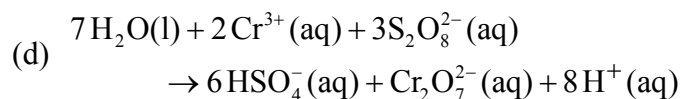
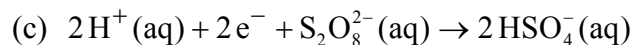
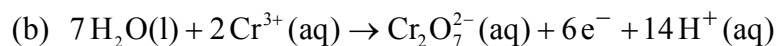
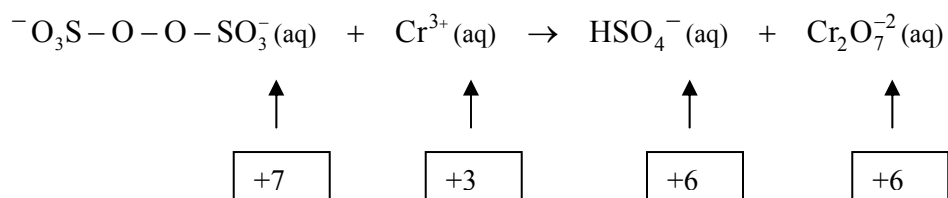


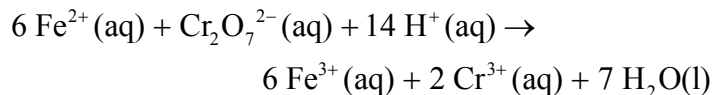
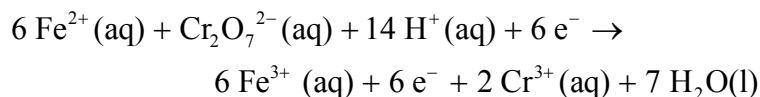
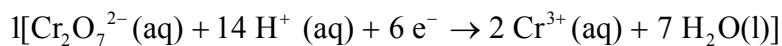
CHAPTER 12

ELECTROCHEMISTRY

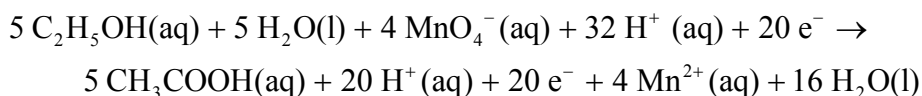
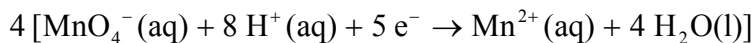
12.2 (a)

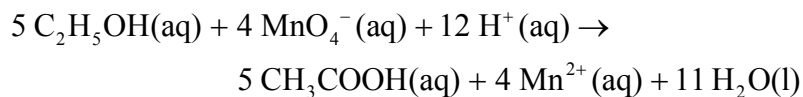


12.4 (a) $6[\text{Fe}^{2+}(\text{aq}) \rightarrow \text{Fe}^{3+}(\text{aq}) + \text{e}^-]$



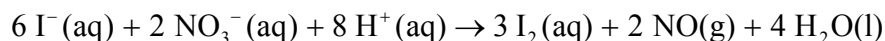
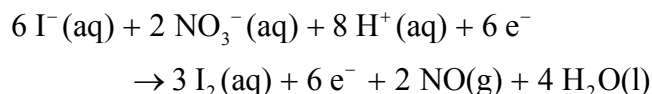
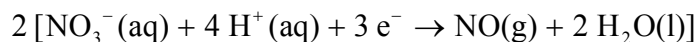
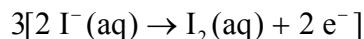
Fe^{2+} is the reducing agent and $\text{Cr}_2\text{O}_7^{2-}$ is the oxidizing agent.





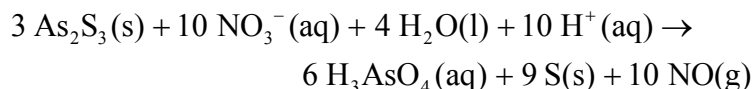
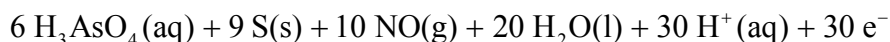
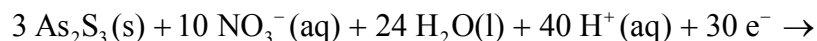
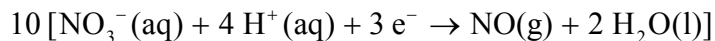
$\text{C}_2\text{H}_5\text{OH}$ is the reducing agent and MnO_4^- is the oxidizing agent.

(c) The reaction is $\text{I}^- (\text{aq}) + \text{NO}_3^- (\text{aq}) \rightarrow \text{I}_2 (\text{aq}) + \text{NO}(\text{g})$.



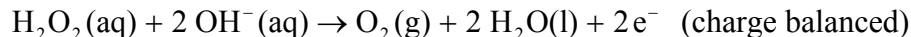
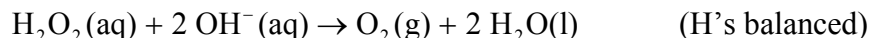
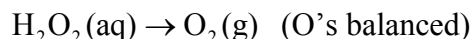
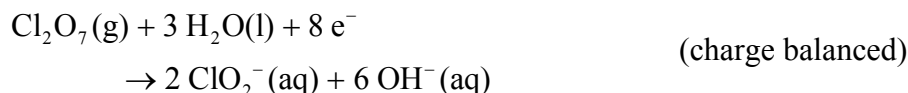
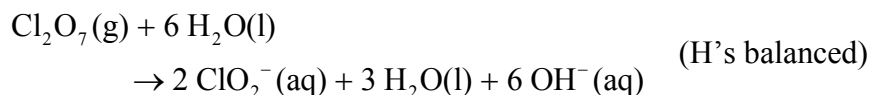
I^- is the reducing agent and NO_3^- is the oxidizing agent.

