CHAPTER - 2

LITERATURE REVIEW
2. LITERATURE REVIEW

2.1 Critical Review

Knowledge of the compositions of equilibrium vapour and liquid phases and the effect of temperature and pressure on these compositions is of primary importance for the development, design and operation of distillation equipment. The importance and influence of petroleum processing industry, the rapid growth of the petro-chemical industry, the increased requirement of pure liquid components and the relatively low cost and uncomplicated nature of the distillation equipment have contributed to the importance of vapour-liquid equilibrium.

Vapour-liquid equilibria are studied for two reasons – to contribute to scientific knowledge and to aid in the design of process equipment. In the first case, a good deal of thought and skill are required, while in the second case, time and money are involved. Because of the number of problems arising from many industrial processes, there is a need for more rapid and accurate method for the determination and prediction of vapour-liquid equilibria. Both the experimental measurements and the development of predictive methods are complimentary to each other. It is necessary to have data of one kind or other for the evaluation of parameters appearing in the thermodynamic equations.

It would be simpler to describe the vapour-liquid equilibrium relationship for a system which exhibits ideal behaviour. The activity coefficient concept is widely used to express quantitatively the departure of the vapour and liquid phase from ideal behaviour. Although many binary systems, both in vapour and liquid states, approximate to ideal behaviour, the great majority of the systems encountered in practice are non-ideal in either or both the states.

At low pressures, the vapour phase approaches ideality because the molecules in the vapour phase are far apart and their interaction becomes less frequent. The liquid phase is much denser and the molecular interactions are of much greater magnitude than the vapour phase and quite often, the assumption that all the non-ideality exists in the liquid phase is justified especially at low and moderate pressures for systems with no appreciable chemical interactions.
Generally, the vapour phase non-ideality effects are combined with those of the liquid phase and are described by the use of a single activity coefficient. For the consideration of vapour-liquid equilibria, the excess free energy of mixing is the most useful property because of its direct relationship to the activity coefficient:

\[ g^E = RT \sum x_i \ln \gamma_i \]

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. The vapour phase non-ideality is described by means of an equation of state and activity coefficient, \( \gamma \), is used to describe liquid phase non-ideality.

In terms of activity coefficients, the unrestricted form of Gibbs-Duhem equation, which is one of the most useful and fundamental thermodynamic equations relating to the partial molal properties of the components to one another in a mixture, can be written as:

\[ \sum x_i \, d \ln \gamma_i = \left( \frac{V^E}{RT} \right) d\pi - \left( \frac{h^E}{RT^2} \right) dT \]

where \( V^E \) and \( h^E \) are the excess volume of mixing and excess enthalpy of mixing respectively.

The following is the Critical Literature Review regarding the systems studied:

Consistent vapour-liquid equilibria were determined for the ternary system ethanol + methycyclohexane + p-xylene and the three binary subsystems at 101.3 kPa at temperatures in the range from 345 to 408 K by Russinyol et al. [348]. The binary systems exhibit positive deviation from ideal behavior and the system ethanol + methycyclohexane presents a minimum-boiling-point azetroppe. The VLE data have been correlated by the Wilson, NRTL and UNIQUAC equations. The ternary system does not present an azetroppe and is well predicted from binary interaction parameters.

Isobaric vapour-liquid equilibria was measured for cyclohexane or n-heptane + o-xylene, + m-xylene, + p-xylene and + ethylbenzene and 1-hexene + p-xylene, + m-xylene, + p-xylene, + toluene and + ethylbenzene at 101.3 kPa using a dynamic
still with circulation of both phases by Diaz et al. [65, 67, 68]. Also vapour-liquid equilibria of methylcyclohexane with 1,4-dimethylbenzene was reported at 348.15 K for the entire concentration range and a graph is represented. Experimental data were tested for thermodynamic consistency and satisfactorily correlated by different equations. A comparative analysis was performed by application of the ASOG, original UNIFAC, modified UNIFAC (Dortmund) and modified UNIFAC (Lyngby) systems and low root-mean-square deviations of vapour mole fraction and temperature were computed.

Isobaric vapour-liquid equilibria data were measured at 101.3 kPa on four oxygenates (acetone, diisopropyl ether, ethanol and methyl ethyl ketone) separately with hydrocarbon mixtures by Peng et al. [286]. Acetone, ethanol and methyl ethyl ketone were mixed with a five-component hydrocarbon mixture and diisopropyl ether was mixed with a four-component hydrocarbon mixture. Calculations of non-ideality of the vapour phase were made with the Soave-Redlich-Kwong equation of state. The experimental data have been correlated with the mole fraction of oxygenate using the Redlich-Kister type and Wisniak-Tamir equations.

Isobaric vapour-liquid equilibria were determined at 101.3 kPa for the binary mixtures containing methanol + propyl acetate, methanol + isopropyl acetate, vinyl acetate + propyl acetate and vinyl acetate + isopropyl acetate by Resa et al. [340]. The thermodynamic consistency of the experimental data was checked by means of a modified Dechema test and was satisfactory. The activity coefficients were correlated with the Margules, van Laar, Wilson and NRTL models and the Wilson model with two suffix equations and the Wilson model with three suffix equations. The ASOG model was also used for prediction.

Isobaric vapour-liquid equilibria have been determined for the partially miscible systems octane + p-xylene + sulfolane, nonane + o-xylene + sulfolane, nonane + p-xylene + sulfolane and nonane + ethylbenzene + sulfolane at 101.325 kPa by Gupta et al. [113]. The data have been compared with those calculated by the UNIFAC-group-contribution model. The calculated vapour-phase compositions and activity coefficients have been compared with the experimental values.

Siddiah et al. [358] reported isobaric vapour-liquid equilibrium data for the binary systems formed by p-xylene with 1,2-dichloroethane, 1,1,1-trichloroethane and
1,1,2,2-tetrachloroethane at 66.5 kPa.

Lores et al. [187] measured vapour-liquid equilibrium data for binary systems of isobutanol with m-xylene, o-xylene and p-xylene at 101.3 kPa using a recirculating still. The results determined were thermodynamically consistent.

Isobaric vapour-liquid equilibria of the p-xylene - 1,1,1-trichloroethane system at 685 mm Hg pressure was measured by Viswanath et al. [416]. Activity coefficients were evaluated and correlated. Vapour pressures of 1,1,1-trichloroethane in the range of 600-1750 mm Hg are also reported.

Isothermal vapour-liquid equilibria for o-, m- and p-xylene with N-methylpyrrolidone (NMP) at 373.15 K and 393.15 K have been measured by Gupta [114]. The results have been correlated using the NRTL, Wilson and three-constant Redlich-Kister models. The root-mean-square deviation (RMSD) between experimental and calculated \(y\) values show that the data for all the three xylenes with NMP are well represented by the Wilson, NRTL and three-constant Redlich-Kister models.

Boiling temperatures were measured for the close boiling ethylbenzene-p-xylene binary system at 500, 780, 1250 and 1500 mm Hg by Chianese et al. [52]. The data were correlated by the NRTL equation and the relative volatility of ethylbenzene to p-xylene was calculated.

Results of total vapour pressure measurements, performed at 313.15 K by a static method, are reported for six binary mixtures: methylcyclohexane-benzene, -toluene, -o-xylene, -p-xylene, -ethylbenzene, -propylbenzene by Asmanovat et al. [15]. The excess Gibbs energy is expressed with a one-constant equation of the type proposed by Hildebrand and Scatchard by using critical volumes instead of molar volumes. Comparison of the experimental results with the UNIFAC method is also noted.

Cabezas et al. [44] reported the standardized results data on the liquid-vapour equilibria of 1,2,3,4-tetrahydronaphthalene and 1,4-dimethylbenzene system for various molar ratios of the liquid and vapour phases at 26.66 kPa and 367.85 - 430.15 K.

Vapour-liquid equilibrium data are reported for the two binary systems acetic acid-ethylbenzene and acetic acid - p-xylene at 725 mm Hg pressure by
Bagga et al. [20]. Both systems formed minimum boiling azeotropes. The activity coefficient-composition data were tested for thermodynamic consistency and correlated by the Wilson equation for the acetic acid-ethylbenzene system and the van Laar equation for the acetic acid-\(p\)-xylene system.

Vapour-liquid equilibria for the title systems have been determined at 760 mm Hg by Wisniak et al. [434]. The two methyl ethyl ketone systems exhibit positive deviations from ideal behaviour, no azeotropes are present and the third system behaves ideally. An empirical equation was used to correlate the boiling points with the composition of the liquid phase.

The vapour-liquid equilibria of the \(p\)-xylene-1,2-dichloroethane system and \(p\)-xylene-1,1,2,2-tetrachloroethane system were measured at 685 mm Hg pressure by Rao et al. [312, 313]. Vapour-pressure data in the range of 500-2700 mm Hg are also reported. The results on enthalpy of mixing and vapour-liquid equilibria show that system behaves like an ideal system.

Isobaric vapour-liquid equilibrium data for the systems ethylbenzene-dimethylformamide and \(p\)-xylene-dimethylformamide were obtained at 760 mm Hg pressure by using a vapour recirculating type of equilibrium still by Bagga et al. [21]. Both the systems form minimum-boiling azeotropes. The activity coefficient data were tested for thermodynamic consistency by the methods of Herrington, Black and Norrish and Twigg and correlated by the van Laar, Wilson and Redlich-Kister equations.

Experimental vapour-liquid equilibrium data were obtained for the binary systems, 2-methoxyethanol-ethylbenzene, 2-methoxyethanol-\(p\)-xylene and 2-ethoxyethanol-\(p\)-xylene at 760 mm Hg by Kumar et al. [173]. The activity coefficients were calculated taking into account the non-ideality of the vapour phase. The data satisfied the thermodynamic consistency tests of Herington, Norrish-Twigg and Black. The correlations of van Laar, Redlich-Kister, Wilson, NRTL and Wiehe-Bagley, with the constants evaluated by the method of nonlinear least squares, represented the data well.

The part 3 of a series of contributions by the critical properties group of the IUPAC Commission 1.2 on Thermodynamics, Subcommittee on Thermodynamic Data [402] presents all known experimental data for the critical constants of aromatic
hydrocarbons, which have been divided into four families: normal alkylbenzenes (5 compounds, C6-C10); other alkylbenzenes (13 compounds, C8-C12); polyphenyls (5 compounds, C12-C18); and condensed polycyclics (7 compounds, C9-C14). Recommendations are given together with uncertainties.

The isobaric vapour-liquid equilibria of the binary systems formed by acetonitrile + benzene, + toluene, + m-xylene, + p-xylene, or + ethylbenzene were measured at 28.0 and 101.3 kPa by Cave et al. [47]. The activity coefficients were correlated by using the NRTL equation.

Vapour-liquid equilibrium data was obtained at 99.992 kPa for 2-butanone + m-xylene, 2-butanone + ethylbenzene, 2-butanone + o-xylene and 2-butanone + p-xylene by Yong et al. [443]. A thermodynamic model proposed by Hayden O’Connell to account for the non-ideal behaviour of the liquid phase and the vapour phase was used for calculating the activity coefficients of liquid phases. All experimental data has been tested by the method proposed by Herington and the results show that the experimental data confirm to the demand of the thermodynamic consistency.

Isothermal vapour-liquid equilibria has been studied for binary mixtures of benzene + alcohols (C1-C4) at 45 °C and toluene, p-xylene + alcohols (C1-C4) at 60 °C by using head space gas chromatography as one of the static measuring methods by Jin et al. [151]. Most of the measured binary systems show minimum boiling azeotropes. These experimental data were correlated with the conventional $g^p$ models. The excess molar volumes have also been measured for the same binary mixtures at 25 °C by using digital vibrating tube densimeter. The experimental data were fitted with 5 parameter Redlich-Kister equation.

Total pressures were measured for the four binary silicon compound systems, tetramethoxy silane with p-xylene and n-nonane (at 390 K) and tetraethoxy silane with p-xylene and n-nonane (at 410 K) by Masahiro et al. [206]. Densities for the mixtures were measured at 298.15 K. Vapour compositions were determined using the Wilson equation from the experimental total pressure and density data.

Separation of the ternary systems water + ethanol + (o-, m-, p-) xylene is discussed by Fele et al. [79]. Vapour-liquid equilibrium (VLE) data were measured in the homogeneous region of the ternary phase diagram for all three systems at two
pressures (49.4 kPa and near atmospheric pressure). The parameters of UNIQUAC and NRTL thermodynamic local composition models were evaluated to describe the three-phase behavior of the systems and to simulate the appropriate distillation column. The system water + ethanol + o-xylene does not form a ternary azeotrope. This fact was confirmed by distillation on a NORMAG spinning band column.

The vapour pressure data given in the International Critical Tables for the xylenes, mesitylene, cumene, pseudocumene, \(n\)-propylbenzene, cumene and isobutylbenzene are based on measurements of Woringer. These results give very strongly curved plots of \(\log p\) against \(1/T\), indicative of serious error and indeed a few measurements made by Linder near 0°C for several of these compounds showed that Woringer's values at the lower temperatures were much too high. Since it became necessary to calculate entropies of vapourization for the xylenes and mesitylene, the vapour pressures of these substances were remeasured by Kassel [161].

Vapour-liquid equilibria for the systems propyl bromide-tert-butyl alcohol and propyl bromide- \(p\)-xylene have been determined at 760 mm Hg by Wisniak et al. [433]. The propyl bromide-tert-butyl alcohol system shows positive deviations from ideal behavior and presents a minimum boiling point azeotrope at 68.55 °C with 23.5 mol % propyl bromide. The system propyl bromide- \(p\)-xylene behaves ideally. The boiling points were well correlated with the composition of the liquid phase.

