Logic Flow of Chapters 7 and 8

Understanding Kinetics
1) Real reaction coordinate diagram are multi dimensional
2) Our normal 2D plots are slices were the reaction coordinate is defined as a vibrational mode undergoing a significant change during the reaction
3) The rate determining step is the step with the highest barrier on the reaction coordinate
4) Rate constants reflect the intrinsic ability of a reactant to achieve the TS for the rate determining step:
   a) Large barriers are slow reactions and have small rate constants
   b) Small barriers are fast reactions and have large rate constants
5) The transition state is really a saddle point on the multi-dimensional surface
6) The TS we usually discuss represents the lowest energy strained structure that transitions to product, but there is really a distribution of TSs that go over the col
7) The Eyring equation can be used to relate rate constants to activation parameters: Gibbs free energy, enthalpy and entropy
8) Most all reactions have positive enthalpies of activation, but the entropies can vary

Postulates
1) Hammond Postulate
2) Reactivity vs Selectivity
3) Curtin-Hammett Principle
4) Microscopic Reversibility
5) Kinetics vs. Thermodynamic Control

How to Perform Kinetics
1) Order of the reaction, and order per reactant
2) First order kinetics
3) Pseudo first order kinetics (try to get everything to fit this)
4) Steady State Approximation for reactive intermediates
5) Pre-Equilibrium kinetics
6) Looking to see how variations in the denominator of the kinetic expression makes the order in reactants vary
7) Looking for order in reactants to determination if that reactant plays its role prior to, at, or after the rate determining step
8) Steps in a mechanism after the rate determining step are not kinetically observable

Calculating Rate Constants
1) Marcus theory
2) Marcus equation

Back to Multi-Dimensional Reaction Coordinate Diagrams

1) Competing reactions are displaced on a 3-D surface with intermediates at the corners
2) A projection of the 3-D surface onto a 2-D surface is a More O'Ferrall Jencks plot
3) Ues the Golden Rules to predict TS structure as chemical parameters change
4) Changes in chemical parameters often lead to counter-intuitive changes in TS structure
5) Visualizing enthalpy and entropy changes on a 3-D reaction coordinate diagram

Isotope Effects
1) Check to see if a particular bond to an atom breaks at or before the rate determining step, usually a bond to H
2) Isotope effects arise from significant differences in any vibrational modes upon isotopic substitution, usually bond stretches
3) Kinetic isotope effects can be primary, secondary and normal, inverse
4) The more thermal neutral a reaction is the larger its isotope effect
5) Secondary effects arise from hybridization changes, which are dominated by out-of-plane bending mode changes

Substituent Effects
1) Field, inductive, resonance, polarizability, solvent, steric effects
2) LFREs are quantitative measurements of substituent effects
3) Hammett plots are used for quantitative comparisons of inductive and resonance effects between substituents and between reactions
4) Taft parameters are used for comparisons of polarity and sterics (we do not cover this)
5) Grunwald-Winstein plots are used for comparisons of solvent polarity and sensitivity of reactions to solvent polarity
6) Swain-Scott plots are used for comparisons of nucleophiles and sensitivity of reactions to nucleophiles
7) Nucleophilicity is a balance of basicity, shape, and polarizability
8) Sensitivity to nucleophility and leaving group ability is measured with Bronsted plots
9) LFERS work because of entropy/enthalpy compensation

Handful of Other Experiments
1) Product identification
2) Trapping intermediates
3) Competition experiments
4) Cross-over experiments
5) Isotope scrambling
6) Radical clocks
7) Transient spectroscopy
8) Stable ion media