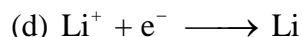
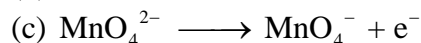
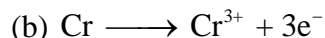
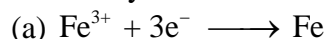


Chemistry 2e
17: Electrochemistry
17.1: Review of Redox Chemistry

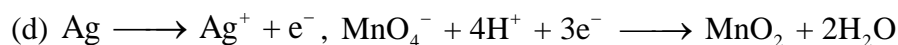
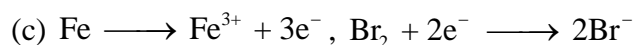
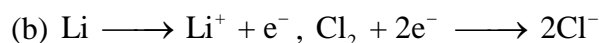
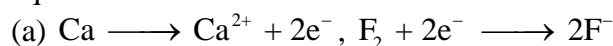
1. Identify each half-reaction below as either oxidation or reduction.



Solution

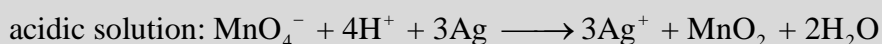
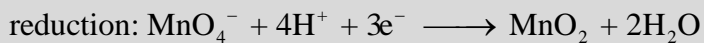
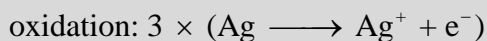
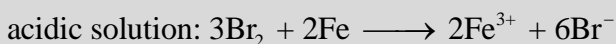
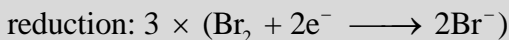
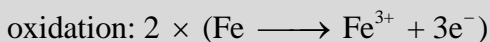
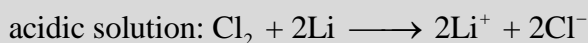
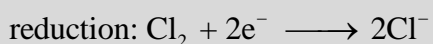
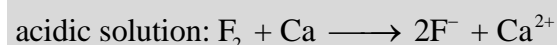
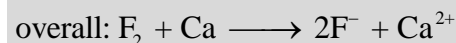
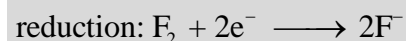
(a) reduction (b) oxidation (c) oxidation (d) reduction

3. Assuming each pair of half-reactions below takes place in an acidic solution, write a balanced equation for the overall reaction.



Solution

(a)



5. Identify the oxidant and reductant of each reaction of the previous exercise.

Solution

Oxidized: (a) Ag; (b) Sn²⁺; (c) Hg; (d) Al, reduced: (a) Hg₂²⁺; (b) H₂O₂; (c) PbO₂; (d) Cr₂O₇²⁻, oxidizing agent: (a) Hg₂²⁺; (b) H₂O₂; (c) PbO₂; (d) Cr₂O₇²⁻, reducing agent: (a) Ag; (b) Sn²⁺; (c) Hg; (d) Al.

7. Identify the oxidant and reductant of each reaction of the previous exercise.

Solution

Oxidized = reducing agent: (a) SO₃²⁻; (b) Mn(OH)₂; (c) H₂; (d) Al; reduced = oxidizing agent: (a) Cu(OH)₂; (b) O₂; (c) NO₃⁻; (d) CrO₄²⁻

9. Why don't hydrogen ions appear in equations for half-reactions occurring in basic solution?

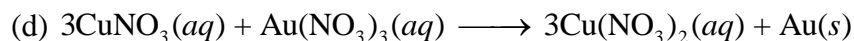
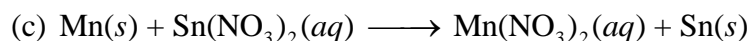
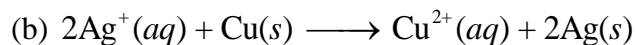
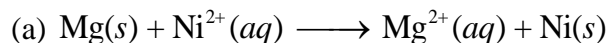
Solution

In basic solution, $[\text{OH}^-] > 1 \times 10^{-7} \text{M} > [\text{H}^+]$. Hydrogen ion cannot appear as a reactant because its concentration is essentially zero. If it were produced, it would instantly react with the excess hydroxide ion to produce water. Thus, hydrogen ion should *not* appear as a reactant or product in basic solution.

This resource file is copyright 2019, Rice University. All Rights Reserved.

