

Chemical Engineering Thermodynamics
Quiz 12 April 14, 2016

- 1) For the water/ethylene glycol mixture we calculated that the freezing temperature for a 0.225 mole percent ethylene glycol was 240 K and $\gamma_1 = 1.86$ using $\Delta H_{f,1} = 6,000$ J/mole, and $T_f = 273$ K in HW problem 14.25. This is typical for an automotive coolant mix partly due to the better heat capacity and lower volatility of water. For aircraft de-icing a propylene glycol/water mixture is used with typically 75% propylene glycol (as well as a polymer additive such as polyetheleneoxide or polypropyleneoxide (Pluronic[®] copolymer)).
- a) Sketch a rough plot of the freezing temperature versus mole fraction propylene glycol showing how the minimum freezing temperature could be determined.
- b) The melting point of pure propylene glycol is 214°K (*ethylene glycol is 260°K*) and the heat of fusion for pure propylene glycol is 8,180 J/mole (*ethylene glycol is 9,900 J/mole*). Assume an ideal solution between propylene glycol and water and calculate the melting (freezing) point of a 0.75 mole percent propylene glycol binary mixture.
- c) Compare your calculation in part b with a calculation using water as the basis. Which is the appropriate value to use, part b or part c? (Refer to the plot you made in part a.)
- d) The literature value for the freezing point of a 75 mole % propylene glycol mixture is -55 °C (218 °K). Calculate the activity coefficient. Does water/propylene glycol show a positive or a negative deviation from Raoult's Law?
- 2) Ethyl Acetate (1) and water (2) form a two-phase liquid at 335°K with an equimolar mixture ($z_1=z_2=0.5$).
- a) Calculate the composition of the two phases, α (water rich) and β (ethyl acetate rich), that form using the one parameter Margules model, $A_{12} = 2.70$. (The final composition is about $x_1^\alpha \sim 0.2$, and $x_1^\beta \sim 0.85$ from Figure 14.5 (shown below). Do the initial estimation and then two iterations to show that you are approaching the observed values in Figure 14.5.
- b) Given that the initial composition is $z = 0.5$ can you estimate the fraction of the total material that is in the α -phase using the graph values for the composition? (This is a calculation based on a tie line construction in Figure 14.5.)

