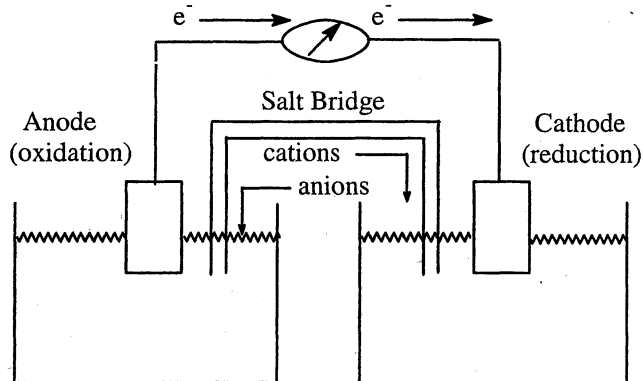


Chapter 11: #17, 18, 19, 26, 29, 32, 39, 46, 53, 55, 56, 91, 95

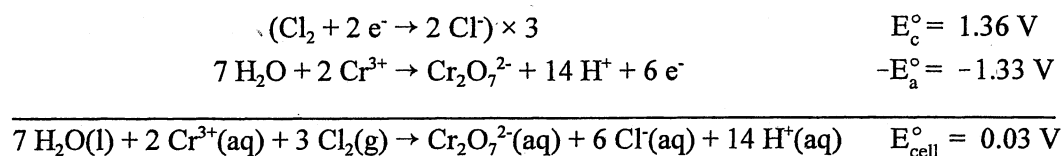
Galvanic Cells, Cell Potentials, and Standard Reduction Potentials

17. A typical galvanic cell diagram is:



The diagram for all cells will look like this. The contents of each half-cell will be identified for each reaction, with all concentrations at 1.0 M and partial pressures at 1.0 atm. Note that cations always flow into the cathode compartment and anions always flow into the anode compartment. This is required to keep each compartment electrically neutral.

- a. Reference Table 11.1 for standard reduction potentials. Remember that  $E_{\text{cell}}^{\circ} = E^{\circ}(\text{cathode}) - E^{\circ}(\text{anode})$ ; in the Solutions Guide, we will represent  $E^{\circ}(\text{cathode})$  as  $E_{\text{c}}^{\circ}$  and represent  $-E^{\circ}(\text{anode})$  as  $-E_{\text{a}}^{\circ}$ . Also remember that standard potentials are not multiplied by the integer used to obtain the overall balanced equation.

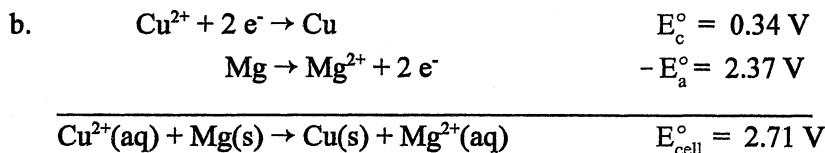


The contents of each compartment is:

Cathode: Pt electrode;  $\text{Cl}_2$  bubbled into solution,  $\text{Cl}^-$  in solution

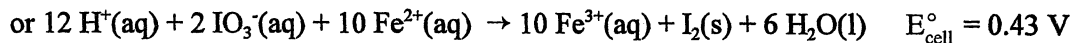
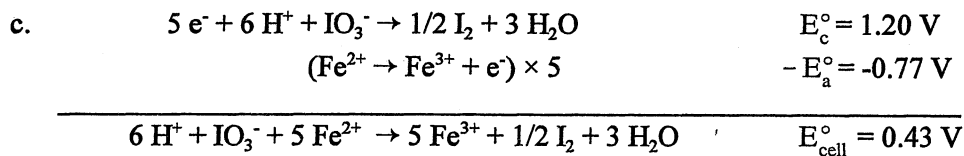
Anode: Pt electrode;  $\text{Cr}^{3+}$ ,  $\text{H}^+$ , and  $\text{Cr}_2\text{O}_7^{2-}$  in solution

We need a nonreactive metal to use as the electrode in each case, since all of the reactants and products are in solution. Pt is the most common choice. Another possibility is graphite.



