

Nevertheless, there are some obvious limitations to the assumption of a constant packing fraction. A little calculation would make it clear that the λ for liquid propane at $T_r = 0.99$ is significantly larger than λ for toluene at $T_r = 0.619$. Thus, a mixture of propane and toluene at 366 K would not be very accurately represented by the Flory-Huggins theory. Note that deviations of λ from each other are related to differences in the compressibilities of the components. Thus, it is common to refer to Flory-Huggins theory as an “incompressible” theory and to develop alternative theories to represent “compressible” polymer mixtures. Not surprisingly, these alternative theories closely resemble the van der Waals’ equation (with a slightly modified temperature dependence of the a parameter). This observation lends added significance to Gibbs’ quote: “The whole is simpler than the sum of its parts” and to Rayleigh’s quote: “I am more than ever an admirer of van der Waals.”

11.6 LOCAL COMPOSITION THEORY

One of the major assumptions of regular solution theory was that the mixture interactions were independent of each other such that quadratic mixing rules would provide reasonable approximations as shown in Section 10.1 on page 322. But in some cases, like radically different strengths of attraction, the mixture interaction can be strongly coupled to the mixture composition. That is, for instance, the cross parameter could be a function of composition, $a_{12} = a_{12}(\mathbf{x})$. One way of treating this prospect is to recognize the possibility that the “local compositions” in the mixture might deviate strongly from the bulk compositions. As an example, consider a lattice consisting primarily of type A atoms but with two B atoms right beside each other. Suppose all these atoms were the same size and that the coordination number was 10. Then the local compositions around a B atom are $x_{AB} = 9/10$ and $x_{BB} = 1/10$ (notation of subscripts is $AB \Rightarrow$ “ A around B ”). Specific interactions such as hydrogen bonding and polarity might lead to such effects, and thus, the basis of the hypothesis is that *energetic differences lead to the nonrandomness that causes the quadratic mixing rules to break down*. Excess Gibbs models based on this hypothesis are termed local composition theories, and were first introduced by Wilson in 1964.¹ To develop the theory, we first introduce nomenclature to identify the local compositions summarized in Table 11.2

Table 11.2 Nomenclature for local composition variables.

Composition around a “1” molecule	Composition around a “2” molecule
x_{21} – mole fraction of “2’s” around “1”	x_{12} – mole fraction of “1’s” around “2”
x_{11} – mole fraction of “1’s” around “1”	x_{22} – mole fraction of “2’s” around “2”
local mole balance, $x_{11} + x_{21} = 1$	local mole balance, $x_{22} + x_{12} = 1$

We assume that the local compositions are given by some weighting factor, Ω_{ij} , relative to the overall compositions.

$$\frac{x_{21}}{x_{11}} = \frac{x_2}{x_1} \Omega_{21} \quad 11.64$$

1. Wilson, G.M., *J. Am. Chem. Soc.* 86:127 (1964).

$$\frac{x_{12}}{x_{22}} = \frac{x_1}{x_2} \Omega_{12} \quad 11.65$$

Therefore, if $\Omega_{12} = \Omega_{21} = 1$, the solution is random. Before introducing the functions that describe the weighting factors, let us discuss how the factors may be used.

Local Compositions around "1" molecules

Let us begin by considering compositions around "1" molecules. We would like to write the local mole fractions x_{21} and x_{11} in terms of the overall mole fractions, x_1 and x_2 . Using the local mole balance

$$x_{11} + x_{21} = 1 \quad 11.66$$

Rearranging Eqn. 11.64

$$x_{21} = x_{11} \frac{x_2}{x_1} \Omega_{21} \quad 11.67$$

Substituting 11.67 into 11.66

$$x_{11} \left(1 + \frac{x_2}{x_1} \Omega_{21} \right) = 1 \quad 11.68$$

Rearranging

$$x_{11} = \frac{x_1}{x_1 + x_2 \Omega_{21}} \quad 11.69$$

Substituting 11.69 into 11.67

$$x_{21} = \frac{x_2 \Omega_{21}}{x_1 + x_2 \Omega_{21}} \quad 11.70$$

Local Compositions around "2" molecules

Similar derivations for molecules of type "2" results in

$$x_{22} = \frac{x_2}{x_1 \Omega_{12} + x_2} \quad 11.71$$

$$x_{12} = \frac{x_1 \Omega_{12}}{x_1 \Omega_{12} + x_2} \quad 11.72$$

Example 11.12 Local compositions in a 2-dimensional lattice

The following lattice contains x's, o's and void spaces. The coordination number of each cell is 8. Estimate the local composition (x_{XO}) and the parameter Ω_{XO} based on rows and columns away from the edges.

		o		o		x		o	
	x		o	x			x		
	x		x	x		o	x	o	
o		x		o			x		
						o			x
	o		x		o			x	
		x		o		o		x	
o	x				x		x		o

Solution:

There are 9 o's and 13 x's that are located away from the edges. The number of x's and o's around each o are:

o#	1	2	3	4	5	6	7	8	9	
#x's	3	3	3	2	1	1	0	2	2	= 17
#o's	2	0	0	0	1	0	3	1	1	= 8
$x_{XO} = 17/25 = 0.68$; $x_o = 9/22$; $\Omega_{XO} = 17/8 \cdot 9/13 = 1.47$										= 1.47

Note: Fluids do not really behave as though their atoms were located on lattice sites, but there are many theories based on the supposition that lattices represent reasonable approximations. In this text, we have elected to omit detailed treatment of lattice theory on the basis that it is too approximate to provide an appreciation for the complete problem and too complicated to justify treating it as a simple theory. This is a judgment call and interested students may wish to learn more about lattice theory. Sandler presents a brief introduction to the theory which may be acceptable for readers at this level.¹

1. Sandler, S.I., *Chemical Engineering Thermodynamics*, 2nd ed, p. 366, Wiley, 1989.

Applying the Local Composition Concept to Obtain the Free Energy of Mixing

We need to relate the local compositions to the excess Gibbs energy. The perspective of representing all fluids by the square-well potential lends itself naturally to the local composition concept. Then the intermolecular energy is given simply by the local composition times the well-depth for that interaction. In equation form, the energy equation for mixtures can be reformulated in terms of local compositions. The local mole fraction can be related to the bulk mole fraction by defining a quantity Ω_{ij} as follows:

$$\frac{x_{ij}}{x_{jj}} \equiv \frac{x_i}{x_j} \Omega_{ij} \quad 11.73$$

The next step in the derivation requires scaling up from the molecular scale, local composition to the macroscopic energy in the mixture. The rigorous procedure for taking this step requires integration of the molecular distributions times the molecular interaction energies, analogous to the procedure for pure fluids as applied in Section 6.8. This rigorous development is presented below in Section 11.9. On the other hand, it is possible to simply present the result of that derivation for the time being. This permits a more rapid exploration of the practical implications of local composition theory. The form of the equation is not so difficult to understand from an intuitive perspective, however. The energy departure is simply a multiplication of the local composition (x_{ij}) by the local interaction energy (ϵ_{ij}). The departure properties are calculated based on a general model known as the *two-fluid theory*. According to the two-fluid theory, any intensive departure function in a binary is given by

$$(M - M^{ig}) = x_1(M - M^{ig})^{(1)} + x_2(M - M^{ig})^{(2)} \quad 11.74$$

Where the local composition environment of the type 1 molecules determines $(M - M^{ig})^{(1)}$, and the local composition environment of the type 2 molecules determines $(M - M^{ig})^{(2)}$. Note that $(M - M^{ig})^{(i)}$ is composition-dependent and is equal to the pure component value only when the local composition is pure i .

