ASSIGNMENT 6 CHE 3473

Solution

#Problem 1:
9.4

We have the following properties for a mixture for mixing at constant T and P:

$$U(T,P,\underline{x}) = \sum N_i \underline{U}_i(T,P)$$

$$V(T,P,\underline{x}) = \sum N_i \underline{V}_i(T,P)$$

$$S(T,P,\underline{x}) = \sum N_i \underline{S}_i(T,P) - R\sum N_i \ln x_i$$

and $\underline{S}_i = \underline{S}_i^0 + C_{V,i}\ln\frac{\underline{U}_i}{\underline{U}_i^0} + R\ln\frac{\underline{V}_i}{\underline{V}_i^0}$

$\underline{S}_i^0$, $\underline{U}_i^0$, $\underline{V}_i^0$ are at some reference state.

(a) Find $\overline{V}_i$, $\overline{U}_i$, $\overline{S}_i$ and $\overline{G}_i$ in terms of $\underline{S}_i^0$, $\underline{U}_i^0$, $\underline{V}_i^0$, $C_{V,i}$, R, T, and $\underline{P}$. Need $\underline{U}_i$, $\underline{V}_i$.

We know $d\underline{U} = Td\underline{S} - Pd\underline{V} \rightarrow \left.\frac{\partial \underline{S}}{\partial \underline{U}}\right|_{\underline{V}} = \frac{1}{T}$; $\left.\frac{\partial \underline{S}}{\partial \underline{V}}\right|_{\underline{U}} = \frac{P}{T}$ and $\underline{S}_i = \underline{S}_i^0 + C_{V,i}\ln\frac{\underline{U}_i}{\underline{U}_i^0} + R\ln\frac{\underline{V}_i}{\underline{V}_i^0}$ for pure component i.

$$\left.\frac{\partial \underline{S}}{\partial \underline{U}}\right|_{\underline{V}} = \frac{1}{T} = C_{V,i}\frac{1}{\underline{U}_i} \rightarrow \underline{U}_i = C_{V,i}T$$

$$\left.\frac{\partial \underline{S}}{\partial \underline{V}}\right|_{\underline{U}} = R\frac{1}{\underline{V}_i} \text{ and } \left.\frac{\partial \underline{S}}{\partial \underline{V}}\right|_{\underline{U}} \cdot \left.\frac{\partial \underline{U}}{\partial \underline{S}}\right|_{\underline{V}} \cdot \left.\frac{\partial \underline{V}}{\partial \underline{U}}\right|_{\underline{S}} = -1$$

$$\left.\frac{\partial \underline{U}}{\partial \underline{S}}\right|_{\underline{V}} = T \left.\frac{\partial \underline{V}}{\partial \underline{U}}\right|_{\underline{S}} = -\frac{1}{P} \Rightarrow \left.\frac{\partial \underline{S}}{\partial \underline{V}}\right|_{\underline{U}} = T\cdot\frac{-1}{P} = -1 \rightarrow \left.\frac{\partial \underline{S}}{\partial \underline{V}}\right|_{\underline{U}} = \frac{R}{\underline{V}_i} = \frac{P}{T}$$

$$\Rightarrow \underline{V}_i = \frac{RT}{P}$$

So $\overline{U}_i = \left.\frac{\partial U}{\partial N_i}\right|_{T,P,N_{j\neq i}} = \frac{\partial}{\partial N_i}\sum N_i C_{V,i}T = C_{V,i}T = \underline{U}_i$

$$\overline{U}_i = C_{V,i}T$$

$$\overline{V}_i = \left.\frac{\partial V}{\partial N_i}\right|_{T,P,N_{j\neq i}} = \frac{\partial}{\partial N_i}\sum N_i \underline{V}_i = \frac{RT}{P} = \overline{V}_i = \underline{V}_i$$