Cathode: Cu electrode;  $\text{Cu}^{2+}$  in solution

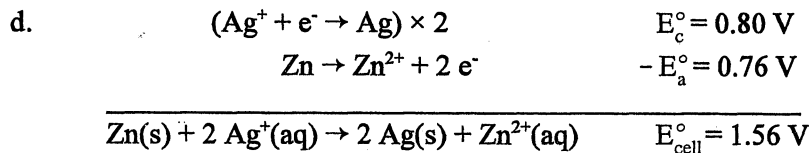
Anode: Mg electrode;  $\text{Mg}^{2+}$  in solution



Cathode: Pt electrode;  $IO_3^-$ ,  $I_2$  and  $H_2SO_4$  ( $H^+$  source) in solution.

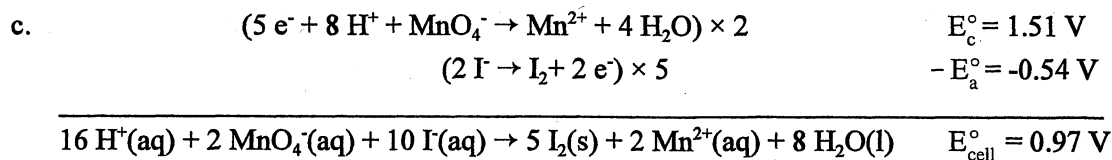
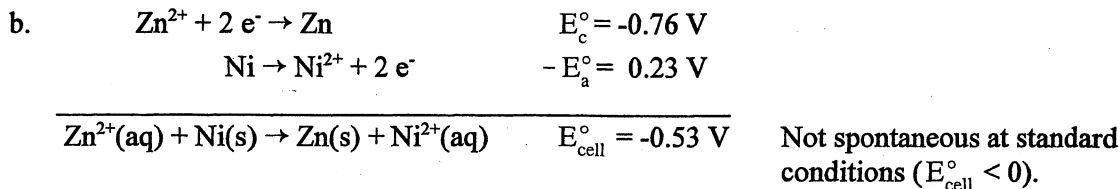
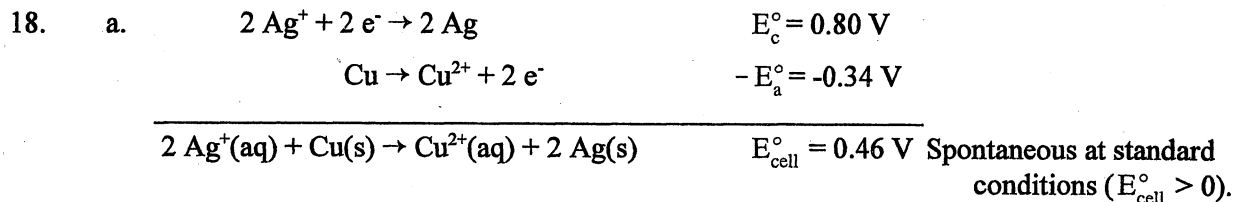
Anode: Pt electrode;  $Fe^{2+}$  and  $Fe^{3+}$  in solution

Note:  $I_2(s)$  would make a poor electrode since it sublimes.

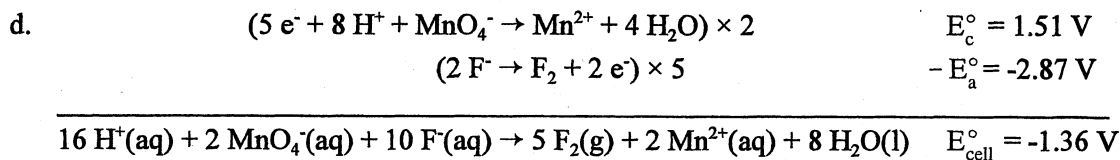


Cathode: Ag electrode;  $Ag^+$  in solution

Anode: Zn electrode;  $Zn^{2+}$  in solution

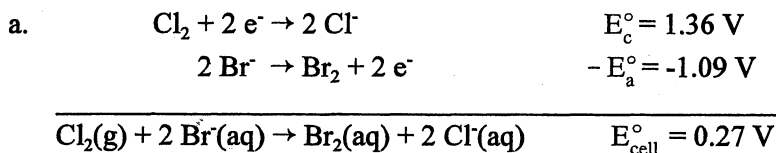


Spontaneous since  $E_{cell}^\circ > 0$ .



