

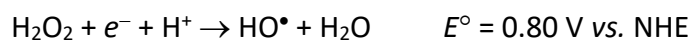
Chemistry 153a
Winter 2020
Due 17 January, 2020

Problem Set 2

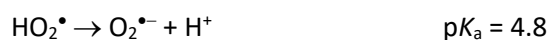
1. Construct a diagram illustrating the dependence of electrode potentials (vs. NHE) on pH (Pourbaix diagram) for the following redox couples:

- a. $\text{O}_2 + e^- + \text{H}^+ \rightarrow \text{HO}_2^\bullet$
- b. $\text{HO}_2^\bullet + e^- + \text{H}^+ \rightarrow \text{H}_2\text{O}_2$
- c. $\text{H}_2\text{O}_2 + e^- + \text{H}^+ \rightarrow \text{HO}^\bullet + \text{H}_2\text{O}$
- d. $\text{HO}^\bullet + e^- + \text{H}^+ \rightarrow \text{H}_2\text{O}$
- e. $\text{O}_2 + 2e^- + 2\text{H}^+ \rightarrow \text{H}_2\text{O}_2$
- f. $\text{H}_2\text{O}_2 + 2e^- + 2\text{H}^+ \rightarrow 2\text{H}_2\text{O}$
- g. $\text{O}_2 + 4e^- + 4\text{H}^+ \rightarrow 2\text{H}_2\text{O}$

In constructing your diagram, use the following standard potentials:



and the following $\text{p}K_a$ 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:

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

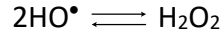
$$[\text{HO}_2^\bullet] + [\text{O}_2^{\bullet-}] = 1 \text{ m}$$

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

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

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

- Using the data from your Pourbaix diagram give the electrode potentials for the redox couples $a-g$ at the following pH values:
 - pH 0
 - pH 7
 - pH 14
- Using the data from your Pourbaix diagram determine the standard free energy change for the following reaction:



- Consider the H_2 and O_2 evolution reactions of several metal oxides depicted in the plot below.
 - Identify which reactions are endothermic and which are exothermic.
 - Identify the algebraic sign of the entropy change for each reaction.
 - Which reaction has the smallest value of $|\Delta H^\circ|$?
 - Which metal oxide pair(s) might be used in a thermal water-splitting cycle? Explain your reasoning.

