# HW # 10

## problem 1

(a) n-pentane

$$f^{L}(T,P) = P^{sat}\,\phi^{sat}\exp\left[\frac{1}{RT}\int_{P^{sat}}^{P} v^{L}\,dP\right]$$

find $T = T^{boil}(P = 1\text{ bar})$

use Antoine eq: $\ln(P[\text{bar}]) = A - \dfrac{B}{T+C}$

$$\frac{B}{T+C} = A - \ln P$$

$$T = \frac{B}{A - \ln P} - C$$

$$T = \frac{2477.07}{9.2131 - \underbrace{\ln(1)}_{0}} - (-39.94)$$

(coefficients from Koretsky Table A1.1)

use this T $\rightarrow$ $\boxed{T^{boil} = 309\text{ K}}$

for $T = 309\text{ K}$, $\underbrace{P^{sat} = 1\text{ bar}}_{}$

low pressure, vapour $\simeq$ ideal

$\phi^{sat}(T = 309\text{ K},\ P = 1\text{ bar}) \simeq 1$

$$F^{L}(T,P) = P^{sat}\exp\underbrace{\left[\frac{V_m^{L}}{RT}(P - P^{sat})\right]}_{\text{assume } V_m^{L} = \text{const}}$$

from NIH (PubChem)

$\rho = 630 \ kg/m^3$

$$V_m^L = \frac{MW}{\rho} = \frac{72.15 \times 10^{-3} \ kg/mol}{630 \ kg/m^3} = 0.000\,115 \ m^3/mol$$

$$F^L = (1 \ bar) \exp\left[\frac{0.000115 \ m^3/mol}{(8.314 \ J/mol \cdot K)(309 K)} (200 \ bar - 1 \ bar) \times 10^5 \ Pa/bar\right]$$

$$\boxed{F^L = 2.4 \ bar}$$

(b) from NIST Chemistry Webbook:

(use diff units) $\log_{10}(P[bar]) = A - \frac{B}{T+C}$

$$T = \frac{B}{A - \log_{10} P} - C$$

$$T = \frac{1099.207}{4.24696 - \underbrace{\log_{10}(1)}_{=0}} - (-8.256)$$

$$\boxed{T = 267 \ K}$$

$$F^L = P^{sat} \exp\left[\frac{V_m^L}{RT}(P - P^{sat})\right]$$

$\rho = 0.626 \ g/mL = 626 \ kg/m^3$ (NIH)

$$~~V_m~~ \ V_m^L = \frac{56.108 \times 10^{-3} \ kg/mol}{626 \ kg/m^3} = 8.96 \times 10^{-5} \ m^3/mol$$

$$\boxed{F^L = 2.2 \ bar}$$

2)

$$g_m^E = x_a x_b \left[ A + B(x_a - x_b) \right]$$

$$\gamma_{H_2O}^{\infty} = \gamma_a^{\infty} = 2.62$$

$$\gamma_{EtOH}^{\infty} = \gamma_b^{\infty} = 7.24$$

$$G^E = \frac{n_a n_b}{n_a + n_b} \left[ A + B \left( \frac{n_a - n_b}{n_a + n_b} \right) \right]$$

$$\overline{G}_a^E = \left( \frac{\partial G^E}{\partial n_a} \right)_{T,P,n_b} = \frac{\partial}{\partial n_a} \left[ A \left( \frac{n_a n_b}{n_a + n_b} \right) + B \frac{n_a n_b (n_a - n_b)}{(n_a + n_b)^2} \right]$$

$$= A \left[ \frac{n_b(n_a + n_b) - n_a n_b}{(n_a + n_b)^2} \right]$$

$$+ B \left[ \frac{(2 n_a n_b - n_b^2)(n_a + n_b)^2 - 2(n_a + n_b) n_a n_b (n_a - n_b)}{(n_a + n_b)^4} \right]$$

$$= A(x_b - x_a x_b)$$

$$+ B \left[ (2 x_a x_b - x_b^2) - 2 x_a x_b (x_a - x_b) \right]$$

$$= A x_b^2 + B \left[ x_b^2 (2x_a - 1) + 2 x_a x_b \underbrace{(1 - x_a)}_{x_b} \right]$$

$$= A x_b^2 + B x_b^2 \left[ 2x_a - 1 + 2x_a \right]$$

$$= A x_b^2 + B x_b^2 \left[ 4(1 - x_b) - 1 \right]$$

$$= A x_b^2 + 3B x_b^2 - 4B x_b^3$$

$$\boxed{\overline{G}_a^E = RT \ln \gamma_a = (A + 3B) x_b^2 - 4B x_b^3}$$

← equivalent to result in Table 7.2

Similarly,

$$\bar{G}_b^E = RT\ln\gamma_b = (A-3B)x_a^2 + 4Bx_a^3 \qquad \text{(also in Table 7.2)}$$

