HW 11 Solutions

1. a) $n_1 = 5$ moles

$n_2 = 10$ moles

$$Pv_m = RT + P^2\left[A y_1 y_2 + B\right]$$

$P = 90$ bar, $T = 298$ K, $y_1 = \frac{5}{15} = \frac{1}{3}$, $y_2 = \frac{10}{15} = \frac{2}{3}$

$$v_m = \frac{RT}{P} + P\left[A y_1 y_2 + B\right]$$

convert P's, A, B to [=] Pa

$$\frac{A}{RT} = -2\times10^{-4}\ \text{bar}^{-2} \times \frac{(1\ \text{bar})^2}{(10^5\ \text{Pa})^2}$$

$$A = (8.314\ \text{J/mol-K})(298\ \text{K})(-2\times10^{-4})(10^{-10}\ \text{Pa}^{-2})$$

$$A = -4.96\times10^{-11}\ \text{m}^3/\text{mol-Pa}$$

$$B = (8.314)(298)(8\times10^{-5})(10^{-10})$$

$$B = 1.98\times10^{-11}\ \text{m}^3/\text{mol-Pa}$$

$$v_m = \frac{(8.314)(298)}{(90\times10^5\ \text{Pa})} + (90\times10^5)\left[(-4.96\times10^{-11})\left(\tfrac{1}{3}\right)\left(\tfrac{2}{3}\right) + 1.98\times10^{-11}\right]$$

$$\boxed{v_m = 0.000355\ \text{m}^3/\text{mol} = 3.55\times10^{-4}\ \text{m}^3/\text{mol}}$$

$$\boxed{V = n v_m = (n_1 + n_2) v_m = 5.32\times10^{-3}\ \text{m}^3}$$

$$\bar{V}_2 = \left(\frac{\partial V}{\partial n_2}\right)_{T,P,n_1}$$

$$V = n v_m = \frac{nRT}{P} + P\left[A\frac{n_1 n_2}{n} + Bn\right]$$

$$\left(\frac{\partial V}{\partial n_2}\right)_{T,P,n_1} = \left[\frac{\partial}{\partial n_2}\left(\frac{nRT}{P} + P\left(A\frac{n_1 n_2}{n} + Bn\right)\right)\right]_{T,P,n_1}$$

Note: $\left(\frac{\partial n}{\partial n_2}\right)_{T,P,n_1} = 1$

$$\bar{V}_2 = \frac{RT}{P} + P\left[B + A\frac{n n_1 - n_1 n_2}{n^2}\right]$$

$$\bar{V}_2 = \frac{RT}{P} + P\left[B + A(y_1 - y_1 y_2)\right]$$

$$\bar{V}_2 = \frac{RT}{P} + P\left[B + A y_1 (\underbrace{1 - y_2}_{= y_1})\right]$$

$$\bar{V}_2 = \frac{RT}{P} + P\left[A y_1^2 + B\right]$$

$$\rightarrow \boxed{\bar{V}_2 = \bar{V}_2(y_1 = 0.33) = 4.04 \times 10^{-4} \ m^3/mol}$$

OR

$$v_{m,2} = \bar{V}_2(y_1 = 0) = v_m(y_1 = 0) = \frac{RT}{P} + PB$$

$$\boxed{v_m = 4.54 \times 10^{-4} \ m^3/mol}$$

1. b) $\hat{\phi}_2 = \dfrac{\hat{f}_2}{y_2 P}$ (mixture)

$$RT \, d \ln \hat{f}_2 = \bar{V}_2 \, dP$$

$$RT \ln\left(\frac{\hat{f}_2}{y_2 P_{low}}\right) = \int_{P_{low}}^{P} \left[\frac{RT}{P} + P\left(Ay_1^2 + B\right)\right] dP$$

$$RT \ln\left(\frac{\hat{f}_2}{y_2 P_{low}}\right) = RT \ln\left(\frac{P}{P_{low}}\right) + \frac{Ay_1^2 + B}{2}\left(P^2 - \underbrace{\cancel{P_{low}^2}}_{\approx 0}\right)$$