(d) $3[\text{As}_2\text{S}_3 (\text{s}) + 8 \text{H}_2\text{O}(\text{l}) \rightarrow 2 \text{H}_3\text{AsO}_4 (\text{aq}) + 3 \text{S}(\text{s}) + 10 \text{H}^+ (\text{aq}) + 10 \text{e}^-]$

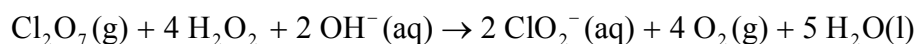
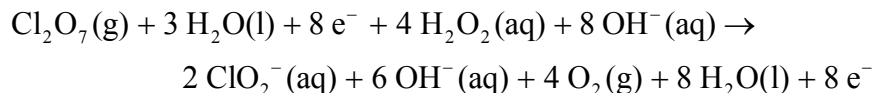
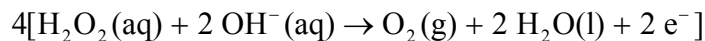
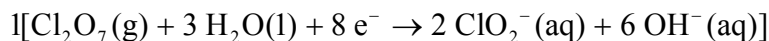


As_2S_3 is the reducing agent (both As and S are oxidized) and NO_3^- is the oxidizing agent.

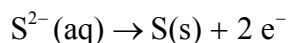
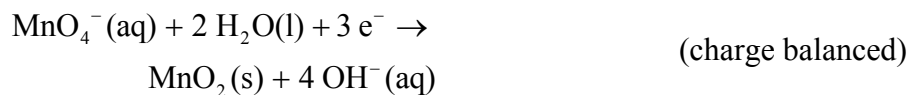
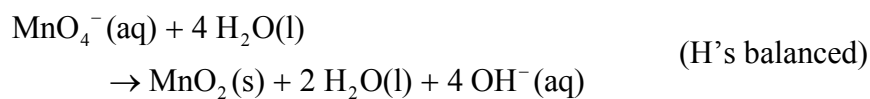
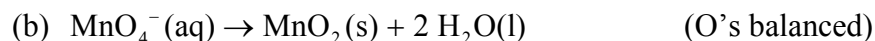
12.6 (a) $\text{Cl}_2\text{O}_7 (\text{g}) \rightarrow 2 \text{ClO}_2^- (\text{aq}) + 3 \text{H}_2\text{O}(\text{l})$ (O's balanced)



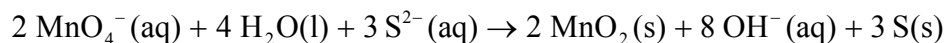
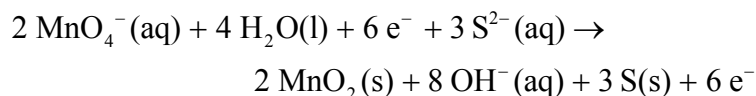
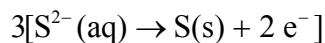
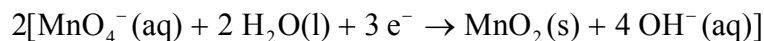
Combining the two half-reactions:



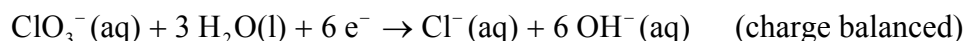
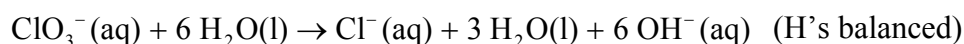
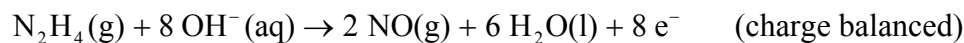
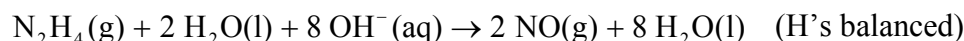
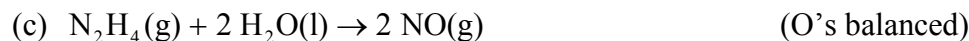
Cl_2O_7 is the oxidizing agent and H_2O_2 is the reducing agent.



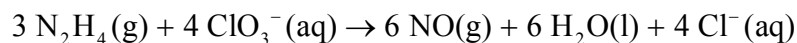
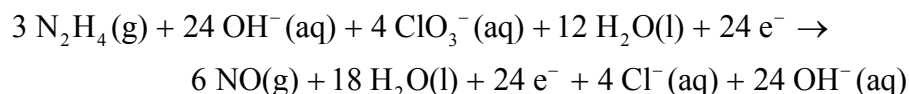
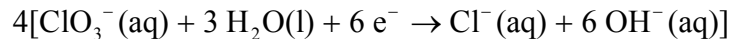
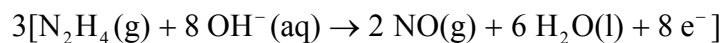
Combining the two half-reactions:



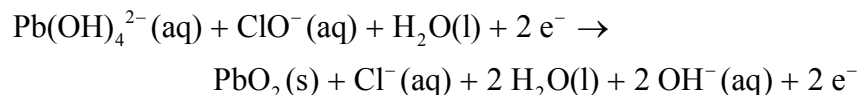
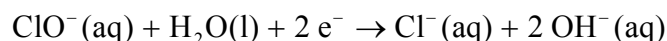
MnO_4^- is the oxidizing agent and S^{2-} is the reducing agent.



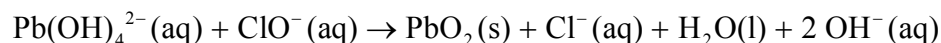
Combining the two half-reactions:



N_2H_4 is the reducing agent and ClO_3^- is the oxidizing agent.



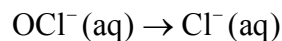
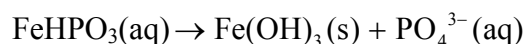
or



$\text{Pb}(\text{OH})_4^{2-}$ is the reducing agent and ClO^- is the oxidizing agent.

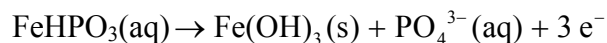
12.8 We first determine the two half-reactions:

Unbalanced:

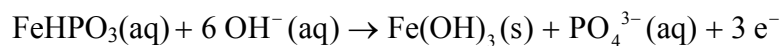


These are then balanced as follows:

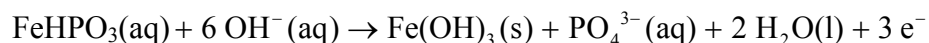
The ferrous hydrogen phosphite reaction is complicated because both iron and phosphorus are oxidized. The Fe atom begins with an oxidation number of +2 and ends with an oxidation number of +3, while phosphorus starts as +3 and ends up as +5. There is a total change of 3 electrons.



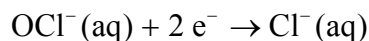
Balancing the charge by addition of hydroxide for basic solution gives



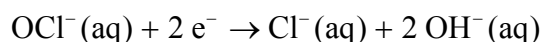
Balancing the hydrogen and oxygen atoms by addition of water gives



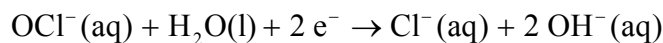
The reduction of hypochlorite is simpler to balance. The oxidation number of chlorine changes from +1 in OCl^- to -1 in Cl^- , giving a change of 2 e^- .



