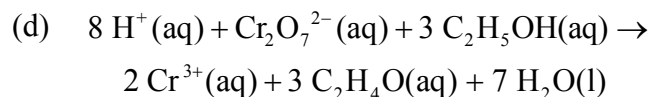
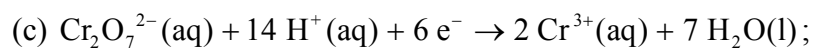


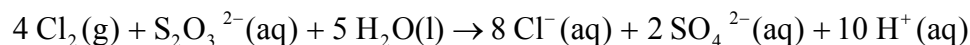
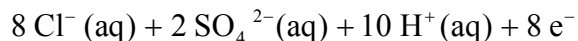
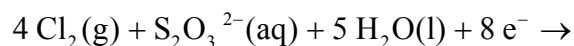
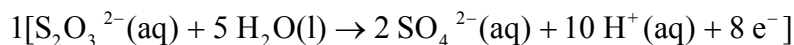
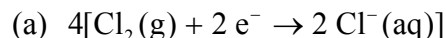
# CHAPTER 12

## ELECTROCHEMISTRY

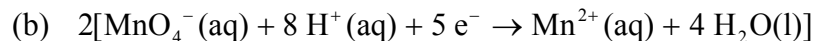
**12.1** (a) Cr reduced from 6+ to 3+; C oxidized from 2- to 1-;

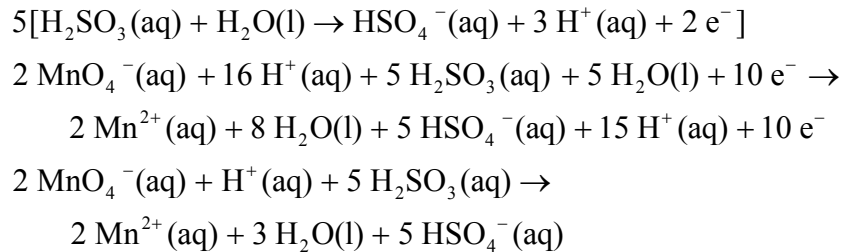


**12.3** In each case, first obtain the balanced half-reactions. Multiply the oxidation and reduction half-reactions by appropriate factors that will result in the same number of electrons being present in both half-reactions. Then add the half-reactions, canceling electrons in the process, to obtain the balanced equation for the whole reaction. Check to see that the final equation is balanced.

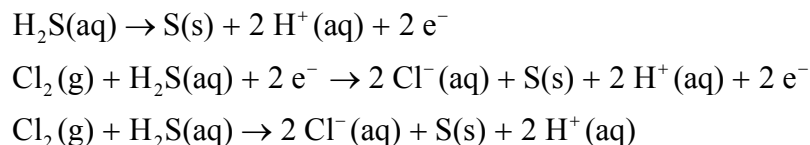
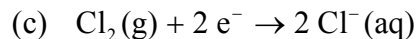


$\text{Cl}_2$  is the oxidizing agent and  $\text{S}_2\text{O}_3^{2-}$  is the reducing agent.

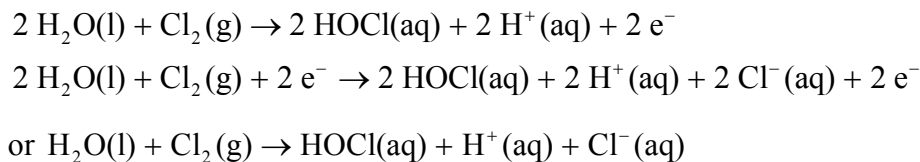
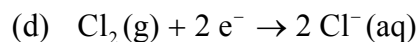




$\text{MnO}_4^-$  is the oxidizing agent and  $\text{H}_2\text{SO}_3$  is the reducing agent.

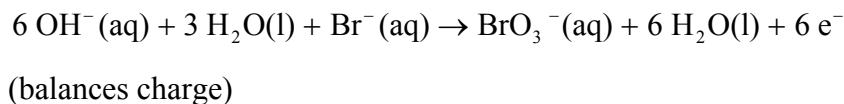
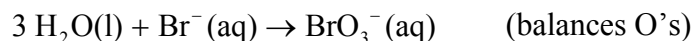
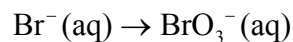
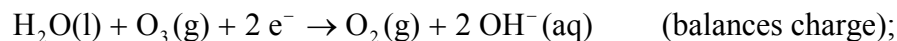
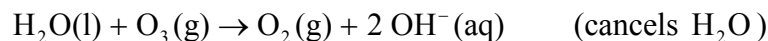
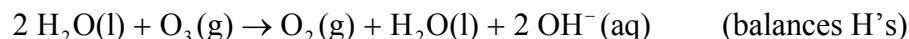
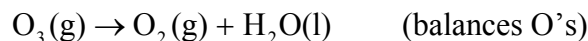


$\text{Cl}_2$  is the oxidizing agent and  $\text{H}_2\text{S}$  is the reducing agent.

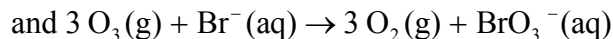
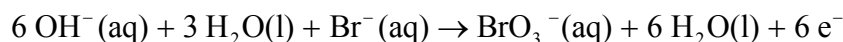
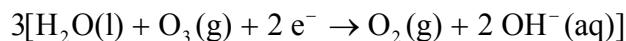


$\text{Cl}_2$  is both the oxidizing and the reducing agent.

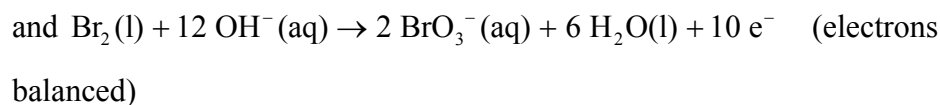
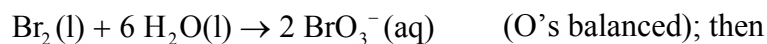
## 12.5 (a) $\text{O}_3(\text{g}) \rightarrow \text{O}_2(\text{g})$



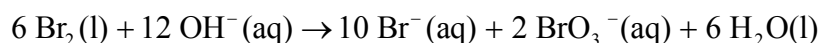
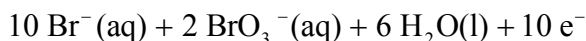
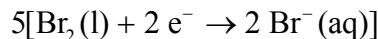
Combining half-reactions yields



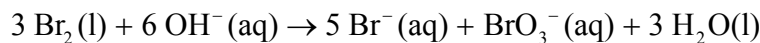
$\text{O}_3$  is the oxidizing agent and  $\text{Br}^-$  is the reducing agent.



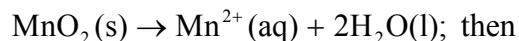
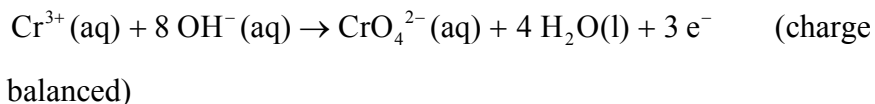
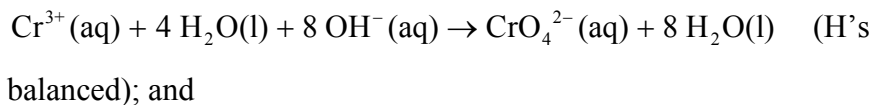
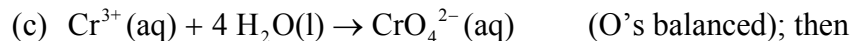
Combining half-reactions yields

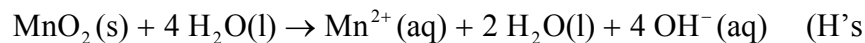


Dividing by 2 gives



$\text{Br}_2$  is both the oxidizing agent and the reducing agent.



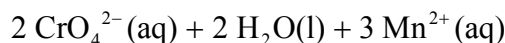
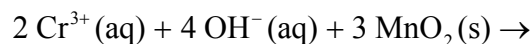
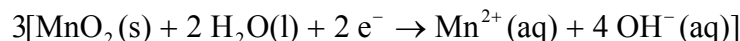


balanced); and

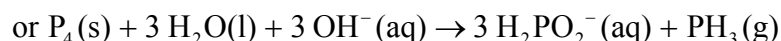
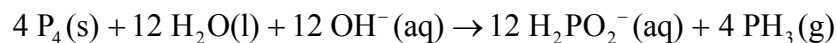
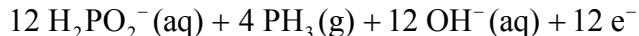
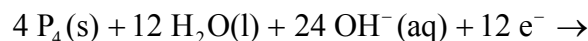
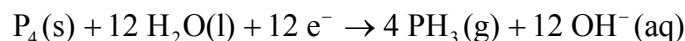
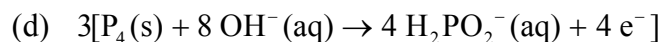


balanced)

Combining half-reactions yields



$\text{Cr}^{3+}$  is the reducing agent and  $\text{MnO}_2$  is the oxidizing agent.

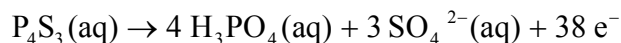


$\text{P}_4(\text{s})$  is both the oxidizing and the reducing agent.



For the oxidation of  $\text{P}_4\text{S}_3$ , both the P and S atoms are oxidized. The assignment of oxidation states to the P and S atoms is complicated by the presence of P—P bonds in the molecule, which leads to non-integral values. As long as we are consistent in our assignments, the end result should be the same. We will assume that S in  $\text{P}_4\text{S}_3$  is  $2-$  and, therefore, loses 8 electrons on going to  $\text{S}^{6+}$  in the sulfate ion. Because  $\text{P}_4\text{S}_3$  is a neutral molecule and, if S has an oxidation number of  $-2$ , then each phosphorus atom will have an oxidation number of  $+1.5$ . Phosphorus in

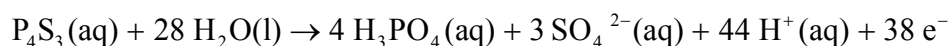
phosphoric acid has an oxidation number of +5. so each P atom of  $\text{P}_4\text{S}_3$  must lose 3.5 electrons. The total number of electrons lost is  $(4 \times 3.5) + (3 \times 8) = 38$ .



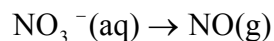
We balance the charge by adding  $\text{H}^+$  in an acidic solution:



The final balance is achieved by adding water to provide the oxygen and hydrogen atoms:

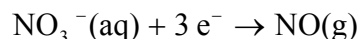


The other half-reaction is simpler.

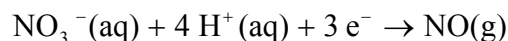


N has an oxidation number of +5 in the nitrate ion and +2 in nitric oxide.

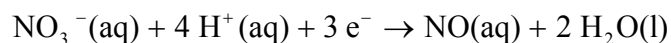
Each nitrogen atom gains three electrons in the course of the reaction.