P_{low}'s equal

$$RT \ln\left(\frac{\hat{f}_2}{y_2 P_{low}}\right) = RT \ln \hat{\phi}_2 = \frac{P^2\left(Ay_1^2 + B\right)}{2}$$

$$\boxed{\hat{\phi}_2 = \exp\left[\frac{P^2\left(Ay_1^2 + B\right)}{2RT}\right]}$$

1. b) pure:

$$\phi_2 = \frac{f_2}{P}$$

molar volume of pure "2"

$$RT\, d\ln f_2 = v_{m,2}\, dP$$

$$RT\int_{P_{low}}^{f_2} d\ln f_2 = \int\left(\frac{RT}{P} + PB\right)dP$$

$$RT\ln\left(\frac{f_2}{\cancel{P_{low}}}\right) = RT\ln\left(\frac{P}{\cancel{P_{low}}}\right) + \frac{BP^2}{2}$$

$$RT\ln\phi_2 = \frac{BP^2}{2} \rightarrow \boxed{\phi_2 = \exp\left[\frac{BP^2}{2RT}\right]}$$

1. c) $\hat{f}_2^L = \mathcal{H}_2 x_2 \gamma_2^H$

and $\ln \gamma_2^H = -7(1-x_1^2)$

$$\gamma_2^H = \underbrace{\exp\left[-7(1-x_1^2)\right]}_{<1 \text{ for all } x_2, x_1}$$

$\therefore$ $\hat{f}_2^L$ is <u>less than</u> fugacity in the ideal solution limit (as $x_2 \to 0$ for Henry's)

$\to$ this means like $(1 \leftrightarrow 1)$ interaction
$(2 \leftrightarrow 2)$

are stronger than unlike $(1 \leftrightarrow 2)$

1.d) $\hat{f}_2^V = \hat{f}_2^L$

$$P y_2 \hat{\phi}_2 = \mathcal{H}_2 x_2 \gamma_2^H$$

know $y_1 = \frac{1}{3}$, $y_2 = \frac{2}{3}$

$$\rightarrow x_2 = \frac{P y_2 \hat{\phi}_2}{\mathcal{H}_2 \gamma_2^H}$$

$$x_2 = \underbrace{\frac{P y_2}{\mathcal{H}_2} \frac{\exp\left[\frac{P^2(A y_1^2 + B)}{2RT}\right]}{\exp\left[-7(1-x_1^2)\right]}}_{\text{solve numerically for } x_1, x_2 \text{ using } x_1 + x_2 = 1}$$

$$\rightarrow \boxed{x_2 = 0.013}$$

2. mole ballance: $\boxed{\underset{(in)}{\dot{F}} = \underbrace{\dot{V} + \dot{L}}_{(out)}}$

VLE: $P y_i \hat{\phi}_i = f_i^L x_i \gamma_i$ (using L-R ref state for liquid)

vapor ideal, $\hat{\phi}_i = 1$ for all "i"

find P_i^{sat}'s,

ideal solution, $\gamma_i = 1$ for all "i"

To find P_i^{sat}'s use Antoine:

$$\ln\left(P^{sat}[bar]\right) = A - \frac{B}{T[K] + C}$$

where T = 290 K for this problem

n-butane: $P_a^{sat} = 1.87$ bar

n-pentane: $P_b^{sat} = 0.50$ bar

n-hexane: $P_c^{sat} = 0.14$ bar

assume $f_i^L \approx P_i^{sat}$

$\longrightarrow$ VLE:

$$\boxed{\begin{aligned} P y_a^V &= P_a^{sat} x_a^L \\ P y_b^V &= P_b^{sat} x_b^L \\ P y_c^V &= P_c^{sat} x_c^L \end{aligned}}$$

Also have: $\boxed{\begin{aligned} x_a^L + x_b^L + x_c^L &= 1 \\ y_a^V + y_b^V + y_c^V &= 1 \end{aligned}}$

and: $\boxed{\begin{aligned} x_a \dot{F} &= y_a^V \dot{V} + x_a^L \dot{L} \\ x_b \dot{F} &= y_b^V \dot{V} + x_b^L \dot{L} \end{aligned}}$ species balance

- 8 eqns
- 8 unknowns: $\dot{V}$, $\dot{L}$, x_a^L, x_b^L, x_c^L, y_a^V, y_b^V, y_c^V

Solving numerically gives:

$\dot{V} = 0.48$ mol/s , $\dot{L} = 0.52$ mol/s

$x_a^L = 0.198$ $\quad y_a^V = 0.617$

$x_b^L = 0.326$ $\quad y_b^V = 0.272$

$x_c^L = 0.476$ $\quad y_c^V = 0.111$

3. @ bub pt, 1 bubble of vap.

