2.1 THERMODYNAMIC CONSIDERATIONS

A large part of chemical engineering design is concerned with separation operations. Many of these are diffusional operations of the phase contacting type, and of them all distillation is the most common. For rational design of such separation operations, we require quantitative information on phase equilibria in multicomponent mixtures.
In the calculations of vapour-liquid systems at equilibrium, we encounter vapour and liquid phases not necessarily ideal ones in their behaviour. For ease in calculations, the phases are separately considered for deviations from ideal behaviour. The departures from ideality of the vapour phase is expressed in terms of fugacity coefficients and those of the liquid phase in terms of activity coefficients. The assumption of ideal gas behaviour for the vapour phase is justified at low and moderate pressures when the components constituting the system do not associate in the vapour phase. Likewise, under similar conditions, slightly polar gases may be treated as being non-polar without much loss of accuracy. On the other hand, for highly polar or associating molecules, such as acetic acid, and for systems at high pressures and for the ones containing components of greatly differing critical constants, the vapour phase nonideality is highly important.

One way of estimating the vapour phase nonideality is to use some equations of state. The most important ones commonly used are: Redlich - Kwong (226), Beattie - Bridgeman (11, 12), and Benedict - Webb - Rubin (14, 15). These equations are of semi-empirical nature with a form chosen to describe the experimental data rather than conform to a theoretical description of the actual molecular behaviour.

The only equation of state which has been shown to have exact physical significance on a molecular scale is the virial expansion for gases, which in its proper form gives the
compressibility factor \( \zeta \) as a power series in density:

\[
\zeta = \frac{P \nu}{\gamma} = 1 + \frac{B}{\nu} + \frac{C}{\nu^2} + \frac{D}{\nu^3} + \ldots \quad \ldots (2.1)
\]

The coefficients \( B, C, D, \ldots \), are known as virial coefficients, with \( B \) designated as the second virial coefficient, \( C \), the third and so on. For a given material they are functions of temperature only. Statistical mechanics attaches them physical significance as reflecting the molecular interactions of particular numbers of molecules. Thus it has been shown that the second virial coefficient accounts for interactions between pairs of molecules; the third three body interactions and so on. In most cases of low pressure equilibrium, the second virial coefficient \( B \) describes the non ideality of the vapour phase quite well.

The fugacity coefficients ( in mixture and pure components ) are found from vapour phase volumetric properties. A number of methods have been proposed from time to time for the estimation of fugacity coefficients. Some of the methods have been reviewed elsewhere (16). The method of Hayden and O'Connell (103) is briefly described below:

At normal pressures, vapour phase fugacity coefficients of pure components and components in mixture may be calculated from second virial coefficients, \( B_{ij} \)

\[
\ln \phi_i = \frac{P}{RT} \left( 2 \sum_{j=1}^{n_i} y_j B_{ij} - B_i \right) \quad \ldots (2.2)
\]
$$b = \sum_{j=1}^{M} y_i y_j b_{ij} \quad \cdots \quad (2.3)$$

$m$ is the number of components in the system.

In Hayden and O'Connell's generalised correlation for predicting second virial coefficients, the overall second virial coefficient is considered as a sum of contributions from free pairs of molecules, metastable pairs, physically bound pairs, and chemically bound pairs

$$b_{\text{total}} = b_{\text{free}} + b_{\text{metastable}} + b_{\text{bound}} + b_{\text{chem}} \quad \cdots \quad (2.4)$$

and equations are presented for each contribution. For associating components such as carboxylic acids, the dimerisation equilibrium constant, $K_p$, is obtained from

$$K_p = \frac{b_{\text{bound}} + b_{\text{metastable}} + b_{\text{chem}}}{b_{\text{bound}}} \quad \cdots \quad (2.5)$$

The Hayden and O'Connell generalised correlation for $b_{ij}$ is applicable to most systems. Input to the correlation consists of (i) pure component information: critical temperature and pressure, Thomson's mean radius of gyration, dipole moment, and an associating factor, which depends only on the type of associating group (hydroxyl, amine, carboxylic acid, etc.); (ii) mixture information: solvation factor; (iii) system temperature. The authors give the input parameters, including association and solvation factors, for a large number of systems.

Liquid phase activity coefficients, using all the four measured variables $P-T-x-y$, may be calculated using the
following equations (259):

\[
\gamma_1 = \frac{P y_1}{x_1^0} \exp \left( \frac{(B_{11} - v_{1}^0)(P - P_1^0) + \delta_{12} y_2}{RT} \right)
\]

\[
\gamma_2 = \frac{P y_2}{x_2^0} \exp \left( \frac{(B_{22} - v_{2}^0)(P - P_2^0) + \delta_{12} y_1}{RT} \right)
\]

... (2.6)

... (2.6a)

where

\[
\delta_{12} = 2B_{12} - B_{11} - B_{22}
\]

... (2.6b)

The interactions \(B_{11}, B_{22}, B_{12}\) are second virial coefficients between pairs of molecules. \(\delta_{12}\) may be taken as zero for non-polar molecules resulting in a simple equation for \(\delta_{12}\) in which only pure component property data is required.

For moderate pressures, Prausnitz-Eckert-Crye-O'Connell (216) presented the above equations in terms of fugacities and fugacity coefficients as:

\[
\gamma_1 = \frac{\phi_1^0 y_1}{(f_1^0 x_1)}
\]

... (2.7)

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

\[
f_1^{OL} = f_1^0 \exp \left( v_1^0 \rho / RT \right)
\]

... (2.8)

The reference fugacity for pure component is calculated using

\[
f_1^0 = \phi_1^0 p_1^0 \exp \left( -v_1^0 \rho_1^0 / RT \right)
\]

... (2.9)
where \( \psi_i \) is the fugacity coefficient of pure vapour \( i \) at temperature \( T \) and saturation pressure \( P_i^\circ \). Lyckman-Eckert-Prasnitz (155) presented an equation for the calculation of \( \psi_i \) in the form

\[
\ln \psi_i = (\ln \psi_i^{(0)}) + \omega_i (\ln \psi_i^{(1)}) \quad \ldots \quad (2.10)
\]

where \( (\ln \psi_i^{(0)}) \) and \( (\ln \psi_i^{(1)}) \) are generalised functions of the reduced temperature. These are presented in a tabular form (155).

The above equations have mostly been used for the calculation of liquid phase activity coefficients where all the measured variables have been involved in the determinations of activity coefficients.

There is a lack of correlation to account for the vapour phase nonideality for highly polar and hydrogen bonding molecules. Rathnagel, Abrams and Prasnitz (155) presented a generalised correlation to account for vapour phase imperfections for a wide variety of vapours and their mixtures including polar and nonpolar components and also strongly hydrogen bonding fluids such as alcohols, aldehydes and carboxylic acids where the extent of dimerisation is large. The correlation is based on chemical theory of compounds.

Barker (16) maintained that the activity coefficients derived from total pressure measurements could be comparable in accuracy with the ones derived from the more difficult partial pressure measurements, particularly for solutions of high relative
voltalities where the difficult of obtaining a vapour sample in the true equilibrium with the liquid is most marked. A procedure based on the method of least squares for calculating activity coefficients for solutions from p-x measurements was described. The activity coefficients and excess chemical potentials can be represented by Scatchard and Raymond equations:

\[
\begin{align*}
\ln \gamma_1 &= \frac{-\Delta F}{RT} = \ln \left( \frac{P}{P_1^0} \right) + \frac{V_1^0 - V_1}{RT} \left( \frac{P}{P_1^0} - 1 \right) \\
&= \ln \left( \frac{P}{P_1^0} \right) + \ln \left( \frac{P}{P_1^0} \right) + \frac{V_1^0 - V_1}{RT} \left( \frac{P}{P_1^0} - 1 \right)
\end{align*}
\]

\[
\ln \gamma_2 = \frac{-\Delta F}{RT} = \ln \left( \frac{P}{P_2^0} \right) + \frac{V_2^0 - V_2}{RT} \left( \frac{P}{P_2^0} - 1 \right)
\]

\[
\gamma_1 = \frac{P}{P_1^0} \exp \left( \frac{V_1^0 - V_1}{RT} \left( \frac{P}{P_1^0} - 1 \right) \right)
\]

\[
\gamma_2 = \frac{P}{P_2^0} \exp \left( \frac{V_2^0 - V_2}{RT} \left( \frac{P}{P_2^0} - 1 \right) \right)
\]

The total pressure is given by

\[
\frac{P}{P_1^0} = \gamma_1 \frac{P}{P_1^0} + \gamma_2 \frac{P}{P_2^0}
\]

