ASSIGNMENT 10

CHEMISTRY 200

Due: 4:30 pm Wednesday 29 November 2006

The Entropy Assignment

1. Consider the adiabatic irreversible compression of 1.53 moles of a perfect gas initially at a volume of 21.5 L and 236 K. This gas is compressed at constant pressure to half its initial volume.
   (a) What are the final pressure and temperature?
   (b) Calculate the entropy change associated with this change in state by each of the following combinations of reversible paths:
      i. an isochore followed by an isobar
      ii. an isotherm followed by an isochore
      iii. an isotherm followed by an isobar
      iv. an adiabat followed by an isochore
      v. an adiabat followed by an isobar
      vi. an abiabat followed by an isotherm

2. The molar heat capacity of gaseous hydrogen is given by $C_p/R = a + bT + cT^2$ where a = 3.4958, b = -1.006 $\times 10^{-4}$ K^{-1}, and c = 2.419 $\times 10^{-7}$ K^{-2}.
   (a) What is the entropy change if the gas is heated at constant pressure from 300 K to 1500 K?
   (b) What is the entropy change if the gas is heated at constant volume from 300 K to 1500 K?
   (c) The heat capacity at constant volume of a gas can be estimated by taking into account the internal motions of the molecule and assuming that there are no intermolecular forces. Each vibrational degree of freedom contributes R to the molar heat capacity while each rotational and each translational degree of freedom contributes $R/2$. On this basis, recalculate the entropy changes, assuming no temperature dependence. Discuss whether the vibrational motion of the molecule affects the heat capacity.

3. The difference between heat capacity at constant pressure and at constant volume is given by:

$$C_p - C_v = T \left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial p}{\partial T}\right)_v$$

   (a) Evaluate this expression for a perfect gas.
   (b) Evaluate this expression for a hard sphere gas.
   (c) Evaluate this expression for a gas with a Berthelot equation of state.

$$P = \frac{nRT}{V - nb} - \frac{n^2 a}{TV^2}$$

   HINT: Use the cyclic rule

$$-1 = \left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial T}{\partial p}\right)_V \left(\frac{\partial p}{\partial V}\right)_T$$

   as necessary.

4. One mole of perfect gas doubles in volume at a constant temperature. What volume change is required for 2.00 mole of an ideal gas to exhibit the same increase in entropy? For 0.500 mol?

5. Calculate the absolute entropy of one mole of S gas at 917 K. At 95.4°C, the enthalpy of the transition from rhombic to monoclinic form is 0.38 kJ mol^{-1}. At 119°C, monoclinic S melts with an enthalpy of fusion of 1.23 kJ mol^{-1}. The boiling point is 444.7°C. The heat capacity of rhombic S between 15 and 370 K is:

$$C_p/R = 0.08 + 2.17 \times 10^{-2}T - 6.2 \times 10^{-5}T^2 + 6.9 \times 10^{-8}T^3$$

Below 15 K, the Debye expression is used:

$$\frac{C_v}{R} = \frac{233.8}{\Theta_D^3}T^3$$

where the Debye temperature,Θ_D for rhombic S is 150.4 K.
The heat capacity of monoclinic S is:

$$C_p/R = 1.96 \times 10^{-2}T - 4.8 \times 10^{-5}T^2 + 4.7 \times 10^{-8}T^3$$

The heat capacity of liquid S is:

$$C_p/R = 7.85$$

Use Trouton's rule:

$$\frac{\Delta H_{vap}}{T_{vap}} = 88 \text{ J K}^{-1} \text{ mol}^{-1}$$

to estimate the enthalpy of vaporization.
In the gas phase, assume that atomic S behaves ideally.