

Problem Set 3

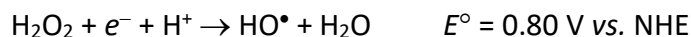
Ch153a – Winter 2023

Due: 20 January 2023

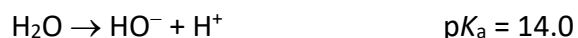
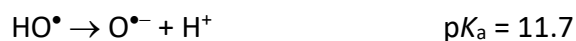
1. Construct a diagram illustrating the dependence of electrode potentials (vs. NHE) on pH (Pourbaix diagram) for the following redox couples:

- $\text{O}_2 + e^- + \text{H}^+ \rightarrow \text{HO}_2^\bullet$
- $\text{HO}_2^\bullet + e^- + \text{H}^+ \rightarrow \text{H}_2\text{O}_2$
- $\text{H}_2\text{O}_2 + e^- + \text{H}^+ \rightarrow \text{HO}^\bullet + \text{H}_2\text{O}$
- $\text{HO}^\bullet + e^- + \text{H}^+ \rightarrow \text{H}_2\text{O}$
- $\text{O}_2 + 2e^- + 2\text{H}^+ \rightarrow \text{H}_2\text{O}_2$
- $\text{H}_2\text{O}_2 + 2e^- + 2\text{H}^+ \rightarrow 2\text{H}_2\text{O}$
- $\text{O}_2 + 4e^- + 4\text{H}^+ \rightarrow 2\text{H}_2\text{O}$

In constructing your diagram, use the following standard potentials:



and the following pK_a values:



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:

$$p\text{O}_2 = 100 \text{ kPa}$$

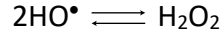
$$[\text{HO}_2^\bullet] + [\text{O}_2^{\bullet-}] = 1 \text{ } m$$

$$[\text{H}_2\text{O}_2] + [\text{HO}_2^-] = 1 \text{ } m$$

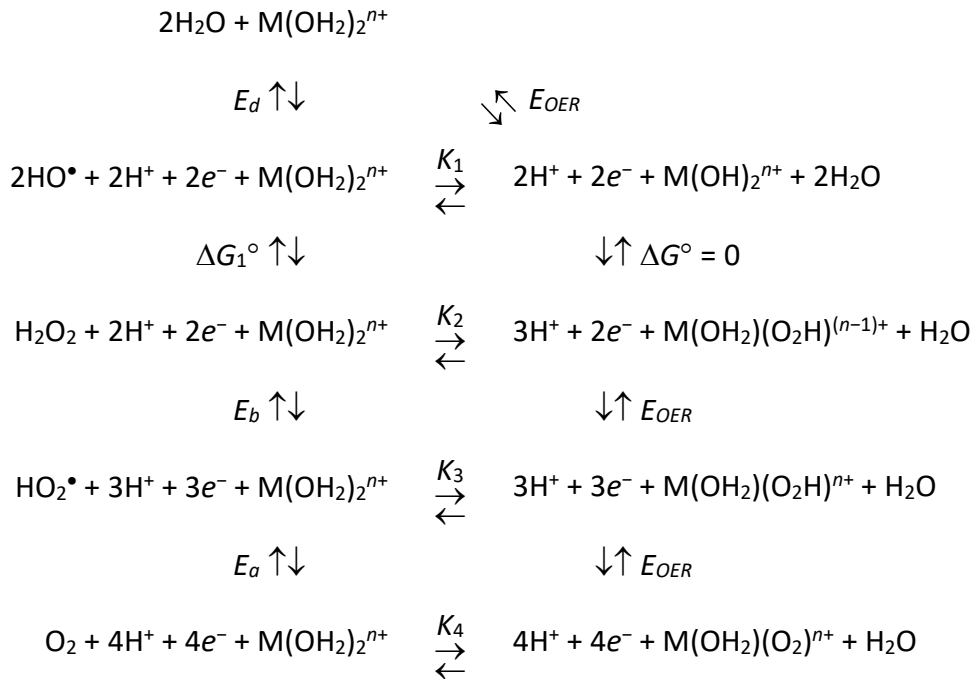
$$[\text{HO}^\bullet] + [\text{O}^{\bullet-}] = 1 \text{ } m$$

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 (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 .