

Problem 1 Solution

Note: In this solution, the subscript "m" indicates an intensive property

a)

$$\bar{G}_{m,1}^E = G_m^E + x_2 \frac{dG_m^E}{dx_1} \quad (+1)$$

$$\bar{G}_{m,2}^E = G_m^E - x_1 \frac{dG_m^E}{dx_1} \quad (+1)$$

Model 1 : $\frac{G_m^E}{RT} = Ax_1 - Ax_1^2$

$$\begin{aligned} \ln \gamma_1 &= \frac{\bar{G}_{m,1}^E}{RT} = Ax_1 - Ax_1^2 + x_2 [A - 2Ax_1] \quad (+1) \\ &= Ax_1 - Ax_1^2 + (1-x_1) [A - 2Ax_1] \\ &= Ax_1^2 - 2Ax_1 + A \\ &= Ax_2^2 \quad (+1) \end{aligned}$$

$$\begin{aligned} \ln \gamma_2 &= \frac{\bar{G}_{m,2}^E}{RT} = Ax_1 - Ax_1^2 - x_1 [A - 2Ax_1] \quad (+1) \\ &= Ax_1^2 \quad (+1) \end{aligned}$$

Model 2 : $\frac{G_m^E}{RT} = Bx_1 - Ax_1^2$

$$\begin{aligned} \ln \gamma_1 &= Bx_1 - Ax_1^2 + (1-x_1) [B - 2Ax_1] \quad (+1) \\ &= B - 2Ax_1 + Ax_1^2 \quad (+1) \end{aligned}$$

$$\begin{aligned} \ln \gamma_2 &= Bx_1 - Ax_1^2 - x_1 [B - 2Ax_1] \quad (+1) \\ &= -Ax_1^2 \quad (+1) \end{aligned}$$

(b)

According to the problem statement

$$\gamma_2 (x_2 \rightarrow 0) \rightarrow 1$$

$$\text{or } \ln \gamma_2 \xrightarrow{(x_2 \rightarrow 0)} 0$$

(+5) $\gamma_1 (x_1 \rightarrow 0)$ is $\gg 1$ or $\ll 1$ or $\ln \gamma_1 \xrightarrow{(x_1 \rightarrow 0)} \gg 0$ or $\ll 0$

Now for both models

$$\ln \gamma_2 = Ax_1^2$$

$$\text{for } x_2 \rightarrow 0 \text{ (or } x_1 \rightarrow 0) \quad \ln \gamma_2 \rightarrow 0$$

$$A \rightarrow 0$$

but $\ln \gamma_1 = Ax_2^2$ for the first model

$\rightarrow 0$ if $A \rightarrow 0$ and will be inconsistent with the model

however for the second model

$$\ln \gamma_1 = B - 2Ax_1 + Ax_1^2$$

for $x_1 \rightarrow 0$ $\ln \gamma_1 \rightarrow B \neq 0$, hence would agree

\therefore Second model would be more appropriate

Another argument would be that the first model is symmetric and cannot satisfy such asymmetric behavior.

c)

at $T = 100^\circ\text{C}$, plugging in the Antoine's eqn.

$$P_1^{\text{sat}} = 61.80 \text{ kPa} \quad (+1)$$

$$P_2^{\text{sat}} = 107.49 \text{ kPa} \quad (+1)$$

Now for VLE, we have

$$\hat{f}_x^V = \hat{f}_x^L \quad (+2)$$

$$\phi_1 y_1 P = x_1 \gamma_1 P_1^{\text{sat}} \quad \text{Ideal gas phase}$$

(+1)

$$\phi_2 y_2 P = x_2 \gamma_2 P_2^{\text{sat}}$$

* It is reasonable to assume that vapor is ideal ($\phi_i = 1$) when the pressures are low, as it turns out below (+2).

Now for an azeotrope $y_1 = x_1$; $y_2 = x_2$ (+2)

Hence the equations reduce to

$$P = \gamma_1 P_1^{\text{sat}}$$

$$P = \gamma_2 P_2^{\text{sat}}$$

$$\Rightarrow \gamma_1 P_1^{\text{sat}} = \gamma_2 P_2^{\text{sat}} \quad (+2)$$

$$\exp[B - 2Ax_1 + Ax_1^2] \cdot 61.86 = \exp[Ax_1^2] \times 107.49$$

$$\Rightarrow \exp[B - 2Ax_1] = 1.7376 \quad (+1)$$

$$B - 2Ax_1 = 0.5525$$

$$3.65 - 3.00(2x_1) = 0.5525$$

$$3.0974 = 6.00x_1 \quad (+1)$$

$$x_1 = 0.516 \quad (+1)$$

$$P = \gamma_1 P_1^{\text{sat}} = \exp(3.0 \times 0.516^2) \times 107.49 = 238 \text{ kPa} \quad (+1)$$