May 1, 2008

Problem 2.

The 2-suffix Margules equation gives the excess Gibbs energy for binary liquid mixtures where the chemical nature of the two components is reasonably similar:

$g^E / RT = A x_1 x_2$,

where A is a function of temperature only. Determine the range of values for A which allow an azeotrope to form given that the ratio of the saturation pressures of the two components: $P_1^{sat}/P_2^{sat} = 1.2$ *and the overall pressure of the system is low.*

Solution:

Begin with the criteria for phase equilibrium:

$$\begin{aligned} \hat{f}_1^v &= \hat{f}_1^L \\ \hat{f}_2^v &= \hat{f}_2^L \end{aligned} \tag{1}$$

Expanding one of these expressions:

$$\hat{\varphi}_1 y_1 P = x_1 \gamma_1 P_1^{sat} \hat{\varphi}^{sat} \mathscr{P} \tag{2}$$

If the overall pressure of the system is low, we can assume ideal behavior in the gas phase and assume the fugacity coefficients and Poynting correction are all 1. At an azeotrope, $y_i = x_i$, so Equation 2 reduces to

$$P = \gamma_1 P_1^{sat} \tag{3a}$$

$$P = \gamma_2 P_2^{sat} \tag{3b}$$

$$where \quad \hat{\varphi}_i = \hat{\varphi}_i^{sat} = \mathscr{P} = 1 \text{ using the ideal gas phase assumption} \tag{4}$$

Setting Equations 3a and 3b equal to each other:

$$\gamma_1 P_1^{sat} = \gamma_2 P_2^{sat} \tag{5}$$

The activity coefficient of a species in a mixture is related to the Gibbs excess energy by the equation

$$\ln \gamma_i = \frac{\overline{g}_i^E}{RT} \tag{6}$$

For the two-suffix Margules equation,

$$RT\,\overline{g}_1^E = \frac{\partial((n_1+n_2)g^E)}{\partial n_1}$$

$$= \frac{\partial}{\partial n_1}\left((n_1+n_2)A\frac{n_1 n_2}{(n_1+n_2)^2}\right)$$

$$= A\frac{\partial}{\partial n_1}\left(\frac{n_1 n_2}{n_1+n_2}\right)$$

$$= A\left(\frac{n_2}{n_1+n_2} - \frac{n_1 n_2}{(n_1+n_2)^2}\right)$$

$$= A(x_2 - x_1 x_2)$$

$$= A(x_2 - (1-x_2)x_2)$$

$$\text{or}\quad \frac{\overline{g}_1^E}{RT} = Ax_2^2 \tag{7}$$

Since the expression for g^E is symmetric,

$$\frac{\overline{g}_2^E}{RT} = Ax_1^2 \tag{8}$$

Plugging into Equation 6

$$\begin{aligned}\gamma_1 &= \exp\left(Ax_2^2\right)\\ \gamma_2 &= \exp\left(Ax_1^2\right)\end{aligned} \tag{9}$$

Substituting these expressions into Equation 5 and using the given ratio of $\frac{P_1^{sat}}{P_2^{sat}} = 1.2$

$$\frac{\gamma_2}{\gamma_1} = \frac{P_1^{sat}}{P_2^{sat}}$$

$$\frac{\exp\left(Ax_1^2\right)}{\exp\left(Ax_2^2\right)} = 1.2$$

$$\frac{\exp\left(Ax_1^2\right)}{\exp\left(A(1-x_1)^2\right)} = 1.2$$

$$\frac{\exp\left(Ax_1^2\right)}{\exp\left(A(1-2x_1+x_1^2)\right)} = 1.2$$

Cancelling the Ax_1^2 terms and rearranging

$$0.833 = \exp(A - 2Ax_1)$$
$$-0.1823 = A - 2Ax_1$$

$$x_1 = \frac{1}{2} + \frac{0.1823}{2A} \qquad (10)$$

An azeotrope can exist when $0 < x_1 < 1$ or

$$0 < \frac{1}{2} + \frac{0.1823}{2A} < 1 \qquad (11)$$

Examining the bound on A from the lower bound on x_1 :

$$0 < \frac{1}{2} + \frac{0.1823}{2A}$$
$$0 < 1 + \frac{0.1823}{A}$$
$$0 < \frac{A + 0.1823}{A}$$
$$\text{then } \; A < -0.1823 \text{ or } A > 0 \qquad (12)$$

Looking now at the upper bound on x_1:

$$\frac{1}{2} + \frac{0.1823}{2A} < 1$$
$$1 + \frac{0.1823}{A} < 2$$
$$-1 + \frac{0.1823}{A} < 0$$
$$\frac{-A + 0.1823}{A} < 0$$
$$\frac{A - 0.1823}{A} > 0$$
$$\text{then } \; A > 0.1823 \text{ or } A < 0 \qquad (13)$$

Combining the bounds on A (Equations 12 and 13),

$\boxed{A > 0.1823 \text{ or } A < -0.1823}$ for an azeotrope to exist.

Grading Scheme:

1. 1 point for $\hat{\varphi}_i = \hat{\varphi}_i^{sat} = \mathscr{P} = 1$ using the ideal gas phase assumption
2. 1 point for $y_1 = x_1$ at an azeotrope
3. 3 points for $\gamma_1 P_1^{sat} = \gamma_2 P_2^{sat}$
4. 1 point for $\ln \gamma_1 = \dfrac{\overline{g}_1^E}{RT} = A x_2^2$
5. 1 point for $\ln \gamma_2 = \dfrac{\overline{g}_2^E}{RT} = A x_1^2$
6. 2 points for a valid expression relating A and x_1 or x_2 such as $x_1 = \dfrac{1}{2} + \dfrac{0.1823}{2A}$
7. 2 points for recognizing that $0 < x_1 < 1$
8. 2 points for recognizing that 0.1823 and -0.1823 are the boundaries for A
9. 2 point for $A > 0.1823$ and $A < -0.1823$