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Vapour–Liquid Equilibrium: Theory

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Introduction

The concept of an equilibrium stage in distillation is based on the assumption that the vapour leaving the stage is in equilibrium with the liquid leaving the same stage. The use of this concept in the design of distillation columns requires a description of how the components of a multicomponent mixture distribute between the two phases in equilibrium. This description is provided by phase equilibrium thermodynamics.

The equilibrium relationship for any component *i* in an equilibrium stage is defined in terms of the distribution coefficient or K value:

$$K_i = \frac{y_i}{x_j} \qquad [1]$$

where y_i is the mole fraction of component i in the vapour phase and x_i is the mole fraction of i in the liquid phase. The more volatile components of a mixture will have higher K values, and vice versa. In distillation, the efficiency of separation of two components is often compared via a quantity called the relative volatility α_{ij}:

$$\alpha_{ij} = \frac{K_i}{K_j} = \frac{y_i/x_i}{y_j/x_j} \qquad [2]$$

A relative volatility close to unity means that the separation of the two components is likely to be difficult, whereas a relative volatility much greater or much less than unity means that few equilibrium stages are likely to be needed for separation. For binary system, eqn [2] can be rearranged to give:

$$y_i = \frac{\alpha_{ij} x_i}{1 + (\alpha_{ij} - 1)x_i} \qquad [3]$$

Eqn [3] is plotted in **Figure 1** for various (constant) values of the relative volatility. Note that an increase in the relative volatility leads to an increase in the concentration of the more volatile component in the vapour phase. When the relative volatility has a value of 1, $y_i = x_i$ and separation is no longer feasible. A relative volatility of 1 also signifies the existence of an azeotrope or a critical point. A framework for the correlation and prediction of K values (and hence relative volatilities) is provided by thermodynamics and is discussed below. A more detailed discussion may be found in textbooks of thermodynamics (see Further Reading).

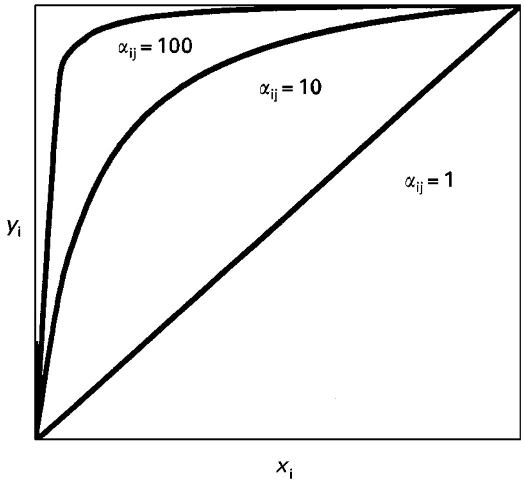

Figure 1 The y–x behaviour of a binary mixture at constant temperature for various values of the relative volatility α_{ij}.

Thermodynamic Framework

Vapour–liquid equlibria (VLE) can be modelled using the thermodynamic relationship for the equality of fugacities of a component i in the vapour and liquid phases. Thus:

$$\hat{f}_i^L = \hat{f}_i^V \quad (i = 1 \text{ to } m) \qquad [4]$$

where m is the total number of components in the system, and L and V represent the liquid phase and the vapour phase, respectively. In order to use this relationship, the fugacities must first be related to the compositions in the two phases in equilibrium. This is done using the following thermodynamic relationship in terms of the variables T, P and n_i:

$$RT \ln\left(\frac{\hat{f}_i}{z_i P}\right) = \int_0^P \left[\left(\frac{\partial V}{\partial n_i}\right)_{T,P,n_j} - \frac{RT}{P}\right] dP \qquad [5]$$

or the equivalent relationship in terms of T, V and n_i:

$$RT \ln\left(\frac{\hat{f}_i}{z_i P}\right) = \int_V^\infty \left[\left(\frac{\partial P}{\partial n_i}\right)_{T,V,n_j} - \frac{RT}{V}\right] dP - RT \ln\left(\frac{PV}{RT}\right) \qquad [6]$$

In the above equations, z_i is either x_i or y_i depending on the phase being considered, and n_i is the number of moles of component i in that phase. The quantity $(\hat{f}_i/z_i P)$ is called the fugacity coefficient $\hat{\phi}_i$ of component i in the mixture.

Ideal Systems

In the case of an ideal gas mixture, substitution of the ideal gas equation $PV = nRT$ into eqn [5] leads to:

$$\hat{f}_i^V = y_i P \qquad [7]$$

Similarly, substitution of the volume additivity relation for ideal liquid mixtures $V = \Sigma n_i v_i^L$ (where v_i^L is the molar volume of component i at the temperature and pressure of the solution) leads to:

$$\hat{f}_i^L = x_i f_i^L \qquad [8]$$

where f_i^L is the fugacity of pure liquid i at the pressure and temperature of the solution. At constant temperature, the effect of pressure on the pure liquid fugacity can be obtained from:

$$d\ln f_{\mathrm{i}}^{\mathrm{L}} = \frac{v_{\mathrm{i}}^{\mathrm{L}}}{RT}\,\mathrm{d}P \qquad [9]$$

Integration of eqn [9] from the saturation pressure to the system pressure leads to:

$$f_{\mathrm{i}}^{\mathrm{L}} = f_{\mathrm{i}}^{\mathrm{sat}} \exp \int_{P_{\mathrm{i}}^{\mathrm{sat}}}^{P} \frac{v_{\mathrm{i}}^{\mathrm{L}}}{RT}\,\mathrm{d}P \qquad [10]$$

where $f_{\mathrm{i}}^{\mathrm{sat}}$ $(=\phi_{\mathrm{i}}^{\mathrm{sat}}P_{\mathrm{i}}^{\mathrm{sat}})$ is the fugacity of pure *i* at saturation, $\phi_{\mathrm{i}}^{\mathrm{sat}}$ is the fugacity coefficient of pure *i* at saturation, and $P_{\mathrm{i}}^{\mathrm{sat}}$ is the vapour pressure of pure *i*. The liquid molar volume $v_{\mathrm{i}}^{\mathrm{L}}$ can often be assumed to be constant with respect to pressure (since liquids are incompressible), thus simplifying the exponential terms of eqn [10], called the Poynting factor, to:

$$\exp\left(-\int_{P_{\mathrm{i}}^{\mathrm{sat}}}^{P} \frac{v_{\mathrm{i}}^{\mathrm{L}}}{RT}\,\mathrm{d}P\right) \approx \exp\left(\frac{v_{\mathrm{i}}^{\mathrm{L}}(P_{\mathrm{i}}^{\mathrm{sat}} - P)}{RT}\right) \qquad [11]$$

