Ch153a
Winter 2019
Due 25 January, 2019

Problem Set 3

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:

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

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

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

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

    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: