

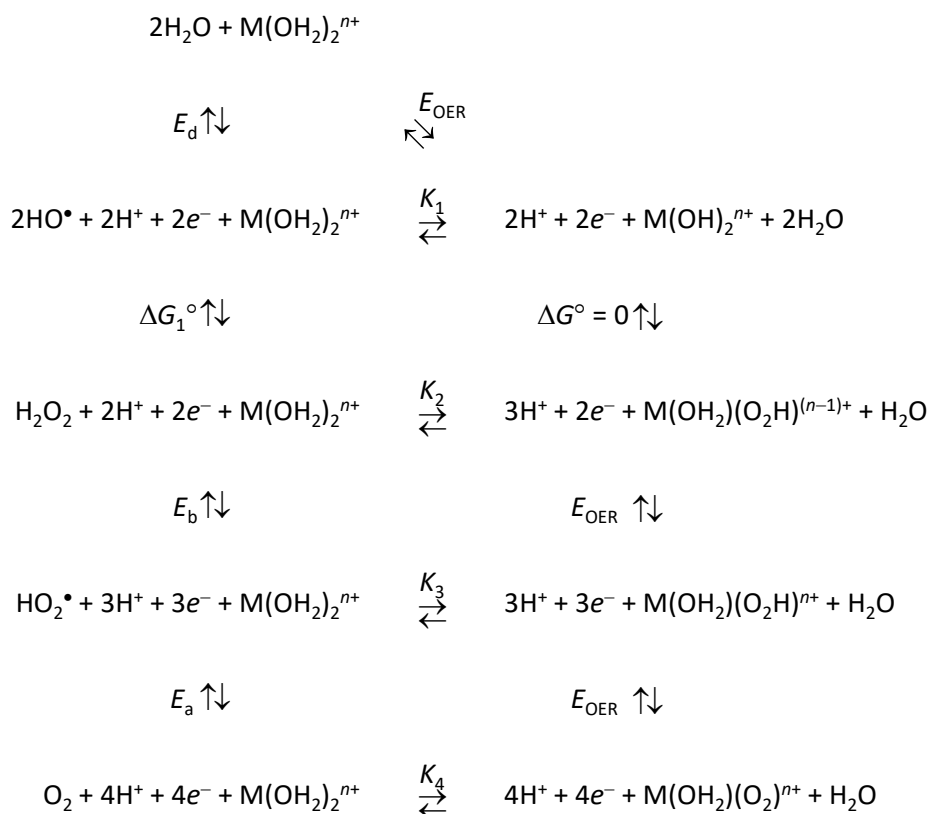
Ch153a

Winter 2019

Due 1 February, 2019

Problem Set 4

1. It should be clear from the Pourbaix diagrams you produced for Problem Set 3 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 in Problem Set 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 .

2. For each reaction *a-i* given below, calculate the standard Gibbs free energies of formation (ΔG_f°) for all reactants and products, as well as the standard Gibbs free energy change (ΔG°) for the transformation. Standard states are 25 °C, concentrations of 1 molal (1 *m*), partial gas pressures of 100 kPa. The ΔG_f° values for elements in their pure forms under standard-state conditions are defined to be 0. The table below contains all of the information that you will need to perform these calculations. Express your Gibbs energies in kJ mol⁻¹.

- $2\text{H}_2\text{CrO}_{4(\text{aq})} \rightarrow 2\text{CrO}_{2(\text{s})} + \text{O}_2 + 2\text{H}_2\text{O}$
- $2\text{H}_2\text{MoO}_{4(\text{aq})} \rightarrow 2\text{MoO}_{2(\text{s})} + \text{O}_2 + 2\text{H}_2\text{O}$
- $2\text{H}_2\text{WO}_{4(\text{s})} \rightarrow 2\text{WO}_{2(\text{s})} + \text{O}_2 + 2\text{H}_2\text{O}$
- $2\text{MnO}_4^-(\text{aq}) + 2\text{H}^+ \rightarrow 2\text{MnO}_{2(\text{s})} + \frac{3}{2}\text{O}_2 + \text{H}_2\text{O}$
- $2\text{TcO}_4^-(\text{aq}) + 2\text{H}^+ \rightarrow 2\text{TcO}_{2(\text{s})} + \frac{3}{2}\text{O}_2 + \text{H}_2\text{O}$
- $2\text{ReO}_4^-(\text{aq}) + 2\text{H}^+ \rightarrow 2\text{ReO}_{2(\text{s})} + \frac{3}{2}\text{O}_2 + \text{H}_2\text{O}$
- $2\text{FeO}_4^{2-}(\text{aq}) + 4\text{H}^+ \rightarrow \text{Fe}_2\text{O}_{3(\text{s})} + \frac{3}{2}\text{O}_2 + 2\text{H}_2\text{O}$
- $\text{RuO}_{4(\text{aq})} \rightarrow \text{RuO}_{2(\text{s})} + \text{O}_2$
- $\text{OsO}_{4(\text{aq})} \rightarrow \text{OsO}_{2(\text{s})} + \text{O}_2$

