

Homework 7: Problem 7.29

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Consider a binary mixture of a and b at 300 K and 1 bar. The vapor pressure of pure a at 300 K is 80 kPa.

(a) Specify the reference state for a .

Based upon the plot of the activity coefficient vs mole fraction for a , we conclude that the reference state is the Lewis/Randall reference state (i.e. pure species). The activity coefficient is defined as $\gamma_a = \frac{f_a^l}{x_a f_a^o}$. From the plot, we can conclude that the activity coefficient limits to unity as the mole fraction approaches unity. If it were the Henry's Law reference state, the activity coefficient would approach unity as the mole fraction approaches zero, which in this case it does not. The fact that $\ln \gamma_a \geq 0$ implies that that $f_a < \mathcal{H}_a$ – i.e., that the a-a interactions are stronger than a-b interactions.

[+1 point]

(b) What is the value of f_a ?

To calculate the pure species fugacity for a at 300 K and 1 bar, we must first calculate the fugacity at the saturation conditions. At 300 K and 80 kPa, the liquid fugacity and vapor fugacity must be equal (from the equilibrium condition). Additionally, the vapor phase fugacity is given by the fugacity coefficient and the vapor pressure. Combined, we get Equation 7.82:

$$f_a^l = \phi_a^{sat} P_a^{sat} \text{ at 300 K and 80 kPa}$$

In theory, in order determine the fugacity coefficient at 1 bar, we would need to use the Poynting correction:

$$f_a^l = \phi_a^{sat} P_a^{sat} \exp \left[\frac{v_a^l}{RT} (P - P_a^{sat}) \right]$$

In our case, we can simplify this equation considerably because (i) the system pressure is quite close to the saturation pressure at the given temperature, and (ii) because the saturation pressure is reasonably low. This is fortunate, since we don't have enough information to solve for the fugacity coefficient and the specific volume of the liquid phase. Instead, we assume that the terms inside the exponential are negligible, and that the fugacity coefficient is unity. The result is that the liquid phase fugacity is approximately equal to the saturation pressure:

$$\begin{aligned} f_a^l &= P_a^{sat} \text{ at 300 K and 1 bar} \\ &= 80 \text{ [kPa]} \end{aligned}$$

To see why it is ok to assume that the Poynting correction is unnecessary, consider what the specific volume would have to be in order for the Poynting correction to be a 1% deviation. The term in brackets would have to be $\left[\frac{v_a^l}{RT} (P - P_a^{sat}) \right] = \ln(1.01)$, which would require a specific volume of $v_a^l \approx 1241 \text{ [cm}^3\text{/mol]}$. Water, in contrast, is $18 \text{ [cm}^3\text{/mol]}$. So the liquid would need to be roughly 70 times lighter than water for the correction to make a difference of 1 percent; it would have to be 660 times lighter to make a 10 percent difference.

[+1 point]

(c) What is the value of \mathcal{H}_a ?

We know that the reference state for the activity coefficient is the Lewis/Randall reference state. We also know that as $x_a \rightarrow 0$, $\hat{f}_a^l \rightarrow x_a \mathcal{H}_a$. Combining these two results, it follows that:

$$\lim_{x_a \rightarrow 0} \gamma_a = \frac{\mathcal{H}_a}{f_a}$$

From the plot, we read that the natural log of the activity coefficient at $x_a = 0$ is 2.5. Thus,

$$\begin{aligned}\lim_{x_a \rightarrow 0} \gamma_a &= \frac{\mathcal{H}_a}{f_a} \\ &= e^{2.5}\end{aligned}$$

Rearranging and solving for \mathcal{H}_a , we get:

$$\begin{aligned}\mathcal{H}_a &= f_a \gamma_a|_{x_a=0} \\ &= 974.6 \text{ [kPa]}\end{aligned}$$

[+2 points]

(d) Come up with the two-suffix Margules parameter, A .

From Equation 7.123, we can relate A to the mole fraction and the activity coefficient:

$$\frac{A}{RT} = \frac{\ln \gamma_a}{(1 - x_a)^2}$$

From the plot, we can easily read the value at $x_a = 0$: $A/RT = 2.5$. It doesn't follow automatically that this is necessarily the best value for A . In this case, however, it does a good job of predicting the values over the range we're interested in, so we'll stick with it. If we read off the first six values on the plot, we get:

x_a	$\ln \gamma_a$	$\frac{A}{RT} = 2.5$
0	2.5	2.5
0.1	2.03	2.025
0.2	1.625	1.6
0.3	1.25	1.225
0.4	0.89	0.9
0.5	0.625	0.625

So $A/RT = 2.5$ does a good job of predicting $\ln \gamma_a$, at least within the significant figures that are readable off the plot. Under our conditions, this parameters works out to: $A = 62.4 \text{ [L bar / mol]}$.

[+2 points]

(e) Given a liquid mixture with 2 moles of a and 3 moles of b at 300 K and 1 bar, find the mole fraction of a in the vapor phase.

From the plot, we can read that at $x_a = 0.4$, $\ln \gamma_a \approx 0.9$. From the equation obtained in part (d), we get $\ln \gamma_a = 0.9$, so that's the value we'll use. Since the liquid and vapor phases are in equilibrium, we can equate the fugacity in the two phases. Combining that result with the value for the activity coefficient, we get:

$$\begin{aligned}\hat{f}_a^v &= \hat{f}_a^l \\ &= x_a \gamma_a f_a^\circ \\ &= 78.71 \text{ [kPa]}\end{aligned}$$

Similarly, we can relate the gas-phase fugacity to the mole fraction with:

$$\hat{f}_a^v = y_a \hat{\phi}_a P_{\text{sys}}$$

In part (b), we made the assumption that a behaves ideally at 300 K and 1 bar, and thus $\hat{\phi}_a = 1$. Therefore,

$$\begin{aligned}y_a &= \frac{\hat{f}_a^v}{P_{\text{sys}}} \\ &= 0.7871\end{aligned}$$

[+2 points]

(f) Calculate γ_b for the above mixture using the Lewis/Randall reference state.

From the results in part (c), the two-suffice Margules equation works well for $0 \leq x_a \leq 0.5$, so it should be fine for $x_a = 0.4$. From Equation 7.124, we know that

$$\begin{aligned}\gamma_b &= \exp \left[\frac{A}{RT} x_a^2 \right] \\ &= \exp [2.5 \times 0.4^2] \\ &= 1.492\end{aligned}$$

[+2 points]