# P Set 5
# Aquatic Chem - 1.76

## PROBLEM 1: Q 7.3 in Morel & Hering

Relevant rxns

① "oxidizing Fe(II) to Fe(III) w/ $O_2$"

| | $pe_o$ |
|---|---|
| $Fe^{2+} + 3H_2O \rightleftharpoons Fe(OH)_3(am) + 3H^+ + e^-$ | $-16.0$ |
| $\frac{1}{4}O_2(g) + H^+ + e^- \rightleftharpoons \frac{1}{2}H_2O$ | $20.75$ |
| $Fe^{2+} + \frac{5}{2}H_2O + \frac{1}{4}O_2(g) \rightleftharpoons Fe(OH)_3(am) + 2H^+$ | $4.75 = pe^\circ_{rxn}$ |

$$pe_{rxn} = pe^\circ_{rxn} - \log Q = pe^\circ_{rxn} - \log \frac{[H^+]^2}{[Fe^{2+}][O_2(g)]^{1/4}}$$

$\Delta G = -2.3nRT(pe_{rxn})$ ; need to find the relevant concentrations to find $pe_{rxn}$.

Assume $pO_2 = 10^{-0.7}$ atm.

$[H^+] = 10^{-pH} = 10^{-8}$ M (given)

$[Fe^{2+}] = K_{sp,FeCO_3(s)}/[CO_3^{2-}] = 10^{-10.7}/[CO_3^{2-}]$

I: Solve for $[CO_3^{2-}]$:

$$C_T = [H_2CO_3^*] + [HCO_3^-] + [CO_3^{2-}]$$

$$= \frac{[H^+]^2[CO_3^{2-}]}{Ka_1 Ka_2} + \frac{[H^+][CO_3^{2-}]}{Ka_2} + [CO_3^{2-}]$$

$$= [CO_3^{2-}]\left(\left([H^+]^2/Ka_1Ka_2\right) + \left([H^+]/Ka_2\right) + 1\right)$$

$$[CO_3^{2-}] = C_T \Big/ \left(1 + 10^{-2pH + 10.33 + 6.35} + 10^{-pH + 10.33}\right)$$

At pH=8, $[CO_3^{2-}] = 10^{-3} \Big/ \left(1 + 10^{0.68} + 10^{2.33}\right) = 4.55 \times 10^{-6} M = 10^{-5.34} M$

Then $[Fe^{2+}] = 10^{-10.7} \Big/ 10^{-5.34} = 10^{-5.36} M$

Then $pe_{rxn} = pe^\circ_{rxn} - \log \dfrac{[H^+]^2}{[Fe^{2+}][O_2(g)]^{1/4}}$

$$= 4.75 - \log \frac{(10^{-8})^2}{(10^{-5.36})(10^{-0.7}\,atm)^{1/4}} = 4.75 - \log 10^{-10.225}$$

$pe_{rxn} = 4.75 + 10.225 = 14.97\underline{5}$

$\Delta G_{rxn} = -2.3\, n\, RT (pe_{rxn})$

$= -2.3(1)(8.31451\ J/mol \cdot K)(298K)(14.97\underline{5})\left(\frac{kJ}{1000J}\right)$

$= \boxed{-85.3\ kJ/mol = \Delta G_{rxn}\ Fe^{2+}\ \text{oxidation by}\ O_2}$

② Fix 1 mol inorg. C with $Fe^{2+}$ as the reductant

| | $pe_o$ |
|---|---|
| $Fe^{2+} + 3H_2O \rightleftarrows Fe(OH)_3(am) + 3H^+ + e^-$ | $-16.0$ |
| $\frac{1}{4}HCO_3^- + \frac{5}{4}H^+ + e^- \rightleftarrows \frac{1}{4}\text{"}CH_2O\text{"} + \frac{1}{2}H_2O$ | $+1.8$ |
| $Fe^{2+} + \frac{5}{2}H_2O + \frac{1}{4}HCO_3^- \rightleftarrows Fe(OH)_3(am) + \frac{1}{4}\text{"}CH_2O\text{"} + \frac{7}{4}H^+$ | $-14.2 = pe^o_{rxn}$ |

$$pe_{rxn} = pe_o - \log Q = pe_{o,rxn} - \log \frac{[H^+]^{7/4}[\text{"}CH_2O\text{"}]^{1/4}}{[HCO_3^-]^{1/4}[Fe^{2+}]}$$

