Model Exam Question "Answer Key"

Everyone: I'm abandoning subscripts and superscripts- trying to be efficient with time. Also, don't maintain hopes of eloquent writing.

Question #1:
Part a: Arrange these ligands in order, from easiest to most difficult to reduce, to determine which would be most likely to be bioavailable to organisms using the reductive approach.

The organism wants to reduce an Fe(III)-Ligand complext to an Fe(II)-Ligand complex. Let L= Ligand, then we can represent an overall reaction as

$$Fe(III)-L + e- = Fe(II)-L$$
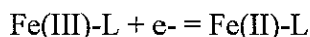
We can figure out eh free energy change associated with the overall process by adding the log Ks of the constituent half reactions.

For the generic reaction:

		$Log\ K = pe^o$
The reduction step:	$Fe^{3+} + e^- = Fe^{2+}$	13.0
Fe(III) DISsocciation	$Fe(III)-L = Fe^{3+} + L$	- X
Fe(II) ASSociation	$Fe^{2+} + L = Fe(II)-L$	Y
Overal RXN	$Fe(III)-L + e^- = Fe(II)-L$	$13 - X + Y$

Example:

	$Log\ K = pe^o$
$Fe^{3+} + e^- = Fe^{2+}$	13.0
$Fe(III)-EDTA = Fe^{3+} + EDTA^{4-}$	- 25.1
$Fe^{2+} + L = Fe(II)-L$	14.3
$Fe(III)-L + e^- = Fe(II)-L$	$13 - 25.1 + 14.3$
	$= 2.2 = log\ K_{Fe-EDTA} = pe^o\ _{Fe-EDTA}$

	$Log\ K = pe^o$
$Fe^{3+} + e^- = Fe^{2+}$	13.0
$Fe(III)-EDTA = Fe^{3+} + EDTA^{4-}$	- 15.9
$Fe^{2+} + L = Fe(II)-L$	8.9
$Fe(III)-L + e^- = Fe(II)-L$	$13 - 15.9 + 8.9$
	$= 6.0 = log\ K_{Fe-NTA} = pe^o\ _{Fe-NTA}$

As log $K_{Fe-EDTA} <$ log K_{Fe-NTA} , the Fe-NTA rxn is more favorable. Thus, the Fe(III)-NTA is easier to reduce and more "bioavailable" for the organism using the reductive approach. If you like to think about pe^o's as REDUCTION POTENTIALS (E_H^o=reduction potential= $2.3RTpe^o/F$), then the larger pe^o has the greater POTENTIAL to be REDUCED.

If you solve for all of this business using the generic equation ($13 - X + Y = \log K$ of the Fe-Ligand reduction, where $X = \log \beta$ for the Fe(III)-L complex, and $Y = \log \beta$ for the Fe(II)-L complex), then you get the following order:
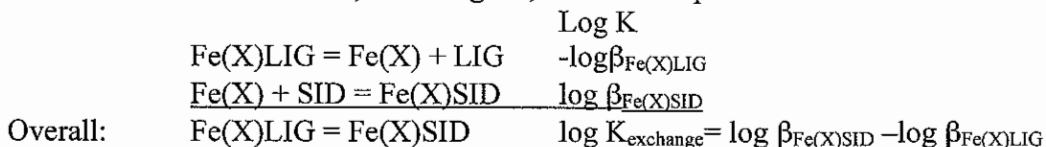
Easiest for organism using reductive approach (top) to hardest for organism to use reductive approach (bottom):

	Log K Fe-L reduction	
1,10-phenanthroline	12.8	$= 13 - 11.4 + 11.2$
NTA	6	$= 13 - 15.9 + 8.9$
EDTA	2.2	$= 13 - 25.1 + 14.3$
CDTA	1.9	$= 13 - 30 + 18.9$
DTPA	1.2	$= 13 - 28 + 16.2$
TETA	-0.2	$= 13 - 26.5 + 13.3$

Part B: arrange them in order, showing which would be most bioavailable to an organism that produces siderophores.

