19.43 What is the difference between a galvanic cell and an electrolytic cell?

**Galvanic (Voltaic) Cell:** A spontaneous process that produces electricity. \(-\Delta G; +E_{\text{cell}}\)

**Electrolytic Cell:** A nonspontaneous process that requires an input of electricity to occur. \(+\Delta G; -E_{\text{cell}}\)

19.46 Consider the electrolysis of molten barium chloride, BaCl₂.

(a) Write the half-reactions and determine the \(E^\circ\) for a standard cell.

The only ions present in molten BaCl₂ are Ba\(^{2+}\) and Cl\(^{-}\). The electrode reactions are:

\[
\text{anode: } \quad 2 \text{Cl}^- (l) \longrightarrow \text{Cl}_2 (g) + 2e^- \quad E_{\text{red}}^\circ = +1.36 \text{ V}
\]

\[
\text{cathode: } \quad \text{Ba}^{2+} (l) + 2e^- \longrightarrow \text{Ba} (s) \quad E_{\text{red}}^\circ = -2.90 \text{ V}
\]

\(E^\circ\) for a standard cell = \(-2.90\text{V} - (+1.36\text{V}) = -4.26 \text{ V}\)

(b) How many grams of barium metal can be produced by supplying 0.50 A for 30 min?

\[
0.50 \text{ A} \times \frac{1 \text{ C}}{1 \text{ A} \cdot \text{s}} \times \frac{60 \text{ s}}{1 \text{ min}} \times 30 \text{ min} = 9.0 \times 10^2 \text{ C}
\]

\[
(9.0 \times 10^2 \text{ C}) \times \frac{1 \text{ mol e}^-}{96,500 \text{ C}} \times \frac{1 \text{ mol Ba}}{2 \text{ mol e}^-} \times \frac{137.3 \text{ g Ba}}{1 \text{ mol Ba}} = 0.64 \text{ g Ba}
\]

19.49 One of the half-reactions for the electrolysis of water is: \(2\text{H}_2\text{O} (l) \rightarrow \text{O}_2 (g) + 4\text{H}^+(aq) + 4e^-\). If 0.076 L of O\(_2\) is collected at 25°C and 755 mm Hg, how many coulombs of electricity had to pass through the solution?

\[
n = \frac{PV}{RT} = \left(\frac{755 \text{ mmHg} \times 1 \text{ atm}}{760 \text{ mmHg}}\right)\left(0.0821 \text{ L} \cdot \text{atm/K} \cdot \text{mol}(298 \text{ K})\right)(0.076 \text{ L}) = 3.1 \times 10^{-3} \text{ mol O}_2
\]

\[
(3.1 \times 10^{-3} \text{ mol O}_2) \times \frac{4 \text{ moles e}^-}{1 \text{ mol O}_2} \times \frac{96,500 \text{ C}}{1 \text{ mole e}^-} = 1197 \text{ C} = 1200 \text{ C}
\]

19.56 In the 1950’s, 60’s and 70’s, most car bumpers were plated with chromium to give a shiny, mirror-like finish. Chromium plating can be accomplished by the electrolysis of a suspended car bumper in an acidified dichromate solution.

(a) The following (unbalanced) reduction half-reaction takes place in the cell. Balance the reduction half-reaction. *(Hint: Balance Cr, then O, then H, than electrons.)*

\[
\text{Cr}_2\text{O}_7^{2-} (aq) + 14 \text{H}^+ (aq) + 12 \text{e}^- \longrightarrow 2 \text{Cr(s)} + 7 \text{H}_2\text{O(l)}
\]

(b) How long would it take (in hours) for a car bumper to be plated with 18 g of chromium if the electrolytic cell carries a current of 25.0 amps.

\[
18 \text{ g Cr} \times \frac{1 \text{ mol Cr}}{52.00 \text{ g Cr}} \times \frac{6 \text{ mol e}^-}{1 \text{ mol Cr}} \times \frac{96,500 \text{ C}}{1 \text{ mol e}^-} \times \frac{1 \text{ s}}{25.0 \text{ C}} \times \frac{1 \text{ h}}{3600 \text{ s}} = 2.3 \text{ h}
\]
19.80 An acidified aqueous solution (has H⁺ ions) was electrolyzed using copper electrodes. A constant current of 1.18 A is applied for 1520 seconds causing the anode to lose 0.584 g of Cu when Cu is oxidized to Cu²⁺.