$$\bar{S}_i = \left.\frac{\partial S}{\partial N_i}\right|_{T,P,Nj\neq i} = \frac{\partial}{\partial N_i}\left(\sum N_i \underline{S_i}(T,P) - R\sum N_i ln x_i\right) = \underline{S_i} - Rlnx_i$$

$$\bar{S}_i = \underline{S}_i^o + C_{v,i}ln\frac{C_{v,i}T}{\underline{U}_i^o} + Rln\frac{RT}{P\underline{V}_i^o} - Rlnx_i$$

$$\bar{G}_i = \left.\frac{\partial G}{\partial N_i}\right|_{T,P,Nj\neq i} = \frac{\partial}{\partial N_i}(H - TS)|_{T,P,Nj\neq i} = \frac{\partial}{\partial N_i}(U + PV - TS)|_{T,P,Nj\neq i}$$

$$\bar{G}_i = \bar{U}_i + P\bar{V}_i - T\left.\frac{\partial S}{\partial N_i}\right|_{T,P,Nj\neq i} = \bar{U}_i + P\bar{V}_i - T\bar{S}_i$$

$$= C_{V,i}T + RT - T(\underline{S}_i^o + C_{v,i}ln\frac{C_{v,i}T}{\underline{U}_i^o} + Rln\frac{RT}{P\underline{V}_i^o} - Rlnx_i)$$

b)

$$V = \sum N_i \underline{V}_i = \sum N_i \frac{RT}{P} = \frac{NRT}{P}$$

$$U = \sum N_i \underline{U}_i = \sum N_i C_{V,i}T$$

c)

$$H = U + PV = \sum N_i \underline{U}_i + P\sum N_i \underline{V}_i = \sum N_i(\underline{U}_i + P\underline{V}_i) = \sum N_i \underline{H}_i$$

$$A = U - TS = \sum N_i \underline{U}_i - T\left(\sum N_i \underline{S}_i(T,P) - R\sum N_i lnx_i\right)$$
$$= \sum N_i\left(\underline{U}_i - T\underline{S}_i + RTlnx_i\right) = \sum N_i \underline{A}_i + RT\sum N_i lnx_i$$

$$G = H - TS = \sum N_i \underline{H}_i - T\left(\sum N_i \underline{S}_i(T,P) - R\sum N_i lnx_i\right)$$
$$= \sum N_i(\underline{H}_i - T\underline{S}_i) + RT\sum N_i lnx_i = \sum N_i \underline{G}_i + RT\sum N_i lnx_i$$

#Problem 2:
9.6

As a preliminary note that, from Eqns. (6.4-27 and 28)

$$\underline{H}(T,P)-\underline{H}^{\text{IG}}(T,P)=RT(Z-1)+\int_{\underline{V}=\infty}^{\underline{V}=ZRT/P}\left[T\left(\frac{\partial P}{\partial T}\right)_{\underline{V}}-P\right]d\underline{V}$$

and

$$\underline{S}(T,P)-\underline{S}^{\text{IG}}(T,P)=R\ln Z+\int_{\underline{V}=\infty}^{\underline{V}=ZRT/P}\left[\left(\frac{\partial P}{\partial T}\right)_{\underline{V}}-\frac{R}{\underline{V}}\right]d\underline{V}$$

vdw E.O.S. $P=\frac{RT}{\underline{V}-b}-\frac{a}{\underline{V}^2}$ so

$$\left(\frac{\partial P}{\partial T}\right)_{\underline{V}}=\frac{R}{\underline{V}-b};\ T\left(\frac{\partial P}{\partial T}\right)_{\underline{V}}-P=\frac{RT}{\underline{V}-b}-\frac{RT}{(\underline{V}-b)}+\frac{a}{\underline{V}^2}=\frac{a}{\underline{V}^2}$$

$$\left(\frac{\partial P}{\partial T}\right)_{\underline{V}}-\frac{R}{\underline{V}}=\frac{R}{(\underline{V}-b)}-\frac{R}{\underline{V}};$$

