CHE 221A

ASSIGNMENT-06

MODEL SOLUTION

[I]

$P = 83.14\ kPa,\ T = 500K$

$n_A = 2\ moles,\ n_B = 3\ moles$

$\rightarrow \bar{V}_A = \left(\frac{\partial V}{\partial n_A}\right)_{T,P,n_B} = \frac{\partial}{\partial n_A}\left((n_A + n_B)\frac{RT}{P}\right)_{T,P,n_B}$ $\left[\because V = \frac{(n_A+n_B)RT}{P}\right.$

$= \frac{RT}{P} = \frac{(8.314)(500)}{(83.14\times10^3)}$

$$\boxed{\bar{V}_A = 0.05\ \frac{m^3}{mol}}$$

$\rightarrow$ Similiarly,

$\bar{V}_B = \left(\frac{\partial V}{\partial n_B}\right)_{T,P,n_A}$

$= RT/P$

$$\boxed{\bar{V}_B = 0.05\ \frac{m^3}{mol}}$$

$\rightarrow V_A = \frac{n_A RT}{P}$

$$\boxed{V_A = 0.1\ m^3}$$

$\therefore \underline{V}_A = \frac{V_A}{n_A} = 0.05\ m^3$

$\rightarrow V_B = \frac{n_B RT}{P}$

$$\boxed{V_B = 0.15\ m^3}$$

$$\rightarrow \boxed{\underline{V}_B = 0.05\ m^3}$$

$\rightarrow V_T = V_A + V_B$

$$\boxed{V_T = 0.25\ m^3}$$

$$\rightarrow \boxed{\underline{V}_T = \frac{0.25}{5} = 0.05\ m^3}$$

→ Using;

$$\Delta B_{mix} = \sum_{i=1}^{2} N_i (\bar{B}_i - \underline{B}_i)$$

For ΔV_{mix};

$$\Delta V_{mix} = N_A(\bar{V}_A - \underline{V}_A) + N_B(\bar{V}_B - \underline{V}_B)$$

$$\boxed{\Delta V_{mix} = 0}$$

$$\Rightarrow \boxed{\Delta \underline{V}_{mix} = 0}$$

2

$$\underline{V} = 100y_a + 80y_b + 2.5y_a y_b \quad — (1)$$

(a) To get pure species molar volume for species a, put $y_a = 1$ & $y_b = 0$ in eq (1)

$$\therefore \boxed{\underline{V}_a = 100 \text{ cm}^3/\text{mol}}$$

(b) For $\bar{V}_a$,

$$\bar{V}_a = \left(\frac{\partial V}{\partial n_A}\right)_{T,P,n_B}$$

$$\rightarrow V = (n_A + n_B)\left[100\left(\frac{n_A}{n_A+n_B}\right) + 80\left(\frac{n_B}{n_A+n_B}\right) + 2.5\frac{n_A n_B}{(n_A+n_B)^2}\right]$$

$$\therefore \bar{V}_a = \frac{\partial}{\partial n_A}\left(100 n_A + 80 n_B + 2.5\frac{n_A \cdot n_B}{(n_A+n_B)}\right)_{T,P,n_B}$$

$\therefore \bar{V}_a = 100 + 2.5 \frac{n_b}{n_a+n_b} - 2.5 \frac{n_a n_b}{(n_a+n_b)^2}$

$\bar{V}_a = 100 + 2.5 y_b^2$ $\quad [\because y_a + y_b = 1]$

$\rightarrow \bar{V}_a^{\infty} = \lim_{y_a \to 0} \bar{V}_a$

$$\boxed{\bar{V}_a^{\infty} = 102.5 \frac{cm^3}{mol}}$$

(c) As we know;

$$\Delta V_{mix} = n_A(\bar{V}_a - V_a) + n_B(\bar{V}_b - V_b) \quad -(2)$$

Now; $\bar{V}_a - V_a = 100 + 2.5 y_b^2 - 100$

$= 2.5 y_b^2$

$$\boxed{\bar{V}_a - V_a > 0}$$

Similiarly; $\bar{V}_b - V_b = 80 + 2.5 y_a^2 - 80$

$= 2.5 y_a^2$

$$\boxed{\bar{V}_b - V_b > 0}$$

$\therefore$ From eq (2);

$$\boxed{\Delta V_{mix} > 0}$$

3

\# of moles of specie 1 : $n_1 = 1$

\# of moles of specie 2 : $n_2 = 4$

$\therefore$ Mole fraction of specie 1 : $x_1 = 0.2$

Mole fraction of specie 2 : $x_2 = 0.8$

→ From the plot;