Here, the organism is producing a siderophore (sider = iron), a compound designed to bind iron strongly. The siderophore will exchange iron with the Fe-L, and then the organism will acquire the Fe from the Fe-siderophore complex. The easier it is to get the Fe from the Fe-L complex, the easier it will be for the siderophore to bind the Fe. We can write the general reaction:

Let X= oxidation state of Fe, LIG = ligand, SID= siderophore.

		Log K
	$Fe(X)LIG = Fe(X) + LIG$	$-\log\beta_{Fe(X)LIG}$
	$Fe(X) + SID = Fe(X)SID$	$\log \beta_{Fe(X)SID}$
Overall:	$Fe(X)LIG = Fe(X)SID$	$\log K_{exchange} = \log \beta_{Fe(X)SID} - \log \beta_{Fe(X)LIG}$

The bigger $\log K_{exchange}$, the more favorable the exchange, and the more bioavailable the Fe is to the organism. $\log K_{exchange}$ is bigger when $\log\beta_{Fe(X)LIG}$ is smaller (this makes sense, right? If $\log\beta_{Fe(X)LIG}$ is small, the complex is weak, and will release Fe more readily than a complex with a larger $\log\beta_{Fe(X)LIG}$.) Thus, the complex with the smallest $\log\beta_{Fe(X)LIG}$ is the most bioavailable for the siderophore-producing organism, and we can make a list:

Most bioavailable (top) to least bioavailable (bottom):
(You all know I don't know I have problems with big vs. small, left vs. right... check these):
Fe(II)-NTA
Fe(II)-1,10-phenanthroline
Fe(III)-1,10-phenanthroline
Fe(II)-TETA
Fe(II)-EDTA

Fe(III)-NTA
Fe(II)-DTPA
Fe(II)-CDTA
Fe(III)-EDTA
Fe(III)-TETA
Fe(III)-DTPA
Fe(III)-CDTA

Part c: A big-shot WHOI Scientist is studying Fe uptake in two marine phytoplankton species, A and B, using a media containing 1uM EDTA and 0.05uM Fe. Due to a careless mistake, he adds 100uM EDTA to the media. He observes an immediate decrease in Fe uptake in A, but the uptake rate in B is unaffected. Based on these data, speculate about which Fe acquisition strategy is used by organism A and which is used by organism B.

After the addition of EDTA, Fe-EDTA is going to be the dominant form of Fe in both media. The organism using the siderophore-production approach has a much easier time sequestering free Fe than Fe-EDTA. As organism A has decreased uptake with increased Fe-EDTA, we can speculate that organism A is the siderophore-producer. The organism using the reduction strategy reduces complexed Fe, and so it should not be greatly affected by the complexation of Fe. (It may be easier for the Fe-reducer to reduce free Fe(III) than complexed Fe(III) (Fe(III)-L), but it will still be able to obtain Fe from the medium using it's reduction strategy).

Part d: Thermodynamics aside, what is an obvious disadvantage for marine organisms using the siderophores production strategy. Why therefore, might organisms use this strategy instead of reduction?

Siderophores are complex biological molecules whose production is energetically expensive (involves complex gene clusters, multiple proteins and/or protein domains). Additionally, it is believed that an organism recovers only a small percentage of the siderophores that it produces. (Granted, the organism may delay siderophore production until is senses a "quorum" of individuals of the same species). In spite of it's pitfalls, the siderophore-production approach might be favored because of the lack of dissolved Fe(III)-complexes in the water column. Recall that Fe(III)-complexes rapidly form colloids and precipitate. Thus, an organism using the reduction strategy would be best suited to an area with a high Fe(III)-colloid (or dust) input, but not to general survival in areas with low Fe inputs. Also, if Fe(II)-L complexes diffuse away from the organism using the reduction strategy, competing organisms could utilize the newly reduced Fe and out-compete the Fe-reducer. (Persumably, the Fe-reducer has some coupled Fe(II)-L uptake mechanism, so as to avoid such losses).