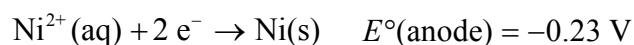
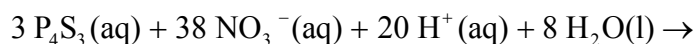
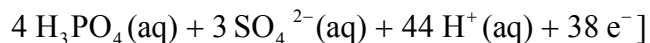
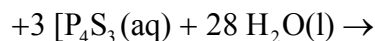
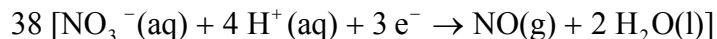
Charge balance is again achieved by adding  $\text{H}^+$ :



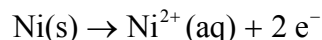
The number of hydrogen and oxygen atoms is completed by the addition of water:



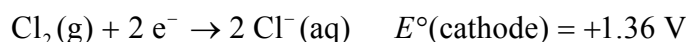
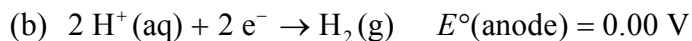
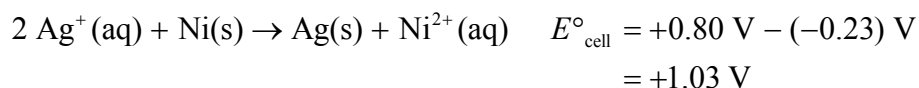
Combining the two half-reactions gives



Reversing the anode half-reaction yields



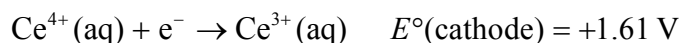
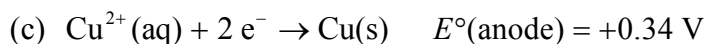
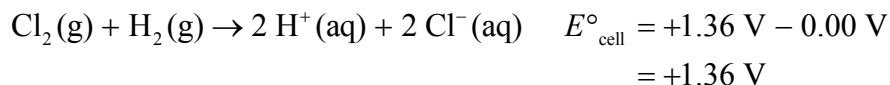
and the cell reaction is, upon addition of the half-reactions,



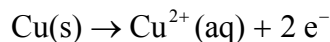
Therefore, at the anode, after reversal,



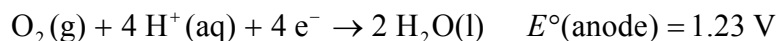
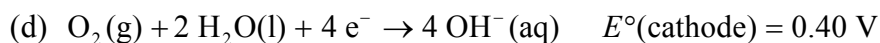
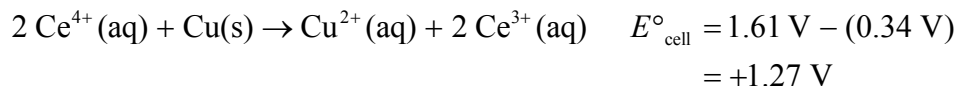
and, the cell reaction is, upon addition of the half-reactions,



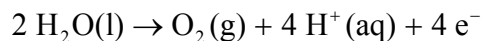
Therefore, at the anode, after reversal,



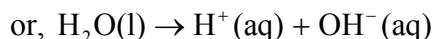
and, the cell reaction is, upon addition of the half-reactions,



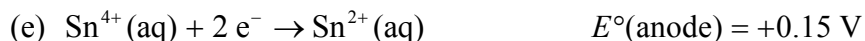
Reversing the anode half-reaction yields



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

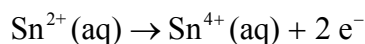


Note: This balanced equation corresponds to the cell notation given. The spontaneous process is the reverse of this reaction.

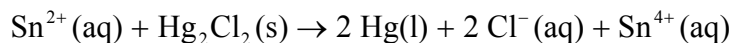




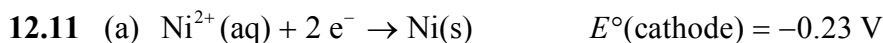
Therefore, at the anode, after reversal,



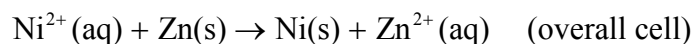
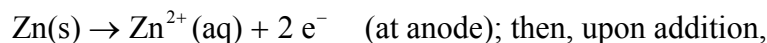
and the cell reaction is, upon addition of the half-reactions,



$$E^\circ_{\text{cell}} = 0.27 \text{ V} - 0.15 \text{ V} = 0.12 \text{ V}$$

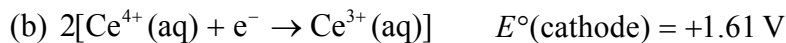


Reversing the anode reaction yields

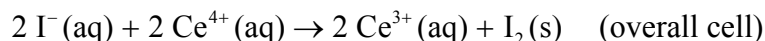
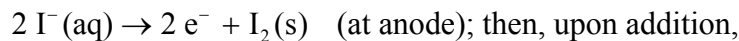


$$E^\circ_{\text{cell}} = -0.23 \text{ V} - (-0.76 \text{ V}) = +0.53 \text{ V}$$

and  $\text{Zn}(\text{s}) | \text{Zn}^{2+}(\text{aq}) || \text{Ni}^{2+}(\text{aq}) | \text{Ni}(\text{s})$



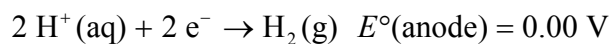
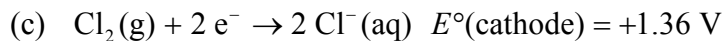
Reversing the anode reaction yields



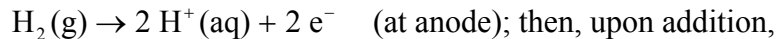
$$E^\circ_{\text{cell}} = +1.61 \text{ V} - 0.54 \text{ V} = +1.07 \text{ V}$$

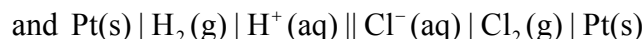
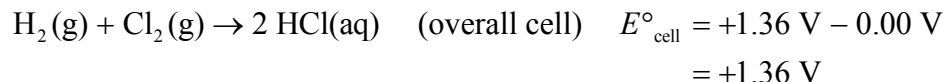
and  $\text{Pt}(\text{s}) | \text{I}^-(\text{aq}) | \text{I}_2(\text{s}) || \text{Ce}^{4+}(\text{aq}), \text{Ce}^{3+}(\text{aq}) | \text{Pt}(\text{s})$

An inert electrode such as Pt is necessary when both oxidized and reduced species are in the same solution.

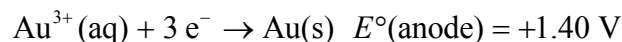
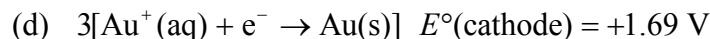


Reversing the anode reaction yields

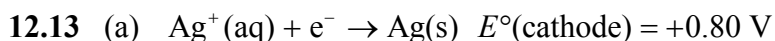
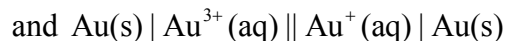
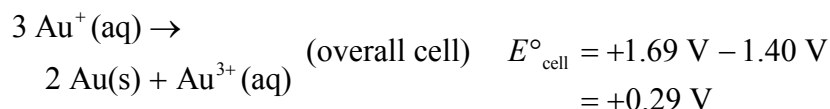
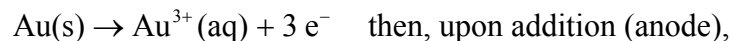




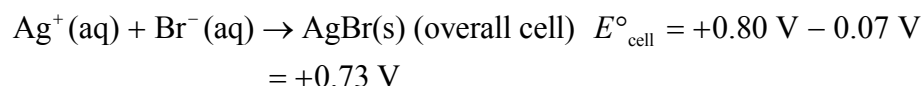
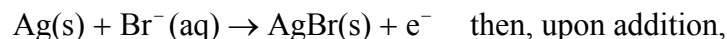
An inert electrode such as Pt is necessary for gas/ion electrode reactions.



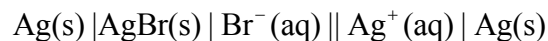
Reversing the anode reaction yields



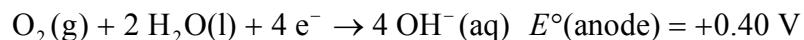
Reversing the anode reaction yields



This is the direction of the spontaneous standard cell reaction that could be used to study the reverse of the given solubility equilibrium. A cell diagram for this favorable process is



(b) To conform to the notation of this chapter, the neutralization is rewritten as



Reversing the anode reaction yields



$4 \text{OH}^{-}(\text{aq}) \rightarrow \text{O}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{l}) + 4 \text{e}^{-}$ ; then, upon addition,



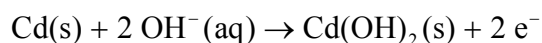
or  $\text{H}^{+}(\text{aq}) + \text{OH}^{-}(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{l})$  (overall cell)  $E^{\circ} = +1.23 \text{ V} - 0.40 \text{ V}$   
 $= +0.83 \text{ V}$

and  $\text{Pt}(\text{s}) | \text{O}_2(\text{g}) | \text{OH}^{-}(\text{aq}) || \text{H}^{+}(\text{aq}) | \text{O}_2(\text{g}) | \text{Pt}(\text{s})$

(c)  $\text{Cd}(\text{OH})_2(\text{s}) + 2 \text{e}^{-} \rightarrow \text{Cd}(\text{s}) + 2 \text{OH}^{-}(\text{aq})$   $E^{\circ}(\text{anode}) = -0.81 \text{ V}$

$\text{Ni}(\text{OH})_3(\text{s}) + \text{e}^{-} \rightarrow \text{Ni}(\text{OH})_2(\text{s}) + \text{OH}^{-}(\text{aq})$   $E^{\circ}(\text{cathode}) = +0.49 \text{ V}$

Reversing the anode reaction and multiplying the cathode reaction by 2 yields



$2 \text{Ni}(\text{OH})_3 + 2 \text{e}^{-} \rightarrow 2 \text{Ni}(\text{OH})_2(\text{s}) + 2 \text{OH}^{-}(\text{aq})$  then, upon addition,



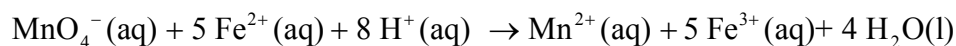
overall cell  $E^{\circ} = +1.30 \text{ V}$

and  $\text{Cd}(\text{s}) | \text{Cd}(\text{OH})_2(\text{s}) | \text{KOH}(\text{aq}) || \text{Ni}(\text{OH})_3(\text{s}) | \text{Ni}(\text{OH})_2(\text{s}) | \text{Ni}(\text{s})$

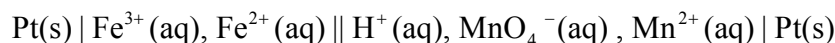
**12.15** (a)  $\text{MnO}_4^{-}(\text{aq}) + 8 \text{H}^{+}(\text{aq}) + 5 \text{e}^{-} \rightarrow \text{Mn}^{2+}(\text{aq}) + 4 \text{H}_2\text{O}(\text{l})$  (cathode half-reaction)

$5[\text{Fe}^{3+}(\text{aq}) + \text{e}^{-} \rightarrow \text{Fe}^{2+}(\text{aq})]$  (anode half-reaction)

(b) Reversing the anode reaction and adding the two equations yields



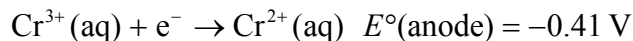
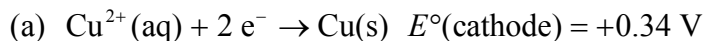
The cell diagram is



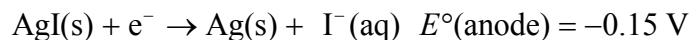
**12.17** A galvanic cell has a positive potential difference; therefore, identify as cathode and anode the electrodes that make  $E^{\circ}(\text{cell})$  positive upon calculating

$$E^{\circ}(\text{cell}) = E^{\circ}(\text{cathode}) - E^{\circ}(\text{anode})$$

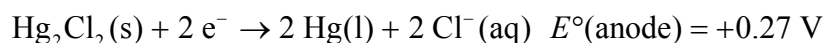
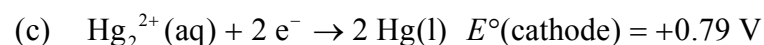
There are only two possibilities: If your first guess gives a negative  $E^\circ$  (cell), switch your identification.