$x_a \approx 0.4$, $x_b \approx 0.2$, $x_c \approx 0.25$, $x_d \approx 0.15$

$$\left.\begin{aligned} P y_a &= P_a^{sat} x_a \\ P y_b &= P_b^{sat} x_b \\ P y_c &= P_c^{sat} x_c \\ P y_d &= P_d^{sat} x_d \end{aligned}\right\} \text{sum} \downarrow$$

$$P^{bub} = \sum_i P y_i = P_a^{sat} x_a + P_b^{sat} x_b + P_c^{sat} x_c + P_d^{sat} x_d$$

P_i^{sat}'s $\rightarrow$ Antoine eq $\rightarrow$ $\boxed{P = P^{bub} = 0.1 \text{ bar}}$

@ dew pt. all vap, tiny liq drop

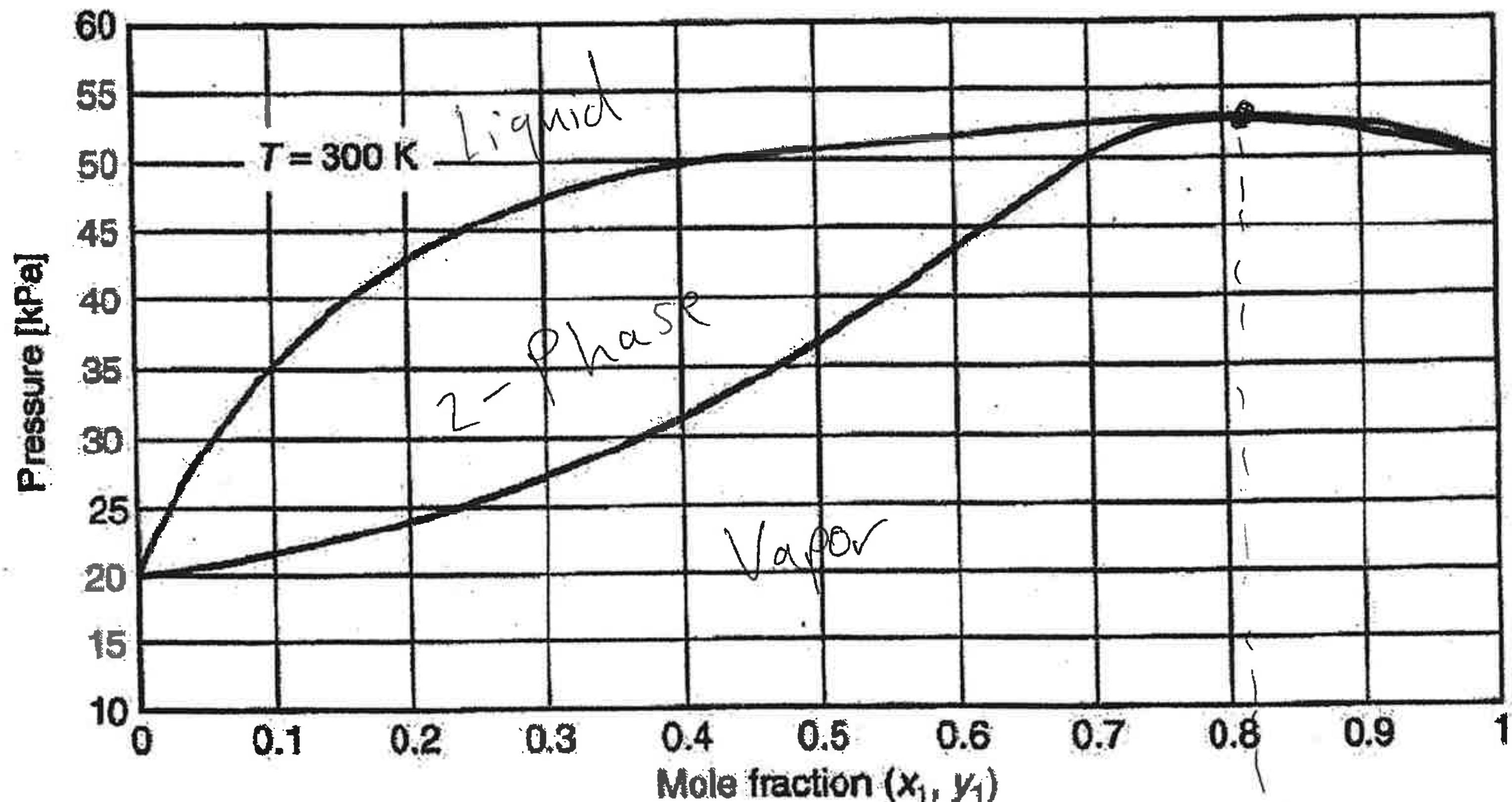
$y_a \approx 0.4$, $y_b \approx 0.2$, $y_c \approx 0.25$, $y_d \approx 0.15$

