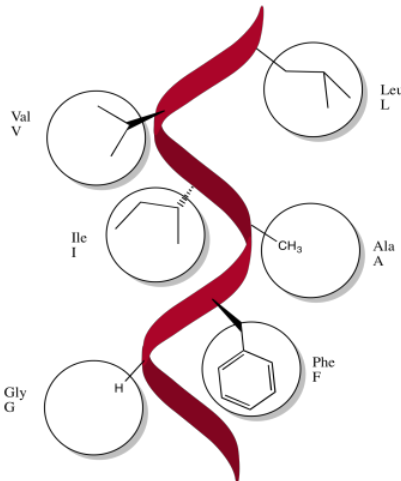
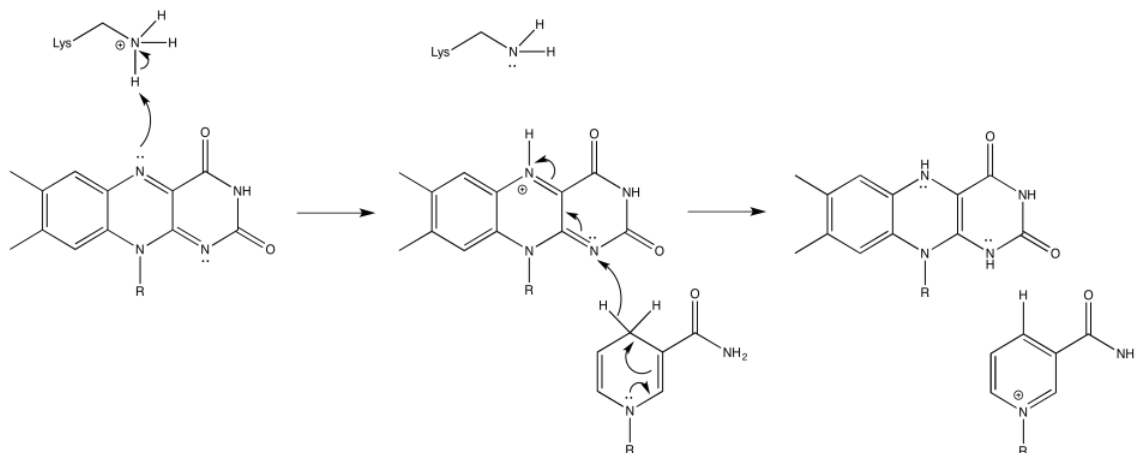


7.7: Solutions for Selected Problems

Exercise 7.2.1:



Exercise 7.2.2:



Exercise 6.2.3:

a) Iron charges: $Fe(II) + Fe(III) = 5^+$

Ligand charges: $2 \text{ sulfides} = 2 \times 2^- = 4^-$; $4 \text{ cysteines} = 4 \times 1^- = 4^-$; $\text{total} = 8^-$

Overall: 3^-

b) Iron charges: $2 \times Fe(II) + Fe(III) = 4^+ + 3^+ = 7^+$

Ligand charges: $4 \text{ sulfides} = 4 \times 2^- = 8^-$; $3 \text{ cysteines} = 3 \times 1^- = 3^-$; $\text{total} = 11^-$

Overall: 4^-

c) Iron charges: $3 \times Fe(II) + Fe(III) = 6^+ + 3^+ = 9^+$

Ligand charges: $4 \text{ sulfides} = 4 \times 2^- = 8^-$; $4 \text{ cysteines} = 4 \times 1^- = 4^-$; $\text{total} = 12^-$

