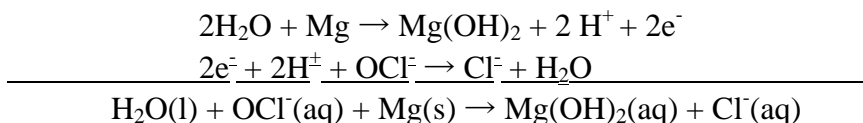
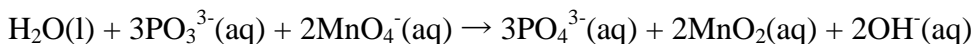
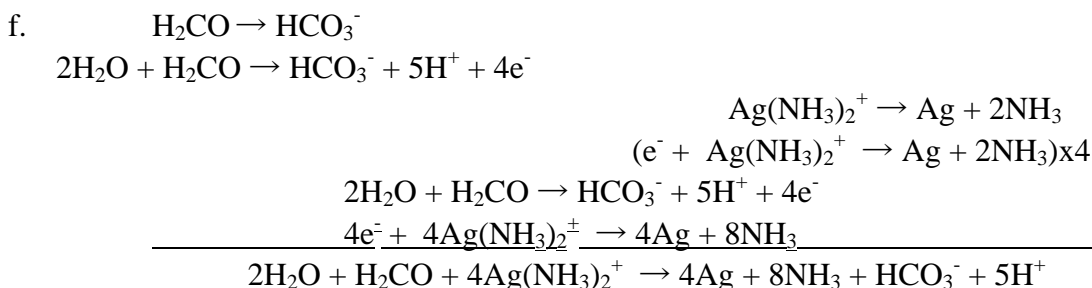


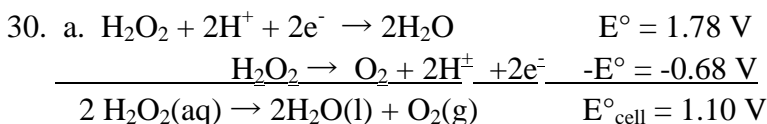
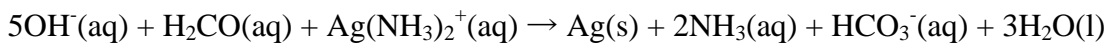
Now convert to a basic solution by adding 2 OH⁻ to both sides. 2 H⁺ + 2OH⁻ → 2H₂O on the reactant side. After concerting H⁺ to OH⁻, simplify the overall equation by crossing off 1 H₂O on each side of the reaction. The overall balanced equation is:



The final overall reaction does not contain H⁺, so we are done.

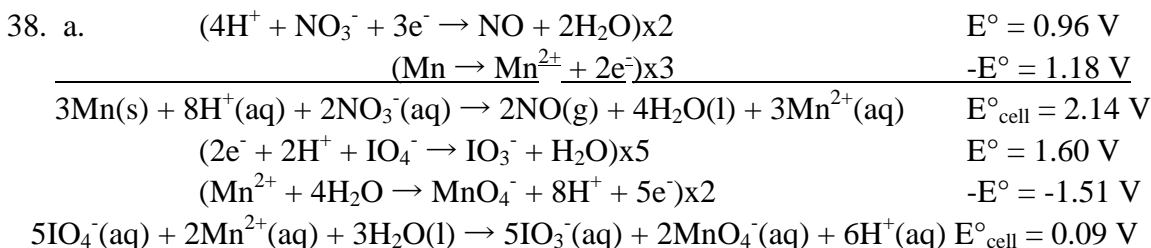
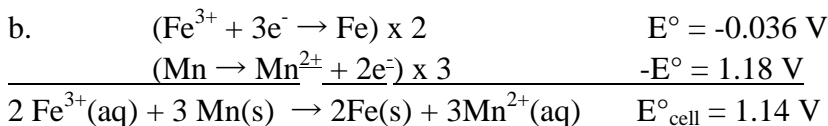


Convert to a basic solution by adding 5 OH⁻ to both sides (5H⁺ + 5OH⁻ → 5H₂O). Then, cross off 2 H₂O on both sides, which gives the overall balanced equation:



