CH301 Fall 2008 Worksheet 12 Answer Key

1. Assume we want to use a bomb calorimeter to determine the specific heat capacity of an unknown liquid. We use 3 L of the unkown liquid and perform a known reaction that releases 400 kJ of heat. We measure an initial and final temperature of 25 °C and 28.7 °C, respectively. If the heat capacity of the calorimeter is 85 $J \cdot K^{-1}$, and the density of the liquid is 2.34 $g \cdot mL^{-1}$, what is the specific heat capacity of the unknown liquid?

ΔH = 400 kJ
m = 3 L * 1000 $mL \cdot L^{-1}$ * 2.34 $g \cdot mL^{-1}$ = 7020 g
$\Delta T = T_f - T_i$ = 28.7 °C - 25 °C = 3.7 °C = 3.7 K
c_{cal} = 85 $J \cdot K^{-1}$ * .001 $kJ \cdot J^{-1}$ = 0.085 $kJ \cdot K^{-1}$
$\Delta H = m \cdot c \cdot \Delta T + c_{cal} \cdot \Delta T$
$c = (\Delta H - c_{cal} \cdot \Delta T)/(m \cdot \Delta T)$
= (400 kJ - 0.085 $kJ \cdot K^{-1}$ * 3.7 K)/(7020 g * 3.7 K)
= 0.01539 $kJ \cdot g^{-1} \cdot K^{-1}$ = 15.39 $J \cdot g^{-1} \cdot K^{-1}$

2. Lets say we filled the calorimeter above with 3 L of water and performed the same known reaction above. We measured a final temperature of 57.56 °C, but forgot to measure the inital temperature. Considering the density and specific heat capacity of water are 1 $g \cdot mL^{-1}$ and 4.184 $J \cdot g^{-1} \cdot K^{-1}$, could we calculate what the initial temperature must have been? If so, what was the initial temperature?

Yes, we can determine T_i. We don't know the value of either ΔT or T_i, so we have two unknowns, but we also have two equation, so we can solve:
$\Delta H = m \cdot c \cdot \Delta T + c_{cal} \cdot \Delta T$ and $\Delta T = T_f - T_i$
$\Delta T = \Delta H/(m \cdot c + c_{cal})$ = 400,000 J/(3000 g * 4.184 $J \cdot g^{-1} \cdot K^{-1}$ + 85 $J \cdot K^{-1}$)
= 32.34 K = 32.34 °C
$T_i = T_f - \Delta T$ = 57.56 °C - 32.34 °C = 25.22 °C
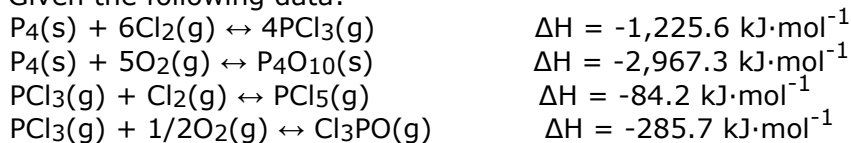
3. Given the following data:
$P_4(s) + 6Cl_2(g) \leftrightarrow 4PCl_3(g)$ ΔH = -1,225.6 $kJ \cdot mol^{-1}$
$P_4(s) + 5O_2(g) \leftrightarrow P_4O_{10}(s)$ ΔH = -2,967.3 $kJ \cdot mol^{-1}$
$PCl_3(g) + Cl_2(g) \leftrightarrow PCl_5(g)$ ΔH = -84.2 $kJ \cdot mol^{-1}$
$PCl_3(g) + 1/2O_2(g) \leftrightarrow Cl_3PO(g)$ ΔH = -285.7 $kJ \cdot mol^{-1}$
calculate ΔH for the reaction
      $P_4O_{10}(s) + 6PCl_5(g) \leftrightarrow 10Cl_3PO(g)$
ΔH_{rxn} = (1 * -1,225.6 $kJ \cdot mol^{-1}$) + (-1 * -2,967.3 $kJ \cdot mol^{-1}$) + (-6 * -84.2 $kJ \cdot mol^{-1}$) + (10 * -285.7 $kJ \cdot mol^{-1}$)
= -610.1 $kJ \cdot mol^{-1}$
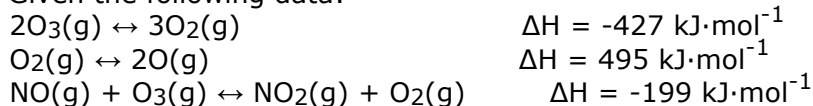
4. Given the following data:
$2O_3(g) \leftrightarrow 3O_2(g)$ ΔH = -427 $kJ \cdot mol^{-1}$
$O_2(g) \leftrightarrow 2O(g)$ ΔH = 495 $kJ \cdot mol^{-1}$
$NO(g) + O_3(g) \leftrightarrow NO_2(g) + O_2(g)$ ΔH = -199 $kJ \cdot mol^{-1}$
calculate ΔH for the reaction
      $NO(g) + O(g) \leftrightarrow NO_2(g)$
ΔH_{rxn} = (-1/2 * -427 $kJ \cdot mol^{-1}$) + (-1/2 * 495 $kJ \cdot mol^{-1}$) + (1 * -199 $kJ \cdot mol^{-1}$)
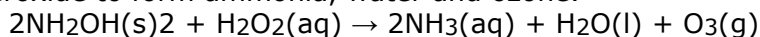= -233 $kJ \cdot mol^{-1}$