At low pressures ($P < 1$ MPa), the Poynting terms and $\phi_{\mathrm{i}}^{\mathrm{sat}}$ both approach unity and eqn [10] reduces to:

$$f_{\mathrm{i}}^{\mathrm{L}} = P_{\mathrm{i}}^{\mathrm{sat}} \qquad [12]$$

Thus, for the simplest case of an ideal gas mixture in equilibrium with an ideal liquid solution at low pressures, eqns [4]–[12] lead to Raoult's law:

$$x_{\mathrm{i}}P_{\mathrm{i}}^{\mathrm{sat}} = y_{\mathrm{i}}P \qquad [13]$$

and, therefore:

$$K_{\mathrm{i}} = \frac{y_{\mathrm{i}}}{x_{\mathrm{i}}} = \frac{P_{\mathrm{i}}^{\mathrm{sat}}}{P} \qquad [14]$$

and:

$$\alpha_{\mathrm{ij}} = \frac{P_{\mathrm{i}}^{\mathrm{sat}}}{P_{\mathrm{j}}^{\mathrm{sat}}} \qquad [15]$$

The relative volatility of a system that obeys Raoult's law is thus a ratio of two vapour pressures and is a function only of the temperature. The y_{i} versus x_{i} behaviour at constant temperature is therefore as shown in Figure 1, and the *P–x–y* behaviour of such a system is shown in **Figure 2**. A feature of this system is that the *P–x* behaviour (or the bubble curve) is linear and given by:

$$P = P_{\mathrm{i}}^{\mathrm{sat}} + x_1(P_1^{\mathrm{sat}} - P_2^{\mathrm{sat}}) \qquad [16]$$

Only a small number of systems containing chemically similar components obey Raoult's law, and then only at low pressures (<1 MPa). As a consequence, *K* values can be predicted from pure component data only for such mixtures. The majority of real systems are nonideal and their thermodynamic description is discussed below.

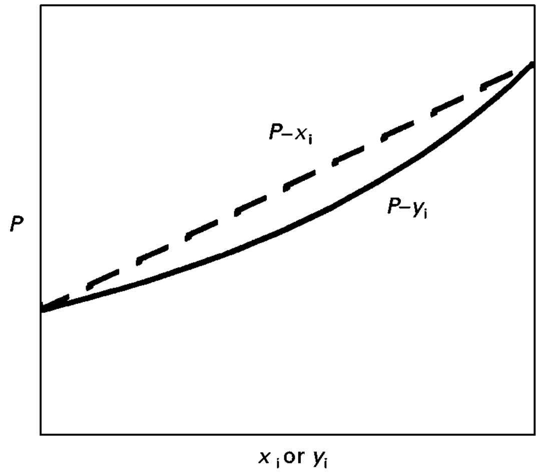

Figure 2 The *P–x–y* behaviour at constant temperature of a binary mixture that obeys Raoult's law. The dashed line shows the *P–x* behaviour or the bubble curve. The solid line represents the *P–y* behaviour or the dew point curve.

Nonideal Systems

Figure 3A, B shows the *P–x–y* behaviour of systems that exhibit small negative and positive deviations from Raoult's law, whereas Figure 3C and D show systems that exhibit large negative and positive deviations from Raoult's law, respectively. Large deviations from Raoult's law often lead to the formation of minimum pressure (maximum boiling) or maximum pressure (minimum boiling) azeotropes, as shown in Figure 3C and D. The relative volatility has a value of unity at the azeotropic composition. Nonideal behaviour depicted in these figures can be described using two approaches – the activity coefficient approach and the equation of state approach.

Activity coefficient approach In this approach, vapour-phase fugacities are written in terms of the vapour-phase composition as follows:

$$\hat{f}_{\mathrm{i}}^{\mathrm{V}} = \hat{\phi}_{\mathrm{i}}^{\mathrm{V}} y_{\mathrm{i}} P \qquad [17]$$

where $\hat{\phi}_{\mathrm{i}}^{\mathrm{V}}$ is the vapour-phase fugacity coefficient of component *i*, y_{i} is the mole fraction of *i* in the vapour phase and *P* is the total system pressure. In addition, liquid-phase fugacities are written in terms of the liquid-phase composition as follows:

$$\hat{f}_{\mathrm{i}}^{\mathrm{L}} = \gamma_{\mathrm{i}} x_{\mathrm{i}} f_{\mathrm{i}}^{0} \qquad [18]$$

