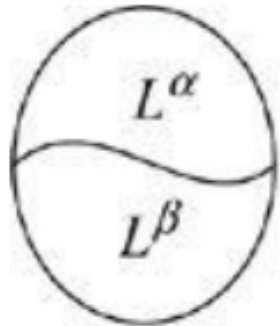


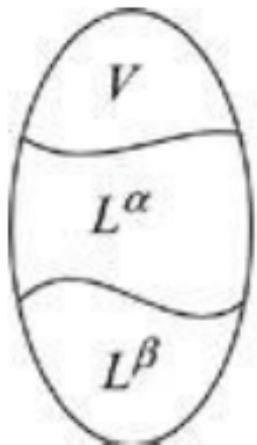
Chapter 14. Liquid-Liquid and Solid-Liquid Phase Equilibria

14.1. The Onset of Liquid-Liquid Instability



$$\hat{f}_i^\alpha = \gamma_i^\alpha x_i^\alpha P_i^{sat} = \gamma_i^\beta x_i^\beta P_i^{sat} = \hat{f}_i^\beta$$
$$\gamma_i^\alpha x_i^\alpha = \gamma_i^\beta x_i^\beta$$

14.1



$$\hat{f}_i^\alpha = \hat{f}_i^\beta = \hat{f}_i^V = \gamma_i^\alpha x_i^\alpha P_i^{sat} = \gamma_i^\beta x_i^\beta P_i^{sat} = y_i P$$

(ig) 14.2

Example 14.1. Simple vapor-liquid-liquid equilibrium (VLLE) calculations

At 25°C, a binary system containing components 1 and 2 is in a state of three-phase LLVE. Analysis of the two equilibrium liquid phases (α and β) yields the following compositions:

$$x_2^\alpha = 0.05; \quad x_1^\beta = 0.01$$

Vapor pressures for the two pure components at 25°C are $P_1^{sat} = 0.7$ bar and $P_2^{sat} = 0.1$ bar.

Making reasonable assumptions, determine good estimates for the following.

- The activity coefficients γ_1 and γ_2 (use Lewis-Randall standard states).
- The equilibrium pressure.
- The equilibrium vapor composition.

Solution

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

Assume $\gamma_1^\alpha \approx 1$, $\gamma_2^\beta \approx 1$ because these are practically pure in the specified phases.

$$y_1 P = \gamma_1^\alpha x_1^\alpha P_1^{sat} = 0.95(0.7); \quad y_2 P = \gamma_2^\beta x_2^\beta P_2^{sat} = 0.99(0.1)$$
$$P = \sum_i y_i P = 0.764 \text{ bar}, \quad y_1 = 0.95(0.7)/0.764 = 0.8704, \quad y_2 = 0.1296$$

$$\gamma_2^\alpha = y_2 P / 0.05(0.1) = 19.8; \quad \gamma_1^\beta = y_1 P / 0.01(0.7) = 95$$

Example 14.2. LLE predictions using Flory-Huggins theory: Polymer mixing

One of the major problems with recycling polymeric products is that different polymers do not form miscible solutions with each other, but form highly nonideal solutions. To illustrate, suppose 1 g each of two different polymers (polymer *A* and polymer *B*) is heated to 127°C and mixed as a liquid. Estimate the mutual solubilities of *A* and *B* using the Flory-Huggins equation. Predict the energy of mixing using the Scatchard-Hildebrand theory. Polymer data:

	<i>MW</i>	<i>V</i> (cm ³ /mol)	δ (J/cm ³) ^{1/2}
<i>A</i>	10,000	1,540,000	19.2
<i>B</i>	12,000	1,680,000	19.4

Solution

This is the same mixture that we considered as an equal-weight-fraction mixture in [Example 12.5](#). Based on that calculation, we know that the solution is highly nonideal. We must now iterate on the guessed solubilities until the implied activity coefficients are consistent. Let's start by guessing that the two polymer phases are virtually pure and infinitely dilute in the other component.

$$\lim_{x_A^\alpha \rightarrow 0} \Phi_A^\alpha = 0 \text{ and } \lim_{x_B^\beta \rightarrow 0} \Phi_B^\beta = 0$$

$$\lim_{x_i \rightarrow 0} \frac{\Phi_i}{x_i} = \lim_{x_i \rightarrow 0} \frac{x_i V_i}{x_i V_i + x_j V_j} \cdot \frac{1}{x_i} = \frac{V_i}{V_j}$$

Using [Eqns. 11.46](#) and [11.47](#),

$$\ln \gamma_A^\alpha = \ln(0.91) + (1 - 0.91) + 1.54\text{E}6(19.4 - 19.2)^2 (1.0)^2 / [8.314(400)] = 18.5$$

$$\ln \gamma_B^\beta = \ln(1.09) + (1 - 1.09) + 1.68\text{E}6(19.4 - 19.2)^2 (1.0)^2 / [8.314(400)] = 20.2$$

Since $\gamma_i^\alpha x_i^\alpha = \gamma_i^\beta x_i^\beta$, then $\gamma_B^\beta x_B^\beta = 1$ and $\gamma_A^\alpha x_A^\alpha = 1$.

$$\Rightarrow \gamma_A^\alpha = 1.1\text{E}8 \Rightarrow x_A^\alpha = 9.1\text{E}-9$$

$$\Rightarrow \gamma_B^\beta = 5.9\text{E}8 \Rightarrow x_B^\beta = 1.7\text{E}-9$$

Good guess. The polymers are totally immiscible. No further iterations are needed.

$$\ln \gamma_1 = \ln(\Phi_1/x_1) + (1 - \Phi_1/x_1) + \frac{V_1}{RT} \Phi_2^2 (\delta_1 - \delta_2)^2 \quad 12.36$$

$$\ln \gamma_2 = \ln(\Phi_2/x_2) + (1 - \Phi_2/x_2) + \frac{V_2}{RT} \Phi_1^2 (\delta_1 - \delta_2)^2 \quad 12.37$$

$$G^E = RT(x_1 \ln(\Phi_1/x_1) + x_2 \ln(\Phi_2/x_2)) + \Phi_1 \Phi_2 (x_1 + x_2 r) \chi RT \quad 12.38$$

Example 12.5. Polymer mixing

One of the major problems with recycling polymeric products is that different polymers do not form miscible solutions with one another; rather, they form highly non-ideal solutions. To illustrate, suppose 1g each of two different polymers (polymer *A* and polymer *B*) is heated to 127°C and mixed as a liquid. Estimate the activity coefficients of *A* and *B* using the Flory-Huggins model.

	<i>MW</i>	<i>V</i> (cm ³ /mol)	δ (J/cm ³) ^{1/2}
<i>A</i>	10,000	1,540,000	19.2
<i>B</i>	12,000	1,680,000	19.4

Solution

$$x_A = (1/10,000)/(1/10,000 + 1/12,000) = 0.546; x_B = 0.454$$

$$\Phi_A = 0.546(1.54)/[0.546(1.54) + 0.454(1.68)] = 0.524; \Phi_B = 0.476$$

$$\begin{aligned} \ln \gamma_A &= \ln (0.5238/0.5455) + (1 - 0.5238/0.5455) + (1.54E6(19.4 - 19.2)^2(0.4762)^2)/(8.314(400)) \\ &= -0.0008 + 4.200 \Rightarrow \gamma_A = 66 \end{aligned}$$

$$\begin{aligned} \ln \gamma_B &= \ln (0.4762/0.4545) + (1 - 0.4762/0.4545) + (1.68E6(19.4 - 19.2)^2(0.5238)^2)/(8.314(400)) \\ &= +0.0008 + 5.544 \Rightarrow \gamma_B = 258 \end{aligned}$$

$$\ln \gamma_1 = \ln(\Phi_1/x_1) + (1 - \Phi_1/x_1) + \frac{V_1}{RT} \Phi_2^2 (\delta_1 - \delta_2)^2 \quad 12.36$$

14.2. Stability and Excess Gibbs Energy

$$G = \Delta G_{mix} + \sum_i x_i G_i = G^E + \Delta G_{mix}^{is} + \sum_i x_i G_i$$

14.3

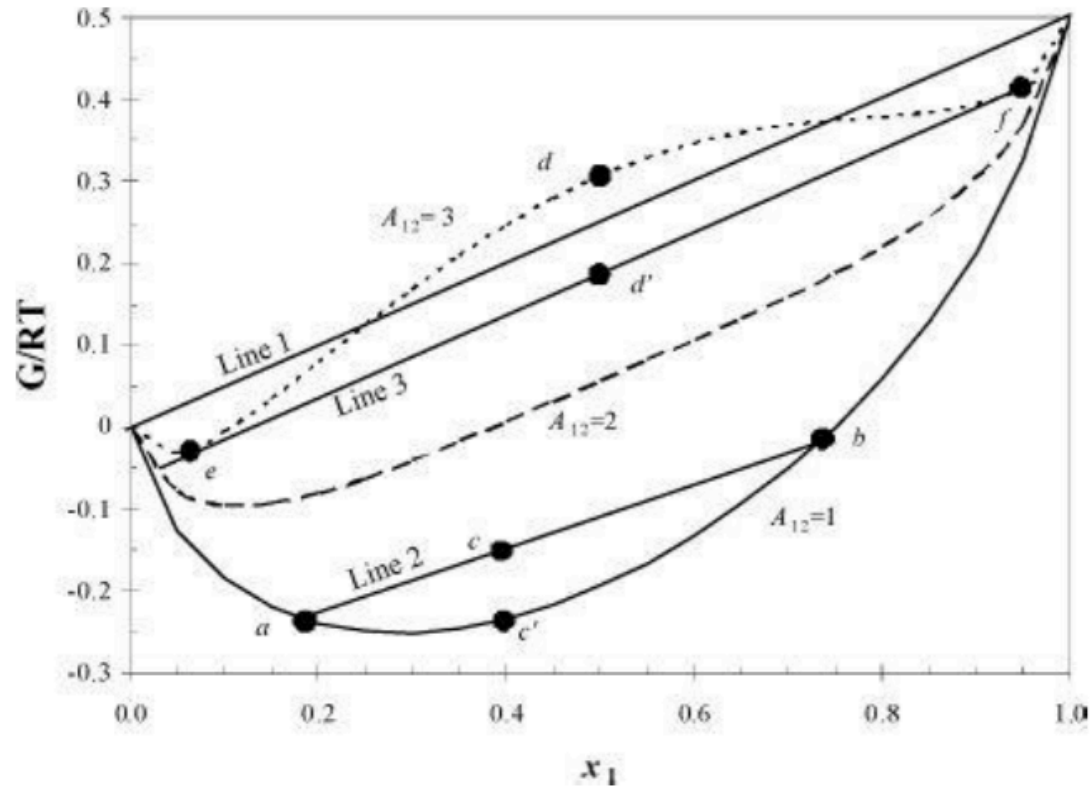


Figure 14.1. Illustration of the Gibbs energy of a mixture represented by the Margules one-parameter equation.

$$G = \Delta G_{mix} + \sum_i x_i G_i = G^E + \Delta G_{mix}^{is} + \sum_i x_i G_i$$