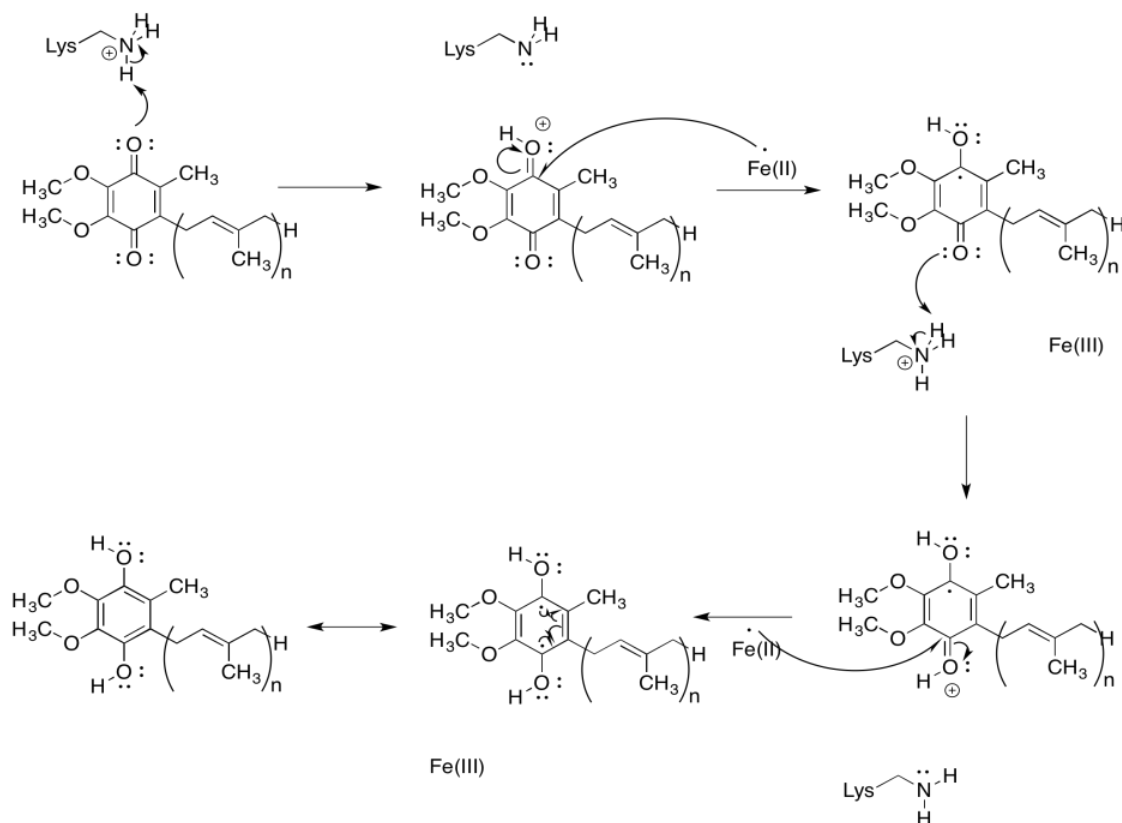
Overall: 3^-

Exercise 7.2.4:

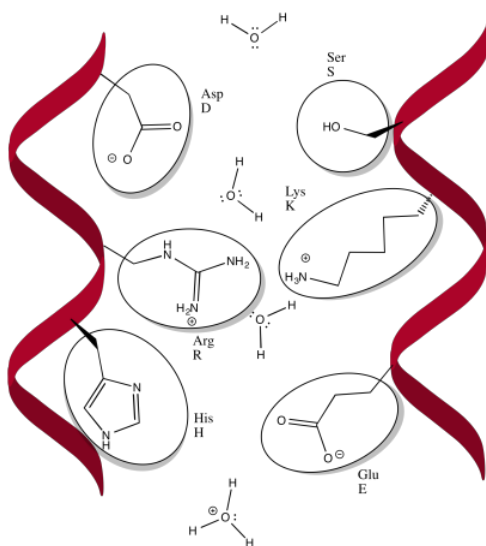
Upon reduction, the charge on a $2Fe_2S$ cluster will increase from 3^- to 4^- , assuming it starts in a mixed $Fe(II)/(III)$ state (whereas if it starts in a $Fe(III)/(III)$ state, the overall charge will increase from 2^- to 3^-). These anions would be stabilised by strong intermolecular interactions such as ion-dipole forces. Both states (oxidised and reduced) will be stabilised by a polar environment, but the more highly charged reduced state will depend even more strongly on stabilisation by the environment. As a result, we

might expect the reduction potential to be lower when surrounded by nonpolar amino acid residues, and higher if surrounded by polar residues.

