SRCC

Scientific Reviews
&
Chemical Communications

Sci. Revs. Chem. Commun.: 2(2), 2012, 158-171
ISSN 2277-2669

VAPOR LIQUID EQUILIBRIA: A REVIEW

MAYA B. MANE[*] and S. N. SHINDE

Master Student in Chemical Engineering, Chemical Engineering Department, Bharati Vidyapeeth Deemed University, College of Engineering, PUNE (M.S.) INDIA

(*Received : 30.05.2012; Revised : 03.06.2012; Accepted : 04.06.2012*)

ABSTRACT

Vapor-liquid equilibrium data may be readily evaluated and extended when they are calculated as activity coefficients. The equations proposed by Van Laar, Margulas, Wilson, NRTL and UNIQUAC, which express the activity coefficients of the components of a mixture as functions of the liquid composition and empirical constants, are capable of fitting most of the available vapor liquid equilibrium data. Equations of state play an important role in chemical engineering design and they have assumed an expanding role in the study of the phase equilibria of fluids and fluid mixtures.

Key words: VLE, Van Laar, Margulas, Wilson, NRTL, UNIQUAC, Equation of States.

INTRODUCTION

The term "Vapor-Liquid Equilibrium (VLE)" refers to systems in which a single liquid phase is in equilibrium with its vapor, schematic diagram of the vapor-liquid equilibrium is illustrated in Fig. 1. In studies of phase equilibrium, however, the phase containing gradients is not considered. Wherever gradients exist there is a tendency for change with time; hence there is no equilibrium. On the other hand, there can be two or more phases, each of which is homogenous throughout, with no tendency for any change in properties with time, even though the phases are in intimate physical contact with one another. The latter is the condition that we denote by the term "phase equilibrium". In a condition of phase equilibrium there are some properties that are drastically different between the phases and others that must be identical for all phases to prevent a change in properties within individual phases from occurring[1]. The thermodynamic equilibrium determines how components in a mixture are distributed between phases.

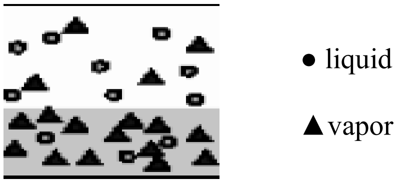

Fig. 1: Schematic diagrams illustrating the vapor-liquid equilibrium of binary system[1]

---

[*] Author for correspondence; E-mail: mayamane29@gmail.com, snshinde@bvucoep.edu.in;
Mo.: +91-7875089217; 91-8805001490

The system is in the equilibrium state, if only reversible process can occur in it.

This verbal formulation makes it possible mathematically to express the condition of equilibrium:

Let us consider a closed system on which a constant pressure is acting as the only external force. In an infinitesimal reversible process at constant temperature and pressure, the free enthalpy of this system does not change; hence at equilibrium we have –

$$dT = 0, \quad dP = 0, \quad dG = 0 \qquad \ldots(1)$$

where T is the absolute temperature, P the pressure and G the free enthalpy of the system. This formulation of the condition of equilibrium is sufficiently general for all cases with which we shall be concerned[2].

Vapour liquid equilibrium laws

Vapour liquid equilibria are best understood with the help of simple, empirical laws which may, however, only apply within certain limits.

Dalton's law

It describes the vapour phase:

$$p_i''/p_t'' = n_i''/n_t'' \qquad \ldots(2)$$

where p is the pressure and n the number of moles of substance. The subscript i denotes component i. since $n_i''/n_t'' = y_i$ (where y_i is the mole fraction of component i in the vapour).

This law generally holds low pressure ($p_t < p_{cr}$, where p_{cr} is the critical pressure). At higher pressure, however, it may require modification instead of using pressure p, the equation is written in terms of fugacity f:

$$f_i'' = y_i f_t'' \qquad \ldots(3)$$

Raoult's law

The liquid phase is described by Raoult's law giving a relation for the partial pressure p_i' of component i over a liquid mixture:

$$p_i' = x_i p_i^o \qquad \ldots(4)$$

According to Equation (4) the partial pressure p_i' depends only on the vapour pressure p_i^o of the pure component i and its liquid mole fraction x_i; it is not affected by the nature and concentration of other substances in the mixture. Raoult's law holds only as the forces of interaction between different types of molecules are equal (ideal mixture). Nonideal liquid phase behavior is described by using the activity coefficient γ_i which is defined as follows:

$$p_i' = \gamma_i x_i p_i^o \qquad \ldots(5)$$

Equations (4) and (5) are valid only for mole fractions. The activity coefficient γ_i is often called as "Raoult's law correction factor" and is highly concentration dependent. Eq. (4) and (5) apply only at temperatures below the critical temperature (T < T_{cr}).

Henry's law

At higher temperatures, Henry's law is applied instead of Raoult's law:

$$p_i' = H_{ij}x_i \qquad \text{…(6)}$$

Where H_{ij} is the Henry's coefficient for substance i in solvent j. Again, a correction must be made for nonideal mixtures by using the activity coefficient γ_i:

$$p_i' = H_{ij}\gamma_i x_i \qquad \text{…(7)}$$

This relationship is analogous to Raoult's law, except that the proportionality constant[3].

