-hand side of Equation 2.47 can be neglected [71, 82, 174, 341, 405]. Coulson, Hales, and Herington [60] reached a similar conclusion on theoretical grounds. For nonpolar systems the right-hand term in Equation 2.47 may be negligible but for polar-nonpolar and polar-polar systems it may be appreciable.
Herington [141, 142] proposed a semiempirical test for the thermodynamic consistency of isobaric, nonisothermal data. The percent deviation, D, defined by

\[
D = \frac{(\text{Area above } x\text{-axis}) - (\text{Area below } x\text{-axis})}{(\text{Area above } x\text{-axis}) + (\text{Area below } x\text{-axis})} \times 100 \quad (2.48)
\]
is obtained from a plot of \( \ln \gamma_1 / \gamma_2 \) vs. \( x_1 \). Herington suggested that D should be compared with J obtained from Equation 2.49

\[
J = 150 |\Theta| / T_m \quad (2.49)
\] where \( |\Theta| \) is the absolute value of the maximum temperature difference for the system and \( T_m \) is the minimum boiling temperature in °K observed over the entire composition range. Herington suggested that if \( D - J < 10 \), the data are probably consistent; if \( D - J > 10 \), the data are probably inconsistent. This method, though an approximation provides, in the absence of heat of mixing data, a technique for testing isobaric binary data.

McDermott [252] modified Herington's test in which he introduced the term \( D^h \) which is evaluated from the excess free energy and boiling point data by Equation 2.50:

\[
D^h = 1/2 \left[ Q_a/T_1 + Q_b/T_2 \right] (T_2 - T_1) \quad (2.50)
\]

where \( Q = \frac{g^E}{RT} \)

\[
T_1 = \text{minimum boiling temperature, °K}
\]

\[
T_2 = \text{maximum boiling temperature, °K}
\]

For testing pairs of points, the equation is

\[
\sum \left[ \frac{x_a + x_b}{2} (\ln \gamma_{2a} - \ln \gamma_{1a}) + \frac{x_{1b} + x_{2b}}{2} (\ln \gamma_{2b} - \ln \gamma_{1b}) \right] = \sum D^h \quad (2.51)
\]

The subscripts a and b indicate the experimental points.
If \( \Sigma D' - 3 \Sigma D^h \leq 0.02 \), the binary data can be considered to be thermodynamically consistent. Ohe [288] proposed a consistency test similar to that of Herington's test by replacing the activity coefficients in the integral by the relative volatilities.

Coulson, Hales, and Herington [60], Röck [355] and Broughton and Brearley [37] obtained the relation

\[
\int_0^1 \left( T \ln \frac{\gamma_1}{\gamma_2} \right) dx_1 = 0
\]

(2.52)

for testing isobaric data. Van Ness [415] discussed the advantage of using the excess entropy of mixing term \( \int_0^1 s^E \left( \frac{dT}{dx_1} \right) dx_1 \) in the consistency tests as \( s^E \) may be small even though \( h^E \) is not and the variation of \( s^E \) with temperature may not be so rapid as compared to \( h^E \). The area test in terms of \( s^E \) is written as

\[
\int_0^1 \left( RT \ln \frac{\gamma_1}{\gamma_2} \right) dx_1 = \int_0^1 s^E \left( \frac{dT}{dx_1} \right) dx_1
\]

(2.53)

Adler, Friend, Egford, and Rosselli [2] developed area tests for the cases of constant temperature and constant pressure in terms of \( K \)-values rather than activity coefficients. These tests are applied to the case where one of the components in the mixture is above its critical temperature. Edmister and Robinson [79] reviewed the area tests. They recommended the \( K \)-value forms for the consistency tests which can be derived from the following forms of the Gibbs–Duhem equation for isothermal and isobaric conditions:

Isothermal

\[
x_1 \frac{d \ln K_1}{d \ln \pi} + x_2 \frac{d \ln K_2}{d \ln \pi} =
\]

\[
z^{-1} + z^{-1}_1 y_1 \left( \frac{1}{K_2} - \frac{1}{K_1} \right) - z^V / K_2
\]

(2.54)
where $Z^l = \text{compressibility factor for the liquid mixture}$

$Z^v = \text{compressibility factor for the vapour mixture}$

$Z^v_1 = \text{partial compressibility factor of component 1 in vapour mixture.}$

Isobaric

$$x_1 \frac{d \ln K_1}{dT} + x_2 \frac{d \ln K_2}{dT} = \frac{h^E}{RT^2}$$  \hspace{1cm} (2.55)

where

$$V_1^o = \frac{f_1}{\pi}$$ \hspace{1cm} (2.55a)

$$V_2^o = \frac{f_2}{\pi}$$ \hspace{1cm} (2.55b)

Equation 2.54 on integration gives

$$\int_{K_1(0)}^{K_1(x_1)} x_1 \frac{d \ln K_1}{K_2(l)} + \int_{K_2(l)}^{K_2(x_2)} x_2 \frac{d \ln K_2}{K_1(1)} + \ln x = \int [Z^l + Z^v_1 y_1] d \ln x$$

(2.56)

Equation 2.56 provides the area test for isothermal data.

Equation 2.55 is integrated to give

$$\int_{T(0)}^{T(x_1)} \frac{h^E}{RT^2} dT$$

(2.57)

Equation 2.57 provides the isobaric area test. Van Ness and Mrazek [418] gave the area test in terms of partial molar excess free energies. At constant temperature and pressure the test requires that

$$\int_0^1 \frac{\xi_1^E}{x_1} dx_1 = \int_0^1 \frac{\xi_2^E}{x_1} dx_1$$

(2.58)
Ramachandran and Laddha [332] proposed a method for the evaluation of the heat of mixing term in Equation 2.40b. The Redlich-Kister expansion for the excess free energy function and the inter-relationship between the excess free energy function and the heat of mixing were used as the basis for the method.

The method involves the evaluation of the Redlich-Kister binary constants from experimental activity coefficient data as a function of temperature which are used in the following equation to calculate the heat of mixing:

\[ h^E = x_1 x_2 \left[ b + c (x_1 - x_2) + \ldots \right] \]  

where

\[ b = 2.303 R \frac{dB}{d \left( \frac{1}{T} \right)} \]  

\[ c = 2.303 R \frac{dC}{d \left( \frac{1}{T} \right)} \]

etc. The values of \( \frac{dB}{d \left( \frac{1}{T} \right)} \), \( \frac{dC}{d \left( \frac{1}{T} \right)} \), etc., are evaluated graphically by plotting B vs. \( \frac{1}{T} \), C vs. \( \frac{1}{T} \), etc. The values of \( \frac{dT}{dx_1} \) are evaluated by plotting T vs. \( x_1 \). For each value of \( x_1 \), \( \left( \frac{h^E}{RT^2} \right) \left( \frac{dT}{dx_1} \right) \) is calculated and by graphical integration value of \( \int_{x_1=0}^{x_1=1} \left( \frac{h^E}{RT^2} \right) \left( \frac{dT}{dx_1} \right) dx_1 \) is obtained. The method has been tested [340] on some binary systems involving polar compounds and found to be fairly good for testing binary isobaric data.

Herington [140] developed general integral tests based on the Duhem - Margules equation which can be used to examine part of a composition range for miscible systems.

A.2 Slope Tests

One of the disadvantages of an integral test is that it does not represent a point-by-point test of the data and thus it is possible because of cancellation of errors, that an integral test is satisfied. Another disadvantage is that the integral methods are weighted with respect to the dilute regions of the composition range where greatest experimental errors are to be expected. A differential test provides a
much stricter examination of thermodynamic consistency than does an integral test.

At constant temperature and pressure for binary systems the Gibbs - Duhem equation can be written as

$$x_1 \left( \frac{d \ln \gamma_1}{dx_1} \right)_{T, \pi} + x_2 \left( \frac{d \ln \gamma_2}{dx_1} \right)_{T, \pi} = 0 \quad (2.60)$$

In other words, for thermodynamically consistent data a definite relationship must exist between the slopes of the curves of ln $\gamma_1$ and ln $\gamma_2$ vs. $x_1$. This test is necessarily an approximate test as the vapour-liquid equilibrium data cannot be isobaric as well as isothermal.

Redlich, Kister, and Turnquist [345] presented equations which enable the testing of isobaric and isothermal data. Under isobaric conditions, the following equation is given which connects the boiling temperature with the composition

$$\frac{dt}{dy_1} = s \left( \frac{x_1 - y_1}{y_1 y_2} \right) \quad (2.61)$$

where $s$, the 'slopefactor' is given by

$$s = 0.4343 / \left[ x_1 \frac{d \log P_1^0}{d t} + x_2 \frac{d \log P_2^0}{d t} \right] \quad (2.61a)$$

Equation 2.61 can be used to predict the slope of the dew point curve at any point for which $x_1$ and $y_1$ are known. A similar relation is given for isothermal data

$$\frac{d \ln \pi}{dy_1} = \left( \frac{y_1 - x_1}{y_1 y_2} \right) \quad (2.62)$$

Equations 2.61 and 2.62 are valid for ideal vapour phase.

Equation 2.41

$$\frac{x - y}{y (1 - y)} \left[ \frac{dy}{dt} \right] = \frac{h^E}{RT^2} \quad (2.41)$$

can be used as a method of testing isobaric binary vapour-liquid
equilibrium data [22, 172, 182, 301]. The $h^E$ term is made up of both heats of vapourisation and liquid heats of mixing. For most of the liquid systems the heat of vapourisation is much larger than the heat of mixing. Consequently, if the liquid heats of mixing are not known and must be estimated, or neglected, the error involved may not be large. The left hand term in Equation 2.41 is computed and compared numerically or graphically with the right-hand term. If the data are consistent and the assumptions are reasonable, the two sides of the equation will be nearly same. The term $h^E$ is calculated using the relation

$$h^E = x_1 h_{v1} + x_2 h_{v2}$$  \hspace{1cm} (2.63)

Bitrich [22] discussed the permissible deviations from this test by considering the likely errors in temperature and composition measurements and in the calculation of $h^E$ from Equation 2.63 which gives the ideal mixture vapourisation enthalpy. The reliability of this test depends on the direction of integration, choice of initial conditions, and choice of the composition intervals.

Van Ness [416] proposed a 'composition resolution' test based on the fact that whereas a given curve for the excess free energy vs. mole fraction can be computed from an infinite number of sets of experimentally determined values of $\gamma_1$ and $\gamma_2$, only one set of $\gamma_1$ and $\gamma_2$ can be calculated from a given curve for the excess free energy. For a binary system, $\gamma_1$ and $\gamma_2$ are related by the Gibbs - Duhem equation and hence, from a curve of $g^E / RT$ vs. $x_1$ only one consistent set of $\gamma_1$ and $\gamma_2$ can be calculated from any individual point on the curve. If the calculated values agree with the experimental ones,
then the data are consistent. The slope of the tangent drawn to the curve $g^E/RT$ vs. $x_1$ at some arbitrary point is $d (g^E/RT) / dx_1$, and the tangent intersects the ordinate at $x_1 = 1$ and $x_1 = 0$ at points, say, a and b respectively, which are given by

$$a = (g^E/RT) + x_2 \frac{d}{dx_1} (g^E/RT)$$

and

$$b = (g^E/RT) - x_1 \frac{d}{dx_1} (g^E/RT)$$

It can be shown, using the relationship between $g^E/RT$ and the activity coefficients and the unrestricted form of the Gibbs - Duhem equation for either isobaric or isothermal conditions, that

$$a = \ln \gamma_1 + x_2 \delta$$

$$b = \ln \gamma_2 - x_1 \delta$$

where

$$\delta = (\nu^E/RT) (d\pi/dx_1)$$

for isothermal data

or

$$\delta = -(h^E/RT) / (dT/dx_1)$$

for isobaric data

The procedure for testing the thermodynamic consistency involves the calculation of a and b from a plot of $g^E/RT$ vs. $x_1$ for a given data point by construction of a tangent and comparison of the values of a and b read from the graph with those calculated using Equations 2.68 and 2.69. If the comparison is satisfactory the data point tested is thermodynamically consistent.

One of the disadvantages of the method is that it is difficult to draw tangents with accuracy. To overcome this disadvantage, Van Ness and Mrazek [418] suggested a plot of $g^E/RT x_1 x_2$ vs. $x_1$ instead of $g^E/RT$ vs. $x_1$. Then the tangent intercepts of this plot, e and f (at $x_1 = 1$ and $x_1 = 0$ respectively) are related to a and b by the
The modified plot is less sensitive to errors in tangent construction. One of the limitations of the composition resolution test is that it requires heat of mixing data for isobaric conditions and volumetric data for isothermal conditions. As discussed in the preceding sections, for low pressure isothermal data, $\delta$ can be neglected whereas for isobaric data this may not be always true.

Barien [15] derived the isothermal equation

$$x_f \left( \frac{d \ln f_1}{d x} \right)_T + x_f \left( \frac{d \ln f_2}{d x} \right)_T = \frac{(V_T/n) \rho}{RT} \quad (2.72)$$

starting from the Gibbs - Duhem equation written in terms of fugacities. Equation 2.72 can be used in the following manner:

$n$ moles of a feed having the composition $x_f$ are added to a container of total volume $V_T$, at temperature $T$, where vapour and liquid phases exist. At equilibrium, $x$, $y$, and $\pi$ values are determined. The experiment is repeated a number of times, varying the number of moles, $n$, or the feed composition $x_f$. Using the experimental $y$, $\pi$, $T$ values, fugacities are calculated by the use of an equation of state. The derivative $\left( \frac{d \ln f_1}{d x} \right)_T$ for each component is then evaluated at the experimental conditions where $x_f$ and $V_T/n$ values are known.

