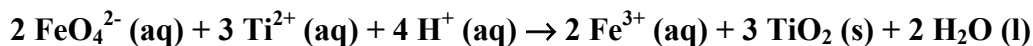
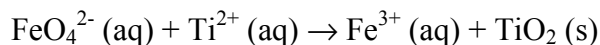


CHEM 121
Supplemental Questions for Electrochemistry

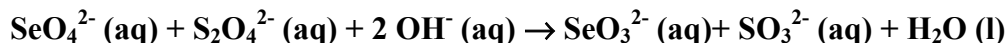
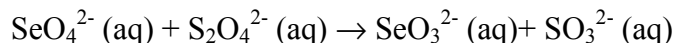
1a. Balance the following redox reaction that takes place in acidic solution. Identify the oxidant and the reductant.



FeO_4^{2-} gets reduced, so it is the oxidant

Ti^{2+} gets oxidized, so it is the reductant

b. Balance the following redox reaction that takes place in basic solution. Identify the chemical species that was reduced and the chemical species that was oxidized.



SeO_4^{2-} is reduced.

$\text{S}_2\text{O}_4^{2-}$ is oxidized

2. An electrochemical cell is constructed of one half-cell in which a silver wire is placed into a 1.00 M aqueous solution of AgNO_3 , and the other half-cell consists of a zinc electrode in an aqueous solution of $\text{Zn}(\text{NO}_3)_2$ that is also 1.00 M.

a. Write the balanced chemical equation for the spontaneous reaction that occurs in this cell under standard conditions.

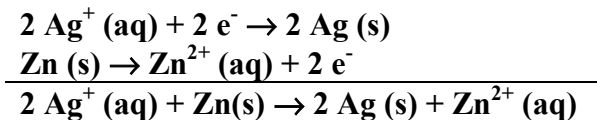
Standard reduction potentials for the half-reactions are



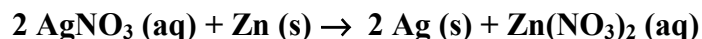
To get a spontaneous reaction we would need to flip the second reduction. Thus Zn will be oxidized and it will be the anode.



Balance the number of electrons and add to get overall net ionic equation.



The overall chemical reaction is



b. What is E^0 for this cell?

$$E^0_{\text{cell}} = E^0_{\text{cathode}} - E^0_{\text{anode}} = +0.80 \text{ V} - (-9.763 \text{ V}) = +1.56 \text{ V}$$

E^0 for this cell is +1.56 V.

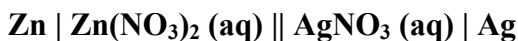
c. What is ΔG^0 for this cell?

$$\Delta G^0 = -n \cdot F \cdot E^0 = -2(96485.309 \text{ C} \cdot \text{mole}^{-1})(+1.56 \text{ J} \cdot \text{C}^{-1})$$

$$\Delta G^0 = -301. \text{ kJ} \cdot \text{mole}^{-1}$$

For this cell ΔG^0 is -301. k J·mole⁻¹.

d. Write this cell in line notation (the short-hand way discussed in class).



e. What would be E for the cell at 35.0 °C when $[\text{Ag}^+]$ is 0.50 m and $[\text{Zn}^{2+}] = 1.00 \text{ m}$?

$$E = E^0 - \frac{RT}{nF} \ln Q = +1.56 \text{ V} - \frac{\left(8.314510 \frac{\text{J}}{\text{K} \cdot \text{mole}}\right)(308.15 \text{ K})}{(2)\left(96485.309 \frac{\text{C}}{\text{mole}}\right)} \ln \left(\frac{[\text{Zn}^{2+}]}{[\text{Ag}^+]^2}\right)$$

$$E = +1.56 \text{ V} - 1.327_{72} \times 10^{-2} \ln \left(\frac{1.00}{(0.50)^2}\right) \text{ V}$$

$$E = +1.53 \text{ V}$$

Under the stated conditions, this cell has a potential of + 1.53 V.

3. We have learned that the ionization energy decreases down a group. So, for the elements of Group 1, it should be easier to remove an electron from K than it is to remove an electron from Na and this is easier than removing an electron from Li. In other words, ΔG for the reaction: $M(g) \rightarrow M^+(g) + e^-$ (where M is Li, Na, or K) should be more negative for K than Na, which is more negative than that of Li.

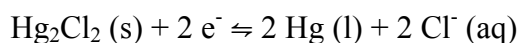
Consult the table of standard reduction potentials, and give the order of ΔG that it predicts for the reaction $M(s) \rightarrow M^+(aq) + e^-$ (where M is Li, Na, or K). What have we forgotten to take into account that might fix the apparent incongruity between the order predicted by the ionization energies and that predicted by the E^0 ?

The E^0 (and therefore ΔG^0) for the reaction $M(s) \rightarrow M^+(aq) + e^-$ (where M is Li, Na, or K) is in the opposite order than that shown in the table. So, Li has the most negative ΔG^0 , followed by K and with Na being the least negative ΔG^0 .

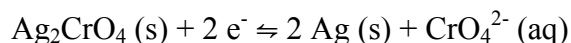
The problem is that the ionization energies are measured in the gaseous state; while the E^0 are measured in condensed states (fancy physics term for solids and liquids). In both the solid and the solution we need to account for the interactions between the particles (in the solid this is the metallic bonding, while in solution it is primarily an ion-dipole interaction between the ion and the polar water). These will affect ΔH . We don't expect ΔS to be very different between Li, Na and K because the reactions are identical. So, the difference in ΔG^0 must arise from ΔH (remember, $\Delta G = \Delta H - T\Delta S$).

FYI The difference between the ionization energy and E^0 is attributed to $\Delta H_{\text{hydration}}$. Because Li^+ is so small the water molecules can not pack around it has effectively as with the larger Na^+ and K^+ .

4. An electrochemical cell is constructed consisting of a saturated calomel electrode (SCE) in one compartment and a silver wire coated with Ag_2CrO_4 in the other compartment. The SCE is an electrode that is composed of liquid mercury in contact with a saturated solution of Hg_2Cl_2 (calomel), which is also saturated with KCl. The SCE is described by the half-reaction that is shown below, and it has E^0 of +0.2412 V versus SHE.

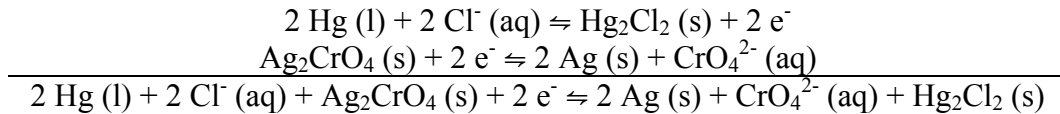


The E^0 for the following half-reaction is +0.466 V relative to SHE.



a. Combine the two half-reactions to get the overall balanced chemical equation for the cell. Calculate E^0 and ΔG^0 for this cell (25.0 °C, $[CrO_4^{2-}] = 1.00$ M).

For a spontaneous reaction we need to reverse the first reaction making the Hg electrode the anode (Hg is oxidized).



$$E^0_{\text{cell}} = E^0_{\text{cathode}} - E^0_{\text{anode}} = +0.466 \text{ V} - (+0.2412 \text{ V}) = +0.225 \text{ V}$$

$$\Delta G^0 = -nFE^0$$

$$\Delta G^0 = -(2) \left(9.6485309 \times 10^4 \frac{\text{C}}{\text{mole}} \right) \left(+0.225 \frac{\text{J}}{\text{C}} \right)$$

$$\Delta G^0 = -43.4 \frac{\text{kJ}}{\text{mole}}$$

For this reaction E^0 is +0.225 V and ΔG^0 is -43.4 kJ/mole.

b. Write the Nernst equation for this cell. Assume that all of the concentrations associated with the SCE are 1.00 m.

