Chapter 5 Solutions

1) $[Fe(ent)]^{3-} \underset{}{\overset{K_d}{\rightleftharpoons}} Fe^{3+} + ent^{6-}$

1-x x x $\}$ $\sum = 1$ M

$K_d = [Fe^{3+}][ent^{6-}] / [Fe(ent)^{3-}] = x^2 / (1-2x)$

$x^2 = K_d*(1-x)$; $x^2 - K_d*(1-x) = 0$

then use quadratic equation, or assume (1-x) = 1 for small x

$x^2 - K_d = 0$; $x^2 = K_d$; $x^2 = K_d$; $x = K_d^{1/2}$

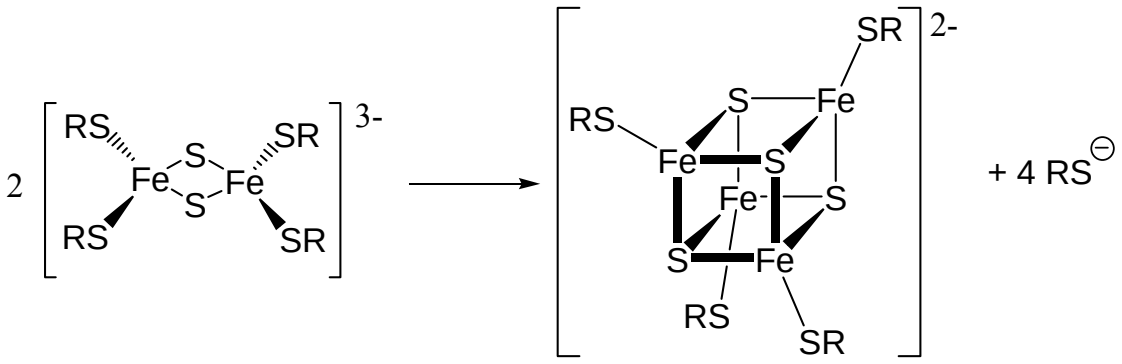
Fe^{3+} ions = $[Fe^{3+}]*V*N_A$

High pH:
$K_d = 10^{-49}$, # Fe^{3+} ions = $(10^{-49})^{1/2}$ M * 1 L * $6.022*10^{23}$ ions/mol = 0.19 ions

Neutral pH:
$K_d = 10^{-25}$, # Fe^{3+} ions = $(10^{-25})^{1/2}$ M * 1 L * $6.022*10^{23}$ ions/mol = $1.9*10^{11}$ ions

2) The enantiomer for enterobactin will chelate iron equally well with a $K_d = 10^{-25}$ at neutral pH, since an iron ion is spherically symmetric in the absence of a ligand field. Molecular recognition in biology depends on multiple small energy interactions (i.e. the sum of hydrogen bonding, hydrophobic interactions, π-stacking interactions, salt bridges, etc.). Recognition of the native enantiomer of enterobactin presumably relies upon this type of recognition; the other enantiomer of enterobactin would not be recognized by the same cellular machinery and there would be no uptake.

3)



