Problem Set 1
Ch153a – Winter 2026
Due: 16 January 2026

1. (10 points) 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 pK_a values:

$HO_2^{\bullet} \rightarrow O_2^{\bullet-} + H^+$	$pK_a = 4.8$
$H_2O_2 \rightarrow HO_2^- + H^+$	$pK_a = 11.62$
$HO^{\bullet} \rightarrow O^{\bullet-} + H^+$	$pK_a = 11.7$
$H_2O \rightarrow HO^- + H^+$	$pK_a = 14.0$

    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. (5 points) 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. (5 points) Using the data from your Pourbaix diagram determine the standard free energy change for the following reaction:

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

4. (10 points) 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}).

$2H_2O + M(OH_2)_2^{n+}$		
E_d ↑↓		↙↗ E_{OER}
$2HO^{\bullet} + 2H^+ + 2e^- + M(OH_2)_2^{n+}$	$\overset{K_1}{\rightleftarrows}$	$2H^+ + 2e^- + M(OH)_2^{n+} + 2H_2O$
ΔG_1° ↑↓		↓↑ $\Delta G^\circ = 0$
$H_2O_2 + 2H^+ + 2e^- + M(OH_2)_2^{n+}$	$\overset{K_2}{\rightleftarrows}$	$3H^+ + 2e^- + M(OH_2)(O_2H)^{(n-1)+} + H_2O$
E_b ↑↓		↓↑ E_{OER}
$HO_2^{\bullet} + 3H^+ + 3e^- + M(OH_2)_2^{n+}$	$\overset{K_3}{\rightleftarrows}$	$3H^+ + 3e^- + M(OH_2)(O_2H)^{n+} + H_2O$
E_a ↑↓		↓↑ E_{OER}
$O_2 + 4H^+ + 4e^- + M(OH_2)_2^{n+}$	$\overset{K_4}{\rightleftarrows}$	$4H^+ + 4e^- + M(OH_2)(O_2)^{n+} + H_2O$

Use the data from your Pourbaix diagram and the answer from question 3 (ΔG_1°) 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.