Start with the general Nernst equation, and then substitute specific values ($n = 2$, and the only chemical species that appear will be CrO_4^{2-} and Cl^- , because they are the only ones in solution).

$$E = E^0 - \frac{RT}{nF} \ln(Q)$$

$$E = E^0 - \frac{RT}{2F} \ln \left(\frac{[\text{CrO}_4^{2-}]}{[\text{Cl}^-]^2} \right)$$

Since the $[\text{Cl}^-]$ is 1.00 m, we can remove it from the Nernst equation for this cell. This leaves with the following Nernst equation for the cell.

$$E = E^0 - \frac{RT}{2F} \ln([\text{CrO}_4^{2-}])$$

c. If the coated silver wire is placed in a solution at 25.0 °C in which $[\text{CrO}_4^{2-}]$ is 1.00×10^{-5} M, what is the expected cell potential?

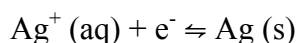
Start with the Nernst equation for the cell, found in part b, and substitute in the known values

$$E = E^0 - \frac{RT}{2F} \ln([\text{CrO}_4^{2-}]) = +0.225V - \frac{(8.314510 \text{ J} \cdot \text{K}^{-1} \cdot \text{mole}^{-1})(298.15 \text{ K})}{(2)(96485.309 \text{ C} \cdot \text{mole}^{-1})} \ln(1.00 \times 10^{-5})$$

$$E = +0.373V$$

Under these conditions the cell potential is +0.373 V.

d. Using data from this problem and the half-reaction shown below ($E^0 = +0.7994$), calculate K_{sp} for Ag_2CrO_4 .



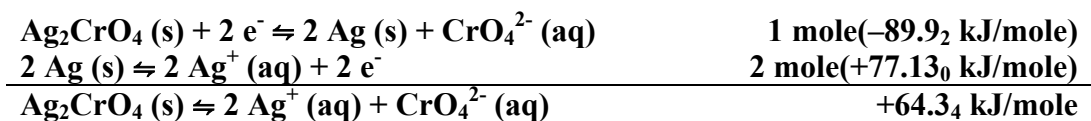
Find ΔG^0 for the reaction $\text{Ag}_2\text{CrO}_4 (\text{s}) + 2 \text{e}^- \rightleftharpoons 2 \text{Ag} (\text{s}) + \text{CrO}_4^{2-} (\text{aq})$.

$$\Delta G^0 = -nFE^0 = -2 \left(96485.309 \frac{\text{C}}{\text{mole}} \right) \left(+0.466 \frac{\text{J}}{\text{C}} \right) = +89.9_2 \frac{\text{kJ}}{\text{mole}}$$

Calculate ΔG^0 for the reaction $\text{Ag} (\text{s}) \rightleftharpoons \text{Ag}^+ (\text{aq}) + \text{e}^-$.

$$\Delta G^0 = -nFE^0 = -1 \left(96485.309 \frac{\text{C}}{\text{mole}} \right) \left(-0.7994 \frac{\text{J}}{\text{C}} \right) = +77.13_0 \frac{\text{kJ}}{\text{mole}}$$

Combining these reactions and using Hess's Law gives ΔG^0 for the desired reaction.



From ΔG^0 for the desired reaction, calculate K .

$$\Delta G^0 = -RT \ln K$$

$$\ln K = -\frac{\Delta G^0}{RT} = -\frac{+64.3_4 \times 10^3 \text{ J} \cdot \text{mole}^{-1}}{(8.31447 \text{ J} \cdot \text{K}^{-1} \cdot \text{mole}^{-1})(298.15 \text{ K})} = -25.9_5$$

$$K = e^{-25.9_5} = 5.3 \times 10^{-12}$$

The K_{sp} for this Ag_2CrO_4 is $5. \times 10^{-12}$.