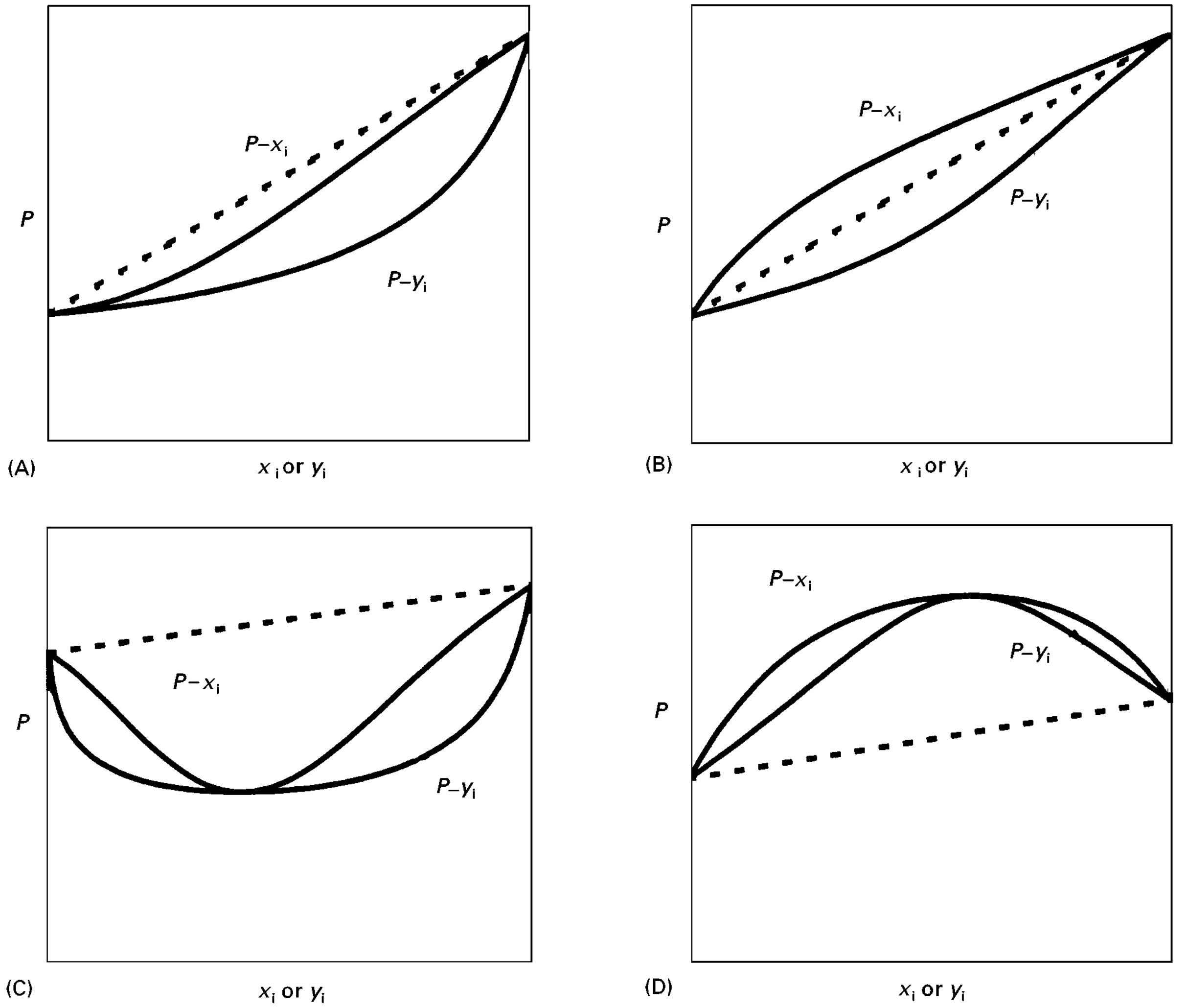

Figure 3 (A) The *P–x–y* behaviour of a system that exhibits small negative deviations from Raoult's law. The *P–x* behaviour of a system that follows Raoult's law is shown by the broken line. (B) The *P–x–y* behaviour of a system that exhibits small postive deviations from Raoult's law. Raoult's law behaviour is shown by the broken line. (C) The *P–x–y* behaviour of a system that exhibits significant negative deviations from Raoult's law leading to the formation of a minimum pressure (maximum boiling) azeotrope. (D) The *P–x–y* behaviour of a system that exhibits significant positive deviations from Raoult's law leading to the formation of a maximum pressure (minimum boiling) azeotrope.

where γ_i is the activity coefficient of component i in the liquid phase, x_i is the mole fraction of i in the liquid phase and f_i^0 is the fugacity of pure liquid i at the pressure and temperature of the system. Combining eqns [17] and [18], we obtain:

$$\gamma_i x_i f_i^0 = \hat{\phi}_i^V y_i P \qquad [19]$$

At low pressures (< 1 MPa), eqn [19] can be simplified further to yield:

$$\gamma_i x_i P_i^{sat} = \hat{\phi}_i^V y_i P \qquad [20]$$

as discussed in the previous section. Often $\hat{\phi}_i^V \sim 1.0$ for vapour phases at moderate pressures.

Hence:

$$\gamma_i x_i P_i^{sat} = y_i P \qquad [21]$$

and:

$$K_i = \gamma_i P_i^{sat}/P \qquad [22]$$

Vapour pressures at subcritical temperatures may be obtained from experimental data using equations such as the Antoine equation. Activity coefficients may be obtained from excess Gibbs energy g^E models, as described below.

Equation of state approach The equation of state approach uses eqn [17] for the vapour phase and an analogous expression for the liquid phase. Thus, for the liquid phase:

$$\hat{f}_i^L = \hat{\phi}_i^L x_i P \qquad [23]$$

Substituting these relationships into eqn [4] results in:

$$\hat{\phi}_i^V y_i = \hat{\phi}_i^L x_i \qquad [24]$$

and:

$$K_i = \hat{\phi}_i^L / \hat{\phi}_i^V \qquad [25]$$

The calculation of K values is therefore reduced to the calculation of fugacity coefficients in the equation of state approach and, at moderate pressures, to the calculation of activity coefficients in the activity coefficient approach.

Calculation of Fugacity Coefficients

Calculation of the fugacity coefficient using eqn [5] or eqn [6] requires knowledge of the P–V–T–x behaviour of the system. This information is obtained from an equation of state. Two representative types of equation of state will be discussed below – a volume-explicit virial equation and a pressure-explicit cubic equation. A more detailed discussion of types of equation of state is available elsewhere (see Further Reading).

