CHAPTER 12 ELECTROCHEMISTRY

12.2 (a)

(b)
$$7 \text{ H}_2\text{O(1)} + 2 \text{ Cr}^{3+}(\text{aq}) \rightarrow \text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 6 \text{ e}^- + 14 \text{ H}^+(\text{aq})$$

(c)
$$2 H^{+}(aq) + 2 e^{-} + S_{2}O_{8}^{2-}(aq) \rightarrow 2 HSO_{4}^{-}(aq)$$

(d)
$$7 H_2 O(l) + 2 Cr^{3+}(aq) + 3 S_2 O_8^{2-}(aq)$$

 $\rightarrow 6 HSO_4^-(aq) + Cr_2 O_7^{2-}(aq) + 8 H^+(aq)$

12.4 (a)
$$6[Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^{-}]$$

$$1[Cr_2O_7^{\ 2-}(aq) + 14\ H^+\ (aq) + 6\ e^- \rightarrow 2\ Cr^{3+}(aq) + 7\ H_2O(l)]$$

 Fe^{2+} is the reducing agent and $Cr_2O_7^{2-}$ is the oxidizing agent.

(b)
$$5[C_2H_5OH(aq) + H_2O(l) \rightarrow CH_3COOH(aq) + 4H^+(aq) + 4e^-]$$

$$4 \left[\text{MnO}_4^{-}(\text{aq}) + 8 \text{ H}^{+}(\text{aq}) + 5 \text{ e}^{-} \rightarrow \text{Mn}^{2+}(\text{aq}) + 4 \text{ H}_2\text{O}(\text{l}) \right]$$

$$5 C_2 H_5 OH(aq) + 5 H_2 O(l) + 4 MnO_4^-(aq) + 32 H^+(aq) + 20 e^- \rightarrow$$

 $5 CH_3 COOH(aq) + 20 H^+(aq) + 20 e^- + 4 Mn^{2+}(aq) + 16 H_2 O(l)$

$$5 C_2H_5OH(aq) + 4 MnO_4^-(aq) + 12 H^+(aq) \rightarrow$$

 $5 CH_3COOH(aq) + 4 Mn^{2+}(aq) + 11 H_2O(l)$

C₂H₅OH is the reducing agent and MnO₄⁻ is the oxidizing agent.

(c) The reaction is
$$I^-(aq) + NO_3^-(aq) \rightarrow I_2(aq) + NO(g)$$
.

$$3[2 I^{-}(aq) \rightarrow I_{2}(aq) + 2 e^{-}]$$

$$2[NO_3^-(aq) + 4 H^+(aq) + 3 e^- \rightarrow NO(g) + 2 H_2O(1)]$$

6 I⁻(aq) + 2 NO₃⁻(aq) + 8 H⁺(aq) + 6 e⁻

$$\rightarrow$$
 3 I₂(aq) + 6 e⁻ + 2 NO(g) + 4 H₂O(l)

$$6 I^{-}(aq) + 2 NO_{3}^{-}(aq) + 8 H^{+}(aq) \rightarrow 3 I_{2}(aq) + 2 NO(g) + 4 H_{2}O(l)$$

I⁻ is the reducing agent and NO₃⁻ is the oxidizing agent.

(d)
$$3[As_2S_3(s) + 8 H_2O(l) \rightarrow 2 H_3AsO_4(aq) + 3 S(s) + 10 H^+(aq) + 10 e^-]$$

 $10[NO_3^-(aq) + 4 H^+(aq) + 3 e^- \rightarrow NO(g) + 2 H_2O(l)]$

$$3 \text{ As}_2\text{S}_3(s) + 10 \text{ NO}_3^-(aq) + 24 \text{ H}_2\text{O}(l) + 40 \text{ H}^+(aq) + 30 \text{ e}^- \rightarrow 6 \text{ H}_3\text{AsO}_4(aq) + 9 \text{ S}(s) + 10 \text{ NO}(g) + 20 \text{ H}_2\text{O}(l) + 30 \text{ H}^+(aq) + 30 \text{ e}^-$$

$$3 \text{ As}_2 \text{S}_3(s) + 10 \text{ NO}_3^-(aq) + 4 \text{ H}_2 \text{O}(l) + 10 \text{ H}^+(aq) \rightarrow 6 \text{ H}_3 \text{AsO}_4(aq) + 9 \text{ S}(s) + 10 \text{ NO}(g)$$

 As_2S_3 is the reducing agent (both As and S are oxidized) and NO_3^- is the oxidizing agent.

12.6 (a)
$$Cl_2O_7(g) \rightarrow 2 ClO_2^-(aq) + 3 H_2O(l)$$
 (O's balanced)

$$Cl_2O_7(g) + 6 H_2O(l)$$

 $\rightarrow 2 ClO_2^-(aq) + 3 H_2O(l) + 6 OH^-(aq)$ (H's balanced)

$$Cl_2O_7(g) + 3 H_2O(l) + 8 e^-$$

 $\rightarrow 2 ClO_2^-(aq) + 6 OH^-(aq)$ (charge balanced)

$$H_2O_2(aq) \rightarrow O_2(g)$$
 (O's balanced)

$$H_2O_2(aq) + 2 OH^-(aq) \rightarrow O_2(g) + 2 H_2O(l)$$
 (H's balanced)

$$\mathrm{H_2O_2(aq)} + 2\ \mathrm{OH^-(aq)} \rightarrow \mathrm{O_2(g)} + 2\ \mathrm{H_2O(l)} + 2\ \mathrm{e^-} \ \ (charge\ balanced)$$

Combining the two half-reactions:

$$1[Cl_2O_7(g) + 3 H_2O(1) + 8 e^- \rightarrow 2 ClO_7(aq) + 6 OH^-(aq)]$$

$$4[H_2O_2(aq) + 2 OH^-(aq) \rightarrow O_2(g) + 2 H_2O(l) + 2 e^-]$$

$$Cl_2O_7(g) + 3 H_2O(l) + 8 e^- + 4 H_2O_2(aq) + 8 OH^-(aq) \rightarrow$$

 $2 ClO_2^-(aq) + 6 OH^-(aq) + 4 O_2(g) + 8 H_2O(l) + 8 e^-$

$$Cl_2O_7(g) + 4 H_2O_2 + 2 OH^-(aq) \rightarrow 2 ClO_2^-(aq) + 4 O_2(g) + 5 H_2O(l)$$

 Cl_2O_7 is the oxidizing agent and H_2O_2 is the reducing agent.

(b)
$$MnO_4^-(aq) \rightarrow MnO_2(s) + 2 H_2O(l)$$
 (O's balanced)

$$MnO_4^-(aq) + 4 H_2O(l)$$

 $\rightarrow MnO_2(s) + 2 H_2O(l) + 4 OH^-(aq)$ (H's balanced)

$$MnO_4^-(aq) + 2 H_2O(l) + 3 e^- \rightarrow$$

$$MnO_2(s) + 4 OH^-(aq)$$
(charge balanced)

$$S^{2-}(aq) \to S(s) + 2e^{-}$$

Combining the two half-reactions:

$$2[MnO_4^-(aq) + 2 H_2O(1) + 3 e^- \rightarrow MnO_2(s) + 4 OH^-(aq)]$$

$$3[S^{2-}(aq) \rightarrow S(s) + 2e^{-}]$$

$$2 \text{ MnO}_4^-(aq) + 4 \text{ H}_2\text{O}(l) + 6 \text{ e}^- + 3 \text{ S}^{2-}(aq) \rightarrow$$

 $2 \text{ MnO}_2(s) + 8 \text{ OH}^-(aq) + 3 \text{ S}(s) + 6 \text{ e}^-$

$$2 \text{ MnO}_4^-(aq) + 4 \text{ H}_2\text{O}(1) + 3 \text{ S}^{2-}(aq) \rightarrow 2 \text{ MnO}_2(s) + 8 \text{ OH}^-(aq) + 3 \text{ S}(s)$$

 $MnO_4^{\;\;-}$ is the oxidizing agent and S^{2-} is the reducing agent.

(c)
$$N_2H_4(g) + 2H_2O(l) \rightarrow 2 NO(g)$$
 (O's balanced)

$$N_2H_4(g) + 2 H_2O(l) + 8 OH^-(aq) \rightarrow 2 NO(g) + 8 H_2O(l)$$
 (H's balanced)

$$N_2H_4(g) + 8 OH^-(aq) \rightarrow 2 NO(g) + 6 H_2O(l) + 8 e^-$$
 (charge balanced)

$$ClO_3^-(aq) \rightarrow Cl^-(aq) + 3 H_2O(l)$$
 (O's balanced)

$$ClO_3^-(aq) + 6 H_2O(l) \rightarrow Cl^-(aq) + 3 H_2O(l) + 6 OH^-(aq)$$
 (H's balanced)

$$\text{ClO}_3^-(\text{aq}) + 3 \text{ H}_2\text{O}(\text{l}) + 6 \text{ e}^- \rightarrow \text{Cl}^-(\text{aq}) + 6 \text{ OH}^-(\text{aq})$$
 (charge balanced)

Combining the two half-reactions:

$$3[N_2H_4(g) + 8 OH^-(aq) \rightarrow 2 NO(g) + 6 H_2O(l) + 8 e^-]$$

$$4[ClO_3^-(aq) + 3 H_2O(l) + 6 e^- \rightarrow Cl^-(aq) + 6 OH^-(aq)]$$

$$3 \text{ N}_2\text{H}_4(g) + 24 \text{ OH}^-(aq) + 4 \text{ ClO}_3^-(aq) + 12 \text{ H}_2\text{O}(l) + 24 \text{ e}^- \rightarrow 6 \text{ NO}(g) + 18 \text{ H}_2\text{O}(l) + 24 \text{ e}^- + 4 \text{ Cl}^-(aq) + 24 \text{ OH}^-(aq)$$

$$3 \text{ N}_2 \text{H}_4(g) + 4 \text{ ClO}_3^-(aq) \rightarrow 6 \text{ NO}(g) + 6 \text{ H}_2 \text{O}(l) + 4 \text{ Cl}^-(aq)$$

N₂H₄ is the reducing agent and ClO₃⁻ is the oxidizing agent.

(d)
$$Pb(OH)_a^{2-}(aq) \rightarrow PbO_2(s) + 2 H_2O(1) + 2 e^{-}$$

$$ClO^{-}(aq) + H_{2}O(l) + 2e^{-} \rightarrow Cl^{-}(aq) + 2OH^{-}(aq)$$

or

$$Pb(OH)_4^{2-}(aq) + ClO^{-}(aq) \rightarrow PbO_2(s) + Cl^{-}(aq) + H_2O(l) + 2OH^{-}(aq)$$

Pb(OH)₄²⁻ is the reducing agent and ClO⁻ is the oxidizing agent.

12.8 We first determine the two half-reactions:

Unbalanced:

$$FeHPO_3(aq) \rightarrow Fe(OH)_3(s) + PO_4^{3-}(aq)$$

$$OCl^{-}(aq) \rightarrow Cl^{-}(aq)$$

These are then balanced as follows:

The ferrous hydrogen phosphite reaction is complicated because both iron and phosphorus are oxidized. The Fe atom begins with an oxidation number of +2 and ends with an oxidation number of +3, while phosphorus starts as +3 and ends up as +5. There is a total change of 3 electrons.

$$FeHPO_3(aq) \rightarrow Fe(OH)_3(s) + PO_4^{3-}(aq) + 3 e^{-}$$

Balancing the charge by addition of hydroxide for basic solution gives

$$\text{FeHPO}_3(\text{aq}) + 6 \text{ OH}^-(\text{aq}) \rightarrow \text{Fe(OH)}_3(\text{s}) + \text{PO}_4^{\ 3-}(\text{aq}) + 3 \text{ e}^-$$

Balancing the hydrogen and oxygen atoms by addition of water gives

$$\text{FeHPO}_3(\text{aq}) + 6 \text{ OH}^-(\text{aq}) \rightarrow \text{Fe(OH)}_3(\text{s}) + \text{PO}_4^{\ 3-}(\text{aq}) + 2 \text{ H}_2\text{O(l)} + 3 \text{ e}^-$$

The reduction of hypochlorite is simpler to balance. The oxidation number of chlorine changes from +1 in OCl⁻ to -1 in Cl⁻, giving a change of 2 e⁻.

$$OCl^{-}(aq) + 2e^{-} \rightarrow Cl^{-}(aq)$$

Balancing the charge by addition of OH⁻:

$$OCl^{-}(aq) + 2e^{-} \rightarrow Cl^{-}(aq) + 2OH^{-}(aq)$$

Balancing oxygen and hydrogen atoms by addition of H₂O:

$$OCl^{-}(aq) + H_{2}O(l) + 2e^{-} \rightarrow Cl^{-}(aq) + 2OH^{-}(aq)$$

Combining the two equations:

$$3[OC1^{-}(aq) + H_2O(1) + 2e^{-} \rightarrow C1^{-}(aq) + 2OH^{-}(aq)]$$

$$2[FeHPO_3(aq) + 6 OH^-(aq)$$

$$\rightarrow$$
 Fe(OH)₃(s) + PO₄³⁻(aq) + 2 H₂O(l) + 3 e⁻]