$$\overline{V_1} \cong 46 \text{ cm}^3/\text{mol}$$

$$\overline{V_2} \approx 69.5 \text{ cm}^3/\text{mol}$$

→ Using;

$$n_T \underline{V} = n_1\overline{V_1} + n_2\overline{V_2}$$

$$\therefore \underline{V} = \frac{(1\times 46) + (4\times 69.5)}{5}$$

$$\boxed{\underline{V} = 64.8 \ \frac{\text{cm}^3}{\text{mol}}}$$

$$\therefore V = 5\times 64.8$$

$$\boxed{V = 324 \text{ cm}^3}$$

→ $\underline{V}_1 = \lim_{x_1\to 1} \overline{V_1}$

$\underline{V}_1 = 50 \text{ cm}^3/\text{mol}$ (From plot)

$\therefore \boxed{V_1 = 50 \text{ cm}^3}$

→ $\underline{V}_2 = \lim_{x_1\to 0} \overline{V_2}$

$\underline{V}_2 = 70 \text{ cm}^3/\text{mol} \Rightarrow \boxed{V_2 = 280 \text{ cm}^3}$

$\rightarrow$ $$\Delta V_{mix} = \sum_{i=1}^{2} n_i (\bar{V}_i - \underline{V}_i)$$

$$= 1(46 - 50) + 4(69.5 - 70)$$

$$\boxed{\Delta V_{mix} = -6 \ cm^3}$$

4 given; $\bar{V}_1$ = constant

→ Using eq^n;

$$x_1\left(\frac{\partial \bar{B}_1}{\partial x_1}\right) + x_2\left(\frac{\partial \bar{B}_2}{\partial x_1}\right) = 0$$

Here $B = V$;

$$\therefore \quad x_1\left(\frac{\partial \bar{V}_1}{\partial x_1}\right) + x_2\left(\frac{\partial \bar{V}_2}{\partial x_1}\right) = 0$$

Since $\bar{V}_1$ = constant,

$$\frac{\partial \bar{V}_2}{\partial x_1} = 0 \Rightarrow \boxed{\bar{V}_2 = \text{constant}}$$

[5] Given:

$$P = \frac{RT}{\underline{V}-b} - \frac{a}{T\underline{V}^2} \quad \text{— (1)}$$

(a) Using;

$$RT\ln\left(\frac{f}{P_0}\right) = \int_{P_0}^{P} \underline{V}\,dP$$

→ Since eq (1) cannot be written in volume explicit form;

$$dP = \left(\frac{-RT}{(\underline{V}-b)^2} + \frac{2a}{T\underline{V}^3}\right) d\underline{V}$$

$$\therefore\ RT\ln\left(\frac{f}{P_0}\right) = \int_{P_0}^{P} \underline{V}\left(\frac{-RT}{(\underline{V}-b)^2} + \frac{2a}{T\underline{V}^3}\right) d\underline{V}$$

$$= \int_{P_0}^{P} \left(\frac{-RT\underline{V}}{(\underline{V}-b)^2} + \frac{2a}{T\underline{V}^2}\right) d\underline{V}$$

$$= \int_{\frac{RT}{P_0}}^{\underline{V}} \frac{-RT\underline{V}}{(\underline{V}-b)^2}\,d\underline{V} + \frac{2a}{T}\int_{P_0}^{P} \frac{1}{\underline{V}^2}\,d\underline{V}$$

→ Using partial fractions,

$$\frac{\underline{V}}{(\underline{V}-b)^2} = \frac{1}{(\underline{V}-b)} + \frac{b}{(\underline{V}-b)^2}$$

$$\therefore RT\ln\left(\frac{f}{P_0}\right) = -RT\int_{RT/P_0}^{V}\left(\frac{1}{(V-b)}+\frac{b}{(V-b)^2}\right)dV + \frac{2a}{T}\int_{RT/P_0}^{V}\frac{1}{V}\,dV$$

$$= \left[\frac{b}{V-b} - \ln(V-b) - \frac{2a}{RT^2V}\right]_{RT/P_0}^{V}$$

$$\ln\left(\frac{f}{P_0}\right) = b\left[\frac{1}{V-b} - \frac{1}{\frac{RT}{P_0}-b}\right] - \ln\left[\frac{V-b}{\frac{RT}{P_0}-b}\right] - \frac{2a}{RT^2}\left[\frac{1}{V} - \frac{P_0}{RT}\right]$$

