

Homework 8: Problem 8.17

April 23, 2008

We're given a binary mixture of 1 and 2 at 298 K and 90 bar. The vapor phase has the following equation of state:

$$\begin{aligned}v &= \frac{RT}{P} + P(Ay_1y_2 + B) \\ \frac{A}{RT} &= -2.0 \times 10^{-4} \text{ [bar}^{-2}\text{]} \\ \frac{B}{RT} &= 8.0 \times 10^{-5} \text{ [bar}^{-2}\text{]} \\ \mathcal{H}_2 &= 7000 \text{ [bar]} \\ \ln \gamma_2^{Henry's} &= -7(1 - x_1^2)\end{aligned}$$

(a) given a vapor composition of 5 moles of 1 and 10 moles of 2, calculate v , V , v_2 , and \bar{V}_2 .

The first two are easy, just plug in the numbers:

$$\begin{aligned}v &= 354.6 \text{ [cm}^3\text{/mol]} \\ V &= 5319 \text{ [cm}^3\text{]}\end{aligned}$$

For v_2 substitute in $y_2 = 1$ into the EOS:

$$v_2 = 453.7 \text{ [cm}^3\text{/mol]}$$

For \bar{V}_2 , start with:

$$\begin{aligned}
\bar{V}_2 &= \left(\frac{\partial V}{\partial n_2} \right)_{T,P,n_1} \\
&= \frac{\partial}{\partial n_2} \left[(n_1 + n_2) \frac{RT}{P} + P \left(A \frac{n_1 n_2}{n_1 + n_2} + B (n_1 + n_2) \right) \right] \\
&= \frac{RT}{P} + P (A y_1^2 + B) \\
&= 404.1 \text{ [cm}^3/\text{mol]}
\end{aligned}$$

(b) Calculate ϕ_2^v and $\hat{\phi}_2^v$.

Start with Equation 7.29:

$$\begin{aligned}
\ln \phi_2^v &= \int_{P_{low}}^P \left[\frac{v_2}{RT} - \frac{1}{P} \right] dP \\
&= \int_{P_{low}}^P \left[\frac{1}{P} + P \frac{B}{RT} - \frac{1}{P} \right] dP \\
&= \frac{B}{RT} \int_{P_{low}}^P P dP \\
&= \frac{B}{RT} (P^2 - P_{low}^2) \quad \text{NOTE: should be } P^2/2.
\end{aligned}$$

If we rearrange and take the limit as $P_{low} \rightarrow 0$, we get:

$$\begin{aligned}
\phi_2^v &= \exp \left[\frac{BP^2}{RT} \right] \\
&= 1.912
\end{aligned}$$

Similarly, start with Equation 7.36

$$\begin{aligned}
RT \ln \frac{\hat{f}_2^v}{y_2 P_{low}} &= \int_{P_{low}}^P \bar{V}_2 dP \\
&= \int_{P_{low}}^P \left[\frac{RT}{P} + P (A y_1^2 + B) \right] dP \\
&= RT \ln \frac{P}{P_{low}} + (A y_1^2 + B) (P^2 - P_{low}^2)
\end{aligned}$$

Next divide by RT , subtract $\ln P$ from both sides, add $\ln P_{low}$ to both sides, rearrange, and take the limit as $P_{low} \rightarrow 0$:

$$\begin{aligned}\ln \hat{\phi}_2^v &= \ln \frac{\hat{f}_2^v}{y_2 P} \\ &= P^2 \left(\frac{A}{RT} y_1^2 + \frac{B}{RT} \right)\end{aligned}$$

Which yields:

$$\hat{\phi}_2^v = 1.597$$

So it seems that the Lewis fugacity rule is not very good under these conditions.

(c) Are the like interactions stronger or weaker?