2. Write balanced equations for the reactions for the following oxidations and reductions:

Follow these steps:
1. Split the reaction into half reactions (if it's not split for you).
2. Balance the species that is changing oxidation state.
3. Balance O's with H2O
4. Balance H's with H+
5. Balance charge with e-'s (The # of electrons should be equal to the change in oxidation state: that is, if you go from Mn(II) to Mn(IV), you must have transferred 2 electrons).
6. Check that the charges and atoms balance.

See attached.

Arrange the following in order of increasing pe

You're used to an equation like this: $pe = pe^o - \log (Red)/(Ox)$.
(Remember that (Red)/(Ox) means: (stuff on the Reduced side of the 1/2 rxn)/(stuff on the Oxidized side of the 1/2 rxn). So, if you have Ox + e- + H+ = Red, then log (Red)/(Ox) = log (Red)/((Ox)*(H+))).

You might be looking for some concentrations of these "Red", "Ox" species, but you have been given very little information. Here is where you need to use all that is available to you and remind yourself that you are quite bright and have a strong chemical intuition. Also, state your assumptions.

We will assume that the **lake** and the **ocean** are oxygenated. Then, the O2/H2O couple will dominate the pe of the system.

$(1/4)*O2(g) + H+ + e- = (1/2)*H2O$
$pe = pe^o - (1/4)*\log (1)/(pO2) - \log \{H+\}$
$\quad = pe^o - (1/4)*\log (1)/(pO2) + pH.$

Increasing pH => decreasing pe.

The lake water (pH 6.5) has a higher pe than seawater (pH 8.3).
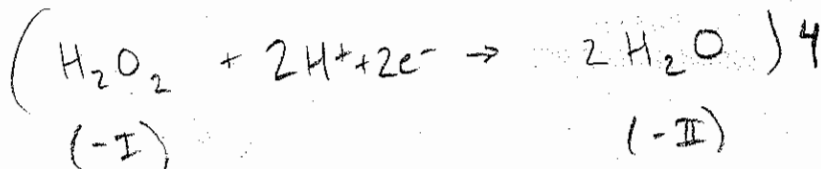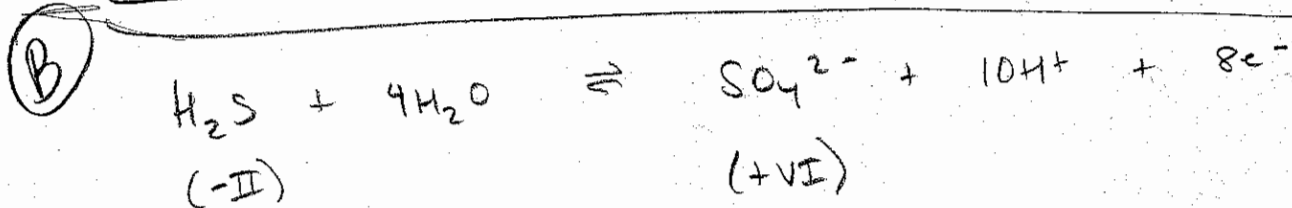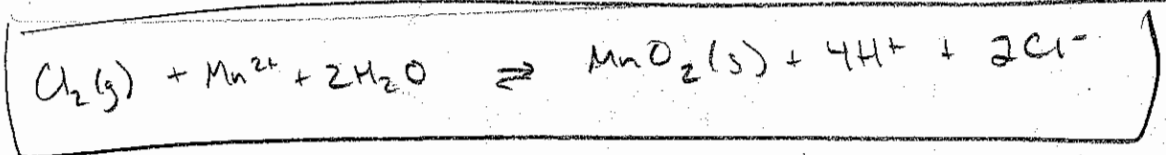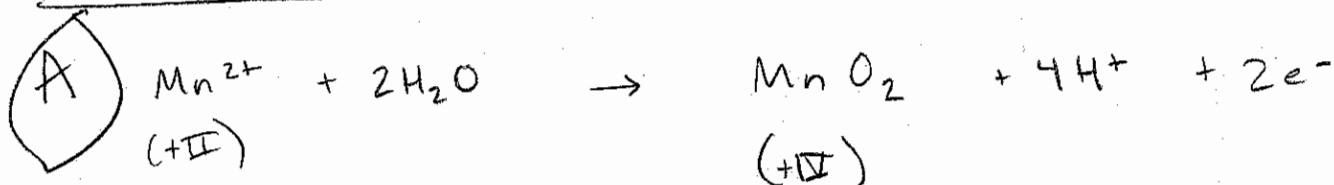(What does this mean? Here is where pe's analogy to pH comes in handy (about the only time). When pH is low, H+ concentration is high. When pe is low, the abstract "{e-}" is high. If there are many e-'s "floating about," the system is reducing (greater chance than an electron will stick on to something and reduce it). Since pe(lake) > pe(seawater), the lake is more oxidizing (the seawater is more reducing, relatively speaking)).

