10.40 Thermodynamics **Fall 2003**
Problem Set 10

Problem 15.29 Text

Solution:

To determine if the Margules equation is applicable for the limit of miscibility of a binary solution, we examine the behavior at the consolute point. In particular, we look at the values of A and B at the consolute point. At the consolute point, the spinodal and binodal curves meet. The limit of stability that corresponds to the spinodal curve, Eq. (15-153), applies to the consulate point.

$$\left(\frac{\partial^2 \Delta G_{mix}}{\partial x_1^2}\right)_{T.P} = 0 \qquad (15\text{-}153)$$

When $\left(\frac{\partial^2 \Delta G_{mix}}{\partial x_1^2}\right)_{T.P} \geq 0$, the solution is stable, which means that only a single phase will be present.

An additional criterion of stability is applicable at the consolute point since it behaves as a critical point. From Section 7.3, at the critical point, or the consulate point in this problem,

$$y^{(m-2)}_{(m-1)(m-1)(m-1)} = 0 \text{ with } m = n + 2 \qquad (7\text{-}39)$$

Following a similar derivation to Section 15.7, the second criteria for the consolute point is:

$$\left(\frac{\partial^3 \Delta G_{mix}}{\partial x_1^3}\right)_{T.P} = 0 \qquad (1)$$

In the problem we are given and equation of state for ΔG_{mix}^{EX}. It can be related to ΔG_{mix} by applying Eq. (9-168).

$$\Delta G_{mix} = \Delta G_{mix}^{EX} + \Delta G_{mix}^{ID} \qquad (2)$$

where $\Delta G_{mix}^{ID} = RT\left(x_1 \ln x_1 + x_2 \ln x_2\right)$ (9-101)

Combining equations for ideal and excess properties yields,

$$\frac{\Delta G_{mix}}{RT} = Ax_1^2\left(1-x_1\right) + Bx_1\left(1-x_1\right)^2 + x_1 \ln x_1 + \left(1-x_1\right)\ln\left(1-x_1\right) \tag{3}$$

Differentiation of Eq. (3) results in,

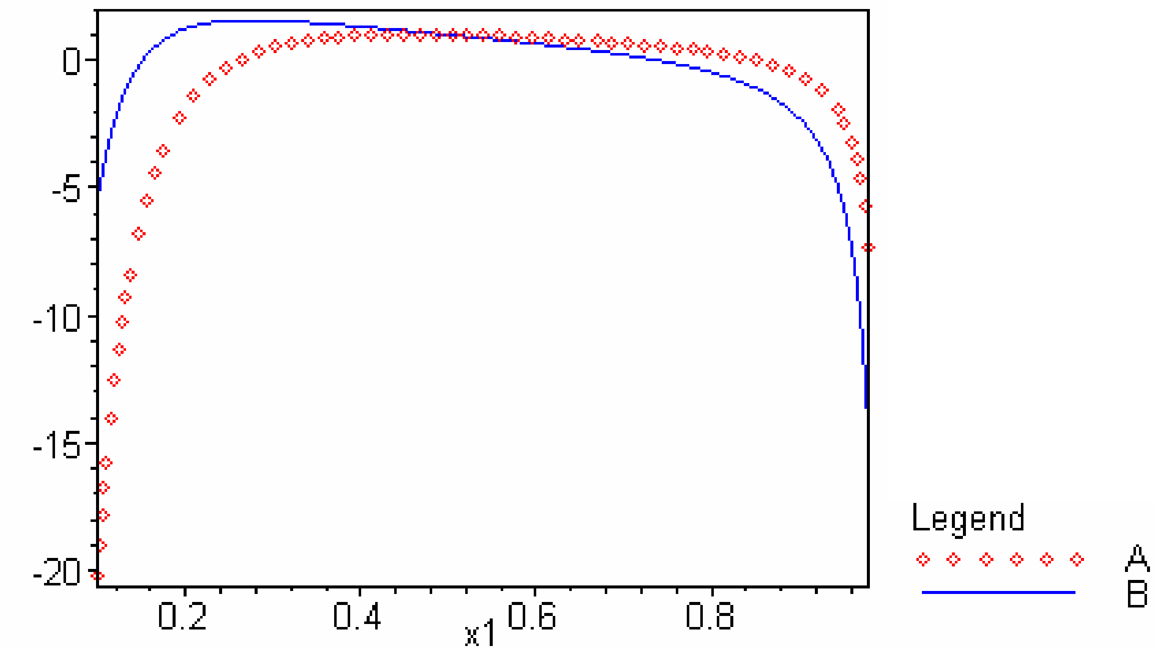
$$\left(\frac{\Delta^2 G_{mix}}{\partial x_1^2}\right)_{T,P} = RT\left[A\left(2-6x_1\right) + B\left(-4+6x_1\right) + \frac{1}{x_1} + \frac{1}{\left(1-x_1\right)}\right] = 0 \tag{4}$$

$$\left(\frac{\Delta^3 G_{mix}}{\partial x_1^3}\right)_{T,P} = RT\left[-6A + 6B - \frac{1}{x_1^2} + \frac{1}{\left(1-x_1\right)^2}\right] = 0 \tag{5}$$