Like interactions are stronger. To see why, consider the equation for the Henry's Law activity coefficient. It is always less than or equal to 1. From Equation 7.73, we know that $\gamma_2^{Henry's} \leq 1$ implies that like interactions dominate. To see why, start with the Henry's law activity coefficient evaluated at $x_1 = 0$:

$$\begin{aligned}\ln \gamma_2^{Henry's} \Big|_{x_1=0} &= \ln \frac{f_2}{\mathcal{H}_2} \\ &= -7\end{aligned}$$

Which implies that

$$\begin{aligned}\frac{f_2}{\mathcal{H}_2} &= \exp[-7] \\ &= 9.12 \times 10^{-4}\end{aligned}$$

Or $f_2 \ll \mathcal{H}_2$, which implies that like interactions are stronger. The like (2-2) interactions are characterized by f_2 , whereas the unlike (1-2) interactions are characterized by the Henry's law constant. Because the Henry's law constant is larger, there is a greater tendency to escape 1-2 interactions than 2-2 interactions;

hence, 2-2 interactions dominate.

(d) Find x_2 for the conditions in part (b):

At equilibrium, we can equation the fugacity of the liquid and vapor phases:

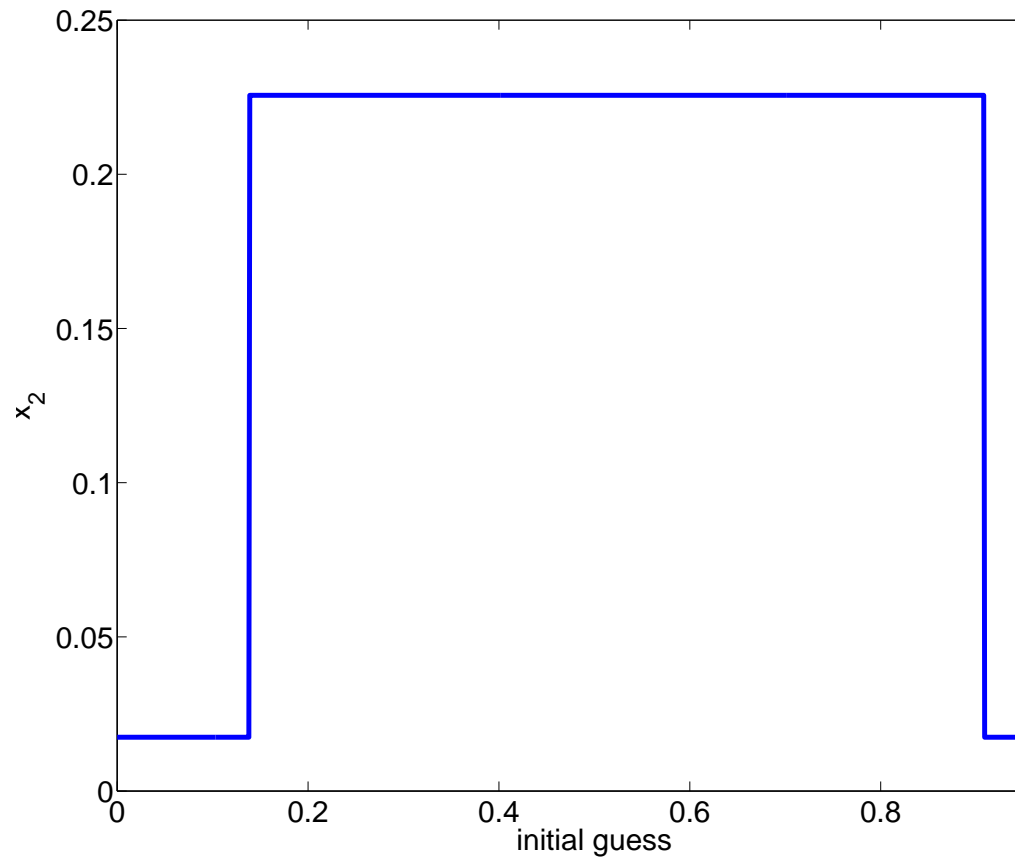
$$\begin{aligned}\hat{f}_2^l &= \hat{f}_2^v \\ x_2 \gamma_2^{Henry's} \mathcal{H}_2 &= y_2 \hat{\phi}_2^v P\end{aligned}$$

which can be rearranged to yield:

$$\begin{aligned}x_2 &= \frac{y_2 \hat{\phi}_2^v P}{\gamma_2^{Henry's} \mathcal{H}_2} \\ &= \frac{y_2 \hat{\phi}_2^v P}{\exp[-7(2x_2 - x_2^2)] \mathcal{H}_2}\end{aligned}$$

