Chapter 20 Homework Answers

20.50 (a) anode: Cd(s) → Cd^{2+}(aq) + 2e^–
cathode: Au^{3+}(aq) + 3e^– → Au(s)
cell: 3Cd(s) + 2Au^{3+}(aq) → 3Cd^{2+}(aq) + 2Au(s)

(b) anode: Fe(s) → Fe^{2+}(aq) + 2e^–
cathode: Br_2(aq) + 2e^– → 2Br^–(aq)
cell: Fe(s) + Br_2(aq) → Fe^{2+}(aq) + 2Br^–(aq)

(c) anode: Cr(s) → Cr^{3+}(aq) + 3e^–
cathode: Cu^{2+}(aq) + 2e^– → Cu(s)
cell: 2Cr(s) + 3Cu^{2+}(aq) → 2Cr^{3+}(aq) + 3Cu(s)

20.52 (a) Pt(s)|Fe^{2+}(aq),Fe^{3+}(aq)||NO_3^–(aq), H^+(aq)||NO(g)|Pt(s)
(b) Pt(s)|Br_2(aq),Br^–(aq)||Cl^–(aq),Cl_2(g)|Pt(s)
(c) Ag(s)|Ag^+(aq)||Au^{3+}(aq)|Au(s)

20.54 (a) Sn(s) (b) Br^–(aq) (c) Zn(s) (d) I^–(aq)

20.56 (a) E°_cell = 0.96 V – (0.77) V = 0.19 V
(b) E°_cell = 1.07 V – (1.36 V) = –0.29 V
(c) E°_cell = 1.42 V – (0.80 V) = 0.62 V

20.58 The reactions are spontaneous if the overall cell potential is positive.
E°_cell = E substance reduced − E substance oxidized

(a) E°_cell = 1.42 V – (0.54 V) = 0.88 V spontaneous
(b) E°_cell = 1.07 V – (0.17 V) = 0.90 V spontaneous
(c) E°_cell = –0.74 V – (–2.76 V) = 2.02 V spontaneous

20.66 First, separate the overall reaction into its two half–reactions:
2Br^–(aq) → Br_2(aq) + 2e^– oxidation
I_2(s) + 2e^– → 2I^–(aq) reduction

E°_cell = E°_reduction − E°_oxidation = 0.54 V − (1.07 V) = –0.53 V
The value of n is 2: ∆G° = –n F E°_cell = –(2)(96,500 C)(–0.53 J/C)
= 1.0 × 10^5 J = 1.0 × 10^2 kJ

20.72 This reaction involves the oxidation of Ag by two electrons and the reduction of Ni by two electrons. The concentration of the hydrogen ion is derived from the pH of the solution: [H^+] = antilog (–pH) = antilog (–2) = 1 × 10^-2 M

E cell = 2.48 V − 0.0592 V log \left[ \frac{[\text{Ag}^+]^2[\text{Ni}^{2+}]}{[\text{H}^+]^3} \right]
= 2.48 V − 0.0592 V log \left[ \frac{3.0 \times 10^{-2}}{1.0 \times 10^{-2}} \right]^2 \left[ \frac{3.0 \times 10^{-2}}{1.0 \times 10^{-2}} \right]^4
E_{cell} = 2.48 V − 0.101 V = 2.38 V
20.76 In the iron half–cell, we are initially given:

\[
0.0500 \text{ L} \times 0.100 \text{ mol/L} = 5.00 \times 10^{-3} \text{ mol Fe}^{2+}(aq)
\]

The precipitation of Fe(OH)_2(s) consumes some of the added hydroxide ion, as well as some of the iron ion: Fe^{2+}(aq) + 2OH^–(aq) \rightarrow \text{Fe(OH)}_2(s). The number of moles of OH^– that have been added to the iron half–cell is:

\[
0.500 \text{ mol/L} \times 0.0500 \text{ L} = 2.50 \times 10^{-2} \text{ mol OH}^–
\]

