CHAPTER 20

ELECTROCHEMISTRY

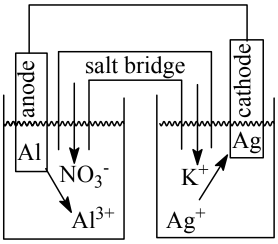
PRACTICE EXAMPLES

1A **(E)** The conventions state that the anode material is written first, and the cathode material is written last.

Anode, oxidation: $\mathrm{Sc(s)} \rightarrow \mathrm{Sc^{3+}(aq)} + 3\mathrm{e^-}$

Cathode, reduction: $\{\mathrm{Ag^+(aq)} + \mathrm{e^-} \rightarrow \mathrm{Ag(s)}\} \quad \times 3$

Net reaction $\mathrm{Sc(s)} + 3\,\mathrm{Ag^+(aq)} \rightarrow \mathrm{Sc^{3+}(aq)} + 3\,\mathrm{Ag(s)}$



1B **(E)** Oxidation of Al(s) at the anode: $\mathrm{Al(s)} \rightarrow \mathrm{Al^{3+}(aq)} + 3\mathrm{e^-}$

Reduction of $\mathrm{Ag^+(aq)}$ at the cathode: $\mathrm{Ag^+(aq)} + \mathrm{e^-} \rightarrow \mathrm{Ag(s)}$

Overall reaction in cell: $\mathrm{Al(s)} + 3\,\mathrm{Ag^+(aq)} \rightarrow \mathrm{Al^{3+}(aq)} + 3\,\mathrm{Ag(s)}$ Diagram: $\mathrm{Al(s)|Al^{3+}(aq)||Ag^+(aq)|Ag(s)}$

2A **(E)** Anode, oxidation: $\mathrm{Sn(s)} \rightarrow \mathrm{Sn^{2+}(aq)} + 2\mathrm{e^-}$

Cathode, reduction: $\{Ag^+(aq) + 1e \rightarrow Ag(s)\} \times 2$

Overall reaction in cell: $Sn(s) + 2Ag^+(aq) \rightarrow Sn^{2+}(aq) + 2Ag(s)$

2B **(E)** Anode, oxidation: $\{In(\mathrm{s}) \rightarrow In^{3+}(\mathrm{aq}) + 3\mathrm{e^-}\} \times 2$

Cathode, reduction: $\{Cd^{2+}(aq) + 2e \rightarrow Cd(s)\} \times 3$

Overall reaction in cell: $2In(s) + 3Cd^{2+}(aq) \rightarrow 2In^{3+}(aq) + 3Cd(s)$

3A **(M)** We obtain the two balanced half-equations and the half-cell potentials from Table 20-1.

Oxidation: $\{\mathrm{Fe^{2+}(aq)} \rightarrow \mathrm{Fe^{3+}(aq)} + \mathrm{e^-}\} \quad \times 2 \qquad -E^\circ = -0.771\,\mathrm{V}$

Reduction: $\mathrm{Cl_2(g)} + 2\mathrm{e^-} \rightarrow 2\,\mathrm{Cl^-(aq)} \qquad E^\circ = +1.358\,\mathrm{V}$

Net: $2\mathrm{Fe^{2+}(aq)} + \mathrm{Cl_2(g)} \rightarrow 2\mathrm{Fe^{3+}(aq)} + 2\mathrm{Cl^-(aq)}; \quad E^\circ_{\text{cell}} = +1.358\,\mathrm{V} - 0.771\,\mathrm{V} = +0.587\,\mathrm{V}$

3B **(M)** Since we need to refer to Table 20-1, in any event, it is perhaps a bit easier to locate the two balanced half-equations in the table. There is only one half-equation involving both $\mathrm{Fe^{2+}(aq)}$ and $\mathrm{Fe^{3+}(aq)}$ ions. It is reversed and written as an oxidation below. The half-equation involving $\mathrm{MnO_4^-(aq)}$ is also written below. [Actually, we need to know that in acidic solution $\mathrm{Mn^{2+}(aq)}$ is the principal reduction product of $\mathrm{MnO_4^-(aq)}$.]

Oxidation: $\{\mathrm{Fe^{2+}(aq)} \rightarrow \mathrm{Fe^{3+}(aq)} + \mathrm{e^-}\} \quad \times 5 \qquad -E^\circ = -0.771\,\mathrm{V}$

Reduction: $\mathrm{MnO_4^-(aq)} + 8\,\mathrm{H^+(aq)} + 5\mathrm{e^-} \rightarrow \mathrm{Mn^{2+}(aq)} + 4\,\mathrm{H_2O(l)} \qquad E^\circ = +1.51\,\mathrm{V}$

Net: $\mathrm{MnO_4^-(aq)} + 5\,\mathrm{Fe^{2+}(aq)} + 8\mathrm{H^+(aq)} \rightarrow \mathrm{Mn^{2+}(aq)} + 5\mathrm{Fe^{3+}(aq)} + 4\mathrm{H_2O(l)}$

$E^{\mathrm{o}}_{\mathrm{cell}} = +1.51\,\mathrm{V} - 0.771\,\mathrm{V} = +0.74\,\mathrm{V}$

4A **(M)** We write down the oxidation half-equation following the method of Chapter 5, and obtain the reduction half-equation from Table 20-1, along with the reduction half-cell potential.

Oxidation: $\{\mathrm{H_2C_2O_4(aq)} \longrightarrow 2\,\mathrm{CO_2\,(aq)} + 2\,\mathrm{H^+(aq)} + 2\,\mathrm{e^-}\}\ \times 3 \qquad -E^{\circ}\{\mathrm{CO_2/H_2C_2O_4}\}$

Reduction: $\mathrm{Cr_2O_7{}^{2-}(aq)} + 14\,\mathrm{H^+(aq)} + 6\,\mathrm{e^-} \rightarrow 2\,\mathrm{Cr^{3+}(aq)} + 7\,\mathrm{H_2O(l)} \qquad E^{\mathrm{o}} = +1.33\,\mathrm{V}$

Net: $\mathrm{Cr_2O_7{}^{2-}(aq)} + 8\,\mathrm{H^+(aq)} + 3\,\mathrm{H_2C_2O_4(aq)} \rightarrow 2\,\mathrm{Cr^{3+}(aq)} + 7\,\mathrm{H_2O(l)} + 6\,\mathrm{CO_2(g)}$

$E^{\mathrm{o}}_{\mathrm{cell}} = +1.81\,\mathrm{V} = +1.33\,\mathrm{V} - E^{\mathrm{o}}\{\mathrm{CO_2/H_2C_2O_4}\};\quad E^{\mathrm{o}}\{\mathrm{CO_2/H_2C_2O_4}\} = 1.33\,\mathrm{V} - 1.81\,\mathrm{V} = -0.48\,\mathrm{V}$

4B **(M)** The 2nd half-reaction must have $\mathrm{O_2(g)}$ as reactant and $\mathrm{H_2O(l)}$ as product.

Oxidation: $\{\mathrm{Cr^{2+}} + \mathrm{(aq)} \longrightarrow \mathrm{Cr^{3+}(aq)} + \mathrm{e^-}\}\ \times 4 \qquad -E^{\circ}\{\mathrm{Cr^{3+}/Cr^{2+}}\}$

Reduction: $\mathrm{O_2(g)} + 4\mathrm{H^+(aq)} + 4\mathrm{e^-} \rightarrow 2\mathrm{H_2O(l)} \qquad E^{\mathrm{o}} = +1.229\mathrm{V}$

Net: $\mathrm{O_2(g)} + 4\mathrm{H^+(aq)} + 4\,\mathrm{Cr^{2+}(aq)} \rightarrow 2\mathrm{H_2O(l)} + 4\mathrm{Cr^{3+}(aq)}$

$E_{\mathrm{cell}}{}^{\mathrm{o}} = +1.653\mathrm{V} = +1.229\mathrm{V} - \mathrm{E^o}\{\mathrm{Cr^{3+}/Cr^{2+}}\};\quad E^{\mathrm{o}}\{\mathrm{Cr^{3+}/Cr^{2+}}\} = 1.229\mathrm{V} - 1.653\mathrm{V} = -0.424\mathrm{V}$

5A **(M)** First we write down the two half-equations, obtain the half-cell potential for each, and then calculate $E^{\mathrm{o}}_{\mathrm{cell}}$. From that value, we determine ΔG^{o}

Oxidation: $\{\mathrm{Al(s)} \rightarrow \mathrm{Al^{3+}(aq)} + 3\mathrm{e^-}\}\ \times 2 \qquad -E^{\mathrm{o}} = +1.676\mathrm{V}$

Reduction: $\{\mathrm{Br_2(l)} + 2\mathrm{e^-} \rightarrow 2\ \mathrm{Br^-(aq)}\}\ \times 3 \qquad E^{\mathrm{o}} = +1.065\mathrm{V}$

Net: $2\,\mathrm{Al(s)} + 3\,\mathrm{Br_2(l)} \rightarrow 2\,\mathrm{Al^{3+}(aq)} + 6\,\mathrm{Br^-(aq)} \quad E^{\mathrm{o}}_{\mathrm{cell}} = 1.676\,\mathrm{V} + 1.065\,\mathrm{V} = 2.741\,\mathrm{V}$

$$\Delta G^{\mathrm{o}} = -nFE^{\mathrm{o}}_{\mathrm{cell}} = -6\,\mathrm{mol\ e^-} \times \frac{96{,}485\ \mathrm{C}}{1\,\mathrm{mol\ e^-}} \times 2.741\,\mathrm{V} = -1.587\times 10^{6}\,\mathrm{J} = -1587\,\mathrm{kJ}$$

5B **(M)** First we write down the two half-equations, one of which is the reduction equation from the previous example. The other is the oxidation that occurs in the standard hydrogen electrode.

Oxidation: $2\mathrm{H_2(g)} \rightarrow 4\mathrm{H^+(aq)} + 4\mathrm{e^-}$

Reduction: $\mathrm{O_2(g)} + 4\,\mathrm{H^+(aq)} + 4\mathrm{e^-} \rightarrow 2\,\mathrm{H_2O(l)}$

Net: $2\ \mathrm{H_2(g)} + \mathrm{O_2(g)} \rightarrow 2\ \mathrm{H_2O(l)} \qquad n = 4$ in this reaction.

This net reaction is simply twice the formation reaction for $\mathrm{H_2O(l)}$ and, therefore,

$$\Delta G^{\mathrm{o}} = 2\Delta G_{\mathrm{f}}{}^{\mathrm{o}}\left[\mathrm{H_2O(l)}\right] = 2\times(-237.1\ \mathrm{kJ}) = -474.2\times 10^{3}\ \mathrm{J} = -nFE^{\mathrm{o}}_{\mathrm{cell}}$$

$$E^{\mathrm{o}}_{\mathrm{cell}} = \frac{-\Delta G^{\mathrm{o}}}{nF} = \frac{-(-474.2\times 10^{3}\ \mathrm{J})}{4\ \mathrm{mol\ e^-} \times \dfrac{96{,}485\,\mathrm{C}}{\mathrm{mol\,e^-}}} = +1.229\,\mathrm{V} = E^{\mathrm{o}}\text{, as we might expect.}$$

6A **(M)** Cu(s) will displace metal ions of a metal less active than copper. Silver ion is one example.

Oxidation: $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$ $-E^\circ = -0.340 V$ (from Table 20.1)

Reduction: $\{Ag^+(aq) + e^- \rightarrow Ag(s)\} \times 2$ $E^\circ = +0.800 V$

Net: $2Ag^+(aq) + Cu(s) \rightarrow Cu^{2+}(aq) + 2Ag(s)$ $E^\circ_{cell} = -0.340 V + 0.800 V = +0.460 V$

6B **(M)** We determine the value for the hypothetical reaction's cell potential.

Oxidation: $\{Na(s) \rightarrow Na^+(aq) + e^-\} \times 2$ $-E^\circ = +2.713 V$

Reduction: $Mg^{2+}(aq) + 2e^- \rightarrow Mg(s)$ $E^\circ = -2.356 V$

Net: $2Na(s) + Mg^{2+}(aq) \rightarrow 2Na^+(aq) + Mg(s)$ $E^\circ_{cell} = 2.713 V - 2.356 V = +0.357 V$

The method is not feasible because another reaction occurs that has a more positive cell potential, i.e., Na(s) reacts with water to form $H_2(g)$ and NaOH(aq):

Oxidation: $\{Na(s) \rightarrow Na^+(aq) + e^-\} \times 2$ $-E^\circ = +2.713 V$

Reduction: $2H_2O + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$ $E^\circ = -0.828 V$

$E^\circ_{cell} = 2.713 V - 0.828 V = +1.885 V$.

7A **(M)** The oxidation is that of SO_4^{2-} to $S_2O_8^{2-}$, the reduction is that of O_2 to H_2O.

Oxidation: $\{2SO_4^{2-}(aq) \rightarrow S_2O_8^{2-}(aq) + 2e^-\} \times 2$ $-E^\circ = -2.01 V$

Reduction: $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$ $E^\circ = +1.229 V$

Net: $O_2(g) + 4H^+(aq) + 2SO_4^{2-}(aq) \rightarrow S_2O_8^{2-}(aq) + 2H_2O(l)$ $E^\circ_{cell} = -0.78 V$

Because the standard cell potential is negative, we conclude that this cell reaction is nonspontaneous under standard conditions. This would not be a feasible method of producing peroxodisulfate ion.

7B **(M) (1)** The oxidation is that of $Sn^{2+}(aq)$ to $Sn^{4+}(aq)$; the reduction is that of O_2 to H_2O.

Oxidation: $\{Sn^{2+}(aq) \rightarrow Sn^{4+}(aq) + 2e^-\} \times 2$ $-E^\circ = -0.154 V$

Reduction: $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$ $E^\circ = +1.229 V$

Net: $O_2(g) + 4H^+(aq) + 2Sn^{2+}(aq) \rightarrow 2Sn^{4+}(aq) + 2H_2O(l)$ $E^\circ_{cell} = +1.075 V$

Since the standard cell potential is positive, this cell reaction is spontaneous under standard conditions.

(2) The oxidation is that of Sn(s) to $Sn^{2+}(aq)$; the reduction is still that of O_2 to H_2O.

Oxidation: $\{Sn(s) \rightarrow Sn^{2+}(aq) + 2e^-\} \times 2$ $-E^\circ = +0.137 V$

Reduction: $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$ $E^\circ = +1.229 V$

Net: $O_2(g) + 4H^+(aq) + 2Sn(s) \rightarrow 2Sn^{2+}(aq) + 2H_2O(l)$

$E^\circ_{cell} = 0.137 V + 1.229 V = +1.366 V$

The standard cell potential for this reaction is more positive than that for situation (1). Thus, reaction (2) should occur preferentially. Also, if $Sn^{4+}(aq)$ is formed, it should react with Sn(s) to form $Sn^{2+}(aq)$.

Oxidation: $Sn(s) \rightarrow Sn^{2+}(aq) + 2e^-$ $\quad -E^o = +0.137\,V$

Reduction: $Sn^{4+}(aq) + 2e^- \rightarrow Sn^{2+}(aq)$ $\quad E^o = +0.154\,V$

Net: $Sn^{4+}(aq) + Sn(s) \rightarrow 2\,Sn^{2+}(aq)$ $\quad E^o_{cell} = +0.137\,V + 0.154\,V = +0.291\,V$

8A **(M)** For the reaction $2\,Al(s) + 3Cu^{2+}(aq) \rightarrow 2\,Al^{3+}(aq) + 3Cu(s)$ we know $n = 6$ and $E^o_{cell} = +2.013\,V$. We calculate the value of K_{eq}.

$$E^o_{cell} = \frac{0.0257}{n} \ln K_{eq}; \quad \ln K_{eq} = \frac{nE^o_{cell}}{0.0257} = \frac{6 \times (+2.013)}{0.0257} = 470; \quad K_{eq} = e^{470} = 10^{204}$$

The huge size of the equilibrium constant indicates that this reaction indeed will go to essentially 100% to completion.

8B **(M)** We first determine the value of E^o_{cell} from the half-cell potentials.

Oxidation: $Sn(s) \rightarrow Sn^{2+}(aq) + 2e^-$ $\quad -E^o = +0.137\,V$

Reduction: $Pb^{2+}(aq) + 2e^- \rightarrow Pb(s)$ $\quad E^o = -0.125\,V$

Net: $Pb^{2+}(aq) + Sn(s) \rightarrow Pb(s) + Sn^{2+}(aq)$ $\quad E^o_{cell} = +0.137\,V - 0.125\,V = +0.012\,V$

$$E^o_{cell} = \frac{0.0257}{n} \ln K_{eq} \quad \ln K_{eq} = \frac{nE^o_{cell}}{0.0257} = \frac{2 \times (+0.012)}{0.0257} = 0.93 \quad K_{eq} = e^{0.93} = 2.5$$

The equilibrium constant's small size (0.001 < K <1000) indicates that this reaction will not go to completion.

9A **(M)** We first need to determine the standard cell voltage and the cell reaction.

Oxidation: $\{Al(s) \rightarrow Al^{3+}(aq) + 3\,e^-\} \times 2$ $\quad -E^o = +1.676\,V$

Reduction: $\{Sn^{4+}(aq) + 2\,e^- \rightarrow Sn^{2+}(aq)\} \times 3$ $\quad E^o = +0.154\,V$

Net: $2\,Al(s) + 3\,Sn^{4+}(aq) \rightarrow 2\,Al^{3+}(aq) + 3\,Sn^{2+}(aq)$ $\quad E^o_{cell} = +1.676\,V + 0.154\,V = +1.830\,V$

Note that $n = 6$. We now set up and substitute into the Nernst equation.

$$E_{cell} = E^o_{cell} - \frac{0.0592}{n} \log \frac{[Al^{3+}]^2 [Sn^{2+}]^3}{[Sn^{4+}]^3} = +1.830 - \frac{0.0592}{6} \log \frac{(0.36\,M)^2 (0.54\,M)^3}{(0.086\,M)^3}$$

$$= +1.830\,V - 0.0149\,V = +1.815\,V$$

9B **(M)** We first need to determine the standard cell voltage and the cell reaction.

Oxidation: $2\,Cl^-(1.0\,M) \rightarrow Cl_2(1\,atm) + 2e^-$ $\quad -E^o = -1.358\,V$

Reduction: $PbO_2(s) + 4H^+(aq) + 2e^- \rightarrow Pb^{2+}(aq) + 2H_2O(l)$ $\quad E^o = +1.455\,V$

Net: $PbO_2(s)+4H^+(0.10\text{ M})+2Cl^-(1.0\text{ M})\rightarrow Cl_2(1\text{ atm})+Pb^{2+}(0.050\text{ M})+2H_2O(l)$

$E^{o}_{cell}=-1.358\text{ V}+1.455\text{ V}=+0.097\text{ V}$ Note that $n=2$. Substitute values into the Nernst equation.

$$E_{cell}=E^{o}_{cell}-\frac{0.0592}{n}\log\frac{P\{Cl_2\}\left[Pb^{2+}\right]}{\left[H^+\right]^4\left[Cl^-\right]^2}=+0.097-\frac{0.0592}{2}\log\frac{(1.0\text{ atm})(0.050\text{ M})}{(0.10\text{ M})^4(1.0\text{ M})^2}$$

$$=+0.097\text{ V}-0.080\text{ V}=+0.017\text{ V}$$

10A **(M)** The cell reaction is $2\text{ Fe}^{3+}(0.35\text{ M})+Cu(s)\rightarrow 2\text{ Fe}^{2+}(0.25\text{ M})+Cu^{2+}(0.15\text{ M})$ with $n=2$ and $E^{o}_{cell}=-0.337\text{ V}+0.771\text{ V}=0.434\text{ V}$ Next, substitute this voltage and the concentrations into the Nernst equation.

$$E_{cell}=E^{o}_{cell}-\frac{0.0592}{n}\log\frac{\left[Fe^{2+}\right]^2\left[Cu^{2+}\right]}{\left[Fe^{3+}\right]^2}=0.434-\frac{0.0592}{2}\log\frac{(0.25)^2(0.15)}{(0.35)^2}=0.434+0.033$$

$E_{cell}=+0.467\text{ V}$ Thus the reaction is spontaneous under standard conditions as written.

10B **(M)** The reaction is not spontaneous under standard conditions in either direction when $E_{cell}=0.000\text{ V}$. We use the standard cell potential from Example 20-10.

$$E_{cell}=E^{o}_{cell}-\frac{0.0592}{n}\log\frac{\left[Ag^+\right]^2}{\left[Hg^{2+}\right]};\qquad 0.000\text{ V}=-0.054\text{ V}-\frac{0.0592}{2}\log\frac{\left[Ag^+\right]^2}{\left[Hg^{2+}\right]}$$

$$\log\frac{\left[Ag^+\right]^2}{\left[Hg^{2+}\right]}=\frac{-0.054\times 2}{0.0592}=-1.82;\qquad \frac{\left[Ag^+\right]^2}{\left[Hg^{2+}\right]}=10^{-1.82}=0.0150$$

11A **(M)** In this concentration cell $E^{o}_{cell}=0.000\text{ V}$ because the same reaction occurs at anode and cathode, only the concentrations of the ions differ. $\left[Ag^+\right]=0.100\text{ M}$ in the cathode compartment. The anode compartment contains a saturated solution of AgCl(aq).

$$K_{sp}=1.8\times10^{-10}=\left[Ag^+\right]\left[Cl^-\right]=s^2;\qquad s=\sqrt{1.8\times10^{-10}}=1.3\times10^{-5}\text{ M}$$

Now we apply the Nernst equation. The cell reaction is

$$Ag^+(0.100\text{ M})\rightarrow Ag^+(1.3\times10^{-5}\text{ M})$$

$$E_{cell}=0.000-\frac{0.0592}{1}\log\frac{1.3\times10^{-5}\text{ M}}{0.100\text{ M}}=+0.23\text{ V}$$

11B **(D)** Because the electrodes in this cell are identical, the standard electrode potentials are numerically equal and subtracting one from the other leads to the value $E^{o}_{cell}=0.000\text{ V}$. However, because the ion concentrations differ, there is a potential difference between the

two half cells (non-zero nonstandard voltage for the cell). $\left[\mathrm{Pb}^{2+}\right] = 0.100\ \mathrm{M}$ in the cathode compartment, while the anode compartment contains a saturated solution of PbI_2.
We use the Nernst equation (with $n = 2$) to determine $\left[\mathrm{Pb}^{2+}\right]$ in the saturated solution.

$$E_{\text{cell}} = +0.0567\ \mathrm{V} = 0.000 - \frac{0.0592}{2}\log\frac{x\,\mathrm{M}}{0.100\,\mathrm{M}};\quad \log\frac{x\,\mathrm{M}}{0.100\,\mathrm{M}} = \frac{2\times 0.0567}{-0.0592} = -1.92$$

$$\frac{x\,\mathrm{M}}{0.100\,\mathrm{M}} = 10^{-1.92} = 0.012;\quad \left[\mathrm{Pb}^{2+}\right]_{\text{anode}} = x\ \mathrm{M} = 0.012\times 0.100\ \mathrm{M} = 0.0012\ \mathrm{M};$$

$$\left[\mathrm{I}^-\right] = 2\times 0.0012\ \mathrm{M} = 0.0024\ \mathrm{M}$$

$K_{\text{sp}} = \left[\mathrm{Pb}^{2+}\right]\left[\mathrm{I}^-\right]^2 = (0.0012)(0.0024)^2 = 6.9\times 10^{-9}$ compared with 7.1×10^{-9} in Appendix D

12A **(M)** From Table 20-1 we choose one oxidations and one reductions reaction so as to get the least negative cell voltage. This will be the most likely pair of ½ -reactions to occur.

Oxidation: $2\mathrm{I}^-(\mathrm{aq}) \to \mathrm{I}_2(\mathrm{s}) + 2\ \mathrm{e}^-$ $\qquad -E^\circ = -0.535\ \mathrm{V}$
$2\,\mathrm{H_2O(l)} \to \mathrm{O_2(g)} + 4\,\mathrm{H^+(aq)} + 4\,\mathrm{e}^-$ $\qquad -E^\circ = -1.229\,\mathrm{V}$
Reduction: $\mathrm{K^+(aq)} + \mathrm{e}^- \to \mathrm{K(s)}$ $\qquad E^\circ = -2.924\ \mathrm{V}$
$2\,\mathrm{H_2O(l)} + 2\,\mathrm{e}^- \to \mathrm{H_2(g)} + 2\,\mathrm{OH^-(aq)}$ $\qquad E^\circ = -0.828\ \mathrm{V}$

The least negative standard cell potential $(-0.535\,\mathrm{V} - 0.828\,\mathrm{V} = -1.363\,\mathrm{V})$ occurs when $\mathrm{I_2(s)}$ is produced by oxidation at the anode, and $\mathrm{H_2(g)}$ is produced by reduction at the cathode.

12B **(M)** We obtain from Table 20-1 all the possible oxidations and reductions and choose one of each to get the least negative cell voltage. That pair is the most likely pair of half-reactions to occur.

Oxidation: $2\,\mathrm{H_2O(l)} \to \mathrm{O_2(g)} + 4\,\mathrm{H^+(aq)} + 4\mathrm{e}^-$ $\qquad -E^\circ = -1.229\mathrm{V}$
$\mathrm{Ag(s)} \to \mathrm{Ag^+(aq)} + \mathrm{e}^-$ $\qquad -E^\circ = -0.800\mathrm{V}$
[We cannot further oxidize $\mathrm{NO_3^-(aq)}$ or $\mathrm{Ag^+(aq)}$.]
Reduction: $\mathrm{Ag^+(aq)} + \mathrm{e}^- \to \mathrm{Ag(s)}$ $\qquad E^\circ = +0.800\mathrm{V}$
$2\,\mathrm{H_2O(l)} + 2\mathrm{e}^- \to \mathrm{H_2(g)} + 2\,\mathrm{OH^-(aq)}$ $\qquad E^\circ = -0.828\mathrm{V}$

Thus, we expect to form silver metal at the cathode and $\mathrm{Ag^+(aq)}$ at the anode.

13A **(M)** The half-cell equation is $\mathrm{Cu^{2+}(aq)} + 2\mathrm{e}^- \to \mathrm{Cu(s)}$, indicating that two moles of electrons are required for each mole of copper deposited. Current is measured in amperes, or coulombs per second. We convert the mass of copper to coulombs of electrons needed for the reduction and the time in hours to seconds.

$$\text{Current} = \frac{12.3\ \text{g Cu} \times \dfrac{1\ \text{mol Cu}}{63.55\ \text{g Cu}} \times \dfrac{2\ \text{mol e}^-}{1\ \text{mol Cu}} \times \dfrac{96{,}485\ \text{C}}{1\ \text{mol e}^-}}{5.50\ \text{h} \times \dfrac{60\ \text{min}}{1\ \text{h}} \times \dfrac{60\ \text{s}}{1\ \text{min}}} = \frac{3.735 \times 10^4\ \text{C}}{1.98 \times 10^4\ \text{s}} = 1.89\ \text{amperes}$$

<u>13B</u> **(D)** We first determine the moles of $O_2(g)$ produced with the ideal gas equation.

$$\text{moles } O_2(g) = \frac{\left(738\ \text{mmHg} \times \dfrac{1\ \text{atm}}{760\ \text{mmHg}}\right) \times 2.62\ \text{L}}{\dfrac{0.08206\ \text{L atm}}{\text{mol K}} \times (26.2 + 273.2)\ \text{K}} = 0.104\ \text{mol } O_2$$

Then we determine the time needed to produce this amount of O_2.

$$\text{elapsed time} = 0.104\ \text{mol } O_2 \times \frac{4\ \text{mol e}^-}{1\ \text{mol } O_2} \times \frac{96{,}485\ \text{C}}{1\ \text{mol e}^-} \times \frac{1\ \text{s}}{2.13\ \text{C}} \times \frac{1\ \text{h}}{3600\ \text{s}} = 5.23\ \text{h}$$

INTEGRATIVE EXAMPLE

14A **(D)** In this problem we are asked to determine E^o for the reduction of $CO_2(g)$ to $C_3H_8(g)$ in an acidic solution. We proceed by first determining ΔG^o for the reaction using tabulated values for ΔG_f^o in Appendix D. Next, E_{cell}^o for the reaction can be determined using $\Delta G^o = -zFE_{cell}^o$. Given reaction can be separated into reduction and oxidation. Since we are in acidic medium, the reduction half-cell potential can be found in Table 20.1. Lastly, the oxidation half-cell potential can be calculated using $E_{cell}^o = E^o(\text{reduction half-cell}) - E^o(\text{oxidation half-cell})$.

Stepwise approach

First determine ΔG^o for the reaction using tabulated values for ΔG_f^o in Appendix D:

	$C_3H_8(g)$	+	$5O_2(g)$	$\rightarrow$	$3CO_2(g)$	+	$4H_2O(l)$
ΔG_f^o	-23.3 kJ/mol		0 kJ/mol		-394.4 kJ/mol		-237.1 kJ/mol

$$\Delta G^o = 3 \times \Delta G_f^o(CO_2(g)) + 4 \times \Delta G_f^o(H_2O(l)) - [\Delta G_f^o(C_3H_8(g)) + 5 \times \Delta G_f^o(O_2(g))]$$

$$\Delta G^o = 3 \times (-394.4) + 4 \times (-237.1) - [-23.3 + 5 \times 0]\text{kJ/mol}$$

$$\Delta G^o = -2108\text{kJ/mol}$$

In order to calculate E_{cell}^o for the reaction using $\Delta G^o = -zFE_{cell}^o$, z must be first determined. We proceed by separating the given reaction into oxidation and reduction:

Reduction: $5\times\{O_2(g)+4H^+(aq)+4e^- \rightarrow 2H_2O(l)\}$ E^o=+1.229 V
Oxidation: $C_3H_8(g) + 6H_2O(l) \rightarrow 3CO_2(g) + 20H^+ + 20e^-$ E^o=xV

Overall: $C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$ E^o=+1.229 V-xV

Since z=20, E_{cell}^o can now be calculated using $\Delta G^o = -zFE_{cell}^o$:

$$\Delta G^o = -zFE^o_{cell}$$

$$-2108 \times 1000\text{J/mol} = -20\text{mol e}^- \times \frac{96485\text{C}}{1\text{mol e}^-} \times E^o_{cell}$$

$$E^o_{cell} = \frac{-2108 \times 1000}{-20 \times 96485} V = 1.092V$$

Finally, E^o(reduction half-cell) can be calculated using

$E^o_{cell} = E^o$(reduction half-cell) – E^o(oxidation half-cell):

1.092 V = 1.229 V – E^o(oxidation half-cell) V

E^o(oxidation half-cell)=1.229 V – 1.092 V = 0.137 V

Therefore, E^o for the reduction of $CO_2(g)$ to $C_3H_8(g)$ in an acidic medium is 0.137 V.

Conversion pathway approach:

Reduction: $5\times\{O_2(g)+4H^+(aq)+4e^- \rightarrow 2H_2O(l)\}$ E^o=+1.229 V

Oxidation: $C_3H_8(g) + 6H_2O(l) \rightarrow 3CO_2(g) + 20H^+ + 20e^-$ E^o=x V

Overall: $C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$ E^o=+1.229 V-x V

ΔG^o_f -23.3 kJ/mol 0 kJ/mol -394.4 kJ/mol -237.1 kJ/mol

$$\Delta G^o = 3 \times \Delta G^o_f(CO_2(g)) + 4 \times \Delta G^o_f(H_2O(l)) - [\Delta G^o_f(C_3H_8(g)) + 5 \times \Delta G^o_f(O_2(g))]$$

$$\Delta G^o = 3 \times (-394.4) + 4 \times (-237.1) - [-23.3 + 5 \times 0]\text{kJ/mol}$$

$$\Delta G^o = -2108\text{kJ/mol}$$

$$\Delta G^o = -zFE^o_{cell}$$

$$-2108 \times 1000\text{J/mol} = -20\text{mol e}^- \times \frac{96485\text{C}}{1\text{mol e}^-} \times E^o_{cell}$$

$$E^o_{cell} = \frac{-2108 \times 1000}{-20 \times 96485} V = 1.092V$$

1.092 V = 1.229 V – E^o(oxidation half-cell) V

E^o(oxidation half-cell)=1.229 V – 1.092 V = 0.137 V

14B **(D)** This is a multi component problem dealing with a flow battery in which oxidation occurs at an aluminum anode and reduction at a carbon-air cathode. Al^{3+} produced at the anode is complexed with OH^- anions from NaOH(aq) to form $[Al(OH)_4]^-$.