Not spontaneous since  $E_{cell}^\circ < 0$ .

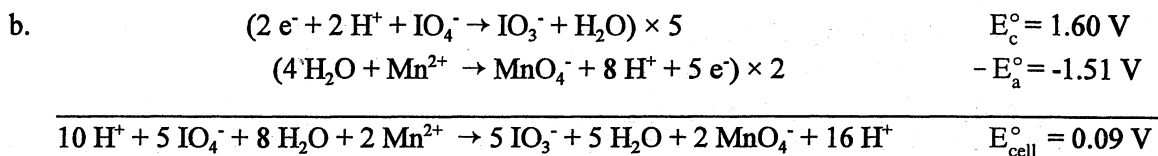
19. Reference Exercise 11.17 for a typical galvanic cell design. The contents of each half-cell compartment is identified below with all solute concentrations at 1.0 M and all gases at 1.0 atm. For each pair of half-reactions, the half-reaction with the largest standard reduction potential will be the cathode reaction and the half-reaction with the smallest reduction potential will be reversed to become the anode reaction. Only this combination gives a spontaneous overall reaction, i.e., a reaction with a positive overall standard cell potential.



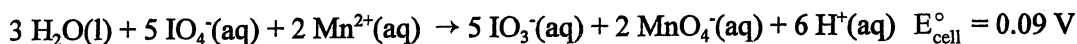
The contents of each compartment is:

Cathode: Pt electrode;  $\text{Cl}_2(\text{g})$  bubbled in,  $\text{Cl}^-$  in solution

Anode: Pt electrode;  $\text{Br}_2$  and  $\text{Br}^-$  in solution

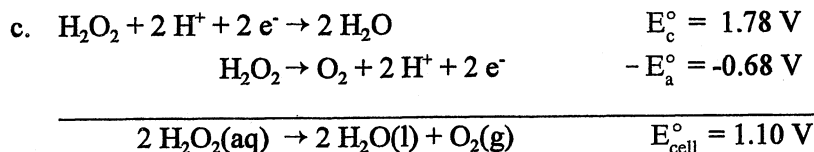


This simplifies to:



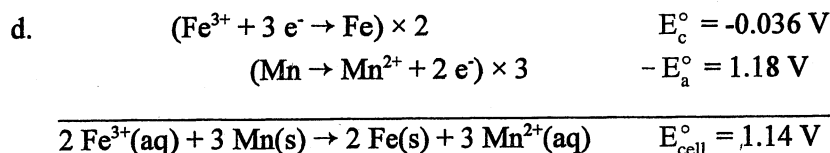
Cathode: Pt electrode;  $\text{IO}_4^-$ ,  $\text{IO}_3^-$ , and  $\text{H}_2\text{SO}_4$  (as a source of  $\text{H}^+$ ) in solution

Anode: Pt electrode;  $\text{Mn}^{2+}$ ,  $\text{MnO}_4^-$  and  $\text{H}_2\text{SO}_4$  in solution

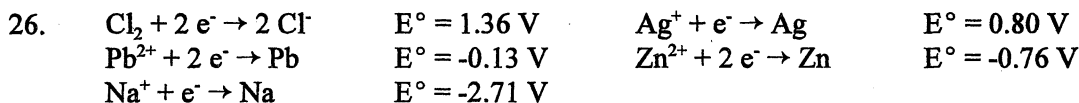


Cathode: Pt electrode;  $\text{H}_2\text{O}_2$  and  $\text{H}^+$  in solution

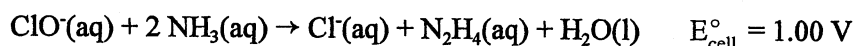
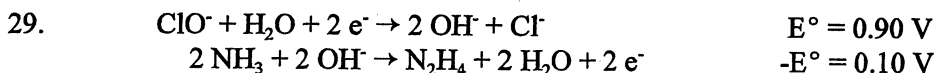
Anode: Pt electrode;  $\text{O}_2(\text{g})$  bubbled in,  $\text{H}_2\text{O}_2$  and  $\text{H}^+$  in solution