The stoichiometry of the precipitation reaction requires that the following number of moles of OH^– be consumed on precipitation of 5.00 \times 10^{-3} \text{ mol of Fe(OH)}_2(s):

\[
5.00 \times 10^{-3} \text{ mol Fe(OH)}_2 \times (2 \text{ mol OH}^–/\text{mol Fe(OH)}_2) = 1.00 \times 10^{-2} \text{ mol OH}^–
\]

The number of moles of OH^– that are unprecipitated in the iron half–cell is:

\[
2.50 \times 10^{-2} \text{ mol} – 1.00 \times 10^{-2} \text{ mol} = 1.50 \times 10^{-2} \text{ mol OH}^–
\]

Since the resulting volume is 50.0 mL + 50.0 mL, the concentration of hydroxide ion in the iron half–cell becomes, upon precipitation of the Fe(OH)_2:

\[
[\text{OH}^–] = 1.50 \times 10^{-2} \text{ mol/0.100 L} = 0.150 \text{ M OH}^–
\]

The standard cell potential is:

\[
E^{\circ}_{\text{cell}} = E^{\circ}_{\text{reduction}} – E^{\circ}_{\text{oxidation}} = 0.3419 \text{ V} – (–0.447 \text{ V}) = 0.7889 \text{ V}
\]

The Nernst equation is:

\[
E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cell}} – \frac{RT}{nF} \ln \left( \frac{[\text{Fe}^{2+}]}{[\text{Cu}^{2+}]} \right)
\]

\[
1.175 = 0.7889 – \frac{(8.314 \text{ J mol}^{-1} \text{K}^{-1})(298 \text{ K})}{2(96,500 \text{ C mol}^{-1})} \ln \left( \frac{[\text{Fe}^{2+}]}{[1.00]} \right)
\]

\[
1.175 = 0.7889 – 0.01284 \ln[\text{Fe}^{2+}]
\]

\[
\ln[\text{Fe}^{2+}] = –30.08
\]

\[
[\text{Fe}^{2+}] = 8.66 \times 10^{-14} \text{ M}
\]

20.80 (a) Fe^{2+}(aq) + 2e^- \rightarrow \text{Fe(s)}

0.20 \text{ mol Fe}^{2+} \times 2 \text{ mol e}^-/\text{mol Fe}^{2+} = 0.40 \text{ mol e}^–

(b) Cl^–(aq) \rightarrow 1/2\text{Cl}_2(g) + e^–

0.70 \text{ mol Cl}^- \times 1 \text{ mol e}^-/\text{mol Cl}^- = 0.70 \text{ mol e}^–

(c) Cr^{3+}(aq) + 3e^- \rightarrow \text{Cr(s)}

1.50 \text{ mol Cr}^{3+} \times 3 \text{ mol e}^-/\text{mol Cr}^{3+} = 4.50 \text{ mol e}^–

(d) \text{Mn}^{2+}(aq) + 4\text{H}_2\text{O(l)} \rightarrow \text{MnO}_4^–(aq) + 8\text{H}^+(aq) + 5e^–

1.0 \times 10^{-2} \text{ mol Mn}^{2+} \times 5 \text{ mol e}^-/\text{mol Mn}^{2+} = 5.0 \times 10^{-2} \text{ mol e}^–

20.86 Mg^{2+} + 2e^- \rightarrow \text{Mg(l)}

The number of Coulombs that will be required is:

\[
\text{Coulombs} = \left(60.0 \text{ g Mg} \times \frac{1 \text{ mol Mg}}{24.31 \text{ g Mg}} \times \frac{2 \text{ mol e}^-}{1 \text{ mol Mg}} \times \frac{96,500 \text{ C}}{1 \text{ mol e}^-} \right) \times 4.76 \times 10^5 = 4.76 \times 10^5 \text{ C}
\]