12.10 The anode (oxidation) is written to the left in a cell diagram, the cathode (reduction) to the right.

(a)
$$Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)$$
 $E^{\circ} = +0.34 \text{ V (anode)}$

$$2[Cu^{+}(aq) + e^{-} \rightarrow Cu(s)]$$
 $E^{\circ} = +0.52 \text{ V (cathode)}$

Therefore, at the anode, after reversal,

$$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^{-}$$

The cell reaction is

$$2 \text{ Cu}^+(\text{aq}) \rightarrow \text{Cu(s)} + \text{Cu}^{2+}(\text{aq})$$
 $E^{\circ}_{\text{cell}} = 0.52 \text{ V} - 0.34 \text{ V} = 0.18 \text{ V}$

(b)
$$2[Au^{3+}(aq) + 3e^{-} \rightarrow Au(s)]$$
 $E^{\circ}(cathode) = +1.40 \text{ V}$

$$3[Cr^{2+}(aq) + 2e^{-} \rightarrow Cr(s)]$$
 $E^{\circ}(anode) = -0.90 \text{ V}$

Therefore, at the anode, after reversal,

$$3[Cr(s) \rightarrow Cr^{2+}(aq) + 2e^{-}]$$

The cell reaction is, upon addition of the half-reactions,

$$3 \operatorname{Cr}(s) + 2 \operatorname{Au}^{3+}(aq) \rightarrow 2 \operatorname{Au}(s) + 3 \operatorname{Cr}^{2+}(aq)$$

$$E_{\text{cell}}^{\circ} = +1.40 \text{ V} - (-0.90 \text{ V}) = +2.30 \text{ V}$$

(c)
$$AgI(s) + e^{-} \rightarrow Ag(s) + I^{-}(aq)$$
 $E^{\circ} = -0.15 \text{ V (anode)}$

$$AgCl(s) + e^- \rightarrow Ag(s) + Cl^-(aq)$$
 $E^\circ = +0.22 \text{ V (cathode)}$

Therefore, at the anode, after reversal,

$$Ag(s) + I^{-}(aq) \rightarrow AgI(s) + e^{-}$$

The cell reaction is, upon addition of the half-reactions,

$$I^{-}(aq) + AgCl(s) \rightarrow AgI(s) + Cl^{-}(aq)$$

$$E_{\text{cell}}^{\circ} = +0.22 \text{ V} - (-0.15 \text{ V}) = +0.37 \text{ V}$$

(d)
$$2[AgCl(s) + e^- \rightarrow Ag(s) + Cl^-(aq)]$$
 $E^\circ = +0.22 \text{ V (cathode)}$

$$Hg_2Cl_2(s) + 2e^- \rightarrow 2Hg(l) + 2Cl^-(aq)$$
 $E^\circ = +0.27 \text{ V (anode)}$

Reverse the anode half-reaction: $2 \text{ Hg(l)} + 2 \text{ Cl}^-(\text{aq}) \rightarrow \text{Hg}_2 \text{Cl}_2(\text{s}) + 2 \text{ e}^$ and the cell reaction is, upon addition of the half-reactions,

$$2 \operatorname{AgCl}(s) + 2 \operatorname{Hg}(l) \rightarrow \operatorname{Hg}_2 \operatorname{Cl}_2(s) + 2 \operatorname{Ag}(s)$$

$$E^{\circ}_{cell} = +0.22 \text{ V} - 0.27 \text{ V} = -0.05 \text{ V}$$

Note: This balanced equation corresponds to the cell notation as given (the cell is an electrolytic one). The spontaneous process is the reverse of this reaction.

(e)
$$5[Hg_2^{2+}(aq) + 2e^- \rightarrow 2Hg(l)]$$

$$E^{\circ}(\text{anode}) = +0.79 \text{ V}$$

$$2[MnO_4^-(aq) + 8 H^+(aq) + 5 e^- \rightarrow Mn^{2+}(aq) + 4 H_2O(l)]$$

$$E^{\circ}(\text{cathode}) = +1.51 \text{ V}$$

Reversing the anode reaction gives

$$5[2 \text{ Hg(l)} \rightarrow \text{Hg}_2^{2+}(\text{aq}) + 2 \text{ e}^-]$$

The cell reaction, upon combination of the half-reactions,

$$2 \text{ MnO}_{4}^{-}(aq) + 10 \text{ Hg(l)} + 16 \text{ H}^{+}(aq)$$

$$\rightarrow 5 \text{ Hg}_{2}^{2+}(aq) + 2 \text{ Mn}^{2+}(aq) + 8 \text{ H}_{2}\text{O(l)}$$

$$E_{\text{cell}}^{\circ} = +1.51 \text{ V} - (+0.79 \text{ V}) = +0.72$$

12.12 (a) cathode:
$$Mn^{2+}(aq) + 2e^{-} \rightarrow Mn(s)$$
 $E^{\circ} = -1.18 \text{ V}$

$$Ti^{2+}(aq) + 2e^{-} \rightarrow Ti(s)$$
 (anode) $E^{\circ} = -1.63 \text{ V}$

Reversing the anode reaction:

anode:
$$Ti(s) \rightarrow Ti^{2+}(aq) + 2e^{-}$$

Adding the half-reactions, we have, for the overall reaction:

$$\operatorname{Mn}^{2+}(\operatorname{aq}) + \operatorname{Ti}(\operatorname{s}) \to \operatorname{Mn}(\operatorname{s}) + \operatorname{Ti}^{2+}(\operatorname{aq})$$

$$E_{\text{cell}}^{\circ} = -1.18 \text{ V} - (-1.63 \text{ V}) = +0.45 \text{ V}$$

The cell diagram is

 $Ti(s)|Ti^{2+}(aq)||Mn^{2+}(aq)|Mn(s)$

(b) cathode:
$$Fe^{3+}(aq) + e^{-} \rightarrow Fe^{2+}(aq)$$
 $E^{\circ} = +0.77 \text{ V}$ (1)

anode:
$$H_2(g) \to 2 H^+(aq) + 2 e^ E^{\circ} = 0.00 V$$
 (2)

Multiplying Eq. 1 by a factor of 2 gives

$$2 \text{ Fe}^{3+}(aq) + 2 e^{-} \rightarrow 2 \text{ Fe}^{2+}(aq)$$
 (3)

Adding Eqs. 2 and 3 gives the overall reaction:

$$2 \text{ Fe}^{3+}(aq) + \text{H}_2(g) \rightarrow 2 \text{ Fe}^{2+}(aq) + 2 \text{ H}^+(aq)$$

$$E_{\text{cell}}^{\circ} = +0.77 \text{ V} - 0.00 \text{ V} = +0.77 \text{ V}$$

The cell diagram is

$$Pt(s)|H_2(g)|H^+(aq)||Fe^{3+}(aq), Fe^{2+}(aq)|Pt(s)$$

(c) cathode:
$$Cu^+(aq) + e^- \rightarrow Cu(s)$$
 $E^\circ = +0.52 \text{ V}$ (1)

anode:
$$Cu(s) \to Cu^{2+}(aq) + 2e^{-}$$
 $E^{\circ} = +0.34 \text{ V}$ (2)

Multiplying Eq. 1 by a factor of 2 gives
$$2 \text{ Cu}^+ + 2 \text{ e}^- \rightarrow 2 \text{ Cu(s)}$$
 (3)

Upon addition of Eqs. 2 and 3, we have

$$2 \text{ Cu}^+(\text{aq}) \rightarrow \text{Cu(s)} + \text{Cu}^{2+}(\text{aq})$$
 $E_{\text{cell}}^{\circ} = 0.52 \text{ V} - 0.34 \text{ V} = 0.18 \text{ V}$

The cell diagram is

$$Cu(s)|Cu^{2+}(aq)||Cu^{+}(aq)|Cu(s)$$

(d)
$$2[MnO_4^-(aq) + 8 H^+ + 5 e^- \rightarrow Mn^{2+}(aq) + 4 H_2O(1)]$$
 (cathode)
 $E^\circ = +1.51 \text{ V}$

$$5[Cl_{2}(g) + 2e^{-} \rightarrow 2Cl^{-}(aq)]$$
 (anode)

$$E^{\circ} = +1.36 \text{ V}$$

Reverse the anode reaction $5[2 \text{ Cl}^-(aq) \rightarrow \text{Cl}_2(g) + 2 \text{ e}^-]$, then upon addition

$$2 \text{ MnO}_4^-(aq) + 16 \text{ H}^+(aq) + 10 \text{ Cl}^-(aq)$$

$$\rightarrow 5 \text{ Cl}_2(g) + 2 \text{ Mn}^{2+}(aq) + 8 \text{ H}_2\text{O}(l)$$

$$E^{\circ}_{cell} = +1.51 \text{ V} - 1.36 \text{ V} = +0.15 \text{ V}$$

The cell diagram is

$$C(gr)|Cl_{2}(g)\,|\,Cl^{\text{-}}(aq)\,\|\,MnO_{4}^{\text{-}}(aq),\,H^{\text{+}}(aq),\,Mn^{2\text{+}}(aq)|Pt$$

12.14 (a) Eliminating the spectator ions, the reaction is

$$Ag^{+}(aq) + I^{-}(aq) \rightarrow AgI(s)$$

$$Ag^{+}(aq) + e^{-} \rightarrow Ag(s)$$
 (cathode) $E^{\circ} = +0.80 \text{ V}$

$$AgI(s) + e^- \rightarrow Ag(s) + I^-(aq)$$
 (anode) $E^{\circ} = -0.15 \text{ V}$

Reverse the anode reaction $Ag(s) + I^{-}(aq) \rightarrow AgI(s) + e^{-}$, then upon addition,

$$Ag^{+}(aq) + I^{-}(aq) \rightarrow AgI(s)$$
 $E^{\circ}_{cell} = +0.80 \text{ V} - (-0.15 \text{ V}) = +0.95 \text{ V}$

The cell diagram is

$$Ag(s)|AgI(s)|I^{-}(aq)||Ag^{+}(aq)|Ag(s)$$

(b) Rewriting in the notation of this chapter, we have

$$H^+(aq, conc) \rightarrow H^+(aq, dil)$$

The oxidation reaction at the anode is $\frac{1}{2} H_2(g) \to H^+(aq) + e^-$ and the reduction at the cathode is $H^+(aq) + e^- \to \frac{1}{2} H_2(g)$.

The cell diagram is $Pt(s)|H_2(g)|H^+(aq, dil)|H^+(aq, conc)|H_2(g)|Pt(s)$.

(c) anode:
$$Zn(s) + 2 OH^{-}(aq) \rightarrow ZnO(s) + H_2O(l) + 2 e^{-}$$

cathode:
$$Ag_2O(s) + H_2O(l) + 2e^- \rightarrow 2Ag(s) + 2OH^-(aq)$$

Adding the two half-reactions gives

$$Ag_2O(s) + Zn(s) \rightarrow 2 Ag(s) + ZnO(s)$$
 $E_{cell}^{\circ} = 1.6 V$

(See Table 12.1.)

The cell diagram is

 $Zn(s)|ZnO(s)|KOH(aq)|Ag_2O(s)|Ag(s)|steel$

12.16 (a)
$$\operatorname{Cr_2O_7}^{2-}(\operatorname{aq}) + 14 \operatorname{H}^+(\operatorname{aq}) + 6 \operatorname{e}^- \to 2 \operatorname{Cr}^{3+}(\operatorname{aq}) + 7 \operatorname{H}_2\operatorname{O}(1)$$

(cathode half-reaction)

$$3[Hg_2^{2+}(aq) \rightarrow 2 Hg^{2+} + 2 e^-]$$
 (anode half-reaction $\times 3$)

(b) Adding half-reactions gives

$$Cr_2O_7^{2-}(aq) + 3 Hg_2^{2+}(aq) + 14 H^+(aq) \rightarrow$$

 $2 Cr^{3+}(aq) + 6 Hg^{2+}(aq) + 7H_2O(1)$

The cell diagram is

$$Pt(s)|Hg_2^{2+}(aq), Hg^{2+}(aq)||H^+(aq), Cr_2O_7^{2-}(aq), Cr^{3+}(aq)|Pt(s)|$$

12.18 (a)
$$Ag^{+}(aq) + e^{-} \rightarrow Ag(s)$$
 $E^{\circ}(cathode) = +0.80 \text{ V}$

$$E^{\circ}$$
(cathode) = +0.80 V

$$Fe^{3+}(aq) + e^{-} \rightarrow Fe^{2+}(aq)$$
 $E^{\circ}(anode) = +0.77 \text{ V}$

$$E^{\circ}(\text{anode}) = +0.77 \text{ V}$$

$$E^{\circ}(\text{cell}) = E^{\circ}(\text{cathode}) - E^{\circ}(\text{anode}) = +0.80 \text{ V} - 0.77 \text{ V} = +0.03 \text{ V}$$

(b)
$$V^{2+}(aq) + 2 e^{-} \rightarrow V(s)$$
 $E^{\circ}(cathode) = -1.19 \text{ V}$

$$E^{\circ}(\text{cathode}) = -1.19 \text{ V}$$

$$U^{3+}(aq) + 3 e^{-} \rightarrow U(s)$$
 $E^{\circ}(anode) = -1.79 \text{ V}$

$$E^{\circ}(\text{anode}) = -1.79 \text{ V}$$

$$E^{\circ}(\text{cell}) = -1.19 \text{ V} - (-1.79 \text{ V}) = +0.60 \text{ V}$$