14.3

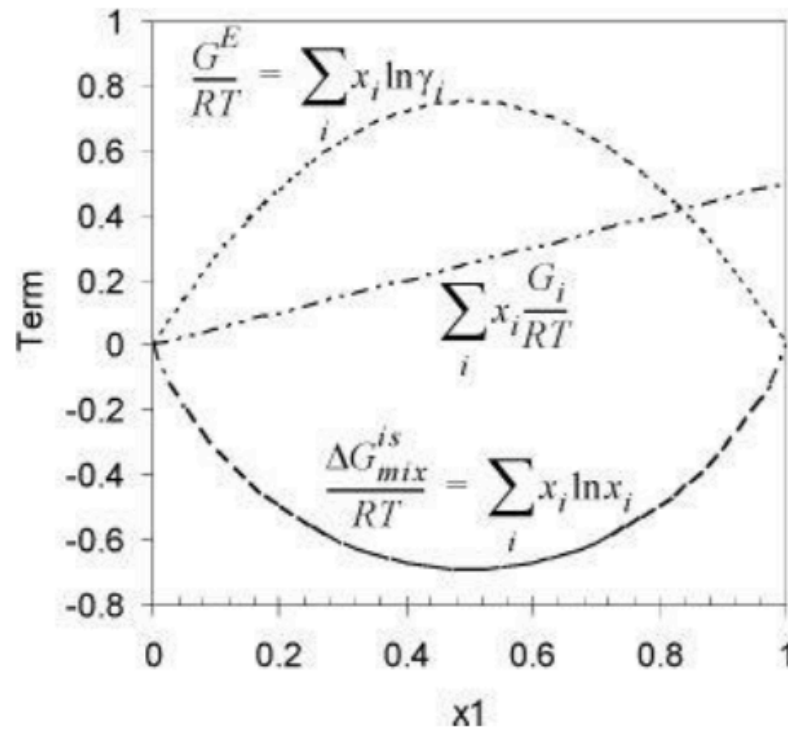


Figure 14.2. Illustration of the contributions to the Gibbs energy of a binary mixture when $A_{12} = 3$ and the pure component Gibbs energies are as in [Fig. 14.1](#).

14.3. Binary LLE by Graphing the Gibbs Energy of Mixing

Example 14.3. LLE predictions by graphing

Arce et al.^a give the compositions for the tie lines in the system water(1) + propanoic acid(2) + methylethylketone (MEK)(3) at 298 K and 1 bar. As limiting conditions, the mutual solubilities of water + MEK (1CH₃ + 1CH₃CO + 1CH₂) binary are also listed as $x_1^\alpha = 0.342$, $x_1^\beta = 0.922$.

- Use MAB to roughly estimate the water + MEK binary mutual solubilities to ± 5 mole%.
- Use UNIFAC to roughly estimate the water + MEK binary mutual solubilities to ± 5 mole%.

Solution

- $A_{12} = (50.13 - 0)(15.06 - 9.70)(90.1 + 18.0)/(4 \cdot 8.314 \cdot 298) = 2.931$, virtually the same as the parameter used above.

Adding $G^E/RT = A_{12}x_1x_2$ and $\Delta G_{mix}^{is}/(RT) = \sum_i x_i \ln x_i$ gives $\Delta G_{mix}/(RT)$. Using the drawing tool shows $x_1^\alpha = 0.93$ and $x_1^\beta = 0.07$

- Selecting the appropriate groups from the UNIFAC menu, then copying the values of the activity coefficient, we can develop [Figs. 14.3](#) and [14.4](#) using increments of $x_w = 0.05$. In MATLAB we can set up a vector $x_1 = 0:0.05:1$, and then insert a loop into

unifacCallerLLE.m. Noting $G^E/(RT) = \sum_i x_i \ln \gamma_i$ and programming the formula for $\Delta G_{mix}/(RT)$.

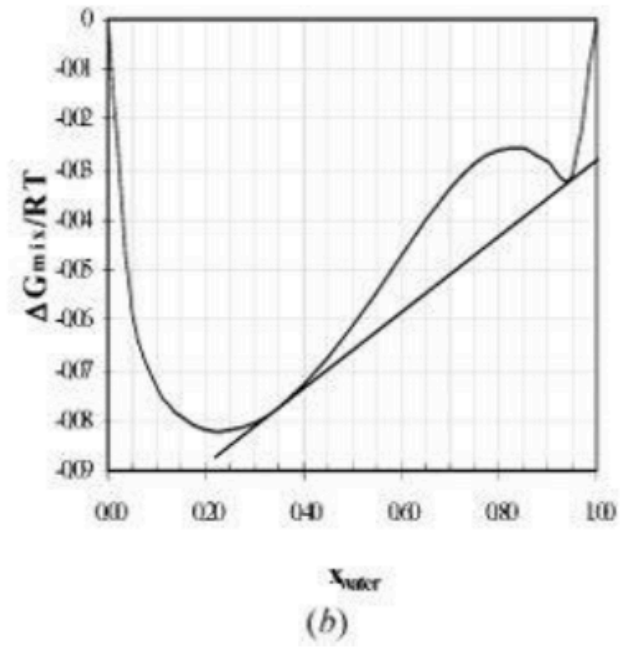
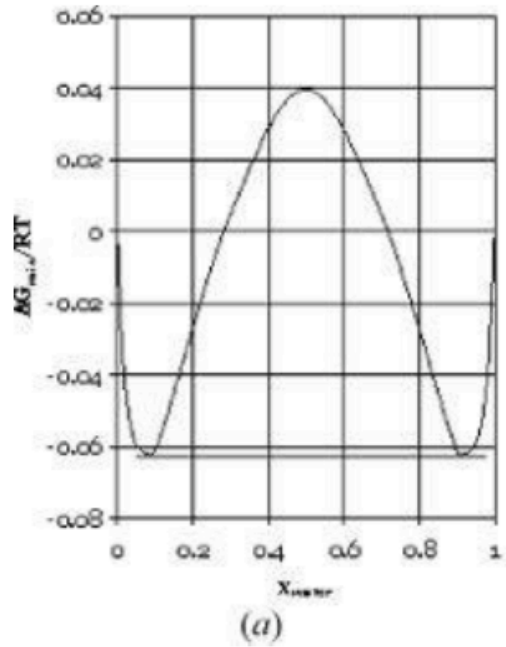


Figure 14.3. Gibbs energy of mixing in the water + MEK system as predicted by (a) MAB and (b) UNIFAC.

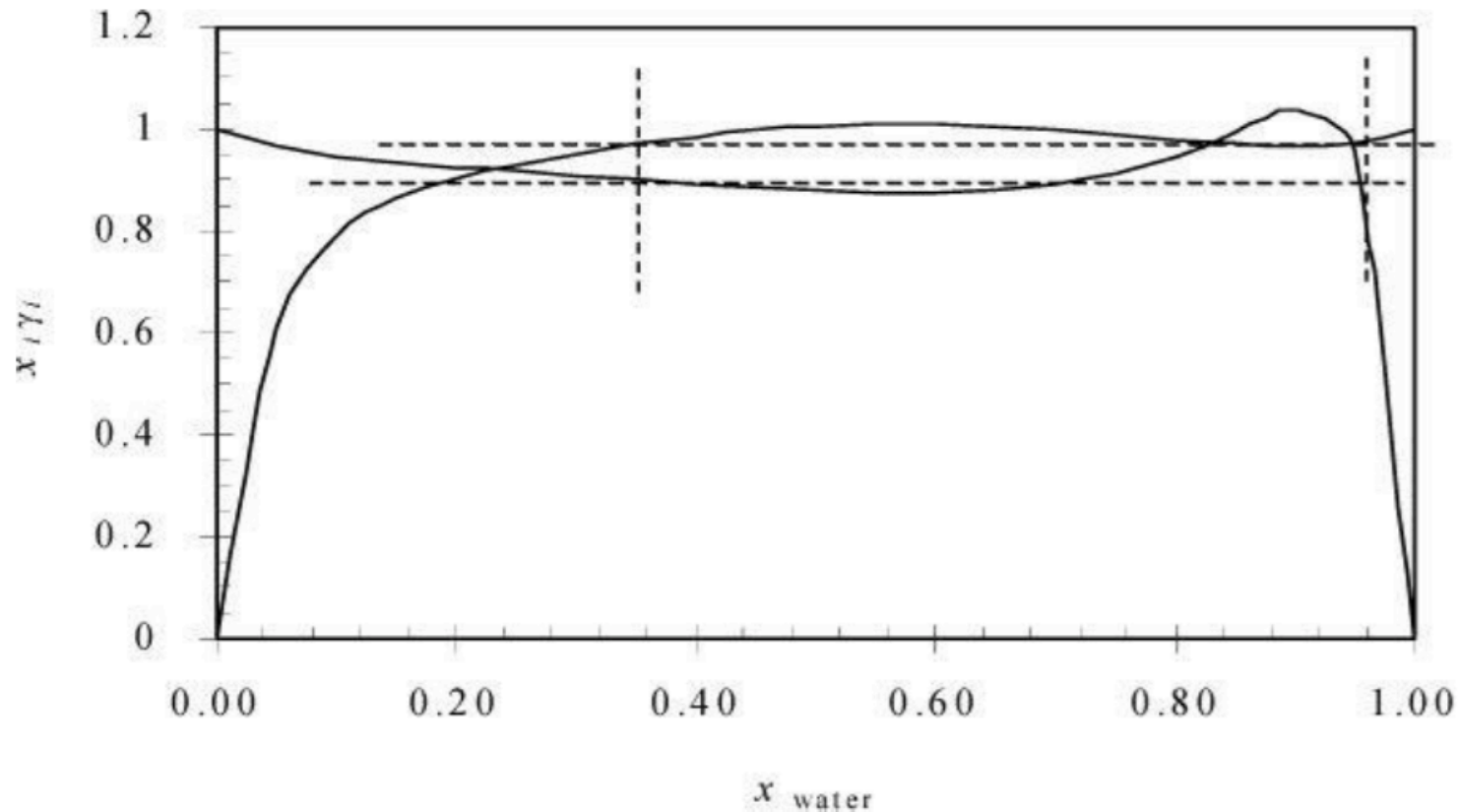


Figure 14.4. Activities of water and MEK as a function of mole fraction water as predicted by UNIFAC. The activity versus mole fraction plots will have a maximum when LLE exists. The dashed lines show the compositions where the activities of components are equal in both phases simultaneously.

Using the line drawing tool we obtain tangents at $x_1^\alpha = 0.35$ and $x_1^\beta = 0.94$.

These are sufficiently precise for the problem statement as given above. Note how the MAB model results in symmetric estimates of the compositions, a serious deficiency for LLE, and UNIFAC happens to be fairly close.