The number of amperes is: 4.76 \times 10^5 \text{ C} \div 7200 \text{ s} = 66.2 \text{ amp}
The electrolysis of NaCl solution results in the reduction of water, together with the formation of hydroxide ion: \(2H_2O + 2e^- \rightarrow H_2(g) + 2OH^-(aq)\). The number of Coulombs is: \(2.00 \text{ A} \times 20.0 \text{ min} \times 60 \text{ s/min} = 2.40 \times 10^3 \text{ C}\). The number of moles of \(OH^-\) is:

\[
\text{mol OH}^- = \left(2.40 \times 10^3 \text{ C}\right) \left(\frac{1 \text{ mol e}^-}{96,500 \text{ C}}\right) \left(\frac{2 \text{ mol OH}^-}{2 \text{ mol e}^-}\right) = 0.0249 \text{ mol OH}^-
\]

\([OH^-] = 0.0249 \text{ mol/0.250 L} = 0.0996 \text{ M}\)

The initial numbers of moles of Ag\(^+\) and Zn\(^{2+}\) are: \(1.00 \text{ mol/L} \times 0.100 \text{ L} = 0.100 \text{ mol}\). The number of Coulombs (A \times s) that have been employed is: \(0.10 \text{ C/s} \times 15.00 \text{ hr} \times 3600 \text{ s/hr} = 5.4 \times 10^3 \text{ C}\). The number of moles of electrons is: \(5.4 \times 10^3 \text{ C} \div 96,500 \text{ C/mol} = 5.6 \times 10^{-2} \text{ mol electrons}\).

For Ag\(^+\), there is 1 mol per mole of electrons, and for Zn\(^{2+}\), there are two moles of electrons per mol of Zn. This means that the number of moles of the two ions that have been consumed or formed is given by:

\[
5.6 \times 10^{-2} \text{ mol e}^- \times 1 \text{ mol Ag}^+/1 \text{ mol e}^- = 5.6 \times 10^{-2} \text{ mol Ag}^+ \text{ reacted.}
\]

\[
5.6 \times 10^{-2} \text{ mol e}^- \times 1 \text{ mol Zn}^{2+}/2 \text{ mol e}^- = 2.8 \times 10^{-2} \text{ mol Zn}^{2+} \text{ formed}
\]

The number of moles of Ag\(^+\) that remain is: \(0.100 - 0.056 = 0.044 \text{ mol of Ag}^+\)

The final concentration of silver ion is: \([Ag^+] = 0.044 \text{ mol/0.100 L} = 0.44 \text{ M}\)

The number of moles of Zn\(^{2+}\) that are present is: \(0.100 + 0.028 = 0.128 \text{ mol Zn}^{2+}\)

The final concentration of zinc ion is: \([Zn^{2+}] = 0.128 \text{ mol/0.100 L} = 1.28 \text{ M}\)

The standard cell potential should be: \(E^\circ_{\text{cell}} = E^\circ_{\text{reduction}} - E^\circ_{\text{oxidation}} = 0.80 - (-0.76) = 1.56 \text{ V}\)

We now apply the Nernst equation:

\[
E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0592 \text{ V}}{2} \log \frac{1.28}{(0.44)^2}
\]

\(E_{\text{cell}} = 1.56 \text{ V} - 0.024 \text{ V} = 1.54 \text{ V}\)

In the iron half–cell, we are initially given:

\(0.0500 \text{ L} \times 0.100 \text{ mol/L} = 5.00 \times 10^{-3} \text{ mol Fe}^{3+}(aq)\)

The precipitation of Fe(OH)\(_2\)(s) consumes some of the added hydroxide ion, as well as some of the iron ion: \(Fe^{3+}(aq) + 2OH^- (aq) \rightarrow Fe(OH)_2(s)\). The number of moles of \(OH^-\) that have been added to the iron half–cell is:

\(0.500 \text{ mol/L} \times 0.0500 \text{ L} = 2.50 \times 10^{-2} \text{ mol OH}^-\)

