Today's Info

- No HW this week
- Bring tables to exam
- Exam is standard length

Key Ideas

- Acids and bases
  - identification-including conjugates
  - proton transfer and hydrolysis
  - complete treatments
  - polyprotic-determining []s of the conjugate bases
  - K_{rxn}
    - leveling effect
    - running downhill
  - Titrations and titration curves
  - Buffers
  - LeChatelier Effects
- Solubility
  - basic relations between Ksp, s, etc
  - use of Ksp
  - precipitation-yes/no and how much
  - separating ions-qualitative and quantitative
  - LeChatelier effects

Summarizing Entropy

- Entropy is time's arrow-the entropy of the universe is increasing
- $\triangle S>0$ favorable $\triangle S<0$ unfavorable $\triangle S=q_{rev}/T$ $\triangle S=\triangle H/T$. We will be limiting our calculations in this area to entropies of phase changes. $S(\triangle S)$ has units J/K-mol or J/K. These are often called entropy units
- Spontaneity requires a total entropy change, system and universe, which is positive. Thus, for changes with $\triangle S<0$, $\triangle H$ must be <0. This loss of heat to the surroundings increases its entropy.
- Predicting the sign of the entropy is usually possible, given sufficient detail about the starting and ending states. Predicting magnitudes is far more difficult
- The combination of entropy and enthalpy is the free energy, $\triangle G$. $\triangle G=\triangle H-T\triangle S$. Spontaneity requires $\triangle G<0$. Equilibrium: $\triangle G=0$
- Four possible sets: $\triangle G^o=\triangle H^o-T\triangle S^o$.(see Table 17.2-p 737)
  - $\triangle H^o>0$ $\triangle S^o>0$ spontaneous above a minimum T
  - $\triangle H^o>0$ $\triangle S^o<0$ never spontaneous
  - $\triangle H^o<0$ $\triangle S^o>0$ always spontaneous
  - $\triangle H^o<0$ $\triangle S^o<0$ spontaneous below a maximum T
- Be aware that spontaneous and nonspontaneous is measured against the Q=1 condition. When the conditions are other than that, the direction of spontaneity can be different. Further, $\triangle G$ represents the thermodynamic stability. The overall nature of a change of state requires consideration of its kinetics, as well.
- $\triangle G_{rxn}=\sum n* \triangle G_{prods}-\sum n* \triangle G_{reacts}$ you need to be able to use this equation
- $\triangle G^o=-RTlnK$ $K=e^{-\triangle Go/RT}$ Note that negative values of $\triangle G^o$ lead to K>1. You need to be able to use these two equations-the homework provides exercises .

Probability Redux

- Entropy is all about probability
- One always uses simple examples like coin flips or binary events. The number of possible arrangements for a binary event system is simple 2^n where n is the count of "coins".
- The Boltzmann relationship states S=kln$W$
- $k=R/N_A=1.38*10^{-23} J/K$
- If you have a mole of molecules totally randomly arranged then S=Rln2=8.314J/K*0.693=5.76J/K
- Variations on a theme.
  - It seems logical that the more room is given to a gas, the greater the number of states and the higher the entropy. $\triangle$S=Rln(V$_f$/V$_i$)
  - If the pressure goes up its equivalent to a volume decrease (why) $\triangle$S=Rln(P$_i$/P$_f$)
- Third Law: The entropy of a perfect crystal at absolute zero=0

△S and phase changes

- $\triangle S = q_{rev}/T$
- The simplest example of a reversible process taking place at constant temperature is the phase change
- $\triangle S_{fus} = q_{fus}/T_{melt}$ and so on

Free Energy and K

- $\triangle G^o = -RTlnK \qquad K = e^{-\triangle Go/RT}$ this is the thermodynamic $R = 8.314$ J/mol·K

- Table 17.4-p.747 summarizes the relationship between K and $\triangle G^o$

- When the system is not at equilibrium, the free enerny is given by the relationship $\triangle G = \triangle G^o + RTlnQ$