14.4. LLE Using Activities

$$\gamma_i^\alpha x_i^\alpha = \gamma_i^\beta x_i^\beta$$

Activity $a_i^\alpha = a_i^\beta$

$$K_i = \frac{x_i^\alpha}{x_i^\beta} = \frac{\gamma_i^\beta}{\gamma_i^\alpha} \quad 14.4$$

for a binary mixture that x_i^α must sum to unity.

$$x_1^\beta K_1 + (1 - x_1^\beta) K_2 = 1.$$

$$x_1^\beta = \frac{1 - K_2}{K_1 - K_2}; \text{ and } x_1^\alpha = x_1^\beta K_1 \quad 14.5$$

Iterative flash procedure for binary LLE.

The method is initialized by assuming the two phases are virtually immiscible with an infinitely dilute trace of the other component. The method is as follows.

1. Assume that phase β is nearly pure 1, $x_1^\alpha = 1/\gamma_1^{\alpha,\infty}$, and α is nearly pure 2, $x_2^\beta = 1/\gamma_2^{\beta,\infty}$. These represent initialization of the iteration procedure. The procedure is most stable with an initial guess of mutual solubility outside the two-phase region.
2. Calculate $K_{i,old} = \gamma_i^\beta / \gamma_i^\alpha$ where the γ_i 's are evaluated at the initial compositions.
3. Calculate $x_{1,new}^\beta = (1 - K_{2,old}) / (K_{1,old} - K_{2,old})$, $x_{2,new}^\beta = 1 - x_{1,new}^\beta$.
4. Calculate $x_{i,new}^\alpha = K_{i,old} x_{i,new}^\beta$.
5. Determine $\gamma_{i,new}$ values for each liquid phase from the $x_{i,new}$ values.
6. Calculate $K_{i,new} = \gamma_i^\beta / \gamma_i^\alpha$.
7. Replace all $x_{i,old}$ and $K_{i,old}$ values with the corresponding new values.
8. Loop to step 3 until calculations converge. The calculations converge slowly.

Example 14.4. The binary LLE algorithm using MAB and SSCED models

Compute the mutual solubilities of water and MEK at 298 K and compare to the experimental data of [Example 14.3](#) assuming the following models: (a) MAB (b) SSCED.

Solution

a. From [Example 14.3](#), $A_{12} = 2.931$. The symmetry of the MAB model gives $x_1^\alpha = x_2^\beta = 1/\exp(2.931) = 0.05335$. Computing γ_i 's at these compositions, $K_W = 1.0084/13.83 = 0.0729$; $K_{MEK} = 13.83/1.0084 = 13.72$. Then [Eqn. 14.5](#) gives $x_{1new}^\alpha = 0.93205$; $x_{1new}^\beta = 0.06795$ for the first iteration. Unfortunately, the LLE calculations converge more slowly than VLE flash calculations. The calculations may drift a couple mole percent in compositions after they are changing at step sizes in the tenths of mole percents, so patience is required in converging the calculations. [Section 14.9](#) provides details on setting up a macro or circular calculation. The table below summarizes the initial iterations. This same model is used above and the results are the same, but numerically known to better precision than the graphical method.

Iteration	x_1^α	x_1^β	$K_{1,new}$	$K_{2,new}$
Initialize	0.9466	0.0534	0.0729	13.72
1	0.9321	0.0680	0.0794	12.59
2	0.9264	0.0736	0.0821	12.18
Converged	0.9225	0.0775	0.0840	11.91

b. The SSCED model gives:

$$k_{12} = (50.13 - 0)(15.06 - 9.70)/(4 \cdot 27.94 \cdot 18.88) = 0.1274.$$

From $\ln \gamma_1^\infty = 18[(27.94-18.88)^2+2(0.1274)27.94(18.88)]/(8.314 \cdot 298) = 1.573$, $x_1^\alpha = 1/\exp(1.573) = 0.2072$.

Applying the same formulas to MEK: $x_2^\beta = 1/2626 = 0.9997$.

The table below shows the improved predictions from SSCED relative to MAB. Note how the molecular size difference is reflected by the much greater activity of trying to squeeze the large molecule among the small ones. This reflects a significantly improved insight for SSCED relative to the MAB model.

Iterating further on x_1^α through [Eqn. 14.5](#) gives $x_1^\alpha = 0.2509$.

Iteration	x_1^α	x_1^β	$K_{1,new}$	$K_{2,new}$
Initialize	0.9997	0.2072	0.2073	2623
1	0.9997	0.2413	0.2414	2515
2	0.9997	0.2487	0.2488	2493
Converged	0.9997	0.2509	0.2510	2486

14.5. VLLE with Immiscible Components

A special case of VLLE is obtained when one of the liquid-phase components is almost entirely insoluble in other components, and all other components are essentially insoluble in it, as occurs with many hydrocarbons with water. When a mixture forms two liquid phases, the mole fractions sum to

Example 14.5. Steam distillation

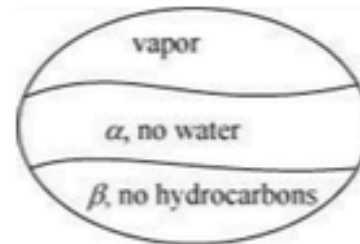
Consider a steam distillation with the vapor leaving the top of the fractionating column and entering the condenser at 0.1 MPa with the following analysis:

	y_i	T_c	P_c	ω
<i>n</i> -C8	0.20	568.8	2.486	0.396
C12 fraction	0.40	660.0	2.000	0.540
H ₂ O	0.40	(use steam tables)		

Assuming no pressure drop in the condenser and that the water and hydrocarbons are completely immiscible, calculate the maximum temperature which ensures complete condensation at 0.1 MPa. Use the shortcut *K*-ratio method for the hydrocarbons.

Solution

Apply the following notation to designate the phases:



The temperature that we seek is a bubble temperature of the liquid phases. The hydrocarbons and the water are essentially immiscible. We may approximate the hydrocarbon liquid phase, α , as an ideal solution of C8 and C12 with no water present. Therefore, two liquid phases will form: one of pure H_2O and the other a mixture of $1/3$ n -C8 + $2/3$ C12 fraction. We may apply Raoult's law with $x_w = 1$ for water in the β phase. The vapor mixture is a single phase, however, and must conform to:

$$1 = \sum_i y_i$$

	Phase	x_i	$VLE K_i(353 \text{ K})$	y_i	$VLE K_i(368 \text{ K})$	y_i
n -C8	α	0.333	0.254	0.084	0.415	0.138
C12 fraction	α	0.667	0.015	0.010	0.028	0.019
H_2O	β	1.0	0.474	0.474	0.846	0.846
				$\Sigma y_i = 0.568$		$\Sigma y_i = 1.0027$

So the bubble temperature with water present is $\sim 95^\circ\text{C}$. Note that the bubble temperature is below the bubble temperature of pure water. What would it be without water?

	x_i	$VLE K_i(400\text{K})$	y_i	$VLE K_i(440\text{K})$	y_i
n -C8	0.333	1.049	0.349	2.727	0.908
C12 fraction	0.667	0.092	0.061	0.319	0.213
			$\Sigma y_i = 0.410$		$\Sigma y_i = 1.121$

Then, interpolating $T \approx 400 + (1 - 0.41)/(1.121 - 0.41) \cdot 40 = 433 \text{ K}$. Thus, we reduced the bubble temperature by 65°C in the steam distillation.

14.6. Binary Phase Diagrams

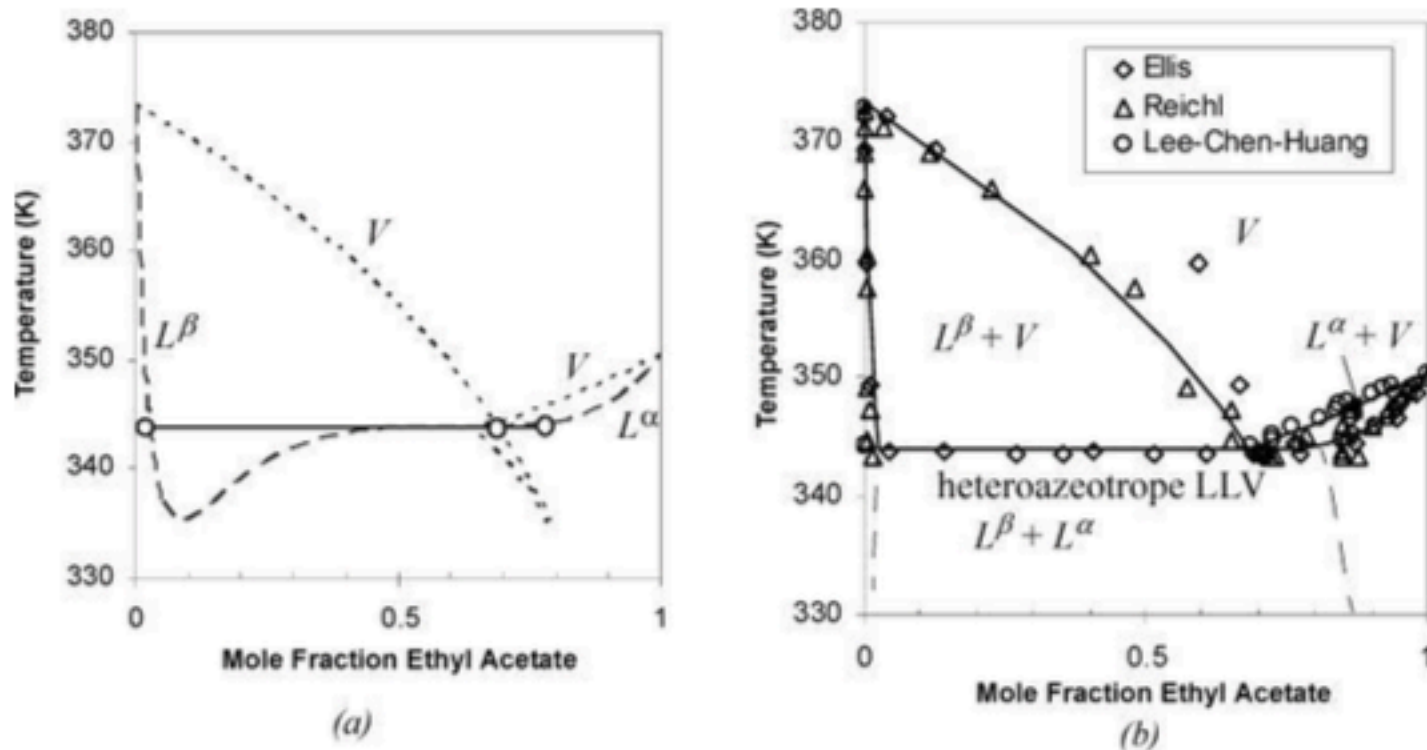


Figure 14.5. (a) VLE predictions of ethyl acetate + water as predicted by literature parameters in ASPEN using UNIQUAC. The horizontal line and the dots have been added manually. (b) The correct phase behavior after specifying to check for VLLE. Note that the liquid-liquid envelope is sketched by hand based on general behavior that may be expected, not predicted, but the two liquid compositions at the bubble temperature are at the ends of the horizontal VLLE line. Data from Ellis, S. R. M.; Garbett, R. D. 1960. *Ind. Eng. Chem.* 52:385-388; Reichl, A.; et al, 1998. *Fluid Phase Equil.* 153:113-134; Lee, L.-S.; et al. 1996. *J. Chem. Eng. Japan* 96:427-438.

