CHM 3400 – Problem Set 2
Due date: Wednesday, January 29th.

Do all of the following problems. Show your work.

"Thermodynamics is a funny subject. The first time you go through it, you don't understand it at all. The second time you go through it, you think you understand it, except for one or two points. The third time you go through it, you know you don't understand it, but by that time you are so used to the subject, it doesn't bother you anymore."

- Arnold Sommerfeld

1) Consider a nonideal gas obeying the following equation of state (an example of a virial equation)

$$\frac{pV}{nRT} = 1 + \frac{nB}{V} + \frac{n^2C}{V^2} \qquad (1.1)$$

where B and C are constants whose values only depend on temperature.

a) Find a general expression for w (work) for the isothermal reversible expansion or compression of n moles of the above substance from an initial volume V_i to a final volume V_f.

b) Using your result in part a, find the value for w when 1.000 mol of argon gas is compressed isothermally and reversibly from an initial volume V_i = 20.00 L to a final volume V_f = 0.200 L, at a temperature T = 300.0 K. For argon at T = 300.0 K, B = - 21.7 cm^3/mol and C = 1200. cm^6/mol^2. Give your final answer in units of J.

c) Find the value for w for the same process, but assuming that argon obeys the ideal gas law. Give your final answer in units of J.

d) Compare your answers in b and c. What is the percent difference between the result found in b an that found in c?

2) Consider the following function of two variables

$$F(x,y) = 4x^3y + 7xy^2 + 3y^2 - 6x + 2 \qquad (2.1)$$

Find the following:

a) $(\partial F/\partial x)_y$

b) $(\partial F/\partial y)_x$

3) The effect of temperature on the molar volume of a liquid is often written as follows

$$V_m = V_{m,0}\,[\,1 + a\,(T - T_0) + b\,(T - T_0)^2\,] \qquad (3.1)$$

where $V_{m,0}$ is the molar volume at a reference temperature T_0, and a and b are constants.

a) Find an expression for α, the coefficient of thermal expansion, for a liquid whose volume is given by eq 3.1. Note that α is defined by the expression

$$\alpha = (1/V_m)\,(\partial V_m/\partial T)_p \qquad (3.2)$$

b) For water, in the temperature range 15-35 °C, the values for the constants in eq 3.1 are T_0 = 20.0 °C, a = 2.037 x 10^{-4} K^{-1}, b = 5.0 x 10^{-6} K^{-2}, and $V_{m,0}$ = 18.0478 cm^3/mol. Based on this information, find the value for α (including correct units) for water at T = 20.0 °C and at T = 30.0 °C.

4) The temperature dependence of the constant pressure molar heat capacity of a pure substance ($C_{p,m}$) is often fit to the following equation (see Atkins, section 2D.3).

$$C_{p,m} = a + bT + (c/T^2) \qquad (4.1)$$

where a, b, and c are constants.

a) Find the value for $C_{p,m}$ for CO_2(g) at T = 300.0 K and T = 400.0 K. Note that for CO_2(g), a = 44.22 J/mol•K, b = 8.79 x 10^{-3} J/mol•K^2, and c = - 8.62 x 10^5 J•K/mol.

b) Find the value for ΔH, the change in enthalpy, when 5.000 mol of CO_2(g) is heated from an initial temperature T_i = 300.0 K to a final temperature T_f = 400.0 K under conditions of constant pressure. Give your final answer in unit of J. (Hint – For the constant pressure heating of a pure substance dH = n $C_{p,m}$ dT)

5) Using the thermochemical data given below (at T = 25.0 °C) find the following for the reaction

$$2\,SnO_2(s) \rightarrow 2\,SnO(s) + O_2(g) \qquad (5.1)$$

a) $\Delta H°_{rxn}$ at T = 25.0 °C.

b) $\Delta H°_{rxn}$ at T = 100.0 °C. To do this problem you may assume that the values for $C_{p,m}$ in the thermochemical data are constant over the range 25.0 – 100.0 °C.

Substance	$\Delta H°_f$ (kJ/mol)	S° (J/mol•K)	$\Delta G°_f$ (kJ/mol)	$C_{p,m}$ (J/mol•K)
O_2(g)	0.0	205.2	0.0	29.36
SnO(s)	- 285.8	56.5	- 256.8	44.31
SnO_2(s)	- 580.7	52.3	- 519.6	52.59