Volume-explicit Virial Equation

Virial equations of state are infinite-series expansions of the compressibility Z as a function either of the density or pressure. The pressure series may be written as:

$$Z = \frac{PV}{RT} = 1 + B'P + C'P^2 + \ldots$$

$$= 1 + \frac{BP}{RT} + \frac{(C - B^2)}{(RT^2)} P^2 + \ldots \qquad [26]$$

where B is the second virial coefficient, C the third virial coefficient, and so on. Typically, the two-terms truncated form of the virial equation is used for gases at low pressures:

$$Z = 1 + B'P = 1 + \frac{BP}{RT} \qquad [27]$$

which can be rearranged in the volume-explicit form:

$$V = \frac{RT}{P} + B \qquad [28]$$

The truncated virial eqn [28] is only applicable to gases at densities that are less than about half the critical density. One of the advantages of the virial equation, however, is that virial coefficients can be calculated from intermolecular potential functions. Also, statistical mechanics provides rigorous expressions for the composition dependence of the virial coefficients. Thus, the mixture second virial coefficient is given by:

$$B = \sum_i \sum_j y_i y_j B_{ij} \qquad [29]$$

where B_{ii} is the second virial coefficient of component i and B_{ij} is a cross second virial coefficient. Substitution of eqns [28] and [29] into eqn [5] leads to:

$$\ln \hat{\phi}_i^V = \frac{P}{RT}[B_{ii} + \tfrac{1}{2}\Sigma\Sigma y_k y_l (2\delta_{ki} - \delta_{kl})] \qquad [30]$$

where $\delta_{kl} = 2B_{kl} - B_{kk} - B_{ll}$. The fugacity coefficient of any component in the vapour phase can thus be calculated if the second virial coefficients of the pure components and the cross second virial coefficients are available. Since the truncated virial equation is only applicable to gases at low to moderate pressures, fugacity coefficients calculated using eqn [30] are generally only employed when eqn [20] is used to calculate VLE.

Pressure-explicit Cubic Equation of State

Cubic equations of state express the pressure as a cubic function of the molar volume, and their origin stems from the van der Waals equation, which was the first cubic equation of state to represent qualitatively both vapour and liquid phases. Several hundred modification of the van der Waals equation have been reported in the literature. An example of a recent modification that is better able to represent P–V–T–x data for both vapour and liquid mixtures is the equation of state proposed by Patel and Teja in 1982. This equation may be written as:

$$P = \frac{RT}{v - b} - \frac{a\alpha}{v^2 + bv + cv - bc} \qquad [31]$$

where:

$$a = \alpha\Omega_a \frac{R^2 T_c^2}{P_c} \qquad [32]$$

$$b = \Omega_b \frac{RT_c}{P_c} \qquad [33]$$

$$c = \Omega_c \frac{RT_c}{P_c} \qquad [34]$$

$$\alpha = [1 + m(1 - \sqrt{T/T_c})]^2 \qquad [35]$$

$$\Omega_a = 3\zeta_c^2 + 3(1 - 2\zeta_c)\Omega_b + \Omega_b^2 + 1 - 3\zeta_c \qquad [36]$$

$$\Omega_c = 1 - 3\zeta_c \qquad [37]$$

$$\zeta_c = P_c v_c / RT_c \qquad [38]$$

and Ω_b is the smallest positive root of:

$$\Omega_b^3 + (2 - 3\zeta_c)\Omega_b^2 + 3\zeta_c^2\Omega_b - \zeta_c^3 = 0 \qquad [39]$$

In the above equations, the subscript c denotes a value at the critical point. Note that by setting the parameter $c = 0$ in eqn [31], the Patel–Teja equation reduces to the Redlich-Kwong-Soave equation of state; and by setting c = b, it reduces to the Peng–Robinson equation of state. Both the Redlich–Kwong–Soave and the Peng–Robinson equations are widely used in process design calculations. For nonpolar fluids, ζ_c and m are calculated from the following relationships in terms of the acentric factor ω:

$$\zeta_c = 0.329032 - 0.076799\omega + 0.0211947\omega^2 \qquad [40]$$

$$m = 0.452413 + 1.30982\omega - 0.295937\omega^2 \qquad [41]$$

A knowledge of P_c, T_c and ω is therefore sufficient to calculated the parameters of the equation of state. Alternatively, ζ_c and m may be calculated from experimental values of the vapour pressure and liquid density of the substance. Several other forms of eqn [35] suitable for complex molecules have been proposed.

The parameters a, b and c for a mixture can be calculated using the following mixing rules:

$$a\alpha = \sum_i \sum_j z_i z_j (a\alpha)_{ij} \qquad [42]$$

$$b = \sum_i z_i b_i \qquad [43]$$

$$c = \sum_i z_i c_i \qquad [44]$$

where z_i can be x_i or y_i and $(a\alpha)_{ij} = (1 - k_{ij}\sqrt{(a\alpha)_i (a\alpha)_j}$. k_{ij} is a binary interaction parameter that is usually obtained by fitting experimental VLE data.

The fugacity coefficient can be obtained by substituting eqns [31]–[44] into eqn [6] leading to:

$$\ln \hat{\phi}_i = \ln\left(\frac{\hat{f}_i}{z_i P}\right) = \frac{b_i}{v - b} - \ln\left[\frac{P}{RT}(v - b)\right]$$

$$- \frac{2\sum x_j \alpha_{ij} a_{ij}}{RT[4bc + (b + c)^2]^{1/2}}$$

$$\times \ln\left(\frac{(2v + b + c) + [4bc + (b + c)^2]^{1/2}}{(2v + b + c) - [4bc + (b + c)^2]^{1/2}}\right)$$

$$+ \frac{2a\alpha(b_i + c_i)}{RT((2v + b + c)^2 - [4bc + (b + c)^2])}$$

$$+ \frac{a\alpha}{RT[4bc + (b + c)^2]^{3/2}}$$

$$\times [c_i(3b + c) + b_i(3c + b)]$$

$$\times \left[\ln\left(\frac{(2v + b + c) + [4bc + (b + c)^2]^{1/2}}{(2v + b + c) - [4bc + (b + c)^2]^{1/2}}\right)\right.$$

$$\left. - \frac{2(2v + b + c)[4bc + (b + c)^2]^{1/2}}{(2v + b + c)^2 - [4bc + (b + c)^2]} \right] \qquad [45]$$

Eqn [45] can be used to calculate both the vapour- and liquid-phase fugacity coefficients. In the case of vapour phase, $z_i = y_i$ and v is the vapour molar volume, whereas for the liquid phase, $z_i = x_i$ and v is the liquid molar volume. The ratio of the two fugacity coefficients yields the K value under the conditions of interest.