Noting that $\epsilon_{12} = \epsilon_{21}$, and recalling that the local mole fractions must sum to unity, we have for a binary mixture

$$U - U^{ig} = \frac{N_A}{2} [x_1 N c_1 (x_{11} \epsilon_{11} + x_{21} \epsilon_{21}) + x_2 N c_2 (x_{12} \epsilon_{12} + x_{22} \epsilon_{22})] \quad 11.75$$

where $N c_j$ is the coordination number (total number of atoms in the neighborhood of the j^{th} species), and where we can identify

$$(U - U^{ig})^{(1)} = \frac{N_A}{2} N c_1 (x_{11} \epsilon_{11} + x_{21} \epsilon_{21}) \quad \text{and} \quad (U - U^{ig})^{(2)} = \frac{N_A}{2} N c_2 (x_{12} \epsilon_{12} + x_{22} \epsilon_{22}) \quad 11.76$$

When x_1 approaches unity, x_2 goes to zero, and from Eqn. 11.64 x_{21} goes to zero, and x_{11} goes to one. The limit applied to Eqn. 11.75 results in $(U - U^{ig})_{pure1} = (N_A/2)Nc_1\epsilon_{11}$. Similarly, when x_2 approaches unity, x_1 goes to zero, x_{12} goes to zero, and x_{22} goes to one, resulting in $(U - U^{ig})_{pure2} = (N_A/2)Nc_2\epsilon_{22}$. For an ideal solution

$$(U - U^{ig})^{is} = x_1(U - U^{ig})_{pure1} + x_2(U - U^{ig})_{pure2} = \frac{N_A}{2}[x_1Nc_1\epsilon_{11} + x_2Nc_2\epsilon_{22}] \quad 11.77$$

The excess energy is obtained by subtracting Eqn. 11.77 from 11.75

$$U^E = U - U^{is} = \frac{N_A}{2}[x_1Nc_1((x_{11}\epsilon_{11} + x_{21}\epsilon_{21}) - \epsilon_{11}) + x_2Nc_2((x_{12}\epsilon_{12} + x_{22}\epsilon_{22}) - \epsilon_{22})] \quad 11.78$$

Collecting terms with the same energy variables, and using the local mole balance from Table 11.2 on page 381, $(x_{11}-1)\epsilon_{11} = -x_{21}\epsilon_{11}$, and $(x_{22}-1)\epsilon_{22} = -x_{12}\epsilon_{22}$, resulting in

$$U^E = \frac{N_A}{2} [x_1x_{21}Nc_1(\epsilon_{21} - \epsilon_{11}) + x_2x_{12}Nc_2(\epsilon_{12} - \epsilon_{22})] \quad 11.79$$

Substituting Eqn. 11.70 and Eqn. 11.72

$$U^E = \frac{N_A}{2} \left[\frac{x_1x_2\Omega_{21}Nc_1(\epsilon_{21} - \epsilon_{11})}{x_1 + x_2\Omega_{21}} + \frac{x_2x_1\Omega_{12}Nc_2(\epsilon_{12} - \epsilon_{22})}{x_1\Omega_{12} + x_2} \right] \quad 11.80$$

At this point, the traditional local composition theories deviate from regular solution theory in a way that really has nothing to do with local compositions. Instead, the next step focuses on one of the subtleties of classical thermodynamics. Recalling, $A = U - TS \Rightarrow A/RT = U/RT - S/R$

$$T \left(\frac{\partial(A/RT)}{\partial T} \right)_V = \frac{T}{RT} \left(\frac{\partial U}{\partial T} \right)_V - \frac{TU}{RT^2} - \frac{T}{R} \left(\frac{\partial S}{\partial T} \right)_V = \frac{C_V}{R} - \frac{U}{RT} - \frac{T}{R} \frac{C_V}{T} = -\frac{U}{RT} \quad 11.81$$

Therefore,

$$\int_{\infty}^T d \left(\frac{A^E}{RT} \right) = \frac{A^E}{RT} - \frac{A^E}{RT} \Big|_{\infty} = - \int_{\infty}^T \frac{U^E}{RT^2} dT \quad 11.82$$

where $A^E/(RT) \Big|_{\infty}$ is the infinite temperature limit at the given liquid density, independent of temperature but possibly dependent on composition or density. We need to insert Eqn 11.80 into Eqn 11.82 and integrate. We need to have some algebraic expression for the dependence of Ω_{ij} on temperature, which is what distinguishes the local composition theories from each other.

Wilson's Equation

Wilson made a bold assumption regarding the temperature dependence of Ω_{ij} . Wilson's original parameter used in the literature is Λ_{ji} , but it is related to Ω_{ij} in a very direct way. Wilson *assumes*,¹

$$\Omega_{ij} = \Lambda_{ji} = \frac{V_i}{V_j} \exp\left(\frac{-N_A N_{c_j}(\epsilon_{ij} - \epsilon_{jj})}{2RT}\right) = \frac{V_i}{V_j} \exp\left(\frac{-A_{ji}}{RT}\right) \quad 11.83$$

(note: $\Lambda_{ii} = \Lambda_{jj} = 1$, and $A_{ij} \neq A_{ji}$ even though $\epsilon_{ij} = \epsilon_{ji}$), and integration with respect to T becomes very simple. Assuming $N_{c_j} = 2$ for all j at all ρ ,

$$\frac{A^E}{RT} = -x_1 \ln(\Phi_1 + \Phi_2 \exp(-A_{12}/RT)) - x_2 \ln(\Phi_1 \exp(-A_{21}/RT) + \Phi_2) + \frac{A^E}{RT} \Big|_{\infty} \quad 11.84$$

A convenient simplifying assumption before proceeding further is that $G^E = A^E$. This corresponds to neglecting the excess volume of mixing relative to the other contributions and is really quite acceptable for liquids. The customary way of interpreting G^E/RT is to separate it into an energetic part known as the *residual* contribution, $(G^E/RT)^{RES}$, that vanishes at infinite temperature or when $\epsilon_{12} - \epsilon_{22} = 0$ and $\epsilon_{21} - \epsilon_{11} = 0$, and a size/shape part known as the *combinatorial* contribution, $(G^E/RT)^{COMB}$, that represents the infinite temperature limit at the liquid density. For Wilson's equation, the first two terms vanish at high T, so

$$(G^E/RT)^{RES} = -x_1 \ln(\Phi_1 + \Phi_2 \exp(-A_{12}/RT)) - x_2 \ln(\Phi_1 \exp(-A_{21}/RT) + \Phi_2) \quad 11.85$$

For the combinatorial contribution, Wilson used Flory's equation,

$$G^E/(RT) \Big|_{\infty} = (G^E/RT)^{COMB} = x_1 \ln(\Phi_1/x_1) + x_2 \ln(\Phi_2/x_2) \quad 11.86$$