Exercise 7.2.5:



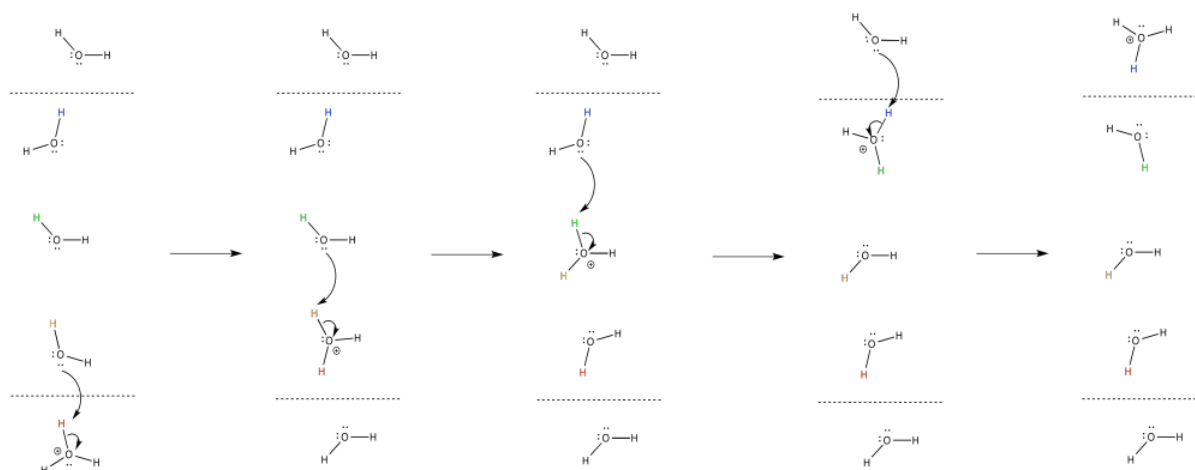
Exercise 7.2.6:



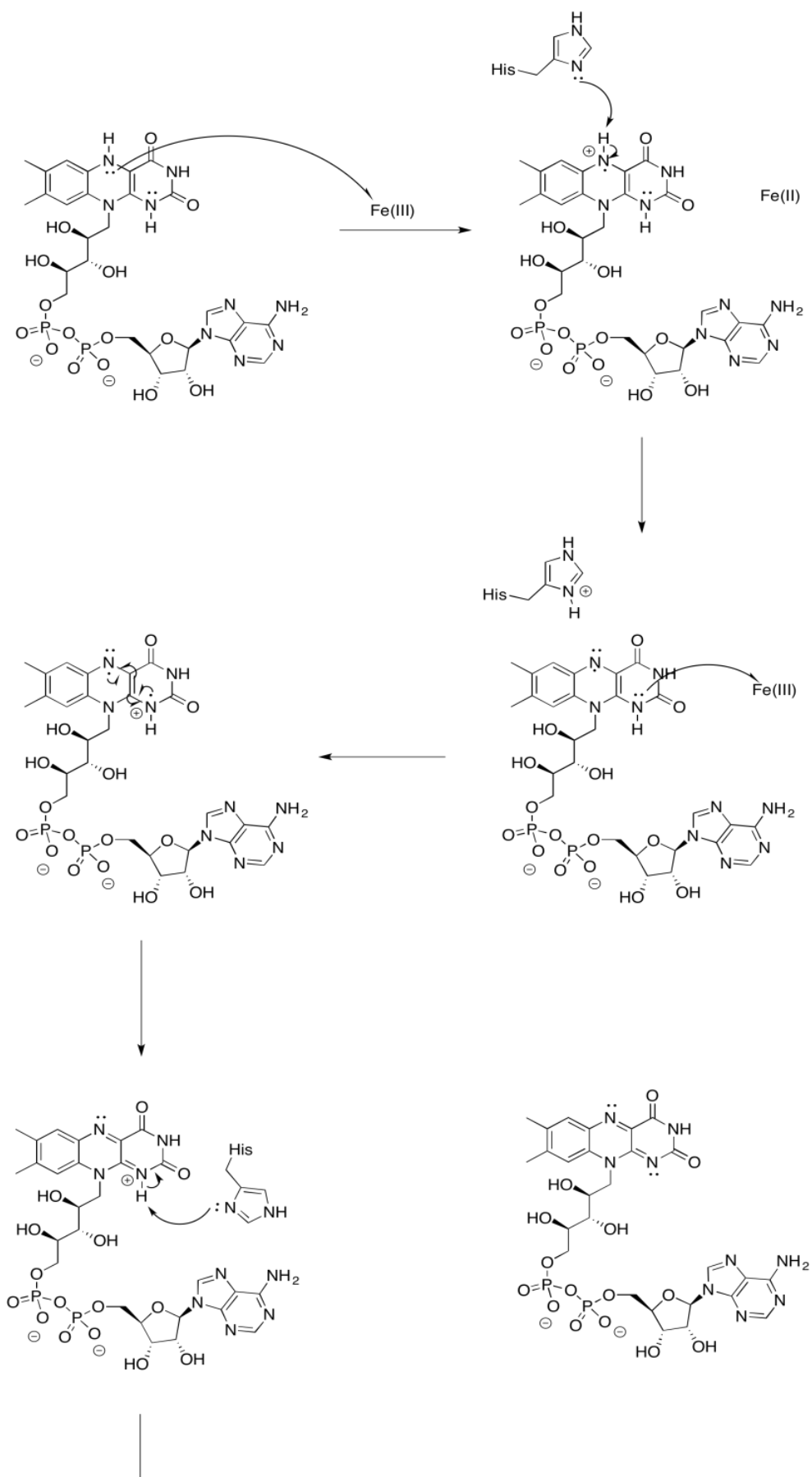
Other possibilities:

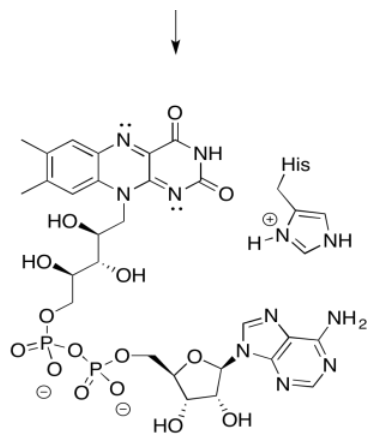
Thr T, Tyr Y, Gln Q, Asn N, Trp W, Cys C, Met M

Exercise 7.2.7:



Exercise 7.2.8:

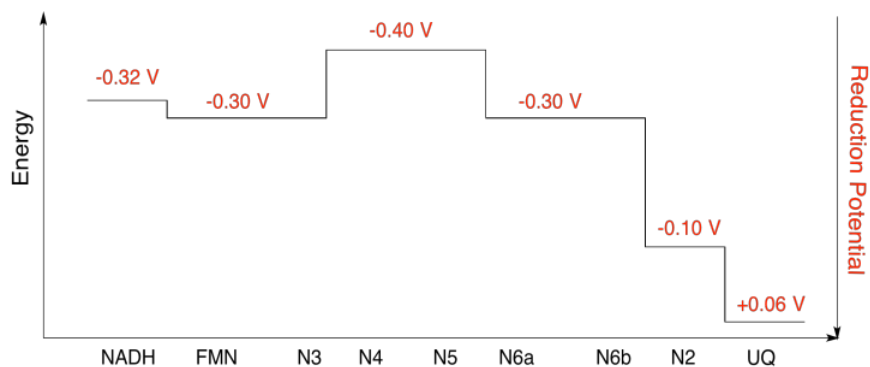




Exercise 7.2.9:

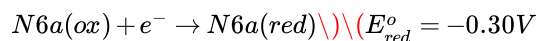
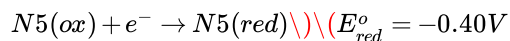
a) N1a and N1b are most likely not involved, because their reduction potentials are too negative.

b)



Exercise 7.2.10:

Assuming the reduction potentials are:



Then the potential difference for the reaction, $\Delta E^o = -0.30 - (-0.40)V = 0.10V$

The Faraday relation $\Delta G = -nF\Delta E^o$ gives

$$\Delta G = -1 \times 96485 \frac{J}{V \text{ mol}} \times 0.10V = 9649 \frac{J}{\text{mol}} = 9.7 \frac{kJ}{\text{mol}}$$

