Prerequisites for Section III (1-2 weeks)

• In this section and in the next section on redox chemistry, we will often draw on fundamental thermodynamic concepts. You should recall the meaning of $\Delta H$, $\Delta S$, and $\Delta G$ for chemical and physical changes — and try to think about systems using these concepts.
• $\Delta G^\circ = -RT \ln K_{eq}$ This relationship is central to relating chemical thermodynamics and equilibrium.
• $\Delta G = \Delta H - T \Delta S$ for a process with a specified $T$ and $P$
• The above two relationships can be combined to provide invaluable guidance in understanding how a chemist can manipulate $\Delta H$ or $\Delta S$ (say, by making changes in solvents or molecular substituents) to dramatically shift equilibria: $K_{eq} = e^{\Delta S^\circ / R} e^{-\Delta H^\circ / RT}$

At room temperature, $RT \approx 2.5$ kJ/mol, so this equation means that, for example, a change in solvent that causes $\Delta H$ to shift by only $\sim 6$ kJ/mol will shift the equilibrium constant for a reaction by a factor of 10 (roughly).

Acids and Bases

  a. Brønsted Acidity — aqueous equilibria, solvent leveling, periodic trends, oxoacids, anhydrous acids and bases, amphotericism, polyoxo ions, nonaqueous solvents

• Brønsted acid = proton donor, Brønsted base = proton acceptor
• $p\text{H} = -\log[H^+]; pK_a = -\log K_a; pK_b = -\log K_b$
• $[H^+][H^+] = 10^{-14}$ in aqueous solutions
• $pK_a + pK_b = 14$ – for any conjugate acid-base pair in dilute aqueous solution
• recall concepts of conjugate acids and bases; strong acids have weak conjugate bases, weak acids have strong conjugate bases
• Things that affect acidity and basicity of organic acids and bases: the ability of a conjugate base (acid) to delocalize negative (positive) charge through inductive effects or resonance affects the strength of an acid (base). What are the relative strengths of organic acids and bases? Examples: sulfonic acids are stronger than carboxylic acids, which are stronger than phenols, which are stronger than aliphatic alcohols. Conversely, alkoxides are stronger bases than phenoxides, which are stronger than carboxylates, which are stronger than sulfonates.
• review important properties of solvents: ability to hydrogen bond, dielectric constant, polarity

  b. Lewis acidity — group 13 compounds, M-L dative bonding, superacids
  c. Acid-base reactions — adduct formation, displacements, double displacements
  d. 'Hard’ and 'soft’ acids and bases

• review the concept of polarizability; molecules with “large” atoms have valence electrons that extend further from the nucleus and tend to be more easily polarized by charges on other molecules. “Hardness” and “softness” are related to polarizability.

  e. Solvents as acids and bases