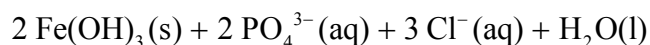
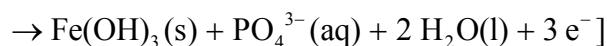
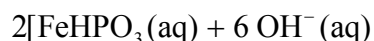
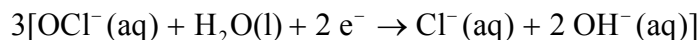
Balancing the charge by addition of OH^- :



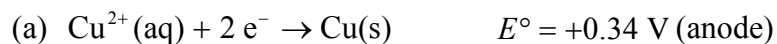
Balancing oxygen and hydrogen atoms by addition of H_2O :



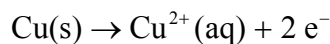
Combining the two equations:



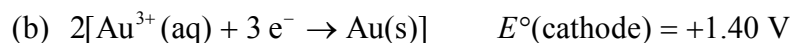
12.10 The anode (oxidation) is written to the left in a cell diagram, the cathode (reduction) to the right.



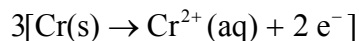
Therefore, at the anode, after reversal,



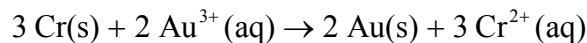
The cell reaction is



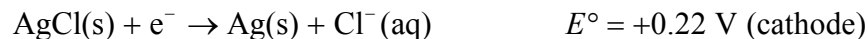
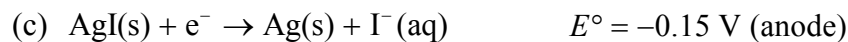
Therefore, at the anode, after reversal,



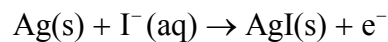
The cell reaction is, upon addition of the half-reactions,



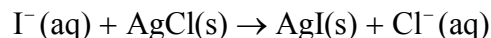
$$E^\circ_{\text{cell}} = +1.40 \text{ V} - (-0.90 \text{ V}) = +2.30 \text{ V}$$



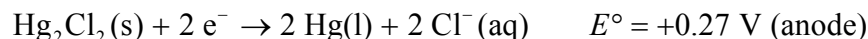
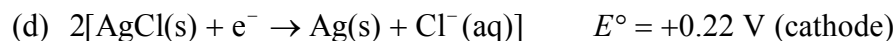
Therefore, at the anode, after reversal,



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

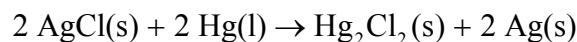


$$E^\circ_{\text{cell}} = +0.22 \text{ V} - (-0.15 \text{ V}) = +0.37 \text{ V}$$



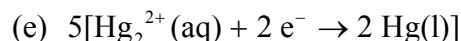
Reverse the anode half-reaction: $2 \text{Hg(l)} + 2 \text{Cl}^-(\text{aq}) \rightarrow \text{Hg}_2\text{Cl}_2(\text{s}) + 2 \text{e}^-$

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

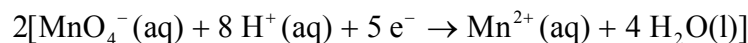


$$E^\circ_{\text{cell}} = +0.22 \text{ V} - 0.27 \text{ V} = -0.05 \text{ V}$$

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

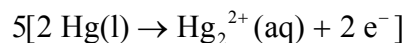


$$E^\circ(\text{anode}) = +0.79 \text{ V}$$

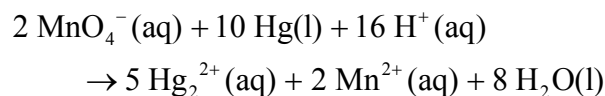


$$E^\circ(\text{cathode}) = +1.51 \text{ V}$$

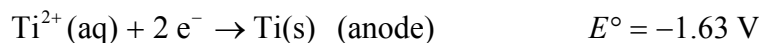
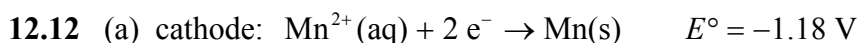
Reversing the anode reaction gives



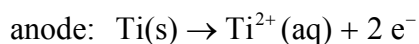
The cell reaction, upon combination of the half-reactions,



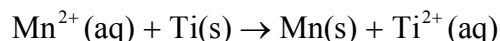
$$E^{\circ}_{\text{cell}} = +1.51 \text{ V} - (+0.79 \text{ V}) = +0.72$$



Reversing the anode reaction:

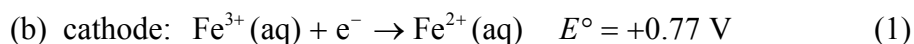


Adding the half-reactions, we have, for the overall reaction:



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

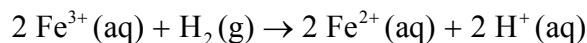
The cell diagram is



Multiplying Eq. 1 by a factor of 2 gives

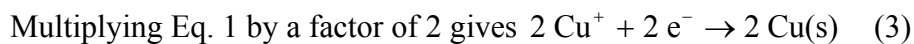
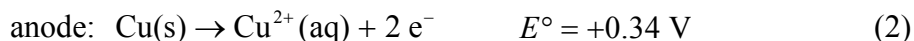
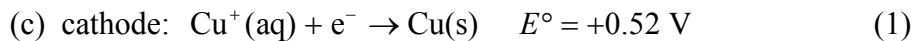
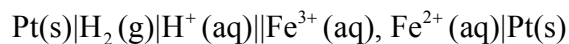


Adding Eqs. 2 and 3 gives the overall reaction:



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

The cell diagram is

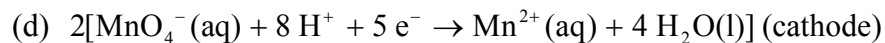


Upon addition of Eqs. 2 and 3, we have

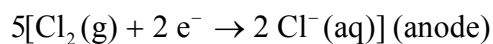


The cell diagram is



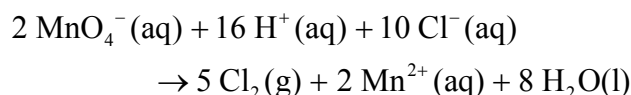


$$E^\circ = +1.51 \text{ V}$$



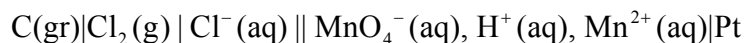
$$E^\circ = +1.36 \text{ V}$$

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

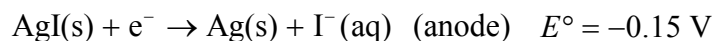
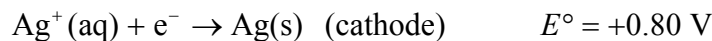
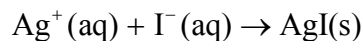


$$E^\circ_{\text{cell}} = +1.51 \text{ V} - 1.36 \text{ V} = +0.15 \text{ V}$$

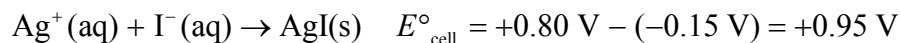
The cell diagram is



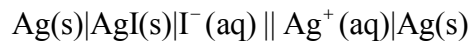
12.14 (a) Eliminating the spectator ions, the reaction is



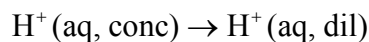
Reverse the anode reaction $\text{Ag}(\text{s}) + \text{I}^- (\text{aq}) \rightarrow \text{AgI}(\text{s}) + \text{e}^-$, then upon addition,



The cell diagram is

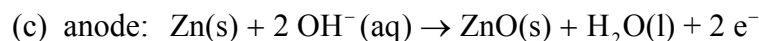


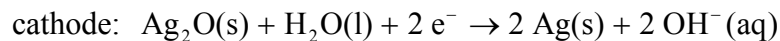
(b) Rewriting in the notation of this chapter, we have



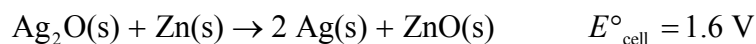
The oxidation reaction at the anode is $\frac{1}{2} \text{H}_2 (\text{g}) \rightarrow \text{H}^+ (\text{aq}) + \text{e}^-$ and the reduction at the cathode is $\text{H}^+ (\text{aq}) + \text{e}^- \rightarrow \frac{1}{2} \text{H}_2 (\text{g})$.

The cell diagram is $\text{Pt}(\text{s})|\text{H}_2 (\text{g}) | \text{H}^+ (\text{aq, dil}) || \text{H}^+ (\text{aq, conc}) | \text{H}_2 (\text{g}) | \text{Pt}(\text{s})$.



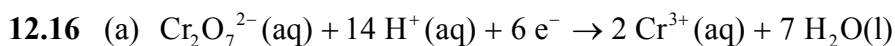
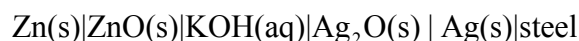


Adding the two half-reactions gives

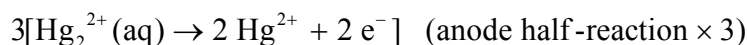


(See Table 12.1.)

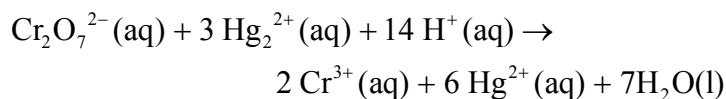
The cell diagram is



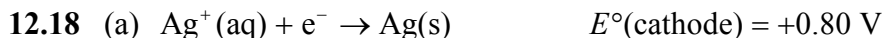
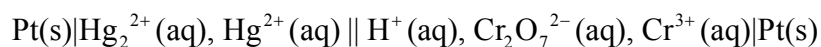
(cathode half-reaction)



(b) Adding half-reactions gives



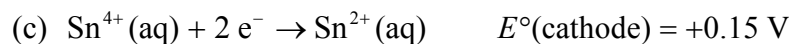
The cell diagram is



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



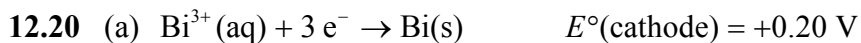
$$E^\circ(\text{cell}) = -1.19 \text{ V} - (-1.79 \text{ V}) = +0.60 \text{ V}$$



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



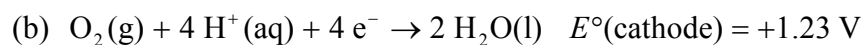
$$E^\circ(\text{cell}) = +1.69 \text{ V} - (+0.34 \text{ V}) = +1.35 \text{ V}$$



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

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

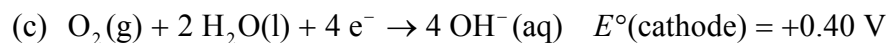
$$\begin{aligned}\Delta G^{\circ}_{\text{r}} &= -nFE^{\circ} = -6(9.6485 \times 10^4 \text{ J} \cdot \text{V}^{-1} \cdot \text{mol}^{-1})(+0.96 \text{ V}) \\ &= -5.6 \times 10^2 \text{ kJ} \cdot \text{mol}^{-1}\end{aligned}$$



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

half-reaction gives $2 \text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{H}_2\text{O}(\text{l})$ $n = 4$, $E^{\circ}_{\text{cell}} = +1.23 \text{ V}$

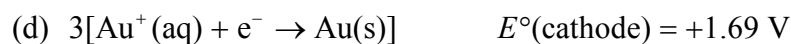
$$\Delta G^{\circ}_{\text{r}} = -nFE^{\circ} = -4 \times 9.6485 \times 10^4 \text{ C} \cdot \text{mol}^{-1} \times 1.23 \text{ V} = -475 \text{ kJ} \cdot \text{mol}^{-1}$$



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

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

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

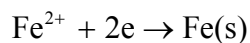


Taking $3[\text{Au}^{+} + \text{e}^{-} \rightarrow \text{Au}(\text{s})]$ and adding it to the reverse of the reduction half-reaction gives $3 \text{Au}^{+} \rightarrow \text{Au}^{3+} + 2 \text{Au}(\text{s})$ $n = 3$

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

$$\begin{aligned}\Delta G^{\circ}_{\text{r}} &= -nFE^{\circ} = -3 \times 9.6485 \times 10^4 \text{ C} \cdot \text{mol}^{-1} \times 0.29 \text{ J} \cdot \text{C}^{-1} \\ &= -84 \text{ kJ} \cdot \text{mol}^{-1}\end{aligned}$$