Stepwise approach:

Part (a): The flow battery consists of aluminum anode where oxidation occurs and the formed Al^{3+} cations are complexes with OH^- anions to form $[Al(OH)_4]^-$. The plausible half-reaction for the oxidation is:

Oxidation: $Al(s) + 4OH^-(aq) \rightarrow [Al(OH)_4]^- + 3e^-$

The cathode, on the other hand consists of carbon and air. The plausible half-reaction for the reduction involves the conversion of O_2 and water to form OH^- anions (basic medium):

Reduction: $O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$

Combining the oxidation and reduction half-reactions we obtain overall reaction for the process:

Oxidation: $\{Al(s) + 4OH^-(aq) \rightarrow [Al(OH)_4]^- + 3e^-\}\times4$

Reduction: $\{O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)\} \times 3$

Overall: $4Al(s) + 4OH^-(aq) + 3O_2(g) + 6H_2O(l) \rightarrow 4[Al(OH)_4]^-(aq)$

Part(b): In order to find E_o for the reduction, use the known value for E^o_{cell} as well as E^o for the reduction half-reaction from Table 20.1:

$$E^o_{cell} = E^o(\text{reduction half-cell}) - E^o(\text{oxidation half-cell})$$

$$E^o_{cell} = +0.401V - E^o(\text{oxidation half-cell}) = +2.73V$$

$$E^o(\text{oxidation half-cell}) = +0.401V - 2.73V = -2.329V$$

Part (c): From the given value for E^o_{cell} (+2.73V) first calculate ΔG^o using $\Delta G^o = -zFE^o_{cell}$ (notice that z=12 from part (a) above):

$$\Delta G^o = -zFE^o_{cell} = -12\text{mol e}^- \times \frac{96485\text{C}}{1\text{mol e}^-} \times 2.73V$$

$$\Delta G^o = -3161\text{kJ/mol}$$

Given the overall reaction (part (a)) and ΔG^o_f for $OH^-(aq)$ anions and $H_2O(l)$, we can calculate the Gibbs energy of formation of the aluminate ion, $[Al(OH)_4]^-$:

Overall reaction:	$4Al(s)$	+	$4OH^-(aq)$	+	$3O_2(g)$	+	$6H_2O(l) \rightarrow$	$4[Al(OH)_4]^-(aq)$
ΔG^o_f	0 kJ/mol		-157 kJ/mol		0 kJ/mol		-237.2 kJ/mol	x

$$\Delta G^o = 4 \times x - [4 \times 0 + 4 \times (-157) + 3 \times 0 + 6 \times (-237.2)\text{kJ/mol} = -3161\text{kJ/mol}$$

$$4x = -3161 - 2051.2 = -5212.2\text{kJ/mol}$$

$$x = -1303\text{kJ/mol}$$

Therefore, $\Delta G^o_f([Al(OH)_4]^-) = -1303\text{kJ/mol}$

Part(d): First calculate the number of moles of electrons:

$$\text{number of mol e}^- = \text{current}(C/s) \times \text{time(s)} \times \frac{1\text{mol e}^-}{96485C}$$

$$\text{number of mol e}^- = 4.00h \times \frac{60\min}{1h} \times \frac{60s}{1\min} \times 10.0\frac{C}{s} \times \frac{1\text{mol e}^-}{96485C}$$

$$\text{number of mol e}^- = 1.49\text{mol e}^-$$

Now, use the oxidation half-reaction to determine the mass of Al(s) consumed:

$$mass(Al) = 1.49\text{mol e}^- \times \frac{1\text{mol Al}}{3\text{mol e}^-} \times \frac{26.98\text{g Al}}{1\text{mol Al}} = 13.4g$$

Conversion pathway approach:

Part (a):

Oxidation: $\{Al(s) + 4OH^-(aq) \rightarrow [Al(OH)_4]^- + 3e^-\} \times 4$

Reduction: $\{O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)\} \times 3$

Overall: $4Al(s) + 4OH^-(aq) + 3O_2(g) + 6H_2O(l) \rightarrow 4[Al(OH)_4]^-(aq)$

Part (b):

$$E^{o}_{cell} = E^{o}(\text{reduction half-cell}) - E^{o}(\text{oxidation half-cell})$$

$$E^{o}_{cell} = +0.401V - E^{o}(\text{oxidation half-cell}) = +2.73V$$

$$E^{o}(\text{oxidation half-cell}) = +0.401V - 2.73V = -2.329V$$

Part (c):

$$\Delta G^{o} = -zFE^{o}_{cell} = -12\text{mol e}^{-} \times \frac{96485\text{C}}{1\text{mol e}^{-}} \times 2.73V$$

$$\Delta G^{o} = -3161\text{kJ/mol}$$

Overall reaction: $4Al(s) + 4OH^{-}(aq) + 3O_2(g) + 6H_2O(l) \rightarrow 4[Al(OH)_4]^{-}(aq)$

ΔG^{o}_{f} 0 kJ/mol -157 kJ/mol 0 kJ/mol -237.2 kJ/mol x

$$\Delta G^{o} = 4 \times x - [4 \times 0 + 4 \times (-157) + 3 \times 0 + 6 \times (-237.2)\text{kJ/mol} = -3161\text{kJ/mol}$$

$$4x = -3161 - 2051.2 = -5212.2\text{kJ/mol}$$

$$x = \Delta G^{o}_{f}([Al(OH)_4]^{-}) = -1303\text{kJ/mol}$$

Part (d):

$$\text{number of mol e}^{-} = \text{current}(C/s) \times \text{time(s)} \times \frac{1\text{mol e}^{-}}{96485C}$$

$$\text{number of mol e}^{-} = 4.00h \times \frac{60\min}{1h} \times \frac{60s}{1\min} \times 10.0\frac{C}{s} \times \frac{1\text{mol e}^{-}}{96485C}$$

$$\text{number of mol e}^{-} = 1.49\text{mol e}^{-}$$

$$mass(Al) = 1.49\text{mol e}^{-} \times \frac{1\text{mol Al}}{3\text{mol e}^{-}} \times \frac{26.98\text{g Al}}{1\text{mol Al}} = 13.4g$$

EXERCISES

Standard Electrode Potential

1. **(E) (a)** If the metal dissolves in HNO_3, it has a reduction potential that is smaller than $E^{o}\{NO_3^{-}(aq)/NO(g)\} = 0.956\,V$. If it also does not dissolve in HCl, it has a reduction potential that is larger than $E^{o}\{H^{+}(aq)/H_2(g)\} = 0.000\,V$. If it displaces $Ag^{+}(aq)$ from solution, then it has a reduction potential that is smaller than $E^{o}\{Ag^{+}(aq)/Ag(s)\} = 0.800\,V$. But if it does not displace $Cu^{2+}(aq)$ from solution, then its reduction potential is larger than $E^{o}\{Cu^{2+}(aq)/Cu(s)\} = 0.340\,V$ Thus, $0.340\text{ V} < E^{o} < 0.800\,V$

(b) If the metal dissolves in HCl, it has a reduction potential that is smaller than $E^{o}\{H^{+}(aq)/H_2(g)\} = 0.000\text{ V}$. If it does not displace $Zn^{2+}(aq)$ from solution, its reduction potential is larger than $E^{o}\{Zn^{2+}(aq)/Zn(s)\} = -0.763\text{ V}$. If it also does not displace $Fe^{2+}(aq)$ from solution, its reduction potential is larger than

$$E^\circ\left\{\mathrm{Fe}^{2+}(\mathrm{aq})/\mathrm{Fe}(\mathrm{s})\right\} = -0.440\ \mathrm{V}. \quad -0.440\,\mathrm{V} < E^\circ < 0.000\,\mathrm{V}$$

2. **(E)** We would place a strip of solid indium metal into each of the metal ion solutions and see if the dissolved metal plates out on the indium strip. Similarly, strips of all the other metals would be immersed in a solution of In^{3+} to see if indium metal plates out. Eventually, we will find one metal whose ions are displaced by indium and another metal that displaces indium from solution, which are adjacent to each other in Table 20-1. The standard electrode potential for the $\mathrm{In/In}^{3+}$(aq) pair will lie between the standard reduction potentials for these two metals. This technique will work only if indium metal does not react with water, that is, if the standard reduction potential of $\mathrm{In}^{3+}(\mathrm{aq})/\mathrm{In}(\mathrm{s})$ is greater than about $-1.8\ \mathrm{V}$. The inaccuracy inherent in this technique is due to overpotentials, which can be as much as 0.200 V. Its imprecision is limited by the closeness of the reduction potentials for the two bracketing metals

3. **(M)** We separate the given equation into its two half-equations. One of them is the reduction of nitrate ion in acidic solution, whose standard half-cell potential we retrieve from Table 20-1 and use to solve the problem.

Oxidation: $\{\mathrm{Pt(s)} + 4\,\mathrm{Cl}^-(\mathrm{aq}) \longrightarrow [\mathrm{PtCl}_4]^{2-}(\mathrm{aq}) + 2\ \mathrm{e}^-\}\ \times 3; \quad -E^\circ\{[\mathrm{PtCl}_4]^{2-}(\mathrm{aq})/\mathrm{Pt(s)}\}$

Reduction: $\{\mathrm{NO}_3^-(\mathrm{aq}) + 4\,\mathrm{H}^+(\mathrm{aq}) + 3\mathrm{e}^- \rightarrow \mathrm{NO}(\mathrm{g}) + 2\,\mathrm{H}_2\mathrm{O(l)}\} \times 2; \quad E^\circ = +0.956\,\mathrm{V}$

Net: $3\,\mathrm{Pt}(\mathrm{s}) + 2\,\mathrm{NO}_3^-(\mathrm{aq}) + 8\,\mathrm{H}^+(\mathrm{aq}) + 12\,\mathrm{Cl}^-(\mathrm{aq}) \rightarrow 3\left[\mathrm{PtCl}_4\right]^{2-}(\mathrm{aq}) + 2\,\mathrm{NO}(\mathrm{g}) + 6\mathrm{H}_2\mathrm{O}(\mathrm{l})$

$$E^\circ_{\mathrm{cell}} = 0.201\,\mathrm{V} = +0.956\ \mathrm{V} - E^\circ\{[\mathrm{PtCl}_4]^{2-}(\mathrm{aq})/\mathrm{Pt(s)}\}$$

$$E^\circ\{[\mathrm{PtCl}_4]^{2-}(\mathrm{aq})/\mathrm{Pt(s)}\} = 0.956\,\mathrm{V} - 0.201\,\mathrm{V} = +0.755\,\mathrm{V}$$

4. **(M)** In this problem, we are dealing with the electrochemical reaction involving the oxidation of Na(in Hg) to Na^+(aq) and the reduction of Cl_2(s) to Cl^-(aq). Given that $E^o_{cell} = 3.20V$, we are asked to find E^o for the reduction of Na^+ to Na(in Hg). We proceed by separating the given equation into its two half-equations. One of them is the reduction of $\mathrm{Cl}_2(\mathrm{g})$ to $\mathrm{Cl}^-(\mathrm{aq})$ whose standard half-cell potential we obtain from Table 20-1 and use to solve the problem.

Stepwise approach:

Separate the given equation into two half-equations:

Oxidation: $\{\mathrm{Na(in\,Hg)} \rightarrow \mathrm{Na}^+(\mathrm{aq}) + \mathrm{e}^-\}\ \times 2 \qquad -E^\circ\{\mathrm{Na}^+(\mathrm{aq})/\mathrm{Na(in\,Hg)}\}$

Reduction: $\mathrm{Cl}_2(\mathrm{g}) + 2\mathrm{e}^- \rightarrow 2\mathrm{Cl}^-(\mathrm{aq}) \qquad E^\circ = +1.358\ \mathrm{V}$

Net: $2\mathrm{Na(in\ Hg)} + \mathrm{Cl}_2(\mathrm{g}) \rightarrow 2\,\mathrm{Na}^+(\mathrm{aq}) + 2\,\mathrm{Cl}^-(\mathrm{aq}) \qquad E^\circ_{\mathrm{cell}} = 3.20\ \mathrm{V}$

Use $E^o_{cell} = E^o(\text{reduction half-cell}) - E^o(\text{oxidation half-cell})$ to solve for $E^o(\text{oxidation half-cell})$:

$$E^\circ_{\mathrm{cell}} = 3.20\ \mathrm{V} = +1.385\ \mathrm{V} - E^\circ\{\mathrm{Na}^+(\mathrm{aq})/\mathrm{Na(in\,Hg)}\}$$

$$E^\circ\{\mathrm{Na}^+(\mathrm{aq})/\mathrm{Na(in\ Hg)}\} = 1.358\ \mathrm{V} - 3.20\ \mathrm{V} = -1.84\ \mathrm{V}$$

Conversion pathway approach:

Oxidation: $\{\mathrm{Na(in\,Hg)} \rightarrow \mathrm{Na}^+(\mathrm{aq}) + \mathrm{e}^-\}\ \times 2 \qquad -E^\circ\{\mathrm{Na}^+(\mathrm{aq})/\mathrm{Na(in\,Hg)}\}$

$\text{Reduction: } Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq) \qquad E^\circ = +1.358\ \text{V}$

$\text{Net: } 2Na(\text{in Hg}) + Cl_2(g) \rightarrow 2\,Na^+(aq) + 2\,Cl^-(aq) \qquad E^\circ_{\text{cell}} = 3.20\ \text{V}$

$3.20V = 1.358 - E^o\{Na^+(aq)/Na(\text{in Hg})\}$

$E^o\{Na^+(aq)/Na(\text{in Hg})\} = 1.358V - 3.20V = -1.84V$

5. **(M)** We divide the net cell equation into two half-equations.

$\text{Oxidation: } \{Al(s) + 4\ OH^-(aq) \rightarrow [Al(OH)_4]^-(aq) + 3\ e^-\} \times 4; \qquad -E^o\{[Al(OH)_4]^-(aq)/Al(s)\}$

$\text{Reduction: } \{O_2(g) + 2\ H_2O(l) + 4e^- \rightarrow 4\ OH^-(aq)\}\ \times 3; \qquad E^o = +0.401\text{V}$

$\text{Net: } 4\,Al(s)\ + 3O_2(g)\ + 6\,H_2O(l) + 4\,OH^-(aq) \rightarrow 4[Al(OH)_4]^-(aq) \qquad E_{\text{cell}}{}^o = 2.71\text{V}$

$E^o_{\text{cell}} = 2.71\text{V} = +0.401\text{V} - E^o\{[Al(OH)_4]^-(aq)/Al(s)\}$

$E^o\{[Al(OH)_4]^-(aq)/Al(s)\} = 0.401\text{V} - 2.71\text{V} = -2.31\text{V}$

6. **(M)** We divide the net cell equation into two half-equations.

$\text{Oxidation: } CH_4(g) + 2H_2O(l) \rightarrow CO_2(g) + 8\,H^+(aq) + 8\,e^- \qquad -E^o\{CO_2(g)/CH_4(g)\}$

$\text{Reduction: } \{O_2(g) + 4H^+(aq) + 4\,e^- \rightarrow 2H_2O(l)\}\ \times 2 \qquad E^o = +1.229\text{V}$

$\text{Net: } CH_4(g)\ + 2\ O_2(g) \rightarrow CO_2(g)\ + 2\,H_2O(l) \qquad E^o_{\text{cell}} = 1.06\text{V}$

$E^o_{\text{cell}} = 1.06\text{V} = +1.229\text{V} - E^o\{CO_2(g)/CH_4(g)\}$

$E^o\{CO_2(g)/CH_4(g)\} = 1.229\text{V} - 1.06\text{V} = +0.17\text{V}$

7. **(M) (a)** We need standard reduction potentials for the given half-reactions from Table 10.1:
$Ag^+(aq)+e^- \rightarrow Ag(s)$ E_o=+0.800 V
$Zn^{2+}(aq)+2e^- \rightarrow Zn(s)$ E_o=-0.763 V
$Cu^{2+}(aq)+2e^- \rightarrow Cu(s)$ E_o=+0.340 V
$Al^{3+}(aq)+3e^- \rightarrow Al(s)$ E_o=-1.676 V
Therefore, the largest positive cell potential will be obtained for the reaction involving the oxidation of Al(s) to $Al^{3+}(aq)$ and the reduction of $Ag^+(aq)$ to Ag(s):
$Al(s) + 3Ag^+(aq) \rightarrow 3Ag(s)+Al^{3+}(aq) \quad E^o_{cell} = +1.676V + 0.800V = 2.476V$
Ag is the anode and Al is the cathode.
(b) Reverse to the above, the cell with the smallest positive cell potential will be obtained for the reaction involving the oxidation of Zn(s) to $Zn^{2+}(aq)$ (anode) and the reduction of $Cu^{+2}(aq)$ to Cu(s) (cathode):
$Zn(s) + Cu^{2+}(aq) \rightarrow Cu(s)+Zn^{2+}(aq) \quad E^o_{cell} = 0.763V + 0.340V = 1.103V$

8. **(M) (a)** The largest positive cell potential will be obtained for the reaction:
$Zn(s) + 4NH_3(aq) + 2VO^{2+}(aq) + 4H^+(aq) \rightarrow [Zn(NH_3)_4]^{2+}(aq)+2V^{3+}(aq)+2H_2O(l)$
$E^o_{cell} = E^o(\text{reduction half-cell}) - E^o(\text{oxidation half-cell}) = 0.340V - (-1.015V) = 1.355V$
Zn is the anode and VO^{2+} is the cathode.

(b) Reverse to the above, the cell with the smallest positive cell potential will be obtained for the reaction involving the oxidation of Ti^{2+}(aq) to Ti^{3+}(aq) (anode) and the reduction of Sn^{+2}(aq) to Sn(s) (cathode):

$2Ti^{2+}(aq) + Sn^{2+}(aq) \rightarrow 2Ti^{3+}(aq)+Sn(aq)$

$E^o_{cell} = E^o(\text{reduction half-cell}) - E^o(\text{oxidation half-cell}) = -0.14V - (-0.37V) = 0.23V$

Predicting Oxidation-Reduction Reactions

9. **(E)** **(a)** Ni^{2+}, **(b)** Cd.

10. **(E)** **(a)** potassium, **(b)** barium.

11. **(M)** **(a)** Oxidation: $Sn(s) \rightarrow Sn^{2+}(aq) + 2e^-$ $\quad -E^o = +0.137$ V

Reduction: $Pb^{2+}(aq) + 2e^- \rightarrow Pb(s)$ $\quad E^o = -0.125$ V

Net: $Sn(s) + Pb^{2+}(aq) \rightarrow Sn^{2+}(aq) + Pb(s)$ $\quad E^o_{cell} = +0.012$ V $\quad$ Spontaneous

(b) Oxidation: $2I^-(aq) \rightarrow I_2(s) + 2e^-$ $\quad -E^o = -0.535$ V

Reduction: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ $\quad E^o = +0.340$ V

Net: $2I^-(aq) + Cu^{2+}(aq) \rightarrow Cu(s) + I_2(s)$ $\quad E^o_{cell} = -0.195$ V $\quad$ Nonspontaneous

(c) Oxidation: $\{2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-\} \times 3$ $\quad -E^o = -1.229$ V

Reduction: $\{NO_3^-(aq) + 4H^+(aq) + 3e^- \rightarrow NO(g) + 2H_2O(l)\} \times 4$ $\quad E^o = +0.956$ V

Net: $4NO_3^-(aq) + 4H^+(aq) \rightarrow 3O_2(g) + 4NO(g) + 2H_2O(l)$ $\quad E^o_{cell} = -0.273$ V
Nonspontaneous

(d) Oxidation: $Cl^-(aq) + 2OH^-(aq) \rightarrow OCl^-(aq) + H_2O(l) + 2e^-$ $\quad -E^o = -0.890$ V

Reduction: $O_3(g) + H_2O(l) + 2e^- \rightarrow O_2(g) + 2OH^-(aq)$ $\quad E^o = +1.246$ V

Net: $Cl^-(aq) + O_3(g) \rightarrow OCl^-(aq) + O_2(g)$ (basic solution) $\quad E^o_{cell} = +0.356$ V
Spontaneous

12. **(M)** It is more difficult to oxidize Hg(l) to Hg_2^{2+} (-0.797 V) than it is to reduce H^+ to H_2 (0.000 V); Hg(l) will not dissolve in 1 M HCl. The standard reduction of nitrate ion to NO(g) in acidic solution is strongly spontaneous in acidic media ($+0.956$ V). This can help overcome the reluctance of Hg to be oxidized. Hg(l) will react with and dissolve in the $HNO_3(aq)$.

13. **(M)** **(a)** Oxidation: $Mg(s) \rightarrow Mg^{2+}(aq) + 2e^-$ $\quad -E^o = +2.356$ V

Reduction: $Pb^{2+}(aq) + 2e^- \rightarrow Pb(s)$ $\quad E^o = -0.125$ V

Net: $Mg(s) + Pb^{2+}(aq) \rightarrow Mg^{2+}(aq) + Pb(s)$ $\quad E^o_{cell} = +2.231$ V

This reaction occurs to a significant extent.

(b) Oxidation: $\mathrm{Sn(s) \rightarrow Sn^{2+}(aq) + 2\,e^-}$ $\quad -E^{o} = +0.137\,\mathrm{V}$

Reduction: $\mathrm{2\,H^+(aq) \rightarrow H_2(g)}$ $\quad E^{o} = 0.000\,\mathrm{V}$

Net: $\mathrm{Sn(s)\ +\ 2H^+(aq) \rightarrow Sn^{2+}(aq)\ +\ H_2(g)}$ $\quad E^{o}_{\mathrm{cell}} = +0.137\,\mathrm{V}$

This reaction will occur to a significant extent.

(c) Oxidation: $\mathrm{Sn^{2+}(aq) \rightarrow Sn^{4+}(aq) + 2\,e^-}$ $\quad -E^{o} = -0.154\,\mathrm{V}$

Reduction: $\mathrm{SO_4^{\,2-}(aq) + 4H^+(aq) + 2\,e^- \rightarrow SO_2(g) + 2H_2O(l)}$ $\quad E^{o} = +0.17\,\mathrm{V}$

Net: $\mathrm{Sn^{2+}(aq) + SO_4^{\,2-}(aq) + 4\,H^+(aq) \rightarrow Sn^{4+}(aq) + SO_2(g) + 2H_2O(l)}$ $\quad E^{o}_{\mathrm{cell}} = +\,0.02\,\mathrm{V}$

This reaction will occur, but not to a large extent.

(d) Oxidation: $\{\mathrm{H_2O_2(aq) \rightarrow O_2(g) + 2\,H^+(aq) + 2e^-}\}\ \times 5$ $\quad -E^{o} = -0.695\,\mathrm{V}$

Reduction: $\{\mathrm{MnO_4^{\,-}(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)}\}\ \times 2$ $\quad E^{o} = +1.51\,\mathrm{V}$

Net: $\mathrm{5H_2O_2(aq) + 2MnO_4^{\,-}(aq) + 6H^+(aq) \rightarrow 5O_2(g) + 2Mn^{2+}(aq) + 8H_2O(l)}$ $\quad E^{o}_{\mathrm{cell}} = +0.82\,\mathrm{V}$

This reaction will occur to a significant extent.

(e) Oxidation: $\mathrm{2\,Br^-(aq) \rightarrow Br_2(aq) + 2\,e^-}$ $\quad -E^{o} = -1.065\,\mathrm{V}$

Reduction: $\mathrm{I_2(s) + 2e^- \rightarrow 2\,I^-(aq)}$ $\quad E^{o} = +0.535\,\mathrm{V}$

Net: $\mathrm{2\,Br^-(aq) + I_2(s) \rightarrow Br_2(aq) + 2\,I^-(aq)}$ $\quad E^{o}_{\mathrm{cell}} = -0.530\,\mathrm{V}$

This reaction will not occur to a significant extent.

14. **(M)** In this problem we are asked to determine whether the electrochemical reaction between Co(s) and $\mathrm{Ni^{2+}}$(aq) to yield $\mathrm{Co^{2+}}$(aq) + Ni(s) will proceed to completion based on the known E^{o}_{cell} value. This question can be answered by simply determining the equilibrium constant.

Stepwise approach

First comment on the value of E^{o}_{cell}:

The relatively small positive value of E^{o}_{cell} for the reaction indicates that the reaction will proceed in the forward direction, but will stop short of completion. A much larger positive value of E^{o}_{cell} would be necessary before we would conclude that the reaction goes to completion.

Calculate the equilibrium constant for the reaction using $E^{o}_{\mathrm{cell}} = \dfrac{0.0257}{n} \ln K_{\mathrm{eq}}$:

$$E^{o}_{\mathrm{cell}} = \frac{0.0257}{n} \ln K_{\mathrm{eq}} \qquad \ln K_{\mathrm{eq}} = \frac{n \times E^{o}_{\mathrm{cell}}}{0.0257} = \frac{2 \times 0.02}{0.0257} = 2$$

$$K_{\mathrm{eq}} = e^{2} = 7$$

Comment on the value of K_{eq}:

K_{eq} is small. A value of 1000 or more is needed before we can describe the reaction as one that goes to completion.

Conversion pathway approach:

$$E^{\circ}_{\text{cell}} = \frac{0.0257}{n} \ln K_{\text{eq}}$$

$$\ln K_{\text{eq}} = \frac{n \times E^{\circ}_{\text{cell}}}{0.0257}$$

$$K_{eq} = e^{\frac{n\times E^{\circ}_{\text{cell}}}{0.0257}} = e^{\frac{2\times 0.02}{0.0257}} = 7$$

K_{eq} is too small. The reaction does not go to completion.

15. **(M)** If E°_{cell} is positive, the reaction will occur. For the reduction of $Cr_2O_7^{2-}$ to $Cr^{3+}(aq)$:

$$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l) \qquad E^{\circ} = +1.33\,V$$

If the oxidation has $-E^{\circ}$ smaller (more negative) than $-1.33\,V$, the oxidation will not occur.

(a) $Sn^{2+}(aq) \rightarrow Sn^{4+}(aq) + 2e^- \qquad -E^{\circ} = -0.154\,V$

Hence, $Sn^{2+}(aq)$ can be oxidized to $Sn^{4+}(aq)$ by $Cr_2O_7^{2-}(aq)$.

(b) $I_2(s) + 6H_2O(l) \rightarrow 2IO_3^-(aq) + 12H^+(aq) + 10e^- \qquad -E^{\circ} = -1.20\,V$

$I_2(s)$ can be oxidized to $IO_3^-(aq)$ by $Cr_2O_7^{2-}(aq)$.

(c) $Mn^{2+}(aq) + 4H_2O(l) \rightarrow MnO_4^-(aq) + 8H^+(aq) + 5e^- \qquad -E^{\circ} = -1.51\,V$

$Mn^{2+}(aq)$ cannot be oxidized to $MnO_4^-(aq)$ by $Cr_2O_7^{2-}(aq)$.

16. **(M)** In order to reduce Eu^{3+} to Eu^{2+}, a stronger reducing agent than Eu^{2+} is required. From the list given, Al(s) and $H_2C_2O_4$(aq) are stronger reducing agents. This is determined by looking at the reduction potentials (-1.676 V for Al^{3+}/Al(s) and -0.49 V for CO_2, $H^+/H_2C_2O_4$(aq)), are more negative than -0.43 V). Co(s), H_2O_2 and Ag(s) are not strong enough reducing agents for this process. A quick look at their reduction potentials shows that they all have more positive reduction potentials than that for Eu^{3+} to Eu^{2+} (-0.277 V for Co^{2+}/Co(s), +0.695 V for O_2, H^+/H_2O_2(aq) and +0.800 V for Ag^+/Ag(s).

17. **(M) (a)** Oxidation: $\{Ag(s) \rightarrow Ag^+(aq) + e^-\} \times 3 \qquad -E^{\circ} = -0.800\,V$

Reduction: $NO_3^-(aq) + 4H^+(aq) + 3e^- \rightarrow NO(g) + 2H_2O(l) \qquad E^{\circ} = +0.956\,V$

Net: $3Ag(s) + NO_3^-(aq) + 4H^+(aq) \rightarrow 3Ag^+(aq) + NO(g) + 2H_2O(l) \qquad E^{\circ}_{\text{cell}} = +0.156\,V$

Ag(s) reacts with $HNO_3(aq)$ to form a solution of $AgNO_3(aq)$.

(b) Oxidation: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^- \qquad -E^{\circ} = +0.763\,V$

Reduction: $2H^+(aq) + 2e^- \rightarrow H_2(g) \qquad E^{\circ} = 0.000\,V$

Net: $Zn(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g) \qquad E^{\circ}_{\text{cell}} = +0.763\,V$

Zn(s) reacts with HI(aq) to form a solution of $ZnI_2(aq)$.

(c) Oxidation: $\mathrm{Au(s) \rightarrow Au^{3+}(aq) + 3e^-}$ $\quad -E^\circ = -1.52\,\mathrm{V}$

Reduction: $\mathrm{NO_3^-(aq) + 4H^+(aq) + 3e^- \rightarrow NO(g) + 2H_2O(l)}$ $\quad E^\circ = +0.956\,\mathrm{V}$

Net: $\mathrm{Au(s) + NO_3^-(aq) + 4H^+(aq) \rightarrow Au^{3+}(aq) + NO(g) + 2\ H_2O(l)}$; $E^\circ_{\mathrm{cell}} = -0.56\,\mathrm{V}$

Au(s) does not react with 1.00 M $\mathrm{HNO_3(aq)}$.

18. **(M)** In each case, we determine whether E^o_{cell} is greater than zero; if so, the reaction will occur.

(a) Oxidation: $\mathrm{Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-}$ $\quad -E^\circ = 0.440\,\mathrm{V}$

Reduction: $\mathrm{Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)}$ $\quad E^\circ = -0.763\,\mathrm{V}$

Net: $\mathrm{Fe(s) + Zn^{2+}(aq) \rightarrow Fe^{2+}(aq) + Zn(s)}$ $\quad E^\circ_{\mathrm{cell}} = -0.323\,\mathrm{V}$

The reaction is not spontaneous under standard conditions as written

(b) Oxidation: $\{\mathrm{2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-}\} \times 5$ $\quad -E^\circ = -1.358\,\mathrm{V}$

Reduction: $\{\mathrm{MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)}\} \times 2$; $E^\circ = 1.51\,\mathrm{V}$

Net: $\mathrm{10Cl^-(aq) + 2MnO_4^-(aq) + 16H^+(aq) \rightarrow 5Cl_2(g) + 2Mn^{2+}(aq) + 8H_2O(l)}$

$E^\circ_{\mathrm{cell}} = +0.15\,\mathrm{V}$. The reaction is spontaneous under standard conditions as written.

(c) Oxidation: $\{\mathrm{Ag(s) \rightarrow Ag^+(aq) + e^-}\} \times 2$ $\quad -E^\circ = -0.800\,\mathrm{V}$

Reduction: $\mathrm{2H^+(aq) + 2e^- \rightarrow H_2(g)}$ $\quad E^\circ = +0.000\,\mathrm{V}$

Net: $\mathrm{2Ag(s) + 2H^+(aq) \rightarrow 2Ag^+(aq) + H_2(g)}$ $\quad E^\circ_{\mathrm{cell}} = -0.800\,\mathrm{V}$

The reaction is not spontaneous under standard conditions as written.

(d) Oxidation: $\{\mathrm{2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-}\} \times 2$ $\quad -E^\circ = -1.358\,\mathrm{V}$

Reduction: $\mathrm{O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)}$ $\quad E^\circ = +1.229\,\mathrm{V}$

Net: $\mathrm{4Cl^-(aq) + 4H^+(aq) + O_2(g) \rightarrow 2Cl_2(g) + 2H_2O(l)}$ $\quad E^\circ_{\mathrm{cell}} = -0.129\,\mathrm{V}$

The reaction is not spontaneous under standard conditions as written.

Galvanic Cells

19. **(M) (a)** Oxidation: $\{\mathrm{Al(s) \rightarrow Al^{3+}(aq) + 3e^-}\} \times 2$ $\quad -E^\circ = +1.676\ \mathrm{V}$

Reduction: $\{\mathrm{Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)}\} \times 3$ $\quad E^\circ = -0.137\ \mathrm{V}$

Net: $\mathrm{2\ Al(s) + 3\ Sn^{2+}(aq) \rightarrow 2\ Al^{3+}(aq) + 3\ Sn(s)}$ $\quad E^\circ_{\mathrm{cell}} = +1.539\ \mathrm{V}$

(b) Oxidation: $\mathrm{Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-}$ $\quad -E^\circ = -0.771\ \mathrm{V}$

Reduction: $\mathrm{Ag^+(aq) + e^- \rightarrow Ag(s)}$ $\quad E^\circ = +0.800\ \mathrm{V}$

Net: $\mathrm{Fe^{2+}(aq) + Ag^+(aq) \rightarrow Fe^{3+}(aq) + Ag(s)}$ $\quad E^\circ_{\mathrm{cell}} = +0.029\ \mathrm{V}$

(c) Oxidation: $\{\mathrm{Cr(s) \rightarrow Cr^{2+}(aq) + 2e^-}\} \times 3$ $\quad -E^\circ = +0.90\,\mathrm{V}$

Reduction: $\{Au^{3+}(aq)+3e^{-} \rightarrow Au(s)\} \times 2$ $E^{o} = 1.52V$

Net: $3Cr(s)+2Au^{3+}(aq) \rightarrow 3Cr^{2+}(aq)+2Au(s)$ $E^{o}_{cell} = 2.42V$

(d) Oxidation: $2H_2O(l) \rightarrow O_2(g)+4H^{+}(aq)+4e^{-}$ $-E^{o} = -1.229V$

Reduction: $O_2(g)+2H_2O(l)+4e^{-} \rightarrow 4OH^{-}(aq)$ $E^{o} = +0.401V$

Net: $H_2O(l) \rightarrow H^{+}(aq)+OH^{-}(aq)$ $E^{o}_{cell} = -0.828V$

20. **(M)** In this problem we are asked to write the half-reactions, balanced chemical equation and determine E^{o}_{cell} for a series of electrochemical cells.

