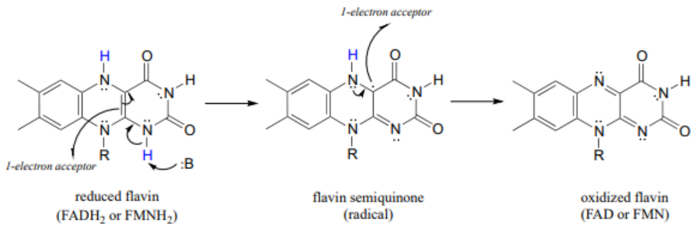
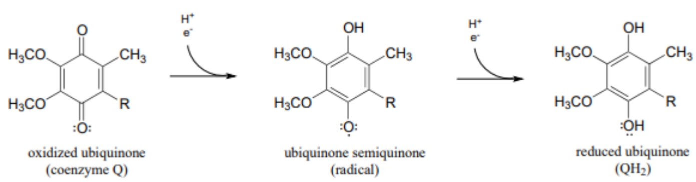
16.7: Flavin as a One-Electron Carrier

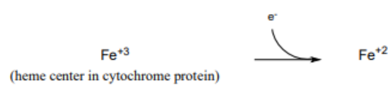
In chapter 15 we saw how a nicotinamide and flavin coenzymes can act as acceptors or donors of two electrons in hydride-transfer redox steps. Recall that it was mentioned that flavin, (but not nicotinamide) can also participate in single-electron transfer steps through a stabilized radical intermediate called a semiquinone.. Frey p. 162 fig 3-30; Silverman p. 122 sch. 3.34; J Phys Chem A. 2013, 117, 11136 fig 2)



Note in this reaction that overall, flavin loses or gains two electrons and two protons, just like in the flavin-dependent redox reactions we saw in chapter 15. The difference here is that the electrons are transferred one at a time, rather than paired in the form of a hydride ion.

Two important examples single-electron acceptor species in human metabolism are ubiquinone (coenzyme Q) and the oxidized form of cytochrome. Ubiquinone is a coenzyme that can transfer single electrons via a semiquinone state analogous to that of flavin, and cytochrome is a protein containing a 'heme' iron center which shuttles between the Fe^{+3} (oxidized) and Fe^{+2} (reduced) state.





Further discussion of the mechanisms of single-electron flavin reactions is beyond our scope here, but when you study the 'respiratory chain' in a biochemistry course you will gain a deeper appreciation for the importance of flavin in single-electron transfer processes.