Solving for A and B from Eqs. (4) and (5) yields their values at the consolute point as a function of solution composition.

$$\begin{aligned} A_c &= \frac{-9x_1^2 + 10x_1 - 2}{6x_1^2\left(1-x_1\right)^2} \\ B_c &= \frac{-9x_1^2 + 8x_1 - 1}{6x_1^2\left(1-x_1\right)^2} \end{aligned} \tag{6}$$

The values of A_c and B_c are applicable over the entire composition range except for where x_1 equals zero or one (where there will be a single pure phase of either component 1 or 2). By inspection of Eq. (4), when A and B are less than their critical values, $\left(\frac{\partial^2 \Delta G_{mix}}{\partial x_1^2}\right)_{T.P} > 0$, so the solutions will be miscible and form a single phase. When A and B are greater than their critical values, the solutions will not be miscible and will form two phases. The values of A and B are constrained by Eq. (6) and are plotted below. As x_1 goes to 0 or 1, the values of A and B go to negative infinity. Since the Margules equation gives conditions for solutions ranging from a single solution through the consolute point and to liquid-liquid equilibrium, it can be used for liquid-liquid equilibrium problems.



Experimental determination of A and B

Values of A and B can be found for a binary mixture based on values of x_1 or x_2 in the two liquid phases. At equilibrium between liquid 1 (α) and liquid 2 (β), the fugacity of each component in the α and β phases are equal.

$$\hat{f}_i^{\alpha} = \gamma_i^{\alpha} x_i^{\alpha} f_i^{\alpha}(T,P) = \gamma_i^{\beta} x_i^{\beta} f_i^{\beta}(T,P) = \hat{f}_i^{\beta} \tag{7}$$

Since f_i^{α} and f_i^{β} is the fugacity of x_i=1 at T and P of interest, they are equivalent. Eq. (7) reduces to:

$$\gamma_1^{\alpha} x_1^{\alpha} = \gamma_1^{\beta} x_1^{\beta} \tag{8}$$

$$\gamma_2^{\alpha} x_2^{\alpha} = \gamma_2^{\beta} x_2^{\beta} \tag{9}$$

and can be rewritten in natural log form as:

$$\ln \gamma_1^{\alpha} - \ln \gamma_1^{\beta} = \ln x_1^{\beta} - \ln x_1^{\alpha} \tag{10}$$

$$\ln \gamma_2^{\alpha} - \ln \gamma_2^{\beta} = \ln x_2^{\beta} - \ln x_2^{\alpha} \tag{11}$$

The Margules equation can be related to the activity coefficient by a combination of Eqs. (9-180) and (9-53).

$$RT\ln\gamma_i = \overline{\Delta G_i^{EX}} = \Delta G_{mix}^{EX} - x_j\left(\frac{\partial \Delta G_{mix}^{EX}}{\partial x_j}\right)_{T,P,x[j,i]} \quad \text{for } j \neq i \tag{12}$$

Plugging the Margules equation into (12) and simplifying yields:

$$\ln\gamma_1 = 2A\left(x_2^2 - x_2^3\right) + B\left(2x_2^3 - x_2^2\right) = \left(B + 2\left(A - B\right)x_1\right)x_2^2 \tag{13}$$

$$\ln\gamma_2 = A\left(2x_1^3 - x_1^2\right) + 2B\left(x_1^2 - x_1^3\right) = \left(A + 2\left(B - A\right)x_2\right)x_1^2 \tag{14}$$

Substituting Eqs. (13) and (14) into (10) and (11) yields two equations with two unknowns (A and B) given experimental pairs of values for x_i^α and x_i^β. These equations can be written as:

$$\left(B + 2\left(A - B\right)x_1^\alpha\right)\left(1 - x_1^\alpha\right)^2 - \left(B + 2\left(A - B\right)x_1^\beta\right)\left(1 - x_1^\beta\right)^2 = \ln x_1^\beta - \ln x_1^\alpha \tag{15}$$

$$\left(A + 2\left(B - A\right)\left(1 - x_1^\alpha\right)\right)\left(x_1^\alpha\right)^2 - \left(A + 2\left(B - A\right)\left(1 - x_1^\beta\right)\right)\left(x_1^\beta\right)^2 = \ln\left(1 - x_1^\beta\right) - \ln\left(1 - x_1^\alpha\right) \tag{16}$$

Thus, A and B can be determined experimentally using Eqs. (15) and (16).