(a) *Stepwise approach*

First write the oxidation and reduction half-reactions and find E_o values from Appendix D:

Oxidation: $Cu(s) \rightarrow Cu^{2+}(aq)+2e^{-}$ $-E^{o} = -0.340$ V

Reduction: $Cu^{+}(aq)+e^{-} \rightarrow Cu(s)$ $E^{o} = +0.520$ V

In order to obtain balanced net equation, the reduction half-reaction needs to be multiplied by 2:

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

Add the two half-reactions to obtain the net reaction:

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

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

Net: $2Cu^{+}(aq) \rightarrow Cu^{2+}(aq)+Cu(s)$

Determine E^{o}_{cell}:

E^{o}_{cell} =-0.340V+0.520V= +0.18 V

Conversion pathway approach:

Oxidation: $Cu(s) \rightarrow Cu^{2+}(aq)+2e^{-}$ $-E^{o} = -0.340$ V

Reduction: $\{Cu^{+}(aq)+e^{-} \rightarrow Cu(s)\} \times 2$ $E^{o} = +0.520$ V

Net: $2Cu^{+}(aq) \rightarrow Cu^{2+}(aq)+Cu(s)$ $E^{o}_{cell} = +0.18V$

Follow the same methodology for parts (b), (c), and (d).

(b) Oxidation: $Ag(s)+I^{-}(aq) \rightarrow AgI(s)+e^{-}$ $-E^{o} = +0.152$ V

Reduction: $AgCl(s)+e^{-} \rightarrow Ag(s)+Cl^{-}(aq)$ $E^{o} = +0.2223$ V

Net: $AgCl(s)+I^{-}(aq) \rightarrow AgI(s)+Cl^{-}(aq)$ $E^{o}_{cell} = +0.3743$ V

(c) Oxidation: $\{Ce^{3+}(aq) \rightarrow Ce^{4+}(aq)+e^{-}\} \times 2$ $-E^{o} = -1.76V$

Reduction: $I_2(s)+2e^{-} \rightarrow 2I^{-}(aq)$ $E^{o} = +0.535$ V

Net: $2Ce^{3+}(aq)+I_2(s) \rightarrow 2Ce^{4+}(aq)+2I^{-}(aq)$ E^{o}_{cell} = -1.225 V

(d) Oxidation: $\{U(s) \rightarrow U^{3+}(aq)+3e^{-}\} \times 2$ $-E^{o} = +1.66V$

Reduction: $\{V^{2+}(aq)+2e^{-} \rightarrow V(s)\} \times 3$ $E^{o} = -1.13V$

Net: $2U(s)+3V^{2+}(aq) \rightarrow 2U^{3+}(aq)+3V(s)$ $E^{o}_{cell} = +0.53\ V$

21. **(M)** In each case, we determine whether E^{o}_{cell} is greater than zero; if so, the reaction will occur.

(a) Oxidation: $H_2(g) \rightarrow 2H^{+} + 2e^{-}(aq)$ $-E^{o} = 0.000\,V$

Reduction: $F_2(g) + 2e^{-} \rightarrow 2F^{-}(aq)$ $E^{o} = 2.866\ V$

Net: $H_2(g) + F_2(g) \rightarrow 2\,H^{+}(aq) + 2\,F^{-}(aq)$ $E^{o}_{cell} = +2.866\,V$

The reaction is spontaneous under standard conditions as written

(b) Oxidation: $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^{-}$ $-E^{o} = -0.340\,V$

Reduction: $Ba^{2+}(aq) + 2e^{-} \rightarrow Ba(s);$ $E^{o} = -2.92\,V$

Net: $Cu(s) + Ba^{2+}(aq) \rightarrow Cu^{2+}(aq) + Ba(s)$ $E^{o}_{cell} = -3.26\ V.$

The reaction is not spontaneous under standard conditions as written.

(c) Oxidation: $\{Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^{-}\} \times 2$ $-E^{o} = -0.771\ V$

Reduction: $Fe^{2+}(aq) + 2e^{-} \rightarrow Fe(s)$ $E^{o} = -0.440\ V$

Net: $3\,Fe^{2+}(aq) \rightarrow Fe(s) + 2\,Fe^{3+}(aq)$ $E^{o}_{cell} = -1.211\ V$

The reaction is not spontaneous as written.

(d) Oxidation: $2\,Hg(l) + 2\,Cl^{-} \rightarrow Hg_2Cl_2(s) + 2\,e^{-}$ $-E^{o} = -(0.2676)\,V$

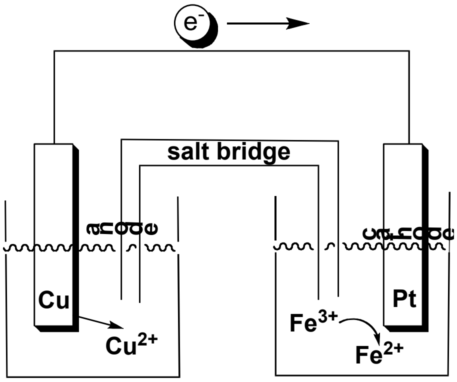
Reduction: $2\,HgCl_2(aq) + 2\,e^{-} \rightarrow Hg_2Cl_2(s) + 2\,Cl^{-}(aq)$ $E^{o} = +0.63V$

Net: $2\,Hg(l) + 2\,HgCl_2(aq) \rightarrow 2\,Hg_2Cl_2(s)$ $E^{o}_{cell} = +0.36\ V$

(divide by 2 to get $Hg(l) + HgCl_2(aq) \rightarrow Hg_2Cl_2(s)$)

The reaction is spontaneous under standard conditions as written.

22. **(M)** **(a)**

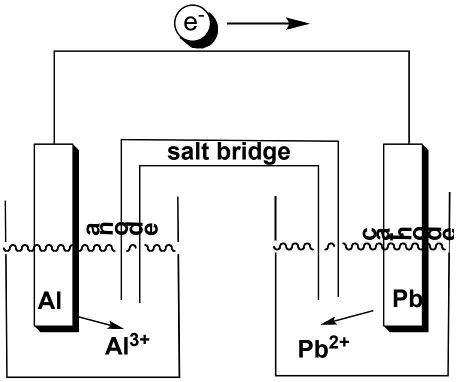


Anode, oxidation: $\mathrm{Cu(s)} \rightarrow \mathrm{Cu^{2+}(aq)} + 2\,\mathrm{e^-}$ $\quad -E^\circ = -0.340\,\mathrm{V}$

Cathode, reduction: $\{\mathrm{Fe^{3+}(aq)} + \mathrm{e^-} \rightarrow \mathrm{Fe^{2+}(aq)}\} \times 2\,;\; E^\circ = +0.771\,\mathrm{V}$

Net: $\mathrm{Cu(s)} + 2\,\mathrm{Fe^{3+}(aq)} \rightarrow \mathrm{Cu^{2+}(aq)} + 2\,\mathrm{Fe^{2+}(aq)}$ $\quad E^\circ_{\mathrm{cell}} = +0.431\,\mathrm{V}$

(b)

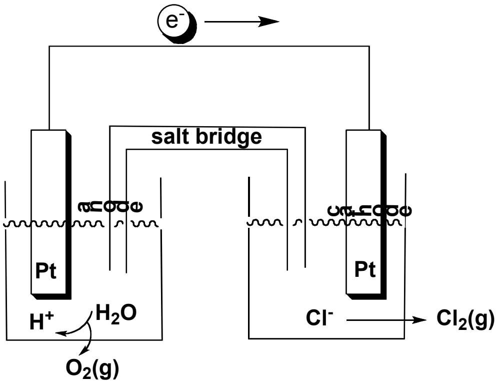


Anode, oxidation: $\{\mathrm{Al(s)} \rightarrow \mathrm{Al^{3+}(aq)} + 3\,\mathrm{e^-}\} \times 2$ $\quad -E^\circ = +1.676\,\mathrm{V}$

Cathode, reduction: $\{\mathrm{Pb^{2+}(aq)} + 2\,\mathrm{e^-} \rightarrow \mathrm{Pb(s)}\} \times 3\,;$ $\quad E^\circ = -0.125\ \mathrm{V}$

Net: $2\mathrm{Al(s)} + 3\mathrm{Pb^{2+}(aq)} \rightarrow 2\mathrm{Al^{3+}(aq)} + 3\mathrm{Pb(s)}$ $\quad E^\circ_{\mathrm{cell}} = +1.551\ \mathrm{V}$

(c)

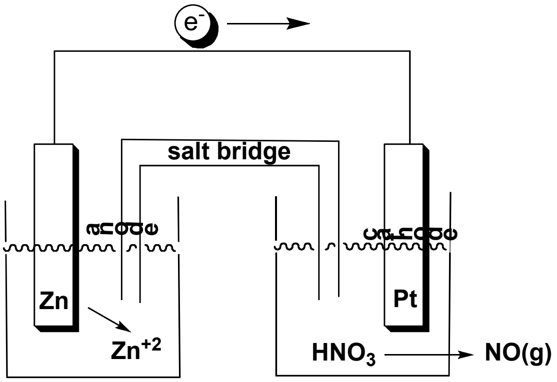


Anode, oxidation: $2\,\mathrm{H_2O(l)} \rightarrow \mathrm{O_2(g)} + 4\,\mathrm{H^+(aq)} + 4\,\mathrm{e^-}$ $\quad -E^\circ = -1.229\,\mathrm{V}$

Cathode, reduction: $\{\mathrm{Cl_2(g)} + 2\,\mathrm{e^-} \rightarrow 2\,\mathrm{Cl^-(aq)}\} \times 2$ $\quad E^\circ = +1.358\,\mathrm{V}$

Net: $2\,H_2O(l) + 2\,Cl_2(g) \rightarrow O_2(g) + 4\,H^+(aq) + 4\,Cl^-(aq)$ $E^o_{cell} = +0.129\,V$

(d)



Anode, oxidation: $\{Zn(s) \rightarrow Zn^{2+}(aq) + 2\,e^-\}$ ×3 $-E^o = +0.763\,V$

Cathode, reduction: $\{NO_3^-(aq) + 4H^+(aq) + 3e^- \rightarrow NO(g) + 2H_2O(l)\} \times 2$; $E^o = +0.956$ V

Net: $3Zn(s) + 2NO_3^-(aq) + 8H^+(aq) \rightarrow 3Zn^{2+}(aq) + 2NO(g) + 4H_2O(l)$ $E^o_{cell} = +1.719\,V$

23. **(M)** In each case, we determine whether E^o_{cell} is greater than zero; if so, the reaction will occur.

(a) Oxidation: $Ag(s) \rightarrow Ag^+(aq) + e^-$ $-E^o = -0.800\,V$

Reduction: $Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$ $E^o = +0.771$ V

Net: $Ag(s) + Fe^{3+}(aq) \rightarrow Ag^+(aq) + Fe^{2+}(aq)$ $E^o_{cell} = -0.029\,V$

The reaction is not spontaneous under standard conditions as written.

(b) Oxidation: $Sn(s) \rightarrow Sn^{2+}(aq) + 2e^-$ $-E^o = +0.137\,V$

Reduction: $Sn^{4+}(aq) + 2e^- \rightarrow Sn^{+2}(aq)$ $E^o = +0.154$ V

Net: $Sn(s) + Sn^{4+}(aq) \rightarrow 2Sn^{2+}(aq)$ $E^o_{cell} = +0.291\,V$

The reaction is spontaneous under standard conditions as written.

(c) Oxidation: $2Br^-(aq) \rightarrow Br_2(l) + 2e^-$ $-E^o = -1.065V$

Reduction: $2Hg^{2+}(aq) + 2e^- \rightarrow Hg_2^+(aq)$ $E^o = +0.630$ V

Net: $2Br^-(aq) + 2Hg^{2+}(aq) \rightarrow Br_2(l) + Hg_2^+$ $E^o_{cell} = -0.435\,V$

The reaction is not spontaneous under standard conditions as written.

(d) Oxidation: $\{NO_3^-(aq) + 2H^+(aq) + e^- \rightarrow NO_2(g) + H_2O(l)\} \times 2$ $-E^o = -2.326V$

Reduction: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ $E^o = +1.563V$

Net: $2NO_3^-(aq) + 4H^+(aq) + Zn(s) \rightarrow 2NO_2(g) + 2H_2O(l) + Zn^{2+}(aq)$ $E^o_{cell} = -0.435\,V$

The reaction is not spontaneous under standard conditions as written.

24. **(M) (a)** $Fe(s)|Fe^{2+}(aq)||Cl^-(aq)Cl_2(g)|Pt(s)$

Oxidation: $Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$ $\quad -E^\circ = +0.440\,V$

Reduction: $Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$ $\quad E^\circ = +1.358\,V$

Net: $Fe(s) + Cl_2(g) \rightarrow Fe^{2+}(aq) + 2Cl^-(aq)$ $\quad E^\circ_{cell} = +1.798\,V$

(b) $Zn(s)|Zn^{2+}(aq)||Ag^+(aq)|Ag(s)$

Oxidation: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ $\quad -E^\circ = +0.763\,V$

Reduction: $\{Ag^+(aq) + e^- \rightarrow Ag(s)\} \times 2$ $\quad E^\circ = +0.800\,V$

Net: $Zn(s) + 2Ag^+(aq) \rightarrow Zn^{2+}(aq) + 2Ag(s)$ $\quad E^\circ_{cell} = +1.563\,V$

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

Oxidation: $Cu^+(aq) \rightarrow Cu^{2+}(aq) + e^-$ $\quad -E^\circ = -0.159\,V$

Reduction: $Cu^+(aq) + e^- \rightarrow Cu(s)$ $\quad E^\circ = +0.520\,V$

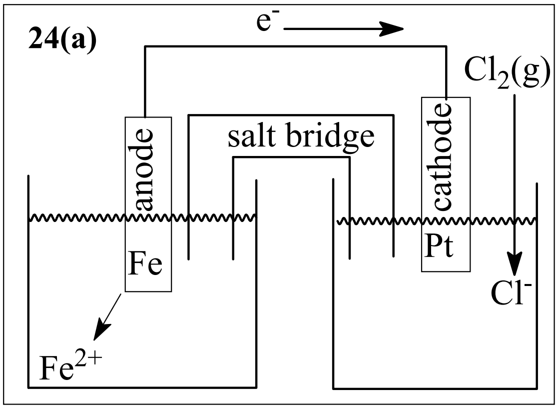
Net: $2Cu^+(aq) \rightarrow Cu^{2+}(aq) + Cu(s)$ $\quad E^\circ_{cell} = +0.361\,V$

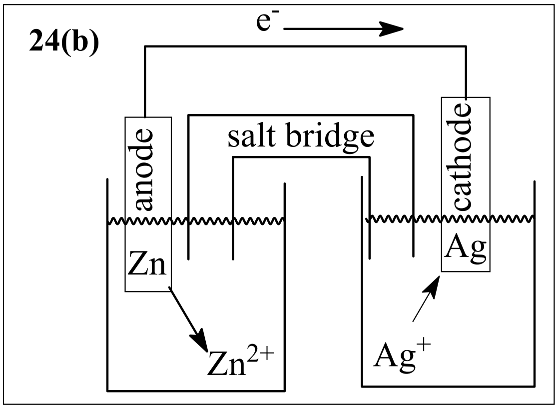
(d) $Mg(s)|Mg^{2+}(aq)||Br^-(aq)Br_2(l)|Pt(s)$

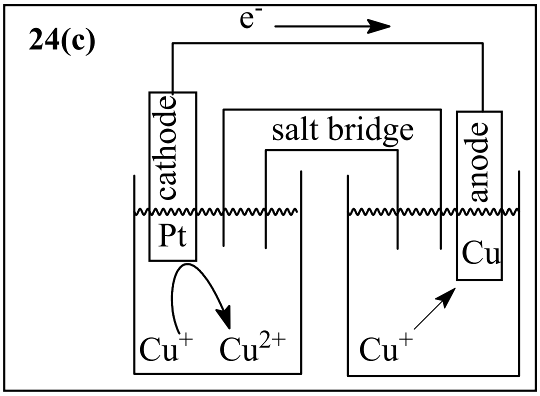
Oxidation: $Mg(s) \rightarrow Mg^{2+}(aq) + 2e^-$ $\quad -E^\circ = +2.356\,V$

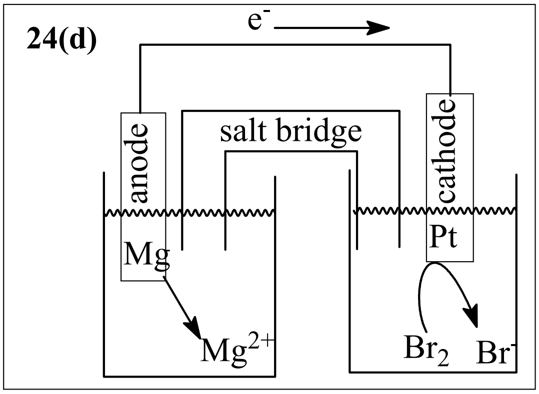
Reduction: $Br_2(l) + 2e^- \rightarrow 2Br^-(aq)$ $\quad E^\circ = +1.065\,V$

Net: $Mg(s) + Br_2(l) \rightarrow Mg^{2+}(aq) + 2Br^-(aq)$ $\quad E^\circ_{cell} = +3.421\,V$









ΔG°, E°_{cell}, and K

25. **(M) (a)** Oxidation: $\{\text{Al(s)} \rightarrow \text{Al}^{3+}\text{(aq)} + 3\,\text{e}^-\} \times 2$ $\qquad -E^\circ = +1.676\,\text{V}$

Reduction: $\{\text{Cu}^{2+}\text{(aq)} + 2\,\text{e}^- \rightarrow \text{Cu(s)}\} \times 3$ $\qquad E^\circ = +0.337\,\text{V}$

Net: $2\,\text{Al(s)} + 3\,\text{Cu}^{2+}\text{(aq)} \rightarrow 2\,\text{Al}^{3+}\text{(aq)} + 3\,\text{Cu(s)}$ $\qquad E^\circ_{\text{cell}} = +2.013\,\text{V}$

$$\Delta G^\circ = -nFE^\circ_{\text{cell}} = -(6\text{ mol e}^-)(96{,}485\text{ C/mol e}^-)(2.013\,\text{V})$$

$$\Delta G^\circ = -1.165\times10^{6}\,\text{J} = -1.165\times10^{3}\text{ kJ}$$

(b) Oxidation: $\{2\,\text{I}^-\text{(aq)} \rightarrow \text{I}_2\text{(s)} + 2\,\text{e}^-\} \times 2$ $\qquad -E^\circ = -0.535\text{ V}$

Reduction: $\text{O}_2\text{(g)} + 4\,\text{H}^+\text{(aq)} + 4\,\text{e}^- \rightarrow 2\,\text{H}_2\text{O(l)}$ $\qquad E^\circ = +1.229\text{ V}$

Net: $4\,\text{I}^-\text{(aq)} + \text{O}_2\text{(g)} + 4\,\text{H}^+\text{(aq)} \rightarrow 2\,\text{I}_2\text{(s)} + 2\,\text{H}_2\text{O(l)}$ $\qquad E^\circ_{\text{cell}} = +0.694\text{ V}$

$$\Delta G^\circ = -nFE^\circ_{\text{cell}} = -(4\text{ mol e}^-)(96{,}485\text{ C/mol e}^-)(0.694\text{ V}) = -2.68\times10^{5}\,\text{J} = -268\text{ kJ}$$

(c) Oxidation: $\{\text{Ag(s)} \rightarrow \text{Ag}^+\text{(aq)} + \text{e}^-\} \times 6$ $\qquad -E^\circ = -0.800\text{ V}$

Reduction: $\text{Cr}_2\text{O}_7^{\;2-}\text{(aq)} + 14\text{ H}^+\text{(aq)} + 6\text{ e}^- \rightarrow 2\text{ Cr}^{3+}\text{(aq)} + 7\text{ H}_2\text{O(l)}$ $\qquad E^\circ = +1.33\,\text{V}$

Net: $6\text{ Ag(s)} + \text{Cr}_2\text{O}_7^{\;2-}\text{(aq)} + 14\,\text{H}^+\text{(aq)} \rightarrow 6\,\text{Ag}^+\text{(aq)} + 2\,\text{Cr}^{3+}\text{(aq)} + 7\,\text{H}_2\text{O(l)}$

$$E^\circ_{\text{cell}} = -0.800\,\text{V} + 1.33\,\text{V} = +0.53\,\text{V}$$

$$\Delta G^\circ = -nFE^\circ_{\text{cell}} = -(6\text{mol e}^-)(96{,}485\text{C/mol e}^-)(0.53\,\text{V}) = -3.1\times10^{5}\,\text{J} = -3.1\times10^{2}\text{ kJ}$$

26. **(M)** In this problem we need to write the equilibrium constant expression for a set of redox reactions and determine the value of K at 25 °C. We proceed by calculating E^o_{cell} from standard electrode reduction potentials (Table 20.1). Then we use the expression $\Delta G^\circ = -nFE^\circ_{\text{cell}} = -RT\ln K$ to calculate K.

(a)

Stepwise approach:

Determine E^o_{cell} from standard electrode reduction potentials (Table 20.1):

Oxidation: $\text{Ni(s)} \rightarrow \text{Ni}^{2+}\text{(aq)} + 2\text{e}^-$ $\qquad -E^\circ = 0.257\text{ V}$

Reduction: $\{\text{V}^{3+}\text{(aq)} + \text{e}^- \rightarrow \text{V}^{2+}\text{(aq)}\} \times 2$ $\qquad E^\circ = -0.255\text{ V}$

Net: $\text{Ni(s)} + 2\text{V}^{3+}\text{(aq)} \rightarrow \text{Ni}^{2+}\text{(aq)} + 2\text{V}^{2+}\text{(aq)}$ $\qquad E^\circ_{\text{cell}} = 0.003\,\text{V}$

Use the expression $\Delta G^\circ = -nFE^\circ_{\text{cell}} = -RT\ln K$ to calculate K:

$$\Delta G^{\circ} = -nFE^{\circ}_{\text{cell}} = -RT\ln K;$$

$$\Delta G^{o} = -2mole^{-} \times 96485\frac{C}{mol} \times 0.003V = -578.9J$$

$$\Delta G^{o} = -RT\ln K \Rightarrow -578.9J = -8.314JK^{-1}mol^{-1} \times 298.15K\ln K$$

$$\ln K = 0.233 \Rightarrow K = e^{0.233} = 1.26$$

$$K = 1.26 = \frac{\left[\text{Ni}^{2+}\right]\left[\text{V}^{2+}\right]^2}{\left[\text{V}^{3+}\right]^2}$$

Conversion pathway approach:

Determine E^{o}_{cell} from standard electrode reduction potentials (Table 20.1):

Oxidation: $\text{Ni(s)} \rightarrow \text{Ni}^{2+}\text{(aq)+2e}^-$ $\quad -E^{\circ} = 0.257\text{ V}$

Reduction: $\{\text{V}^{3+}\text{(aq)+e}^- \rightarrow \text{V}^{2+}\text{(aq)}\} \times 2$ $\quad E^{\circ} = -0.255\text{ V}$

Net: $\text{Ni(s)+2V}^{3+}\text{(aq)} \rightarrow \text{Ni}^{2+}\text{(aq)+2V}^{2+}\text{(aq)}$ $\quad E^{\circ}_{\text{cell}}\text{=0.003V}$

$$\Delta G^{\circ} = -nFE^{\circ}_{\text{cell}} = -RT\ln K \Rightarrow \ln K_{eq} = \frac{nFE^{o}_{cell}}{RT} = \frac{n \times 96485Cmol^{-1}}{8.314JK^{-1}mol^{-1} \times 298.15K}E^{o}_{cell}$$

$$\ln K_{\text{eq}} = \frac{n}{0.0257}E^{\circ}_{\text{cell}} = \frac{2\text{ mol e}^- \times 0.003V}{0.0257} = 0.233$$

$$K_{\text{eq}} = e^{0.233} = 1.26 = \frac{\left[\text{Ni}^{2+}\right]\left[\text{V}^{2+}\right]^2}{\left[\text{V}^{3+}\right]^2}$$

Similar methodology can be used for parts (b) and (c)

(b) Oxidation: $2\text{Cl}^-(\text{aq}) \rightarrow \text{Cl}_2(\text{g}) + 2\text{ e}^-$ $\quad -E^{\circ} = -1.358\text{ V}$

Reduction: $\text{MnO}_2(\text{s}) + 4\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{Mn}^{2+}(\text{aq}) + 2\text{H}_2\text{O(l)}$ $\quad E^{\circ} = +1.23\text{V}$

Net: $2\text{ Cl}^-(\text{aq}) + \text{MnO}_2(\text{s}) + 4\text{ H}^+(\text{aq}) \rightarrow \text{Mn}^{2+}(\text{aq}) + \text{Cl}_2(\text{g}) + 2\text{ H}_2\text{O(l)}$ $\quad E^{\circ}_{\text{cell}} = -0.13\text{V}$

$$\ln\ K_{\text{eq}} = \frac{2\text{ mol e}^- \times (-0.13\text{ V})}{0.0257} = -10._1;\ K_{\text{eq}} = \text{e}^{-10.1} = 4\times10^{-5} = \frac{\left[\text{Mn}^{2+}\right]P\{\text{Cl}_2(\text{g})\}}{\left[\text{Cl}^-\right]^2\left[\text{H}^+\right]^4}$$

(c) Oxidation: $4\text{ OH}^-(\text{aq}) \rightarrow \text{O}_2(\text{g}) + 2\text{H}_2\text{O(l)} + 4\text{ e}^-$ $\quad -E^{\circ} = -0.401\text{ V}$

Reduction: $\{\text{OCl}^-\text{(aq)+H}_2\text{O(l)+2e}^- \rightarrow \text{Cl}^-\text{(aq)+2OH}^-\} \times 2$ $\quad E^{\circ} = +0.890\text{ V}$

Net: $2\text{OCl}^-\text{(aq)} \longrightarrow 2\text{Cl}^-\text{(aq)} + \text{O}_2\text{(g)}$ $\quad E^{\circ}_{\text{cell}} = +0.489\text{ V}$

$$\ln K_{\text{eq}} = \frac{4\text{ mol e}^-(0.489\text{ V})}{0.0257} = 76.1 \qquad K_{\text{eq}} = \text{e}^{76.1} = 1\times10^{33} = \frac{\left[\text{Cl}^-\right]^2\text{P}\{\text{O}_2\text{(g)}\}}{\left[\text{OCl}^-\right]^2}$$

27. **(M)** First calculate E^{o}_{cell} from standard electrode reduction potentials (Table 20.1). Then use $\Delta G^{\circ} = -nFE^{\circ}_{\text{cell}} = -RT\ln K$ to determine ΔG^{o} and K.

(a)

$$\text{Oxidation: } \{Ce^{3+}(aq) \rightarrow Ce^{4+}(aq) + e^-\} \times 5 \qquad -E^\circ = -1.61\text{ V}$$

$$\text{Reduction: } \mathrm{MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)} \qquad E^\circ = +1.51\text{V}$$

$$\text{Net: } \mathrm{MnO_4^-(aq) + 8H^+(aq) + 5Ce^{3+}(aq) \rightarrow Mn^{2+}(aq) + 4H_2O(l) + 5Ce^{4+}(aq)} \quad E^o_{cell} = -0.100V$$

(b)

$$\Delta G^\circ = -nFE^\circ_{\text{cell}} = -RT\ln K;$$

$$\Delta G^o = -5 \times 96485\frac{\text{C}}{\text{mol}} \times (-0.100V) = 48.24\text{kJmol}^{-1}$$

(c)

$$\Delta G^o = -RT\ln K \Rightarrow 48.24 \times 1000\text{Jmol}^{-1} = -8.314\text{JK}^{-1}\text{mol}^{-1} \times 298.15\text{K}\ln K$$

$$\ln K = -19.46 \Rightarrow K = e^{-19.46} = 3.5 \times 10^{-9}$$

(d) Since K is very small the reaction will not go to completion.

28. **(M)** First calculate E^o_{cell} from standard electrode reduction potentials (Table 20.1). Then use $\Delta G^\circ = -nFE^\circ_{\text{cell}} = -RT\ln K$ to determine ΔG^o and K.

(a)

$$\text{Oxidation: } \mathrm{Pb^{2+}(aq) \rightarrow Pb^{4+}(aq) + 2e^-} \qquad E_o = -0.180V$$

$$\text{Reduction: } \mathrm{Sn^{4+}(aq) + 2e^- \rightarrow Sn^{2+}(aq)} \qquad E_o = +0.154V$$

$$\text{Net: } \mathrm{Pb^{2+}(aq) + Sn^{4+}(aq) \rightarrow Pb^{4+}(aq) + Sn^{2+}(aq)} \qquad E^o_{cell} = -0.026V$$

(b) $\Delta G^\circ = -nFE^\circ_{\text{cell}} = -RT\ln K \Rightarrow \quad \Delta G^o = -2 \times 96485\frac{\text{C}}{\text{mol}} \times (-0.026) = 5017\text{Jmol}^{-1}$

(c)

$$\Delta G^o = -RT\ln K \Rightarrow 5017\text{Jmol}^{-1} = -8.314\text{JK}^{-1}\text{mol}^{-1} \times 298.15\text{K}\ln K$$

$$\ln K = -2.02 \Rightarrow K = e^{-2.02} = 0.132$$

(d) The value of K is small and the reaction does not go to completion.

29. **(M) (a)** A negative value of E°_{cell} (-0.0050 V) indicates that $\Delta G^\circ = -nFE^\circ_{\text{cell}}$ is positive which in turn indicates that K_{eq} is less than one $\left(K_{\text{eq}} < 1.00\right)$; $\Delta G^\circ = -RT\ln K_{\text{eq}}$.

$$K_{\text{eq}} = \frac{\left[\text{Cu}^{2+}\right]^2\left[\text{Sn}^{2+}\right]}{\left[\text{Cu}^{+}\right]^2\left[\text{Sn}^{4+}\right]}$$

Thus, when all concentrations are the same, the ion product, *Q*, equals 1.00. From the negative standard cell potential, it is clear that K_{eq} must be (slightly) less than one. Therefore, all the concentrations cannot be 0.500 M at the same time.

(b) In order to establish equilibrium, that is, to have the ion product become less than 1.00, and equal the equilibrium constant, the concentrations of the products must decrease and those of the reactants must increase. A net reaction to the left (towards the reactants) will occur.

30. **(D) (a)** First we must calculate the value of the equilibrium constant from the standard cell potential.

$$E^\circ_{\text{cell}} = \frac{0.0257}{n}\ln K_{\text{eq}};\ \ln K_{\text{eq}} = \frac{nE^\circ_{\text{cell}}}{0.0257} = \frac{2\text{ mol e}^- \times (-0.017)\text{V}}{0.0257} = -1.32$$

$$K_{\text{eq}} = \text{e}^{-1.32} = 0.266$$

To determine if the described solution is possible, we compare K_{eq} with Q. Now $K_{\text{eq}} = \frac{\left[\text{BrO}_3^-\right]\left[\text{Ce}^{4+}\right]^2}{\left[\text{H}^+\right]^2\left[\text{BrO}_4^-\right]\left[\text{Ce}^{3+}\right]^2}$. Thus, when $\left[\text{BrO}_4^-\right]=\left[\text{Ce}^{4+}\right]=0.675\text{ M}$, $\left[\text{BrO}_3^-\right]=\left[\text{Ce}^{3+}\right]=0.600\text{ M}$ and pH=1 ($\left[\text{H}^+\right]$=0.1M the ion product, $Q = \frac{0.600 \times 0.675^2}{0.1^2 \times 0.675 \times 0.600^2} = 112.5 > 0.266 = K_{\text{eq}}$. Therefore, the described situation can occur

(b) In order to establish equilibrium, that is, to have the ion product (112.5) become equal to 0.266, the equilibrium constant, the concentrations of the reactants must increase and those of the products must decrease. Thus, a net reaction to the left (formation of reactants) will occur.

