

## CHAPTER II

### THEORY

In this chapter presents a general treatment of a class of solution properties known as excess properties. Of particular interest for vapor-liquid equilibrium is the excess Gibbs free energy and a related property, the activity coefficient. Two simple activity coefficient models (Wilson, and UNIQUAC) were presented in detail. All such models are empirical in nature and represent the activity coefficient of a component in a mixture in terms of an equation that contains a set of parameters. Finally, relations of heat of mixing to interaction parameters are discussed.

#### 2.1 Thermodynamic relations between excess properties

An excess property is defined as the difference between an actual property and the property that would be calculated at the same conditions of  $T$ ,  $P$ , and  $x$  by the equations for an ideal solution.

$$\begin{aligned} M^E &= M - M^{id} \\ &= \sum x_i M_i(T, P) + \Delta M - M^{id} \end{aligned} \quad (2.1)$$

where  $M^E$  and  $\Delta M$  are the excess solution property and the property change of mixing, respectively. For internal energy ( $U$ ), enthalpy ( $H$ ), volume ( $V$ ) and heat capacities ( $C_p$  and  $C_v$ ), the ideal property,  $M^{id}$ , is

$$M^{id} = \sum x_i M_i \quad (2.2)$$

For Gibbs free energy ( $G/R$ ) and entropy ( $S/R$ ), the ideal property is

$$M^{id} = \sum x_i M_i - \sum x_i \ln x_i \quad (2.3)$$

The excess Gibbs free energy property,  $G^E$ , is related to the activity coefficients of the components as follows.

$$\begin{aligned}\frac{G^E}{RT} &= \frac{\Delta G}{RT} - \sum x_i \ln x_i \\ &= \sum x_i \ln \hat{a}_i - \sum x_i \ln x_i \\ &= \sum x_i \ln \gamma_i\end{aligned}\quad (2.4)$$

where  $\hat{a}_i$  and  $\gamma_i$  are the activity and activity coefficient of component  $i$ .

The total derivative of  $(G^E/RT)$  for a binary mixture is

$$d\left[\frac{G^E}{RT}\right] = \left[\frac{\partial(G^E/RT)}{\partial T}\right]_{P,x_i} dT + \left[\frac{\partial(G^E/RT)}{\partial P}\right]_{T,x_i} dP + \sum \left[\frac{\bar{G}^E}{RT}\right] dx_i \quad (2.5)$$

where  $\bar{G}^E$  is the partial molar Gibbs free energy of component  $i$ . The derivative term,

$\left[\frac{\partial(G^E/RT)}{\partial T}\right]_{P,x_i}$  can be related to the excess enthalpy by thermodynamic identities.

$$\left[\frac{\partial(G^E/RT)}{\partial T}\right]_{P,x_i} = -\left[\frac{H^E}{RT^2}\right] \quad (2.6)$$

Equation (2.4) and (2.6) provides the following expression involving the activity coefficients:

$$H^E = -RT^2 \sum x_i \left(\frac{\partial \ln \gamma_i}{\partial T}\right)_{P,x} \quad (2.7)$$

## 2.2 Activity coefficient models

In order to represent activity coefficients as a function of temperature and composition at constant pressure, some kind of thermodynamic model is required.

Typical activity coefficient models contain parameters that are fitted to experimental data on binary mixtures.

The oldest of the models still in common use is that of Margules equations which amounts to representing the logarithm of the activity coefficient by a power series in composition for each component. A model with some theoretical basis, the van Laar equation, was based on van der Waals' equation of state and, although it can represent experimental data rather well when the two constants are treated as empirical parameters, its predictive capabilities are limited (Van Ness and Abbott, 1982). The modern development of activity coefficient models began with the work of Wilson (1964), in which he introduced the "local composition" model. Later developments include the Non Random Two Liquid model (NRTL) (Renon, and Prausnitz, 1968) and the UNIQUAC equations (Abrams, and Prausnitz, 1975).

The models that will be mentioned in this chapter are the Wilson and UNIQUAC models.