We know $[H^+] = 10^{-8} M$, $[Fe^{2+}] = 10^{-5.36} M$; Assume $[CH_2O] = 10^{-5} M$ (Morel, p. 435)

Need $[HCO_3^-]$:

$$C_T = [H_2CO_3^*] + [HCO_3^-] + [CO_3^{2-}]$$

$$= \frac{[H^+][HCO_3^-]}{Ka_1} + [HCO_3^-] + \frac{[HCO_3^-]Ka_2}{[H^+]}$$

$$C_T = [HCO_3^-]\left([H^+]/Ka_1 + 1 + Ka_2/[H^+]\right)$$

$$[HCO_3^-] = C_T \Big/ \left([H^+]/Ka_1 + 1 + Ka_2/[H^+]\right)$$

$$= 10^{-3} \Big/ \left(10^{-pH+6.35} + 1 + 10^{-10.33+pH}\right)$$

$$= 10^{-3} \Big/ \left(10^{-1.65} + 1 + 10^{-2.33}\right) = 10^{-3.01} \; (\approx 10^{-3} M)$$

$$pe_{rxn} = -14.2 - \log \frac{(10^{-8})^{7/4}(10^{-5})^{1/4}}{(10^{-3.01})^{1/4}(10^{-5.36})} = -14.2 - \log(10^{-9.14})$$

$$= -14.2 + 9.142 = -5.06 = pe_{rxn}$$

$$\Delta G_{rxn} = -2.3nRT\,pe_{rxn} = \boxed{28.8 \text{ kJ/mol } Fe^{2+} \text{ oxidized } (= \tfrac{1}{4} \text{mol C fixed})}$$

Assuming perfect efficiency,

$$\left| \frac{\left(28.8 \text{ kJ}/\tfrac{1}{4}\text{mol C reduced}\right)(4)}{\left(-85.3 \text{ kJ/mol Fe}^{2+}\text{ oxid.}\right)} \right| = 1.35 \text{ mol Fe}^{2+}\text{ ox.}/\text{mol C reduced}$$

At 10% efficiency,

$$1.35 \text{ mol Fe}^{2+}\text{ ox}/0.1 \text{ mol C red} = 13.5 \text{ mol Fe}^{2+}\text{ oxid}/\text{mol C reduced}.$$

Survival would be easier if I could get more energy out of $Fe^{2+} + 5/2\, H_2O + 1/4\, O_2(g) \rightleftharpoons Fe(OH)_3(am) + 2H^+$ this rxn.

If $pe_{rxn} = pe_{O_2/H_2O} - pe_{Fe(OH)_3(am)/Fe^{2+}}$

$$= pe^\circ_{rxn} - \log \frac{[H^+]^2}{[Fe^{2+}][O_2(g)]^{1/4}}$$

and

$$\Delta G = -2.3nRT(pe_{rxn}) = -2.3nRT\left(pe^\circ_{rxn} - \underbrace{\log \frac{[H^+]^2}{[Fe^{2+}][O_2(g)]^{1/4}}}\right),$$

can make $\Delta G$ more negative if we ↓ this term

This can happen if we 1) reduce $[H^+]$ or
2) increase $[Fe^{2+}]$.

An increase in pH is beneficial for organism's survival.
Fe(II) chelation generally reduces $[Fe^{2+}]$, so it would not aid survival unless an organic ligand sequestered $Fe^{2+}$ into the organism, thereby ↑ intracellular $[Fe^{2+}]$.
Fe(III) chelation would solubilize $Fe(OH)_3(am)$, which might drive $Fe^{2+} + 3H_2O \rightleftharpoons Fe(OH)_3(am) + 3H^+ + e^-$ to the right (indirectly), & reduce $Fe^{2+}$ — not favorable. Clearly, as an organism living on the solid $Fe(OH)_3(am)$, solubilization of the substrate is disfavored.

Survival would also we easier if this rxn

$Fe^{2+} + \frac{5}{2} H_2O + \frac{1}{4} HCO_3^- \rightleftarrows Fe(OH)_3(am) + \frac{1}{4}\text{"}CH_2O\text{"} + \frac{7}{4} H^+$

required less energy.

$$\Delta G_{rxn} = -2.3nRT \left( \text{"}pe^\circ_{rxn}\text{"} - \underbrace{\log \frac{[H^+]^{7/4} [\text{"}CH_2O\text{"}]^{1/4}}{[HCO_3^-]^{1/4} [Fe^{2+}]}}_{\text{becomes smaller.}} \right)$$

This rxn becomes more favorable as this term becomes smaller.

Again, an increase in pH is favored. (will reduce $[HCO_3^-]$, not significant until pH>10.33), a drop in $[Fe^{2+}]$ is favored, and solubilization of $Fe(OH)_3(am)$ is disfavored.

# PROBLEM 2 : Fe in the Arabian Sea

**Part 1:**

At 150(m), Fe(II) = 0.7 nM

$\{H^+\} = 10^{-7.6}$

$pO_2 = 0.004$ atm

$Fe_T = 1.3\ nM = [Fe(II)]_T + [Fe(III)]_T$

The pe is controlled by the $O_2/H_2O$ couple:

$$\tfrac{1}{4}O_2(g) + H^+ + e^- = \tfrac{1}{2}H_2O \qquad pe^\circ = 20.75$$

$$pe = pe^\circ - \log\frac{1}{(pO_2)^{1/4}\{H^+\}} = 20.75 - \log\frac{1}{(0.004\,atm)^{1/4}\,10^{-7.6}}$$

$$= 20.75 - \log 10^{+8.20} = 20.75 - 8.20 \ \boxed{= 12.55 \\ = \text{pe of the system}}$$

We want to solve for $[Fe^{2+}]$ at Thermodynamic Equilibrium.

$$Fe^{3+} + e^- = Fe^{2+} \qquad pe^\circ = 13.0$$

$$pe_{Fe\,rxn} = pe^\circ - \log\frac{\{Fe^{2+}\}}{\{Fe^{3+}\}} = pe^\circ - \log\frac{\gamma_{Fe^{2+}}}{\gamma_{Fe^{3+}}} - \log\frac{[Fe^{2+}]}{[Fe^{3+}]}$$

At equilibrium $pe_{sys} = pe_{Fe\,rxn}$,

$$\log\frac{[Fe^{2+}]}{[Fe^{3+}]} = pe^\circ - pe_{sys} - \log\frac{\gamma_{Fe^{2+}}}{\gamma_{Fe^{3+}}} \ *$$

$$= 13.0 - 12.55 - 0.61 = -0.16$$

Eqn 1 $$\boxed{\frac{[Fe^{2+}]}{[Fe^{3+}]} = 10^{-0.16}}$$ (so $[Fe^{3+}] > [Fe^{2+}]$)

$$* \ \log\gamma = -Az_i^2\left[\frac{I^{1/2}}{1+I^{1/2}} - bI\right]; \quad b = 0.3,\ I = 0.7,\ z_{Fe^{2+}} = 2,\ z_{Fe^{3+}} = 3$$

$\log\gamma_{Fe^{2+}} = -0.491;\ \gamma_{Fe^{2+}} = 0.323$

$\log\gamma_{Fe^{3+}} = -1.105;\ \gamma_{Fe^{3+}} = 0.0785$

$$-\log\frac{\gamma_{Fe^{2+}}}{\gamma_{Fe^{3+}}} = -\log\frac{10^{-0.491}}{10^{-1.105}} = -\log 10^{0.614}$$

Now, we will consider complexation, where $OH^-$ is the only ligand considered.