Determine A & B using $\gamma_a^\infty$, $\gamma_b^\infty$ data

$$RT\ln\gamma_a^\infty = \bar{G}_a^E(x_a \approx 0) = A + 3B - 4B$$

$x_b \approx 1$
dilute conditions

$$RT\ln\gamma_a^\infty = A - B$$

and:

$$RT\ln\gamma_b^\infty = \bar{G}_b^E(x_a = 1) = A - 3B + 4B = A + B$$

$$RT\ln(\gamma_a^\infty \gamma_b^\infty) = 2A$$

$$A = \frac{RT}{2}\ln(\gamma_a^\infty \gamma_b^\infty)$$

$$T = 70 + 273 \text{ K}$$

$$\boxed{A = 4195 \text{ J/mol}}$$

$$B = A - RT\ln\gamma_a^\infty$$

$$\boxed{B = 1449 \text{ J/mol}}$$

$\hat{f}_a(x_a = 0.4)$ ?

$$\hat{f}_a = \underset{\substack{\uparrow \\ \text{pure liquid}}}{f_a^L} x_a \gamma_a$$

Note: $P_a^{sat}(70°C) = 31.2$ kPa $\ll$ 1 bar $\rightarrow \phi_a^v \approx 1$

If $P = 1$ bar, ignore $\exp\left[\frac{v_m^L}{RT}(P - P_a^{sat})\right] \approx 1$

Thus, $$f_a^L(T,P) = P_a^{sat} \underset{\substack{\uparrow \\ \approx 1}}{\phi_a^v} \underbrace{\exp\left[\frac{1}{RT}\int_{P_a^{sat}}^{P} v_m^L \, dP\right]}_{\approx 1}$$

$$f_a^L(T,P) \approx P_a^{sat}(70°C) = 31.2 \text{ kPa}$$

$$\hat{f}_a = P_a^{sat} \underset{\substack{\uparrow \\ 0.4}}{x_a} \exp\left[\frac{1}{RT}\left((A+3B)x_b^2 - 4Bx_b^3\right)\right]$$

$x_b = 1 - x_a = 0.6$

$$\boxed{\hat{f}_a = 23.65 \text{ kPa}}$$

ii) both Lewis

$\ln \gamma_a \to 0$ $(\gamma_a \to 1)$ as $x_a \to 1$

$\ln \gamma_b \to 0$ $(\gamma_b \to 1)$ as $x_b \to 1$

(b) G-D eqn:

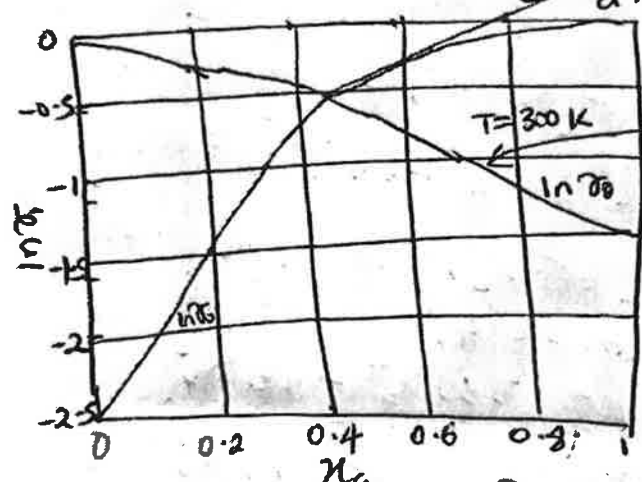
$\sum x_i \, d\ln \gamma_i = 0$

$x_a \, d\ln \gamma_a + x_b \, d\ln \gamma_b = 0$

$$x_a \frac{d\ln \gamma_a}{dx_a} + x_b \frac{d\ln \gamma_b}{dx_a} = 0$$

estimate from slopes @ $x_a = 0.6$

$$\left.\frac{d\ln \gamma_a}{dx_a}\right|_{x_a=0.6} \approx \frac{0.25}{0.175} \approx 1.43$$




$$\left.\frac{d\ln \gamma_b}{dx_a}\right|_{x_a=0.6} \approx \frac{-0.2}{0.1} \approx -2$$

$\to (0.6)(1.43) + (0.4)(-2) = 0.06 \approx 0$

(c) cannot use two-suffix Margules:

$\gamma_a = \exp\left[\frac{A}{RT} x_b^2\right]$, $\gamma_b = \exp\left[\frac{A}{RT} x_a^2\right]$

because this $g^E_m$ model requires the $\gamma_i$'s to be symmetric with $x_a$

Let's try 3-suffix Margules.

