Chemistry 153a
Winter 2020
Due 17 January, 2020

Problem Set 2

1. Construct a diagram illustrating the dependence of electrode potentials (*vs.* NHE) on pH (Pourbaix diagram) for the following redox couples:

   a. $O_2 + e^- + H^+ \rightarrow HO_2^\bullet$

   b. $HO_2^\bullet + e^- + H^+ \rightarrow H_2O_2$

   c. $H_2O_2 + e^- + H^+ \rightarrow HO^\bullet + H_2O$

   d. $HO^\bullet + e^- + H^+ \rightarrow H_2O$

   e. $O_2 + 2e^- + 2H^+ \rightarrow H_2O_2$

   f. $H_2O_2 + 2e^- + 2H^+ \rightarrow 2H_2O$

   g. $O_2 + 4e^- + 4H^+ \rightarrow 2H_2O$

   In constructing your diagram, use the following standard potentials:

   $O_2 + e^- \rightarrow O_2^{\bullet-}$ $\quad E^\circ = -0.35$ V *vs.* NHE

   $HO_2^\bullet + e^- \rightarrow HO_2^-$ $\quad E^\circ = 0.76$ V *vs.* NHE

   $H_2O_2 + e^- + H^+ \rightarrow HO^\bullet + H_2O$ $\quad E^\circ = 0.80$ V *vs.* NHE

   $HO^\bullet + e^- + H^+ \rightarrow H_2O$ $\quad E^\circ = 2.72$ V *vs.* NHE;

   and the following pK_a values:

   $HO_2^\bullet \rightarrow O_2^{\bullet-} + H^+$ $\quad$ p$K_a = 4.8$

   $H_2O_2 \rightarrow HO_2^- + H^+$ $\quad$ p$K_a = 11.62$

   $HO^\bullet \rightarrow O^{\bullet-} + H^+$ $\quad$ p$K_a = 11.7$

   $H_2O \rightarrow HO^- + H^+$ $\quad$ p$K_a = 14.0$

   The standard state for potentials is 25 °C, concentrations of 1 molal (1 *m*), partial gas pressures of 100 kPa, and the activity of water is taken to be unity. For the purposes of your diagram, assume the following conditions:

   $pO_2 = 100$ kPa

   $[HO_2^\bullet] + [O_2^{\bullet-}] = 1\ m$

   $[H_2O_2] + [HO_2^-] = 1\ m$

   $[HO^\bullet] + [O^{\bullet-}] = 1\ m$

   Your plot should span the range from pH 0 to pH 14.

2. Using the data from your Pourbaix diagram give the electrode potentials for the redox couples *a-g* at the following pH values:

   a. pH 0 b. pH 7 c. pH 14

3. Using the data from your Pourbaix diagram determine the standard free energy change for the following reaction:

   $2HO^{\bullet} \rightleftharpoons H_2O_2$

4. Consider the H_2 and O_2 evolution reactions of several metal oxides depicted in the plot below.

   a. Identify which reactions are endothermic and which are exothermic.

   b. Identify the algebraic sign of the entropy change for each reaction.

   c. Which reaction has the smallest value of $|\Delta H^{\circ}|$?

   d. Which metal oxide pair(s) might be used in a thermal water-splitting cycle? Explain your reasoning.