Scatchard (17) presented an equation for the dependence of excess Gibbs free energy of mixing which, with sufficient number of terms, can represent measured values of excess Gibbs free energy of mixing with any desired accuracy.
\[
\frac{\gamma}{\gamma_0} = x_1 x_2 \left[ A + B (x_1 - x_2) + C (x_1 - x_2)^2 + \ldots \right] \\
\ldots \quad (2.15)
\]

This results into the following equations for the activity coefficients:

\[
\ln \gamma_1 = A l_1 + B m_1 + C n_1 + \ldots \quad \ldots \quad (2.16)
\]

\[
\ln \gamma_2 = A l_2 + B m_2 + C n_2 + \ldots \quad \ldots \quad (2.16a)
\]

where

\[
\begin{align*}
l_1 &= x_2^2, \quad m_1 = -x_2^2 (1 - 4x_1), \quad n_1 = x_2^2 (1 - 3x_1 + 12x_1^2) \\
l_2 &= x_1^2, \quad m_2 = x_2^2 (1 - 4x_2), \quad n_2 = x_1^2 (1 - 3x_2 + 12x_2^2)
\end{align*}
\]

The procedure consists in determining the constants, A, B, C by a process of successive approximations. The first approximation is to assume that the solution behaves like a regular solution, so that B = C are zero. A is given by

\[
A = 4 \ln \left( \frac{\rho^*}{\rho_1^0 + \rho_2^0} \right) \quad \ldots \quad (2.17)
\]

where \( \rho^* \) is the pressure for eqimolar mixture. Using this value of A, an approximate value of \( \gamma \) is calculated from Equations 2.11 and 2.11a, \( \rho_1 \) and \( \rho_2 \) are calculated from experimental \( x \) values.

With the first approximation of A, \( \gamma_1 \) and \( \gamma_2 \) are obtained from Equations 2.16 and 2.16a, \( P \) by equation 2.12, pressure residuals, \( R = \frac{\rho_{\text{expt.}}}{\rho_{\text{calc.}}} \), and the derivatives by
\[
\frac{\delta p}{\delta a} = l_1 \gamma_1 p'_1 + l_2 \gamma_2 p'_2 \\
\frac{\delta p}{\delta b} = m_1 \gamma_1 p'_1 + m_2 \gamma_2 p'_2 \\
\frac{\delta p}{\delta c} = n_1 \gamma_1 p'_1 + n_2 \gamma_2 p'_2
\]

\[\text{.... (2.13)}\]

The changes \(\delta A, \delta B, \delta C\) in \(A, B, C\) are determined to make pressure residuals equal zero by fitting by least squares to the equation

\[
\left(\frac{\delta p}{\delta a}\right) \delta a + \left(\frac{\delta p}{\delta b}\right) \delta b + \left(\frac{\delta p}{\delta c}\right) \delta c = 0
\]

\[\text{.... (2.19)}\]

That is, the solution to the following equations:

\[
\delta A \sum_{i=1}^{n} (\partial p/\partial a)(\partial a_i/\partial A) + \delta B \sum_{i=1}^{n} (\partial p/\partial b)(\partial a_i/\partial B) + \delta C \sum_{i=1}^{n} (\partial p/\partial c)(\partial a_i/\partial C) = \sum_{i=1}^{n} \delta A_i \frac{\partial p}{\partial a} \\
\delta A \sum_{i=1}^{n} (\partial p/\partial b)(\partial a_i/\partial B) + \delta B \sum_{i=1}^{n} (\partial p/\partial a)(\partial a_i/\partial A) + \delta C \sum_{i=1}^{n} (\partial p/\partial c)(\partial a_i/\partial C) = \sum_{i=1}^{n} \delta B_i \frac{\partial p}{\partial b} \\
\delta A \sum_{i=1}^{n} (\partial p/\partial c)(\partial a_i/\partial C) + \delta B \sum_{i=1}^{n} (\partial p/\partial a)(\partial a_i/\partial B) + \delta C \sum_{i=1}^{n} (\partial p/\partial c)(\partial a_i/\partial C) = \sum_{i=1}^{n} \delta C_i \frac{\partial p}{\partial c}
\]

Abbot and Van Ness (1) found that highly nonideal systems, even those merging on instability, might be very precisely fit by
one of the two single equations, the 5-suffix Margules equation or a new equation called the Modified Margules equation. They concluded that reliable P-x data only are required to provide reliable vapour liquid equilibrium relationships. This conclusion was also supported by Kemeny and Hanczinger (135) and according to them measured data sets of only three variables should be treated and that the simultaneous regression of all the four variables is erroneous, since the number of degrees of freedom allows two independent and two dependent variables. It was shown by Abbot and Van Ness (1) that use of the measured y values along with P-x data in the data reduction process distorted the correlation of both the P-x and y-x relationships. They used Barker's method in conjunction with the two types of Margules equations — 5-suffix Margules equation and Modified Margules Equation. The method involves the following steps:

The concentration dependence of excess Gibbs free energy of mixing can be described by Margules 5-suffix equation

\[
\frac{\Delta G}{R T x_1 x_2} = \lambda_{21} x_1 + \lambda_{12} x_2 - (\lambda_{21} x_1 + \lambda_{12} x_2) x_1 x_2
\]

or Modified Margules equation

\[
\frac{\Delta G}{R T x_1 x_2} = A_{21} x_1 + A_{12} x_2 = \frac{\alpha_{21} \alpha_{12} x_1 x_2}{\alpha_{11} x_1 + \alpha_{22} x_2 + \gamma x_1 x_2}
\]

For an i j binary,
\[
\frac{y_i}{x_i} = x_j \text{ in } Y_i + x_j \text{ in } Y_j \quad \text{..... (2.23)}
\]

\[
p = \frac{x_i}{n} \frac{\exp \left( \frac{y_i}{n} \right) + x_j \frac{\exp \left( \frac{y_j}{n} \right)}{\Delta n} + \frac{x_i \frac{\exp \left( \frac{y_i}{n} \right)}{\Delta n} + x_j \frac{\exp \left( \frac{y_j}{n} \right)}{\Delta n}}{x_i \frac{\exp \left( \frac{y_i}{n} \right)}{\Delta n} + x_j \frac{\exp \left( \frac{y_j}{n} \right)}{\Delta n}} = x_i \frac{\exp \left( \frac{y_i}{n} \right)}{\Delta n} \quad \text{..... (2.24)}
\]

where

\[
Y_i = \frac{\frac{\exp \left( \frac{y_i}{n} \right)}{\Delta n}}{x_i \frac{\exp \left( \frac{y_i}{n} \right)}{\Delta n} + x_j \frac{\exp \left( \frac{y_j}{n} \right)}{\Delta n}} \quad \text{..... (2.25)}
\]

and \( \varphi_i = \exp \left( \frac{(1 - \varphi_i)(R - \varphi_i) + R y_j \varphi_i}{R T} \right) \quad \text{..... (2.26)} \)

Since the terms on the right hand side of Equation 2.24 represent the partial pressures, \( y_i P \) and \( y_j P \), the \( y \)'s are calculated by division of the values of these terms by the calculated values of \( P \). Barker's method is applied through application of Equation 2.24 in conjunction with a correlation for \( G^0/k T \), here Equation 2.21 or Equation 2.22. The procedure is to seek through regression a set of values for the parameters in the correlating equation for \( G^0/k T \) that minimises the sum of the squares of the pressure residuals calculated by Equation 2.24.

2.2 PHYSICAL PROPERTIES

Pure component properties in the determination of activity coefficients and the thermodynamic analysis of vapour-liquid systems.
usually are vapour pressures, second virial coefficients and liquid
molar volumes, all of which are functions of temperature only.
Experimental values of this data are not always available at the
desired conditions. It is always helpful to use reliable general-
ised correlations for the estimation of these properties under
varied conditions of pressure and temperature.

Reid and Sherwood (223) have given an excellent review of
the physical property estimation methods, most of which are depend-
dent upon the pure component constants like molecular weight, normal
boiling point, critical constants, dipole moments etc. Recommen-
dations are given for the choice of these correlations for varied
situations.

In the isothermal vapour-liquid equilibrium studies, the
experimental values of the properties like vapour pressures, liquid
molar volumes and second virial coefficients are normally available
in some standard handbooks or reference books. In case the values
are not available at the conditions of interest, a suitable corre-
lation can be tested and used. An exhaustive review of the above
and other properties is presented by Shushan Kumar (16).