### 2.2.1 Wilson model

The model proposed by Wilson (1964) is based on the concept of local composition and leads to an expression for the Gibbs free energy from which the activity coefficients can be obtained. Wilson recognized that, in a mixture with specific interactions, the distribution of molecules is not purely random and that non-ideal mixing is associated with this fact. Consider a binary mixture of component 1 and 2 with bulk mole fractions  $x_1$  and  $x_2$ . The composition in the immediate vicinity of a molecule of species 1 will not usually be the same as the mean bulk composition. Instead, Wilson suggested that the local compositions  $x_{11}$  and  $x_{21}$  of components 1 and 2 around a molecule of species 1 are given by Boltzmann-weighted averages of the bulk mole fractions. Thus

$$\frac{x_{11}}{x_{21}} = \frac{x_1 \exp(-\epsilon_{11}/RT)}{x_2 \exp(-\epsilon_{21}/RT)} = \frac{x_1}{x_2} \exp(\lambda_{12}/RT) \quad (2.8)$$

where  $\varepsilon_{11}$  and  $\varepsilon_{21}$  are energies of interaction defined in a manner similar to the attractive part of the van der Waals potential (Assael, Trusler, and Tsolakis, 1996) and  $\lambda_{12} = \varepsilon_{21} - \varepsilon_{11}$ . As one might expect, the compositional ordering of the fluid is determined not by the absolute magnitude of the molecular interactions but by the difference between the like and unlike interactions.

Equation (2.8) is next used to evaluate the local volume fraction,  $z_1$ , of species 1 around itself, with the result

$$z_1 = \frac{x_{11}V_1}{x_{11}V_1 + x_{21}V_2} = \frac{x_1}{x_1 + \Lambda_{12}x_2} \quad (2.9)$$

where

$$\Lambda_{12} = V_{12} \exp\left(-\frac{\lambda_{12}}{RT}\right) \text{ and } V_{12} = \frac{V_2}{V_1}. \quad (2.10)$$

Here,  $V_1$  and  $V_2$  are respectively the partial molar volumes of species 1 and 2 in the liquid mixture.

In a similar manner, the local volume fraction  $z_2$  occupied by molecules of type 2 around a molecule of the same species is found to be

$$z_2 = \frac{x_{22}V_2}{x_{22}V_2 + x_{12}V_1} = \frac{x_2}{x_2 + \Lambda_{21}x_1} \quad (2.11)$$

where

$$\Lambda_{21} = V_{21} \exp\left(-\frac{\lambda_{21}}{RT}\right) \text{ and } V_{21} = \frac{V_1}{V_2}. \quad (2.12)$$

It should be noted that  $\Lambda_{ij}$  cannot be negative, that  $\Lambda_{11} = \Lambda_{22} = 1$ , and that, in general,  $\Lambda_{12} \neq \Lambda_{21}$ .

In order to obtain an expression for the excess Gibbs free energy of the mixture, Wilson employed the Flory-Huggins theory (Walas, 1985). Thus, the Wilson model becomes:

$$\frac{G^E}{RT} = -x_1 \ln(x_1 + \Lambda_{12}x_2) - x_2 \ln(\Lambda_{21}x_1 + x_2) \quad (2.13)$$

The activity coefficients are written

$$\left. \begin{aligned} \ln \gamma_1 &= -\ln(x_1 + x_2 \Lambda_{12}) + x_2 \left( \frac{\Lambda_{12}}{x_1 + x_2 \Lambda_{12}} - \frac{\Lambda_{21}}{x_2 + x_1 \Lambda_{21}} \right) \\ \ln \gamma_2 &= -\ln(x_2 + x_1 \Lambda_{21}) - x_1 \left( \frac{\Lambda_{12}}{x_1 + x_2 \Lambda_{12}} - \frac{\Lambda_{21}}{x_2 + x_1 \Lambda_{21}} \right) \end{aligned} \right\} \quad (2.14)$$

Generalized expressions for multi-component mixtures are given in Table 2.1 and may be used to obtain the activity coefficient of each component  $i$  in a mixture of  $n$  components provided that all the binary parameters  $\lambda_{ij}$  and the partial molar volumes are known. No additional parameters are required. Typically, partial molar volumes are approximated by the molar volume of the pure liquids and, provided that this is done consistently in both parameter determination and application, the results are generally satisfactory.

Table 2.1 The Wilson Model (1964)

	$\ln \gamma_i = 1 - \ln \left( \sum_{j=1}^n x_j \Lambda_{ij} \right) - \sum_{k=1}^n \frac{x_k \Lambda_{ki}}{\sum_{j=1}^n x_j \Lambda_{kj}} \quad (2.15)$
where	$\Lambda_{ij} = V_{ij} \exp \left( -\frac{\lambda_{ij}}{RT} \right) \quad V_{ij} = \frac{V_j}{V_i} \quad (2.16)$
and	$\Lambda_{ii} = \Lambda_{jj} = 1 \quad \Lambda_{ij} \neq \Lambda_{ji} \quad (2.17)$

In most cases, these parameters are assumed to be independent of temperature. The binary parameters  $\lambda_{12}$  and  $\lambda_{21}$  are usually determined by fitting either experimentally determined excess Gibbs free energies to Eq.(2.13) or experimentally determined

activity coefficients to Eqs.(2.14). In either case Eq.(2.16) is used to relate  $\lambda_{ij}$  and  $\Lambda_{ij}$ . Usually, results over a range of liquid compositions are employed and the optimum parameters found by a non-linear regression analysis.

