Entropy and Gibbs Free Energy

Entropy

1. Calculate the change in entropy of a large vat of molten copper when 50 J of energy is removed reversible from it as heat at 1100 °C.

2. Calculate the change in entropy of 1.0 L of water at 0 °C when it absorbs 235 J of energy from a heater. (b) If the 1.0 L of water is at 99 °C, what is its entropy change? (c) Explain any difference in entropy change.

3. What is the standard entropy of vaporization of acetone at it normal boiling point of 56.7 °C? The standard enthalpy of vaporization for acetone is 29.1 kJ/mol.

4. Calculate the entropy change for the vaporization of 50.0 g of ethanol at 351.5 K. $\Delta H_{vap}°$(ethanol) = 43.5 kJ/mol.

5. Calculate the entropy of fusion of mercury at its freezing point (234.3 K). $\Delta H_{fus}°$(mercury) = 2.292 kJ/mol.

6. The entropy of vaporization of benzene is approximately 85 J/(K*mol) and the enthalpy of vaporization of benzene is 30 kJ/mol. What is the boiling point of benzene?

7. Suppose that 104 g of cyclohexane at 17°C is mixed with 234 g of cyclohexane at 77°C at constant atmospheric pressure in a thermally insulated vessel. What is the ΔS_{syst} for the process? The specific heat capacity for cyclohexane is, $C_{P,m}$ = 156.5 J/(K*mol)

8. Using data of $S_m°$ from the Appendix in your book, calculate the standard entropy change for each of the following reactions at 25°C. For each reaction, interpret the sign and magnitude of the reaction entropy.

    $CaCO_3(s) \rightarrow CO_2(g) + CaO(s)$

    $4\ KClO_3(s) \rightarrow 3\ KClO_4(s) + KCl(s)$

The Familiar Process of Water Boiling

Imagine you start with a pot of 54 g of water. The initial temperature of this mixture is 100 °C. If you leave this pot in a room that has a constant temperature of 105 °C, the water will *spontaneously* boil and you will end up with all water vapor at 100 °C.

Here we will calculate the entropy change for the process of the water boiling (note: after the water boils the temperature of the resulting water vapor will rise until it is the same temperature as the room. We are just looking at the first step where the liquid water boils).

1. First identify what the system and surroundings are. (what are they composed of, what is their temperature, etc…) Often it is helpful to make a sketch or diagram.

2. Now identify what the initial and final states of the system are. Again a diagram, equation, or sketch can be helpful.

3. Now look at the energy change for this process. Does energy flow into or out of the system? If so, as heat or work?

4. Given that $\Delta_{vap}H° = 40.7$ kJ mol^{-1}, what is the change in enthalpy for system for this process (in Joules)?

5. Given that this process is at constant temperature, q = ΔH. This is the *reversible heat*. What then is the change in entropy for the system?

6. What is the heat from the perspective of the surroundings? (did the energy go up? Down? How much?)

7. What is the entropy change for the surroundings?

8. What is the entropy change for the universe for this process? Does this make sense with what physically is happening?

9. The answer to part 8 is extensive (this for the 54 g of liquid water that boils in this process). What is the entropy change per mole of liquid water that boils under these conditions?

10. Redo steps 7 and 8 but with a room that has a constant temperature of 95 °C. Explain any observed differences or similarities.

Gibb's Free Energy

Gibb's Free Energy Equation: $\Delta G = \Delta H - T\Delta S$

1. Under what conditions is the equation above true?

2. If ΔH of a process is positive and ΔS of that same process is positive, what can you conclude about the spontaneity of the process?
   a. The process is spontaneous. How do you know that?

   b. The process is not spontaneous. How do you know that?

   c. There is not enough information to conclude. If this is the case, what information would you need to be able to make a conclusion?

3. If ΔH of a process is negative and ΔS of that same process is negative, what can you conclude about the spontaneity of the process?
   a. The process is spontaneous. How do you know that?

   b. The process is not spontaneous. How do you know that?

   c. There is not enough information to conclude. If this is the case, what information would you need to be able to make a conclusion?