2.3 THERMODYNAMIC CONSISTENCY
OF VAPOUR- LIQUID
EQUILIBRIUM DATA

Equilibrium measurements are always subject to errors
which might result from fractionation occurring in the contactor
as a result of slight heat leakages from the still, incorrect
sampling, entrainment of liquid droplets by the uprising vapours due to flashing at low pressures, attainment of nonequilibrium steady states or in the measurements and analysis either due to the faulty instruments or humanistic reasons. Hence there is a great need of the methods to check the reliability and thermodynamic consistency of the experimental data.

The raw experimental data are normally subjected to preliminary checks aimed at ascertaining the internal consistency. These checks primarily involve plotting the data in different ways and weeding out the erroneous observations on the basis of scatter from the regular curve. This type of check can detect random errors and is not helpful in pointing the systematic errors.

For any liquid phase of a multicomponent mixture, the Gibbs-Duhem equation applicable under isothermal conditions is:

\[ \sum x_i \ln \gamma_i = \frac{y_i}{\mu_i} \mathrm{d} \rho \]  

(2.27)

If the molal volumes of organic compounds do not differ by more than a factor of 2 to 4, the volume change of mixing is usually less than 0.5 cc/mole at temperatures below the normal boiling point. For many nonideal mixtures, the right hand side of Equation 2.27 does not exceed 0.002 per cent of either term on the left hand side: for example, Ibl and Lodge (12) calculated a value of 0.007 per cent for an equimolar mixture of acetone and carbon disulphide at 35°C. This corresponds to the negligible effect
or pressure on the properties of a pure liquid when in a condition
far removed from its critical state.

As a close approximation, the equation 2.27 becomes

\[ \sum x_i \frac{d \ln \gamma_i}{d x_i} = J \quad (T \text{ constant}) \quad \ldots \quad (2.29) \]

Thus:

\[ x_i \frac{d \log \gamma_i}{d x_i} + (1 - x_i) \frac{d \log \gamma_i}{d x_i} = 0 \quad \ldots \quad (2.29) \]

Gibbs-Duhem equation 2.29 is a differential equation which has been
applied to test the absolute consistency of isothermal vapour-
liquid equilibrium data, e.g., by measuring tangency or by graphical
integration. These types of calculation for testing the consistency
of isothermal data are less convenient and probably less accurate
than the method based upon the Nerington-Redlich-Kister equation.

Nerington (103), Coulson, Seales and Nerington (48), and
Redlich and Kister (224) derived an equation which depends upon,
but is more convenient than, the Gibbs-Duhem equation. Under
isothermal conditions for binary system

\[ x = 1 \]

\[ \ln \frac{\gamma_1}{\gamma_2} d x_i = \frac{1}{x_i} \int \left( V^2 d P \right) \quad \ldots \quad (2.30) \]

\[ x = 0 \]

\[ \bar{\rho} = \bar{\rho}_0 \]

\[ P = P_0 \]

If therefore the areas above and below \( \log \frac{\gamma_1}{\gamma_2} = c \) line
are equal, the binary data are thermodynamically consistent.

For near-ideal solutions the effect of scatter on the ratio of the areas is much more pronounced. It is usually impossible to decide whether the departure has occurred at all concentrations or only in part of the concentration range.

Brown, Smith and coworkers (31 to 34) tested the consistency of isothermal vapour-liquid equilibrium data for ten organic binary mixtures. The ratio of areas ranged from 1.001 to 1.09 with a mean of 1.025 and a standard deviation of 0.025 from the theoretical value of 1.00. Ellis and Bourne (63) reported the ratio of areas in the range 1.001 to 1.03.

It is well known that the random experimental errors in the determination of vapour-liquid equilibria are greatest in dilute solutions, particularly when the method of analysis has a constant absolute error (e.g., refractometry or densimetry (233,251)). The largest contribution to the areas above and below the line \( \log \frac{Y_A}{Y_2} = 0 \) arise from the most dilute regions, where experimental accuracy is lowest and measurements on equimolar solution are given least and not most weight. This is the major drawback of this important method.

Fraunitz (214) suggested the following condition as sufficient to satisfy the area test:

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

The integral test suffer from the drawback that the errors
in one part yet compensated for in the other part of composition range and it is difficult to draw a correct line through the scatter in the dilute concentration regime. On the other hand, the differential or point by point tests can be considered to be more reliable.

Van Ness (257) proposed the "Composition Resolution Test" based on Gibbs-Duhem equation which suffers from the disadvantage that it requires the measurements of the slope of the curve. This difficulty was overcome using the suggestion of Van Ness and Mrazek (261) according to which, plot \( \frac{G^*}{R T} x_1 x_2 \) vs. \( x_1 \) instead of plotting \( \frac{G^*}{R T} \) vs. \( x_1 \). The new plot is less sensitive to errors of tangency.

Using Gibbs-Duhem equation, Barreau (3) derived an equation in fugacities for testing the isothermal data. This equation does not involve any of the thermodynamic properties of the liquid phase.

From the discussion of Carlson and Coulburn (39) on the application of Gibbs-Duhem equation, Lu (152) and Lu, Simpson and Ho (154) proposed some local consistency tests at strategic liquid compositions. These tests take use of the assumption that pressure has a negligible effect on activity coefficients which were correlated by the van Javaa, Margules and Redlich-Kister equations. These tests are given below:

1. \( \ln \gamma_1 \) \( x_1 = 0.25 \) ; \( \ln \gamma_2 \) \( x_1 = 0.75 \).
2. At $x_1 = 0.50$
(a) in $\gamma_1 \approx 0.25 \theta$
(b) in $\gamma_2 \approx 0.25 \alpha$

where

$\alpha = (\ln \gamma_1) x_1 = 0$

$\theta = (\ln \gamma_2) x_1 = 1$

3. If $\alpha > \theta$

$(\ln \gamma_1) x_1 = 0.50 < (\ln \gamma_2) x_1 = 0.50$

4. If $\alpha < \theta$

$(\ln \gamma_1) x_1 = 0.50 > (\ln \gamma_2) x_1 = 0.50$

5. Both the $\ln \gamma$ curves on a $\ln \gamma$ vs. $x$ plot approach their zero values with a horizontal tendency.

6. If there is a maxima or minima on one of the curves, there is a corresponding minima or maxima on the other curve at the same composition.

7. If there is no maxima or minima, both the $\ln \gamma$ vs. $x$ curves are on the same side of $\ln \gamma = 0$ line.

The departures from the above requirements have also been given limits which largely depend upon the values of $\alpha$ and $\theta$, the end values of the activity coefficients.
These limits are:

(1) \( (\log \gamma_1)_{x_1=0.25} = (\log \gamma_2)_{x_1=0.75} \)

<table>
<thead>
<tr>
<th>( \beta/\alpha ) or ( \alpha/\beta )</th>
<th>( (\log \gamma_1)_{x_1=0.25} )</th>
<th>or</th>
<th>( (\log \gamma_2)_{x_1=0.75} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1 ± 0.01</td>
<td>or</td>
<td>1 ± 0.01</td>
</tr>
<tr>
<td>2</td>
<td>1 ± 0.03</td>
<td>or</td>
<td>1 ± 0.03</td>
</tr>
<tr>
<td>3</td>
<td>1 ± 0.09</td>
<td>or</td>
<td>1 ± 0.09</td>
</tr>
</tbody>
</table>

(2) \( (\log \gamma_1)_{x_1=0.50} = 0.25 \beta \)

\( (\log \gamma_2)_{x_1=0.50} = 0.25 \alpha \)

<table>
<thead>
<tr>
<th>( \beta/\alpha ) or ( \alpha/\beta )</th>
<th>( (\log \gamma_1)_{x_1=0.50} /\beta )</th>
<th>or</th>
<th>( (\log \gamma_2)_{x_1=0.50} /\alpha )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.25 ± 0.015</td>
<td>or</td>
<td>0.25 ± 0.015</td>
</tr>
<tr>
<td>2</td>
<td>0.24 ± 0.025</td>
<td>or</td>
<td>0.24 ± 0.025</td>
</tr>
<tr>
<td>3</td>
<td>0.22 ± 0.035</td>
<td>or</td>
<td>0.22 ± 0.035</td>
</tr>
</tbody>
</table>

Using van Leer equations, Black (18,19) suggested a plot of \((\ln \gamma_1)^{0.5} \) vs. \((\ln \gamma_2)^{0.5} \), a straight line, as a thermodynamic consistency test of the data. If the coefficients were less than
unity, a plot of \((-\ln \gamma_1)^{0.5}\) vs. \((-\ln \gamma_2)^{0.5}\) should yield a straight line for thermodynamically consistent data.

Van Ness-Heyl-Gibbs (260) put forth the view that the widely used area test, which requires the area for a plot of \(\ln (\gamma_1 / \gamma_2)\) vs. \(x_1\) to be zero, is a consistency test only in the most restrictive sense because only data needed to construct the plot are \(x\) and \(y\) values and the ratio \(P_2^0 / P_1^0\). The pressures which represent the resonating data, are not involved, except for the limiting values \(P_1^0\) and \(P_2^0\). Thus the only testing done by the area test as applied to isothermal data is of whether the vapour pressure ratio \(P_2^0 / P_1^0\) is appropriate to the set of \(x-y\) data. Of the four measurements, \(P-x-y\), the two most reliable are \(P-x\). Therefore Van Ness proposed a thermodynamic consistency test by comparison of calculated values of \(P\) or of \(y\) with experimental values that were not used in any way to generate the correlation. Where \(x\) and \(y\) data were alone used, the plot of \(\Delta y\) vs. \(x_1\) provides a consistency test. Where \(P-x\) data alone were used, the plot of \(\Delta y\) vs. \(x_1\) provides the test. In either case, the consistency requires that the \(\Delta\) values scatter randomly about zero. Where there is bias from \(\Delta = 0\) axis, the data must be judged to be inconsistent. This could, of course, result also from use of a correlating equation of a form not capable of adequately representing the data.

Most recently Kuschel, Kraetsch, Kahlen, and Zzechmann (143) proposed a consistency test of isothermal vapour-liquid equilibrium
data which requires the calculation of the molar excess Gibbs function \( \frac{\gamma}{RT} \) from isothermal \( P-x-y \) data by conventional procedure. Because of the Gibbs-Duhem equation there exists also the possibility of calculating \( \frac{\gamma}{RT} \) only from \( P-x \) data using Barker's method.

To test the consistency of data measured at \( n \) different mole fractions \( x_i \), the consistency parameter \( K \) is calculated:

\[
K = \frac{\sum_{i=1}^{n} \left( \frac{\gamma_i}{RT(x_i - y)} \right) (x_i) - \frac{\gamma}{RT(P)} (x_1)}{n}
\]  

(2.31)

For good consistency, the requirement is \( K \leq 15 \) J/mole. For high relative volatility cases there is a considerable difference between \( \frac{\gamma}{RT(P-x)} \) and \( \frac{\gamma}{RT(P)} \) and the question arises whether \( \frac{\gamma}{RT(P)} \) or \( \frac{\gamma}{RT(P-x)} \) possesses the higher reliability. The authors concluded, for such cases, that \( \frac{\gamma}{RT(P-x)} \) values should be preferred which are superior especially for systems with large \( \alpha \) values. In these systems, the inclusion of \( y \) values produced considerable deterioration of calculated \( \frac{\gamma}{RT} \) values.

2.4 Correlation of Vapour-Liquid Equilibrium Data

2.4.1 Correlations

Vapour-liquid equilibrium correlations are needed for the solution of many chemical engineering problems involving vapour-liquid systems. The required data can be, and often are, directly obtained by experimental measurements. However, such measurements are difficult, even for binary systems, and they become increasingly
tedious as the number of components grows. This is one of the incentives for the application of thermodynamics to the calculation of phase equilibrium correlations. However, thermodynamics does not generate data, it provides only the mathematical framework which allows maximum use of whatever data are available. Thus there is a basis for systematic correlation, extension, generalisation, evaluation, and interpretation of data. Moreover, it provides the means by which predictions of various theories of molecular physics and statistical mechanics may be applied to practical purposes.

The activity coefficients determined from experimental data are generally correlated by an equation. The activity coefficients for a given system are related to Gibbs excess free energy of mixing,

\[ \frac{G^E}{RT} = \sum x_i \ln \gamma_i \]

and

\[ \ln \gamma_i = \frac{G^E}{RT} - \sum_k x_k \left( \frac{\partial (G^E / RT)}{\partial x_k} \right)_{T, P, x_k = x_{k-1}} \]

it is best to build correlations around this function. The excess Gibbs free energy \( \frac{G^E}{RT} \) is a function of \( T, P \) and \( x_i \), but for liquids it is a weak function of \( P \). Hence, assume that at low pressures the pressure dependence of \( \frac{G^E}{RT} \) can be neglected. Thus, for a given temperature and composition, \( \frac{G^E}{RT} \) can be determined from the activity coefficients and conversely the activity
coefficients can be determined if \( \frac{d \gamma}{d \mu} \) is known as a function of concentration. A number of expressions for \( \frac{d \gamma}{d \mu} \) as a function of concentration have been proposed (1,224,225,229,270,273). Thus under isothermal conditions

\[
\frac{d \gamma}{d \mu} = \gamma (x_1, x_2, \ldots, x_n). \quad \ldots \ldots (2.33)
\]

A number of other equations are also in common use for the correlation of the activity coefficients. For binary systems, the function often most conveniently represented by an equation is

\[
\frac{d \gamma}{d \mu} = B + C (x_1 - x_2) + L (x_1 - x_2)^2 + \ldots \ldots \quad \ldots \ldots (2.34)
\]

By means of several assumptions on the \( \frac{d \gamma}{d \mu} \) or \( \frac{d \gamma}{d \mu} \) expressions, the well known correlations of van Laar (39,255,256), Margules (1,150) can be deduced. For binary systems there are:

van Laar:

\[
\ln \gamma_1 = \frac{A_{12}}{(1 + \frac{A_{12}}{A_{21}} x_2)^2} \quad \ldots \ldots (2.35)
\]

\[
\ln \gamma_1 = \frac{A_{21}}{(1 + \frac{A_{21}}{A_{12}} x_1)^2}
\]
Margsules : 

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

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

\[ \ln \gamma_1 = x_2^2 \left( \lambda + 2x_1 (\lambda_{21} - \lambda_{12}) + 3x_1^2 \lambda_{12} \right) \]

\[ \ln \gamma_2 = x_1^2 \left( \lambda + 2x_2 (\lambda_{12} - \lambda_{21}) + 3x_2^2 \lambda_{21} \right) \]

\[ \ln \gamma_1 = x_2^2 \left( \lambda_{12} + 2x_1 (\lambda_{21} - \lambda_{12}) + 2x_1 \left( \lambda_{21} x_1 + \lambda_{12} x_2 \right)(x_1 - x_2) \right) \]

\[ - \lambda_{21} x_1^2 \]

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

\[ - \lambda_{12} x_2^2 \]

Ellis and Bourne (63) gave the following conditions under which van Leer and Margsules equations give fairly close fit of isothermal binary vapour-liquid equilibrium data when:

1. the ratio of the end values are less than 1.6,
2. the end values are less than 1.3,
3. the ratio of molar volumes of the components are less than 2, and
4. one component is not strongly associated whilst the other is not associated.
Only Margules equation would fit the data well when one of the activity coefficients passes through a maximum. The van Laar equation is usually more accurate than the Margules equation.

Various modifications of van Laar and Margules equations have been proposed from time to time to extend the effectiveness of these equations under involved conditions (1, 17, 19, 23, 39, 206, 260, 267, 276). Abbot and Van Ness (1) modified the 5-suffix Margules equation by introducing a fifth parameter to extend its effectiveness to a system which could not be satisfactorily represented by unmodified Margules equation.

Black (119) modified van Laar equations for isothermal conditions by introducing an empirical term \( c_{ij} \) to account for the overall influence of physical interaction, association and inter-association among molecules

\[
\ln \gamma_i = a_{ij}^2 / (1 + \frac{a_{ij}^2 x_i}{a_{ji}^2 x_j})^2 + E_i \quad \text{**** (2.39)}
\]

where

\[
E_i = c_{ij} x_j (x_i - x_j) \left[ 2(x_i x_j - x_j^3)(1 - x_i) + 2x_j \right] \quad \text{**** (2.39a)}
\]

This equation is extremely flexible and can fairly well represent the behaviour of even highly nonideal systems and is suitable for polar-nonpolar and polar-polar mixtures.