Using a static manometric technique, vapour pressures of \(p\)-xylene + tetrachloromethane have been measured at 313.15 \(K\) and 323.15 \(K\) over the mole-fraction range 0 to 1 by Yadav [437]. Activity coefficients of components and excess molar Gibbs energies for the mixture have been calculated from the vapour pressures and compositions using Barker's method. The results have been interpreted in terms of the intermolecular interactions of unlike molecules in the mixture.

Total vapour pressure measurements made by a modified static method for the binary systems of benzene, toluene, ethylbenzene and \(p\)-xylene with \(n\)-hexane, \(n\)-heptane, \(n\)-octane and \(n\)-decane at 313.15 \(K\) are reported by Goral [105]. The results were correlated with four equations for excess Gibbs energy. Comparison of their correlating ability was made. Agreement with literature data was checked. Experimental results were compared with prediction by the UNIFAC method and with the Hildebrand-Scatchard equation.
Vapour-liquid equilibrium data of 1-butanol + benzene, or toluene, or o-, or m-, or p-xylene measured by the static method at 308.15 ± 0.01 K over the entire composition range are reported by Maken et al. [200]. The excess molar Gibbs free energies of mixing $G_m^E$ for these binary systems have been calculated from total vapour pressure data using Barker’s method. The $G_m^E$ for these binary systems are also analyzed in terms of the Mecke-Kempter type of association model with a Flory contribution term using two interaction parameters and it has been found that this model describes well the $G_m^E$ values of these binary systems.

Excess molar volumes of organic carbonate + p-xylene systems and dynamic viscosities of organic carbonate + n-octane, n-dodecane or p-xylene systems are reported by Moreiras et al. [230]. All the $V_m^E$ values were positive for dimethyl carbonate + p-xylene whereas they were negative for diethyl carbonate + p-xylene. The dynamic viscosity deviations are negative for the organic carbonate + n-alkane or p-xylene systems in all the composition range.

Isobaric vapour–liquid equilibria were measured for the binary systems n-heptane + o-xylene, m-xylene, p-xylene or ethylbenzene at 101.3 kPa using a dynamic method with circulation in both phases by Diaz et al. [66]. In thermodynamic calculations using the data, the vapour phase was considered to be non-ideal and activity coefficients of the components in the mixtures indicate positive deviations from Raoult’s law. After reduction of the data and verification of thermodynamic consistency, various group-contribution models were applied to estimate the isobaric VLE data.

A vapour-liquid equilibrium cell of a new design to withstand high temperature, high pressure and corrosive fluids was constructed by Chen et al. [51]. Vapour-liquid equilibrium was measured for mixtures of 1-propanol and p-xylene at 160.0 and 221.1 °C at pressure of 26 bar. The VLE data are correlated with Wong and Sandler’s equation of state method using activity coefficient model parameters.

Total vapour pressure measurements using a modified static method at 313.15 K are reported for binary mixtures of CCl₄ with benzene, toluene, o-xylene, p-xylene, hexane, heptane, octane, nonane and decane and 2,2,4-trimethylpentane with benzene, toluene, ethylbenzene, o-xylene, p-xylene and propylbenzene by
Goral et al. [103, 104]. The results were correlated with the generalized Redlich-Kister equation for excess Gibbs energy. A comparison with literature vapour-liquid equilibrium data and excess enthalpy was made. Consistency within homologous series was checked. Predictions made using the UNIFAC method and the Hildebrand-Scatchard equation were compared.

Boiling temperatures were measured for four binary systems of methyl isobutyl ketone with chlorobenzene, o-dichlorobenzene, bromobenzene and p-xylene at 300, 500 and 700 mm Hg by Ramanjaneyulu et al. [311]. The data were correlated using the Wilson equation.

Total vapour pressure measurements made at 313.15 K by the modified static method for 12 binary mixtures of methanol, ethanol, 1-propanol and 1-butanol with benzene, toluene and p-xylene are presented and compared with literature data by Oracz et al. [257, 258]. The alcohol high dilution region of these systems is thoroughly studied. The different expressions for $G^i$ suitable for correlation of these measurements are tested. The internal consistency of data for various systems is also studied.

Vapour-liquid equilibrium data for carbon dioxide-benzene, carbon dioxide-toluene and carbon dioxide-p-xylene were measured for pressures up to 6.5 MPa and at temperatures of 353 K, 373 K and 393 K by Kim et al. [165]. The solubility of benzene in the dense carbon dioxide vapour phase is higher than that of either toluene or p-xylene. In the liquid phase, carbon dioxide is more soluble in p-xylene than in toluene or benzene. The experimental data obtained were compared with calculations from three correlations: the Peng-Robinson equation, the UNIFAC activity coefficient correlation and the Perturbed-Anisotropic-Chain Theory (PACT). All three correlations predict phase compositions in good agreement with the experimental data.

Bubble pressures and vapour-liquid equilibria are reported for four binary hydrocarbon mixtures at three temperatures: (cyclohexane + benzene), (methylocyclopentane + benzene), (ethylbenzene + n-heptane) and (p-xylene + n-heptane) by Mentzer et al. [219]. The isothermal dependence of bubble pressure on liquid-phase composition is determined in a static apparatus. Equilibrium vapour-
phase compositions are calculated from Barker’s procedure using the three-parameter Redlich Kister equation for the excess Gibbs free energy.

A model employing the correction factors of Marek and Standart, but using a concentration-dependent liquid phase association factor of Jenkins-Robinson, has been used to model vapour-liquid equilibrium data for mixtures of acetic acid with benzene, toluene, o-xylene and p-xylene by Stevanovic et al. [369]. With the aim to use systems of acetic acid-benzene and acetic acid-toluene as the test mixtures for distillation columns, the examination of the systems of acetic acid-aromatic hydrocarbons was undertaken. The model promises to be useful in modelling isobaric and isothermal data of acetic acid-benzene, acetic acid-toluene, acetic acid-p-xylene and acetic acid-o-xylene systems. Deviation plots show that the isothermal and isobaric data are represented well.

2.2 Physical Properties Estimation

For the calculation of activity coefficients, vapour pressures, second virial coefficients and liquid molar volumes of pure components, which are all functions of temperature, are required. It is not always possible to have experimental data on these properties. Reliable generalized correlations for the estimation of these properties under varied conditions of temperature and pressure are of immense use in obtaining the activity coefficient data.

Reid and Sherwood [334] have given an excellent review of the property estimation methods, most of which are dependent upon the pure component constants like molecular weight, normal boiling point, critical properties, dipole moment, etc. In case the experimental values of the constants are not available, the methods for their estimation have also been discussed. Also comments are given for the choice of different correlations.

2.2.1 Vapour Pressure

Most of the correlations for the estimation of vapour pressure are based on the well known Clapeyron equation. A detailed study covering a number of general types of equations was made by Miller [224]. It covers a pressure range of 10 to 1500 mm of Hg and temperature range from the normal boiling point to the critical temperature. These equations were divided into three classes of reduced, semi-reduced and non-
reduced types. It was concluded that the reduced equations are superior in the temperature range of $T_h$ to $T_c$ whereas the semi-reduced or non-reduced types are superior in the pressure range of 10 to 1500 mm of Hg. MRA [224] correlation was found to be most accurate in the low pressure region whereas RPMH [223, 224] correlation proved to be excellent for the high pressure region.

Othmer and Huang [263], after comparing the reference substance correlation proposed by Othmer et al. [262] with those studied by Miller [222, 223, 224], found that the reference substance correlation gives comparable results for each group of compounds over the entire pressure range and better results in the high pressure region between $T_h$ and $T_c$ than those in Miller’s study. A number of extensions for the reference substance correlation were published by Othmer and his coworkers in a series of articles [260, 261, 268, 269, 270].

Thek and Stiel [388] proposed an equation to predict the vapour pressure of polar and hydrogen bonding substances. Halm and Stiel [121] extended Pitzer’s acentric factor [293] approach by the introduction of a polarity term. It has improved the ability to correlate vapour pressures of highly polar compounds at low reduced temperature. Harlacher and Braun [124] used fourth parameter in the extension of the corresponding states principle to give an equation which gives satisfactory results especially for associating compounds.

Smialek and Thodos [363] gave an equation for normal paraffins which gives an average deviation of 1.81 percent.

Asija [14] developed an equation in the following form:

$$\log P_r = -a f(T_r)$$

(2.3)

where $a$ is a constant for the substance.

The values of $f(T_r)$ are tabulated for $0.5 < T_r < 1.0$ and the equation is claimed to give a mean deviation of 1.5 percent when tested for fifteen typical substances.

Stitzell and Kammermeyer [371] described a method for writing a computer programme for the selection of the best equation for finding out vapour pressure. The choice of the method depends on the pressure range and the known parameters. It was
concluded that for low pressures, Othmer’s reference substance method [261, 268] gives better results.

Experimental vapour pressure data for a large number of compounds are available in literature [8, 72, 372, 394, 423]. Some of the important correlations for the estimation of vapour pressure are given in Table 2.1.

2.2.2 Second Virial Coefficient

Reid and Sherwood [334] discussing the application of potential functions for the estimation of second virial coefficients recommended that Lennard-Jones potential should be used for non-polar molecules and Stockmayer potential for polar molecules.

Polak and Lu [295] used the least squares analysis to calculate the parameters of the Stockmayer potential function from the experimental data of sixty polar substance. A mean standard deviation of 3.2 percent was obtained. The possibility of extrapolating second virial coefficients from high to low temperature was also demonstrated. Martin [204, 205] used an expansion in Chebyshev polynomials to give least squares surface fits of the calculated data for the reduced second virial coefficients and collision integral for the Stockmayer and Lennard-Jones potential. Lawley and Smith [177] discussed the limitations of the Stockmayer potential in describing polar molecules, for which the dipole moment is displaced from the centre of the molecules and in the representation of the behaviour of polar-nonpolar mixtures, for which dipole induced dipole effects may be significant. Lawley and Smith [177] and Dymond and Smith [73] modified the Stockmayer potential with a model involving a point dipole displaced from the centre of the molecule.

Kunz and Kapner [175] developed an analytical technique based on the method of least squares to fit the experimental second virial coefficients to the functional form derived from the Lennard-Jones potential. Experimental second virial coefficients for as many as sixty materials including hydrocarbons, halides, alcohols and cyclic compounds were fitted to the Lennard-Jones potential function. The force constants for these materials, as determined from fitting the data in this manner, were found to be related to structural parameters. The final correlation with the potential related to the critical temperature and collision diameter, calculated from a set of group contributions with appropriate correction for polarity and association, produced
### Table 2.1 Correlations for Vapour Pressure

<table>
<thead>
<tr>
<th>Name</th>
<th>Equation</th>
<th>No.</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Antoine</td>
<td>( \log P^0 = A - B/(C + t) )</td>
<td>(2.4)</td>
<td>[37]</td>
</tr>
<tr>
<td>MRA</td>
<td>( \log P^0_{\text{m}} = (k/T_r) [T_r^2 (0.60706 T_r - 1.44779) - I_c T_r - 0.98045'] )</td>
<td>(2.5)</td>
<td>[224]</td>
</tr>
<tr>
<td></td>
<td>( I_b = -1.44779 ) ( (T_{\alpha} - 1/T_{\alpha}) + 0.60706 ) ( (T_{\alpha}^2 - 4/T_{\alpha}) )</td>
<td>(2.5a)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( k = \log P_r / (I_c - I_b) )</td>
<td>(2.5b)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( I_c = -1.82118' )</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>* obtained by putting ( T_i = T_r ) in Eq. 2.5a</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EB2</td>
<td>( \log P^0 = A - B' \log (1 - C_{\theta}) )</td>
<td>(2.6)</td>
<td>[224]</td>
</tr>
<tr>
<td></td>
<td>( B' = 0.4343 ) ( [1.03 \Delta H_s / RT_h + C_{\theta} / (1 - C_{\theta})] )</td>
<td>(2.6a)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( A = B' \log (1 - C_{\theta}) )</td>
<td>(2.6b)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( \theta = T/T_h )</td>
<td>(2.6c)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( C_{\theta} = 0.512 + 4.3 ) ( 10^4 T_h ) (Organics)</td>
<td>(2.6d)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( C_{\theta} = 0.59 ) (Inorganics)</td>
<td>(2.6e)</td>
<td></td>
</tr>
<tr>
<td>RPME</td>
<td>( \log P^0 = -(G/T_r) [1 - T_r^2 + k(3 + T_r) (1 - T_r)^2] )</td>
<td>(2.7)</td>
<td>[223]</td>
</tr>
<tr>
<td></td>
<td>( G = 0.21 + 0.20a )</td>
<td>(2.7a)</td>
<td></td>
</tr>
</tbody>
</table>
\[
\begin{align*}
\alpha &= \frac{T_m \ln P_c}{(1 - T_m)} \\
\beta &= \frac{T_m \ln P_c}{(1 - T_m) (1 - T_m)^2} \\
L &= 2.3026
\end{align*}
\]

\[
\begin{align*}
\log P^0 &= -\frac{(G/T_s) [1 - T^2 + k(1 - T)^3]} {0.2271 + 0.19654 [T_m \ln P_c/(1 - T_m)]} \\
k &= \frac{T_m}{(1 - T_m)^2} [G \left(\frac{2.88014 + \log P_c}{1 - T_m}\right) \\
&\quad - \left(1 - T_m^2\right)/(1 - T_m)^3]
\end{align*}
\]