The left-hand term is calculated and compared with the known right-hand term for each experimental point. If the two sides agree, the data are thermodynamically consistent. This test can be extended to multicomponent systems.
Carlson and Colburn [46] discussed the application of the differential form of the Gibbs–Duhem equation for testing the thermodynamic consistency of binary data qualitatively by means of log $\gamma$ vs. $x$ which has prompted Lu [230] and Lu, Spinner, and Ho [233] to develop the following visual thermodynamic consistency tests using the van Laar, Margules, and Redlich and Kister forms of the integrated Gibbs–Duhem equation:

\[(\log \gamma_1)_{x_1=0.25} \approx (\log \gamma_2)_{x_1=0.75}\] (2.73)

At $x_1 = 0.5$

(a) $\log \gamma_1 \approx 0.25 \beta$ (2.74a)

(b) $\log \gamma_2 \approx 0.25 \alpha$ (2.74b)

where $\alpha = (\log \gamma_1)_{x_1=0}$

$\beta = (\log \gamma_2)_{x_1=1}$ (2.74c)

(3) If $\alpha > \beta$

\[(\log \gamma_1)_{x_1=0.5} < (\log \gamma_2)_{x_1=0.5}\] (2.75)

(4) If $\alpha < \beta$

\[(\log \gamma_1)_{x_1=0.5} > (\log \gamma_2)_{x_1=0.5}\] (2.75a)

(5) Both the log $\gamma$ curves on a log $\gamma$ vs. $x$ plot approach their zero values with a horizontal tangency.

(6) If there is a maximum or minimum on one of the log $\gamma$ curves, there is a corresponding minimum or maximum on the other curve at the same composition.

(7) If there is no maximum or minimum, both log $\gamma$ curves are on the same side of the log $\gamma = 0$ line.
These tests are valid at constant temperature with negligible effect of pressure on the activity coefficients. The applicability of these tests further depends on the applicability of the van Laar, Margules or Redlich-Kister equations to represent the vapour-liquid equilibrium data. Guidelines regarding the allowable deviations were discussed. One of the advantages in applying these tests is their simplicity.

Black [24, 25] has shown that the van Laar equations for binary systems can be rearranged to the form

\[(\log \gamma_1)^{0.5} = A^{0.5} - (A/B)^{0.5} (\log \gamma_2)^{0.5} \] (2.76a)

\[(\log \gamma_2)^{0.5} = B^{0.5} - (B/A)^{0.5} (\log \gamma_1)^{0.5} \] (2.76b)

From equations 2.76a and 2.76b it can be seen that a plot of \((\log \gamma_1)^{0.5}\) vs. \((\log \gamma_2)^{0.5}\) should give a straight line for thermodynamically consistent data since the van Laar equations are based on the Gibbs - Duhem equation. For systems for which the activity coefficients are less than one, \((-\log \gamma_1)^{0.5}\) vs. \((-\log \gamma_2)^{0.5}\) is plotted.

Norrish and Twigg [282] suggested the following equation which uses \(x - y\) and the pure component molar heat of vapourisation data to evaluate the consistency of the isobaric binary data:

\[Z = \ln \left( \frac{y_1 x_2^k}{y_2 x_1^k} \right) \] (2.77)

where \(k\) = ratio of the molar heats of vapourisation of the lower boiling component to that of the higher boiling component. For the data to be consistent, a plot of \(Z\) vs. \(x_1\) should give a straight line in the middle concentration range. The relationship was tested on 25 isobaric systems involving a wide range of compounds.
Techo [4-02] gave a method for testing isothermal binary data by fitting the experimental total pressure and vapour composition data as functions of the liquid compositions into two sets of polynomials, \( \pi = \pi (x) \) and \( y = y (x) \). These polynomials are used to calculate the excess chemical potentials which are substituted into the Gibbs – Duhem equation. Criteria are given for determining whether or not the data are thermodynamically consistent.

Myles and Wingard [267] discussed a chi-square statistical method for testing the internal consistency of experimental vapour-liquid equilibrium data. It is considered that the data should be experimentally consistent and reproducible even if thermodynamic consistency requirements are not met.

**A.3 Other Tests**

Schuberth [371] developed a method for testing the thermodynamic consistency of binary data with limited miscibility in the liquid phase. Five conditions for testing the data are given. Hala [128] also developed a test for application to binary systems with limited miscibility which can be extended to multicomponent systems. Kogan et al. [192] derived equations for testing the thermodynamic consistency for systems with chemically interacting components.

Tao [397, 398] developed a test which is applicable to binary as well as multicomponent systems for local and overall consistency. The method takes into account the vapour phase imperfections and involves the following equations:

\[
Q = \frac{g^E}{RT} = \sum_{i} x_i \ln \gamma_i = Q_e \quad (2.78)
\]
\[ \alpha_1 = - \left( \frac{h^E}{RT^2} \right) \left( \frac{dT}{dx_1} \right) + \left( \frac{v^E}{RT} \right) \left( \frac{d\alpha}{dx} \right) + \]

\[ \bar{\Xi} \left( \frac{dx_1}{dx_1} \right) \ln \gamma_1 = \alpha_{le} \]

\[ \frac{dx_1}{dx_1} = \left( x_{1a} - x_{1b} \right) / \left( x_{1a} - x_{1b} \right) \]

\[ Q_{x_{1b}} - Q_{x_{1a}} = \int_{x_{1a}}^{x_{1b}} \alpha_1 \, dx_1 = \Delta Q_c \]

\[ \alpha_1 = \frac{dQ}{dx_1} = \alpha_{lc} \]

Since \( Q \) and \( \alpha_1 \) can be calculated directly from experimental data according to Equations 2.78 and 2.79 and also indirectly from Equations 2.81 and 2.81a, an integral method with Equations 2.78 and 2.81 and a differential method with Equations 2.79 and 2.81a are available to test an overall linear path as well as local points. Equations are given to estimate the propagation of the errors in experimental measurements for the computed values of \( \gamma, Q, \) and \( \alpha_1 \). The application of the method requires the heats of mixing and volumetric properties in its rigorous form. Stevenson and Sater [387] and Redlich, Gargrave, and Krostek [343] gave local consistency tests which can be applied to limited data. Chang and Lu [49] discussed a general consistency method for binary and multicomponent systems which does not involve activity coefficients. The test can be applied even if one of the components is above its critical state. Data can be tested point-by-point along any arbitrarily chosen path. A method similar to that of Tao [397] was employed to obtain the maximum experimental error bounds. The test is applicable to isobaric or isothermal data.
Friend, Scheller, and Weber [108] developed relationships based on the Gibbs–Duhem equation which will permit the evaluation of net deviations in any one of the four measured variables, \( \pi - t - x - y \) using the Gibbs–Duhem equation assuming that the values of the other measured variable is correct. The method takes into consideration vapour phase nonideality. The method was tested on four typical isothermal binary systems exhibiting ideal to nonideal azeotropic behaviour. Both narrow as well as large pressure difference systems were included. In many instances the calculated liquid compositions differed from the experimental ones by less than 0.02 mole percent, which is less than the experimental error. This indicates the existence of compensating errors. One of the drawbacks of the method is the assumption that three out of four measured quantities are correct and lumping the deviations into the fourth measured value.

B. Multicomponent Systems

The excess free energy function for a multicomponent system is given by Equation 2.78:

\[
Q = \frac{g^E}{RT} = \sum \frac{x_i}{\ln y_i} \quad (2.78)
\]

\[
dQ = \sum \ln y_i \, dx_i + \frac{\nu}{RT} \, dx - \frac{h^E}{RT^2} \, dT \quad (2.82)
\]

Different consistency tests have been proposed which depend on integration of Equation 2.82 in different ways.

Herington [143] has suggested two methods for ternary systems one of which involves integration along a line parallel to one of the bases of the triangular coordinates, thus keeping the mole fraction of one component constant. The other method involves integration along a straight line connecting one of the vertices to a point in
the opposite base. In this method, the ratio of two of the mole fractions is kept constant. These methods are applicable to systems with more than one liquid phase provided that the whole liquid is treated as a single phase by using the overall mole fractions and activity coefficients. Krishnamurthy and Rao [207] suggested a linear paths method for ternary systems with one component at constant composition. Prausnitz and Snider [322] gave an equation which may be used for tests along linear paths connecting to pure components.

Li and Lu [224] presented a method by which the integration of the Gibbs–Duhem equation can be performed along any curvilinear path for a ternary system, especially along the curve of constant temperature and pressure for which the method becomes thermodynamically exact. At constant temperature and pressure for a ternary system, Equation 2.82 becomes

\[ dQ = \ln \gamma_1 \, dx_1 + \ln \gamma_2 \, dx_2 + \ln \gamma_3 \, dx_3 \] \hspace{1cm} (2.83)

Since \( Q = 0 \) at the three vertices of the triangular coordinates, an integration of Equation 2.83 along a curve connecting two of the vertices gives

\[ \int_{x_1=a}^{x_1=b} \ln \gamma_1 \, dx_1 + \int_{x_1=a}^{x_1=b} \ln \gamma_2 \, dx_2 + \int_{x_1=a}^{x_1=b} \ln \gamma_3 \, dx_3 = 0 \] \hspace{1cm} (2.84)

Equation 2.84 can be applied to isobaric ternary data, provided that the temperature change along the curve is small so that the heat of mixing effects can be neglected:

\[ Q_b - Q_a = \int_a^b \ln \gamma_1 \, dx_1 + \int_a^b \ln \gamma_2 \, dx_2 + \int_a^b \ln \gamma_3 \, dx_3 \] \hspace{1cm} (2.85)
a and b refer to the points between which the integrals are evaluated. The integrals can be evaluated graphically by plotting \( \ln \gamma_i \) vs. \( x_i \) or numerically by taking the points from the path chosen in the sequence from point a to point b. The number of plots required can be reduced to two if the activity coefficient ratios are plotted against composition. Equation 2.85 in terms of the activity coefficient ratios becomes

\[
Q_b - Q_a = \int_a^b \ln \gamma_1 / \gamma_2 \, dx_1 + \int_a^b \ln \gamma_2 / \gamma_3 \, dx_2 \tag{2.86}
\]

Closed or open paths over limited areas can be chosen for the integration. If closed paths are chosen or if a and b coincide with two vertices of the triangular coordinates, the sum of the values of the integrals reduce to zero. The test involves the selection of the paths and the evaluation of the right-hand side of Equation 2.86 for a number of data pairs which is then compared to the left-hand side evaluated from the corresponding activity coefficient-composition data for each point using Equation 2.78. If the two sides agree within reasonable limits the data are consistent.

McDermott and Ellis [253] rederived the Li and Lu [224] equations in a form which permits testing the consistency of points individually in pairs for isothermal multicomponent systems which can be extended to isobaric data with small temperature differences between the points. The isothermal-isobaric Gibbs–Duhem equation is integrated round a loop of points a, b, c, ... y, z by the trapezoidal rule to give

\[
\sum_{i=1}^{n} \left[ \frac{x_{ia} + x_{ib}}{2} \left( \ln \gamma_{ib} - \ln \gamma_{ia} \right) + \frac{x_{ib} + x_{ic}}{2} \left( \ln \gamma_{ic} - \ln \gamma_{ib} \right) + \ldots + \frac{x_{iz} + x_{iy}}{2} \left( \ln \gamma_{iz} - \ln \gamma_{iy} \right) \right] = 0 \tag{2.87}
\]
The individual terms in Equation 2.87 give a direct comparison of each point with its neighbour offering a two-point consistency test. If any particular point is common to several pairs and gives large deviations, then it may be taken as inconsistent. Equation 2.87 to any pair of points, a and b can be written as

$$\sum_{i=1}^{n} (x_{ia} + x_{ib}) (\ln \gamma_{ib} - \ln \gamma_{ia})$$

(2.88)

Because of finite distances between the points, the numerical integration method used in deriving Equation 2.87 is an approximation. The error arising out of this approximation can be minimised by selecting the data pairs so that their compositions differ to a small extent. The method can be applied to isobaric data by carefully selecting the data pairs so that their temperatures do not differ by more than about 3°C. This test is simple to apply and can be used to check the results as they are experimentally performed.

Pak and Kogan [308] developed methods to reduce a ternary system into a pseudo-binary one for three different cases considering change in composition along (i) a straight line connecting one of the vertices to a point in the opposite base, (ii) a line parallel to one of the bases, and (iii) along the solubility curve in triangular coordinates. They have introduced the concept of an average activity coefficient to describe the properties of the pseudo component, consisting of components 1 and 2, in the mixture. They have illustrated the application of the binary consistency tests to the pseudo-binary systems.

Ravindran, Srinivasan, and Laddha [339] gave the following

$$n^i (x_{ia} + x_{ib}) (\ln \gamma_{ib} - \ln \gamma_{ia})$$

(2.88)
equation for testing thermodynamic consistency of ternary isobaric data:

\[ Q_a - Q_b = \int_a^b \ln \gamma_1/\gamma_2 \, dx_1 - \int_a^b \frac{h^E}{RT^2} \left( \frac{dT}{dx_1} \right) \, dx_1 \] (2.89)

where \( a \) and \( b \) refer to the two vertices of the triangular coordinates with \( x_1 = 0 \) and \( x_2 = 0 \) respectively. They have extended the method proposed by Ramachandran and Laddha [332] for the evaluation of the heat of mixing term using the Redlich-Kister expansion on the assumption that the ternary effects are negligible. This method gives the overall consistency of the data and therefore, cannot detect errors which compensate each other.