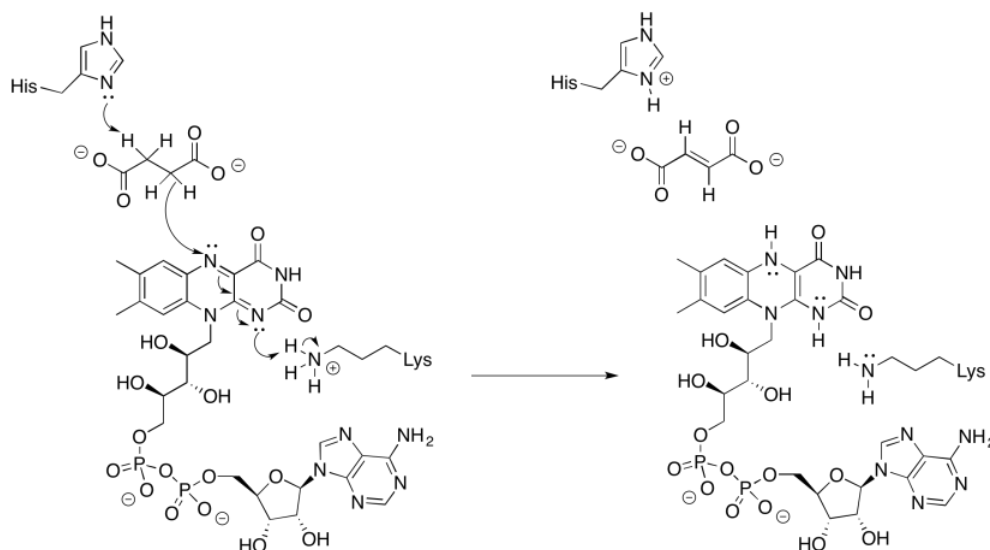
Exercise 7.3.1:

Heme b.

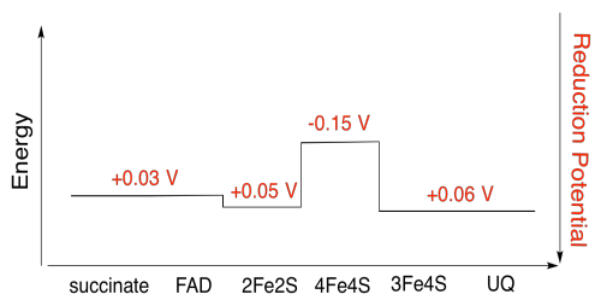
Exercise 7.3.2:

A porphyrin contains four pyrrole rings (five-membered, aromatic ring containing a nitrogen) arranged to form a 16-membered macrocycle.

Exercise 7.3.3:

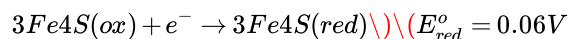
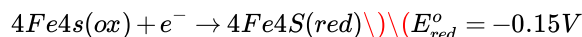


Exercise 7.3.4:



Exercise 7.3.5:

Assuming the reduction potentials are:



Then the potential difference for the reaction, $\Delta E^o = 0.06 - (-0.15)V = 0.21V$

The Faraday relation $\Delta G = -nF\Delta E^o$ gives

$$\Delta G = -1 \times 96485 \frac{J}{V \cdot mol} \times 0.21V = 20262 \frac{J}{mol} = 20 \frac{kJ}{mol}$$

Exercise 7.3.6:

a) Iron charges: $2 \times Fe(III) = 6^+$

Ligand charges: $2 \text{ sulfides} = 2 \times 2^- = 4^-$; $4 \text{ cysteines} = 4 \times 1^- = 4^-$; $total = 8^-$

Overall: 2^-

b) Iron charges: $3 \times Fe(III) = 9^+$

Ligand charges: $4 \text{ sulfides} = 4 \times 2^- = 8^-$; $3 \text{ cysteines} = 3 \times 1^- = 3^-$; $total = 11^-$

Overall: 2^-

c) Iron charges: $4 \times Fe(III) = 12^+$

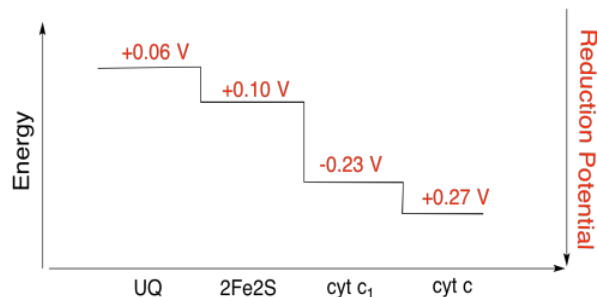
Ligand charges: $4 \text{ sulfides} = 4 \times 2^- = 8^-$; $4 \text{ cysteines} = 4 \times 1^- = 4^-$; $total = 12^-$

Overall: 0

Exercise 7.4.1:

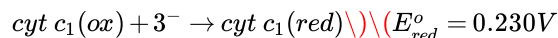
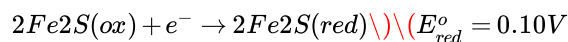
Arginine and lysine are positively charged at neutral pH.