\textit{RPMH}

\[
\begin{align*}
\log P^0 &= m \log P_c \\
\text{Othmer}
\end{align*}
\]

\[
\begin{align*}
\alpha &= \frac{\Delta H_m}{[RT_m(1 - T_m)^{0.77}]} \\
\beta &= -T_m \ln \left[\frac{P_c}{(T_m - 1)}\right] \\
\alpha_c &= \text{Slope}_c(d \ln P^0_c / d \ln T_c) \text{ at } T_c \text{ and } P_c
\end{align*}
\]

\textit{Thel and Stiel}
| Ambrose and Townsend | \[
\log_{10} P_{\text{am}}^n = A - B(i(C + t)) - Dt + E(t - F)^3
\]
| | (2.11) |
| | \[
\log_{10} P_{\text{am}}^n = A - B(i(C + t))
\]
| | (2.11a) |
| | \[\text{For } t > G\] |
| RPML | \[
\log P_r^0 = -(G/T_r) \left[1 - T_r^2 + k(1 - T_r)^3\right]
\]
| | (2.12) |
| | \[
G = 0.2471 + 0.19654 \left[T_n \ln P_r / (1 - T_n)\right]
\]
| | (2.12a) |
| | \[
k = \left[T_n / (1 - T_n)^2\right]G \left[-2.880814 + \log P_r\right]
\]
| | (2.12b) |
| | \[
-[(1 - T_n)^2 / (1 - T_n)^3]
\]
| | \[k \text{ is obtained from Eq. 2.12 by substitution of } T_n \text{ for } T \text{ and rearrangement}\] |
| K (Reduced Kirchhoff's Equation) | \[
\log P_r^0 = A(1 - 1/T_r)
\]
| | (2.13) |
| | \[
A = T_n \log P_r / (1 - T_n)
\]
| | (2.13a) |
| FK | \[
\log P_r^0 = [(5/9) C - (40/27)] \left[(1/T_r) - 1\right] + C \log T_r
\]
| | (2.14) |
| | \[
+ 0.1832 \left[(P_r / T_r^3) - 1\right]
\]
| | \[C \text{ is obtained from Eq. 2.14 by substitution of } T_n \text{ for } T \text{ and rearrangement}\] |
an average deviation of 10 to 15 percent or 100 cm$^3$ mol$^{-1}$ whichever is greater. In many cases the agreement was found to be much better. Eisenman and Stiel [74] developed procedures for the calculation of interaction virial coefficients for the non-polar mixtures based on the theoretical relationships for the Kihara core potential. Improved relationships for the non-polar fluids of large size can be obtained by the inclusion of an additional shape parameter as provided by the planner core model. Combining rules for the molecular parameters permit the calculation of the interaction virial coefficients for the spherical core relationships for pure fluids to within the experimental errors of non-polar mixtures including mixtures containing components of dissimilar size. Several authors [59, 141, 301] dealt with the development of macroscopic combining rules for the calculation of second virial coefficients of non-polar mixtures.

Hirschfelder, Curtiss and Bird [134] and Prausnitz [302] discussed most of the potential functions and their application for the estimation of the second virial coefficients. More information for the correlations based on potential functions can be had from literature [167, 170, 345, 382].

Many correlations, based on the principle of corresponding states, have been developed [213, 232, 292, 435]. The correlation of McGlashan and Potter [214], which involves the use of reduced temperature and critical volume, gives good results for small non-polar molecules. For larger molecules, the correlation has been extended by introducing carbon number as the third parameter [213]. Wohl’s generalized correlation [435], which involves reduced temperature and critical pressure is satisfactory for simple non-polar molecules. Pitzer and Curl [292] proposed an equation, excellent for normal fluids, by introducing the acentric factor, $\omega$, as the third parameter. Nagahama and Hirata [232], correlated the second virial coefficients of pure compounds as a power series of the reduced temperatures. The three parameters of the equation used were calculated for polar and non-polar compounds.

There is a lack of well developed correlation for polar gases because no simple parameter, to characterize the effect of polarity on thermodynamic properties, is available. The correlations of Black [32] and O’Connell and Prausnitz [255] are only approximations for the estimation of second virial coefficients for polar compounds. Black’s correlation [32] is based on a van der Waals type equation developed for non-polar gases. For polar gases, to account for polarity, additional constant terms were introduced. The correlation of O’Connell and Prausnitz [255], which is an
extension of Pitzer-Curl correlation [292], takes into account the contributions due to
the polarity and association. The acentric factor, \( \omega \), has been replaced by the acentric
factor, \( \omega_h \), of a homomorph which is a non-polar molecule having approximately the
same size and shape. Mixing rules for non-polar–non-polar, polar–non-polar and
polar–polar systems were also given. The association factor, \( \eta \), to be used in the
correlation, may be determined from one experimental second virial coefficient data
point.

Halm et al. [123] developed relationships for the calculation of second virial
coefficients of polar fluids from the critical constants, acentric factor and Stiel’s polar
parameter, \( \chi \), of the substance. Good results were obtained for most polar fluids. The
relationships were extended for mixtures of non-polar or polar components. Additional theoretical studies are required to account for the effect of dispersion of
polarity on the second virial coefficients of large size molecules.

Stiel [370] developed a generalized procedure for the accurate calculation of
thermodynamic properties of non-polar and polar compounds and their mixtures. It
was shown that the concept of van der Waals for simple fluids can be extended to
complex substances and the properties of a wide range of fluids can be calculated
from a number of macroscopic parameters defined through the vapour pressure.
Relationships were presented for the calculation of interaction virial coefficients of
binary mixtures based on composition and temperature dependence of the second
virial coefficients. The relationships also enable the calculation of the thermodynamic
properties of a mixture.

Blanks and Prausnitz [34] presented a method to calculate the cross virial
coefficients for binary mixtures for polar-polar and polar-non-polar pairs. They
showed that for polar-polar pairs, the use of Stockmayer potential alone is not
satisfactory. But the use of corrected collision diameter in the Stockmayer potential
improved the accuracy of prediction. Kreglewski [169] and Reid and Sherwood [334]
also discussed mixing rules. Reid and Sherwood [334] have presented a brief review
of the application of the virial equation to mixtures and gave recommendations
regarding the method to be used to determine the potential parameters.

The important correlations for the estimation of second virial coefficient are
given in Table 2.2.
Table 2.2 Correlations for Second Virial Coefficient

<table>
<thead>
<tr>
<th>Name</th>
<th>Equation</th>
<th>No.</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wohl</td>
<td>( B \frac{P_r}{RT_r} = 0.197 - 0.012T_r - 0.4/T_r - 0.146/T_r^2 ), ( x )</td>
<td>(2.15)</td>
<td>[435]</td>
</tr>
<tr>
<td>Pitzer and Curl</td>
<td>( B \frac{P_r}{RT_r} = f_s^{(0)}(T_r) + \omega f_s^{(1)}(T_r) )</td>
<td>(2.16)</td>
<td>[292]</td>
</tr>
<tr>
<td></td>
<td>( f_s^{(0)}(T_r) = 0.1445 - 0.33/T_r - 0.1385/T_r^2 - 0.0121/T_r^3 )</td>
<td>(2.16a)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( f_s^{(1)}(T_r) = 0.073 + 0.46/T_r - 0.50/T_r^2 - 0.097/T_r^3 )</td>
<td>(2.16b)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( -0.0073/T_r^8 )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pitzer and Curl Eq. modified by Tsonopoulos</td>
<td>( B \frac{P_r}{RT_r} = f_s^{(0)}(T_r) + \omega f_s^{(1)}(T_r) )</td>
<td>(2.17)</td>
<td>[403]</td>
</tr>
<tr>
<td></td>
<td>( f_s^{(0)}(T_r) = 0.1445 - 0.330/T_r - 0.1385/T_r^2 )</td>
<td>(2.17a)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( -0.0121/T_r^3 - 0.000607/T_r^6 )</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>( f_s^{(1)}(T_r) = 0.0637 + 0.331/T_r^2 - 0.423/T_r^3 - 0.008/T_r^8 )</td>
<td>(2.17b)</td>
<td></td>
</tr>
<tr>
<td>O’Connell and Prausnitz</td>
<td>( B \frac{P_r}{RT_r} = f_s^{(0)}(T_r) + \omega f_s^{(1)}(T_r) + f_s(\mu, T_r) - \eta f_s(T_r) )</td>
<td>(2.18)</td>
<td>[255]</td>
</tr>
<tr>
<td></td>
<td>( f_s^{(0)}(T_r) = 0.1445 - 0.33/T_r - 0.1385/T_r^2 - 0.0121/T_r^3 )</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>( f_s^{(1)}(T_r) = 0.073 + 0.46/T_r - 0.50/T_r^2 - 0.097/T_r^3 )</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>( -0.0073/T_r^8 )</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
\begin{align*}
\mu_* &= 10^5 \mu^2 P_c / T_c^3 \\
f_\mu(\mu_*, T_c) &= -5.23722 + 5.665807 \ln \mu_* \\
&\quad + \frac{2.133816 (\ln \mu_*)^2 + 0.2525373 (\ln \mu_*)^3}{2.28327 (\ln \mu_*)^2 - 0.2649074 (\ln \mu_*)^3} + (1/T_c) \left[ 5.76977 - 6.181427 \ln \mu_* \right] \\
f_\sigma(T_c) &= \exp \left[ 6.6(0.7 - T_c) \right] \\
\omega_n &= \text{acentric factor for homomorph}
\end{align*}

\[ (2.18a) \]

\[ (2.18b) \]

\[ (2.18c) \]

<table>
<thead>
<tr>
<th>Black</th>
<th>( B = b - a e^\circ / RT )</th>
<th>( a = 27bRT_c / 8 )</th>
<th>( e^\circ = A' + B' / T_c - C' / T_c^2 + D' / T_c^3 + 64E' / 27T_c^4 )</th>
<th>( A' = 0.396 )</th>
<th>( B' = 1.181 )</th>
<th>( C' = 0.864 )</th>
<th>( D' = 0.384 )</th>
<th>( E' = 0.000 )</th>
</tr>
</thead>
</table>

\[ (2.19a) \]
\[ (2.19b) \]
\[ (2.19c) \]
\[ (2.19d) \]

[32] Nonpolar Compounds
\( A', B', C' \) are same as in Eq. 2.19d

\( D' = 0.384 \) 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 Eq. 2.19c

\( D' \) for chlorinated, fluorine, sulphur and other compounds might be estimated using experimental vapour density or second virial coefficient data putting \( E' = 0.0 \) in Eq. 2.19c

<table>
<thead>
<tr>
<th>Halm and Stiel</th>
<th>( B^* = B_0^* + \omega \ B_1^* + x \ B_1^* + x^2 B_2^* + \omega^2 B_2^* + \omega \ x \ B_3^* )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( B_0^<em>, B_1^</em>, B_2^<em>, B_3^</em>, B_4^<em>, B_5^</em> ) are tabulated for ( 0.6 \leq T_v \leq 0.94 )</td>
</tr>
</tbody>
</table>
2.2.3 Liquid Molar Volume

Several correlations have been presented in literature for the estimation of liquid molar volumes [20, 36, 39, 55, 102, 108, 109, 122, 137, 194, 195, 217, 272, 365, 442].

Othmer et al. [272] extended Othmer’s reference substance correlation [262] to liquid densities and prepared a nomograph which permits direct determination of liquid densities at any temperature using experimental values at two temperatures.

Lydersen et al. [195] presented a generalized correlation for pure component liquid densities over a wide range of temperature and pressure. This correlation is considered to be one of the best corresponding states correlations but the only drawback is that it is not easily amenable for computer applications.

Yen and Woods [442] developed an analytical equation based on a modified corresponding states principle and the correlation of Lydersen et al. [195]. When tested over a number of experimental data, the deviations were found to be within about two percent. The correlation has been extended to mixtures and compressed mixtures with good accuracy.

Meisner [217] derived a set of equations to predict liquid molar volume based on the carbon number and temperature for homologous unbranched liquid hydrocarbons. Gunn and Yamada [109] presented a corresponding state correlation, valid for $T_r$ between 0.2 and 1.0, using critical temperature, acentric factor and a scaling volume. Average absolute deviation was found to be 0.25 percent when tested for 26 compounds.

Prausnitz et al. [55, 194] improved upon Pitzer’s generalized correlation [294]. It was found that the accuracy for nonpolar liquids was quite good and the deviations for polar liquids were also not large. The correlation is particularly useful for liquids with large acentric factors.

Halm and Stiel [122] extended Pitzer’s acentric factor approach using Stiel’s polar factor [121] as the fourth parameter. It gave good agreement for polar fluids including large molecules.

Bondi and Simkin [36] developed a correlation particularly suitable for high molecular weight compounds which decompose before attaining the critical state. It makes use of a group contribution technique.
Barile and Thodos [23] correlated the reduced compressibility factor as a function of reduced pressure for the prediction of pure component liquid density. The average deviation for 23 polar and nonpolar compounds was found to be 2.7 percent. A graphical relation of this type was given by Hobson and Weber [137]. A correlation for hydrocarbons based on the reduced temperature and critical compressibility factor, giving an average deviation of 1.1 percent over the entire temperature range up to the critical, was presented by Bradford and Thodos [39].

Goyal and Doraiswamy [108] developed a correlation, based on Watson’s expansion factor [422], reduced temperature and critical compressibility factor, which is claimed to be applicable to nonpolar and polar compounds.