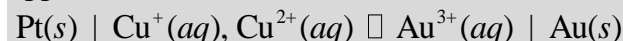
Chemistry 2e
17: Electrochemistry
17.2: Galvanic Cells

11. Write cell schematics for the following cell reactions, using platinum as an inert electrode as needed.



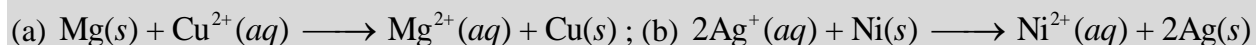
Solution

(a) $\text{Mg}(s) \mid \text{Mg}^{2+}(aq) \parallel \text{Ni}^{2+}(aq) \mid \text{Ni}(s)$; (b) Stoichiometric coefficients do not appear in cell notation $\text{Cu}(s) \mid \text{Cu}^{2+}(aq) \parallel \text{Ag}^{+}(aq) \mid \text{Ag}(s)$; (c) Spectator ions do not appear in cell notation $\text{Mn}(s) \mid \text{Mn}^{2+}(aq) \parallel \text{Sn}^{2+}(aq) \mid \text{Sn}(s)$ (d) Neither stoichiometric coefficients nor spectator ions appear in cell notation. Platinum electrode needed



13. Write a balanced equation for the cell reaction of each cell in the previous exercise.

Solution



15. Identify the oxidant and reductant in each reaction of the previous exercise.

Solution

Species oxidized = reducing agent: (a) $\text{Al}(s)$; (b) $\text{NO}(g)$; (c) $\text{Mg}(s)$ and (d) $\text{MnO}_2(s)$. Species reduced = oxidizing agent: (a) $\text{Zr}^{4+}(aq)$; (b) $\text{Ag}^{+}(aq)$; (c) $\text{SiO}_3^{2-}(aq)$; and (d) $\text{ClO}_3^{-}(aq)$.

17. Why is a salt bridge necessary in galvanic cells like the one in Figure 17.3?

Solution

Without the salt bridge, the circuit would be open (or broken) and no current could flow. With a salt bridge, each half-cell remains electrically neutral and current can flow through the circuit.

19. An active (metal) electrode was found to lose mass as the oxidation-reduction reaction was allowed to proceed. Was the electrode an anode or a cathode? Explain.

Solution

Active electrodes participate in the oxidation-reduction reaction. Since metals form cations, the electrode would lose mass if metal atoms in the electrode were to oxidize and go into solution. Oxidation occurs at the anode.

Chemistry 2e
17: Electrochemistry
17.3: Electrode and Cell Potentials

21. Calculate the standard cell potential for each reaction below, and note whether the reaction is spontaneous under standard state conditions.

- (a) $\text{Mg}(s) + \text{Ni}^{2+}(aq) \longrightarrow \text{Mg}^{2+}(aq) + \text{Ni}(s)$
(b) $2\text{Ag}^{+}(aq) + \text{Cu}(s) \longrightarrow \text{Cu}^{2+}(aq) + 2\text{Ag}(s)$
(c) $\text{Mn}(s) + \text{Sn}(\text{NO}_3)_2(aq) \longrightarrow \text{Mn}(\text{NO}_3)_2(aq) + \text{Sn}(s)$
(d) $3\text{Fe}(\text{NO}_3)_2(aq) + \text{Au}(\text{NO}_3)_3(aq) \longrightarrow 3\text{Fe}(\text{NO}_3)_3(aq) + \text{Au}(s)$

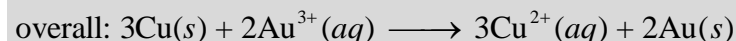
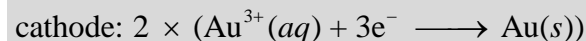
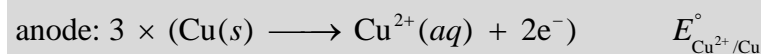
Solution

- (a) $E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ} = -0.257 \text{ V} - (-2.372 \text{ V}) = +2.115 \text{ V}$ (spontaneous);
(b) $E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ} = 0.7996 \text{ V} - (+0.337 \text{ V}) = +0.4626 \text{ V}$ (spontaneous);
(c) $E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ} = -0.1262 \text{ V} - (-1.185 \text{ V}) = +1.0589 \text{ V}$ (spontaneous);
(d) $E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ} = 1.498 \text{ V} - (+0.771 \text{ V}) = +0.727 \text{ V}$ (spontaneous)

23. Write the balanced cell reaction for the cell schematic below, calculate the standard cell potential, and note whether the reaction is spontaneous under standard state conditions.



