Chem 312 – Spring 2008
Problem Set #4
Due Friday, Mar 28, 10:10am in class.

Question 1

(a) Use average bond energy data to calculate the value of ΔH_f^o for $H_2O_{2(l)}$ (liquid hydrogen peroxide). The enthalpy of vaporization of H_2O_2 is 51.47 kJ/mol. Compare your calculated value to the experimental value of –187.78 kJ/mol.

(b) Assuming one of the Kekule structures of benzene (3 C=C and 3 C-C bonds), calculate the enthalpy of combustion for benzene using bond energy data, assuming all species are in the gas phase for this reaction. Explain the discrepancy with the experimental value of –3225 kJ/mol. What values should be used for the carbon-carbon bond energies instead? Comment on your result.

Bond Energy (kJ/mol)

	C	**N**	**S**	**O**	**Cl**	**F**	**H**
H–	414	389	368	464	431	569	435
F–	490	280	343	213	255	159	
Cl–	326	201	272	205	243		
O–	326	230	423	142			
O=	803	590	523	498			
N–	285	159					
N=	515	473					
C–	331						
C=	590						

Question 2

(a) Calculate ΔS for reversibly cooling 1 mol of an ideal monatomic gas from 25°C to 0°C under constant volume conditions. Does the "randomness" of the system increase or decrease?

(b) Repeat the calculation in (a) for a reversible isobaric cooling of the gas. Compare and the two results and comment on the difference.

(c) If the gas condenses at 0°C under isobaric conditions and ΔH^o_{vap} is 38.3 kJ/mol for this substance, calculate ΔS. Comment on your result.

(d) What correction factor is needed to change entropy values listed in handbooks at 25°C and 1 atm to 25°C and 1 bar for ideal gases?

Question 3

(a) A Carnot engine operates between two thermal reservoirs at 100°C and 0°C. What is the efficiency of the engine? How much work can it produce for each 1000 J of heat absorbed from the warm reservoir? [Assume the temperatures do not change during the process.]

(b) Consider 1.00 mol of liquid water at 100°C to be the warm reservoir for a Carnot engine. As heat is drawn from this reservoir by the engine, the temperature of the hot heat reservoir drops drops. How much work can be obtained from this reservoir as it cools to the temperature of the cold heat reservoir at 0°C? What is the efficiency of this process? How does it compare to the efficiency in (a)? [You may assume $C_{p,m}$ = 75 J K^{-1} mol^{-1} for water over this temperature range.]

Question 4

A 25.00-g sample of water at 25.0°C was mixed reversibly with a 75.00-g sample of water at 75.0°C. For $H_2O_{(l)}$, $C_{p,m}$ = 75.3 J K^{-1} mol^{-1} stays constant in this temperature range. [Molar mass of H_2O is 18.015-g.]

(a) Calculate the final temperature of the system (based on conservation of energy).

(b) Calculate the entropy change for each sample of water separately, and then calculate the entropy change for the combined system.

(c) If this mixing process is performed irreversibly (direct transfer, no change to thermal surroundings), would it be spontaneous?

Question 5

Using absolute entropies from tables, calculate the entropy change for the following reactions under standard conditions and explain if the sign and magnitudes make sense:

(a) decomposition of nitrogen dioxide into nitrogen monoxide and oxygen gas

(b) (i) combustion of methane (products in their standard states)

(ii) combustion of methane again (but this time with all gaseous products)

(c) Qualitatively explain the trend in absolute entropy values for each substance that you used in part (a).