14.7. Plotting Ternary LLE Data

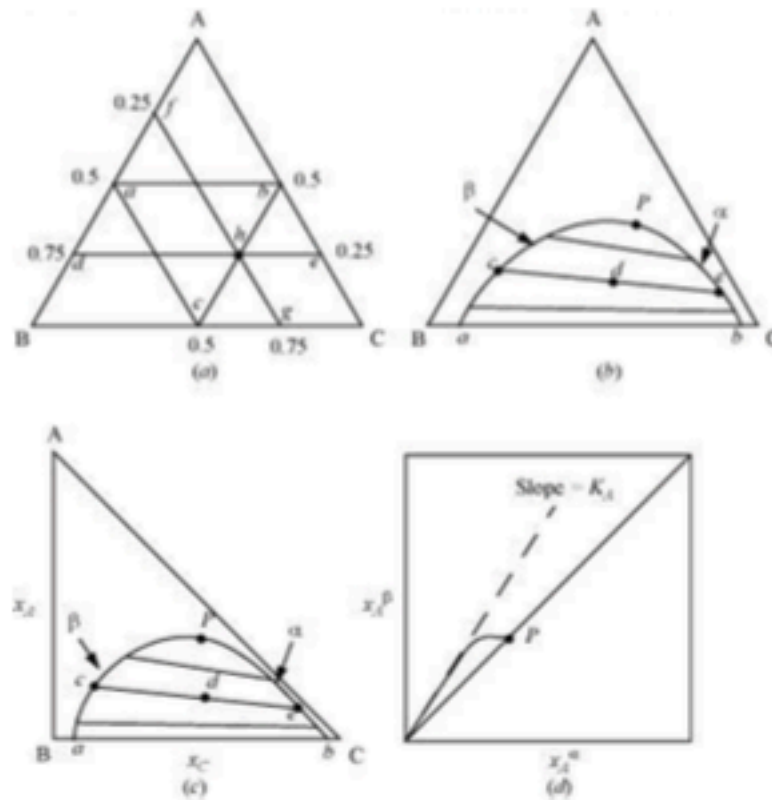


Figure 14.6. Illustrations of graphical representation of ternary data on triangular diagrams. (a) Illustration of grid lines on an equilateral triangle; (b) illustration of LLE on an equilateral triangle; (c) illustration of LLE on a right triangle; (d) illustration of tie-line data on a right triangle.

Other Examples of LLE Behavior

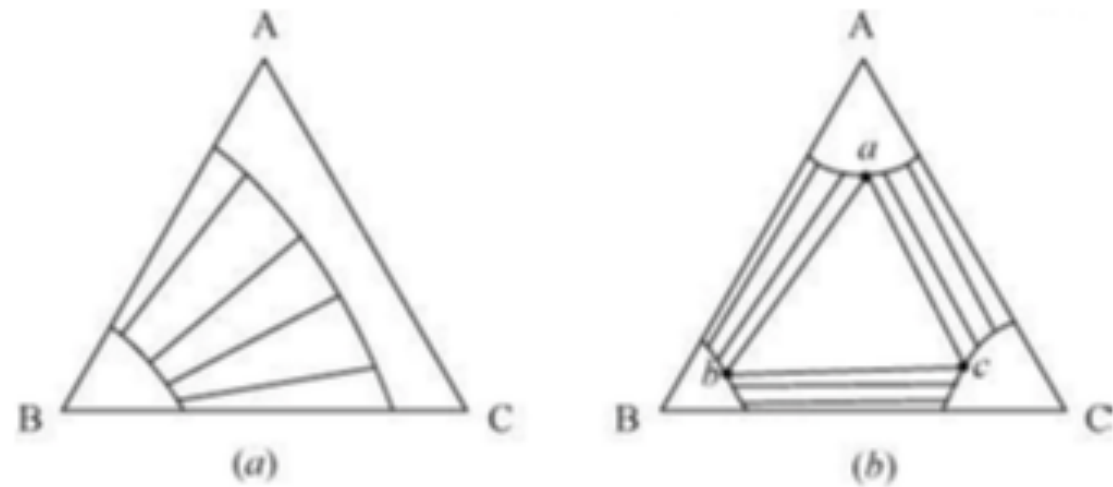
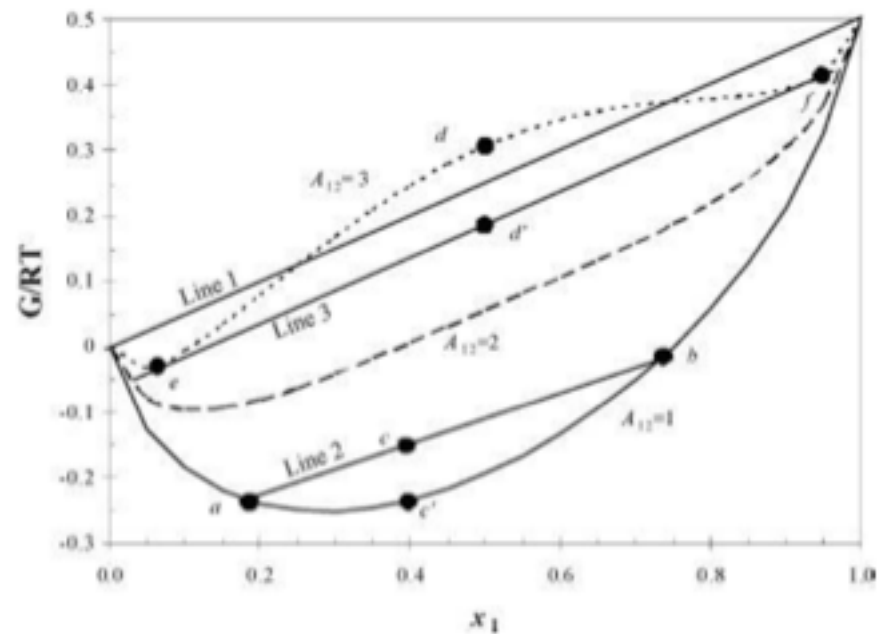


Figure 14.7. Illustration of other types of LLE behavior.

14.8. Critical Points in Binary Liquid Mixtures

$$\frac{\partial^2 G}{\partial x_1^2} = 0; \quad \frac{\partial^3 G}{\partial x_1^3} = 0 \quad 14.6$$

$$\frac{\partial^2 (G/(RT))}{\partial n_1^2} = 0; \quad \frac{\partial^3 (G/(RT))}{\partial n_1^3} = 0 \quad 14.7$$



$$\boxed{\gamma_i^\infty = \exp(A_{12}) = \exp(2) = 7.4} \quad \text{limit for Margules one-parameter miscibility} \quad 14.11$$

Example 14.6. Liquid-liquid critical point of the Margules one-parameter model

Based on [Fig. 14.1](#) and the discussion of concavity above, it looks like the value of $A_{12} = 2$ may be close to the critical point. Use [Eqns. 14.6](#) and [14.7](#) to determine the exact value of the critical parameter.

Solution

Multiplying through by n and recognizing that we have previously performed the initial part of this derivation (see [Eqns. 11.29–11.31](#)) gives

$$\begin{aligned} \underline{G}/(RT) &= n_1 \ln x_1 + n_2 \ln(1-x_1) + A_{12} n_2 x_1 \\ \frac{\partial(\underline{G}/(RT))}{\partial n_1} &= \frac{\partial(\underline{G}^{is}/(RT))}{\partial n_1} + \frac{\partial(\underline{G}^E/(RT))}{\partial n_1} = \ln x_1 + \ln \gamma_1 = \ln x_1 \gamma_1 = \ln x_1 + A_{12} x_1^2 \end{aligned} \quad 14.8$$

Since this is a binary solution, there is a simple finite relationship between the derivative with respect to mole number and the derivative with respect to mole fraction, leading expeditiously to the expected conclusion:

$$\begin{aligned} \frac{\partial^2(\underline{G}/(RT))}{\partial n_1^2} &= \frac{\partial^2(\underline{G}/(RT))}{\partial x_1^2} \left(\frac{\partial x_1}{\partial n_1} \right)^2 = 0 \Rightarrow \frac{\partial^2(\underline{G}/(RT))}{\partial x_1^2} = 0 = \frac{1}{x_1} - 2(1-x_1)A_{12} \\ \frac{\partial^3(\underline{G}/(RT))}{\partial n_1^3} &= \frac{\partial^3(\underline{G}/(RT))}{\partial x_1^3} \left(\frac{\partial x_1}{\partial n_1} \right)^3 = 0 \Rightarrow \frac{\partial^3(\underline{G}/(RT))}{\partial x_1^3} = 0 = \frac{-1}{x_1^2} + 2A_{12} \end{aligned} \quad 14.9$$

$$2A_{12} = \frac{1}{x_1^2} \Rightarrow 1 - \frac{1-x_1}{x_1} \Rightarrow x_{1,c} = \frac{1}{2}$$

$$\boxed{\frac{1}{x_{1,c}} = 0.5; \quad A_{12,c} = 2} \text{ one-parameter Margules model} \quad 14.10$$

Example 14.7. Liquid-liquid critical point of the Flory-Huggins model

Determine the critical value of the Flory-Huggins χ parameter considering the degrees of polymerization of each component.

Solution

Note that we have already solved this problem for the special case where the two components are identical in size. Then the excess entropy is zero, the volume fractions are equal to the mole fractions, and the Margules one-parameter model is recovered with A_{12} having nearly the same meaning as the Flory-Huggins χ parameter. To consider the problem of including the degree of polymerization, N_d , we must define the parameter with respect to a standard unit of volume. N_d is the number of monomer repeat units in the polymer. In the presentation below (and most other presentations of the same material), the volume of a *monomer* of component 1 is assigned as this standard volume ($\chi' = V_{std} \cdot [\delta_1 - \delta_2]^2 / RT$; $V_{std} = V_1 / N_{d,1}$). Note that we are introducing temperature dependence into χ' . Recalling the formula for the activity coefficient with this notational adaptation, the starting point (Eqn. 11.46) for this derivation becomes:

$$\begin{aligned} \frac{\partial(G/(RT))}{\partial n_1} &= \frac{\partial(G^{is}/(RT))}{\partial n_1} + \frac{\partial(G^E/(RT))}{\partial n_1} = \ln x_1 \gamma_1 \\ &= \ln \Phi_1 + (1 - \Phi_1/x_1) + N_{d,1} \chi' \Phi_2^2 \end{aligned}$$

The next step is greatly simplified if we recognize a simple relationship that is very similar to the formula for computing the number average molecular weight from the weight fractions of each component. The analogous formula for the volume can be rearranged in terms of the volume ratio $r = V_2/V_1$ as follows:

$$\begin{aligned} V &= \left[\frac{\Phi_1}{V_1} + \frac{\Phi_2}{V_2} \right]^{-1} \Rightarrow \frac{\Phi_1}{x_1 V_1} = \frac{1}{V} = \frac{\Phi_1}{V_1} + \frac{\Phi_2}{V_2} \\ \Rightarrow \frac{\Phi_1}{x_1} &= \Phi_1 + \Phi_2(1/r) \Rightarrow 1 - \frac{\Phi_1}{x_1} = \Phi_2(1 - 1/r) \end{aligned}$$

