van Laar Correlation

Another two-parameter excess Gibbs energy model was developed from an expansion of $(RTx_1x_2)/G^E$ instead of G^E/RTx_1x_2. The end results are:

$$\frac{G^E}{RTx_1x_2} = \frac{A'_{12}A'_{21}}{A'_{12}x_1 + A'_{21}x_2} \qquad (12.16)$$

for the excess Gibbs energy and:

$$\ln\gamma_1 = A'_{12}\left(1 + \frac{A'_{12}x_1}{A'_{21}x_2}\right)^{-2} \qquad (12.17a)$$

$$\ln\gamma_2 = A'_{21}\left(1 + \frac{A'_{21}x_2}{A'_{12}x_1}\right)^{-2} \qquad (12.17b)$$

for the activity coefficients.

Note that: as $x_1 \to 0$, $\ln\gamma_1^\infty \to A'_{12}$

and as $x_2 \to 0$, $\ln\gamma_2^\infty \to A'_{21}$

Example 2 (Problem 5, Practice Problem Set #4)

P5. Vapour liquid data for the system 1,4 dioxane(1)/ethylbenzene(2) at 85 ^{o}C are provided below. From these data obtain estimates of the van Laar coefficients (estimates based on smoothly drawn curves on the enclosed graph paper are sufficient). Estimate values of P-x_1-y_1 for x_1=0.5 based on these parameter values.

Table 2: VLE data for the system 1,4 dioxane/ethylbenzene at 85 ^{o}C

P (kPa)	x_1	y_1
20.2	0	0
23.4	0.065	0.15
35.2	0.29	0.55
41.6	0.44	0.7
52.4	0.78	0.91
57.8	1	1

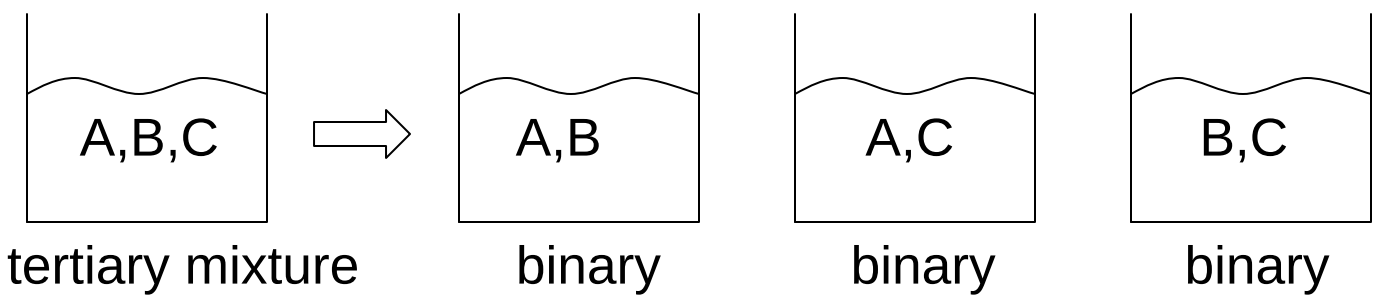
Local Composition Models

Unfortunately, the previous approach cannot be extended to systems of 3 or more components. For these cases, local composition models are used to represent multi-component systems.

- Wilson's Theory
- Non-Random-Two-Liquid Theory (NRTL)
- Universal Quasichemical Theory (Uniquac)

While more complex, these models have two advantages:

- the model parameters are temperature dependent
- the activity coefficients of species in multi-component liquids can be calculated using information from binary data.



Wilson's Equations for Binary Solution Activity

A versatile and reasonably accurate model of excess Gibbs Energy was developed by Wilson in 1964. For a binary system, G^E is provided by:

$$\frac{G^E}{RT} = x_1 \ln(x_1 + x_2\Lambda_{12}) - x_2 \ln(x_2 + x_1\Lambda_{21}) \qquad (12.18)$$

where

$$\Lambda_{12} = \frac{V_2}{V_1}\exp\left[\frac{-a_{12}}{RT}\right] \qquad \Lambda_{21} = \frac{V_1}{V_2}\exp\left[\frac{-a_{21}}{RT}\right] \qquad (12.24)$$

V_i is the molar volume at T of the pure component *i*.
a_{ij} is determined from experimental data.

The notation varies greatly between publications. This includes,

- $a_{12} = (\lambda_{12} - \lambda_{11})$, $a_{21} = (\lambda_{12} - \lambda_{22})$ that you will encounter in Holmes, M.J. and M.V. Winkle (1970) *Ind. Eng. Chem.* **62**, 21-21.