("What about the pO2?" you might ask. Since the "log(1)/(pO2)" term is divided by 4, order-of-magnitude changes in pO2 have little effect on the overall pe. Thus, while we

Question #2

(A)

$$Mn^{2+} + 2H_2O \rightarrow MnO_2 + 4H^+ + 2e^-$$

$(+II)$ $\qquad\qquad (+IV)$

$$Cl_2(g) + 2e^- \rightarrow 2Cl^-$$

0 $\qquad\qquad (-I)$

$$Cl_2(g) + Mn^{2+} + 2H_2O \rightleftharpoons MnO_2(s) + 4H^+ + 2Cl^-$$

(B)

$$H_2S + 4H_2O \rightleftharpoons SO_4^{2-} + 10H^+ + 8e^-$$

$(-II)$ $\qquad\qquad (+VI)$

$$\left(H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \right)4$$

$(-I)$ $\qquad\qquad (-II)$

$$H_2S + 4H_2O_2 \quad = \quad 2H^+ + 4H_2O + SO_4^{2-}$$

(C)

$$\left(MnO_2 + 4H^+ + 2e^- \rightarrow 2H_2O + Mn^{2+} \right)4$$

$$H_2S + 4H_2O \rightleftharpoons SO_4^{2-} + 10H^+ + 8e^-$$

$$4MnO_2 + 6H^+ + H_2S \quad = \quad 4H_2O + 4Mn^{2+} + SO_4^{2-}$$
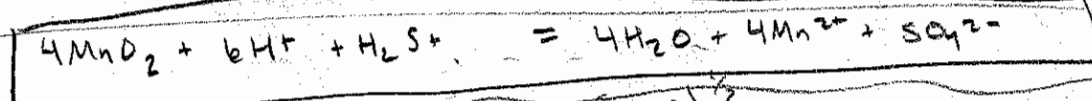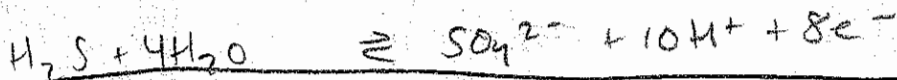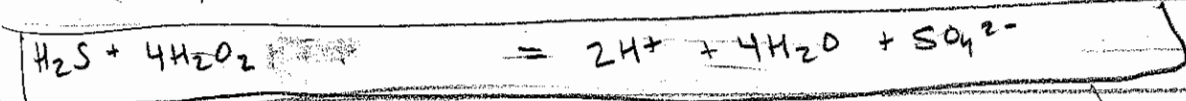
$$pe_{sys} = pe_{O_2/H_2O} = pe^0 - \log \frac{(H_2O)^2}{(pO_2)^{1/4} \{H^+\}}$$

$$= pe^0 - \left(\frac{1}{4}\log \frac{1}{(pO_2)} + \log\{H^+\} \right)$$
$$\qquad\qquad\qquad\qquad (+ pH)$$

$$= pe^0 - \frac{1}{4}\log \frac{1}{(pO_2)} - pH$$

$\downarrow pH, \quad \uparrow pe_{sys}.$

lake > ocean > seds > gd water must be very reducing.

can assume that pO2(lake) is roughly equal to pO2(seawater), even if they were very different, there would be a small overall effect on the pe's).