5. Hyrdoiodic acid (HI) and sodium hydroxide (NaOH) are a strong acid and strong base respectively. Calculate the change in enthalpy for their neutralization reaction:
$HI(g) + NaOH(s) \rightarrow NaI(s) and H_2O(l)$
Consult Appendix 2 in your ebook for standard enthalpy of formation values.
$\Delta H_{rxn} = \Sigma H_{f,products} - \Sigma H_{f,reactants}$
= (-287.78 $kJ \cdot mol^{-1}$ + -285.83 $kJ \cdot mol^{-1}$) - (26.48 $kJ \cdot mol^{-1}$ + -425.61 $kJ \cdot mol^{-1}$)
= -174.48 $kJ \cdot mol^{-1}$
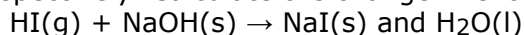
6. Calculate the change in enthalpy for the reaction of hydroxylamine and hydrogen peroxide to form ammonia, water and ozone.

$2NH_2OH(s)2 + H_2O_2(aq) \rightarrow 2NH_3(aq) + H_2O(l) + O_3(g)$

Consult Appendix 2 in your ebook for standard enthalpy of formation values.

$\Delta H_{rxn} = \Sigma H_{f,products} - \Sigma H_{f,reactants}$
$= (2*-80.29 \text{ kJ·mol}^{-1} + -285.83 \text{ kJ·mol}^{-1} + 142.7 \text{ kJ·mol}^{-1}) - (2*-114.2 \text{ kJ·mol}^{-1} + -191.17 \text{ kJ·mol}^{-1})$
$= 115.86 \text{ kJ·mol}^{-1}$

7. Using bond enthalpies, approximate the change in enthalpy for the reaction in question 6 above. Would the reaction be more or less endothermic with every species in the gas phase? Consult tables 6.7 and 6.8 in your ebook for mean bond enthalpies

$\Delta H_{rxn} = \Sigma BE_{reactants} - \Sigma BE_{products}$
$= (2*N\text{-}H + N\text{-}O + 3*O\text{-}H + O\text{-}O) - (3*N\text{-}H + 2*O\text{-}H + O\text{-}O + O\text{=}O)$
$= (2*388 \text{ kJ·mol}^{-1} + 210 \text{ kJ·mol}^{-1} + 3*463 \text{ kJ·mol}^{-1} + 157 \text{ kJ·mol}^{-1}) - (3*388 \text{ kJ·mol}^{-1} + 2*463 \text{ kJ·mol}^{-1} + 157 \text{ kJ·mol}^{-1} + 496 \text{ kJ·mol}^{-1})$
$= -211 \text{ kJ·mol}^{-1}$

The reaction would be less endothermic in the gas phase; it would in fact be exothermic.

8. Calculate the change in standard molar entropy for the reaction in question 6 above. Consult Appendix 2 in your ebook for standard molar entropy values. Assume that hydroxyalmine has a standard molar entropy of 0. Also, discuss whether we are overestimating or underestimating the change in standard molar entropy for the reaction .

$\Delta S_{rxn} = \Sigma S_{m,products} - \Sigma S_{m,reactants}$
$= (2*111.3 \text{ J·mol}^{-1}\text{·K}^{-1} + 69.91 \text{ J·mol}^{-1}\text{·K}^{-1} + 238.93 \text{ J·mol}^{-1}\text{·K}^{-1}) - (143.9 \text{ J·mol}^{-1}\text{·K}^{-1})$
$= 387.54 \text{ J·mol}^{-1}\text{·K}^{-1}$

By assuming that a reactant has no entropy, we are overestimating ΔS_{rxn}.