(c)
$$\text{Sn}^{4+}(\text{aq}) + 2 \text{ e}^{-} \rightarrow \text{Sn}^{2+}(\text{aq})$$
 $E^{\circ}(\text{cathode}) = +0.15 \text{ V}$

$$E^{\circ}(\text{cathode}) = +0.15 \text{ V}$$

$$\operatorname{Sn}^{2+}(\operatorname{aq}) + 2 \operatorname{e}^{-} \to \operatorname{Sn}(\operatorname{s})$$

$$E^{\circ}(anode) = -0.14 \text{ V}$$

$$E^{\circ}(\text{cell}) = +0.15 \text{ V} - (-0.14 \text{ V}) = +0.29 \text{ V}$$

(d)
$$Au^+(aq) + e^- \rightarrow Au(s)$$
 $E^{\circ}(cathode) = +1.69 \text{ V}$

$$E^{\circ}(\text{cathode}) = +1.69 \text{ V}$$

$$Cu^{2+}(aq) + 2 e^{-} \rightarrow Cu(s)$$
 $E^{\circ}(anode) = +0.34 \text{ V}$

$$E^{\circ}(\text{anode}) = +0.34 \text{ V}$$

$$E^{\circ}(\text{cell}) = +1.69 \text{ V} - (+0.34 \text{ V}) = +1.35 \text{ V}$$

12.20 (a)
$$Bi^{3+}(aq) + 3e^{-} \rightarrow Bi(s)$$
 $E^{\circ}(cathode) = +0.20 \text{ V}$

$$Zn^{2+}(aq) + 2e^{-} \rightarrow Zn(s)$$
 $E^{\circ}(anode) = -0.76 \text{ V}$

For the equation, $3 \operatorname{Zn}(s) + 2 \operatorname{Bi}^{3+}(aq) \to 3 \operatorname{Zn}^{2+}(aq) + 2 \operatorname{Bi}(s), n = 6$

$$E_{\text{cell}}^{\circ} = +0.20 \text{ V} - (-0.76 \text{ V}) = +0.96 \text{ V}$$

$$\Delta G_{\rm r}^{\circ} = -nFE^{\circ} = -6(9.6485 \times 10^{4} \,\text{J} \cdot \text{V}^{-1} \cdot \text{mol}^{-1})(+0.96 \,\text{V})$$
$$= -5.6 \times 10^{2} \,\text{kJ} \cdot \text{mol}^{-1}$$

(b)
$$O_2(g) + 4 H^+(aq) + 4 e^- \rightarrow 2 H_2O(1)$$
 $E^{\circ}(cathode) = +1.23 V$

$$2 \text{ H}^+(\text{aq}) + 2 \text{ e}^- \rightarrow \text{H}_2(\text{g})$$
 $E^{\circ}(\text{anode}) = 0.00 \text{ V}$

Taking $2[2 \text{ H}^+(\text{aq}) + 2 \text{ e}^- \rightarrow \text{H}_2(\text{g})]$, reversing it and adding it to the cathode:

half-reaction gives
$$2 H_2(g) + O_2(g) \rightarrow 2 H_2O(l)$$
 $n = 4$, $E_{cell}^{\circ} = +1.23 \text{ V}$

$$\Delta G^{\circ}_{r} = -nFE^{\circ} = -4 \times 9.6485 \times 10^{4} \text{ C} \cdot \text{mol}^{-1} \times 1.23 \text{ V} = -475 \text{ kJ} \cdot \text{mol}^{-1}$$

(c)
$$O_2(g) + 2 H_2O(l) + 4 e^- \rightarrow 4 OH^-(aq)$$
 $E^{\circ}(cathode) = +0.40 V$

$$2 \text{ H}_2\text{O(1)} + 2 \text{ e}^- \rightarrow \text{H}_2(\text{g}) + 2 \text{ OH}^-(\text{aq})$$
 $E^\circ(\text{anode}) = -0.83 \text{ V}$

Taking $2[H_2O(1) + 2 e^- \rightarrow H_2(g) + 2 OH^-(aq)]$, reversing it and adding it to the cathode half-reaction gives $2 H_2(g) + O_2(g) \rightarrow 2 H_2O(1)$

$$n = 4$$
, $E^{\circ}_{cell} = +1.23 \text{ V}$

$$\Delta G^{\circ}_{r} = nFE^{\circ} = -475 \text{ kJ} \cdot \text{mol}^{-1} \text{ (same as part b)}$$

(d)
$$3[Au^{+}(aq) + e^{-} \rightarrow Au(s)]$$
 $E^{\circ}(cathode) = +1.69 \text{ V}$

$$Au^{3+}(aq) + 3e^{-} \rightarrow Au(s)$$
 $E^{\circ}(anode) = +1.40 \text{ V}$

Taking $3[Au^+ + e^- \rightarrow Au(s)]$ and adding it to the reverse of the reduction

half-reaction gives $3 \text{ Au}^+ \rightarrow \text{Au}^{3+} + 2 \text{ Au}(s)$ n = 3

$$E^{\circ}_{cell} = +1.69 \text{ V} - 1.40 \text{ V} = 0.29 \text{ V}$$

$$\Delta G_{\rm r}^{\circ} = -nFE^{\circ} = -3 \times 9.6485 \times 10^{4} \text{ C} \cdot \text{mol}^{-1} \times 0.29 \text{ J} \cdot \text{C}^{-1}$$

= $-84 \text{ kJ} \cdot \text{mol}^{-1}$

12.22 The unknown metal ions are reduced, increasing the weight of the unknown metal electrode. The cell can be written as Fe(s)|Fe²⁺(aq)||M⁺(aq)|M(s) showing that the M⁺/M electrode is the cathode, because this is where reduction is occurring.

Fe²⁺ + 2e
$$\rightarrow$$
 Fe(s)
E° = -0.44 V
E° (cathode) = +1.24 V + E° (anode)
E° (cathode) = +1.24 V + (-0.44 V) = +0.80 V

12.24 (a)
$$Co^{2+}$$
 $E^{\circ} = -0.28 \text{ V}$

$$Cl_{2} \qquad E^{\circ} = +1.36 \text{ V}$$

$$Ce^{4+} \qquad E^{\circ} = +1.61 \text{ V}$$

$$In^{3+} \qquad E^{\circ} = -0.34 \text{ V}$$

The best oxidizing agent has the highest E° : $Ce^{4+} > Cl_2 > Co^{2+} > In^{3+}$

(b)
$$NO_3^ E^\circ = +0.96 \text{ V}$$
 $CIO_4^ E^\circ = +1.23 \text{ V}$
 $E^\circ = +1.60 \text{ V}$
 $Cr_2O_7^{2-}$ $E^\circ = +1.33 \text{ V}$

The best oxidizing agent has the highest

$$E^{\circ}$$
: HBrO > Cr₂O₇²⁻ > ClO₄⁻ > NO₃⁻

(c)
$$O_2 + 4 H^+ + 4 e^- \rightarrow 2 H_2 O$$
 $E^\circ = +1.23 V$

$$O_3 + 2 H^+ + 2 e^- \rightarrow O_2 + H_2 O$$
 $E^\circ = +2.07 V$

$$2 HCIO + 2 H^+ + 2 e^- \rightarrow Cl_2 + 2 H_2 O$$
 $E^\circ = +1.63 V$

$$2 HBrO + 2 H^+ + 2 e^- \rightarrow Br_2 + 2 H_2 O$$
 $E^\circ = +1.60 V$

The order of oxidizing ability in acidic solution (which corresponds to the ease of reduction of the reagent) is $O_3 > HClO > HBrO > O_2$.

(d)
$$O_2 + H_2O + 4e^- \rightarrow 4OH^ E^{\circ} = +0.40 \text{ V}$$

$$O_3 + H_2O + 2 e^- \rightarrow O_2 + 2 OH^- E^\circ = +1.24 V$$

 $ClO^- + H_2O + 2 e^- \rightarrow Cl^- + 2 OH^- E^\circ = +0.89 V$
 $BrO^- + H_2O + 2 e^- \rightarrow Br^- + 2 OH^- E^\circ = +0.76 V$

The order of oxidizing ability in basic solution (which corresponds to the ease of reduction of the reagent) is $O_3 > ClO^- > BrO^- > O_2$. Notice that the order in (c) is the same as here, but the relative amounts of difference may be significantly different. For example, HClO and HBrO have very similar oxidizing abilities in acidic solution, but in basic solution the ClO-ion is substantially more oxidizing than BrO^- . Note also that the oxidizing ability of all of these species is somewhat less in the basic medium.

12.26 (a)
$$Pt^{2+}/Pt$$
 $E^{\circ} = +1.20 \text{ V}$, Pt^{2+} is oxidizing agent (cathode)
 AgF/Ag , F^{-} $E^{\circ} = +0.78 \text{ V}$, Ag is reducing agent (anode)
 $Ag(s)|AgF(s)|F^{-}(aq)||Pt^{2+}(aq)|Pt(s)$
 $E^{\circ}_{cell} = E^{\circ}(cathode) - E^{\circ}(anode) = +1.20 \text{ V} - 0.78 \text{ V} = +0.42 \text{ V}$
(b) I_{3}^{-}/I^{-} $E^{\circ} = +0.53 \text{ V}$, I_{3}^{-} is oxidizing agent (cathode)
 Cr^{3+}/Cr^{2+} $E^{\circ} = -0.41 \text{ V}$, Cr^{2+} is reducing agent (anode)
 $Pt(s)|Cr^{2+}(aq), Cr^{3+}(aq)||I^{-}(aq), I_{3}^{-}(aq)||Pt(s)$
 $E^{\circ}_{cell} = +0.53 \text{ V} - (-0.41 \text{ V}) = +0.94 \text{ V}$
(c) H^{+}/H_{2} $E^{\circ} = 0.00 \text{ V}$, H^{+} is oxidizing agent (cathode)
 Ni^{2+}/Ni $E^{\circ} = -0.23 \text{ V}$, Ni is reducing agent (anode)
 $Ni(s)|Ni^{2+}(aq)||H^{+}(aq)|H_{2}(g)|Pt(s)$
 $E^{\circ}_{cell} = 0.00 \text{ V} - (-0.23 \text{ V}) = +0.23 \text{ V}$
(d) O_{3} , H^{+}/O_{2} $E^{\circ} = +2.07 \text{ V}$, O_{3} is oxidizing agent (cathode)
 O_{3}/O_{2} , OH^{-} $E^{\circ} = +1.24 \text{ V}$, O_{2} is reducing agent (anode)
 $Pt(s)|O_{3}(g), O_{2}(g)|OH^{-}(aq)||O_{3}(g), O_{2}(g)|H^{+}(aq)|Pt(s)$

$$E^{\circ}_{cell} = +2.07 \text{ V} - 1.24 \text{ V} = +0.83 \text{ V}$$

12.28 (a)
$$Mg^{2+} + Cu \rightarrow \text{no reaction}$$
; E° for $Cu^{2+}/Cu > E^{\circ}$ for Mg^{2+}/Mg

(b)
$$2 \text{ Al} + 3 \text{ Pb}^{2+} \rightarrow 2 \text{ Al}^{3+} + 3 \text{ Pb}$$

$$Pb^{2+} + 2e^{-} \rightarrow Pb$$
 reduction (cathode) $E^{\circ} = -0.13 \text{ V}$

$$Al \rightarrow Al^{3+} + 3e^{-}$$
 oxidation (anode) $E^{\circ} = -1.66 \text{ V}$

$$E_{\text{cell}}^{\circ} = E^{\circ}(\text{cathode}) - E^{\circ}(\text{anode}) = -0.13 \text{ V} - (-1.66 \text{ V}) = +1.53 \text{ V}$$

$$\Delta G_{\rm r}^{\circ} = -nFE^{\circ} = -(6)(9.6485 \times 10^{4} \text{ C} \cdot \text{mol}^{-1})(+1.53 \text{ J} \cdot \text{C}^{-1})$$

= -886 kJ·mol⁻¹; therefore, the reaction is spontaneous

(c)
$$Hg_2^{2+} + 2 Ce^{3+} \rightarrow 2 Ce^{4+} + 2 Hg$$

 E° for $Ce^{4+}/Ce^{3+} > E^{\circ}$ for Hg_2^{2+}/Hg : the reaction is not spontaneous.