It should be noted that the assumption of the temperature dependence of Eqn 11.83 has been made for convenience, but there is some justification for it, as we show in Section 11.9. Wilson's equation becomes

$$\frac{G^E}{RT} = -x_1 \ln\left(\Phi_1 + \Phi_2 \exp\left(\frac{-A_{12}}{RT}\right)\right) - x_2 \ln\left(\Phi_1 \exp\left(\frac{-A_{21}}{RT}\right) + \Phi_2\right) + x_1 \ln \frac{\Phi_1}{x_1} + x_2 \ln \frac{\Phi_2}{x_2} \quad 11.87$$

Algebraic rearrangement of Wilson's equation results in the form that is usually cited,

$$\boxed{\frac{G^E}{RT} = -x_1 \ln(x_1 + x_2 \Lambda_{12}) - x_2 \ln(x_1 \Lambda_{21} + x_2)} \quad 11.88$$

One limitation of Wilson's equation is that it is unable to model liquid-liquid equilibria, but it is reasonably accurate for modeling the liquid phase when correlating the vapor-liquid equilibria of many mixtures. Extending Eqn. 11.88 to a multicomponent solution,

$$\boxed{\frac{G^E}{RT} = -\sum_j x_j \ln\left(\sum_i x_i \Lambda_{ji}\right)} \Rightarrow \frac{G^E}{RT} = -\frac{1}{n} \sum_j n_j \ln\left(\sum_i \frac{n_i \Lambda_{ji}}{n}\right) \quad 11.89$$

1. Advanced readers may note that our definition of local compositions differs slightly from Wilson's. Wilson's original derivation combined the two-fluid theory of local compositions with an *ad hoc* "one-fluid" Flory equation. The same result can be derived more consistently using a two-fluid theory. The difference is that the local compositions are dependent on size as well as energies as defined by Eqns. 11.64, 11.65, and 11.83. This gives $x_{ij}/x_{jj} = (\Phi_i/\Phi_j) \exp(-A_{ji}/(RT))$ where the original was $x_{ij}/x_{jj} = (x_i/x_j) \exp(-A_{ji}/(RT))$.

$$\frac{G^E}{RT} = - \left[\sum_j n_j \ln \left(\sum_i n_i \Lambda_{ji} \right) - n \ln(n) \right] \quad 11.90$$

To determine activity coefficients, the excess Gibbs energy is differentiated. Differentiating the last term,

$$\left(\frac{\partial(n \ln n)}{\partial n_k} \right)_{T, P, n_{i, j \neq k}} = \ln n + 1$$

and letting “sum” stand for the summation of Eqn. 11.90

$$\left(\frac{\partial(\text{sum})}{\partial n_k} \right)_{T, P, n_{i, j \neq k}} = - \ln \left(\sum_i n_i \Lambda_{ki} \right) - \sum_j \left(\frac{n_j \Lambda_{jk}}{\sum_i n_i \Lambda_{ji}} \right)$$

combining,

$$\boxed{\ln \gamma_k = 1 - \ln \left(\sum_i x_i \Lambda_{ki} \right) - \sum_j \left(\frac{x_j \Lambda_{jk}}{\sum_i x_i \Lambda_{ji}} \right)} \quad 11.91$$

For a binary system, the activity coefficients from the Wilson equation are:

$$\ln \gamma_1 = 1 - \ln(x_1 \Lambda_{11} + x_2 \Lambda_{12}) - \frac{x_1 \Lambda_{11}}{x_1 \Lambda_{11} + x_2 \Lambda_{12}} - \frac{x_2 \Lambda_{21}}{x_1 \Lambda_{21} + x_2 \Lambda_{22}}$$

$$\ln \gamma_2 = 1 - \ln(x_1 \Lambda_{21} + x_2 \Lambda_{22}) - \frac{x_1 \Lambda_{12}}{x_1 \Lambda_{11} + x_2 \Lambda_{12}} - \frac{x_2 \Lambda_{22}}{x_1 \Lambda_{21} + x_2 \Lambda_{22}}$$

Noting that $\Lambda_{11} = \Lambda_{22} = 1$, and looking back at Eqn. 11.69 we can also see that for the first equation

$1 - \frac{x_1}{x_1 + x_2 \Lambda_{12}} = x_{21} = \frac{x_2 \Lambda_{12}}{x_1 + x_2 \Lambda_{12}}$. We can rearrange this expression to obtain the slightly more

compact relation:

$$\boxed{\ln \gamma_1 = - \ln(x_1 + x_2 \Lambda_{12}) + x_2 \left(\frac{\Lambda_{12}}{x_1 + x_2 \Lambda_{12}} - \frac{\Lambda_{21}}{x_1 \Lambda_{21} + x_2} \right)} \quad 11.92$$

Wilson's Equation.

Similar rearrangement of the second expression gives:

$$\boxed{\ln \gamma_2 = - \ln(x_1 \Lambda_{21} + x_2) - x_1 \left(\frac{\Lambda_{12}}{x_1 + x_2 \Lambda_{12}} - \frac{\Lambda_{21}}{x_1 \Lambda_{21} + x_2} \right)} \quad 11.93$$

$$\text{where } \Lambda_{12} = \frac{V_2}{V_1} \exp\left(\frac{-A_{12}}{RT}\right) \text{ and } \Lambda_{21} = \frac{V_1}{V_2} \exp\left(\frac{-A_{21}}{RT}\right) \quad 11.94$$

Example 11.13 Application of Wilson's equation to VLE

For the binary system *n*-pentanol(1) + *n*-hexane(2), the Wilson equation constants are $A_{12} = 1718$ cal/mol, $A_{21} = 166.6$ cal/mol. Assuming the vapor phase to be an ideal gas, determine the composition of the vapor in equilibrium with a liquid containing 20 mole% *n*-pentanol at 30°C. Also calculate the equilibrium pressure.

Given: $P_1^{sat} = 3.23$ mmHg; $P_2^{sat} = 187.1$ mmHg

Solution: From CRC, $\rho_1 = 0.8144$ g/ml (1mole/88g) $\Rightarrow V_1 = 108$ cm³/mole

$$\rho_2 = 0.6603 \text{ g/ml (1mole/86g)} \Rightarrow V_2 = 130 \text{ cm}^3/\text{mole}$$

Note: ρ_1 and ρ_2 are functions of T but $\rho_1/\rho_2 \approx \text{const.}$

$$V_2/V_1 = 1.205$$

utilizing Eqn. 11.94

$$\Lambda_{12} = 1.205 \exp(-1718/1.987/303) = 0.070$$

$$\Lambda_{21} = 1/1.205 \exp(-166.6/1.987/303) = 0.625$$

$$\begin{aligned} \frac{\Lambda_{12}}{x_1 + x_2 \Lambda_{12}} - \frac{\Lambda_{21}}{x_1 \Lambda_{21} + x_2} \\ = 0.070 / (0.2 + 0.8 \cdot 0.070) - 0.625 / (0.8 + 0.2 \cdot 0.625) \\ = -0.4022 \end{aligned}$$

$$\ln \gamma_1 = 1.0408 \Rightarrow \gamma_1 = 2.824$$

$$\ln \gamma_2 = 0.1584 \Rightarrow \gamma_2 = 1.172$$

$$P = (y_1 + y_2)P = x_1 \gamma_1 P_1^{sat} + x_2 \gamma_2 P_2^{sat} = 0.2 \cdot 2.824 \cdot 3.23 + 0.8 \cdot 1.172 \cdot 187.1 = 177.2 \text{ mmHg}$$

$$y_1 = x_1 \gamma_1 P^{sat} / P = 0.2 \cdot 2.824 \cdot 3.23 / 177.2 = 0.0103$$

! Bubble pressure calculation.