4. If ΔH of a process is positive and ΔS of that same process is negative, what can you conclude about the spontaneity of the process?
   a. The process is spontaneous. How do you know that?

   b. The process is not spontaneous. How do you know that?

   c. There is not enough information to conclude. If this is the case, what information would you need to be able to make a conclusion?

5. If ΔH of a process is negative and ΔS of that same process is positive, what can you conclude about the spontaneity of the process?
    a. The process is spontaneous. How do you know that?

    b. The process is not spontaneous. How do you know that?

    c. There is not enough information to conclude. If this is the case, what information would you need to be able to make a conclusion?


6. (7.47 end) Calculate the standard enthalpy change, entropy change, and free-energy change at 298°C for each of the following reactions by using data in the Appendix in the back of your book. For each case, confirm that the value obtained from the free energies of formation is the same as that obtained by using the relation $\Delta G_r° = \Delta H_r°$ - T $\Delta S_r°$.
    The oxidation of magnetite to hematite: $2Fe_3O_4(s) + \frac{1}{2} O_2(g) \rightarrow 3 Fe_2O_3(s)$

    The dimerization of NO_2: $2 NO_2(g) \rightarrow N_2O_4(g)$

7. (7.51) Use the standard free energies of formation in the Appendix in the back of your book to calculate ΔG_r° for each of the following reactions at 25 °C. Comment on the spontaneity of each reaction under the standard conditions at 25 °C.

$$CaCO_3(s, \text{calcite}) \rightarrow CaO(s) + CO_2(g)$$

$$2\ C_8C_{18}(l) + 25\ O_2(g) \rightarrow 16\ CO_2(g) + 18\ H_2O(l)$$
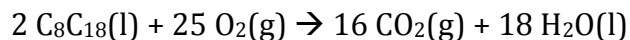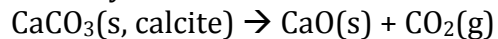
8. (7.59) Assume that ΔH_r° and ΔS_r° are independent of temperature and use data in the Appendix in the back of your book to calculate ΔG_r° for each of the following reactions at 80 °C. Over what termperature range will each reaction be spontaneous under standard conditions?

$$B_2O_3(s) + 6\ HF(g) \rightarrow 2\ BF_3(g) + 3\ H_2O(l)$$

$$C(s, \text{graphite}) \rightarrow C(s, \text{diamond})$$
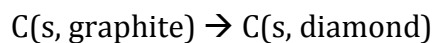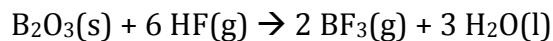
The Familiar Process of Ice Melting and Water Boiling

1. Looking back at the worksheet done in class where we calculated ΔS_{syst}, ΔS_{surr}, and $\Delta S_{universe}$ of 36 g of ice melting and in the section of this worksheet where we calculated ΔS_{syst}, ΔS_{surr}, and $\Delta S_{universe}$ of 54 g of water boiling, what was the purpose of these calculations?

There is another method of coming to these same conclusions using the Gibb's Free Energy Equation. Using data about the enthalpy and entropy of fusion and vaporization of water and the Gibb's Free Energy Equation calculate, the change of Gibb's Free Energy for each process. You should reach the same conclusions as those found on the previous worksheets.

2. Are the conditions needed in order to use the Gibb's Free Energy Equation met?

3. What is ΔG for 36 g of ice in a room with a constant temperature of 25 °C? What can you conclude about the spontaneity of the process?

4. What is ΔG for 36 g of ice in a room with a constant temperature of 0.1 °C? What can you conclude about the spontaneity of the process?

5. What is ΔG for 54 g of water in an oven with a constant temperature of 105 °C? What can you conclude about the spontaneity of the process?

6. What is ΔG for 54 g of water in an oven with a constant temperature of 95 °C? What can you conclude about the spontaneity of the process?

7. Which method, calculating $\Delta S_{universe}$ or calculating ΔG, do you prefer? Why?