Redlich and Kister (224, 225) developed a convenient and flexible equation representing \( \log(\gamma_1 / \gamma_2) \) as a function of composition of a binary system.
\[
\log \frac{\gamma_1}{\gamma_2} = b (x_2 - x_1) + c (3x_1 x_2 - 1) + d (x_1 - x_2)(3x_1 x_2 - 1) \\
+ \varepsilon (x_1 - x_2)^2 (10x_1 x_2 - 1) + \cdots \cdots (2.40)
\]

and

\[
\log \gamma_1 = x_2^2 (b + c (3x_1 - x_2) + d (x_1 - x_2)(5x_1 - x_2) \\
+ \varepsilon (x_1 - x_2)^2 (7x_1 - x_2) + \cdots \cdots) \cdots \cdots (2.41)
\]

The principal advantage of these equations over other solutions of Gibbs-Duhem equation is that of flexibility, because if an adequate fit of the experimental data cannot be obtained with, say, two constants, a third and, if necessary, a fourth constant may easily be incorporated. After a thorough study of the equation for the number of constants, Bourne (25) found that the three constant equation is usually satisfactory as the fourth constant did not significantly improve upon the correlation for polar nonideal systems.

Wilson (276) represented excess Gibbs free energy of mixing as a logarithmic function of composition by analogy with the Flory-Huggins expression (69,125) for athermal mixtures in which the overall volume fraction was replaced by local volume fraction. Wilson expression for excess Gibbs free energy of mixing as given by Orye and Prausnitz (194) is

\[
G^E / k T = -x_1 \ln (x_1 + x_2 \Lambda_{1c}) - x_2 \ln (x_2 + x_1 \Lambda_{2c}) \cdots \cdots (2.42)
\]
where
\[ \Lambda_{12} = \frac{\nu_2^0}{\nu_1^0} \exp \left( - \frac{\Lambda_{12} - \Lambda_{11}}{x_1} \right) \]  
\[ \Lambda_{41} = \frac{\nu_4^0}{\nu_2^0} \exp \left( - \frac{\Lambda_{12} - \Lambda_{22}}{x_2} \right) \]  
\[ \Lambda_{21} = \frac{\nu_2^0}{\nu_1^0} \exp \left( - \frac{\Lambda_{21} - \Lambda_{22}}{x_2} \right) \]

and
\[ \ln \gamma_1 = \ln \left( x_1 + x_2 \Lambda_{12} \right) + x_2 \left( \frac{\Lambda_{12}}{x_1 + x_2 \Lambda_{12}} - \frac{\Lambda_{21}}{x_2 + x_1 \Lambda_{21}} \right) \]  
\[ \ln \gamma_2 = -\ln \left( x_2 + x_1 \Lambda_{21} \right) - x_1 \left( \frac{\Lambda_{12}}{x_1 + x_2 \Lambda_{12}} - \frac{\Lambda_{21}}{x_2 + x_1 \Lambda_{21}} \right) \]  
\[ \ln \gamma_4 = -\ln \left( x_4 + x_2 \Lambda_{24} \right) - x_2 \left( \frac{\Lambda_{24}}{x_4 + x_2 \Lambda_{24}} - \frac{\Lambda_{41}}{x_4 + x_1 \Lambda_{41}} \right) \]  
\[ \ln \gamma_4 = -\ln \left( x_4 + x_2 \Lambda_{24} \right) - x_2 \left( \frac{\Lambda_{24}}{x_4 + x_2 \Lambda_{24}} - \frac{\Lambda_{41}}{x_4 + x_1 \Lambda_{41}} \right) \]  

Here energy parameters, \( \Lambda_{12} - \Lambda_{11} \) and \( \Lambda_{12} - \Lambda_{22} \), are independent of temperature for a moderate temperature interval. Wilcox equation, as given above, is suitable for a wide variety of binaries even with high nonideality. This is particularly more effective in case of alcohols in nonpolar solvents. The correlation fails in the case of partially miscible systems and also in systems which exhibit maxima or minima on plots of \( \ln \gamma \times x \). In order to make this equation applicable to partially miscible systems, Wilcox suggested that his original equation for molar excess Gibbs free energy of the mixture, be multiplied by a constant \( c \neq 1 \).

Hayata, Yamada, Gotoh and Kazuma (133) made use of Wilcox's suggestion for the additional constant. They established the concentration dependence of energy parameters in the form of an empirical expression and thus modified the Wilcox equation for
phase splitting.

Holmes and Van Winkle (124) and Hudson and Van Winkle (117) have discussed the superiority of this correlation for representing vapor-liquid equilibria for all types of solutions. Nagata (140) pointed instances where the Wilson equation failed.

Hatkovics (44) modified the Wilson equation for systems containing associating components which form dimers.

Hirano (111) worked on Ronon-Prausnitz finding, that
c = z/2 where z is the coordination number of the liquid, and
discussed a method to determine the value of z. Cuckor and Prausnitz found z for typical liquids between 6 and 12, even this
did not give good fit of experimental data for partially miscible systems. Hirano divided the liquids into four groups and the
value of z determined according to the combination of these groups
in a mixture.

Nagata, Nagashima, Ogura (131) modified Wilson equations for
partially miscible systems making use of the suggestion of some
authors (137, 138, 151) that extension of Wilson equation for
partially miscible systems might be made by adding another equation
to the original Wilson equation. Thus

\[
\frac{U}{L} = - \left( x_1 \ln(x_1 + \Lambda_{12} x_2) + x_2 \ln(x_2 + \Lambda_{21} x_1) \right) + \beta \phi_1 \phi_2 \left( x_1 v_1 + x_2 v_2 \right)
\]

where \( \beta \) is determined from solubility parameters.
Islamoka and Katayama (254) modified Wilson equation for vapour-liquid and liquid-liquid equilibria. The new equation has been derived on the basis of an equation of excess free energy with Wilson local volume fractions and Gibbs-Helmholtz correlation. This modified Wilson equation has only two parameters for a binary system. The equations are:

$$\frac{v^c_i}{v_i} = -x_1 \ln (x_1 + x_2 \Lambda_{21}) - x_2 \ln (x_2 + x_1 \Lambda_{12})$$
$$+ x_1 \ln (x_1 + x_2 \rho_{21}) + x_2 \ln (x_2 + x_1 \rho_{12}) \quad \ldots \ldots (2.45)$$

and

$$\ln \gamma_1 = -\ln (x_1 + x_2 \Lambda_{21}) + x_2 \left( \frac{\Lambda_{21}}{x_1 + x_2 \Lambda_{21}} - \frac{\Lambda_{12}}{x_1 \Lambda_{12} + x_2} \right)$$
$$+ \ln (x_1 + x_2 \rho_{21}) - x_2 \left( \frac{\rho_{21}}{x_1 + x_2 \rho_{21}} - \frac{\rho_{12}}{x_1 \rho_{12} + x_2} \right) \quad \ldots \ldots (2.46)$$

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

with

$$\Lambda_{ij} = \rho_{ij} \exp \left[ - \left( \gamma_{ij} - \gamma_{ii} \right) \right] \quad \ldots \ldots (2.47)$$

$$\rho_{ij} = \frac{v_i}{v_j} \quad \ldots \ldots (2.48)$$

Ammon and Prausnitz (229) developed an equation, which is
known as NRTL equation, based on Scott’s two liquid theory of mixtures (239) and on the assumption based on the Guggenheim’s quasi-chemical approximation (99).

\[
\frac{G^E}{x_1} = x_1 \frac{\tau_{21} G_{21}}{x_1 + x_2 G_{21}} + \frac{\tau_{12} G_{12}}{x_2 + x_1 G_{12}} \ldots\ldots\ldots\ldots(2.49)
\]

where

\[
\tau_{12} = \exp \left( -\alpha_{12} \frac{\psi_{12}}{R T} \right) \ldots\ldots\ldots\ldots(2.49a)
\]

\[
\tau_{21} = \exp \left( -\alpha_{12} \frac{\psi_{21}}{R T} \right) \ldots\ldots\ldots\ldots(2.49b)
\]

\[
\tau_{12} = \left( \psi_{12} - \psi_{22} \right) / R T \ldots\ldots\ldots\ldots(2.49c)
\]

\[
\tau_{21} = \left( \psi_{21} - \psi_{11} \right) / R T \ldots\ldots\ldots\ldots(2.49d)
\]

\[
\psi_{12} = \psi_{21} \ldots\ldots\ldots\ldots(2.49e)
\]

\(\tau_{12}\) and \(\tau_{21}\) are temperature dependent parameters and the non-random parameter \(\alpha_{12}\); to a good approximation, is independent of temperature. The activity coefficient expressions based on the above excess free energy expression of mixing are:

\[
\ln \gamma_1 = x_2^2 \left( \frac{\tau_{21} \psi_{21}^2}{(x_1 + x_2 \psi_{21})^2} + \frac{\tau_{12} \psi_{12}}{(x_2 + x_1 \psi_{12})^2} \right) \ldots\ldots\ldots\ldots(2.50)
\]

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

Rosen and Reusnitz give the value of \(\alpha_{12}\) for typical nonelectrolytes.
in the range of 0.2 to 0.47 depending upon the chemical nature of the systems. Renon and Prausnitz (231) also presented method for the evaluation of NRTL parameters. NRTL equation is capable of representing vapour-liquid equilibrium data of partially miscible systems as compared to the original Wilson equation which fails on such systems. Also, NRTL equation is simpler without any logarithmic terms and can describe ternary equilibrium data well. For extending this equation to multicomponent systems, no additional assumptions are involved. The only drawback with this equation is that all the three constants have to be used even for miscible systems.

