

Consider a mixture of species 1, 2, and 3. The following equation of state is available for the vapor phase:

$$Pv = RT + P^2 [A(y_1 - y_2) + B]$$

Where

$$\frac{A}{RT} = -9.0 \times 10^{-5} \left[\frac{1}{\text{atm}^2} \right], \quad \frac{B}{RT} = 3.0 \times 10^{-5} \left[\frac{1}{\text{atm}^2} \right]$$

Consider a vapor mixture with

$$n_1 = 1, n_2 = 2, \text{ and } n_3 = 2$$

$$P = 50 \text{ atm}, T = 500\text{K}$$

Find:

- (i) v , molar volume of the vapor mixture
- (ii) V , Total volume of vapor mixture
- (iii) v_1 , molar volume of species 1
- (iv) v_2 , molar volume of species 2
- (v) v_3 , molar volume of species 3
- (vi) \bar{V}_1 , partial molar volume of species 1 in the vapor mixture

Solution:(i) v , molar volume of the vapor mixture

Using the given equation of state and rearranging,

$$v = \frac{RT}{P} + P[A(y_1 - y_2) + B]$$

$$v = \frac{(0.08206 \frac{\text{Latm}}{\text{molK}})(500\text{K})}{50\text{atm}} + (50\text{atm}) \left[(-9.0 \times 10^{-5}) \left(\frac{1}{5} - \frac{2}{5} \right) + (3.0 \times 10^{-5}) \right] (0.08206 \frac{\text{Latm}}{\text{molK}})(500\text{K})$$

(1 point)

$$v = 0.9191 \frac{\text{L}}{\text{mol}}$$

(1 point)

(ii) V , Total volume of vapor mixture

$$V = n_{\text{Total}} v$$

(1/2 point)

$$V = (5\text{mol}) \left(0.9191 \frac{\text{L}}{\text{mol}} \right)$$

$$V = 4.595\text{L}$$

(1/2 point)

(iii) v_1 , molar volume of species 1Assuming that there is only species 1 present, $y_1 = 1$, $y_2 = 0$, $y_3 = 0$

(1/2 point)

$$v_1 = \frac{RT}{P} + P[A(y_1 - y_2) + B]$$

$$v_1 = \frac{(0.08206 \frac{\text{Latm}}{\text{molK}})(500\text{K})}{50\text{atm}} + (50\text{atm}) \left[(-9.0 \times 10^{-5})(1 - 0) + (3.0 \times 10^{-5}) \right] (0.08206 \frac{\text{Latm}}{\text{molK}})(500\text{K})$$

$$v_1 = 0.6975 \frac{\text{L}}{\text{mol}}$$

(1/2 point)

(iv) v_2 , molar volume of species 2

Assuming that there is only species 2 present, $y_1 = 0$, $y_2 = 1$, $y_3 = 0$

(1/2 point)

$$v_2 = \frac{RT}{P} + P[A(y_1 - y_2) + B]$$

$$v_2 = \frac{(0.08206 \frac{\text{Latm}}{\text{molK}})(500\text{K})}{50\text{atm}} + (50\text{atm})[(-9.0 \times 10^{-5})(0 - 1) + (3.0 \times 10^{-5})](0.08206 \frac{\text{Latm}}{\text{molK}})(500\text{K})$$

$$v_2 = 1.0668 \frac{\text{L}}{\text{mol}}$$

(1/2 point)

(v) v_3 , molar volume of species 3

Assuming that there is only species 3 present, $y_1 = 0$, $y_2 = 0$, $y_3 = 1$

(1/2 point)

$$v_3 = \frac{RT}{P} + P[A(y_1 - y_2) + B]$$

$$v_3 = \frac{(0.08206 \frac{\text{Latm}}{\text{molK}})(500\text{K})}{50\text{atm}} + (50\text{atm})[(-9.0 \times 10^{-5})(0 - 0) + (3.0 \times 10^{-5})](0.08206 \frac{\text{Latm}}{\text{molK}})(500\text{K})$$

$$v_3 = 0.8821 \frac{\text{L}}{\text{mol}}$$

(1/2 point)

(vi) \bar{V}_1 , partial molar volume of species 1 in the vapor mixture

$$\bar{V}_1 = \left(\frac{\partial V}{\partial n_1} \right)_{T, P, n_2, n_3} \quad \text{Equation (6.29)}$$

Using the given equation of state,

$$V = n_{\text{Total}} v = (n_1 + n_2 + n_3) v$$

$$V = (n_1 + n_2 + n_3) \frac{RT}{P} + (n_1 + n_2 + n_3) P \left[A \left(\frac{n_1}{n_1 + n_2 + n_3} - \frac{n_2}{n_1 + n_2 + n_3} \right) + B \right]$$

$$V = (n_1 + n_2 + n_3) \frac{RT}{P} + PA(n_1 - n_2) + (n_1 + n_2 + n_3) PB$$

(2 points for correct expression of V)

Differentiating V with respect to n_1 and keeping other factors constant,

$$\bar{V}_1 = \left(\frac{\partial V}{\partial n_1} \right)_{T, P, n_2, n_3}$$

$$\bar{V}_1 = \frac{RT}{P} + PA + PB$$

(1 point for correct evaluation of \bar{V}_1)

$$\bar{V}_1 = \frac{(0.08206 \frac{\text{Latm}}{\text{molK}})(500\text{K})}{50\text{atm}} + (50\text{atm})(-9.0 \times 10^{-5} + 3.0 \times 10^{-5})(0.08206 \frac{\text{Latm}}{\text{molK}})(500\text{K})$$

$$\boxed{\bar{V}_1 = 0.6975 \frac{\text{L}}{\text{mol}}}$$

(1 point)