The outstanding features of the Wilson equations include the generally superior representation of activity coefficients for both polar and non-polar mixtures, and the ability to treat multi-component systems with only binary parameters.

### 2.2.2 The UNIQUAC equations

The UNIQUAC (Universal Quasi-Chemical) equations, were developed by Abrams and Prausnitz (1975) and are based on a semi-theoretical approach to the mixture problem that includes a local composition model. It was also recognized that the non-ideality of liquid mixtures has contributions not only from specific interactions but also from the differences in the size and shape of the molecules. Consequently, in the UNIQUAC model, the excess Gibbs free energy of the mixture is correlated by the sum of two separate terms,

$$G^E / RT = (G_{con}^E + G_{res}^E) / RT \quad (2.18)$$

which comprise:

- a contribution  $G_{con}^E$ , known as the configurational term, due to differences in sizes and shapes; and
- a contribution  $G_{res}^E$ , known as the residual term, due to energetic interactions between the molecules.

Function  $G_{con}^E$  contains pure-species parameters only, whereas function  $G_{res}^E$  incorporates two binary parameters for each pair of molecules. For a multicomponent system,

$$G_{con}^E = \sum_i x_i \ln \frac{\phi_i}{x_i} + \frac{z}{2} \sum_i q_i x_i \ln \frac{r_i}{\phi_i} \quad (2.19)$$

and

$$G_{res}^E = -\sum_i q_i x_i \ln \left( \sum_i \theta_i' \tau_{ji} \right) \quad (2.20)$$

the following expressions for a binary mixture:

$$\left. \begin{aligned} G_{con}^E/RT &= x_1 \left[ \ln \left( \frac{\phi_1}{x_1} \right) + \frac{1}{2} q_1 z \ln \left( \frac{\theta_1}{\phi_1} \right) \right] + x_2 \left[ \ln \left( \frac{\phi_2}{x_2} \right) + \frac{1}{2} q_2 z \ln \left( \frac{\theta_2}{\phi_2} \right) \right] \\ G_{res}^E/RT &= -x_1 q_1' \ln(\theta_1' + \theta_2' \tau_{21}) - x_2 q_2' \ln(\theta_1' \tau_{12} + \theta_2') \end{aligned} \right\} \quad (2.21)$$

The quantities  $\phi_i$ ,  $\theta_i$  and  $\theta_i'$  which appear here are pure-substance parameters given by

$$\phi_i = \frac{x_i r_i}{x_1 r_1 + x_2 r_2}, \theta_i = \frac{x_i q_i}{x_1 q_1 + x_2 q_2}, \text{ and } \theta_i' = \frac{x_i q_i'}{x_1 q_1' + x_2 q_2'} \quad (2.22)$$

where  $r_i$  is volume parameter and  $q_i$  is surface area parameter for species  $i$ . Usually,  $q_i' = q_i$  so that  $\theta_i' = \theta_i$ .  $z$  is a co-ordination number to which the value 10 is usually, but not necessarily, assigned. Finally, the model contains two adjustable binary energy parameter  $u_{12}$  and  $u_{21}$  that enter the residual part of the excess Gibbs free energy through the quantities  $\tau_{12}$  and  $\tau_{21}$  which are defined by

$$\tau_{ij} = \exp \left( -\frac{u_{ij}}{RT} \right) = \exp \left( -\frac{a_{ij}}{T} \right) \quad (2.23)$$

Consequently, the logarithm of the activity coefficient for each component also has configurational and residual contributions:

$$\ln \gamma_i = \ln \gamma_i^{con} + \ln \gamma_i^{res} \quad (2.24)$$

The contributions to the activity coefficient of component  $i$  which result from this formulation are:



$$\left. \begin{aligned} \ln \gamma_i^{con} &= \ln \left( \frac{\phi_i}{x_i} \right) + \frac{z}{2} \ln \left( \frac{\theta_i}{\phi_i} \right) + \phi_j (l_i - r_i l_j / r_j) \\ \ln \gamma_i^{res} &= -q_i' \ln (\theta_i' + \theta_j' \tau_{ji}) + \theta_j' q_i' \left( \frac{\tau_{ji}}{\theta_i' + \theta_j' \tau_{ji}} - \frac{\tau_{ij}}{\theta_i' \tau_{ji} + \theta_j'} \right) \end{aligned} \right\} \quad (2.25)$$

where

$$l_i = \frac{z}{2} (r_i - q_i) - (r_i - 1). \quad (2.26)$$

The corresponding results for a multi-component system are given in Table 2.2. Table A.2 of Appendix A. gives values of the parameter  $r_i$ , and  $q_i$  for a selection of compounds.