9. Based on the values of ΔH_{rxn} and ΔS_{rxn} calculated in question 6 and question 8, how would the reactions spontaneity be effected by temperature? Explain your answer.

The reaction would become more spontaneous as temperature increases. Based on the Maxwell free energy equation, $\Delta G_{rxn} = \Delta H_{rxn} + T\Delta S_{rxn}$, and the convention that a negative free energy corresponds to a spontaneous process, we can state that in spite of the change in enthalpy being positive (non-spontaneous), if the temperature is sufficiently high, then the change in entropy (also positive, i.e spontaneous) can drive the reaction and make it spontaneous.

10. Based on the values of ΔH_{rxn} and ΔS_{rxn} calculated in question 6 and question 8, at what temperature would the reaction switch from being non-spontaneous to spontaneous. In other words, what would T be if $\Delta G_{rxn} = 0$. Considering your answer to number 8, are we overestimating or underestimating the temperature at which the reaction switches from non-spontaneous to spontaneous?
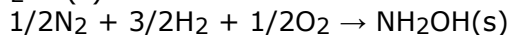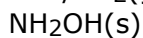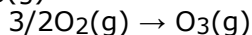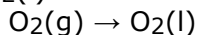
$\Delta G_{rxn} = \Delta H_{rxn} - T\Delta S_{rxn} = 0$
$T = \Delta H_{rxn}/\Delta S_{rxn} = 115,860 \text{ kJ·mol}^{-1}/387.54 \text{ J·mol}^{-1}\text{·K}^{-1} = 299 \text{ K}$

Because the equilibrium temperature is inversely proportional to ΔS_{rxn}, overestimating ΔS_{rxn} would mean underestimating T.

11. In the list of elements below, mark (circle, underline, etc.) all of the elements that are not shown in their standard state.

C_diamond(s)   Ca(s)   **B_2(s)**   Na(s)   Fe(s)   **Hg(s)**
Br_2(l)   Mo(s)   **H(g)**   He(g)   Xe(g)   **Rb_2(s)**
Cd(l)   As(s)   **N_2(l)   O_2(l)**   **Si_60(s)**   F_2(g)

12. Write the standard formation reactions for the following chemical species
$NH_3(g)$
    $1/2N_2(g) + 3/2H_2(g) \rightarrow NH_3(g)$
$Fe_2O_3(s)$
    $2Fe(s) + 3/2O_2(g) \rightarrow Fe_2O_3(s)$
$O_2(l)$
    $O_2(g) \rightarrow O_2(l)$
$O_3(g)$
    $3/2O_2(g) \rightarrow O_3(g)$
$NH_2OH(s)$
    $1/2N_2 + 3/2H_2 + 1/2O_2 \rightarrow NH_2OH(s)$
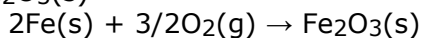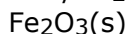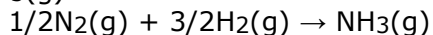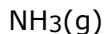
13. State in your own words the first law of thermodynamics. What are some of the consequences of the first law?
    The energy of the universe is a constant. Some important consequences are that the energy of a system can be increased or decreased by adding/subtracting heat or doing work on/by the system. Etc...

14. What is a state function? List all of the state functions you can.
    A state function is a parameter or value of a system that depends only on the state of the system (whence the name), and not on how the system arrived at that state. Etc...
    Temperature, pressure, volume, density, enthalpy, entropy, Gibbs free energy, Helmholz free energy, fugacity, internal energy, mass, chemical potential, number of moles etc...

15. If we were harnessing a combustion reaction that produces lots of gaseous products to do work (like in a car's engine), how would lowering the temperature effect the amount of work we could do?
    Because $w = -\Delta n_{gas}RT$, as we lower T we also decrease the amount of work we can do. In other words, work done by expanding gases is directly proportional to the temperature.

Consider the following molecules for questions 16-20: O_3, N_2, CH_4, SF_6
16. Which has the fewest rotational modes? how many? why?
    N_2 has the fewest because it is linear (2 rotational modes) rather than non-linear (3 rotational modes).

17. Which has most vibrational modes? how many? why?
    SF_6 has the most rotational modes because it has $3*7 = 21$ total modes, and 6 of those are rotational and translation, leaving 15 vibrational modes.

18. Do any have more or less than 3 translational modes? why?
    No, all molecules have 3 translational modes.

19. Which has the most total modes? how many? why?
    SF_6 has the most total modes, because total modes is equal to three times the number of atoms, 21 in this case.

20. Which has 9 vibrational modes?
    CH4 has 15 total modes minus 3 translational and 3 rotational, leaving 9 vibrational modes.