Vapour liquid equilibrium in ideal systems

(I) Binary systems

(a) At constant temperature

Let us first consider a system with the two constituents A and B; according to equation (4)

$$P_A = x_A p_A^o, \qquad \text{…(8)}$$

$$P_B = x_B p_B^o, \qquad \text{…(9)}$$

The total pressure, according to Dalton's law, is given by the sum of the partial pressures:

$$p = \mathrm{pA} + \mathrm{pB} = x_A p_A^o + x_B p_B^o \qquad \text{…(10)}$$

As the system is binary, it is possible to substitute (1-x_A) for x_B; after this modification:

$$P = x_A(p_A^o - p_B^o) + p_B^o) \qquad \text{…(11)}$$

Equation (11) states that the total pressure over an ideal solution is, at constant temperature, a linear function of composition.

According to Dalton's law we have for the vapour phase:

$$p_A = y_A p, \qquad \text{…(12)}$$

$$p_B = y_B p = (1 - y_A)p, \qquad \text{…(13)}$$

where y_A denotes the mole fraction of constituent A in the vapour phase and similarly for y_B.

It follows from the relations (8), (9), (12) and (13) that

$$y_A p = x_A p_A^o, \qquad \text{…(14)}$$

$$y_B p = x_B p_B^o, \qquad \text{…(15)}$$

On taking the ratio of these equations we find

$$\frac{y_A}{y_B} / \frac{x_A}{x_B} = \frac{y_A(1-x_A)}{x_A(1-y_A)} = \frac{p_A^o}{p_B^o} = \boldsymbol{\alpha}; \quad \ldots(16)$$

For an ideal solution α is a constant independent of the composition; it is called the relative volatility or enrichment ratio.

Equation (16) states that the ratio of the mole fractions of the constituents A and B in the vapour phase divided by the corresponding ratio in the liquid phase is constant.

From (11) and (12) it is possible after elimination of x_A to obtain a relation expressing the isothermal dependence of the total pressure on the composition of the vapour phase

$$p = \frac{p_A^o}{\boldsymbol{\alpha} - y_A(\boldsymbol{\alpha} - 1)'} \quad \ldots(17)$$

or

$$p = \frac{p_A^o p_B^o}{p_A^o - y_A(p_A^o - p_B^o)'} \quad \ldots(18)$$

The relation giving the dependence between the mole fraction of constituent A in the liquid phase and its mole fraction in the vapour phase is obtained from equation (18) by a simple rearrangement:

$$y_A = \frac{\boldsymbol{\alpha} x_A}{1 + x_A(\boldsymbol{\alpha} - 1)'} \quad \ldots(19)$$

(b) At constant pressure

Practically speaking however knowledge of the isobaric vapour-liquid equilibrium is more important. In this case we have by equation (14) -

$$p = p_A + p_B = x_A p_A^o(T) + (1 - x_A) p_B^o(T) \quad \ldots(20)$$

We write p_i^o(T) to emphasize that the vapour pressures of the pure constituent i dependes on the temperature, which in this case is not constant.

The relation giving the dependence between the compositions of the vapour and liquid phases is given by the equation –

$$y_A = \frac{x_A \boldsymbol{\alpha}(T)}{1 + x_A[\boldsymbol{\alpha}(T) - 1]} \quad \ldots(21)$$

α(T) = $p_A^o(T) / p_B^o(T)$ is generally speaking a function of temperature; however the ratio of the vapour pressures of the pure constituents varies but little in a short range of temperatures, so that α can often be considered as constant over the entire range of compositions.

(II) Multicomponent systems

In a multicomponent system containing an ideal liquid phase and a vapour phase that obeys the ideal gas laws, it is possible to derive relations similar to those for binary systems.

For an arbitrary constituent I we have

$$p_I = x_I p_I^o \qquad \text{…(22)}$$

$$y_I = \frac{p_I}{p} = \frac{x_I p_I^o}{\sum_{J=A}^{K} x_J p_J^o} \qquad \text{…(23)}$$

By division of the numerator and denominator of the right side of (23) by p_K^o we obtain after a simple rearrangement.

$$y_I = \frac{x_I \boldsymbol{\alpha}_{IK}}{1 + x_A(\boldsymbol{\alpha}_{IK} - 1) + x_B(\boldsymbol{\alpha}_{BK} - 1) + \ldots + x_{K-1}(\boldsymbol{\alpha}_{K-1,K} - 1)'} \qquad \text{…(24)}$$

where $\alpha_{IK} = {p_A^o}\big/{p_K^o}, \boldsymbol{\alpha}_{AK} = {p_A^o}\big/{p_K^o}$ etc.