Since this is a binary solution, there is a simple finite relationship between the derivative with respect to mole number and the derivative with respect to *volume* fraction, leading expeditiously to the *general* conclusion (note $d\Phi_1 = -d\Phi_2$):

$$\begin{aligned} \frac{\partial^2(\underline{G}/RT)}{\partial n_1^2} &= \frac{\partial^2(\underline{G}/RT)}{\partial \Phi_1^2} \left(\frac{\partial \Phi_1}{\partial n_1} \right)^2 = 0 \Rightarrow \frac{\partial^2(\underline{G}/RT)}{\partial \Phi_1^2} = 0 \\ &= \frac{1}{\Phi_1} - (1 - 1/r) - 2(1 - \Phi_1)N_{d,1}\chi' \end{aligned} \quad 14.12$$

$$\frac{\partial^3(\underline{G}/RT)}{\partial n_1^3} = \frac{\partial^3(\underline{G}/RT)}{\partial \Phi_1^3} \left(\frac{\partial \Phi_1}{\partial n_1} \right)^3 = 0 \Rightarrow \frac{\partial^3(\underline{G}/RT)}{\partial \Phi_1^3} = 0 = \frac{-1}{\Phi_1^2} + 2N_{d,1}\chi'$$

which leads to two important results:

$$\begin{aligned} 2N_{d,1}\chi' = \frac{1}{\Phi_1^2} \Rightarrow 0 &= \frac{1}{\Phi_1} - (1 - 1/r) - \frac{(1 - \Phi_1)}{\Phi_1^2} \Rightarrow \Phi_{1,c} = \frac{1}{1 + \sqrt{1/r}} = \frac{\sqrt{V_2}}{\sqrt{V_1} + \sqrt{V_2}} \\ \chi'_c = \frac{1}{2N_{d,1}}(1 + \sqrt{1/r})^2 &= \frac{V_1}{2N_{d,1}} \left(\frac{1}{\sqrt{V_1}} + \frac{1}{\sqrt{V_2}} \right)^2 \Rightarrow \frac{(\delta_1 - \delta_2)^2}{RT_c} = \frac{1}{2} \left(\frac{1}{\sqrt{V_1}} + \frac{1}{\sqrt{V_2}} \right)^2 \end{aligned} \quad 14.13$$

These results suggest that critical concentration decreases to zero with increasing polymer size but the critical temperature approaches a finite limit that is related to the solvent size.

14.10. Solid-Liquid Equilibria

Solid-liquid equilibria (SLE) calculations begin just as VLE and LLE calculations, by equating fugacities. From [Eqn. 11.13](#), $\hat{f}_i^L = x_i \gamma_i f_i^*$. The next step is to equate $\hat{f}_i^L = \hat{f}_i^S$ and derive an equation to solve for temperature or composition depending on the problem statement. We have deliberately

Pressure Effects

For [SLE](#), as for [LLE](#), pressure changes usually have very small effects on the equilibria unless the pressure changes are large (10 to 100 MPa), because the enthalpies and entropies of *condensed* phases are only weakly pressure-dependent. Since $dG = RT d \ln f = dH - T dS = V dP$ for a pressure

SLE in a Single Component System

The effect of temperature on the Gibbs energy of any phase may be determined most easily at constant pressure. We may write $dG = -S dT + V dP$, and recognize using the concepts of [Chapter 6](#)

$$(\partial G / \partial T)_P = -S$$

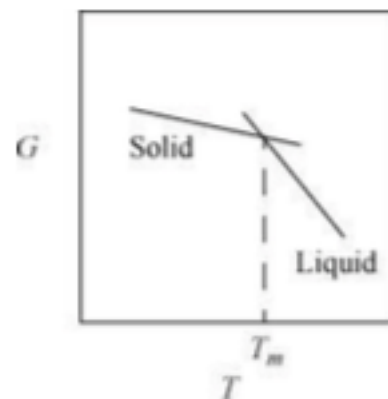


Figure 14.8. Illustration of Gibbs energies for pure SLE.

The Calculation Pathway for Mixtures

Let us consider a practical example of dissolving naphthalene (2) in *n*-hexane (1) at 298 K. Since the normal melting temperature for pure naphthalene is 353.3 K, how can we explain the phenomenon

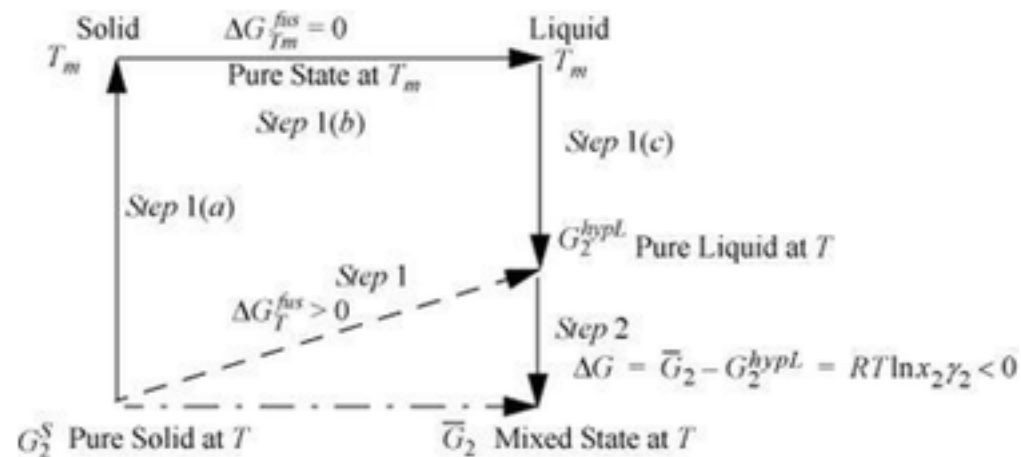


Figure 14.9. Illustration of the two-step process for calculating solubility of solids in liquids. Overall, $G_2^S = \bar{G}_2$. Note that the Gibbs energy goes up in Step 1 to create liquid, below the normal melting T_m , but the Gibbs energy goes down when the liquid is mixed.

Step 1. Naphthalene is melted to form a hypothetical liquid at 298 K. The Gibbs energy change for this step is positive as discussed above. The Gibbs energy change is:

$$\Delta G_T^{fus} = G_2^{hypL} - G_2^S \quad 14.15$$

where the superscript *hypL* indicates a hypothetical liquid.

Step 2. The hypothetical liquid naphthalene is mixed with liquid *n*-hexane. If the solution is nonideal, the Gibbs energy change for component 2 is

$$\bar{G}_2 - G_2^{hypL} = RT \ln(x_2 \gamma_2) \quad 14.16$$

The Gibbs energy change for this step is always negative if mixing occurs spontaneously, and must be large enough to cancel the Gibbs energy change from step 1.

❗ Solubility is determined by a balance between the positive ΔG^{fus} and the negative Gibbs energy effect of mixing.

Then clearly, from [Fig. 14.9](#) and [Eqns. 14.14](#) through [14.16](#),

$$\bar{G}_2 - G_2^S = (\bar{G}_2 - G_2^{hypL}) + (G_2^{hypL} - G_2^S) = RT \ln(x_2 \gamma_2) + \Delta G_T^{fus}$$

or

$$\boxed{\Delta G_T^{fus} = -RT \ln(x_2 \gamma_2)} \quad 14.17$$

where *T* is 298 K for our example. Relations for the activity coefficients in the right-hand side of

Formation of a Hypothetical Liquid

$$\Delta H_T^{fus} = H_T^{hypL} - H_T^S = \Delta H_{T_m}^{fus} + \int_{T_m}^T (C_P^L - C_P^S) dT \quad 14.19$$

$$\Delta S_T^{fus} = \Delta S_{T_m}^{fus} + \int_{T_m}^T \frac{(C_P^L - C_P^S)}{T} dT \quad 14.20$$

$$\Delta S_{T_m}^{fus} = \frac{\Delta H_{T_m}^{fus}}{T_m} \quad 14.21$$

$$\Delta G_T^{fus} = \Delta H_{T_m}^{fus} - T \Delta S_{T_m}^{fus} = \Delta H_{T_m,2}^{fus} \left(1 - \frac{T}{T_{m,2}} \right) \quad 14.22$$

Criteria for Equilibrium

In general, combining [Eqn. 14.22](#) with [Eqn. 14.17](#), we arrive at the equation for the solubility of component 2,

$$\ln(x_2\gamma_2) = \frac{-\Delta H_2^{fus}}{R} \left(\frac{1}{T} - \frac{1}{T_{m,2}} \right) = \frac{-\Delta S_2^{fus}}{R} \left(\frac{T_{m,2}}{T} - 1 \right) \quad 14.23$$

❶ Solubility equation for crystalline solids.

where heat of fusion is at the normal melting temperature of 2, and heat capacity integrals are neglected.

Example 14.8. Variation of solid solubility with temperature

Estimate the solubility of naphthalene in *n*-hexane for the range $T = [298, 350\text{K}]$ using the SSCED model. Plot $\log_{10}(x_N)$ versus $1000/T$.

Solution

From [Appendix E](#), $T_{m,2} = 353.3\text{ K}$ and $\Delta H^{fus} = 18,800\text{J/mol}$.

We can begin at 298 K, assuming an ideal solution. Then

$$x_N = \exp[(-18800/8.314) \cdot (1/298 - 1/353.3)] = 0.305.$$

Starting with $x_N = 0.305$ as an initial guess,

$$\Phi_N = 0.305 \cdot 130.6 / (0.695 \cdot 130.3 + 0.305 \cdot 130.6) = 0.306.$$

Noting that $\delta_1' = 14.93$, $\delta_2' = 19.19$ and $k_{12} = 0.0052 \Rightarrow \gamma_2 = 1.693$.

$x_N = 0.305/1.693 = 0.1802$. Iterating on x_N to achieve consistency, $x_N = 0.135$. Repeating this procedure at other temperatures gives [Fig. 14.10](#).

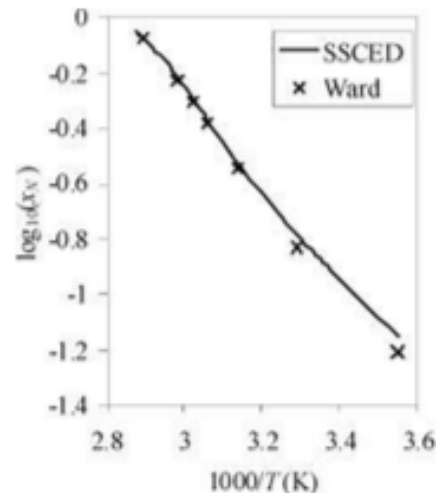


Figure 14.10. Freezing curve for the system *n*-hexane(1) + naphthalene(2). Experimental data of H.L. Ward, 1926. *J. Phys. Chem.*, 30:1316.