The stoichiometry of the precipitation reaction requires that the following number of moles of \(OH^-\) be consumed on precipitation of \(5.00 \times 10^{-3} \text{ mol of Fe(OH)}_2(s)\):

\(5.00 \times 10^{-3} \text{ mol Fe(OH)}_2 \times (2 \text{ mol OH}^-/\text{mol Fe(OH)}_2) = 1.00 \times 10^{-2} \text{ mol OH}^-\)

The number of moles of \(OH^-\) that are unprecipitated in the iron half–cell is:

\(2.50 \times 10^{-2} \text{ mol} - 1.00 \times 10^{-2} \text{ mol} = 1.50 \times 10^{-2} \text{ mol OH}^-\)

Since the resulting volume is 50.0 mL + 50.0 mL, the concentration of hydroxide ion in the iron half–cell becomes, upon precipitation of the Fe(OH)\(_2\):

\([OH^-] = 1.50 \times 10^{-2} \text{ mol/0.100 L} = 0.150 \text{ M OH}^-\)
We have assumed that the iron hydroxide that forms in the above precipitation reaction is completely insoluble. This is not accurate, though, because some small amount does dissolve in water according to the following equilibrium:

\[
\text{Fe(OH)}_2(s) \rightleftharpoons \text{Fe}^{2+}(aq) + 2\text{OH}^-(aq)
\]

This means that the true \([\text{OH}^-]\) is slightly higher than 0.150 \(M\) as calculated above. Thus we must set up the usual equilibrium table, in order to analyze the extent to which \(\text{Fe(OH)}_2(s)\) dissolves in 0.150 \(M\) \(\text{OH}^-\) solution:

<table>
<thead>
<tr>
<th></th>
<th>([\text{Fe}^{2+}])</th>
<th>([\text{OH}^-])</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>–</td>
<td>0.150</td>
</tr>
<tr>
<td>C</td>
<td>+(x)</td>
<td>+2(x)</td>
</tr>
<tr>
<td>E</td>
<td>+(x)</td>
<td>0.150 + 2(x)</td>
</tr>
</tbody>
</table>

The quantity \(x\) in the above table is the molar solubility of \(\text{Fe(OH)}_2\) in the solution that is formed in the iron half–cell.

\[
K_{sp} = [\text{Fe}^{2+}][\text{OH}^-]^2 = (x)(0.150 + 2x)^2
\]

The standard cell potential is:

\[
E_{\text{cell}}^\circ = E_{\text{reduction}}^\circ - E_{\text{oxidation}}^\circ = 0.3419 \text{ V} - (-0.447 \text{ V}) = 0.7889 \text{ V}
\]

The Nernst equation is:

\[
E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{RT}{nF} \ln \left( \frac{[\text{Fe}^{2+}]}{[\text{Cu}^{2+}]} \right)
\]

\[
1.175 = 0.7889 - \frac{(8.314 \text{ J mol}^{-1} \text{K}^{-1})(298 \text{ K})}{2(96,500 \text{ C mol}^{-1})} \ln \left( \frac{[\text{Fe}^{2+}]}{[1.00]} \right)
\]

\[
1.175 = 0.7889 - 0.01284 \ln [\text{Fe}^{2+}]
\]

\[
\ln [\text{Fe}^{2+}] = -30.07
\]

\[
[\text{Fe}^{2+}] = 8.72 \times 10^{-14} \text{ M}
\]

This is the concentration of \(\text{Fe}^{2+}\) in the saturated solution, and it is the value to be used for \(x\) in the above expression for \(K_{sp}\).

\[
K_{sp} = (x)(0.150 + 2x)^2 = (8.72 \times 10^{-14})(0.150 + (2)(8.72 \times 10^{-14}))^2
\]

\[
K_{sp} = 1.96 \times 10^{-15}
\]

115 and 119 are discussion questions.