12.22 The unknown metal ions are reduced, increasing the weight of the unknown metal electrode. The cell can be written as $\text{Fe(s)}|\text{Fe}^{2+}(\text{aq})||\text{M}^{+}(\text{aq})|\text{M(s)}$ showing that the M^{+}/M electrode is the cathode, because this is where reduction is occurring.



$$E^{\circ} = -0.44 \text{ V}$$

$$E^{\circ}(\text{cathode}) = +1.24 \text{ V} + E^{\circ}(\text{anode})$$

$$E^{\circ}(\text{cathode}) = +1.24 \text{ V} + (-0.44 \text{ V}) = +0.80 \text{ V}$$

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

$$\text{Cl}_2 \quad E^{\circ} = +1.36 \text{ V}$$

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

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

The best oxidizing agent has the highest E° : $\text{Ce}^{4+} > \text{Cl}_2 > \text{Co}^{2+} > \text{In}^{3+}$

(b) $\text{NO}_3^{-} \quad E^{\circ} = +0.96 \text{ V}$

$$\text{ClO}_4^{-} \quad E^{\circ} = +1.23 \text{ V}$$

$$\text{HBrO} \quad E^{\circ} = +1.60 \text{ V}$$

$$\text{Cr}_2\text{O}_7^{2-} \quad E^{\circ} = +1.33 \text{ V}$$

The best oxidizing agent has the highest

$$E^{\circ}: \text{HBrO} > \text{Cr}_2\text{O}_7^{2-} > \text{ClO}_4^{-} > \text{NO}_3^{-}$$

(c) $\text{O}_2 + 4 \text{H}^{+} + 4 \text{e}^{-} \rightarrow 2 \text{H}_2\text{O} \quad E^{\circ} = +1.23 \text{ V}$

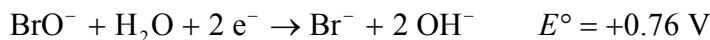
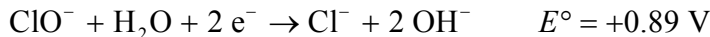
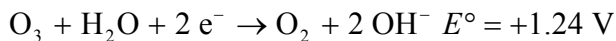
$$\text{O}_3 + 2 \text{H}^{+} + 2 \text{e}^{-} \rightarrow \text{O}_2 + \text{H}_2\text{O} \quad E^{\circ} = +2.07 \text{ V}$$

$$2 \text{HClO} + 2 \text{H}^{+} + 2 \text{e}^{-} \rightarrow \text{Cl}_2 + 2 \text{H}_2\text{O} \quad E^{\circ} = +1.63 \text{ V}$$

$$2 \text{HBrO} + 2 \text{H}^{+} + 2 \text{e}^{-} \rightarrow \text{Br}_2 + 2 \text{H}_2\text{O} \quad E^{\circ} = +1.60 \text{ V}$$

The order of oxidizing ability in acidic solution (which corresponds to the ease of reduction of the reagent) is $\text{O}_3 > \text{HClO} > \text{HBrO} > \text{O}_2$.

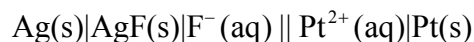
(d) $\text{O}_2 + \text{H}_2\text{O} + 4 \text{e}^{-} \rightarrow 4 \text{OH}^{-} \quad E^{\circ} = +0.40 \text{ V}$



The order of oxidizing ability in basic solution (which corresponds to the ease of reduction of the reagent) is $\text{O}_3 > \text{ClO}^- > \text{BrO}^- > \text{O}_2$. Notice that the order in (c) is the same as here, but the relative amounts of difference may be significantly different. For example, HClO and HBrO have very similar oxidizing abilities in acidic solution, but in basic solution the ClO^- ion is substantially more oxidizing than BrO^- . Note also that the oxidizing ability of all of these species is somewhat less in the basic medium.

12.26 (a) Pt^{2+}/Pt $E^\circ = +1.20 \text{ V}$, Pt^{2+} is oxidizing agent (cathode)

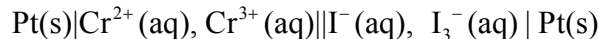
$\text{AgF}/\text{Ag}, \text{F}^-$ $E^\circ = +0.78 \text{ V}$, Ag is reducing agent (anode)



$$E^\circ_{\text{cell}} = E^\circ(\text{cathode}) - E^\circ(\text{anode}) = +1.20 \text{ V} - 0.78 \text{ V} = +0.42 \text{ V}$$

(b) I_3^-/I^- $E^\circ = +0.53 \text{ V}$, I_3^- is oxidizing agent (cathode)

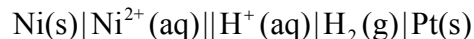
$\text{Cr}^{3+}/\text{Cr}^{2+}$ $E^\circ = -0.41 \text{ V}$, Cr^{2+} is reducing agent (anode)



$$E^\circ_{\text{cell}} = +0.53 \text{ V} - (-0.41 \text{ V}) = +0.94 \text{ V}$$

(c) H^+/H_2 $E^\circ = 0.00 \text{ V}$, H^+ is oxidizing agent (cathode)

Ni^{2+}/Ni $E^\circ = -0.23 \text{ V}$, Ni is reducing agent (anode)



$$E^\circ_{\text{cell}} = 0.00 \text{ V} - (-0.23 \text{ V}) = +0.23 \text{ V}$$

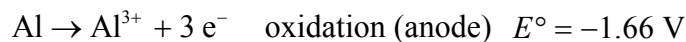
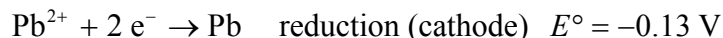
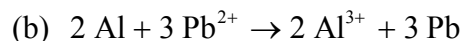
(d) $\text{O}_3, \text{H}^+/\text{O}_2$ $E^\circ = +2.07 \text{ V}$, O_3 is oxidizing agent (cathode)

$\text{O}_3/\text{O}_2, \text{OH}^-$ $E^\circ = +1.24 \text{ V}$, O_2 is reducing agent (anode)



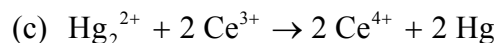
$$E^\circ_{\text{cell}} = +2.07 \text{ V} - 1.24 \text{ V} = +0.83 \text{ V}$$

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

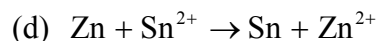


$$E^\circ_{\text{cell}} = E^\circ(\text{cathode}) - E^\circ(\text{anode}) = -0.13 \text{ V} - (-1.66 \text{ V}) = +1.53 \text{ V}$$

$$\begin{aligned} \Delta G^\circ_{\text{r}} &= -nFE^\circ = -(6)(9.6485 \times 10^4 \text{ C} \cdot \text{mol}^{-1})(+1.53 \text{ J} \cdot \text{C}^{-1}) \\ &= -886 \text{ kJ} \cdot \text{mol}^{-1}; \text{ therefore, the reaction is spontaneous} \end{aligned}$$



E° for $\text{Ce}^{4+}/\text{Ce}^{3+} > E^\circ$ for $\text{Hg}_2^{2+}/\text{Hg}$: the reaction is not spontaneous.