Table 2.2 UNIQUAC Equations (Abrams and Prausnitz, 1975)

$$\ln \gamma_i = \ln \gamma_i^{con} + \ln \gamma_i^{res} \quad (2.27)$$

where

$$\ln \gamma_i^{con} = \ln \left( \frac{\phi_i}{x_i} \right) + \frac{z}{2} \ln \left( \frac{\theta_i}{\phi_i} \right) + l_i - \frac{\phi_i}{x_i} \sum_{j=1}^n x_j l_j \quad (2.28)$$

$$\ln \gamma_i^{res} = q_i' \left[ 1 - \ln \left( \sum_{k=1}^n \theta_k' \tau_{ki} \right) - \frac{\sum_{j=1}^n \theta_j' \tau_{ij}}{\sum_{k=1}^n \theta_k' \tau_{kj}} \right] \quad (2.29)$$

$$\text{and } \tau_{ij} = \exp \left( -\frac{u_{ij}}{RT} \right), \quad \tau_{ii} = \tau_{jj} = 1, \quad l_i = \frac{z}{2} (r_i - q_i) - (r_i - 1), \quad \text{and } z = 10 \quad (2.30)$$

$$\phi_i = \frac{x_i r_i}{\sum_{j=1}^n x_j r_j}, \quad \theta_i = \frac{x_i q_i}{\sum_{j=1}^n x_j q_j}, \quad \theta_i' = \frac{x_i q_i'}{\sum_{j=1}^n x_j q_j'} \quad (2.31)$$



### 2.3 Relations of heat of mixing to interaction parameters

The excess enthalpy is related to the derivatives of the activity coefficients with respect to temperature at constant pressure and composition leads to

$$H^E = -RT^2 \sum x_i \left( \frac{\partial \ln \gamma_i}{\partial T} \right)_{P,x} \quad (2.7)$$

In terms of the Wilson equation (Section 2.2.1), the needed relationship is developed with the following sequence of formulas:

$$\frac{\partial \Lambda_{12}}{\partial T} = \frac{\lambda_{12} \Lambda_{12}}{RT^2}, \quad \text{and} \quad \frac{\partial \Lambda_{21}}{\partial T} = \frac{\lambda_{21} \Lambda_{21}}{RT^2}, \quad (2.32)$$

so that

$$H^E = x_1 x_2 \left[ \frac{\lambda_{12} \Lambda_{12}}{x_1 + \Lambda_{12} x_2} + \frac{\lambda_{21} \Lambda_{21}}{\Lambda_{21} x_1 + x_2} \right] \quad (2.33)$$

which assumes that the  $\lambda_{ij}$  are constant.

When the UNIQUAC equation (Section. 2.2.2) is differentiated and substituted into Equation (2.7), assuming all parameters  $a_{ij}$  and  $a_{ji}$  to be independent of temperature, gives

$$H^E = R \left[ \frac{q_1 x_1}{\theta_1 + \theta_2 \tau_{21}} (\theta_2' \tau_{21} a_{21}) + \frac{q_2 x_2}{\theta_1' \tau_{12} + \theta_2} (\theta_1' \tau_{12} a_{12}) \right] \quad (2.34)$$

Equations (2.33) and (2.34) are simple because all parameters are assumed independent of temperature. In Table B.1 the complex expressions for excess enthalpy are given if parameters are taken to vary linearly with temperature.

## 2.4 Parameter estimation

In this work, The parameters of the activity coefficient model are determined by two approaches

### 2.4.1. Parameter estimation of the VLE data

In principle, two parameters in an activity coefficient model may be obtained from a pair of activity coefficients measured in a binary system at a single composition. Provided that due attention is paid to the possibility of multiple roots, the resulting parameters may permit useful predictions to be made over a range of compositions.

Here, two non-linear simultaneous equations must be solved for the two model parameters and the Newton-Raphson method is employed. For this method the partial derivatives of the two equations with respect to the unknown parameters are required.

