Chapter 9 Solutions

1) A monodentate carboxylate is a σ-only donor, whereas a cysteinate is a σ- and π-donor. Mutating a cysteine to an aspartate will eliminate the band (~600 nm) in the optical spectrum associated with ligand-to-metal charge-transfer and probably ipsochromically shift the d-d transition band (because RCO_2^- is not as weak field as RS^-).

2) Cytochrome *c* contains a coordinatively-saturated, O_h iron in the active site and does not change coordination number during redox processes. In comparison, myoglobin alternates between five- and six-coordinate depending on redox state. Consequently, the ruthenium-modified myoglobin will have an higher reorganization energy and thus a lower rate constant for electron transfer.

3) The maximum rate constant for electron transfer, k_{ET}^0, at van der Waals contact (R_0 = 3.6 Å) through covalent linkages (β = 0.7 $Å^{-1}$) is 10^{13} s^{-1}. Using this, one can express T_{DA}^0 as follows:

$k_{ET}^0 = (4\pi^2/h)*(T_{DA}^0)^2*(FC)$
$(T_{DA}^0)^2 = k_{ET}^0 / [(4\pi^2/h)*(FC)]$
where FC will remain constant. We can then determine the electron transfer rate constant using the given values:

$k_{ET} = (4\pi^2/h)*(T_{DA})^2*(FC) = (4\pi^2/h)*(T_{DA}^0)^2*\exp[-\beta(R-R_0)]*(FC)$
$= (4\pi^2/h)*\{k_{ET}^0 / [(4\pi^2/h)*(FC)]\}*\exp[-\beta(R-R_0)]*(FC)$
$= k_{ET}^0 * \exp[-\beta(R-R_0)]$

a) for electron transfer over 30 Å through covalent bonds:
$k_{ET} = 10^{13}\ s^{-1} * \exp[-0.7\ Å^{-1} * (30\ Å - 3.6\ Å)] = 9.4*10^4\ s^{-1}$

b) for electron transfer over 30 Å through a protein (β = 1.4 $Å^{-1}$)
$k_{ET} = 10^{13}\ s^{-1} * \exp[-1.4\ Å^{-1} * (30\ Å - 3.6\ Å)] = 8.9*10^{-4}\ s^{-1}$

4) Given that electron transfer rate for used pathway is 100 times faster than unused pathway (k_{ET}'/k_{ET} = 1/100), β = 1.4 $Å^{-1}$, $-\Delta G^0$ = 0.2 eV, λ = 0.2 eV, and kT = 0.026 eV

a) assume difference in rate constant is due to difference in distance, find ΔR:
$k_{ET}'/k_{ET} = [(4\pi^2/h)(T_{DA}')^2(FC')] / [(4\pi^2/h)(T_{DA})^2(FC)]$
where FC' = FC

$k_{ET}'/k_{ET} = (T_{DA}')^2/(T_{DA})^2 = \{(T_{DA}^0)^2*\exp[-\beta(R'-R_0)]\} / \{(T_{DA}^0)^2*\exp[-\beta(R-R_0)]\}$
$= \exp[-\beta(R'-R_0)] / \exp[-\beta(R-R_0)] = \exp[-\beta(R'-R_0) + \beta(R-R_0)] = \exp[-\beta(R'-R)]$
$= 1/100$

$-\ln(100) = -\beta(R'-R)$
$R' = \ln(100)/\beta + R = 13.3$ Å
$\Delta R = 3.3$ Å

b) assume difference in rate constant is due to difference in driving force, find $\Delta(-\Delta G)$:
$k_{ET}'/k_{ET} = [(4\pi^2/h)(T_{DA}')^2(FC')] / [(4\pi^2/h)(T_{DA})^2(FC)]$
where $(T_{DA}')^2 = (T_{DA})^2$

k_{ET}'/k_{ET}
$= \{(4\pi\lambda kT)^{-1/2}*\exp[-(-\Delta G^{0'} - \lambda)^2/(4\lambda kT)]\} / \{(4\pi\lambda kT)^{-1/2}*\exp[-(-\Delta G^0 - \lambda)^2/(4\lambda kT)]\}$

since $-\Delta G^0 = 0.2$ eV $= \lambda$,
$= \exp[-(-\Delta G^{0'} - \lambda)^2/(4\lambda kT)] = 1/100$