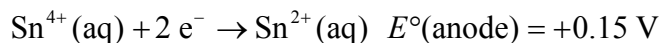
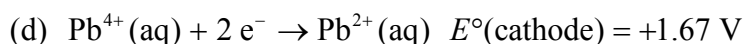
$$E^\circ(\text{cell}) = +0.34 \text{ V} - (-0.41 \text{ V}) = +0.75 \text{ V}$$



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



$$E^\circ(\text{cell}) = +0.79 \text{ V} - (+0.27 \text{ V}) = +0.52 \text{ V}$$

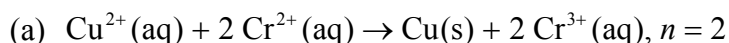


$$E^\circ(\text{cell}) = +1.67 \text{ V} - (+0.15 \text{ V}) = +1.52 \text{ V}$$

**12.19** See Exercise 12.17 solutions for  $E^\circ$  (cell) values. In each case,

$$\Delta G^\circ_{\text{r}} = -nFE^\circ.$$

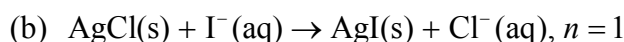
$1 \text{ V} = 1 \text{ J} \cdot \text{C}^{-1}$ .  $n$  is determined by balancing the equation for the cell reaction constructed from the half-reactions given in Exercise 12.17.



$$E^\circ_{\text{cell}} = +0.75 \text{ V} \text{ and } \Delta G^\circ_{\text{r}} = -nFE^\circ$$

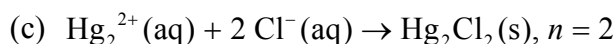
$$= -(2)(9.6485 \times 10^4 \text{ C} \cdot \text{mol}^{-1})(0.75 \text{ J} \cdot \text{C}^{-1})$$

$$= -145 \text{ kJ} \cdot \text{mol}^{-1}$$

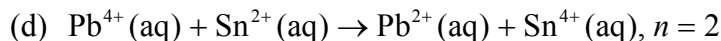


$$E^\circ_{\text{cell}} = +0.37 \text{ V} \text{ and } \Delta G^\circ_{\text{r}} = -nFE^\circ$$

$$= -1 \times 9.6485 \times 10^4 \text{ C} \cdot \text{mol}^{-1} \times 0.37 \text{ J} \cdot \text{C}^{-1} = -36 \text{ kJ} \cdot \text{mol}^{-1}$$



$$\begin{aligned}
 E^\circ_{\text{cell}} &= +0.52 \text{ V and } \Delta G^\circ_r = -nFE^\circ \\
 &= -(2)(9.6485 \times 10^4 \text{ C} \cdot \text{mol}^{-1})(0.52 \text{ J} \cdot \text{C}^{-1}) \\
 &= -100 \text{ kJ} \cdot \text{mol}^{-1}
 \end{aligned}$$

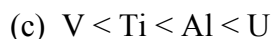


$$\begin{aligned}
 E^\circ_{\text{cell}} &= +1.52 \text{ V and } \Delta G^\circ_r = -nFE^\circ \\
 &= -(2)(9.6485 \times 10^4 \text{ C} \cdot \text{mol}^{-1})(1.52 \text{ J} \cdot \text{C}^{-1}) \\
 &= -293 \text{ kJ} \cdot \text{mol}^{-1}
 \end{aligned}$$

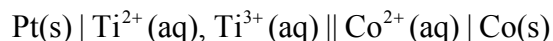
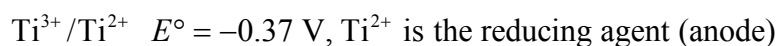
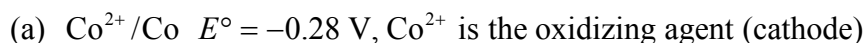
**12.21** The cell, as written  $\text{Cu(s)} | \text{Cu}^{2+}(\text{aq}) || \text{M}^{2+}(\text{aq}) | \text{M(s)}$ , makes the  $\text{Cu}/\text{Cu}^{2+}$  electrode the anode, because this is where oxidation is occurring; the  $\text{M}^{2+}/\text{M}$  electrode is the cathode. The calculation is

$$\begin{aligned}
 E^\circ &= E^\circ(\text{cathode}) - E^\circ(\text{anode}) \\
 0.689 \text{ V} &= E^\circ(\text{cathode}) - (+0.34 \text{ V}) \\
 E^\circ(\text{cathode}) &= +1.03 \text{ V}
 \end{aligned}$$

**12.23** Refer to Appendix 2B. The more negative (less positive) the standard reduction potential, the stronger is the metal as a reducing agent.



**12.25** In each case, identify the couple with the more positive reduction potential. This will be the couple at which reduction occurs, and therefore which contains the oxidizing agent. The other couple contains the reducing agent.



$$E^\circ_{\text{cell}} = E^\circ(\text{cathode}) - E^\circ(\text{anode}) = -0.28 \text{ V} - (-0.37 \text{ V}) = +0.09 \text{ V}$$

(b)  $\text{U}^{3+}/\text{U}$   $E^\circ = -1.79 \text{ V}$ ,  $\text{U}^{3+}$  is the oxidizing agent (cathode)

$\text{La}^{3+}/\text{La}$   $E^\circ = -2.52 \text{ V}$ ,  $\text{La}$  is the reducing agent (anode)

$\text{La(s)} \mid \text{La}^{3+}(\text{aq}) \parallel \text{U}^{3+}(\text{aq}) \mid \text{U(s)}$

$$E^\circ_{\text{cell}} = -1.79 \text{ V} - (-2.52 \text{ V}) = +0.73 \text{ V}$$

(c)  $\text{Fe}^{3+}/\text{Fe}^{2+}$   $E^\circ = +0.77 \text{ V}$ ,  $\text{Fe}^{3+}$  is the oxidizing agent (cathode)

$\text{H}^+/\text{H}_2$   $E^\circ = 0.00 \text{ V}$ ,  $\text{H}_2$  is the reducing agent (anode)

$\text{Pt(s)} \mid \text{H}_2(\text{g}) \mid \text{H}^+(\text{aq}) \parallel \text{Fe}^{2+}(\text{aq}), \text{Fe}^{3+}(\text{aq}) \mid \text{Pt(s)}$

$$E^\circ_{\text{cell}} = +0.77 \text{ V} - 0.00 \text{ V} = +0.77 \text{ V}$$

(d)  $\text{O}_3/\text{O}_2, \text{OH}^-$   $E^\circ = +1.24 \text{ V}$ ,  $\text{O}_3$  is the oxidizing agent (cathode)

$\text{Ag}^+/\text{Ag}$   $E^\circ = +0.80 \text{ V}$ ,  $\text{Ag}$  is the reducing agent (anode)

$\text{Ag(s)} \mid \text{Ag}^+(\text{aq}) \parallel \text{OH}^-(\text{aq}) \mid \text{O}_3(\text{g}), \text{O}_2(\text{g}) \mid \text{Pt(s)}$

$$E^\circ_{\text{cell}} = +1.24 \text{ V} - 0.80 \text{ V} = +0.44 \text{ V}$$

**12.27** (a)  $E^\circ(\text{Cl}_2, \text{Cl}^-) = +1.36 \text{ V}$  (cathode)

$E^\circ(\text{Br}_2, \text{Br}^-) = +1.09 \text{ V}$  (anode)

Because  $E^\circ(\text{Cl}_2, \text{Cl}^-) > E^\circ(\text{Br}_2, \text{Br}^-)$  the reaction favors products.

$$E^\circ_{\text{cell}} = +1.36 \text{ V} - 1.09 \text{ V} = +0.27 \text{ V}$$

$\text{Cl}_2(\text{g})$  is the oxidizing agent.

(b)  $E^\circ(\text{Ce}^{4+}/\text{Ce}^{3+}) = +1.61 \text{ V}$  (anode)

$E^\circ(\text{MnO}_4^-/\text{Mn}^{2+}) = +1.51 \text{ V}$  (cathode)

Because  $E^\circ(\text{Ce}^{4+}/\text{Ce}^{3+}) > E^\circ(\text{MnO}_4^-/\text{Mn}^{2+})$ , the reaction does not favor products.

(c)  $E^\circ(\text{Pb}^{4+}/\text{Pb}^{2+}) = +1.67 \text{ V}$  (anode)

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

Because  $E^\circ(\text{Pb}^{4+}/\text{Pb}^{2+}) > E^\circ(\text{Pb}^{2+}/\text{Pb})$ , the reaction does not favor products.

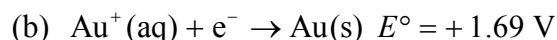
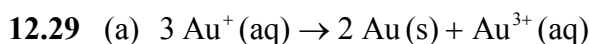
(d)  $E^\circ(\text{NO}_3^-/\text{NO}_2/\text{H}^+) = +0.80 \text{ V}$  (cathode)

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

Because  $E^\circ(\text{NO}_3^-/\text{NO}_2/\text{H}^+) > E^\circ(\text{Zn}^{2+}/\text{Zn})$ , the reaction favors products.

$$E^\circ_{\text{cell}} = +0.80 \text{ V} - (-0.76 \text{ V}) = +1.56 \text{ V}$$

$\text{NO}_3^-$  is the oxidizing agent.

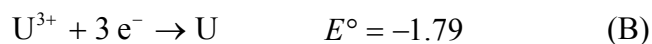


Multiplying the first equation by three and subtracting the second equation gives the net equation desired. The potential is given simply by subtracting the second from the first:

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

Because  $E^\circ$  is positive, the process should be spontaneous for standard state conditions.

**12.31** The appropriate half-reactions are:



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



In order to calculate the potential of a *half-reaction*, we need to convert the  $E^\circ$  values into  $\Delta G^\circ$  values:

$$\Delta G^\circ(\text{A}) = -nFE^\circ(\text{A}) = -1F(-0.61 \text{ V})$$

$$\Delta G^\circ(\text{B}) = -nFE^\circ(\text{B}) = -3F(-1.79 \text{ V})$$

$$\Delta G^\circ(\text{C}) = -nFE^\circ(\text{C}) = -4FE^\circ(\text{C})$$

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

$$-4FE^\circ(\text{C}) = -1F(-0.61 \text{ V}) + [-3F(-1.79 \text{ V})]$$

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

$$-4E^\circ(\text{C}) = -1(-0.61 \text{ V}) - 3(-1.79 \text{ V})$$

$$E^\circ(\text{C}) = -[0.61 \text{ V} + 5.37 \text{ V}]/4 = -1.50 \text{ V}$$

**12.33** (a)  $E^\circ_{\text{cell}} = E^\circ(\text{cathode}) - E^\circ(\text{anode}) = 0.34 \text{ V} - (-0.41 \text{ V}) = 0.75 \text{ V}$ , and

$$\ln K = \frac{nFE^\circ}{RT} \text{ at } 25^\circ\text{C} = \frac{nE^\circ}{0.02569 \text{ V}} \ln K = \frac{(2)(0.75 \text{ V})}{0.02569 \text{ V}} = 58 \text{ and}$$

$$K = 10^{25}$$



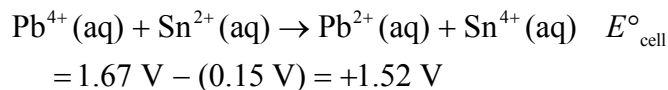
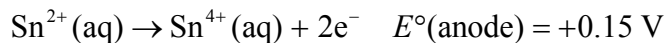
Note: These equations represent the cathode and anode half-reactions for the overall reaction as written. The spontaneous direction of this reaction under standard conditions is the opposite of that given.

$$E^\circ_{\text{cell}} = E^\circ(\text{cathode}) - E^\circ(\text{anode}) = -1.63 \text{ V} - (-1.18 \text{ V}) = -0.45 \text{ V}, \text{ and}$$

$$\ln K = \frac{nFE^\circ}{RT} \text{ at } 25^\circ\text{C} = \frac{nE^\circ}{0.02569 \text{ V}} \ln K = \frac{(2)(-0.45 \text{ V})}{0.02569 \text{ V}} = -35 \text{ and}$$