Cathode: Fe electrode;  $\text{Fe}^{3+}$  in solution; Anode: Mn electrode;  $\text{Mn}^{2+}$  in solution

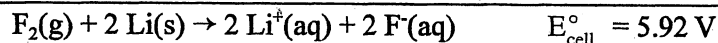
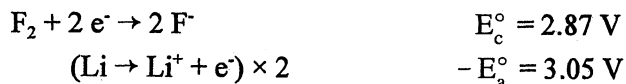


- a. Oxidizing agents (species reduced) are on the left side of the above reduction half-reactions. Of the species available,  $\text{Ag}^+$  would be the best oxidizing agent since it has the most positive  $E^\circ$  value.
- b. Reducing agents (species oxidized) are on the right side of the reduction half-reactions. Of the species available,  $\text{Zn}$  would be the best reducing agent since it has the most positive  $-E^\circ$  value.
- c.  $\text{SO}_4^{2-} + 4 \text{H}^+ + 2 e^- \rightarrow \text{H}_2\text{SO}_3 + \text{H}_2\text{O}$   $E_c^\circ = 0.20 \text{ V}$ ;  $\text{SO}_4^{2-}$  can oxidize  $\text{Pb}$  and  $\text{Zn}$  at standard conditions. When  $\text{SO}_4^{2-}$  is coupled with these reagents,  $E_{\text{cell}}^\circ$  is positive.
- d.  $\text{Al} \rightarrow \text{Al}^{3+} + 3 e^-$   $-E_a^\circ = 1.66 \text{ V}$ ;  $\text{Al}$  can oxidize  $\text{Ag}^+$  and  $\text{Zn}^{2+}$  at standard conditions since  $E_{\text{cell}}^\circ > 0$ .



Since  $E_{\text{cell}}^\circ$  is positive for this reaction, then at standard conditions  $\text{ClO}^-$  can spontaneously oxidize  $\text{NH}_3$  to the somewhat toxic  $\text{N}_2\text{H}_4$ .

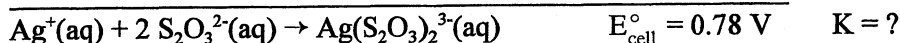
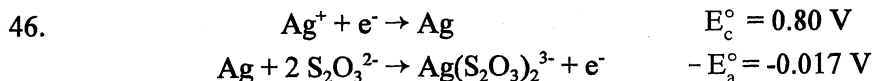
32. Consider the strongest oxidizing agent combined with the strongest reducing agent from Table 11.1:



The claim is impossible. The strongest oxidizing agent and reducing agent when combined only give  $E_{\text{cell}}^\circ$  of about 6 V.

39.  $\Delta G^\circ = -nFE^\circ = \Delta H^\circ - T\Delta S^\circ$ ,  $E^\circ = \frac{T\Delta S^\circ}{nF} - \frac{\Delta H^\circ}{nF}$

If we graph  $E^\circ$  vs.  $T$  we should get a straight line ( $y = mx + b$ ). The slope of the line ( $m$ ) is equal to  $\Delta S^\circ/nF$  and the y-intercept ( $b$ ) is equal to  $-\Delta H^\circ/nF$ .



For this overall reaction,  $E_{\text{cell}}^\circ = \frac{0.0591}{n} \log K$

$\log K = \frac{nE^\circ}{0.0591} = \frac{(1)(0.78)}{0.0591} = 13.20$ ,  $K = 10^{13.20} = 1.6 \times 10^{13}$

Cell Potential,  
Free Energy, and  
Equilibrium

# Galvanic Cells: Concentration Dependence

53. a.  $n = 2$  for this reaction (lead goes from  $\text{Pb} \rightarrow \text{Pb}^{2+}$  in  $\text{PbSO}_4$ ).

