**Problem Set 3**
**Ch153a – Winter 2024**
**Due: 22 January 2024**

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:

    | | |
    |---|---|
    | $O_2 + e^- \rightarrow O_2^{\bullet-}$ | $E^\circ = -0.35$ V *vs.* NHE |
    | $HO_2^\bullet + e^- \rightarrow HO_2^-$ | $E^\circ = 0.76$ V *vs.* NHE |
    | $H_2O_2 + e^- + H^+ \rightarrow HO^\bullet + H_2O$ | $E^\circ = 0.80$ V *vs.* NHE |
    | $HO^\bullet + e^- + H^+ \rightarrow H_2O$ | $E^\circ = 2.72$ V *vs.* NHE |

    and the following p$K_a$ values:

    | | |
    |---|---|
    | $HO_2^\bullet \rightarrow O_2^{\bullet-} + H^+$ | p$K_a = 4.8$ |
    | $H_2O_2 \rightarrow HO_2^- + H^+$ | p$K_a = 11.62$ |
    | $HO^\bullet \rightarrow O^{\bullet-} + H^+$ | p$K_a = 11.7$ |
    | $H_2O \rightarrow HO^- + H^+$ | 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

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

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

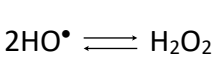
    $[HO^\bullet] + [O^{\bullet-}] = 1\ m$

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

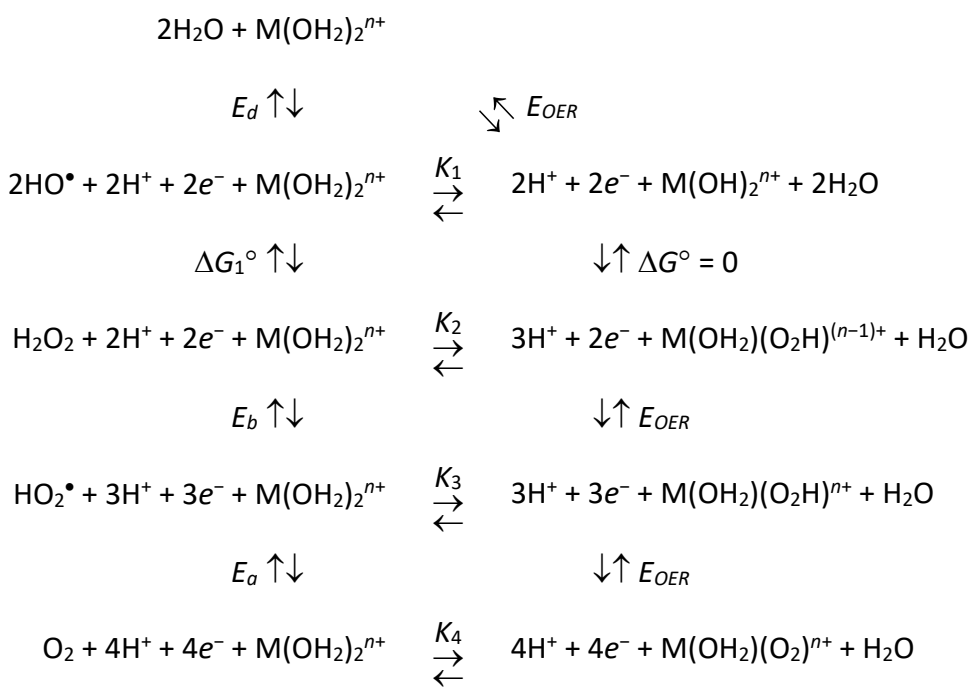
2. Using the data from your Pourbaix diagram give the electrode potentials for the redox couples *a*-*g* at the following pH values:

   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:



4. It should be clear from your Pourbaix diagram that the electrode potential for the four-electron, four-proton oxidation of water is substantially lower than those for some of the steps in the sequential one-electron oxidation of water to dioxygen. The stepwise oxidation of water, then, requires large overpotentials; these overpotentials can be reduced if the intermediates in the water oxidation sequence are bound to metal complexes as illustrated below. Define the potential for redox reaction *g* from question 1 (pH 7, 25 °C) to be equal to that for the oxygen evolving reaction ($E_{OER}$).



Use the data from your Pourbaix diagram and the answer from question 3 ($\Delta G_1^\circ$) to estimate values for the equilibrium constants for binding to a generic metal center ($M(OH_2)_2^{n+}$) of the intermediates in the water oxidation sequence, *i.e.*, $K_1$, $K_2$, $K_3$, and $K_4$.