| Species | Conditions | ΔG_f° kJ mol ⁻¹ |
|---|-----------------------|---|
| H ⁺ | 1 m, aqueous solution | 0 |
| Half-reaction | | E° , V vs. NHE |
| $\text{O}_2 + 4\text{H}^+ + 4e^- \rightarrow 2\text{H}_2\text{O}$ | | 1.229 |
| $\text{H}_2\text{CrO}_{4(\text{aq})} + 6\text{H}^+ + 6e^- \rightarrow \text{Cr}_{(\text{s})} + 4\text{H}_2\text{O}$ | | 0.325 |
| $\text{CrO}_{2(\text{s})} + 4\text{H}^+ + 4e^- \rightarrow \text{Cr}_{(\text{s})} + 2\text{H}_2\text{O}$ | | -0.191 |
| $\text{H}_2\text{MoO}_{4(\text{aq})} + 6\text{H}^+ + 6e^- \rightarrow \text{Mo}_{(\text{s})} + 4\text{H}_2\text{O}$ | | 0.114 |
| $\text{MoO}_{2(\text{s})} + 4\text{H}^+ + 4e^- \rightarrow \text{Mo}_{(\text{s})} + 2\text{H}_2\text{O}$ | | -0.152 |
| $\text{H}_2\text{WO}_{4(\text{s})} + 6\text{H}^+ + 6e^- \rightarrow \text{W}_{(\text{s})} + 4\text{H}_2\text{O}$ | | -0.089 |
| $\text{WO}_{2(\text{s})} + 4\text{H}^+ + 4e^- \rightarrow \text{W}_{(\text{s})} + 2\text{H}_2\text{O}$ | | -0.154 |
| $\text{MnO}_4^-(\text{aq}) + 8\text{H}^+ + 7e^- \rightarrow \text{Mn}_{(\text{s})} + 4\text{H}_2\text{O}$ | | 0.698 |
| $\text{MnO}_{2(\text{s})} + 4\text{H}^+ + 4e^- \rightarrow \text{Mn}_{(\text{s})} + 2\text{H}_2\text{O}$ | | 0.024 |
| $\text{TcO}_4^-(\text{aq}) + 8\text{H}^+ + 7e^- \rightarrow \text{Tc}_{(\text{s})} + 4\text{H}_2\text{O}$ | | 0.472 |
| $\text{TcO}_{2(\text{s})} + 4\text{H}^+ + 4e^- \rightarrow \text{Tc}_{(\text{s})} + 2\text{H}_2\text{O}$ | | 0.272 |
| $\text{ReO}_4^-(\text{aq}) + 8\text{H}^+ + 7e^- \rightarrow \text{Re}_{(\text{s})} + 4\text{H}_2\text{O}$ | | 0.376 |
| $\text{ReO}_{2(\text{s})} + 4\text{H}^+ + 4e^- \rightarrow \text{Re}_{(\text{s})} + 2\text{H}_2\text{O}$ | | 0.216 |
| $\text{FeO}_4^{2-}(\text{aq}) + 8\text{H}^+ + 6e^- \rightarrow \text{Fe}_{(\text{s})} + 4\text{H}_2\text{O}$ | | 1.505 |
| $\text{Fe}_2\text{O}_{3(\text{s})} + 6\text{H}^+ + 6e^- \rightarrow 2\text{Fe}_{(\text{s})} + 3\text{H}_2\text{O}$ | | -0.055 |
| $\text{RuO}_{4(\text{aq})} + 8\text{H}^+ + 8e^- \rightarrow \text{Ru}_{(\text{s})} + 4\text{H}_2\text{O}$ | | 1.039 |
| $\text{RuO}_{2(\text{s})} + 4\text{H}^+ + 4e^- \rightarrow \text{Ru}_{(\text{s})} + 2\text{H}_2\text{O}$ | | 0.673 |
| $\text{OsO}_{4(\text{aq})} + 8\text{H}^+ + 8e^- \rightarrow \text{Os}_{(\text{s})} + 4\text{H}_2\text{O}$ | | 0.838 |
| $\text{OsO}_{2(\text{s})} + 4\text{H}^+ + 4e^- \rightarrow \text{Os}_{(\text{s})} + 2\text{H}_2\text{O}$ | | 0.687 |

3. On the basis of your ΔG° values for the reactions from problem 5, which of the metal dioxides would be likely candidates for water oxidation catalysts? Would the one sesquioxide be a candidate? Explain your reasoning.