Chapter 10 Problems

1. Solutions of two organic liquids A and B have the following partial pressures:

x_B	partial pressure of B mm Hg	partial pressure of A mm Hg
0.0000	0.0	344.5
0.0588	9.2	323.2
0.1232	20.4	299.3
0.1853	31.9	275.4
0.2910	55.4	230.3
0.4232	88.9	174.3
0.5143	117.8	135.0
0.5812	139.9	108.5
0.6635	170.2	79.0
0.7997	224.4	37.5
0.9175	267.1	13.0
1.0000	293.1	0.0

   Calculate and plot

   (a) the total vapor pressure.

   (b) the Raoultian activities of A and B. What standard state for Raoultian activities did you use?

   (c) the Raoultian activity coefficients of A and B.

   (d) Fit a Regular Solution equation to the activity coefficients to find w_G (how to do this is shown in Figures 14.7 and 14.8).

   (e) Derive an expression for a_B in terms of w_G and x_B.

   (f) Differentiate this equation to find da_B/dx_B, and evaluate this at $x_B = 0$. This gives the Henryan slope, assuming Regular Solution theory.

   (g) Using this slope, calculate Henryan activity coefficients for B

   (h) If you are unable to derive these equations, plot the slope graphically and determine the Henryan activity coefficients of B that way.

2. Fugacity coefficients for CO_2 and H_2O in H_2O-CO_2 solutions at 2000 bars, 600°C are[1]

[1] Bowers, T.S., and Helgeson, H.C., 1983, Calculation of the thermodynamic and geochemical consequences of nonideal mixing in the system H_2O-CO_2-NaCl on phase relations in geological systems: Equation of state for H_2O-CO_2-NaCl fluids at high temperatures and pressures. Geochim. Cosmochim. Acta, v. 47, pp. 1247–1275.

x_{CO_2}	γ_{f,CO_2}	γ_{f,H_2O}
0	5.026	0.474
0.1	3.371	0.483
0.2	2.664	0.503
0.3	2.303	0.528
0.4	2.097	0.555
0.5	1.973	0.583
0.6	1.896	0.612
0.7	1.848	0.641
0.8	1.820	0.671
0.9	1.805	0.702
1.0	1.801	0.732

Claculate and plot vs. x_{CO_2}

(a) Partial pressure of CO_2.

(b) fugacity of CO_2 and H_2O.

(c) activity of CO_2 and H_2O. What standard states did you use?

(d) Raoultian activity coefficients for CO_2 and H_2O.

(e) Fit the CO_2 Raoultian activity coefficients to one of equations (10.105) to determine w_{G_1} and w_{G_2}. This can be done with the solver option in a spreadsheet, or any other curve-fitting program.

(f) Use w_{G_1} and w_{G_2} to calculate values of CO_2 activity and plot these on graph containing the experimental values.

(g) Plot the Henry's Law line. Note that the Henry's Law slope is given by the fugacity coefficient at $x_{CO_2} = 0$ calculated from equation (10.105).