January 16, 2002

CH 342 S02, Homework 2

due Wednesday, January 23, 2002

Problems marked with a $\star$ must be done using a computer (spreadsheet or symbolic math package).

Phase Diagrams : Pure Materials

1. $\star$ The following information has been gathered for ethanol: $\Delta_{fus}\bar{H}$ = 5.0 kJ/mol, $\Delta_{vap}\bar{H}$ = 38.56 kJ/mol, ρ_l = 0.7873 Mg/m^3, and ρ_s = 0.815 Mg/m^3. Ethanol has a triple point at 150 K with a vapor pressure of 0.43 mPa.

   Using the appropriate variations of the equation $dp/dT = \Delta_{trs}\bar{S}/\Delta_{trs}\bar{V}$, construct a phase diagram for ethanol near its triple point. The equations developed will be for the solid-gas, solid-liquid, and liquid-gas boundaries. The temperature should extend from 140 K to 160 K and the pressure from 0 to 2 mPa. The solid-gas, solid-liquid, and liquid-gas boundaries should meet at the triple point.

   Notes: The above problem is similar to P 6.10 of the textbook. The enthalpies of fusion, vaporization, and sublimation can be related appropriately through a simple Born-Haber thermodynamic cycle in order to determine the missing enthalpy of sublimation.

2. Using the above information, determine the vapor pressure of liquid ethanol (in bar) at 273 K and at its normal boiling point of 350 K.

3. Using the above information, determine the solid-liquid and liquid-gas transition temperatures at 1 mPa pressure.

Extra Credit: Using the above information, construct a hypothetical plot of chemical potential versus temperature for ethanol at a pressure of 1 mPa from 140 K to 150 K. Assume the chemical potential and molar entropy of solid ethanol at 140 K are zero.

Hint: The slope of the plot of chemical potential versus temperature is $-\bar{S}$. The difference in slopes for a transition between one phase to another is therefore $-\Delta_{trs}\bar{S} = -\Delta_{trs}\bar{H}/T_{trs}$. See P 6.4 of the textbook for similar information.

Mixtures : Partial Molar Quantities

4. E 7.1b

5. P 7.2

6. A liquid mixture with 10 mol A and 20 mol B is formed at STP. The mixture has a molar enthalpy of -107 kJ/mol. The chemical potential of component B is determined to be 25 kJ/mol. One mole of B is added to the mixture. Determine the molar enthalpy of the new mixture.

Extra Credit: The total volume of a mixture of two liquids A and B is fit by the expression $V = A + Bx_B + Cx_B^2 + D/x_B$, where x_B is the mole fraction B. Determine the expression for the partial molar volumes of A and B ($\hat{V}_A$ and $\hat{V}_B$) as a function of x_B.

Mixtures : Thermodynamics of Mixing

7. E 7.9b

8. E 7.10b