Now for the **sediment/groundwater:**

The reduction potential of sediment porewaters is a function of depth in the sediments (more reducing as you go deeper), rain rate of organic matter to the sediments (becomes reducing faster if there is a larger organic matter flux), and the relative concentration of electron acceptors (OXIDANTS that OXIDIZE organic matter. (e.g. the Fe(III)/Fe(II) redox couple can't control the pe if there is no Fe in your sediment...)). It is difficult for us to say for sure how reducing the sediments are without additional information, but we can expect that they will be more reducing than oxygenated waters at some point in the sediment column.

While we can not say for sure what the pe of the sediments is, we know that conditions must be very reducing in order for there to be 10^{-4} M (!!) Fe(II) in solution. (That's a whole lot of soluble Fe(II)). It is pretty safe to say that the groundwater is more reducing than the sediment porewater. It is true that, with increasing depth, the sediments may become more reducing than the groundwater, but if we assume that the sediments are in contact with oxygenated bottom water, they will be less reducing than the Fe-containing groundwater (at least at the sediment-water interface).

From most oxidizing/least reducing/ highest pe to
least oxidizing/most reducing/lowest pe:
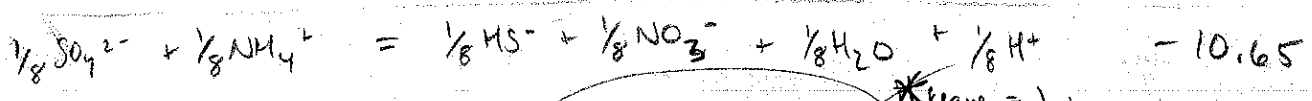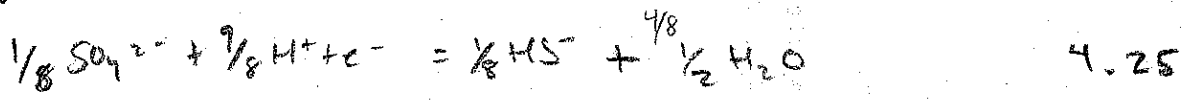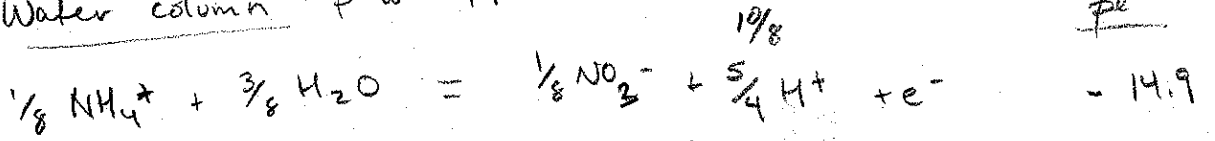   Lake water, pH 6.5
      Seawater, pH 8.3
      Sediment porewater
      Groundwater containing 10^{-4} M Fe(II)

Can the oxidation of ammonia to nitrate by sulfate be mediated by bacteria at pH 7?
Is the oxidation of HS⁻ to SO_4^{2-} by NO_3^- thermodynamically possible at pH 9?

Again, for these calculations, you are given little concentration information. You can take the "pew" approach, where you use as much information as you have (here, you only have pH) to give an improved estimate of the reaction favorability.

See the attached chicken scratch. You should be more through with your answers (e.g. calculate a dG estimate... I just wrote down the equation).

Water column - "pe" approach.

The $10/8$ notation above NO3

pe^0 (JM

$$\tfrac{1}{8}NH_4^+ + \tfrac{3}{8}H_2O = \tfrac{1}{8}NO_3^- + \tfrac{5}{4}H^+ + e^-$$ -14.9

$$\tfrac{1}{8}SO_4^{2-} + \tfrac{9}{8}H^+ + e^- = \tfrac{1}{8}HS^- + \tfrac{4}{8}\tfrac{1}{2}H_2O$$ 4.25

$$\tfrac{1}{8}SO_4^{2-} + \tfrac{1}{8}NH_4^+ = \tfrac{1}{8}HS^- + \tfrac{1}{8}NO_3^- + \tfrac{1}{8}H_2O + \tfrac{1}{8}H^+$$ -10.65

$10^{-3}M$

$$pe_{rxn} = pe^0_{rxn} - \tfrac{1}{8}\log\frac{[NO_2^-][HS^-]}{[NH_4^+][SO_4^{2-}]} \quad \tfrac{?}{8}\log[H^+]$$

leave = 1.

very low   *leave = 1.*

µmol   µmol   mM

* contribution of this term is small, & we have no [ ] information.