Spencer and Danner [365] evaluated the available methods for predicting the saturated liquid density for pure hydrocarbons and concluded that the revised Rackett equation [365], with one constant determined from experimental data is more accurate. A list of constants is also given with the help of which one can predict the saturated liquid density over the entire temperature range from the triple point to the critical point.

Reid and Sherwood [334] and Gold and Ogle [102] have reviewed most of the correlations with recommendations for their choice. According to Gold and Ogle, the Surface Tension method is generally the most accurate.

In general, the Lydersen et al. [195] or the Surface Tension method can be expected to give good accuracy. The correlation of Lyckman et al. [193] gives good accuracy for nonpolar compounds whereas the correlation of Halm and Stiel [123] appear to be fairly accurate for polar liquids.

Table 2.3 gives some of the important correlations discussed in the above paragraphs for the estimation of liquid molar volume.
Table 2.3 Correlations for liquid molar volume

<table>
<thead>
<tr>
<th>Name</th>
<th>Equation</th>
<th>No.</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface-Tension</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Modified Goldhammer)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>( \rho_c = \rho_v + \rho_i [1 - T_i]^{0.5} )</td>
<td>(2.21)</td>
<td>[174]</td>
</tr>
<tr>
<td></td>
<td>( \log \rho_v / \rho_i = 5 (T / T_i - 1) )</td>
<td>(2.21a)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( \rho_{sh} = M / (82.06 T_i) )</td>
<td>(2.21b)</td>
<td></td>
</tr>
<tr>
<td>Lydersen, Greenkorn and Hougen</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>( V_1 \rho_n = V_2 \rho_n ) or ( V_1 = V / \rho_n )</td>
<td>(2.22)</td>
<td>[195]</td>
</tr>
<tr>
<td></td>
<td>( \rho_v = f(T_v, P_v, Z_v) ) from tables</td>
<td>(2.22a)</td>
<td></td>
</tr>
<tr>
<td>Yen and Woods</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>( \rho_n = 1 + A (1 - T_v)^{1/3} + B (1 - T_v)^{2/3} + D (1 - T_v)^{4/3} )</td>
<td>(2.23)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( A = 17.4425 - 214.578 Z_v + 989.625 Z_v^2 - 1522.06 Z_v^3 )</td>
<td>(2.23a)</td>
<td>[442]</td>
</tr>
<tr>
<td></td>
<td>( B = -3.28257 + 13.6377 Z_v + 107.4844 Z_v^2 - 384.211 Z_v^3 )</td>
<td>(2.23b)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( D = 60.2091 - 402.063 Z_v + 501 Z_v^2 + 641 Z_v^3 )</td>
<td>(2.23c)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( 0.93 - B )</td>
<td>(2.23d)</td>
<td></td>
</tr>
<tr>
<td>Lyckman, Eckerts and Prausnitz</td>
<td>$V_r = V_r^{(0)} + \omega V_r^{(1)} + \omega^2 V_r^{(2)}$</td>
<td>(2.24)</td>
<td></td>
</tr>
<tr>
<td>-----------------------------</td>
<td>-------------------------------------------------</td>
<td>--------</td>
<td></td>
</tr>
<tr>
<td></td>
<td>For $0.56 \leq T_r \leq 0.99,$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$V_r^{(0)} = 0.11917 + 0.009513 \ T_r + 0.21091 \ T_r^2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$-0.06922 \ T_r^3 + 0.0748 / \ T_r$</td>
<td>(2.24a)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$-0.084476 \ \ln (1 - T_r)$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$V_r^{(1)} = 0.98465 - 1.60378 \ T_r + 1.82484 \ T_r^2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$-0.61432 \ T_r^3 - 0.34546 / \ T_r$</td>
<td>(2.24b)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$+ 0.087037 \ \ln (1 - T_r)$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$V_r^{(2)} = -0.55314 - 0.15793 \ T_r - 1.01601 \ T_r^2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$+ 0.34095 \ T_r^3 + 0.46795 / \ T_r$</td>
<td>(2.24c)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$-0.239938 \ \ln (1 - T_r)$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| Halm and Stiel              | $V^* = P_c V / RT_c = V^{(0)} + \omega V^{(1)} + \chi V^{(2)} + \omega^2 V^{(3)}$ | (2.25) |
|                            | $+ \chi^2 V^{(4)} + \omega \chi V^{(5)}$                | [122]  |
|                            | $V^{(0)}, V^{(1)}, V^{(2)}, V^{(3)}, V^{(4)}$ and $V^{(5)}$ |        |
|                            | are tabulated for $0.56 \leq T_r \leq 1.0$               |        |

| Bradford and Thodos         | $\rho_s = 1 + \beta (1 - T_r) + \gamma (1 - T_r)^2 + \delta (1 - T_r)^n$ | (2.26) |
|                            | [39]                                                        |        |
\[ n = 0.16 + 0.586 \ Z_c \]  
\[ \delta = 2.785 - 3.544 \ Z_c \]  
\[ \beta = 2.924 - 7.34 \ Z_c \]  
\[ \gamma = \delta - \beta - 1 \]  

<table>
<thead>
<tr>
<th>Barile and Thodos</th>
<th>[ n ]</th>
<th>( n = 0.16 + 0.586 \ Z_c )</th>
<th>(2.26a)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \delta )</td>
<td>( \delta = 2.785 - 3.544 \ Z_c )</td>
<td>(2.26b)</td>
</tr>
<tr>
<td></td>
<td>( \beta )</td>
<td>( \beta = 2.924 - 7.34 \ Z_c )</td>
<td>(2.26c)</td>
</tr>
<tr>
<td></td>
<td>( \gamma )</td>
<td>( \gamma = \delta - \beta - 1 )</td>
<td>(2.26d)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>( \rho_i )</th>
<th>( \rho_i = \frac{P_r P_i}{Z_n T} )</th>
<th>(2.27)</th>
</tr>
</thead>
<tbody>
<tr>
<td>For ( 0.1 \leq P_r \leq 1.0 ),</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( Z_n )</td>
<td>( = \alpha P_r + \beta P_r' + \gamma' P_r' )</td>
<td>(2.27a)</td>
</tr>
<tr>
<td>At the critical point, ( \alpha + \beta + \gamma' = 1.0 )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \alpha )</td>
<td>( = 0.2094 + 1.2375 \ Z_c )</td>
<td>(2.27b)</td>
</tr>
<tr>
<td>( \beta )</td>
<td>( = 0.269 - 0.298 \ Z_c )</td>
<td>(2.27c)</td>
</tr>
<tr>
<td>( \gamma ' )</td>
<td>( = 9.659 - 50.597 \ Z_c + 114.49 \ Z_c^2 )</td>
<td>(2.27d)</td>
</tr>
<tr>
<td>( \tau )</td>
<td>( = 34 )</td>
<td>(2.27e)</td>
</tr>
</tbody>
</table>

For \( P_r \leq 0.10 \),
| \( Z_n \) | \( = \delta + \epsilon P_r \) | (2.27f) |
| \( \delta \) | \( = 0.011536 \ Z_c - 0.002071 \) | (2.27g) |
| \( \epsilon \) | \( = 1.0715 - 5.5875 \ Z_c + 13.4886 \ Z_c^2 \) | (2.27h) |
2.3 Activity Coefficient: Prediction and Correlations

Predictive Methods

The knowledge of vapour-liquid equilibria is essential for the design of distillation columns & other related equipments. If the vapour phase obeys perfect gas laws and for liquid phase at constant temperature & pressure, the partial molar Gibb’s free energy of each species in mixture is dependent only on mole fraction, then a simple relation describing the equilibrium between liquid and vapour phase in a binary system can be obtained. This condition is in the case of an ideal solution. The formation of an ideal solution occurs without absorption or evolution of heat and without change in volume.

The deviations from ideal behaviour are expressed in terms of fugacity coefficients for the vapour phase and activity coefficients for the liquid phase. The assumption of ideal vapour phase is justified at low pressure with systems whose constituents do not associate in the vapour phase. At atmospheric pressure, the correction for the vapour phase non ideality amounts to about 5 to 10 percent. Likewise under the same conditions, slightly polar gases may be treated as being non-polar without great loss of accuracy. But on the other hand, for highly polar or associating molecules, such as acetic acid, for systems at high pressure and for systems containing components whose critical constants differ greatly, such as methane-butane-decane, the gas phase non-ideality is extremely important.

The equations of state can be used to estimate the contribution of the vapour phase non-ideality to the overall non-ideality of the system as given below. The Redlich-Kwong [330], Beattie-Bridgeman [24] and Benedict-Webb-Rubin [25, 26] equations of state are of semi-empirical nature.

The Virial equation of state

It can be written as:

\[ PV = RT + \frac{B(T)}{V} + \frac{C(T)}{V^2} + \frac{D(T)}{V^3} + \ldots \]  

(2.28)

where the functions \( B(T), C(T), D(T), \ldots \) are called the second, third, fourth, \ldots Virial coefficients respectively. Eq. 2.28 is widely used for estimating the vapour phase non-ideality. The Virial coefficients are functions of temperature only. It can be shown [134] that the Virial coefficients are directly related to the molecular forces.
that exist between groups of molecules. For example, \( B(T) \) describes interactions between pairs of molecules, \( C(T) \) describes interactions between groups of three molecules and so on. These interactions may be expressed in terms of complicated integrals of the intermolecular forces. Unfortunately, these calculations are extremely complex and have not been successfully completed except for certain simplified intermolecular force potentials. In the case of small deviations from ideal behaviour, only the second virial coefficient need to be considered and the higher coefficients may be neglected. Physical theory (equation of state) forms the basis of most of the earlier work on fugacity coefficients [54, 331, 333].

Van Ness [408] gave the following equations for binary mixtures to account for the vapour phase non-ideality along with the liquid phase:

\[
\gamma_i = (\pi y_i / P_i^o x_i) \exp\left\{ \left( (B_1 - V_1)(\pi - P_i^o) / RT \right) + \left( \pi \delta_{i2} y_2^2 / RT \right) \right\} \\
\gamma_2 = (\pi y_2 / P_2^o x_2) \exp\left\{ \left( (B_2 - V_2)(\pi - P_2^o) / RT \right) + \left( \pi \delta_{12} y_1^2 / RT \right) \right\} \\
\text{where } \delta_{12} = 2B_{12} - B_{11} - B_{22}
\]

(2.29)

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.

The above equations are applicable for moderate pressures and for slight vapour phase imperfections. As suggested by Mertes and Colburn [220], \( \delta_{12} \) can be taken as zero for non-polar molecules to give a simple equation whose application requires only the pure component properties for the estimation of vapour phase non-idealities.

Prausnitz et al. [300] presented the following equations in terms of the fugacity coefficients which are applicable for moderate pressures:

\[
\gamma_i = \varphi_i (\pi y_i / f_i^{\infty} x_i)
\]

(2.30)

The fugacity coefficient, \( \varphi_i \), is given by:

\[
\ln \varphi_i = 2 / V \sum_{j=1}^{\infty} y_j B_{ij} - \ln Z
\]

(2.31)
The compressibility factor, \( Z \), is evaluated from the Virial equation truncated after the second term.

\[
Z = \frac{PV}{RT} = 1 + \sum_{i=1}^{N} \sum_{j=1}^{N} y_i y_j B_{ij} / V \tag{2.32}
\]

The liquid phase fugacity in the reference state \( f_i^{0*} \) is:

\[
f_i^{0*} = f_i^0 \exp(V_i \pi / RT) \tag{2.33}
\]

The reference state fugacities for pure components are calculated by:

\[
f_i^0 = \varphi_i^* P_i^* \exp(-V_i P_i^* / RT) \tag{2.34}
\]

where \( \varphi_i^* \) is the fugacity coefficient of pure vapour \( i \) at temperature \( T \) and saturation pressure \( P_i^* \). \( \varphi_i^* \) can be calculated from the generalized three parameter correlation of Lyckman-Eckert-Prausnitz [193].

\[
\ln \varphi_i^* = (\ln \varphi_i^{0*})^{(0)} + \omega_i (\ln \varphi_i^*)^{(1)} \tag{2.35}
\]

where \( (\ln \varphi_i^{0*})^{(0)} \) and \( (\ln \varphi_i^*)^{(1)} \) are generalized functions of the reduced temperature, given in tabular form [193]. This correlation is finding increasing use in the calculation of activity coefficients for moderately non-ideal vapour phase.