→ In ~~[illegible]~~ order to simplify, for very low P_0,

$$\frac{RT}{P_0} \gg b$$

$$\therefore \ln(f) - \ln(P_0) = b\left[\frac{1}{V-b} - \frac{P_0}{RT}\right] - \ln\left(\frac{(V-b)P_0}{RT}\right) - \frac{2a}{RT^2}\left[\frac{1}{V} - \frac{P_0}{RT}\right]$$

$$\therefore \ln(f) = \frac{b}{(V-b)} - \ln\left(\frac{(V-b)}{RT}\right) - \frac{2a}{RT^2V}$$

$$\Rightarrow \boxed{f = \left(\frac{RT}{V-b}\right)\exp\left[\frac{b}{V-b} - \frac{2a}{RT^2V}\right]}$$

→ To obtain ϕ,

$$\boxed{\phi = \frac{f}{P} = \frac{RT}{P(V-b)}\exp\left[\frac{b}{V-b} - \frac{2a}{RT^2V}\right]}$$

[b] Using results of Problem 4.29;

$$V_c = 3b = \frac{3RT_c}{8P_c}$$

$$a = \frac{9}{8} V_c R T_c^{2}$$

$$\rightarrow \phi = \frac{RT_r \cdot T_c}{P_r \cdot P_c\left(V - \frac{V_c}{3}\right)} \exp\left[\frac{V_c/3}{V - V_c/3} - \frac{2\cdot\frac{9}{\cancel{8}_{4}}\left(RT_c^{2}V_c\right)}{RT^2 V}\right]$$

$$= \left(\frac{3RT_c}{P_c}\right)\left(\frac{1}{V_c}\right)\frac{T_r}{P_r(3V_r-1)} \exp\left[\frac{1}{3V_r-1} - \frac{9}{4T_r^2V_r}\right]$$

$$= \left(8\cancel{V_c}\right)\left(\frac{1}{\cancel{V_c}}\right)\frac{T_r}{P_r(3V_r-1)} \exp\left[\frac{1}{3V_r-1} - \frac{9}{4T_r^2V_r}\right]$$

$$\boxed{\phi = \frac{8T_r}{P_r(3V_r-1)} \exp\left[\frac{1}{3V_r-1} - \frac{9}{4T_r^2V_r}\right]}$$

[6] Given;

$$f = P\exp(-CP) \quad -(1)\quad ; \quad P \text{ is in bar}, \; C \text{ is constant}$$

$$C = -0.065 + \frac{30}{T} \quad -(2)\quad ; \quad T \text{ is in kelvin}$$

(a) Using eq (1);

$$\ln f = \ln P - CP$$

→ Differentiating wrt P;

$$\left(\frac{\partial \ln f}{\partial P}\right)_T = \frac{1}{P} - C$$

$$\left(\frac{\partial \ln f}{\partial P}\right)_T = \frac{1}{P} + 0.065 - \frac{30}{T} \qquad [\text{Using eq } (2)]$$

→ Moreover; $\left(\frac{\partial \ln f}{\partial P}\right)_T = \frac{V}{RT}$

$$\therefore \boxed{V = RT\left[\frac{1}{P} + 0.065 - \frac{30}{T}\right]} \Rightarrow \text{Eq}^n \text{ of state}$$

(b) At $T = 80°C$ | $P = 30\text{bar}$

$T = 353\,K$

$V = ?$

$$\therefore V = \left(8.314 \times 10^{-5} \times 353\right)\left[\frac{1}{30} + 0.065 - \frac{30}{353}\right]$$

$$\therefore \boxed{\underline{V} = 3.92 \times 10^{-4} \ \frac{m^3}{mol}}$$

[7] given;

$$P\underline{V} = RT + P^2[A(y_1 - y_2) + B]$$

$$\therefore \underline{V} = \frac{RT}{P} + P[A(y_1 - y_2) + B] \quad -① $$

(a) To determine pure specie-1 fugacity coefficient we use;

$$RT \ln\left(\frac{f_1^V}{P_0}\right) = \int_{P_0}^{P} \underline{V}_1 \, dP$$

To obtain $\underline{V}_1$, put $y_1 = 1$ in eq ①;

$$RT \ln\left(\frac{f_1^V}{P_0}\right) = \int_{P_0}^{P} \left[\frac{RT}{P} + P(A+B)\right] dP$$

$$\ln\left(\frac{f_1^V}{P_0}\right) = \int_{P_0}^{P} \left[\frac{1}{P} + \frac{P(A+B)}{RT}\right] dP$$

$$= \left[\ln P + \frac{P^2}{2RT}(A+B)\right]_{P_0}^{P}$$

$$\ln\left(\frac{f_1^V}{P_0}\right) = \ln\left(\frac{P}{P_0}\right) + \frac{(A+B)}{2RT} \cdot (P^2 - P_0^2)$$

$$\therefore \ln(f_1^v) = \ln(P) + \frac{(A+B)}{RT}\left(\frac{P^2}{2} - \frac{P_0^2}{2}\right)$$