Calculation of Activity Coefficients

Activity coefficients, γ_i are generally calculated by differentiation of the excess Gibbs energy g^E:

$$RT \ln \gamma_i = \left(\frac{\partial n g^E}{\partial n_i}\right)_{T,P,n_j} \qquad [46]$$

A number of expressions have been proposed for g^E as a function of composition. Some of the more popular of these are outlined below.

Margules Equation

The Margules equation is one of the simplest expressions for the molar excess Gibbs energy. For a binary solution:

$$\frac{g^E}{RT} = x_1 x_2 (A_{21} x_1 + A_{12} x_2) \qquad [47]$$

where A_{12} and A_{21} are binary parameters dependent on temperature, but not on the composition. The Margules activity coefficients in a binary mixture are obtained by differentiation of eqn [47] and are given by:

$$\ln \gamma_1 = [A_{12} + 2(A_{21} - A_{12})x_1]x_2^2 \qquad [48]$$

$$\ln \gamma_2 = [A_{21} + 2(A_{12} - A_{21})x_2]x_1^2 \qquad [49]$$

A_{12} and A_{21} are generally obtained by fitting VLE data. Note that the value of the activity coefficient of each component tends to unity as the mole fraction of that component goes to unity. This behaviour is inherent in all g^E models. The Margules equation works well for binary systems in which the two components are very similar in size, shape and chemical nature. Margules parameters for a large number of systems are tabulated in DECHEMA books on VLE data.

Van Laar Equation

The van Laar equation for the excess Gibbs energy may be written as:

$$\frac{g^E}{RT} = \frac{2a_{12}x_1x_2q_1q_2}{x_1q_1 + x_2q_2} \qquad [50]$$

where q_1 and q_2 are the effective volumes of the two molecules and a_{12} is an interaction parameter. Differentiation according to eqn [46] leads to the following expressions for the activity coefficients:

$$\ln \gamma_1 = \frac{A_{12}}{\left[1 + \dfrac{A_{12}}{A_{21}}\dfrac{x_1}{x_2}\right]^2} \qquad [51]$$

$$\ln \gamma_2 = \frac{A_{21}}{\left[1 + \dfrac{A_{21}}{A_{12}}\dfrac{x_2}{x_1}\right]^2} \qquad [52]$$

where $A_{12} = 2q_1a_{12}$ and $A_{21} = q_2a_{12}$. As in the case of the Margules equation, the two parameters A_{12} and A_{21} are obtained by fitting VLE data. The van Laar equations have been shown to work well for a number of binary systems where the size, shape and chemical nature of the components are dissimilar, and parameters for many binary systems have been tabulated in the DECHEMA data books.

Wilson Equation

The Margules equation is based on the assumption that the ratio of species 1 to species 2 molecules surrounding any molecule is the same as the ratio of the mole fractions of species 1 and 2. A different class of g^E models has been proposed based on the assumption that, around each molecule, there is a local composition that is different from the bulk composition. The Wilson equation is such a local composition model and the Wilson excess Gibbs energy has the following form for a binary system:

$$\frac{g^E}{RT} = x_1 \ln(x_1 + \Lambda_{12}x_2) - x_2 \ln(x_2 + \Lambda_{21}x_1) \qquad [53]$$

where Λ_{12} and Λ_{21} are parameters specific to the binary pair. These parameters are defined in terms of the molar liquid volume v_i of the pure component i, and the energies of interaction λ_{ij} between the molecules i and j as follows:

$$\Lambda_{ij} = \frac{v_j}{v_i} \exp\left[-\frac{\lambda_{ij} - \lambda_{ii}}{RT}\right] \qquad [54]$$

The expression for the liquid activity coefficients are:

$$\ln \gamma_1 = -\ln(x_1 + \Lambda_{12}x_2) + x_2\left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{x_2 + \Lambda_{21}x_1}\right) \qquad [55]$$

$$\ln \gamma_2 = -\ln(x_2 + \Lambda_{21}x_1) + x_1\left(\frac{\Lambda_{21}}{x_2 + \Lambda_{21}x_1} - \frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2}\right) \qquad [56]$$

The Wilson equation has two parameters Λ_{12} and Λ_{21} (or equivalently, $\lambda_{12} - \lambda_{11}$ and $\lambda_{21} - \lambda_{22}$) and is able to correlate VLE data for a wide variety of miscible systems, including those containing polar or associating components in nonpolar solvents. However, the equation is incapable of predicting liquid–liquid immiscibility in a system.

For multicomponent mixtures, the Wilson equation is written as follows:

$$\ln \gamma_k = -\ln\left[\sum_{j=1}^{m} x_j\Lambda_{kj}\right] + 1 - \sum_{i=1}^{m} \frac{x_i\Lambda_{ik}}{\sum_{j=1}^{m} x_j\Lambda_{ij}} \qquad [57]$$

Note that only binary parameters Λ_{ij} are required to evaluate activity coefficients in multicomponent systems. These parameters are obtained by fitting VLE data for the binary pairs, and many of these parameters have been tabulated in the DECHEMA data books. Moreover, because a temperature dependence is included in eqn [54], the same binary parameters may be used over a range of temperatures (although no more that about 50 K).

NRTL Equation

The NRTL (non-tandom two-liquid theory) equation is also based on a local composition model for the excess Gibbs energy. However, it is applicable to miscible as well as partially miscible systems due to the inclusion of a third binary parameter in the model. The expression for the molar excess Gibbs energy is:

$$\frac{g^E}{RT} = x_1x_2\left[\frac{\tau_{21}G_{21}}{x_1 + x_2G_{21}} + \frac{\tau_{12}G_{12}}{x_2 + x_1G_{12}}\right] \qquad [58]$$

where τ_{ij} and G_{ij} are defined as:

$$G_{ij} = \exp(-\zeta_{ij}\tau_{ij}) \qquad [59]$$

$$\tau_{ij} = \frac{g_{ij} - g_{jj}}{RT} \qquad [60]$$

g_{ij} describes the energy of interaction between component i and j and ζ_{ij} ($=\zeta_{ji}$) is a nonrandomness parameter which is often set equal to 0.3. Thus, only two parameters τ_{ij} and τ_{ji} (or, equivalently, $g_{ij} - g_{jj}$ and $g_{ji} - g_{ii}$) are required per binary pair.

