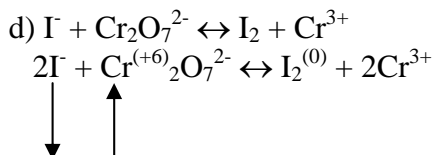
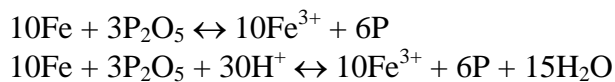
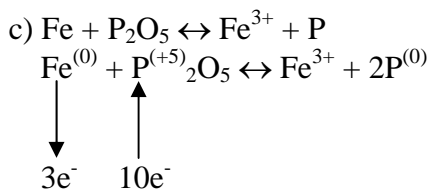
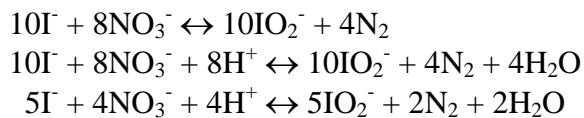
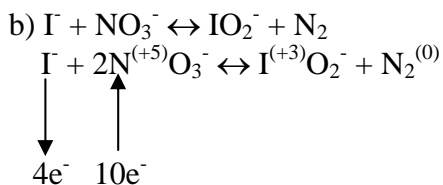
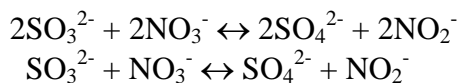
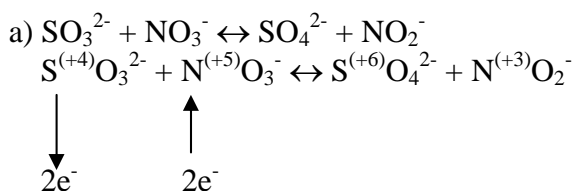


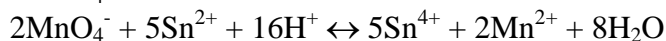
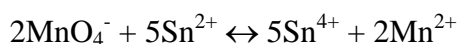
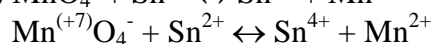
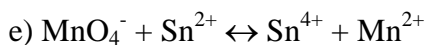
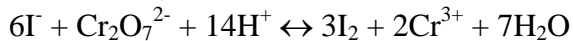
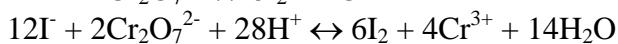
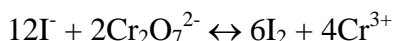
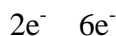
**PRINCIPLES OF GEOCHEMISTRY**  
**GEOL 423**  
**FALL 2009**  
**PROBLEM SET #6**  
**ANSWERS**

Problem 1:

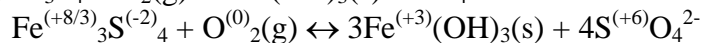
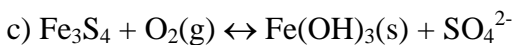
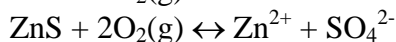
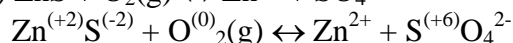
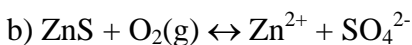
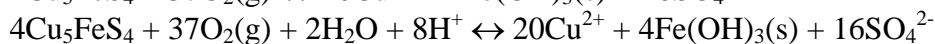
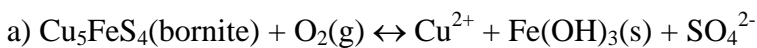
- a) P in  $\text{H}_3\text{PO}_4$ ; +5
- b) Cr in  $\text{Cr}_2\text{O}_4^{2-}$ ; +3
- c) Cl in  $\text{NaClO}_2$ ; +3
- d) N in  $\text{NO}_2^-$ ; +3
- e) N in  $\text{N}_2\text{O}$ ; +1

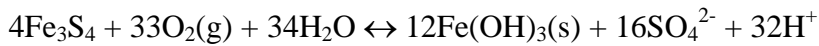
Problem 2: Balance the following overall oxidation-reduction reactions:





Problem 3:

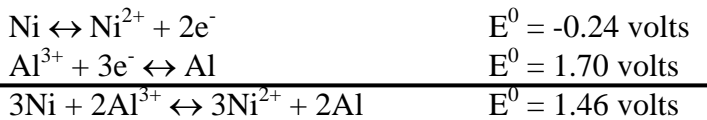




Reaction c) is the only one that generates acid. Reaction a) actually consumes acid, and reaction b) neither generates nor consumes acid.

Generation of acid is important because it can result in the lowering of pH of stream and lake waters below that optimal for enzyme function for many forms of life. Moreover, many toxic metals are more soluble at low pH, so acid generation from the oxidation of sulfides can result in elevated toxic metal concentrations in natural waters.

