1. (20 pts). For the following cell, what is $E_{\text{cell}}$, the net cell reaction, $\Delta G_{\text{rxn}}$ and $K_{eq}$? Also indicate the direction of electron flow and whether the cell is electrolytic or galvanic.

**Galvanic** $\rightarrow \Delta G \text{ in reaction}$

Pt/Sn$^{4+}$ (0.065 M), Sn$^{2+}$ (0.12 M)// Ag$^+$ (0.0015 M)/Ag

$\text{Sn}^{4+} + 2e^- = \text{Sn}^{2+} \quad E^o = 0.15 \text{V}$

$\text{Ag}^+ + e^- = \text{Ag} \quad E^o = 0.799 \text{V}$

$E_{\text{anode}} = E^o + \frac{0.0592 \ \log \left(\frac{\text{[Sn}^{4+}\]}{\text{[Sn}^{2+}\]}\right)}{n} = 0.15 + \frac{0.0592 \ \log \left(\frac{0.065}{0.12}\right)}{2} = 0.142 \text{V}$

$E_{\text{cathode}} = E^o + \frac{0.0592 \ \log \left(\frac{\text{[Ag}^+\]}{\text{[Ag]}\right)} = 0.799 + \frac{0.0592 \ \log \left(\frac{0.0015}{1}\right)}{1} = 0.632 \text{V}$

$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} = 0.632 - 0.142 = 0.490 \text{V}$

$2 \left( \text{Ag}^+ + e^- \rightarrow \text{Ag} \right)$

$\text{Sn}^{2+} \rightarrow \text{Sn}^{4+} + 2e^-$

$\Delta G = -nFE_{\text{cell}} = - (2)(96,500 \ \text{C/mole})(0.490) = -9.45 \times 10^4 \text{ J/mole}$

$V = \frac{V}{F}$

$K = 3.77 \times 10^{16}$ (far to right)

$2 \text{Ag}^+ + \text{Sn}^{2+} \rightarrow 2 \text{Ag} + 2 \text{Sn}^{4+}$

$\ln K = -nFE_{\text{cell}} = -(2)(96,500 \ \text{C/mole})(0.490) = -38.17$

2. (10 pts). Describe the differences in theory of operation and equipment needed for potentiometric and voltammetric measurements. List any guiding theoretical expressions that relate activity or concentration of an analyte to a measured electrochemical signal.

For a potentiometric measurement, one only needs a high impedance voltmeter, an indicator electrode and a reference electrode.

For voltammetry, one needs a potentiostat to apply controlled voltage and to measure current + 3 electrodes.

$E_{\text{in}} = L + \frac{0.0592 \ \log a_i}{2}$

$E_{\text{cell}} = E_{\text{in}} - E_{\text{ref}}$
3. (20 pts). Researchers from NASA proposed that the Ag\(^+\) used as the biocide in potable water onboard the International Space Station could be monitored potentiometrically using an electrode of the first kind (that is, the metal used to detect its corresponding cation). The nominal concentration is about 100 ppb (1 ppb = \(\mu\)g/L, Ag = 108 g/mol) and changes from this level (decreases) would be reflective of increased bioactivity. The potable water is pretty much devoid of other ions except a little Cl\(^-\). Do the following: (i) draw a schematic of how this cell might be constructed, (ii) write the short hand notation for the cell, (iii) determine what the sensitivity for the measurement is, (iv) indicate what interferences might exist in the measurement and (v) calculate the potential recording for the sensor assuming \(L = 0.100 \text{ V}\) and no chemical interferences.

\[
\text{Ag} / \text{AgCl} / \text{C}_1 = \text{Ag}^+ \quad E^\circ_{\text{AgCl}} = \text{?} / \text{Ag}
\]

\[
E_{\text{cell}} = L + 0.0592 \frac{\text{V}}{\text{decade}} \log [\text{Ag}^+] \quad \text{sensitivity is 0.0592 V/decade}
\]