(d)
$$Zn + Sn^{2+} \rightarrow Sn + Zn^{2+}$$

$$E^{\circ}$$
 for $\operatorname{Sn}^{2+}/\operatorname{Sn} > \operatorname{E}^{\circ}$ for $\operatorname{Zn}^{2+}/\operatorname{Zn}$

$$\operatorname{Sn}^{2+} + 2 \operatorname{e}^{-} \rightarrow \operatorname{Sn} \quad E^{\circ}(\operatorname{cathode}) = -0.14 \operatorname{V}$$

$$Zn \to Zn^{2+} + 2 e^{-} E^{\circ} (anode) = -0.76 V$$

$$\Delta E^{\circ} = E^{\circ}(\text{cathode}) - E^{\circ}(\text{anode}) = -0.14 \text{ V} - (-0.76 \text{ V})$$

= +0.62 V

$$\Delta G_{\rm r}^{\circ} = -nFE^{\circ} = -(2)(9.6485 \times 10^{4} \text{ C} \cdot \text{mol}^{-1})(0.62 \text{ J} \cdot \text{C}^{-1})$$

= -120 kJ·mol⁻¹,

the reaction is spontaneous

(e)
$$O_2 + H^+ + Hg \rightarrow H_2O + Hg_2^{2+}$$
 (unbalanced)

$$E^{\circ}$$
 for $O_2/H_2O > E^{\circ}$ for Hg_2^{2+}/Hg

$$O_2 + 4 H^+ + 4 e^- \rightarrow 2 H_2 O$$
 E° (cathode) = +1.23 V

$$2 \text{ Hg} \rightarrow \text{Hg}_2^{2+} + 2 \text{ e}^- \quad E^{\circ}(\text{anode}) = +0.79 \text{ V}$$

Multiplying the second half-reaction by two and adding to the cathode half-reaction gives $4 \text{ Hg} + \text{O}_2 + 4 \text{ H}^+ \rightarrow 2 \text{ Hg}_2^{2+} + 2 \text{ H}_2\text{O}$ (balanced)

$$\Delta E^{\circ} = E^{\circ} (\text{cathode}) - E^{\circ} (\text{anode}) = +1.23 \text{ V} - (+0.79 \text{ V})$$

= +0.44 V
$$\Delta G^{\circ}_{r} = -nFE^{\circ} = -(4)(9.6485 \times 10^{4} \text{ C} \cdot \text{mol}^{-1})(0.44 \text{ J} \cdot \text{C}^{-1})$$

= -170 kJ·mol⁻¹,

the reaction is spontaneous

12.30 (a)
$$2 \operatorname{Sn}^{2+}(aq) \rightarrow \operatorname{Sn}(s) + \operatorname{Sn}^{4+}(aq)$$

(b)
$$\operatorname{Sn}^{2+}(\operatorname{aq}) + 2 \operatorname{e}^{-} \to \operatorname{Sn}(\operatorname{s}) \quad E^{\circ} = -0.14 \text{ V}$$

$$\operatorname{Sn}^{4+}(aq) + 2 e^{-} \rightarrow \operatorname{Sn}^{2+}(aq) \quad E^{\circ} = +0.15 \text{ V}$$

The desired reaction is obtained by subtracting the second equation from the first.

The E° value is obtained also by subtracting the second value from the first:

$$E^{\circ} = -0.14 \text{ V} - (+0.15 \text{ V}) = -0.29 \text{ V}$$

Because the E° value is negative, the process is not spontaneous.

12.32 The appropriate half-reactions are

$$Ti^{3+} + e^{-} \rightarrow Ti^{2+}$$
 $E^{\circ} = -0.37$ (A)

$$Ti^{2+} + 2e^{-} \rightarrow Ti$$
 $E^{\circ} = -1.63$ (B)

(A) and (B) add to give the desired half-reaction (C):

$$Ti^{3+} + 3e^- \rightarrow Ti E^\circ = ?$$
 (C)

In order to calculate the potential of a *half-reaction*, we need to convert the E° values into ΔG° values:

$$\Delta G^{\circ}(A) = -nFE^{\circ}(A) = -1F(-0.37 \text{ V})$$

$$\Delta G^{\circ}(B) = -nFE^{\circ}(B) = -2F(-1.63 \text{ V})$$

$$\Delta G^{\circ}(C) = -nFE^{\circ}(C) = -3FE^{\circ}(C)$$

$$\Delta G^{\circ}(C) = \Delta G^{\circ}(A) + \Delta G^{\circ}(B)$$

$$-3FE^{\circ}(C) = -1F(-0.37 \text{ V}) + [-2F(-1.63 \text{ V})]$$

The constant *F* will cancel from both sides, leaving:

$$-3E^{\circ}(C) = -1(-0.37 \text{ V}) - 2(-1.63 \text{ V})$$

 $E^{\circ}(C) = -[0.37 \text{ V} + 3.26 \text{ V}]/3 = -1.21 \text{ V}$

12.34 (a) The balanced cell reaction is

2 Fe³⁺(aq) + H₂(g)
$$\rightarrow$$
 2 Fe²⁺(aq) + 2 H⁺(aq) $n = 2$
 $E^{\circ}_{cell} = E^{\circ}(cathode) - E^{\circ}(anode) = +0.77 \text{ V} - (0.00) \text{ V} = +0.77 \text{ V}$
 $\ln K = \frac{nFE^{\circ}}{RT} = \frac{2(+0.77 \text{ V})}{0.025693 \text{ V}}$
 $\ln K = \frac{(2)(0.77 \text{ V})}{0.025693 \text{ V}} = 59.9$

$$K = 10^{26}$$

(b)
$$\operatorname{Cr}(s) + \operatorname{Zn}^{2+}(aq) \to \operatorname{Cr}^{2+}(aq) + \operatorname{Zn}(s)$$
 $n = 2$

$$E^{\circ}_{\text{cell}} = E^{\circ}(\text{cathode}) - E^{\circ}(\text{anode}) = -0.76 \text{ V} - (-0.91 \text{ V}) = 0.15 \text{ V} \text{ and}$$

$$\ln K = \frac{nFE^{\circ}}{RT} = \frac{(2)(+0.15 \text{ V})}{0.025 693 \text{ V}}$$

$$\ln K = \frac{(2)(0.15 \text{ V})}{0.025 693 \text{ V}} = +12$$

and
$$K = 10^5$$

12.36 (a)
$$ClO_4^-(aq) + 2 H^+(aq) + 2 e^- \rightarrow ClO_3^-(aq) + H_2O(1)$$

 $E^{\circ}(cathode) = +1.23 \text{ V}$

$$Ag^+(aq) + e^- \rightarrow Ag(s)$$
 $E^\circ(anode) = +0.80 \text{ V}$

Reversing the latter half-reaction, multiplying by 2, and adding, we have

$$ClO_4^-(aq) + 2 H^+(aq) + 2 Ag(s) \rightarrow ClO_3^-(aq) + H_2O(l) + Ag^+(aq)$$

$$n = 2$$
, $E^{\circ}_{cell} = +0.43 \text{ V}$

Then, using the Nernst equation, $E = E^{\circ} - \frac{RT}{nF} \ln Q$, we have

$$E = E^{\circ} - \frac{0.025 \ 693}{n} \ln Q$$

$$0.40 \text{ V} = 0.43 \text{ V} - \frac{0.025 \text{ 693 V}}{2} \ln Q$$

$$\ln Q = -\frac{(2)(-0.03 \text{ V})}{0.025693 \text{ V}} = 2$$

$$\ln Q = 10^{1}$$

(b) cathode: $Au^{3+}(aq) + 3e^{-} \rightarrow Au(s)$ $E^{\circ}(cathode) = +1.40 \text{ V}$ anode: [reduction potential for

$$Cl_2(g) + 2 e^- \rightarrow 2 Cl^-(aq) is + 1.36 V = E^{\circ}(anode)$$

Multiplying, we have $2[Au^{3+}(aq) + 3e^{-} \rightarrow Au(s)]$

$$3[2 \text{ Cl}^-(\text{aq}) \rightarrow \text{Cl}_2(\text{g}) + 2 \text{ e}^-]$$

Adding yields $2 \text{ Au}^{3+}(aq) + 6 \text{ Cl}^{-}(aq) \rightarrow 2 \text{ Au}(s) + 3 \text{ Cl}_{2}(g)$

$$E_{\text{cell}}^{\circ} = 0.04 \text{ V}$$

Then, n = 6

$$E = E^{\circ} - \frac{0.025\ 693}{n} \ln Q$$

$$0.00 \text{ V} = 0.04 \text{ V} - \frac{0.025 693}{6} \ln Q$$

$$\ln Q = -\frac{(6)(-0.04 \text{ V})}{0.025693 \text{ V}} = 9$$

$$Q = 10^4$$

12.38 (a) Cell reaction: $Pb^{2+}(aq, 0.10 \text{ mol} \cdot L^{-1}) \rightarrow Pb^{2+}(aq, x \text{ mol} \cdot L^{-1})$

$$n = 2$$
, $E_{\text{cell}} = 0.050 \text{ V}$

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{RT}{nF} \ln Q = -\frac{0.025 693 \text{ V}}{2} \ln \left(\frac{x}{0.10 \text{ mol} \cdot \text{L}^{-1}} \right) = 0.050 \text{ V}$$

$$\ln\left(\frac{x}{0.10 \text{ M}}\right) = -\frac{2 \times 0.050 \text{ V}}{0.025 \text{ 693 V}} = -3.9$$

$$\left(\frac{x}{0.10 \text{ M}}\right) = 2 \times 10^{-2}; x = [\text{Pb}^{2+}] = 2 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$$

(b) Cathode:
$$Fe^{3+}$$
 (aq, xM) + $e^{-} \rightarrow Fe^{3+}$ (aq, 0.0010 M)
Anode: Fe^{3+} (aq, 0.10 M) + $e^{-} \rightarrow Fe^{2+}$ (aq, 1.0 M)
overall reaction: Fe^{3+} (aq, xM) + Fe^{2+} (aq, 1.0 M) \rightarrow
 Fe^{2+} (aq, 0.0010 M) + Fe^{3+} (aq, 0.10 M)

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{RT}{nF} \ln Q$$

$$= -\frac{0.025 693 \text{ V}}{1} \ln \left(\frac{0.0010 \text{ M} \times 0.10 \text{ M}}{x \text{M} \times 1.0 \text{ M}} \right) = 0.10 \text{ V}$$

$$\ln \left(\frac{1.0 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}}{x} \right) = -\frac{0.10 \text{ V}}{0.025 693 \text{ V}} = -3.9$$

$$\frac{1.0 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}}{x} = 2 \times 10^{-2}, x = [\text{Fe}^{3+}] = 5 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$$

12.40 (a) anode:
$$Cr(s) \rightarrow Cr^{3+}(aq) + 3 e^{-}$$
 $E^{\circ}(anode) = -0.74 \text{ V}$ cathode: $Pb^{2+}(aq) + 2 e^{-} \rightarrow Pb(s)$ $E^{\circ}(cathode) = -0.13 \text{ V}$ Multiplying half-reactions gives

$$3[Pb^{2+}(aq) + 2e^{-} \rightarrow Pb(s)]$$

 $2[Cr(s) \rightarrow Cr^{3+}(aq) + 3e^{-}]$

overall reaction:
$$3 \text{ Pb}^{2+}(\text{ag}) + 2 \text{ Cr}(\text{s}) \rightarrow 3 \text{ Pb}(\text{s}) + 2 \text{ Cr}^{3+}(\text{ag})$$

$$E_{\text{cell}}^{\circ} = +0.61 \text{ V}, n = 6$$

$$E = E^{\circ} - \frac{0.025 693 \text{ V}}{n} \ln \frac{[\text{Cr}^{3+}]^2}{[\text{Pb}^{2+}]^3}$$

$$E = +0.61 \text{ V} - \frac{0.025 \text{ 693 V}}{6} \ln \frac{(0.37)^2}{(9.5 \times 10^{-3})^3}$$

$$E = +0.61 \text{ V} - 0.0043 \text{ V} \ln 1.6 \times 10^5 = +0.61 \text{ V} - 0.051 \text{ V} = +0.56 \text{ V}$$

(b)
$$Hg_2Cl_2(s) + 2e^- \rightarrow 2Hg(l) + 2Cl^-(aq)$$
 $E^{\circ}(cathode) = +0.27 \text{ V}$

$$2 \text{ H}^+(\text{aq}) + 2 \text{ e}^- \rightarrow \text{H}_2(\text{g}) \quad E^\circ(\text{anode}) = 0.00 \text{ V}$$

Reversing the latter half-reaction and adding, we have

$$Hg_2Cl_2(s) + H_2(g) \rightarrow 2 Hg(l) + 2 H^+(aq) + 2 Cl^-(aq)$$
 $E^{\circ}_{cell} = +0.27 V$

$$E = E^{\circ} - \frac{0.025 693 \text{ V}}{n} \ln \frac{[\text{H}^{+}]^{2} [\text{Cl}^{-}]^{2}}{P_{\text{H}_{2}}}$$

$$E = +0.27 \text{ V} - \frac{0.025 \text{ 693 V}}{2} \ln \frac{(10^{-3.5})^2 (0.75)^2}{2.0} = +0.27 \text{ V} + 0.22 \text{ V}$$
$$= +0.5 \text{ V}$$