$$\Rightarrow \underline{H}(T,P)-\underline{H}^{\text{IG}}(T,P)=RT(Z-1)+\int_{\underline{V}=\infty}^{\underline{V}=ZRT/P}\frac{a}{\underline{V}^2}d\underline{V}=RT(Z-1)-\frac{a}{\underline{V}}=RT(Z-1)-\frac{RTA}{Z}$$

and

$$\underline{S}(T,P)-\underline{S}^{\text{IG}}(T,P)=R\ln Z+\int_{\underline{V}=\infty}^{\underline{V}=ZRT/P}\left[\frac{R}{\underline{V}-b}-\frac{R}{\underline{V}}\right]d\underline{V}$$

$$=R\ln Z+R\ln\frac{(\underline{V}-b)}{\underline{V}}\Bigg|_{\underline{V}=\infty}^{ZRT/P}=R\ln(Z-B)$$

Now on to solution of problem.

(a) $\underline{V}^{\text{ex}}=\underline{V}_{\text{mix}}-\sum x_i\underline{V}_i=\frac{RT}{P}\left(Z_{\text{mix}}-\sum x_iZ_i\right)=\Delta_{\text{mix}}\underline{V}$

$Z_{\text{mix}}=$ compressibility of mixture at T and P

$Z_i=$ compressibility of pure fluid i at T and P

Will leave answer to this part in this form since the analytic expression for Z_i and Z_{mix} (solution to cubic) is messy. Though it can be analytically and symbolically with a computer algebra program such as Mathcad, Mathematica, Maple, etc.)

(b) $\underline{H}^{\text{ex}}=\underline{H}_{\text{mix}}-\sum x_i\underline{H}_i=\frac{RT}{Z_{\text{mix}}-1}-\frac{RTA_{\text{mix}}}{Z_{\text{mix}}}-\sum_i x_i\left[RT(Z_i-1)-\frac{RTA_i}{Z_{\text{mix}}}\right]$

$$= RT\left(Z_{\text{mix}} - \sum x_i Z_i\right) + \sum RT\left(\frac{x_i A_i}{Z_i}\right) - \frac{RTA_{\text{mix}}}{Z_{\text{mix}}}$$

$$= RT\left(Z_{\text{mix}} - \sum x_i Z_i\right) + RT\left(\sum \frac{x_i A_i}{Z_i} - \frac{A_{\text{mix}}}{Z_{\text{mix}}}\right)$$

$$\underline{U}^{\text{ex}} = \left(\underline{H}_{\text{mix}} - P\underline{V}_{\text{mix}}\right) - \sum x_i\left(\underline{H}_i - P\underline{V}_i\right)$$

$$= \left(\underline{H}_{\text{mix}} - \sum x_i \underline{H}_i\right) - P\left(\underline{V}_{\text{mix}} - \sum x_i \underline{V}_i\right)$$

$$= RT\left(Z_{\text{mix}} - \sum x_i Z_i\right) + RT\left(\sum \frac{x_i A_i}{Z_i} - \frac{A_{\text{mix}}}{Z_{\text{mix}}}\right) - RT\left(Z_{\text{mix}} - \sum x_i Z_i\right)$$

$$= +RT\left(\sum \frac{x_i A_i}{Z_i} - \frac{A_{\text{mix}}}{Z_{\text{mix}}}\right)$$

(c) $\underline{S}_{\text{mix}} - \sum x_i S_i - R\sum x_i \ln x_i$

$$= \underline{S}^{\text{ex}}$$

$$= P\ln(Z_{\text{mix}} - B_{\text{mix}}) - R\left[X_i \ln(Z_i - B_i) - R\sum x_i \ln x_i\right]$$

$$= R\ln(Z_{\text{mix}} - B_{\text{mix}}) - R\sum x_i\left[\ln(Z_i - B_i) + \ln x_i\right]$$

$$= R\ln(Z_{\text{mix}} - B_{\text{mix}}) - R\left[x_i\left[\ln x_i(Z_i - B_i)\right]\right]$$