Thus in a ternary system-

$$p_A = x_A p_A^o \qquad \text{…(25)}$$

$$p_B = x_B p_B^o, \qquad \text{…(26)}$$

$$p_C = x_C p_C^o, \qquad \text{…(27)}$$

$$p = x_A p_A^o + x_B p_B^o + (1 - x_A - x_B) p_C^o, \qquad \text{…(28)}$$

$$y_A = \frac{p_A}{p} = \frac{x_A p_A^o}{x_A p_A^o + x_B p_B^o + (1 - x_A - x_B) p_C^{o\prime}} \qquad \text{…(29)}$$

$$y_B = \frac{p_B}{p} = \frac{x_B p_B^o}{x_A p_A^o + x_B p_B^o + (1 - x_A - x_B) p_C^{o\prime}} \qquad \text{…(30)}$$

By division of numerator and denominator of the right sides of (29) and (30) by p_C^o and by substitution of $\boldsymbol{\alpha}_{AC} = p_A^o / p_C^o$ and $\boldsymbol{\alpha}_{BC} = p_B^o / p_C^o$ we obtain –

$$y_A = \frac{x_A \boldsymbol{\alpha}_{AC}}{1 - x_A(\boldsymbol{\alpha}_{AC} - 1) + x_B(\boldsymbol{\alpha}_{BC} - 1)} \qquad \text{…(31)}$$

$$y_B = \frac{x_B \boldsymbol{\alpha}_{BC}}{1 - x_A(\boldsymbol{\alpha}_{AC} - 1) + x_B(\boldsymbol{\alpha}_{BC} - 1)} \qquad \text{…(32)}$$

Strictly speaking, equations (31) and (32) are valid only at constant temperature; they can however be used for the case of constant pressure in many problems, since the ratio of the vapour pressures of the pure constituents is only weakly dependent on temperature, and the ranges of temperature that occur in distillation problems are frequently small[2].

Vapour liquid equilibrium in real systems

Deviations from ideal behavior are more likely to occur in the liquid phase than in the vapur phase. As a result of smaller intermolecular distances, the forces of interaction between molecules in the liquid are considerably stronger. In contrast, the vapur phase can be assumed to behave ideally at moderate pressure. At higher pressures, the vapur phase must be described by equation of state. The phase behavior of real liquids is usually described by means of the activity coefficient $\gamma^{2,3}$.

The method for calculating phase equilibrium in systems that are nonideal in liquid phase only is based on the activity coefficient models such as Margules, Van Laar, Wilson, NRTL, UNIQUAC and UNIFAC whereas at higher pressure, nonideality in vapor phase is described by equations of state.

Calculation of phase equilibrium from excess enthlpy

(1) Margules Equation

Max Margules introduced in 1895, a simple thermodynamic model for the excess Gibbs free energy of a liquid mixture. After Lewis had introduced the concept of the activity coefficient, the model could be used to derive an expression for the activity coefficients γ_i of a compound *i* in a liquid and the activity coefficient is a measure for the deviation from ideal solubility. In Chemical Engineering the Margules' Gibbs free energy model for liquid mixtures is better known as the Margules activity or activity coefficient model. Although the model is old it has the characteristic feature to describe extrema in the activity coefficient, while modern models like UNIQUAC, NRTL and Wilson cannot.

Margules expressed the excess Gibbs free energy of binary liquid mixtures is as follow,

$$\frac{g^E}{RT} = x_1 x_2 \left(A_{21} x_1 + A_{12} x_2\right) \qquad \ldots(33)$$

The activity coefficient of component i is found by differentiation of the excess Gibbs energy towards x_i. This yields, when applied only to the first term and using the Gibbs-Duhem equation,

$$\ln \gamma_1 = x_2^2 (A_{12} + 2(A_{21} - A_{12}) x_1) \qquad \ldots(34)$$

$$\ln \gamma_2 = x_1^2 (A_{21} + 2(A_{12} - A_{21}) x_2) \qquad \ldots(35)$$

In here A_{12} and A_{21} are constants which are equal to the logarithm of the limiting activity coefficients: $\ln \gamma_1^\infty$ and $\ln \gamma_2^\infty$ respectively[4].

(2) Van Laar Equation

The Van Laar equation is an activity model, which was developed by Johannes Van Laar in 1910-1913, to describe phase equilibria of liquid mixtures. The equation was derived from the Van der Waals equation. The original Van der Waals parameters didn't give good description of vapor-liquid phase equilibria, which forced the user to fit the parameters to experimental results. Because of this, the model lost the connection to molecular properties, and therefore it has to be regarded as an empirical model to correlate experimental results.

Van Laar expressed the excess Gibbs free energy of binary liquid mixtures is as follow,

$$\frac{g^E}{RT} = \frac{A_{12} x_1 x_2}{x_1 (A_{12} / A_{21}) + x_2} \qquad \ldots(36)$$

In here A_{12} and A_{21} are constants, which are obtained by regression of experimental vapor-liquid equilibria data.