⟹ Take "pe" approach & use only the info you have. leave other [ ] = 1. Then, $pe^0_{rxn} + pH = -10.65 + \tfrac{7}{8} = -9.775 = \log k$

small.

$$\boxed{\Delta G^0 = -2.3nRT(pe_{rxn})} = 5.6 \times 10^4 \, J/mol\,e^- > 0 \quad \text{not favored}$$

For 1 mol NH_4^+ $\left(5.6\times10^4 \, \tfrac{J}{mol\cdot e^-}\right)\left(\frac{mol\,e^-}{\tfrac{1}{8}mol\,NH_4^+}\right) = 446 \, kJ/mol\,NH_4^+$

$45/40$

$$\tfrac{1}{8}HS^- + \tfrac{1}{2}H_2O = \tfrac{1}{8}SO_4^{2-} + \tfrac{9}{8}H^+ + e^-$$ -4.25

$$\tfrac{1}{2}NO_3^- + \tfrac{6}{5}H^+ + e^- = \tfrac{1}{2}NO_2^- + \tfrac{1}{2}H_2O$$ 14.15

$48/40$

$$\tfrac{1}{8}HS^- + \tfrac{1}{2}NO_3^- + \tfrac{9}{40}H^+ = \tfrac{1}{2}NO_2^- + \tfrac{1}{8}SO_4^{2-}$$ 9.9
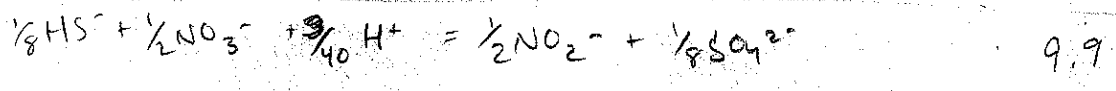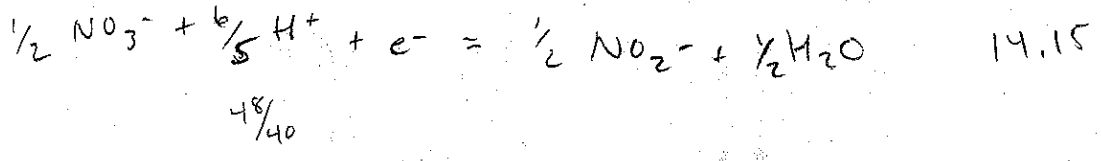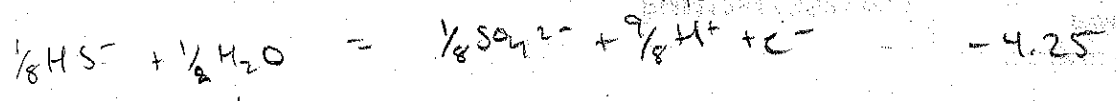
$$pe_{rxn} = pe^0_{rxn} - \tfrac{3}{40}\log\{H^+\} = pe^0_{rxn} - \tfrac{3}{40}(9) = 9.225$$

plug into $\Delta G = -2.3nRT(pe_{rxn})$ $\boxed{\Delta G < 0}$ <u>favored</u>.