(a) Write the half-reaction that occurs at the anode, the half-reaction than occurs at the cathode and the balanced overall reaction. Then calculate E° of a standard cell.

\[
\begin{align*}
\text{anode:} & \quad \text{Cu} (s) \rightarrow \text{Cu}^{2+} (aq) + 2e^- & E_{\text{red}}^o &= +0.34 \text{ V} \\
\text{cathode:} & \quad 2\text{H}^+ (aq) + 2e^- \rightarrow \text{H}_2 (g) & E_{\text{red}}^o &= 0 \text{ V}
\end{align*}
\]

Overall Rxn: \( \text{Cu} (s) + 2\text{H}^+ (aq) \rightarrow \text{Cu}^{2+} (aq) + \text{H}_2 (g) \)  \( E_{\text{cell}}^o = 0 - (0.34 \text{V}) = -0.34 \text{V} \)

(b) What gas is produced at the cathode? \( \text{H}_2 \) What volume of this gas would be collected if the gas was collected at STP?

\[
V_{\text{H}_2} = \left(9.20 \times 10^{-3} \text{ mol H}_2\right) \times \frac{22.41 \text{ L}}{1 \text{ mol}} = 0.206 \text{ L}
\]

(c) Calculate the quantity of electricity (in coulombs) used in this cell.

\[
1.18 \text{ A} \times \frac{1 \text{ C}}{1 \text{ A} \cdot \text{s}} \times (1.52 \times 10^3 \text{ s}) = 1.79 \times 10^3 \text{ C}
\]

(d) How many electrons were used? 1 electron has a charge of \(1.6022 \times 10^{-19} \text{ C}.\)

\[
\frac{(1.79 \times 10^3 \text{ C}) \times 1 \text{ e}^-}{1.6022 \times 10^{-19} \text{ C}} = 1.12 \times 10^{22} \text{ e}^-
\]

(e) Calculate Avogadro’s number (# electrons/1 mole e⁻) based on the data in this question

\[
\frac{1.12 \times 10^{22} \text{ e}^-}{9.20 \times 10^{-3} \text{ mol H}_2} \times \frac{1 \text{ mol H}_2}{2 \text{ mol e}^-} = 6.09 \times 10^{23} \text{ e}^- / \text{ mol e}^-
\]

19.89 Industrially, copper is purified by electrolysis. The impure copper acts as the anode, and the cathode is made of pure copper. The electrodes are immersed in a CuSO₄ solution. During electrolysis, copper at the anode enters the solution as Cu²⁺ while Cu²⁺ ions are reduced at the cathode.

(a) Write the half-cell reactions and the overall rxn for the cell.

Anode (impure Cu): \( \text{Cu} (s) \rightarrow \text{Cu}^{2+} (aq) + 2e^- \)

Cathode (pure Cu): \( \text{Cu}^{2+} (aq) + 2e^- \rightarrow \text{Cu} (s) \)

Overall rxn: \( \text{Cu} (s) \rightarrow \text{Cu} (s) \)

Cu is transferred from the impure Cu anode to pure copper cathode.

(b) Suppose the impure copper anode was contaminated with Zn and Ag. Explain what happens to these impurities during electrolysis. (Hint: Use a reduction chart to determine whether either Zn or Ag is more easily oxidized than Cu. Then determine if there are now any new reduction reactions that would occur.)

- Zn is more easily oxidized than Cu, so Zn will be oxidized to form Zn²⁺.
- However, the newly formed Zn²⁺ will not be reduced at the cathode because Zn²⁺ is less easily reduced than Cu²⁺.
- Ag will not be oxidized at the anode because it is less easily oxidized than Cu.