

Problem Set #5 – Chemistry 102 – Spring 2008

Due Wednesday, March 12th at the beginning of class

Please answer the following questions from the Exercises in Whitten:

Chapter 15: # 89, 101, 113 (*replace 650 K with 700 K in question*)

1. The following quotes are taken from the play *Arcadia* by Tom Stoppard, the best play by the best living playwright, says a chemist with no authority whatsoever.

Thomasina: When you stir your rice pudding, Septimus, the spoonful of jam spreads itself round making red trails like the picture of a meteor in my astronomical atlas. But if you stir backward, the jam will not come together again. Indeed, the pudding does not notice and continues to turn pink just as before. Do you think this is odd?

Septimus: No.

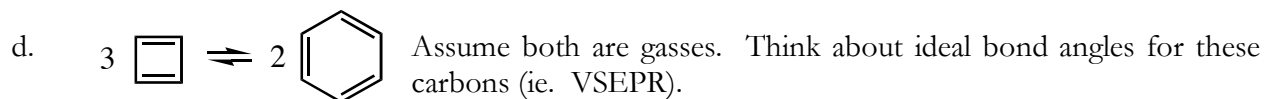
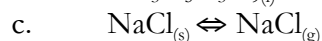
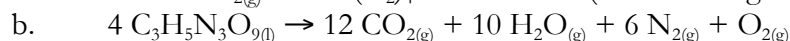
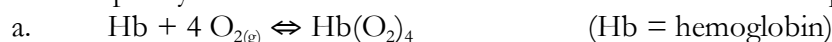
Thomasina: Well, I do. You cannot stir things apart.

a. What thermodynamic principles dictate that stirring jam into pudding is only spontaneous in one direction?

Valentine: Heat goes to cold. It's a one-way street. Your tea will end up at room temperature. What's happening to your tea is happening to everything everywhere. The sun and the stars. It'll take a while but we're all going to end up at room temperature.

b. Without taking this too literally, why will we end up at “room temperature”? Think about changes in entropy to the system, surroundings and universe. Why is heat spontaneously transferred from warm things to cold things?

2. Identify whether the following reactions are spontaneous, and whether they are enthalpically or entropically favorable or unfavorable. Provide one sentence explanations.



3. There are two allotropes of tin: white and gray (an allotrope is a structurally distinct form of an element) The following thermodynamic data applies:

$$\text{Sn}_{\text{white}} \quad \Delta H_f^\circ = 0.00 \text{ kJ/mol} \quad S^\circ = 51.55 \text{ J/molK}$$

$$\text{Sn}_{\text{gray}} \quad \Delta H_f^\circ = -2.09 \text{ kJ/mol} \quad S^\circ = 44.14 \text{ J/molK}$$

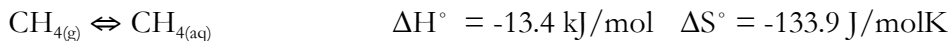
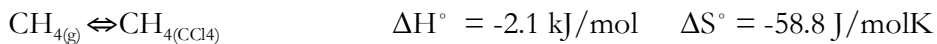
a. Is the reaction $\text{Sn}_{\text{white}} \rightarrow \text{Sn}_{\text{gray}}$ spontaneous at 298 K?

b. Is the reaction enthalpically favorable? Is it entropically favorable?

c. Will the reaction be spontaneous in above direction at all temperatures? If not, over what temperatures will gray tin be favored over white tin?

Additional question on back.

4. Oil and water don't mix. Why not? This is a general observation – non-polar molecules do not dissolve well in water. Let's take methane as a stand-in for oil, since they are both non-polar. We will consider two phase transfers, one from the gas phase to CCl₄ (a non-polar liquid) and one from the gas phase to water (a polar liquid).



- What are the changes in free energies for each of these two transfers at 25°C?
- What is the change in free energy for the reaction: $\text{CH}_{4(\text{CCl}_4)} \rightleftharpoons \text{CH}_{4(aq)}$? (this mimics the transfer of a non-polar solute from a non-polar environment to a polar environment, similar to oil being transferred to water.) Will methane be spontaneously transferred from CCl₄ to water?
- Is the reaction in “b” enthalpically favorable or unfavorable? Is it entropically favorable or unfavorable? Do the necessary calculations.
- See the following web page: <http://www.aw-bc.com/mathews/ch02/clathrat.htm>
Why doesn't oil dissolve in water?