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

Problem 1:

a) P in H_3PO_4; +5
b) Cr in $Cr_2O_4^{2-}$; +3
c) Cl in $NaClO_2$; +3
d) N in NO_2^-; +3
e) N in N_2O; +1

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

a) $SO_3^{2-} + NO_3^- \leftrightarrow SO_4^{2-} + NO_2^-$

$S^{(+4)}O_3^{2-} + N^{(+5)}O_3^- \leftrightarrow S^{(+6)}O_4^{2-} + N^{(+3)}O_2^-$

$\downarrow$ $2e^-$ (from S) $\uparrow$ $2e^-$ (to N)

$2SO_3^{2-} + 2NO_3^- \leftrightarrow 2SO_4^{2-} + 2NO_2^-$

$SO_3^{2-} + NO_3^- \leftrightarrow SO_4^{2-} + NO_2^-$

b) $I^- + NO_3^- \leftrightarrow IO_2^- + N_2$

$I^- + 2N^{(+5)}O_3^- \leftrightarrow I^{(+3)}O_2^- + N_2^{(0)}$

$\downarrow$ $4e^-$ (from I) $\uparrow$ $10e^-$ (to N)

$10I^- + 8NO_3^- \leftrightarrow 10IO_2^- + 4N_2$

$10I^- + 8NO_3^- + 8H^+ \leftrightarrow 10IO_2^- + 4N_2 + 4H_2O$

$5I^- + 4NO_3^- + 4H^+ \leftrightarrow 5IO_2^- + 2N_2 + 2H_2O$

c) $Fe + P_2O_5 \leftrightarrow Fe^{3+} + P$

$Fe^{(0)} + P^{(+5)}{}_2O_5 \leftrightarrow Fe^{3+} + 2P^{(0)}$

$\downarrow$ $3e^-$ (from Fe) $\uparrow$ $10e^-$ (to P)

$10Fe + 3P_2O_5 \leftrightarrow 10Fe^{3+} + 6P$

$10Fe + 3P_2O_5 + 30H^+ \leftrightarrow 10Fe^{3+} + 6P + 15H_2O$

d) $I^- + Cr_2O_7^{2-} \leftrightarrow I_2 + Cr^{3+}$

$2I^- + Cr^{(+6)}{}_2O_7^{2-} \leftrightarrow I_2^{(0)} + 2Cr^{3+}$

$\downarrow$ (from I) $\uparrow$ (to Cr)

$2e^-$ $6e^-$

$12I^- + 2Cr_2O_7^{2-} \leftrightarrow 6I_2 + 4Cr^{3+}$
$12I^- + 2Cr_2O_7^{2-} + 28H^+ \leftrightarrow 6I_2 + 4Cr^{3+} + 14H_2O$
$6I^- + Cr_2O_7^{2-} + 14H^+ \leftrightarrow 3I_2 + 2Cr^{3+} + 7H_2O$

e) $MnO_4^- + Sn^{2+} \leftrightarrow Sn^{4+} + Mn^{2+}$
$Mn^{(+7)}O_4^- + Sn^{2+} \leftrightarrow Sn^{4+} + Mn^{2+}$

$5e^-$ $2e^-$

$2MnO_4^- + 5Sn^{2+} \leftrightarrow 5Sn^{4+} + 2Mn^{2+}$
$2MnO_4^- + 5Sn^{2+} + 16H^+ \leftrightarrow 5Sn^{4+} + 2Mn^{2+} + 8H_2O$

Problem 3:

a) Cu_5FeS_4(bornite) $+ O_2(g) \leftrightarrow Cu^{2+} + Fe(OH)_3(s) + SO_4^{2-}$
$Cu^{(+6/5)}{}_5Fe^{(+2)}S^{(-2)}{}_4 + O^{(0)}{}_2(g) \leftrightarrow 5Cu^{2+} + Fe^{(+3)}(OH)_3(s) + 4S^{(+6)}O_4^{2-}$

$4e^-$ $1e^-$ $32e^-$ $4e^-$

$37e^-$

$4Cu_5FeS_4 + 37O_2(g) \leftrightarrow 20Cu^{2+} + 4Fe(OH)_3(s) + 16SO_4^{2-}$
$4Cu_5FeS_4 + 37O_2(g) + 2H_2O + 8H^+ \leftrightarrow 20Cu^{2+} + 4Fe(OH)_3(s) + 16SO_4^{2-}$

b) $ZnS + O_2(g) \leftrightarrow Zn^{2+} + SO_4^{2-}$
$Zn^{(+2)}S^{(-2)} + O^{(0)}{}_2(g) \leftrightarrow Zn^{2+} + S^{(+6)}O_4^{2-}$

$8e^-$ $4e^-$

$4ZnS + 8O_2(g) \leftrightarrow 4Zn^{2+} + 4SO_4^{2-}$
$ZnS + 2O_2(g) \leftrightarrow Zn^{2+} + SO_4^{2-}$

c) $Fe_3S_4 + O_2(g) \leftrightarrow Fe(OH)_3(s) + SO_4^{2-}$
$Fe^{(+8/3)}{}_3S^{(-2)}{}_4 + O^{(0)}{}_2(g) \leftrightarrow 3Fe^{(+3)}(OH)_3(s) + 4S^{(+6)}O_4^{2-}$

$33e^-$ $4e^-$

$4Fe_3S_4 + 33O_2(g) \leftrightarrow 12Fe(OH)_3(s) + 16SO_4^{2-}$

$4Fe_3S_4 + 33O_2(g) + 34H_2O \leftrightarrow 12Fe(OH)_3(s) + 16SO_4^{2-} + 32H^+$

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:

$Ni \leftrightarrow Ni^{2+} + 2e^-$	$E^0 = -0.24$ volts
$Al^{3+} + 3e^- \leftrightarrow Al$	$E^0 = 1.70$ volts
$3Ni + 2Al^{3+} \leftrightarrow 3Ni^{2+} + 2Al$	$E^0 = 1.46$ volts

$E = 1.46 + (0.0592/6) \log ([Ni^{2+}]^3/[Al^{3+}]^2)$
$E = 1.46 + 0.00987 \log (10^{-2}) = 1.44$ V

Problem 5:

We first write: $Cu \leftrightarrow Cu^{2+} + 2e^-$ 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:

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

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

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

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

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:

$$4Fe^{3+} + 2H_2O \leftrightarrow 4Fe^{2+} + 4H^+ + O_2(g)$$
$$\Delta G_r^\circ = 4\Delta G_f^\circ(Fe^{2+}) + 4\Delta G_f^\circ(H^+) + \Delta G_f^\circ(O_2) - 4\Delta G_f^\circ(Fe^{3+}) - 2\Delta G_f^\circ(H_2O)$$
$$= 4(-18.85) + 4(0) + (0) - 4(-1.12) - 2(-56.687) = 42.454 \text{ kcal mol}^{-1}$$

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

$$K = \frac{[Fe^{2+}]^4[H^+]^4 \, p_{O_2}}{[Fe^{3+}]^4}$$

$$\log K = -31.12 = 4 \log([Fe^{2+}]/[Fe^{3+}]) - 4\text{ pH} + \log p_{O_2}$$

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Comparison of $[Fe^{2+}]/[Fe^{3+}] = 3.89$ from part a with $[Fe^{2+}]/[Fe^{3+}] = 622$ 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., Ce^{3+}/Ce^{4+}, Fe^{2+}/Fe^{3+}, and H_2O/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.