The activity coefficient of component i is derived by differentiation to x_i. This yields:

$$\ln \gamma_1 = A_{12}\left(\frac{A_{21}x_2}{A_{12}x_{21} + A_{21}x_2}\right)^2 \qquad \ldots(37)$$

$$\ln \gamma_2 = A_{21}\left(\frac{A_{21}x_2}{A_{12}x_1 + A_{21}x_2}\right)^2 \qquad \ldots(38)$$

This shows that the constants A_{12} and A_{21} are equal to logarithmic limiting activity coefficients $\ln \gamma_1^\infty$ and $\ln \gamma_2^\infty$, respectively. The model gives increasing (A_{12} and $A_{21} > 0$) or only decreasing (A_{12} and $A_{21} > 0$) activity coefficients with decreasing concentration. The model can not describe extrema in the activity coefficient along the concentration range[5].

(3) Wilson Equation

Based on molecular considerations, Wilson (1964) presented the following expression for the excess Gibbs energy of a binary solution:

$$\frac{g^E}{RT} = -x_1 \ln (x_1 + A_{12}x_2) - x_2 \ln (x_2 + A_{21}x_1) \qquad \ldots(39)$$

Activity coefficients derived from this equation are –

$$\ln \gamma_1 = -\ln (x_1 + A_{12}x_2) + x_2 \left[\frac{A_{12}}{x_1 + A_{21}x_2} - \frac{A_{21}}{x_2 + A_{21}x_1}\right] \qquad \ldots(40)$$

$$\ln \gamma_2 = -\ln (x_2 + A_{21}x_1) - x_1 \left[\frac{A_{12}}{x_1 + A_{12}x_2} - \frac{A_{21}}{x_2 + A_{21}x_1}\right] \qquad \ldots(41)$$

In Equation (39) the excess Gibbs energy is defined with reference to an ideal solution in the sense of Raoult's law; Equation (39) obeys the boundary condition that g^E vanishes as either x_1 or x_2 becomes zero.

Wilson's equation has two adjustable parameters, A_{12} and A_{21}. In wilson derivation, these are related to the pure-component molar volumes and to characteristic energy differences by –

$$A_{12} = \frac{v_2}{v_1} \exp\left(-\frac{\lambda_{12} - \lambda_{11}}{RT}\right) \qquad \ldots(42)$$

$$A_{21} = \frac{v_1}{v_2} \exp\left(-\frac{\lambda_{21} - \lambda_{22}}{RT}\right) \qquad \ldots(43)$$

Wilson equation has two disadvantages that are not serious for many applications. First, Eqs. (40) and (41) are not useful for systems where the logarithms of the activity coefficients, when plotted against x, exhibits maxima or minima. (Van Laar equations are also not useful for this case). Such systems, however, are not common. The second and more serious disadvantage of Wilson's equation lies in its inability to predict limited miscibility. When Wilson's equation is substituted into the equations of thermodynamic stability for a binary system, no parameters A_{12} and A_{21} can be found that indicates the existence of two stable liquid phases. Wilson's equation, therefore, should be used only for liquid systems that are completely miscible or else for those limited regions of partially miscible systems where only one liquid phase is present.

For a solution of m components, Wilson's equation is –

$$\frac{g^E}{RT} = -\sum_{i=1}^{m} x_i \ln\left(\sum_{j=1}^{m} x_j A_{ij}\right) \qquad \text{…(44)}$$

Where

$$A_{\mathrm{ij}} = \frac{v_j}{v_i} \exp\left(-\frac{\lambda_{ij} - \lambda_{ii}}{RT}\right) \qquad \text{…(45)}$$

$$A_{\mathrm{ji}} = \frac{v_i}{v_j} \exp\left(-\frac{\lambda_{ji} - \lambda_{jj}}{RT}\right) \qquad \text{…(46)}$$

The activity coefficient for any component *k* is given by –

$$\ln \gamma_{\mathrm{k}} = -\ln\left(\sum_{j=1}^{m} x_j A_{kj}\right) + 1 - \sum_{i=1}^{m} \frac{x_i A_{ik}}{\sum_{j=1}^{m} x_j A_{ij}} \qquad \text{…(47)}$$

Equation (47) requires only parameters that can be obtained from binary data; for each possible binary pair in the multicomponent solution, two parameters are needed[6].

(4) NRTL Equation

The basic idea in Wilson's derivation of Eq. (39) follows from the concept of local composition. This concept was also used by Renon (1968) in his derivation of the NRTL (nonrandom, two-liquid) equation; however, Renon's equation, unlike Wilson's is applicable to partially miscible as well as completely miscible systems. The NRTL equation for the excess Gibbs energy is –

$$\frac{g^E}{RT} = x_1 x_2 \left(\frac{\tau_{21} G_{21}}{x_1 + x_2 G_{21}} + \frac{\tau_{21} G_{21}}{x_1 + x_2 G_{21}}\right) \qquad \text{…(48)}$$

Where

$$T_{12} = \frac{g_{12} - g_{22}}{RT} \qquad T_{21} = \frac{g_{21} - g_{11}}{RT} \qquad \text{…(49)}$$

$$G_{12} = \exp\left(-\alpha_{12}\tau_{12}\right) \qquad G_{21} = \exp\left(-\alpha_{12}\tau_{21}\right) \qquad \text{…(50)}$$