(c) anode:
$$\operatorname{Sn}^{2+}(\operatorname{aq}) \to \operatorname{Sn}^{4+}(\operatorname{aq}) + 2 \operatorname{e}^{-} E^{\circ}(\operatorname{anode}) = +0.15 \text{ V}$$
 cathode: $\operatorname{Fe}^{3+}(\operatorname{aq}) + \operatorname{e}^{-} \to \operatorname{Fe}^{2+}(\operatorname{aq}) E^{\circ}(\operatorname{cathode}) = +0.77 \text{ V}$ Multiplying half-reactions,

$$2[Fe^{3+}(aq) + e^{-} \rightarrow Fe^{2+}(aq)]$$

 $Sn^{2+}(aq) \rightarrow Sn^{4+}(aq) + 2e^{-}$

Adding,
$$2 \text{ Fe}^{3+}(aq) + \text{Sn}^{2+}(aq) \rightarrow 2 \text{ Fe}^{2+}(aq) + \text{Sn}^{4+}(aq)$$

$$E_{\text{cell}}^{\circ} = +0.62 \text{ V}$$

$$E = E^{\circ} - \frac{0.025 693 \text{ V}}{n} \ln \frac{[\text{Fe}^{2+}]^2 [\text{Sn}^{4+}]}{[\text{Fe}^{3+}]^2 [\text{Sn}^{2+}]}$$

$$E = +0.62 \text{ V} - \frac{0.025 693 \text{ V}}{2} \ln \frac{(0.15)^2 (0.059)}{(0.15)^2 (0.059)}$$

$$E = +0.62 \text{ V} - 0.0129 \text{ V} \ln 1 = +0.62 \text{ V}$$

(d) anode:
$$Ag(s) + I^{-}(aq) \rightarrow AgI(s) + e^{-}$$
 $E^{\circ}(anode) = -0.15 \text{ V}$

cathode:
$$AgCl(s) + e^- \rightarrow Ag(s) + Cl^-(aq)$$
 $E^{\circ}(cathode) = +0.22 \text{ V}$

$$Ag(s) + I^{-}(aq) \rightarrow AgI(s) + e^{-}$$

Adding,
$$AgCl(s) + I^{-}(aq) \rightarrow AgI(s) + Cl^{-}(aq)$$
 $E^{\circ}_{cell} = +0.37 \text{ V}$

$$E = E^{\circ} - \frac{0.025 \text{ 693 V}}{n} \ln \frac{[\text{Cl}^{-}]}{[\text{I}^{-}]}$$

$$E = +0.37 \text{ V} - (0.025 693 \text{ V}) \ln \frac{0.67}{0.025}$$

$$E = +0.37 \text{ V} - 0.084 \text{ V} = +0.29 \text{ V}$$

12.42 (a) anode:
$$H_2(g) \rightarrow 2 H^+(aq) + 2 e^- E^\circ(anode) = 0.00 V$$
 cathode: $AgCl(s) + e^- \rightarrow Ag(s) + Cl^-(aq) E^\circ(cathode) = 0.22 V$ Multiplying,

$$2[AgCl(s) + e^{-} \rightarrow Ag(s) + Cl^{-}(aq)]$$

$$H_2(g) \to 2 H^+(aq) + 2 e^-$$

Adding,
$$2 \operatorname{AgCl}(s) + \operatorname{H}_{2}(g) \rightarrow 2 \operatorname{H}^{+}(aq) + 2 \operatorname{Ag}(s) + 2 \operatorname{Cl}^{-}(aq)$$

$$E_{\text{cell}}^{\circ} = +0.22 \text{ V}$$

$$E = E^{\circ} - \frac{0.025 693 \text{ V}}{n} \ln[\text{H}^{+}]^{2} [\text{Cl}^{-}]^{2}$$

0.30 V = 0.22 V -
$$\frac{0.025693 \text{ V}}{2} \ln \frac{[\text{H}^+]^2 (1.0)}{(1.0)}$$

$$0.08 \text{ V} = -0.0129 \text{ V} \ln[\text{H}^+]^2$$

$$0.08 \text{ V} = -0.025 693 \text{ V} \ln[\text{H}^+] = -0.059 \text{ V} \times \log[\text{H}^+]$$

$$\frac{0.08 \text{ V}}{0.059 \text{ V}} = -\log[\text{H}^+] = \text{pH} = 1.4$$

(b)
$$\text{Ni}^{2+}(\text{aq}) + 2 \text{ e}^- \rightarrow \text{Ni}(\text{s}) \ E^{\circ}(\text{cathode}) = -0.23 \text{ V}$$

$$Pb(s) \to Pb^{2+}(aq) + 2e^{-}$$
 $E^{\circ}(anode) = -0.13V$

Adding half-reactions gives

$$Ni^{2+}(aq) + Pb(s) \rightarrow Ni(s) + Pb^{2+}(aq)$$

$$E^{\circ}_{\text{cell}} = -0.10 \text{ V}$$

$$E = E^{\circ} - \frac{0.025 \text{ 693 V}}{\text{n}} \ln \frac{[\text{Pb}^{2+}]}{[\text{Ni}^{2+}]}$$

$$0.040 \text{ V} = -0.10 \text{ V} - \frac{0.025 \text{ 693 V}}{2} \ln \frac{[\text{Pb}^{2+}]}{0.10}$$

0.14 V = -(0.0129 V)
$$\ln \frac{[Pb^{2+}]}{0.10}$$
 = -0.0129 V (ln[Pb²⁺] - ln[0.10])

$$0.14 \text{ V} = -0.0129 \text{ V} \ln[\text{Pb}^{2+}] - 0.030 \text{ V}$$

$$0.17 \text{ V} = -0.0129 \text{ V} \ln[Pb^{2+}]$$

$$\frac{0.17 \text{ V}}{-0.0129 \text{ V}} = \ln[\text{Pb}^{2+}] = -13$$

$$[Pb^{2+}] = 2 \times 10^{-6} \text{ mol} \cdot L^{-1}$$

12.44 Cathode:
$$Pb^{2+}(aq, 0.010M) + 2e^{-} \rightarrow Pb(s)$$
 $E^{\circ} = -0.13 \text{ V}$

Anode:
$$H_2(g, 1.0bar) \rightarrow 2H^+(aq, pH) + 2e^ E^{\circ} = 0 \text{ V}$$

Total:
$$Pb^{2+}(aq, 0.010M) + H_2(g, 1.0bar) \rightarrow Pb(s) + 2H^+(aq, pH)$$

$$E^{\circ} = -0.13 \text{ V}$$

$$E = E^{\circ} - \frac{0.05916 \text{ V}}{2} \lg \frac{\left[H^{+}\right]^{2}}{\left[Pb^{2+}\right]}$$

$$0.057 \text{ V} = -0.13 \text{ V} - \frac{0.05916 \text{ V}}{2} \lg \frac{\left[H^{+}\right]^{2}}{0.010}$$

$$0.187 \text{ V} = (-0.05916 \text{ V}) \log \left[H^{+}\right] + 0.05916 \text{ V}$$

$$pH = \frac{0.187}{0.05916} - 1.000 = 2.2$$

12.46 (a)
$$Ag_2CrO_4(s) + 2e^- \rightarrow 2Ag(s) + CrO_4^{2-}(aq)$$

(b) To calculate this value we need to determine the E° value for the solubility reaction:

$$Ag_2CrO_4(s) \rightarrow 2 Ag^+(aq) + CrO_4^{2-}(aq) E^{\circ} = ?$$

The relationship $\Delta G^{\circ} = -RT \ln K = -nFE^{\circ}$ can be used to calculate the value of $K_{\rm sp}$. The equations that will add to give the net equation we want, are:

$$Ag_2CrO_4(s) + 2e^- \rightarrow 2 Ag(s) + CrO_4^{2-}(aq)$$
 $E^\circ = +0.446 V$
 $Ag(s) \rightarrow Ag^+(aq) + e^ E^\circ = -0.80 V$

Notice that the second equation is reversed from the reduction reaction given in the Appendix, and consequently the E° value is changed in sign. Adding the first equation to twice the second gives the desired net reaction, and summing the E° values will give the E° value for that process (note that we do not multiply the second equation's E° value by 2).

$$E^{\circ} = (+0.446 \text{ V}) + (-0.80 \text{ V}) = -0.35 \text{ V}$$

$$\ln K_{\text{sp}} = \frac{nFE^{\circ}}{RT} = \frac{(2)(9.65 \times 10^{4} \text{ C} \cdot \text{mol}^{-1})(-0.35 \text{ V})}{(8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298.2 \text{ K})} = -27$$

$$K_{\rm sp} = 10^{-12}$$

12.48 (a) $E^{\circ} = E^{\circ} (Pb^{2+}/Pb) - E^{\circ} (Ag^{+}/Ag) = -0.13 \text{ V} - 0.80 \text{ V} = -0.93 \text{ V}$ Total cell reaction is:

$$2Ag(s) + Pb^{2+}(aq, 0.10 \text{ mol } L^{-1}) \rightarrow 2Ag^{+}(aq, 2.1 \times 10^{-4} \text{ mol } L^{-1}) + Pb(s)$$

$$E = E^{\circ} - \frac{0.025 693 \text{ V}}{2} \ln \frac{\left[\text{Ag}^{+}\right]^{2}}{\left[\text{Pb}^{2+}\right]}$$
$$= -0.93 \text{ V} - \frac{0.025693 \text{ V}}{2} \ln \frac{\left(2.1 \times 10^{-4}\right)^{2}}{0.10} = -0.74 \text{ V}$$

This cell can do work. However, its spontaneous direction is opposite to what we have so far assigned. The maximum work it performs after consuming 1 mol of Pb is

$$w = nFE = (2 \text{ mol})(96500 \text{ C} \cdot \text{mol}^{-1})(0.74 \text{ V}) = 1.4 \times 10^5 \text{ J}$$

(b) The cell reaction in the spontaneous direction should be:

$$2Ag^{+}(aq, 2.1 \times 10^{-4} \text{ mol } L^{-1}) + Pb(s) \rightarrow 2Ag(s) + Pb^{2+}(aq, 0.10 \text{ mol } L^{-1})$$

$$\Delta G_r = -nFE = -2 \times 96 \text{ 485 C} \cdot \text{mol}^{-1} \times 0.74V = -140 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta H_r^{\circ} = \Delta H_f^{\circ}(Pb^{2+}) - 2\Delta H_f^{\circ}(Ag^{+}) = -1.7 \text{ kJ} \cdot \text{mol}^{-1} - 2 \times 105.58 \text{ kJ} \cdot \text{mol}^{-1}$$
$$= -212.9 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta H_r \approx \Delta H_r^{\circ}$$

$$\Delta S_r = \frac{\Delta H_r - \Delta G_r}{T} = \frac{-212.9 \text{ kJ} \cdot \text{mol}^{-1} + 140 \text{ kJ} \cdot \text{mol}^{-1}}{298.15 \text{ K}} = -240 \text{ J} \cdot \text{K}^{-1} \text{mol}^{-1}$$
(negative)

12.50 The change in concentration of Cl⁻ ions will affect the potential of the calomel electrode. The difference in the potential, relative to the standard potential, will be given by the Nernst equation. First, we calculate the concentration of Cl⁻ in a saturated KCl solution:

$$[KCl] = [Cl^{-}] = \frac{\left(\frac{35 \text{ g}}{74.55 \text{ g} \cdot \text{mol}^{-1}}\right)}{0.100 \text{ L}} = 4.7 \text{ mol} \cdot \text{L}^{-1}$$

$$Hg_{2}Cl_{2}(s) + 2 \text{ e}^{-} \rightarrow 2 \text{ Hg(l)} + 2 \text{ Cl}^{-}(\text{aq})$$

$$E = E^{\circ} - \frac{RT}{nF} \ln Q$$

$$(8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298.2 \text{ K}) + 0.00$$

$$E = E^{\circ} - \frac{RP}{nF} \ln Q$$

$$= 0.27 \text{ V} - \frac{(8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298.2 \text{ K})}{2(9.65 \times 10^{5} \text{ C} \cdot \text{mol}^{-1})} \ln Q$$

$$= 0.27 \text{ V} - \frac{(8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298.2 \text{ K})}{2(9.65 \times 10^{5} \text{ C} \cdot \text{mol}^{-1})} \ln[\text{Cl}^{-}]^{2}$$

$$= 0.27 \text{ V} - \frac{(8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298.2 \text{ K})}{2(9.65 \times 10^{4} \text{ C} \cdot \text{mol}^{-1})} \ln(4.7)^{2}$$

$$= 0.23 \text{ V}$$

If this electrode were now set to equal 0, all other potentials would be decreased by 0.23 V (instead of 0.27 V as in Exercise 12.53). The standard hydrogen electrode's potential would be 0.00-0.23~V=-0.23~V; the standard reduction potential for Cu^{2+}/Cu would be 0.34~V-0.23~V=+0.11~V.

12.52 (a) cathode:
$$2 H_2O(1) + 2 e^- \rightarrow H_2(g) + 2 OH^-(aq)$$

$$E^{\circ}$$
(cathode) = -0.42 V (pH = 7)

(rather than
$$K^+(aq) + e^- \rightarrow K(s)$$
 $E^\circ = -2.93 \text{ V}$)

(b) anode:
$$2 \text{ H}_2\text{O}(1) \rightarrow \text{O}_2(g) + 4 \text{ H}^+(aq) + 4 \text{ e}^- \qquad E^\circ(\text{anode}) = +0.82 \text{ V}$$

(pH = 7)

(rather than
$$2 \operatorname{Br}^{-}(aq) \to \operatorname{Br}_{2}(g) + 2 \operatorname{e}^{-} E^{\circ}(anode) = +1.09 \operatorname{V}$$
)

(c)
$$E_{\text{cell}}^{\circ} = E^{\circ}(\text{cathode}) - E^{\circ}(\text{anode}) = -0.42 \text{ V} - (+0.82 \text{ V})$$

$$E_{\text{cell}}^{\circ} = -1.24 \text{ V}$$

Therefore, E(minimum supplied) = + 1.24 V

12.54 (a)
$$Cr(s) \rightarrow Cr^{2+}(aq) + 2e^{-}$$
 $E^{\circ} = -0.91 \text{ V}$

$$Cr(s) \to Cr^{3+}(aq) + 3 e^{-}$$
 $E^{\circ} = -0.74 \text{ V}$

$$2 \text{ H}_2\text{O(l)} \rightarrow \text{O}_2(g) + 4 \text{ H}^+(aq) + 4 \text{ e}^- \qquad E^\circ = +0.81 \text{ V (pH} = 7)$$

Because $E^{\circ}(Cr) < E^{\circ}(H_2O)$, oxidation of the electrode will occur.