UNIQUAC¹

UNIQUAC (short for UNiversal QUAsi Chemical model) builds on the work of Wilson by making three primary refinements. First, the temperature dependence of Ω_{ij} is modified to depend on surface areas rather than volumes, based on the hypothesis that the interaction energies that determine local compositions are dependent on the relative surface areas of the molecules. If the parameter q_i is proportional to the surface area of molecule i ,

$$\Omega_{ij} = \frac{q_i}{q_j} \exp\left(\frac{-N_A z (\epsilon_{ij} - \epsilon_{jj})}{2RT}\right) = \frac{q_i}{q_j} \exp\left(\frac{-a_{ij}}{T}\right) = \frac{q_i}{q_j} \tau_{ij} \quad 11.95$$

1. Abrams, E.S., Prausnitz, J.M., *AIChE J.* 21:116 (1975).

where $z = 10$. The intermediate parameter τ_{ij} is used for compact notation.¹

$$\tau_{ij} = \exp\left(\frac{a_{ij}}{T}\right) \quad 11.96$$

where $\tau_{ii} = \tau_{jj} = 1$. In addition, when the energy equation 11.80 is written with $Nc_j = zq_j = 10q_j$ for all j at all ρ , the different sizes and shapes of the molecules are implicitly taken into account. Qualitatively, the number of molecules that can contact a central molecule increases as the size of the molecule increases. Using surface fractions attempts to recognize the branching and overlap that can occur between segments in a polyatomic molecule. The inner core of these segments is not accessible, only the surface is accessible for energetic interactions. Therefore, the model of the energy is proposed to be proportional to surface area. Unfortunately, it is not straightforward to construct a more rigorous argument in favor of surface fractions from the energy equation itself. Inserting Eqn. 11.95 and 11.80 into 11.82, the excess Helmholtz for a binary solution becomes

$$A^E/(RT) = -x_1q_1 \ln(\theta_1 + \theta_2\tau_{21}) - x_2q_2 \ln(\theta_1\tau_{12} + \theta_2) + A^E/(RT)\Big|_{\infty} \quad 11.97$$

where θ_i is the surface area fraction, and $\theta_i = x_iq_i/(x_1q_1 + x_2q_2)$ for a binary. Analogous to Wilson's equation, G^E is calculated as A^E , which is a good approximation. The first two terms represent $(G^E/RT)^{RES}$

$$(G^E/RT)^{RES} = -x_1q_1 \ln(\theta_1 + \theta_2\tau_{21}) - x_2q_2 \ln(\theta_1\tau_{12} + \theta_2) \quad 11.98$$

that can be compared with Eqn 11.85 and the final term represents $(G^E/RT)^{COMB}$. The $(G^E/RT)^{COMB}$ term is attributed to the entropy of mixing hard chains, and an approximate expression for this contribution is applied by Maurer and Prausnitz.² This representation of the entropy of mixing traces its roots back to the work of Staverman³ and Guggenheim⁴ and discussed more recently by Lichtenthaler et al.⁵ It is very similar to the Flory term, but it corrects for the fact that large molecules are not always large balls, but sometimes long "strings." By noting that the ratio of surface area to volume for a sphere is different from that for a string, Guggenheim's form (the form actually applied in UNIFAC and UNIQUAC) provides a simple but general correction, giving an indication of the degree of branching and non-sphericity. Nevertheless, the Staverman-Guggenheim term represents a relatively small correction to Flory's term. As shown in the Figure 11.7, the extra correction of including the "surface to volume" parameter serves to decrease the excess entropy to some value between zero and the Flory-Huggins estimate. The combinatorial part of UNIQUAC for a binary system takes the form

$$\left(\frac{G^E}{RT}\right)^{COMB} = \left(x_1 \ln \frac{\Phi_1}{x_1} + x_2 \ln \frac{\Phi_2}{x_2}\right) - 5 \left[q_1 x_1 \ln \left(\frac{\Phi_1}{\theta_1}\right) + q_2 x_2 \ln \left(\frac{\Phi_2}{\theta_2}\right) \right] \quad 11.99$$

that can be compared with 11.86.

1. Note that these assumptions create local compositions of the form $x_{ij}/x_{jj} = (\theta_i/\theta_j) \exp(-a_{ij}/T)$. Compare this with the form of Wilson's equation (footnote page 386). Note that the use of the subscripts for the local composition energetic parameters τ and a are switched for the UNIQUAC relative to the Wilson equation.

2. Maurer, G., Prausnitz, J.M., *Fluid Phase Equilibria*, 2:91 (1978).

3. Staverman, A.J., *Recl. Trav. Chem. Pays Bas*, 69:163 (1950).

4. Guggenheim, E.A., *Mixtures*, Oxford University Press, 1952.

5. Lichtenthaler, R.N., Abrams, D.S., Prausnitz, J.M., *Can. J. Chem.* 51:3071 (1973).

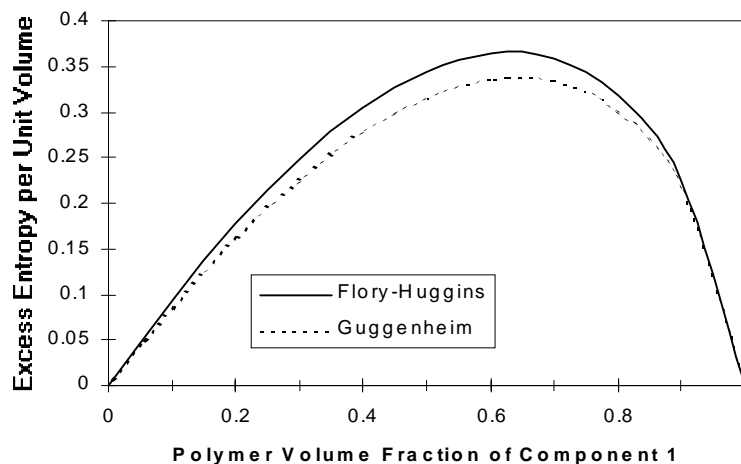


Figure 11.7 Excess entropy according to the Flory-Huggins equation vs. Guggenheim's equation at $V_2/V_1 = 1695$ for a polymer solvent mixture.