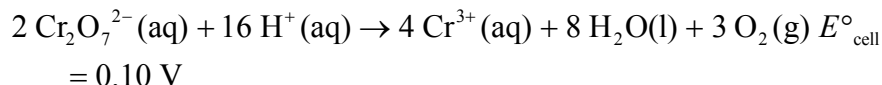
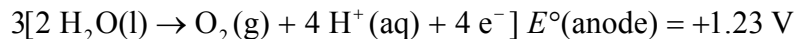
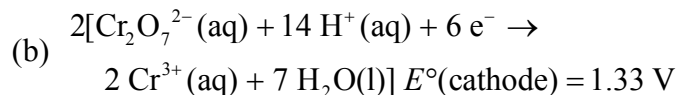
$$K = 10^{-15}$$

**12.35** (a)  $\text{Pb}^{4+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Pb}^{2+}(\text{aq})$   $E^\circ(\text{cathode}) = +1.67 \text{ V}$



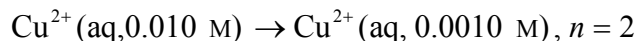
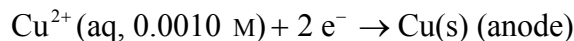
$$\text{Then, } E = E^\circ - \left( \frac{0.025693 \text{ V}}{n} \right) \ln Q; 1.33 \text{ V} = 1.52 \text{ V} - \left( \frac{0.025693 \text{ V}}{2} \right) \ln Q$$

$$\ln Q = \frac{1.52 \text{ V} - 1.33 \text{ V}}{0.0129 \text{ V}} = \frac{0.19 \text{ V}}{0.0129 \text{ V}} = 15 \quad Q = 10^6$$



$$\text{Then, } E = E^\circ - \left( \frac{0.0257 \text{ V}}{n} \right) \ln Q; \quad 0.10 \text{ V} = +0.10 \text{ V} - \left( \frac{0.0257 \text{ V}}{12} \right) \ln Q$$

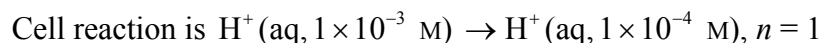
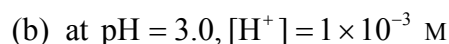
$$\ln Q = 0.00 \quad Q = 1.0$$



$$E^\circ_{\text{cell}} = E^\circ(\text{cathode}) - E^\circ(\text{anode}) = 0 \text{ V}$$

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \left( \frac{RT}{nF} \right) \ln Q = - \left( \frac{0.025693 \text{ V}}{2} \right) \ln Q \text{ at } 25^\circ\text{C}$$

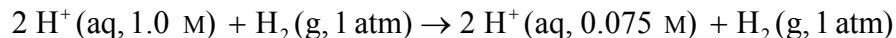
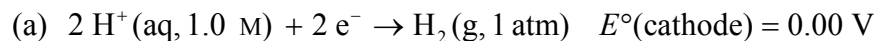
$$E_{\text{cell}} = - \left( \frac{0.025693 \text{ V}}{2} \right) \ln \left( \frac{0.0010 \text{ M}}{0.010 \text{ M}} \right) = +0.030 \text{ V}$$



$$E^\circ_{\text{cell}} = 0 \text{ V} \quad E_{\text{cell}} = E^\circ_{\text{cell}} - \left( \frac{RT}{nF} \right) \ln Q = - \left( \frac{0.025693 \text{ V}}{1} \right) \ln \left( \frac{1 \times 10^{-4}}{1 \times 10^{-3}} \right)$$

$$= +6 \times 10^{-2} \text{ V}$$

**12.39** In each case,  $E^\circ_{\text{cell}} = E^\circ(\text{cathode}) - E^\circ(\text{anode})$ . Recall that the values for  $E^\circ$  at the electrodes refer to the electrode potential for the half-reaction written as a reduction reaction. In balancing the cell reaction, the half-reaction at the anode is reversed. However, this does not reverse the sign of electrode potential used at the anode, because the value always refers to the reduction potential.

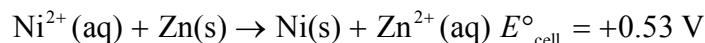
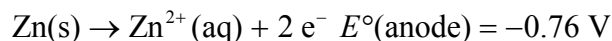
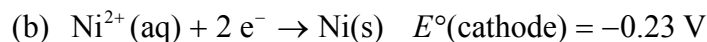


$$E^{\circ}_{\text{cell}} = 0.00 \text{ V}$$

$$\text{Then, } E = E^{\circ} - \left( \frac{0.025693 \text{ V}}{n} \right) \ln \left( \frac{[\text{H}^+, 0.075 \text{ M}]^2 P_{\text{H}_2}}{[\text{H}^+, 1.0 \text{ M}]^2 P_{\text{H}_2}} \right)$$

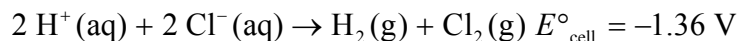
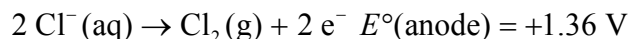
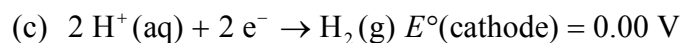
$$E = 0.00 \text{ V} - \left( \frac{0.025693 \text{ V}}{2} \right) \ln \left( \frac{(0.075 \text{ M})^2 \times 1 \text{ atm}}{(1.0 \text{ M})^2 \times 1 \text{ atm}} \right)$$

$$E = -0.0129 \text{ V} \ln (0.075)^2 = +0.067 \text{ V}$$



$$\text{Then, } E = E^{\circ} - \left( \frac{0.025693 \text{ V}}{n} \right) \ln \left( \frac{[\text{Zn}^{2+}]}{[\text{Ni}^{2+}]} \right)$$

$$E = 0.53 \text{ V} - \left( \frac{0.025693 \text{ V}}{2} \right) \ln \left( \frac{0.37}{0.059} \right) = 0.53 \text{ V} - 0.02 \text{ V} = 0.51 \text{ V}$$



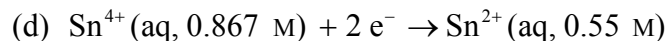
Then,

$$E = E^{\circ} - \left( \frac{0.025693 \text{ V}}{n} \right) \ln \left( \frac{P_{\text{H}_2} P_{\text{Cl}_2}}{[\text{H}^+]^2 [\text{Cl}^-]^2} \right)$$

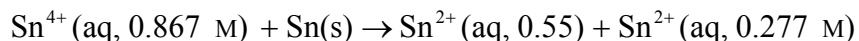
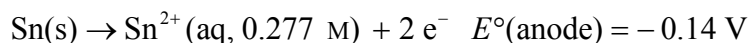
$$E = -1.36 \text{ V} - \left( \frac{0.025693 \text{ V}}{2} \right) \ln \left( \frac{\left( \frac{125}{760} \right) \left( \frac{250}{760} \right)}{(0.85)^2 (1.0)^2} \right) (1.01325)^2$$

$$E = -1.36 \text{ V} + 0.03 \text{ V}$$

$$= -1.33 \text{ V}$$



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



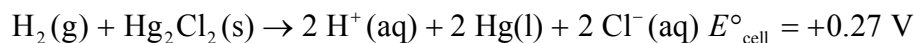
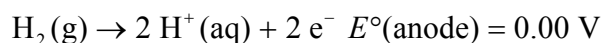
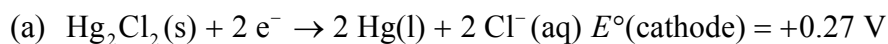


$$E^{\circ}_{\text{cell}} = 0.29 \text{ V}$$

$$E = E^{\circ} - \left( \frac{0.025\,693 \text{ V}}{2} \right) \ln \left( \frac{(0.55)(0.277)}{(0.867)} \right)$$

$$E = 0.29 \text{ V} + 0.02 \text{ V} = 0.31 \text{ V}$$

**12.41** In each case, obtain the balanced equation for the cell reaction from the half-cell reactions at the electrodes, by reversing the reduction equation for the half-reaction at the anode, multiplying the half-reaction equations by an appropriate factor to balance the number of electrons, and then adding the half-reactions. Calculate  $E^{\circ}_{\text{cell}} = E^{\circ}(\text{cathode}) - E^{\circ}(\text{anode})$ . Then write the Nernst equation for the cell reaction and solve for the unknown.



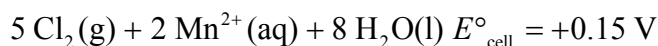
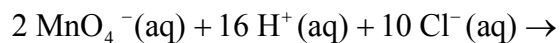
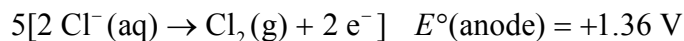
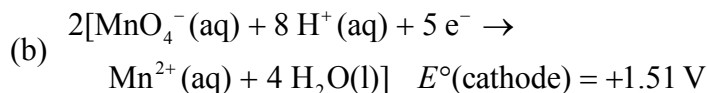
$$E = E^{\circ} - \left( \frac{0.025\,693 \text{ V}}{n} \right) \ln \left( \frac{[\text{H}^{+}]^2 [\text{Cl}^{-}]^2}{[\text{H}_2]} \right)$$

$$0.33 \text{ V} = 0.27 \text{ V} - \left( \frac{0.025\,693 \text{ V}}{2} \right) \ln \left( \frac{[\text{H}^{+}]^2 (1)^2}{(1)} \right)$$

$$= 0.27 \text{ V} - (0.0129 \text{ V}) \ln [\text{H}^{+}]^2$$

$$0.06 \text{ V} = -0.0257 \text{ V} \ln [\text{H}^{+}] = -0.0257 \text{ V} \times (2.303 \log [\text{H}^{+}])$$

$$\text{pH} = \frac{0.06 \text{ V}}{(2.303)(0.025\,693 \text{ V})} = 1.0$$



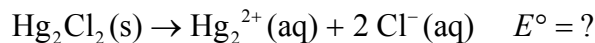
$$E = E^{\circ} - \left( \frac{0.0257 \text{ V}}{n} \right) \ln \left( \frac{[\text{Cl}_2]^5 [\text{Mn}^{2+}]^2}{[\text{MnO}_4^{-}]^2 [\text{H}^{+}]^{16} [\text{Cl}^{-}]^{10}} \right)$$

$$\begin{aligned}
-0.30 \text{ V} &= +0.15 \text{ V} - \left( \frac{0.0257 \text{ V}}{10} \right) \ln \left( \frac{(1)^5 (0.10)^2}{(0.010)^2 (1 \times 10^{-4})^{16} (\text{Cl}^-)^{10}} \right) \\
-0.45 \text{ V} &= -(0.002 5693 \text{ V}) \log \left( \frac{1 \times 10^{-2}}{(1 \times 10^{-4}) (1 \times 10^{-64}) [\text{Cl}^-]^{10}} \right) \\
&= -0.002 5693 \text{ V} \left[ \ln (1 \times 10^{66}) + \ln \left( \frac{1}{[\text{Cl}^-]^{10}} \right) \right] \\
&= -0.390 \text{ V} + (0.0025 693 \text{ V}) \ln [\text{Cl}^-]^{10} \\
-0.0594 \text{ V} &= 0.002 5693 \text{ V} \ln [\text{Cl}^-]^{10} \\
&= (0.025 693 \text{ V}) \ln [\text{Cl}^-] \\
\ln [\text{Cl}^-] &= \frac{-0.06 \text{ V}}{0.025 693 \text{ V}} = -2 \\
[\text{Cl}^-] &= 10^{-1} \text{ mol} \cdot \text{L}^{-1}
\end{aligned}$$

**12.43** Since the reduction potential of tin(II) is negative relative to the S.H.E., we will assume the tin electrode to be the anode such that the standard cell potential would be positive. Then we can use the Nernst equation to solve for the hydrogen ion activity in order to calculate the pH. The cell reaction is  $\text{Sn(s)} + 2 \text{H}^+ \rightarrow \text{Sn}^{2+} + \text{H}_2(\text{g})$ .

