Solution for Problem 8-15 | **10.213**

Consider the system of ethanol (1) / benzene (2) at 25 ˚C. This system exhibits an azeotrop at a mole fraction of x_1 = 0.28 and a pressure of 122.3 torr.

Part 1: Determine the values of the parameters in the Van Laar equation.

Calculate P^{sat} using the Antoine Equation: $\ln\left(P^{sat}\left[bar\right]\right) = A - \dfrac{B}{T\left[K\right] - C}$

Using Table A.1.1

	A	B	C
Ethanol	12.2917	3803.98	-41.68
Benzene	9.2806	2788.51	-52.36

Substituting these values into the Antoine Equation, at T = 25 ˚C,

$$P_1^{sat} = 0.0788 \text{ bar}$$ (1/2 point)

$$P_2^{sat} = 0.1269 \text{ bar}$$ (1/2 point)

To determine the activity coefficients

$$P = 122.3 \text{ torr} = 0.163 \text{ bar}$$

$$\gamma_1 = \frac{P}{P_1^{sat}} = \frac{0.163 bar}{0.0788 bar} = 2.07$$ (1/2 point)

$$\gamma_2 = \frac{P}{P_2^{sat}} = \frac{0.163 bar}{0.1269 bar} = 1.28$$ (1/2 point)

The Van Laar equation, from Table 7.1

$$RT\ln\gamma_1 = A\left(\frac{Bx_2}{Ax_1 + Bx_2}\right)^2 \quad (1)$$

$$RT\ln\gamma_2 = B\left(\frac{Ax_1}{Ax_1 + Bx_2}\right)^2 \quad (2)$$

(1 point)

Substitute γ_1, γ_2, $x_1 = 0.28$, $x_2 = 0.72$ into Equations (1) and (2).

Solving using MATLAB

$$\boxed{A = 6323 \, {}^{J}\!/_{mol}} \qquad \text{(1 point)}$$

$$\boxed{B = 2819 \, {}^{J}\!/_{mol}} \qquad \text{(1 point)}$$

Part 2: Estimate the liquid composition and pressure in equilibrium with a vapor of y_1 = 0.75 at 25°C.

The pressure is low, thus can assume the vapor phase behaves ideally.

$$Py_1 = x_1\gamma_1 P_1^{sat} \tag{3}$$

$$Py_2 = x_2\gamma_2 P_2^{sat} = (1-x_1)\gamma_2 P_2^{sat} \tag{4}$$

(1 point)

Summing the above equations, the system pressure is

$$P = y_1 P + y_2 P = x_1\gamma_1 P_1^{sat} + (1-x_1)\gamma_2 P_2^{sat} \tag{5}$$

(1/2 point)

Substitute Equation (5) into (3) and rearrange

$$y_1 = \frac{x_1\gamma_1 P_1^{sat}}{x_1\gamma_1 P_1^{sat} + (1-x_1)\gamma_2 P_2^{sat}} \tag{6}$$

(1/2 point)

Using the values of A and B calculated earlier, substitute Equation (1) and (2) into Equation (6)

$$y_1 = \frac{x_1 \exp\left(\frac{A}{RT}\left(\frac{B(1-x_1)}{Ax_1 + B(1-x_1)}\right)^2\right)P_1^{sat}}{x_1 \exp\left(\frac{A}{RT}\left(\frac{B(1-x_1)}{Ax_1 + B(1-x_1)}\right)^2\right)P_1^{sat} + (1-x_1)\exp\left(\frac{B}{RT}\left(\frac{Ax_1}{Ax_1 + B(1-x_1)}\right)^2\right)P_2^{sat}}$$

(1 point)

Substitute in the values and solve for x_1

$$\boxed{x_1 = 0.9334}$$

$$\boxed{x_2 = 0.0666}$$

(1 point)

Solving for Pressure,

$$\gamma_1 = \exp\left(\frac{A}{RT}\left(\frac{B(1-x_1)}{Ax_1 + B(1-x_1)}\right)^2\right)$$

$$\gamma_1 = \exp\left(\frac{6323 \, {}^{J}\!/\!{}_{mol}}{0.08314 \frac{J}{mol-K} \times 298.15K}\left(\frac{2819 \, {}^{J}\!/\!{}_{mol} \times 0.0666}{6323 \, {}^{J}\!/\!{}_{mol} \times 0.9334 + 2819 \, {}^{J}\!/\!{}_{mol} \times 0.0666}\right)^2\right)$$

$$\gamma_1 = 1.27$$

$$P = \frac{x_1 \gamma_1 P_1^{sat}}{y_1}$$

$$P = \frac{0.9334 \times 1.27 \times 0.0788 bar}{0.75}$$

$$\boxed{P = 0.125 bar}$$ (1 point)