Electrochem-2

Thursday, April 13, 2017 8:09 AM

Electrochemistry

1. For each of the following reactions: identify the oxidizing agent, balance the reaction using the half-reaction approach, calculate E°, state whether the reaction is spontaneous or not, and determine ΔG°.
   a. $Fe^{2+} + Pb^{2+} \rightarrow Fe^{3+} + Pb(s)$

$(Fe^{2+} \rightarrow Fe^{3+} + e^-)2 \quad E° = -0.77V$

$Pb^{2+} + 2e^- \rightarrow Pb(s) \quad E° = -0.13V$

$2Fe^{2+} + Pb^{2+} \rightarrow 2Fe^{3+} + Pb(s) \quad E° = -0.9V$

NOT spontaneous

$\Delta G° = -2(96485)(-0.9)$

$\Delta G° = 173,673 \frac{J}{mol}$

   b. $Ni^{2+} + Mg(s) \rightarrow Mg^{2+} + Ni(s)$

$Ni^{2+} + 2e^- \rightarrow Ni(s) \quad E° = -0.25V$

$Mg(s) \rightarrow Mg^{2+} + 2e^- \quad E° = 2.37V$

$Ni^{2+} + Mg(s) \rightarrow Mg^{2+} + Ni(s) \quad E° = 2.12V$

Spontaneous

$\Delta G° = -2(96485)(2.12)$

$\Delta G° = -409,096 \frac{J}{mol}$

   c. $Fe^{2+} + O_2 \rightarrow Fe^{3+} + H_2O$

$4(Fe^{2+} \rightarrow Fe^{3+} + e^-) \quad E° = -0.77V$

$4H^+ + 4e^- + O_2 \rightarrow 2H_2O \quad E° = 1.23V$

$4Fe^{2+} + 4H^+ + O_2 \rightarrow 4Fe^{3+} + 2H_2O \quad E° = 0.46V$

spontaneous

$\Delta G° = -4(96485)(0.46)$

$\Delta G° = -177,532 \frac{J}{mol}$

2. Calculate the equilibrium constant for reaction 1c. $\Delta G° = RT \ln K$

$-177,532 = 8.314(298.15) \ln K \qquad K = 1.27 \times 10^{31}$

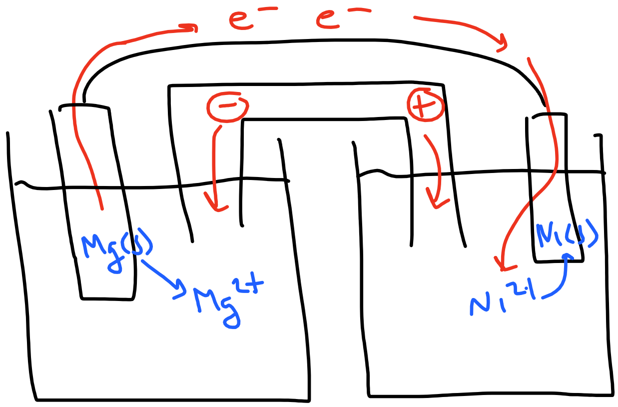
3. Determine ΔG at 25°C for reaction 1a if $[Fe^{2+}]$ = 1.2 M, $[Fe^{3+}]$ = 26.5 nM, and $[Pb^{2+}]$ = 820 mM.

$\Delta G = \Delta G° + RT \ln Q \qquad Q = \frac{[Fe^{3+}]^2}{[Fe^{2+}]^2[Pb^{2+}]} = \frac{(26.5 \times 10^{-9})^2}{(1.2)^2(0.82)} = 5.95 \times 10^{-16}$

$\Delta G = -177532 + 8.314(298.15) \ln 5.95 \times 10^{-16}$

$\Delta G = -264,434 \ J/mol$

4. Sketch an electrochemical call (battery diagram) for reaction 1b. Show this as a complete sketch and as well as the shorthand method.



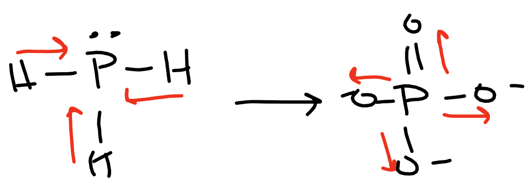
$Mg(s)|Mg^{2+}||Ni^{2+}|Ni(s)$

5. Consider each pair: determine with is the stronger oxidizing agent. For the first two, you can use the table at the end of the activity. In the last example, you will need to think about which molecule is more likely to get reduced.

Cl_2 vs. F_2 $\quad$ Ni^{2+} vs. Co^{2+} $\quad$ NO_3^- vs. $I_2(s)$ $\quad$ Na^+ vs. K^+

Na^+ has a higher electron affinity than K^+ because the incoming e^- is placed closer to the nucleus. This means the reduction is more favorable

6. How many electrons are required to oxidize PH_3 to PO_4^{3-}?
   a. Use oxidation states to determine this (note that P is more electronegative than H).
   b. Confirm your answer using the half-reaction approach.



$$P^{-3} \longrightarrow P^{+5} + 8e^-$$

$$4H_2O + PH_3 \longrightarrow PO_4^{3-} + 11H^+ + 8e^-$$