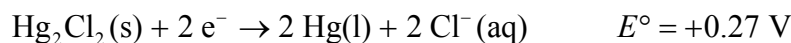
$$\begin{aligned}
E &= E^\circ - \left( \frac{0.025 693 \text{ V}}{n} \right) \ln \left( \frac{[\text{Sn}^{2+}] p_{\text{H}_2}}{[\text{H}^+]^2} \right) \\
0.061 \text{ V} &= 0.14 \text{ V} - \left( \frac{0.025 693 \text{ V}}{2} \right) \ln \left( \frac{[0.015][1]}{[\text{H}^+]^2} \right) \\
&= 0.14 \text{ V} - (0.01284 \text{ V}) (\ln(0.015) - \ln [\text{H}^+]^2) \\
\frac{0.079 \text{ V}}{0.01284 \text{ V}} &= \ln(0.015) - 2 \ln [\text{H}^+] \\
-10.352 &= 2 \ln [\text{H}^+] \\
\ln [\text{H}^+] &= -5.176, \quad [\text{H}^+] = 5.650 \times 10^{-3} \\
\text{pH} &= -\log(5.650 \times 10^{-3}) = 2.25
\end{aligned}$$

**12.45** To calculate this value, we need to determine the  $E^\circ$  value for the solubility reaction:



The relationship  $\Delta G^\circ = -nRT \ln K = -nFE^\circ$  can be used to calculate the value of  $K_{\text{sp}}$ .

The equations that will add to give the net equation we want are



Notice that the second equation is reversed from the reduction reaction given in the Appendix, and consequently the  $E^\circ$  value is changed in sign.

Adding these two equations together gives the desired net reaction, and summing the  $E^\circ$  values will give the  $E^\circ$  value for that process:

$$E^\circ = (+0.29 \text{ V}) + (-0.79 \text{ V}) = -0.50 \text{ V}$$

$$\ln K_{\text{sp}} = \frac{nFE^\circ}{RT} = \frac{(2)(9.65 \times 10^4 \text{ C} \cdot \text{mol}^{-1})(-0.50 \text{ V})}{(8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298 \text{ K})} = -38.95$$

$$K_{\text{sp}} = 1.2 \times 10^{-17}$$

(b) This value is a factor of 10 greater than the value in Table 11.6 ( $1.3 \times 10^{-18}$ ).

**12.47** This cell uses two silver electrodes, so  $E^\circ = 0$  and  $E$  is determined by the ratio of  $[\text{Ag}^+]_{\text{anode}}$  to  $[\text{Ag}^+]_{\text{cathode}}$ . Since  $[\text{Ag}^+]_{\text{anode}} < [\text{Ag}^+]_{\text{cathode}}$ , the ratio is less than 1 and  $E > 0$ , so the cell can do work because

$$\Delta G = w_{\text{max}} = -nFE$$

$$E = -\left(\frac{0.025693 \text{ V}}{n}\right) \ln \left(\frac{[\text{Ag}^+]_{\text{anode}}}{[\text{Ag}^+]_{\text{cathode}}}\right) = -\left(\frac{0.025693 \text{ V}}{1}\right) \ln \left(\frac{5.0 \times 10^{-3}}{0.15}\right)$$

$$= 0.0874 \text{ V}$$

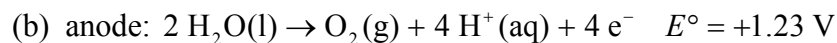
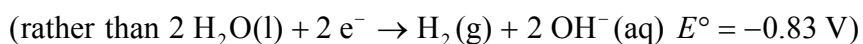
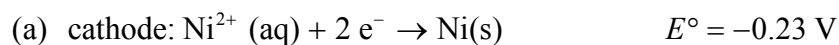
$$\Delta G = w_{\text{max}} = -nFE = -(1 \text{ mol})(96485 \text{ J V}^{-1} \text{mol}^{-1})(0.0874 \text{ V})$$

$$= -8.4 \text{ kJ}$$

**12.49** For the standard calomel electrode,  $E^\circ = +0.27 \text{ V}$ . If this were set equal to 0, all other potentials would also be decreased by 0.27 V. (a) Therefore, the standard hydrogen electrode's standard reduction potential would be

0.00 V – 0.27 V or –0.27 V. (b) The standard reduction potential for  $\text{Cu}^{2+}/\text{Cu}$  would be 0.34 V – 0.27 V or +0.07 V.

**12.51** The strategy is to consider the possible competing cathode and anode reactions. At the cathode, choose the reduction reaction with the most positive (least negative) standard reduction potential ( $E^\circ$  value). At the anode, choose the oxidation reaction with the least positive (most negative) standard reduction potential ( $E^\circ$  value, as given in the table). Then calculate  $E^\circ_{\text{cell}} = E^\circ(\text{cathode}) - E^\circ(\text{anode})$ . The negative of this value is the minimum potential that must be supplied.

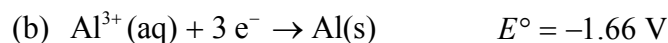


(the  $\text{SO}_4^{2-}$  ion will not oxidize)

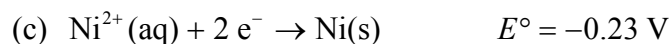


Therefore E (supplied) must be  $> +1.46\text{ V}$  (1.46 V is the minimum).

**12.53** In each case, compare the reduction potential of the ion to the reduction potential of water ( $E^\circ = -0.42\text{ V}$ ) and choose the process with the least negative  $E^\circ$  value.

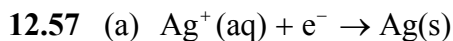
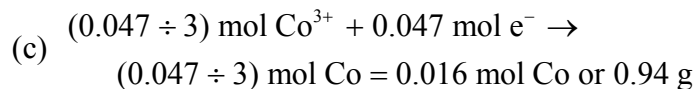
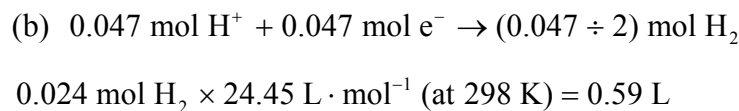
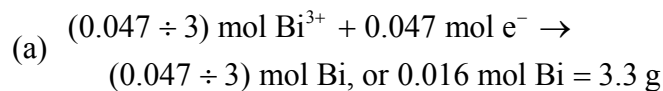


The reactions in (a) and (b) evolve hydrogen rather than yield a metallic deposit because water is reduced, according to



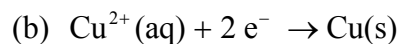
In (c) and (d) the metal ion will be reduced.

**12.55**  $4500 \text{ C} \div 9.65 \times 10^4 \text{ C} \cdot \text{F}^{-1} = 0.047 \text{ F} = 0.047 \text{ mol e}^{-}$



$$\text{time} = (1.50 \text{ g Ag}) \left( \frac{1 \text{ mol Ag}}{107.98 \text{ g Ag}} \right) \left( \frac{1 \text{ mol e}^{-}}{1 \text{ mol Ag}} \right)$$

$$\left( \frac{9.65 \times 10^4 \text{ C}}{1 \text{ mol e}^{-}} \right) \left( \frac{1 \text{ A} \cdot \text{s}}{1 \text{ C}} \right) \left( \frac{1}{0.0136} \right) = 9.9 \times 10^4 \text{ s or } 27 \text{ h}$$



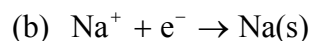
$$\text{mass Cu} = (9.9 \times 10^4 \text{ s})(0.0136 \text{ A}) \left( \frac{1 \text{ C}}{1 \text{ A} \cdot \text{s}} \right) \left( \frac{1 \text{ mol e}^{-}}{9.65 \times 10^4 \text{ C}} \right)$$

$$\left( \frac{0.50 \text{ mol Cu}}{1 \text{ mol e}^{-}} \right) \left( \frac{63.5 \text{ g Cu}}{1 \text{ mol Cu}} \right) = 0.44 \text{ g Cu}$$



$$\text{current} = \frac{\text{charge}}{\text{time}}$$

$$\begin{aligned} & 2.5 \text{ g Cr} \left( \frac{1 \text{ mol Cr}}{52.00 \text{ g Cr}} \right) \left( \frac{6 \text{ mol e}^{-}}{1 \text{ mol Cr}} \right) \left( \frac{9.65 \times 10^4 \text{ C}}{1 \text{ mol e}^{-}} \right) \\ &= \frac{\phantom{2.5 \text{ g Cr} \left( \frac{1 \text{ mol Cr}}{52.00 \text{ g Cr}} \right) \left( \frac{6 \text{ mol e}^{-}}{1 \text{ mol Cr}} \right) \left( \frac{9.65 \times 10^4 \text{ C}}{1 \text{ mol e}^{-}} \right)}}{12 \text{ h} \times 3600 \text{ s} \cdot \text{h}^{-1}} \\ &= 0.64 \text{ C} \cdot \text{s}^{-1} = 0.64 \text{ A} \end{aligned}$$



$$\text{current} = \frac{2.5 \text{ g Na} \left( \frac{1 \text{ mol Na}}{22.99 \text{ g Na}} \right) \left( \frac{1 \text{ mol e}^-}{1 \text{ mol Na}} \right) \left( \frac{9.65 \times 10^4 \text{ C}}{1 \text{ mol e}^-} \right)}{12 \text{ h} \times 3600 \text{ s} \cdot \text{h}^{-1}}$$

$$= 0.24 \text{ C} \cdot \text{s}^{-1} = 0.24 \text{ A}$$

**12.61**  $\text{Ru}^{n+}(\text{aq}) + n \text{ e}^- \rightarrow \text{Ru}(\text{s})$ ; solve for  $n$

$$\text{moles of Ru} = (0.0310 \text{ g Ru}) \left( \frac{1 \text{ mol}}{101.07 \text{ g Ru}} \right) = 3.07 \times 10^{-4} \text{ mol}$$

$$\text{total charge} = (500 \text{ s}) (120 \text{ mA}) \left( \frac{10^{-3} \text{ A}}{1 \text{ mA}} \right) \left( \frac{1 \text{ C} \cdot \text{s}^{-1}}{1 \text{ A}} \right) = 60 \text{ C}$$

$$\text{moles of e}^- = (60 \text{ C}) \left( \frac{1 \text{ mol e}^-}{96\,500 \text{ C}} \right) = 6.2 \times 10^{-4} \text{ mol e}^-$$

$$n = \frac{6.2 \times 10^{-4} \text{ mol e}^-}{3.07 \times 10^{-4} \text{ mol}} = \frac{2 \text{ mol charge}}{1 \text{ mol}}$$

Therefore, oxidation number of  $\text{Ru}^{2+}$  is +2.

**12.63**  $\text{Hf}^{n+} + n \text{ e}^- \rightarrow \text{Hf}(\text{s})$ ; solve for  $n$ .

$$\text{charge consumed} = 15.0 \text{ C} \cdot \text{s}^{-1} \times 2.00 \text{ h} \times 3600 \text{ s} \cdot \text{h}^{-1} = 1.08 \times 10^5 \text{ C}$$

$$\text{moles of charge consumed} = (1.08 \times 10^5 \text{ C}) \left( \frac{1 \text{ mol e}^-}{9.65 \times 10^4 \text{ C}} \right) = 1.12 \text{ mol e}^-$$

$$\text{moles of Hf plated} = (50.0 \text{ g Hf}) \left( \frac{1 \text{ mol Hf}}{178.49 \text{ g Hf}} \right) = 0.280 \text{ mol Hf}$$

$$\text{Then, } n = \frac{1.12 \text{ mol e}^-}{0.280 \text{ mol Hf}} = 4.00 \text{ mol e}^- / \text{mol Hf}$$

Therefore, the oxidation number is 4, that is,  $\text{Hf}^{4+}$ .