Because we cannot solve for x_2 analytically, we'll use fsolve. The solution depends upon the initial guess, as shown in the plot below.

$$x_2 = \begin{cases} 0.01743 & \text{if } 0 \leq x_2^0 < 0.139 \\ 0.22563 & \text{if } 0.139 \leq x_2^0 < 0.909 \\ 0.01743 & \text{if } 0.909 \leq x_2^0 < 0.996 \\ 0.22563 & \text{if } 0.996 \leq x_2^0 < 1 \end{cases}$$



(e) Estimate the saturation pressure of pure species 2 at 298 K.

At the saturation point, the liquid and vapor fugacity must be equal: $\hat{f}_2^v = \hat{f}_2^l$. Instead of using the Henry's Law limit for the activity coefficient, it would be more natural to use the Lewis/Randall reference state, since the Lewis/Randall reference state can be related to the saturation pressure.

$$\begin{aligned}\hat{f}_2^l &= x_2 \gamma_2 \phi_2^{sat} P_2^{sat} \mathcal{P} \\ &= x_2 \gamma_2^{Henry's} \mathcal{H}\end{aligned}$$

From which it follows:

$$\begin{aligned}
x_2 \gamma_2 \phi_2^{sat} P_2^{sat} \mathcal{P} &= x_2 \gamma_2^{Henry's} \mathcal{H} \\
&\text{or} \\
P_2^{sat} &= \frac{\gamma_2^{Henry's} \mathcal{H}}{\gamma_2 \phi_2^{sat} \mathcal{P}}
\end{aligned}$$

Unfortunately, we do not have an expression for γ_2 , the activity coefficient for the Lewis/Randall reference state. However, we can relate the two activity coefficients by applying Equations 7.75 through 7.78 to show that:

$$\begin{aligned}
\gamma_2 &= \frac{\gamma_2^{Henry's}}{\gamma_2^{Henry's} \Big|_{x_1=0}} \\
&= \exp [7x_1^2]
\end{aligned}$$

For simplicity, we assume that the Poynting correction is negligible: $\mathcal{P} = 1$. This correction may or may not be good, but since we have no way to estimate the molar volume of the liquid, it is the best we can do. To calculate the fugacity coefficient at the saturation condition, we return to the equation for the pure species fugacity coefficient at the start of part (b):

$$\begin{aligned}
\ln \phi_2^v &= \int_{P_{low}}^{P_2^{sat}} \left[\frac{v_2}{RT} - \frac{1}{P} \right] dP \\
&\text{or} \\
\phi_2^{sat} &= \exp \left[\frac{B}{RT} (P_2^{sat})^2 \right]
\end{aligned}$$

Combining these results, we can rewrite the equation for P_2^{sat} as:

$$\begin{aligned}
P_2^{sat} &= \frac{\gamma_2^{Henry's} \mathcal{H}}{\gamma_2 \phi_2^{sat} \mathcal{P}} \\
&= \frac{e^{-7} \mathcal{H}}{e^{\frac{B}{RT} (P_2^{sat})^2}}
\end{aligned}$$

Notice that all the terms with x_2 have dropped out, which is good, since we are looking for a pure component property. Once again, we have a nonlinear equation,

this time in terms of P_2^{sat} . To find a reasonable initial guess, we assume that: $\phi_2^{sat} = 1$. Note that this assumption only makes sense if the saturation pressure is low – much lower than the current system pressure. Nonetheless, it is a logical initial guess.

$$\begin{aligned} P_2^{sat, guess} &= e^{-7} \mathcal{H} \\ &= 6.38 \text{ [bar]} \end{aligned}$$

Using fsolve, we get:

$$P_2^{sat} = 6.36 \text{ [bar]}$$