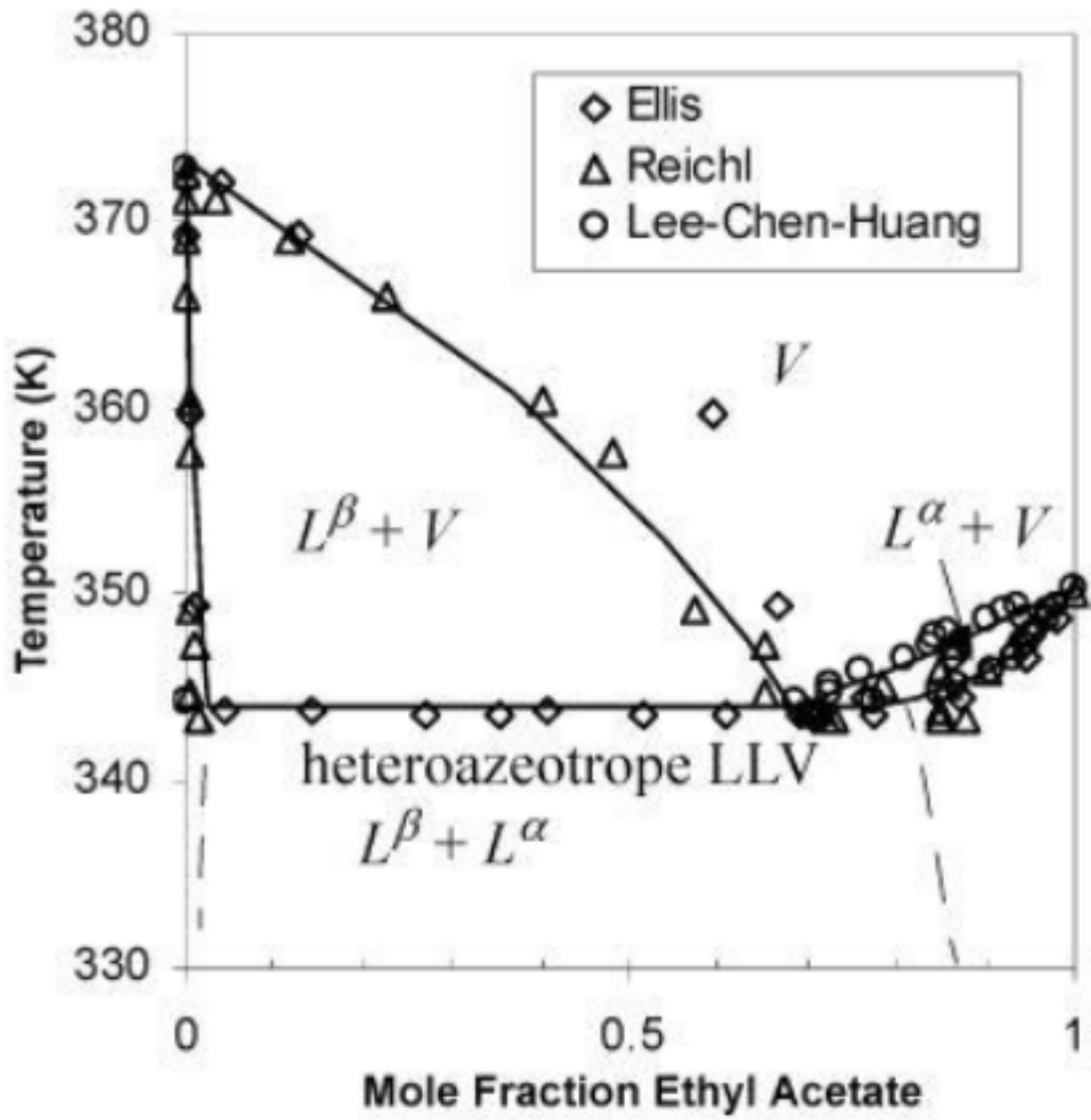


Figure 14.5

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.

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

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

$$\gamma_i^\alpha x_i^\alpha = \gamma_i^\beta x_i^\beta \quad 14.1$$

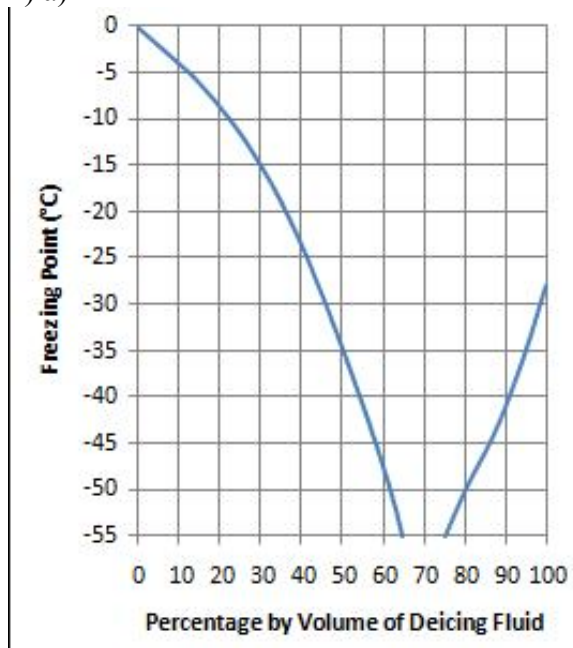
❗ The one-parameter Margules equation is the simplest excess Gibbs expression.

$$\begin{aligned} \frac{G^E}{RT} &= A_{12} x_1 x_2 & 11.5 \\ \ln \gamma_1 &= A_{12} x_2^2 \\ \ln \gamma_2 &= A_{12} x_1^2 \end{aligned}$$

$$R = 8.314 \text{ J/(mole } ^\circ\text{K)}$$

**ANSWERS: Chemical Engineering Thermodynamics
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1) a)



From Wikipedia. Percent propylene glycol is shown on the x-axis of the plot. A green pigment has been added to the propylene glycol/water mixture in the image. Notice that adding water reduces the freezing point. The eutectic occurs at about 70 volume percent propylene glycol (or about 75 mole percent).

1) b)

$$\ln(x_2 \gamma_2) = \frac{-\Delta H_f}{R} \left(\frac{1}{T} - \frac{1}{T_{m2}} \right)$$