Kogan and Sedletskaya [196] proposed a method for testing the consistency of ternary and multicomponent systems based on the properties of mixed derivatives of the free energy with respect to composition. The method can be used in a restricted composition range.

Tao [400] has developed an isobaric consistency test for multicomponent systems with large temperature variation based on the following rigorous thermodynamic equation relating the phase enthalpy difference, temperature, and phase composition [394]:

\[ \sum \left( x_i - y_i \right) \ln f_i^V / dT = \left( \Delta H - \Delta H^* \right) / RT^2 \] (2.90)

where \( \Delta H = (\text{saturated vapour enthalpy}) - (\text{saturated liquid enthalpy}) \)

\( \Delta H^* = (\text{Ideal gas enthalpy with vapour phase composition}) - (\text{Ideal gas enthalpy with liquid phase composition}) \)

\( f_i^V = \text{fugacity of component i in the saturated vapour phase.} \)

\( \Delta H \), the phase enthalpy difference, can be estimated as follows:

As a first approximation, a linear interpolation of \( \Delta H \) may be made by using the pure component heats of evaporation. The difference, \( \delta \), between the real \( \Delta H \) and the first approximation may be defined by
Equation 2.91 as a second approximation:

$$\delta = \Delta H - \frac{\Xi}{2} y_1 \Delta H_1^0 \tag{2.91}$$

where $\Delta H_i^0$ = heat of vapourisation of pure component $i$. $\delta$ may be estimated using two experimental points or a similarity concept assuming that $\delta$ of a given system has the same magnitude as that of a similar system where the thermodynamic consistency has been established by using the conventional Gibbs-Duhem equation. Using $\delta$ and $\Delta H_1^0$ in Equation 2.91, $\Delta H$ is calculated. From $t$, $x$, $y$ data and the vapour phase fugacities, the left-hand term of Equation 2.90 is calculated which is then compared to the right-hand term calculated from $\Delta H$ estimated from Equation 2.91 and $\Delta H^*$ either taken from literature or estimated from heat capacity data. Equation 2.90 can be used in a differential test or integrated to given an integral test.

For many systems with pressures far below the critical region, the gas phase fugacities can usually be assumed to be equal to $wy_i$. This results in the following simplified equation:

$$\Xi \left[ \frac{x_i}{y_i} \left( \frac{dy_i}{dT} \right) \right] = \left( \Delta H - \Delta H^* \right) / RT^2 \tag{2.92}$$

Kogan et al. [193, 197] gave equations which permit testing the consistency of ternary data involving components that react in the vapour phase.

Subbarao [389] proposed a method of obtaining ternary vapour-liquid equilibrium data experimentally, in which the analysis of the equilibrium liquid sample can be avoided, and discussed its utility in checking the thermodynamic consistency of isothermal ternary data.
2.5 Correlation and Prediction of Vapour-Liquid Equilibria

2.5.1 Binary Systems

A. Based on Excess Free Energy Function

The relationship between activity coefficients and composition is conveniently expressed by the molar excess free energy, $g^E$. If $g^E$ can be expressed as a function of liquid composition, activity coefficients can be calculated from the exact relationship

$$ \text{RT} \ln \gamma_i = (\frac{\partial n_i^E}{\partial n_i^E})_{T,P,n_j \neq i} \quad (2.93) $$

For a given temperature and composition $g^E$ can be determined from the activity coefficients, and conversely the activity coefficients can be determined if $g^E$ is known as a function of composition using Equation 2.93. Thus it has been the objective of most efforts to develop equations relating $g^E$ to composition. The simplest case is when $g^E = 0$ at all compositions, and consequently $\gamma_i = 1$ for all compositions, which represents a complete definition of an ideal solution. Adding the assumption that the vapour phase is an ideal gas results in Raoult's law.

For a binary mixture Wohl [440] proposed the following expansion for $g^E$ using the effective volume fraction $z$ for the composition variable:

$$ g^E / \text{RT} (x_1 q_1 + x_2 q_2) = 2 a_{12} z_1 z_2 + 3 a_{112} z_1^2 z_2 + 3 a_{122} z_1 z_2^2 + ... \quad (2.94) $$

where $z_1 = x_1 q_1 / (x_1 q_1 + x_2 q_2)$ and $z_2 = x_2 q_2 / (x_1 q_1 + x_2 q_2) \quad (2.94a)$

The q's are size factors or effective molar volumes and the a's are
proportionality factors to reflect the interactions among various groups of molecules. The a's and q's are independent of composition but dependent on temperature. Though Equation 2.94 has no precise theoretical foundation, it has the built-in flexibility to allow a variety of simplifying assumptions. If we assume $q_1 = q_2$ and neglect higher terms in Equation 2.94, then Equations 2.93 and 2.94 yield the familiar three-suffix Margules equations

$$\ln \gamma_1 = x_1^2 \left[ A_{12} + 2x_1 (A_{21} - A_{12}) \right]$$

$$\ln \gamma_2 = x_1^2 \left[ A_{21} + 2x_2 (A_{12} - A_{21}) \right]$$

If we retain only the first term in $q_2 / q_1 = A_{21} / A_{12}$, then we obtain the well-known equations of van Laar [46, 412, 413]:

$$\ln \gamma_1 = \frac{A_{12}}{1 + \frac{A_{12} x_1}{A_{21} x_2}}$$

$$\ln \gamma_2 = \frac{A_{21}}{1 + \frac{A_{21} x_2}{A_{12} x_1}}$$

If we assume that $A_{12} = A_{21}$, both the Margules and van Laar equations simplify to the form

$$\ln \gamma_1 = \frac{A_{12} x_2^2}{x_1}$$

$$\ln \gamma_2 = \frac{A_{12} x_1^2}{x_2}$$

which are the second/third order Symmetrical equations. If we assume that $q_1 = V_1$ and $q_2 = V_2$, Scatchard and Hamer equations [365] are obtained:

$$\ln \gamma_1 = z_2^2 \left[ A_{12} + 2 z_2 (A_{21} V_1/V_2 - A_{12}) \right]$$

$$\ln \gamma_2 = z_1^2 \left[ A_{21} + 2 z_1 (A_{12} V_2/V_1 - A_{21}) \right]$$
Ellis and Bourne [82] observed that the van Laar and Margules equations might be expected to give a fairly close fit of isothermal data if (i) the ratio of the end values of $\gamma$ is less than 1.5 to 1.6, (ii) the end values are less than 1.3, (iii) the ratio of molar volumes of the components is less than 2.0, (iv) both the components are either associated or nonassociated, and (v) the mixture exhibits either positive or negative deviations. If one of the activity coefficients passes through a maximum, only the Margules equation can fit the data. The van Laar or Scatchard-Hamer equations are frequently suitable compared to the Margules equations if the ratio of the pure component volumes differ largely. If the constants $A_{12}$ and $A_{21}$ are equal, the van Laar and Margules equations become identical. In general, the van Laar equations are superior to the Margules or Scatchard and Hamer equations. Since these equations are obtained from Wohl's expansion which holds for constant temperature and pressure, the constants in these equations are functions of temperature and pressure. For isobaric systems, the pressure effect is zero, but the temperature effect is not necessarily negligible. These equations are applicable if the temperature range is small. The Scatchard and Hamer equations have not received much attention in the literature because they are mathematically more complex.

Various modifications of the van Laar and Margules equations have been proposed from time to time mainly to facilitate the application of the equations to the correlation of data [23, 25, 26, 46, 306, 427, 449]. The original van Laar equations [412, 413]

$$T \ln \gamma_1 = \frac{A_{21}}{(1 + \frac{A_{12} x_1}{x_2})^2}$$

$$T \ln \gamma_2 = \frac{A_{12} A_{21}}{(A_{12} + \frac{x_2}{x_1})^2}$$

(2.99)

contain a temperature term which was omitted in the Carlson and Colburn modification (Equation 2.95). Otterstedt and Missen [306] showed that the
van Laar and Margules equations are reciprocally related and can be written as

\[
\frac{g}{x_1 x_2} = \sum_{k=0}^n a_k x_1^k \quad \text{(Margules)} \quad (2.100)
\]

\[
\frac{x_1 x_2}{g} = \sum_{k=0}^n b_k x_1^k \quad \text{(van Laar)} \quad (2.101)
\]

They have observed that the van Laar equations cannot be used if the excess function changes sign. Since \( g \) cannot change sign, the van Laar equations are successful. But if other excess functions are used, change of sign can occur. They developed a square-root analogue of the Margules equation

\[
\frac{g}{x_1 x_2} = \sum_{k=1}^n c_k x_1^{(k-2)/2} \quad (2.102)
\]

which is empirical in nature and represented data better for methanol-carbon tetrachloride mixtures. Equation 2.102 is, however, not sound theoretically.

Fleck and Prausnitz [96] developed an approximate correlation for relative volatility based on the single-parameter van Laar equations.

Black [25] modified the van Laar equations which can be applied to polar-nonpolar or polar-polar mixtures. It was shown that the van Laar equations can be rearranged to give

\[
(\ln \gamma_1)^{0.5} = A_{12}^{0.5} - (A_{12} / A_{21})^{0.5} (\ln \gamma_2)^{0.5} \quad (2.103)
\]

\[
(\ln \gamma_2)^{0.5} = A_{21}^{0.5} - (A_{21} / A_{12})^{0.5} (\ln \gamma_1)^{0.5}
\]

This form gives a straight line when plotted as \((\ln \gamma_1)^{0.5}\) vs. \((\ln \gamma_2)^{0.5}\). Some systems deviate from this relationship due to association and to account for these deviations, Black added an
empirical term to the isothermal van Laar equation:

$$\ln \gamma_i = \frac{a^2_{ij}}{1 + a^2_{ij} \frac{x_i}{a^2_{ji} x_j}} + E_i$$  \hspace{1cm} (2.104)

where

$$E_i = c_{ij} x_j (x_i - x_j) [3 (x_i - x_j) (1-x_i) + 2x_j]$$  \hspace{1cm} (2.104a)

The term $c_{ij}$ is an empirical constant. Black's equations are very flexible and can express the behaviour of even highly nonideal systems.

Recently Lowell and Van Winkle [2293 * proposed the following equations starting with the Margules equations and making use of the excess heat capacity expressed as a function of temperature and its relationship with the activity coefficients:

$$\ln \gamma_1 = \sum_{n=1}^{N} \left[ D_{n,1} + (D_{n,2} / T) + D_{n,3} \ln T + \sum_{m=4}^{M} D_{n,m} T^{m-3} \right] x_2^{n+1}$$

$$\ln \gamma_2 = \sum_{n=1}^{N} \left[ D_{n,1} + (D_{n,2} / T) + D_{n,3} \ln T + \sum_{m=4}^{M} D_{n,m} T^{m-3} \right]$$

$$\left[ x_2^{n+1} - \frac{(n+1)}{n} x_2^n + 1/n \right]$$

where $D_{n,m} =$ constants

$M =$ number of temperature terms used in temperature series expansion

$N =$ number of composition terms used in composition series expansion

Similar equations are given for the excess enthalpies from which heats of mixing can be calculated using the relation

$$h^E = x_1 (\bar{h}_1 - \bar{h}_1^*) + x_2 (\bar{h}_2 - \bar{h}_2^*)$$  \hspace{1cm} (2.106)

where $\bar{h}_1 =$ partial molar enthalpy of component $i$, cal / g mole

$\bar{h}_2 =$ heat of mixing cal / g mole.

$\bar{h}_1^*$ = pure component enthalpy of component $i$, cal / g mole.
A number of papers appeared in the literature on the determination of constants in the binary correlations [46, 131, 264, 374, 407]. Hala et al. [132] discussed some of the methods which need not be considered here. These methods involve the use of limited data such as the azeotropic point or a few experimental points. Tierney [407] proposed a rigorous statistical method taking into consideration the sources of experimental error.

Mir and Steidler [264] proposed a least squares method for the evaluation of the binary van Laar constants by combining the van Laar equation with the equilibrium relationships

\[ \gamma_i x_i = P_i \ (2.107a) \]

and

\[ \alpha_{ij} = \frac{y_i x_j}{y_j x_i} \]  
\[ \frac{\ln \left( \frac{p_i^0}{p_j^0} \right)}{\alpha_{ij}} = A_{21} \left[ \frac{(x_i / x_j)^2 - A_{21} / A_{12}}{(x_i / x_j)^2 + (A_{21} / A_{12})^2} \right] \]  
\[ (2.107c) \]

Equation 2.107c is solved for \( A_{12} \) and \( A_{21} \) by a least squares regression technique.

The development of large number of variants for the van Laar and Margules equations did not diminish the popularity of the Carlson and Colburn type van Laar and Margules equations for application to binary systems. The omission of the temperature term in the van Laar type equations resulted in most of the cases no disadvantage. Moreover, the constants in the Carlson and Colburn type equations became identical with the end values of the activity coefficients, which was not the case with the equations containing the temperature term. The Black equations
improve the accuracy of prediction for alcohol-hydrocarbon systems
but with the use of an additional constant.