*again neglecting contribution of NO_2^-, NO_3^-, HS^-, SO_4^{2-}

(really, leaving their [ ]s = 1,) not a great assumption

(should normalize to 1 mol HS^-, the thing being oxidized not don't normalize to the oxidant & Just make sure you specify what you're normalizing ...)
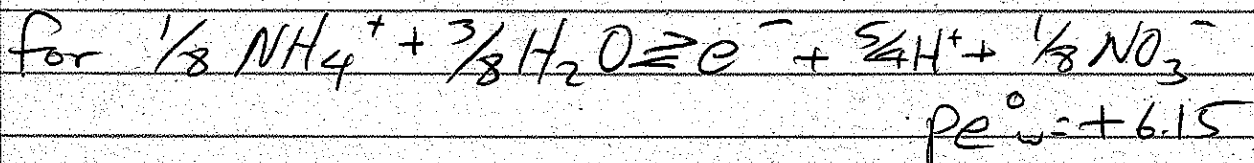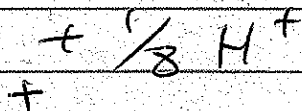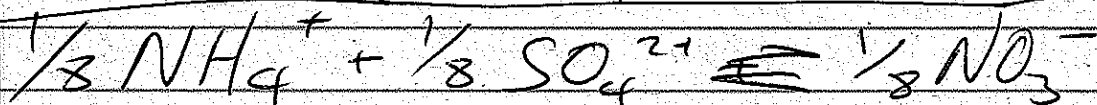
p 10, lines 1 and 2

JIM'S ANSWER - follows p. 440 in M&H.

$$\tfrac{1}{8} NH_4^+ + \tfrac{1}{8} SO_4^{2-} \rightleftharpoons \tfrac{1}{8} NO_3^-$$
$$+ \tfrac{1}{8} H^+$$
$$+$$

for $\tfrac{1}{8} NH_4^+ + \tfrac{3}{8} H_2O \rightleftharpoons e^- + \tfrac{5}{4} H^+ + \tfrac{1}{8} NO_3^-$

$pe^\circ_w = +6.15$

$$\tfrac{1}{8} SO_4^{2-} + \tfrac{5}{4} H^+ + e^- \rightleftharpoons \tfrac{1}{8} HS^- + \tfrac{1}{2} H_2O$$

$$Ox_1 + Red_2 \rightleftharpoons Red_1 + Ox_2$$
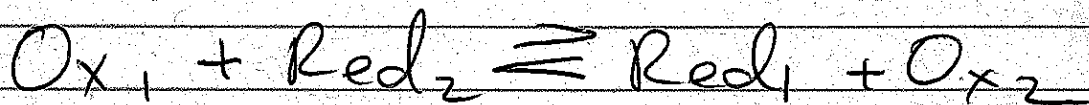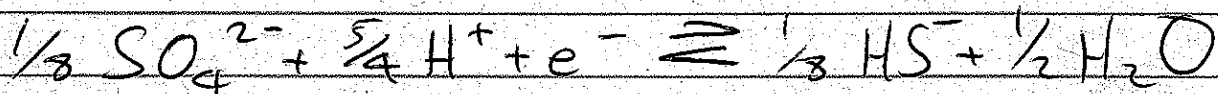
$$\log K = n(pe_1 \cdots$$

$$\Delta G_r^\circ \approx -5.7\, n\, (pe^\circ_{w_1} - pe^\circ_{w_2})\ kJ\ mol^{-1}$$

$$= -5.7 \times 8\,(-3.6 - 6.15)$$

$$= 440$$

$R = 8.3145\,1 \times 10^{-3}\ kJ/mol \cdot K$

$-5.7 \approx -2.3\,RT$, $T = 298K$ (not great assumption for many natural systems) but ok for a ball park.

other way around

$HS^5 \rightarrow SO_4{}^{2-}$ $pe^0_{w(9)} = 4.25 - \left(\frac{9}{8}\right)9 = -5.875$

$NO_3{}^- \rightarrow NO_2{}^-$

$pe^0_{w(9)} = 14.15 - 9 = 5.15$
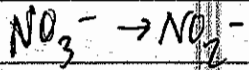
$$-5.7 \times 8 \left(\cancel{14.15}\ 5.15 - (-5.875)\right)$$

calc'ing a
"$pe_{w(9)}$"
instead of
$pe_{w(7)}$

$$= -5.7 \times 8 \left(\right)$$

$$= -501.6$$

normalizing to mol S.