Cathode: Pt electrode; H₂O₂ and H⁺ in solution

Anode: Pt electrode; O₂(g) bubbled in, H₂O₂ and H⁺ in solution



54. As is the case for all concentration cells, $E^\circ_{\text{cell}} = 0$, and the smaller ion concentration is always in the anode compartment. The general Nernst equation for the $\text{Ni} | \text{Ni}^{2+}(\text{xM}) || \text{Ni}^{2+}(\text{y M}) | \text{Ni}$ concentration cell is:

$$E_{\text{cell}} = E^\circ_{\text{cell}} - 0.0591/n \log Q = -0.0591/2 \log [\text{Ni}^{2+}]_{\text{anode}}/[\text{Ni}^{2+}]_{\text{cathode}}$$

a. Since both compartments are at standard conditions ($[\text{Ni}^{2+}] = 1.0 \text{ M}$), then $E_{\text{cell}} = E^\circ_{\text{cell}} = 0 \text{ V}$. No electron flow occurs.

b. Cathode = 2.0 M Ni^{2+} ; Anode = 1.0 M Ni^{2+} ; Electron flow is always from the anode to the cathode, so electrons flow to the right in the diagram.

$$E_{\text{cell}} = -0.0591/2 \log [\text{Ni}^{2+}]_{\text{anode}}/[\text{Ni}^{2+}]_{\text{cathode}} = -0.0591/2 \log 1.0/2.0 = 8.9 \cdot 10^{-3} \text{ V}$$

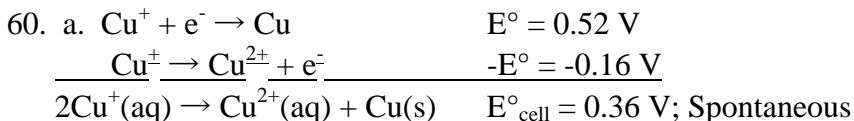
c. Cathode = 1.0 M Ni^{2+} ; Anode = 0.10 M Ni^{2+} ; Electrons flow to the left in the diagram.

$$E_{\text{cell}} = -0.0591/2 \log [\text{Ni}^{2+}]_{\text{anode}}/[\text{Ni}^{2+}]_{\text{cathode}} = -0.0591/2 \log 0.10/1.0 = 0.030 \text{ V}$$

d. Cathode = 1.0 M Ni^{2+} ; Anode = $4.0 \cdot 10^{-5} \text{ M Ni}^{2+}$; Electrons flow to the left in the diagram.

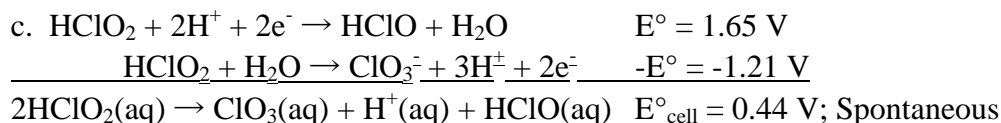
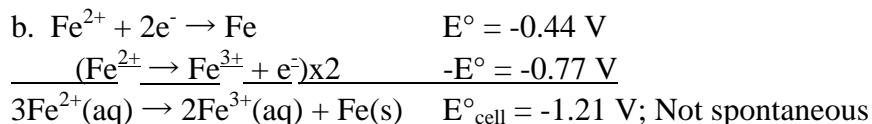
$$E_{\text{cell}} = -0.0591/2 \log [\text{Ni}^{2+}]_{\text{anode}}/[\text{Ni}^{2+}]_{\text{cathode}} = -0.0591/2 \log 4.0 \cdot 10^{-5}/1.0 = 0.13 \text{ V}$$

e. Since both concentrations are equal, $\log(2.5/2.5) = \log 1.0 = 0$ and $E_{\text{cell}} = 0$. No electron flow occurs.



$$\Delta G^\circ = -nFE^\circ_{\text{cell}} = -(1 \text{ mol e}^-)(96,485 \text{ C/mol e}^-)(0.36 \text{ J/C}) = -34,700 \text{ J} = -35 \text{ kJ}$$

$$E^\circ_{\text{cell}} = 0.0591/n \log K, \log K = nE^\circ/0.0591 = 1(0.36)/0.0591 = 6.09, K = 10^{6.09} = 1.2 \cdot 10^6$$