Bruin and Prausnitz (15) modified the NRTL equation by substituting local volume fractions in place of local mole fractions. The equation contains only one parameter and the correlations relating the value of this parameter to molecular structure were established for several classes of systems. This equation correlates the activity coefficients for all types of systems as a function of temperature with a small number of variable parameters.

Andiappan and Maclean (5) proposed a semiempirical correlation based on Scott's Two Liquid Theory. There are two adjustable parameters and a binary constant and it is claimed that the correlation describes highly nonideal solutions and even those on the verge of instability.
2.4.2 Evaluation of Parameters

Most of the correlations representing activity coefficients involve constant terms which are dependent upon temperature. In the treatment of vapour-liquid equilibrium data, optimum values of these constant terms are determined using some optimisation technique. Before selecting any optimisation technique, it is always advisable to know which function is to be minimised. Various minimisation functions have been used by many workers (119,123,135, 173,179,182,186,216,263).

\[ F_Q = \sum_{i=1}^{n} (C_{\text{expt}} - C_{\text{calc}})^2 \]  \hspace{1cm} \text{(2.51)}

\[ F_Y = \sum_{i=1}^{n} \left[ (\gamma_1 \text{expt} - \gamma_1 \text{calc})^2 + (\gamma_2 \text{expt} - \gamma_2 \text{calc})^2 \right] \]  \hspace{1cm} \text{(2.51a)}

\[ F_\left(\frac{\gamma_1}{\gamma_2}\right) = \sum_{i=1}^{n} \left[ \ln \left(\frac{\gamma_1}{\gamma_2}\right) \text{expt} - \ln \left(\frac{\gamma_1}{\gamma_2}\right) \text{calc} \right]^2 \]  \hspace{1cm} \text{(2.51b)}

\[ = \frac{\sum_{i=1}^{k} (\gamma_1 \text{expt} - \gamma_1 \text{calc})^2}{\sum_{i=1}^{k} (\gamma_1 \text{expt} - 1.0)^2} + \frac{\sum_{i=1}^{k} (\gamma_2 \text{expt} - \gamma_2 \text{calc})^2}{\sum_{i=1}^{k} (\gamma_2 \text{expt} - 1.0)^2} \]  \hspace{1cm} \text{(2.51c)}

\[ F_Y = \sum_{i=1}^{n} (y \text{expt} - y \text{calc})^2 \]  \hspace{1cm} \text{(2.51d)}
\[ h_y = \sum_{i=1}^{n} \left( \frac{y_{\text{expt.}} - y_{\text{calc.}}}{y_{\text{calc.}}} \right)_i^2 \]  
\[ \ldots (2.51e) \]

\[ f_y = \sum_{i=1}^{n} \left( 1 - y_{\text{calc.}} - y_{\text{calc.}} \right)_i^2 \]  
\[ \ldots (2.51f) \]

\[ z_y = \sum_{i=1}^{n} \left( \frac{y_{\text{expt.}} - y_{\text{calc.}}}{y_{\text{calc.}}} \right)_i^2 \]  
\[ \ldots (2.51g) \]

\[ z_p = \sum_{i=1}^{n} \left( \frac{y_{\text{expt.}} - y_{\text{calc.}}}{y_{\text{calc.}}} \right)_i^2 \]  
\[ \ldots (2.51h) \]

\[ c = \sum_{i=1}^{n} \left( y_{1,\text{expt.}} - y_{1,\text{calc.}} \right)_i^2 \]  
\[ \ldots (2.51i) \]

\[ + \sum_{i=1}^{k} \left( \frac{y_{\text{expt.}} - y_{\text{calc.}}}{y_{\text{calc.}}} \right)_i^2 \]  
\[ \ldots (2.51j) \]

\[ \Gamma_{\gamma_{1,2}} = \sum_{i} \left[ \ln \left( \frac{y_{1i}}{y_{2i}} \right)_{\text{expt.}} - \ln \left( \frac{y_{1i}}{y_{2i}} \right)_{\text{calc.}} \right]^2 \]  
\[ \sigma_i^2 \left( \ln \frac{y_1}{y_2} \right)_i^2 \]

\[ + \sum_{i} \left( \frac{y_{1,\text{expt.}} - y_{1,\text{calc.}}}{\sigma_i} \right)_i^2 \]  
\[ \ldots (2.51j) \]
Nagahama, Suzuki and Hiraeta (173) employed $F_t$, $F_y$ and $F_y$ minimisation functions in their determination of Wilson constants while using the following optimisation techniques:

1. Nonlinear least squares method (50)
2. Gradient search method (161)
3. Pattern search method (55)
4. Complex search method (27)

These are well known optimisation methods. The first one is described below because this has been used in the estimation of constants in various correlating equations in this work.

The minimisation function is written as

$$i = \sum_{i=1}^{n} \epsilon_i$$

For a binary system $x_1 = x; x_2 = 1-x$,

$$\epsilon_i = (C_{\text{expt.}} - C_{\text{calc.}})$$

$$= C_{\text{expt.}} + x \ln (x + \Lambda_{12} (1-x)) + (1-x) \ln (\Lambda_{21} x + (1-x))$$

... (2.53)

Procedure runs as follows:

(a) Starting from the independent variables $\Lambda_{12}$ and $\Lambda_{21}$, the corrections $\Delta \Lambda_{12}$ and $\Delta \Lambda_{21}$ to $\Lambda_{12}$ and $\Lambda_{21}$ respectively are evaluated by solving the following set of simultaneous equations...
\[
\sum_{i=1}^{n} \frac{\partial r_i}{\partial \Lambda_{12}} \frac{\partial r_i}{\partial \Lambda_{21}} \Delta \Lambda_{12} + \sum_{i=1}^{n} \frac{\partial r_i}{\partial \Lambda_{12}} \frac{\partial r_i}{\partial \Lambda_{21}} \Delta \Lambda_{21} = \sum_{i=1}^{n} \frac{\partial r_i}{\partial \Lambda_{12}} \quad \cdots (2.54a)
\]

\[
\sum_{i=1}^{n} \frac{\partial r_i}{\partial \Lambda_{12}} \frac{\partial r_i}{\partial \Lambda_{21}} \Delta \Lambda_{12} + \sum_{i=1}^{n} \frac{\partial r_i}{\partial \Lambda_{12}} \frac{\partial r_i}{\partial \Lambda_{21}} \Delta \Lambda_{21} = \sum_{i=1}^{n} \frac{\partial r_i}{\partial \Lambda_{21}} \quad \cdots (2.54b)
\]

where

\[
\frac{\partial r_i}{\partial \Lambda_{12}} = \frac{x (1 - x)}{\Lambda_{12} (1 - x) + x} \quad \cdots (2.55a)
\]

\[
\frac{\partial r_i}{\partial \Lambda_{21}} = \frac{x (1 - x)}{(1 - x) + \Lambda_{21}} \quad \cdots (2.55b)
\]

the \(r_i\)'s and \(\partial r_i / \partial \Lambda_{12}\) and \(\partial r_i / \partial \Lambda_{21}\) are evaluated at the starting values of \(\Lambda_{12}\) and \(\Lambda_{21}\).

(b) The new values of \(\Lambda_{12}\) and \(\Lambda_{21}\) are computed by subtracting the correction \(\Delta \Lambda_{12}\) and \(\Delta \Lambda_{21}\) from the old values of \(\Lambda_{12}\) and \(\Lambda_{21}\). With the new values of \(\Lambda_{12}\) and \(\Lambda_{21}\), the procedure in step (a) is repeated till \(\Delta \Lambda_{12}\) and \(\Delta \Lambda_{21}\) become suitably small. The advantage of this Gaussian technique is that the partial derivatives are evaluated with each iteration.
Nagahama, Suzuki and Hirata (178) concluded that the results calculated by above different techniques with the same objective function were not much different and, therefore, the method of nonlinear least squares be preferred over other methods because this is simpler and gives reasonably good estimates of the constants within 5 to 10 iterations whereas other methods require some 30 to 40 iterations to reach the same final value of the minimised function. According to them the nonlinear least squares method coupled with the use of a function is to be preferred over any other method for obtaining Wilson parameters.

