Redox Chemistry Problem Set

1. Question 7.3 in Morel and Hering

2. Figure 1, below, shows a depth profile of Fe(II) and total dissolved Fe in the Arabian Sea. Note that Fe(II) reaches its highest values where the dissolved oxygen is very low. This is a typical feature of Fe(II) in low O_2 environments.

At 150m, the following parameters were measured:

Fe(II) = 0.7nMTotal dissolved Fe (i.e. Fe(II) + Fe(III)) = 1.3nM PO₂ = 0.004atm pH = 7.6

Assuming pe is controlled by the O_2/H_2O couple, determine if the observed Fe(II) concentrations can be accounted for by thermodynamics. Assume only hydrolysis complexes for Fe(II) and Fe(III) and that Fe(OH)₃ (am) is not present. Also, you may use the constants in Table 6.3 from Morel and Hering.

If your calculations predict a lower value of Fe(II) than observed, one possibility is that the Fe(II) is stabilized by organic ligands. If 10^{-8} M of an Fe(II) binding ligand was detected, what would its stability constant need to be in order to give rise to the required concentration?

Figure 2 shows another profile in the Arabian Sea along with nitrite. In general Fe(II) tracks the deep nitrite maxima (a feature associated with denitrification). Determine whether Fe(II) could be controlled by the NO_3^-/NO_2^- couple using the conditions above and assuming nitrite = $10^{-6}M$ and nitrate = $10^{-7}M$.

The high near-surface concentrations of Fe(II) in Figure 1 have not been seen elsewhere and may be contamination. However, they could arise from photochemical processes. Provide a brief summary of the photochemical reactions that would give rise to Fe(II) (from Morel and Hering).

Finally, suggest why there may be a local maximum in total dissolved Fe coincident with the Fe(II) maximum.



Figure 1



Figure 2