For example, the Wilson parameters for the mixture will be found, given temperature, pressure, composition, and the activity coefficients. The Wilson equations are written in the forms,

$$f = \ln \gamma_1 + \ln(x_1 + \Lambda_{12}x_2) - x_2 \left( \frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2} \right) = 0, \quad (2.35)$$

$$g = \ln \gamma_2 + \ln(x_2 + \Lambda_{21}x_1) + x_1 \left( \frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2} \right) = 0. \quad (2.36)$$

The derivatives are

$$\frac{\partial f}{\partial \Lambda_{12}} = \Lambda_{12} \left( \frac{x_2}{x_1 + \Lambda_{12}x_2} \right)^2, \quad (2.37)$$

$$\frac{\partial f}{\partial \Lambda_{21}} = \left( \frac{x_2}{x_2 + \Lambda_{21}x_1} \right)^2, \quad (2.38)$$

$$\frac{\partial g}{\partial \Lambda_{12}} = \left( \frac{x_1}{x_1 + \Lambda_{12}x_2} \right)^2, \quad (2.39)$$

$$\frac{\partial g}{\partial \Lambda_{21}} = \Lambda_{21} \left( \frac{x_1}{x_2 + \Lambda_{21} x_1} \right)^2. \quad (2.40)$$

The Newton-Raphson equations for the corrections,  $h$  and  $k$ , to initial estimates of  $\Lambda_{12}$  and  $\Lambda_{21}$  are

$$f_0 + h \left( \frac{\partial f}{\partial \Lambda_{12}} \right)_0 + k \left( \frac{\partial f}{\partial \Lambda_{21}} \right)_0 = 0, \quad (2.41)$$

$$g_0 + h \left( \frac{\partial g}{\partial \Lambda_{12}} \right)_0 + k \left( \frac{\partial g}{\partial \Lambda_{21}} \right)_0 = 0. \quad (2.42)$$

where  $\Lambda_{y,0}$  is initial estimate. Require the values to be correct to 0.0001.

In addition, the UNIQUAC parameters for the binary systems are found by using the excess gibbs energy ( $G^E$ ) relation:

$$G^E = RT(x_1 \ln \gamma_1 + x_2 \ln \gamma_2) \quad (2.43)$$

The UNIQUAC equations are written in the forms

$$f = x_1 \ln \gamma_1 + x_2 \ln \gamma_2 - G_{con}^E - G_{res}^E \quad (2.44)$$

In equation 2.21, it can be observed that the interaction energy parameters are shown in the residual term. Then this term is differentiated with respect to UNIQUAC parameters.

The derivatives are

$$\frac{\partial f}{\partial \tau_{12}} = \frac{x_2 q_2 \theta_1'}{\theta_1' \tau_{12} + \theta_2'} \quad (2.45)$$

$$\frac{\partial f}{\partial \tau_{21}} = \frac{x_1 q_1 \theta_2'}{\theta_2' \tau_{21} + \theta_1'} \quad (2.46)$$

These parameter were found by means of the Newton method.

### 2.4.2. Parameter estimation of the $H^E$ model

The values for a set of parameters  $\{\theta_i\}$  were obtained through regression by a weighted least squares technique that minimized the objective function

$$S = \sum \left( \frac{H_{\text{exp}}^E - H_{\text{cal}}^E}{H_{\text{exp}}^E} \right)^2 \quad (2.47)$$

Newton Raphson solution of linearized equations is required to determine the best values of the parameters.

Equations (2.33) and (2.34) were employed in the evaluation of parameters in this investigation. The calculation procedure may be briefly outlined as follows:

1. For a given value of excess enthalpy, and the assumed values of parameters calculate excess enthalpy by means of Equation (2.33) which expressed in terms of the Wilson parameters.
2. Calculate the objective function (Equation 2.47).
3. Calculate derivatives of equation (2.33) with respect to parameters.
4. Substitute values obtained from step 1 through 3 into Newton Raphson 's equation and solve simultaneously for another set of roots of parameters.
5. Substitute new parameters from step 4 into Equation (2.33) and calculate new excess enthalpy and compare it with the experimental data

An iteration loop in Newton method is thus built up until the change of value of parameters is less than the specified tolerance. The final set of the parameter values is used to obtain activity coefficients values from Equations (2.14). The tolerance used in this investigation is 0.0001.

For UNIQUAC equation, substitute Equation (2.34) into Equation (2.33) and repeat the steps 1-5 finding the new values of UNIQUAC parameters. The activity coefficients in Equations (2.24) were determined using these new values.



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