Guiding Questions #3: To be used with the handout on Thermodynamics along with the standard state thermodynamic data.

Due by Wednesday 3/3/2010

1) The first law of thermodynamics results in a variable called Enthalpy which is the flow of heat when work is done to or by a system. By convention, energy changes are calculated for any reaction by subtracting the sum of the enthalpies (multiplied by their stoichiometric coefficients) of the reactants from the enthalpies of the products (equation 13.19 from your first reading). Explain why the sign (+ or -) of the enthalpy change of a reaction indicates whether a reaction is exothermic or endothermic. (Do not simply restate the meaning of exothermic and endothermic…rather, interpret the math. Remember, by convention, enthalpy state changes are determined by subtracting the reactants state from the products state.)

2) Calculate the enthalpy change (in kJ/mole) for the following reaction… (use the data from the table handed out in class. The data in the table is all at standard state which is 25°C and 1 atmosphere (bar) pressure. In some tables the minerals and other species list more than one value, if that is so, use the first one listed)…Use equation 13.19.

Use “alpha quartz” for Quartz

Calcite (CaCO$_3$(s)) + Quartz (SiO$_2$(s)) = Wollastonite (CaSiO$_3$(s)) + CO$_2$(g)

Does this reaction absorb or give off heat as written?

3) What is the heat capacity (specific heat capacity) and why is it important? Compare the specific heat capacity of water to that of Quartz.
4) We can tell whether a chemical reaction will proceed as written (from left to right) based on the Gibb’s free energy change of the reaction. i.e. reactions will proceed in the direction of decreasing free energy (systems are more stable in the lowest energy state). Using equation 13.48 from the reading (same format as equation 13.19), will the reaction in question 2 proceed as written at 25°C and 1 atmosphere (bar)? Explain.

5) Write the equilibrium constant for the reaction in question 2.

i.e. \[ K = \frac{A^a B^b}{C^c D^d} \] for the generic reaction \( cC + dD = aA + bB \) (C, D, A, and B are the activities of species like Quartz or CO2(g) and a, b, c, d are the stoichiometric coefficients)

6) By convention, the activities of pure phases are equal to 1. Minerals that are not solid solutions are considered pure phases (in this case, they are all pure). Also, if water is in the reaction, it may be considered a pure phase. Gases are not typically treated as pure phases and, therefore, must remain in the expression. Rewrite the equilibrium expression you created in question 5 considering Quartz, Calcite and Wollastonite are pure phases.
7) What is the value of the equilibrium constant for the reaction in question 2 at standard state (25°C and 1 bar...approximately 1 atmosphere) (hint use the answer for question 4 along with equation 13.74 from the reading.... If you've never used logs (ln) before, equation 13.74 can be rearranged to be...

\[ e^{\left(\frac{\Delta G^o_R}{RT}\right)} = K \]  
(You can use the \( \Delta G^o_r \) to calculate the value of the equilibrium constant using this equation. The \( e \) should be on your calculator as \( e^x \) or as Exp and should be connected to the button that says LN).

You can also convert the natural log expression to base 10 logs... \( \Delta G^o_r = -RT2.303\log K \) or

\[ 10^{\left(\frac{\Delta G^o_R}{RT2.303}\right)} = K \]

\( R \) is the universal gas constant equal to 8.3145 J K\(^{-1}\) mol\(^{-1}\) and \( T \) is in Kelvin.

BE CAREFUL OF YOUR UNITS... \( G \) is in kJ (killaJoules; \( 1000J = 1kJ \)).
\( (T(K) = T(^oC) + 273.15) \)

8) Now that you know the value of K for the above reaction, calculate the equilibrium fugacity (partial pressure) of CO\(_2\) in equilibrium with Quartz, Calcite and Wollastonite at 25°C and 1 atmosphere (bar).

9) The partial pressure of CO\(_2\) in the atmosphere is \( 10^{-3.5} \) or (0.000316). Can the above reaction ever be in equilibrium with CO\(_2\) in the atmosphere at 25°C and 1 atmosphere pressure? Explain.
10) When performing thermodynamic calculations, why do we use activity and fugacity in place of concentration and pressure respectively?

11) What is LeChatelier’s Principle and why is it valuable to a geochemist?

12) Based on your response to question 11, what direction will the reaction proceed if CO₂ is increased while in equilibrium with Quartz, Calcite and Wollastonite (we will assume that the reaction is occurring at a higher temperature than 25°C so that it can be in equilibrium)?

13) Use the van’t Hoff equation (equation 13.97) to calculate the value of the equilibrium constant at 100°C. Did it increase, decrease, stay the same? Interpret the change in value of the equilibrium constant with respect to LeChatilier’s principle (what happens to the reaction when heat is added?)