<u>To simplify further;</u>

Let $P_0 \to 0$

$$\therefore \ln(f_1^v) - \ln(P) = \frac{A+B}{RT}\left(\frac{P^2}{2}\right)$$

$$\therefore \ln\left(\frac{f_1^v}{P}\right) = \frac{(A+B)P^2}{2RT}$$

$$\therefore \boxed{\ln \phi_1^v = \frac{P^2(A+B)}{2RT}} \Rightarrow$$ Expression for pure species fugacity coefficient of species-1

→ <u>To determine $\hat{\phi}_i^v$, of species 1 in the mixture;</u>

$$RT \ln\left(\frac{\hat{f}_i^v}{y_i P_0}\right) = \int_{P_0}^{P} \bar{V}_i \, dP$$

<u>To determine $\bar{V}_1$;</u>

$$V = (N_1 + N_2 + N_3)\left[\frac{RT}{P} + P((y_1 - y_2)A + B)\right]$$

$$V = (N_1 + N_2 + N_3)\frac{RT}{P} + P[A(N_1 - N_2) + B(N_1 + N_2 + N_3)]$$

$$\therefore \bar{V}_1 = \left(\frac{\partial V}{\partial N_1}\right)_{T, P, N_2, N_3}$$

$$\therefore \bar{V}_1 = \frac{RT}{P} + P(A+B) \quad \text{--- (2)}$$

→ Substituting eq (2) in;

$$RT \ln\left(\frac{\hat{f}_1^V}{y_i P_0}\right) = \int_{P_0}^{P} \left[\frac{RT}{P} + P(A+B)\right] dP$$

→ Integrating and simplifying as done before;

$$\boxed{\ln(\hat{\phi}_1^V) = \frac{P^2}{2RT}(A+B)} \quad \text{--- (3)}$$

(b) Given; $\hat{f}_1^L = 15 \text{ atm}$

→ For VLE;

$$\hat{f}_1^L = \hat{f}_1^V$$

Using;

$$\hat{\phi}_1^V = \frac{\hat{f}_1^V}{y_1 P}$$

$$\exp\left(\frac{P^2}{2RT}(A+B)\right) = \frac{\hat{f}_1^V}{y_1 P} \qquad \text{[From (3)]}$$

$$\therefore y_1 = \left(\frac{15}{50}\right) \cdot \frac{1}{\exp\left[\frac{50}{2}^2\left(-9\times10^{-5} + 3\times10^{-5}\right)\right]}$$

$$\boxed{y_1 = 0.32}$$

8 Gibbs free energy can be written as;

$$dg_i = -s_i dT + v_i dP$$

→ Differentiating wrt P keeping T constant we get;

$$\left(\frac{\partial g_i}{\partial P}\right)_T = \left[\frac{\partial}{\partial P}\left(-s_i \partial T + v_i \partial P\right)\right]_T$$

$$\boxed{\left(\frac{\partial g_i}{\partial P}\right)_T = v_i} \quad - (1)$$

→ Using;

$$g_i - g_i^{\circ} = RT \ln\left(\frac{f_i}{P_0}\right)$$

$$\therefore g_i = RT\left[\ln(f_i) - \ln(P_0)\right] + g_i^{\circ}$$

Differentiating wrt P at constant T;

$$\left(\frac{\partial g_i}{\partial P}\right)_T = RT\left(\frac{\partial}{\partial P}\left[\ln(f_i) - \ln(P_0)\right]\right)_T + \left(\frac{\partial g_i^{\circ}}{\partial P}\right)_T$$

$$\boxed{\left(\frac{\partial g_i}{\partial P}\right)_T = RT\left(\frac{\partial \ln f_i}{\partial P}\right)_T} \quad - (2)$$

→ Using (1) & (2);

$$\boxed{\left(\frac{\partial g_i}{\partial P}\right)_T = v_i = RT\left(\frac{\partial \ln f_i}{\partial P}\right)_T}$$

Hence verified.