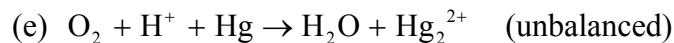
E° for $\text{Sn}^{2+}/\text{Sn} > E^\circ$ for Zn^{2+}/Zn



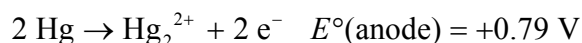
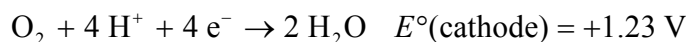
$$\begin{aligned} \Delta E^\circ &= E^\circ(\text{cathode}) - E^\circ(\text{anode}) = -0.14 \text{ V} - (-0.76 \text{ V}) \\ &= +0.62 \text{ V} \end{aligned}$$

$$\begin{aligned} \Delta G^\circ_{\text{r}} &= -nFE^\circ = -(2)(9.6485 \times 10^4 \text{ C} \cdot \text{mol}^{-1})(0.62 \text{ J} \cdot \text{C}^{-1}) \\ &= -120 \text{ kJ} \cdot \text{mol}^{-1}, \end{aligned}$$

the reaction is spontaneous



E° for $\text{O}_2/\text{H}_2\text{O} > E^\circ$ for $\text{Hg}_2^{2+}/\text{Hg}$



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

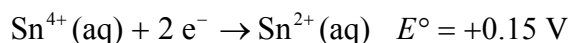
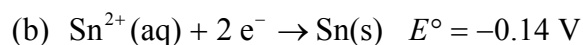
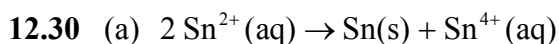
$$\Delta E^\circ = E^\circ(\text{cathode}) - E^\circ(\text{anode}) = +1.23 \text{ V} - (+0.79 \text{ V})$$

$$= +0.44 \text{ V}$$

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

$$= -170 \text{ kJ} \cdot \text{mol}^{-1},$$

the reaction is spontaneous



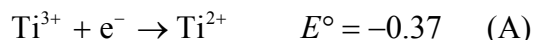
The desired reaction is obtained by subtracting the second equation from the first.

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

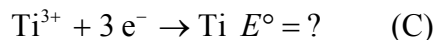
$$E^\circ = -0.14 \text{ V} - (+0.15 \text{ V}) = -0.29 \text{ V}$$

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

12.32 The appropriate half-reactions are



(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° values into ΔG° values:

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

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

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

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

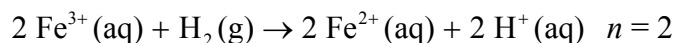
$$-3FE^\circ(\text{C}) = -1F(-0.37 \text{ V}) + [-2F(-1.63 \text{ V})]$$

The constant F will cancel from both sides, leaving:

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

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

12.34 (a) The balanced cell reaction is



$$E^\circ_{\text{cell}} = E^\circ(\text{cathode}) - E^\circ(\text{anode}) = +0.77 \text{ V} - (0.00) \text{ V} = +0.77 \text{ V}$$

$$\ln K = \frac{nFE^\circ}{RT} = \frac{2(+0.77 \text{ V})}{0.025693 \text{ V}}$$

$$\ln K = \frac{(2)(0.77 \text{ V})}{0.025693 \text{ V}} = 59.9$$

$$K = 10^{26}$$



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

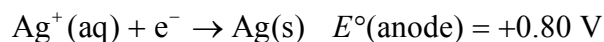
$$\ln K = \frac{nFE^\circ}{RT} = \frac{(2)(+0.15 \text{ V})}{0.025693 \text{ V}}$$

$$\ln K = \frac{(2)(0.15 \text{ V})}{0.025693 \text{ V}} = +12$$

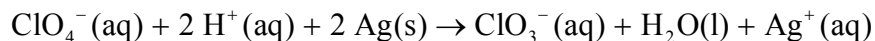
$$\text{and } K = 10^5$$

12.36 (a) $\text{ClO}_4^-(\text{aq}) + 2 \text{H}^+(\text{aq}) + 2 \text{e}^- \rightarrow \text{ClO}_3^-(\text{aq}) + \text{H}_2\text{O}(\text{l})$

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



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



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

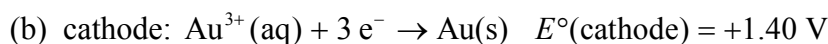
Then, using the Nernst equation, $E = E^\circ - \frac{RT}{nF} \ln Q$, we have

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

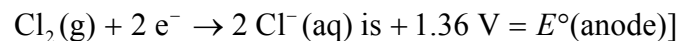
$$0.40\text{ V} = 0.43\text{ V} - \frac{0.025\,693\text{ V}}{2} \ln Q$$

$$\ln Q = -\frac{(2)(-0.03\text{ V})}{0.025\,693\text{ V}} = 2$$

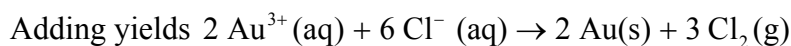
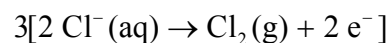
$$\ln Q = 10^1$$



anode: [reduction potential for



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



$$E^\circ_{\text{cell}} = 0.04\text{ V}$$

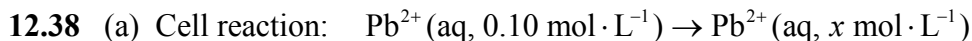
Then, $n = 6$

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

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

$$\ln Q = -\frac{(6)(-0.04\text{ V})}{0.025\,693\text{ V}} = 9$$

$$Q = 10^4$$

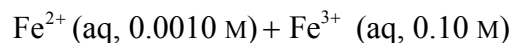
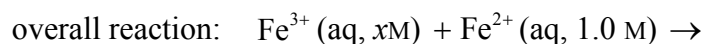
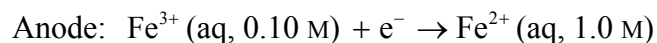
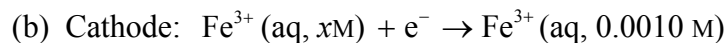


$$n = 2, E_{\text{cell}} = 0.050\text{ V}$$

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

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

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

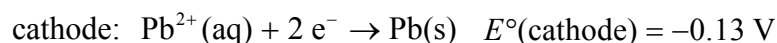
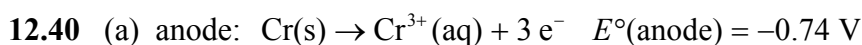


