

## Problem Set 2

Ch153a – Winter 2026

Due: 23 January 2026

1. (15 points) For each reaction *a-i* given below, calculate the standard Gibbs free energies of formation ( $\Delta G_f^\circ$ ) for all reactants and products, as well as the standard Gibbs free energy change ( $\Delta G^\circ$ ) for the transformation. Standard states are 25 °C, concentrations of 1 molal (1 *m*), partial gas pressures of 100 kPa. The  $\Delta G_f^\circ$  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<sup>-1</sup>.

- $2\text{H}_2\text{CrO}_{4(\text{aq})} \rightarrow 2\text{CrO}_{2(\text{s})} + \text{O}_2 + 2\text{H}_2\text{O}$
- $2\text{H}_2\text{MoO}_{4(\text{aq})} \rightarrow 2\text{MoO}_{2(\text{s})} + \text{O}_2 + 2\text{H}_2\text{O}$
- $2\text{H}_2\text{WO}_{4(\text{s})} \rightarrow 2\text{WO}_{2(\text{s})} + \text{O}_2 + 2\text{H}_2\text{O}$
- $2\text{MnO}_{4^-(\text{aq})} + 2\text{H}^+ \rightarrow 2\text{MnO}_{2(\text{s})} + \frac{3}{2}\text{O}_2 + \text{H}_2\text{O}$
- $2\text{TcO}_{4^-(\text{aq})} + 2\text{H}^+ \rightarrow 2\text{TcO}_{2(\text{s})} + \frac{3}{2}\text{O}_2 + \text{H}_2\text{O}$
- $2\text{ReO}_{4^-(\text{aq})} + 2\text{H}^+ \rightarrow 2\text{ReO}_{2(\text{s})} + \frac{3}{2}\text{O}_2 + \text{H}_2\text{O}$
- $2\text{FeO}_{4^{2-}(\text{aq})} + 4\text{H}^+ \rightarrow \text{Fe}_2\text{O}_3(\text{s}) + \frac{3}{2}\text{O}_2 + 2\text{H}_2\text{O}$
- $\text{RuO}_{4(\text{aq})} \rightarrow \text{RuO}_{2(\text{s})} + \text{O}_2$
- $\text{OsO}_{4(\text{aq})} \rightarrow \text{OsO}_{2(\text{s})} + \text{O}_2$

Species	Conditions	$\Delta G_f^\circ$ kJ mol <sup>-1</sup>
$\text{H}^+$	1 <i>m</i> , aqueous solution	0
$\text{HO}^-$	1 <i>m</i> , aqueous solution	-157.3
$\text{H}_2\text{O}$	liquid	-237.2
Half-reaction		$E^\circ$ , 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

- (5 points) On the basis of your  $\Delta G^\circ$  values for the reactions from problem 1, which of the metal dioxides would be likely candidates for water oxidation catalysts? Would the one sesquioxide be a candidate? Explain your reasoning.
- (10 points) Consider the  $\text{H}_2$  and  $\text{O}_2$  evolution reactions of several metal oxides depicted in the plot on the following page.
  - 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.