For the generic complexation rxn:

$$m\,Fe^{x+} + n\,OH^- \rightleftharpoons Fe_mOH_n^{(x-n)}$$

Have $$\beta = \frac{\{Fe_mOH_n^{(x-n)}\}}{\{Fe^{x+}\}^m\ \{OH^-\}^n} = \frac{\gamma_{Fe_mOH_n^{(x-n)}}\,[Fe_mOH_n^{(x-n)}]}{(\gamma_{Fe^{x+}})^m\,[Fe^{x+}]^m\ \underset{\substack{\uparrow\\ \text{leaving in } \{OH^-\},\\ \text{because we have}\\ \{H^+\}=10^{-pH},\\ K_w=\{H^+\}\{OH^-\}\\ \Rightarrow \{OH^-\}=K_w/\{H^+\}}}{\{OH^-\}^n}}$$

Let $$\beta_{app} = \frac{[Fe_mOH_n^{(x-n)}]}{[Fe^{x+}]^m\ \{OH^-\}^n} = \beta\,\frac{(\gamma_{Fe^{x+}})^m}{(\gamma_{Fe_mOH^{(x-n)}})}$$

$$\log\beta_{app} = \log\beta_{in\,book} - \log\gamma_{Fe_mOH^{(x-n)}} + m\log\gamma_{Fe^{x+}}$$

Will will use values given in Table 6.5 (p. 346)... even though these should really be measured.

| Spp | $\log\gamma_{spp}$ |
|---|---|
| $i^{-1}$ | $-0.17$ |
| $i^{0}$ | $0.05$ |
| $i^{+1}$ | $-0.17$ |
| $i^{+2}$ | $-0.491$ |
| $i^{+3}$ | $-1.105$ |
| $i^{+4}$ | $-1.964$ |

| Complex | $\log\beta_{in\,book}$ | $-\log\gamma_{Fe_mOH^{(x-n)}} + m\log\gamma_{Fe^{x+}}$ | $\log\beta_{app}$ (keep only 1 sig fig after decimal) |
|---|---|---|---|
| Fe(II) $FeOH^+$ | 4.5 | $-(-0.17) + (1)(-0.491)$ | $4.1\underline{79} = 4.2$ |
| $Fe(OH)_2^0$ | 7.4 | $-(0.05) + (1)(-0.491)$ | $6.8\underline{59} = 6.9$ |
| $Fe(OH)_3^-$ | 11.0 | $-(-0.17) + (1)(-0.491)$ | $10.6\underline{79} = 10.7$ |
| Fe(III) $FeOH^{2+}$ | 11.8 | $-(-0.491) + (1)(-1.105)$ | $11.1\underline{86} = 11.2$ |
| $Fe(OH)_2^+$ | 22.3 | $-(-0.17) + (1)(-1.105)$ | $21.3\underline{65} = 21.4$ |
| $Fe(OH)_4^-$ | 34.4 | $-(-0.17) + (1)(-1.105)$ | $33.4\underline{65} = 33.5$ |
| $Fe_2(OH)_2^{4+}$ | 25.5 | $-(-1.964) + (2)(-1.105)$ | $25.2\underline{54} = 25.3$ |

From complexation reactions (hydrolysis only), we have

$$[Fe(II)]_T = [Fe^{2+}] + [FeOH^+] + [Fe(OH)_2^\circ] + [Fe(OH)_3^-]$$

$$= [Fe^{2+}]\left(1 + \beta^{app}_{FeOH^+}\{OH^-\} + \beta^{app}_{Fe(OH)_2^\circ}\{OH^-\}^2 + \beta^{app}_{Fe(OH)_3^-}\{OH^-\}^3\right)$$

$$\frac{[Fe^{2+}]}{[Fe(II)]_T} = \frac{1}{\left(1 + 10^{4.2}(10^{-14+pH}) + 10^{6.9}(10^{-28+2pH}) + 10^{10.7}(10^{-42+3pH}\right)}$$

$$= 1/\left(1 + 10^{-2.2} + 10^{-5.9} + 10^{-8.5}\right) = \boxed{10^{-0.00273} = \frac{[Fe^{2+}]}{[Fe(II)]_T}}$$