**12.65**  $\text{MCl}_3 \rightarrow \text{M}^{3+} + 3 \text{ Cl}^-$      $\text{M}^{3+} + 3 \text{ e}^- \rightarrow \text{M}(\text{s})$

First, determine the number of moles of electrons consumed; the number of moles of  $\text{M}^{3+}$  reduced is one-third of this number.

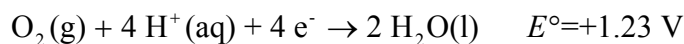
$$\text{charge used} = (6.63 \text{ h}) \left( \frac{3600 \text{ s}}{1 \text{ h}} \right) \left( \frac{0.700 \text{ C}}{1 \text{ s}} \right) = 1.67 \times 10^4 \text{ C}$$

$$\text{number of moles of } e^- = (1.67 \times 10^4 \text{ C}) \left( \frac{1 \text{ mol } e^-}{9.65 \times 10^4 \text{ C}} \right) = 0.173$$

$$\begin{aligned} \text{number of moles of } M^{3+} \text{ (and } M) &= 0.173 \text{ mol } e^- \times \frac{1 \text{ mol } M^{3+}}{3 \text{ mol } e^-} \\ &= 0.0577 \end{aligned}$$

$$\text{molar mass } M = \frac{3.00 \text{ g}}{0.0577 \text{ mol}} = 52.0 \text{ g} \cdot \text{mol}^{-1} \text{ (Cr)}$$

**12.67** Assuming all the energy comes from reduction of oxygen focuses attention on this half reaction:



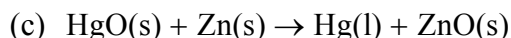
Body conditions are far from standard state values, so the actual value of  $E$  would be reduced by about 0.5 V if we take pH,  $p_{\text{O}_2}$  and T into account. However, we are only estimating an average current to one significant digit, so  $E = 1.23 \pm 0.5 \text{ V} \approx 1 \text{ V}$  is adequate. With these approximations in mind, we can calculate the current.

$$It = nF = \frac{\Delta G}{-E} \quad \text{or}$$

$$I = \frac{\Delta G}{-Et} = \frac{(-10 \times 10^6 \text{ J})}{-(1 \text{ V})(24 \text{ h})(3600 \text{ s} \cdot \text{h}^{-1})} \cdot \frac{1 \text{ V} \cdot \text{C}}{1 \text{ J}} = 115 \text{ A} \approx 100 \text{ A}$$

**12.69** (a) The electrolyte is KOH(aq)/HgO(s), which will have the consistency of a moist paste.

(b) The oxidizing agent is HgO(s).

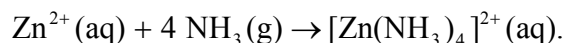


**12.71** See Table 12.1.

The anode reaction is  $\text{Zn(s)} \rightarrow \text{Zn}^{2+}(\text{aq}) + 2 \text{e}^-$ ; this reaction supplies the electrons to the external circuit. The cathode reaction is

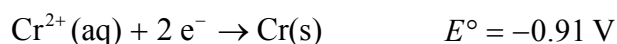
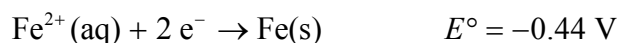
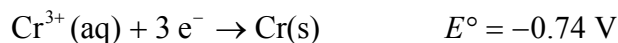
$\text{MnO}_2(\text{s}) + \text{H}_2\text{O(l)} + \text{e}^- \rightarrow \text{MnO(OH)}_2(\text{s}) + \text{OH}^-(\text{aq})$ . The  $\text{OH}^-(\text{aq})$  produced reacts with  $\text{NH}_4^+(\text{aq})$  from the  $\text{NH}_4\text{Cl(aq)}$  present:

$\text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{H}_2\text{O(l)} + \text{NH}_3(\text{g})$ . The  $\text{NH}_3(\text{g})$  produced complexes with the  $\text{Zn}^{2+}(\text{aq})$  produced in the anode reaction



The overall reaction is complicated.

**12.73** See Table 12.1 (a)  $\text{KOH(aq)}$  (b) In the charging process, the cell reaction is the reverse of what occurs in discharge. Therefore, at the anode,  $2 \text{Ni(OH)}_2(\text{s}) + 2 \text{OH}^-(\text{aq}) \rightarrow 2 \text{Ni(OH)}_3 + 2 \text{e}^-$ .



Comparison of the reduction potentials shows that Cr is more easily oxidized than Fe, so the presence of Cr retards the rusting of Fe. At the position of the scratch, the gap is filled with oxidation products of Cr, thereby preventing contact of air and water with the iron.

**12.77** (a)  $n_{\text{e}^-} = n_{\text{Ag}^+} = \frac{It}{F} = \frac{(3.5 \text{ A})(395.0 \text{ s})}{(96\,485 \text{ C} \cdot \text{mol}^{-1})} = 1.43 \times 10^{-2} \text{ mol Ag}$

$$1.43 \times 10^{-2} \text{ mol Ag} \left( \frac{107.87 \text{ g Ag}}{\text{mol Ag}} \right) = 1.55 \text{ g Ag}$$

$$\frac{1.55 \text{ g}}{2.69 \text{ g}} \times 100 = 57.4\% \text{ Ag}$$

(b)  $2.69 \text{ g} - 1.55 \text{ g} = 1.14 \text{ g X}$



Since the salt is 1:1 Ag:X, the molar mass of X is

$$\frac{1.14 \text{ g}}{1.43 \times 10^{-2} \text{ mol}} = 79.7 \text{ g} \cdot \text{mol}^{-1}$$

This molar mass is closest to bromine, so the formula is AgBr.

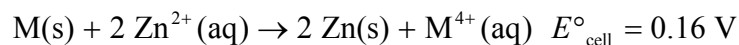
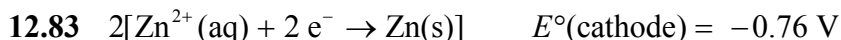
**12.79** (a)  $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$  (b)  $\text{H}_2\text{O}$  and  $\text{O}_2$  jointly oxidize iron. (c) Water is more highly conducting if it contains dissolved ions, so the rate of rusting is increased.

**12.81** (a) aluminum or magnesium; both are below titanium in the electrochemical series.

(b) cost, availability, and toxicity of products in the environment



Fe could act as the anode of an electrochemical cell if  $\text{Cu}^{2+}$  or  $\text{Cu}^{+}$  were present; therefore, it could be oxidized at the point of contact. Water with dissolved ions would act as the electrolyte.



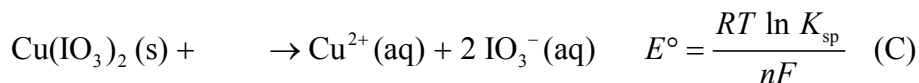
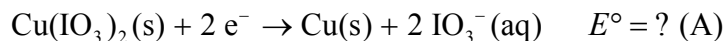
$$E^{\circ}_{\text{cell}} = E^{\circ}(\text{cathode}) - E^{\circ}(\text{anode})$$

$$+0.16 \text{ V} = -0.76 \text{ V} - (x)$$

$$x = -0.92 \text{ V} = E^{\circ}(\text{M}^{4+}/\text{M})$$

**12.85** The strategy is to find the  $E^{\circ}$  value for the solubility reaction and then find appropriate half-reactions that add to give that solubility reaction.

One of these half-reactions is our unknown, the other is obtained from Appendix 2B:

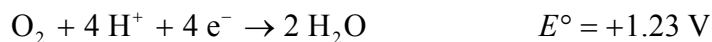


$$\begin{aligned} E^\circ &= \frac{RT \ln K_{\text{sp}}}{nF} \\ &= \frac{(8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298.2 \text{ K}) \ln (1.4 \times 10^{-7})}{2(9.65 \times 10^4 \text{ C} \cdot \text{mol}^{-1})} \\ &= -0.20 \text{ V} \end{aligned}$$

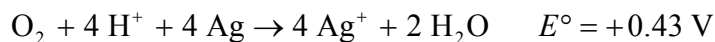
$$-0.20 \text{ V} = E^\circ(\text{A}) + (-0.34 \text{ V})$$

$$E^\circ(\text{A}) = +0.14 \text{ V}$$

**12.87** (a) In acidic solution, the relevant reactions are



Overall reaction:



Because the potential is positive, the reaction should be spontaneous and would be expected to occur. We should also consider the conditions; because air is only 20.95%  $\text{O}_2$ , the potential may be different from that calculated for standard conditions. If air is the source of oxygen, then it will be present at  $0.2095 \times 1.01325 \text{ bar} = 0.2123 \text{ bar}$ .

$$\begin{aligned} E &= E^\circ - \frac{0.0592}{4} \log \frac{[\text{Ag}^+]^4}{P_{\text{O}_2} [\text{H}^+]^4} \\ &= +0.43 \text{ V} - \frac{0.0592}{4} \log \frac{[1.0]^4}{(0.2123)[1.0]^4} \end{aligned}$$

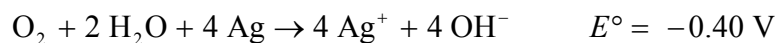
$$\begin{aligned}
&= +0.43 \text{ V} - \frac{0.0592}{4} \log \frac{1}{0.2123} \\
&= +0.43 \text{ V} - 0.010 \text{ V} \\
&= +0.42 \text{ V}
\end{aligned}$$

The potential is still positive and the reaction is expected to be spontaneous.

(b) In basic solution, the relevant reactions are



Overall reaction:



This process as written is nonspontaneous and is not predicted to occur.

However, AgOH forms an insoluble precipitate, changing the nature of the reaction. The  $K_{\text{sp}}$  value for AgOH is  $1.5 \times 10^{-8}$ . We use the Nernst

equation to calculate the potential under these conditions:

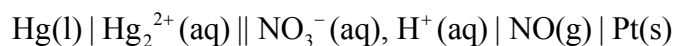
$$\begin{aligned}
E &= E^\circ - \frac{0.0592}{4} \log \frac{[\text{Ag}^+]^4 [\text{OH}^-]^4}{P_{\text{O}_2}} \\
&= -0.40 \text{ V} - \frac{0.0592}{4} \log \frac{K_{\text{sp}}^4}{P_{\text{O}_2}} \\
&= -0.40 \text{ V} - \frac{0.0592}{4} \log \frac{(1.5 \times 10^{-8})^4}{0.2132} \\
&= -0.40 \text{ V} + 0.45 \text{ V} \\
&= +0.05 \text{ V}
\end{aligned}$$

Under these conditions, the potential is slightly positive and the oxidation should be spontaneous.