Hexane also dissolves in a hexane–naphthalene solution below its melting temperature. The general relationship for solving SLE can be written as:

$$\ln(x_i \gamma_i) = \frac{-\Delta H_i^{fus}}{R} \left(\frac{1}{T} - \frac{1}{T_{m,i}} \right) \quad 14.24$$

where the heat of fusion is for the pure i^{th} component at its normal melting temperature, $T_{m,i}$. Note that [Eqns. 14.23](#) and [14.24](#) may be used to determine crystallization temperatures at specified compositions.

Example 14.9. Eutectic behavior of chloronitrobenzenes

[Fig. 14.11](#) illustrates application to the system *o*-chloronitrobenzene (1) + *p*-chloronitrobenzene (2). The compounds are chemically similar; thus, the liquid phase may be assumed to be ideal, and the activity coefficients may be set to 1. The two branches represent calculations performed from [Eqns. 14.23](#) and [14.24](#), each giving one-half the diagram. The curves are hypothetical below the point of intersection. This temperature at the point of intersection of the two curves is called the **eutectic temperature**, and the composition is the **eutectic composition**.

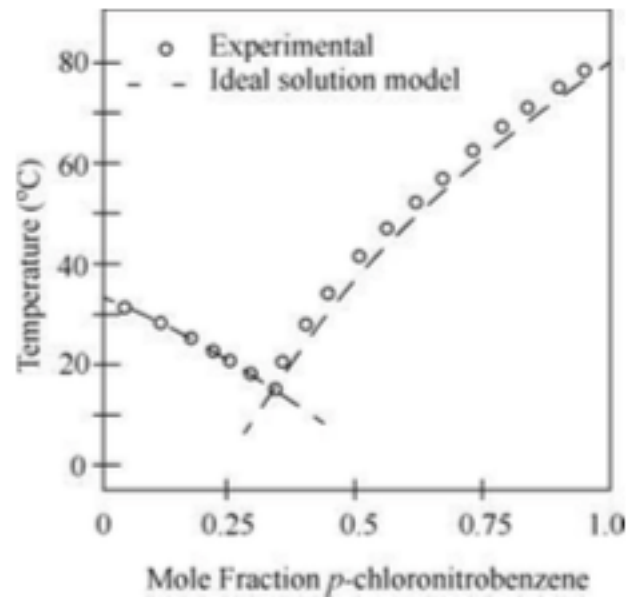


Figure 14.11. Freezing curves for the system *o*-chloronitrobenzene(1) + *p*-chloronitrobenzene(2).

Example 14.10. Eutectic behavior of benzene + phenol

In most systems, an activity coefficient model must be included. [Fig. 14.12](#) shows an example where the ideal solution model is not a good approximation, and the activity coefficients are modelled with the UNIFAC activity coefficient model. To solve for solubility given a temperature, the following procedure may be used (taking component 2, for example):

1. Assume the $\gamma_2 = 1$.
2. Solve [Eqn. 14.23](#) for x_2 .
3. At this value of x_2 , determine γ_2 from the activity model.
4. Return to step 2, including the value of γ_2 in [Eqn. 14.23](#), iterating to converge.

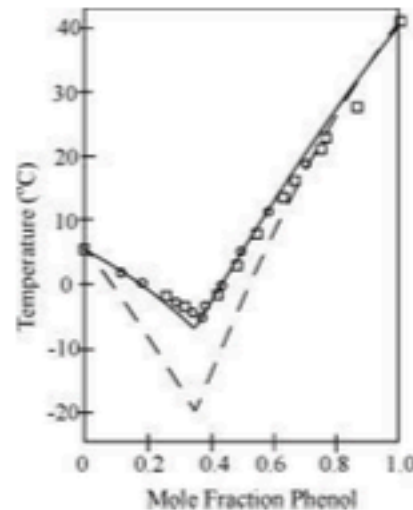


Figure 14.12. Freezing curves for the system benzene(1) + phenol(2). Solid line, UNIFAC prediction; dashed line, ideal solution prediction; squares, Tsakalotos, D., Guye, P. 1910. *J. Chim. Phys.* 8:340; circles, Hatcher, W., Skirrow, F. J. *Am. Chem. Soc.*, 1917. 39:1939. Based on figure of Gmehling, J., Anderson, T., Prausnitz, 1978. *J. Ind. Eng. Chem Fundam.* 17:269.

Example 14.11. Precipitation by adding antisolvent

Ephedrine is a commonly used stimulant, appetite suppressant, and decongestant, related to pseudoephedrine. It can be extracted from the Chinese herb, ma huang. Ephedrine is to be crystallized from ethanol at 278 K by adding water as an antisolvent.

- Estimate the mole fraction of water needed to reduce the concentration of ephedrine in solution to 0.1 mol% using the SSCED model.
- Yalkowsky and Valvani (1980) have suggested that $\Delta S^{fus} = 56.5 \text{ J/mol-K}$ for rigid molecules.^a Evaluate this relation in comparison to the estimated value of $\Delta H^{fus} = 25 \text{ kJ/mol}$.

Additional data for ephedrine are $M_w = 165.2$; $T_m = 313 \text{ K}$; and $\Delta H^{fus} = 25 \text{ kJ/mol}$.

Comp.	$\alpha(\text{J/cm}^3)^{0.5}$	$\beta(\text{J/cm}^3)^{0.5}$	$\delta(\text{J/cm}^3)^{0.5}$	$V^L(\text{cm}^3/\text{mol})$
Ethanol(1)	12.58	13.29	18.68	58.3
Water(2)	50.13	15.06	27.94	18.0
Ephedrine(3)	7.70	12.60	16.36	172.3

Solution

- From [Eqn. 14.25](#), $T_{m,i} = 313 \text{ K}$ and $\Delta H^{fus} = 25,000 \text{ J/mol}$. We can begin by solving for the target value of the activity coefficient, noting that the concentration of drug is practically infinitely dilute. Then using $x_i = 1\text{E-}3$ to approximate infinite dilution,

$$\gamma_i^\infty = \exp\left[\frac{-25000}{8.314} \left(\frac{1}{278} - \frac{1}{313}\right)\right] \cdot 0.001 = 245 \text{ is what we seek to find.}$$

The solution requires iteration using [Eqn. 12.55](#). As the mole fraction of water is increased, the activity coefficient of ephedrine increases because water is the antisolvent.

Since we have worked the problem before, “Guessing” a value of $x_1 = 0.2102$,

$$\Phi_1 = 0.2102(58.3) / (0.2102 \cdot 58.3 + 0.7898 \cdot 18.0) = 0.4627$$

$$\langle \delta^* \rangle = 0.4627(18.68) + 0.5373(27.94) = 23.66$$

From [Eqn. 12.51](#),

$$k_{12} = 0.0318; k_{13} = 0.0028; k_{23} = 0.0571;$$

$$\Rightarrow \langle k_{3m} \rangle = 0.4627(18.68)0.0028 + 0.5373(27.94)0.0571 = 0.8808;$$

$$\text{Similarly, } \langle k_{1m} \rangle = 0.4779; \langle k_{2m} \rangle = 0.2752;$$

$$\langle\langle k_{mm} \rangle\rangle = 0.4627(18.68)0.4779 + 0.5373(27.94)0.2752 = 8.262.$$

By [Eqn. 12.55](#), $RT \ln \gamma_3 = 172.3((16.36 - 23.66)^2 + 2(16.36)0.8808 - 8.262) \Rightarrow \gamma_3 = 245$. So the solution should be 79 mol% water. Good “guess!”

b. With $\Delta S^{fus} = 56.5$ and $T_m = 313\text{K}$, $\Delta H^{fus} = 56.5(313) = 17,700 \text{ J/mol}$, 29% lower than 25,000. The rule does not appear to apply to this compound.

[a.](#) Connors, K.A. 2002. *Thermodynamics of Pharmaceutical Systems: An Introduction for Students of Pharmacy*, Hoboken, NJ: Wiley, p. 129.

A special feature of [Example 14.11](#) is the way it shows how to tailor a solvent to achieve a particular environment for a target solute. A similar approach could be applied to compatibilizing a liquid solvent to avoid LLE. For example, how much methanol should be added to isooctane to reduce the activity coefficient of water below a value of 7.4? This is the calculation behind “dry gas,” used to dissolve water from gas tanks.

SLE with Solid Mixtures

solutions and pure liquids. For each component in the mixtures:

$$-RT\ln(x_i^S \gamma_i^S) + \Delta G_i^{fus} + RT\ln(x_i^L \gamma_i^L) = 0$$

14.25

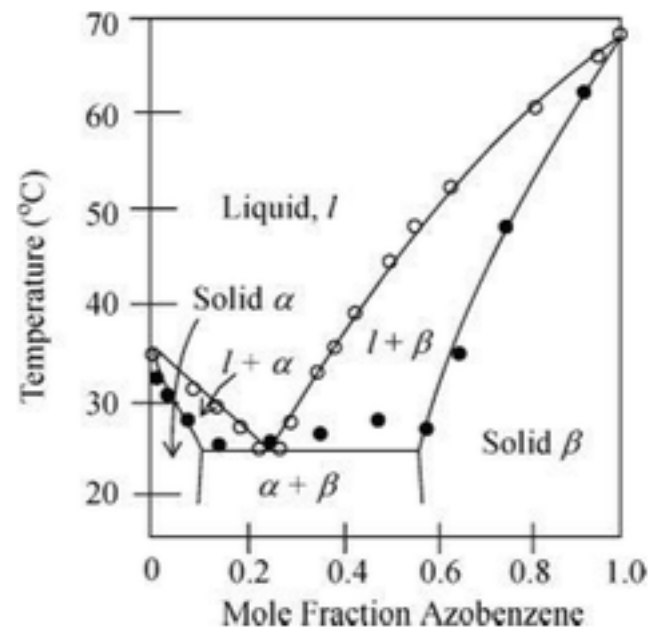


Figure 14.13. Freezing curves for the Azoxybenzene(1) + azobenzene(2) system illustrating a system with solid-solid solubility. Based on Hildebrand, J.H., Scott, R.L., Solubility of Nonelectrolytes, New York, NY: Dover, 1964.