Eqn 2

$$[Fe(III)]_T = [Fe^{3+}] + [FeOH^{2+}] + [Fe(OH)_2^+] + [Fe(OH)_4^-] + 2[Fe_2(OH)_2^{4+}]$$

$$= [Fe^{3+}]\left(1 + \beta^{app}_{FeOH^{2+}}\{OH^-\} + \beta^{app}_{Fe(OH)_2}\{OH^-\}^2 + \beta^{app}_{Fe(OH)_4^-}\{OH^-\}^4 + 2\beta_{Fe_2(OH)_2^{4+}}[Fe^{3+}]\{OH^-\}^2\right)$$

$$\frac{[Fe^{3+}]}{[Fe(III)]_T} = \frac{1}{\left(1 + 10^{11.2-6.4} + 10^{21.4-6.4-6.4} + 10^{33.5-(6.4\times4)} + 2(10^{25.3-(2\times6.4)})[Fe^{3+}]\right)}$$

at most = $10^{-8.9}$ = 1.3nM

$$= \frac{1}{\left(1 + 10^{4.8} + 10^{8.6} + 10^{7.9} + \underbrace{2(10^{12.5})(10^{-8.9})}_{10^{3.9}\text{, at most} \ll 10^{8.6}}\right)}$$

can neglect

$$\boxed{= 10^{-8.68} = \frac{[Fe^{3+}]}{[Fe(III)]_T}}$$

Eqn 3

Now, we can be very clever and find:

Eqn 4

$$\frac{[Fe(II)]_T}{[Fe(III)]_T} = \left(\frac{[Fe^{3+}]/[Fe(III)]_T}{[Fe^{2+}]/[Fe(II)]_T}\right)\left(\frac{[Fe^{2+}]}{[Fe^{3+}]}\right) = \left(\frac{\text{Eqn 3}}{\text{Eqn 2}}\right)(\text{Eqn 1})$$

$$\boxed{\frac{[Fe(II)]_T}{[Fe(III)]_T} = \left(\frac{10^{-8.68}}{10^{-0.00278}}\right)\left(10^{-0.16}\right) = 10^{-8.84}}$$

Then $[Fe(III)]_T >> [Fe(II)]_T$ ,

and $Fe_T = 10^{-8.9} M = \underset{\text{negligable}}{\cancel{[Fe(II)]_T}} + [Fe(III)]_T$

$$[Fe(III)]_T = 10^{-8.9} M$$

Use Eqn 4 to solve for $[Fe(II)]_T$

$$[Fe(II)]_T = (10^{-8.84})(10^{-8.9}) = 10^{-17.74} M$$ at T.D. equilibrium, where only $OH^-$ ligands are considered.

This certainly is <u>not</u> what was observed in the Arabian Sea ($[Fe(II)]_{T,\text{Arabian Sea}} = 0.7 nM = 10^{-9.15} M >>$

$[Fe(II)]_{T,TD} = 10^{-17.74} M$ ).

Something is acting to increase the dissolved $[Fe(II)]_T$ !
Maybe it's an organic ligand ($L_1$), where $[L_1] = 10^{-8} M$.

### Binding Constant of Organic ligand, $L_1$:

From

Eqn 5
$$\frac{[Fe^{2+}]}{[Fe(II)]_T} = \frac{1}{\left(\underbrace{1 + 10^{-2.2} + 10^{-3.9} + 10^{-8.5}}_{\text{From Eqn 2.}} + \underbrace{\beta_{L_1}[L_1]}_{\text{new term to account for } L_1}\right)}$$

↑ need to solve for this; rearrange eqn 4:

assumes $L_1$ forms a mono-nuclear complex w/ $Fe^{2+}$
$L_1 : Fe^{2+}$ ratio in complex $= 1:1$