Solution

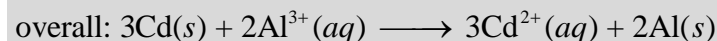
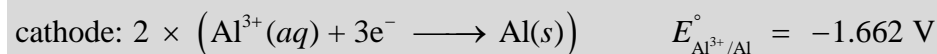
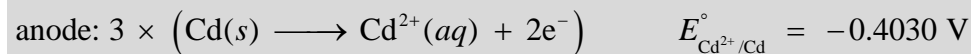


$$E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ} = 1.498 \text{ V} - (+0.34 \text{ V}) = +1.16 \text{ V} \quad (\text{spontaneous})$$

25. Determine the cell reaction and standard cell potential at 25 °C for a cell made from an anode half-cell containing a cadmium electrode in 1 M cadmium nitrate and a cathode half-cell consisting of an aluminum electrode in 1 M aluminum nitrate solution. Is the reaction spontaneous at standard conditions?

Solution

Oxidation occurs at the anode and reduction at the cathode:



$$E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ} = -1.662 \text{ V} - (-0.4030 \text{ V}) = -1.259 \text{ V} \quad (\text{nonspontaneous})$$

This resource file is copyright 2019, Rice University. All Rights Reserved.

Chemistry 2e
17: Electrochemistry
17.4: Potential, Free Energy, and Equilibrium

27. For each pair of standard cell potential and electron stoichiometry values below, calculate a corresponding standard free energy change (kJ).

- (a) 0.000 V, $n = 2$
(b) +0.434 V, $n = 2$
(c) -2.439 V, $n = 1$

Solution

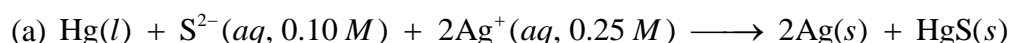
$$\Delta G^\circ = -nFE_{\text{cell}}^\circ$$

$$(a) \Delta G^\circ = -nFE_{\text{cell}}^\circ = -(2) \left(96485 \frac{\text{C}}{\text{V mol}} \right) (0.000 \text{ V}) = 0 \text{ J/mol} = 0 \text{ kJ/mol}$$

$$(b) \Delta G^\circ = -nFE_{\text{cell}}^\circ = -(2) \left(96485 \frac{\text{C}}{\text{V mol}} \right) (+0.434 \text{ V}) = -83749 \text{ J/mol} = -83.7 \text{ kJ/mol}$$

$$(c) \Delta G^\circ = -nFE_{\text{cell}}^\circ = -(1) \left(96485 \frac{\text{C}}{\text{V mol}} \right) (-2.439 \text{ V}) = +235327 \text{ J/mol} = +235.3 \text{ kJ/mol}$$

29. Determine the standard cell potential and the cell potential under the stated conditions for the electrochemical reactions described. State whether each is spontaneous or nonspontaneous under each set of conditions at 298.15 K.

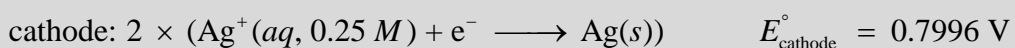
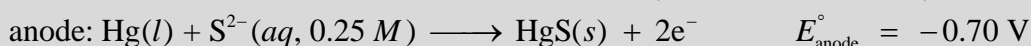


(b) The cell made from an anode half-cell consisting of an aluminum electrode in 0.015 M aluminum nitrate solution and a cathode half-cell consisting of a nickel electrode in 0.25 M nickel(II) nitrate solution.

(c) The cell comprised of a half-cell in which aqueous bromine (1.0 M) is being oxidized to bromide ion (0.11 M) and a half-cell in which Al^{3+} (0.023 M) is being reduced to aluminum metal.