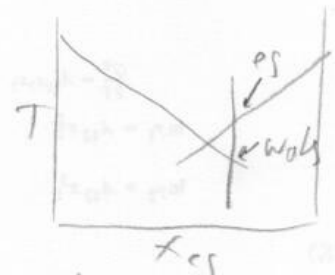
for ideal $\gamma_2 = 1$

$$\left(\frac{-R \ln(x_2)}{\Delta H_f} + \frac{1}{T_{m2}} \right)^{-1} = T$$

$$\left(\frac{-8.314 \text{ J/molK} \ln(0.75)}{8,180 \text{ J/mol}} + \frac{1}{214 \text{ K}} \right)^{-1} = 201 \text{ K} \quad (-71^\circ\text{C})$$

c) for water

$$\left(\frac{-8.314 \text{ J/molK} \ln(0.25)}{6,000 \text{ J/mol}} + \frac{1}{273 \text{ K}} \right)^{-1} = 179 \text{ K} \quad (-94^\circ\text{C})$$



use part (b) for ethylene glycol

d) Solve top equation for γ_2

$$\begin{aligned} \gamma_2 &= \frac{1}{x_2} \exp\left(\frac{-\Delta H_f}{R} \left(\frac{1}{T} - \frac{1}{T_{m2}} \right)\right) \\ &= \frac{1}{0.75} \exp\left(\frac{-8180 \text{ J/mol}}{8.314 \text{ J/molK}} \left(\frac{1}{218} - \frac{1}{214} \right)\right) = 1.45 \end{aligned}$$

②

Positive deviation from Raoult

$$\gamma > 1$$

2)

water

ethyl alcohol

(2)

(1)

α

β

1) B is pure 1 so $\gamma_1^B = 1$ ($\gamma_2^A = 1$)

$$x_1^B \gamma_1^A = x_1^A \gamma_1^\alpha \qquad x_2^A \gamma_2^B = x_2^B \gamma_2^\beta$$

$$x_1^\alpha = \frac{1}{\gamma_1^\alpha} \qquad (x_2^\beta = \frac{1}{\gamma_2^\beta})$$

$$\ln \gamma_1^\alpha = A_{12} (x_2^\alpha)^2$$

$$\gamma_1^\alpha = \exp(2.70) \\ = 14.9$$

$$\gamma_2^\beta = \exp(2.70) \\ = 14.9$$

$$x_1^\alpha = \frac{1}{14.9} = 0.067 \qquad x_2^\alpha = 1 - 0.067 = 0.933$$

$$x_2^\beta = 0.067 \qquad x_1^\beta = 0.933$$

$$2) \quad K_1 = \frac{\gamma_1^B}{\gamma_1^\alpha} = 0.0965 \quad \gamma_1^B = \exp(A_2 (x_2^B)^2) = 1.012 \quad \textcircled{3}$$

$$\gamma_1^\alpha = \exp(A_2 (x_2^\alpha)^2) = 10.49$$

$$K_2 = \frac{\gamma_2^B}{\gamma_2^\alpha} = 10.36 \quad \gamma_2^B = \exp(A_2 (x_1^B)^2) = 10.49$$

$$\gamma_2^\alpha = \exp(A_2 (x_1^\alpha)^2) = 1.012$$

$$3) \quad x_1^B = \left(\frac{1 - K_2}{K_1 - K_2} \right) = 0.912 \quad x_2^B = 1 - x_1^B = 0.088$$

$$4) \quad x_1^\alpha = K_1 x_1^B = 0.088 \quad x_2^\alpha = 1 - x_1^\alpha = 0.912$$

$$5) \quad K_1 = \frac{\gamma_1^B}{\gamma_1^\alpha} = 0.108 \quad \gamma_1^B = \exp(A_2 (x_2^B)^2) = 1.021$$

$$6) \quad \gamma_1^\alpha = \exp(A_2 (x_2^\alpha)^2) = 9.447$$

$$K_2 = \frac{\gamma_2^B}{\gamma_2^\alpha} = 9.25 \quad \gamma_2^B = \exp(A_2 (x_1^B)^2) = 9.447$$

$$\gamma_2^\alpha = \exp(A_2 (x_1^\alpha)^2) = 1.021$$

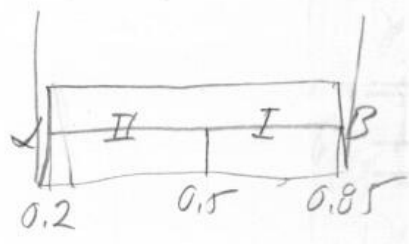
$$7) \quad x_1^B = \left(\frac{1 - K_2}{K_1 - K_2} \right) = 0.903 \quad x_2^B = 0.097$$

$$x_1^\alpha = 0.106 \quad x_1^B = 0.907 \quad x_2^\alpha = 0.903$$

(x_1^α is approaching 0.2
 x_1^B is approaching 0.85)

④

b)



$$\text{Fraction of } \alpha \text{ phase} = \frac{I}{II + I} = \frac{0.85 - 0.2}{0.85 - 0.2}$$
$$= 0.54$$

54 mol% α
46 mol% β