Exercise 7.4.2:



Exercise 7.4.3:

Assuming the reduction potentials are:



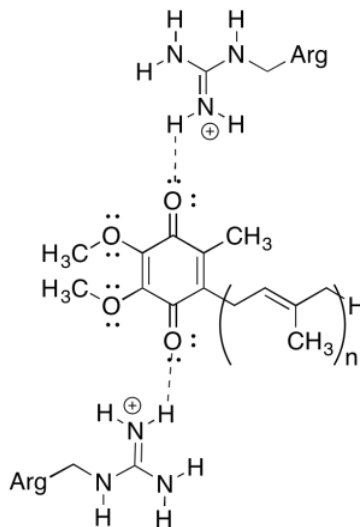
Then the potential difference for the reaction, $\Delta E^o = 0.23 - (0.10)V = 0.13V$

The Faraday relation $\Delta G = -nF\Delta E^o$ gives

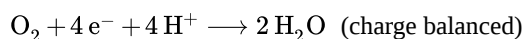
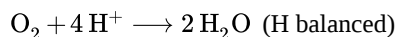
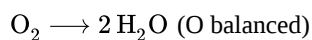
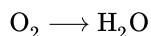
$$\Delta G = -1 \times 96485 \frac{J}{V\ mol} \times 0.13V = 12543 \frac{J}{mol} = 12.5 \frac{kJ}{mol}$$

Exercise 7.4.4:

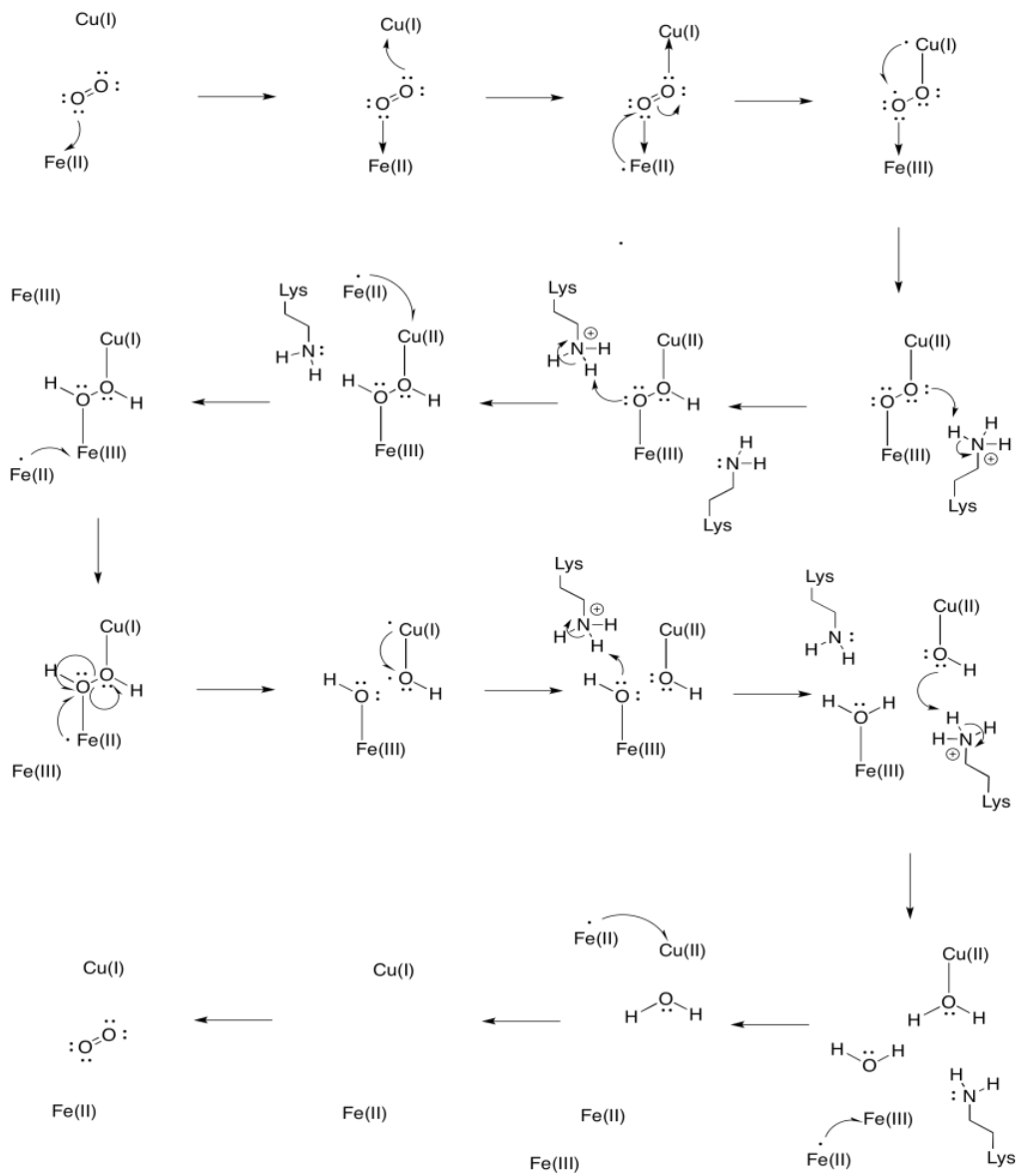
The positive arginine residues would confer partial positive charge on the ubiquinone via hydrogen bonding; the ubiquinone would have a more positive reduction potential as a result.



