1) We are given the data that a solution of an unknown salt of vanadium is electrolyzed with 95.0% efficiency, and we get 3.558 g of vanadium. We are also told that we apply 2.75 amps for 2.15 hours. We are asked a) how many faradays are used to deposit the vanadium; and b) what is the charge on the vanadium? We'll approach these in order.

   a) The number of coulombs (and thereby, faradays) can be determined from the amperage and the time. \[ ?C = (2.75 \text{ A})(2.15 \text{ h})(3600 \text{ sec/h}) = 21285 \text{ C} \]

   which, given that 1 F = 96500 C, yields 0.221 F, of which 95%, or 0.210 F is used to deposit the vanadium.

   b) Vanadium has an atomic mass of 50.9415 g/mol, so 3.558 g of vanadium corresponds to 0.06984 mole vanadium. We used 0.210 Faradays, which is 0.210 moles of electrons to deposit 0.06984 moles of vanadium metal. Taking the ratio of these, we get: \[ \frac{0.210 \text{ mol}}{0.06984 \text{ mol}} = 3 \text{ mole electrons/mole vanadium} \]

   which leads us to conclude that the charge on vanadium is +3 (i.e. we have V^{3+})

2) We are given the following cell, and asked to get the \( \Delta G^\circ \).

   \[
   \text{Rb}|\text{Rb}^+(aq)||\text{Pb}^{2+}|\text{Pb}.
   \]

   The balanced equation for this cell is:

   \[
   2\text{Rb} + \text{Pb}^{2+} \rightarrow 2\text{Rb}^+ + \text{Pb}
   \]

   \[\Delta G^\circ = -24.3 -282.2 \quad 0.0 \quad \text{(kJ/mol)}\]

   which data leads to a \( \Delta G^\circ_{\text{rxn}} = (2(-282.2) + 0.0) - (0.0 + (-24.3)) = -540.1 \text{kJ} \).

   This \( \Delta G^\circ \) value, given an \( n = 2 \), leads, via \( \Delta G^\circ = -nF E^\circ_{\text{cell}} \) to: \[ E^\circ_{\text{cell}} = \frac{-540100}{-2(96500 C)} = 2.80 V. \]

   Given that \( E^\circ_{\text{Pb/Pb}^{2+}} = -0.13 \), and that \( E^\circ_{\text{cell}} = E^\circ_{\text{cath}} - E^\circ_{\text{an}} \) which leads to: 2.80 = -0.13 - (x), and \( x = E^\circ_{\text{Rb}^+/\text{Rb}} = -2.93 \text{ V.} \)

3) We have the following equation, mostly under standard conditions:

   \[
   \text{O}_3(g) + 2\text{H}^+(aq) + 2\text{Co}^{2+}(aq) \rightarrow \text{O}_2(g) + \text{H}_2\text{O}(l) + 2\text{Co}^{3+}(aq)
   \]
which means that \([\text{Co}^{2+}] = [\text{Co}^{3+}] = 1.0 \, \text{M}\), and that \(P(\text{O}_2) = P(\text{O}_3) = 1 \, \text{atm}\). First, let’s find the \(E^{\circ}_{\text{cell}}\): \(\text{O}_3(\text{g}) + 2\text{H}^+ (\text{aq}) + 2e^- \rightarrow \text{O}_2(\text{g}) + \text{H}_2\text{O}(\text{l})\) is the cathode and has \(E^{\circ} = 2.07 \, \text{V}\), whereas \(2\text{Co}^{2+} (\text{aq}) \rightarrow 2\text{Co}^{3+} (\text{aq}) + 2e^-\) is the anode and has \(E^{\circ} = 1.82 \, \text{V}\) so the \(E^{\circ}_{\text{cell}} = 2.07 - 1.82 = 0.25 \, \text{V}\) (so yes, we’ve confirmed that it is spontaneous.)

The buffer conditions tell us that we have \(\text{pH} = \text{pK}_a + \log \left( \frac{[\text{ClO}^-]}{[\text{HClO}]} \right) = 7.456 + \log \left( \frac{0.1}{0.15} \right) = 7.280\), which yields an \([H^+] = 5.25 \times 10^{-8}\).