**The Wilson equation [432]**

In this activity coefficient equation applicable to homogeneous systems, the activity coefficient of component \( i \) in an \( N \) component system is given by:

\[
\ln \gamma_i = -\ln[\sum_{j=1}^{N} x_j \Lambda_{ij}] + 1 - \sum_{j=1}^{N} x_j \Lambda_{ij} / \sum_{j=1}^{N} x_j \Lambda_{ij} \tag{2.36}
\]

where

\[
\Lambda_{ij} = (v_j / v_i) \exp[-(\lambda_{ij} - \lambda_i) / RT] \quad (\lambda_{ij} = \lambda_j) \tag{2.36a}
\]

In Eq. 2.36a, \( (\lambda_i - \lambda_j) \) and \( (\lambda_i - \lambda_j) \) are two Wilson parameters characteristic of the components \( i \) and \( j \), obtainable from binary data. The parameters \( (\lambda_i - \lambda_j) \) are assumed to be independent of temperature over a narrow temperature range. \( v_j \) is the liquid molar volume of pure component \( j \).
The NRTL (Non-Random, Two-Liquid) Equation [2, 337]

This activity coefficient equation is applicable to both heterogeneous and homogeneous systems. The activity coefficient of component $i$ in an $N$ component system is given by:

$$
\ln \gamma_i = \frac{\sum_{j=1}^{N} \tau_{ji} G_j x_j}{\sum_{j=1}^{N} G_j x_j } + \sum_{j=1}^{N} \frac{[x_j G_j / \sum_{j=1}^{N} G_j x_j ](\tau_{ji} - \sum_{j=1}^{N} x_j G_j / \sum_{j=1}^{N} G_j x_j )}{\sum_{j=1}^{N} x_j G_j / \sum_{j=1}^{N} G_j x_j }$$

where

$$
\tau_{ji} = \frac{(g_j - g_i)}{RT} \quad (g_j = g_i) \quad (2.37a)
$$

$$
G_j = \exp(-\alpha_j \tau_{ji}) \quad (\alpha_j = \alpha_i) \quad (2.37b)
$$

In Eq. 2.37a, $(g_j - g_i)$ and $(g_j - g_i)$ are two NRTL parameters (equivalent to Wilson parameters) characteristic of the components $i$ and $j$. In Eq. 2.37b, $\alpha_j$ is a third parameter, a constant varying roughly between 0.2 and 0.47 according to the type of system concerned.

The UNIQUAC (Universal Quasi Chemical) Equation

In this activity coefficient equation, applicable to both heterogeneous and homogenous systems, the activity coefficient of component $i$ in an $N$ component system is given by:

$$
\ln \gamma_i = \frac{\ln \phi_i/(x_i) + (z/2)q_i \ln \theta_i / \phi_i + l_i}{1} - \frac{\ln \phi_i / \sum_{j=1}^{N} x_j l_j + q[1 - \ln \sum_{j=1}^{N} \theta_{ji} - \sum_{j=1}^{N} \theta_{ji} / \sum_{j=1}^{N} \tau_{ji}]}{1}
$$

where

$$
l_i = (z/2)(r_i - q_i) - (r_i - 1) \quad ; \quad z = 10 \quad (2.38a)
$$

$$
\theta_j = (q_j x_j) / \sum_{j=1}^{N} q_j x_j \quad ; \quad \phi_j = (r_j x_j) / \sum_{j=1}^{N} r_j x_j \quad (2.38b)
$$

$$
\tau_{ji} = \exp[-(u_{ji} - u_i) / RT] \quad (u_{ji} = u_i) \quad (2.38c)
$$
In Eq. 2.38c, \((u_i - u_j)\) and \((u_j - u_i)\) are two parameters characteristic of the components \(i\) and \(j\) that can be obtained from binary data. In Eq. 2.38b, \(\theta_i\) is the area fraction and \(\phi_i\) the segment fraction; \(r_i\) and \(g_i\) are measures of, respectively, molecular van der Waals volumes and molecular surface and are constants for a pure component.

The binary parameters necessary for predicting vapour-liquid equilibria by the three activity coefficient equations discussed above appear in the following references: Wilson [98, 133, 138, 300], NRTL [98, 221, 235] and UNIQUAC [2, 98].

Commonly, \(N(N - 1)\) parameters are necessary for predicting the vapour-liquid equilibria for an \(N\) component system if the equation used is like the Wilson, NRTL, and UNIQUAC equations, which contain just the parameters characteristic of a binary system and which predict the vapour-liquid equilibrium of multicomponent systems only from binary data. As \(N(N - 1)/2\) binary data are needed to determine these parameters, the number of parameters increases rapidly with the increase in the number of components. In fact, often we cannot predict a multicomponent vapour-liquid equilibrium in the absence of binary data. For this purpose, the group contribution method for predicting activity coefficients is extremely useful as it can predict multicomponent vapour-liquid equilibria with binary data.

Scheibel [353] presented a nomograph account for the vapour phase non-ideality at moderate pressure. The nomograph is based on the equation [220]:

\[
Z = \exp\left\{\frac{(B - V)(\pi - P^\theta)}{RT}\right\}
\] (2.39)

which has been reduced to a form requiring knowledge of only the critical properties of the pure components by substitution of Wohl’s correlation [435] for the second Virial coefficients and Meissner and Redding correlation [218] for the liquid molar volumes.

There is a lack of correlations to account for the vapour phase non-ideality for highly polar and hydrogen bonding components. Earlier several authors [355] used the chemical theory of vapour imperfections to account for the vapour phase non-ideality of carboxylic acids but no general methods were presented. Nothnagel, Abrams and Prausnitz [253] developed a generalized correlation, based on
the chemical theory to account for vapour phase imperfections for a wide variety of
vapours and vapour mixtures including polar as well as non-polar components
including strongly hydrogen bonding fluids such as alcohols, aldehydes and acids
where the extent of dimerisation is large. The following equation of state was used:

\[ P = n_r RT / (V - n_r b_m) \]  \hspace{1cm} (2.40)

where \( n_r b_m \) is the excluded volume due to the finite size of molecules
(a mixture of monomers and dimers). The total number of moles depend upon the
equilibrium constant and the pressure for a pure component.

Considering component A dimerises to give:

\[ 2A \xrightarrow{\leftrightarrow} A_2 \]

The final equation takes the form:

\[ PK \exp(b_i P / RT) = a(1 - \alpha / 2) / [2(1 - \alpha)^2] \]  \hspace{1cm} (2.41)

where

- \( b_i \) = excluded volumes for the monomer
- \( K \) = dimerisation constant
- \( \alpha \) = fraction of molecules dimerised

Several authors [131, 135, 209] showed that the chemical theory of gas
imperfections leads to an equation of state of the Virial form for the situation where
\( \alpha \to 0 \) and the second viral coefficient is related to \( b \) and \( k \) by the relation

\[ \text{Limit } B = b - RTK \]  \hspace{1cm} (2.42)

It is therefore possible to find the value of the equilibrium constant for
dimerisation from experimental Virial coefficients obtained at low densities where \( \alpha \)
is much less than unity. But for highly polar fluids, this condition is only attained at
very low pressures. The chemical theory of gas imperfections is applicable for the
entire range \( 0 < \alpha < 1 \), but is limited to moderate pressures because with rise in
pressure, trimers and higher aggregates are formed for which, very few quantitative
data are available on chemical equilibria beyond dimerisation. For weakly interacting
fluids, the chemical theory and the Virial equation of state give similar results but the
former has the advantage of being applicable to strongly polar and hydrogen bonding fluids as well as normal non-polar fluids.

The most successful methods presently used for calculating the activity coefficients in the liquid phase are the group contribution methods as described below:

**Group Contribution Methods**

**ASOG Method**

In this method, the monograph deals with prediction of vapour-liquid equilibria by the group contribution method referred to as the Analytical Solutions of Groups (ASOG). The group contribution method is considered to be a very useful approach because it takes into account the groups making up of a liquid solution in order to predict the activity coefficients of the components in the solution. The fundamental assumption of a group contribution method is additivity: the contribution made by one group within a molecule is assumed to be independent of that made by any other group in that molecule. Prediction of activity coefficients by group contribution was proposed by Wilson and Deal [431]. Later, a model for Analytical Solutions of Groups (ASOG) was developed by Rone and Ratcliff [346, 347] and Palmer and Smith [280], leading to universal application of this model. The group interaction parameters necessary for predicting activity coefficients by ASOG have been discussed by Tochigi and Kojima [396, 397].

ASOG is simplest method of all the group contribution methods and yields good predictions. The monograph provides, for 31 groups, the group pair parameters necessary for predicting activity coefficients by ASOG and discusses the method of prediction together with the predicted results.

In ASOG method [166], the activity coefficient of component \( i \) in a solution is commonly represented by \( \gamma_i \). The excess chemical potential \( \ln \gamma_i \) is assumed to be the sum of the contribution \( \ln \gamma_i^{\text{m}} \), due to differences in molecular sizes and the group interaction contribution \( \ln \gamma_i^{\text{i}} \), due to differences in intermolecular forces.

\[
\ln \gamma_i = \ln \gamma_i^{\text{m}} + \ln \gamma_i^{\text{i}}
\]  

(2.43)
The contribution due to the differences in molecular sizes is calculated by applying Eq. 2.44 which is similar to the Flory-Huggins equation.

\[
\ln \gamma^{HN}_i = \ln \left( \frac{v_i^{HN}}{\sum_j v_j^{HN} x_j} \right) + 1 - \left( \frac{v_i^{HN}}{\sum_j v_j^{HN} x_j} \right) x_i
\]

(2.44)

where

\( v_j^{HN} \) = the number of atoms (other than hydrogen atoms) in the molecule \( j \).

\( x_i \) = the mole fraction of component \( j \) in liquid solution.

The summations in Eq. 2.44 cover all components in liquid solution. From this \( \gamma^{HN}_i \) is calculated, with due attention to the chemical structure of the pure components making up the solution.

The contribution of group interaction is obtained from Eq. 2.45, the sum of the contribution of the individual groups making up the solution:

\[
\ln \gamma^{G}_i = \sum_k v_k \left( \ln \Gamma_k - \ln \Gamma_k^{i(i)} \right)
\]

(2.45)

where

\( v_k \) = the number of atoms (other than hydrogen atoms) in group \( k \) in molecule \( i \).

\( \Gamma_k \) = the group activity coefficient of group \( k \).

\( \Gamma_k^{i(i)} \) = the group activity coefficient of group \( k \) at standard state (pure component \( i \)).

The summation in Eq. 2.45 covers all groups in liquid solution. This method of counting the number of atoms \( v_k \) in the equation is an improvement on past techniques.

The group activity coefficient \( \Gamma_k \) is a function of temperature and the fraction of each group in liquid solution; it is given analytically by the Wilson equation as follows:

\[
\ln \Gamma_k = -\ln \sum_j X_j a_{ij} + \sum_j \left( X_j a_{ij} / \sum_m X_m a_{im} \right)
\]

(2.46)
where

\[ a_{kl} = \text{the group interaction parameters characteristic of groups } k \text{ and } l \]

\( (a_{kl} \neq a_{lu} ) \).

\[ X_i = \text{the group fraction of group } l \text{ in liquid solution and is given by} \]

Eq. 2.47.

\[ X_i = \frac{\sum_i x_i v_i}{\sum_i x_i v_i} \quad (2.47) \]

The summations in Eq. 2.46 cover all groups. In Eq. 2.47 \( \sum_i \) covers all components and \( \sum_k \) all groups. The group activity coefficient \( \Gamma_k^{(i)} \) of group \( k \) at standard state can also be calculated with Eq. 2.46.

Activity coefficients can be calculated from the group interaction parameters \( a_{kl} \) using Eqs. 2.43 to 2.47. However, \( a_{kl} \) is a function of temperature even for the same group pair and we must take this into consideration. Temperature dependence of group interaction is expressed here in Eq. 2.48, obtained on the basis of past study [396, 397].

\[ \ln a_{kl} = m_{kl} + n_{kl} / T \quad (2.48) \]

where

\[ m_{kl}, n_{kl} = \text{the group pair parameters characteristic of groups } k \text{ and } l, \]

independent of temperature.

\[ T = \text{temperature, } K. \]

To apply Eq. 2.48 in ASOG for predicting activity coefficients, group pair parameters \( m_{kl}, n_{kl} \) must be determined from a minimum of experimental data. The group interaction parameter \( a_{kl} \) at any desired temperature is calculated by determining \( m_{kl} \) and \( n_{kl} \) and this makes it possible to predict the activity coefficients of a wide range of components in a liquid solution containing the same group pairs.
UNIFAC Model

The UNIFAC (UNIQUAC Functional Group Activity Coefficients) group-contribution method [88] is a reliable and fast method for predicting liquid-phase activity coefficients in nonelectrolyte, nonpolymeric mixtures at low to moderate pressures and temperatures between 300 and 425 K. It has become widely used in practical chemical engineering applications, most notably in phase equilibrium calculations in cases where little or no relevant experimental information is available.

It has already been used successfully in many areas [99], e.g., (1) for calculating vapour-liquid equilibria [88], (2) for calculating liquid-liquid equilibria [198], (3) for calculating solid-liquid equilibria [101], (4) for determining activities in polymer solutions [256, 130], (5) for determining vapour pressures of pure components [150], (6) for determining the influence of solvent on reaction rate [185], (7) for determining flash points of solvent mixtures [99], (8) for determining solubilities of gases [251, 350].

Revised UNIFAC interaction parameters are presented for a number of groups, especially the aniline [100]. Parameters are given for 52 pairs of groups where the parameters have not previously been available. N-Methylpyrrolidone has been introduced as a new group and interaction parameters with five important groups are given [99, 196].

UNIFAC method [425] is used for calculating coefficients in terms of composition and temperature. The group UNIFAC parameters used are the ones reported earlier [88]. In a multicomponent mixture, the UNIFAC equation for the activity coefficient of component \( i \) is:

\[
\ln \gamma_i = \ln \gamma_i^r + \ln \gamma_i^n
\]

(2.49)

where

\[
\ln \gamma_i^n = \sum_{k=1}^{N} v_i^{(k)} \frac{1}{(\Gamma_i - \Gamma_k^{(0)})}
\]

(2.49a)

\[
k = 1, 2 \ldots N \text{ (number of different groups in the mixture)}
\]

\[
\Gamma_k = \text{residual activity coefficient of group } k \text{ in a solution.}
\]
\( \Gamma_i^{(0)} \) = residual activity coefficient of group \( k \) in a reference solution containing only molecules of type \( i \).