Potential interferes is Cl\(^-\) which would reduce the activity of Ag\(^+\) according to the reaction: Ag\(^+\) + Cl\(^-\) \rightleftharpoons AgCl. If Cl\(^-\) present, the measurement would underdetermine the true [Ag\(^+\)] in solution.

\[
(100 \times 10^{-6} \text{ g Ag}) \left( \frac{\text{mol}}{108 \text{ g Ag}} \right) = 9.26 \times 10^{-7} \text{ mol/L} \quad E_{\text{cell}} = -0.257 \text{ V}
\]

\[
E_{\text{cell}} = L + 0.0592 \frac{\text{V}}{\text{decade}} \log [\text{Ag}^+] = 0.100 \text{ V} + 0.0592 \log (9.26 \times 10^{-7})
\]

4. (10 pts). You are a materials scientist at Air Liquide and you are tasked with developing a new metal alloy to use in your gas handling systems for Cl\(_2\). The alloy you have developed and want to test contains (20%) Fe and (80%) Au. What is your prediction about how susceptible this alloy would be to corrosion during exposure to Cl\(_2\) gas? Assume there is some moisture in the gas.

Metal alloy: Treat individual metals separately. Assume standard conditions.

**Is Cl\(_2\) an oxidant?**

- **(E\(_a\))** Cl\(_2\) + 2e\(^-\) \rightleftharpoons 2Cl\(^-\)  \(E_{\text{cathode}} = 1.36 \text{ V}\)
- **(E\(_a\))** Au \rightleftharpoons Au\(^+\) + e\(^-\)  \(E_{\text{anode}} = 1.83 \text{ V}\)

Since E\(_{\text{cell}}\) is negative, Au would be negative. No tendency to corrode (Au).
\[ E_c \quad Cl_2 + 2e^- \rightarrow 2Cl^- \quad E^0 = 1.36\text{V} \]
\[ E_a \quad Fe \rightarrow Fe^{2+} + 2e^- \quad E^0 = -0.44\text{V} \]

\[ E_{cell} = E_c - E_a = 1.36\text{V} - (-0.44\text{V}) = 1.80\text{V} \]

Since \( E_{cell} \) is positive, \( \Delta G \) is negative, so \( Fe \) would have a tendency to corrode in presence of \( Cl_2 \).

Tendency to corrode \( (Fe) \)
5. (20 pts). Last Friday, we discussed the operation of an interesting Ca^{2+} ion selective electrode developed by Bakker. Describe the operating principles of this electrode? What is the equation that relates its response to the activity Ca^{2+} in the external solution? How would the response of the sensor change if the normal internal solution, 0.01 M CaCl\(_2\), is replaced with 0.02 M NaCl?

\[
E_{\text{NHE}} = L + 0.0592 \log \left(\frac{[\text{Ca}^{2+}]}{2}\right)
\]

6. (20 pts). In your research, assume you synthesized a new molecule, A\(^{3+}\). Furthermore, assume you know the following is the redox reaction: A\(^{3+}\) + 2e \leftrightarrow A\(^{+}\), \(E^0 = -0.500\) V vs. NHE. Sketch what the i-E curves would look like for fast and slow electron transfer at a working electrode. Design a set of electrochemical experiments to test whether or not A\(^{3+}\) complexes with Cl\(^-\). Assuming there is some interaction then how would your measured electrochemical signal change if the activity of A\(^{3+}\) was reduced by 15%.

\[
E^0 = E^0 + 0.0592 \log \left(\frac{[A^{3+}]}{2}\right)
\]

\[
\text{when } [A^{3+}] = [A^{+}] \text{ then } E^{0'} = E^0 = -0.500\text{V}
\]

\[
\text{when } [A^{3+}] < [A^{+}] \text{ then } E^{0'} < E^0
\]

A shift would occur.

\[
E^{0'} = -0.500 + 0.0592 \log \left(\frac{0.85}{2}\right) = -0.502\text{V}
\]

The shift would be small but one could measure i-E curves as a function of Cl\(^-\). If there is complexation, then \(E^{0'}\) would shift slightly negatively.