CHM 3400 – Problem Set 3

Due date: Wednesday, February 3rd (by 11:59pm). Please turn in your homework by sending it to me at my FIU email address joensj@fiu.edu Indicate in your email that you are sending me your Homework 3 solutions.

Do all of the following problems. Show your work.

"I have always been more interested in chemistry than physics." – Thomas Edison

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

$$V_m = V_{m,0} [1 + a (T - T_0) + b (T - T_0)^2] \quad (1.1)$$

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 1.1. Note that α is defined by the formula

$$\alpha = (1/V_m) (\partial V_m/\partial T)_p \quad (1.2)$$

b) For water, in the temperature range 15-35 °C, the values for the constants in eq 1.1 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 = 15.0 °C.

NOTE: This may not seem like an important problem, but as least half of the rise in sea level predicted to occur due to global warming is from the increase in the average temperature of the ocean.

2) For an ideal monatomic gas the constant volume molar heat capacity is $C_{V,m} = (^3/_2)$ R = 12.472 J/mol•K. This value is independent of temperature..

a) What is the numerical value for $C_{p,m}$, the constant pressure molar heat capacity of an ideal monatomic gas?

b) The temperature of 1.000 mol of an ideal monatomic gas is changed from an initial value T_i = 300.0 K to a final value T_f = 350.0 K by a constant pressure reversible process. Find the values for q, w, ΔU, and ΔH for the process.

c) Find the values for q, w, ΔU, and ΔH if the temperature of the ideal monatomic gas is changed from the same initial value to the same final value of temperature as in part b, but by an unspecified irreversible process. If it is not possible to find some or all of the values asked for, briefly explain why those values cannot be found.

3) Heat capacity data can be used to find the amount of heat required to change the temperature of a substance. Consider a 500.0 g block of lead (Pb(s), MW = 207.19 g/mol). Find the amount of heat needed to change the temperature of this lead block from room temperature (T = 25.0 °C) to the normal melting point for lead (T_{fus} = 327.5 °C) by a constant pressure process. Do your calculation in two ways:

a) Assume the heat capacity for lead is independent of temperature, with $C_{p,m}$ = 26.70 J/mol•K, the value for heat capacity at T = 25.0 °C.

b) Use the following formula for $C_{p,m}$, one commonly used to model data on heat capacity

$$C_{p,m} = a + bT + c/T^2 \quad (3.1)$$

For lead, a = 22.13 J/mol•K, b = 1.172 x 10^{-2} J/mol•K^2, c = 9.6 x 10^4 J•K/mol.

4) Argonne National Laboratory (ANL) maintains a website that critically evaluates thermochemical data from the scientific literature. Based on these data, the website provides the best current values for the enthalpy of formation for hundreds of chemical substances at 0. K (absolute zero) and 298.15 K (T = 25.0 °C). The address for the website is:

https://atct.anl.gov/Thermochemical%20Data/version%201.122p/index.php

Values for ΔH°_f can be found by entering the appropriate chemical formula into the "species" box .

a) Using the information available at the ANL website, find the value for ΔH°_{rxn} for the following chemical reactions. Assume T = 25.0 °C.

i) $N_2O_5(g) + H_2O(\ell) \rightarrow 2\ HNO_3(aq)$	reaction contributing to acid rain formation in the lower atmosphere
ii) $3\ N_2H_4(\ell) \rightarrow 4\ NH_3(g) + N_2(g)$	main decomposition reaction for hydrazine, used as a rocket propellant
iii) $H_2CO(g) + O_2(g) \rightarrow CO_2(g) + H_2O(g)$	gas phase oxidation reaction of formaldehyde

b) For reaction iii above, use the table of average bond enthalpies in the Chapter 2 handout (Table 1) and the method discussed in class to estimate the value for ΔH°_{rxn}.

5) Thermochemical data for bromine (Br_2, MW = 159.82 g/mol) are given below (at T = 25.0 °C) and may be used in doing the following problem.

substance	ΔH°_f (kJ/mol)	ΔG°_f (kJ/mol)	S° (J/mol•K)	$C_{p,m}$ (J/mol•K)
$Br_2(\ell)$	0.0	0.0	152.23	75.69
$Br_2(g)$	30.907	3.110	245.46	36.02

Evaporazation of liquid bromine at room pressure corresponds to the process

$$Br_2(\ell) \rightarrow Br_2(g) \qquad (5.1)$$

Find the value for ΔH°_{rxn} for the above process at the following two temperatures.

a) At T = 25.0 °C

b) At T = 100.0 °C. For this part of the problem you will need to use the heat capacity data. You may assume that the values for $C_{p,m}$ for liquid bromine and bromine vapor are independent of temperature.

c) It is possible to estimate the value for w when evaporization of liquid bromine takes place at a constant pressure p = 1.000 atm. Estimate the value for w when evaporization of bromine liquid occurs at T = 25.0 °C and p = 1.000 atm. State any approximations in your calculation.