10.213 Chemical Engineering Thermodynamics
Spring 2002

Problem Set I
Due Wednesday, April 24, 2002 in lecture

Problem 29
The Redlich-Kwong equation can be written as:

$$P = \frac{RT}{V-b} - \frac{a}{T^{0.5}V(V+b)} \text{ and manipulated to provide that}$$

$$Z = 1 + \frac{b}{V-b} - \frac{a}{RT^{1.5}(V+b)}, \text{ where } a = \frac{0.42748R^2T_c^{2.5}}{P_c} \text{ and } b = \frac{0.08664RT_c}{P_c}.$$

a) Show that $\ln\phi = -\ln(1-\frac{b}{V}) - \frac{a\ln(1+\frac{b}{V})}{bRT^{1.5}} + Z - 1 - \ln Z$. As a hint, consider the use of either $\frac{G^R}{RT} = \int_0^P (Z-1)\frac{dP}{P}$ (eq 6.46) or $\frac{G^R}{RT} = \int_0^\rho (Z-1)\frac{d\rho}{\rho} + Z - 1 - \ln Z$ (eq 6.57) where $\rho = \frac{1}{V}$.
b) Determine the fugacity of *n*-butane gas at 500 K and 50 bar using the equation derived in a).
c) Determine the fugacity of *n*-butane gas at 500 K and 50 bar using the values of H^R = -4.51 kJ/mol and S^R = -6.55 J/mol-K determined in Example 6.4 for n-butane under these conditions (pp 215-216 in SVN&A).
d) Determine the fugacity of *n*-butane gas at 500 K and 50 bar using generalized correlations.

Problem 30
The excess Gibbs free energy of a binary liquid mixture at T and P is given by:

$$\frac{G^E}{RT} = (-2.6x_1 - 1.8x_2)x_1x_2$$

a) Find expression of $\ln\gamma_1$ and $\ln\gamma_2$ at T and P.
b) Show that when these expressions are combined in accord with Eq 11.95 that the given equation for G^E/RT is recovered.
c) Show that the expressions in a) satisfy the Gibbs-Duhem equation.
d) Show that $(d\ln\gamma_1/dx_1)_{x_1=1} = (d\ln\gamma_2/dx_1)_{x_1=0} = 0$.
e) Plot G^E/RT, $\ln\gamma_1$, and $\ln\gamma_2$ as calculated by the given equation for G^E/RT and by the equations developed in a) vs. x_1. Label points $\ln\gamma_1^\infty$ and $\ln\gamma_2^\infty$ and show their values.
f) Plot $\Delta G/RT$ vs x_1.
g) Does $\Sigma(x_i\, d\gamma_i) = 0$? Should it? Hint: consider the definition of the Gibbs-Duhem equation.

Problem 31

The data tabulated below are experimental values of H^E for binary liquid mixtures of 1,2-dichloroethane (1) and dimethyl carbonate (2) at 313.15 K and 1 atm

(from R. Francesconi et al. *Int. DATA Ser. A*, Vol. 25, No. 3, p. 225, 1997).

x_1	H^E (J/mol)	x_1	H^E (J/mol)
0.0426	-23.3	0.5163	-204.2
0.0817	-45.7	0.6156	-191.7
0.1177	-66.5	0.6810	-174.1
0.1510	-86.6	0.7621	-141.0
0.2107	-118.2	0.8181	-116.8
0.2624	-144.6	0.8650	-85.6
0.3472	-176.6	0.9276	-43.5
0.4158	-195.7	0.9624	-22.6

a) Determine from the data numerical values of the parameters a, b, and c in the correlating equation:

$$H^E = x_1 x_2 (a + b x_1 + c x_1^2)$$

(Hint: consider plotting $H^E/(x_1 x_2)$ vs. x_1 as a way to determine values of a, b, and c.)

b) Determine the minimum value of H^E from the results in part a). At what value of x_1 does this occur?

c) Determine expressions for $\overline{H}_1^E$ and $\overline{H}_2^E$ from the results of part a). Prepare a plot of $\overline{H}_1^E$ and $\overline{H}_2^E$ vs. x_1 and discuss its features.

d) Plot ΔH vs. x_1. What is the relationship between ΔH and H^E?

e) Determine values of H^E, $\overline{H}_1^E$, and $\overline{H}_2^E$ for $x_1 = 0$ and $x_1 = 1$. For cases where $H^E = 0$ and either $\overline{H}_1^E$ or $\overline{H}_2^E \neq 0$, explain how H^E can equal 0 while either $\overline{H}_1^E$ or $\overline{H}_2^E$ do not.

Problem 32.

Steam undergoes an isothermal change in state from 9000 kPa and 400 ºC to 300 kPa and 400 ºC. Determine *using steam tables*, the ratio of the fugacity in the final state to that in the initial state. (Hint: this question requires only a little bit of calculation, so think first about how to connect fugacities (or rather, fugacity ratios) given the type of data in a steam table.)