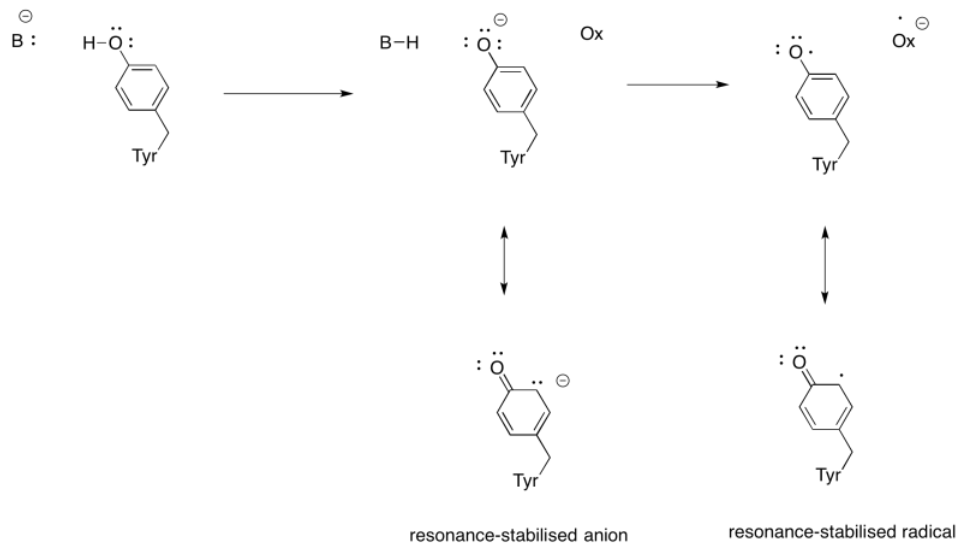
Exercise 7.5.1:



Exercise 7.5.2:

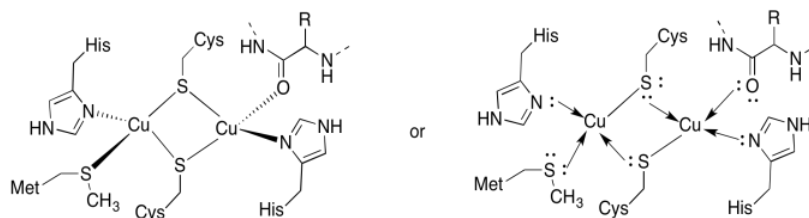


Exercise 7.5.3:



Exercise 7.5.4:

a)



b) tetrahedral

c) $\text{Cu(I)} = d^{10}$

4 donors = $8 e^-$

total = $18 e^-$

d) $2 \times \text{Cu(I)} = 2^+$

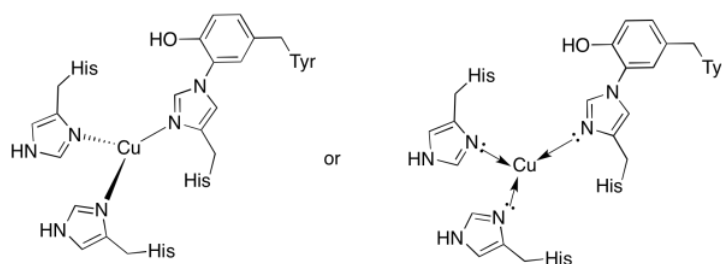
$2 \times \text{Cys-S}^- = 2^-$

All others neutral

Total = 0

Exercise 7.5.5:

a)