Question 3. A student is studying the oxidation kinetics of Cu(I) in seawater by molecular oxygen in seawater. She notices that the reaction deviates significantly from pseudo-first order kinetics. She assumes that this is because the reaction is reversible, so she adds 10^{-5} M EDTA to the solution. The reaction now displays pseudo-first order kinetics, but the initial rate is about 10x faster than in the original solution.

Let's assume that this is the
reaction of interest:

$$Cu(I) + O_2 = Cu(II) + O_2-$$
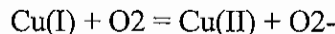
a) How did he determine that the reaction was pseudo-first order in the presence of EDTA?

We can write an expression for the dissapearance of Cu(I):

$-d(Cu(I))/dt = k[Cu(I)][O_2]$, where k is the first-order degradation rate constant.

If we hold [O2] at some steady-state concentration, then we can say
$-d(Cu(I))/dt = k'[Cu(I)]$; where $k'=k[O_2]$ and k' is the pseudo-first order rate constant.

If we integrate this from 0 to t (see you recitation notes for the integration if you need it), we find that $\ln((Cu(I)t)/(Cu(I)o)) = -k't$. If we plot $\ln((Cu(I)t)/(Cu(I)o))$ vs. t, the slope will be $-k'$. If the reaction obeys first-order (or pseudo-first order) kinetics, a plot of $\ln((Cu(I)t)/(Cu(I)o))$ vs. t will give a straight line.

How did he show that it departed from pseudo-first order behavior in the first place?

If the plot of $\ln((Cu(I)t)/(Cu(I)o))$ vs. t did not give a straight line (or if the Cu(I) vs. t plot approached some steady state value, instead of continually decreasing like one would expect for a 1st-order decay process), the wicked smaht student might think that either (1) the reaction is second order, (2) the experiment is flawed, and the O2 concentration is not constant, or (3) there is a back reaction occurring. Option 1 is unlikely: biomolecular reactions involving trace metals will be rare (there just aren't enough of them around... they're TRACE). Option 2 is unlikely because the student is wicked smaht and is monitoring the O2 concentration or keeping it at some high, steady-state value. Option 3 is worth investigating because....

How could this reaction be reversible? What is the reductant?

...this reaction could be reversible! It's the "reaction of interest" in reverse, where O2- (superoxide) is the reductant (right? O2- is a reduced form of O, so it's got electrons to donate to Cu(II), thereby reducing Cu(II) to Cu(I), and rendering O2- a reductant). Jim says that superoxide will react readily with oxidized metals to reduce the metal.

b) How would EDTA affect the reverse reaction? Why is the initial rate so much faster?

If the Cu(II)-EDTA complex is strong and resistant to reduction, the back reaction of Cu(II) to Cu(I) will be hindered. (Cu(II)-EDTA + O2- = Cu(I)-EDTA + O2 is much, much less favorable than Cu(II) + O2- = Cu(I) + O2).

By chelating Cu(II), EDTA is essentially pulling the "reaction of interest" to the right, speeding up the forward reaction, resulting in an increased reaction rate. The stability constant Cu(II)-EDTA is roughly15 orders of magnitude stronger than Cu(I)-EDTA.

Question 3

Bad sketches to accompany Q3:

$[Cu(I)]$ (vertical axis)

t (horizontal axis)

← back rxn of Cu(II) preventing dissapearance of Cu(I) that you might expect for 1st-order (or pseudo-1st order decay process).

add EDTA — prevent back rxn of
$$O_2^{\cdot -} + Cu(II) \longrightarrow Cu(I) + O_2$$

$\ln \dfrac{[Cu(I)]_t}{[Cu(I)]_0}$ (vertical axis)

t (horizontal axis)

← Smothing, not straight. (maybe not this curved...)

$R^2 = 0.9987$

w/o the back rxn, can find $k' = k[O_2]$ from ~~these~~ slope, where
$$-\frac{d[Cu]}{dt} = k[O_2][Cu(I)].$$