$$= R\ln\frac{Z_{\text{mix}} - B_{\text{mix}}}{\prod_i (Z_i - B_i)^{x_i}}$$

(d) $\underline{G}^{\text{ex}} = \underline{H}^{\text{ex}} - T\underline{S}^{\text{ex}} = RT\left(Z_{\text{mix}} - \sum x_i Z_i\right) + RT\left(\sum \frac{x_i A_i}{Z_i} - \frac{A_{\text{mix}}}{Z_{\text{mix}}}\right)$

$$-RT\ln\frac{Z_{\text{mix}} - B_{\text{mix}}}{\prod_i (Z_i - B_i)^{x_i}}$$

$$\underline{A}^{\text{ex}} = \underline{U}^{\text{ex}} - T\underline{S}^{\text{ex}} = +RT\left(\sum \frac{x_i A_i}{Z_i} - \frac{A_{\text{mix}}}{Z_{\text{mix}}}\right) - RT\ln\frac{Z_{\text{mix}} - B_{\text{mix}}}{\prod_i (Z_i - B_i)^{x_i}}$$

#Problem 3:
9.22

2 (a) The two-constant Redlich-Kister expansion, which leads to the two-constant Margules equation is

$$\underline{G}^{\text{ex}} = x_1x_2\{A + B(x_1 - x_2)\}$$

Thus

$$\frac{\underline{G}^{\text{ex}}}{x_1x_2} = A + B(2x_1 - 1) \qquad (1)$$

which is a linear function of x.
The form of the Wohl Equation which leads to the van Laar Equation is

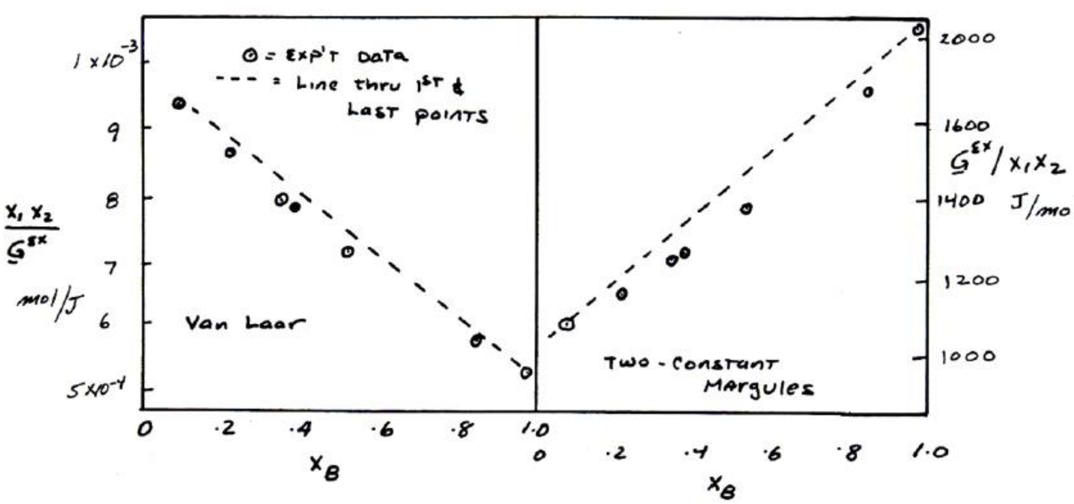
$$\underline{G}^{\text{ex}} = \frac{2RTa_{12}x_1q_1x_2q_2}{x_1q_1 + x_2q_2}$$

which can be rearranged to

$$\frac{x_1x_2}{\underline{G}^{\text{ex}}} = \frac{x_1q_1 + (1-x_1)q_2}{2RTa_{12}q_1q_2} \qquad (2)$$

which is also a linear function of x. Equations (1) and (2) provide the justification for the procedure.