Solution

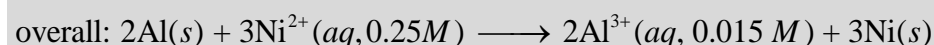
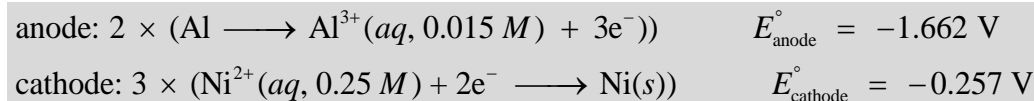
All reactions are at 298.15 K and use $E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{RT}{nF} \ln Q = E_{\text{cell}}^\circ - \frac{0.0592}{n} \log Q$:



$$E_{\text{cell}}^\circ = E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ = 0.7996 \text{ V} - (-0.70 \text{ V}) = 1.50 \text{ V} \quad (\text{spontaneous})$$

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.0592 \text{ V}}{2} \log \frac{1}{0.10 \times 0.25^2} = 1.43 \text{ V} \quad (\text{spontaneous})$$

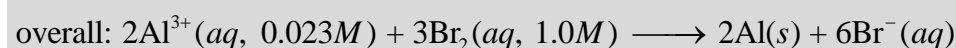
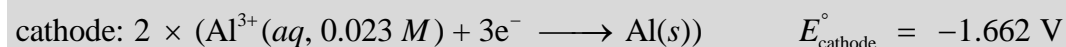
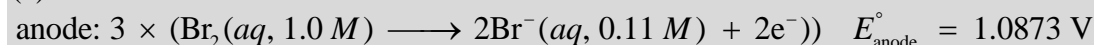
(b)



$$E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ} = -0.257 \text{ V} - (-1.662 \text{ V}) = 1.405 \text{ V} \quad (\text{spontaneous})$$

$$E_{\text{cell}}^{\circ} = E_{\text{cell}}^{\circ} - \frac{0.0592 \text{ V}}{6} \log \frac{0.015^2}{0.25^3} = 1.423 \text{ V} \quad (\text{spontaneous})$$

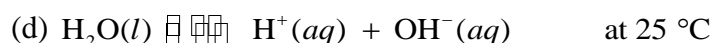
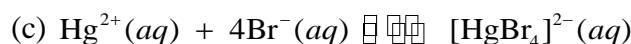
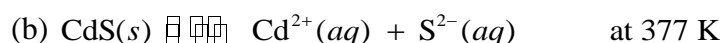
(c) Oxidation occurs at the anode and reduction at the cathode.



$$E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ} = -1.662 \text{ V} - 1.0873 \text{ V} = -2.749 \text{ V} \quad (\text{nonspontaneous})$$

$$E_{\text{cell}}^{\circ} = E_{\text{cell}}^{\circ} - \frac{0.0592 \text{ V}}{6} \log \frac{0.11^6}{0.23^2 \cdot 1.0^3} = -2.757 \text{ V} \quad (\text{nonspontaneous})$$

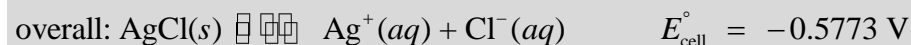
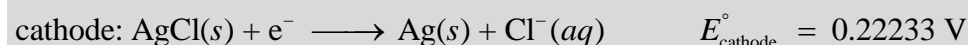
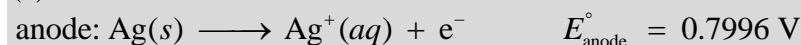
31. Use the data in Appendix L to calculate equilibrium constants for the following reactions. Assume 298.15 K if no temperature is given.



Solution

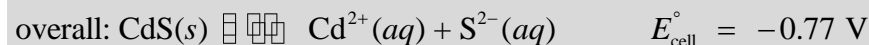
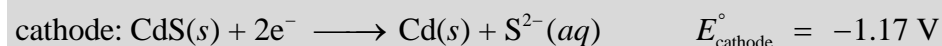
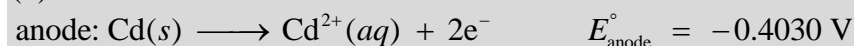
All use $K = e^{nFE_{\text{cell}}^{\circ}/RT}$ with $E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ}$

(a)



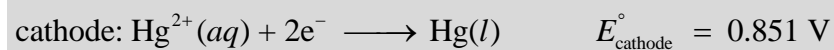
$$n = 1 \text{ and } K = e^{-22.4707} = 1.7 \times 10^{-10}$$

(b)



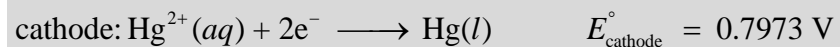
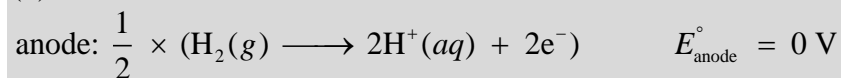
$$n = 2 \text{ and } K = e^{-47.41} = 2.6 \times 10^{-21}$$

(c)



$$n = 2 \text{ and } K = e^{49.90} = 4.693 \times 10^{21}$$

(d)



$$n = \frac{1}{2}(2) \text{ and } K = e^{-32.22} = 1.0 \times 10^{-14}$$

This resource file is copyright 2019, Rice University. All Rights Reserved.