$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{RT}{nF} \ln Q$$

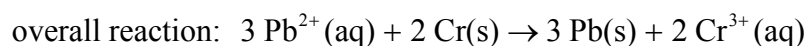
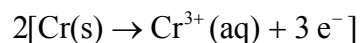
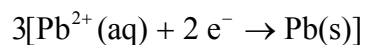
$$= -\frac{0.025\,693\text{ V}}{1} \ln \left(\frac{0.0010\text{ M} \times 0.10\text{ M}}{x\text{M} \times 1.0\text{ M}} \right) = 0.10\text{ V}$$

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

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



Multiplying half-reactions gives

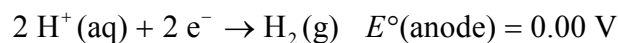
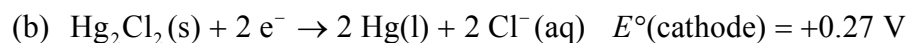


$$E^{\circ}_{\text{cell}} = +0.61\text{ V}, n = 6$$

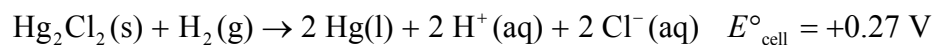
$$E = E^{\circ} - \frac{0.025\,693\text{ V}}{n} \ln \frac{[\text{Cr}^{3+}]^2}{[\text{Pb}^{2+}]^3}$$

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

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

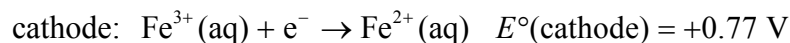
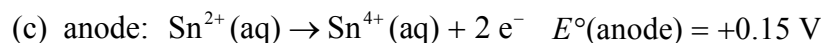


Reversing the latter half-reaction and adding, we have

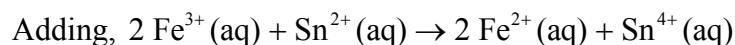
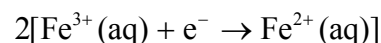


$$E = E^{\circ} - \frac{0.025\,693\text{ V}}{n} \ln \frac{[\text{H}^+]^2 [\text{Cl}^-]^2}{P_{\text{H}_2}}$$

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



Multiplying half-reactions,

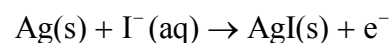
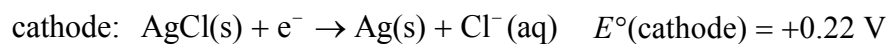


$$E^{\circ}_{\text{cell}} = +0.62\text{ V}$$

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

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

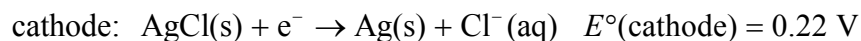
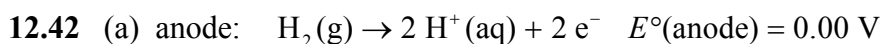
$$E = +0.62\text{ V} - 0.0129\text{ V} \ln 1 = +0.62\text{ V}$$



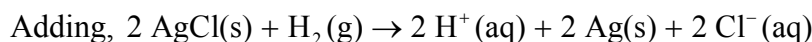
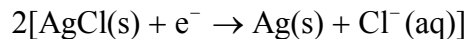
$$E = E^{\circ} - \frac{0.025\,693\text{ V}}{n} \ln \frac{[\text{Cl}^-]}{[\text{I}^-]}$$

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

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



Multiplying,



$$E^\circ_{\text{cell}} = +0.22 \text{ V}$$

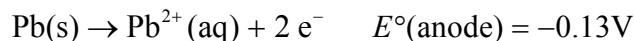
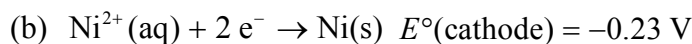
$$E = E^\circ - \frac{0.025693 \text{ V}}{n} \ln[\text{H}^+]^2[\text{Cl}^-]^2$$

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

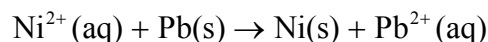
$$0.08 \text{ V} = -0.0129 \text{ V} \ln[\text{H}^+]^2$$

$$0.08 \text{ V} = -0.025693 \text{ V} \ln[\text{H}^+] = -0.059 \text{ V} \times \log[\text{H}^+]$$

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



Adding half-reactions gives



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

$$E = E^\circ - \frac{0.025693 \text{ V}}{n} \ln \frac{[\text{Pb}^{2+}]}{[\text{Ni}^{2+}]}$$

$$0.040 \text{ V} = -0.10 \text{ V} - \frac{0.025693 \text{ V}}{2} \ln \frac{[\text{Pb}^{2+}]}{0.10}$$

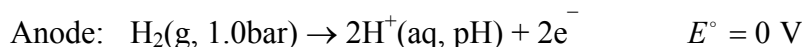
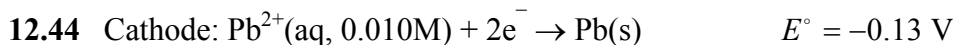
$$0.14 \text{ V} = -(0.0129 \text{ V}) \ln \frac{[\text{Pb}^{2+}]}{0.10} = -0.0129 \text{ V} (\ln[\text{Pb}^{2+}] - \ln[0.10])$$

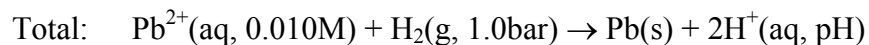
$$0.14 \text{ V} = -0.0129 \text{ V} \ln[\text{Pb}^{2+}] - 0.030 \text{ V}$$

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

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

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





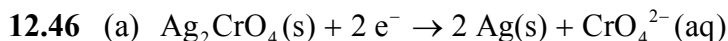
$$E^\circ = -0.13 \text{ V}$$

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

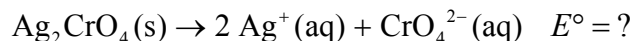
$$0.057 \text{ V} = -0.13 \text{ V} - \frac{0.05916 \text{ V}}{2} \lg \frac{[\text{H}^+]^2}{0.010}$$

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

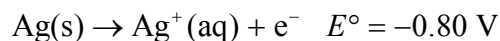
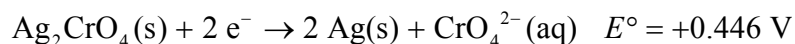
$$\text{pH} = \frac{0.187}{0.05916} - 1.000 = 2.2$$



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



The relationship $\Delta G^\circ = -RT \ln K = -nFE^\circ$ can be used to calculate the value of K_{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° value is changed in sign. Adding the first equation to twice the second gives the desired net reaction, and summing the E° values will give the E° value for that process (note that we do not multiply the second equation's E° value by 2).