Eqn 6
$$\frac{[Fe^{2+}]}{[Fe(II)]_T} = \left(\frac{[Fe^{3+}]/[Fe(III)]_T}{[Fe(II)]_T/[Fe(III)]_T}\right)\left(\frac{[Fe^{2+}]}{[Fe^{3+}]}\right)$$ ; where $\frac{[Fe^{2+}]}{[Fe^{3+}]} = 10^{-0.16}$ (Eqn 1),

$\frac{[Fe^{3+}]}{[Fe(III)]_T} = 10^{-8.68}$ (Eqn 3),

solve for $\frac{[Fe(II)]_T}{[Fe(III)]_T}$

$$\frac{[Fe(II)]_T}{[Fe(III)]_T} = \frac{\left(10^{-9.15}\right)}{\left(\underbrace{10^{-8.9}}_{[Fe]_T} - \underbrace{10^{-9.15}}_{[Fe(II)]_T}\right)} = \frac{10^{-9.15}}{10^{-9.026}} = 10^{-0.124}$$

Then, Eqn 6 gives

$$\frac{[Fe^{2+}]}{[Fe(II)]_T} = \left(\frac{10^{-8.68}}{10^{-0.124}}\right)\left(10^{-0.16}\right) = 10^{-8.72}$$

If we assume $\beta_{L_1}[L_1] \gg$ all other $\beta$ [ligand] terms, then Eqn 5 reduces to:

$$\frac{[Fe^{2+}]}{[Fe(II)]_T} = \frac{1}{\beta_{L_1}[L_1]}$$

$$\beta_{L_1} = \frac{1}{\left([Fe^{2+}]/[Fe(II)]_T\right)\left([L_1]\right)} = \frac{1}{\left(10^{-8.72}\right)\left(10^{-8}\right)} = \frac{1}{10^{-16.72}}$$

$$= 10^{16.72}$$

Check assumption: is $\beta_{L_1}[L_1] = 10^{+8.72} \gg$ "$\beta$ [ligand]" terms in Eqn 5 ?

$$10^{8.72} \gg 1,\ 10^{-2.2},\ 10^{-3.9},\ 10^{-8.5} \quad ✓$$

So assumption is satisfied. Wicked.

Part 2: what if $NO_3^-/NO_2^-$ couple controls pe in the OMZ in the Arabian Sea? (maybe I should become a rapper...)

$\uparrow$ "$O_2$ minimum zone"

$$\tfrac{1}{2}NO_3^- + H^+ + e^- \rightleftharpoons \tfrac{1}{2}NO_2^- + \tfrac{1}{2}H_2O \qquad pe^\circ = 14.15$$

$$pe = pe^\circ - \log\frac{\{NO_2^-\}^{1/2}}{\{NO_3^-\}^{1/2}\{H^+\}} = pe^\circ - \log\frac{\{\gamma_{NO_2^-}\}^{1/2}[NO_2^-]^{1/2}}{\{\gamma_{NO_3^-}\}^{1/2}[NO_3^-]^{1/2}\{H^+\}}$$

$$= pe^\circ \underbrace{\cancel{-\tfrac{1}{2}\log\left(\frac{\gamma_{NO_2^-}}{\gamma_{NO_3^-}}\right)}}_{0\text{, as we are assuming } \gamma_{NO_2^-} = \gamma_{NO_3^-}} - \log\frac{[NO_2^-]^{1/2}}{[NO_3^-]^{1/2}\{H^+\}},$$

if $[NO_2^-] = 10^{-6}\,M$

$[NO_3^-] = 10^{-7}\,M$,

$\gamma_{NO_2^-} = \gamma_{NO_3^-}$,

$\{H^+\} = 10^{-7.6}$

$$pe = 14.15 - 0 - 8.1 = 6.05 = \text{pe of the system.}$$

As we found earlier,

$$\log\frac{[Fe^{2+}]}{[Fe^{3+}]} = pe^\circ_{Fe^{2+}/Fe^{3+}} - pe_{sys} - \log\frac{\gamma_{Fe^{2+}}}{\gamma_{Fe^{3+}}}$$