The significance of g_{ij} is similar to that of λ_{ij} in Wilson's equation; g_{ij} is an energy parameter characteristic of the *i-j* interaction. Parameter α_{12} is related to the non randomness in the mixture; when α_{12} is zero, the mixture is completely random and Eq. (48) reduces to the two-suffix Margules equation. The NRTL equation contains three parameters, but reduction of experimental data for a large number of binary systems indicates that α_{12} varies from about 0.20 to 0.47; when experimental data are scarce, the value of α_{12} can often be set arbitrary; a typical choice is $\alpha_{12} = 0.3$. From Eq. (48), the activity coefficients are –

$$\ln \gamma_1 = -\, x_2^2 \left[\tau_{21} \left(\frac{G_{12}}{x_1 + x_2 G_{21}} \right)^2 + \frac{\tau_{12} G_{12}}{(x_2 + x_1 G_{12})^2} \right] \qquad \ldots(51)$$

$$\ln \gamma_2 = -\, x_1^2 \left[\tau_{12} \left(\frac{G_{12}}{x_2 + x_1 G_{12}} \right)^2 + \frac{\tau_{21} G_{21}}{(x_1 + x_2 G_{21})^2} \right] \qquad \ldots(52)$$

For a solution of m components, the NRTL equation is –

$$\frac{g^E}{RT} = -\sum_{i=1}^{m} x_i \frac{\sum_{j=1}^{m} \tau_{ji} G_{li} x_j}{\sum_{l=1}^{m} G_{li} x_j} \qquad \ldots(53)$$

Where

$$T_{ji} \, \frac{g_{ji} - g_{ii}}{RT} \qquad \ldots(54)$$

$$G_{ji} = \exp\,(-\alpha_{ji}\tau_{ji}) \qquad (\alpha_{ji} = \alpha_{ij}) \qquad \ldots(55)$$

The activity coefficient for any component *i* is given by -

$$\ln \gamma_i = \frac{\sum_{j=1}^{m} \tau_{ji} G_{ji} x_j}{\sum_{l=1}^{m} G_{li} x_l} + \sum_{j=1}^{m} \frac{x_j G_{ij}}{\sum_{l=1}^{m} G_{lj} x_l} \left(\tau_{ij} - \frac{\sum_{j=1}^{m} x_r \tau_{rj} G_{rj}}{\sum_{l=1}^{m} G_{lj} x_l} \right) \qquad \ldots(56)$$

Equations (53) and (56) contain only parameters obtained from binary data[6].

(5) Uniquac Equation

A critical examination of the derivation of the NRTL equation shows that this equation, like those obtained from Wohl's expansion is more suitable for h^E than g^E (Renon and Prausnitz, 1969). Further, because experimental data for typical binary mixtures are usually not sufficiently plentiful or precise to yield three meaningful binary parameters, attempts were made (Abrams, 1975; Maurer 1978; Anderson, 1978; Kemeny and Rasmussen, 1981) to derive a two-parameter equation for g^E that retains at least some of the advantages of the equation of Wilson without restriction to completely miscible mixtures. Abrams derived an equation that in a sense, extends the quasichemical theory of Guggenheim for nonrandom mixtures to solutions containing molecules of different size. This extension was therefore called the universal quasi-chemical theory. The UNIQUAC equation for g^E consists of two parts, a combinatorial part that attempts to describe the dominant entropic contribution, and a residual part that is due primarily to intermolecular forces that are responsible for the enthalpy of mixing. The combinatorial part is determined only by the composition and by the sizes and shapes of the molecules; it requires only pure component data. The residual part, however, depend also on intermolecular forces; the two adjustable binary parameters, therefore, appear only in the residual part. The UNIQUAC equation is –

$$\frac{g^E}{RT} = \left(\frac{g^E}{RT} \right)_{combinatorial} + \left(\frac{g^E}{RT} \right)_{residal} \qquad \ldots(57)$$

For a binary mixture,

$$\left(\frac{g^E}{RT}\right)_{combinatorial} = x_1 \ln \frac{\phi_1^*}{x_1} + x_2 \ln \frac{\phi_2^*}{x_2} + \frac{z}{2}\left(x_1 q_1 \ln \frac{\theta_1}{\phi_1^*} + x_2 q_2 \ln \frac{\theta_2}{\phi_2^*} \right) \qquad \ldots(58)$$

$$\left(\frac{g^E}{RT}\right)_{residal} = x_1 q_1' \ln (\theta_1' + \theta_2' \tau_{21}) - x_2 q_2' \ln (\theta_2' + \theta_1' \tau_{12}) \qquad \ldots(59)$$

Where the coordination number z is set equal to 10. Segment fraction, ϕ^* and area fractions, θ and θ', are given by –

$$\phi_1^* = \frac{x_1 r_1}{x_1 r_1 + x_2 r_2} \qquad \phi_2^* = \frac{x_2 r_2}{x_1 r_1 + x_2 r_2} \qquad \ldots(60)$$

$$\theta_1^* = \frac{x_1 q_1'}{x_1 q_1' + x_2 q_2'} \qquad \theta_2' = \frac{x_1 q_2'}{x_1 q_1' + x_2 q_2'} \qquad \ldots(61)$$

Parameters *r, q* and *q*' are pure component molecular structure constants depending on molecular size and external surface areas.