The second type of solution for $g^E$ for binary systems was proposed
by Redlich and Kister [344, 345]:

$$
\frac{g^E}{RT} = x_1 x_2 \left[ B + C (x_1 - x_2) + D (x_1 - x_2)^2 + \ldots \right] \quad (2.108)
$$

where $B$, $C$, $D$, $\ldots$ are constants found from the binary data. If the
equation has only the first three constants it is known as the Redlich
and Kister fourth order equation. By differentiation of Equation 2.108
with respect of $x_1$ and $x_2$, the Redlich and Kister equation for activity
coefficient ratio is obtained:

$$
\ln \gamma_1 / \gamma_2 = B (x_2 - x_1) + C (6x_1 x_2 - 1) + D (x_2 - x_1)
\left(1 - 8x_1 x_2\right) + \ldots \quad (2.109)
$$

If $D$ and higher constants are set to zero in Equation 2.109, the
Redlich and Kister equation reduces to the Margules equation. For the
individual activity coefficients the equations are:

$$
\ln \gamma_1 = x_2^2 \left[ B + C (3x_1 - x_2) + D (x_1 - x_2) (5x_1 - x_2) + \ldots \right] \quad (2.110)
\ln \gamma_2 = x_1^2 \left[ B + C (x_1 - 3x_2) + D (x_1 - x_2) (x_1 - 5x_2) + \ldots \right]
$$

The principal advantage of the Redlich and Kister equations is
their flexible nature. If the data cannot be fitted adequately by the
use of the three-constant form, four-constant form can be used. For
nearly ideal systems, the use of only one constant will be sufficient
whereas highly nonideal systems containing an alcohol or an acid three
terms may be used. Bourne [32] has made a thorough study of the Redlich
and Kister equations with the objective of determining quantitatively

1) whether the two and four-constant forms differ significantly
from the three-constant form
ii) whether the vapour phase can be treated as an (a) ideal solution or (b) an ideal gas at subatmospheric pressures

iii) how the numerical method adopted in fitting an equation to the experimental values influences the correlation obtained.

The study covered a number of binary systems including some highly nonideal systems with polar-nonpolar combinations and also some near-ideal systems. The conclusions were in favour of the three-constant Redlich and Kister equation as the four-constant equation did not significantly improve the correlation for the polar, nonideal systems. Two and one-constant equations are not sufficiently accurate. The assumption that the vapour phase is ideal deteriorates the data fit in the correlation irrespective of the number of constants used. The trend of the errors indicates that the calculations are not simple curve fitting but have a thermodynamic significance. Comparison between the least squares method and the graphical method of residues for the evaluation of the constants gave comparable accuracy. On the other hand, graphical methods in the van Laar and Margules equations can lead to large errors because of the errors involved in extrapolating the activity coefficients to their infinite dilution values. Nonlinear extrapolation in the least accurate regions gives rise to appreciable errors.

Hala et al. [132] summarised the graphical method generally used for the evaluation of the constants in the Redlich and Kister equation. The method involves plotting $\ln \frac{\gamma_1}{\gamma_2}$ as a function of $x_1$ from which
values of $\ln \gamma_1 / \gamma_2$ at strategic compositions are read off and substituted in Equation 2.109, to give equations which are solved for $B, C, D, \ldots$ constants. Scatchard's [364] observation, that while the error in an activity coefficient is not equally weighted with respect to composition, values of the excess free energy function, $g^E / RT$, are approximately equally weighted, can be used to apply the least squares method to Equation 2.108 to evaluate the constants. This method is used in this work in evaluating the constants in various correlations.

Chao [50] added an empirical constant, $a$, to the isothermal Redlich and Kister equation (Equation 2.109) in order to extend its applicability to isobaric conditions. At constant pressure, Chao proposed that

$$\int_0^1 \ln \gamma_1 / \gamma_2 \, dx_1 = a \quad (2.111)$$

where $a$, a function of pressure, may or may not be equal to zero. Addition of the constant $a$ to Equation 2.109, requires adjustment of the other constants and the modified Redlich and Kister equation is written as

$$\ln \gamma_1 / \gamma_2 = a + b (x_2 - x_1) + c (6x_1 x_2 - 1) + d (x_2 - x_1) (1 - 8x_1 x_2) + \ldots \quad (2.112a)$$

in which the constants $b, c, d, \ldots$ are somewhat different from $B, C, D, \ldots$ in Equation 2.109. Chao [51] showed that the constants in Equation 2.112a have the following relationship to the constants in Equation 2.109 if the terms containing the constants $d, D, \ldots$ are neglected:

$$B = b$$
$$C = c - a \quad (2.112b)$$
Wichterle [429] examined carefully selected literature experimental data for about 400 binary azeotropic and nonazeotropic systems containing polar and nonpolar components for fit in various correlations including those of the van Laar, Scatchard-Hamer, Margules, and Redlich-Kister using a weighted least squares method. Both third and fourth order Margules and Redlich-Kister correlations were used. All the systems chosen were in the low-pressure range up to two atmospheres and ideal behaviour for the vapour phase was examined. It was concluded that the most commonly used third order van Laar and Redlich and Kister equations are equally suitable. The Scatchard and Hamer equation was found not too reliable.

In both the Wohl and Redlich-Kister expansion, $g^E$ has been expressed as a power series of composition. Wilson [438] has proposed a completely different expression, writing $g^E$ as a logarithmic function of liquid composition. As shown by Orye and Prausnitz [290]

$$
\frac{g^E}{RT} = -x_1 \ln (x_1 + \frac{\Lambda_{12}}{\Lambda_{21}} x_2) - x_2 \ln (x_2 + \frac{\Lambda_{21}}{\Lambda_{12}} x_1)
$$

(2.113)

where

$$
\frac{\Lambda_{12}}{\Lambda_{21}} = \frac{(V_2/V_1) \exp \left[ - \left( \frac{\Lambda_{12}}{\Lambda_{11}} - \frac{\Lambda_{12}}{\Lambda_{22}} \right) / RT \right]}{V_2 / V_1}
$$

and

$$
\frac{\Lambda_{21}}{\Lambda_{12}} = \frac{(V_1/V_2) \exp \left[ - \left( \frac{\Lambda_{12}}{\Lambda_{11}} - \frac{\Lambda_{12}}{\Lambda_{22}} \right) / RT \right]}{V_1 / V_2}
$$

The energy parameters, $\Lambda_{12}$, $\Lambda_{11}$ and $\Lambda_{22}$, are, to a good approximation, independent of temperature, at least over a modest temperature interval. The corresponding expressions for the activity coefficients are:

$$
\ln \gamma_1 = -\ln (x_1 + \frac{\Lambda_{12}}{\Lambda_{11}} x_2) - x_2 \left[ \frac{\Lambda_{12}}{\Lambda_{11} x_2} - \frac{\Lambda_{21}}{\Lambda_{21} x_1 + x_2} \right]
$$

$$
\ln \gamma_2 = -\ln (x_2 + \frac{\Lambda_{21}}{\Lambda_{12}} x_1) - x_1 \left[ \frac{\Lambda_{12}}{\Lambda_{11} x_2} - \frac{\Lambda_{21}}{\Lambda_{21} x_1 + x_2} \right]
$$

(2.114)
These equations, because of their built-in temperature dependence, are useful for isobaric conditions. These equations have proved suitable for the representation of vapour-liquid equilibrium data for a wide variety of binary systems including highly nonideal systems. In recent years a large number of binary systems have been fitted to the Wilson correlation which represented the data generally better than some of the more complicated equations containing more than two constants.

Though the Wilson correlation is in general found to be superior to the other two-constant equations, especially for highly nonideal systems, it suffers from two disadvantages. First, the correlation is not suitable for partially miscible systems. Second, it is not capable of representing systems that give rise to maxima or minima on a \( \ln \gamma \) vs. \( x \) plot. To extend the correlation to represent partially miscible systems, Wilson [438] introduced a third parameter in the correlating equations. But the three-parameter model does not offer any significant advantage over other correlations and also restricts its application to only binary systems.

Heil and Prausnitz [138] modified the Wilson equation to represent vapour-liquid equilibrium data for strongly nonideal polymer solutions.

The parameters in the Wilson equation are evaluated from a series of experimental data points, either isobaric or isothermal. Prausnitz et al. [320], Neretnieks [279] and Holmes and Van Winkle [161] used different minimum seeking techniques to obtain the parameters.
Their techniques operate to minimise the following error functions to obtain the best parameters:

\[ E_x = \sum_{i=1}^{k} \left( \frac{\pi_{\text{exptl}} - \pi_{\text{calcd}}}{\pi_{\text{exptl}}} \right)^2 \quad \text{(Prausnitz et al.)} \quad (2.115a) \]

\[ E_y = \sum_{i=1}^{k} \left( \frac{y_{\text{exptl}} - y_{\text{calcd}}}{y_{\text{calcd}}} \right)^2 \quad \text{(Neretnieks)} \quad (2.115b) \]

\[ E_y = \sum_{i=1}^{k} (\gamma_{1\text{exptl}} - \gamma_{1\text{calcd}})^2 + \sum_{i=1}^{k} (\gamma_{2\text{exptl}} - 1.0) \quad \text{(Helmes and Van Winkle)} \quad (2.115c) \]

No detailed comparison of these techniques has been made although Hudson and Van Winkle [167] pointed that the function defined by Equation 2.115c gave generally better fit of the experimental compositions compared to that when Equation 2.115a is used.

Renon and Prausnitz [349] proposed the following equation for \( g^E \), based on Scott's two-fluid theory of mixtures [372] :

\[ g^E / RT = x_1 x_2 \left( \frac{\tau_{21} G_{21}}{x_1 + x_2} \right) + \frac{\tau_{12} G_{12}}{x_2 + x_1} \quad (2.116) \]

where

\[ G_{12} = \exp \left( -\alpha_{12} \tau_{12} \right) \quad (2.116a) \]

\[ G_{21} = \exp \left( -\alpha_{12} \tau_{21} \right) \quad (2.116b) \]

\[ \tau_{12} = (g_{12} - g_{22}) / RT \quad (2.116c) \]

\[ \tau_{21} = (g_{21} - g_{11}) / RT \quad (2.116d) \]

with

\[ g_{12} = g_{21} \quad (2.116e) \]

Equation 2.116 contains two temperature-dependent parameters, \((g_{12} - g_{22})\) and \((g_{21} - g_{11})\), in addition to a nonrandomness parameter,
\( \alpha_{12} \), which, to a good approximation does not depend on temperature. From equation 2.116, the following expressions for activity coefficients can be obtained:

\[
\ln \gamma_1 = x_2 \left[ \frac{\tau_{21} \alpha_{21}^2}{(x_1 + x_2 \alpha_{21})^2} + \frac{\tau_{12} \alpha_{12}^2}{(x_2 + x_1 \alpha_{12})^2} \right]
\]

\( \ln \gamma_2 = x_1 \left[ \frac{\tau_{12} \alpha_{12}^2}{(x_2 + x_1 \alpha_{12})^2} + \frac{\tau_{21} \alpha_{21}^2}{(x_1 + x_2 \alpha_{21})^2} \right]
\]

Equation 2.116 is called the NRTL (Non-Random Two-Liquid) equation. This equation, unlike the Wilson equation, is applicable to both miscible and partially miscible systems. Unlike the Wilson three-parameter equation which has been proposed to extend the original Wilson equation to partially miscible binary systems, the NRTL equation can easily be extended to multicomponent systems. Renon and Prausnitz have applied the NRTL equation to a large number of binary systems and found it to be accurately representing the experimental data.

Renon and Prausnitz [351] discussed methods for the estimation of the parameters in the NRTL equation and gave charts to facilitate the evaluation of the parameters. For typical non-electrolyte systems, \( \alpha_{12} \) varies from 0.2 to 0.47. If complete experimental data are available the parameters can be determined by a suitable least squares method. These can also be estimated from limiting activity coefficient data, or, for partially miscible systems, from mutual solubilities. Renon and Prausnitz [349] have classified binary systems into seven types based on their chemical nature and recommended values of \( \alpha_{12} \).
Values of $\alpha_{12}$ thus selected, the other two parameters can be found from the charts presented \[351\] for different values of $\alpha_{12}$.

Asselineau and Renon \[13\] have extended the NRTL equation to represent the properties of binary systems over a large temperature range. They showed that the parameters can be calculated by least squares method from available vapour-liquid, liquid-liquid equilibria, activity coefficients at infinite dilution and enthalpy of mixing.

Bruin \[40\] derived equations relating the excess free energy to the composition of a liquid mixture based on Guggenheim's quasilattice model of multicomponent solutions. In this model the enthalpic and entropic contributions to the excess free energy appear as separate terms. He showed that the introduction of the Wilson parameters in this model assuming the excess entropy to be zero (regular solutions) gives the 'enthalpic Wilson' equations:

$$\ln \gamma_1 = -\frac{x_2 \ln \left(\frac{\Lambda_{12}}{\Lambda_{21}}\right)}{(x_1 + \Lambda_{12} x_2)(x_2 + \Lambda_{21} x_1)} \left[ 1 + x_1 \left(1 - \frac{1}{x_1 + \Lambda_{12} x_2}\right) \right] \frac{\Lambda_{21}}{x_2 + \Lambda_{21} x_1}$$

(2.118)

For $\ln \gamma_2$ an analogous expression results by rotation of indices 1 2 1. In a similar manner, the 'extended van Laar' (EVL) equations were obtained by the introduction of the van Laar parameters into the model:

$$\ln \gamma_1 = 1 - \ln \left(\frac{x_1 + A_{12} x_2}{A_{21}}\right) - \frac{1}{x_1 + A_{12} x_2 / A_{21}} + \frac{A_{21} x_2}{(x_2 + A_{21} x_1 / A_{12})^2}$$

(2.119)
The relation for \( \ln \gamma_2 \) results when indices are rotated in the sequence 1 2 1.