$$= 13.0 - 6.05 - 0.61 = 6.34$$

$$\frac{[Fe^{2+}]}{[Fe^{3+}]} = 10^{6.34}$$

Complexation should be unchanged (if pH is unchanged), so we can plug this $[Fe^{2+}]/[Fe^{3+}]$ into Eqn 4;

$$\frac{[Fe(II)]_T}{[Fe(III)]_T} = \left(\frac{10^{-8.68}}{10^{-0.00279}}\right)\left(10^{6.34}\right) = 10^{-2.34}$$

$$[Fe(II)]_T = 10^{-2.34}\,[Fe(III)]_T$$

$$= 10^{-2.34}\left([Fe]_T - [Fe(II)]_T\right)$$

$$[Fe(II)]_T + 10^{-2.34}\left([Fe(II)]_T\right) = 10^{-2.34}\left([Fe]_T\right)$$

$$[Fe(II)]_T = \frac{10^{-2.34}\left([Fe]_T\right)}{\left(1+10^{-2.34}\right)} = \frac{\left(10^{-2.34}\right)\left(10^{-8.9}\right)}{\left(1+10^{-2.34}\right)} = 10^{-11.2}\,M$$

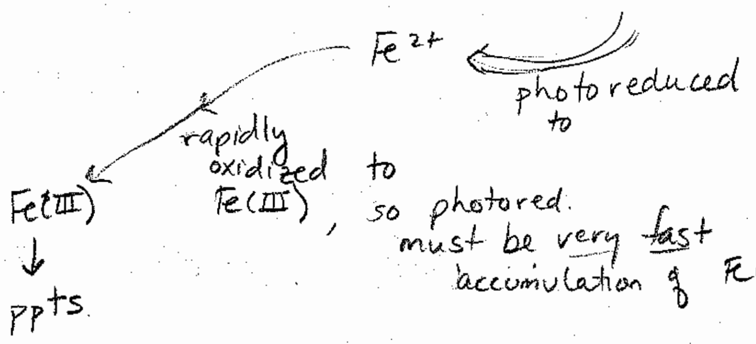
So, even when $NO_3^-/NO_2^-$ couple controls $Fe^{2+}/Fe^{3+}$, we still find that the T.D.'lly favored $[Fe(II)]_T = 10^{-11.2}\,M$ $<<$ $[Fe(II)]_{T,\text{observed}} = 10^{-9.15}\,M$ (but it is certainly much closer than if the $H_2O/O_2$ couple controls $Fe^{2+}/Fe^{3+}$).

## photochemistry - causing surface Fe(II) spike?

The very-brief summary:

$$FeOH^{2+} \xrightarrow[\substack{k\sim\text{order}\\ s-min}]{h\nu} Fe^{2+} + \cdot OH$$

- net effect of iron photoreduction:
  - dissolve Fe(III) minerals
  - dissociate Fe(III) chelation complexes



so photored. must be very fast to result in accumulation of Fe(II)

## Why is there a TDFe max coincident with TDFe(II) max?

The ferric ion (Fe(III)) is much less soluable than the ferrous ion (Fe(II)). Fe(III) solids rapidly form and precipitate, while Fe(II) is quite stable as a dissolved species. If there is a process acting to increase Fe(II), TDFe will also increase. However, Fe(II) is terribly disfavored by oxidizing conditions, and one would expect that it would be nearly nonexistent at thermodynamic equilibrium. Why is it showing up in seawater? Perhaps microorganisms growing in the ocean have evolved an enzyme that can reduce Fe(III) (which should be abundant on colloidal Fe(III)-mineral phases) to Fe(II). Perhaps the oxidation of Fe(II) is kinetically hindered (slow), and so any Fe(II) produced by microbial activity or photochemical reactions in the euphotic zone would persist at depth. I'm sure there are many creative explanations of this phenomenon that we can all share together over a nice cup of cocoa.