Wilson's Equations for Binary Solution Activity

Activity coefficients are derived from the excess Gibbs energy using the definition of a partial molar property:

$$RT\ln\gamma_i = \overline{G}_i^E = \left.\frac{\partial nG^E}{\partial n_i}\right|_{T,P,n_j}$$

When applied to equation 11.16, we obtain:

$$\ln\gamma_1 = -\ln(x_1 + x_2\Lambda_{12}) + x_2\left(\frac{\Lambda_{12}}{x_1 + x_2\Lambda_{12}} - \frac{\Lambda_{21}}{x_2 + x_1\Lambda_{21}}\right) \quad (12.19a)$$

$$\ln\gamma_2 = -\ln(x_2 + x_1\Lambda_{21}) - x_1\left(\frac{\Lambda_{12}}{x_1 + x_2\Lambda_{12}} - \frac{\Lambda_{21}}{x_2 + x_1\Lambda_{21}}\right) \quad (12.19b)$$

Wilson's Equations for Multi-Component Mixtures

The strength of Wilson's approach resides in its ability to describe multi-component (3+) mixtures using binary data.

- Experimental data of the mixture of interest (ie. acetone, ethanol, benzene) is not required
- We only need data (or parameters) for acetone-ethanol, acetone-benzene and ethanol-benzene mixtures

The excess Gibbs energy for multicomponent mixtures is written:

$$\frac{G^E}{RT} = -\sum_i x_i \ln(\sum_j x_j \Lambda_{ij}) \qquad (12.22)$$

and the activity coefficients become:

$$\ln \gamma_i = 1 - \ln \sum_i x_j \Lambda_{ij} - \sum_k \frac{x_k \Lambda_{ki}}{\sum_j x_j \Lambda_{kj}} \qquad (12.23)$$

where Λ_{ij} = 1 for i=j. Summations are over all species.

Wilson's Equations for 3-Component Mixtures

For three component systems, activity coefficients can be calculated from the following relationship:

$$\ln\gamma_i = 1 - \ln(x_1\Lambda_{i1} + x_2\Lambda_{i2} + x_3\Lambda_{i3}) - \frac{x_1\Lambda_{1i}}{x_1 + x_2\Lambda_{12} + x_3\Lambda_{13}} - \frac{x_2\Lambda_{2i}}{x_1\Lambda_{21} + x_2 + x_3\Lambda_{23}} - \frac{x_3\Lambda_{3i}}{x_1\Lambda_{31} + x_2\Lambda_{32} + x_3}$$

Model coefficients are defined as (Λ_{ij} = 1 for i=j):

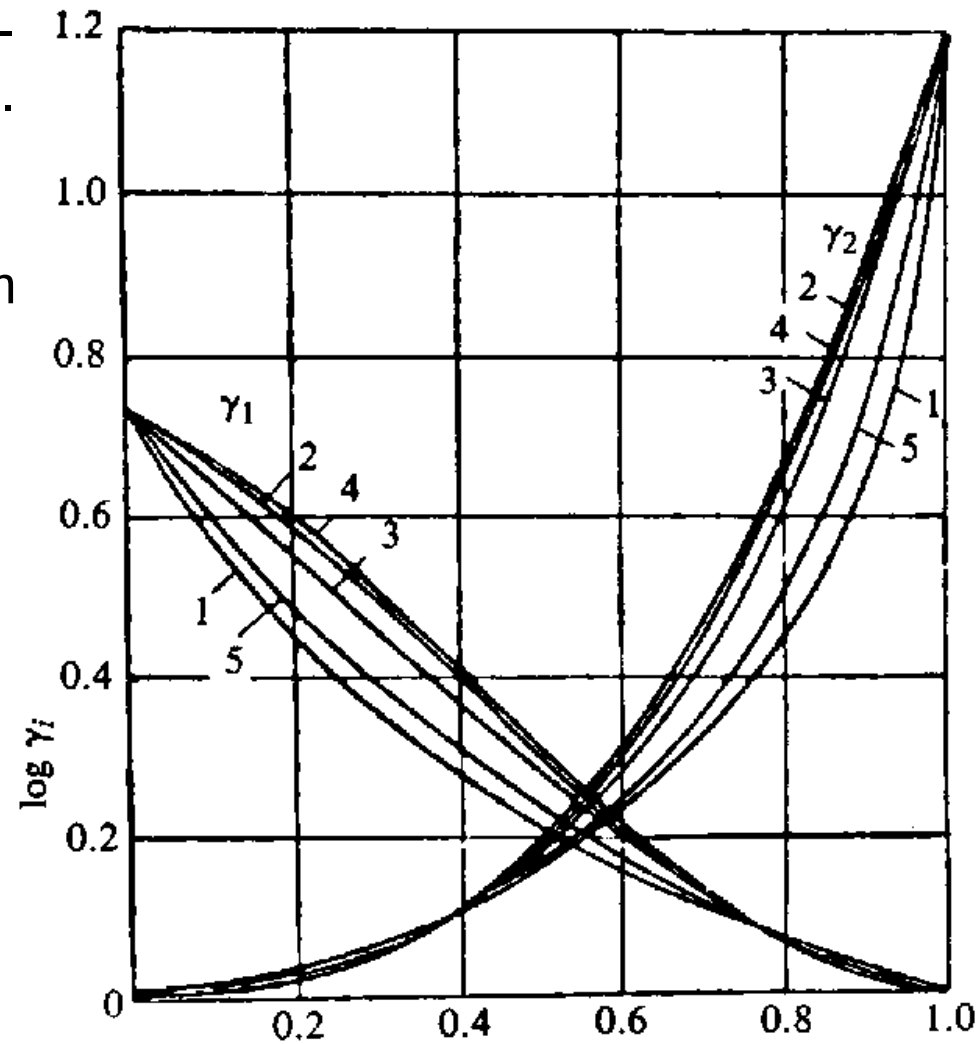
$$\Lambda_{ij} = \frac{V_j}{V_i}\exp\left[\frac{-a_{ij}}{RT}\right]$$