Equations 2.118 and 2.119 were tested for sixteen binary systems, five of which show limited miscibility and for four ternary systems. The Wilson [290] and the van Laar equations [46] were also included in the programme which used the fitting procedure proposed by Prausnitz et al. [320]. The EVL equations gave poorer results when compared to the van Laar equations. The enthalpic Wilson equations gave good representation for most of the systems, in many cases better than the van Laar and Wilson equations. The major advantage of the enthalpic Wilson equations is in their application to partially miscible systems with only two binary parameters. The Wilson or NRTL equations require three binary parameters to represent such systems. As in the case of the Wilson and NRTL equations, there is a built-in temperature dependence of the activity coefficients. A nomograph is given for the estimation of the parameters in the enthalpic Wilson equation using infinite dilution activity coefficient data.

Several other mathematical fitting techniques have been used in representing the excess properties for binary systems. Jost and Röck [184] and Klaus and Van Ness [187] represented the thermodynamic excess functions by orthogonal polynomials and showed how these can be applied to experimental vapour-liquid equilibrium data.

A number of papers appeared in literature on alcohol-hydrocarbon systems [23-26, 53, 338, 350, 432, 433]. Wiehe and Bagley [433] and Renon and Prausnitz [350] obtained equations which
are applicable to miscible alcohol-hydrocarbon systems taking into consideration hydrogen bonding. Chao et al. [53] developed a group interaction theory of heat of mixing for binary alcohol-paraffin systems.

B. Based on Equilibrium Phase Compositions

Hala et al. [132] reviewed a number of equations for the correlation of x - y and relative volatility data. Clark [56] related the vapour and liquid compositions for binary systems by the following equations:

\[ \frac{y_1}{y_2} = a \frac{x_1}{x_2} + b \] (2.120a)
\[ \frac{y_2}{y_1} = a' \frac{x_2}{x_1} + b' \] (2.120b)

Equation 2.120a is used for large values of \( x_1 / x_2 \) and Equation 2.120b is used when \( x_2 / x_1 \) is large. The constants are related by the equation

\[ \sqrt{(a' - a)} + \sqrt{(b' - b)} = 1 \] (2.120c)

Clark equations are quite simple and fairly good for representing the relationship between the equilibrium phases. Prahl [317] proposed the equation

\[ y_1 = \frac{C_{x_1} (A - x_1)}{C_{x_1} (A - x_1) + x_2 (B + x_1)} \] (2.121)

which has been modified by Lu, Li, and Ting [232] to the following general form based on cluster theory:

\[ \frac{y_1}{y_2} = \frac{x_1}{x_2} \left( \frac{C_{x_1} + D_{x_2}}{E_{x_1} + x_2} \right) \] (2.122)

Nagata [269] proposed a method, which uses Equation 2.122 for the prediction of boiling temperatures of binary and ternary systems. Tamura and Nagata [393] used Equation 2.122 to develop a method for
studying the effect of pressure on $x - y$ data. Nagata [272] further showed that Equation 2.122 can be used for the prediction of vapour-liquid equilibria at reduced or higher pressures from data at atmospheric pressure. Other equations of this type include the equations of Kretschmer and Wiebe [206] and Spinner, Lu, and Graydon [384]. The later method permits the estimation of equilibria between two components, provided that data are available for each component on two of the related binaries. Tassios and Van Winkle [401] presented a method for the prediction of infinite dilution activity coefficients in binary systems consisting of a common solvent and the individual members of a homologous series from existing data on two of these binaries. Recently Hsi and Lu [165] proposed a method for obtaining the limiting slopes of the binary $x - y$ curves making use of the Clark equation. They showed that

$$\left(\frac{dy}{dx}\right)_{x_1=1} = \frac{1}{a} \quad (2.123a)$$

$$\left(\frac{dy}{dx}\right)_{x_1=0} = \frac{1}{a'} \quad (2.123b)$$

where $a$ and $a'$ are constants in the Clark equation. Equations of Prahl and Kretschmer and Wiebe were also used to obtain the limiting slopes. The limiting activity coefficients can be obtained from the equation

$$(\ln \gamma_1)_{x_1=0} = \ln \left[ \left(\frac{dy_1}{dx_1}\right) \left(\frac{P_2^0}{P_1^0}\right) \right]_{x_1=0} + \left(\frac{P_2^0 - P_1^0}{B_1 - v_1}/RT\right)$$

$$\quad (2.124)$$

A similar equation can be written for $(\ln \gamma_2)_{x_1=1}$. Hala et al. [132] gave the following general form of the algebraic equations:

$$a_{12}^2 = a_{12}^o \left(1 + a_{12}^o x_2\right) / \left(1 + a_{21} x_1 + a_{211} x_1^2\right) \quad (2.125)$$
where $\alpha_{12}$ is the relative volatility and $\alpha_{12}'$, $\alpha_{21}$, and $\alpha_{211}$ are all constants. The theoretical significance of this form of equation has been given in terms of cluster theory. Wichterle [429] reported, on the basis of tests carried out on about 400 carefully selected binary systems that Equation 2.125 is quite reliable to represent vapour-liquid equilibrium data for a wide variety of systems.

Hirata [148, 149] proposed a method according to which the $y - x$ curve is replaced by three straight lines on a log-log graph in which the ordinate is

$$y = y_1 / y_2$$  \hspace{1cm} (2.126a)

and the abscissa is

$$x = x_1 / x_2$$  \hspace{1cm} (2.126b)

For ideal systems this relationship may be expressed in the form

$$y_1 / y_2 = \alpha x_1 / x_2$$  \hspace{1cm} (2.126c)

where $\alpha$ is a constant. Hirata’s method has been applied to a large number of isobaric and isothermal systems and in general gives three straight line segments each represented by the equation

$$\ln Y = n \ln X + \ln \alpha$$  \hspace{1cm} (2.127)

where $n$ is the slope and $\alpha$ is the ordinate of the intersection of the segment with the vertical axis $X = 1$.

Gilmont and co-workers [118-120] proposed an expansion for binary systems expressing the dependence of $\ln \alpha$ on $x$. Hirata et al. [152] gave a correlation which gives parallel lines when plotted as $\ln \alpha$ vs. $x$ when the total pressure is chosen as parameter. Di Cave [66] gave a graphical method for representing the equilibrium phase compositions as a function of relative volatility.
The empirical relationships are simple to apply and therefore have practical advantages to represent equilibrium data. The main drawback in these equations is that they do not represent complete vapour-liquid equilibrium as the temperature (isobaric data) or total pressure (isothermal) data do not enter the correlations.

2.5.2 Multicomponent Systems

The interest in the thermodynamic description of multicomponent systems has increased in recent years and a number of correlations are available from which, using primarily binary data, the behaviour of multicomponent systems can be predicted with reasonable accuracy. Many of the correlations discussed in Section 2.5.1 can be extended to multicomponent systems. The correlations of Margules [248], van Laar [413], Redlich and Kister [344, 345] and Wilson [290, 438] have been extensively applied for the prediction of multicomponent data.

Wohl [440] derived the following fourth order Margules equation for representing ternary isothermal vapour-liquid equilibria:

\[ \frac{g^E}{RT} = x_1 x_2 \left( x_1 a_{21} + x_2 a_{12} - x_1 x_2 d_{12} \right) + x_1 x_3 \left( x_1 a_{31} + x_3 a_{13} - x_1 x_3 d_{13} \right) + x_2 x_3 \left( x_2 a_{32} + x_2 a_{23} - x_2 x_3 d_{23} \right) + x_1 x_2 x_3 \left[ \frac{1}{2} \left( a_{12} + a_{21} + a_{13} + a_{31} + a_{23} + a_{32} \right) - (x_1 x_2 x_3) \right] \] (2.128)

The equations for the activity coefficients can be obtained by the appropriate differentiation of Equation 2.128 [132]:

\[ \ln \gamma_1 = x_1^2 \left( a_{21} - 2x_1 (a_{21} - a_{12} - d_{12}) + 3x_1^2 d_{12} \right) + x_2^2 \left( a_{13} + 2x_1 \right) \left( a_{31} - a_{13} - d_{13} \right) + 3x_1^2 d_{13} \] + \( x_2 x_3 \left[ a_{21} + a_{13} - a_{32} + 2x_1 \right] \left( a_{31} - a_{13} \right) + 2x_3 \left( a_{32} - a_{23} \right) + 3x_2 x_3 d_{23} - c_1 x_1 (2 - 3x_1) - c_2 x_2 (1 - 3x_1) - c_3 x_3 (1 - 3x_1) \] (2.129)
The equations for $\ln \gamma_2$ and $\ln \gamma_3$ are obtained from Equation 2.129 by the rotation principle 1 2 3 1 etc. The constants $D_{12}$, $D_{23}$, and $D_{13}$ are set to zero in Equations 2.128 and 2.129 to obtain the third order equations. In most cases, the third order correlation with a simple ternary constant $C$ in place of the three constants $C_1$, $C_2$, and $C_3$ would suffice to obtain adequate representation of the data. The constants $A_{ij}$ and $D_{ij}$ are obtained from the data on the three constituent binaries.

The Margules equation is one of the most commonly used equations for representing ternary systems. The application of this equation to ternary vapour-liquid equilibria has been discussed by several workers [1, 3, 82, 115, 132, 183, 375]. Severns et al. [375] concluded that, if all the binary systems exhibit positive or positive and zero deviations from ideality, the ternary constant $C$ in the Margules equations is not significantly different from zero for isothermal conditions. In their study, they found that the ternary constant was necessary when both positive and negative deviations are involved. They have pointed out that the ternary constant should be evaluated corresponding to the concentrations where the $C$ term will have its greatest effect. Adler, Friend, and Pigford [1] made an extensive study of the application of the third and fourth order Margules equations covering a large number of highly nonideal ternary systems. The third order equations were found to be successful in many cases. The fourth order equations were needed for some systems which contained one or more polar compounds. The ternary constant $C$ in general varies from $-1.0$ to $+1.0$. (These values correspond to the equations in which the logarithms used are to the base 10). Ellis [81]

Ellis [81]
observed that the ternary isothermal equations like the Margules equations can be applied to isobaric data if the temperature difference does not exceed 20°C.

Brown and Smiley [38] gave generalised Margules equations to include second, third, and fourth order equations for multicomponent systems. Hala [129] also derived Margules type equations suitable for multicomponent systems with unlimited number of components. Adler, Ozkardesh, and Schreiner [3] gave Margules fourth order equations for multicomponent systems and pointed out that for most of the low pressure systems, the third order equations are sufficient to represent the data well but the systems containing such compounds as acetone, methanol, carbon tetrachloride, water, ethanol, benzene, toluene, and furfural may require the application of the fourth order equations for improved results.

Wohl [440] extended the van Laar equations to ternary systems which can be written as

\[
\ln \gamma_1 = \left[ \frac{x_1^2 A_{12} \left(A_{21}/A_{12}\right)^2 + x_2^2 A_{13} \left(A_{31}/A_{13}\right)^2 + x_3 x_2 A_{21} A_{13} / \left(A_{12} A_{13}\right)}{x_1 + x_2 A_{21} / A_{12} + x_3 A_{31} / A_{13}} \right]^2 \left(A_{12} + A_{13} - A_{21} A_{13} / A_{31}\right)
\]

(2.130)

The corresponding expressions for the other components can be obtained by the rotation principle. Equation 2.130 involves no ternary constants. The binary constants should satisfy Equation 2.130a:

\[
\frac{A_{12}}{A_{21}} \cdot \frac{A_{23}}{A_{32}} \cdot \frac{A_{31}}{A_{13}} = 1
\]

(2.130a)
Often the parameters obtained by the least squares method do not satisfy Equation 2.130a. Though this condition is a definite disadvantage in applying Equation 2.130 to ternary data, it becomes a convenient method for the estimation of the constants of one of the constituent binaries which is close to ideality. When a binary system is nearly ideal, the constants for that system are close to zero and small errors in the constants would be exaggerated. This can be avoided by calculating the constants using the relationship 2.130a.

Li and Coull [223], Bonham [31], Black [26], and Null and Palmer [283] have extended binary van Laar type correlations to ternary and multicomponent systems. In both the Li and Coull and Bonham correlations, the ln γ term is multiplied by temperature. These correlations also require the binary constants which are related by conditions similar to Equation 2.130a. The Black correlation requires three parameters for each binary. No ternary constants are used. Null and Palmer gave fourth order van Laar type equations involving three constants for each binary. They claimed that the correlation could be successfully employed for systems exhibiting mixed deviations and limited miscibility.