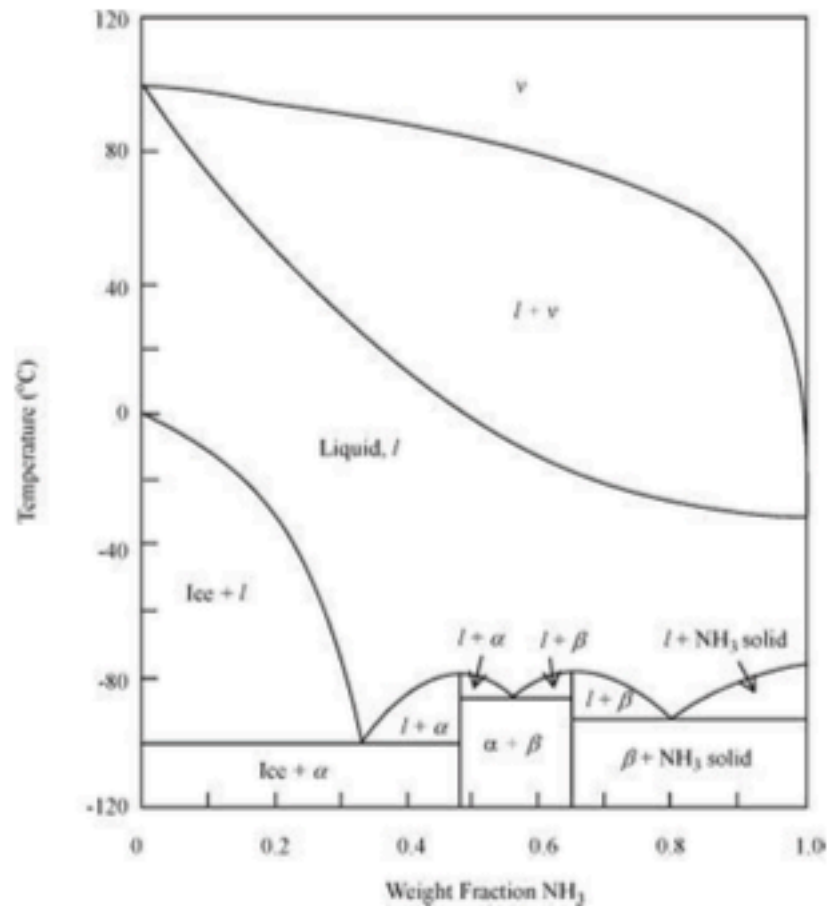


Figure 14.14. Solid-liquid and vapor-liquid behavior for the ammonia(1) + water(2) system at 1.013 bar. NH₃ and H₂O form two crystals in the stoichiometries: (α) NH₃·H₂O; (β) 2NH₃·H₂O. (Based on Landolt-Börnstein, 1960. II/2a:377.)

$$-RT \ln(x_i^S \gamma_i^S) + \Delta G_i^{fus} + RT \ln(x_i^L \gamma_i^L) = 0 \quad 14.25$$

Thus, we can recognize an SLE K -ratio on the left-hand side, $K_{SLE} = (x_i^L \gamma_i^L) / (x_i^S \gamma_i^S)$,

$$RT \ln \frac{(x_i^L \gamma_i^L)}{(x_i^S \gamma_i^S)} = -\Delta G_i^{fus} \quad \text{or} \quad \boxed{RT \ln K_{SLE} = -\frac{\Delta H_i^{fus}}{R} \left(\frac{1}{T} - \frac{1}{T_{m,i}} \right)} \quad 14.26$$

and we can recognize [Eqn. 14.24](#) as a simplification where for a pure solid, $x_i^S \gamma_i^S = 1$.

Petroleum Wax Precipitation

An especially difficult problem in the recovery of natural gas is the clogging of pipes caused by small amounts of wax that accumulate over time. In the Gulf of Mexico, natural gas at the bottom of the well can be 250 bars and 100°C, but it must be reduced to 100 bars to be permitted in the pipeline, and the sea floor can drop to 5°C. The reduction in pressure and temperature results in a loss of carrying power and the small amounts of heavy liquid hydrocarbons can condense, eventually coating the walls with viscous liquid. After the liquid has formed, further cooling can cause solid wax to deposit on the walls of the pipe. These deposits cause constrictions and larger pressure drops that lead to more deposits, and so forth.

Table 14.1. Summary of Data for Wax Fractions and Calculations of the Precipitate Composition as Calculated by [Example 14.12](#)

Species	Wt%	M_i	$\rho(g/cm^3)$	$\rho^p(g/cm^3)$	z_i^{tot}	z_i^w	T^{fus}	ΔH^{fus} (J/mol)	K_i^{320}	x_i^S
<c4	0.031	29	0.416	0.619	0.003	0.000	---	---		
c5	0.855	71	0.632	0.679	0.031	0.000	92	3904		
c6	0.377	82	0.695	0.689	0.012	0.000	131	6386		
c7	2.371	91	0.751	0.696	0.068	0.021	155	8419	28.98	0.0007
c8	2.285	103	0.778	0.704	0.058	0.016	181	11134	24.75	0.0006
c9	2.539	116	0.793	0.712	0.057	0.015	204	14080	20.81	0.0007
c10	2.479	132	0.798	0.721	0.049	0.013	225	17714	16.78	0.0008
c11	1.916	147	0.803	0.728	0.034	0.009	241	21128	13.67	0.0006
c12	2.352	163	0.817	0.735	0.038	0.009	255	24777	10.95	0.0008
c13	2.091	175	0.836	0.740	0.031	0.007	264	27519	9.26	0.0008
c14	3.677	190	0.843	0.746	0.051	0.011	273	30952	7.49	0.0015
c15	3.722	205	0.849	0.751	0.047	0.010	281	34393	6.04	0.0017
c16	2.034	215	0.853	0.754	0.025	0.005	286	36691	5.22	0.0010
c17	4.135	237	0.844	0.761	0.046	0.010	296	41757	3.78	0.0026
c18	3.772	251	0.846	0.764	0.039	0.008	301	44989	3.07	0.0027
c19	3.407	262	0.857	0.767	0.034	0.007	304	47532	2.60	0.0026
c20	2.781	268	0.868	0.769	0.027	0.005	306	48921	2.38	0.0021
c21	3.292	284	0.862	0.773	0.030	0.006	311	52631	1.86	0.0031
c22	3.14	299	0.863	0.776	0.027	0.005	315	56116	1.48	0.0035
c23	3.445	315	0.963	0.780	0.029	0.003	319	59841	1.15	0.0027
c24	3.254	330	0.865	0.783	0.026	0.005	322	63340	0.91	0.0052
c25	2.975	342	0.867	0.785	0.023	0.004	324	66144	0.75	0.0054
c26	3.038	352	0.869	0.787	0.023	0.004	326	68485	0.64	0.0061
c27	2.085	371	0.873	0.791	0.015	0.002	330	72941	0.47	0.0052
c28	2.74	385	0.877	0.793	0.019	0.003	332	76231	0.37	0.0079
c29	3.178	399	0.881	0.796	0.021	0.003	334	79527	0.29	0.0107
>c30	31.12	578	0.905	0.821	0.141	0.011	355	122213	0.01	0.9308

The fusion (melting) temperatures and heats of fusion for n -paraffins can be calculated according to the correlations of Won.³

$$T_i^{fus}(K) = 374.5 + 0.02617M_i - 20172/M_i \quad 14.27$$

$$\Delta H_i^{fus}(\text{cal/mol}) = 0.1426M_iT_i^{fus} \quad 14.28$$

$$z_i^W = z_i^{tot} \left[1 - \left(0.8824 + \frac{0.5353M_i}{1000} \right) \left(\frac{\rho_i - \rho_i^P}{\rho_i^P} \right)^{0.1144} \right] \quad 14.29$$

$$\rho_i^P(\text{g/cm}^3) = 0.3915 + 0.0675 \ln(M_i) \quad 14.30$$

where z_i^{tot} is the species overall mole fraction in the initial sample.

z_i^W is the portion of that fraction which is wax-forming (i.e., n -paraffin).

Example 14.12. Wax precipitation

Use the data from the first four columns of [Table 14.1](#) and correlations for wax to estimate the solid wax phase amount and the composition of the solid as a function of temperature. Use your estimates to predict the temperature at which wax begins to precipitate. Hansen et al. give the experimental value as 304 K.

Solution

This problem is basically a multicomponent variation of the binary solid-liquid equilibrium problems discussed above. The main difference is that the solid phase is not pure. We can adapt the algorithm as follows.

Assuming ideal solution behavior for both the solid and liquid phases, we define $K_i = x_i^L/x_i^S$, and as before, we assume the difference in heat capacities between liquid and solid is negligible relative to the heat of fusion,

$$K_i = \exp\left[\frac{-\Delta H_i^{fus}}{RT}\left(1 - \frac{T}{T_i^{fus}}\right)\right] \quad 14.31$$

which is independent of the compositions of the liquid and solid phases because of the ideal solution assumptions. The solid solution mole fraction is given by $x_i^S = x_i^L/K_i$. Compare this method to the vapor-liquid calculations using the shortcut K -ratio in [Chapter 9](#). This is a liquid-solid freezing temperature analog to the vapor-liquid dew-temperature procedure. The liquid mole fractions are given by the z_i^W values in the table below. All that remains is to guess values of T , which changes all

K_i until $\sum_i x_i^S = 1.0$. Hand calculations would be easy with a couple of components, but spreadsheets are recommended for a multicomponent mixture. Using Solver for spreadsheet Wax.xlsx distributed with the textbook software gives $T = 320.7$ K. Intermediate results are tabulated in [Table 14.1](#). The T is slightly higher than the experimental value, but reasonably accurate considering the complex nature of the petroleum fractions and their variabilities from one geographic location to another.

14.11. Summary

$$\hat{f}_i = \gamma_i^x f_i^\circ$$

11.13

Suspect LLE if $\gamma_i^\infty > 7.4$, in which case $x_i \approx 1/\gamma_i^\infty$ is a good initial guess.⁶

$$\gamma_i^\alpha x_i^\alpha = \gamma_i^\beta x_i^\beta$$

14.1

$$\ln(x_i \gamma_i) = (-\Delta H^{fus}/R)(1/T - 1/T_m)$$

14.24

12.2. The van Laar Model

$$A_{12} = \frac{QV_1}{RT}; \quad A_{21} = \frac{QV_2}{RT}; \quad \frac{A_{12}}{A_{21}} = \frac{V_1}{V_2} \quad 12.11$$

$$\boxed{\frac{G^E}{RT} = \frac{U^E}{RT} = \frac{A_{12}A_{21}x_1x_2}{(x_1A_{12} + x_2A_{21})}} \quad 12.12$$

2.12 gives expressions for the activity coefficients. To show this for γ_1 ,

$$\frac{G^E}{RT} = \frac{n_2n_1A_{12}A_{21}}{(n_1A_{12} + n_2A_{21})} \quad 12.13$$

$$\boxed{\ln \gamma_1 = \frac{A_{12}}{\left[1 + \frac{A_{12}x_1}{A_{21}x_2}\right]^2}}; \quad \boxed{\ln \gamma_2 = \frac{A_{21}}{\left[1 + \frac{A_{21}x_2}{A_{12}x_1}\right]^2}} \quad 12.15$$

$$A_{12} = (\ln \gamma_1) \left[1 + \frac{x_2 \ln \gamma_2}{x_1 \ln \gamma_1}\right]^2 \quad A_{21} = (\ln \gamma_2) \left[1 + \frac{x_1 \ln \gamma_1}{x_2 \ln \gamma_2}\right]^2 \quad 12.16$$