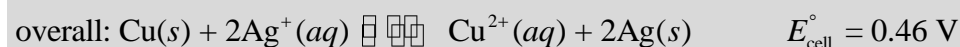
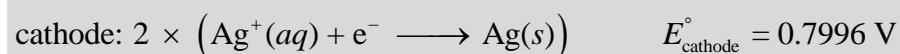
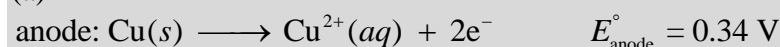
Chemistry 2e
17: Electrochemistry
17.5: Batteries and Fuel Cells

33. Consider a battery with the overall reaction: $\text{Cu}(s) + 2\text{Ag}^+(aq) \longrightarrow 2\text{Ag}(s) + \text{Cu}^{2+}(aq)$.

- (a) What is the reaction at the anode and cathode?
(b) A battery is “dead” when its cell potential is zero. What is the value of Q when this battery is dead?
(c) If a particular dead battery was found to have $[\text{Cu}^{2+}] = 0.11\text{ M}$, what was the concentration of silver ion?

Solution

(a)



(b) Using the Nernst equation with $n = 2$:

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

$$0 = 0.46\text{ V} - \frac{0.0592\text{ V}}{2} \log Q \quad \text{or} \quad Q = 10^{2 \times 0.46\text{ V} / 0.0592\text{ V}} = 10^{15.54} = 3.5 \times 10^{15};$$

(c) Using the value of Q just calculated:

$$Q = 3.5 \times 10^{15} = \frac{[\text{Cu}^{2+}]}{[\text{Ag}^+]^2} \quad \text{or} \quad [\text{Ag}^+] = \sqrt{\frac{[\text{Cu}^{2+}]}{3.5 \times 10^{15}}} = 5.6 \times 10^{-9}\text{ M}.$$

34. Why do batteries go dead but fuel cells do not?

Solution

Batteries are self-contained and have a limited supply of reagents to expend before going dead. Alternatively, battery reaction byproducts accumulate and interfere with the reaction. Because a fuel cell is constantly resupplied with reactants and products are expelled, it can continue to function as long as reagents are supplied.

36. Using the information thus far in this chapter, explain why battery-powered electronics perform poorly in low temperatures.

Solution

E_{cell} , as described in the Nernst equation, has a term that is directly proportional to temperature. At low temperatures, this term is decreased, resulting in a lower cell voltage provided by the battery to the device—the same effect as a battery running dead.

Chemistry 2e
17: Electrochemistry
17.6: Corrosion

38. Consider the following metals: Ag, Au, Mg, Ni, and Zn. Which of these metals could be used as a sacrificial anode in the cathodic protection of an underground steel storage tank? Steel is an alloy composed mostly of iron, so use -0.447 V as the standard reduction potential for steel.

Solution

For cathodic protection, the overall reaction must be spontaneous. Thus, the standard cell potential of the anode must be less than the standard reduction potential of steel/iron (the metal to be protected), which, from the problem, has $E_{\text{cathode}}^{\circ} = -0.447\text{ V}$. With standard reductions in parentheses: Mg (-1.185 V), and Zn (-0.7618 V) could be used as a sacrificial anode, while Ag ($+0.7996\text{ V}$), Au ($+1.629\text{ V}$), and Ni (-0.257 V) could not.

40. If a sample of iron and a sample of zinc come into contact, the zinc corrodes but the iron does not. If a sample of iron comes into contact with a sample of copper, the iron corrodes but the copper does not. Explain this phenomenon.

Solution

Both examples involve cathodic protection. The (sacrificial) anode is the metal that corrodes (oxidizes or reacts). In the case of iron (-0.447 V) and zinc (-0.7618 V), zinc has a more negative standard reduction potential and so serves as the anode. In the case of iron and copper (0.34 V), iron has the smaller standard reduction potential and so corrodes (serves as the anode).

