

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 $\text{Cr}_2\text{O}_4^{2-}$; 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) $\text{SO}_3^{2-} + \text{NO}_3^- \leftrightarrow \text{SO}_4^{2-} + \text{NO}_2^-$
b) $\text{I}^- + \text{NO}_3^- \leftrightarrow \text{IO}_2^- + \text{N}_2$
c) $\text{Fe} + \text{P}_2\text{O}_5 \leftrightarrow \text{Fe}^{3+} + \text{P}$
d) $\text{I}^- + \text{Cr}_2\text{O}_7^{2-} \leftrightarrow \text{I}_2 + \text{Cr}^{3+}$
e) $\text{MnO}_4^- + \text{Sn}^{2+} \leftrightarrow \text{Sn}^{4+} + \text{Mn}^{2+}$

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

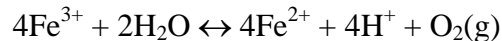
- a) $\text{Cu}_5\text{FeS}_4(\text{bornite}) + \text{O}_2(\text{g}) \leftrightarrow \text{Cu}^{2+} + \text{Fe}(\text{OH})_3(\text{s}) + \text{SO}_4^{2-}$
b) $\text{ZnS} + \text{O}_2(\text{g}) \leftrightarrow \text{Zn}^{2+} + \text{SO}_4^{2-}$
c) $\text{Fe}_3\text{S}_4 + \text{O}_2(\text{g}) \leftrightarrow \text{Fe}(\text{OH})_3(\text{s}) + \text{SO}_4^{2-}$

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

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

Problem 6:

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



if $\text{pH} = 8.2$ and seawater is in equilibrium with the Earth's atmosphere?

b) E° for the reaction $\text{Ce}^{3+} \leftrightarrow \text{Ce}^{4+} + \text{e}^-$ is 1.61 volts. The ratio $\text{Ce}^{3+}/\text{Ce}^{4+}$ 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 $\text{Fe}^{2+} \leftrightarrow \text{Fe}^{3+} + \text{e}^-$ at 25 °C, what should be the $[\text{Fe}^{2+}]/[\text{Fe}^{3+}]$ ratio in these waters? If there is a significant difference, why?