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{2} \log \left( \frac{1}{[\text{H}^+]^2 [\text{HSO}_4^-]^2} \right) = 2.04 \text{ V} - \frac{0.0591}{2} \log \frac{1}{(4.5)^2 (4.5)^2}$$

$$2.04 \text{ V} - (-0.077 \text{ V}) = 2.12 \text{ V}$$

- b. We can calculate  $\Delta G^{\circ}$  from  $\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$  and then  $E^{\circ}$  from  $\Delta G^{\circ} = -nFE^{\circ}$ ; or we can use the equation derived in Exercise 11.39.

$$E_{-20}^{\circ} = \frac{T\Delta S^{\circ} - \Delta H^{\circ}}{nF} = \frac{(253 \text{ K})(263.5 \text{ J/K}) + 315.9 \times 10^3 \text{ J}}{(2 \text{ mol } e^-)(96,485 \text{ C/mol } e^-)} = 1.98 \text{ J/C} = 1.98 \text{ V}$$

c.  $E_{-20} = E_{-20}^{\circ} - \frac{RT}{nF} \ln Q = 1.98 \text{ V} - \frac{RT}{nF} \ln \frac{1}{[\text{H}^+]^2 [\text{HSO}_4^-]^2}$

$$E_{-20} = 1.98 \text{ V} - \frac{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(253 \text{ K})}{(2 \text{ mol } e^-)(96,485 \text{ C/mol } e^-)} \ln \frac{1}{(4.5)^2 (4.5)^2} = 1.98 \text{ V} - (-0.066 \text{ V}) = 2.05 \text{ V}$$

- d. As the temperature decreases, the cell potential decreases. Also, oil becomes more viscous at lower temperatures, 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.

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

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

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

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

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

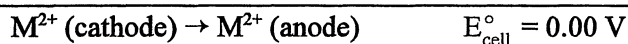
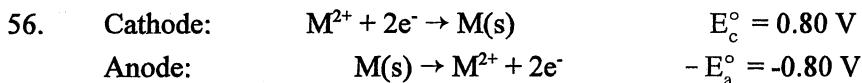
- c. Cathode =  $1.0 \text{ M Ni}^{2+}$ ; Anode =  $0.10 \text{ M Ni}^{2+}$ ; Electrons flow to the left in the diagram.

$$E_{\text{cell}} = \frac{-0.0591}{2} \log \frac{0.10}{1.0} = 0.030 \text{ V}$$

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

$$E_{\text{cell}} = \frac{-0.0591}{2} \log \frac{4.0 \times 10^{-5}}{1.0} = 0.13 \text{ V}$$

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



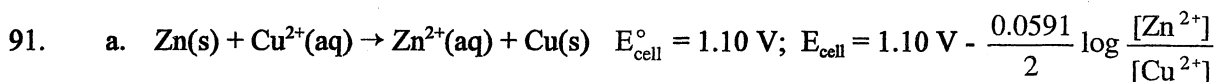
$$E_{\text{cell}} = 0.44 \text{ V} = 0.00 \text{ V} - \frac{0.0591}{2} \log \frac{[M^{2+}]_{\text{anode}}}{[M^{2+}]_{\text{cathode}}}, \quad 0.44 = - \frac{0.0591}{2} \log \frac{[M^{2+}]_{\text{anode}}}{1.0}$$

$$\log [M^{2+}]_{\text{anode}} = - \frac{2(0.44)}{0.0591} = -14.89, \quad [M^{2+}]_{\text{anode}} = 1.3 \times 10^{-15} \text{ M}$$

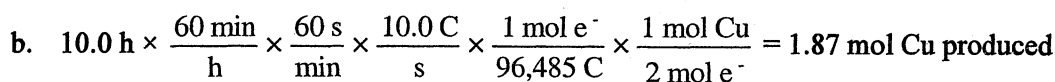
Since we started with equal numbers of moles of  $\text{SO}_4^{2-}$  and  $M^{2+}$ , then  $[M^{2+}] = [\text{SO}_4^{2-}]$  at equilibrium.

$$K_{\text{sp}} = [M^{2+}][\text{SO}_4^{2-}] = (1.3 \times 10^{-15})^2 = 1.7 \times 10^{-30}$$

### Challenge Problems



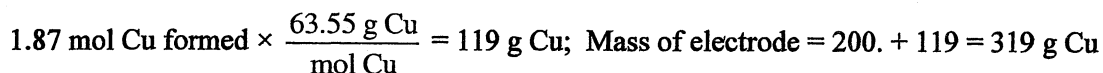
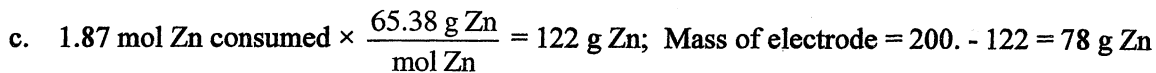
$$E_{\text{cell}} = 1.10 \text{ V} - \frac{0.0591}{2} \log \frac{0.10}{2.50} = 1.10 \text{ V} - (-0.041 \text{ V}) = 1.14 \text{ V}$$