(b)
$$Pt(s) \rightarrow Pt^{2+}(aq) + 2e^{-}$$
 $E^{\circ} = +1.20 \text{ V}$

Because $E^{\circ}(Pt) > E^{\circ}(H_2O)$, oxidation of water will occur.

(c)
$$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^{-}$$
 $E^{\circ} = +0.34 \text{ V}$

$$Cu(s) \to Cu^{+}(aq) + e^{-}$$
 $E^{\circ} = +0.52 \text{ V}$

Because $E^{\circ}(Cu) < E^{\circ}(H_2O)$, oxidation of the electrode will occur.

(d)
$$Ni(s) \rightarrow Ni^{2+}(aq) + 2e^{-}$$
 $E^{\circ} = -0.23 \text{ V}$

Because $E^{\circ}(Ni) < E^{\circ}(H_2O)$, oxidation of the electrode will occur.

12.56 96.5 kC =
$$9.65 \times 10^4$$
 C $\cong 1.00$ F = 1.00 mol e

- (a) $1.00 \text{ mol Ag}^+(\text{aq}) + 1.00 \text{ mol e}^- \rightarrow 1.00 \text{ mol Ag, or } 108 \text{ g}$
- (b) $1.00 \text{ mol Cl}^- \rightarrow 0.500 \text{ mol Cl}_2(g) + 1.00 \text{ mol } e^-$

 0.500 mol Cl_2 at 298 K = $0.500 \text{ mol} \times 24.45 \text{ L} \cdot \text{mol}^{-1} = 12.2 \text{ L}$

(c) $0.500 \text{ mol } \text{Cu}^{2+}(\text{aq}) + 1.00 \text{ mol } \text{e}^- \rightarrow 0.500 \text{ mol } \text{Cu}(\text{s});$

mass of copper = $0.500 \text{ mol Cu} \times 63.54 \text{ g} \cdot \text{mol}^{-1} = 31.8 \text{ g}$

12.58 (a)
$$2 F^- \rightarrow F_2(g) + 2 e^-$$

moles of
$$e^- = (7.0 \text{ h}) \left(\frac{3600 \text{ s}}{1 \text{ h}}\right) (324 \text{ mA}) \left(\frac{10^{-3} \text{A}}{1 \text{ mA}}\right) \left(\frac{1 \text{ C} \cdot \text{s}^{-1}}{1 \text{ A}}\right)$$

$$\left(\frac{1 \text{ mol } e^{-}}{9.6485 \times 10^{4} \text{ C}}\right) = 8.5 \times 10^{-2} \text{ mol } e^{-}$$

volume of
$$F_2(g) = (8.5 \times 10^{-2} \text{ mol e}^-) \left(\frac{1 \text{ mol } F_2(g)}{2 \text{ mol e}^-} \right) \left(\frac{24.45 \text{ L } F_2(g)}{1 \text{ mol } F_2(g)} \right)$$

= 1.0 L F₂(g)

(b) as in part (a),

volume of
$$O_2(g) = (8.5 \times 10^{-2} \text{ mol e}^-) \left(\frac{1 \text{ mol } O_2}{4 \text{ mol e}^-} \right) \left(\frac{24.45 \text{ L}}{1 \text{ mol } O_2} \right) = 0.52 \text{ L}$$

Note: We have assumed that the gases are ideal and so occupy $24.45 \text{ L} \cdot \text{mol}^{-1}$ at 298 K and 1.0 atm.

12.60 (a)
$$Au^{3+}(aq) + 3e^{-} \rightarrow Au(s)$$

$$current = (6.66 \ \mu g \ Au) \left(\frac{10^{-6} \ g}{1 \ \mu g}\right) \left(\frac{1 \ mol \ Au}{196.97 \ g \ Au}\right) \left(\frac{3 \ mol \ e^{-}}{1 \ mol \ Au}\right)$$

$$\left(\frac{9.6485 \times 10^{4} \ C}{1 \ mol \ e^{-}}\right) \left(\frac{1 \ A}{1 \ C \cdot s^{-1}}\right) \left(\frac{1}{1800 \ s}\right) = 5.44 \times 10^{-6} \ A$$
(b) $Cr_{2}O_{7}^{2-}(aq) + 14 \ H^{+}(aq) + 12 \ e^{-} \rightarrow 2 \ Cr(s) + 7 \ H_{2}O(l)$

$$time = (6.66 \ \mu g \ Cr) \left(\frac{10^{-6}}{1 \ \mu g}\right) \left(\frac{1 \ mol \ Cr}{52.00 \ g \ Cr}\right) \left(\frac{6 \ mol \ e^{-}}{1 \ mol \ Cr}\right)$$

$$\left(\frac{9.6485 \times 10^{4} \ C}{1 \ mol \ e^{-}}\right) \left(\frac{1 \ A}{1 \ C \cdot s^{-1}}\right) \left(\frac{1}{0.100 \ A}\right) = 0.741 \ s$$

12.62
$$\text{Mn}^{n+}(\text{aq}) + n\text{e}^{-} \to \text{Mn(s)}$$
; solve for n
moles of $\text{Mn} = (4.9 \text{ g Mn}) \left(\frac{1 \text{ mol Mn}}{54.94 \text{ g}} \right) = 0.089 \text{ mol Mn}$

total charge used = (13.7 h)(3600 s·h⁻¹)(350 mA)
$$\left(\frac{10^{-3} \text{ A}}{1 \text{ mA}}\right) \left(\frac{1 \text{ C} \cdot \text{s}^{-1}}{1 \text{ A}}\right)$$

= 1.73×10⁴ C

moles of
$$e^- = (1.73 \times 10^4 \text{ C}) \left(\frac{1 \text{ mol } e^-}{9.6485 \times 10^4} \right) = 0.179 \text{ mol } e^-$$

 $= 0.179 \text{ mol } e^- = 2 \text{ mol charge}$ the species is

$$n = \frac{0.179 \text{ mol e}^{-}}{0.089 \text{ mol Hg}} = \frac{2 \text{ mol charge}}{1 \text{ mol Hg}}; \text{ therefore the species is}$$

$$Mn^{2+}(\text{ox. no.} = +2)$$

12.64 $\operatorname{Ti}^{n+} + ne^{-} \rightarrow \operatorname{Ti}(s)$; solve for n.

Charge consumed =
$$4.70 \text{ C} \cdot \text{s}^{-1} \times 6.00 \text{ h} \times 3600 \text{ s} \cdot \text{h}^{-1} = 1.02 \times 10^5 \text{ C}$$

Moles of charge consumed =
$$\frac{1.02 \times 10^5 \text{ C}}{9.6485 \times 10^4 \text{ C} \cdot \text{mol}^{-1}} = 1.06 \text{ mol e}^{-1}$$

Moles of Ti lost =
$$\frac{12.57 \text{ g Ti}}{47.88 \text{ g Ti/mol Ti}} = 0.2625 \text{ mol Ti}$$

$$n = \frac{1.06 \text{ mol e}^{-}}{0.2625 \text{ mol Ti}} = \frac{4.04 \text{ mol e}^{-}}{1.0 \text{ mol Ti}} = (\text{necessarily}) \frac{4 \text{ mol e}^{-}}{1 \text{ mol Ti}}$$

Therefore, the oxidation number is 4, i.e., the species is Ti⁴⁺.

12.66 (a) $Zn^{2+} + 2e^{-} \rightarrow Zn(s)$ (2 mol $e^{-}/1$ mol Zn)

charge used =
$$(1.0 \text{ mA}) \left(\frac{10^{-3} \text{ A}}{1 \text{ mA}} \right) (31 \text{ d}) \left(\frac{24 \text{ h}}{1 \text{ d}} \right) \left(\frac{3600 \text{ s}}{1 \text{ h}} \right)$$

= $2.7 \times 10^3 \text{ C}$

moles of
$$e^-$$
 used = $(2.7 \times 10^3 \text{ C}) \left(\frac{1 \text{ mol } e^-}{96500 \text{ C}} \right) = 2.8 \times 10^{-2} \text{ mol } e^-$

moles of
$$Zn = (2.8 \times 10^{-2} \text{ mol e}^{-}) \left(\frac{1 \text{ mol } Zn}{2 \text{ mol e}^{-}} \right) = 1.4 \times 10^{-2} \text{ mol } Zn$$

mass of Zn =
$$(1.4 \times 10^{-2} \text{ mol Zn}) \left(\frac{65.37 \text{ g Zn}}{1 \text{ mol Zn}} \right) = 0.92 \text{ g Zn}$$

(b) Given $2 H^+ + 2 e^- \rightarrow H_2(g)$ (hydrogen reduction), corresponding to

 $Zn^{2+} + 2e^{-} \rightarrow Zn(s)$ (zinc reduction), then 1 mol H₂ = 1 mol Zn.

moles of
$$Zn = \frac{0.92 \text{ g Zn}}{65.37 \text{ g} \cdot \text{mol}^{-1} \text{ Zn}} = 1.4 \times 10^{-2} \text{ mol Zn}$$

 1.4×10^{-2} mol H₂ is thus formed.

$$PV = nRT \text{ and } V = \frac{nRT}{P}$$

$$= \frac{(1.4 \times 10^{-2} \text{ mol H}_2)(0.083 \text{ 14 L} \cdot \text{bar} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298 \text{ K})}{1 \text{ bar}}$$

$$V = 0.35 L$$

(c) Neither method is ideal for measuring the amount of current compared to today's ammeters. The Zn method has the advantage that the solid zinc is more robust and masses tend to be easier to measure than volumes. Hydrogen, as a gas, is more difficult to keep for long periods of time. It can be readily lost, leading to inaccurate readings. H₂ gas is also potentially hazardous and explosions could result.

12.68 cathode:
$$2H^{+}(aq) + 2e^{-} \rightarrow H_{2}(g)$$
 $E^{\circ}(H^{+}/H_{2}) = 0 \text{ V}$
anode: $Si(s) + 2 H_{2}O(l) \rightarrow SiO_{2}(s) + 4H^{+}(aq) + 4e^{-} E^{\circ}(SiO_{2}/Si) = -0.84 \text{ V}$
Total: $Si(s) + 2 H_{2}O(l) \rightarrow SiO_{2}(s) + 2 H_{2}(g)$
 $E^{\circ} = E^{\circ}(H^{+}/H_{2}) - E^{\circ}(H^{+},SiO_{2}/Si) = 0 \text{ V} - (-0.84 \text{ V}) = 0.84 \text{ V}$

- **12.70** See Box 12.1 and Table 12.2.
 - (a) $H_2SO_4(aq)$
 - (b) $PbO_2(s)$
 - (c) $PbSO_4(s) + H^+(aq) + 2e^- \rightarrow Pb(s) + HSO_4^-(aq)$
- **12.72** The overall reaction in discharge is the sum of the anode and cathode reactions in Table 12.2.

$$PbO_2(s) + Pb(s) + 2 H_2SO_4(aq) \rightarrow 2 PbSO_4(s) + 2 H_2O(l)$$

So, as the reaction progresses, H_2SO_4 is converted to H_2O . Because the density of H_2SO_4 is greater than that of H_2O , the density of the electrolyte in the battery decreases as the battery is discharged.

- **12.74** (a) Lead-antimony grids have a larger surface area than smooth plates, so the battery can generate large currents (briefly) for starting a car; also, precipitate can adhere to grids better than to a smooth surface.
 - (b) $PbSO_4(s)(Pb^{2+})$; see the anode reaction in Table 12.2.
 - (c) Generally, 6 separate cells are linked in series: $6 \times 2 \text{ V} = 12 \text{ V}$.

12.76 In order to answer this exercise, we need to identify the reduction potentials of the metal ions.

There are

$$Ag^{+} + e^{-} \rightarrow Ag$$
 $E^{\circ} = +0.80 \text{ V}$
 $Cu^{2+} + 2e^{-} \rightarrow Cu$ $E^{\circ} = +0.34 \text{ V}$
 $Ni^{2+} + 2e^{-} \rightarrow Ni$ $E^{\circ} = -0.23 \text{ V}$

- (a) Metals that have reduction potentials in the range
- -0.23 V to +0.34 V will satisfy this requirement. The metals from Appendix 2B that are appropriate include Sn, In, Pb, Fe, and Bi.
- (b) Metals that have reduction potentials in the range +0.34 to +0.80 would be appropriate. The only metal in this range that is appropriate is Hg.
- (c) Any metal with a reduction potential higher than 0.80 V will leave all three metal ions in solution. These include Au and Pt. Notice that Hg has a potential in this range for oxidation to Hg^{2^+} ; however, the reduction potential of the $\mathrm{Hg_2}^{2^+}/\mathrm{Hg}$ couple is lower, so that Hg can reduce Ag^+ with the formation of the $\mathrm{Hg_2}^{2^+}$ ion.
- (d) It is not possible to find a metal that will reduce Ag^+ and Ni^{2+} but not Cu^{2+} , as the Cu^{2+} potential lies between those of Ag^+ and Ni^{2+} . Any metal that would not reduce Cu^{2+} would also not reduce Ni^{2+} .