The fourth order Redlich and Kister correlation for ternary systems can be written as [132]:

\[
\frac{g^E}{RT} = x_1x_2 \left[ B_{12} + C_{12} (x_1 - x_2) + D_{12} (x_1 - x_2)^2 \right] + \\
\frac{x_1x_3}{3} \left[ B_{13} + C_{13} (x_1 - x_3) + D_{13} (x_1 - x_3)^2 \right] + \\
\frac{x_2x_3}{3} \left[ B_{23} + C_{23} (x_2 - x_3) + D_{23} (x_2 - x_3)^2 \right] + \\
\frac{x_1x_2x_3}{3} \left[ C + D_1 x_1 + D_2 x_2 \right] 
\] (2.131)
and

\[
\ln \gamma_1 = (1 - x_1) (x_2 B_{12} + x_3 B_{31}) + x_2 c_{12} [ 2x_1 (1 - x_1 + x_2) - x_2 ] + x_3 D_{12} \left[ x_1^2 + 3x_1^2 (1 - x_1) - x_1x_2 (4 - 6x_1 + 3x_2) \right] + x_3^2 [ x_3 - 2x_1 (1 - x_1 + x_3) C_{31} + x_2^2 + 3x_1^2 (1 - x_1) - x_1x_3 ] (4 - 6x_1 + 3x_2) D_{31} ] - x_2x_3 \left[ B_{23} + (x_2 - x_3) 2 C_{23} + 3(x_2 - x_3) \right] D_{23} - (1 - 2x_1) C_{2} - (1 - 3x_1) (x_2 - x_3) D_1 + (x_3 - x_1) D_2 + x_1 D_3]
\]

Equations for \( \ln \gamma_2 \) and \( \ln \gamma_3 \) can similarly be written. Equations 2.131 and 2.132 lead to the third order equations if \( D_{12} = D_{13} = D_{23} = 0 \). \( C, D_1, \) and \( D_2 \) are ternary constants which can be replaced by a single constant \( C \).

Chao and Hougen [52] and Nagata [270] gave equations for isobaric ternary systems based on the Redlich and Kister correlations by modifying the constants. The excess free energy for ternary systems is expressed as

\[
\Delta G_{123}^E = \Delta G_{12}^E + \Delta G_{23}^E + \Delta G_{31}^E + RT x_1x_2x_3 \left[ B + C_1 (x_2 - x_3) + c_2 (x_3 - x_1) + c_3 (x_1 - x_2) + \ldots \right]
\]

The corresponding expression for \( \ln \gamma_1 \) is

\[
\ln \gamma_1 = a_{12} x_2 - a_{31} x_3 + (\Delta G_{123}/RT) + \left[ x_2 (x_2 + x_3) - x_1 x_2 \right] \left[ b_{12} + c_{12} (x_1 - x_2) + \ldots \right] - 2x_2x_3 \left[ b_{23} + c_{23} (x_2 - x_3) + \ldots \right] + [ (x_3 - x_1) (x_2 + x_3) + x_1 x_2 ] \left[ b_{31} + c_{31} (x_3 - x_1) + \ldots \right] + [ x_1 x_2 (x_2 + x_3) + x_1 x_3^2 ] (c_{12} + \ldots) + [ x_2 x_3 (x_2 + x_3) - 2x_3^2 x_3 ] (c_{23} + \ldots) + [ -2x_3 x_1 (x_2 + x_3) + x_1 x_2 x_3 ] (c_{31} + \ldots) + [ (x_2 + x_2) (x_2 x_3 - x_1 x_2) - x_2 (x_1 x_3 - x_1 x_2) ] [b + c_1 (x_2 - x_3) + c_2 (x_3 - x_1) + c_3 (x_1 - x_2) + \ldots] + x_1 x_2 x_3 \left[ (x_2 + x_3) (c_1 - 2c_2 + c_3) - x_2 (2c_1 - c_2 - c_3) + \ldots \right]
\]

(2.134)
Equation 2.134 has been proposed by Nagata which becomes identical to the Chao and Hougen equation if the binary constants $a_{12}$ and $a_{31}$ are assumed to be zero.

The Wilson equation [290] for multicomponent systems can be written as

$$\frac{\varepsilon^E}{RT} = -\sum_{i=1}^{N} x_i \ln \left[ \sum_{j=1}^{N} \frac{x_j \wedge x_i}{A_{i,j}} \right]$$

(2.135)

The expression for the activity coefficients becomes

$$\ln y_i = 1 - \ln \left[ \sum_{j=1}^{N} \frac{x_j \wedge A_{i,j}}{x_k \wedge k_1} \right]$$

(2.136)

An advantage of this equation is that it involves only binary parameters with no restrictions such as those that limit the van Laar, Li and Coull, and Bonham equations. Orye and Prausnitz [290] observed that there is a built-in temperature dependence effect. They have applied the Wilson equation to some ternary systems including one system composed of one binary with negative deviations and the other two with positive deviations [375] and found that it gives better fit of the experimental data than the van Laar equation [440].

The NRTL correlation proposed by Renon and Prausnitz [349] can be applied to multicomponent systems and it is claimed that this correlation can be applied to partially miscible systems for which the Wilson correlation fails. This advantage extends the NRTL correlation to the prediction of liquid-liquid equilibria. The excess free energy function and activity coefficients, according to the NRTL correlation, can be represented by Equations 2.137 and 2.138 for multicomponent systems:
\[
g^F / RT = \sum_{i=1}^{N} x_i \sum_{j=1}^{N} \tau_{ji} G_{ji} x_j / \sum_{l=1}^{N} G_{li} x_l
\]  
(2.137)

where

\[
\tau_{ji} = (g_{ji} - g_{ii}) / RT \quad (g_{ji} = g_{ij})
\]  
(2.137a)

\[
G_{ji} = \exp [- \alpha_{ji} \tau_{ji}]
\]  
(2.137b)

\[
\ln \gamma_i = \sum_{j=1}^{N} \frac{\tau_{ij} G_{ji} x_j}{\sum_{l=1}^{N} G_{li} x_l} + \sum_{j=1}^{N} \frac{x_i G_{ij}}{\sum_{l=1}^{N} G_{lj} x_l} \left[ \tau_{ij} - \sum_{r=1}^{N} x_r \tau_{ri} G_{ri} \right]
\]  
(2.138)

Equations 2.137 and 2.138 contain only binary parameters and require no additional data on the multicomponent systems. Renon and Prausnitz [349] applied the NRTL equation to nine ternary systems using only binary data. WoHn's equation, with and without a ternary constant, was also used for comparison purposes, the results being taken from Adler et al. [1]. The data tested include some of the highly nonideal systems. It was found that the NRTL equation gave a better fit than the Wohl equation even with optimised ternary constants. The NRTL equation was also applied to ternary liquid-liquid equilibria with promising results.

Many papers appeared in the literature comparing the ternary or multicomponent van Laar, Margules, Redlich and Kister, and Wilson correlations. McDermott and Ellis [254] and Ellis, McDermott, and Chiang [85] applied the Margules, Redlich and Kister, and Wilson equations to three isobaric ternary systems [21, 269, 435] and found that these equations are equally satisfactory to predict the vapour compositions from the boiling point-liquid composition data.
Neretnieks [279] compared the Black and Wilson equations for the prediction of activity coefficient-composition data for ternary and quaternary systems and found the Wilson equation to be generally better than the Black equation.

Holmes and Van Winkle [161] compared the capabilities of the Wilson, van Laar, third order Margules, and Bonham equations to predict multicomponent vapour-liquid equilibria for 19 ternary systems using only binary parameters. They found that for almost all the ternary systems studied, the Wilson equation is superior followed by the Margules, van Laar, and Bonham equations ranked in the same order of superiority, the Bonham equation being the least accurate of the four. For systems exhibiting near-ideal behaviour, all the equations gave almost the same accuracy whereas for the highly nonideal systems, the Wilson equation gave much better fit than any of the other equations.

Hudson and Van Winkle [167] demonstrated the accuracy of the Wilson equation on a wide variety of multicomponent systems, including azeotropic systems. They have applied the equation to one quinary, three quaternary, and twenty ternary systems. The ternary systems were selected to include all possible types of miscible systems. Even when the binary parameters were obtained based on a single data point, they found that the multicomponent system is fitted with sufficient accuracy to the Wilson equation. They pointed out that the Wilson equation provides an excellent basis for predicting low pressure, multicomponent vapour-liquid equilibria from limited binary data.

There are many other methods in literature that are aimed at the prediction of ternary or multicomponent vapour-liquid equilibrium
data using information on the constituent binaries \([80, 147, 153, 195, 198, 200, 273, 360, 384, 390]\). Spinner, Lu, and Graydon [384] extended their correlation for ternary systems which predicts ternary vapour compositions which requires data for a minimum of two of the constituent binaries. Edwards, Hashmall, Gilmont, and Othmer [80] extended the method of Gilmont et al. [118 - 120] to multicomponent systems which requires parameters determined from the relative volatility data of the constituent binaries. The method is applicable to both isobaric and isothermal conditions.

Hala [127] extended the relative volatility expansion correlation for multicomponent systems which permits the prediction of multicomponent equilibria from data on the corresponding binaries. The correlation is flexible and can be applied even to highly nonideal systems.

Hirata [151] observed that in any ternary system containing components 1, 2 and 3, if any one component, say 3, is present in high concentration, (i) the relative volatility, \(\alpha_{12}\), remains constant over a wide range of concentration ratio between components 1 and 2 and

\[
(\alpha_{12})_{x_3 \to 1.0} \approx (\alpha_{13})_{x_2 \to 1.0} = (\alpha_{23})_{x_2 \to 1.0}
\]  

(2.139)

Tao [395] and Lu and Jones [231] gave interpolation and extrapolation methods for ternary and multicomponent systems. Hutchison and Fletcher [171] proposed an empirical method using orthogonal polynomials in two dimensions for fitting surfaces to sets of experimental points at uneven intervals of the prime variables. It has been applied to represent the composition and temperature surfaces in the ternary vapour-liquid equilibrium data. Garner, Ellis, and Pearce [113] gave an
interpolation method for ternary data based on the Margules equation. Schiebel and Friedland [368] gave a graphical interpolation method for ternary activity coefficient data and claimed that the method gives satisfactory results for systems for which all the constituent binaries show positive deviations.

2.5.3 Prediction from Physical Properties and Molecular Structure

A. From Physical Properties

The prediction of vapour-liquid equilibrium data from the properties of the pure components would be of great value to the practicing chemical engineer. In principle it should be possible to carry out such a prediction from molecular considerations. However, only very limited progress has been made in this direction though the problem has received a great deal of attention in recent years.

One of the most reliable methods for estimating solution behaviour from component physical properties is that of Scatchard [363] and Hildebrand [145] who expressed the activity coefficients as a function of liquid molar volumes and solubility parameters:

\[
\ln \gamma_1 = \frac{V_1}{RT} \left( \delta_1 - \delta_2 \right)^2 \quad (2.140a)
\]
\[
\ln \gamma_2 = \frac{V_2}{RT} \left( \delta_1 - \delta_2 \right)^2 \quad (2.140b)
\]

The solubility parameter, \( \delta \), can be calculated from the pure component heats of vapourisation, from boiling points and the Hildebrand rule, from internal pressures, from an equation of state and critical constants, from surface tension data of pure components, from optical data, and from solubility data. Hildebrand preferred the use of heats of vapourisation data for the estimation of solubility parameters. At
low pressures the solubility parameter is related to the heat of vapourisation by
\[ \delta \approx \left( \frac{H_v - RT}{V} \right)^{0.5} \] (2.141)

The application and extension of the Scatchard-Hildebrand theory has been studied extensively \([10, 86, 91, 95, 121, 139, 213, 249, 283, 319, 321, 410, 425]\). Van Arkel \([410]\) proposed a theoretical model to account for the effect of polar properties on the Scatchard-Hildebrand equation. The model involves the use of dipole moments, molar volumes, and solubility parameters for the pure components. Finch and Van Winkle \([95]\) have extended Van Arkel's theory empirically to enable the prediction of vapour-liquid equilibria for polar-nonpolar systems that are essentially free from hydrogen bonding. Gilmont, Zudkevitch, and Othmer \([121]\) developed a weighted least squares prediction method which is complex to use but appears to be generally applicable as it was tested on 500 binary systems giving close agreement between the predicted and experimental vapour compositions. Weimer and Prausnitz \([425]\) have used a combination of nonpolar and polar solubility parameters with an entropy of mixing effect for the prediction of infinite dilution activity coefficients for hydrocarbons in polar solvents. The correlation can be written as
\[ \ln \gamma_1 = \left( \frac{V_1}{RT} \right) \left[ (\delta_1 - \lambda_2)^2 + \tau_2^2 - 2 \gamma_{12} \right] + 1 - \frac{V_1}{V_2} + \ln \frac{V_1}{V_2} \] (2.142)
The quantities \( \lambda_2 \) and \( \tau_2 \) for the polar solvent are related to the conventional solubility parameter by
\[ \frac{\lambda_2^2}{\lambda_2^2 + \tau_2^2} = \delta_2^2 \] (2.142a)
values of $\lambda_2$ are obtained as function of molar volumes and reduced temperatures from plots given. For several families of solutes, correlations for $\Psi_{12}$ are also given. Humphrey and Van Winkle [170] pointed out that the Weimer-Prausnitz correlation might give rise to gross errors when applied to strong hydrogen-bonding solvents and proposed methods for the extension of Weimer-Prausnitz model to the prediction of selectivities in saturated-unsaturated hydrocarbon systems with a strong hydrogen-bonding solvent as the solvent concentration approaches unity.

Helpinstill and Van Winkle [139] extended the Weimer-Prausnitz model to include polar-polar interactions. Null and Palmer [283] further extended the Weimer-Prausnitz and Helpinstill-Van Winkle approach to include associating and highly polar systems. The methods based on the Scatchard-Hildebrand regular solution theory are particularly useful in the screening of solvents for azeotropic and extractive distillation and liquid-liquid extraction.