) trigonal planar

c) $\text{Cu(I)} = d^{10}$

3 donors = $6 e^-$

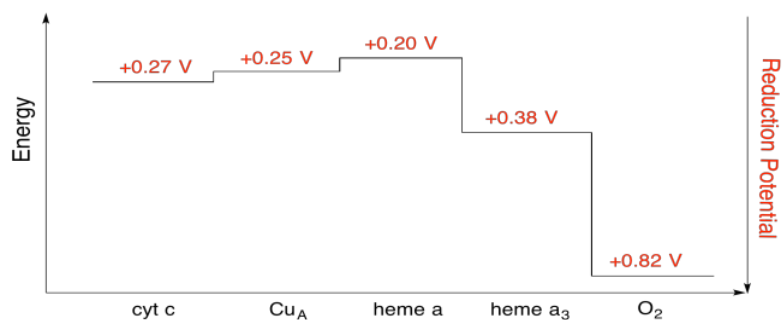
total = $16 e^-$

d) $\text{Cu(I)} = 1^+$

histidines neutral

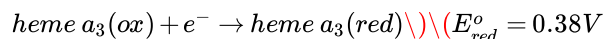
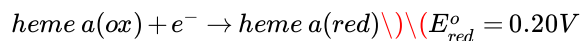
Total = 1^+

Exercise 7.5.6:



Exercise 7.5.7:

Assuming the reduction potentials are:



Then the potential difference for the reaction, $\Delta E^{\circ} = 0.38 - (0.20)V = 0.18V$

The Faraday relation $\Delta G = -nF\Delta E^{\circ}$ gives

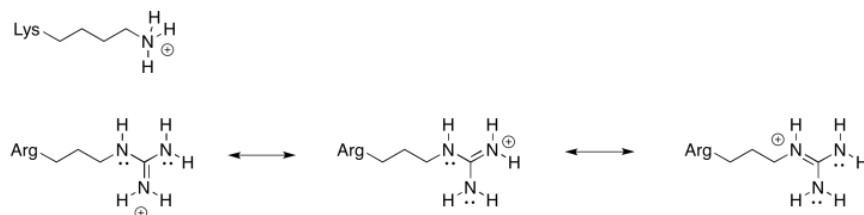
$$\Delta G = -1 \times 96485 \frac{J}{V \text{ mol}} \times 0.18V = 17367 \frac{J}{\text{mol}} = 17.4 \frac{kJ}{\text{mol}}$$

Exercise 7.6.1:

These amino acids would probably be non-polar: alanine, glycine, methionine, isoleucine, leucine, methionine, phenylalanine, tryptophan, valine.

Exercise 7.6.2:

There is always an equilibrium between the protonated state and the deprotonated state in a charged amino acid residue. For this position, an amino acid is needed that is more reliably in the protonated state; that is, the equilibrium lies more heavily to the protonated side of the equation. Because of the resonance-stabilised cation that results from protonation, arginine is much more likely to remain in a protonated state than lysine. That will make for a more efficient millwheel.

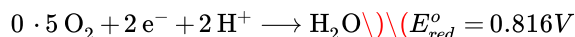
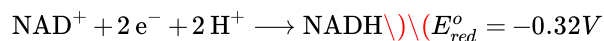


Exercise 7.6.3:

ADP and phosphate are both anions; they would repel normally each other. When bound in the active site, their charges are likely neutralized by complementary charges in the active site.

Exercise 7.6.4:

Assuming the reduction potentials are:



Then the potential difference for the reaction, $\Delta E^{\circ} = 0.816 - (-0.32)V = 1.136V$

The Faraday relation $\Delta G = -nF\Delta E^{\circ}$ gives

$$\Delta G = -2 \times 96475 \frac{J}{V \text{ mol}} \times 1.136V = 219213 \frac{J}{\text{mol}} = 219 \frac{kJ}{\text{mol}}$$

$$\text{so } \frac{219 \frac{kJ}{\text{mol}}}{30 \frac{kJ}{\text{mol}}} = 7.3$$

With 100% efficiency, 7 moles of ATP could be produced per mole of NADH. In reality, about half that amount is produced (closer to 3 moles ATP per mole NADH).

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