\( v_i^{(0)} \) = number of structural groups of kind \( k \) in molecule \( i \).

and

\[
\ln \gamma_i' = \ln(\Phi_i/x_i) + \frac{z}{2} q_i \ln(\theta_i/\Phi_i) + l_i - (\Phi_i/x_i) \sum_j x_j f_j
\]  
(2.50)

\[
l_i = \frac{z}{2}(r_i - q_i) - (r_i - 1) ; \quad z = 10
\]  
(2.50a)

\[
\theta_i = (q_i x_i)/(\sum_j q_j x_j) ; \quad \Phi_i = (r_i x_i)/(\sum_j r_j x_j)
\]  
(2.50b)

\[
r_i = \sum_k v_i^{(0)} R_i ; \quad q_i = \sum_k v_i^{(0)} Q_i
\]  
(2.50c)

\( j = 1, 2 \ldots \ldots M \) (number of components)

\( k = 1, 2 \ldots \ldots N \) (number of groups in molecule \( i \))

Here \( \Phi, \theta, r \) and \( q \) are respectively, the molecular volume fraction, molecular surface area fraction, van der Waals volume and van der Waals surface area. Parameter \( r \) and \( q \) are calculated as the sum of the group volume and group area parameters, \( R_i \) and \( Q_i \). The residual group activity coefficient for group \( k \) is found from Eq. 2.51:

\[
\ln \Gamma_i = Q_i [1 - \ln(\sum \theta_n \psi_{mn}) - \sum \left( \theta_n \psi_{mn} / \sum \psi_{mn} \right)]
\]  
(2.51)

where

\[
\theta_n = (Q_n X_n) / \sum Q_j X_j
\]

\[
X_n = \left( \sum v_n^{(i)} x_j \right) / \sum \sum v_n^{(i)} x_j
\]

\( \psi_{mn} = \exp(-a_{mn} / T) \)  
(2.51a)

\( j = 1, 2, \ldots \ldots M \).

\( n = 1, 2, \ldots \ldots N \)
Here $\theta_n$, $X_m$, $a_{nm}$ and $\psi_{nm}$ are, respectively, the group surface area fraction, group fraction, UNIFAC binary interaction parameter and UNIFAC group interaction parameter between groups $n$ and $m$.

However, Thomas et al. [390] made clear that the results obtained for the calculation of activity coefficients at infinite dilution were in most cases unsatisfactory especially when systems with molecules very different in size were considered. However, the exact knowledge of this quantity is particularly important for separation techniques, since the number of plates can be particularly high for very dilute systems. The original UNIFAC was not able to calculate enthalpies of mixing and thus the temperature dependence of the Gibbs excess energy to the required degree of exactness. It was thus modified in such a way that vapour-liquid equilibria, activity coefficients at infinite dilution and enthalpies of mixing could be calculated sufficiently exactly using only one set of parameters.

Modified UNIFAC method [425] required variations not only of the combinatorial part with respect to the form and size of the molecules but also the residual part with regard to the description of the temperature dependence of the activity coefficients. Eqs. 2.52 to 2.52b show the relations for the combinatorial part in the original UNIFAC model:

\[
\ln \gamma_i' = 1 - \phi_i' + \ln \phi_i' - 5q_i'[1 - (\phi_i' / \theta_i') + \ln(\phi_i' / \theta_i')] 
\] (2.52)

where

\[
\phi_i' = r_i' / \sum_j r_jx_j 
\] (2.52a)

\[
\theta_i = q_i' / \sum_j q_jx_j 
\] (2.52b)

After the preliminary investigations, an empirical $\frac{1}{4}$ term was introduced, which was determined by simultaneously optimizing activity coefficients at infinite dilution for various alkane/alkane, alkane/alcohol and alcohol/alcohol measurement series into the combinatorial part. Thomas et al. [390] obtained a similar result. Eq. 2.52 was thus modified as:-

\[
\ln \gamma_i' = 1 - \phi_i' + \ln \phi_i' - 5q_i'[1 - (\phi_i' / \theta_i') + \ln(\phi_i' / \theta_i')] 
\] (2.53)
The expressions for $\phi_j$ and $\theta_j$ remain unchanged.

Temperature dependent interaction parameters were introduced into the residual part. Eq. 2.54 and 2.55 show the relationships for the group interaction parameters $\psi_{nm}$ in the original and modified UNIFAC approach.

**Original UNIFAC**

\[ \psi_{nm} = \exp(-a_{nm}/T) \]  \hspace{1cm} (2.54)

**Modified UNIFAC**

\[ \psi_{nm} = \exp[-(a_{nm} + b_{nm}T + c_{nm}T^2)/T] \]  \hspace{1cm} (2.55)

The relative van der Waal’s volumes and surfaces of the structural groups (Rk and Qk values) were not calculated from molecular parameters as in original UNIFAC approach but fit together with interaction parameters ($a_{nm}$, $b_{nm}$, $c_{nm}$) to the experimental values. In addition, special Rk and Qk values were introduced for the cyclic CH2 and CH groups in order to permit a better description of systems containing cycloalkanes, which differ in some cases relatively strongly from the acyclic alkanes.

Vapour-liquid equilibria for system containing tertiary alcohols were not always satisfactorily described by UNIFAC [426, 427]. This is taken into account in the modified UNIFAC model by introducing separate vander Waal’s volumes and surfaces for the primary, secondary and tertiary alcohol groups. Additional main groups are not introduced. The cyclic structure groups are assigned to the main group alkane (CH2) and the different alcohol groups to the main group alcohol (OH). A 6 x 6 parameter matrix was built up, which contains the following main groups: CH2, alkanes; C = C, alkenes; ACH, aromatics; ACCH2, substituted aromatics; OH, alcohols; CH2CO, ketones.
Correlations

The main uses of correlating equations for vapour-liquid equilibrium data are to:

- correlate scattered data
- calculate vapour-liquid equilibrium data over the entire composition range
- calculate $x-y$ curves at one temperature from those at another
- aid in the prediction and correlation of the vapour-liquid equilibrium data for multi component systems, which are difficult to obtain experimentally
- facilitate the presentation of the data in an abridged form convenient for computer applications

The correlations can be divided into those based on excess free energy function and those based on equilibrium phase compositions. The activity coefficients are related to the excess free energy of the liquid phase by equations:

$$\frac{g'}{RT} = \sum x_i \ln \gamma_i, \quad (2.56)$$

and

$$\ln \gamma_i = \frac{g'}{RT} - \sum x_i \left[ \left( \frac{\partial g'}{\partial x_i} \right) / \frac{\partial \ln \gamma_i}{\partial x_i} \right] \quad (2.57)$$

Thus for a given temperature and composition, $g'$ can be determined from the activity coefficients and conversely the activity coefficients can be determined, if $g'$ is known as a function of composition. A number of treatments have been proposed for expressing $g'$ as a function of composition [329, 337, 432, 436]. Wohl [436] has proposed an expansion which can be written in the following form for a binary mixture, using the effective volume function $Z$ for the composition variable:

$$\frac{g'}{(RT(x_1q_1 + x_2q_2))} = 2a_{12}Z_1Z_2 + 3a_{112}Z_1^2Z_2 + 3a_{122}Z_1Z_2^2 + \ldots \quad (2.58)$$

where

\[
Z_1 = x_1q_1 / (x_1q_1 + x_2q_2) \quad (2.58a)
\]

and

\[
Z_2 = x_2q_2 / (x_1q_1 + x_2q_2) \quad (2.58b)
\]

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 upon temperature.

By means of several assumptions, the well known correlations by van Laar \[46, 303\], Scatchard-Hamer \[352\] and Margules \[303\] can be deduced from Eqs. 2.58 and 2.58a. These equations in terms of activity coefficients for binary systems can be written as:

van Laar

\[
\begin{align*}
\ln \gamma_1 &= A_{12} / (1 + A_{12} x_1 / A_{21} x_2) \\
\ln \gamma_2 &= A_{21} / (1 + A_{21} x_2 / A_{12} x_1)
\end{align*}
\]

\((2.59)\)

Scatchard - Hamer

\[
\begin{align*}
\ln \gamma_1 &= Z_1^1 [A_{12} + 2 Z_1 (A_{12} V_1 / V_2) - A_{12}] \\
\ln \gamma_2 &= Z_2^2 [A_{21} + 2 Z_2 (A_{12} V_2 / V_1) - A_{21}]
\end{align*}
\]

\((2.60)\)

Margules

\[
\begin{align*}
\ln \gamma_1 &= x_1 [A_{12} + 2 x_1 (A_{11} - A_{12})] \\
\ln \gamma_2 &= x_2 [A_{21} + 2 x_2 (A_{22} - A_{21})]
\end{align*}
\]

\((2.61)\)

Ellis and Bourne \[75\] have discussed the conditions under which the van Laar and Margules equations are expected to give good results for isothermal data. Various modifications of van Laar and Margules equations have been proposed from time to time to extend the effectiveness of these equations \[29, 30, 31, 46, 276, 429\]. van Laar and Margules equations are adequate only for simple and not highly non-ideal systems. They do not give generally satisfactory results for systems consisting of associating components. van Laar equation is more suited to unsymmetrical systems whereas the Margules equation is flexible and can represent the maxima and minima in the $\ln \gamma - x$ plot.

Black \[30\] modified the isothermal van Laar equation by introducing an empirical term containing an additional empirical constant $c_o$ to account for the overall influence of physical interaction, association and inter-association among molecules:
\[ \ln \gamma_j = \frac{a_j^2}{[1 + a_j^2 x_j / a_j^2 x_j]^2 + E_j} \]  
(2.62)

where

\[ E_j = c_j x_j (x_j - x_j) [3(x_j - x_j)(1 - x_j) + 2x_j] \]  
(2.62a)

Eq. 2.62 is extremely flexible and can represent very well the behaviour of even highly non-ideal systems. It can follow paths of maxima and minima in the activity coefficient-composition plots. This equation can be applied to polar-non-polar or polar-polar mixtures.

Lowell and Van Winkle [188] proposed an equation relating heat capacity and activity coefficients. Another solution of excess molar free energy expressed as a power series of composition was proposed by Redlich and Kister [329]:

\[ \frac{g^e}{RT} = x_1 x_2 [B + C(x_1 - x_2) + D(x_1 - x_2)^2 + ...] \]  
(2.63)

This equation has the advantage of being flexible and can be used to represent the behaviour of highly non-ideal systems by using the four constant form of the equation. The equation has an additional advantage that the constants represent the whole data and are not the end values of activity coefficient-composition plot as are in van Laar and Margules equations. Hala et al. [119] have discussed the graphical method for the evaluation of the constants in the Redlich-Kister equation. Chao [50] extended the isothermal Redlich-Kister equation to isobaric data by introducing an additional empirical constant:

\[ \ln \left( \frac{\gamma_j}{\gamma_j} \right) = a + b(x_2 - x_j) + c(6x_1x_j - 1) + d(x_2 - x_j)(1 - 8x_1x_j) + ... \]  
(2.64)

in which the constants \( b, c, d, \ldots \) are somewhat different from \( B, C, D, \ldots \) in Eq. 2.63.

Wichterle [430] concluded that the third order van Laar and Redlich-Kister equations are equally suitable whereas the Scatchard-Hamer equations are not suitable to represent most of the non-ideal systems.

Wilson [432] obtained an expression for the excess free energy as a logarithmic function of composition by analogy with the Flory-Huggins expression for athermal mixtures [83] in which the overall volume fraction was replaced by local volume fraction. The Wilson equation for the excess free energy function is given as:
\[ g^e / RT = -x_1 \ln(x_1 + \Lambda_{12}x_2) - x_2 \ln(x_2 + \Lambda_{21}x_1) \]  
(2.65)

where

\[ \Lambda_{12} = (V_2 / V_1) \exp[-(\lambda_{12} - \lambda_{11}) / RT] \]  
(2.65a)
\[ \Lambda_{21} = (V_1 / V_2) \exp[-(\lambda_{12} - \lambda_{22}) / RT] \]

The energy parameters, \( \lambda_{12} - \lambda_{11} \) and \( \lambda_{12} - \lambda_{22} \), are independent of temperature at least over a moderate interval. The corresponding expression for the activity coefficients can be written as:

\[ \ln \gamma_1 = -\ln(x_1 + \Lambda_{12}x_2) + x_2[(\Lambda_{12}/(x_1 + \Lambda_{12}x_2)) - (\Lambda_{21}/(\Lambda_{21}x_1 + x_2))] \]  
(2.66)
\[ \ln \gamma_2 = -\ln(x_2 + \Lambda_{21}x_1) - x_1[(\Lambda_{12}/(x_1 + \Lambda_{12}x_2)) - (\Lambda_{21}/(\Lambda_{21}x_1 + x_2))] \]  
(2.66a)

Wilson’s treatment, though suitable for a wide variety of binary systems including those with high non-ideality, is particularly successful for mixtures containing alcohols in non-polar solvents. The correlation is not suitable for partially miscible systems and systems which exhibit maxima and minima on \( \ln \gamma \) vs. \( x \) plots. Wilson [432] extended his correlation by introducing a third parameter to represent partially miscible systems, which however cannot be extended to multi-component systems.

Holmes and Van Winkle [138] and Hudson and Van Winkle [140] have discussed about the superiority of the correlation for representing vapour-liquid equilibria for all types of solutions.

