## What you should now know about the 2<sup>nd</sup> and 3<sup>rd</sup> Laws ...Boland

- The concepts of spontaneous and reversible change
- Concept of entropy and the requirement that total entropy of the universe (system + surroundings) increases during any spontaneous change (2nd law)
- Qualitative understanding of the Boltzmann (S=k In W) and Clausius ( $\Delta$ S = q/T) expressions for entropy and entropy change
- Realize that the increase in entropy and NOT the reduction in energy is the reason why things happen (e.g. evaporation: energy <u>increases</u> due to broken bonds in liquid (ΔH > 0) but entropy increase is even bigger)
- Qualitative estimate of entropy change during reactions and quantitative evaluation of ∆S° for a reaction given standard values
- Given the entropy of the solid and the enthalpy of sublimation calculate the entropy of the vapor (and all other phase change problems of this type)
- The 3rd law of thermodynamics... what is it, and how is it consistent with the definition of entropy
- The Gibbs free energy G and the criterion for spontaneous and reversible change how is this consistent with increase in the increase in entropy of the universe
- Understand that  $\Delta S_{univ} = -\Delta G / T$  and that you can calculate this if you have to (and you do!).
- ΔG=ΔH-TΔS where does it come from? Since H and S refer to the system, how does this expression include changes that occur in the surroundings (as required by 2nd Law)
- Why can strong bond formation during a chemical reaction be consistent with the 2nd Law since bond formation increases the local order (i.e. decreases entropy of system)
- How is the spontaneous formation of ordered structures, e,g., crystals, consistent with the 2nd Law
- What does the superscript zero refer to, e.g.  $\Delta S^{\circ}$
- Calculation of the standard free energy change  $\Delta G^{\circ}$  for a reaction
- Effect of temperature on  $\Delta G^{\circ}$  and predicting the temperature where a reaction changes from being non-spontaneous to spontaneous and vice-versa
- The relationship between  $\Delta G$  and  $\Delta G^{o}$  and K and Q

- How  $\Delta G$  changes during the course of a reaction, but  $\Delta G^{\circ}$  is a constant
- The reaction quotient Q; how it determines the value of  $\Delta G$  during a reaction, and controls the direction of reaction
- The significance of the magnitude of the equilibrium constant K and how it relates to  $\Delta G^{\circ}$
- Calculation involving the equilibrium constant K at some temperature given  $\Delta G^o$  or  $\Delta H^o$  and  $\Delta S^o$

## Homework Problems: Kotz Treichel and Weaver Chapter 19

1, 3, 5, 11, 13, 17, 19, 23, 25, 29, 33, 35, 37, 41, 43, 49, 51, 55, 61, 67,