**12.89** In each case, determine the cathode and anode half-reactions corresponding to the reactions *as written*. Look up the standard reduction potentials for these half-reactions and then calculate  $E^\circ_{\text{cell}} = E^\circ(\text{cathode}) - E^\circ(\text{anode})$ . If  $E^\circ_{\text{cell}}$  is positive, the reaction is spontaneous under standard conditions.

$$(a) \quad E^\circ_{\text{cell}} = E^\circ(\text{cathode}) - E^\circ(\text{anode}) = +0.96 \text{ V} - (+0.79 \text{ V}) = +0.17 \text{ V}.$$

Therefore, spontaneous galvanic cell:



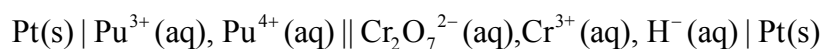
$$\Delta G^\circ_r = -nFE^\circ = -(6)(9.65 \times 10^4 \text{ C} \cdot \text{mol}^{-1})(+0.17 \text{ J} \cdot \text{C}^{-1}) = -98 \text{ kJ} \cdot \text{mol}^{-1}$$

$$(b) \quad E^\circ_{\text{cell}} = E^\circ(\text{cathode}) - E^\circ(\text{anode}) = +0.92 \text{ V} - (+1.09 \text{ V}) = -0.17 \text{ V}$$

Therefore, not spontaneous.

$$(c) \quad E^\circ_{\text{cell}} = E^\circ(\text{cathode}) - E^\circ(\text{anode}) = +1.33 \text{ V} - (+0.97 \text{ V}) = +0.36 \text{ V}$$

Therefore, spontaneous galvanic cell.



$$\Delta G^\circ_r = -nFE^\circ = -(6)(9.65 \times 10^4 \text{ C} \cdot \text{mol}^{-1})(0.36 \text{ J} \cdot \text{C}^{-1}) = -208 \text{ kJ} \cdot \text{mol}^{-1}$$

$$12.91 \quad (a) \quad M_{\text{Ag}^+} V_{\text{Ag}^+} = M_{\text{I}^-} V_{\text{I}^-}$$

$$\begin{aligned} M_{\text{Ag}^+} &= \frac{M_{\text{I}^-} V_{\text{I}^-}}{V_{\text{Ag}^+}} = \frac{(0.015 \text{ M})(16.7 \text{ mL})}{(25.0 \text{ mL})} \\ &= 1.0 \times 10^{-2} \text{ M} \end{aligned}$$

(b) We can find  $[\text{Ag}^+]$  by using the Nernst equation appropriately.

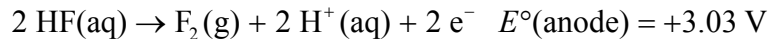
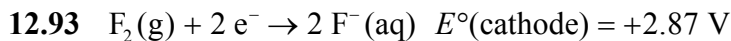
$$E = E^\circ - \left( \frac{0.025693 \text{ V}}{n} \right) \ln \left( \frac{1}{[\text{Ag}^+]} \right)$$

Since the standard reduction potential of silver(I) is +0.80 V, it will be the reduction half reaction versus the S.H.E., so  $[\text{Ag}^+]$  appears in the denominator of  $Q$ . In addition,  $n = 1$  and  $E^\circ = 0.080 \text{ V}$ .

$$\begin{aligned} 0.325 \text{ V} &= 0.80 \text{ V} - \left( \frac{0.025693 \text{ V}}{1} \right) \ln \left( \frac{1}{[\text{Ag}^+]} \right) \\ -0.475 \text{ V} &= (-2.567 \times 10^{-2} \text{ V})(\ln 1 - \ln[\text{Ag}^+]) \\ -18.50 &= \ln[\text{Ag}^+] \\ [\text{Ag}^+] &= 9.23 \times 10^{-9} \text{ M} \end{aligned}$$

Recalling that  $K_{sp} = [\text{Ag}^+][\text{I}^-]$ , and assuming  $[\text{Ag}^+] = [\text{I}^-]$  at the stoichiometric point of the titration,

$$K_{sp} = [\text{Ag}^+][\text{I}^-] = (9.23 \times 10^{-9})^2 = 8.5 \times 10^{-17}$$



$$E^\circ_{\text{cell}} = E^\circ(\text{cathode}) - E^\circ(\text{anode}) = +2.87 \text{ V} - (+3.03 \text{ V}) = -0.16 \text{ V}$$

For the above reaction,  $K = \frac{[\text{H}^+]^2 [\text{F}^-]^2}{[\text{HF}]^2}$  and  $\ln K = \frac{nFE^\circ}{RT}$

$$\text{at } 25^\circ\text{C} = \frac{nE^\circ}{0.02569 \text{ V}} = \frac{(2)(-0.16 \text{ V})}{0.02569 \text{ V}} = -12$$

$$K = 10^{-5}$$

$$K_a = \sqrt{K} = \sqrt{10^{-5}} = 10^{-3}$$

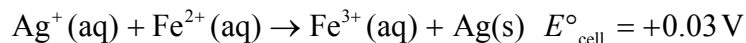
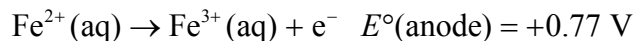
**12.95** The wording of this exercise suggests that  $\text{K}^+$  ions participate in an electrolyte concentration cell reaction. Therefore,  $E^\circ_{\text{cell}} = 0.00 \text{ V}$ , because the two half cells would be identical under standard conditions.

Then,

$$\begin{aligned} E &= E^\circ - \left( \frac{0.0257 \text{ V}}{n} \right) \ln \left( \frac{[\text{K}_{\text{out}}^+]}{[\text{K}_{\text{in}}^+]} \right) = 0.00 \text{ V} - \left( \frac{0.0257 \text{ V}}{1} \right) \ln \left( \frac{1}{30} \right) \\ &= +0.09 \text{ V} \end{aligned}$$

$$\text{and } E = 0.00 \text{ V} - \left( \frac{0.0257 \text{ V}}{1} \right) \ln \left( \frac{1}{20} \right) = +0.08 \text{ V}$$

The range of potentials is 0.08 V to 0.09 V.



$$E_{\text{cell}} = E^\circ_{\text{cell}} - \left( \frac{0.0257 \text{ V}}{n} \right) \ln \left( \frac{[\text{Fe}^{3+}]}{[\text{Ag}^+][\text{Fe}^{2+}]} \right)$$

$$\begin{aligned}
&= 0.03 \text{ V} - (0.0257 \text{ V}) \ln \left( \frac{1}{(0.010)(0.0010)} \right) = 0.03 \text{ V} - 0.30 \text{ V} \\
&= -0.27 \text{ V}
\end{aligned}$$

*Comment:* The cell changes from spontaneous to nonspontaneous as a function of concentration.

**12.99** Since the number of electrons transferred in each half-reaction is different, the Gibbs free energy relationship must be used rather than just the reduction potentials themselves (see Example 12.6).

$$\begin{aligned}
\Delta G_3^\circ &= \Delta G_1^\circ + \Delta G_2^\circ \\
(-n_3 F E_3^\circ) &= (-n_1 F E_1^\circ) + (-n_2 F E_2^\circ) \\
n_3 E_3^\circ &= n_1 E_1^\circ + n_2 E_2^\circ \\
E_3^\circ &= \frac{(1)(-0.256 \text{ V}) + (2)(-1.175 \text{ V})}{3} \\
&= -0.869 \text{ V}
\end{aligned}$$

**12.101** buffer system  $\text{HA} \rightarrow \text{H}^+ + \text{A}^-$

$$Q = \frac{(\text{H}^+)(\text{A}^-)}{(\text{HA})}$$

Note:  $(\text{H}^+)$ , as opposed to  $[\text{H}^+]$ , indicates a nonequilibrium molarity.

Because in a buffer system  $(\text{A}) \approx (\text{HA})$ , we can write

$$Q = (\text{H}^+)$$

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{RT}{nF} \ln (\text{H}^+)$$

$$0.060 \text{ V} = E_{\text{cell}}^\circ - \left( \frac{0.025693}{1} \right) (2.303) (\log(\text{H}^+))$$

Because  $\log(\text{H}^+) = -[-\log(\text{H}^+)] = -\text{pH}$ , we have

$$0.060 \text{ V} = E_{\text{cell}}^\circ - 0.0592 \times (-\text{pH})$$

$$0.060 \text{ V} = E_{\text{cell}}^\circ + 0.0592 \times \text{pH}$$

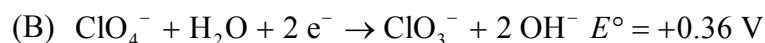
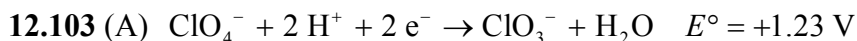
$$0.060 \text{ V} = E_{\text{cell}}^\circ + 0.0592 \times 9.40$$

$$0.060 \text{ V} = E^\circ_{\text{cell}} + 0.556 \text{ V}$$

$$E^\circ = 0.060 \text{ V} - 0.556 \text{ V} = -0.496 \text{ V}$$

$$\text{Similarly, } 0.22 \text{ V} = -0.496 \text{ V} + 0.0592 \text{ V} \times \text{pH}$$

$$\text{pH} = \frac{0.22 \text{ V} + 0.496 \text{ V}}{0.0592 \text{ V}} = 12$$



(a) The Nernst equation can be used to derive the potential as a function of pH:

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

$$\text{For (A), } E(\text{A}) = 1.23 \text{ V} - \frac{0.05916}{2} \log \frac{[\text{ClO}_3^-]}{[\text{ClO}_4^-][\text{H}^+]^2}$$

We are only interested in varying  $[\text{H}^+]$ , so the  $[\text{ClO}_3^-]$  and  $[\text{ClO}_4^-]$  will be left at the standard values of 1 M.

$$\begin{aligned} E(\text{A}) &= +1.23 \text{ V} - \frac{0.05916}{2} \log \frac{1}{[\text{H}^+]^2} \\ &= +1.23 \text{ V} - \frac{0.05916}{2} \times 2 \log \frac{1}{[\text{H}^+]} \\ &= +1.23 \text{ V} - 0.05916 (-\log [\text{H}^+]) \\ &= +1.23 \text{ V} - 0.05916 \text{ pH} \end{aligned}$$

Similarly, for (B):

$$E(\text{B}) = +0.36 \text{ V} - \frac{0.05916}{2} \log \frac{[\text{ClO}_3^-][\text{OH}^-]^2}{[\text{ClO}_4^-]}$$

As above, we are only interested in varying

$[\text{OH}^-]$ , so  $[\text{ClO}_3^-]$  and  $[\text{ClO}_4^-]$  will be left at the standard value of 1 M.

$$\begin{aligned}
E(\text{B}) &= +0.36 \text{ V} - \frac{0.05916}{2} \log [\text{OH}^-]^2 \\
&= +0.36 \text{ V} - \frac{0.05916}{2} \times 2 \log [\text{OH}^-] \\
&= +0.36 \text{ V} - 0.05916 \times \log [\text{OH}^-] \\
&= +0.36 \text{ V} + 0.05916 \text{ pOH}
\end{aligned}$$

Because  $\text{pOH} + \text{pH} = \text{p}K_w = 14.00$ , we can write:

$$\begin{aligned}
\text{pOH} &= 14.00 - \text{pH} \\
E(\text{B}) &= +0.36 \text{ V} + 0.05916[14.00 - \text{pH}] \\
&= +0.36 \text{ V} + 0.83 \text{ V} - 0.05916 \text{ pH} \\
&= +1.19 \text{ V} - 0.05916 \text{ pH}
\end{aligned}$$

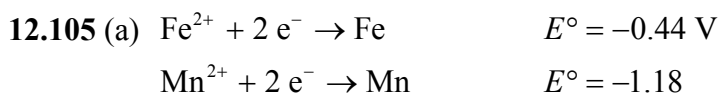
If we compare this to  $E^\circ(\text{A})$ , we find that the equations are essentially the same. They should be identical, the difference being due to the limitation of the number of significant figures available for the calculations.

(b) From the discussion above, we can see that the potential in neutral solution should be the same, regardless of which half-reaction we use to calculate the value.

$$\text{Using } E^\circ(\text{A}) = +1.23 \text{ V} - 0.05916 \text{ pH} = +1.23 \text{ V} - 0.05916 (7.00) = 0.82$$

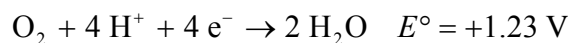
$$\text{Using } E(\text{B}) = +0.36 \text{ V} + 0.05916 \text{ pOH} = +0.36 + 0.05916 (7.00) = 0.77$$

Although these numbers differ slightly, they should be identical; again the difference lies in the limitation of the number of significant figures.



