Chapter 6: Phase Equlibria I: Problem Formulation

1. To manufacture diamonds at 25°C requires increasing the pressure until graphite and diamond are in equilibrium. The following data are available at 25°C:

$$\Delta g(25°C, 1\ atm) = g_{diamond} - g_{graphite} = 2866\ J/mol$$
$$\rho_{diamond} = 3.51\ g/cm^3$$
$$\rho_{graphite} = 2.26\ g/cm^3.$$

   Estimate the pressure at which these two forms of carbon are in equilibrium at 25°C.

2. The vapor pressure of silver (between 1234 K and 2485 K) is given by the following expression:

$$\ln P = -\frac{14260}{T} - 0.458 \ln T + 12.23$$

   with P in torr, and T in K. Estimate the enthalpy of vaporization at 1500 K. State the assumptions that you make.

3. Pure ethanol boils at a temperature of 63.5°C at a pressure of 400 torr. It also boils at 78.4°C and 760 torr. Using only these data, estimate the saturation pressure for ethanol at 100°C.

4. An alternative criteria for chemical equilibrium between two phases of pure species i can be written:

$$\left(\frac{g_i}{T}\right)^{\alpha} = \left(\frac{g_i}{T}\right)^{\beta}$$

   Apply the thermodynamic web to show that the partial derivative of this function with respect to temperature at constant pressure is given by:

$$\left[\frac{\partial\left(\frac{g_i}{T}\right)}{\partial T}\right]_P = -\frac{h_i}{T^2}.$$

5. At 900 K, solid Sr has values of enthalpy and entropy of 20.285 $kJ/(mol)$ and 91.222 $J/(mol\ K)$, respectively. At 1500 K, liquid Sr has values of enthalpy and entropy of 49.179 kJ/mol and 116.64 $J/(mol\ K)$, respectively. The heat capacity for the solid and liquid phases is given by:

$$(c_p)_{Sr}^{(s)} = 37.656\ J/(mol\ K),\ (c_p)_{Sr}^{(l)} = 35.146\ J/(mol\ K)$$

respectively. Using only these data, determine the temperature of the phase transition between solid and liquid. What is the enthalpy of fusion? Hint: The result of Problem 4 could be useful.

6. Determine the second virial coefficient, B, for CS_2 at $100°C$ from the following data. The saturation pressure of carbon disulfide (CS_2) has been fit to the following equation:

$$\ln P_{CS_2}^{sat} = 62.7839 - \frac{4.7063 \times 10^3}{T} - 6.7794 \ln T + 8.0194 \times 10^{-3} T$$

where T is in K and $\ln P_{CS_2}^{sat}$ is in Pa. The enthalpy of vaporization for CS_2 at $100°C$ has been reported as

$$\Delta h_{vap,CS_2} = 24.050\ KJ/mol.$$

Compare the reported value of

$$B_{CS_2} = -492\ cm^3/mol. \tag{1}$$

7. Consider a mixture of species 1, 2, and 3. The following equation of state is available for the vapor phase:

$$Pv = RT + P^2[A(y_1 - y_2) + B],$$

where

$$\frac{A}{RT} = -9.0 \times 10^{-5}\ atm^{-2},\ \frac{B}{RT} = 3.0 \times 10^{-5}\ atm^{-2}$$

and $y_1,\ y_2$, and y_3 are the mole fractions of species 1, 2 and 3, respectively. Consider a vapor mixture with 1 mole of species 1, 2 moles of species 2, and 2 moles of species 3 at a pressure of 50 atm and a temperature of $500K$. Calculate the following quantities: $v, V, v_1, v_2, v_3, \overline{V_1}$

8. Enthalpies of mixing for binary mixtures of cadmium (Cd) and tin (Sn) have been fit to the following equation at $500°C$:

$$\Delta h_{mix} = 13000 X_{Cd} X_{Sn}\ J/mol.$$

where X_{Cd}, X_{Sn} are the cadmium and tin mole fractions, respectively. Consider a mixture of 3 moles Cd and 2 moles Sn.

(a) Show that

$$(\overline{\Delta H}_{mix})_{Cd} = \bar{H}_{Cd} - h_{Cd}.$$

(b) Based on the equations above, calculate values for $\overline{H}_{Cd} - h_{Cd}$, and $\overline{H}_{Sn} - h_{Sn}$ at $500°C$.

(c)Show that the results are consistent with the Gibbs-Duhem equation.