For each binary mixture, there are two adjustable parameters, τ_{12} and τ_{21}. These, in turn, are given in terms of characteristic energies Δu_{12} and Δu_{21}, by –

$$\tau_{12} = \exp\left(-\frac{\Delta u_{12}}{RT}\right) = \exp\left(-\frac{\alpha_{12}}{T}\right) \qquad \ldots(62)$$

$$\tau_{21} = \exp\left(-\frac{\Delta u_{21}}{RT}\right) = \exp\left(-\frac{\alpha_{21}}{T}\right) \qquad \ldots(63)$$

For many cases, Eqs. (62) and (63) give the primary effect of temperature on τ_{12} and τ_{21} characteristic energies Δu_{12} and Δu_{21} are often only weakly dependent on temperature.

Activity coefficients γ_1 and γ_2 are given by –

$$\ln \gamma_1 = \ln \frac{\phi_1^*}{x_1} + \frac{z}{2} q_1 \ln \frac{\theta_2'}{\theta_1^*} + \theta_2^* \left(l_1 q_1 - \frac{r_1}{r_2} l_2 \right)$$

$$- q_2' \ln(\theta_1' + \theta_2' \tau_{21}) + \theta_2' q_1' \left(\frac{\tau_{21}}{\theta_1' + \theta_2' \tau_{21}} - \frac{\tau_{12}}{\theta_2' + \theta_1' \tau_{12}} \right) \qquad \ldots(64)$$

$$\ln \gamma_2 = \ln \frac{\phi_2^*}{x_2} + \frac{z}{2} q_2 \ln \frac{\theta_2'}{\theta_2^*} + \theta_2^* \left(l_2 - \frac{r_2}{r_1} l_2 \right)$$

$$- q_2' \ln (\theta_2' + \theta_1' \tau_{12}) + \theta_1' q_2' \left(\frac{\tau_{12}}{\theta_2' + \theta_1' \tau_{12}} - \frac{\tau_{21}}{\theta_1' + \theta_2' \tau_{21}} \right) \qquad \ldots(65)$$

Where

$$l_1 = \frac{z}{2}(r_1 - q_1) - (r_1 - {}_1) \qquad \text{…(66)}$$

$$l_2 = \frac{z}{2}(r_2 - q_2) - (r_2 - {}_1) \qquad \text{…(67)}$$

For a multicomponent system, the UNIQUAC equation for the molar excess Gibbs energy is given by the sum of –

$$\frac{g^E_{(combinatorial)}}{RT} = \sum_{i=1}^{m} x_i \ln\frac{\phi_i^*}{xi} + \frac{z}{2}\sum_{i=1}^{m} q_i x_i \ln\frac{\theta_i}{\phi_i^*} \qquad \text{…(68)}$$

and

$$\frac{g^E_{(residual)}}{RT} = -\sum_{i=1}^{m} q'_i x_i \ln\left(\sum_{i=1}^{m} q'_j \tau_{ji}\right) \qquad \text{…(69)}$$

Where segment fraction ϕ^* and area fractions θ and θ' are given by –

$$\phi_i^* = \frac{r_i x_i}{\sum_{j=1}^{m} r_j x_j} \qquad \theta_i = \frac{q_i x_i}{\sum_{j=1}^{m} q_j x_j} \qquad \theta'_i \frac{q'_i x_i}{\sum_{j=1}^{m} q'_i x_j} \qquad \text{…(70)}$$

and

$$\tau_{ij} = \exp\left(-\frac{a_{ij}}{T}\right) \text{ and } \tau_{ji} = \exp\left(-\frac{a_{ji}}{T}\right)$$

The coordination number *z* is set equal to 10. For any component *i*, the activity coefficient is given by -

$$\ln \gamma i = \ln\frac{\phi_i^*}{x_i} + \frac{z}{2} q_i \ln\frac{\theta_i}{\phi_i^* x_i} + l_i - \frac{\phi_i^*}{x_i}\sum_{j=1}^{m} x_j l_j - q'_i \ln\left(\sum_{j=1}^{m} \theta'_j \tau_{ji}\right) + q'_i$$

$$- q'_i \sum_{j=1}^{m} \frac{\theta_i \tau_{ij}}{\sum_{k=1}^{m} \theta'_k \tau_{kj}} \qquad \text{…(70)}$$

Equation (70) requires only pure component and binary parameters[6].

(6) UNIFAC Equation

UNIFAC provides a method for estimating activity coefficients in non electrolyte liquid mixtures. To use this method, no experimental data are required for the particular mixture of interest. In addition to the temperature and composition of the system, it is necessary only to know the molecular structure of every component in the mixture and the necessary group parameters. A large number of group-interaction parameters of different groups have been calculated.

The UNIFAC model is developed as a combination of the UNIQUAC (Universal Quasi-Chemical) model and the solution of functional groups concept.

