

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:

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

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:

$$pO_2 = 100 \text{ kPa}$$

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

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

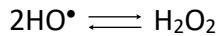
$$[HO^\bullet] + [O^\bullet -] = 1 \text{ } m$$

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

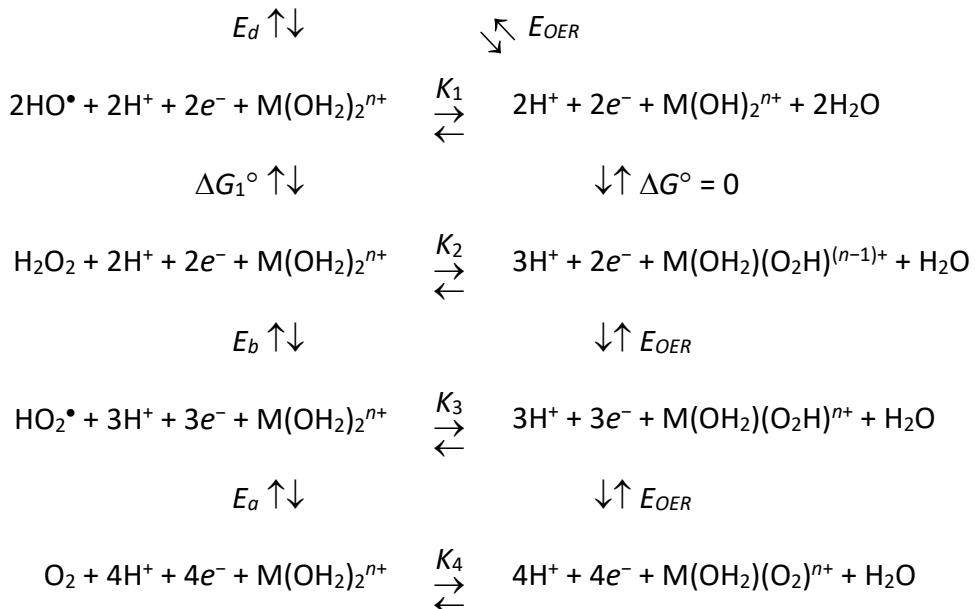
2. (5 points) Using the data from your Pourbaix diagram give the electrode potentials for the redox couples *a-g* at the following pH values:

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:



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}).



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 ($\text{M}(\text{OH}_2)_2^{n+}$) of the intermediates in the water oxidation sequence, *i.e.*, K_1 , K_2 , K_3 , and K_4 .