Tassios [381] has modified the Wilson equation requiring only one adjustable parameter per binary as compared to two adjustable parameters in the Wilson equation. It was claimed that the equation is superior to van Laar equation, though inferior to the original Wilson equation, as should be expected since only one adjustable parameter is involved. For the prediction of ternary data the equation is claimed to be comparable to the Wilson equation.

Heil and Prausnitz [125] proposed a semi-empirical equation for representing free energy of mixing for polymer solutions in single and mixed solvents. Two adjustable parameters are involved per binary and the equation can be extended to multi-component systems. This equation is claimed to give good representation of the
properties of polymer solutions including those which form hydrogen bonding.

Renon and Prausnitz [337] developed the following equation called NRTL (Non Random Two Liquid) equation. It is based on Scott’s two liquid theory of mixtures [354]:

\[ g^E / RT = x_1 x_2 \left[ \frac{(\tau_{12} G_{12})}{(x_1 + x_2 G_{12})} + \frac{(\tau_{21} G_{21})}{(x_2 + x_1 G_{12})} \right] \]  \hspace{1cm} (2.67)

where

\[ G_{12} = \exp(-\alpha_{12} \tau_{12}) \]  \hspace{1cm} (2.67a)

\[ G_{21} = \exp(-\alpha_{12} \tau_{21}) \]  \hspace{1cm} (2.67b)

\[ \tau_{12} = \exp(g_{12} - g_{22}) / RT \]  \hspace{1cm} (2.67c)

\[ \tau_{21} = \exp(g_{21} - g_{11}) / RT \]  \hspace{1cm} (2.67d)

with

\[ g_{12} = g_{21} \]  \hspace{1cm} (2.67e)

\( \tau_{12} \) and \( \tau_{21} \) are temperature dependent parameters whereas the non random parameter \( \alpha_{12} \), to a good approximation, does not depend on temperature. The corresponding expressions for activity coefficients are:

\[ \ln \gamma_1 = x_1 \left[ \frac{(\tau_{12} G_{12})^2}{(x_1 + x_2 G_{12})^2} + \frac{(\tau_{21} G_{21})^2}{(x_2 + x_1 G_{12})^2} \right] \]  \hspace{1cm} (2.68)

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

Renon and Prausnitz observed that the value of \( \alpha_{12} \) for typical non-electrolyte systems varies from 0.2 to 0.47 depending upon the chemical nature of the systems. Renon and Prausnitz [336] gave methods for the estimation of parameters in the NRTL equation. When complete equilibrium data are available, the constants can be determined by a suitable least squares method. In the case of limited data for miscible systems, the parameters can be estimated from the activity coefficient data at infinite dilution. For partially miscible systems, mutual solubility data can be used.

Heil and NRTL equations can represent thermodynamic properties of binary mixtures with two liquid phases in which the Wilson equation is not applicable. The NRTL equation is simple without any logarithmic terms and represents the ternary
data well. It can be extended to the multi-component systems without introducing any additional assumptions. But the disadvantage of the NRTL equation is that even for miscible systems, all the three constants are to be used.

Asselineau and Renon [16] extended the NRTL equation to represent the properties of binary systems over a large temperature range. The parameters were calculated by the method of least squares from available data. Bruin and Prausnitz [42] modified the NRTL equation by substituting local volume fractions for local mole fractions. The equation contains only one parameter and the correlations relating the value of the parameter to molecular structure were established for several classes of systems. Palmer and Smith [280] developed a two parameter equation similar to the NRTL to correlate partially miscible systems. The equation was claimed to be correlating activity coefficients for all types of systems as a function of temperature and composition with a small number of variable parameters.

Lowell and Van Winkle [188] proposed a correlating method based on the combination of the thermodynamically derived expression for \( \ln y \) as a power series in composition and an integrated power series in temperature. The correlation is easily adaptable to computer calculations and was found to predict data with reasonable accuracy.

The discussion in the preceding paragraphs pertains to the correlations based on excess free energy. There are some equations which directly correlate equilibrium phase compositions. Hala et al. [119] have reviewed a number of such correlations. Clark [56] related the vapour and liquid compositions for a binary system by a set of equations. These equations are quite simple and fairly good for representing the relationship between the equilibrium phases. Hsi and Lu [139] proposed a method for obtaining the limiting slopes of the binary \( x-y \) curves making use of the Clark equation. Prahl [298] proposed an equation relating the vapour-liquid equilibrium phase compositions. The equation was modified by Lu et al. [189] and the modified equation was used by Nagata [236] to predict the boiling temperatures of binary and ternary mixtures. Kretschmer et al. [172] and Spinner et al. [366] also presented equations of this type.
Tassios and Van Winkle [380] 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.

Hala et al. [119] gave an equation relating the relative volatility and the composition. It was reported by Wichterle [430] that this equation is quite reliable to represent vapour-liquid equilibria of a wide variety of systems. Another equation relating \( \ln \alpha \) and \( x \) was proposed by Gilmont et al. [96]. Hirata [132] gave a correlation which gives parallel lines on a plot of \( \ln \alpha \) vs \( x \) with total pressure as the parameter.

Hirata [132] proposed a method according to which three straight lines are obtained on an \( x_1/x_2 \) vs \( y_1/y_2 \) plot on log-log graph. The method was applied to a large number of isobaric and isothermal systems.

The empirical relationships have the advantage of their simple application but the main drawback is that they cannot represent complete vapour-liquid equilibria because the temperature or the total pressure do not enter into these correlations.

**Evaluation of Parameters**

Most of the correlations representing activity coefficient data involve constant terms which are temperature dependent. Although the use of limited data is enough for the evaluation of constants in the correlations, it is generally more sound to obtain the constants using experimental data over the entire composition range. For the treatment of experimental isobaric data, especially for wide boiling systems, either the heat of mixing term should be introduced or the optimum average values of the constants should be determined using an optimization technique. The principal advantage of an optimization method is that it eliminates the need for individual judgement in smoothening and extrapolating data. Before an optimization technique is selected, it is important to know which function is to be minimised. Various minimisation functions used by several workers are given below [138, 233, 234, 248, 300, 415].

\[
F_q = \sum_{i=1}^{n} (Q_{exp} - Q_{cal})^2
\]  

(2.69a)
No detailed comparison of these functions has been made although Hudson and Van Winkle [140] pointed out that the minimised function represented by Eq. 2.69d gave generally better fit of the experimental data compared to Eq. 2.69h used by Prausnitz et al. [300].

Nagahama et al. [233] employed $F_y$, $F_y$ and $F_y$ minimisation functions to find the constants in the Wilson equation using the following optimisation techniques.

- non-linear least squares method [63]
These are well known optimization techniques. The first one, a Gaussian nonlinear least squares technique, is described below in detail. This technique was used in obtaining the constants in different correlations for the systems studied in this work. The minimisation function is written as:

\[ F = \sum_{i=1}^{n} r_i^2 \]  (2.70)

taking \( x_i = x \) \( x_2 = 1 - x \)

\[ r_i = (Q_{exp} - Q_{cal}) = [Q_{exp} + x \ln(x + \Lambda_{12}(1-x)) + (1-x) \ln(\Lambda_{21}x + 1-x)] \]  (2.70a)

The procedure is as follows:

(1) 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:

\[
\sum_{i=1}^{n} \left[ (\partial r_i / \partial \Lambda_{12}) (\partial r_i / \partial \Lambda_{12}) \Delta \Lambda_{12} \right] + \sum_{i=1}^{n} \left[ (\partial r_i / \partial \Lambda_{12}) (\partial r_i / \partial \Lambda_{21}) \Delta \Lambda_{21} \right] = \sum_{i=1}^{n} (\partial r_i / \partial \Lambda_{12}) r_i \]  (2.71a)

\[
\sum_{i=1}^{n} \left[ (\partial r_i / \partial \Lambda_{21}) (\partial r_i / \partial \Lambda_{12}) \Delta \Lambda_{12} \right] + \sum_{i=1}^{n} \left[ (\partial r_i / \partial \Lambda_{21}) (\partial r_i / \partial \Lambda_{21}) \Delta \Lambda_{21} \right] = \sum_{i=1}^{n} (\partial r_i / \partial \Lambda_{21}) r_i \]  (2.71b)

where

\[
\partial r_i / \partial \Lambda_{12} = x(1-x)/[\Lambda_{12}(1-x) + x] \]  (2.71c)

\[
\partial r_i / \partial \Lambda_{21} = x(1-x)/(1-x + \Lambda_{21}x) \]  (2.71d)
the $r_i$'s and $\partial r_i / \partial \Lambda_{12}$ and $\partial r_i / \partial \Lambda_{21}$ are evaluated at the assumed values of $\Lambda_{12}$ and $\Lambda_{21}$.

(2) 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 (1) is repeated till $\Delta \Lambda_{12}$ and $\Delta \Lambda_{21}$ become suitably small. The advantage of this Gaussain technique is that the partial derivatives are evaluated with each iteration.

Nagahama et al. [233] concluded that the difference among the converged results calculated by means of the above mentioned techniques for the same objective function, is not much. But the method of non-linear least squares is very simple and gives the most reasonable final estimate after the evaluation of the objective function, with 5 to 10 iterations, whereas the other methods required about 30 to 40 iterations to reach the same minimum value. Also the non-linear least squares method always converged for values of the constants between zero and 5. They have claimed that the non-linear least squares method, coupled with the use of the $Q$ function as an objective function, is to be preferred over any other method for obtaining the Wilson parameters.

Verhoeye [414, 415] employed $F_q$, $F(\gamma_1/\gamma_2)$ and $F_x$ or $E_x$ as the minimisation criteria. The $F_x$ function was minimized by the Newton-Raphson method in which the function is expanded by Taylor series neglecting the higher derivative terms. The Newton-Raphson method is quite efficient if the approximate constants are in the neighbourhood of the optimum values but is quite inefficient if the constants are far removed from the optimum values and the method may even diverge. This method was also used by McDermott and Ellis [211] for the prediction of isothermal vapour-liquid equilibrium data from total pressure measurements. A method of weighted least squares for the Wilson equation was also developed by Verhoeye [414, 415] by awarding a statistical weight to each experimental point.

Kaliaguine and Ramalho [155] discussed about the choice of a regression method to estimate the coefficients in the Wilson equation. Miyahara et al. [228] presented a graphical method to evaluate the parameters in Wilson equation from $Q$...
function. Miyahara et al. [229] presented a method to obtain the Wilson parameters by nomographs which relate them to the activity coefficients at infinite dilution. Asselineau and Renon [16] gave a method to calculate the constants in the NRTL equation by the method of least squares.

Mir and Steidler [226] proposed a least squares method for the evaluation of the binary van Laar constants by combining the van Laar equation with the equilibrium relationships:

\[ \pi y_i = p_i^0 x_i y_i \]  
\[ \alpha_y = y_i x_i / y_j x_j \]

(2.72a)

(2.72b)

to give

\[ \ln(p_i^0 / p_j^0) \alpha_y = A_{2j}[(x_i / x_j)^2 - A_{2j} / A_{1j}] \bigg/ [(x_i / x_j)^2 + (A_{2j} / A_{1j})^2] \]

(2.72c)

The Eq. 2.72c is solved for \( A_{1j} \) and \( A_{2j} \) by a least squares regression technique.

Tierney [392] developed an exact method based on the weighted least squares procedure suitable for the evaluation of Margules and van Laar three-suffix constants. Carli [45] minimised the \( \pi \) function by a non-linear technique to evaluate the constants in the van Laar and Margules equations. Ho et al. [136] employed \( F_n \) as the minimisation function to evaluate the optimum values of the Redlich-Kister constants by the method of least squares. It was found that on the average four iterations are adequate for a tolerance of 10\(^{-5}\) in the constants.

Wichterle [430] described that for energy balance of distillation columns, it is desirable to minimise \( F(\gamma_1 / \gamma_2) \) function and for mass balance, it is desirable to minimise the \( F_r \) function. But for the purpose of statistical thermodynamics, it is convenient to adjust the excess enthalpy. It was concluded that out of all these, the minimisation of \( F(\gamma_1 / \gamma_2) \) 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:

\[ W = \left[ \frac{1}{x^2(1-x)^2} + \frac{1}{y^2(1-y)^2} + \left( \frac{\partial F(x)}{\partial x} \right)^2 \right]^{-1} \quad (2.73) \]

where

\[ F(x) = \ln \left( \frac{y_1}{y_2} \right) \quad (2.73a) \]

Nagata and Yamada [234] used the Simplex method using objective functions (of Eqs. 2.69j, 2.69k) based on excess free energy and excess enthalpy. They have observed that the Simplex method gives much better results compared to the non-linear least squares and the modified steepest descent methods. They assumed the parameters as linear function of temperature. The method usually leads to convergence irrespective of the initial values of parameters as could be noted from the data tested by them. However the disadvantage of the method is that it requires large number of iterations. Nagata and Yamada have proposed the use of this method in the case of a complicated objective function.

2.4 Consistency Tests for Vapour-Liquid Equilibrium Data

Equilibrium measurements are always subjected to errors which might result from fractionation taking place in the equilibrium still, incorrect sampling, entrainment, attainment of non equilibrium steady state or in the measurement and analysis either due to the faulty instruments or human factors. Obviously there is a great need for methods to check the reliability 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 readings on the basis of scatter. This type of checking can detect only random errors and often fails to detect systematic errors.

Thermodynamic consistency tests based on Gibbs-Duhem equation are aimed at finding out the systematic errors. This equation, in terms of the activity coefficients, can be written as:

\[ \sum_i x_i \ln \gamma_i = 0 \quad (2.74) \]

The Gibbs-Duhem equation can be applied to:
- verify the thermodynamic consistency of the experimental data.
- calculate activity coefficients of one component from the knowledge of the other, even when there is a wide difference in the relative volatilities of the components.
- convert isothermal $\pi - x$ data or isobaric $T - x$ data into the equilibrium $x - y$ data.

Detailed information regarding the application of the equation can be had from the literature [46, 49, 53, 60, 132, 136, 142, 149, 184, 186, 197, 211, 227, 273, 285, 304, 310, 377, 379, 409]. The data which do not satisfy the Gibbs-Duhem equation can be safely rejected as erroneous. But compliance with tests based on this equation is not a sufficient condition since incorrect data might satisfy this equation.

There are a variety of methods available in literature for testing thermodynamic consistency of vapour-liquid equilibrium data. Some of the tests are rigorous based on unrestricted forms of the Gibbs-Duhem equation. Often these tests are difficult to apply as all the data required for their application might not be available. For this reason a number of appropriate tests, semi-empirical in nature, were developed. Application of one or more of these tests gives an indication about the thermodynamic consistency of the data. Some of the important thermodynamic consistency tests, confining to binary vapour-liquid equilibrium data, are reviewed briefly in the following paragraphs. These tests can be divided into two classes, namely (i) Integral or overall consistency tests and (ii) Differential or local consistency tests.

### 2.4.1 Integral Tests

It can be shown [57, 329] that at constant temperature and pressure:

$$\int_0^1 \ln(\gamma_1/\gamma_2) \, dx_1 = 0 \quad (2.75)$$

which means that a plot of $\ln(\gamma_1/\gamma_2)$ vs $x$ should mark off equal areas on the positive and negative side. The above equation is valid thermodynamically at constant temperature and pressure under conditions far from critical where the molar volume of the liquid phase is negligible as compared to that of the vapour phase. For isobaric
conditions, the deviations from the test depend on the integral heat of mixing and the
temperature range as discussed by several workers [70, 76, 129, 153, 389]. The area
test may not be very reliable as the departure from equilibrium in one part of the
composition range may compensate for deviations in another part. Prausnitz [302]
suggested the following condition as sufficient to satisfy the area test:

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

In practice, either the isothermal or the isobaric data are obtained and the
Gibbs-Duhem equation takes the following forms for the isothermal and isobaric data
respectively:

\[
\int_{\alpha_i=0}^{\alpha_i=1} \ln \left( \frac{\gamma_1}{\gamma_2} \right) \, d\alpha_i = \int_{\alpha_i=0}^{\alpha_i=1} \frac{\nabla v}{RT} \, d\alpha 
\]  

(2.76)

\[
\int_{\alpha_i=0}^{\alpha_i=1} \ln \left( \frac{\gamma_1}{\gamma_2} \right) \, d\alpha_i = -\int_{\alpha_i=0}^{\alpha_i=1} \frac{h^k}{RT^2} \, dT 
\]

(2.77)

Ellis and Bourne [75] have observed that for isothermal data the right hand
side of Eq. 2.76 is frequently less than 0.001 and can be safely taken as zero whereas
for the isobaric data and for boiling range not exceeding 10°C, the right hand side of
the Eq. 2.77 can be neglected as discussed by a number of workers [70, 75, 76, 389].
Coulson et al. [57] reached a similar conclusion on theoretical grounds that for
nonpolar systems the right hand term in Eq. 2.77 may be negligible but for polar-
nonpolar and polar-polar systems, it may be appreciable.

A semi-empirical test for isobaric data was proposed by Herington [129]. The
following quantities are evaluated and compared in this test.

\[
\int_{\alpha_i=0}^{\alpha_i=1} \ln \left( \frac{\gamma_1}{\gamma_2} \right) \, d\alpha_i = I 
\]

(2.78)

\[
D = \frac{100 |I|}{\Sigma} 
\]

(2.79)

where \(\Sigma\) is the sum of the absolute magnitudes of positive and negative areas
and \(|I|\) is the absolute value of the integral \(I\). Function \(D\) is then compared with
another function \(J\) which depends on the overall boiling range, \(\theta\), of the system at the
given pressure and the lowest measured boiling temperature, $T_{mm}$, in °K.

$$J = \frac{150 | \theta |}{T_{mm}} \quad (2.80)$$

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 [212] modified Herington’s test by introducing a term, $D^h$, which is evaluated from the excess free energy and the boiling point data. The procedure was adopted for pairs of data points.

Coulson et al. [57] and Broughton et al. [41] accounted for the temperature as:

$$\int_0^1 T \ln(y_1/y_2) \, dx_1 = 0 \quad (2.81)$$

As the variation of excess entropy, $s^F$, with temperature is small as compared to that of excess enthalpy, $h^F$, Van Ness [409] proposed the area test for isobaric systems in the following form:

$$\int_0^1 RT \ln(y_1/y_2) \, dx_1 = \int_0^1 s^F(dT/dx_1) \, dx_1 \quad (2.82)$$

Ramachandran and Laddha [309] proposed a method for testing isobaric data by taking into account heat of mixing which was calculated by employing the Redlich-Kister expansion for the excess free energy function.

Herington [128] developed general integral tests based on the Duhem-Margules equation. A family of symmetrical area tests were presented. These new tests were claimed to be more powerful tools for the examination of experimental data than the area tests previously developed by Herington [129]. In addition, these tests can be used to examine part of a composition range and to identify regions of poor observation. Also, the tests can sometimes be used to identify the quantities that are in error.
2.4.2. Differential Tests

The integral tests suffer from the disadvantages that the errors may compensate in different parts of the composition range and it is difficult to draw a correct line through the scattered data in the dilute region. But on the other hand, the differential or point by point tests can be considered to be more reliable. The following equation

\[ \frac{(x - y)}{y(1 - y)} \frac{dy}{dt} = \frac{h}{RT^2} \]  

(2.83)

can be used for testing the isobaric binary vapour-liquid equilibrium data [142, 153, 273]. It is based on the assumption that the heat of vapourisation is much larger than the heat of mixing which can be safely taken as zero in the evaluation of \( h \) term in above equation. The test is applicable for systems with ideal vapour phase. Also instead of partial molal heats of vapourisation, molal average heats of vapourisation should be used in the above equation.

Van Ness [410] proposed the ‘Composition Resolution Test’, based on the Gibbs-Duhem equation. It suffers from the disadvantage that the measurement of the slope of the curve is difficult. This difficulty was overcome by Van Ness and Mrazek [407] by suggesting a plot of \( g^f / (RT x_1 x_2) \) vs \( x_1 \) instead of \( g^f / RT \) vs \( x_1 \). The new plot is less sensitive to errors in tangent construction.

Based on Gibbs-Duhem equation, Barieau [22] derived an equation in terms of fugacities for testing the isothermal data. The test proposed can be extended to multicomponent systems.

From the discussion of Carlson and Colburn [46] on the application of Gibbs-Duhem equation, Lu [190] and Lu et al. [191] proposed some local consistency tests at strategic liquid compositions. These tests are based on the assumption that pressure has negligible effect on activity coefficients which were represented by the van Laar, Margules and Redlich-Kister equations. These tests are summarised below:

1. \( (\ln \gamma_1)_{x_1=0.25} = (\ln \gamma_1)_{x_1=0.75} \)

2. \( \ln \gamma_1 = 0.25 \beta \)

(a) \( (\ln \gamma_2)_{x_1=0.5} \approx 0.25 \alpha \)

(b) \( (\ln \gamma_2)_{x_1=0.5} \approx 0.25 \alpha \)

(2.84)

(2.85a)

(2.85b)
where \( \alpha = (\ln \gamma_1)_{x_i=0} \)  
(2.85c) 

\( \beta = (\ln \gamma_2)_{x_i=1} \)  
(2.85d) 

- If \( \alpha > \beta \) 
  
  \[
  (\ln \gamma_1)_{x_i=0.5} < (\ln \gamma_2)_{x_i=0.5} 
  \]  
  (2.86) 

- If \( \alpha < \beta \) 
  
  \[
  (\ln \gamma_1)_{x_i=0.5} > (\ln \gamma_2)_{x_i=0.5} 
  \]  
  (2.86a) 

- Both the \( \ln \gamma \) curves on a \( \ln \gamma \) vs \( x \) plot approach their zero values with a horizontal tangency. 
- If there is a maxima or minima on one of the \( \ln \gamma \) curves, there is a corresponding minima or maxima on the other curve at the same composition. 
- If there is no maxima or minima, both the \( \ln \gamma \) curves are on the same side of the \( \ln \gamma = 0 \) line.

The limits for the departure of the data from these tests were also suggested [191] which depend largely on the end values of the activity coefficients and the boiling range of the system.

Tao [376, 378] 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 involve the following equations:

\[
Q = \frac{g^V}{RT} = \sum x_i \ln \gamma_i = Q_e 
\]  
(2.87) 

\[
\alpha_i = -\left(\frac{h^V}{RT^2}\right)\left(\frac{dT}{dx_i}\right) + \left(\frac{v^V}{RT}\right)\left(\frac{d\pi}{dx_i}\right) + \sum (dx_i / dx_j) \ln \gamma_j = \alpha_{ie} 
\]  
(2.88) 

\[
\frac{dx_i}{dx_i} = (x_i - x_{ib})/(x_i - x_{ib}) 
\]  
(2.89) 

\[
Q x_{ib} - Q x_{ib} = \int_{x_i}^{x_{ie}} \alpha_i \, dx_i = \Delta Q 
\]  
(2.90) 

\[
\alpha_i = \frac{dQ}{dx_i} = \alpha_{ie} 
\]  
(2.90a) 

Since \( Q \) and \( \alpha_i \) can be calculated directly from experimental data according
to Eqs. 2.87 and 2.88 and also indirectly from Eqs. 2.90 and 2.90a, an integral method with Eqs. 2.87 and 2.90 and a differential method with Eqs. 2.88 and 2.90a are available to test an overall linear path as well as local paths. Equations are given to estimate the propagation of the errors in experimental measurements for the computed values of $\gamma_1$, $Q$, and $\alpha$. The application of the method in its rigorous form, requires the heats of mixing and volumetric properties. Tao [376] has given a method to treat azeotropic and non-azeotropic isobaric data. The method is better than the usual graphical method and covers both integral and differential tests.

2.4.3 Miscellaneous Tests

Based on the van Laar equation, Black [30, 32] proposed a thermodynamic consistency test whose validity results when a plot of $(\ln \gamma_1)^{0.5}$ vs $(\ln \gamma_2)^{0.5}$ produces a straight line. In case the activity coefficients are less than unity, $(-\ln \gamma_1)^{0.5}$ vs. $(-\ln \gamma_2)^{0.5}$ is plotted.

Norrish and Twigg [252] proposed a consistency test for isobaric data by using the relationship:

$$Z = \ln \left[(y_1/y_2)^{0.5}(x_1^y/x_2^y)\right]$$

(2.91)

where $k$ is the ratio of the molal heats of vapourisation. The data are claimed to be consistent, when a plot of $Z$ vs liquid composition $x_1$ results in a straight line in the middle composition region. The scatter of points should only be confined to the ends of the line where the sensitivity of $Z$ to changes in $x$ and $y$ increases rapidly to infinity.

Fried [91] developed two consistency tests for binary mixtures by using excess property functions, $Z_1^e/x_1^y$ and $Z_2^e/x_2^y$ which are more sensitive to errors than the commonly used functions $Z_1^r$ and $Z_2^r$. It was claimed that the test can check individual data points or the experimental curve as a whole.

Francesconi and Trevissoi [87] developed a direct semi-integral criterion for the consistency of vapour-liquid equilibrium data under isobaric and isothermal conditions for binary mixtures with association between the components in the two phases. The method permits the introduction of fugacity and activity coefficients which are more
convenient to use. Furthermore, it does not require any information on the state of association in the liquid phase. The consistency of the data throughout the whole concentration range can be examined without any analytical or graphical difficulty.

**Hirata Test**

Hirata test [133] is based on the fact that in binary systems, the equilibrium \( X - Y \) curve can be represented by three straight lines on a log-log graph in which the ordinate is the ratio of the mole fractions of the constituents in vapour phase.

\[
Y = \frac{y}{1-y} \quad (2.92)
\]

and the abscissa is the ratio of the mole fractions of the constituents in the liquid phase.

\[
X = \frac{x}{1-x} \quad (2.93)
\]

For the systems that form ideal solutions in the liquid phase, this relation is represented by a straight line parallel to the \( 45^\circ \) diagonal, since Raoult’s law may be expressed in the form

\[
Y = \alpha X \quad (2.94)
\]

Hirata examined a large amount of data from the literature on the vapour-liquid equilibrium relations of real systems at constant pressure as well as at constant temperature and found the following general properties of the \( X - Y \) curves in the range \( x = 0.001 \) to \( x = 0.999 \).

1. The \( X - Y \) curve consist of three straight line segments. The equation of each straight line segment is \( \log Y = n \log X + \log \alpha \), where \( n \) is the slope and \( \alpha \) gives the ordinate of the intersection of the segment with the vertical axis \( X = 1 \).

2. The upper portion of the curve where \( X \to \infty \), that is \( x \to 1 \), is a straight line whose slope is equal to 1.

3. The lower portion, where \( X \to 0 \), that is \( x \to 0 \), is a straight line of slope approximately 0.985.

4. The middle segment has a slope between 0 and 1 which is the characteristic of the system.