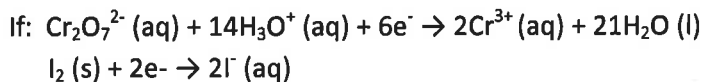


Electrochemistry & Gibbs Practice

1) A galvanic cell is constructed in which the overall reaction is:



$$E^\circ = 1.33\text{V}$$

$$E^\circ = 0.53\text{V} \quad \text{ox} \rightarrow -0.53\text{V}$$

(a) Calculate the E°_{cell} , ΔG° , and K_{eq} of the reaction.

$$E^\circ = 1.33\text{V} - 0.53\text{V}$$

$$= \boxed{0.80\text{V}}$$

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

$$= -6 \left(\frac{96,485\text{ C}}{\text{mol}} \right) \left(0.80 \frac{\text{J}}{\text{C}} \right)$$

$$= -463,128\text{ J}$$

$$= \boxed{-463\text{ kJ}}$$

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

$$-463\text{ kJ} = -(8.13 \times 10^3\text{ J})(298.15\text{ K}) \ln K$$

$$\ln K = 1.87 \times 10^5$$

$$K = \boxed{e^{1.87 \times 10^5}}$$

(b) At pH=0, with a $[\text{Cr}_2\text{O}_7^{2-}] = 1.5\text{M}$ and $[\text{I}^-] = 0.40\text{M}$, the cell voltage is found to be equal to 0.87V. Calculate the $[\text{Cr}^{3+}]$ in the cell.

$$\text{pH} = 0 \therefore [\text{H}^+] = 1.0\text{M}, [\text{Cr}_2\text{O}_7^{2-}] = 1.5\text{M}, [\text{I}^-] = 0.40\text{M}$$

$$Q = \frac{[\text{Cr}^{3+}]^2}{[\text{Cr}_2\text{O}_7^{2-}][\text{H}^+]^{14}[\text{I}^-]^6} = \frac{x^2}{0.00614}$$

$$\boxed{[\text{Cr}^{3+}] = 2.22 \times 10^{-5}\text{M}}$$

$$E = E^\circ - \frac{0.0592\text{V}}{n} \log Q$$

$$0.87\text{V} = 0.80\text{V} - \frac{0.0592}{6} \log \left(\frac{x^2}{0.00614} \right)$$

$$-7.095 = \log \frac{x^2}{0.00614}$$

$$8.04 \times 10^{-5} = \frac{x^2}{0.00614} \Rightarrow x = 2.22 \times 10^{-5}\text{M}$$

2) What mass of platinum would be plated on an electrode from the electrolysis of a $\text{Pt}(\text{NO}_3)_2$ solution with a current of 0.500A for 55 minutes?

$$q = It$$

$$= (0.500\text{ A}) \left(55\text{ min} \cdot \frac{60\text{ sec}}{1\text{ min}} \right)$$

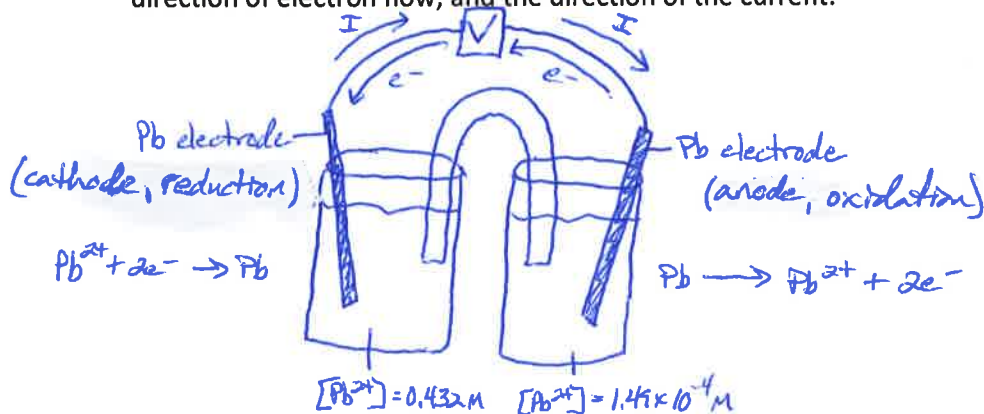
$$= 1650\text{ C}$$

$$1650\text{ C} \left(\frac{1\text{ mole}^-}{96,485\text{ C}} \right) \left(\frac{1\text{ mol Pt}}{2\text{ mole}^-} \right) \left(\frac{195.08\text{ g}}{1\text{ mol Pt}} \right) = \boxed{1.7\text{ g Pt}}$$

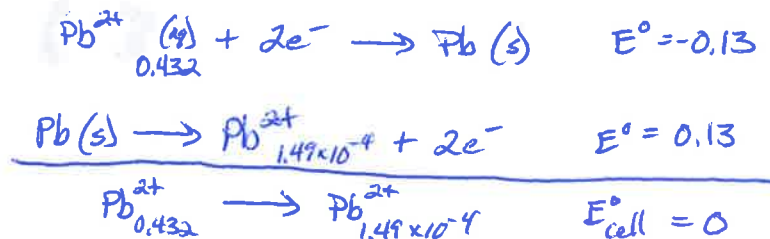


3) A concentration cell contains Pb electrodes in $[Pb^{2+}] = 0.432M$ and $[Pb^{2+}] = 1.49 \times 10^{-4}M$ solutions of equal volume.

