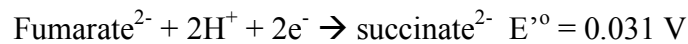


Last Time:

1. The transfer of electrons (Redox rxn) from compounds with relatively low electron affinities (e.g. sugars, fatty acids, amino acids) to compounds with high electron affinities (e.g. O₂) occurs with the release of free energy, which can be used to perform biological work (e.g. ATP synthesis).
2. Most electron transfers are enzymatically catalyzed. Electrons are most frequently passed to electron carriers such as NAD⁺ or FAD prior to their eventual transfer to O₂.
3. Electrons are frequently transferred as either hydrogen atoms (H), or hydride ions (H⁻). The source of these electrons are the more reduced compounds (sugars, fats, etc.). It's important to understand how we assign ownership of electrons in carbon compounds, and how to recognize whether a particular C has been oxidized or reduced in the course of a redox rxn.
4. The standard reduction potential (E^o) is the quantitative measure of affinity that a particular compound has for electrons, e.g.:



Remember that superscripts such as ' and ° refer to standard conditions. These are reference points, and will need adjustments for “real world” conditions. The more positive the E'^o value, the higher the affinity the “acceptor” compound (fumarate in this case) has for electrons. This equation states that Fumarate can accept 2 electrons and 2 protons (or two H) to become succinate. Fumarate has a relatively weak affinity compared to H⁺ (E'^o = 0.00), but still higher than that of a lot of other compounds, which have negative E'^o values (i.e. they have weaker affinities for electrons than H⁺).

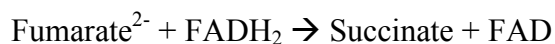
5. As written above, the electrons appear to come out of nowhere. This is NOT the case. Some other compound must provide these electrons (serve as the reductant). Because E'^o values are constant, the only compounds that could serve as electron “donors” for the reduction of fumarate would be compounds with lower E'^o values (lower affinities for electrons). An example “donor” reaction might be:



However, this reaction is written as if FAD will be receiving the electrons (as all half-reactions are). To combine these equations into a sensible form we must reverse the “donor” half reaction to read like a reaction that will be donating electrons:



We then combine the two reactions and cancel common terms to create the overall Redox reaction:



6. The free energy change for this redox reaction is directly proportional to the difference in E'° values for the two half reactions: $\Delta G'^{\circ} = -nF\Delta E'^{\circ}$, where n = no. of electrons transferred, and F = Faraday constant (96.5 kJ/V mol) and $\Delta E'^{\circ} = E'^{\circ}_{\text{acceptor } \frac{1}{2} \text{ rxn}} - E'^{\circ}_{\text{donor half reaction}}$. Please note that although we reversed the donor half reaction, to account for the fact that it will be donating, not accepting, electrons in the redox rxn, we do NOT reverse the sign for its E'° value. Thus,

$$\Delta E'^{\circ} = (0.031 \text{ V} - (-0.219 \text{ V})) = 0.25 \text{ V}, \text{ and}$$

$$\Delta G'^{\circ} = -(2)(96.5 \text{ kJ/V mol})(0.25 \text{ V}) = -48.3 \text{ kJ/mol}$$

Note the magnitude of the $\Delta G'^{\circ}$ term. This constitutes a significant release of free energy (compare to $\text{ATP} \rightarrow \text{ADP} + \text{P}_i$ $\Delta G'^{\circ} = -31 \text{ kJ/mol}$).

7. If only things were this simple. Under actual conditions, the concentrations of “acceptor” and “donor” compounds will not be 1M to begin with. To account for these changes we must adjust the E'° value to account for their actual concentrations (E). The **Nernst Equation** serves as our converter:

$$E = E'^{\circ} + \frac{RT}{nF} \ln \frac{[\text{acceptor}]}{[\text{donor}]}$$

R and T are the gas constant and Temperature (K), n is the number of electrons transferred and F is the Faraday constant. $[\text{acceptor}]$ is the concentration of the compound “accepting” electrons in the $\frac{1}{2}$ reaction and $[\text{donor}]$ is the concentration of the donor compound. For the fumarate example above, fumarate would be the acceptor and succinate would be the donor. For the FAD $\frac{1}{2}$ reaction, FAD is the acceptor and FADH₂ is the donor. The E'° value, of course, is taken from table 13-7.

8. For an “actual conditions” redox reaction, the Nernst equation must be solved twice; once for the “acceptor” $\frac{1}{2}$ reaction (e.g fumarate) that will be receiving electrons and once for the “donor” $\frac{1}{2}$ reaction (e.g FAD) that will be donating electrons. I know this is confusing, but you must be able to distinguish between “acceptor” and “donor” compounds in individual $\frac{1}{2}$ reactions, and “acceptor” and “donor” $\frac{1}{2}$ reactions involved in redox reactions. The difference is crucial to setting up and solving such reactions correctly.

9. As under standard conditions, the actual free energy change (ΔG) available from a redox reaction is directly proportional to the difference in E values between the “acceptor” and “donor” $\frac{1}{2}$ reactions: $\Delta G = -nF\Delta E$. Remember, do not reverse the sign for E_{donor} . A good example of such a problem is the one found in your text on pages 510-511.

Key words: electron acceptor, electron donor, electron carrier, electron ownership, $\frac{1}{2}$ reaction, redox reaction, oxidant, oxidizes, oxidized, reductant, reduces, reduced, reduction potential, standard conditions, actual conditions.

Today:

1. Carbohydrates, in general, and glucose, in particular, are major sources of biological fuel, as well as serving as important precursors for the synthesis of other carbohydrates, fatty acids, amino acids and nucleotides.
2. Carbohydrate digestion
3. Glycolysis: overview
4. Glycolysis: preparatory phase
5. Glycolysis: payoff phase
6. Fate of Glycolysis products
7. Glycogen and starch (endogenous) degradation
8. "Side doors" to glycolysis: fructose, galactose and mannose