31. **(M)** Cell reaction: $\text{Zn(s)} + \text{Ag}_2\text{O(s)} \rightarrow \text{ZnO(s)} + 2\text{Ag(s)}$. We assume that the cell operates at 298 K.

$$\begin{aligned}\Delta G^\circ &= \Delta G^\circ_f\left[\text{ZnO(s)}\right] + 2\Delta G^\circ_f\left[\text{Ag(s)}\right] - \Delta G^\circ_f\left[\text{Zn(s)}\right] - \Delta G^\circ_f\left[\text{Ag}_2\text{O(s)}\right] \\ &= -318.3\text{ kJ/mol} + 2(0.00\text{ kJ/mol}) - 0.00\text{ kJ/mol} - (-11.20\text{ kJ/mol}) \\ &= -307.1\text{ kJ/mol} = -nFE^\circ_{\text{cell}}\end{aligned}$$

$$E^\circ_{\text{cell}} = -\frac{\Delta G^\circ}{nF} = -\frac{-307.1\times10^3\text{ J/mol}}{2\text{ mol e}^-\text{/mol rxn}\times 96,485\text{ C/mol e}^-} = 1.591\text{ V}$$

32. **(M)** From equation (20.15) we know $n = 12$ and the overall cell reaction. First we must compute value of ΔG°.

$$\Delta G^\circ = -n\,FE^\circ_{\text{cell}} = -12\text{ mol e}^- \times \frac{96485\text{ C}}{1\text{ mol e}^-} \times 2.71\text{ V} = -3.14\times10^6\text{ J} = -3.14\times10^3\text{ kJ}$$

Then we will use this value, the balanced equation and values of ΔG_f° to calculate $\Delta G^\circ_f\left[\text{Al(OH)}_4\right]^-$.

$$4\text{ Al(s)} + 3\text{O}_2\text{(g)} + 6\text{H}_2\text{O(l)} + 4\text{OH}^-\text{(aq)} \rightarrow 4\left[\text{Al(OH)}_4\right]^-\text{(aq)}$$

$$\Delta G^\circ = 4\Delta G^\circ_f\left[\text{Al(OH)}_4\right]^- - 4\Delta G^\circ_f[\text{Al(s)}] - 3\Delta G^\circ_f[\text{O}_2\text{(g)}] - 6\Delta G^\circ_f[\text{H}_2\text{O(l)}] - 4\Delta G^\circ_f[\text{OH}^-\text{(aq)}]$$

$$-3.14\times10^3\text{ kJ} = 4\Delta G_f^\circ\left[\text{Al}(\text{OH})_4\right]^- - 4\times0.00\text{ kJ} - 3\times0.00\text{ kJ} - 6\times(-237.1\text{ kJ}) - 4\times(-157.2)$$

$$= 4\Delta G_f^\circ\left[\text{Al}(\text{OH})_4\right]^- + 2051.4\text{ kJ}$$

$$\Delta G_f^\circ\left[\text{Al}(\text{OH})_4\right]^- = (-3.14\times10^3\text{ kJ} - 2051.4\text{ kJ})\div4 = -1.30\times10^3\text{ kJ/mol}$$

33. **(D)** From the data provided we can construct the following Latimer diagram.

$$\underset{\text{(IV)}}{\text{IrO}_2} \xrightarrow{0.223\text{ V}} \underset{\text{(III)}}{\text{Ir}^{3+}} \xrightarrow{1.156\text{ V}} \underset{(0)}{\text{Ir}} \quad \text{(Acidic conditions)}$$

Latimer diagrams are used to calculate the standard potentials of non-adjacent half-cell couples. Our objective in this question is to calculate the voltage differential between IrO_2 and iridium metal (Ir), which are separated in the diagram by Ir^{3+}. The process basically involves adding two half-reactions to obtain a third half-reaction. The potentials for the two half-reactions cannot, however, simply be added to get the target half-cell voltage because the electrons are not cancelled in the process of adding the two half-reactions. Instead, to find $E^\circ_{1/2\text{ cell}}$ for the target half-reaction, we must use free energy changes, which are additive. To begin, we will balance the relevant half-reactions in acidic solution:

$4\text{ H}^+(aq) + \text{IrO}_2(s) + e^- \rightarrow \text{Ir}^{3+}(aq) + 2\text{ H}_2\text{O}(l) \qquad E^\circ_{1/2\text{red(a)}} = 0.223\text{ V}$

$\text{Ir}^{3+}(aq) + 3\text{ e}^- \rightarrow \text{Ir}(s) \qquad E^\circ_{1/2\text{red(b)}} = 1.156\text{V}$

$4\text{ H}^+(aq) + \text{IrO}_2(s) + 4e^- \rightarrow 2\text{ H}_2\text{O}(l) + \text{Ir}(s) \qquad E^\circ_{1/2\text{red(c)}} = ?$

$E^\circ_{1/2\text{red(c)}} \neq E^\circ_{1/2\text{red(a)}} + E^\circ_{1/2\text{red(b)}}$ but $\Delta G^\circ_{(a)} + \Delta G^\circ_{(b)} = \Delta G^\circ_{(c)}$ and $\Delta G^\circ = -nFE^\circ$

$-4F(E^\circ_{1/2\text{red(c)}}) = -1F(E^\circ_{1/2\text{red(a)}}) + -3F(E^\circ_{1/2\text{red(b)}})$

$-4F(E^\circ_{1/2\text{red(c)}}) = -1F(0.223) + -3F(1.156)$

$$E^\circ_{1/2\text{red(c)}} = \frac{-1F(0.223) + -3F(1.156)}{-4F} = \frac{-1(0.223) + -3(1.156)}{-4} = 0.923\text{ V}$$

In other words, $E^\circ_{(c)}$ is the weighted average of $E^\circ_{(a)}$ and $E^\circ_{(b)}$

34. **(D)** This question will be answered in a manner similar to that used to solve 31. Let's get underway by writing down the appropriate Latimer diagram:

$$\begin{tikzcd}
\underset{\text{(VI)}}{\text{H}_2\text{MoO}_4} \arrow[r, "0.646\text{ V}"] \arrow[rr, bend right, "0.428\text{ V}"'] & \underset{\text{(IV)}}{\text{MoO}_2} \arrow[r, "?\text{ V}"] & \underset{\text{(III)}}{\text{Mo}^{3+}} & \text{(Acidic conditions)}
\end{tikzcd}$$

This time we want to calculate the standard voltage change for the 1 e^- reduction of MoO_2 to Mo^{3+}. Once again, we must balance the half-cell reactions in acidic solution:

$\text{H}_2\text{MoO}_4(aq) + 2\text{ e}^- + 2\text{ H}^+(aq) \rightarrow \text{MoO}_2(s) + 2\text{ H}_2\text{O}(l) \qquad E^\circ_{1/2\text{red(a)}} = 0.646\text{ V}$

$\text{MoO}_2(s) + 4\text{ H}^+(aq) + 1\text{ e}^- \rightarrow \text{Mo}^{3+}(aq) + 2\text{ H}_2\text{O}(l) \qquad E^\circ_{1/2\text{red(b)}} = ?\text{ V}$

$\text{H}_2\text{MoO}_4(aq) + 3\text{ e}^- + 6\text{ H}^+(aq) \rightarrow \text{Mo}^{3+}(aq) + 4\text{ H}_2\text{O}(l) \qquad E^\circ_{1/2\text{red(c)}} = 0.428\text{ V}$

So, $-3F(E^\circ_{1/2\text{red(c)}}) = -2F(E^\circ_{1/2\text{red(a)}}) + -1F(E^\circ_{1/2\text{red(b)}})$

$-3F(0.428\text{ V}) = -2F(0.646) + -1F(E^\circ_{1/2\text{red(b)}})$

$-1FE^\circ_{1/2\text{red(b)}} = -3F(0.428\text{ V}) + 2F(0.646)$

$$E°_{1/2\text{red(c)}} = \frac{-3F(0.428\text{ V}) + 2F(0.646)}{-1F} = 1.284\text{ V} - 1.292\text{ V} = -0.008\text{ V}$$

Concentration Dependence of E_{cell}—the Nernst Equation

35. **(M)** In this problem we are asked to determine the concentration of [Ag^+] ions in electrochemical cell that is not under standard conditions. We proceed by first determining E^o_{cell}. Using the Nerst equation and the known value of E, we can then calculate the concentration of [Ag^+].

Stepwise approach:

First, determine E^o_{cell}:

$$\begin{array}{ll} \text{Oxidation: } \mathrm{Zn(s) \rightarrow Zn^{2+}(aq) + 2\,e^-} & -E^\circ = +0.763\text{ V} \\ \text{Reduction: } \{\mathrm{Ag^+(aq) + e^- \rightarrow Ag(s)}\} \times 2 & E^\circ = +0.800\text{ V} \\ \hline \text{Net: } \mathrm{Zn(s) + 2\,Ag^+(aq) \rightarrow Zn^{2+}(aq) + 2Ag(s)} & E^\circ_{\text{cell}} = +1.563\text{ V} \end{array}$$

Use the Nerst equation and the known value of E to solve for $[Ag]^+$:

$$E = E^\circ_{\text{cell}} - \frac{0.0592}{n}\log\frac{[\mathrm{Zn^{2+}}]}{[\mathrm{Ag^+}]^2} = +1.563\text{ V} - \frac{0.0592}{2}\log\frac{1.00}{x^2} = +1.250\text{ V}$$

$$\log\frac{1.00\text{ M}}{x^2} = \frac{-2\times(1.250-1.563)}{0.0592} = 10.6;\quad x = \sqrt{2.\underline{5}\times10^{-11}} = 5\times10^{-6}\text{ M}$$

Therefore, [Ag^+] = 5 × 10^{-6} M

Conversion pathway approach:

$$\begin{array}{ll} \text{Oxidation: } \mathrm{Zn(s) \rightarrow Zn^{2+}(aq) + 2\,e^-} & -E^\circ = +0.763\text{ V} \\ \text{Reduction: } \{\mathrm{Ag^+(aq) + e^- \rightarrow Ag(s)}\} \times 2 & E^\circ = +0.800\text{ V} \\ \hline \text{Net: } \mathrm{Zn(s) + 2\,Ag^+(aq) \rightarrow Zn^{2+}(aq) + 2Ag(s)} & E^\circ_{\text{cell}} = +1.563\text{ V} \end{array}$$

$$E = E^\circ_{\text{cell}} - \frac{0.0592}{n}\log\frac{[\mathrm{Zn^{2+}}]}{[\mathrm{Ag^+}]^2} \Rightarrow \log\frac{[\mathrm{Zn^{2+}}]}{[\mathrm{Ag^+}]^2} = -\frac{n}{0.0592}(E - E^o_{cell})$$

$$[\mathrm{Ag^+}]^2 = \frac{[\mathrm{Zn^{2+}}]}{10^{-\frac{n}{0.0592}(E-E^o_{cell})}} \Rightarrow [\mathrm{Ag^+}] = \sqrt{\frac{[\mathrm{Zn^{2+}}]}{10^{-\frac{n}{0.0592}(E-E^o_{cell})}}}$$

$$[\mathrm{Ag^+}] = \sqrt{\frac{1.00}{10^{-\frac{2}{0.0592}(1.250-1.563)}}} = 5\times10^{-6}$$

36. **(M)** In each case, we employ the equation $E_{\text{cell}} = 0.0592\text{ pH}$.

(a) $E_{\text{cell}} = 0.0592\text{ pH} = 0.0592\times5.25 = 0.311\text{ V}$

(b) $\text{pH} = -\log(0.0103) = 1.987 \quad E_{\text{cell}} = 0.0592\text{ pH} = 0.0592\times1.987 = 0.118\text{ V}$

(c) $K_a = \dfrac{\left[\mathrm{H}^+\right]\left[\mathrm{C_2H_3O_2^-}\right]}{\left[\mathrm{HC_2H_3O_2}\right]} = 1.8\times10^{-5} = \dfrac{x^2}{0.158 - x} \approx \dfrac{x^2}{0.158}$

$x = \sqrt{0.158\times1.8\times10^{-5}} = 1.7\times10^{-3}\ \mathrm{M}$

$\mathrm{pH} = -\log(1.7\times10^{-3}) = 2.77$

$E_{\text{cell}} = 0.0592\ \mathrm{pH} = 0.0592\times2.77 = 0.164\,\mathrm{V}$

37. **(M)** We first calculate $E^{\mathrm{o}}_{\text{cell}}$ for each reaction and then use the Nernst equation to calculate E_{cell}.

(a) Oxidation: $\{\mathrm{Al(s)} \rightarrow \mathrm{Al^{3+}(0.18\ M)} + 3\ \mathrm{e^-}\}\ \times 2 \qquad -E^{\mathrm{o}} = +1.676\,\mathrm{V}$

Reduction: $\{\mathrm{Fe^{2+}(0.85\,M)} + 2\,\mathrm{e^-} \rightarrow \mathrm{Fe(s)}\}\ \times 3 \qquad E^{\mathrm{o}} = -0.440\,\mathrm{V}$

Net: $2\,\mathrm{Al(s)} + 3\,\mathrm{Fe^{2+}(0.85\ M)} \rightarrow 2\,\mathrm{Al^{3+}(0.18\ M)} + 3\mathrm{Fe(s)} \qquad E^{\mathrm{o}}_{\text{cell}} = +1.236\,\mathrm{V}$

$$E_{\text{cell}} = E^{\mathrm{o}}_{\text{cell}} - \frac{0.0592}{n}\log\frac{\left[\mathrm{Al^{3+}}\right]^2}{\left[\mathrm{Fe^{2+}}\right]^3} = 1.236\,\mathrm{V} - \frac{0.0592}{6}\log\frac{(0.18)^2}{(0.85)^3} = 1.249\ \mathrm{V}$$

(b) Oxidation: $\{\mathrm{Ag(s)} \rightarrow \mathrm{Ag^+(0.34\,M)} + \mathrm{e^-}\}\ \times 2 \qquad -E^{\mathrm{o}} = -0.800\,\mathrm{V}$

Reduction: $\mathrm{Cl_2(0.55\ atm)} + 2\ \mathrm{e^-} \rightarrow 2\ \mathrm{Cl^-(0.098\ M)} \qquad E^{\mathrm{o}} = +1.358\,\mathrm{V}$

Net: $\mathrm{Cl_2(0.55\,atm)} + 2\ \mathrm{Ag(s)} \rightarrow 2\ \mathrm{Cl^-(0.098\,M)} + 2\,\mathrm{Ag^+(0.34\,M)};\ E^{\mathrm{o}}_{\text{cell}} = +0.558\,\mathrm{V}$

$$E_{\text{cell}} = E^{\mathrm{o}}_{\text{cell}} = \frac{0.0592}{n}\log\frac{\left[\mathrm{Cl^-}\right]^2\left[\mathrm{Ag^+}\right]^2}{P\{\mathrm{Cl_2(g)}\}} = +0.558 - \frac{0.0592}{2}\log\frac{(0.34)^2(0.098)^2}{0.55} = +0.638\ \mathrm{V}$$

38. **(M) (a)** Oxidation: $\mathrm{Mn(s)} \rightarrow \mathrm{Mn^{2+}(0.40\,M)} + 2\,\mathrm{e^-} \qquad -E^{\mathrm{o}} = +1.18\,\mathrm{V}$

Reduction: $\{\mathrm{Cr^{3+}(0.35\,M)} + 1\mathrm{e^-} \rightarrow \mathrm{Cr^{2+}(0.25\ M)}\}\ \times 2 \qquad E^{\mathrm{o}} = -0.424\ \mathrm{V}$

Net: $2\,\mathrm{Cr^{3+}(0.35\,M)} + \mathrm{Mn(s)} \rightarrow 2\,\mathrm{Cr^{2+}(0.25\,M)} + \mathrm{Mn^{2+}(0.40\,M)} \quad E^{\mathrm{o}}_{\text{cell}} = +0.76\,\mathrm{V}$

$$E_{\text{cell}} = E^{\mathrm{o}}_{\text{cell}} - \frac{0.0592}{n}\log\frac{\left[\mathrm{Cr^{2+}}\right]^2\left[\mathrm{Mn^{2+}}\right]}{\left[\mathrm{Cr^{3+}}\right]^2} = +0.76\,\mathrm{V} - \frac{0.0592}{2}\log\frac{(0.25)^2(0.40)}{(0.35)^2} = +0.78\,\mathrm{V}$$

(b) Oxidation: $\{\mathrm{Mg(s)} \rightarrow \mathrm{Mg^{2+}(0.016M)} + 2\mathrm{e^-}\}\ \times 3 \qquad -E^{\mathrm{o}} = +2.356\,\mathrm{V}$

Reduction: $\{\left[\mathrm{Al(OH)_4}\right]^-(0.25\mathrm{M}) + 3\ \mathrm{e^-} \rightarrow 4\mathrm{OH^-}(0.042\ \mathrm{M}) + \mathrm{Al(s)}\} \times 2;\ E^{\mathrm{o}} = -2.310\,\mathrm{V}$

Net: $3\ \mathrm{Mg(s)} + 2[\mathrm{Al(OH)_4}]^-(0.25\mathrm{M}) \rightarrow 3\mathrm{Mg^{2+}}(0.016\ \mathrm{M}) + 8\mathrm{OH^-}(0.042\mathrm{M}) + 2\mathrm{Al(s)};$

$E^{\mathrm{o}}_{\text{cell}} = +0.046\,\mathrm{V}$

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0592}{6}\log\frac{\left[\text{Mg}^{2+}\right]^3\left[\text{OH}^-\right]^8}{\left[\left[\text{Al(OH)}_4\right]^-\right]^2} = +0.046 - \frac{0.0592}{6}\log\frac{(0.016)^3(0.042)^8}{(0.25)^2}$$

$$= 0.046\text{ V} + 0.150\text{ V} = 0.196\text{ V}$$

39. **(M)** All these observations can be understood in terms of the procedure we use to balance half-equations: the ion—electron method.

(a) The reactions for which E depends on pH are those that contain either $\text{H}^+(\text{aq})$ or $\text{OH}^-(\text{aq})$ in the balanced half-equation. These reactions involve oxoacids and oxoanions whose central atom changes oxidation state.

(b) $\text{H}^+(\text{aq})$ will inevitably be on the left side of the reduction of an oxoanion because reduction is accompanied by not only a decrease in oxidation state, but also by the loss of oxygen atoms, as in $\text{ClO}_3^- \rightarrow \text{ClO}_2^-$, $\text{SO}_4^{2-} \rightarrow \text{SO}_2$, and $\text{NO}_3^- \rightarrow \text{NO}$. These oxygen atoms appear on the right-hand side as H_2O molecules. The hydrogens that are added to the right-hand side with the water molecules are then balanced with $\text{H}^+(\text{aq})$ on the left-hand side.

(c) If a half-reaction with $\text{H}^+(\text{aq})$ ions present is transferred to basic solution, it may be re-balanced by adding to each side $\text{OH}^-(\text{aq})$ ions equal in number to the $\text{H}^+(\text{aq})$ originally present. This results in $\text{H}_2\text{O(l)}$ on the side that had $\text{H}^+(\text{aq})$ ions (the left side in this case) and $\text{OH}^-(\text{aq})$ ions on the other side (the right side.)

40. **(M)** Oxidation: $2\text{Cl}^-(\text{aq}) \rightarrow \text{Cl}_2(\text{g}) + 2\text{e}^-$ $\quad -E^{\circ} = -1.358\text{V}$

Reduction: $\text{PbO}_2(\text{s}) + 4\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{Pb}^{2+}(\text{aq}) + 2\text{H}_2\text{O(l)}$ $\quad E^{\circ} = +1.455\text{V}$

Net: $\text{PbO}_2(\text{s}) + 4\text{H}^+(\text{aq}) + 2\text{Cl}^-(\text{aq}) \rightarrow \text{Pb}^{2+}(\text{aq}) + 2\text{H}_2\text{O(l)} + \text{Cl}_2(\text{g})$; $E^{\circ}_{\text{cell}} = +0.097\text{ V}$

We derive an expression for E_{cell} that depends on just the changing $\left[\text{H}^+\right]$.

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0592}{2}\log\frac{P\{\text{Cl}_2\}[\text{Pb}^{2+}]}{[\text{H}^+]^4[\text{Cl}^-]^2} = +0.097 - 0.0296\log\frac{(1.00\text{ atm})(1.00\text{ M})}{[\text{H}^+]^4(1.00)^2}$$

$$= +0.097 + 4\times 0.0296\log[\text{H}^+] = +0.097 + 0.118\log[\text{H}^+] = +0.097 - 0.118\text{ pH}$$

(a) $E_{\text{cell}} = +0.097 + 0.118\ \log(6.0) = +0.189\text{ V}$

$\therefore$ Forward reaction is spontaneous under standard conditions

(b) $E_{\text{cell}} = +0.097 + 0.118\ \log(1.2) = +0.106\text{ V}$

$\therefore$ Forward reaction is spontaneous under standard conditions

(c) $E_{\text{cell}} = +0.097 - 0.118 \times 4.25 = -0.405 \text{ V}$

$\therefore$ Forward reaction is nonspontaneous under standard conditions

The reaction is spontaneous in strongly acidic solutions (very low pH), but is nonspontaneous under standard conditions in basic, neutral, and weakly acidic solutions.

41. **(M)** Oxidation: $\text{Zn(s)} \rightarrow \text{Zn}^{2+}\text{(aq)} + 2\,\text{e}^-$ $\quad -E^\circ = +0.763\,\text{V}$

Reduction: $\text{Cu}^{2+}\text{(aq)} + 2\,\text{e}^- \rightarrow \text{Cu(s)}$ $\quad E^\circ = +0.337\,\text{V}$

Net: $\text{Zn(s)} + \text{Cu}^{2+}\text{(aq)} \rightarrow \text{Cu(s)} + \text{Zn}^{2+}\text{(aq)}$ $\quad E^\circ_{\text{cell}} = +1.100\,\text{V}$

(a) We set $E = 0.000\text{V}$, $[\text{Zn}^{2+}] = 1.00\text{M}$, and solve for $[\text{Cu}^{2+}]$ in the Nernst equation.

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0592}{2}\log\frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}; \quad 0.000 = 1.100 - 0.0296\,\log\frac{1.0\,\text{M}}{[\text{Cu}^{2+}]}$$

$$\log\frac{1.0\,\text{M}}{[\text{Cu}^{2+}]} = \frac{0.000 - 1.100}{-0.0296} = 37.2; \quad [\text{Cu}^{2+}] = 10^{-37.2} = 6 \times 10^{-38}\,\text{M}$$

(b) If we work the problem the other way, by assuming initial concentrations of $[\text{Cu}^{2+}]_{initial} = 1.0\,\text{M}$ and $[\text{Zn}^{2+}]_{initial} = 0.0\,\text{M}$, we obtain $[\text{Cu}^{2+}]_{final} = 6 \times 10^{-38}\,\text{M}$ and $[\text{Zn}^{2+}]_{final} = 1.0\,\text{M}$. Thus, we would conclude that this reaction goes to completion.

42. **(M)** Oxidation: $\text{Sn(s)} \rightarrow \text{Sn}^{2+}\text{(aq)} + 2\,\text{e}^-$ $\quad -E^\circ = +0.137\text{ V}$

Reduction: $\text{Pb}^{2+}\text{(aq)} + 2\,\text{e}^- \rightarrow \text{Pb(s)}$ $\quad E^\circ = -0.125\text{ V}$

Net: $\text{Sn(s)} + \text{Pb}^{2+}\text{(aq)} \rightarrow \text{Sn}^{2+}\text{(aq)} + \text{Pb(s)}$ $\quad E^\circ_{\text{cell}} = +0.012\,\text{V}$

Now we wish to find out if $\text{Pb}^{2+}\text{(aq)}$ will be completely displaced, that is, will $[\text{Pb}^{2+}]$ reach 0.0010 M, if $[\text{Sn}^{2+}]$ is fixed at 1.00 M? We use the Nernst equation to determine if the cell voltage still is positive under these conditions.

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0592}{2}\log\frac{[\text{Sn}^{2+}]}{[\text{Pb}^{2+}]} = +0.012 - \frac{0.0592}{2}\log\frac{1.00}{0.0010} = +0.012 - 0.089 = -0.077\text{ V}$$

The negative cell potential tells us that this reaction will not go to completion under the conditions stated. The reaction stops being spontaneous when $E_{\text{cell}} = 0$. We can work this the another way as well: assume that $[\text{Pb}^{2+}] = (1.0 - x)\,\text{M}$ and calculate $[\text{Sn}^{2+}] = x\text{ M}$ at equilibrium, that is,

where $E_{\text{cell}} = 0$. $\quad E_{\text{cell}} = 0.00 = E^\circ_{\text{cell}} - \dfrac{0.0592}{2}\log\dfrac{[\text{Sn}^{2+}]}{[\text{Pb}^{2+}]} = +0.012 - \dfrac{0.0592}{2}\log\dfrac{x}{1.0 - x}$

$$\log\frac{x}{1.0-x}=\frac{2\times 0.012}{0.0592}=0.41 \quad x=10^{0.41}(1.0-x)=2.6-2.6x \quad x=\frac{2.6}{3.6}=0.72\text{ M}$$

We would expect the final $[\text{Sn}^{2+}]$ to equal 1.0 M (or at least 0.999 M) if the reaction went to completion. Instead it equals 0.72 M and consequently, the reaction fails to go to completion.

43. **(M) (a)** The two half-equations and the cell equation are given below. $E^{\circ}_{\text{cell}}=0.000\text{ V}$

Oxidation: $H_2(g)\rightarrow 2\,H^+(0.65\text{ M KOH})+2e^-$

Reduction: $2H^+(1.0\text{ M})+2\,e^-\rightarrow H_2(g)$

Net: $2H^+(1.0\text{ M})\rightarrow 2H^+(0.65\text{ M KOH})$

$$[H^+]_{\text{base}}=\frac{K_w}{[OH^-]}=\frac{1.00\times10^{-14}\text{ M}^2}{0.65\text{ M}}=1.5\times10^{-14}\text{ M}$$

$$E_{\text{cell}}=E^{\circ}_{\text{cell}}-\frac{0.0592}{2}\log\frac{[H^+]^2_{\text{base}}}{[H^+]^2_{\text{acid}}}=0.000-\frac{0.0592}{2}\log\frac{(1.5\times10^{-14})^2}{(1.0)^2}=+0.818\text{ V}$$

(b) For the reduction of $H_2O(l)$ to $H_2(g)$ in basic solution, $2\,H_2O(l)+2\,e^-\rightarrow 2\,H_2(g)+2\,OH^-(aq)$, $E^{\circ}=-0.828\text{ V}$. This reduction is the reverse of the reaction that occurs in the anode of the cell described, with one small difference: in the standard half-cell, $[OH^-]$ = 1.00 M, while in the anode half-cell in the case at hand, $[OH^-]$ = 0.65 M. Or, viewed in another way, in 1.00 M KOH, $[H^+]$ is smaller still than in 0.65 M KOH. The forward reaction (dilution of H^+) should be even more spontaneous, (i.e. a more positive voltage will be created), with 1.00 M KOH than with 0.65 M KOH. We expect that E°_{cell} (1.000 M NaOH) should be a little larger than E_{cell} (0.65 M NaOH), which, is in fact, the case.

44. **(M) (a)** Because $NH_3(aq)$ is a weaker base than KOH(aq), $[OH^-]$ will be smaller than in the previous problem. Therefore the $[H^+]$ will be higher. Its logarithm will be less negative, and the cell voltage will be less positive. Or, viewed as in Exercise 41(b), the difference in $[H^+]$ between 1.0 M H^+ and 0.65 M KOH is greater than the difference in $[H^+]$ between 1.0 M H^+ and 0.65 M NH_3. The forward reaction is "less spontaneous" and E_{cell} is less positive.

(b)

Reaction:	$NH_3(aq)+H_2O(l)$	$\rightleftharpoons$	$NH_4^+(aq)+$	$OH^-(aq)$
Initial:	0.65M		0 M	$\approx 0\text{ M}$
Changes:	$-x\text{ M}$		$+x\text{M}$	$+x\text{ M}$
Equil:	$(0.65-x)\text{M}$		$x\text{ M}$	$x\text{ M}$

$$K_b=\frac{[NH_4^+][OH^-]}{[NH_3]}=1.8\times10^{-5}=\frac{x\cdot x}{0.65-x}\approx\frac{x^2}{0.65}$$

$$x=[OH^-]=\sqrt{0.65\times1.8\times10^{-5}}=3.4\times10^{-3}\text{ M};\qquad [H_3O^+]=\frac{1.00\times10^{-14}}{3.4\times10^{-3}}=2.9\times10^{-12}\text{ M}$$

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0592}{2}\log\frac{[\text{H}^+]^2_{\text{base}}}{[\text{H}^+]^2_{\text{acid}}} = 0.000 - \frac{0.0592}{2}\ \log\frac{(2.9\times10^{-12})^2}{(1.0)^2} = +0.683\ \text{V}$$

45. **(M)** First we need to find $\left[\text{Ag}^+\right]$ in a saturated solution of Ag_2CrO_4.

$$K_{\text{sp}} = \left[\text{Ag}^+\right]^2\left[\text{CrO}_4^{2-}\right] = (2s)^2(s) = 4s^3 = 1.1\times10^{-12} \quad s = \sqrt[3]{\frac{1.1\times10^{-12}}{4}} = 6.5\times10^{-5}\ \text{M}$$

The cell diagrammed is a concentration cell, for which $E^{\circ}_{\text{cell}} = 0.000\,\text{V}$, $n = 1$,
$\left[\text{Ag}^+\right]_{\text{anode}} = 2s = 1.3\times10^{-4}\text{M}$

Cell reaction: $\text{Ag(s)} + \text{Ag}^+(0.125\ \text{M}) \rightarrow \text{Ag(s)} + \text{Ag}^+\left(1.3\times10^{-4}\text{M}\right)$

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0592}{1}\ \log\frac{1.3\times10^{-4}\text{M}}{0.125\ \text{M}} = 0.000 + 0.177\ \text{V} = 0.177\ \text{V}$$

46. **(M)** First we need to determine $\left[\text{Ag}^+\right]$ in the saturated solution of Ag_3PO_4.
The cell diagrammed is a concentration cell, for which $E^{\circ}_{\text{cell}} = 0.000\text{V}$, $n = 1$.
Cell reaction: $\text{Ag(s)} + \text{Ag}^+(0.140\ \text{M}) \rightarrow \text{Ag(s)} + \text{Ag}^+(x\ \text{M})$

$$E_{\text{cell}} = 0.180\text{V} = E^{\circ}_{\text{cell}} - \frac{0.0592}{1}\log\frac{x\ \text{M}}{0.140\ \text{M}}; \quad \log\frac{x\ \text{M}}{0.140\text{M}} = \frac{0.180}{-0.0592} = -3.04$$

$$x\text{M} = 0.140\ \text{M}\times10^{-3.04} = 0.140\ \text{M}\times9.1\times10^{-4} = 1.3\times10^{-4}\ \text{M} = \left[\text{Ag}^+\right]_{\text{anode}}$$

$$K_{\text{sp}} = \left[\text{Ag}^+\right]^3\left[\text{PO}_4^{3-}\right] = (3s)^3(s) = \left(1.3\times10^{-4}\right)^3\left(1.3\times10^{-4}\div3\right) = 9.5\times10^{-17}$$

47. **(D) (a)** Oxidation: $\text{Sn(s)} \rightarrow \text{Sn}^{2+}(0.075\ \text{M}) + 2\ \text{e}^-$ $\qquad -E^{\circ} = +0.137\ \text{V}$

Reduction: $\text{Pb}^{2+}(0.600\ \text{M}) + 2\ \text{e}^- \rightarrow \text{Pb(s)}$ $\qquad E^{\circ} = -0.125\ \text{V}$

Net: $\text{Sn(s)} + \text{Pb}^{2+}(0.600\text{M}) \rightarrow \text{Pb(s)} + \text{Sn}^{2+}(0.075\ \text{M}); E^{\circ}_{\text{cell}} = +0.012\text{V}$

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0592}{2}\ \log\frac{\left[\text{Sn}^{2+}\right]}{\left[\text{Pb}^{2+}\right]} = 0.012 - 0.0296\ \log\frac{0.075}{0.600} = 0.012 + 0.027 = 0.039\ \text{V}$$

(b) As the reaction proceeds, $[\text{Sn}^{2+}]$ increases while $[\text{Pb}^{2+}]$ decreases. These changes cause the driving force behind the reaction to steadily decrease with the passage of time. This decline in driving force is manifested as a decrease in E_{cell} with time.

(c) When $\left[\text{Pb}^{2+}\right] = 0.500\,\text{M} = 0.600\,\text{M} - 0.100\,\text{M}$, $\left[\text{Sn}^{2+}\right] = 0.075\text{M} + 0.100\ \text{M}$, because the stoichiometry of the reaction is 1:1 for Sn^{2+} and Pb^{2+}.