Verhoeve (263, 264) used $F_q$, $F(\gamma_1/\gamma_2)$ and $X_4$ as the minimisation criteria. $F_q$ function was minimised by Newton-Raphson method in which the function is expanded by Taylor series neglecting the higher derivative terms. Newton-Raphson method is effective if the starting values of the constants are in the neighbourhood of the optimum values but is quite inefficient when the values are far removed from the optimum values and even the method might diverge. This method was also used by McDermott and Ellis (165) for the predictions of vapour-liquid equilibria from total pressure measurements. A method of weighted least squares for the Wilson equation was also developed by Verhoeve by giving statistical weight to each experimental point.

Kaliaguine and Kamalho (133) discussed the choice of regression method to estimate the coefficients in Wilson equation.

Asselineau and Renon (7) gave a method to calculate the constants in the NRDL equation by the method of least squares.
Tierney (251) developed an exact method based on the weighted least squares procedure suitable for the evaluation of Marxules and van Laar 3-suffix constants. Carli (39a) minimised the a function by a nonlinear technique to evaluate the constants in van Laar and Marxules equations. Ho-Soang-Lo (117) employed m as the minimisation function to estimate the optimum values of the Redlich-Kister constants by the method of least squares. The mathematical approach is similar to Barker's (10) and it was found that on the average 4 iterations are adequate for a tolerance of 10^-5 in the constants.

Hichterle (263) concluded that out of all the minimisation functions, F (γ1 / γ2) function was the best. Also it was found possible to improve the adjustment for the individual experimental data by introducing statistical weights given by the following equation:

\[
\lambda = \left( \frac{1}{x^2 (1 - x)^2} + \frac{1}{y^2 (1 - y)^2} + \left( \frac{\partial \gamma_1(x)}{\partial x} \right)^2 \right)^{-1}
\]

\(\cdots (2.56)\)

where

\[
F(x) = \ln \left( \frac{\gamma_1}{\gamma_2} \right)
\]

\(\cdots (2.56a)\)

Most recently Kemény and Menczinger (135) have evaluated various methods for the estimation of Wilson constants. Different estimation criteria on a statistical basis and their experience with correlations of three and four data points were discussed.
It was found that the unweighted regression for three (T-x-y and P-x-x) and for four (P-x-x-y) variables, yields different values of parameters. The values of the parameters depend upon the type of the function of variables used in the minimised sum of squared deviations between measured and calculated values. It has been shown that the properly weighted regression of the T-x-y data or P-x-x data gives the estimated parameters which do not depend upon LGC. It was also concluded that measured data sets of only three variables should be treated and that the simultaneous regression of all the four variables is erroneous, since the number of degrees of freedom allows two independent and two dependent variables.

2.5 Prediction of Vapour-Liquid Equilibria from Molecular Structure

Langmuir (146) gave the idea of the estimation of thermodynamic properties of liquid mixtures from group contributions. He suggested that the partial molal excess Gibbs energy of component i (i.e., R T ln i ) could be considered as the summation of interactions between molecular segments (groups) in molecule i and all other molecular segments in the mixture. By molecular groups, we mean any functional group such as CH₂, CHO, OH, CN, CCCH etc. The idea received little attention until Perr and coworkers (52,223) used group contributions to correlate heats
of mixing followed by Wilson and Ieal (271), Derr and Ieal (51), andnone and Ratcliff (234) proposed their Analytical Solution of Groups (ASOG) model for activity coefficients. Upon combining the concept of functional groups with analytical results of Universal Quasi-chemical Theory (UNIQUAC), Prausnitz, Jones and Fredenslund (74) presented their Functional-Group-ActivityCoefficients method known as UNIFAC method for the calculation of activity coefficients.

Derr and Ieal (51) and none and Ratcliff (234) ASOG model separates the molecular activity coefficient into two parts: one part provides the contribution due to differences in molecular size and the other provides the contribution due to molecular interactions. The first part of this is arbitrarily calculated on the basis of athermal Flory-Huggins equation and the second part is determined by using Wilson equation when applied to functional groups. Most of this arbitrariness is eliminated by combining ASOG with the UNIQUAC equation. This is because, firstly, the UNIQUAC model contains a combinatorial part, essentially due to differences in size and shape of the molecules in the mixture, and a residual part, essentially due to energy interactions, and secondly, functional group sizes and interaction surface areas are entered from pure component and molecular structure data.

Abrams and Prausnitz (2) showed that the UNIQUAC equation gives good representation of both vapour-liquid and liquid-liquid equilibria for binary and multicomponent mixtures containing a variety of nonelectrolytes such as hydrocarbons, alcohols, ketones, amines, esters, nitriles etc.
Ronec and Ratcliff (234) ASCG model is similar to UNIFAC in principle but not in detail. From application point of view, UNIFAC provides three advantages:

1. **Flexibility**, because UNIFAC provides priori estimates of sizes and areas;

2. **Simplicity**, because UNIFAC parameters, unlike ASCG parameters, are essentially independent of temperature for the temperature range considered in this, typically 30°C to 125°C, and

3. **Due to the application of the method to a wide variety of mixtures.**

UNIFAC parameters are now available for a considerably larger number of functional groups (73) than ASCG parameters, therefore the range of applicability of UNIFAC is larger.

In the UNIFAC method, the combinatorial part of the UNICUAC activity coefficients is used directly because only pure component properties enter into this equation. Parameters \( r_1 \) and \( q_1 \) are calculated as the sum of the group volume and area parameters, \( a_k \) and \( t_k \), given in tables. These group parameters \( a_k \) and \( t_k \) are obtained from the van der Waals group volume and surface areas \( V_k \) and \( a_k \) given by Bondi (24). The residual part of the activity coefficient is replaced by the solution-of-groups concept. The group activity coefficient \( \Gamma_k \) is found from an expression similar to the one in UNICUAC method. The governing equations in the
The above two methods are given below:

\[ \ln \gamma_1 = \ln \gamma^c_1 + \ln \gamma^u_1 \]

(combinatorial) (residual) 

I. COMBINATORIAL PART:

This is same in the two models.

\[ \ln \gamma^c_1 = \ln \frac{\phi_1}{x_1} + \frac{z}{2} q_1 \ln \frac{\phi_1}{\sigma_1} + l_1 - \frac{\phi_1}{x_1} \sum_j x_j i_j \]

\[ l_1 = \frac{z}{2} (r_1 - q_1) - (r_1 - 1) \]

\[ z = 10 \]

\[ e_1 = \frac{x_1}{\sum_j x_1 x_j} \]

\[ \phi_1 = \frac{x_1}{\sum_j x_j} \]

\[ r_1 = \sum_k \psi_k \bar{r}_k \]

\[ q_1 = \sum_k \psi_k \bar{c}_k \]

\[ \bar{r}_k = \frac{v_k}{15.17} \]

\[ \bar{c}_k = \frac{v_k}{(2.5 \times 10^9)} \]
II. RESIDUAL PART A (UNIQUAC EQUATION):

\[ \ln \gamma_i^R = q_i \left[ 1 - \ln \left( \frac{\sum_j \theta_j \gamma_j^R}{\gamma_j^R} \right) + \sum_j \left( \theta_j \frac{\gamma_j^R}{\sum_k \theta_k \gamma_k^R} \right) \right] \]

\[ \gamma_j^R = \exp \left( - \frac{u_{ji} - u_{ji}^0}{R} \right) \]

For small temperature range, the effect of temperature on \( \gamma_j^R \) can be approximated by a linear form:

\[ \gamma_j^R = \gamma_j^{(0)} + \gamma_j^{(1)} T \]

where \( \gamma_j^{(0)} \) and \( \gamma_j^{(1)} \) are the coefficients related to characteristic energy interaction difference, \( u_{ji} - u_{ji}^0 \).