12.78 (a)
$$Cu^{+}(aq) + e^{-} \rightarrow Cu$$
 (s)

$$Q = (3.05 \,\mathrm{g} \,\mathrm{Cu}) \left(\frac{1 \,\mathrm{mol} \,\mathrm{Cu}}{63.546 \,\mathrm{g} \,\mathrm{Cu}} \right) \left(\frac{1 \,\mathrm{mol} \,\mathrm{e}^{-}}{1 \,\mathrm{mol} \,\mathrm{Cu}} \right) \left(\frac{96485 \,\mathrm{C}}{1 \,\mathrm{mol} \,\mathrm{e}^{-}} \right) = 4631 \,\mathrm{C}$$

$$Sn^{2+} (aq) + 2 \,\mathrm{e}^{-} \rightarrow Sn \,\mathrm{(s)}$$

$$m \,\mathrm{(Sn \,deposited)} = (4631 \,\mathrm{C}) \left(\frac{1 \,\mathrm{mol} \,\mathrm{e}^{-}}{96485 \,\mathrm{C}} \right) \left(\frac{1 \,\mathrm{mol} \,\mathrm{Sn}}{2 \,\mathrm{mol} \,\mathrm{e}^{-}} \right) \left(\frac{118.7 \,\mathrm{g} \,\mathrm{Sn}}{1 \,\mathrm{mol} \,\mathrm{Sn}} \right)$$

$$= 2.85 \,\mathrm{g} \,\mathrm{Sn}$$

$$Fe^{3+} (aq) + 3 \,\mathrm{e}^{-} \rightarrow Fe \,\mathrm{(s)}$$

$$m ext{ (Fe deposited)} = (4631 ext{ C}) \left(\frac{1 \text{mol e}^-}{96485 ext{ C}} \right) \left(\frac{1 \text{mol Fe}}{3 \text{mol e}^-} \right) \left(\frac{55.847 \text{ g Fe}}{1 \text{mol Fe}} \right)$$

$$= 0.893 \text{ g Fe}$$

(b)
$$Q = It$$
; $t = Q/I = \frac{4631 \text{ C}}{3.5 \text{ A}} = 1.3 \times 10^3 \text{ seconds}$

- 12.80 (a) Water containing dissolved ions.
 - (b) Galvanizing steel (coating it with a film of zinc) is a form of rust protection. Zinc lies below iron in the electrochemical series, so if a scratch exposes the iron, the more strongly reducing zinc can release electrons to the iron. The zinc, not the iron, is oxidized. A sacrificial anode is one that is more easily oxidized than the metal to be preserved from oxidation. Therefore, it is preferentially oxidized, affording the desired protection.
 - (c) Elements below iron in the electrochemical series, for example Mg, are used as sacrificial anodes to protect the steel hulls of ships. Pb, below iron in the series, would work but would pose environmental hazards.
- **12.82** (a) Perhaps. Technically speaking, its potential is below the iron couple. From a practical point of view, however, owing to its passivation, it may not readily interact with its surrounding aqueous medium.
 - (b) Zn: yes, E° below iron couple.

Ag: no, E° above iron couple.

Cu: no, E° above iron couple.

Mg: yes, E° below iron couple.

- (c) the moisture (and its dissolved ions) in the surrounding soil
- **12.84** The appropriate half-reactions are:

$$Ti^{4+} + e^{-} \rightarrow Ti^{3+}$$
 $E^{\circ} = 0.00$ (A)

$$Ti^{3+} + e^{-} \rightarrow Ti^{2+}$$
 $E^{\circ} = -0.37$ (B)

$$Ti^{2+} + e^{-} \rightarrow Ti$$
 $E^{\circ} = -1.63$ (C)

(A), (B), and (C) add to give the desired half-reaction (D):

$$Ti^{4+} + 4e^{-} \rightarrow Ti$$
 $E^{\circ} = ?$ (D)

In order to calculate the potential of a half-reaction we need to convert the E° values into ΔG° values:

$$\Delta G^{\circ}(A) = -nFE^{\circ}(A) = -1 F(0.00 \text{ V})$$

$$\Delta G^{\circ}(B) = -nFE^{\circ}(B) = -1 F(-0.37 \text{ V})$$

$$\Delta G^{\circ}(C) = -nFE^{\circ}(C) = -2 F(-1.63 \text{ V})$$

$$\Delta G^{\circ}(D) = \Delta G^{\circ}(A) + \Delta G^{\circ}(B) + \Delta G^{\circ}(C)$$

$$-4 FE^{\circ}(C) = [-1 F(0.00 \text{ V})] + [-1 F(-0.37 \text{ V})] + [-2 F(-1.63 \text{ V})]$$

The constant -F will cancel from both sides leaving:

4
$$E^{\circ}(C) = 1(0.00 \text{ V}) + [1(-0.37 \text{ V})] + [2(-1.63 \text{ V})]$$

 $E^{\circ}(C) = -3.63 \text{ V}/4 = -0.91 \text{ V}$

12.86 The strategy is to find the E° value for the solubility reaction and then find appropriate half-reactions that add to give that solubility reaction. One of these half-reactions (A) is our unknown, the other (B) is obtained from Appendix 2B. The potential for the combination of (A) and (B) is obtained using the K_{sp} value.

$$Ni(OH)_2(s) + 2 e^- \rightarrow Ni(s) + 2 OH^-(aq)$$
 $E^{\circ} = ?$ (A)

$$Ni(s) \rightarrow Ni^{2+}(aq) + 2e^{-}$$
 $E^{\circ} = +0.23 \text{ V}$ (B)

$$Ni(OH)_{2}(s) \rightarrow Ni^{2+}(aq) + 2OH^{-}(aq)$$
 $E^{\circ} = -0.51 \text{ V}$ (C)

$$E^{\circ}(C) = \frac{RT \ln K_{sp}}{nF}$$

$$= \frac{(8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298.2 \text{ K}) \ln(6.5 \times 10^{-18})}{2(9.65 \times 10^{4} \text{ C} \cdot \text{mol}^{-18})}$$

$$= -0.51 \text{ V}$$

$$-0.51 \text{ V} = E^{\circ}(A) + (+0.23 \text{ V})$$

$$E^{\circ}(A) = -0.74 \text{ V}$$

12.88 See Appendix 2B or Table 12.1.

(a)
$$O_2 + 4 H^+ + 4 e^- \rightarrow 2 H_2 O$$
 E° (cathode) = +1.23 V

(b)
$$O_2 + 2 H_2 O + 4 e^- \rightarrow 4 O H^ E^{\circ}$$
 (cathode) = +0.40 V

(1)
$$\text{MnO}_4^- + \text{e}^- \rightarrow \text{MnO}_4^{2-}$$
 $E^\circ = +0.56 \text{ V}$

(2)
$$\text{MnO}_4^- + 8 \text{ H}^+ + 5 \text{ e}^- \rightarrow \text{Mn}^{2+} + 4 \text{ H}_2\text{O}$$
 $E^\circ = +1.51 \text{ V}$

The possible combinations of the half-reactions in (a) and (b) with (1) and (2) are

(1) and (a)
$$4 \text{ MnO}_4^- + 2 \text{ H}_2\text{O} \rightarrow 4 \text{ MnO}_4^{2-} + \text{O}_2 + 4 \text{ H}^+ \quad E^{\circ} = -0.67$$

(1) and (b)
$$4 \text{ MnO}_4^- + 4 \text{ OH}^- \rightarrow 4 \text{ MnO}_4^{2-} + \text{O}_2 + 2 \text{ H}_2\text{O}$$
 $E^{\circ} = +0.16$

(2) and (a)
$$4 \text{ MnO}_4^- + 12 \text{ H}^+ \rightarrow 4 \text{ Mn}^{2+} + 5 \text{ O}_2 + 6 \text{ H}_2 \text{O}$$
 $E^{\circ} = +0.28$

((2) and (b) give the same result as (2) and (a)).

From these potentials we see that the reduction of MnO_4^{-} to MnO_4^{2-} is spontaneous in basic solution, whereas reduction to Mn^{2+} is spontaneous in acidic solution. The potential for the reduction in basic solution is less positive, so MnO_4^{-} is more stable in basic solution.

12.90 Consider $Al^{3+}(aq) + 3e^- \rightarrow Al(s)$ ($E^{\circ} = -1.66$). With this half-reaction as the anode reaction and one or both of the given reduction reactions, a cell with a positive potential can be constructed. Two adjacent filled teeth, simultaneously in contact with the aluminum, could behave as two independent cells at different potentials, corresponding to the two possible reduction half-reactions. Current will then flow between them, stimulating the pain sensors.

The two possible cell reactions are

$$3 \operatorname{Hg}_{2}^{2+}(aq) + 4 \operatorname{Ag}(s) + 2 \operatorname{Al}(s)$$

 $\rightarrow 2 \operatorname{Ag}_{2} \operatorname{Hg}_{3}(s) + 2 \operatorname{Al}^{3+}(aq)$ $E^{\circ}_{cell} = +2.51 \,\mathrm{V}$

$$3 \operatorname{Sn}^{2+}(\operatorname{aq}) + 9 \operatorname{Ag}(s) + 2 \operatorname{Al}(s)$$

 $\rightarrow 3 \operatorname{Ag}_3 \operatorname{Sn}(s) + 2 \operatorname{Al}^{3+}(\operatorname{aq})$ $E^{\circ}_{\text{cell}} = +1.61 \text{ V}$

12.92
$$n \text{ (KBr needed)} = n \text{ (Cu}^+ \text{ initial)} = 0.035 \text{ L} \times 0.012 \text{ M} = 4.2 \times 10^{-4} \text{ mol}$$

$$V(\text{KBr added}) = \frac{4.2 \times 10^{-4} \text{ mol}}{0.010 \text{ M}} \times \frac{1000 \text{ mL}}{1 \text{ L}} = 42.0 \text{ mL}$$

$$Cu^{+}(aq) + e^{-} \rightarrow Cu(s)$$
 $E^{\circ} = +0.521 \text{ V}$

$$E = E^{\circ} - \frac{0.025693 \text{ V}}{\text{n}} \ln \frac{1}{[\text{Cu}^+]}$$

Need [Cu⁺] at equivalence point.

$$CuBr(s) \rightarrow Cu^{+}(aq) + Br^{-}(aq) \quad K_{sp} = 5.2 \times 10^{-9}$$

$$K_{sp} = [Cu^+][Br^-] = s^2 = 5.2 \times 10^{-9}$$

 $s = 7.2 \times 10^{-5} \text{ M} = [\text{Cu}^+]$ at the equivalence point

$$E = +0.521 \text{ V} - \frac{0.025693 \text{ V}}{1 \text{ mol}} \ln \frac{1}{(7.2 \times 10^{-5})}$$

E = +0.276 V is the potential at the equivalence point.

- 12.94 (a) The chrome-plated piece of metal is the anode. It is immersed in 200 mL of 0.0080 M CrCl₃(aq) in one of the 250-mL beakers. The copper wire is the cathode in 200 mL of 0.12 M CuSO₄(aq) in the other beaker. These two electrodes are connected to each other through the voltmeter by clips and wires. Each end of the salt bridge is submerged in one of the two solutions in the beakers to complete the circuit.
 - (b) at cathode: $Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)$ $E^{\circ}(cathode) = +0.34 \text{ V}$

at anode:
$$Cr(s) \rightarrow Cr^{3+}(aq) + 3e^{-}$$
 $E^{\circ}(anode) = -0.74 \text{ V}$

(c)
$$3 \text{ Cu}^{2+}(\text{aq}) + 2 \text{ Cr}(\text{s}) \rightarrow 3 \text{ Cu}(\text{s}) + 2 \text{ Cr}^{3+}(\text{aq})$$
 $E_{\text{cell}}^{\circ} = +1.08 \text{ V}$

(d)
$$Cr(s) \mid 0.0080 \text{ M } CrCl_3(aq) \mid \mid 0.12 \text{ M } CuSO_4(aq) \mid Cu(s)$$

(e)
$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.025 693 \text{ V}}{n} \ln \frac{[\text{Cr}^{3+}]^2}{[\text{Cu}^{2+}]^3}$$

$$E_{\text{cell}} = 1.08 \text{ V} - \frac{0.025 693 \text{ V}}{6} \ln \frac{(0.0080)^2}{(0.12)^3}$$

$$E_{\text{cell}} = 1.08 \text{ V} - 0.004 28 \ln 0.037$$

$$E_{\text{cell}} = 1.08 \text{ V} + 0.014 \text{ V} = 1.09 \text{ V}$$

12.96 (a)
$$Pb^{2+}(aq) + 2e^{-} \rightarrow Pb(s)$$
 $E^{\circ}(cathode) = -0.13 \text{ V}$