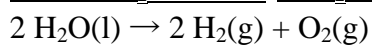
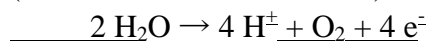
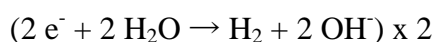
$$\Delta G^\circ = -nFE^\circ_{\text{cell}} = -(2 \text{ mol e}^-)(96,485 \text{ C/mol e}^-)(0.44 \text{ J/C}) = -84,900 \text{ J} = -85 \text{ kJ}$$

$$E^\circ_{\text{cell}} = 0.0591/n \log K, \log K = nE^\circ/0.0591 = 2(0.44)/0.0591 = 14.89, K = 10^{14.89} = 7.8 \cdot 10^{14}$$

74. The oxidation state of bismuth in BiO^+ is +3 because oxygen has a -2 oxidation state in this ion. Therefore, 3 moles of electrons are required to reduce the bismuth in BiO^+ to Bi(s) .

$$10.0 \text{ g Bi} \times 1 \text{ mol Bi}/209.0 \text{ g Bi} \times 3 \text{ mol e}^-/\text{mol Bi} \times 96,485 \text{ C/mol e}^- \times 1 \text{ s}/25.0 \text{ C} = 554 \text{ s} = 9.23 \text{ min}$$

80. The half-reactions for the electrolysis of water are:



Note: $4\text{H}^+ + 4\text{OH}^- \rightarrow 4\text{H}_2\text{O}$ and $n = 4$ for this reaction as it is written.

$$15.0 \text{ min} \times 60 \text{ s/min} \times 2.50 \text{ C/s} \times 1 \text{ mol e}^-/96,485 \text{ C} \times 2 \text{ mol H}_2/4 \text{ mol e}^- = 1.17 \cdot 10^{-2} \text{ mol H}_2$$

At STP, 1 mol of an ideal gas occupies a volume of 22.42 L (see Chapter 5 of the text).

$$1.17 \cdot 10^{-2} \text{ mol H}_2 \times 22.42 \text{ L/mol H}_2 = 0.262 \text{ L} = 262 \text{ mL H}_2$$

$$1.17 \cdot 10^{-2} \text{ mol H}_2 \times 1 \text{ mol O}_2/2 \text{ mol H}_2 \times 22.42 \text{ L/mol O}_2 = 0.131 \text{ L} = 131 \text{ mL O}_2$$

106. a. We can calculate ΔG° from $\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$ and then E° from $\Delta G^\circ = -nFE^\circ$; or we can use the equation derived in Exercise 17.105. For this reaction, $n = 2$ (from oxidation states).

$$E^\circ_{-20} = (T \Delta S^\circ - \Delta H^\circ)/nF = \frac{[(253 \text{ K})(263.5 \text{ J/K}) + 315.9 \cdot 10^3 \text{ J}]}{(2 \text{ mol e}^-)(96,485 \text{ C/mol e}^-)}$$

$$= 1.98 \text{ J/C} = 1.98 \text{ V}$$

$$\text{b. } E^\circ_{-20} = E^\circ_{-20} - RT/nF \ln Q = 1.98 \text{ V} = RT/nF (1/[\text{H}^+]^2[\text{HSO}_4^-]^2)$$

$$E^\circ_{-20} = 1.98 \text{ V} - (8.3145 \text{ J/K}\cdot\text{mol})(253 \text{ K})/(1 \text{ mol e}^-)(96,485 \text{ C/mol e}^-)$$

$$\ln(1/(4.5)^2(4.5)^2) = 1.98 \text{ V} + 0.066 \text{ V} = 2.05 \text{ V}$$

- c. From Exercise 17.56, $E = 2.12 \text{ V}$ at 25°C . As the temperature decreases, the cell potential decreases. Also, oil more viscous at lower temperature, which adds to the difficulty of starting an engine on a cold day. The combination of these two factors results in batteries failing more often on cold days than on warm days.