Other methods that make use of physical properties of the components include the methods of Ohe [287] which make use of critical constants, molar volumes, mutual solubilities, and azeotropic data and the methods of Vaněček [411] and Krishnan and Laddha [208] which use viscosity data for the prediction of vapour-liquid equilibria.

B. From Molecular Structure

The concept of group activity coefficients has received much attention in recent years because of the promise it holds for the prediction of vapour-liquid equilibria from molecular parameters. The method is based on the assumption that molecular mixtures and pure
molecules themselves should be regarded as group mixtures. The partial molar excess free energy of a component could be considered as the summation of interactions between molecular segments (groups) in the molecule and all other molecular segments in the mixture. Any functional group such as CH₂, CH, CN, COOH, etc., are termed as molecular groups. Of the qualitative methods available, the classification of Ewell, Harrison, and Berg [92] is one of the most useful. They have classified liquids into five groups according to their ability to form hydrogen bonds. A number of investigators have shown structural parallelisms based on observed changes of the infinite dilution activity coefficients with molecular weight, molecular configuration, and functional groups. Pierotti, Deal, and Derr [313] developed the following correlation for infinite dilution activity coefficients for many structurally related binary systems:

$$\ln \gamma^\infty = K + \frac{Bn_i}{n_x} + C \frac{n_i}{n_1} + D \left( n_1 - n_k \right)^2 + \frac{F}{n_k} \quad (2.143)$$

where K, B, C, D, F are constants whose values are tabulated for individual groups and nᵢ, nₓ are the numbers of carbon atoms in the structural groups i, k. Many extensions and modifications to the Pierotti, Deal, and Derr correlation have appeared in the literature [27, 63, 64, 309, 342, 369, 439]. This approach uses the 'solution of groups' concept and the assumption that the activity coefficient of a component can be regarded as the product of two independent contributions, one due to molecular size and one due to molecular interactions. Thus

$$\ln \gamma_i = \ln \gamma_i^S + \ln \gamma_i^G \quad (2.144)$$

where \( \ln \gamma_i^S \) represents contributions due to differences in molecular size and \( \ln \gamma_i^G \) represents contributions due to intermolecular forces.
between molecular groups in its surroundings. For \( \ln \gamma_i^g \), an expression of the Flory-Huggins [98, 169] type which depends only on the sizes of the various molecular groups present, was used. For \( \ln \gamma_i^G \), a summation of \( \ln \gamma_k \) terms, where \( \gamma_k \) is the activity coefficient of group k, was used. Ratcliff and Chao [337] used the Brönsted-Koefoed [36] principle of congruence in place of the Flory-Huggins model in extending the group contribution model to binary systems consisting of n-paraffins.

Rodger, Hsu, and Furter [356] have developed an empirical group contribution method for the prediction of vapour-liquid equilibria based on Barkers' theory of solutions [18, 19]. The method appears to be promising but requires further testing to determine its limits of applicability.

2.6 Azeotropes

2.6.1 General

An accurate knowledge of the phenomenon of azeotrope formation and the way in which the azeotropic composition varies with temperature and pressure is often needed in distillation processes. The azeotropic parameters, which are available in literature [162, 219, 424] for a large number of binary and ternary systems can be used to predict vapour-liquid equilibria. Swietoslawski [392] and Malesinski [242] presented detailed treatment of the phenomenon of azeotropism.

Azeotropes may be classified into homo- and hetero-, binary and multicomponent, positive, negative, and positive-negative or saddle azeotropes. For binary azeotropic systems, the temperature-composition or pressure-composition curves exhibit either maxima or
minima. A maximum in the temperature - composition curve is always accompanied by a minimum in the pressure - composition curve. These deductions are called the Gibbs - Konowalow laws.

Rowlinson [358] gave the following generalisations on the basis of the properties of the \( \pi - t - x \) surface:

i) The closer the vapour pressures of the components the more likely is azeotropy.

ii) If the excess free energy is symmetrical in the composition, then a positive azeotrope is richer in the more volatile component, and conversely for a negative azeotrope.

iii) An increase of temperature and of vapour pressure in a positive azeotrope increases the mole fraction of the component whose vapour pressure increases more rapidly with temperature. The converse holds for a negative azeotrope.

iv) The closer the vapour pressures of the pure components, the more rapidly does the azeotropic composition change with temperature.

Ewell, Harrison, and Berg [92] gave a qualitative classification for liquid mixtures which divides all liquids into five classes, depending upon their ability to form intermolecular bonds. From this classification, it is possible to know qualitatively the combinations of compounds that might give rise to positive or negative deviations from ideality. Yoshimoto and Mashiko [447] grouped azeotropic mixtures into four classes according to the type of molecular interaction and discussed the conditions for azeotrope formation.
2.6.2 Prediction of Azeotropes

Reed [346], Nagarajan, Rao, and Satyanarayana [268], Baradarajan and Satyanarayana [14], and Raju [328] have proposed methods for the prediction of azeotropic conditions based on the regular solution theory [145]. Reed's method involves the use of pure component properties like liquid molar volumes and solubility parameters and is applicable to nonpolar binary systems. The methods of Baradarajan and Satyanarayana and Raju can be applied to polar-nonpolar systems. The later method is based on the Van Arkel's theory of solutions [410] and has been extended to ternary systems. For systems involving hydrogen bonds the method is not satisfactory. This method is claimed to be more accurate for polar-nonpolar systems than the method of Reed. Nakanishi [275, 277] gave a method for the prediction of azeotropic conditions in binary systems containing alcohols. Azeotropic diagrams were prepared for each alcohol and the expressions for the azeotropic temperature and composition were obtained by combining the correlation between the limiting value of the activity coefficient and the 'hydrogen bond shift' of the hydroxyl group in infrared spectra for the binary solutions containing alcohols and the regular solution equations. The method has been tested on a number of binary systems containing alcohols and found to be accurate.

Kuhn and Kuhn [211] have reported a condition for azeotrope formation for binary systems based on boiling temperature difference for the pure components, heats of mixing of equimolar solutions, and molar heats of vapourisation of pure components. This method is particularly useful for systems containing similar compounds like
isomers. Malesinski [243] has developed equations for predicting azeotropic conditions for binary systems based on the regular solution theory. The method uses the boiling temperatures of equimolar mixtures.

Jaques and Lee [175] derived conditions for azeotrope formation at constant temperature in binary systems using the third-order Redlich and Kister equations [132] to express the relationship between the activity coefficients and composition. Raju and Rao [330] proposed a method for the prediction of binary and ternary azeotropes making use of the Calingaert and Davis [45] equation to represent the temperature – vapour pressure relationship and the Chao [51] correlation to represent the activity coefficient – composition data. The constants in the Chao correlation are estimated from a knowledge of infinite dilution activity coefficients obtained by the Ellis and Jonah method [84] and the approximate relationships between the activity coefficients at certain strategic compositions and the infinite dilution activity coefficients deduced by Lu et al. [230, 233]. The method has been tested on limited binary and ternary systems and found to be representing the azeotrophic data well. This method has been modified in this work in which its application to binary systems using the Antoine vapour pressure equation [12] in place of the Calingaert and Davis equation. The activity coefficient – composition relationships are represented by the Redlich and Kister equation for systems with negligible heats of mixing and the Chao equation for systems with appreciable heats of mixing. The method has been tested on a wide variety of systems and found to be promising for predicting the azeotropic conditions. The details of the method have been given in
Chapter V. Nakanishi [274] discussed the application of an Antoine type vapour pressure equation for the prediction of azeotrope formation in binary systems.

Several empirical methods have been proposed for the prediction of azeotropes [65, 156, 163, 178, 217, 241, 258, 302, 377, 378]. Many of the proposed methods [65, 156, 163, 258, 378] are graphical correlations. Horsley [163] plotted the difference in the boiling points of the pure components versus the weight percent of the more volatile component in the azeotrope to give a straight line relationship for binary systems. Meissner and Greenfield [258] plotted graphs between the function $T_2^2 \left( T_H - T_S \right) / 100,000$ versus composition of the azeotrope for binary systems which gave straight lines in most of the cases. Different straight lines were obtained for different combinations of the solvent types with the hydro- or halo-carbons. A plot relating the atmospheric boiling temperature of the azeotropes to those of the pure components has also been shown to be a straight line. The correlation is based on extensive experimental data involving different classes of compounds that give rise to azeotropes. Equivalent algebraic equations were also given. One of the disadvantages of this method is that it is not sensitive to slight variations in azeotropic effect on passing from one type of compounds to another and its precision is about ± 2 to 5°C for the azeotropic temperature and ± 5 to 10 percent for the composition. Skolnik [378] proposed a method for the prediction of azeotropes based on the relations between (a) the azeotrope boiling point and the logarithm of the azeotrope composition, (b) the azeotrope boiling point and the boiling points of the pure components, and (c) the boiling points of the pure components and the logarithm of
azeotrope composition. Relations (a) and (b) are straight line functions from which the relation (c) can be derived. These three relations are employed for the correlation of the azeotropic data of benzene with various hydrocarbons, benzene with alcohols, and ethanol with hydrocarbons. This method allows more accurate predictions of unknown azeotropes than that of Meissner and Greenfield. Johnson and Madonis [178] have extended the Meissner-Greenfield correlation to cover different combinations of compounds that are not covered by the Meissner-Greenfield correlation. The modified correlations were claimed to be giving better results for systems such as halogenated hydrocarbons - donor atom liquids, ketones - esters, hydrocarbons - hydrocarbons, and hydrocarbons - associated liquids. The methods of Meissner and Greenfield and Johnson and Madonis do not predict the formation of an azeotrope. Hirose [156] proposed plotting $1/T_{az}$ vs. $\log x_{az}$ which gave straight lines. Shorr [377] proposed an empirical correlation which is based on the linear relationship that exists between two compounds when the azeotropic compositions of each with a series of functionally related compounds are compared.

Several methods have been presented in the literature for the prediction of ternary and multiazeotropes, some of which have been discussed by Swietoslawski [392] and Malesinski [242]. Malesinski [244] showed that the mole fractions of components 1 and 3 in a ternary azeotrope are the same as their mole fractions in the two binary azeotropes 1 and 2 and 2 and 3, and discussed a graphical method [245] for the prediction of ternary azeotropes based on data for binary azeotropes. Yorizane and Nishimoto [446] discussed a thermodynamic...
method for the prediction of azeotropic conditions from only one experimental point for both binaries and ternaries, taking into consideration the excess free energy of azeotropes. Klein [188] presented two methods for the prediction of ternary azeotropes. In one method, an analytical equation depicting a second-order surface is fitted by the least squares method to the experimental points of the vapour curve for the binary systems. The maximum or minimum value of this equation represents the ternary azeotrope. The second method requires two binary azeotropes, one point on the third binary $t - x - y$ diagram and the boiling points of the pure components. The second method was applied to the ternary system carbon disulphide - methanol - ethylbromide. The predicted ternary azeotrope was close to the experimental value. Horvath [164] has presented a trial-and-error graphical method for the prediction of ternary azeotropes which has been claimto be accurately predicting ternary azeotropes for systems containing either heteroazeotrope or homoazeotrope binary pairs or combinations of them. For nonazeotropic systems the trials lead to divergence. A total of eight systems representing different combinations of binary azeotrope types were tested. The agreement in all the cases was good. Hirose [155] discussed a method of finding ternary azeotropic saddle point semiempirically.

2.6.3 Variation of Azeotropic Conditions

The variation of azeotropic composition as a function of pressure has been studied by several workers who presented predictive methods for change in composition with pressure [25, 46, 177, 225, 284, 295, 302]. Smith [380] and Hala et al. [132] discussed some of these methods.
Nutting and Horsley [284] plotted the azeotropic temperature as a function of pressure on a Cox chart to obtain a straight line. Licht and Densler [225] showed that the pressure - temperature relationship for all types of azeotropes can be correlated by a Claypeyron-type equation which has been extended by Othmer and Ten Eyck [302] to show that both the azeotropic composition and the partial pressures of the components in the azeotrope are essentially straight line functions of the total system pressure on a log - log plot. The location of these straight lines requires knowledge of the azeotropic conditions at two pressures. If the azeotrope is known at only one pressure, some knowledge of the heat effects is necessary for establishing the slope.

Another approach that received attention in the separation of azeotropic mixtures is the effect of inorganic salts on the azeotropic composition. Furter and Cook [111] and Furter [110] have presented thorough reviews of this subject. Johnson, Ward, and Furter [179] found that sodium propionate shifted the azeotrope considerably for the system, n-octane - propionic acid. Garwin and Hutchison [114] investigated the effect of various concentrations of calcium chloride on the acetic acid-water system, finding that the affinity of calcium chloride for water was sufficiently strong to reduce the low relative volatility of the system to reversal even at relatively low salt concentrations. Ramalho et al. [334] studied the effect of various alkaline earth chlorides on this system and found that all the salts introduced an azeotrope and reversed the relative volatility order of the two components.