(a) Draw the cell and label all of the components, where oxidation vs reduction is occurring, the direction of electron flow, and the direction of the current.



(b) Write the spontaneous half reactions for each half cell and the overall cell process.



(c) What will be the cell potential when the cell is first connected, when it is allowed to flow for an extended period of time, and at equilibrium?

$$\begin{array}{l}
 E = E^\circ - \frac{0.0592V}{n} \log Q \\
 \textcircled{1} \quad = 0 - \frac{0.0592V}{2} \log \left(\frac{1.49 \times 10^{-4}}{0.432} \right) \\
 = -0.102V
 \end{array}$$

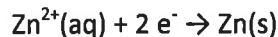
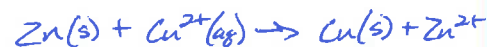
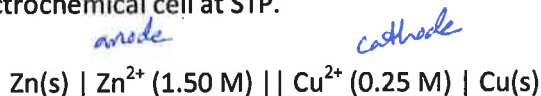
② Between 0 & -0.102 V
 ③ 0 V

(d) What will be the final $[Pb^{2+}]$ in each cell?

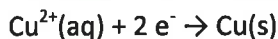
@ Equilibrium $[Pb^{2+}]$ is equal in both half cells, assume both are 1 L

$$\frac{0.432 \text{ mol} + 1.49 \times 10^{-4} \text{ mol}}{2} = 0.216 \text{ mol in each} \Rightarrow 0.216 M Pb^{2+}$$

4) For the following electrochemical cell at STP.



$$E^\circ_{\text{red}} = -0.762 \text{ volts}$$



$$E^\circ_{\text{red}} = +0.339 \text{ volts}$$

$$E^\circ_{\text{cell}} = 1.101 \text{ V}$$

(a) Is it a galvanic or electrolytic cell?

Galvanic (positive E°)

(b) What would be the signs for ΔG° , K_{eq} , and E° ?

Spontaneous $\therefore +E^\circ, -\Delta G, K \gg 1$

(c) Calculate the values for ΔG and E .

$$E = E^\circ - \frac{RT}{nF} \ln Q$$

$$= 1.101 \text{ V} - \frac{0.0257 \text{ V}}{2} \ln \left(\frac{1.5}{0.25} \right)$$

$$= \boxed{1.078 \text{ V}}$$

$$\Delta G = -nFE_{\text{cell}}$$

$$= -2 \text{ mol} \left(96,485 \frac{\text{C}}{\text{mol}} \right) (1.078 \frac{\text{J}}{\text{C}})$$

$$= -208,000 \text{ J}$$

$$= \boxed{-208 \text{ KJ}}$$

(d) Calculate the values for ΔG° and K_{eq} .

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

$$= -2 \left(96,485 \frac{\text{C}}{\text{mol}} \right) (1.101 \text{ V})$$

$$= -212,460 \text{ J}$$

$$= \boxed{-212 \text{ KJ}}$$

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

$$-212 \text{ KJ} = - \left(8.314 \times 10^{-3} \frac{\text{KJ}}{\text{K}} \right) \ln K$$

$$\ln K = 85.5$$

$$K = e^{85.5} = \boxed{1.39 \times 10^{37}}$$

(e) Determine the $[\text{Zn}^{2+}]$ and $[\text{Cu}^{2+}]$ at equilibrium. Calculate and explain.

$$K = \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

	Cu^{2+}	Zn^{2+}
I	0.25	1.5
C	-x	+x
E	0.25-x	1.5+x

K is so large, goes to completion (x is insignificant)

$$1.39 \times 10^{37} = \frac{(1.5+x)}{(0.25-x)}$$

$$3.48 \times 10^{36} - 1.39 \times 10^{37} x = 1.5 + x$$

insignificant

$$\left(3.48 \times 10^{36} - 1.5 \right) = \left(1.39 \times 10^{37} x + x \right)$$

$$x = 0.25$$

$$[\text{Zn}^{2+}] = 0.25 - x = 0.25 - 0.25 = \boxed{0 \text{ M}}$$

$$[\text{Cu}^{2+}] = 1.5 + 0.25 = \boxed{1.75 \text{ M}}$$