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0592}{2}\log\frac{\left[\text{Sn}^{2+}\right]}{\left[\text{Pb}^{2+}\right]} = 0.012 - 0.0296\log\frac{0.175}{0.500} = 0.012 + 0.013 = 0.025\ \text{V}$$

(d)

Reaction:	Sn(s) +	$Pb^{2+}(aq)$	$\rightarrow$	$Pb(s)$	+	$Sn^{2+}(aq)$
Initial:	—	0.600 M		—		0.075 M
Changes:	—	$-x$ M		—		$+x$ M
Final:	—	$(0.600-x)$ M		—		$(0.075+x)$ M

$$E_{\text{cell}} = E^{\text{o}}_{\text{cell}} - \frac{0.0592}{2}\log\frac{[Sn^{2+}]}{[Pb^{2+}]} = 0.020 = 0.012 - 0.0296\log\frac{0.075+x}{0.600-x}$$

$$\log\frac{0.075+x}{0.600-x} = \frac{E_{\text{cell}}-0.012}{-0.0296} = \frac{0.020-0.012}{-0.0296} = -0.27;\ \frac{0.075+x}{0.600-x} = 10^{-0.27} = 0.54$$

$$0.075+x = 0.54(0.600-x) = 0.324-0.54x;\ x = \frac{0.324-0.075}{1.54} = 0.162\text{ M}$$

$$[Sn^{2+}] = 0.075+0.162 = 0.237\text{ M}$$

(e) Here we use the expression developed in part (d).

$$\log\frac{0.075+x}{0.600-x} = \frac{E_{\text{cell}}-0.012}{-0.0296} = \frac{0.000-0.012}{-0.0296} = +0.41$$

$$\frac{0.075+x}{0.600-x} = 10^{+0.41} = 2.6;\quad 0.075+x = 2.6(0.600-x) = 1.6-2.6x$$

$$x = \frac{1.6-0.075}{3.6} = 0.42\text{ M}$$

$$[Sn^{2+}] = 0.075+0.42 = 0.50\text{ M};\qquad [Pb^{2+}] = 0.600-0.42 = 0.18\text{ M}$$

48. **(D) (a)** Oxidation: $Ag(s) \rightarrow Ag^{+}(0.015\text{ M}) + e^{-}$ $\qquad -E^{\text{o}} = -0.800\text{ V}$

Reduction: $Fe^{3+}(0.055\text{ M}) + e^{-} \rightarrow Fe^{2+}(0.045\text{ M})$ $\qquad E^{\text{o}} = +0.771\text{V}$

Net: $Ag(s) + Fe^{3+}(0.055\text{ M}) \rightarrow Ag^{+}(0.015\text{ M}) + Fe^{2+}(0.045\text{ M})$ $\quad E^{\text{o}}_{\text{cell}} = -0.029\text{V}$

$$E_{\text{cell}} = E^{\text{o}}_{\text{cell}} - \frac{0.0592}{1}\log\frac{[Ag^{+}][Fe^{2+}]}{[Fe^{3+}]} = -0.029 - 0.0592\log\frac{0.015\times0.045}{0.055}$$

$$= -0.029\text{ V} + 0.113\text{ V} = +0.084\text{V}$$

(b) As the reaction proceeds, $[Ag^{+}]$ and $[Fe^{2+}]$ will increase, while $[Fe^{3+}]$ decrease. These changes cause the driving force behind the reaction to steadily decrease with the passage of time. This decline in driving force is manifested as a decrease in E_{cell} with time.

(c) When $[Ag^{+}] = 0.020\text{M} = 0.015\text{M} + 0.005\text{M}$, $[Fe^{2+}] = 0.045\text{M} + 0.005\text{M} = 0.050\text{M}$ and $[Fe^{3+}] = 0.055\text{ M} - 0.005\text{M} = 0.500\text{M}$, because, by the stoichiometry of the reaction, a mole of Fe^{2+} is produced and a mole of Fe^{3+} is consumed for every mole of Ag^{+} produced.

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0592}{1}\log\frac{[\text{Ag}^+][\text{Fe}^{2+}]}{[\text{Fe}^{3+}]} = -0.029 - 0.0592\log\frac{0.020\times 0.050}{0.050}$$
$$= -0.029\text{ V} + 0.101\text{ V} = +0.072\text{ V}$$

(d) Reaction: $\text{Ag(s)} + \text{Fe}^{3+}(0.055\text{ M}) \rightleftharpoons \text{Ag}^+(0.015\text{ M}) + \text{Fe}^{2+}(0.045\text{ M})$

Initial:	0.055 M	0.015 M	0.045 M
Changes:	$-x$ M	$+x$ M	$+x$ M
Final:	$(0.055-x)$ M	$(0.015+x)$ M	$(0.045+x)$ M

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0592}{1}\log\frac{[\text{Ag}^+][\text{Fe}^{2+}]}{[\text{Fe}^{3+}]} = -0.029 - 0.0592\log\frac{(0.015+x)(0.045+x)}{(0.055-x)}$$

$$\log\frac{(0.015+x)(0.045+x)}{(0.055-x)} = \frac{E_{\text{cell}}+0.029}{-0.0592} = \frac{0.010+0.029}{-0.0592} = -0.66$$

$$\frac{(0.015+x)(0.045+x)}{(0.055-x)} = 10^{-0.66} = 0.22$$

$$0.00068 + 0.060x + x^2 = 0.22(0.055-x) = 0.012 - 0.22x \qquad x^2 + 0.28x - 0.011 = 0$$

$$x = \frac{-b\pm\sqrt{b^2-4ac}}{2a} = \frac{-0.28\pm\sqrt{(0.28)^2+4\times 0.011}}{2} = 0.035\text{ M}$$

$[\text{Ag}^+] = 0.015\text{ M} + 0.035\text{ M} = 0.050\text{ M}$

$[\text{Fe}^{2+}] = 0.045\text{ M} + 0.035\text{ M} = 0.080\text{ M}$

$[\text{Fe}^{3+}] = 0.055\text{ M} - 0.035\text{ M} = 0.020\text{ M}$

(e) We use the expression that was developed in part (d).

$$\log\frac{(0.015+x)(0.045+x)}{(0.055-x)} = \frac{E_{\text{cell}}+0.029}{-0.0592} = \frac{0.000+0.029}{-0.0592} = -0.49$$

$$\frac{(0.015+x)(0.045+x)}{(0.055-x)} = 10^{-0.49} = 0.32$$

$$0.00068 + 0.060x + x^2 = 0.32(0.055-x) = 0.018 - 0.32x \qquad x^2 + 0.38x - 0.017 = 0$$

$$x = \frac{-b\pm\sqrt{b^2-4ac}}{2a} = \frac{-0.38\pm\sqrt{(0.38)^2+4\times 0.017}}{2} = 0.040\text{ M}$$

$[\text{Ag}^+] = 0.015\text{ M} + 0.040\text{ M} = 0.055\text{ M}$

$[\text{Fe}^{2+}] = 0.045\text{ M} + 0.040\text{ M} = 0.085\text{ M}$

$[\text{Fe}^{3+}] = 0.055\text{ M} - 0.040\text{ M} = 0.015\text{ M}$

49. **(M)** First we will need to come up with a balanced equation for the overall redox reaction. Clearly, the reaction must involve the oxidation of $Cl^-(aq)$ and the reduction of $Cr_2O_7^{2-}(aq)$:

$14\ H^+(aq) + Cr_2O_7^{2-}(aq) + 6\ e^- \rightarrow 2\ Cr^{3+}(aq) + 7\ H_2O(l)$ $\qquad E°_{1/2red} = 1.33$ V
$\{Cl^-(aq) \rightarrow 1/2\ Cl_2(g) + 1\ e^-\} \times 6$ $\qquad E°_{1/2ox} = -1.358$ V

$14\ H^+(aq) + Cr_2O_7^{2-}(aq) + 6\ Cl^-(aq) \rightarrow 2\ Cr^{3+}(aq) + 7\ H_2O(l) + 3\ Cl_2(g)$ $E°_{cell} = -0.03$ V

A negative cell potential means, the oxidation of $Cl^-(aq)$ to $Cl_2(g)$ by $Cr_2O_7^{2-}(aq)$ at standard conditions will not occur spontaneously. We could obtain some $Cl_2(g)$ from this reaction by driving it to the product side with an external voltage. In other words, the reverse reaction is the spontaneous reaction at standard conditions and if we want to produce some $Cl_2(g)$ from the system, we must push the non-spontaneous reaction in its forward direction with an external voltage, (i.e., a DC power source). Since $E°_{cell}$ is only slightly negative, we could also drive the reaction by removing products as they are formed and replenishing reactants as they are consumed.

50. **(D)** We proceed by first deriving a balanced equation for the reaction occurring in the cell:
Oxidation: $Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$
Reduction: $\{Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)\} \times 2$

Net: $Fe(s) + 2Fe^{3+}(aq) \rightarrow 3Fe^{2+}(aq)$

(a) ΔG^o and the equilibrium constant K_{eq} can be calculated using

$$\Delta G^o = -nFE^o_{cell} = -RT\ln K_{eq}:$$

$$\Delta G^o = -nFE^o_{cell} = -2 \times 96485\text{Cmol}^{-1} \times 1.21\text{V} = -233.5\text{kJmol}^{-1}$$

$$\Delta G^o = -RT\ln K = -8.314\text{JK}^{-1}\text{mol}^{-1} \times 298.15\text{K} \times \ln K = -233.5 \times 1000\text{Jmol}^{-1}$$

$$\ln K = 94.2 \Rightarrow K = e^{94.2} = 8.1 \times 10^{40}$$

(b) Before calculating voltage using the Nernst equation, we need to re-write the net reaction to take into account concentration gradient for $Fe^{2+}(aq)$:
Oxidation: $Fe(s) \rightarrow Fe^{2+}(aq, 1.0 \times 10^{-3}M) + 2e^-$
Reduction: $\{Fe^{3+}(aq, 1.0 \times 10^{-3}M) + e^- \rightarrow Fe^{2+}(aq, 0.10M)\} \times 2$

Net: $Fe(s) + 2Fe^{3+}(aq, 1.0 \times 10^{-3}) \rightarrow Fe^{2+}(aq, 1.0 \times 10^{-3}M) + 2Fe^{2+}(aq, 0.10M)$
Therefore,

$$Q = \frac{1.0 \times 10^{-3} \times (0.10)^2}{(1.0 \times 10^{-3})^2} = 10$$

Now, we can apply the Nerst equation to calculate the voltage:

$$E_{cell} = E^o_{cell} - \frac{0.0592}{n}\log(Q) = 1.21\text{ V} - \frac{0.0592}{2}\log 10 = 1.18\text{ V}$$

(c) From parts (a) and (b) we can conclude that the reaction between Fe(s) and $Fe^{3+}(aq)$ is spontaneous. The reverse reaction (i.e. disproportionation of $Fe^{2+}(aq)$) must therefore be nonspontaneous.

Batteries and Fuel Cells

51. **(M)** *Stepwise approach:*

(a) The cell diagram begins with the anode and ends with the cathode.
Cell diagram: $\mathrm{Cr(s)|Cr^{2+}(aq),Cr^{3+}(aq)||Fe^{2+}(aq),Fe^{3+}(aq)|Fe(s)}$

(b) Oxidation: $\mathrm{Cr^{2+}(aq) \rightarrow Cr^{3+}(aq) + e^-}$ $\qquad -E^\circ = +0.424\,\mathrm{V}$

Reduction: $\mathrm{Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)}$ $\qquad E^\circ = +0.771\,\mathrm{V}$

Net: $\mathrm{Cr^{2+}(aq) + Fe^{3+}(aq) \rightarrow Cr^{3+}(aq) + Fe^{2+}(aq)}$ $\qquad E^\circ_{\mathrm{cell}} = +1.195\,\mathrm{V}$

Conversion pathway approach:

$\mathrm{Cr(s)|Cr^{2+}(aq),Cr^{3+}(aq)||Fe^{2+}(aq),Fe^{3+}(aq)|Fe(s)}$

$-E^\circ = +0.424\,\mathrm{V} \qquad E^\circ = +0.771\,\mathrm{V}$

$E^\circ_{\mathrm{cell}} = +0.424V + 0.771V = +1.195V$

52. **(M) (a)** Oxidation: $\mathrm{Zn(s) \rightarrow Zn^{2+}(aq) + 2\,e^-}$ $\qquad -E^\circ = +0.763\,\mathrm{V}$

Reduction: $\mathrm{2MnO_2(s) + H_2O(l) + 2\,e^- \rightarrow Mn_2O_3(s) + 2OH^-(aq)}$

Acid-base: $\mathrm{\{NH_4^+(aq) + OH^-(aq) \rightarrow NH_3(g) + H_2O(l)\}}$ $\qquad \times 2$

Complex: $\mathrm{Zn^{2+}(aq) + 2NH_3(aq) + 2Cl^-(aq) \rightarrow \left[Zn(NH_3)_2\right]Cl_2(s)}$

Net: $\mathrm{Zn(s) + 2\,MnO_2(s) + 2\,NH_4^+(aq) + 2\,Cl^-(aq) \rightarrow Mn_2O_3(s) + H_2O(l) + [Zn(NH_3)_2]Cl_2(s)}$

(b) $\Delta G^\circ = -nFE^\circ_{\mathrm{cell}} = -\left(2\ \mathrm{mol\ e^-}\right)\left(96485\ \mathrm{C/mol\ e^-}\right)\left(1.55\ \mathrm{V}\right) = -2.99\times10^5\,\mathrm{J/mol}$

This is the standard free energy change for the entire reaction, which is composed of the four reactions in part (a). We can determine the values of ΔG° for the acid-base and complex formation reactions by employing the appropriate data from Appendix D and $\mathrm{p}K_f = -4.81$ (the negative log of the K_f for $\mathrm{[Zn(NH_3)_2]^{2+}}$).

$$\Delta G^\circ_{\mathrm{a-b}} = -RT\ln K_\mathrm{b}^{\,2} = -\left(8.3145\ \mathrm{J\ mol^{-1}\ K^{-1}}\right)\left(298.15\ \mathrm{K}\right)\ln\left(1.8\times10^{-5}\right)^2 = 5.417\times10^4\ \mathrm{J/mol}$$

$$\Delta G^\circ_{\mathrm{cmplx}} = -RT\ln K_f = -\left(8.3145\,\mathrm{J\ mol^{-1}\ K^{-}}\right)\left(298.15\ \mathrm{K}\right)\ln\left(10^{4.81}\right) = -2.746\times10^4\ \mathrm{J/mol}$$

Then $\Delta G^\circ_{\mathrm{total}} = \Delta G^o_{\mathrm{redox}} + \Delta G^o_{\mathrm{a-b}} + \Delta G^\circ_{\mathrm{cmplx}}$ $\qquad \Delta G^o_{\mathrm{redox}} = \Delta G^\circ_{\mathrm{total}} - \Delta G^o_{\mathrm{a-b}} - \Delta G^\circ_{\mathrm{cmplx}}$

$$= -2.99\times10^5\ \mathrm{J/mol} - 5.417\times10^4 + 2.746\times10^4\ \mathrm{J/mol} = -3.26\times10^5\ \mathrm{J/mol}$$

Thus, the voltage of the redox reactions alone is

$$E^\circ = \frac{-3.26\times10^5\,\mathrm{J}}{-2\mathrm{mol\ e^-}\times 96485\ \mathrm{C/mol\ e^-}} = 1.69\ \mathrm{V} \qquad 1.69\mathrm{V} = +0.763\mathrm{V} + E^\circ\left\{\mathrm{MnO_2/Mn_2O_3}\right\}$$

$$E^\circ\left\{\mathrm{MnO_2/Mn_2O_3}\right\} = 1.69\mathrm{V} - 0.763\mathrm{V} = +0.93\mathrm{V}$$

The electrode potentials were calculated by using equilibrium constants from Appendix D. These calculations do not take into account the cell's own internal resistance to the flow of electrons, which makes the actual voltage developed by the electrodes less than the theoretical values derived from equilibrium constants. Also because the solid species (other than Zn) do not appear as compact rods, but rather are dispersed in a paste, and since very little water is present in the cell, the activities for the various species involved in the electrochemical reactions will deviate markedly from unity. As a result, the equilibrium constants for the reactions taking place in the cell will be substantially different from those provided in Appendix D, which apply only to dilute solutions and reactions involving solid reactants and products that posses small surface areas. The actual electrode voltages, therefore, will end up being different from those calculated here.

53. **(M) (a)** Cell reaction: $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$

$$\Delta G_{rxn}{}^{o} = 2\Delta G_f{}^{o}\left[H_2O(l)\right] = 2(-237.1\text{ kJ/mol}) = -474.2\text{ kJ/mol}$$

$$E_{\text{cell}}{}^{o} = -\frac{\Delta G^{o}}{nF} = -\frac{-474.2\times10^{3}\text{ J/mol}}{4\text{ mol e}^{-}\times96485\text{ C/mol e}^{-}} = 1.229\text{ V}$$

(b) Anode, oxidation: $\{Zn(s) \rightarrow Zn^{2+}(aq) + 2e^{-}\}\ \times 2$ $\qquad -E^{o} = +0.763V$

Cathode, reduction: $O_2(g) + 4\,H^{+}(aq) + 4e^{-} \rightarrow 2H_2O(l)$ $\qquad E^{o} = +1.229\text{ V}$

Net: $2\,Zn(s) + O_2(g) + 4H^{+}(aq) \rightarrow 2\,Zn^{2+}(aq) + 2\,H_2O(l)$ $\qquad E^{o}_{\text{cell}} = +1.992\,V$

(c) Anode, oxidation: $Mg(s) \rightarrow Mg^{2+}(aq) + 2e^{-}$ $\qquad -E^{o} = +2.356\,V$

Cathode, reduction: $I_2(s) + 2e^{-} \rightarrow 2\,I^{-}(aq)$ $\qquad E^{o} = +0.535\,V$

Net: $Mg(s) + I_2(s) \rightarrow Mg^{2+}(aq) + 2\,I^{-}(aq)$ $\qquad E^{o}_{\text{cell}} = +2.891\,V$

54. **(M) (a)** Oxidation: $Zn(s) \rightleftharpoons Zn^{2+}(aq) + 2\,e^{-}$

Precipitation: $Zn^{2+}(aq) + 2\,OH^{-}(aq) \rightleftharpoons Zn(OH)_2(s)$

Reduction: $2\,MnO_2(s) + H_2)(l) + 2\,e^{-} \rightleftharpoons Mn_2O_3(s) + 2\,OH^{-}(aq)$

Net : $Zn(s) + 2\,MnO_2(s) + H_2O(l) + 2\,OH^{-}(aq) \rightleftharpoons Mn_2O_3(s) + Zn(OH)_2(s)$

(b) In 50, we determined that the standard voltage for the reduction reaction is +0.93 V ($n = 2\,e^{-}$). To convert this voltage to an equilibrium constant (at 25 °C) use:

$$\log K_{\text{red}} = \frac{nE^{o}}{0.0592} = \frac{2(0.93)}{0.0592} = 31.\underline{4}; \qquad K_{\text{red}} = 10^{31.42} = 3\times10^{31}$$

and for $Zn(s) \rightleftharpoons Zn^{2+}(aq) + 2\,e^{-}$ ($E° = 0.763$ V and $n = 2\,e^{-}$)

$$\log K_{\text{ox}} = \frac{nE^{o}}{0.0592} = \frac{2(0.763)}{0.0592} = 25.\underline{8}; \qquad K_{\text{ox}} = 10^{25.78} = 6\times10^{25}$$

$$\Delta G^{\circ}_{\text{total}} = \Delta G^{\circ}_{\text{precipitation}} + \Delta G^{\circ}_{\text{oxidation}} + \Delta G^{\circ}_{\text{reduction}}$$

$$\Delta G^{\circ}_{\text{total}} = -RT\ln\frac{1}{K_{\text{sp, Zn(OH)}_2}} + (-RT\ln K_{\text{ox}}) + (-RT\ln K_{\text{red}})$$

$$\Delta G^\circ_{\text{total}} = -RT\,(\ln \frac{1}{K_{\text{sp, Zn(OH)}_2}} + \ln K_{\text{ox}} + \ln K_{\text{red}})$$

$$\Delta G^\circ_{\text{total}} = -0.0083145 \frac{\text{kJ}}{\text{K mol}} (298\text{ K})\,(\ln \frac{1}{1.2\times10^{-17}} + \ln(6.0\times10^{25}) + \ln(2.6\times10^{31}))$$

$$\Delta G^\circ_{\text{total}} = -423\text{ kJ} = -nFE^\circ_{\text{total}}$$

Hence, $E^\circ_{\text{total}} = E^\circ_{\text{cell}} = \dfrac{-423\times10^3\text{ J}}{-(2\text{ mol})(96485\text{ C mol}^{-1})} = 2.19\text{ V}$

55. **(M)** Aluminum-Air Battery: $2\text{ Al(s)} + 3/2\text{ O}_2\text{(g)} \rightarrow \text{Al}_2\text{O}_3\text{(s)}$
Zinc-Air Battery: $\text{Zn(s)} + ½\text{ O}_2\text{(g)} \rightarrow \text{ZnO(s)}$
Iron-Air Battery $\text{Fe(s)} + ½\text{ O}_2\text{(g)} \rightarrow \text{FeO(s)}$
Calculate the quantity of charge transferred when 1.00 g of metal is consumed in each cell.

Aluminum-Air Cell:

$$1.00\text{ g Al(s)}\times\frac{1\text{ mol Al(s)}}{26.98\text{ g Al(s)}}\times\frac{3\text{ mol e}^-}{1\text{ mol Al(s)}}\times\frac{96{,}485\text{C}}{1\text{ mol e}^-}=1.07\times10^4\text{ C}$$

Zinc-Air Cell:

$$1.00\text{ g Zn(s)}\times\frac{1\text{ mol Zn(s)}}{65.39\text{ g Zn(s)}}\times\frac{2\text{ mol e}^-}{1\text{ mol Zn(s)}}\times\frac{96{,}485\text{ C}}{1\text{ mol e}^-}=2.95\times10^3\text{ C}$$

Iron-Air Cell:

$$1.00\text{ g Fe(s)}\times\frac{1\text{ mol Fe(s)}}{55.847\text{ g Fe(s)}}\times\frac{2\text{ mol e}^-}{1\text{ mol Fe(s)}}\times\frac{96{,}485\text{ C}}{1\text{ mol e}^-}=3.46\times10^3\text{ C}$$

As expected, aluminum has the greatest quantity of charge transferred per unit mass (1.00 g) of metal oxidized. This is because aluminum has the smallest molar mass and forms the most highly charged cation (3+ for aluminum vs 2+ for Zn and Fe).

56. **(M) (a)** A voltaic cell with a voltage of 0.1000 V would be possible by using two half-cells whose standard reduction potentials differ by approximately 0.10 V, such as the following pair.

Oxidation: $2\text{ Cr}^{3+}(\text{aq})+7\text{ H}_2\text{O(l)}\rightarrow\text{Cr}_2\text{O}_7{}^{2-}(\text{aq})+14\text{ H}^+(\text{aq})+6\text{ e}^-\quad -E^\circ=-1.33\text{ V}$

Reduction: $\{\text{PbO}_2(\text{s})+4\text{ H}^+(\text{aq})+2\text{e}^-\rightarrow\text{Pb}^{2+}(\text{aq})+2\text{ H}_2\text{O(l)}\}\ \times3\quad E^\circ=+1.455\text{ V}$

Net: $2\text{Cr}^{3+}(\text{aq})+3\text{PbO}_2(\text{s})+\text{H}_2\text{O(l)}\rightarrow\text{Cr}_2\text{O}_7{}^{2-}(\text{aq})+3\text{Pb}^{2+}(\text{aq})+2\text{H}^+(\text{aq})\ E^\circ_{\text{cell}}=0.12\underline{5}\text{ V}$

The voltage can be adjusted to 0.1000 V by a suitable alteration of the concentrations. $[\text{Pb}^{2+}]$ or $[\text{H}^+]$ could be increased or $[\text{Cr}^{3+}]$ could be decreased, or any combination of the three of these.

(b) To produce a cell with a voltage of 2.500 V requires that one start with two half-cells whose reduction potentials differ by about that much. An interesting pair follows.

Oxidation: $\text{Al(s)}\rightarrow\text{Al}^{3+}(\text{aq})+3\text{e}^-\qquad -E^\circ=+1.676\text{ V}$

Reduction: $\{Ag^+(aq)+e^- \rightarrow Ag(s)\} \times 3$ $E^o = +0.800\text{ V}$

Net: $Al(s)+3Ag^+(aq) \rightarrow Al^{3+}(aq)+3Ag(s)$ $E^o_{cell} = +2.476\text{ V}$

Again, the desired voltage can be obtained by adjusting the concentrations. In this case increasing $[Ag^+]$ and/or decreasing $[Al^{3+}]$ would do the trick.

(c) Since no known pair of half-cells has a potential difference larger than about 6 volts, we conclude that producing a single cell with a potential of 10.00 V is currently impossible. It is possible, however, to join several cells together into a battery that delivers a voltage of 10.00 V. For instance, four of the cells from part (b) would deliver ~10.0 V at the instant of hook-up.

57. **(M)** Oxidation (anode): $Li(s) \rightarrow Li^+(aq)+e^-$ $-E^o = +3.040V$

Reduction (cathode): $MnO_2(s)+2H_2O(l)+e^- \rightarrow Mn(OH)_3(s)+OH^-(aq)$ $E^o = -0.20V$

Net: $MnO_2(s)+2H_2O(l)+Li(s) \rightarrow Mn(OH)_3(s)+OH^-(aq)+Li^+(aq)$ $E^o_{cell} = 2.84V$

Cell diagram: $Li(s), Li^+(aq)|KOH(satd)|MnO_2(s), Mn(OH)_3(s)|$

58. **(M)** **(a)** Oxidation (anode): $Zn(s) \rightarrow Zn^{+2}(aq)+2e^-$ $-E^o = +0.763V$

Reduction (cathode): $Br_2(l)+2e^- \rightarrow 2Br^-(aq)$ $E^o = +1.065V$

Net: $Zn(s)+Br_2(l) \rightarrow Zn^{2+}(aq)+2Br^-(aq)$ $E^o_{cell} = 1.828V$

(b) Oxidation (anode): $\{Li(s) \rightarrow Li^+(aq)+e^-\} \times 2$ $-E^o = +3.040V$

Reduction (cathode): $F_2(g)+2e^- \rightarrow 2F^-(aq)$ $E^o = +2.866V$

Net: $2Li(s)+F_2(g) \rightarrow 2Li^+(aq)+2F^-(aq)$ $E^o_{cell} = 4.868V$

Electrochemical Mechanism of Corrosion

59. **(M) (a)** Because copper is a less active metal than is iron (i.e. a weaker reducing agent), this situation would be similar to that of an iron or steel can plated with a tin coating that has been scratched. Oxidation of iron metal to $Fe^{2+}(aq)$ should be enhanced in the body of the nail (blue precipitate), and hydroxide ion should be produced in the vicinity of the copper wire (pink color), which serves as the cathode.

(b) Because a scratch tears the iron and exposes "fresh" metal, it is more susceptible to corrosion. We expect blue precipitate in the vicinity of the scratch.

(c) Zinc should protect the iron nail from corrosion. There should be almost no blue precipitate; the zinc corrodes instead. The pink color of OH^- should continue to form.

60. **(M)** The oxidation process involved at the anode reaction, is the formation of $Fe^{2+}(aq)$. This occurs far below the water line. The reduction process involved at the cathode, is the formation of $OH^-(aq)$ from $O_2(g)$. It is logical that this reaction would occur at or near the water line close to the atmosphere (which contains O_2). This reduction reaction requires $O_2(g)$ from the atmosphere and $H_2O(l)$ from the water. The oxidation reaction, on the other hand simply requires iron from the pipe together with an aqueous solution into which the $Fe^{2+}(aq)$ can disperse and not build up to such a high concentration that corrosion is inhibited.

Anode, oxidation: $Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$

Cathode, reduction: $O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$

61. **(M)**During the process of corrosion, the metal that corrodes loses electrons. Thus, the metal in these instances behaves as an anode and, hence, can be viewed as bearing a latent negative polarity. One way in which we could retard oxidation of the metal would be to convert it into a cathode. Once transformed into a cathode, the metal would develop a positive charge and no longer release electrons (or oxidize). This change in polarity can be accomplished by hooking up the metal to an inert electrode in the ground and then applying a voltage across the two metals in such a way that the inert electrode becomes the anode and the metal that needs protecting becomes the cathode. This way, any oxidation that occurs will take place at the negatively charged inert electrode rather than the positively charged metal electrode.

62. **(M)** As soon as the iron and copper came into direct contact, an electrochemical cell was created, in which the more powerfully reducing metal (Fe) was oxidized. In this way, the iron behaved as a sacrificial anode, protecting the copper from corrosion. The two half-reactions and the net cell reaction are shown below:

Anode (oxidation)	$Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$	$-E° = 0.440$ V
Cathode (reduction)	$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	$E° = 0.337$ V
Net:	$Fe(s) + Cu^{2+}(aq) \rightarrow Fe^{2+}(aq) + Cu(s)$	$E°_{cell} = 0.777$ V

Note that because of the presence of iron and its electrical contact with the copper, any copper that does corrode is reduced back to the metal.

Electrolysis Reactions

63. **(M)** Here we start by calculating the total amount of charge passed and the number of moles of electrons transferred.

$$\text{mol } e^- = 75 \text{ min} \times \frac{60 \text{ s}}{1 \text{ min}} \times \frac{2.15 \text{ C}}{1 \text{ s}} \times \frac{1 \text{ mol } e^-}{96485 \text{ C}} = 0.10 \text{ mol } e^-$$

(a) $$\text{mass Zn} = 0.10 \text{ mol } e^- \times \frac{1 \text{ mol Zn}^{2+}}{2 \text{ mol } e^-} \times \frac{1 \text{ mol Zn}}{1 \text{ mol Zn}^{2+}} \times \frac{65.39 \text{ g Zn}}{1 \text{ mol Zn}} = 3.3 \text{ g Zn}$$

(b) $$\text{mass Al} = 0.10 \text{ mol } e^- \times \frac{1 \text{ mol Al}^{3+}}{3 \text{ mol } e^-} \times \frac{1 \text{ mol Al}}{1 \text{ mol Al}^{3+}} \times \frac{26.98 \text{ g Al}}{1 \text{ mol Al}} = 0.90 \text{ g Al}$$

(c) $$\text{mass Ag} = 0.10 \text{ mol } e^- \times \frac{1 \text{ mol Ag}^{+}}{1 \text{ mol } e^-} \times \frac{1 \text{ mol Ag}}{1 \text{ mol Ag}^{+}} \times \frac{107.9 \text{ g Ag}}{1 \text{ mol Ag}} = 11 \text{ g Ag}$$

(d) $$\text{mass Ni} = 0.10 \text{ mol e}^- \times \frac{1 \text{ mol Ni}^{2+}}{2 \text{ mol e}^-} \times \frac{1 \text{ mol Ni}}{1 \text{ mol Ni}^{2+}} \times \frac{58.69 \text{ g Ni}}{1 \text{ mol Ni}} = 2.9 \text{ g Ni}$$

64. **(M)** We proceed by first writing down the net electrochemical reaction. The number of moles of hydrogen produced in the reaction can be calculated from the reaction stoichiometry. Lastly, the volume of hydrogen can be determined using ideal gas law.
Stepwise approach:
The two half reactions follow: $Cu^{2+}(aq) + 2\ e^- \rightarrow Cu(s)$ and $2\ H^+(aq) + 2\ e^- \rightarrow H_2(g)$
Thus, two moles of electrons are needed to produce each mole of Cu(s) and two moles of electrons are needed to produce each mole of $H_2(g)$. With this information, we can compute the moles of $H_2(g)$ that will be produced.

$$\text{mol } H_2(g) = 3.28 \text{ g Cu} \times \frac{1 \text{ mol Cu}}{63.55 \text{ g Cu}} \times \frac{2 \text{ mol e}^-}{1 \text{ mol Cu}} \times \frac{1 \text{ mol } H_2(g)}{2 \text{ mol e}^-} = 0.0516 \text{ mol } H_2(g)$$

Then we use the ideal gas equation to find the volume of $H_2(g)$.

$$\text{Volume of } H_2(g) = \frac{0.0516 \text{ mol } H_2 \times \dfrac{0.08206 \text{ L atm}}{\text{mol K}} \times (273.2 + 28.2) \text{ K}}{763 \text{ mmHg} \times \dfrac{1 \text{ atm}}{760 \text{ mmHg}}} = 1.27 \text{ L}$$

This answer assumes the $H_2(g)$ is not collected over water, and that the $H_2(g)$ formed is the only gas present in the container (i.e. no water vapor present)
Conversion pathway approach:
$Cu^{2+}(aq) + 2\ e^- \rightarrow Cu(s)$ and $2\ H^+(aq) + 2\ e^- \rightarrow H_2(g)$

$$\text{mol } H_2(g) = 3.28 \text{ g Cu} \times \frac{1 \text{ mol Cu}}{63.55 \text{ g Cu}} \times \frac{2 \text{ mol e}^-}{1 \text{ mol Cu}} \times \frac{1 \text{ mol } H_2(g)}{2 \text{ mol e}^-} = 0.0516 \text{ mol } H_2(g)$$

$$V(H_2(g)) = \frac{0.0516 \text{ mol } H_2 \times \dfrac{0.08206 \text{ L atm}}{\text{mol K}} \times (273.2 + 28.2)\text{K}}{763 \text{ mmHg} \times \dfrac{1 \text{ atm}}{760 \text{ mmHg}}} = 1.27 \text{ L}$$

65. **(M)** Here we must determine the standard cell voltage of each chemical reaction. Those chemical reactions that have a negative voltage are the ones that require electrolysis.

(a) Oxidation: $2\,H_2O(l) \rightarrow 4H^+(aq) + O_2(g) + 4e^-$ $\quad -E^\circ = -1.229 \text{ V}$
Reduction: $\{2\,H^+(aq) + 2e^- \rightarrow H_2(g)\} \times 2$ $\quad E^\circ = 0.000 \text{ V}$

Net: $2\,H_2O(l) \rightarrow 2\,H_2(g) + O_2(g)$ $\quad E^\circ_{cell} = -1.229 \text{ V}$
This reaction requires electrolysis, with an applied voltage greater than $+1.229\text{V}$.

