Homework 5

1. The standard Gibbs energy of formation of rhombic sulfur is 0 and that of monoclinic sulfur is +0.33 kJ mol^{-1} at 25°C. Which polymorph is the more stable at that temperature? The density of rhombic sulfur is 2.070 g cm^{-3} and that of monoclinic sulfur is 1.957 g cm^{-3}. Can the application of pressure be expected to make monoclinic sulfur more stable than rhombic sulfur? The standard molar entropy of rhombic sulfur is 31.80 J K^{-1} mol^{-1} and that of monoclinic sulfur is 32.6 J K^{-1} mol^{-1}. Can an increase in temperature be expected to make monoclinic sulfur more stable than rhombic sulfur? If so, at what temperature will the transition occur at 1 bar?

2. The standard molar entropy of benzene is 173.3 J K^{-1} mol^{-1}. Calculate the change in its standard molar Gibbs energy when it is heated from 20ºC to 50ºC.

3. A sample of water vapor at 200ºC is compressed isothermally from 300 mL to 100 mL. What is the change in its molar Gibbs energy?

4. Calculate $\Delta_r G^{\varnothing}(375\ \mathrm{K})$ for the reaction $2\ CO(g) + O_2(g) \rightarrow 2\ CO_2(g)$ from the value of $\Delta_r G^{\varnothing}(298\ \mathrm{K})$, $\Delta_r H^{\varnothing}(298\ \mathrm{K})$, and the Gibbs-Helmholtz equation.

5. The fugacity coefficient of a certain gas at 200 K and 50 bar is 0.72. Calculate the difference of its molar Gibbs energy from that of a perfect gas in the same state.

6. Two of the four Maxwell relations were derived in the text, but two were not. Complete their derivation by showing that $(\partial S/\partial V)_T = (\partial p/\partial T)_V$ and $(\partial T/\partial p)_S = (\partial V/\partial S)_p$.

7. Use the Maxwell relations to show that the entropy of a perfect gas depends on the volume as $S \propto R \ln V$.

8. Use the phase diagram for CO_2 in Fig. 4.8 (Atkins) to state what would be observed when a sample of carbon dioxide, initially at 1.0 atm and 298 K, is subjected to the following cycle: (a) constant-pressure heating to 320 K, (b) isothermal compression to 100 atm, (c) constant-pressure cooling to 210 K, (d) isothermal decompression to 1.0 atm, (e) constant-pressure heating to 298 K.

9. The vapor pressure of pyridine is 50.0 kPa at 365.7 K and the normal boiling point is 388.4 K. What is the enthalpy of vaporization of pyridine?

10. When benzene freezes at 5.5°C its density changes from 0.879 g cm^{-3} to 0.891 g cm^{-3}. Its enthalpy of fusion is 10.59 kJ mol^{-1}. Estimate the freezing point of benzene at 1000 atm.