42. Why would a sacrificial anode made of lithium metal be a bad choice?

Solution

While the reduction potential of lithium would make it capable of protecting the other metals, this high potential is also indicative of how reactive lithium is: It would have a spontaneous reaction with most substances. This means that the lithium would react quickly with other substances, even those that would not oxidize the metal it is attempting to protect. Reactivity like this means the sacrificial anode would be depleted rapidly and need to be replaced frequently. (Optional additional reason: fire hazard in the presence of water.)

This resource file is copyright 2019, Rice University. All Rights Reserved.

Chemistry 2e
17: Electrochemistry
17.7: Electrolysis

46. What mass of each product is produced in each of the electrolytic cells of the previous problem if a total charge of $3.33 \times 10^5 \text{ C}$ passes through each cell?

Solution

The charge given in the problem corresponds to $3.33 \times 10^5 \text{ C} \times \frac{1 \text{ mol e}^-}{96485 \text{ C}} = 3.45 \text{ mol e}^-$

(a)

$$\text{mass Ca} = 3.45 \text{ mol e}^- \times \frac{1 \text{ mol}}{2 \text{ mol e}^-} \times \frac{40.078 \text{ g}}{\text{mol}} = 69.1 \text{ g}$$

$$\text{mass Cl}_2 = 3.45 \text{ mol e}^- \times \frac{1 \text{ mol}}{2 \text{ mol e}^-} \times \frac{70.906 \text{ g}}{\text{mol}} = 122 \text{ g}$$

(b)

$$\text{mass Li} = 3.45 \text{ mol e}^- \times \frac{2 \text{ mol}}{2 \text{ mol e}^-} \times \frac{6.941 \text{ g}}{\text{mol}} = 23.9 \text{ g}$$

$$\text{mass H}_2 = 3.45 \text{ mol e}^- \times \frac{1 \text{ mol}}{2 \text{ mol e}^-} \times \frac{2.0158 \text{ g}}{\text{mol}} = 3.48 \text{ g}$$

(c)

$$\text{mass Al} = 3.45 \text{ mol e}^- \times \frac{2 \text{ mol}}{6 \text{ mol e}^-} \times \frac{26.9815 \text{ g}}{\text{mol}} = 31.0 \text{ g}$$

$$\text{mass Cl}_2 = 3.45 \text{ mol e}^- \times \frac{3 \text{ mol}}{6 \text{ mol e}^-} \times \frac{70.906 \text{ g}}{\text{mol}} = 122 \text{ g}$$

(d)

$$\text{mass Cr} = 3.45 \text{ mol e}^- \times \frac{2 \text{ mol}}{6 \text{ mol e}^-} \times \frac{51.9961 \text{ g}}{\text{mol}} = 59.8 \text{ g}$$

$$\text{mass Br}_2 = 3.45 \text{ mol e}^- \times \frac{3 \text{ mol}}{6 \text{ mol e}^-} \times \frac{159.808 \text{ g}}{\text{mol}} = 276 \text{ g}$$

48. A current of 2.345 A passes through the cell shown in Figure 17.19 for 45 minutes. What is the volume of the hydrogen collected at room temperature if the pressure is exactly 1 atm? (Hint: Is hydrogen the only gas present above the water?)

Solution

Water vapor and hydrogen gas will be collected, so the *total* pressure is exactly 1 atm. Using the data in Appendix E, determine that the vapor pressure of water at room temperature is 24.0 mm Hg, or 0.0316 atm. The pressure of the hydrogen gas is then 0.9684 atm. From the figure, 2 moles of electrons are required per mole of hydrogen gas produced so that

$$\text{mol H}_2 = \frac{2.345 \text{ C}}{\text{s}} \times 45.0 \text{ min} \times \frac{60 \text{ s}}{\text{min}} \times \frac{1 \text{ mol e}^-}{96485 \text{ C}} \times \frac{1 \text{ mol H}_2}{2 \text{ mol e}^-} = 0.0328 \text{ mol} = n_{\text{H}_2}$$

Using the ideal gas equation with n_{H_2} , the pressure of the hydrogen, and reducing the value because the efficiency is only 95%, gives:

$$V = \frac{n_{\text{H}_2} \times RT}{P} = \frac{(0.0328 \text{ mol})(0.08206 \text{ L} \cdot \text{atm}/\text{mol} \cdot \text{K})(298.15 \text{ K}) \left(\frac{95\%}{100\%} \right)}{0.9684 \text{ atm}} = 0.79 \text{ L}$$

This resource file is copyright 2019, Rice University. All Rights Reserved.