(b) Oxidation: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ $\quad -E^\circ = +0.763 \text{ V}$
Reduction: $Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$ $\quad E^\circ = -0.440 \text{ V}$

Net: $Zn(s)+Fe^{2+}(aq)\rightarrow Fe(s)+Zn^{2+}(aq)$ $E^{o}_{cell}=+0.323\text{ V}$

This is a spontaneous reaction under standard conditions.

(c) Oxidation: $\{Fe^{2+}(aq)\rightarrow Fe^{3+}(aq)+e^{-}\}\ \times 2$ $-E^{o}=-0.771\text{ V}$

Reduction: $I_2(s)+2e^{-}\rightarrow 2I^{-}(aq)$ $E^{o}=+0.535\text{ V}$

Net: $2Fe^{2+}(aq)+I_2(s)\rightarrow 2Fe^{3+}(aq)+2I^{-}(aq)$ $E^{o}_{cell}=-0.236\text{ V}$

This reaction requires electrolysis, with an applied voltage greater than $+0.236\text{V}$.

(d) Oxidation: $Cu(s)\rightarrow Cu^{2+}(aq)+2e^{-}$ $-E^{o}=-0.337\text{ V}$

Reduction: $\{Sn^{4+}(aq)+2e^{-}\rightarrow Sn^{2+}(aq)\}\ \times 2$ $E^{o}=+0.154\text{ V}$

Net: $Cu(s)+Sn^{4+}(aq)\rightarrow Cu^{2+}(aq)+Sn^{2+}(aq)$ $E^{o}_{cell}=-0.183\text{V}$

This reaction requires electrolysis, with an applied voltage greater than $+0.183\text{V}$.

66. **(M) (a)** Because oxidation occurs at the anode, we know that the product cannot be H_2 (H_2 is produced from the reduction of H_2O), SO_2, (which is a reduction product of $SO_4{}^{2-}$), or SO_3 (which is produced from $SO_4{}^{2-}$ without a change of oxidation state; it is the dehydration product of H_2SO_4). It is, in fact O_2 that forms at the anode. The oxidation of water at the anode produces the $O_2(g)$.

(b) Reduction should occur at the cathode. The possible species that can be reduced are H_2O to $H_2(g)$, $K^{+}(aq)$ to $K(s)$, and $SO_4^{2-}(aq)$ to perhaps $SO_2(g)$. Because potassium is a highly active metal, it will not be produced in aqueous solution. In order for $SO_4^{2-}(aq)$ to be reduced, it would have to migrate to the negatively charged cathode, which is not very probable since like charges repel each other. Thus, $H_2(g)$ is produced at the cathode.

(c) At the anode: $2H_2O(l)\rightarrow 4H^{+}(aq)+O_2(g)+4e^{-}$ $-E^{o}=-1.229\text{V}$

At the cathode: $\{2H^{+}(aq)+2e^{-}\rightarrow H_2(g)\}\ \times 2$ $E^{o}=0.000\text{V}$

Net cell reaction: $2H_2O(l)\rightarrow 2H_2(g)+O_2(g)$ $E^{o}_{cell}=-1.229\text{V}$

A voltage greater than 1.229 V is required. Because of the high overpotential required for the formation of gases, we expect that a higher voltage will be necessary.

67. **(M) (a)** The two gases that are produced are $H_2(g)$ and $O_2(g)$.

(b) At the anode: $2\ H_2O(l)\rightarrow 4\ H^{+}(aq)+O_2(g)+4e^{-}$ $-E^{o}=-1.229\text{V}$

At the cathode: $\{2H^{+}(aq)+2e^{-}\rightarrow H_2(g)\}\ \times 2$ $E^{o}=0.000\text{V}$

Net cell reaction: $2H_2O(l)\rightarrow 2H_2(g)+O_2(g)$ $E^{o}_{cell}=-1.229\text{V}$

68. **(M)** The electrolysis of $Na_2SO_4(aq)$ produces molecular oxygen at the anode. $-E^{o}\{O_2(g)/H_2O\}=-1.229\text{ V}$. The other possible product is $S_2O_8^{2-}(aq)$. It is however,

unlikely to form because it has a considerably less favorable half-cell potential.
$-E^\circ\left\{S_2O_8^{2-}(aq)/SO_4^{2-}(aq)\right\} = -2.01\text{ V}$.
$H_2(g)$ is formed at the cathode.

$$\text{mol } O_2 = 3.75\text{ h} \times \frac{3600\text{ s}}{1\text{ h}} \times \frac{2.83\text{ C}}{1\text{ s}} \times \frac{1\text{ mol e}^-}{96485\text{ C}} \times \frac{1\text{ mol } O_2}{4\text{ mol e}^-} = 0.0990\text{ mol } O_2$$

The vapor pressure of water at 25°C, from Table 12-2, is 23.8 mmHg.

$$V = \frac{nRT}{P} = \frac{0.0990\text{ mol} \times 0.08206\text{ L atm mol}^{-1}\text{ K}^{-1} \times 298\text{ K}}{(742 - 23.8)\text{ mmHg} \times \dfrac{1\text{ atm}}{760\text{ mmHg}}} = 2.56\text{ L } O_2(g)$$

<u>69.</u> **(M) (a)** $Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$

$$\text{mass of Zn} = 42.5\text{ min} \times \frac{60\text{ s}}{1\text{ min}} \times \frac{1.87\text{ C}}{1\text{ s}} \times \frac{1\text{ mol e}^-}{96{,}485\text{ C}} \times \frac{1\text{ mol Zn}}{2\text{ mol e}^-} \times \frac{65.39\text{ g Zn}}{1\text{ mol Zn}} = 1.62\text{ g Zn}$$

(b) $2I^-(aq) \rightarrow I_2(s) + 2e^-$

$$\text{time needed} = 2.79\text{ g } I_2 \times \frac{1\text{ mol } I_2}{253.8\text{ g } I_2} \times \frac{2\text{ mol e}^-}{1\text{ mol } I_2} \times \frac{96{,}485\text{ C}}{1\text{ mol e}^-} \times \frac{1\text{ s}}{1.75\text{ C}} \times \frac{1\text{ min}}{60\text{ s}} = 20.2\text{ min}$$

70. **(M) (a)** $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

$$\text{mmol } Cu^{2+}\text{consumed} = 282\text{ s} \times \frac{2.68\text{ C}}{1\text{ s}} \times \frac{1\text{ mol e}^-}{96{,}485\text{ C}} \times \frac{1\text{ mol } Cu^{2+}}{2\text{ mol e}^-} \times \frac{1000\text{ mmol}}{1\text{ mol}}$$
$$= 3.92\text{ mmol } Cu^{2+}$$

$$\text{decrease in } \left[Cu^{2+}\right] = \frac{3.92\text{ mmol } Cu^{2+}}{425\text{ mL}} = 0.00922\text{ M}$$

$$\text{final } \left[Cu^{2+}\right] = 0.366\text{ M} - 0.00922\text{ M} = 0.357\text{ M}$$

(b) $\text{mmol } Ag^+\text{consumed} = 255\text{ mL}\left(0.196\text{ M} - 0.175\text{ M}\right) = 5.3\underline{6}\text{ mmol } Ag^+$

$$\text{time needed} = 5.36\text{ mmol } Ag^+ \times \frac{1\text{ mol } Ag^+}{1000\text{ mmol } Ag^+} \times \frac{1\text{ mol e}^-}{1\text{ mol } Ag^+} \times \frac{96485\text{C}}{1\text{ mol e}^-} \times \frac{1\text{ s}}{1.84\text{ C}}$$
$$= 28\underline{1}\text{ s} \approx 2.8 \times 10^2\text{ s}$$

<u>71.</u> **(M) (a)** $\text{charge} = 1.206\text{ g Ag} \times \dfrac{1\text{ mol Ag}}{107.87\text{ g Ag}} \times \dfrac{1\text{ mol e}^-}{1\text{ mol Ag}} \times \dfrac{96{,}485\text{ C}}{1\text{ mol e}^-} = 1079\text{ C}$

(b) $\text{current} = \dfrac{1079\text{ C}}{1412\text{ s}} = 0.7642\text{ A}$

72. **(D) (a)**

$$\begin{array}{lr}
\text{Anode, oxidation: } 2H_2O(l) \rightarrow 4H^+(aq) + 4e^- + O_2(g) & -E^\circ = -1.229\text{V} \\
\text{Cathode, reduction: } \{Ag^+(aq) + e^- \rightarrow Ag(s)\} \ \times 4 & E^\circ = +0.800\text{V} \\
\hline
\text{Net: } 2H_2O(l) + 4Ag^+(aq) \rightarrow 4H^+(aq) + O_2(g) + 4Ag(s) & E^\circ_{\text{cell}} = -0.429\text{V}
\end{array}$$

(b) $$\text{charge} = (25.8639 - 25.0782)\text{ g Ag} \times \frac{1\text{ mol Ag}}{107.87\text{ g Ag}} \times \frac{1\text{ mol e}^-}{1\text{ mol Ag}} \times \frac{96,485\text{ C}}{1\text{ mol e}^-} = 702.8\text{C}$$

$$\text{current} = \frac{702.8\text{C}}{2.00\text{ h}} \times \frac{1\text{h}}{3600\text{ s}} = 0.0976\text{A}$$

(c) The gas is molecular oxygen.

$$V = \frac{nRT}{P} = \frac{\left(702.8\text{ C} \times \frac{1\text{ mol e}^-}{96485\text{ C}} \times \frac{1\text{mol O}_2}{4\text{mol e}^-}\right) 0.08206 \frac{\text{L atm}}{\text{mol K}} (23{+}273)\text{ K}}{755\text{ mmHg} \times \frac{1\text{ atm}}{760\text{ mmHg}}}$$

$$= 0.0445\text{ L O}_2 \times \frac{1000\text{ mL}}{1\text{ L}} = 44.5\text{ mL of O}_2$$

73. **(D)** **(a)** The electrochemical reaction is:

$$\begin{array}{lll}
\text{Anode (oxidation):} & \{Ag(s) \rightarrow Ag^+(aq){+}e^-(aq)\} \times 2 & -E^o = -0.800V \\
\text{Cathode (reduction):} & Cu^{2+}(aq){+}2e^- \rightarrow Cu(s) & E_o = +0.340V \\
\hline
\text{Net:} & 2Ag(s){+}Cu^{2+}(aq) \rightarrow Cu(s){+}2Ag^+(aq) & E^o_{cell} = -0.46V
\end{array}$$

Therefore, copper should plate out first.

(b) $$\text{current} = \frac{\text{charge}}{2.50\text{hmin}} \times \frac{1\text{h}}{3600\text{ s}} = 0.75A \Rightarrow \text{charge} = 6750\text{C}$$

$$\text{mass} = 6750\text{ C} \times \frac{1\text{ mole}^-}{96485\text{ C}} \times \frac{1\text{mol Cu}}{2\text{ mol e}^-} \times \frac{63.546\text{ g Cu}}{1\text{ mol Cu}} = 2.22\text{ g Cu}$$

(c) The total mass of the metal is 3.50 g out of which 2.22g is copper. Therefore, the mass of silver in the sample is 3.50g-2.22g=1.28g or (1.28/3.50)x100=37%.

74. **(D)** First, calculate the number of moles of electrons involved in the electrolysis:

$$1.20C/s \times 32.0\text{min} \times \frac{60\text{sec}}{1\text{min}} \times \frac{1\text{mole e}^-}{96485C} = 0.0239\text{mol e}^-$$

From the known mass of platinum, determine the number of moles:

$$2.12\text{gPt} \times \frac{1\text{mol Pt}}{195.078\text{gPt}} = 0.0109\text{molPt}$$

Determine the number of electrons transferred:

$$\frac{0.0239\text{ mol e}^-}{0.0109\text{ mol Pt}} = 2.19$$

Therefore, 2.19 is shared between Pt^{2+} and Pt^{x+}. Since we know the mole ratio between Pt^{2+} and Pt^{x+}, we can calculate x:

$2.19 = 0.90\times(+2) + 0.10\times(x)$.

$2.19 = 1.80 + 0.10 \times x \Rightarrow x \approx 4$

(a) The oxidation state of the contaminant is +4.

INTEGRATIVE AND ADVANCED EXERCISES

75. **(M)** Oxidation: $V^{3+} + H_2O \longrightarrow VO^{2+} + 2\ H^+ + e^-$ $\qquad -E^\circ_a$

Reduction: $Ag^+ + e^- \longrightarrow Ag(s)$ $\qquad E^\circ = +0.800\ V$

Net: $V^{3+} + H_2O + Ag^+ \longrightarrow VO^{2+} + 2\ H^+ + Ag(s)$ $\qquad E^\circ_{cell} = 0.439\ V$

$0.439\ V = -E^\circ_a + 0.800\ V \qquad E^\circ_a = 0.800\ V - 0.439\ V = 0.361\ V$

Oxidation: $V^{2+} \longrightarrow V^{3+} + e^-$ $\qquad -E^\circ_b$

Reduction: $VO^{2+} + 2\ H^+ + e^- \longrightarrow V^{3+} + H_2O$ $\qquad E^\circ = +0.361\ V$

Net: $V^{2+} + VO^{2+} + 2\ H^+ \longrightarrow 2\ V^{3+} + H_2O$ $\qquad E^\circ_{cell} = +0.616\ V$

$0.616\ V = -E^\circ_b + 0.361\ V \quad E^\circ_b = 0.361\ V - 0.616\ V = -0.255\ V$

Thus, for the cited reaction: $V^{3+} + e^- \longrightarrow V^{2+}$ $\qquad E^\circ = -0.255\ V$

76. **(M)**The cell reaction for discharging a lead storage battery is equation (20.24).

$Pb(s) + PbO_2(s) + 2\ H^+(aq) + 2\ HSO_4^-(aq) \longrightarrow PbSO_4(s) + 2\ H_2O(l)$

The half-reactions with which this equation was derived indicates that two moles of electrons are transferred for every two moles of sulfate ion consumed. We first compute the amount of H_2SO_4 initially present and then the amount of H_2SO_4 consumed.

$$\text{initial amount } H_2SO_4 = 1.50\ L \times \frac{5.00\ mol\ H_2SO_4}{1\ L\ soln} = 7.50\ mol\ H_2SO_4$$

$$\text{amount } H_2SO_4 \text{ consumed} = 6.0\ h \times \frac{3600\ s}{1\ h} \times \frac{2.50\ C}{1\ s} \times \frac{1\ mol\ e^-}{96485\ C} \times \frac{2\ mol\ SO_4^{2-}}{2\ mol\ e^-} \times \frac{1\ mol\ H_2SO_4}{1\ mol\ SO_4^{2-}}$$

$$= 0.56\ mol\ H_2SO_4$$

$$\text{final}\,[H_2SO_4] = \frac{7.50\ mol - 0.56\ mol}{1.50\ L} = 4.63\ M$$

77. **(M)** The cell reaction is $2\ Cl^-(aq) + 2\ H_2O(l) \longrightarrow 2\ OH^-(aq) + H_2(g) + Cl_2(g)$

We first determine the charge transferred per 1000 kg Cl_2.

$$\text{charge} = 1000\ kg\ Cl_2 \times \frac{1000\ g}{1\ kg} \times \frac{1\ mol\ Cl_2}{70.90\ g\ Cl_2} \times \frac{2\ mol\ e^-}{1\ mol\ Cl_2} \times \frac{96,485\ C}{1\ mol\ e^-} = 2.72 \times 10^9\ C$$

(a) $\text{energy} = 3.45\ \text{V} \times 2.72 \times 10^{9}\ \text{C} \times \dfrac{1\ \text{J}}{1\ \text{V}\cdot\text{C}} \times \dfrac{1\ \text{kJ}}{1000\ \text{J}} = 9.38 \times 10^{6}\ \text{kJ}$

(b) $\text{energy} = 9.38 \times 10^{9}\ \text{J} \times \dfrac{1\ \text{W}\cdot\text{s}}{1\ \text{J}} \times \dfrac{1\ \text{h}}{3600\ \text{s}} \times \dfrac{1\ \text{kWh}}{1000\ \text{W}\cdot\text{h}} = 2.61 \times 10^{3}\ \text{kWh}$

78. **(D)** We determine the equilibrium constant for the reaction.

$$\begin{array}{lll}
\text{Oxidation:} & \text{Fe(s)} \longrightarrow \text{Fe}^{2+}\text{(aq)} + 2\text{e}^- & -E° = +0.440\ \text{V} \\
\text{Reduction:} & \{\text{Cr}^{3+}\text{(aq)} + \text{e}^- \longrightarrow \text{Cr}^{2+}\text{(aq)}\} \times 2 & E° = -0.424\ \text{V} \\
\hline
\text{Net:} & \text{Fe(s)} + 2\ \text{Cr}^{3+}\text{(aq)} \longrightarrow \text{Fe}^{2+}\text{(aq)} + 2\ \text{Cr}^{2+}\text{(aq)} & \text{E}^{\circ}_{\text{cell}} = +0.016\ \text{V}
\end{array}$$

$$\Delta G^{o} = -nFE^{o}_{cell} = -RT\ln K \Rightarrow \ln K = \frac{nFE^{o}_{cell}}{RT}$$

$$\ln\ K = \frac{2\ \text{mol e}^- \times 96485\ \text{Coul/mol e}^- \times 0.016\ \text{V}}{8.3145\ \text{J mol}^{-1}\ \text{K}^{-1} \times 298\ \text{K}} = 1.2 \qquad K = \text{e}^{1..2} = 3.3$$

Reaction:	Fe(s) +	$2\ \text{Cr}^{3+}\text{(aq)} \rightleftharpoons$	$\text{Fe}^{2+}\text{(aq)}$ +	$2\text{Cr}^{2+}\text{(aq)}$
Initial :		1.00 M	0 M	0 M
Changes :		$-2x$ M	$+x$ M	$+2x$ M
Equil:		$(1.00 - 2x)$M	x M	$2x$ M

$$K = \frac{[\text{Fe}^{2+}][\text{Cr}^{2+}]^2}{[\text{Cr}^{3+}]^2} = 3.3 = \frac{x\,(2x)^2}{(1.00 - 2x)^2}$$

Let us simply substitute values of x into this cubic equation to find a solution. Notice that x cannot be larger than 0.50, (values > 0.5 will result in a negative value for the denominator.

$$x = 0.40 \quad K = \frac{0.40\,(0.80)^2}{(1.00 - 0.80)^2} = 6.4 > 3.3 \qquad x = 0.35 \quad K = \frac{0.35\,(0.70)^2}{(1.00 - 0.70)^2} = 1.9 > 3.3$$

$$x = 0.37 \quad K = \frac{0.37\,(0.74)^2}{(1.00 - 0.74)^2} = 3.0 < 3.3 \qquad x = 0.38 \quad K = \frac{0.38\,(0.76)^2}{(1.00 - 0.76)^2} = 3.8 > 3.3$$

Thus, we conclude that $x = 0.37\ \text{M} = [\text{Fe}^{2+}]$.

79. **(D)** First we calculate the standard cell potential.

$$\begin{array}{lll}
\text{Oxidation:} & \text{Fe}^{2+}\text{(aq)} \longrightarrow \text{Fe}^{3+}\text{(aq)} + \text{e}^- & -E^{\text{o}} = -0.771\ \text{V} \\
\text{Reduction:} & \text{Ag}^{+}\text{(aq)} + \text{e}^- \longrightarrow \text{Ag(s)} & E^{\text{o}} = +0.800\ \text{V} \\
\hline
\text{Net:} & \text{Fe}^{2+}\text{(aq)} + \text{Ag}^{+}\text{(aq)} \longrightarrow \text{Fe}^{3+}\text{(aq)} + \text{Ag(s)} & E^{\text{o}}_{\text{cell}} = 0.029\ \text{V}
\end{array}$$

Next, we use the given concentrations to calculate the cell voltage with the Nernst equation.

$$E_{\text{cell}} = E^{\text{o}}_{\text{cell}} - \frac{0.0592}{1}\log\frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}][\text{Ag}^{+}]} = 0.029 - 0.0592\log\frac{0.0050}{0.0050 \times 2.0} = 0.029 + 0.018 = 0.047\ \text{V}$$

The reaction will continue to move in the forward direction until concentrations of reactants decrease and those of products increase a bit more. At equilibrium, $E_{\text{cell}} = 0$, and we have the following.

$$E^{\circ}_{\text{cell}} = \frac{0.0592}{1}\log\frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}][\text{Ag}^{+}]} = 0.029 \qquad \log\frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}][\text{Ag}^{+}]} = \frac{0.029}{0.0592} = 0.49$$

Reaction:	$\text{Fe}^{2+}(\text{aq})$	+	$\text{Ag}^{+}(\text{aq})$	$\rightleftharpoons$	$\text{Fe}^{3+}(\text{aq})$	+	Ag(s)
Initial:	0.0050 M		2.0 M		0.0050 M		–
Changes:	$-x$ M		$-x$ M		$+x$ M		–
Equil:	$(0.0050 - x)$ M		$(2.0 - x)$ M		$(0.0050 + x)$ M		–

$$\frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}][\text{Ag}^{+}]} = 10^{0.49} = 3.1 = \frac{0.0050 + x}{(0.0050 - x)(2.0 - x)} \approx \frac{0.0050 + x}{2.0(0.0050 - x)}$$

$$6.2(0.0050 - x) = 0.0050 + x = 0.031 - 6.2\,x \qquad 7.2\,x = 0.026 \qquad x = \frac{0.026}{7.2} = 0.0036\text{ M}$$

Note that the assumption that $x << 2.0$ is valid. $[\text{Fe}^{2+}]$ = 0.0050 M – 0.0036 M = 0.0014 M

80. **(D)** We first note that we are dealing with a concentration cell, one in which the standard oxidation reaction is the reverse of the standard reduction reaction, and consequently its standard cell potential is precisely zero volts. For this cell, the Nernst equation permits us to determine the ratio of the two silver ion concentrations.

$$E_{\text{cell}} = 0.000\text{ V} - \frac{0.0592}{1}\log\frac{[\text{Ag}^{+}(\text{satd AgI})]}{[\text{Ag}^{+}(\text{satd AgCl, } x \text{ M Cl}^{-})]} = 0.0860\text{ V}$$

$$\log\frac{[\text{Ag}^{+}(\text{satd AgI})]}{[\text{Ag}^{+}(\text{satd AgCl, } x \text{ M Cl}^{-})]} = \frac{-0.0860}{0.0592} = -1.45 \qquad \frac{[\text{Ag}^{+}(\text{satd AgI})]}{[\text{Ag}^{+}(\text{satd AgCl, } x \text{ M Cl}^{-})]} = 10^{-1.45} = 0.035$$

We can determine the numerator concentration from the solubility product expression for AgI(s)

$$K_{\text{sp}} = [\text{Ag}^{+}][\text{I}^{-}] = 8.5\times10^{-17} = s^{2} \qquad s = \sqrt{8.5\times10^{-17}} = 9.2\times10^{-9}\,\text{M}$$

This permits the determination of the concentration in the denominator.

$$[\text{Ag}^{+}(\text{satd AgCl}, x\,\text{M Cl}^{-})] = \frac{9.2\times10^{-9}}{0.035} = 2.6\times10^{-7}\text{ M}$$

We now can determine the value of x. Note: Cl^{-} arises from two sources, one being the dissolved AgCl.

$$K_{\text{sp}} = [\text{Ag}^{+}][\text{Cl}^{-}] = 1.8\times10^{-10} = (2.6\times10^{-7})(2.6\times10^{-7} + x) = 6.8\times10^{-14} + 2.6\times10^{-7}\,x$$

$$x = \frac{1.8\times10^{-10} - 6.8\times10^{-14}}{2.6\times10^{-7}} = 6.9\times10^{-4}\,\text{M} = [\text{Cl}^{-}]$$

81. **(M)** The Faraday constant can be evaluated by measuring the electric charge needed to produce a certain quantity of chemical change. For instance, let's imagine that an electric circuit contains the half-reaction $\text{Cu}^{2+}(\text{aq}) + 2\text{ e}^{-} \rightleftharpoons \text{Cu(s)}$. The electrode on which the solid copper plates out is weighed before and after the passage of electric current. The mass gain is the mass of copper reduced, which then is converted into the moles of copper reduced. The number of moles of electrons involved in the reduction then is computed from the stoichiometry for the reduction half-reaction. In addition, the amperage is measured during the reduction, and the time is recorded. For simplicity, we assume the amperage is constant. Then the total charge (in coulombs) equals the current (in amperes, that is, coulombs per second) multiplied by the time (in seconds). The ratio of the total charge (in coulombs) required by the reduction divided by the amount (in moles) of electrons is the Faraday constant. To determine the Avogadro constant, one uses the charge of the electron, 1.602×10^{-19} C and the Faraday constant in the following calculation.

$$N_A = \frac{96{,}485\text{ C}}{1\text{ mol electrons}} \times \frac{1\text{ electron}}{1.602 \times 10^{-19}\text{ C}} = 6.023 \times 10^{23}\ \frac{\text{electrons}}{\text{mole}}$$

82. **(M)** In this problem we are asked to determine ΔG_f^o for $N_2H_4(aq)$ using the electrochemical data for hydrazine fuel cell. We first determine the value of ΔG^o for the cell reaction, a reaction in which $n = 4$. ΔG_f^o can then be determined using data in Appendix D.

Stewise approach:

Calculate ΔG^o for the cell reaction (n=4):

$$\Delta G^o = -n\,FE^o_{cell} - 4\text{ mol e}^- \times \frac{96{,}485\text{ C}}{1\text{ mol e}^-} \times 1.559\text{ V} = -6.017 \times 10^5\text{ J} = -601.7\text{ kJ}$$

Using the data in Appendix D, determine ΔG_f^o for hydrazine (N_2H_4):

$$\begin{aligned} -601.7\text{ kJ} &= \Delta G_f^o[N_2(g)] + 2\,\Delta G_f^o[H_2O(l)] - \Delta G_f^o[N_2H_4(aq)] - \Delta G_f^o[O_2(g)] \\ &= 0.00\text{ kJ} + 2 \times (-237.2\text{ kJ}) - \Delta G_f^o[N_2H_4(aq)] - 0.00\text{ kJ} \end{aligned}$$

$$\Delta G_f^o[N_2H_4(aq)] = 2 \times (-237.2\text{ kJ}) + 601.7\text{ kJ} = +127.3\text{ kJ}$$

Conversion pathway approach:

$$\Delta G^o = -n\,FE^o_{cell} - 4\text{ mol e}^- \times \frac{96{,}485\text{ C}}{1\text{ mol e}^-} \times 1.559\text{ V} = -6.017 \times 10^5\text{ J} = -601.7\text{ kJ}$$

$$\begin{aligned} -601.7\text{ kJ} &= \Delta G_f^o[N_2(g)] + 2\,\Delta G_f^o[H_2O(l)] - \Delta G_f^o[N_2H_4(aq)] - \Delta G_f^o[O_2(g)] \\ &= 0.00\text{ kJ} + 2 \times (-237.2\text{ kJ}) - \Delta G_f^o[N_2H_4(aq)] - 0.00\text{ kJ} \end{aligned}$$

$$\Delta G_f^o[N_2H_4(aq)] = 2 \times (-237.2\text{ kJ}) + 601.7\text{ kJ} = +127.3\text{ kJ}$$

83. **(M)** In general, we shall assume that both ions are present initially at concentrations of 1.00 M. Then we shall compute the concentration of the more easily reduced ion when its reduction potential has reached the point at which the other cation starts being reduced by electrolysis. In performing this calculation we use the Nernst equation, but modified for use with a half-reaction. We find that, in general, the greater the difference in $E°$ values for two reduction half-reactions, the more effective the separation.

(a) In this case, no calculation is necessary. If the electrolysis takes place in aqueous solution, $H_2(g)$ rather than K(s) will be produced at the cathode. Cu^{2+} can be separated from K^+ by electrolysis.

(b) $Cu^{2+}(aq) + 2\,e^- \rightarrow Cu(s)\ E^o = +0.340\text{ V}$ $\quad Ag^+(aq) + e^- \rightarrow Ag(s)\quad E^o = +0.800\text{ V}$

Ag^+ will be reduced first. Now we ask what $[Ag^+]$ will be when $E = +0.337$ V.

$$0.337\text{ V} = 0.800\text{ V} - \frac{0.0592}{1}\log\frac{1}{[Ag^+]} \qquad \log\frac{1}{[Ag^+]} = \frac{0.800 - 0.340}{0.0592} = +7.77$$

$[Ag^+] = 1.7 \times 10^{-8}$ M. Separation of the two cations is essentially complete.

(c) $Pb^{2+}(aq) + 2\,e^- \rightarrow Pb(s)\ E^o = -0.125$ V $\qquad Sn^{2+}(aq) + 2\,e^- \rightarrow Sn(s) \qquad E^o = -0.137$ V

Pb^{2+} will be reduced first. We now ask what $[Pb^{2+}]$ will be when $E° = -0.137$ V.

$$-0.137\text{ V} = -0.125\text{ V} - \frac{0.0592}{2}\log\frac{1}{[Pb^{2+}]} \qquad \log\frac{1}{[Pb^{2+}]} = \frac{2(0.137-0.125)}{0.0592} = 0.41$$

$[Pb^{2+}] = 10^{-0.41} = 0.39$ M Separation of Pb^{2+} from Sn^{2+} is not complete.

84. **(D)** The efficiency value for a fuel cell will be greater than 1.00 for any exothermic reaction ($\Delta H^o < 0$) that has $\Delta G°$ that is more negative than its ΔH^o value. Since $\Delta G^o = \Delta H^o - T\Delta S^o$, this means that the value of ΔS^o must be positive. Moreover, for this to be the case, Δn_{gas} is usually greater than zero. Let us consider the situation that might lead to this type of reaction. The combustion of carbon-hydrogen-oxygen compounds leads to the formation of $H_2O(l)$ and $CO_2(g)$. Since most of the oxygen in these compounds comes from $O_2(g)$ (some is present in the C-H-O compound), there is a balance in the number of moles of gas produced—$CO_2(g)$—and those consumed—$O_2(g)$—which is offset in a negative direction by the $H_2O(l)$ produced. Thus, the combustion of these types of compounds will only have a positive value of Δn_{gas} if the number of oxygens in the formula of the compound is more than twice the number of hydrogens. By comparison, the decomposition of NOCl(g), an oxychloride of nitrogen, does produce more moles of gas than it consumes. Let us investigate this decomposition reaction.

$$NOCl(g) \longrightarrow \tfrac{1}{2}N_2(g) + \tfrac{1}{2}O_2(g) + \tfrac{1}{2}Cl_2(g)$$

$$\Delta H^o = \tfrac{1}{2}\Delta H_f^o\,[N_2(g)] + \tfrac{1}{2}\Delta H_f^o\,[O_2(g)] + \tfrac{1}{2}\Delta H_f^o\,[Cl_2(g)] - \Delta H_f^o\,[NOCl(g)]$$

$$= 0.500\,(0.00\text{ kJ/mol} + 0.00\text{ kJ/mol} + 0.00\text{ kJ/mol}) - 51.71\text{ kJ/mol} = -51.71\text{ kJ/mol}$$

$$\Delta G^o = \tfrac{1}{2}\Delta G_f^o\,[N_2(g)] + \tfrac{1}{2}\Delta G_f^o\,[O_2(g)] + \tfrac{1}{2}\Delta G_f^o\,[Cl_2(g)] - \Delta G_f^o\,[NOCl(g)]$$

$$= 0.500\,(0.00\text{ kJ/mol} + 0.00\text{ kJ/mol} + 0.00\text{ kJ/mol}) - 66.08\text{ kJ/mol} = -66.08\text{ kJ/mol}$$

$$\varepsilon = \frac{\Delta G^o}{\Delta H^o} = \frac{-66.08\text{ kJ/mol}}{-51.71\text{ kJ/mol}} = 1.278$$

Yet another simple reaction that meets the requirement that $\Delta G^o < \Delta H^o$ is the combustion of graphite: $C(graphite) + O_2(g) \longrightarrow CO_2(g)$ We see from Appendix D that $\Delta G_f^o[CO_2(g)] = -394.4$ kJ/mol is more negative than $\Delta H_f^o[CO_2(g)] = -393.5$ kJ/mol. (This reaction is accompanied by an increase in entropy; $\Delta S = 213.7 - 5.74 - 205.1 = 2.86$ J/K, $\varepsilon = 1.002$.) $\Delta G^o < \Delta H^o$ is true of the reaction in which CO(g) is formed from the elements. From Appendix D, $\Delta H_f^o\{CO(g)\} = -110.5$ kJ/mol, and $\Delta G_f^o\{CO(g)\} = -137.2$ kJ/mol, producing $\varepsilon = (-137.2/-110.5) = 1.242$.