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^{-} E^{\circ}(anode) = -0.76 \text{ V}$$

$$Pb^{2+}(aq) + Zn(s) \rightarrow Zn^{2+}(aq) + Pb(s) E^{\circ}_{cell} = +0.63 \text{ V}$$

$$E_{cell} = E^{\circ}_{cell} - \left(\frac{0.0257 \text{ V}}{n}\right) ln\left(\frac{[Zn^{2+}]}{[Pb^{2+}]}\right)$$

$$0.66 \text{ V} = 0.63 \text{ V} - \left(\frac{0.0257 \text{ V}}{2}\right) ln\left(\frac{[Zn^{2+}]}{0.10}\right)$$

$$-2.33 = ln\left(\frac{[Zn^{2+}]}{0.10}\right)$$

$$[Zn^{2+}] = 9.7 \times 10^{-3} \text{ mol} \cdot L^{-1}$$

(b) We begin with the Nernst equation from part (a)

$$\begin{split} E_{\text{cell}} &= 0.63 \text{ V} - \left(\frac{0.0257 \text{ V}}{2}\right) \ln \frac{[\text{Zn}^{2+}]}{(0.10)} \\ E_{\text{cell}} &= 0.63 \text{ V} - (0.0128 \text{ V}) [\ln [\text{Zn}^{2+}] - \ln (0.10)] \\ E_{\text{cell}} &= 0.63 \text{ V} - (0.0128 \text{ V}) [\ln [\text{Zn}^{2+}] + 2.30] \\ E_{\text{cell}} &= 0.60 \text{ V} - 0.0128 \ln [\text{Zn}^{2+}] \end{split}$$

12.98 Cell reaction:

The equilibrium constant is related to E° for the cell,

$$E^{\circ} = \frac{0.025693 \,\text{V}}{n} \ln \,\text{K}$$

We can use the Nernst Equation to get E° .

$$E = E^{\circ} - \frac{0.025693 \,\mathrm{V}}{6} \,\ln Q$$

$$1.18 = E^{\circ} - \frac{0.025693 \text{ V}}{6} \ln \frac{(0.01)^{2} (1 \times 10^{-4})^{6}}{(0.1)(1.0)^{6}}$$

$$1.18 = E^{\circ} + 0.27$$

$$E^{o} = 0.91 \text{ V} = \frac{0.025693 \text{ V}}{6} \ln \text{K}$$
$$\ln \text{K} = 2.125 \times 10^{2}$$
$$\text{K} = 2.0 \times 10^{92}$$

12.100 (a)
$$Cu^{2+} + 2e^{-} \rightarrow Cu$$
 $E^{\circ} = +0.34 \text{ V}$
 $Cu^{2+} + e^{-} \rightarrow Cu^{+}$ $E^{\circ} = +0.15 \text{ V}$

Here, we do not combine the half-reactions to obtain an overall cell reaction; instead, we combine them to obtain a new half-reaction. Therefore, the procedure $E^{\circ} = E^{\circ}(\text{cathode}) - E^{\circ}(\text{anode})$ cannot be used here to obtain $E^{\circ}_{\text{Cu}^+/\text{Cu}}$. Reduction potentials are not extensive physical properties and therefore cannot be directly added or subtracted to obtain a third reduction potential. However, the related $\Delta G^{\circ}_{\text{r}}$ value for the half-reactions is an extensive property, so we first calculate $\Delta G^{\circ}_{\text{r,Cu}^+/\text{Cu}}$ and from it obtain $E^{\circ}_{\text{Cu}^+/\text{Cu}^{\circ}}$. Then,

$$Cu^{2+} + 2e^{-} \rightarrow Cu$$

 $Cu^{+} \rightarrow Cu^{2+} + e^{-}$

 $Cu^+ + e^- \rightarrow Cu$ (new half-reaction)

$$Cu^{2+}/Cu^{+}$$
 $\Delta G^{\circ}_{r} = -nFE^{\circ} = -(2)(9.65 \times 10^{4} \text{ C} \cdot \text{mol}^{-1})(+0.34 \text{ J} \cdot \text{C}^{-1})$
= $-66 \text{ kJ} \cdot \text{mol}^{-1}$

Cu⁺/Cu
$$\Delta G_{r}^{\circ} = -nFE^{\circ} = -(1)(9.65 \times 10^{4} \text{ C} \cdot \text{mol}^{-1})(-0.15 \text{ J} \cdot \text{C}^{-1})$$

= +15 kJ·mol⁻¹

$$\Delta G^{\circ}_{r,Cu^{+}/Cu} = \Delta G^{\circ}_{r,Cu^{2+}/Cu^{+}} + \Delta G^{\circ}_{r,Cu^{+}/Cu} = -66 \text{ kJ} + 15 \text{ kJ}$$
$$= -51 \text{ kJ} \cdot \text{mol}^{-1}$$

Then,
$$E^{\circ}_{\text{Cu}^+/\text{Cu}} = \frac{\Delta G^{\circ}_{\text{r,Cu}^+/\text{Cu}}}{-nF} = \frac{-51 \times 10^3 \text{ J}}{-(1)(9.65 \times 10^4 \text{ C} \cdot \text{mol}^{-1})} = +0.53 \text{ V}$$

12.102 Set up a cell in which one electrode is the silver-silver chloride electrode and the other is the hydrogen electrode. The E of this cell will be sensitive to $[H^+]$ and can be used to obtain pH.

$$2 \text{ H}^+(\text{aq}) + 2 \text{ e}^- \rightarrow \text{H}_2(\text{g})$$
 $E^{\circ}(\text{cathode}) = 0.00 \text{ V}$

$$2 \text{ AgCl(s)} + 2 \text{ e}^{-} \rightarrow 2 \text{ Ag(s)} + 2 \text{ Cl}^{-}(\text{aq})$$
 $E^{\circ}(\text{anode}) = -0.22 \text{ V}$

$$2 \text{ AgCl(s)} + \text{H}_{2}(g, 1 \text{ atm}) \rightarrow 2 \text{ Ag(s)} + 2 \text{ Cl}^{-}(aq) + 2 \text{ H}^{+}(aq)$$

$$E^{\circ}_{cell} = 0.22 \text{ V}$$

(a) If $[C1^-] = 1.0 \text{ mol} \cdot L^{-1}$:

$$E = E^{\circ} - \left(\frac{0.0257 \text{ V}}{2}\right) \ln \left(\left[H^{+}\right]^{2}\right) = 0.22 \text{ V} - (0.0257) \ln\left[H^{+}\right]$$

$$ln[H^+] = 2.303 log [H^+] = -2.303(pH),$$

so
$$E = 0.22 \text{ V} + 0.0592 \text{ V} \times \text{pH}$$
, and

$$pH = \frac{E - 0.22 \text{ V}}{0.0592 \text{ V}}$$

By measuring *E* of this cell, pH can be obtained.

- (b) pOH = 14.00 pH
- 12.104 (a) The variation of potential for

$$Ag^+ + e^- \rightarrow Ag \quad E^\circ = +0.80 \text{ V}$$

with Ag⁺ concentration is derived from the Nernst equation:

$$E = E^{\circ} - \frac{RT}{nF} \ln Q$$

$$E = +0.80 \text{ V} - \frac{0.05916}{1} \log \frac{1}{[\text{Ag}^+]}$$

$$E = +0.80 \text{ V} + 0.05916 \log[\text{Ag}^+]$$

(b) The potentials for $AgX + e^- \rightarrow Ag + X^-$ and K_{sp} values for AgX are

Compound	E°	$K_{ m sp}$
AgCl	+0.22 V	1.6×10^{-10}
AgBr	+0.07 V	7.7×10^{-13}
AgI	-0.15 V	1.5×10^{-16}

From the $K_{\rm sp}$ values, we can determine [Ag⁺] at 1 M X⁻ for each: [Ag⁺] = $K_{\rm sp}$ (because $K_{\rm sp}$ = [Ag⁺][X⁻]). If we use these values in the relationship E = +0.80 V + 0.059 16 log[Ag⁺], we calculate the following potentials:

AgX	$[Ag^+]$, $mol \cdot L^{-1}$	E = +0.80 V + 0.059 16 $\log[\text{Ag}^+], \text{ V}$
AgCl	1.6×10^{-10}	+0.22
AgBr	7.7×10^{-13}	+0.08
AgI	1.5×10^{-16}	-0.14

As can be seen, these values are essentially, within the limitations of the data, the values obtained as the reduction potentials of the silver halides. This tells us that the solubility determines the concentration of Ag⁺ ion in solution, which is the reason the potentials differ.

12.106 The potential for electrolyzing a metal cation will change as the concentration of the metal decreases during an electrolysis reaction. This will require increasing the potential across the cell. We do not need to know the actual beginning concentration in order to calculate this answer. The Nernst equation will allow us to calculate the potential difference between *E*1 and *E*2:

$$E1 = E^{\circ} - \frac{0.05916}{1} \log \frac{1}{[M^{+}(1)]}$$
$$E2 = E^{\circ} - \frac{0.05916}{1} \log \frac{1}{[M^{+}(2)]}$$

Subtracting the first equation from the second gives

$$E2 - E1 = -\frac{0.05916}{1} \left\{ \log \frac{1}{[M^{+}(2)]} - \log \frac{1}{[M^{+}(1)]} \right\}$$
$$E2 - E1 = -\frac{0.05916}{1} \log \frac{[M^{+}(1)]}{[M^{+}(2)]}$$

Because we want 99.99% of the metal to be plated out, the final concentration $[M^+(2)]$ will be $0.0001 \times [M^+(1)]$:

$$E2 - E1 = -\frac{0.05916}{1} \log \frac{[M^{+}(1)]}{0.0001 \times [M^{+}(1)]} = -0.24 \text{ V}$$

The potential will need to be increased by about 0.24 V in order to plate out 99.99% of the metal.

12.108 (a) Galvanic from half cell (1) to half cell (2); therefore, half cell (1) is anode (M is oxidized by X^{2+}). Hence $E^{\circ}(M^{+}/M) \le E^{\circ}(X^{+2}/X)$.

Galvanic from half cell (1) to SHE; therefore, half cell (1) is anode (M is oxidized by H_3O^+). Hence $E^{\circ}(M^+/M) \le E^{\circ}(SHE) = 0$.

$$E^{\circ}(M^{+}/M) < 0$$
; $E^{\circ}(M^{+}/M) = -0.25 \text{ V}$

$$E^{\circ}(X^{+2}/X) > 0$$
; $E^{\circ}(X^{+2}/X) = +0.65 \text{ V}$

(b) Anode:
$$M \to M^+ + e^ E^{\circ} = 0.25 \text{ V}$$

Cathode:
$$X^{2+} + 2 e^{-} \rightarrow X$$
 $E^{\circ} = 0.65 \text{ V}$

Net:
$$X^{2+} + 2 M \rightarrow 2 M^{+} + X$$
 $E^{\circ} = 0.90 V$

12.110
$$P_{\text{Cl}_2} = P_{\text{total}} - P_{\text{H}_2\text{O}}$$

= 770. Torr -17.54 Torr = 752 Torr $\left(\frac{1 \text{ atm}}{760 \text{ Torr}}\right)$
= 0.990 atm
 $n_{\text{Cl}_2} = \frac{P_{\text{Cl}_2}V}{RT} = \frac{(0.990 \text{ atm})(20.0 \text{ L})}{(0.08206 \text{ atm} \cdot \text{L} \cdot \text{K}^{-1} \text{mol}^{-1})(293.15 \text{ K})} = 0.823 \text{ mol}$
 $Q = (0.823 \text{ mol Cl}_2) \left(\frac{2 \text{ mol e}^-}{1 \text{ mol Cl}_2}\right) \left(\frac{96 \text{ 485 C}}{\text{mol e}^-}\right) = 1.59 \times 10^5 \text{ C}$

$$t = \frac{1.59 \times 10^5 \text{ C}}{2.0 \text{ A}} = 7.94 \times 10^4 \text{ s} \left(\frac{1 \text{ hour}}{3600 \text{ s}}\right) = 22 \text{ hours}$$

12.112 The reaction of interest is

(1)
$$\operatorname{HF}(\operatorname{aq}) \leftrightarrow \operatorname{H}^{+}(\operatorname{aq}) + \operatorname{F}^{-}(\operatorname{aq})$$
 $K_{\operatorname{a}} = \frac{\left[\operatorname{H}^{+}\right]\left[\operatorname{F}^{-}\right]}{\left[\operatorname{HF}\right]} = ?$

We have

(2)
$$F_2(g) + 2 H^+(aq) + 2e^- \rightarrow 2 HF(aq)$$
 $E^\circ = +3.03 V$ and from Appendix 2B,

(3)
$$F_2(g) + 2e^- \rightarrow 2 F^-(aq)$$
 $E^\circ = +2.87 V$
Since combining reactions $(1/2)(3) - (1/2)(2) = (1)$,

$$E_{(1)}^{\circ} = +2.87 \text{ V} - 3.03 \text{ V} = -0.16 \text{ V}$$

$$\Delta G^{\circ} = -nFE^{\circ} = -RT \ln K$$

$$K = e^{\frac{nFE^{\circ}}{RT}} = e^{\frac{(96 \cdot 485)(-0.16)}{(8.314)(298.15)}} = e^{-6.228} = 2.0 \times 10^{-3}$$

(We note that this value for K_a does not match the one given in Table 10.1 on page 376, 3.5×10^{-4} . There may be a mistake in the data given here or the thermodynamic values may have been determined from different experiments.)