The solution of functional groups concept is a flexible method with a large range of applicability. Instead of considering a liquid as a solution of molecules it is considered as a solution of groups where the groups are structural units or building blocks such as CH_3, OH, CH. These building blocks form the molecule. In the group contribution method it is assumed that a physical property of a fluid is the sum of the contributions made by the molecules' functional groups. So, the activity coefficients are determined by the properties of the groups rather than by the properties of the molecules.

$$\ln \gamma_i = \ln \gamma_i^c + \ln \gamma_i^R \quad \ldots(71)$$

C = combinatorial and R = Residual

I. Combinatorial Part: The combinatorial contribution is -

$$\ln \gamma_i^c = \ln\frac{\phi_i}{x_i} + \frac{z}{2} q_i \ln\frac{\theta i}{\phi i} + l_i - \frac{\phi i}{xi}\sum_j x_j l_j \quad \ldots(72)$$

Where,

$$l_i = \frac{z}{2}(r_i - q_i) - (r_i - 1); z = 10$$

$$\theta_i = \frac{q_i x_i}{\sum_j q_j x_j}; \quad \phi_i = \frac{r_i x_i}{\sum_j r_j x_j} \quad \ldots(74)$$

Pure-component parameters r_i and q_i are respectively measures of molecular van der Waals volumes and molecular surface areas. They are calculated as the sum of the group volume and group-area parameters, R_k and Q_k (Bondi, 1968).

$$r_i = \sum_k v_k^{(i)} R_k; q_i = \sum_k v_k^{(i)} Q_k \quad \ldots(75)$$

where $v_k^{(i)}$, always an integer, is the number of groups of type k in molecule i. Group parameters R_k and Q_k are obtained from Van der Waals group volumes and surface area V_k and A_k, given by Bondi (1968).

$$R_k = V_k/15.17; Q_k = A_k/(2.5*10\text{^}9) \quad \ldots(76)$$

II. Residual part:

The contribution from group interactions, the residual part, is assumed to be the sum of the individual contributions of each solute group in the solution less the sum of the individual contributions in the pure component environment.

$$\ln \gamma_i^R = \sum_{ks\ groups} v_k^{(i)}(\ln\Gamma_k - \ln\Gamma_k^{(i)} \quad \ldots(77)$$

All groups

Γ_k is the group residual activity coefficient and $\Gamma_k^{(i)}$ is the residual activity coefficient of group *k* in a reference solution containing only molecules of type *i*.

The individual group contributions in any environment containing groups of kinds 1,2, ...N are assumed to be only a function of group contributions and temperature.

$$\ln \Gamma_k = Qk\left[1 - \ln\left(\sum_m \theta_m \psi_{mk}\right) - \sum_m \frac{\theta_m \psi_{km}}{\sum_n \theta_n \psi_{nm}}\right] \quad \ldots(78)$$

$$\theta_m = \frac{Q_m X_m}{\sum_n Q_m X_m} ; X_m = \frac{\sum_i v_m^{(i)} x_i}{\sum_i \sum_k v_k^{(i)} x_i} \qquad \text{…(79)}$$

X_m is the fraction of group m in the mixture.

$$\Psi_{mn} = \exp\left(-\frac{U_{mn} - U_{nn}}{RT}\right) = \exp\left(-\frac{a_{mn}}{T}\right) \qquad \text{…(80)}$$

The group interaction parameter Ψ_{mn} is given in equation (81) where U_{mn} is the interaction energy between the groups m and n. Parameter a_{mn} is the group interaction parameter for groups m and n. There are two parameters for each group-group interaction, a_{mn} and a_{nm}, where $a_{mn} \neq a_{nm}$. The group interaction parameters are evaluated from experimental phase equilibria data.

The equation for Γ_k can also be used for calculating $\Gamma_k^{(i)}$ except that the group composition variable θ_k is changed to be the group fraction of group k in pure fluid i[7,8].

Calculation of phase equilibrium from equation of state

(1) Van der Waals Equation

The Van der Waals equation of state, proposed in 1873 (Rowlinson, 1988), was the first equation capable of representing vapor-liquid coexistence.

$$Z = \frac{v}{v-b} - \frac{a}{RT\,v} \qquad \text{…(81)}$$

where,

$$a = \frac{27R2T_{cr}^2}{64\, p_{cr}}; \qquad b = \frac{RT_{cr}}{8\, p_{cr}}$$

where Z is the compressibility factor $Z = pV / RT$; T is temperature, V is volume, p is the pressure, and R is the molar universal gas constant. The parameter a is a measure of the attractive forces between the molecules, and the parameter b is the volume occupied by the molecules. The and b parameters can be obtained from the critical properties of the fluid[9].