(b) The figure below is the required plot. Clearly, neither equation is an accurate fit of the data. [The 2-constant Wohl (or van Laar) equation plot of the data, i.e., the form of Eq. (2), is closest to being linear, and therefore should be the better of the two-constant fits of the data. The data can, however, be fit quite well with a 3-constant Redlich-Kister expansion—See Illustration 10.1-4]



#Problem 4:
9.30

a)

$i := 0, 1 .. 10 \qquad x_i := 0.1 \cdot i$

$$fma_i := x_i \cdot \exp\left[1.06 \cdot (1 - x_i)^2\right] \cdot 1.126$$

$$fm_i := (1 - x_i) \cdot \exp\left[1.06 \cdot (x_i)^2\right] \cdot 0.847$$

x =

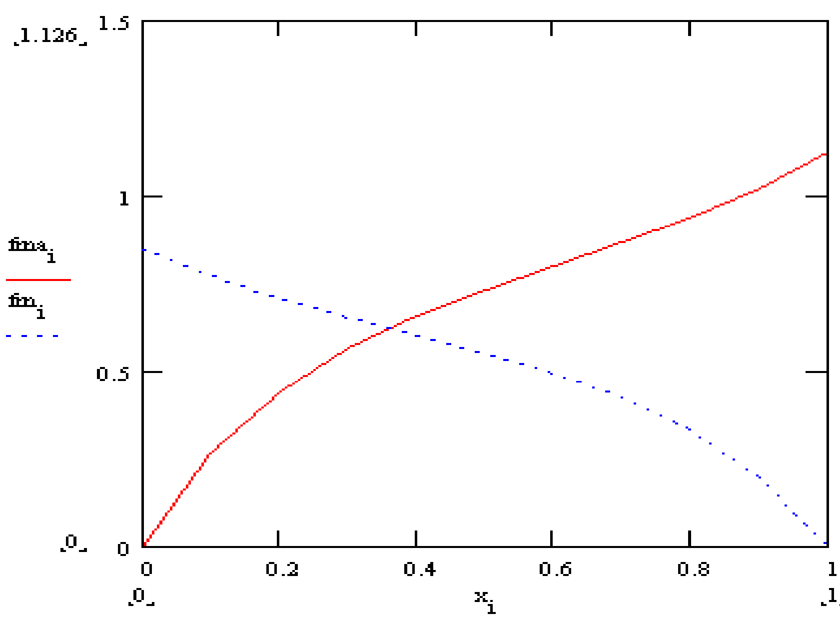
	0
0	0
1	0.1
2	0.2
3	0.3
4	0.4
5	0.5
6	0.6
7	0.7
8	0.8
9	0.9
10	1

fma =

	0
0	0
1	0.266
2	0.444
3	0.568
4	0.66
5	0.734
6	0.8
7	0.867
8	0.94
9	1.024
10	1.126

fm =

	0
0	0.847
1	0.77
2	0.707
3	0.652
4	0.602
5	0.552
6	0.496
7	0.427
8	0.334
9	0.2
10	0



b) from equation (9.7-12), we have

$$H_1 = \gamma_1(T, P, x_1 = 0) f_1^L = \exp\left[\frac{A}{RT}(1 - x_1)^2\right] * 1.126 = \exp(1.06) * 1.126 \ \ (x_1 \to 0)$$

$$H_2 = \gamma_2(T, P, x_2 = 0) f_2^L = \exp\left[\frac{A}{RT}(x_1)^2\right] * 0.847 = \exp(1.06) * 0.847 \ \ (x_2 \to 0)$$

Because of this, the hypothetical pure component fugacity based on the Henry's law standard state for methyl acetate and methanol would be, respectively:

exp(1.06)*1.126 = 3.25

exp(1.06)*0.847 = 2.445

which are different from values obtained from the usual pure component standard state

#Problem 5:
Consider an equimolar binary mixture of species a and b. The activity coefficients at infinite dilution are given by $\gamma 1\infty$ ($x2 \approx 1$) = 2 and $\gamma 2\infty$ ($x1 \approx 1$) = 1.5, calculate the activity coefficient of species a and b using the two-constant Margules expansion, Van Laar equation, and the Wilson equation