$-\ln(100) = -(-\Delta G^{0'} - \lambda)^2/(4\lambda kT)$
$(4\lambda kT)*\ln(100) = (-\Delta G^{0'} - \lambda)^2$
$(\Delta G^{0'})^2 + 2\lambda(\Delta G^{0'}) + \lambda^2 - (4\lambda kT)*\ln(100) = 0$
$(\Delta G^{0'})^2 + 0.4(\Delta G^{0'}) - 0.056 = 0$

use quadratic equation to get
$\Delta G^{0'} = 0.11$ eV or -0.51 eV

thus
$-\Delta G^{0'} = -0.11$ eV or 0.51 eV

so
$\Delta(-\Delta G) = -\Delta G^{0'} - (-\Delta G^0) = -0.11\text{ eV} - (0.2\text{ eV}) = -0.31$ eV

or
$\Delta(-\Delta G) = -\Delta G^{0'} - (-\Delta G^0) = 0.51\text{ eV} - (0.2\text{ eV}) = 0.31$ eV

c) assume difference in rate constant is due to difference in reorganization energy, find $\Delta\lambda$:

$k_{ET}'/k_{ET} = [(4\pi^2/h)(T_{DA}')^2(FC')] / [(4\pi^2/h)(T_{DA})^2(FC)]$
where $(T_{DA}')^2 = (T_{DA})^2$

k_{ET}'/k_{ET}
$= \{(4\pi\lambda' kT)^{-1/2}*\exp[-(-\Delta G^0 - \lambda')^2/(4\lambda' kT)]\} / \{(4\pi\lambda kT)^{-1/2}*\exp[-(-\Delta G^0 - \lambda)^2/(4\lambda kT)]\}$
$= \{(\lambda')^{-1/2}*\exp[-(-\Delta G^0 - \lambda')^2/(4\lambda' kT)]\} / \{(\lambda)^{-1/2}*\exp[-(-\Delta G^0 - \lambda)^2/(4\lambda kT)]\}$

since $-\Delta G^0 = 0.2$ eV $= \lambda$,
$= (\lambda'/\lambda)^{-1/2}*\exp[-(-\Delta G^0 - \lambda')^2/(4\lambda' kT)] = 1/100$

$-\ln(100) = -{}^1/_2*\ln(\lambda'/\lambda) - [(-\Delta G^0 - \lambda')^2/(4\lambda' kT)]$
$-(4\lambda' kT)*\ln(100) = -(2\lambda' kT)*\ln(\lambda') + (2\lambda' kT)*\ln(\lambda) - (-\Delta G^0 - \lambda')^2$
$\lambda'*[(4kT)*\ln(100)] = \lambda'\ln(\lambda')*[2kT] - \lambda'*[(2kT)*\ln(\lambda)] + [(\Delta G^0)^2 + 2\lambda'\Delta G^0 + (\lambda')^2]$

$0 = (\lambda')^2 + \lambda'*[2\Delta G^0 - (2kT)*\ln(\lambda) - (4kT)*\ln(100)] + \lambda'\ln(\lambda')*[2kT] + (\Delta G^0)^2$
$= (\lambda')^2 + \lambda'*[-0.4 + 0.084 - 0.48] + \lambda'\ln(\lambda')*[0.052] + 0.04$

$$= (\lambda')^2 + \lambda'*[-0.796] - \lambda'\ln(\lambda')*[0.052] + 0.04$$

solving numerically for λ':
$\lambda' = 0.76$ eV

thus:
$\Delta\lambda = 0.56$ eV

5) Given R = 20 Å, $k_{ET} = 200\ s^{-1}$, and $\beta = 1.4$ Å^{-1}, find k_{ET}' when R is increased to 25 Å:

in general
$k_{ET} = (4\pi^2/h)*(T_{DA})^2*(FC)$

where
$(T_{DA})^2 = (T_{DA}^0)^2*\exp[-\beta(R-R_0)]$
$(FC) = (4\pi\lambda kT)^{-1/2}*\exp[-(-\Delta G^0 - \lambda)^2/(4\lambda kT)]$

using the following ratio
$k_{ET}'/k_{ET} = [(4\pi^2/h)(T_{DA}')^2(FC')] / [(4\pi^2/h)(T_{DA})^2(FC)]$

since FC has no dependence on R, and all other variables are held constant
$k_{ET}'/k_{ET} = (T_{DA}')^2/(T_{DA})^2 = \{(T_{DA}^0)^2*\exp[-\beta(R'-R_0)]\} / \{(T_{DA}^0)^2*\exp[-\beta(R-R_0)]\}$
$= \exp[-\beta(R'-R_0)] / \exp[-\beta(R-R_0)] = \exp[-\beta(R'-R_0) + \beta(R-R_0)] = \exp[-\beta(R'-R)]$

thus, the new rate constant can be determined
$k_{ET}' = k_{ET}*\exp[-\beta(R'-R)] = 200\ s^{-1} * \exp[-1.4$ Å $* (25$ Å $- 20$ Å$)] = 0.18\ s^{-1}$