The activity coefficients expressions are as follows:

$$\ln \gamma_1 = x_2^2\left[\tau_{21}\left(\frac{G_{21}}{x_1 + G_{21}x_2}\right)^2 + \frac{\tau_{12}G_{12}}{(x_2 + G_{12}x_1)^2}\right] \qquad [61]$$

$$\ln \gamma_2 = x_1^2\left[\tau_{12}\left(\frac{G_{12}}{x_2 + G_{12}x_1}\right)^2 + \frac{\tau_{21}G_{21}}{(x_1 + G_{21}x_2)^2}\right] \qquad [62]$$

A major advantage of the NRTL equation lies in its ability to represent highly nonideal systems, particularly partially miscible systems.

For multicomponent mixtures, the liquid-phase activity coefficients are expressed as:

$$\ln \gamma_i = \frac{\sum_{j=1}^{m} \tau_{ji}G_{ji}x_j}{\sum_{l=1}^{m} G_{li}x_l} + \sum_{j=1}^{m} \frac{x_j G_{ij}}{\sum_{l=1}^{m} G_{lj}x_l}\left(\tau_{ij} - \frac{\sum_{r=1}^{m} x_r \tau_{rj} G_{rj}}{\sum_{l=1}^{m} G_{lj}x_l}\right) \qquad [63]$$

As with the Wilson equation, only binary data are needed to calculate activity coefficients in multicomponent systems, and these parameters have been tabulated in the DECHEMA data books for many systems. Furthermore, because of the inclusion of the temperature in eqn [60] the parameters obtained by fitting VLE data at one temperature may be used to calculated VLE at other temperatures (within a range of about 50 K).

UNIQUAC Equation

The UNIQUAC (universal quasi-chemical theory) equation expresses the molar excess Gibbs energy as a sum of a combinatorial part and residual part.

$$g^E = g^E(\text{combinatorial}) + g^E(\text{residual}) \qquad [64]$$

The combinatorial part accounts for differences in the size and shape of the molecules, whereas the residual contribution accounts for energetic interactions.

$$\frac{g^E(\text{combinatorial})}{RT} = x_1 \ln\frac{\Phi_1}{x_1} + x_2 \ln\frac{\Phi_2}{x_2} + \frac{z}{2}\left(q_1 x_1 \ln\frac{\theta_1}{\Phi_1} + q_2 x_2 \ln\frac{\theta_2}{\Phi_2}\right) \qquad [65]$$

$$\frac{g^E(\text{residual})}{RT} = -q_1 x_1 \ln(\theta_1 + \theta_2\tau_{21}) - q_2 x_2 \ln(\theta_2 + \theta_1\tau_{12}) \qquad [66]$$

where:

$$\Phi_i = \frac{x_i r_i}{\sum_j x_j r_j} \qquad [67]$$

$$\theta_i = \frac{x_i q_i}{\sum_j x_j q_j} \qquad [68]$$

$$\tau_{ji} = \exp\left(-\frac{a_{ji}}{RT}\right) \qquad [69]$$

In eqn [65] z is a coordination number ($=10$ usually), Φ_i are volume fractions, and θ_i are surface area fractions for component i. The volume and surface area parameters r_i and q_i can be evaluated from pure component molecular structure information and are tabulated in the DECHEMA data books. Thus, there are two binary parameters a_{ij} and a_{ji} in the UNIQUAC model and these are found by fitting binary VLE data. The activity coefficient expressions become:

$$\ln \gamma_1 = \ln\frac{\Phi_1}{x_1} + \left(\frac{z}{2}\right)q_1 \ln\frac{\theta_1}{\Phi_1} + \Phi_2\left(l_1 - \frac{r_1}{r_2}l_2\right) - q_1 \ln(\theta_1 + \theta_2\tau_{21}) + \theta_2 q_1\left(\frac{\tau_{21}}{\theta_1 + \theta_2\tau_{21}} - \frac{\tau_{12}}{\theta_2 + \theta_1\tau_{12}}\right) \qquad [70]$$

$$\ln \gamma_2 = \ln\frac{\Phi_2}{x_2} + \left(\frac{z}{2}\right)q_2 \ln\frac{\theta_2}{\Phi_2} + \Phi_1\left(l_2 - \frac{r_2}{r_1}l_1\right) - q_2 \ln(\theta_2 + \theta_1\tau_{12}) + \theta_1 q_2\left(\frac{\tau_{12}}{\theta_2 + \theta_1\tau_{12}} - \frac{\tau_{21}}{\theta_1 + \theta_2\tau_{21}}\right) \qquad [71]$$

where:

$$l_i = \left(\frac{z}{2}\right)(r_i - q_i) - (r_i - 1) \qquad [72]$$

The UNIQUAC equation is applicable to a wide range of systems, including partially miscible systems.

For multicomponent systems, the UNIQUAC equation becomes:

$$\ln \gamma_i = \ln \frac{\Phi_i}{x_i} + \frac{z}{2} q_i \ln \frac{\theta_i}{\Phi_i} + l_i - \frac{\Phi_i}{x_i} \sum_{j=1}^{m} x_j l_j - q_i \ln\left(\sum_{j=1}^{m} \theta_j \tau_{ji} \right) + q_i - q_i \sum_{j=1}^{m} \frac{\theta_j \tau_{ij}}{\sum_{j=1}^{m} \theta_k \tau_{kj}} \quad [73]$$

Once again, only pure component and binary data are needed to calculate the parameters. UNIQUAC parameters for over 6000 binary systems have been tabulated in the DECHEMA data series on VLE.

UNIFAC Group Contribution Method

When values of Margules, van Laar, Wilson, NRTL or UNIQUAC parameters are not available in the literature, or when no VLE data for the system of interest have been measured, the UNIFAC (UNIQUAC functional group activity coefficients) method may be used to estimate activity coefficients. The UNIFAC method is a group contribution technique for the estimation of the parameters a_{mn} of the excess Gibbs energy model. The method expresses the molar excess Gibbs energy as a sum of a combinatorial part and a residual part and uses the same combinatorial part as the UNIQUAC equation. In terms of the activity coefficient:

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \quad [74]$$

$$\ln \gamma_i^C = \ln \frac{\Phi_i}{x_i} + \left(\frac{z}{2}\right) q_i \ln \frac{\theta_i}{\Phi_i} + \Phi_i \left(l_i - \frac{r_i}{r_j} l_j \right) \quad [75]$$

$$r_i = \sum_k v_{ki} R_k \quad [76]$$

$$q_i = \sum_k v_{ki} Q_k \quad [77]$$

The group R_k, and the group area Q_k have been tabulated for a large number of groups. v_{ki} is the number of groups of k kind in molecule i.