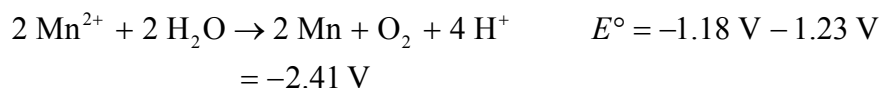
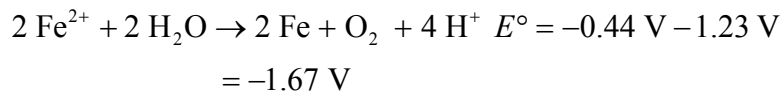
Because these are reduction reactions, we need a corresponding oxidation.

The nitrate ion contains N in its highest oxidation state so it cannot be oxidized further. The logical choice is the oxidation of water. The appropriate reduction potential is



The two overall reactions will be:





(b) The actual potentials, however, will differ from these standard potentials because the concentrations of the metal ions and hydrogen ions are not 1 M, and the pressure of  $\text{O}_2$  is not 1 bar. To calculate the actual values, the Nernst equation is used.

$$\text{For the Fe reaction: } E = -1.67 \text{ V} - \frac{0.05916}{4} \log \frac{P_{\text{O}_2} [\text{H}^+]^4}{[\text{Fe}^{2+}]^2}$$

In an open beaker, with the metal ions dissolved in water with pH = 5.00, the pressure of  $\text{O}_2$  will be  $0.2095 \times 1.00 \text{ atm} \times 0.987 \text{ bar} \cdot \text{atm}^{-1} = 0.207$  bar. Substituting the specific values will give

$$E = -1.67 \text{ V} - \frac{0.05916}{4} \log \frac{(0.207)(1.00 \times 10^{-5})^4}{(0.0950)^2} \\ = -1.67 \text{ V} + 0.276 \text{ V} = -1.39 \text{ V}$$

For the Mn reaction:

$$E = -2.41 \text{ V} - \frac{0.05916}{4} \log \frac{(0.207)(1.00 \times 10^{-5})^4}{(0.115)^2} \\ = -2.41 \text{ V} + 0.278 \text{ V} = -2.13 \text{ V}$$

In order to plate out iron from this mixture, 1.39 V must be applied, and 2.13 V must be applied to cause the reduction of  $\text{Mn}^{2+}$ .

(c) Because the potential for reducing iron(II) is more positive than the potential for reducing manganese(II), the iron will plate out first.

(d) The answer to this question is obtained from the Nernst equation by determining the concentration of  $\text{Fe}^{2+}$  when the applied potential reaches 2.13 V:

$$-2.13 \text{ V} = -1.67 \text{ V} - \frac{0.05916}{4} \log \frac{(0.207)[\text{H}^+]^4}{[\text{Fe}^{2+}]^2}$$

$$-0.46 \text{ V} = -\frac{0.05916}{4} \log \frac{(0.207)[\text{H}^+]^4}{[\text{Fe}^{2+}]^2}$$

$$31.10 = \log 0.207 + \log \frac{[\text{H}^+]^4}{[\text{Fe}^{2+}]^2}$$

$$31.78 = \log \frac{[\text{H}^+]^4}{[\text{Fe}^{2+}]^2}$$

$$\frac{[\text{H}^+]^4}{[\text{Fe}^{2+}]^2} = 6.0 \times 10^{31}$$

$$\frac{[\text{H}^+]^2}{[\text{Fe}^{2+}]} = 7.7 \times 10^{15}$$

For the last ratio to be  $7.7 \times 10^{15}$ , essentially all of the  $\text{Fe}^{2+}$  must be converted to  $\text{Fe(s)}$ . This means that  $[\text{H}^+]$  will essentially be  $0.190$

$\text{mol} \cdot \text{L}^{-1}$ . Substituting this number gives  $[\text{Fe}^{2+}] = 5 \times 10^{-18} \text{ mol} \cdot \text{L}^{-1}$ . We can say that the iron is quantitatively precipitated by this point.

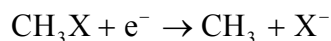
We might note, however, that the potential of  $2.13 \text{ V}$  is now no longer the potential at which  $\text{Mn}^{2+}$  will begin to be reduced. Because the reduction of  $\text{Fe}^{2+}$  has produced a considerable amount of acid, the original reduction of  $\text{Mn}^{2+}$  should be recalculated:

$$E = -2.41 \text{ V} - \frac{0.05916}{4} \log \frac{(0.207)(0.190)^4}{(0.115)^2} = -2.39 \text{ V}$$

Thus, even less iron will remain in solution.

- 12.107** (a) Addition of an electron to any molecule should have the electron enter the molecule's lowest unoccupied molecular orbital (LUMO) first. (b) For  $\text{CH}_3\text{X}$ , one would predict that the LUMO would be antibonding between C and one of the atoms attached to it. Because the C—H bond strength ( $412 \text{ kJ} \cdot \text{mol}^{-1}$ ) is greater than all of the C—X bond strengths given (C—Cl,  $338 \text{ kJ} \cdot \text{mol}^{-1}$ ; C—Br,  $276 \text{ kJ} \cdot \text{mol}^{-1}$ ; C—I,  $238$

$\text{kJ} \cdot \text{mol}^{-1}$ ) we would expect the LUMO to be the antibonding orbital for the C—X bond. Adding an electron to this orbital should then result in a weakening of the C—X bond. The result is the elimination of  $\text{X}^-$  and the formation of a  $\text{CH}_3$  radical:



(c) We would expect this reduction process to follow the C—X bond strengths so that the formation of  $\text{X}^-$  and generation of  $\text{CH}_3$  radicals would be easiest for  $\text{X} = \text{I}$ , followed by  $\text{Br}$ , and then  $\text{Cl}$ .

**12.109** In order to determine the current applied, we need to find the number of moles of electrons transferred. The electrolysis of water to produce gaseous oxygen and hydrogen,

$$2 \text{H}_2\text{O}(\text{l}) \rightarrow \text{O}_2(\text{g}) + 2 \text{H}_2(\text{g}),$$

transfers 4 moles of electrons for each mole of oxygen gas produced:  $4 \text{OH}^-(\text{aq}) \rightarrow \text{O}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{l}) + 4 \text{e}^-$ . We can determine the number of moles of oxygen from its volume, partial pressure, and temperature.

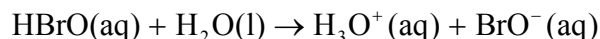
$$\begin{aligned} n_{\text{O}_2} &= \frac{p_{\text{O}_2} V}{RT} = \frac{(p_{\text{tot}} - p_{\text{H}_2\text{O}}) V}{RT} \\ &= \frac{(722 \text{ Torr} - 19.83 \text{ Torr})(25.0 \text{ mL})}{(0.08206 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(295 \text{ K})} \cdot \frac{1 \text{ L}}{1000 \text{ mL}} \cdot \frac{1 \text{ atm}}{760 \text{ Torr}} \\ &= 9.542 \times 10^{-4} \text{ mol O}_2 \text{ produced} \end{aligned}$$

$$\begin{aligned} n_{\text{e}^-} &= n_{\text{O}_2} \times \frac{4 \text{ mol e}^-}{\text{mol O}_2} = 9.542 \times 10^{-4} \text{ mol O}_2 \times \frac{4 \text{ mol e}^-}{\text{mol O}_2} \\ &= 3.817 \times 10^{-3} \text{ mol e}^- \end{aligned}$$

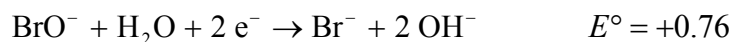
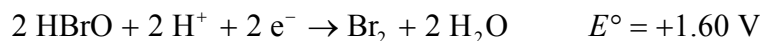
$$It = nF$$

$$\begin{aligned} I &= \frac{nF}{t} = \frac{(3.817 \times 10^{-3} \text{ mol e}^-)}{(30.0 \text{ min})(60 \text{ s} \cdot \text{min}^{-1})} \cdot \left( 96\,485 \frac{\text{C}}{\text{mol e}^-} \right) \\ &= 0.205 \text{ A} \end{aligned}$$

**12.111** The strategy for working this problem is to create a set of equations that will add to the desired equilibrium reaction:



From Appendix 2B, we find

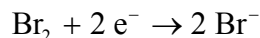
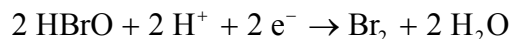


On examination of these equations, it is clear that we will also need a half-reaction that, when combined with the two above, will eliminate

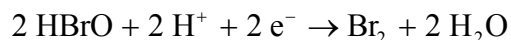
$\text{Br}_2$  and  $\text{Br}^-$ . The obvious choice is



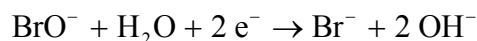
We combine these by adding twice the reverse reaction to the other two:



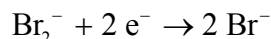
*Caution:* We must be careful here in adding the  $E^\circ$  values—we have created essentially a new half-reaction by summing these reactions, which requires that we convert to  $\Delta G$  values. Whenever one sums more than two half-reactions, it is necessary to convert to the  $\Delta G$  values using  $\Delta G^\circ = nFE^\circ$ , in order to work the problem:



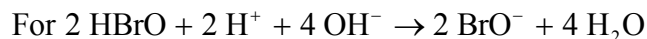
$$\Delta G^\circ = -2(9.65 \times 10^4 \text{ C} \cdot \text{mol}^{-1})(+1.60 \text{ V}) = -309 \text{ kJ} \cdot \text{mol}^{-1}$$



$$\Delta G^\circ = -2(9.65 \times 10^4 \text{ C} \cdot \text{mol}^{-1})(+0.76 \text{ V}) = -147 \text{ kJ} \cdot \text{mol}^{-1}$$



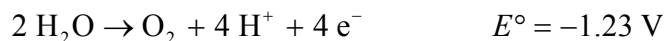
$$\Delta G^\circ = -2(9.65 \times 10^4 \text{ C} \cdot \text{mol}^{-1})(+1.09 \text{ V}) = -210 \text{ kJ} \cdot \text{mol}^{-1}$$



$$\Delta G^\circ = -309 \text{ kJ} + 2(+147 \text{ kJ}) - 210 \text{ kJ} = -225 \text{ kJ} \cdot \text{mol}^{-1}$$

We now see that we will need to eliminate  $\text{OH}^-$  from the left side of the equation. This can be done in one of two ways: we can use the  $K_w$  value

for the autoprotolysis of water or, equivalently, we can use appropriate half-reactions that sum to the autoprotolysis of water. The appropriate half-reactions are



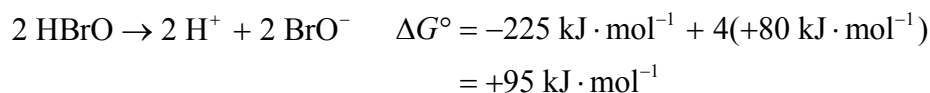
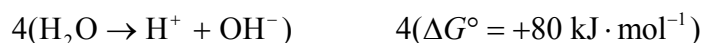
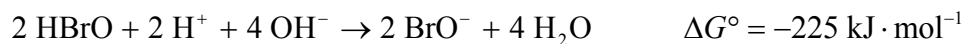
These sum to give



This is a  $4 \text{e}^-$  reaction. Alternatively, one can write the  $1 \text{e}^-$  process that will have the same  $E^\circ$  value.



$$\Delta G^\circ = -(1)(9.65 \times 10^4 \text{ C} \cdot \text{mol}^{-1})(-0.83 \text{ V}) = +80 \text{ kJ} \cdot \text{mol}^{-1}$$



The desired reaction is half of this, for which  $\Delta G^\circ = +48 \text{ kJ} \cdot \text{mol}^{-1}$ .

Using  $\Delta G^\circ = -RT \ln K$ , we obtain  $K = 4 \times 10^{-9}$ , which is in reasonable agreement for this type of calculation with the value of  $2 \times 10^{-9}$  given in Table 10.1.