$g^E_m = x_a x_b \left[ A + B (x_a - x_b) \right]$

find A, B

Table 7.2:

$RT\ln \gamma_a = (A+3B) x_b^2 - 4B x_b^3$

$RT\ln \gamma_b = (A-3B) x_a^2 + 4B x_a^3$

Use data at infinite dilution.

$\to RT \ln \gamma_a^{\infty} = RT \ln \gamma_a (x_a \to 0) = -2.5RT = A + 3B - 4B$ ($x_b \to 1$)

$\boxed{A - B = -2.5\,RT}$

$\rightarrow RT\ln \gamma_b = RT\ln \gamma_b \ (x_b \to 0) = -1.5RT$

$$\boxed{A + B = -1.5RT}$$

$\Downarrow$ sum eqns

$$(A-B)+(A+B) = -4RT$$
$$2A = -4RT$$
$$A = -2RT$$
$$\boxed{A = -4988.4 \text{ J/mol}}$$
$$B = 1247.1 \text{ J/mol}$$

for $\boxed{g_m^E = x_a x_b \left[A + B(x_a - x_b)\right]}$

ⓓ It will not seperate into two liq phases.

- $\gamma_a$ and $\gamma_b$ are always $< 1$
  So system is more stable as a mixture

- Note:
$$g_m^E = x_a x_b [\underset{= -4988.4}{A} + \underbrace{B(x_a - x_b)}_{\substack{\text{max: } 1247 \ (\text{when } x_a \to 1) \\ \text{min: } -1247 \ (\text{where } x_a \to 0)}}]$$

$g_m^E < 0$ always.

and

$\therefore \Delta g_{m,mix} < 0$ always

$\rightarrow$ stable as a mixture (1 liq phase)

(4)

$$g_m^E = \left[\frac{1}{Ax_a} + \frac{1}{Bx_b}\right]^{-1} + C x_a x_b (x_a - x_b)^2$$

$$g_m^G = \left[\frac{n}{An_a} + \frac{n}{Bn_b}\right]^{-1} + \frac{C n_a n_b}{n^4}(n_a - n_b)^2$$

$$G^E = \frac{\cancel{n}}{\cancel{n}\left(\frac{1}{An_a} + \frac{1}{Bn_b}\right)} + \frac{C n_a n_b (n_a - n_b)^2}{n^3}$$

$$G^E = \frac{1}{\left(\frac{1}{An_a} + \frac{1}{Bn_b}\right)} + \frac{C n_a n_b (n_a - n_b)^2}{n^3}$$

$$\bar{G}_a^E = \left(\frac{\partial G^E}{\partial n_a}\right)_{T,P,n_b} = \frac{-\left(-\frac{1}{An_a^2}\right)}{\left(\frac{1}{An_a} + \frac{1}{Bn_b}\right)^2} + \frac{C n^3 (n_b (n_a - n_b)^2 + 2n_a n_b (n_a - n_b))}{n^6}$$

$$- \frac{3C n_a n_b (n_a - n_b)^2 n^2}{n^6}$$

$$\bar{G}_a^E = \frac{1}{An^2\left(\frac{1}{An_a} + \frac{1}{Bn_b}\right)^2} + C\left[\frac{n^3 n_b - 3n_a n_b n^2}{n_6}(n_a - n_b)^2 + \frac{2n_a n_b (n_a - n_b)}{n^3}\right]$$

$$\bar{G}_a^E = \frac{1}{A\left(\frac{1}{Ax_a} + \frac{1}{Bx_b}\right)^2} + C\left[(x_b - 3x_a x_b)(x_a - x_b)^2 + 2x_a x_b (x_a - x_b)\right]$$

$$RT \ln \gamma_a = \frac{1}{A\left(\frac{1}{Ax_a} + \frac{1}{Bx_b}\right)^2} + C\left[(x_b - 3x_a x_b)(x_a - x_b)^2 + 2x_a x_b (x_a - x_b)\right]$$

$$\boxed{RT \ln \gamma_a = A\left(\frac{Bx_b}{Ax_a + Bx_b}\right)^2 + Cx_b\left[(1 - 3x_a)(x_a - x_b)^2 + 2x_a(x_a - x_b)\right]}$$

$$\bar{G}_b^E = \left(\frac{\partial G^E}{\partial n_b}\right)_{T,P,n_a} = \frac{1}{Bn^2\left(\frac{1}{An_a} + \frac{1}{Bn_b}\right)^2}$$

$$+ C\left[\frac{n^3 n_a - 3n^2 n_a n_b}{n^6}(n_a - n_b)^2 + \frac{2n_a n_b (n_a - n_b)}{n^3}\right]$$

$$\boxed{RT \ln \gamma_b = B\left(\frac{Ax_a}{Ax_a + Bx_b}\right)^2 + Cx_a\left[(1 - 3x_b)(x_a - x_b) + 2x_b(x_a - x_b)\right]}$$