Soltuion

- Two-constant Margules expansion

RTln γ_1^∞ = (A + 3B) – 4B = A – B

RTln γ_2^∞ = (A – 3B) + 4B = A + B

with γ_1^∞ ($x_2 \approx 1$) = 2 and γ_2^∞ ($x_1 \approx 1$) = 1.5

plug back into above equations, we obtain

$$A = RTln\sqrt{3}$$

$$B = RTln\frac{\sqrt{3}}{2}$$

For an equimolar mixture

RTln γ_1 = (A + 3B)$(0.5)^2$ – 4B*$(0.5)^3$

RTln γ_2 = (A – 3B)$(0.5)^2$ + 4B*$(0.5)^3$

Substitute the values of A and B into the above equations, we find
$\gamma_1 = 1.11$
$\gamma_2 = 1.19$

- Van Laar equation
  $\ln \gamma_1^\infty = \alpha = \ln(2)$
  $\ln \gamma_2^\infty = \beta = \ln(1.5)$

at equimolar mixture, we have

$$ln\gamma_1 = \frac{\alpha}{[1+\frac{\alpha}{\beta}]^2} = \frac{ln2}{[1+\frac{ln2}{ln1.5}]^2}$$

$$\gamma_1 = 1.1$$

Similarly we have

$$ln\gamma_2 = \frac{\beta}{[1+\frac{\beta}{\alpha}]^2} = \frac{ln1.5}{[1+\frac{ln1.5}{ln2}]^2}$$

$$\gamma_2 = 1.18$$

- Wilson equation

$$ln\gamma_1^\infty = -ln\Lambda_{12} + 1 - \Lambda_{21} = ln2$$

$$ln\gamma_2^\infty = -ln\Lambda_{21} - \Lambda_{12} + 1 = \ln(1.5)$$

Solving these two equations, we obtain

$$\Lambda_{12} = 0.407$$

$$\Lambda_{21} = 1.21$$

For an equimolar mixture

$$ln\gamma_1 = -\ln(0.5 + 0.5\Lambda_{12}) + 0.5[\frac{\Lambda_{12}}{0.5 + 0.5 * \Lambda_{12}} - \frac{\Lambda_{21}}{0.5 * \Lambda_{21} + 0.5}]$$

$$ln\gamma_2 = -\ln(0.5 + 0.5\Lambda_{21}) - 0.5[\frac{\Lambda_{12}}{0.5 + 0.5 * \Lambda_{12}} - \frac{\Lambda_{21}}{0.5 * \Lambda_{21} + 0.5}]$$

Solving the equations to get

$$\gamma_1 = 1.1$$

$$\gamma_2 = 1.17$$

#Problem 6:

The activity coefficients at infinite dilution of a binary mixture are given as γ1∞ (x2 ≈ 1) = 1.27, γ2∞ (x1 ≈ 1) = 1.34; calculate the activity coefficient of species 1 in the mixture, using one-constant Margules equation, at the following compositions x1 = 20%; x1 = 50%; x1 = 90%

Solution

With the one-constant Margules equation, we have

$RT\ln \gamma_1^\infty = A = RT\ln(1.27)$

$RT\ln \gamma_2^\infty = A = RT\ln(1.34)$

The value of A would be taken as the average, which is

A = 0.5*RT*[ln(1.27) + ln(1.34)] = 0.266RT

At x_1 = 20% → x_2 = 80%

$RT\ln \gamma_1 = (0.8)^2 * A = 0.64 * 0.266RT$

$\gamma_1 = 1.186$

At x_1 = 50% → x_2 = 50%

$RT\ln \gamma_1 = (0.5)^2 * A = 0.25 * 0.266RT$

$\gamma_1 = 1.069$

At x_1 = 90% → x_2 = 10%

$RT\ln \gamma_1 = (0.1)^2 * A = 0.01 * 0.266RT$

$\gamma_1 = 1.003$