Comparison of Liquid Solution Models

Activity coefficients of 2-methyl-2-butene + n-methylpyrollidone.

Comparison of experimental values with those obtained from several equations whose parameters are found from the infinite-dilution activity coefficients.

(1) Experimental data.
(2) Margules equation.
(3) van Laar equation.
(4) Scatchard-Hamer equation.
(5) Wilson equation.



Non-Ideal VLE to Moderate Pressures: **Overview** **SVNA 14.1**

We now have the tools required to describe and calculate vapour-liquid equilibrium conditions for even the most non-ideal systems.

1. Equilibrium Criteria:
   - In terms of chemical potential

$$\mu_i^v = \mu_i^l$$

   - In terms of mixture fugacity

$$\hat{f}_i^v = \hat{f}_i^l$$

2. Fugacity of a component in a non-ideal gas mixture:

$$\hat{f}_i^v(T,P,y_1,y_2,...,y_n) = y_i\,\hat{\phi}_i^v(T,P,y_1,y_2,...,y_n)P$$

3. Fugacity of a component in a non-ideal liquid mixture:

$$\hat{f}_i^l(T,P,x_1,x_2,...,x_n) = x_i\,\gamma_i(T,P,x_1,x_2,...,x_n)f_i^l$$

$$= x_i\,\gamma_i(T,P,x_1,x_2,...,x_n)\phi_i^{sat}P_i^{sat}\exp\left[\frac{V_i(P-P_i^{sat})}{RT}\right]$$

γ, ϕ Formulation of VLE Problems

To this point, Raoult's Law was only description we had for VLE behaviour:

$$y_i P = x_i P_i^{sat}$$

We know that calculations based on Raoult's Law do not predict actual phase behaviour due to over-simplifying assumptions.

<u>Accurate</u> treatment of non-ideal phase equilibrium requires the use of mixture fugacities. At equilibrium, the fugacity of each component is the same in all phases. Therefore,

$$\hat{f}_i^v = \hat{f}_i^l$$

or,

$$y_i \hat{\phi}_i^v P = x_i \gamma_i \phi_i^{sat} P_i^{sat} \exp\left[\frac{V_i (P - P_i^{sat})}{RT}\right]$$

determines the VLE behaviour of non-ideal systems where Raoult's Law fails.

Non-Ideal VLE to Moderate Pressures

A simpler expression for non-ideal VLE is created upon defining a lumped parameter, Φ.

$$\Phi_i = \frac{\hat{\phi}_i^v}{\phi_i^{sat}} \exp\left[\frac{-V_i^l(P - P_i^{sat})}{RT}\right]$$

$$\approx \frac{\hat{\phi}_i^v}{\phi_i^{sat}}$$

The final expression becomes,

$$\boxed{y_i \Phi_i P = x_i \gamma_i P_i^{sat}} \qquad (i = 1,2,3,\ldots,N) \qquad 14.1$$

To perform VLE calculations we therefore require vapour pressure data (P_i^{sat}), vapour mixture and pure component fugacity correlations (Φ_i) and liquid phase activity coefficients (γ_i).

Non-Ideal VLE to Moderate Pressures

Sources of Data:

1. Vapour pressure: Antoine's Equation (or similar correlations)

$$\ln P_i^{sat} = A_i - \frac{B_i}{T + C_i} \qquad 14.3$$

2. Vapour Fugacity Coefficients: Viral EOS (or others)

$$\Phi_i = \exp\left[\frac{B_{ii}(P - P_i^{sat}) + 0.5P\sum_j\sum_k y_j y_k (2\delta_{ji} - \delta_{jk})}{RT}\right] \qquad 14.6$$

3. Liquid Activity Coefficients
   - Binary Systems - Margules,van Laar, Wilson, NRTL, Uniquac
   - Ternary (or higher) Systems - Wilson, NRTL, Uniquac