The residual contribution is expressed as follows:

$$\ln \gamma_i^R = \sum_k Q_k (\ln \Gamma_k - \ln \Gamma_k^{(i)}) \quad [78]$$

$$\ln \Gamma_k = Q_k (1 - \ln E_k - F_k) \quad [79]$$

$$\ln \Gamma_k^{(k)} = Q_k^{(i)} (1 - \ln E_k^{(i)} - F_k^{(i)}) \quad [80]$$

$$E_k = \theta_1 \psi_{1k} + \theta_2 \psi_{2k} + \theta_3 \psi_{3k} + \ldots \quad [81]$$

$$F_k = \frac{\theta_1 \psi_{k1}}{E_1} + \frac{\theta_2 \psi_{k2}}{E_2} + \frac{\theta_3 \psi_{k3}}{E_3} + \ldots \quad [82]$$

$$\theta_m = \frac{X_m Q_m}{\sum_n X_n Q_n} \quad [83]$$

$$\psi_{mn} = \exp\left(-\frac{a_{mn}}{T} \right) \quad [84]$$

$$X_m = \frac{\sum_i x_i v_{mi}}{\sum_i \left(x_i \sum_k v_{ki} \right)} \quad [85]$$

Since the group volume parameters R_k and the group area parameters Q_k are known, the only unknowns in the UNIFAC equations are the group interaction parameters a_{mn} and a_{nm}. These have been tabulated for a large number of groups. Moreover, updated parameters are published regularly in the literature. The UNIFAC method has been successfully applied to a wide variety of binary and multicomponent systems.

Examples of Use

Subcritical Vapour–Liquid Equilibria

Figure 4 shows the P–x–y behaviour of the methanol–water system at 313 K calculated using the activity coefficient approach. Activity coefficients were obtained from the Wilson equation using parameters $\Lambda_{12} = -449.3$ and $\Lambda_{21} = -835.9$ reported in DECHEMA data books. Fugacity coefficients in the vapour phase were assumed to be equal to 1.0. Note that the Wilson parameters were obtained by fitting the data, and therefore reproduce the experimental

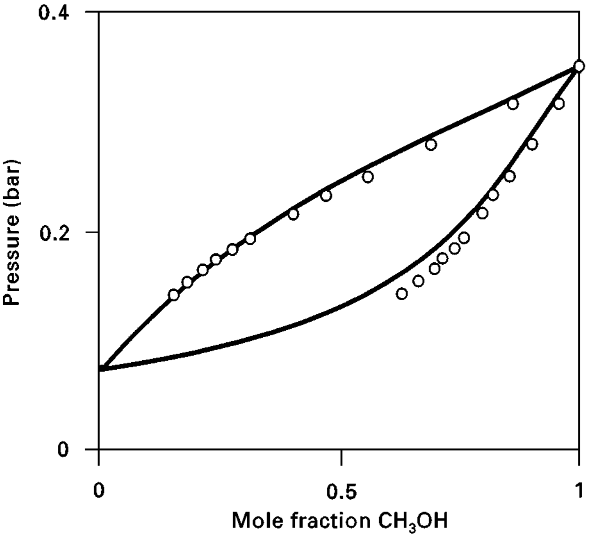

Figure 4 The P–x–y behaviour of methanol–water at 313 K correlated with the Wilson equation.

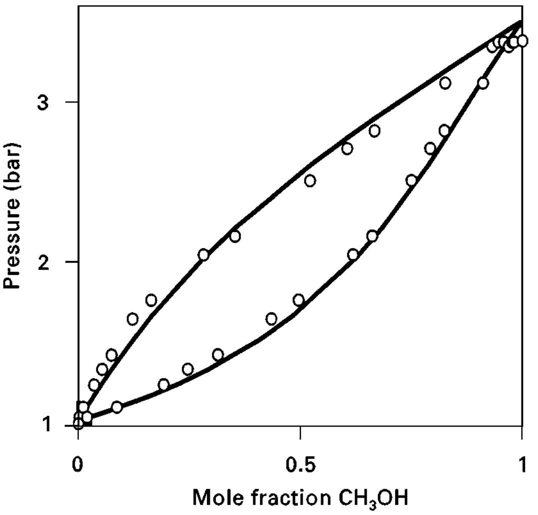

Figure 5 The *P–x–y* behaviour of methanol–water at 373 K predicted using Wilson equation constants obtained at 313 K.

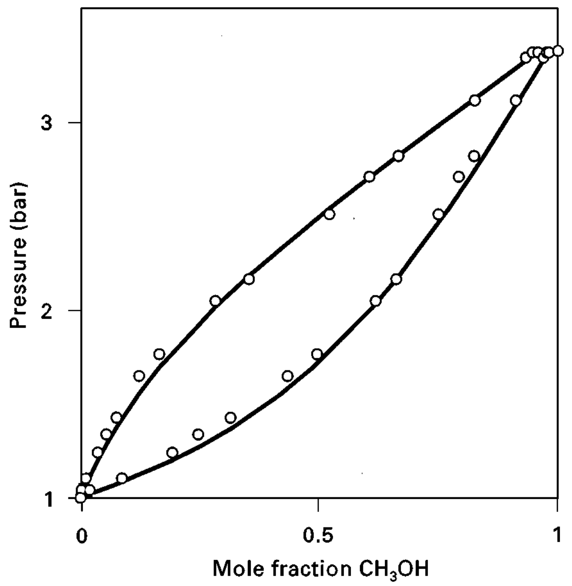

Figure 7 The *P–x–y* behaviour of methanol–water at 373 K predicted with Patel–Teja equation using binary parameters obtained at 313 K.

data (open circles) reasonably well in this system. **Figure 5** shows that when the same parameters are used to calculate VLE data for methanol–water at 373 K, good agreement is obtained with experimental data.