The  $\text{Cu}^{2+}$  concentration decreases by 1.87 mol/L and the  $\text{Zn}^{2+}$  concentration will increase by 1.87 mol/L.

$$[\text{Cu}^{2+}] = 2.50 - 1.87 = 0.63 \text{ M}; \quad [\text{Zn}^{2+}] = 0.10 + 1.87 = 1.97 \text{ M}$$

$$E_{\text{cell}} = 1.10 \text{ V} - \frac{0.0591}{2} \log \frac{1.97}{0.63} = 1.10 \text{ V} - 0.015 \text{ V} = 1.09 \text{ V}$$



d. Three things could possibly cause this battery to go dead:

1. All of the Zn is consumed.
2. All of the  $\text{Cu}^{2+}$  is consumed.
3. Equilibrium is reached ( $E_{\text{cell}} = 0$ ).

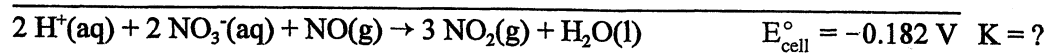
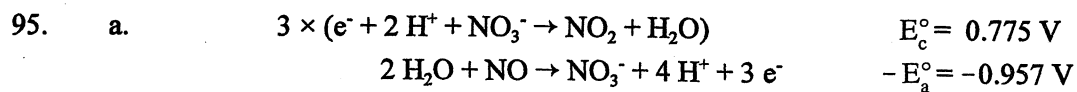
We began with 2.50 mol  $\text{Cu}^{2+}$  and  $200. \text{ g Zn} \times 1 \text{ mol Zn}/65.38 \text{ g Zn} = 3.06 \text{ mol Zn}$ .  $\text{Cu}^{2+}$  is the limiting reagent and will run out first. To react all the  $\text{Cu}^{2+}$  requires:

$$2.50 \text{ mol Cu}^{2+} \times \frac{2 \text{ mol } e^-}{\text{mol Cu}^{2+}} \times \frac{96,485 \text{ C}}{\text{mol } e^-} \times \frac{1 \text{ s}}{10.0 \text{ C}} \times \frac{1 \text{ h}}{3600 \text{ s}} = 13.4 \text{ h}$$

For equilibrium to be reached:  $E = 0 = 1.10 \text{ V} - \frac{0.0591}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$

$$\frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} = K = 10^{2(1.10)/0.0591} = 1.68 \times 10^{37}$$

This is such a large equilibrium constant that virtually all of the  $\text{Cu}^{2+}$  must react to reach equilibrium. So, the battery will go dead in 13.4 hours.



$$\log K = \frac{nE^\circ}{0.0591} = \frac{3(-0.182)}{0.0591} = -9.239, \quad K = 10^{-9.239} = 5.77 \times 10^{-10}$$

b. Let  $C = \text{concentration of HNO}_3 = [\text{H}^+] = [\text{NO}_3^-]$

$$5.77 \times 10^{-10} = \frac{P_{\text{NO}_2}^3}{P_{\text{NO}} \times [\text{H}^+]^2 \times [\text{NO}_3^-]^2} = \frac{P_{\text{NO}_2}^3}{P_{\text{NO}} \times C^4}$$

If 0.20 mol %  $\text{NO}_2$  and  $P_{\text{tot}} = 1.00 \text{ atm}$ :

$$P_{\text{NO}_2} = \frac{0.20 \text{ mol NO}_2}{100. \text{ mol total}} \times 1.00 \text{ atm} = 2.0 \times 10^{-3} \text{ atm}; \quad P_{\text{NO}} = 1.00 - 0.0020 = 1.00 \text{ atm}$$

$$5.77 \times 10^{-10} = \frac{(2.0 \times 10^{-3})^3}{(1.00) C^4}, \quad C = 1.9 \text{ M HNO}_3$$