Note that any reaction that has $\varepsilon > 1.00$ will be spontaneous under standard conditions at all temperatures. (There, of course, is another category, namely, an endothermic reaction that has $\Delta S^o < 0$. This type of reaction is nonspontaneous under standard conditions at all temperatures. As such it consumes energy while it is running, which is clearly not a desirable result for a fuel cell.)

85. **(M)** We first write the two half-equations and then calculate a value of ΔG° from thermochemical data. This value then is used to determine the standard cell potential.

Oxidation: $\text{CH}_3\text{CH}_2\text{OH(g)} + 3\ \text{H}_2\text{O(l)} \longrightarrow 2\ \text{CO}_2(g) + 12\ \text{H}^+\text{(aq)} + 12\ \text{e}^-$

Reduction: $\{\text{O}_2(\text{g}) + 4\ \text{H}^+\text{(aq)} + 4\text{e}^- \longrightarrow 2\ \text{H}_2\text{O(l)}\} \times 3$

Overall: $\text{CH}_3\text{CH}_2\text{OH(g)} + 3\ \text{O}_2(\text{g}) \longrightarrow 3\ \text{H}_2\text{O(l)} + 2\ \text{CO}_2(g)$

Thus, $n = 12$

(a) $\Delta G^\circ = 2\Delta G_f^\circ[\text{CO}_2(\text{g})] + 3\Delta G_f^\circ[\text{H}_2\text{O(l)}] - \Delta G_f^\circ[\text{CH}_3\text{CH}_2\text{OH(g)}] - 3\Delta G_f^\circ[\text{O}_2(\text{g})]$

$= 2(-394.4\text{ kJ/mol}) + 3(-237.1\text{ kJ/mol}) - (-168.5\text{ kJ/mol}) - 3(0.00\text{ kJ/mol}) = -1331.6\text{ kJ/mol}$

$$E^\circ_{\text{cell}} = -\frac{\Delta G^\circ}{n\ F} = -\frac{-1331.6 \times 10^3\ \text{J/mol}}{12\ \text{mol e}^- \times 96{,}485\ \text{C/mol e}^-} = +1.1501\ \text{V}$$

(b) $E^\circ_{\text{cell}} = E^\circ[\text{O}_2(\text{g})/\text{H}_2\text{O}] - E^\circ[\text{CO}_2(\text{g})/\text{CH}_3\text{CH}_2\text{OH(g)}] = 1.1501\ \text{V}$

$= 1.229\ \text{V} - E^\circ[\text{CO}_2(\text{g})/\text{CH}_3\text{CH}_2\text{OH(g)}]$

$E^\circ[\text{CO}_2(\text{g})/\text{CH}_3\text{CH}_2\text{OH(g)}] = 1.229 - 1.1501 = +0.079\ \text{V}$

86. **(M)** First we determine the change in the amount of H^+ in each compartment.

Oxidation: $2\ \text{H}_2\text{O(l)} \rightarrow \text{O}_2(g) + 4\ \text{H}^+\text{(aq)} + 4\ \text{e}^-$ Reduction: $2\ \text{H}^+\text{(aq)} + 2\ \text{e}^- \rightarrow \text{H}_2(\text{g})$

$$\Delta\ \text{amount H}^+ = 212\ \text{min} \times \frac{60\ \text{s}}{1\ \text{min}} \times \frac{1.25\ \text{C}}{1\ \text{s}} \times \frac{1\ \text{mol e}^-}{96{,}485\ \text{C}} \times \frac{1\ \text{mol H}^+}{1\ \text{mol e}^-} = 0.165\ \text{mol H}^+$$

Before electrolysis, there is 0.500 mol H_2PO_4^- and 0.500 mol HPO_4^{2-} in each compartment. The electrolysis adds 0.165 mol H^+ to the anode compartment, which has the effect of transforming 0.165 mol HPO_4^{2-} into 0.165 mol H_2PO_4^-, giving a total of 0.335 mol HPO_4^{2-} (0.500 mol – 0.165 mol) and 0.665 mol H_2PO_4^- (0.500 mol + 0.165 mol). We can use the Henderson-Hasselbalch equation to determine the pH of the solution in the anode compartment.

$$\text{pH} = \text{p}K_{a_2} + \log\frac{[\text{HPO}_4^{\ 2-}]}{[\text{H}_2\text{PO}_4]} = 7.20 + \log\frac{0.335\ \text{mol HPO}_4^{\ 2-}/0.500\ \text{L}}{0.665\ \text{mol H}_2\text{PO}_4^{\ -}/0.500\ \text{L}} = 6.90$$

Again we use the Henderson-Hasselbalch equation in the cathode compartment. After electrolysis there is 0.665 mol HPO_4^{2-} and 0.335 mol H_2PO_4^-. Again we use the Henderson-Hasselbalch equation.

$$\text{pH} = \text{p}K_{a_2} + \log\frac{[\text{HPO}_4^{\ 2-}]}{[\text{H}_2\text{PO}_4^{\ -}]} = 7.20 + \log\frac{0.665\ \text{mol HPO}_4^{\ 2-}/0.500\ \text{L}}{0.335\ \text{mol H}_2\text{PO}_4^{\ -}/0.500\ \text{L}} = 7.50$$

<u>87</u>. **(M)** We first determine the change in the amount of M^{2+} ion in each compartment.

$$\Delta\text{M}^{2+} = 10.00\text{h} \times \frac{3600\ \text{s}}{1\ \text{h}} \times \frac{0.500\ \text{C}}{1\ \text{s}} \times \frac{1\text{mol e}^-}{96485\ \text{C}} \times \frac{1\text{mol M}^{2+}}{2\text{mol e}^-} = 0.0933\ \text{mol M}^{2+}$$

This change in amount is the increase in the amount of Cu^{2+} and the decrease in the amount of Zn^{2+}. We can also calculate the change in each of the concentrations.

$$\Delta[\mathrm{Cu}^{2+}]=\frac{+0.0933\ \mathrm{mol\ Cu}^{2+}}{0.1000\ \mathrm{L}}=+0.933\ \mathrm{M}\qquad \Delta[\mathrm{Zn}^{2+}]=\frac{-0.0933\ \mathrm{mol\ Zn}^{2+}}{0.1000\ \mathrm{L}}=-0.933\ \mathrm{M}$$

Then the concentrations of the two ions are determined.

$[\mathrm{Cu}^{2+}]=1.000\ \mathrm{M}+0.933\ \mathrm{M}=1.933\ \mathrm{M}\qquad [\mathrm{Zn}^{2+}]=1.000\ \mathrm{M}-0.933\ \mathrm{M}=0.067\ \mathrm{M}$

Now we run the cell as a voltaic cell, first determining the value of $E_{\mathrm{cell}}°$.

$$\begin{array}{llll}
\text{Oxidation}: & \mathrm{Zn(s)} \longrightarrow \mathrm{Zn^{2+}(aq)} + 2\ \mathrm{e^-} & -E° = +0.763 & \mathrm{V}\\
\text{Reduction}: & \mathrm{Cu^{2+}(aq)} + 2\ \mathrm{e^-}\quad \mathrm{Cu(s)} & E° = +0.340 & \mathrm{V}\\
\hline
\text{Net}: & \mathrm{Zn(s)} + \mathrm{Cu^{2+}(aq)} \longrightarrow \mathrm{Cu(s)} & E°_{\mathrm{cell}} = +1.103 & \mathrm{V}
\end{array}$$

Then we use the Nernst equation to determine the voltage of this cell.

$$E_{\mathrm{cell}}=E°_{\mathrm{cell}}-\frac{0.0592}{2}\log\frac{[\mathrm{Zn}^{2+}]}{[\mathrm{Cu}^{2+}]}=1.103-\frac{0.0592}{2}\log\frac{0.067\ \mathrm{M}}{1.933\ \mathrm{M}}=1.103+0.043=1.146\ \mathrm{V}$$

88. (M)(a)

$$\begin{array}{lll}
\text{Anode: } \mathrm{Zn(s)} \longrightarrow \mathrm{Zn^{2+}(aq)} + 2\mathrm{e^-} & & -E° = +0.763\ \mathrm{V}\\
\text{Cathode: } \{\mathrm{AgCl(s)} + \mathrm{e^-(aq)} \longrightarrow \mathrm{Ag(s)} + \mathrm{Cl^-(1\ M)}\} & \times\ 2 & E°{=}{+}0.2223\ \mathrm{V}\\
\hline
\text{Net: } \mathrm{Zn(s)} + 2\mathrm{AgCl(s)} \longrightarrow \mathrm{Zn^{2+}(aq)} + 2\mathrm{Ag(s)} + 2\mathrm{Cl^-(1\ M)} & & E°_{\mathrm{cell}} = +0.985\ \mathrm{V}
\end{array}$$

(b) The major reason why this electrode is easier to use than the standard hydrogen electrode is that it does not involve a gas. Thus there are not the practical difficulties involved in handling gases. Another reason is that it yields a higher value of $E°_{\mathrm{cell}}$, thus, this is a more spontaneous system.

(c)

$$\begin{array}{lll}
\text{Oxidation:} & \mathrm{Ag(s)} \longrightarrow \mathrm{Ag^+(aq)} + \mathrm{e^-} & -E° = -0.800\ \mathrm{V}\\
\text{Reduction:} & \mathrm{AgCl(s)} + \mathrm{e^-} \longrightarrow \mathrm{Ag(s)} + \mathrm{Cl^-(aq)} & E = +0.2223\ \mathrm{V}\\
\hline
\text{Net:} & \mathrm{AgCl(s)} \longrightarrow \mathrm{Ag^+(aq)} + \mathrm{Cl^-(aq)} & E°_{\mathrm{cell}} = -0.578\ \mathrm{V}
\end{array}$$

The net reaction is the solubility reaction, for which the equilibrium constant is K_{sp}.

$\Delta G° = -nFE° = -RT\ \ln\ K_{\mathrm{sp}}$

$$\ln K_{\mathrm{sp}}=\frac{nFE°}{RT}=\frac{1\ \mathrm{mol\ e^-}\times\dfrac{96485\ \mathrm{C}}{1\ \mathrm{mol\ e^-}}\times(-0.578\ \mathrm{V})\times\dfrac{1\ \mathrm{J}}{1\ \mathrm{V.C}}}{8.3145\ \mathrm{J\ mol^{-1}\ K^{-1}}\times 298.15\ \mathrm{K}}=-22.5$$

$K_{\mathrm{sp}}=e^{-22.5}=1.7\times10^{-10}$

This value is in good agreement with the value of 1.8×10^{-10} given in Table 18-1.

89. (D) (a)

$$\begin{array}{lll}
\mathrm{Ag(s)} \rightarrow \mathrm{Ag^+(aq)} + \mathrm{e^-} & & -E° = -0.800\ \mathrm{V}\\
\underline{\mathrm{AgCl(s)} + \mathrm{e^-} \rightarrow \mathrm{Ag(s)} + \mathrm{Cl^-(aq)}} & & \underline{E° = 0.2223\ \mathrm{V}}\\
\mathrm{AgCl(s)} \rightarrow \mathrm{Ag^+(aq)} + \mathrm{Cl^-(aq)} & & E°_{\mathrm{cell}} = -0.577\underline{7}\ \mathrm{V}
\end{array}$$

$$E_{\mathrm{cell}}=E°_{\mathrm{cell}}-\frac{0.0592}{1}\left(\log\frac{[\mathrm{Ag^+}][\mathrm{Cl^-}]}{1}\right)=-0.577\underline{7}\ \mathrm{V}-\frac{0.0592}{1}\log\left(\frac{[1.00][1.00\times10^{-3}]}{1}\right)=-0.400\ \mathrm{V}$$

(b) 10.00 mL of 0.0100 M $\mathrm{CrO_4^{2-}}$ + 100.0 mL of 1.00×10^{-3} M $\mathrm{Ag^+}$ (V_{total} = 110.0 mL)

Concentration of CrO_4^{2-} after dilution: 0.0100 M×10.00 mL /110.00 mL = 0.000909 M
Concentration of Ag^+ after dilution: 0.00100 M×100.0 mL /110.00 mL = 0.000909 M

$Ag_2CrO_4(s) \xrightleftharpoons{K_{sp}=1.1\times10^{-12}}$	$2Ag^+(aq)$ +	$CrO_4^{2-}(aq)$
Initial	0.000909 M	0.000909 M
Change(100% rxn)	-0.000909 M	-0.000455 M
New initial	0 M	0.000455 M
Change	$+2x$	$+x$
Equilibrium	$2x$	$0.000455\text{ M}+x \approx 0.000455\text{ M}$

$1.1 \times 10^{-12} = (2x)^2(0.000454)$
$x = 0.0000246$ M Note: 5.4% of 0.000455 M (assumption may be considered valid)
(Answer would be $x = 0.0000253$ using method of successive approx.)
$[Ag^+] = 2x = 0.0000492$ M (0.0000506 M using method of successive approx.)

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0592}{1}\log[Ag^+][Cl^-] = -0.577\underline{7} - \frac{0.0592}{1}\log[1.00M][4.92\times10^{-4}M]$$

$$= -0.323\text{ V } (-0.306\text{ V for method of successive approximations})$$

(c) 10.00 mL 0.0100 M NH_3 + 10.00 mL 0.0100 M CrO_4^{2-} + 100.0 mL 1.00×10^{-3} M Ag^+
(V_{total} = 120.0 mL)
Concentration of NH_3 after dilution: 10.0 M×10.00 mL /120.00 mL = 0.833 M
Concentration of CrO_4^{2-} after dilution: 0.0100 M×10.00 mL /110.00 mL = 0.000833 M
Concentration of Ag^+ after dilution: 0.00100 M×100.0 mL /110.00 mL = 0.000833 M

In order to determine the equilibrium concentration of free $Ag^+(aq)$, we first consider complexation of $Ag^+(aq)$ by $NH_3(aq)$ and then check to see if precipitation occurs.

	$Ag^+(aq)$ +	$2NH_3(aq) \xrightleftharpoons{K_f=1.6\times10^7}$	$Ag(NH_3)_2^+(aq)$
Initial	0.000833 M	0.833 M	0 M
Change(100% rxn)	-0.000833 M	-0.00167 M	+0.000833 M
New initial	0 M	0.831 M	0.000833 M
Change	$+x$	$+2x$	$-x$
Equilibrium	x	$(0.831+2x)$ M	$(0.000833 - x)$ M
Equilibrium ($x \approx 0$)	x	0.831 M	0.000833 M

$1.6 \times 10^7 = 0.000833 / x(0.831)^2$ $x = 7.5\underline{4}\times10^{-11}\text{ M} = [Ag^+]$
Note: The assumption is valid
Now we look to see if a precipitate forms: $Q_{sp} = (7.5\underline{4}\times10^{-11})^2(0.000833) = 4.7\times10^{-24}$
Since $Q_{sp} < K_{sp}$ (1.1×10^{-12}), no precipitate forms and $[Ag^+] = 7.5\underline{4}\times10^{-11}$ M

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0592}{1}\log[Ag^+][Cl^-] = -0.577\underline{7}\text{ V} - \frac{0.0592}{1}\log[1.00M][7.5\underline{4}\times10^{-11}M]$$

$$E_{\text{cell}} = 0.021\underline{5}\text{ V}$$

90. **(M)** We assume that the $Pb^{2+}(aq)$ is "ignored" by the silver electrode, that is, the silver electrode detects only silver ion in solution.

$$\begin{array}{ll} \text{Oxidation : } H_2(g) \longrightarrow 2\ H^+(aq) + 2\ e^- & -E° = 0.000\ \text{V} \\ \text{Reduction: } \{Ag^+(aq) + e^- \longrightarrow Ag(s)\} \times 2 & E° = \ 0.800\ \text{V} \\ \hline \text{Net: } \quad H_2(g) + 2\ Ag^+ \longrightarrow 2\ H^+(aq) + 2\ Ag(s) & E°_{\text{cell}} = 0.800\ \text{V} \end{array}$$

$$E_{\text{cell}} = E°_{\text{cell}} - \frac{0.0592}{2}\log\frac{[H^+]^2}{[Ag^+]^2} \qquad 0.503\ \text{V} = 0.800\ \text{V} - \frac{0.0592}{2}\log\frac{1.00^2}{[Ag^+]^2}$$

$$\log\frac{1.00^2}{[Ag^+]^2} = \frac{2(0.800 - 0.503)}{0.0592} = 10.0 \qquad \frac{1.00^2}{[Ag^+]^2} = 10^{+10.0} = 1.0\times10^{10}$$

$$[Ag^+]^2 = 1.0\times10^{-10}\text{M}^2 \Rightarrow [Ag^+] = 1.0\times10^{-5}$$

$$\text{mass Ag} = 0.500\ \text{L}\times\frac{1.0\times10^{-5}\ \text{mol Ag}^+}{1\ \text{L soln}}\times\frac{1\ \text{mol Ag}}{1\ \text{mol Ag}^+}\times\frac{107.87\ \text{g Ag}}{1\ \text{mol Ag}} = 5.4\times10^{-4}\ \text{g Ag}$$

$$\%\ \text{Ag} = \frac{5.4\times10^{-4}\ \text{g Ag}}{1.050\ \text{g sample}}\times100\ \% = 0.051\%\ \text{Ag (by mass)}$$

91. **(M)** 250.0 mL of 0.1000 M $CuSO_4$ = 0.02500 moles Cu^{2+} initially.

$$\text{moles of } Cu^{2+} \text{ plated out} = \frac{3.512\,\text{C}}{\text{s}}\times1368\ \text{s}\times\frac{1\ \text{mol e}^-}{96{,}485\ \text{C}}\times\frac{1\ \text{mol Cu}^{2+}}{2\ \text{mole}^-} = 0.02490\,\text{mol Cu}^{2+}$$

moles of Cu^{2+} in solution = 0.02500 mol – 0.02490 mol = 0.00010 mol Cu^{2+}

$[Cu^{2+}]$ = 0.00010 mol Cu^{2+}/0.250 L = 4.0×10^{-4} M

	$Cu^{2+}(aq)$ +	$4NH_3(aq) \xrightleftharpoons{K_f=1.1\times10^{13}}$	$Cu(NH_3)_4^{2+}(aq)$
Initial	0.00040 M	0.10 M	0 M
Change(100% rxn)	-0.00040M	maintained	+0.00040 M
New initial	0 M	0.10 M	0.00040 M
Change	+*x*	maintained	-*x*
Equilibrium	*x*	0.10 M	(0.00040 –*x*) M ≈ 0.00040 M

$$K_f = \frac{[Cu(NH_3)_4^{2+}]}{[Cu^{2+}][NH_3]^4} = \frac{0.00040}{[Cu^{2+}](0.10)^4} = 1.1\times10^{13} \qquad [Cu^{2+}] = 3.6\times10^{-13}\,M$$

Hence, the assumption is valid. The concentration of $Cu(NH_3)_4^{2+}(aq)$ = 0.00040 M which is 40 times greater than the 1×10^{-5} detection limit. Thus, the blue color should appear.

<u>92</u>. **(M)** First we determine the molar solubility of AgBr in 1 M NH_3 .

*S*um	$AgBr(s) + 2NH_3(aq)$ ⇌	$Ag(NH_3)^{2+}(aq) +$	$Br^-(aq)$	$K = K_{sp}\times K_f = 8.0\times10^{-6}$
Initial	1.00 M	0 M	0 M	
*E*quil.	1.00-2s	s	s	{s ⇒ AgBr molar solubility}

$$K = \frac{[Ag(NH_3)_2{}^+][Br^-]}{[NH_3(aq)]} = \frac{s^2}{(1-2s)^2} = 8.0\times10^{-6} \qquad s = 2.8\underline{1}\times10^{-3}\ \text{M (also } [Br^-])$$

$$\text{So } [Ag^+] = \frac{K_{sp}}{[Br^-]} = \frac{5.0\times10^{-13}}{2.8\underline{1}\times10^{-3}} = 1.8\times10^{-10}\,M$$

$$\mathrm{AgBr(s)} \rightleftharpoons \mathrm{Ag^+ + Br^-} \qquad \mathrm{K_{sp} = 5.0\times10^{-13}}$$

$$\underline{\mathrm{Ag^+ + 2NH_3} \rightleftharpoons \mathrm{Ag(NH_3)_2^+}} \qquad \mathrm{K_f = 1.6\times10^{7}}$$

$$\text{(sum)}\ \mathrm{AgBr(s) + 2NH_3(aq)} \rightleftharpoons \mathrm{Ag(NH_3)_2^+ + Br^-} \quad \mathrm{K = K_{sp}\ \times\ K_f = 8.0\times10^{-6}}$$

Now, let's construct the cell, guessing that the standard hydrogen electrode is the anode.

$$\text{Oxidation:}\quad H_2(\mathrm{g}) \longrightarrow 2\ \mathrm{H^+} +\ 2\ \mathrm{e^-} \qquad E^\circ = -0.000\ \mathrm{V}$$

$$\text{Reduction:}\quad \underline{\{\mathrm{Ag^+(aq)} +\ \mathrm{e^-} \longrightarrow A\mathrm{g(s)}\ \}\ \times\ 2 \qquad E^\circ = +0.800\ \mathrm{V}}$$

$$\text{Net:}\quad 2\ \mathrm{Ag^+(aq) + H_2(g)} \longrightarrow 2\ \mathrm{Ag(s)}\ + 2\ \mathrm{H^+(aq)} \qquad E^\circ_{\mathrm{cell}} = +0.800\mathrm{V}$$

From the Nernst equation:

$$\mathrm{E\ =\ E^\circ} - \frac{0.0592}{\mathrm{n}}\log_{10} Q = \mathrm{E^\circ} - \frac{0.0592}{\mathrm{n}}\log\frac{[H^+]^2}{[Ag^+]^2} = 0.800\ \mathrm{V} - \frac{0.0592}{2}\log_{10}\frac{1^2}{(1.7\underline{8}\times10^{-10})^2}$$

and $\mathrm{E} = 0.22\underline{3}$ V. Since the voltage is positive, our guess is correct and the standard hydrogen electrode is the anode (oxidizing el*ectrode*).

93. **(M) (a)**

$$\text{Anode:}\qquad 2\mathrm{H_2O(l)} \rightarrow\ 4\ \mathrm{e^-} + 4\ \mathrm{H^+(aq)} + \mathrm{O_2(g)}$$

$$\text{Cathode:}\qquad \underline{2\ \mathrm{H_2O(l)} + 2\ \mathrm{e^-} \rightarrow\ 2\ \mathrm{OH^-(aq)} + \mathrm{H_2(g)}}$$

$$\text{Overall:}\qquad 2\ \mathrm{H_2O(l)} + \cancel{4\ \mathrm{H_2O(l)}} \rightarrow\ \cancel{4\ \mathrm{H^+(aq)}} + \cancel{4\ \mathrm{OH^-(aq)}} + 2\ \mathrm{H_2(g)} + \mathrm{O_2(g)}$$

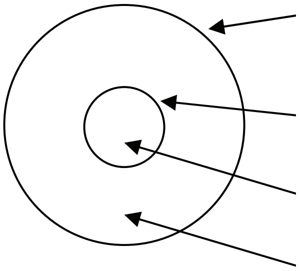
$$2\ \mathrm{H_2O(l)} \rightarrow\ 2\ \mathrm{H_2(g)} + \mathrm{O_2(g)}$$

(b) 21.5 mA = 0.0215 A or 0.0215 C $\mathrm{s^{-1}}$ for 683 s

$$\mathrm{mol\ H_2SO_4} = \frac{0.0215\ \mathrm{C}}{\mathrm{s}} \times 683\mathrm{s} \times \frac{1\ \mathrm{mol\ e^-}}{96485\mathrm{C}} \times \frac{1\ \mathrm{mol\ H^+}}{1\ \mathrm{mol\ e^-}} \times \frac{1\ \mathrm{mol\ H_2SO_4}}{2\ \mathrm{mol\ H^+}} = 7.61\times10^{-5}\ \mathrm{mol\ H_2SO_4}$$

7.61×10^{-5} mol $\mathrm{H_2SO_4}$ in 10.00 mL. Hence $[\mathrm{H_2SO_4}] = 7.61\times10^{-5}$ mol / 0.01000 L $= 7.61\times10^{-3}$M

94. **(D)** First we need to find the total surface area



Outer circumference = 2πr = 2π(2.50 cm) = 15.7 cm
Surface area = circumference × thickness = 15.7 cm × 0.50 cm = $7.8\underline{5}\ \mathrm{cm^2}$

Inner circumference = 2πr = 2π(1.00 cm) = 6.28 cm
Surface area = circumference × thickness = 6.28 cm × 0.50 cm = $3.1\underline{4}\ \mathrm{cm^2}$

Area of small circle = $\pi r^2 = \pi(1.00\ \mathrm{cm})^2 = 3.14\ \mathrm{cm^2}$

Area of large circle = $\pi r^2 = \pi(2.50\ \mathrm{cm})^2 = 19.6\ \mathrm{cm^2}$

$$\text{Total area} = 7.85\ \mathrm{cm^2} + 3.14\ \mathrm{cm^2} + 2\times(19.6\ \mathrm{cm^2}) - 2\times(3.1\underline{4}\ \mathrm{cm^2}) = 43.9\underline{1}\ \mathrm{cm^2}$$

Volume of metal needed = surface area × thickness of plating = $43.9\underline{1}\ \mathrm{cm^2} \times 0.0050\ \mathrm{cm} = 0.22\ \mathrm{cm^3}$

$$\text{Charge required} = 0.22\ \mathrm{cm^3} \times \frac{8.90\ \mathrm{g}}{\mathrm{cm^3}} \times \frac{1\ \mathrm{mol\ Ni}}{58.693\ \mathrm{g\ Ni}} \times \frac{2\ \mathrm{mol\ e^-}}{1\ \mathrm{mol\ Ni}} \times \frac{96485\ \mathrm{C}}{1\ \mathrm{mol\ e^-}} = 6437.5\ \mathrm{C}$$

Time = charge/time = 6437.5 C / 1.50 C/s = 4291.7 s or 71.5 min

95. (M) The overall reaction for the electrolytic cell is:

$$\text{Cu(s)+Zn}^{2+}\text{(aq)} \rightarrow \text{Cu}^{2+}\text{(aq)+Zn(s)} \qquad E^{o}_{cell} = -1.103\text{V}$$

Next, we calculate the number of moles of Zn^{2+}(aq) plated out and number of moles of Cu^{2+}(aq) formed:

$$n(\text{Cu}^{2+}) = = \frac{0.500\text{C}}{\text{s}} \times 10\text{ h} \times \frac{60\,\text{min}}{1\text{h}} \times \frac{60\,\text{s}}{1\,\text{min}} \times \frac{1\text{ mol e}^{-}}{96{,}485\text{ C}} \times \frac{1\text{ mol Cu}^{2+}}{2\text{ mol e}^{-}} = 0.0935\,\text{mol Cu}^{2+}$$

$$n(\text{Zn}^{2+}) = n(\text{Cu}^{2+})\text{=0.0935}\,\text{mol}$$

Initially, solution contained $1.00\text{molL}^{-1} \times 0.100\text{L=0.100 mol}\,\text{Zn}^{2+}$(aq). Therefore, at the end of electrolysis we are left with:

$$\text{n(Zn}^{2+})_{\text{LEFT}}\text{=(0.100-0.0935)mol=6.5} \times 10^{-3}\text{mol} \Rightarrow [\text{Zn}^{2+}]\text{=}\frac{6.5 \times 10^{-3}\text{mol}}{0.1\text{L}}\text{=6.5} \times 10^{-2}\text{M}$$

$$\text{n(Cu}^{2+})_{\text{FORMED}}\text{=0.0935mol} \Rightarrow [\text{Cu}^{2+}]\text{=}\frac{0.0935\text{mol}}{0.1\text{L}}\text{=0.936M}$$

The new potential after the cell was switched to a voltaic one can be calculated using Nernst equation:

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0592}{2}\log\frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} = 1.103 - \frac{0.0592}{2}\log\frac{6.5 \times 10^{-3}\text{ M}}{0.935\text{ M}} = 1.103 + 0.064 = 1.167\text{ V}$$

96. **(M) (a)** The metal has to have a reduction potential more negative than -0.691 V, so that its oxidation can reverse the tarnishing reaction's -0.691 V reduction potential. Aluminum is a good candidate, because it is inexpensive, readily available, will not react with water and has an E^{o} of -1.676 V. Zinc is also a possibility with an E^{o} of -0.763 V, but we don't choose it because there may be an overpotential associated with the tarnishing reaction.

(b)

$$\begin{array}{ll} \text{Oxidation:} & \{\text{Al(s)} \longrightarrow \text{Al}^{3+}\text{(aq)} + \ 3\text{ e}^{-}\ \} \times 2 \\ \text{Reduction:} & \{\text{Ag}_2\text{S(s)} \ + 2\text{ e}^{-} \longrightarrow \text{Ag(s)} + \ \text{S}^{2-}\text{(aq)}\ \} \times 3 \\ \hline \text{Net:} & 2\text{ Al(s)} + 3\text{ Ag}_2\text{S(s)} \longrightarrow 6\text{Ag(s)} \ + \ 2\text{ Al}^{3+}\text{(aq)} + \ 3\text{ S}^{2-}\text{(aq)} \end{array}$$

(c) The dissolved $NaHCO_3$(s) serves as an electrolyte. It would also enhance the electrical contact between the two objects.

(d) There are several chemicals involved: Al, H_2O, and $NaHCO_3$. Although the aluminum plate will be consumed very slowly because silver tarnish is very thin, it will, nonetheless, eventually erode away. We should be able to detect loss of mass after many uses.

