

Study Guide – Lehninger Principles 4th Edition

Chapter Thirteen

By Frank Deis

Homework: 2,3,6,10,18,19. **Bioenergetics and Metabolism, page 481.** Understand the difference between metabolism, anabolism, and catabolism (Fig 3). Familiarize yourself with the five types of chemical reactions found in metabolism (pages 485-488). Oxidation (Type 1) often doesn't involve addition of oxygen but rather removal of electrons from substrate. Making or breaking carbon carbon bonds (Type 2) is difficult in aqueous solution at near pH 7. Many of the reactions that do this are related to Aldol Cleavage or Condensation. Please read the "Electron Sink" handout, and see Fig 8. Enzymes that catalyze internal rearrangements (Type 3) are often called "Mutase" or "Isomerase" enzymes. The most common group transfer (Type 4) is the transfer of phosphate from ATP. Enzymes that catalyze that reaction are called "Kinase" enzymes.

13.1 Bioenergetics and Thermodynamics. The concept of Gibbs' Free Energy was introduced in Chapter 1. You should understand the discussion of enthalpy and entropy, and the Laws of Thermodynamics on 490-1. You should learn the equation relating the equilibrium constant to the standard free energy change (492) and be able to use it. You should also be able to use concentration data to calculate the actual free energy change (493-4). If you wanted to learn the K_{eq} for a series of reactions, you would have to multiply the individual K_{eq} 's together. But with standard free energy changes you can simply sum the ΔG° for all reactions (494-5).

13.2 Phosphoryl Group Transfers and ATP. Know that the ΔG° for ATP cleavage to ADP + Pi is -30.5 kJ/mol, and that this is considered a "high energy" reaction. The main two reasons why ATP is a "high energy compound" are in the caption for Fig 13-1: charge repulsion and resonance stabilization. PEP or Phosphoenolpyruvate has a ΔG° for hydrolysis twice as large, -61.9 kJ/mol, and standard sugar phosphates are about half as large (Glu-6-P, -13.8 kJ/mol), see Fig 13-9. In general ATP isn't simply hydrolyzed – rather it participates in phosphoryl group transfers that couple it to other reactions. See Fig 13-8 for Glutamine Synthetase. When two reactions are coupled you can learn the overall ΔG° simply by adding the individual ΔG° values. Read through 502-506 but we won't do this material in detail just now.

13.3 Biological Oxidation-Reduction Reactions. Understanding this material will prepare you for future chapters covering photosynthesis and mitochondrial respiration. The math in this section is rather simple, in fact it is basically a conversion of units, $\Delta G^\circ = -nF\Delta E^\circ$ where "n" is the number of electrons per transaction, "F" is the Faraday, 96.5 kJ/ V mol) and ΔE° is the standard potential difference in Volts. I consider Table 13-7 to be upside down. The negative half reaction potentials have the highest energies and should be at the top. Voltage is an intensive quantity and free energy is extensive, so voltage is independent of how many electrons are transferred. You should be able to draw NAD⁺ and FAD as "stick and P" figures, and be able to tell the various forms apart (NADP⁺, NADH, FADH₂, FMN etc.). Read about redox cofactors on 512-516.