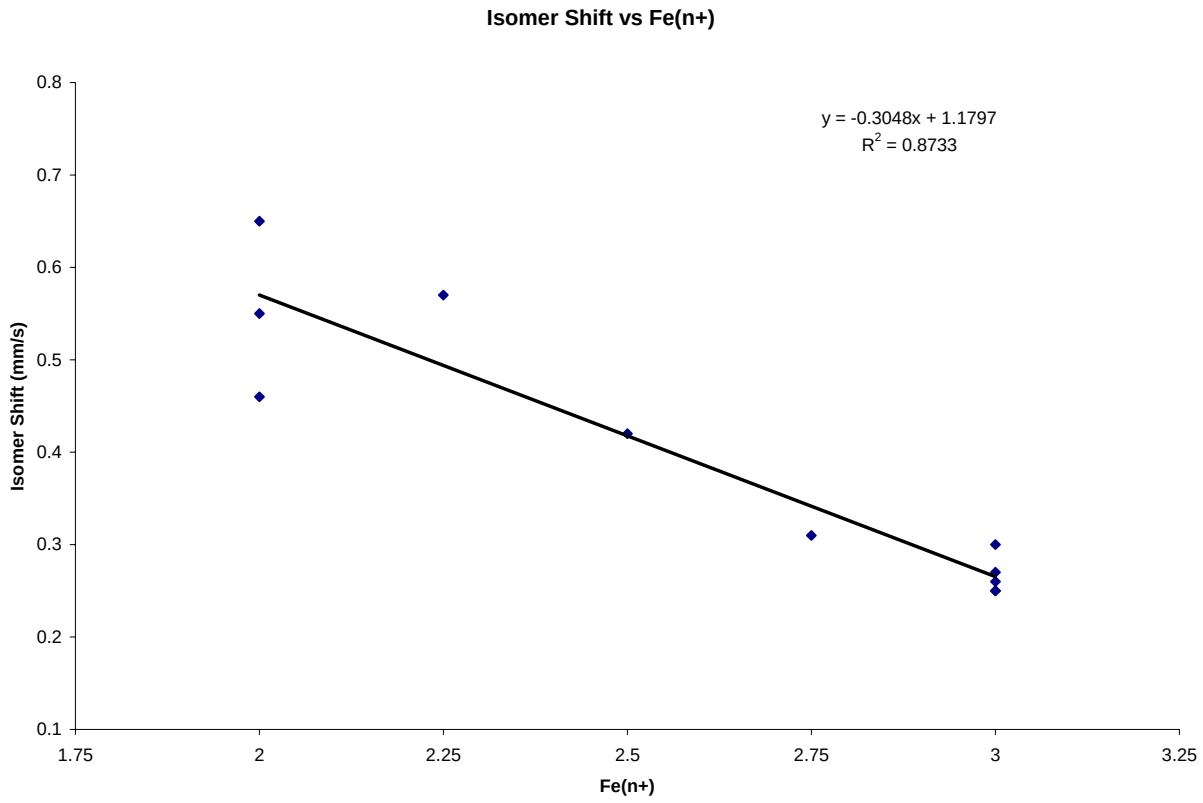
The oxidized form of $[Fe_2S_2(SR)_4]^{2-}$, which is diiron(III), will bind the thiolates much more tightly than the Fe(II)Fe(III) and disfavor their release. Furthermore, the tetrairon(III) cluster that would result is unknown in nature and cannot be supported with this ligand set.

To inhibit dimerization, one could tinker with thermochemical or entropic properties. Increasing the steric demands of the R group will increase the activation barrier for dimerization; this alteration would be especially useful if the dimerization occurs through an associative pathway. Conversely, changing from two monodentate thiolates to one bidentate dithiolate on iron will disfavor ligand dissociation, which would be especially useful if the dimerization occurs through a ligand-dissociative pathway.

4) Given 10 particles per generation, edge length of 500 Å and $\rho = 5.18$ g/cm^3:

$10 * N_{Fe} = 10 * 3N_{Fe3O4} = 30 * m_{Fe3O4} / MW_{Fe3O4} = 30 * \rho V / (231.55 \text{ g/mol})$
$= 30 * 5.18 \text{ g/cm}^3 * (5.00*10^{-6} \text{ cm})^3 / (231.55 \text{ g/mol}) = 8.39*10^{-17}$ moles Fe

5)



For Fe^{n+}, given n = -0.3048*(isomer shift) + 1.1797 and the observed isomer shift of 0.37 mm/s, the predicted iron valence from the fit is n = 2.66. This non-integral number for the valence of iron indicates that an averaging process is taking place to produce a mixed-valence species (i.e. six $Fe^{2.66+}$). To get the formal oxidation states of the iron ions, we first multiply the

average valence by the number of ions: 2.66*6 = 16. Assuming that only the 2+ and 3+ oxidation states are available to iron, and given that the number of iron ions is 6, we can write the following equation: $2n + 3m = 16$, where $n + m = 6$. The unique solution to this is $m = 4$ and $n = 2$. This suggests that the $MoFe_6$ in nitrogenase formally contains two Fe^{2+} ions and four Fe^{3+} ions.