Instead of using experimental data to calculate volume fractions and surface fractions, they may be calculated from molecular size and surface area parameters that have been tabulated. The size parameters are ratios to the equivalent size for the $-\text{CH}_2-$ group in a long chain alkane. These parameters may be calculated in the same manner as the UNIFAC variation discussed in the next section as given in Table 11.3 on page 391. In the table, the uppercase R_k parameter is for the group volume, and the uppercase Q_k parameter is for group surface area. From these values, the molecular size (r_j) and shape (q_j) parameters may be calculated by multiplying the group parameter by the number of times each group appears in the molecule, and summing over all the groups in the molecule.

$$r_j = \sum_k v_k^{(j)} R_k; \quad q_j = \sum_k v_k^{(j)} Q_k; \quad 11.100$$

where $v_k^{(j)}$ is the number of groups of the k th type in the j th molecule. The subdivision of the molecule into groups is sometimes not obvious because there may appear to be more than one way to subdivide, but the conventions have been set forth in examples in the table and these conventions should be followed. The Guggenheim form of the excess entropy is based on the molecular volume fractions, Φ_j , and the surface fractions, θ_j ,

$$\Phi_j \equiv \frac{x_j r_j}{\sum_i x_i r_i} \quad \theta_j \equiv \frac{x_j q_j}{\sum_i x_i q_i} \quad 11.101$$

where R_k and Q_k are group contributions to the molecular parameters r_j and q_j .

Table 11.3 Group parameters for the UNIFAC and UNIQUAC equations. AC in the table means aromatic carbon. The Main groups serve as categories for similar Sub-groups as explained in the UNIFAC section.¹

Main Group	Sub-group	R(rel.vol.)	Q(rel.area)	Example
CH ₂	CH ₃	0.9011	0.8480	
	CH ₂	0.6744	0.5400	<i>n</i> -hexane: 4 CH ₂ + 2 CH ₃
	CH	0.4469	0.2280	isobutane: 1CH + 3 CH ₃
	C	0.2195	0	neopentane: 1C + 4 CH ₃
C=C	CH ₂ =CH	1.3454	1.1760	1-hexene: 1 CH ₂ =CH + 3 CH ₂ + 1 CH ₃
	CH=CH	1.1167	0.8670	2-hexene: 1 CH=CH + 2 CH ₂ + 2 CH ₃
	CH ₂ =C	1.1173	0.9880	
	CH=C	0.8886	0.6760	
	C=C	0.6605	0.4850	
ACH	ACH	0.5313	0.4000	benzene: 6 ACH
	AC	0.3652	0.1200	benzoic acid: 5 ACH + 1 AC + 1 COOH
ACCH ₂	ACCH ₃	1.2663	0.9680	toluene: 5 ACH + 1 ACCH ₃
	ACCH ₂	1.0396	0.6600	ethylbenzene: 5 ACH + 1 ACCH ₂ + 1 CH ₂
	ACCH	0.8121	0.3480	
OH	OH	1.0000	1.2000	<i>n</i> -propanol: 1 OH + 1 CH ₃ + 2 CH ₂
CH ₃ OH	CH ₃ OH	1.4311	1.4320	methanol is an independent group
water	H ₂ O	0.9200	1.4000	water is an independent group
furfural	furfural	3.1680	2.484	furfural is an independent group
DOH	(CH ₂ OH) ₂	2.4088	2.2480	ethylene glycol is an independent group
ACOH	ACOH	0.8952	0.6800	phenol: 1 ACOH + 5 ACH
CH ₂ CO	CH ₃ CO	1.6724	1.4880	dimethylketone: 1 CH ₃ CO + 1 CH ₃ methyl ethyl ketone: 1 CH ₃ CO + 1 CH ₂ + 1 CH ₃
	CH ₂ CO	1.4457	1.1800	diethylketone: 1 CH ₂ CO + 2 CH ₃ + 1 CH ₂
CHO	CHO	0.9980	0.9480	acetaldehyde: 1 CHO + 1 CH ₃
CCOO	CH ₃ COO	1.9031	1.7280	methyl acetate: 1 CH ₃ COO + 1 CH ₃
	CH ₂ COO	1.6764	1.4200	methyl propanate: 1 CH ₂ COO + 2 CH ₃
COOH	COOH	1.3013	1.2240	benzoic acid: 5 ACH + 1 AC + 1 COOH

The parameters to characterize the volume and surface area fractions have already been tabulated, so no more adjustable parameters are really introduced by writing it this way. The only real problem is that including all these group contributions into the formulas makes hand calculations extremely tedious. Fortunately, computers and hand calculators make this task much simpler. As such, we can apply the UNIQUAC method almost as easily as the van Laar method. We should also note, however, that using an equation of state is similarly simplified by using a computer, so the

1. Alcohols are usually treated in UNIQUAC without using the group contribution method. Accepted UNIQUAC values for the set of alcohols [MeOH, EtOH, 1-PrOH, 2-PrOH, 1-BuOH] are $r = [1.4311, 2.1055, 2.7799, 2.7791, 3.4543]$, $q = [1.4320, 1.9720, 2.5120, 2.5080, 3.0520]$. See Gmehling, J., Oken, U., Vapor-Liquid Equilibrium Data Collection, DECHEMA, Frankfurt, 1977-.

basic motivation for developing solution models specific to liquids is simultaneously undermined by requiring computers for implementation. From this perspective, what we should be doing is analyzing the mixing rules and models of interaction energies in equations of state if we intend to use a computer anyway. We return to this point in Unit IV, when we discuss hydrogen-bonding equations of state for non-ideal solutions.

Extending Eqn. 11.97 to a multicomponent solution, the UNIQUAC equation becomes

$$\frac{G^E}{RT} = \sum_j x_j \ln(\Phi_j/x_j) - 5 \sum_j q_j x_j \ln(\Phi_j/\theta_j) - \sum_j q_j x_j \ln \left(\sum_i \theta_i \tau_{ij} \right) \quad 11.102$$

Note that the leading term is simply Flory's equation. The second term is the correction for non-sphericity, so these terms are purely geometric. The first two terms are called the *combinatorial* terms to indicate their geometric significance for combining molecules of different shapes and sizes. The energetic parameters are included in the last term, which is called the *residual* term. Since the terms are linearly combined, the combinatorial and residual parts can be individually differentiated to find their contribution to the activity coefficients,

$$\ln \gamma_k = \ln \gamma_k^{COMB} + \ln \gamma_k^{RES} \quad 11.103$$

$$\ln \gamma_k^{COMB} = \ln(\Phi_k/x_k) + (1 - \Phi_k/x_k) - 5q_k [\ln(\Phi_k/\theta_k) + (1 - \Phi_k/\theta_k)] \quad 11.104$$

$$\ln \gamma_k^{RES} = q_k \left[1 - \ln \left(\sum_i \theta_i \tau_{ik} \right) - \sum_j \frac{\theta_j \tau_{kj}}{\sum_i \theta_i \tau_{ij}} \right] \quad 11.105$$

For a binary mixture, the activity equations become

$$\begin{aligned} \ln \gamma_1 = & \ln \frac{\Phi_1}{x_1} + \left(1 - \frac{\Phi_1}{x_1} \right) - 5q_1 \left[\ln \frac{\Phi_1}{\theta_1} + \left(1 - \frac{\Phi_1}{\theta_1} \right) \right] \\ & + q_1 \left[1 - \ln(\theta_1 + \theta_2 \tau_{21}) - \frac{\theta_1}{\theta_1 + \theta_2 \tau_{21}} - \frac{\theta_2 \tau_{12}}{\theta_1 \tau_{12} + \theta_2} \right] \end{aligned} \quad 11.106$$

$$\begin{aligned} \ln \gamma_2 = & \ln \frac{\Phi_2}{x_2} + \left(1 - \frac{\Phi_2}{x_2} \right) - 5q_2 \left[\ln \frac{\Phi_2}{\theta_2} + \left(1 - \frac{\Phi_2}{\theta_2} \right) \right] \\ & + q_2 \left[1 - \ln(\theta_1 \tau_{12} + \theta_2) - \frac{\theta_1 \tau_{21}}{\theta_1 + \theta_2 \tau_{21}} - \frac{\theta_2}{\theta_1 \tau_{12} + \theta_2} \right] \end{aligned} \quad 11.107$$