Figure 6 shows the *P–x–y* behaviour at 313 K of the same system correlated using the Patel–Teja equation of state. Two k_{ij} values were required to correlate the data ($k_{12} = -0.0923$ and $k_{21} = 0.0748$) and, in general, excellent agreement was obtained between calculated and experimental values. Moreover, the equation of state was successful in predicting data at 373 K using the same values of the k_{ij} parameters, as shown in **Figure 7**.

Supercritical Vapour–Liquid Equilibria

Figure 8 shows the *P–x–y* behaviour of the carbon dioxide–propane system at 328 K predicted using the equation of state approach with the Patel-Teja equation of state. The two binary interaction

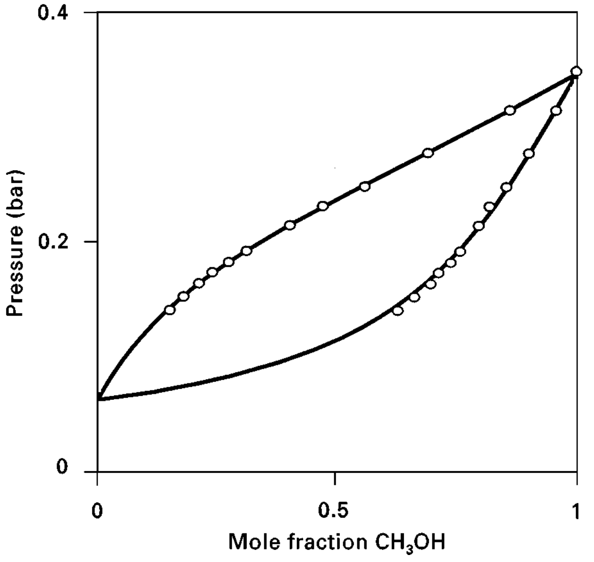

Figure 6 The *P–x–y* behaviour of methanol–water at 313 K correlated with the Patel–Teja equation.

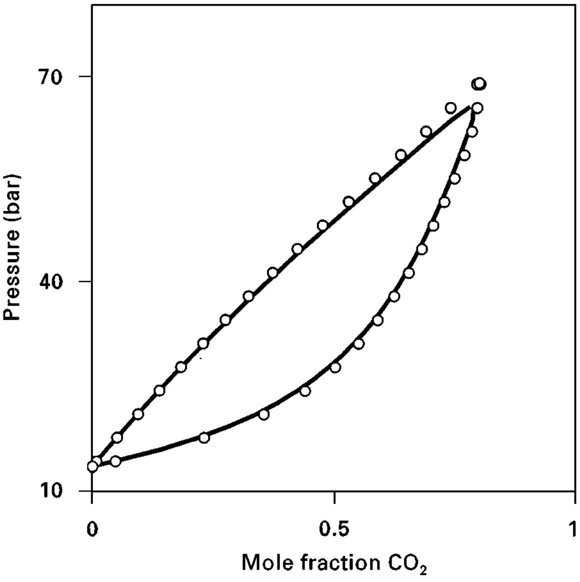

Figure 8 The *P–x–y* behaviour of CO_2–propane mixtures at 328 K predicted using the Patel–Teja equation of state with binary parameters obtained from data at 244 K.

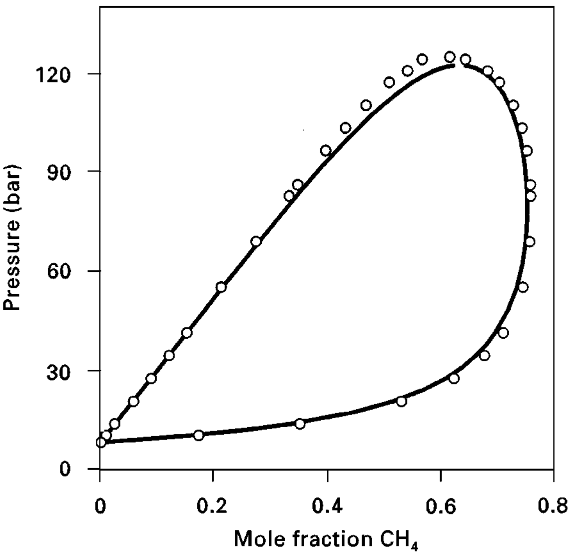

Figure 9 The *P–x–y* behaviour of methane-*n*-butane mixtures at 344 K predicted using the Patel–Teja equation of state with binary parameters obtained from data at 186 K.

parameters ($k_{12} = 0.143$ and $k_{21} = 0.121$) were obtained by fitting data at a much lower temperature of 244 K. The predictions are in excellent agreement with experiment, even though the extrapolation is to a temperature that is above the critical temperature of carbon dioxide (304 K). A similar extrapolation using the Patel–Teja equation of state is shown in **Figure 9** where VLE in the methane-*n*-butane system at 344 K have been predicted using binary parameters ($k_{12} = 0.021$ and $k_{21} = 0.002$) obtained at 186 K. Note that the extrapolation is carried out to a temperature that is well above the critical temperature of methane (190 K). Finally, it should be added that the activity coefficient approach described above cannot be used to correlate or predict supercritical VLE behaviour.

See also: **II/Distillation:** Historical Development; Modelling and Simulation; Multicomponent Distillation; Theory of Distillation; Vapour-Liquid Equilibrium: Correlation and Prediction.

Further Reading

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ELECTROPHORESIS

Agarose Gels

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Development

Agarose is a uniquely nonadhesive hydrocolloid that has found many uses in the separation sciences following Araki's preparation of it in 1937 as an apparently sulfate-free component distinct from the sulfate-rich agaropectin in agar. Agar and many of the other hydrocolloids derived from certain species of seaweed had been used mainly in food preparation dating back to the seventeenth century in Japan. Agar was introduced as a medium for immunoelectrophoresis by Grabar and Williams in 1953, and the original technique is occasionally used today. Citrated agar electrophoresis is the current principal method for identification of haemoglobin variants. Agar was