PRINCIPLES OF GEOCHEMISTRY
GEOL 423
FALL 2009
PROBLEM SET #6

Problem 1: Provide the oxidation number for the indicated element in each of the following:

a) P in H_3PO_4; b) Cr in $Cr_2O_4^{2-}$; c) Cl in $NaClO_2$; d) N in NO_2^-; e) N in N_2O

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

a) $SO_3^{2-} + NO_3^- \leftrightarrow SO_4^{2-} + NO_2^-$
b) $I^- + NO_3^- \leftrightarrow IO_2^- + N_2$
c) $Fe + P_2O_5 \leftrightarrow Fe^{3+} + P$
d) $I^- + Cr_2O_7^{2-} \leftrightarrow I_2 + Cr^{3+}$
e) $MnO_4^- + Sn^{2+} \leftrightarrow Sn^{4+} + Mn^{2+}$

Problem 3: Balance the following three overall redox reactions. Which reactions ***generate*** acid and why is this a problem?

a) Cu_5FeS_4(bornite) + $O_2(g) \leftrightarrow Cu^{2+} + Fe(OH)_3(s) + SO_4^{2-}$
b) $ZnS + O_2(g) \leftrightarrow Zn^{2+} + SO_4^{2-}$
c) $Fe_3S_4 + O_2(g) \leftrightarrow Fe(OH)_3(s) + SO_4^{2-}$

Problem 4: Combine the Al and Ni electrode half reactions and calculate the EMF when $[Ni^{2+}]^3/[Al^{3+}]^2 = 10^{-2}$.

Problem 5: Calculate the Eh of a water in equilibrium with native Cu for which the dissolved Cu^{2+} concentration is 10^{-3} mol L^{-1}. Does pH need to be taken into account in this problem? Why?

Problem 6:

a) Assuming equilibrium, what is the ratio $[Fe^{2+}]/[Fe^{3+}]$ in seawater that you would calculate from

$$4Fe^{3+} + 2H_2O \leftrightarrow 4Fe^{2+} + 4H^+ + O_2(g)$$

if pH = 8.2 and seawater is in equilibrium with the Earth's atmosphere?

b) $E°$ for the reaction $Ce^{3+} \leftrightarrow Ce^{4+} + e^-$ is 1.61 volts. The ratio Ce^{3+}/Ce^{4+} in surface waters in the ocean has been estimated to be 10^{17}. If the redox half-reaction for Ce is in equilibrium with the half-reaction $Fe^{2+} \leftrightarrow Fe^{3+} + e^-$ at 25 °C, what should be the $[Fe^{2+}]/[Fe^{3+}]$ ratio in these waters? If there is a significant difference, why?