PART B UNIFAC METHOD (Group Contribution)

\[ \ln \gamma_i^R = \sum_k \gamma_k^{(i)} (\ln \gamma_k^R - \ln \gamma_k^{(i)}) \]

(all groups)

\( \gamma_k^R \) is the group residual activity coefficient, and \( \gamma_k^{(i)} \) is the residual activity coefficient of group \( k \) in a reference solution containing only molecules of type \( i \).

\[ \ln \gamma_k^R = \tilde{c}_k \left[ 1 - \ln \left( \frac{\sum_n \tilde{\theta}_n \tilde{\gamma}_n}{\tilde{\gamma}_n} \right) - \sum_n \tilde{\theta}_n \frac{\tilde{\gamma}_n}{\sum_m \tilde{\theta}_m \tilde{\gamma}_m} \right] \]

\[ \tilde{\theta}_n = \frac{\tilde{c}_m \tilde{\lambda}_m}{\sum_n \tilde{c}_n \tilde{\lambda}_n} \]
\[ \lambda_m = \sum_i \left( \sum_m x_i \right) / \sum_k \left( \sum_i x_i \right) \quad \text{...(2.61b)} \]

\( \lambda_k \) is the group fraction of group \( m \) in the mixture.

\[ \psi_{nm} = \exp\left( - \frac{a_{nm}}{T} \right) \quad \text{...(2.62)} \]

\( a_{nm} \) characterises the interaction between groups \( n \) and \( m \).
\( a_{nm} \neq \chi_{nm} \). All equations here also hold for \( \chi_k \) except that the group composition variable, \( \chi_k \), is now the group fraction of group \( k \) in pure fluid \( i \).

The original work on UNIFAC considered 25 different functional groups. Extension of the work continued and now UNIFAC group-interaction parameters for more than 50 different groups based upon nearly 70 per cent of all the published vapour-liquid equilibrium data at low to moderate pressures are available (73). The revised tables of these parameters are based upon vapour-liquid equilibrium data for nearly 2500 binary systems.

Nitta, Turek, Greenkorn and Chao (199) developed a group contribution model for the thermodynamic properties of polar and nonpolar liquids and their solutions, including the energy of vaporisation, PVT relations, excess properties and activity coefficients. The model is based on cell theory in which the repulsive forces of molecules are expressed with a modified cell partition function derived from the Carnahan-Starling equation (40) of state for hard spheres. The attractive forces are made up of group pair interaction contributions. Group interaction properties
have been determined for methyl, methylene, hydroxyl, and carbonyl. Extensive comparisons of the predicted values with literature data have been made at conditions for which the cell model is known to be applicable: where the liquids are not expanded, the reduced density is greater than 1, and the temperature is not much above the normal boiling point.

All group-contribution methods are necessarily approximations because any group within a molecule is not completely independent of the other groups within that molecule. But it is precisely this independence which is the essential basis of every group contribution method. Increasing distinction of groups also increases the number of group interactions that must be characterised. Judgment and experience must tell us how to define functional groups so as to achieve a compromise between accuracy of prediction and engineering utility.

2.6 MEASUREMENT OF VAPOUR-LIQUID EQUILIBRIUM DATA

The design of stagewise or differential contacting equipment such as a distillation column requires reliable vapour-liquid equilibrium data. It has been the general practice to determine such basic equilibrium data experimentally. This experimental attempt at obtaining thermodynamically consistent data is a difficult physico-chemical technique and should not be approached in a very casual manner. There is a large number of equilibrium
stills for the purpose.

The methods for the direct determination of equilibrium data can be classified into the following five groups:

1. Distillation method
2. Circulation method
3. Static method
4. Dew and Bubble point method
5. Flow method.

Distillation is the oldest method where a negligible amount of liquid is distilled off from the boiling flask containing a large charge. The disadvantage of this simple method is a large quantity of liquids as charge and it permits a very small amount of vapour sample for analysis, so that the liquid composition is practically constant. Large errors crop up due to partial condensation of vapour sample on the cold walls of the flask at the start of the experiment. This method is very seldom used.

Static methods are deceptively simple in principle but quite difficult and time consuming in practice. They are used especially for the isothermal and high pressure vapour-liquid equilibria. These methods are also helpful when relatively small quantities of liquids are available. The problems encountered in these stills are that complete degasification of both the apparatus and the liquids is necessary with each charge to ensure the accuracy of the pressure measurements. In these stills, generally the equilibration times are long and they involve difficulty in
removing the gas samples especially at low pressures where the amount of vapour samples required for analysis of the same order as the amount of vapour phase in equilibrium bombs. So the vapour sampling would change the equilibrium.

Gibbs-Van Ness (31) discussed the advantages of static stills over recirculatory stills and designed a new static vapour-liquid equilibrium still.

circulation methods are advantageous due to the fact that steady state is relatively quickly attained. Also, due to the thorough mixing of the liquid masses, the possibility of concentration gradients is highly reduced. They suffer from the disadvantage that relatively large amounts of chemicals are required and the mechanical stirring of the liquid masses in the still is also a problem. These stills are not suitable for partially miscible systems and the pressure fluctuations are also large.

In the design and operation of these stills the most common sources of error are due to partial condensation of equilibrium vapour or superheating of vapour in the jacket, occurrence of concentration gradients in the boiling liquid, imperfect mixing of cold condensate with boiling liquid, entrainment of liquid droplets in the vapour, and the presence of concentration gradients in the condensate receiver. The most important stills in this category are those of Chmer (135), Carey and Lewis (33), Jones-Schoenborn-Colburn (139), Gillespie (32), Ellis (62) and many others based on these designs.
Although these stills have been used with some degree of success, certain sources of error (mentioned above) appear to be inherent in each type, there is real need of an apparatus which is not only free from many of the usual sources of error but also simple in design, construction and operation. Other apparatus and those based on it are simple in design and construction and need very little attention during operation for a run.

Paul (203) modified other still to prevent or minimise the various sources of error listed above. The entire vapour space has been surrounded by an evacuated silvered jacket to reduce partial condensation in the vapour space. The concentration gradients in the boiler have been eliminated by using thermosyphon heat exchanger actuated on the temperature induced density difference principle. The entrainment has been eliminated by providing a baffle to the vapour tube of the still. For quick attainment of equilibrium, the hold up of the receiver is minimised by making receiver taper downwards. Equilibration time has been claimed to be 45 minutes.

Hipkin and Myers (110) described a vapour-recirculatory type of still in which the usual compensatory heater winding on the vapour-liquid contactor is replaced by a vapour jacket. External heater windings have several disadvantages—installation is difficult particularly at the ends of the vessel or over any irregular shapes or projections. Hot spots are unavoidable and precise control is difficult if not impossible. Thus the vapour
jacket eliminates the problem of externalwinding. Any reasonably pure liquid can be used in the vapour jacket. Vapour bubbling through the liquid in the contactor blankets the contactor and the vapour tube ensuring adiabatic operation. The concentration gradients in the liquid sample are prevented by the bubbling action of the vapour through the Cottrell tube in the contactor.

Kleekers and Schellin (136) used Hipkin-Myers still for isothermal vapour-liquid equilibrium measurements using a jacket fluid whose boiling point was maintained manually within 0.1°C of the desired still temperature.

Loel and Schellin (150) modified Hipkin-Myers still such that the contactor is self-lagged with its own vapour and the vapour jacket of the original still is replaced by an evacuated and silvered space with a provision of 0.5" viewing window.

Neal, Cooke and Best (218) described a vapour-liquid equilibrium still which embodies the efficient mixing characteristics of Jones-Colburn design with a novel adaptation of the Cottrell pump to provide accurate temperature measurement and to ensure adiabatic operation of the equilibrium chamber at all operating temperatures. The still is not suitable for low pressure operations.

The bubble and dew point methods have the advantage of not involving the determination of composition. These methods can be applied for the determination of critical conditions and volumetric behaviour of mixtures at high pressures.
The flow methods have the advantage of providing rapid approach to equilibrium and relatively easier change of feed composition. They are well suited to heat sensitive materials due to their small residence time in the reboiler. Also these methods, with proper choice of operating conditions, can be used for partially miscible liquids. But on the other hand, they are more complex and use more materials than the other methods.

Several authors (90, 140, 192, 201, 232) have described in detail the techniques of measurement and types of equilibrium stills. Hada-Fick-Fried-Vill (96) have also described the auxiliary devices such as pressure gauges, thermometers, thermocouples, thermostat etc. Raju (219) has given an exhaustive review of the various methods used for the measurements of vapour-liquid equilibria. Aleksander, Bojan and Busan (3) have reviewed different methods for the determination of vapour-liquid equilibrium data and compared them on the basis of equilibrium data for some typical systems.

The selection of still is governed largely by the properties of the components constituting the system, operating conditions, the time, quantity of chemicals available and the nature of the analytical techniques used.