(2) Redlich Kwong Equation

The most important model for the modification of the Van der Waals equation of state is the Redlich-Kwong equation (Redlich and Kwong, 1949). It retains the original van der Waals hard-sphere term with the addition of a temperature- dependent attractive term[9,10].

$$Z = \frac{v}{v-b} - \frac{a}{RT^{3/2}(v+b)} \qquad \text{…(82)}$$

where, $a = 0.42748\, R^2\, T_{cr}^{2.5} / P_{cr}$; $b = 0.08664\, RT_{cr} / P_{cr}$

(3) Redlich Kwong Soave Equation

The success of the Redlich-Kwong equation has been the impetus for many further empirical improvements Soave (1972). Suggested replacing the term $a/a/T^{1.5}$ with a more general temperature-dependent term $a(T)$, that is –

$$Z = \frac{v}{v-b} - \frac{a(T)}{RT\,(v+b)} \qquad \ldots(83)$$

$$\text{where, } a(T) = 0.42748\ \frac{R^2T_{cr}^2}{p_{cr}}\boldsymbol{\alpha}(T)$$

$$\alpha(T) = \left(1 + (0.48 + 1.574\boldsymbol{\omega} - 0.176\,\boldsymbol{\omega}^2)\left(1 - \sqrt{T/T_{cr}}\right)\right)^2$$

$$b = 0.08664\ RT_{cr}/p_{cr}; \quad (\omega = \text{accentric factor})$$

To test the accuracy of Soave-Redlich-Kwong (SRK) equation, the vapor pressures of a number of hydrocarbons and several binary systems were calculated and compared with experimental data (Soave, 1972). In contrast to the original Redlich-Kwong equation, Soave's modification fitted the experimental curve well and was able to predict the phase behavior of mixtures in the critical region[9].

(4) Peng Robinson Equation

The Peng-Robinson (PR) equation of state slightly improves the prediction of liquid volumes and predicts a critical compressibility factor of $Z_c = 0.307$. Peng and Robinson (1976) gave examples of the use of their equation for predicting the vapor pressure and volumetric behavior of single-component systems, and the phase behavior and volumetric behavior of the binary, ternary, and multicomponent system and concluded that Eq. (84) can be used to accurately predict the vapor pressures of pure substances and equilibrium ratios of mixtures. The Peng-Robinson equation performed as well as or better than the Soave-Redlich-Kwong equation. Han et al. (1988) reported that the Peng-Robinson equation was superior for predicting vapor-liquid equilibrium in hydrogen and nitrogen containing mixtures.

$$Z = \frac{v}{v-b} - \frac{a(T)v}{RT\,(v(v+b)+b(v-b))} \qquad \ldots(84)$$

$$\text{where, } a(T) = 0.45724\ \frac{R^2T_{cr}^2}{p_{cr}}\boldsymbol{\alpha}(T)$$

$$\alpha(T) = \left(1 + (0.37464 + 1.54226\,\boldsymbol{\omega} - 0.26992\,\boldsymbol{\omega}^2)\left(1 - \sqrt{T/T_{cr}}\right)\right)^2$$

$$b = 0.0778\ RT_{cr}/p_{cr}; \quad (\omega = \text{accentric factor})$$

The Peng-Robinson and Soave-Redlich-Kwong equations are used widely in industry. The advantages of these equations are that they can accurately and easily represent the relation among temperature, pressure, and phase compositions in binary and multicomponent systems. They only require the critical properties and acentric factor for the generalized parameters[9].

CONCLUSION

In ideal system, activity coefficient is equal to one and Roult's, Dalton laws are used. Activity coefficient models are applicable to systems that are nonideal in the liquid phase and equations of state are effective to describe both the vapour and liquid phase but at high pressure. Therefore, activity coefficient models and equation of states are useful for phase equilibria in non-ideal system.

REFERENCES

1. R. N. Harold, Phase Equilibrium in Process Design, Wiley-Interscience Publisher, New York (1970).
2. Eduard Hala, Vapour Liquid Equilibrium, Pregamon Press, 3rd Edition, London (1967) pp. 3-24.
3. J. G. Stichlmair and J. R. Fair, Distillation Principles and Practice, Wiley-VCH (1998) pp. 6-69.
4. Harrison C. Carlson and Allan P. Colburn, Vapor-Liquid Equilibria of Nonideal Solutions, Ind. Eng. Chem., **34(5)**, 581-589 (1942).
5. J. D. Seader and Ernest J. Henley, Separation Process Principles, 2nd Ed., Wiley India (2001) pp. 52-53
6. J. M. Prausnitz, R. N. Lichtenhaler and E. G. de Azevedo, Molecular Thermodynamics of Fluid Phase Equilibria, 3rd Ed., Prentice-Hall (1999) pp. 258-291.
7. A. Bondi, Physical Prosperities of Molecular Crystals, Liquids and Glasses, Wiley, New York (1968).
8. Group-Contribution Estimation of Activity Coefficients in Nonideal Liquid Mixtures, AIChE Journal, **21(6)**, November, 1086-1099 (1975).
9. Ya Song Wei and Richard J. Sadus, Equations of State for the Calculation of Fluid-Phase Equilibria, AIChE Journal, **46(1)**, 169-196 (2000).
10. D. D. Fussfll and J. L. Yanosik, An Iterative Sequence for Phase-Equilibria Calculations Incorporating the Redlich-Kwong Equation of State, Soc. Petrol. Eng. J., 173-182 (1978).