$$\sum_i x_i = 1$$

$$\Rightarrow \frac{P y_a}{P_a^{sat}} + \frac{P y_b}{P_b^{sat}} + \frac{P y_c}{P_c^{sat}} + \frac{P y_d}{P_d^{sat}} = 1$$

$$\boxed{P = P^{dew} = 0.07 \text{ bar}}$$

#4



$x^{az} \approx 0.82$

$x_1^{az} = y_1^{az}$

5. azotrope @ 0.64 bar

$x_1 = 0.4$

$P y_i \hat{\phi}_i = f_i^L x_i \gamma_i$

P is low $\rightarrow \tilde{\text{ideal}} \rightarrow \hat{\phi}_i = 1$

$\rightarrow f_i^L \approx P_i^{sat}$

$P y_i = P_i^{sat} x_i \gamma_i$

$P_1^{sat} = 0.468$ bar

$P_2^{sat} = 0.56$ bar

$\leftarrow$ from Antoine eq, Appendix A.

At azeotrope, $x_1 = y_1$ and $x_2 = y_2$

$P = P_1^{sat} \gamma_1$ $\qquad$ $P = P_2^{sat} \gamma_2$

$\gamma_1 (x_1 = 0.4) = \dfrac{P}{P_1^{sat}}$ $\qquad$ $\gamma_2 (x_2 = 0.6) = \dfrac{P}{P_2^{sat}}$

$\gamma_1 (x_1 = 0.4) = 1.37$ $\qquad$ $\gamma_2 (x_2 = 0.6) = 1.14$

For two-suffix Margules,

$$g_m^E = A x_1 x_2$$

$$\gamma_1 = \exp\left[\frac{A}{RT} x_2^2\right] \qquad \gamma_2 = \exp\left[\frac{A}{RT} x_1^2\right]$$

$$A_{(1)} = \frac{RT \ln \gamma_1}{x_2^2} \qquad A_{(2)} = \frac{RT \ln \gamma_2}{x_1^2}$$

at az

$$A_{(1)} = \frac{(8.314)(333)\ln(1.37)}{(0.6)^2}$$

at az,

$$A_{(2)} = \frac{(8.314)(333)\ln(1.14)}{(0.4)^2}$$

$$A_{(1)} = 2407.11 \text{ J/mol} \qquad A_{(2)} = 2310.56 \text{ J/mol}$$

take avg.

$$A \approx \frac{A_{(1)} + A_{(2)}}{2} = \frac{2407.11 + 2310.56}{2}$$

$$\boxed{A = 2359 \text{ J/mol}}$$

b)

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

$$y_1 = \left(\frac{P_1^{sat} x_1}{P}\right) \exp\left[\frac{A}{RT} x_2^2\right]$$

$$x_1 = 0.8, \quad x_2 = 0.2$$

$$\boxed{y_1 = 0.61, \quad y_2 = 0.39}$$