Like the Wilson equation, the UNIQUAC equation requires that two adjustable parameters be characterized from experimental data for each binary system. The inclusion of the excess entropy in UNIQUAC by Abrams et al. (1975) is more correct theoretically, but Wilson's equation can be as accurate as the UNIQUAC method for many binary vapor-liquid systems, and much simpler to apply by hand. UNIQUAC supersedes the Wilson equation for describing liquid-liquid systems,

however, because the Wilson equation is incapable of representing liquid-liquid equilibria as long as the Λ_{ij} parameters are held positive (as implied by their definition as exponentials, and noting that exponentials cannot take on negative values).¹

UNIFAC²

This is an extension of UNIQUAC with no adjustable parameters for the user to input or fit to experimental data. Instead, all of the adjustable parameters have been characterized by the developers of the model based on group contributions that correlate the data in a very large data base. The assumptions regarding coordination numbers, etc., are similar to the assumptions in UNIQUAC. The same strategy is applied,

$$\ln \gamma_k = \ln \gamma_k^{COMB} + \ln \gamma_k^{RES}$$

The combinatorial term is therefore identical and given by Eqn. 11.104. The major difference between UNIFAC (short for UNiversal Functional Activity Coefficient model) and UNIQUAC is that, *for the residual term*, UNIFAC considers interaction energies between *functional groups* (rather than the whole molecule). Interactions of functional groups are added to predict relative interaction energies of molecules. The large number of possible functional groups are divided into *main groups* and further subdivided into *subgroups*. Examples are shown in Table 11.3. Each of the subgroups has a characteristic size and surface area; however, the energetic interactions are considered to be the same for all subgroups with a particular main group. Thus, representative interaction energies (a_{ij}) are tabulated for only the main functional groups, and it is implied that all subgroups will use the same energetic parameters. An illustrative sample of values for these interactions is given in Table 11.4. Full implementations of the UNIFAC method with large numbers of functional groups are typically available in chemical engineering process design software. A subset of the

Table 11.4 VLE interaction energies a_{ij} for the UNIFAC equation in units of Kelvin.

Main Group, i	CH2 $j = 1$	ACH $j = 3$	ACCH2 $j = 4$	OH $j = 5$	CH3OH $j = 6$	water $j = 7$	ACOH $j = 8$	CH2CO $j = 9$	CHO $j = 10$	COOH $j = 20$
1,CH2	---	61.13	76.5	986.5	697.2	1318	1333	476.4	677	663.5
3,ACH	-11.12	---	167	636.1	637.3	903.8	1329	25.77	347.3	537.4
4,ACCH2	-69.7	-146.8	---	803.2	603.3	5695	884.9	-52.1	586.8	872.3
5,OH	156.4	89.6	25.82	---	-137.1	353.5	-259.7	84	-203.6	199
6,CH3OH	16.51	-50	-44.5	249.1	---	-181	-101.7	23.39	306.4	-202.0
7,water	300	362.3	377.6	-229.1	289.6	---	324.5	-195.4	-116.0	-14.09
8,ACOH	275.8	25.34	244.2	-451.6	-265.2	-601.8	---	-356.1	-271.1	408.9
9,CH2CO	26.76	140.1	365.8	164.5	108.7	472.5	-133.1	---	-37.36	669.4
10,CHO	505.7	23.39	106.0	529	-340.2	480.8	-155.6	128	---	497.5
20,COOH	315.3	62.32	89.86	-151	339.8	-66.17	-11.00	-297.8	-165.5	---

1. Another modification of the Wilson equation that can represent LLE is the NRTL model. See also Appendix D.

2. Fredenslund, Aa., Jones, R.L.; Prausnitz, J.M. *AIChE J.* 21:1086 (1975).

parameters is provided on the UNIFAC spreadsheet in the ACTCOEFF.xls spreadsheet included with the text. Knowing the values of these interaction energies permits estimation of the properties for a really impressive number of chemical solutions. The limitation is that we are *not always entirely sure of the accuracy* of these predictions.

Although UNIFAC is closely related to UNIQUAC, keep in mind that there is no direct extension to a correlative equation like UNIQUAC. If you want to fit experimental data that might be on hand, you cannot do it within the defined framework of UNIFAC; UNIQUAC is the preferred choice when adjustable parameters are desired. Although it is tedious to estimate the a_{ij} parameters of UNIQUAC from UNIFAC, some implementations of chemical engineering process design software have included facilities for estimating UNIQUAC parameters from UNIFAC. This approach can be useful for estimating interactions for a few binary pairs in a multicomponent mixture when most of the binary pairs are known from experimental data specific to those binary interactions.

The basic approach is the generalization of the residual activity coefficient. To understand the development of the predictive technique, imagine the interactions of a CH_3 group in a mixture of isopropanol (1) and component (2). The isopropanol consists of $2(\text{CH}_3) + 1(\text{CH}) + 1(\text{OH})$. Therefore, in the mixture, a CH_3 will encounter CH_3 , CH , OH groups, and the groups of component (2), and the interaction energies depend on the number of each type of group available in the solution. Therefore, the interaction energy of CH_3 groups can be calculated relative to a hypothetical solution of 100% CH_3 groups. The mixture can be approximated as a solution of groups (SOG)¹ (rather than a solution of molecules), and the interaction energies can be integrated with respect to temperature to arrive at chemical potential in a manner similar to the development of Eqns. 11.81 and 11.82.

Therefore, it is possible to calculate $\frac{\mu_{\text{CH}_3}^{\text{SOG}} - \mu_{\text{CH}_3}^o}{RT} = \ln \Gamma_{\text{CH}_3}$ where $\mu_{\text{CH}_3}^o$ is the chemical potential in a hypothetical solution of 100% CH_3 groups and Γ_{CH_3} is the activity coefficient of CH_3 in the solution of groups. The chemical potential of CH_3 groups in pure isopropanol (1), given by $\mu_{\text{CH}_3}^{(1)}$, will differ from $\mu_{\text{CH}_3}^o$ because even in pure isopropanol CH_3 will encounter a mixture of CH_3 , CH , and OH groups in the ratio that they appear in pure isopropanol, and therefore the activity coefficient of CH_3 groups in pure isopropanol, $\Gamma_{\text{CH}_3}^{(1)}$, is not unity, where the superscript (1) indicates pure component (1). The difference that is desired is the effect of mixing the CH_3 groups in isopropanol with component (2), relative to pure isopropanol,

$$\frac{\mu_{\text{CH}_3}^{\text{SOG}} - \mu_{\text{CH}_3}^{(1)}}{RT} = \frac{\mu_{\text{CH}_3}^{\text{SOG}} - \mu_{\text{CH}_3}^o}{RT} - \frac{\mu_{\text{CH}_3}^{(1)} - \mu_{\text{CH}_3}^o}{RT} = \ln \Gamma_{\text{CH}_3} - \ln \Gamma_{\text{CH}_3}^{(1)}$$

Fig. 11.8 provides an illustration of the differences that we seek to calculate, with water as a component (2).