The Nernst Equation relates \(E_{\text{cell}}\) and \(E^{\circ}_{\text{cell}}\): \(E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{RT}{nF} \ln(Q)\). The \(Q\) in this case is: \(Q = \frac{[\text{Co}^{3+}]^2 P(\text{O}_2)}{[\text{Co}^{2+}]^2 [H^+]^2 P(\text{O}_3)}\); the only condition which is not standard is \([H^+]\); all the others are so this nasty \(Q\) reduces to: \(Q = \frac{1}{(5.25 \times 10^{-8})^2} = 3.629 \times 10^{14}\). Plugging it all in to the Nernst Equation, we get: \(E_{\text{cell}} = 0.25 \, \text{V} - \frac{(8.314)(298.15)}{2(96500)} \ln(3.629 \times 10^{14}) = 0.25 - 0.431 = -0.181 \, \text{V and the reaction is not spontaneous.}\)

4) We are told that this cell is: \(\text{Hg}_2^{2+} (\text{aq}) + \text{H}_2(\text{g}) \rightarrow 2\text{Hg}(\text{l}) + 2\text{H}^+ (\text{aq})\) in which the concentration of mercuric ion is controlled by the \(K_{sp}\) of \(\text{Hg}_2\text{Cl}_2\), which we are asked to find. We need to obtain the \(E^{\circ}_{\text{cell}}\) and, using the Nernst Equation, obtain the \([\text{Hg}_2^{2+}]\) and from this, the \(K_{sp}\) of \(\text{Hg}_2\text{Cl}_2\). We know the \(E^{\circ}_{\text{S.H.E.}} = 0.0 \, \text{V}\) (definition) and we can find \(E^{\circ}_{\text{Hg}^+/\text{Hg}} = 0.80 \, \text{V}\). This yields the \(E^{\circ}_{\text{cell}} = 0.80 - 0.00 = 0.80 \, \text{V}\). We are also given the \(E_{\text{cell}} = 0.268 \, \text{V}\), and we can determine \(Q = \frac{[H^+]^2}{P_{\text{H}_2}[\text{Hg}_2^{2+}]^2} = \frac{[1.0]^2}{10[\text{Hg}_2^{2+}]^2} = \frac{1}{[\text{Hg}_2^{2+}]^2}.\) Lastly, \(n = 2\).

Substituting, we get: \(0.268 \, \text{V} = 0.80 \, \text{V} - (1.285 \times 10^{-2}) \ln \left( \frac{1}{[\text{Hg}_2^{2+}]^2} \right)\) which further leads to - \(0.532 \, \text{V} = -(1.285 \times 10^{-2}) \ln \left( \frac{1}{[\text{Hg}_2^{2+}]^2} \right) = 41.401\) which gives us (careful!)
\[ \text{[Hg}_2^{2+}] = 1.047 \times 10^{-18}. \text{ With a [Cl] = 1.0 M, we have, finally, a } K_{sp} = (1.023 \times 10^{-9})^2 = 1.047 \times 10^{-18}. \]

5) Here are the three (yes, three!) reduction potentials we need:

\[
\begin{align*}
\text{Fe}^{3+} + e^- & \rightarrow \text{Fe}^{2+} \quad E^\circ = 0.77 \text{ V} \\
\text{Fe}^{2+} + 2e^- & \rightarrow \text{Fe(s)} \quad E^\circ = -0.45 \text{ V} \\
\text{Fe}^{3+} + 3e^- & \rightarrow \text{Fe(s)} \quad E^\circ = -0.04 \text{ V}
\end{align*}
\]

Clearly \(-0.04 \neq 0.77 + (-0.45)\) (The term on the right equals 0.32 V)

The reason this simple addition does not work is because cell potentials are not state functions \(i.e.,\) they do not take into account how much material there is, and how many moles of electrons are transferred.

You could use the first two cell potentials to get the third if you first convert the cell potentials to standard free energies, \(\Delta G^\circ\), which are state functions. Proceeding in this manner, we get (recall \(\Delta G^\circ = -nFE^\circ_{\text{cell}}\)):

\[
\begin{align*}
\text{Fe}^{3+} + e^- & \rightarrow \text{Fe}^{2+} \quad E^\circ = 0.77 \text{ V} \quad \Delta G^\circ = -(1)(96500)(0.77) = -74305 J \\
\text{Fe}^{2+} + 2e^- & \rightarrow \text{Fe(s)} \quad E^\circ = -0.41 \text{ V} \quad \Delta G^\circ = -(2)(96500)(-0.41) = 86850 J
\end{align*}
\]

Adding these two \(\Delta G^\circ\) values, we get: 86850-74305 = 12545 J. Now, using this \(\Delta G^\circ\) value, we can calculate our last \(E^\circ\) value, that for \(\text{Fe}^{3+} + 3e^- \rightarrow \text{Fe(s)}\):

\[
E^\circ = \frac{\Delta G^\circ}{-nF} = \frac{12545}{-3(96500)} = -0.0433 \text{ V}, \text{ which agrees fairly well with the value given in our text.}\]