ChE 621: Problem Set #4
Due: February 25, 2009 (11:00 am)

1.) The coexistence (vapor-liquid) line of methylmercaptan is described by the following equation:

$$\ln P^{vap}(mm\ Hg) = 16.1909 - \frac{2338.38}{T(K) - 34.44}$$

a. What phase is methylmercaptan in at 273 K and 1 bar? What is the fugacity of methylmercaptan at 273 K and 1 bar?
b. What phase is methylmercaptan in at 273 K and 0.5 bar? What is the fugacity of methylmercaptan at 273 K and 0.5 bar?

2.) Water obeys a third-order virial equation of state, up to moderate pressures:

$$\frac{P\upsilon}{RT} = 1 + B'(T)P + C'(T)P^2$$

where v is the molar volume and B' and C' are the pressure-based virial coefficients. Calculate the fugacity of liquid water at 528 K and 1000 bar. The virial coefficients for water at 528 K are $B' = -0.00303$ bar^{-1} and $C' = -1.17\text{x}10^{-5}$ bar^{-2}. Also, the density of water vapor at saturation at 528 K is 0.02471 g/ml.

3.) The Peng-Robinson equation of state has the following form:

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)+b(v-b)}$$

where

$$a = 0.45724\frac{R^2T^2}{P_c}\alpha(T) \qquad b = 0.07780\frac{RT_c}{P_c}$$

$$\alpha = \left[1 + \left(0.37464 + 1.54226\omega - 0.26992\omega^2\right)\left(1-\sqrt{T_r}\right)\right]^2 \qquad T_r = \frac{T}{T_c}$$

and T_c and P_c are the critical temperature and pressure, respectively, and ω is the acentric factor. Given this equation of state, derive the following expression for the fugacity coefficient of a pure species.

$$\ln\frac{f}{P} = (Z-1) - \ln\left(Z - \frac{bP}{RT}\right) - \frac{a}{2\sqrt{2}bRT}\ln\left[\frac{Z + \left(1+\sqrt{2}\right)bP/RT}{Z + \left(1-\sqrt{2}\right)bP/RT}\right]$$