12.3. Scatchard-Hildebrand Theory

Scatchard and Hildebrand recognized the unknown parameters in terms of volume fractions and disperse attraction energies that could be related to the pure component values. Defining a term called the “**solubility parameter**,”

$$U^E = \Phi_1 \Phi_2 (\delta_1 - \delta_2)^2 (x_1 V_1 + x_2 V_2) \quad 12.19$$

$$\text{where } \Phi_i = x_i V_i / \sum_i x_i V_i \text{ is known as the “volume fraction” and} \quad 12.20$$

$$\delta_i = \sqrt{a_{ii}} / V_i \text{ is known as the “solubility parameter.”} \quad 12.21$$

To estimate the value of δ_i , Scatchard and Hildebrand suggested that experimental data be used

such that

$$\delta_i = \sqrt{\frac{\Delta U_i^{vap}}{V_i}} = \sqrt{\frac{\Delta H_i^{vap} - RT}{V_i}} \quad 12.22$$

Table 12.1. Solubility Parameters in $(\text{J}/\text{cm}^3)^{1/2}$ and Molar Volumes (cm^3/mol) for Various Substances as liquids at 298 K

1-Olefins	δ	V^L	Napthenics	δ	V^L	Aromatics	δ	V^L
1-pentene	14.11	109	cyclopentane	17.80	93	benzene	18.82	88
1-hexene	15.14	124	cyclohexane	16.77	107	toluene	18.20	106
1,3 butadiene	14.52	86	Decalin	18.00	156	ethylbenzene	18.00	122
Amines	δ	V^L	Ketones	δ	V^L	styrene	19.02	114
ammonia	33.34	28	acetone	20.25	73	<i>n</i> -propylbenzene	17.59	139
methyl amine	22.91	46	2-butanone	19.02	89	anthracene	20.25	145
ethyl amine	20.45	65	2-pentanone	17.80	106	phenanthrene	20.05	186
pyridine	29.86	80	2-heptanone	17.39	139	naphthalene	20.25	125
<i>n</i> -Alkanes	δ	V^L	Alcohols	δ	V^L	Ethers	δ	V^L
<i>n</i> -pentane	14.32	114	water	47.86	18	dimethyl ether	18.00	68
<i>n</i> -hexane	14.93	130	methanol	29.66	40	diethyl ether	15.14	103
<i>n</i> -heptane	15.14	145	ethanol	25.57	58	dipropyl ether	15.95	136
<i>n</i> -octane	15.55	162	<i>n</i> -propanol	21.48	74	furan	19.23	72
<i>n</i> -nonane	15.95	177	<i>n</i> -butanol	27.82	91	THF	18.61	81
<i>n</i> -decane	16.16	194	<i>n</i> -hexanol	21.89	124			
			<i>n</i> -dodecanol	20.25	222			

$$G^E = U^E = \Phi_1 \Phi_2 (\delta_1 - \delta_2)^2 (x_1 V_1 + x_2 V_2)$$

by coefficients are

$$RT \ln \gamma_1 = V_1 \Phi_2^2 (\delta_1 - \delta_2)^2$$

Hildebrand theory.

$$RT \ln \gamma_2 = V_2 \Phi_1^2 (\delta_1 - \delta_2)^2$$

$$RT \ln \gamma_1 = V_1 \Phi_2^2 [(\delta_1 - \delta_2)^2 + 2k_{12} \delta_1 \delta_2] \quad RT \ln \gamma_2 = V_2 \Phi_1^2 [(\delta_1 - \delta_2)^2 + 2k_{12} \delta_1 \delta_2] \quad 12.26$$

12.4. The Flory-Huggins Model

Solution

$$G^E = RT(\delta_2 - \delta_1)^2 (n_1 V_1 + n_2 V_2) \Phi_1 \Phi_2$$

$$RT \ln \gamma_1 = RT(\delta_2 - \delta_1)^2 [V_1 \Phi_1 \Phi_2 + (x_1 V_1 + x_2 V_2) (\Phi_2 n \partial \Phi_1 / \partial n_1 + \Phi_1 n \partial \Phi_2 / \partial n_1)]$$

$$\Phi_1 = x_1 V_1 / (x_1 V_1 + x_2 V_2) = n_1 V_1 / (n_1 V_1 + n_2 V_2); \Phi_2 = x_2 V_2 / (x_1 V_1 + x_2 V_2) = n_2 V_2 / (n_1 V_1 + n_2 V_2).$$

$$RT \ln \gamma_1 = RT(\delta_2 - \delta_1)^2 [V_1 \Phi_2^2]$$

$$G^E = RT(x_1 \ln(\Phi_1/x_1) + x_2 \ln(\Phi_2/x_2)) + \Phi_1 \Phi_2 (x_1 + x_2 r) \chi RT$$

12.38

12.5. MOSCED and SSCED Theories

The MOSCED model is given by,⁹

$$\ln \gamma_2^\infty = \frac{V_2}{RT} \left[(\lambda_2 - \lambda_1)^2 + q_1^2 q_2^2 \frac{(\tau_2^T - \tau_1^T)^2}{\psi_1} + \frac{(\alpha_2^T - \alpha_1^T)(\beta_2^T - \beta_1^T)}{\xi_1} \right] + d_{12} \quad 12.39$$

$$d_{12} = 1 - \left(\frac{V_2}{V_1} \right)^{aa} + aa \ln \left(\frac{V_2}{V_1} \right) \quad 12.40$$

$$aa = 0.953 - 0.002314 \left((\tau_2^T)^2 + \alpha_2^T \beta_2^T \right) \quad 12.41$$

$$\alpha_i^T = \alpha_i \left(\frac{293}{T(K)} \right)^{0.8}; \beta_i^T = \beta_i \left(\frac{293}{T(K)} \right)^{0.8}; \tau_i^T = \tau_i \left(\frac{293}{T(K)} \right)^{0.4} \quad 12.42$$

$$\psi_1 = POL + 0.002629 \alpha_1^T \beta_1^T \quad 12.43$$

$$\xi_1 = 0.68(POL - 1) + [3.24 - 2.4 \exp(-0.002687(\alpha_1 \beta_1)^{1.5})]^{(293/T)^2} \quad 12.44$$

$$POL = 1 + 1.15 q_1^4 [1 - \exp(-0.002337(\tau_1^T)^3)] \quad 12.45$$

Table 12.2. Dispersion (λ) and Polarity (τ) Parameters in $(\text{J}/\text{cm}^3)^{1/2}$ liquids at 293 K

1-Olefins	λ	τ	Napthenics	λ	τ	Aromatics	λ	τ
1-pentene	14.6	0.25	Cyclopentane	16.6	0	Benzene	16.7	3.95
1-hexene	15.2	0.23	Cyclohexane	16.7	0	Toluene	16.6	3.22
Amines	λ	τ	Ketones	λ	τ	Ethylbenzene	16.8	2.98
Aniline	16.5	9.41	Acetone	13.7	8.30	Naphthalene	17.8	4.53
Pyridine	16.4	6.13	2-butanone	14.7	6.64	Phenanthrene	18.5	5.31
			2-pentanone	15.1	5.49	Naphthalene	17.8	4.53
			2-heptanone	14.7	4.20			
n-Alkanes	λ	τ	Alcohols	λ	τ	Ethers	λ	τ
n-pentane	14.4	0.0	Water	10.6	10.5	Diethyl ether	14.0	2.79
n-hexane	14.9	0.0	Methanol	14.4	3.77	Dipropyl ether	15.2	2.00
n-heptane	15.2	0.0	Ethanol	14.4	2.53	MTBE	15.2	2.48
n-octane	15.4	0.0	n-propanol	14.0	1.95	THF	15.8	4.41
n-nonane	15.6	0.0	n-butanol	14.8	1.86			
n-decane	15.7	0.0	n-hexanol	15.0	1.27			
			n-octanol	15.1	1.31			

The SSCED Model

$$G^E = V\Phi_1\Phi_2[(\delta_2' - \delta_1')^2 + 2k_{12}\delta_2'\delta_1'] \quad 12.48$$

$$RT\ln\gamma_k = V_k(1 - \Phi_k)^2[(\delta_2' - \delta_1')^2 + 2k_{12}\delta_2'\delta_1'] \quad 12.49$$

$$(\delta_i')^2 = \delta_i^2 - 2\alpha_i\beta_i \quad 12.50$$

$$k_{12} = \frac{(\alpha_2 - \alpha_1)(\beta_2 - \beta_1)}{4\delta_2'\delta_1'} \quad 12.51$$

13.4. UNIQUAC

UNIQUAC⁵ (short for UNiversal QUAsi Chemical model)

$$\left(\frac{G^E}{RT}\right)^{COMB} = \left(x_1 \ln \frac{\Phi_1}{x_1} + x_2 \ln \frac{\Phi_2}{x_2}\right) - 5 \left[q_1 x_1 \ln \left(\frac{\Phi_1}{\theta_1}\right) + q_2 x_2 \ln \left(\frac{\Phi_2}{\theta_2}\right) \right]. \quad 13.42$$

$$\Phi_j = \frac{x_j r_j}{\sum_i x_i r_i} \quad \theta_j = \frac{x_j q_j}{\sum_i x_i q_i} \quad 13.43$$

$$r_j = \sum_k v_k^{(j)} R_k ; \quad q_j = \sum_k v_k^{(j)} Q_k \quad 13.44$$

Main Group	Sub-group	$R(\text{rel.vol.})$	$Q(\text{rel.area})$	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: 1 CH + 3 CH ₃
	C	0.2195	0	Neopentane: 1 C + 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 ^b	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 Methylethylketone: 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
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

a. AC in the table means aromatic carbon. The main groups serve as categories for similar subgroups as explained in the UNIFAC section.

b. 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. 1977-*Vapor-Liquid Equilibrium Data Collection*. Frankfurt, Germany: DECHEMA.

$$\ln \gamma_1 = \ln(\Phi_1/x_1) + (1 - \Phi_1/x_1) - 5q_1[\ln(\Phi_1/\theta_1) + (1 - \Phi_1/\theta_1)] + q_1[1 - \ln(\theta_1 + \theta_2 \tau_{21}) - \theta_1/(\theta_1 + \theta_2 \tau_{21}) - \theta_2 \tau_{12}/(\theta_1 \tau_{12} + \theta_2)] \quad 13.49$$

$$\ln \gamma_2 = \ln(\Phi_2/x_2) + (1 - \Phi_2/x_2) - 5q_2[\ln(\Phi_2/\theta_2) + (1 - \Phi_2/\theta_2)] + q_2[1 - \ln(\theta_1 \tau_{12} + \theta_2) - \theta_1 \tau_{21}/(\theta_1 + \theta_2 \tau_{21}) - \theta_2/(\theta_1 \tau_{12} + \theta_2)] \quad 13.50$$

$$\tau_{ij} = \exp\left(\frac{-a_{ij}}{T}\right) \quad 13.51$$

13.5. UNIFAC

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

$$\ln \gamma_1^{RES} = \frac{\mu_1 - \mu_1^o}{RT} = \sum_m v_m^{(1)} [\ln \Gamma_m - \ln \Gamma_m^{(1)}] \quad 13.56$$

Table 13.3. Selected 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	---

Table 13.4. 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

13.6. COSMO-RS Methods