

Example 9.1

Use the van Laar activity coefficient expression to predict the compositions of co-existing liquid phases (I and II) comprised of two partially miscible liquids (1) and (2) at 50°C and 4 bar. At these conditions the van Laar equations are given by:

$$\ln \gamma_1 = \frac{A_{12}}{[1 + \frac{A_{12}x_1}{A_{21}x_2}]^2}; \ln \gamma_2 = \frac{A_{21}}{[1 + \frac{A_{21}x_2}{A_{12}x_1}]^2}; A_{12} = 2.5; A_{21} = 3.5$$

Solution:

This system is a binary; however, there are 2 phases since '1' and '2' are partially miscible. One of the phases (I) is rich in component '1' (with some '2' dissolved in it); while the second phase (II) is rich in component '2' (with some '1' dissolved in it). Estimates of the composition of both phases are required. We use two equations of type 9.34 as there are 2 components.

For component 1:

$$x_1^I \gamma_1^I = x_1^I \exp\left(\frac{\alpha}{[1 + \frac{\alpha x_1^I}{\beta(1-x_1^I)}]^2}\right) = x_1^{II} \exp\left(\frac{\alpha}{[1 + \frac{\alpha x_1^{II}}{\beta(1-x_1^{II})}]^2}\right) = x_1^{II} \gamma_1^{II} \quad \text{..(a)}$$

For component 2:

$$x_2^I \gamma_2^I = x_2^I \exp\left(\frac{\beta}{[1 + \frac{\beta x_2^I}{\alpha(1-x_2^I)}]^2}\right) = x_2^{II} \exp\left(\frac{\beta}{[1 + \frac{\beta x_2^{II}}{\alpha(1-x_2^{II})}]^2}\right) = x_2^{II} \gamma_2^{II} \quad \text{..(b)}$$

$$\text{Lastly } x_1^I + x_2^I = 1 \quad \text{..(c)}$$

$$\text{And: } x_1^{II} + x_2^{II} = 1 \quad \text{..(d)}$$

Equations I – IV need to be solved simultaneously using a suitable algorithm to obtain the final solution: $x_1^I = 0.12$, $x_1^{II} = 0.85$; and $x_2^I = 0.88$, $x_2^{II} = 0.15$

Example 9.2

Estimate solubility of a solid A in a liquid B at 300°K, using (i) ideal solution assumption, (ii) regular solution model for liquid-phase. The following data are available: $V_A^L = 100\text{cm}^3 / \text{mol}$; $V_B^L = 125\text{cm}^3 / \text{mol}$; $\delta_A = 9.5(\text{cal} / \text{cc})^{1/2}$; $\delta_B = 7.5(\text{cal} / \text{cc})^{1/2}$. Heat of fusion for A: 17.5 kJ/mol. Melting point for A = 350°K.

Assuming that solid-phase is pure naphthalene (which is in equilibrium with solution of naphthalene in hexane), $z_1 = 1$, $\gamma_1^S = 1$, we start with the simplified equation:

$$\ln x_A = -\ln \gamma_A - \left[\frac{\Delta H_{T_m, A}^{fus}}{R} \left(\frac{1}{T} - \frac{1}{T_{m, A}} \right) \right]$$

For ideal solution the above equation reduces to:

$$\ln x_A = - \left[\frac{\Delta H_{T_m, A}^{fus}}{R} \left(\frac{1}{T} - \frac{1}{T_{m, A}} \right) \right]$$

$$\text{Using the data provided: } \ln x_A = - \left[\frac{17500}{8.314} \left(\frac{1}{300} - \frac{1}{350} \right) \right]$$

Thus, the ideal solubility $x_A = 0.38$.

By Regular solution theory: $RT \ln \gamma_A = V_A^L (\delta_A - \delta_B)^2 \Phi_B^2$

$$\therefore \ln x_A = - \frac{V_A^L \Phi_B^2 (\delta_A - \delta_B)^2}{RT} - \frac{\Delta H^{fus}}{RT} \left[1 - \frac{T}{T_{m, A}} \right] \quad \text{..(1)}$$

$$\text{Also } \Phi_B = \frac{x_B V_B^L}{x_A V_A^L + x_B V_B^L} \quad \text{..(2)}$$

$T = 300 \text{ K}$, $T_{m_1} = 350^\circ\text{K}$

$V_A^L = 100\text{cm}^3 / \text{mol}$; $V_B^L = 125\text{cm}^3 / \text{mol}$; $\delta_A = 9.5(\text{cal} / \text{cc})^{1/2}$; $\delta_B = 7.5(\text{cal} / \text{cc})^{1/2}$. Solution algorithm:

- (1) Assume x_A (to start with assume $x_A = 0$)
- (2) Calculate Φ_B from eqn 2
- (3) Use equation (1) to calculate new x_A
- (4) If $x_{A, i+1} - x_{A, i} < 0.01$, $x_{A, i+1}$ is the solution or else, return to step '1'.

The final converged value for $x_A \approx 0.08$

Note that the result differs significantly from that obtained by assuming ideal solution behaviour for the liquid phase.

Example 9.3

Compute the eutectic composition and temperature for a mixture of two substances A and B using the following data:

Property	A	B
Normal T_m ($^{\circ}\text{K}$)	180	181
ΔH^{fus} (J/mol)	6600	9075

We use the ideal solution behaviour for the liquid phase. The following equation then holds at the eutectic point:

$$\exp\left[\frac{\Delta H_A^{\text{fus}}}{RT_{m,A}}\left(\frac{T - T_{m,A}}{T}\right)\right] + \exp\left[\frac{\Delta H_B^{\text{fus}}}{RT_{m,B}}\left(\frac{T - T_{m,B}}{T}\right)\right] = 1$$

On substituting all relevant data:

$$\exp\left[\frac{6600}{8.314 \times 180}\left(\frac{T - 180}{T}\right)\right] + \exp\left[\frac{9075}{8.314 \times 181}\left(\frac{T - 180}{T}\right)\right] = 1$$

On solving by trial and error, $T(\text{eutectic}) \approx 150^{\circ}\text{K}$

The eutectic composition is found from the following equation:

$$x_A = \exp\left[\frac{\Delta H_A^{\text{fus}}}{RT_{m,A}}\left(\frac{T - T_{m,A}}{T}\right)\right]$$

Substituting all the available data with $T = 150^{\circ}\text{K}$, the eutectic composition is found to be:

$$x_A \approx 0.5.$$

Example 9.4

A certain solid A has a vapour pressure of 0.01 bar at 300⁰K. Compute its solubility at the same temperature in a gas B at a pressure of 1.0bar. The molar volume of the solid is 125cc/mol.

We start with the following equation:

$$P_A^{sat} \phi_A^{sat} \exp \left[\frac{V_A^S (P - P_A^{sat})}{RT} \right] = y_A \hat{\phi}_A P$$

Since $P_A^{sat} = 10^{-2} \text{ bar}$, $\phi_A^{sat} \approx 1.0$

Further as the total system pressure is 1.0bar, it follows that

$$\hat{\phi}_A \cong 1.0$$

Thus the solubility of the solid at the system pressure is given by:

$$y_A = (P_A^{sat} / P) \exp \left[\frac{V_A^S (P - P_A^{sat})}{RT} \right]$$

Substituting all relevant data the solubility is:

$$y_A = 1.05 \times 10^{-2}.$$