Many investigators studied the effect of inorganic salts on ethanol - water system [59, 68, 69, 116]. Costa Novella and Moragues Tarraso [59] observed that potassium acetate and cupric chloride
destroyed the azeotrope. Dobroserdov and Il'ina [68] found that sodium and potassium acetates and zinc chloride destroyed the azeotrope. In another study, Dobroserdov and Il'ina [70] and Dobroserdov [67] reported that calcium chloride destroyed the azeotropes in the systems n-propanol - water and isopropanol - water. Ghosh and Ghosal [116] found that sodium chloride at saturation destroys the azeotrope for ethanol - water systems at 495 mm of Hg pressure whereas in the absence of the salt the azeotrope disappears at a much lower pressure of 70 mm of Hg. Hirata et al. [154] studied the effect of calcium chloride on ethanol-water, i-propanol - water, and n-propanol - water and found that azeotropes disappeared at atmospheric pressure. In another study, Hashitani and Hirata [137] observed that the effect of calcium chloride on the systems, methanol - methylacetate, ethanol - ethylacetate, and n-butanol - n-butylacetate at atmospheric pressure, was to shift the azeotropic composition to higher ester concentrations.

2.7 Measurement of Vapour-Liquid Equilibria

The direct measurement of vapour-liquid equilibria to obtain thermodynamically consistent data, though appears to be simple, is not inherently easy, even for binary systems. Considerable experimental effort may be required which increases very rapidly with the complexity of the system.

There are many techniques for the measurement of vapour-liquid equilibria. Robinson and Gilliland [354], Othmer and Gilmont [295a], Hala et al. [132], and Krell and Lumb [205] discussed in detail the various kinds of equilibrium stills with illustrations pointing out the desirable and undesirable features of many different types. Hala
et al. [132] also discussed the auxiliary techniques for the measurement of temperature, pressure, and composition. The techniques for the direct measurement of equilibrium data can be classified into five groups, namely distillation, circulation, static, dew and bubble point, and flow methods.

2.7.1 Distillation Method

The method of distillation is one of the oldest and simple to use. It can be adopted for obtaining vapour-liquid equilibrium data either at constant temperature or constant pressure. For operation at constant temperature, the pressure on the system is continuously adjusted while the liquid, maintained at constant temperature, boils at a uniform rate. Superheating of vapours, entrainment of liquid or refluxing due to condensation can cause large errors. One of the disadvantages of the method is that it requires large quantity of liquid charge and permits the withdrawing of very small sample of condensate for analysis. In recent years this method has been used by Ramalho et al. [43, 335] who claimed that the method is reliable for obtaining vapour-liquid equilibria for binary and multicomponent systems at constant pressure. They have also pointed out that the entire vapour-liquid equilibrium curve for a binary system can be obtained in a single experiment lasting two or three hours.

2.7.2 Circulation Method

Of all the five methods, the most commonly used method is the circulation method. The equilibrium still employing this technique, can be divided into those involving the recirculation of the vapour phase only and those involving the recirculation of both vapour and liquid phases.
A. Equilibrium Stills with Circulation of Vapour Phase

The first still that functioned satisfactorily with vapour recirculation was constructed by Othmer [291]. Several modifications of this still have been reported in the literature which are too numerous to mention here. Some of these have been described by Hala et al. [132], Othmer and Gilmont [295a], and Krell and Lumb [205].

This still or its modifications have found wide use for the determination of vapour-liquid equilibria. Othmer, Gilmont, and Conti [296] developed a modification to minimise, through vacuum jacketing, the errors caused by heat losses. By using interchangeable parts, data can be obtained on partially miscible systems and normal boiling points can be compared with Cottrell-type boiling and external boiling. Kojima and Hirata [199] described a modified Othmer still that enables the determination of six data points from one feed mixture.

Smith and Bonner [381] described a modified Othmer type still for partially miscible systems. A magnetic mixer is used for stirring the condensate. This still can be used for a solution that is homogeneous at the boiling temperature as magnetic mixing is not adequate to ensure perfect mixing. Othmer still has also been modified [209, 300] for application to high pressure equilibria replacing glass by metal for its construction. It is also possible, however, to place an ordinary glass apparatus inside a pressure vessel [370].

Though Othmer type stills have been widely used, they often give rise to errors due to the occurrence of concentration gradients in the boiling flask as a result of inadequate mixing of the liquid and disturbance of equilibrium by the withdrawal of excessively large samples.
in addition to other errors arising in circulation type stills out of the liquid, partial condensation above the boiling vessel, and entrainment of liquid droplets. Attempts have been made to reduce these sources of error by modifications in the design of the stills and by standardising the conditions of operation. In one method flow refractometers were used for continuous measurement of the composition of the vapour and liquid phases without actually withdrawing the samples [385].

Jones, Schoenborn, and Colburn [180] designed an equilibrium still in which the condensate recycle is totally vapourised in a flask boiler. These vapours bubble through the liquid in the boiling tube ensuring vigorous stirring of the contents. This still requires small amounts of feed liquid and eliminates the concentration gradients that exist in Othmer type stills. The still is very precise but requires careful control of the heating loads. It is particularly suitable for mixtures with wide difference in boiling points and densities. At reduced pressures, it avoids erratic boiling and gives reliable results. This type of still is not suitable for partially miscible systems. If the mixture is heat sensitive, decomposition can take place on the walls of the vapourising tube if the temperature of the walls is too high. Amick et al. [9] made several modifications in this apparatus of simplify its operation. In this work (cf. Chapter III) an entrainment eliminator was added above the boiling tube. Barr-David and Dodge [20] proposed a similar apparatus for the determination of high pressure equilibria.

Raju, Ranganathan, and Rao [329] developed a vapour circulation type still which is suitable for partially miscible systems. This still
similar to the Jones still in operation except that the vapours from the boiling tube bubble through the condensate receiver to provide thorough mixing in it before they are totally condensed. As in the Jones still, the condensate is vapourised completely and allowed to bubble through the liquid in the boiler. Thus complete mixing is ensured in both the boiler and condensate receiver. This still with some modifications has been adapted for most part of this work (cf. Chapter III).

Ellis and Garbett [83] described a still with vapour circulation which employed mechanical stirring of the liquid in the boiler and condensate. This still is useful for partially miscible systems.

Lydersen and Hamer [238] and Williams [434] developed vapour circulation type equilibrium stills that are suitable for pressures as low as 1.0 to 0.1 mm of Hg. In the former one, mixing of the boiling liquid and the condensate is achieved by rotation of the apparatus.


Penske et al. [94] were the first to use a two-stage still. Reed and Myers [347] showed how to treat data from multistage stills. Several multistage equilibrium stills, which permit a greater difference in composition between the liquid in the still pot and the vapour over the top plate than in other types of stills, have been described in literature [41, 94, 220, 257]. This feature is especially advantageous for systems with low relative volatility. These stills
require comparatively less time for obtaining equilibrium data. Ridgway and Butler [352] derived equations for the calculation of equilibration times for circulation type of stills.

B. Equilibrium Stills with Circulation of Vapour and Liquid Phases

Gillespie [117] introduced the idea of circulating both the liquid and vapour phases, employing at the same time a Cottrell tube for accurate temperature measurement. In the still described by Gillespie, the vapours from the boiling chamber carry slugs of liquid up the Cottrell tube into a disengaging chamber. The temperature is measured at this point, where both the phases are present. The liquid from the disengaging chamber returns to the boiling chamber and the vapours are totally condensed. The condensate from the receiver overflows into the boiling chamber. The main advantage of this still is the accurate measurement of temperatures. The possibility of partial condensation and existence of concentration gradients in the liquid are very slight. The drawbacks of this still are the relatively long time required for attainment of equilibrium and the possibility of fractionation occurring in the Cottrell tube which would produce a vapour not in equilibrium with the residual liquid. Thornton [406] attempted to solve this problem by using a separate liquid phase trap as suggested by Fowler [103]. The receivers for collecting the condensate and liquid samples are placed inside the vapour space which makes the still especially useful for mixtures that separate into two phases on cooling. Fowler and Norris [104] and Otsuki and Williams [305] used similar arrangements but did not place the sampling reservoirs inside the still body.
Chao and Hougen [52] and Raal and Cobe [324] described stills that combine the operating characteristics of the Jones and Gillespie stills. Rane, Mehta, and Mene [336] and Mainkar and Mene [240] developed an equilibrium still which combines some of the best features of Othmer, Jones, and Gillespie stills. This still can be used for a variety of systems including those with wide boiling components and components with large density differences. Fleck and Prausnitz [97] described an apparatus for liquid-liquid-gas equilibrium in which all the three phases are recirculated. Hala et al. [132] described several other stills in which recirculation of vapour and liquid phases takes place.

2.7.3 Static Method

In this method, the mixture is charged into a closed and evacuated cylinder, which is placed in a thermostat. The cylinder with its contents is rotated or shaken until equilibrium is established, when samples are removed from the vapour and liquid phases. The stills based on this principle are used especially for the determination of isothermal vapour-liquid equilibria and also for high pressure equilibria. In recent years, with the development of modern analytical techniques like chromatography, the static type stills are finding increasing use for isobaric measurements at atmospheric and higher pressures. These stills are also of value when only relatively small quantities of the liquids are available, for systems with large density differences and with limited miscibility.

One of the disadvantages of this method is in the difficulty to sample the vapour phase especially at low pressures because under these
conditions, the amount of the equilibrium vapour phase in the still is of the same order as the amount required for analysis. This causes a marked disturbance of the equilibrium. This is one of the main reasons for not using these stills for low pressure measurements. Scatchard et al. [366] developed a method suitable for low pressures and for systems with very large differences between vapour and liquid compositions. The method, though tedious, yields exceptionally accurate results. Wichterle and Hala [430] developed a rapid semi-micro method based on the sampling of very small volumes of the vapour phase which is then analysed by gas chromatography. Once the apparatus has been set up, a single experimental point can be obtained in about five minutes from about two ml of liquid charge. Hala et al. [132] gave references for a number of static methods for high pressure equilibria.

Rabe and Harris [325] described a static equilibrium cell which is simple in construction. They have described a mercury displacement method for sampling the gas phase which overcomes the inherent difficulties encountered in the use of static equilibrium cells. Ellis et al. [87] described a high pressure static equilibrium still using a magnetic stirring device. Galata et al. [112] described two static equilibrium stills, for operation at pressures below twelve atmospheres and temperatures below 60°C., which use magnetic agitation.

2.7.4. Dew and Bubble Point Method

In this method, mixture of known composition is introduced into an evacuated equilibrium chamber of variable volume which is maintained at constant temperature by submerging in a thermostat. By varying the volume, the pressure is observed at which condensation commences and completes. The dew and bubble point curves of pressure vs. temperature
for a number of these prepared samples are obtained and, by crossplotting, vapour-liquid equilibrium data can be obtained by locating points at which saturated liquid and vapour phases of different compositions exist at the same temperature and pressure.

This method has been used for a long time for the determination of the phase behaviour of low boiling hydrocarbons. The main advantage of this method is that it does not involve determination of compositions. It can be applied for the determination of critical conditions and volumetric behaviour of mixtures at high pressures. Some of the disadvantages are that sometimes it is difficult to obtain clearly defined dew and bubble points and it can be applied only to binary mixtures. Hala et al. [132] presented a detailed description of an apparatus [93] that can be used to determine dew and bubble points of mixtures that are liquid at normal temperature and pressure conditions.

2.7.5 Flow Method

In this method a steady stream of constant composition is fed to an equilibrium chamber. The feed can be either vapour or liquid or a mixture of the two. In the Colburn flow still [57] feed vapour of constant composition is prepared by mixing the vapours of the pure components obtained from different boiling vessels. The composition of the mixture is adjusted by carefully controlling the heat load on the boiling vessels. The vapour bubbles through the liquid in the equilibrium chamber which is jacketed with vapour. When equilibrium is attained, the vapour leaving the chamber will have the same composition as that entering. The vapour and liquid samples are withdrawn for analysis at equilibrium conditions which are established very quickly. This still can be used for partially miscible systems by
proper choice of operating conditions. Mertes and Colburn [260] used several equilibrium chambers.

Cathala, et al. [47] described a flow still in which superheated vapour and preheated liquid are brought into intimate contact between two sintered glass discs and allowed the flow together in a Cottrell tube splashing over a thermometer bulb. Under equilibrium conditions the two phases are sampled and analysed. The accuracy depends to a large extent on the control of the feed streams. This apparatus is particularly useful for systems with limited miscibility or systems in which long times of contact at boiling temperatures lead to decomposition or reaction of the components.

Vilim et al. [421] developed a flow still in which the feed liquid is partially vapourised and the mixture of liquid and vapour splashed on a thermometer bulb before the phases are separated. This still is simple in construction and gives reliable results establishing equilibrium conditions within 10 to 15 minutes. Stechel and Zinn [386] described a high pressure flow still for difficulty liquefiable gases which can be used up to 100 atmospheres.

Hala et al. [132] presented an evaluation of various types of equilibrium apparatus and gave summaries regarding the precision, suitability to various types of systems and operating conditions, and the approximate equilibration times needed. The selection of a still depends largely on the physical properties of the components constituting the system, the operating conditions, the time and quantities of the components available, and the nature of analytical techniques used.

In recent years more and more stress is laid on the use of modern analytical techniques such as gas chromatography, spectrophotometric
methods, and other instrumental techniques. It is, however, considered that the relatively older techniques of analysis using density and refractive index are as reliable as the modern techniques for most of the purposes. Unless the instruments are carefully calibrated with known standards the instrumental methods are likely to give erroneous results. The principal advantage of the modern techniques is in the analysis of multicomponent mixtures and mixtures in which some of the components are present in low concentrations.