97. (M) (a) Overall: $C_3H_8(g) + 5\ O_2(g) \rightarrow 3\ CO_2(g) + 4\ H_2O(l)$

Anode: $6\ H_2O(l) + C_3H_8(g) \rightarrow 3\ CO_2(g) + 20\ H^{+}(g) + 20\ e^{-}$

Cathode: $20\ e^{-} + 20\ H^{+}(g) + 5\ O_2(g) \rightarrow 10\ H_2O(l)$

$\Delta G^{\circ}_{rxn} = 3(-394.4\text{ kJ/mol}) + 4(-237.1\text{ kJ/mol}) - 1(-23.3\text{ kJ/mol}) = -2108.3\text{ kJ/mol}$

ΔG°_{rxn} = -2108.3 kJ/mol = -2,108,300 J/mol
ΔG°_{rxn} = $-nFE^\circ_{cell}$ = -20 mol e^- × (96485 C/mol e^-) × E°_{cell}
E°_{cell} = +1.0926 V

$20\ e^- + 20\ H^+(g) + 5\ O_2(g) \rightarrow 10\ H_2O(l)$ $E^\circ_{cathode}$ = +1.229 V

Hence $E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$ $+1.0926\text{ V} = +1.229\text{ V} - E^\circ_{anode}$

E°_{anode} = +0.136 V (reduction potential for $3\ CO_2(g) + 20\ H^+(g) + 20\ e^- \rightarrow 6\ H_2O(l) + C_3H_8(g)$)

(b) Use thermodynamic tables for $3\ CO_2(g) + 20\ H^+(g) + 20\ e^- \rightarrow 6\ H_2O(l) + C_3H_8(g)$

ΔG°_{rxn} = 6(-237.1 kJ/mol) + 1(-23.3 kJ/mol) – [(-394.4 kJ/mol) + 20(0kJ/mol)]= -262.7 kJ/mol

ΔG°_{red} = -262.7 kJ/mol = -262,700 J/mol = $-nFE^\circ_{red}$ = -20 mol e^-×(96,485 C/mol e^-)×E°_{red}

E°_{red} = 0.136 V (Same value, as found in (a))

98. (D) (a) Equation 20.15 ($\Delta G^o = -zFE^o_{cell}$) gives the relationship between the standard Gibbs energy of a reaction and the standard cell potential. Gibbs free energy also varies with temperature ($\Delta G^o = \Delta H^o - T\Delta S^o$). If we assume that ΔH^o and ΔS^o do not vary significantly over a small temperature range, we can derive an equation for the temperature variation of E^o_{cell}:

$$\Delta G^o = \Delta H^o - T\Delta S^o = zFE^o_{cell} \Rightarrow E^o_{cell} = \frac{\Delta H^o - T\Delta S^o}{zF}$$

Considering two different temperatures one can write:

$$E^o_{cell}(T_1) = \frac{\Delta H^o - T_1\Delta S^o}{zF} \text{ and } E^o_{cell}(T_2) = \frac{\Delta H^o - T_2\Delta S^o}{zF}$$

$$E^o_{cell}(T_1) - E^o_{cell}(T_2) = \frac{\Delta H^o - T_1\Delta S^o}{zF} - \frac{\Delta H^o - T_2\Delta S^o}{zF}$$

$$E^o_{cell}(T_1) - E^o_{cell}(T_2) = \frac{-T_1\Delta S^o + T_2\Delta S^o}{zF} = \frac{\Delta S^o}{zF}(T_2 - T_1)$$

(b) Using this equation, we can now calculate the cell potential of a Daniel cell at 50 °C:

$$E^o_{cell}(25^o C) - E^o_{cell}(50^o C) = \frac{-10.4 JK^{-1}mol^{-1}}{2 \times 96485 Cmol^{-1}}(50 - 25)K = -0.00135$$

$$E^o_{cell}(50^o C) = 1.103V + 0.00135 = 1.104V$$

99. (D) Recall that under non-standard conditions $\Delta G = \Delta G^o + RT\ln K$. Substituting $\Delta G^o = \Delta H^o - T\Delta S^o$ and $\Delta G = -zFE_{cell}$ one obtains:

$$-zFE_{cell} = \Delta H^o - T\Delta S^o + RT\ln Q$$

For two different temperatures (T_1 and T_2) we can write:

$$-zFE_{cell}(T_1) = \Delta H^o - T_1\Delta S^o + RT_1 \ln Q$$

$$-zFE_{cell}(T_2) = \Delta H^o - T_2\Delta S^o + RT_2 \ln Q$$

$$-E_{cell}(T_1) + E_{cell}(T_2) = \frac{\Delta H^o - T_1\Delta S^o + RT_1 \ln Q - \Delta H^o + T_2\Delta S^o - RT_2 \ln Q}{zF}$$

$$-E_{cell}(T_1) + E_{cell}(T_2) = \frac{-T_1\Delta S^o + RT_1 \ln Q + T_2\Delta S^o - RT_2 \ln Q}{zF}$$

$$E_{cell}(T_1) - E_{cell}(T_2) = \frac{T_1\Delta S^o - RT_1 \ln Q}{zF} - \frac{T_2\Delta S^o + RT_2 \ln Q}{zF}$$

$$E_{cell}(T_1) - E_{cell}(T_2) = T_1\left(\frac{\Delta S^o - R\ln Q}{zF}\right) - T_2\left(\frac{\Delta S^o - R\ln Q}{zF}\right)$$

$$E_{cell}(T_1) - E_{cell}(T_2) = (T_1 - T_2)\left(\frac{\Delta S^o - R\ln Q}{zF}\right)$$

The value of Q at 25 °C can be calculated from E^o_{cell} and E_{cell}. First calculate E^o_{cell}:

Oxidation:	$\text{Cu(s)} \rightarrow \text{Cu}^{2+}\text{(aq)+2e}^-$	$-E_o = -0.340V$
Reduction:	$\text{2Fe}^{3+}\text{(aq)+2e}^- \rightarrow \text{2Fe}^{2+}\text{(aq)}$	$-E_o = +0.771V$
Overall:	$\text{Cu(s)+2Fe}^{3+} \rightarrow \text{Cu}^{2+}\text{(aq)+2Fe}^{2+}$	$E^o_{cell} = 0.431V$

$$0.370 = 0.431 - \frac{0.0592}{2}\log Q \Rightarrow 0.296\log Q = 0.431 - 0.370 = 0.061$$

$$\log Q = 0.206 \Rightarrow Q = 10^{0.206} = 1.61$$

Now, use the above derived equation and solve for ΔS^o:

$$0.394 - 0.370 = (50 - 25)\left(\frac{\Delta S^o - 8.314 \times \ln 1.61}{2 \times 96485}\right)$$

$$0.024 = 25 \times (\frac{\Delta S^o - 3.96}{192970}) \Rightarrow \Delta S^o - 3.96 = 185.3 \Rightarrow \Delta S^o = 189.2\text{JK}^{-1}$$

Since $\Delta G^o = \Delta H^o - T\Delta S^o = -zFE^o_{cell}$ we can calculate ΔG^o, K (at 25 °C) and ΔH^o:

$$\Delta G^o = -zFE^o_{cell} = -2 \times 96485 \times 0.431 = -83.2\text{kJ}$$

$$\Delta G^o = -RT\ln K \Rightarrow -83.2 \times 1000 = -8.314 \times 298.15 \times \ln K$$

$$\ln K = 33.56 \Rightarrow K = e^{33.56} = 3.77 \times 10^{14}$$

$$\text{-83.2kJ=}\Delta\text{H}^o - 298.15 \times \frac{189.2}{1000}\text{kJ} \Rightarrow \Delta H^o = -83.2 + 56.4 = -26.8\text{kJ}$$

Since we have ΔH^o and ΔS^o we can calculate the value of the equilibrium constant at 50 °C:

$$\Delta G^o = \Delta H^o - T\Delta S^o = -26.8\text{kJ} - (273.15 + 50)\text{K} \times \frac{189.2}{1000}\text{kJK}^{-1} = -87.9\text{kJ}$$

$$-87.9 \times 1000\text{J} = -8.314\text{JK}^{-1}\text{mol}^{-1} \times (273.15 + 50)\text{K} \times \ln K$$

$$\ln K = 32.7 \Rightarrow K = e^{32.7} = 1.59 \times 10^{14}$$

Choose the values for the concentrations of Fe^{2+}, Cu^{2+} and Fe^{3+} that will give the value of the above calculated Q. For example:

$$Q=\frac{\left[Fe^{2+}\right]^2\left[Cu^{2+}\right]}{\left[Fe^{3+}\right]^2}=1.61$$

$$\frac{0.1^2\times 1.61}{0.1^2}=1.61$$

Determine the equilibrium concentrations at 50 °C. Notice that since Q<K, a net change occurs from left to right (the direction of the forward reaction):

$$Cu(s)+2Fe^{3+}\rightarrow Cu^{2+}(aq)+2Fe^{2+}$$

Initial:	0.1	1.61	0.1
Change:	0.1-x	1.61+x	0.1+x

$$K=\frac{\left[Fe^{2+}\right]_{eq}^2\left[Cu^{2+}\right]_{eq}}{\left[Fe^{3+}\right]_{eq}^2}=1.59\times 10^{14}=\frac{(0.1+x)^2\times(1.61+x)}{(0.1-x)^2}$$

Obviously, the reaction is almost completely shifted towards products. First assume that the reaction goes to completion, and then let the equilibrium be shifted towards reactants:

$$Cu(s)+2Fe^{3+}\rightarrow Cu^{2+}(aq)+2Fe^{2+}$$

Initial:	0.1	1.61	0.1
Final	0	1.71	0.2
Equilibrium	0+x	1.71-x	0.2-x

$$K=\frac{\left[Fe^{2+}\right]_{eq}^2\left[Cu^{2+}\right]_{eq}}{\left[Fe^{3+}\right]_{eq}^2}=1.59\times 10^{14}=\frac{(0.2-x)^2\times(1.71-x)}{(x)^2}\approx\frac{0.2^2\times 1.71}{x^2}$$

$$x^2\approx\frac{0.2^2\times 1.71}{1.59\times 10^{14}}\approx 4.3\times 10^{-16}$$

$$x\approx 2.1\times 10^{-8}\,M$$

Therefore, $[Cu^{2+}]\approx 1.7M$, $[Fe^{2+}]\approx 0.2M$ and $[Fe^{3+}]\approx 2.1x10^{-8}M$

100. **(D)** This problem can be solved by utilizing the relationship between ΔG^o and E^o_{cell} (ΔG^o=-zFE^o_{cell}):

Consider a hypothetical set of the following reactions:

$$A+ne^-\rightarrow A^{n-}\quad E^o_1\text{ and }\Delta G^o_1$$

$$B+me^-\rightarrow B^{m-}\quad E^o_2\text{ and }\Delta G^o_2$$

Overall: $A+B+ne^-+me^-\rightarrow A^{n-}+B^{m-}\quad E^o_{rxn}=?\text{ and }\Delta G^o_{rxn}=\Delta G^o_1+\Delta G^o_2$

$$\Delta G^o_{rxn}=\Delta G^o_1+\Delta G^o_2=-nFE^o_1-mFE^o_2$$

$$-(n+m)FE^o_{rxn}=-nFE^o_1-mFE^o_2$$

$$(n+m)FE^o_{rxn}=nFE^o_1+mFE^o_2\Rightarrow E^o_{rxn}=\frac{nFE^o_1+mFE^o_2}{n+m}$$

Therefore, for n-sets of half-reactions:

$$E^o = \frac{\sum n_i E_i^o}{\sum n_i}$$

The E_o for the given half-reaction can be determined by combining four half-reactions:

$$\mathrm{H_6IO_6{+}H^{+}{+}2e^{-} \rightarrow IO_3^{-}{+}3H_2O} \Rightarrow \quad \mathrm{E}_o = 1.60V$$

$$\mathrm{IO_3^{-}{+}6H^{+}{+}5e^{-} \rightarrow \frac{1}{2}I_2{+}3H_2O} \Rightarrow \quad \mathrm{E}_o = 1.19V$$

$$\mathrm{I_2{+}2H_2O \rightarrow 2HIO{+}2H^{+}{+}2e^{-}} \Rightarrow \mathrm{E}_o = -1.45V$$

$$2I^- \rightarrow I_2 + 2e^- \Rightarrow \mathrm{E}_o = -0.535V$$

Overall :

$$\mathrm{H_6IO_6{+}H^{+}{+}2e^{-} + IO_3^{-}{+}6H^{+}{+}5e^{-} + I_2{+}2H_2O{+}2}I^- \rightarrow \mathrm{IO_3^{-}{+}3H_2O{+}\frac{1}{2}I_2{+}3H_2O{+}2HIO{+}2H^{+}{+}2e^{-}} + I_2 + 2e^-$$

$$\mathrm{H_6IO_6{+}5H^{+}{+}2I^{-}{+}3e^{-} \rightarrow \frac{1}{2}I_2{+}4H_2O{+}2HIO}$$

$$\mathrm{E}^o = \frac{1.60 \times 3 + 1.19 \times 5 - 1.45 \times 2 - 0.535 \times 2}{2 + 5 - 2 - 2} = 2.26V$$

FEATURE PROBLEMS

101. (D) (a) Anode: $\mathrm{H_2(g, 1\ atm) \rightarrow 2H^+(1\,M) + 2e^-}$ $\quad -E^\circ = -0.0000\,\mathrm{V}$

Cathode: $\{\mathrm{Ag^+}(x\,\mathrm{M}) + \mathrm{e^-} \rightarrow \mathrm{Ag(s)}\} \times 2$ $\quad E^\circ = 0.800\,\mathrm{V}$

Net: $\mathrm{H_2(g, 1atm) + 2Ag^+(aq) \rightarrow 2H^+(1\,M) + 2Ag(s)}$ $\quad E^\circ_{\mathrm{cell}} = 0.800$

(b) Since the voltage in the anode half-cell remains constant, we use the Nernst equation to calculate the half-cell voltage in the cathode half-cell, with two moles of electrons. This is then added to $-E$ for the anode half-cell. Because $-E^\circ = 0.000$ for the anode half cell, $E_{\mathrm{cell}} = E_{\mathrm{cathode}}$

$$E = E^\circ - \frac{0.0592}{2}\log\frac{1}{[\mathrm{Ag^+}]^2} = 0.800 + 0.0592\ \log[\mathrm{Ag^+}] = 0.800 + 0.0592 \log x$$

(c) **(i)** Initially $[\mathrm{Ag^+}] = 0.0100$; $\quad E = 0.800 + 0.0592\ \log\ 0.0100 = 0.682\ \mathrm{V} = E_{\mathrm{cell}}$

Note that 50.0 mL of titrant is required for the titration, since both $\mathrm{AgNO_3}$ and KI have the same concentrations and they react in equimolar ratios.

(ii) After 20.0 mL of titrant is added, the total volume of solution is 70.0 mL and the unreacted $\mathrm{Ag^+}$ is that in the untitrated 30.0 mL of $0.0100\ \mathrm{M\ AgNO_3(aq)}$.

$$\left[\mathrm{Ag}^+\right]=\frac{30.0\ \mathrm{mL}\times 0.0100\ \mathrm{M\ Ag}^+}{70.0\ \mathrm{mL}}=0.00429\mathrm{M}$$

$$E=0.800+0.0592\log(0.00429)=0.660\ \mathrm{V}=E_{\mathrm{cell}}$$

(iii) After 49.0 mL of titrant is added, the total volume of solution is 99.0 mL and the unreacted Ag^+ is that in the untitrated 1.0 mL of $0.0100\ \mathrm{M\ AgNO_3(aq)}$.

$$\left[\mathrm{Ag}^+\right]=\frac{1.0\ \mathrm{mL}\times 0.0100\ \mathrm{M\ Ag}^+}{99.0\ \mathrm{mL}}=0.00010\ \mathrm{M}$$

$$E=0.800+0.0592\log(0.00010)=0.563\ \mathrm{V}=E_{\mathrm{cell}}$$

(iv) At the equivalence point, we have a saturated solution of AgI, for which

$$\left[\mathrm{Ag}^+\right]=\sqrt{K_{\mathrm{sp}}(\mathrm{AgI})}=\sqrt{8.5\times10^{-17}}=9.2\times10^{-9}$$

$$E=0.800+0.0592\log\left(9.2\times10^{-9}\right)=0.324\ \mathrm{V}=E_{\mathrm{cell}}\,.$$

After the equivalence point, the $\left[\mathrm{Ag}^+\right]$ is determined by the $\left[\mathrm{I}^-\right]$ resulting from the excess KI(aq).

(v) When 51.0 mL of titrant is added, the total volume of solution is 101.0 mL and the excess I^- is that in 1.0 mL of 0.0100 M KI(aq).

$$\left[\mathrm{I}^-\right]=\frac{1.0\ \mathrm{mL}\times 0.0100\ \mathrm{M\ I}^-}{101.0\ \mathrm{mL}}=9.9\times10^{-5}\ \mathrm{M}\qquad \left[\mathrm{Ag}^+\right]=\frac{K_{sp}}{\left[\mathrm{I}^-\right]}=\frac{8.5\times10^{-17}}{0.000099}=8.6\times10^{-13}\ \mathrm{M}$$

$$E=0.800+0.0592\ \log\left(8.6\times10^{-13}\right)=0.086\ \mathrm{V}=E_{\mathrm{cell}}$$

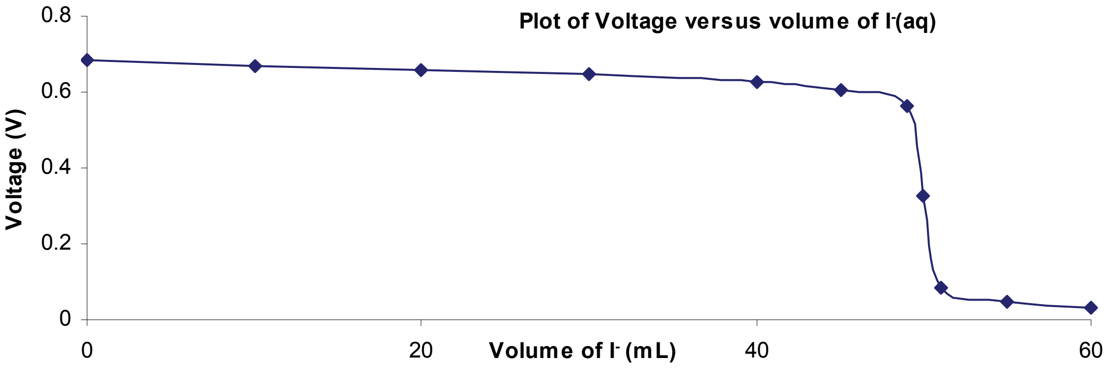
(vi) When 60.0 mL of titrant is added, the total volume of solution is 110.0 mL and the excess I^- is that in 10.0 mL of 0.0100 M KI(aq).

$$\left[\mathrm{I}^-\right]=\frac{10.0\ \mathrm{mL}\times 0.0100\ \mathrm{M\ I}^-}{110.0\ \mathrm{mL}}=0.00091\ \mathrm{M}$$

$$\left[\mathrm{Ag}^+\right]=\frac{\mathrm{K_{sp}}}{\left[\mathrm{I}^-\right]}=\frac{8.5\times10^{-17}}{0.00091}=9.3\times10^{-14}\ \mathrm{M}$$

$$E=0.800+0.0592\ \log\left(9.3\times10^{-14}\right)=0.029\ \mathrm{V}=E_{\mathrm{cell}}$$

(d) The titration curve is presented below.



102. **(D) (a)** **(1)** anode: $\text{Na(s)} \rightarrow \text{Na}^+(\text{in ethylamine}) + \text{e}^-$

cathode: $\text{Na}^+(\text{in ethylamine}) \rightarrow \text{Na(amalgam, 0.206 \%)}$

$$\overline{\text{Net: Na(s)} \rightarrow \text{Na(amalgam, 0.206\%)}}$$

(2) anode: $2\text{Na(amalgam, 0.206\%)} \rightarrow 2\text{Na}^+(1\text{ M}) + 2\text{e}^-$

cathode: $2\text{H}^+(\text{aq,1M}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g,1 atm})$

$$\overline{\text{Net: 2Na (amalgam, 0.206 \%)} + 2\text{H}^+(\text{aq,1M}) \rightarrow 2\ \text{Na}^+(1\text{ M}) + \text{H}_2(\text{g,1 atm})}$$

(b) **(1)** $\Delta G = -1\text{ mol e}^- \times \dfrac{96{,}485\text{ C}}{1\text{mol e}^-} \times 0.8453\text{ V} = -8.156 \times 10^4\text{ J or } -81.56\text{ kJ}$

(2) $\Delta G = -2\text{ mol e}^- \times \dfrac{96{,}485\text{C}}{1\text{ mol e}^-} \times 1.8673\text{ V} = -36.033 \times 10^4\text{ J or } -360.33\text{ kJ}$

(c) **(1)** $2\text{Na(s)} \rightarrow 2\text{Na(amalgam, 0.206\%)}$ $\qquad \Delta G_1 = -2 \times 8.156 \times 10^4\text{ J}$

(2) $2\text{Na (amalg, 0.206\%)} + 2\text{H}^+(\text{aq,1M}) \rightarrow 2\,\text{Na}^+(1\text{M}) + \text{H}_2(\text{g, 1 atm})$

$\Delta G_2 = -36.033 \times 10^4\text{ J}$

Overall: $2\text{Na(s)} + 2\text{H}^+(\text{aq}) \rightarrow 2\,\text{Na}^+(1\text{M}) + \text{H}_2(\text{g, 1 atm})$

$\Delta G = \Delta G_1 + \Delta G_2 = -16.312 \times 10^4\text{J} - 36.033 \times 10^4\text{J} = -52.345 \times 10^4\text{J or } -523.45\text{ kJ}$

Since standard conditions are implied in the overall reaction, $\Delta G = \Delta G^\circ$.

(d) $$E_{cell}^{\circ} = -\frac{-52.345 \times 10^4\text{ J}}{2\text{ mol e}^- \times \dfrac{96{,}485\text{ C}}{1\text{ mol e}^-} \times \dfrac{1\text{ J}}{1\text{ V}\cdot\text{C}}} = E^\circ\{\text{H}^+(1\text{ M})/\text{H}_2(1\text{ atm})\} - E^\circ\{\text{Na}^+(1\text{ M})/\text{Na(s)}\}$$

$E^\circ\{\text{Na}^+(1\text{ M})/\text{Na(s)}\} = -2.713\text{ V}$. This is precisely the same as the value in Appendix D.

103. **(D)** The question marks in the original Latimer diagram have been replaced with letters in the diagram below to make the solution easier to follow:

$$\begin{tikzcd}
BrO_4^- \arrow[r, "1.025\ \text{V}"] & BrO_3^- \arrow[r, "(a)"] \arrow[rrr, bend right, "(e)\ 0.584\ \text{V}"'] & BrO^- \arrow[r, "(b)"] \arrow[rr, bend right, "(d)"'] & Br_2 \arrow[r, "(c)"] & Br^-
\end{tikzcd}$$

By referring to Appendix D and by employing the correct procedure for adding together half-reactions of the same type we obtain:

$$\begin{array}{lll}
\text{(c)} & Br_2(l) + 2e^- \rightarrow 2Br^-(aq) & E_c^\circ = 1.065\,\text{V} \quad \text{(Appendix D)} \\
\text{(d)} & BrO^-(aq) + H_2O(l) + 2e^- \rightarrow Br^-(aq) + 2OH^-(aq) & E_d^\circ = 0.766\,\text{V} \quad \text{(Appendix D)} \\
\text{(b)} & 2BrO^-(aq) + 2H_2O(l) + 2e^- \rightarrow Br_2(l) + 4OH^-(aq) & E_b^\circ = 0.455\,\text{V} \quad \text{(Appendix D)}
\end{array}$$

$$\begin{array}{lll}
\text{(a)} & \{BrO_3^-(aq) + 2H_2O(l) + 4e^- \rightarrow BrO^-(aq) + 4OH^-(aq)\} \times 2 & E_a^\circ = ? \\
\text{(b)} & 2BrO^-(aq) + 2H_2O(l) + 2e^- \rightarrow Br_2(l) + 4OH^-(aq) & E_b^\circ = 0.455\,\text{V} \\
\text{(c)} & Br_2(l) + 2e^- \rightarrow 2Br^-(aq) & E_c^\circ = 1.065\,\text{V} \\
\hline
\text{(e)} & 2BrO_3^-(aq) + 6H_2O(l) + 12e^- \rightarrow 12OH^-(aq) + 2Br^-(aq) & E_e^\circ = 0.584\,\text{V}
\end{array}$$

$$\Delta G^\circ_{Total} = \Delta G^\circ_{(a)} + \Delta G^\circ_{(b)} + \Delta G^\circ_{(c)}$$

$$-12F\left(E_e^\circ\right) = -8F\left(E_a^\circ\right) + \text{-}2F\left(E_b^\circ\right) + \text{-}2F\left(E_c^\circ\right)$$

$$-12F\left(0.584\,\text{V}\right) = -8F\left(E_a^\circ\right) + \text{-}2F\left(0.455\,\text{V}\right) + \text{-}2F\left(1.065\,\text{V}\right)$$

$$E_a^\circ = \frac{-12F\left(0.584\,\text{V}\right) + 2F\left(0.455\,\text{V}\right) + 2F\left(1.065\,\text{V}\right)}{-8F} = 0.496\ \text{V}$$

104. **(D) (a)** The capacitance of the cell membrane is given by the following equation,

$$C = \frac{\varepsilon_0 \varepsilon A}{l}$$

where $\varepsilon_0\varepsilon = 3 \times 8.854 \times 10^{-12}\ C^2\ N^{-1}\ m^{-2}$;
$A = 1 \times 10^{-6}\ cm^2$; and $l = 1 \times 10^{-6}$ cm.
Together with the factors necessary to convert from cm to m and from cm^2 to m^2, these data yield

$$C = \frac{(3)\left(8.854 \times 10^{-12}\ \frac{C^2}{N^1\ m^2}\right)(1 \times 10^{-6}\ cm^2)\left(\frac{1\ m}{100\ cm}\right)^2}{(1 \times 10^{-6} cm)\left(\frac{1\ m}{100\ cm}\right)} = 2.66 \times 10^{-13}\ \frac{C^2}{N\,m}$$

$$C = \left(2.66 \times 10^{-13}\ \frac{C^2}{N\,m}\right)\left(\frac{1F}{1\frac{C^2}{N\,m}}\right) = 2.66 \times 10^{-13}\ F$$

(b) Since the capacitance *C* is the charge in coulombs per volt, the charge on the membrane, *Q*, is given by the product of the capacitance and the potential across the cell membrane.

$$Q = 2.66 \times 10^{-13}\ \frac{\text{C}}{\text{V}} \times 0.085\ \text{V} = 2.26 \times 10^{-14}\ \text{C}$$

(c) The number of K^+ ions required to produce this charge is

$$\frac{Q}{\text{e}} = \frac{2.26\times10^{-14}\ \text{C}}{1.602\times10^{-19}\ \text{C/ion}} = 1.41\times10^{5}\ \text{K}^+\ \text{ions}$$

(d) The number of K^+ ions in a typical cell is

$$\left(6.022\times10^{23}\,\frac{\text{ions}}{\text{mol}}\right)\left(155\times10^{-3}\,\frac{\text{mol}}{\text{L}}\right)\left(\frac{1\text{L}}{1000\ \text{cm}^3}\right)(1\times10^{-8}\ \text{cm}^3) = 9.3\times10^{11}\ \text{ions}$$

(e) The fraction of the ions involved in establishing the charge on the cell membrane is

$$\frac{1.4\times10^{5}\ \text{ions}}{9.3\times10^{11}\ \text{ions}} = 1.5\times10^{-7}\ (\sim 0.000015\ \%)$$

Thus, the concentration of K^+ ions in the cell remains constant at 155 mM.

105. **(M)** Reactions with a positive cell potential are reactions for which $\Delta G^o < 0$, or reactions for which K>1. ΔS^o, ΔH^o and ΔU^o cannot be used alone to determine whether a particular electrochemical reaction will have a positive or negative value.

106. **(M)** The half-reactions for the first cell are:

Anode (oxidation): $\text{X(s)} \rightarrow \text{X}^+\text{(aq)+e}^-$ $\quad -E^o_{X^+/X}$

Cathode (reduction): $2\text{H}^+\text{(aq)+2e}^- \rightarrow \text{H}_2\text{(g)} \quad E^o = 0V$

Since the electrons are flowing from metal X to the standard hydrogen electrode, $E^o_{X^+/X} < 0V$.

The half-reactions for the second cell are:

Anode (oxidation): $\text{X(s)} \rightarrow \text{X}^+\text{(aq)+e}^-$ $\quad -E^o_{X^+/X}$

Cathode (reduction): $\text{Y}^{2+}\text{+2e}^- \rightarrow \text{Y(s)} \quad E^o_{Y^{2+}/Y}$

Since the electrons are flowing from metal X to metal Y, $-E^o_{X^+/X} + E^o_{Y^{2+}/Y} > 0$.

From the first cell we know that $E^o_{X^+/X} < 0V$. Therefore, $E^o_{X^+/X} > E^o_{Y^{2+}/Y}$.

107. **(M)** The standard reduction potential of the Fe^{2+}(aq)/Fe(s) couple can be determined from:

$\text{Fe}^{2+}\text{(aq)} \rightarrow \text{Fe}^{3+}\text{(aq)+e}^- E_o = -0.771V$

$\text{Fe}^{3+}\text{(aq)+3e}^- \rightarrow \text{Fe(s)} \quad \text{E}_o = -0.04V$

Overall:

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

We proceed similarly to the solution for 100:

$$E^o = \frac{\sum n_i E_i^o}{\sum n_i} = \frac{-0.771 \times (1) - 0.04 \times 3}{3-1} = -0.445V$$

SELF-ASSESSMENT EXERCISES

108. **(E)** **(a)** A standard electrode potential E^o measures the tendency for a reduction process to occur at an electrode.

(b) F is the Faraday constant, or the electric charge per mole of electrons (96485 C/mol).

(c) The anode is the electrode at which oxidation occurs.

(d) The cathode is the electrode at which reduction occurs.

109. **(E)** **(a)** A salt bridge is a devise used to connect the oxidation and reduction half-cells of a galvanic (voltaic) cell.

(b) The standard hydrogen electrode (abbreviated SHE), also called normal hydrogen electrode (NHE), is a redox electrode which forms the basis of the thermodynamic scale of oxidation-reduction potentials. By definition electrode potential for SHE is 0.

(c) Cathodic protection is a technique commonly used to control the corrosion of a metal surface by making it work as a cathode of an electrochemical cell. This is achieved by placing in contact with the metal to be protected another more easily corroded metal to act as the anode of the electrochemical cell.

(d) A fuel cell is an electrochemical cell that produces electricity from fuels. The essential process in a fuel cell is fuel+oxygen→oxidation products.

110. **(E)** **(a)** An overall cell reaction is a combination of oxidation and reduction half-reactions.

(b) In a galvanic (voltaic) cell, chemical change is used to produce electricity. In an electrolytic cell, electricity is used to produce a nonspontaneous rection.

(c) In a primary cell, the cell reaction is not reversible. In a secondary cell, the cell reaction can be reversed by passing electricity through the cell (charging).

(d) E^o_{cell} refers to the standard cell potential (the ionic species are present in aqueous solution at unit activity (approximately 1M), and gases are at 1 bar pressure (approximately 1 atm).

111. **(M)** **(a)** False. The cathode is the positive electrode in a voltaic cell and negative in electrolytic cell.

(b) False. The function of the salt bridge is to permit the migration of the ions not electrons.

(c) True. The anode is the negative electrode in a voltaic cell.

(d) True.

(e) True. Reduction always occurs at the cathode of an electrochemical cell. Because of the removal of electrons by the reduction half-reaction, the cathode of a voltaic cell is positive. Because of the electrons forced onto it, the cathode of an electrolytic cell is negative. For both types, the cathode is the electrode at which electrons enter the cell.

(f) False. Reversing the direction of the electron flow changes the voltaic cell into an electrolytic cell.
(g) True. The cell reaction is an oxidation-reduction reaction.

112. **(M)** The correct answer is (b), $Hg^{2+}(aq)$ is more readily reduced than $H^{+}(aq)$.

113. **(M)** Under non-standard conditions, apply the Nernst equation to calculate E_{cell}:

$$E_{cell} = E^{o}_{cell} - \frac{0.0592}{z}\log Q$$

$$E_{cell} = 0.66 - \frac{0.0592}{2}\log\frac{0.10}{0.01} = 0.63V$$

The correct answer is (d).

114. **(E)** **(c)** The displacement of Ni(s) from the solution will proceed to a considerable extent, but the reaction will not go to completion.

115. **(E)** The gas evolved at the anode when K_2SO_4(aq) is electrolyzed between Pt electrodes is most likely oxygen.

116. **(M)** The electrochemical reaction in the cell is:

Anode (oxidation): $\{\text{Al(s)} \rightarrow \text{Al}^{3+}\text{(aq)+3e}^{-}\} \times 2$
Cathode (reduction): $\{\text{H}_2\text{(g)+2e}^{-} \rightarrow \text{2H}^{+}\text{(aq)}\} \times 3$
Overall: $\text{2Al(s)+3H}_2\text{(g)} \rightarrow \text{2Al}^{3+}\text{(aq)+6H}^{+}\text{(aq)}$

$$4.5\text{g Al} \times \frac{1\text{mol Al}}{26.98\text{g Al}} \times \frac{3\text{ mol H}_2}{2\text{ mol Al}} = 0.250\text{mol H}_2$$

$$0.250\text{ mol H}_2 \times \frac{22.4\text{L H}_2}{1\text{mol H}_2} = 5.6\text{L H}_2$$

117. **(E)** The correct answer is (a) ΔG.

118. **(M)** Anode (oxidation): $\{\text{Zn(s)} \rightarrow \text{Zn}^{2+}\text{(aq)+2e}^{-}\} \times 3$ $\quad -E^{o} = 0.763V$
Cathode (reduction): $\{\text{NO}_3^{-}\text{(aq)+4H}^{+}\text{(aq)+3e}^{-} \rightarrow \text{NO(g)+2H}_2\text{O(l)}\} \times 2$ $\quad E^{o} = +0.956V$

Overall: $\text{3Zn(s)+2NO}_3^{-}\text{(aq)+8H}^{+}\text{(aq)} \rightarrow \text{3Zn}^{2+}\text{(aq)+2NO(g)+4H}_2\text{O(l)}$ $\quad E^{o}_{cell} = 1.719V$
Cell diagram: $\text{Zn(s)}|\text{Zn}^{2+}\text{(1M)}\|\text{H}^{+}\text{(1M),NO}_3^{-}\text{(1M)}|\text{NO(g,1atm)}|\text{Pt(s)}$

119. **(M)** Apply the Nernst equation:

$$E_{cell} = E^o_{cell} - \frac{0.0592}{z}\log Q$$

$$0.108 = 0 - \frac{0.0592}{2}\log x^2 \Rightarrow \log x^2 = -3.65$$

$$x^2 = 10^{-3.65} \Rightarrow x = 0.0150M$$

$$pH = -\log(0.0150) = 1.82$$

120. **(M)** **(a)** Since we are given E^o_{cell}, we can calculate K for the given reaction:

$$E^o_{cell} = \frac{RT}{nF}\ln K$$

$$-0.0050V = \frac{8.314JK^{-1}mol^{-1} \times 298K}{2 \times 96485Cmol^{-1}}\ln K \Rightarrow \ln K = -0.389$$

$$K = e^{-0.389} = 0.68$$

Since for the given conditions Q=1, the system is not at equilibrium.

(b) Because Q>K, a net reaction occurs to the left.

121. **(M)** **(a)** $\text{Fe(s)+Cu}^{2+}\text{(1M)} \rightarrow \text{Fe}^{2+}\text{(1M)+Cu(s)}$, $E^o_{cell} = -0.780V$, electron flow from B to A

(b) $\text{Sn}^{2+}\text{(1M)+2Ag}^{+}\text{(1M)} \rightarrow \text{Sn}^{4+}\text{(aq)+2Ag(s)}$, $E^o_{cell} = +0.646V$, electron flow from A to B.

(c) $\text{Zn(s)+Fe}^{2+}\text{(0.0010M)} \rightarrow \text{Zn}^{2+}\text{(0.10M)+Fe(s)}$, $E^o_{cell} = +0.264V$,electron flow from A to B.

122. **(M)** **(a)** Cl_2(g) at anode and Cu(s) at cathode.

(b) O_2(g) at anode and H_2(g) and OH^-(aq) at cathode.

(c) Cl_2(g) at anode and Ba(l) at cathode.

(d) O_2(g) at anode and H_2(g) and OH^-(aq) at cathode.