1. A model exists in the literature that is called ASOG, which is different than the UNIFAC approach, but also uses functional groups.

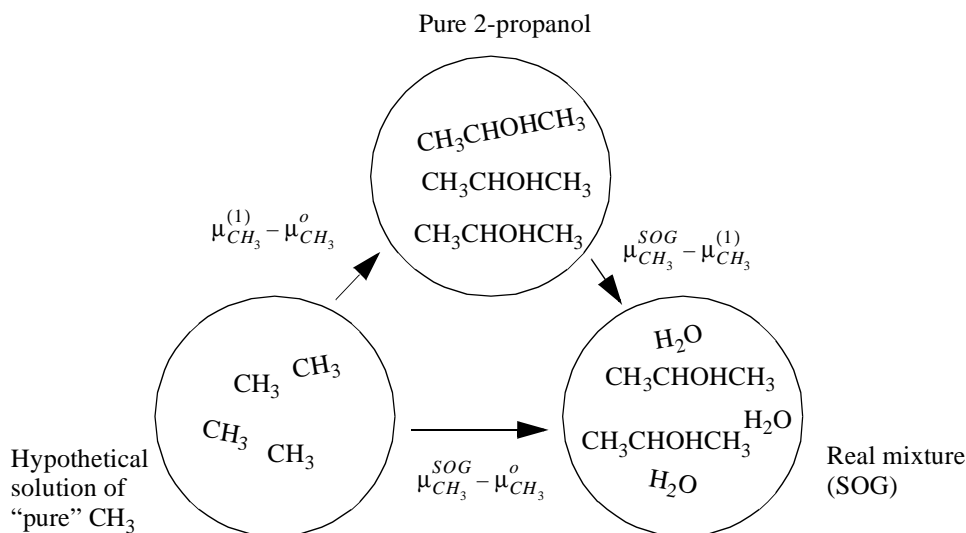


Figure 11.8 Illustration relating the chemical potential of CH_3 groups in pure 2-propanol, a real solution of groups where water is component (2), and a hypothetical solution of CH_3 groups. The number of groups sketched in each circle is arbitrary and chosen to illustrate the types of groups present. The chemical potential change that we seek is $\mu_{\text{CH}_3}^{\text{SOG}} - \mu_{\text{CH}_3}^{(1)}$. We calculate this difference by taking the difference between the other two paths.

If the chemical potential of a molecule consists of the sum of interactions of the groups,

$$\mu_1 = 2\mu_{\text{CH}_3}^{\text{SOG}} + \mu_{\text{CH}}^{\text{SOG}} + \mu_{\text{OH}}^{\text{SOG}}$$

$$\mu_1^o = 2\mu_{\text{CH}_3}^{(1)} + \mu_{\text{CH}}^{(1)} + \mu_{\text{OH}}^{(1)}$$

Therefore, we arrive at the important result that is utilized in UNIFAC,

$$\ln \gamma_1^{\text{RES}} = \frac{\mu_1 - \mu_1^o}{RT} = \sum_m v_m^{(1)} [\ln \Gamma_m - \ln \Gamma_m^{(1)}] \quad 11.108$$

where the sum is over all function groups in molecule (1) and $v_m^{(1)}$ is the number of occurrences of group m in the molecule. The activity coefficient formula for any other molecular component can be found by substituting for (1) in Eqn. 11.108. Note that Γ_m is calculated in a solution of groups for all molecules in the mixture, whereas $\Gamma_m^{(1)}$ is calculated in the solution of groups for just component (1). Note that we use uppercase letters to represent the group property analog of the molecular properties, with the following exceptions: uppercase τ looks too much like T , so we substitute Ψ , and the a_{ij} for UNIFAC is understood to be a group property even though the same symbol is represented by a molecular property in UNIQUAC. The relations are shown in Table 11.5.

Table 11.5 Comparison of group variables and molecular variables for UNIFAC.

	Group Variable	Molecular Variable
volume	R	r
surface area	Q	q
activity coefficient	Γ	γ
surface fraction	Θ	θ
energy variable	Ψ_{ij}	τ_{ij}
energy parameter	a_{ij}	a_{ij}
mole fraction	X	x

! UNIFAC.

$\ln \Gamma_m$ is calculated by generalizing the UNIQUAC expression for $\ln \gamma_m^{RES}$. Generalizing Eqn. 11.105 and supporting equations

$$\ln \Gamma_m = Q_m \left[1 - \ln \sum_i \Theta_i \Psi_{im} - \sum_j \frac{\Theta_j \Psi_{mj}}{\sum_i \Theta_i \Psi_{ij}} \right] \quad 11.109$$

$$\Theta_j = (\text{surface area fraction of group } j) \equiv \frac{X_j Q_j}{\sum_i X_i Q_i} \quad 11.110$$

$$\Psi_{mj} = \exp\left(\frac{-a_{mj}}{T}\right) \quad 11.111$$

$$X_j = \frac{\sum_{\text{molecules } i} v_j^{(i)} x_i}{\sum_{\text{molecules } i} \sum_{\text{groups } k} v_k^{(i)} x_i} \quad 11.112$$

where $v_k^{(i)}$ is the number of groups of type k in molecule i .

Example 11.14 Calculation of group mole fractions

Calculate the group mole fraction for CH₃ in a mixture of 60 mole% 2-propanol and 40 mole% water.

Solution: The two molecules are illustrated in Example 11.2 on page 360 and the group assignments are tabulated there. On a basis of 10 moles of solution, there are six moles of 2-propanol, and four moles of H₂O. The table below summarizes the totals of the functional groups.

Group	moles	X_j
CH ₃	12	0.429
CH	6	0.214
OH	6	0.214
H ₂ O	4	0.143
Σ	28	

The mole fraction of CH₃ groups is then $x_{CH_3} = 12/28 = 0.429$. The mole fractions of the other groups are found analogously and also summarized in the table. The results are consistent with Eqn. 11.112 which is more easily programmed,

$$X_{CH_3} = \frac{2(0.6) + 0(0.4)}{(2(0.6) + 1(0.6) + 1(0.6)) + (1(0.4))} = 0.429$$

Example 11.15 Detailed calculations of activity coefficients via UNIFAC

 Actcoeff.xls,
UNIFAC

Let's return to the example for the IPA + water system mentioned in Example 11.2. Compute the surface fractions, volume fractions, group interactions and the summations that go into the activity coefficients for this system at its azeotropic conditions. The isopropyl alcohol (IPA) + water (W) system is known to form an azeotrope at atmospheric pressure and 80.37°C ($x_W = 0.3146$).¹

Solution: (this calculation can be followed interactively in the UNIFAC spreadsheet):

The molecular size and surface area parameters are found by applying Eqn. 11.94. Isopropanol has 2 CH₃, 1 OH, and 1 CH group. The group parameters are taken from Table 11.3.