Problem 4:



$$E = 1.46 + (0.0592/6) \log ([\text{Ni}^{2+}]^3/[\text{Al}^{3+}]^2)$$

$$E = 1.46 + 0.00987 \log (10^{-2}) = 1.44 \text{ V}$$

Problem 5:

We first write:  $\text{Cu} \leftrightarrow \text{Cu}^{2+} + 2\text{e}^-$  for which  $E^0 = 0.34$  volts according to Table 14.3 in Faure. Alternatively  $E^0$  can be calculated from the Gibbs free energy change of reaction according to:

$$\Delta G_r^\circ = \Delta G_f^\circ(\text{Cu}^{2+}) + \Delta G_f^\circ(\text{e}^-) - \Delta G_f^\circ(\text{Cu}) = 15.65 + (0) - (0) = 15.65 \text{ kcal mol}^{-1}$$

$$E^0 = \Delta G_r^\circ / (n\mathfrak{F}) = 15.65 / (2 \cdot 23.06) = 0.34 \text{ V}$$

$$Eh = E^0 + (0.0592/2) \log ([\text{Cu}^{2+}])$$

$$Eh = 0.34 + 0.0296(-3) = 0.251$$

The pH does not need to be taken into account because the important reaction here is pH-independent!

Problem 6:

a) First we calculate  $\log K$  for the reaction:

$$\begin{array}{l} 4\text{Fe}^{3+} + 2\text{H}_2\text{O} \leftrightarrow 4\text{Fe}^{2+} + 4\text{H}^+ + \text{O}_2(\text{g}) \\ \Delta G_r^\circ = 4\Delta G_f^\circ(\text{Fe}^{2+}) + 4\Delta G_f^\circ(\text{H}^+) + \Delta G_f^\circ(\text{O}_2) - 4\Delta G_f^\circ(\text{Fe}^{3+}) - 2\Delta G_f^\circ(\text{H}_2\text{O}) \\ = 4(-18.85) + 4(0) + (0) - 4(-1.12) - 2(-56.687) = 42.454 \text{ kcal mol}^{-1} \end{array}$$

$$\log K = -\Delta G_r^\circ / (2.3025RT) = -42,454 / (2.3025 \cdot 1.987 \cdot 298.15) = -31.12$$

$$K = \frac{[\text{Fe}^{2+}]^4 [\text{H}^+]^4 p_{\text{O}_2}}{[\text{Fe}^{3+}]^4}$$

$$\log K = -31.12 = 4 \log ([\text{Fe}^{2+}]/[\text{Fe}^{3+}]) - 4 \text{pH} + \log p_{\text{O}_2}$$

$$-31.12 = 4 \log ([\text{Fe}^{2+}]/[\text{Fe}^{3+}]) - 4(8.2) + \log (0.21)$$

$$4 \log ([\text{Fe}^{2+}]/[\text{Fe}^{3+}]) = 2.36$$

$$[\text{Fe}^{2+}]/[\text{Fe}^{3+}] = 3.89$$

b) The approach is to first calculate the  $Eh$  fixed by the Ce reaction, and then use that value to calculate the value of  $[\text{Fe}^{2+}]/[\text{Fe}^{3+}]$  assuming it is in equilibrium with the Ce reaction.

$$Eh = 1.61 + 0.0592 \log ([\text{Ce}^{4+}]/[\text{Ce}^{3+}])$$

$$[\text{Ce}^{3+}]/[\text{Ce}^{4+}] = 10^{17} \text{ so } [\text{Ce}^{4+}]/[\text{Ce}^{3+}] = 10^{-17}$$

$$Eh = 1.61 + 0.0592(10^{-17}) = 0.604$$

Now, for the half-reaction  $\text{Fe}^{2+} \leftrightarrow \text{Fe}^{3+} + e^-$  we calculate:

$$\Delta G_r^\circ = \Delta G_f^\circ(\text{Fe}^{3+}) + \Delta G_f^\circ(e^-) - \Delta G_f^\circ(\text{Fe}^{2+}) = (-1.12) + (0) - (-18.85) = 17.73 \text{ kcal mol}^{-1}$$

$$E^0 = \Delta G_r^\circ / (n\mathcal{F}) = 17.73 / (1 \cdot 23.06) = 0.769 \text{ V}$$

$$Eh = E^0 + 0.0592 \log ([\text{Fe}^{3+}]/[\text{Fe}^{2+}])$$

$$0.604 = 0.769 + 0.0592 \log ([\text{Fe}^{3+}]/[\text{Fe}^{2+}])$$

$$\log ([\text{Fe}^{3+}]/[\text{Fe}^{2+}]) = -2.79$$

$$[\text{Fe}^{3+}]/[\text{Fe}^{2+}] = 0.0016$$

$$[\text{Fe}^{2+}]/[\text{Fe}^{3+}] = 622$$

Comparison of  $[\text{Fe}^{2+}]/[\text{Fe}^{3+}] = 3.89$  from part a with  $[\text{Fe}^{2+}]/[\text{Fe}^{3+}] = 622$  from part b shows that these two values are quite different. The likely cause of the difference is that not all of the redox couples involved, i.e.,  $\text{Ce}^{3+}/\text{Ce}^{4+}$ ,  $\text{Fe}^{2+}/\text{Fe}^{3+}$ , and  $\text{H}_2\text{O}/\text{O}_2$  are in equilibrium with one another. Recall that we discussed in class how redox reactions are very slow to equilibrate and are often out of equilibrium.