For IPA: $r = 2 \cdot 0.9011 + 0.4469 + 1.0 = 3.2491$; $q = 2 \cdot 0.8480 + 0.2280 + 1.2 = 3.124$

For water: $r = 0.920$; $q = 1.40$

At $x_W = 0.3146$, $\Phi_W = 0.1150$, and $\theta_W = 0.1706$

1. Perry, R.H., Chilton, C.H., *Chemical Engineers' Handbook*, 5 ed., Chapter 13, McGraw-Hill (1973).

Fortunately, the spreadsheet and calculator program save us from doing the tedious calculations for UNIFAC, although an understanding of the principles is important.

11.7 FITTING ACTIVITY MODELS TO DATA (OPTIONAL)

Fitting of the Margules and van Laar equations to limited data has been discussed in Examples 11.5, 11.6, and 11.7. Fits to multiple points are preferred, which requires regression of the parameters to optimize the fit.

Fitting of the van Laar Model

Eqn. 11.27 can be rearranged:

$$\frac{x_1 x_2 RT}{G^E} = \left(\frac{1}{A_{21}} - \frac{1}{A_{12}} \right) x_1 + \frac{1}{A_{12}} \quad 11.113$$

Therefore, if numerical values for the left-hand side are determined using G^E from experimental data as illustrated in Example 11.3 on page 363 and plotted versus x_1 , the slope will yield $\left(\frac{1}{A_{21}} - \frac{1}{A_{12}} \right)$, and the intercept will yield $\frac{1}{A_{12}}$. The value of $\frac{1}{A_{21}}$ can also be determined by the value at $x_1 = 1$. Sometimes plots of the data are non-linear when fitting is attempted. This does not necessarily imply that the data are in error. It implies that an alternative model may fit the data better. Another model that is easy to fit is the two-parameter Margules.

! van Laar and Margules models can be linearized for fitting of parameters.

Fitting the Margules equation

Eqn. 11.18 can be linearized:

$$\frac{G^E}{x_1 x_2 RT} = (A_{21} - A_{12}) x_1 + A_{12} \quad 11.114$$

Therefore, plotting $\frac{G^E}{x_1 x_2 RT}$ versus x_1 gives a slope of $(A_{21} - A_{12})$ and an intercept of A_{12} . The value of A_{21} can also be determined by the value at $x_1 = 1$.

! Non-linear parameter fitting is possible in Excel.

Alternative fitting techniques

Parameters for excess Gibbs models besides the van Laar and Margules equations are usually non-linearly related to G^E or γ . The Solver tool in EXCEL provides the capability for non-linear fitting techniques. These can be applied to the Wilson equation or the UNIQUAC equation as well as the

Example 11.15 Detailed calculations of activity coefficients via UNIFAC (Continued)

$$\ln \gamma_k^{COMB} = \ln(\Phi_k/x_k) + (1 - \Phi_k/x_k) - 5q_k[\ln(\Phi_k/\theta_k) + (1 - \Phi_k/\theta_k)]$$

$$\ln \gamma_W^{COMB} = \ln(\Phi_W/x_W) + (1 - \Phi_W/x_W) - 5q_W[\ln(\Phi_W/\theta_W) + (1 - \Phi_W/\theta_W)] = 0.10724$$

$$\ln \gamma_I = \ln(\Phi_I/x_I) + (1 - \Phi_I/x_I) - 5q_I[\ln(\Phi_I/\theta_I) + (1 - \Phi_I/\theta_I)] = -0.00204$$

Note that these combinatorial contributions are computed on the basis of the total molecule. This is because the space-filling properties are the same whether we consider the functional groups or the whole molecules.

For the residual term, we break the solution into a solution of groups. Then we compute the contribution to the activity coefficients arising from each of those groups. We have four functional groups altogether (2CH₃, CH, OH, H₂O). We will illustrate the concepts by calculating $\ln \Gamma_{CH_3}^{(1)}$ and simply tabulate the results for the remainder of the calculations since they are analogous. First, let us tabulate the energetic parameters we will need.

We can summarize the calculations in tabular form as follows:

$\Psi_{\text{row-col}}$	CH ₃	CH	OH	H ₂ O
CH ₃	1	1	0.061	0.024
CH	1	1	0.061	0.024
OH	0.642	0.642	1	0.368
H ₂ O	0.428	0.428	1.912	1

For pure isopropanol, we tabulate the mole fractions of functional groups, and calculate the surface fractions

j	$v_j^{(1)}$	X_j	Q_j	Θ_j
CH ₃	2	0.5	0.848	0.543
CH	1	0.25	0.228	0.073
OH	1	0.25	1.2	0.384
			$\sum_j X_j Q_j = 0.781$	

Example 11.15 Detailed calculations of activity coefficients via UNIFAC (Continued)

Applying Eqn. 11.109,

$$\ln \Gamma_{CH_3}^{(1)} = 0.848 \left\{ 1 - \ln[0.543 + 0.073 + 0.384(0.642)] - \frac{0.543}{0.543 + 0.073 + 0.384(0.642)} - \frac{0.073}{0.543 + 0.073 + 0.384(0.642)} - \frac{0.384(0.061)}{0.543(0.061) + 0.073(0.061) + 0.384} \right\} = 0.3205$$

The same type of calculations can be repeated for the other functional groups. The calculation of $\ln \Gamma_{H_2O}^{(2)}$ is not necessary, since the whole water molecule is considered a functional group.

Performing the calculations in the mixture, the mole fractions, X_j need to be recalculated to reflect the compositions of groups in the overall mixture. Table 11.6 summarizes the calculations.

Table 11.6 Summary of calculations for mixture of isopropanol and water at 80.37 °C and $x_w = 0.3146$.

	CH3 $j = 1$	CH $j = 2$	OH $j = 3$	H2O $j = 4$
Q_j	0.848	0.228	1.200	1.400
Θ_j	0.4503	0.0605	0.3186	0.1706
$\sum_i \Theta_i \Psi_{ij}$	0.7885	0.7885	0.6762	0.3000
$\ln \Gamma_j$	0.4641	0.1248	0.3538	0.6398
$\ln \Gamma_j^{(2)}$	Not Applicable	NA	NA	0
$\ln \Gamma_j^{(1)}$	0.3205	0.0862	0.5927	NA
$\ln \Gamma_j - \ln \Gamma_j^{(i)}$	0.1336	0.0386	-0.2388	0.6398

The pure component values of $\ln \Gamma_j^{(i)}$ can be easily verified on the spreadsheet after un hiding the columns with the intermediate calculations. Entering γ values of 0 and 1 for the respective molecular species mole fractions causes the values of $\ln \Gamma_j^{(i)}$ to be calculated. (Note that values will appear on the spreadsheet computed for infinite dilution activity coefficients of the groups which do not exist in the pure component limits, but these are not applicable to our calculation so we can ignore them.) Subtracting the appropriate pure component limits gives the final row in Table 11.6. All that remains is to combine the group contributions together to form the molecules, and to add the residual part to the combinatorial part.

$$\ln \gamma_I = \ln \gamma_{I, RES} + \ln \gamma_{I, COMB} = [2(0.1336) + 0.0386 - 0.2388] - 0.00204 = 0.0848; \gamma_I = 1.0885$$

$$\ln \gamma_W = \ln \gamma_{W, RES} + \ln \gamma_{W, COMB} = [0.6398] + 0.1072 = 0.7470; \gamma_W = 2.1108$$