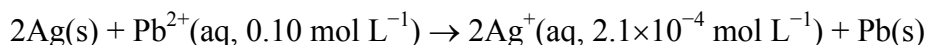
$$E^\circ = (+0.446 \text{ V}) + (-0.80 \text{ V}) = -0.35 \text{ V}$$

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

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

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

Total cell reaction is:

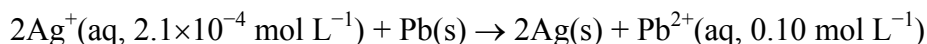


$$\begin{aligned} E &= E^\circ - \frac{0.025693 \text{ V}}{2} \ln \frac{[\text{Ag}^+]^2}{[\text{Pb}^{2+}]} \\ &= -0.93 \text{ V} - \frac{0.025693 \text{ V}}{2} \ln \frac{(2.1 \times 10^{-4})^2}{0.10} = -0.74 \text{ V} \end{aligned}$$

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

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

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



$$\Delta G_r = -nFE = -2 \times 96485 \text{ C} \cdot \text{mol}^{-1} \times 0.74 \text{ V} = -140 \text{ kJ} \cdot \text{mol}^{-1}$$

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

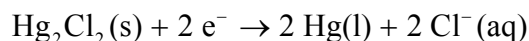
$$\Delta H_r \approx \Delta H_r^\circ$$

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

(negative)

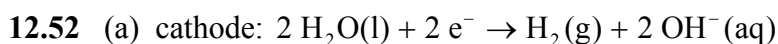
12.50 The change in concentration of Cl^- ions will affect the potential of the calomel electrode. The difference in the potential, relative to the standard potential, will be given by the Nernst equation. First, we calculate the concentration of Cl^- in a saturated KCl solution:

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

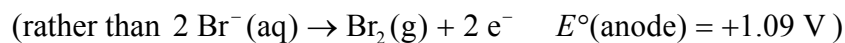
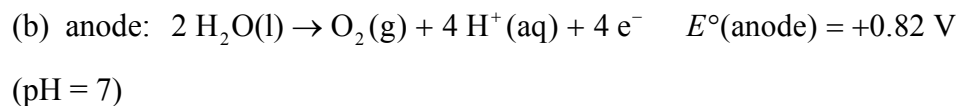
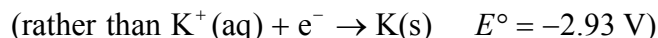


$$\begin{aligned} E &= E^\circ - \frac{RT}{nF} \ln Q \\ &= 0.27 \text{ V} - \frac{(8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298.2 \text{ K})}{2(9.65 \times 10^5 \text{ C} \cdot \text{mol}^{-1})} \ln Q \\ &= 0.27 \text{ V} - \frac{(8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298.2 \text{ K})}{2(9.65 \times 10^5 \text{ C} \cdot \text{mol}^{-1})} \ln[\text{Cl}^-]^2 \\ &= 0.27 \text{ V} - \frac{(8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298.2 \text{ K})}{2(9.65 \times 10^4 \text{ C} \cdot \text{mol}^{-1})} \ln(4.7)^2 \\ &= 0.23 \text{ V} \end{aligned}$$

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



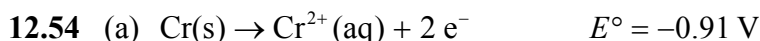
$$E^\circ(\text{cathode}) = -0.42 \text{ V} \quad (\text{pH} = 7)$$

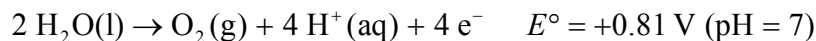


$$(c) \quad E^\circ_{\text{cell}} = E^\circ(\text{cathode}) - E^\circ(\text{anode}) = -0.42 \text{ V} - (+0.82 \text{ V})$$

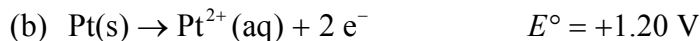
$$E^\circ_{\text{cell}} = -1.24 \text{ V}$$

Therefore, $E(\text{minimum supplied}) = +1.24 \text{ V}$

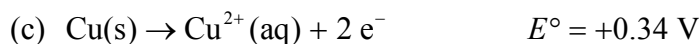




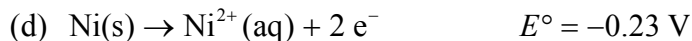
Because $E^{\circ}(\text{Cr}) < E^{\circ}(\text{H}_2\text{O})$, oxidation of the electrode will occur.



Because $E^{\circ}(\text{Pt}) > E^{\circ}(\text{H}_2\text{O})$, oxidation of water will occur.

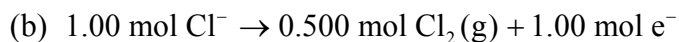
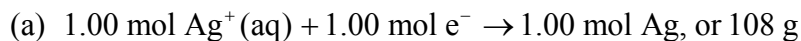


Because $E^{\circ}(\text{Cu}) < E^{\circ}(\text{H}_2\text{O})$, oxidation of the electrode will occur.

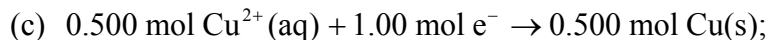


Because $E^{\circ}(\text{Ni}) < E^{\circ}(\text{H}_2\text{O})$, oxidation of the electrode will occur.

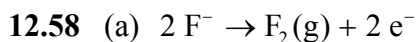
12.56 $96.5 \text{ kC} = 9.65 \times 10^4 \text{ C} \cong 1.00 \text{ F} = 1.00 \text{ mol e}^{-}$



$$0.500 \text{ mol Cl}_2 \text{ at } 298 \text{ K} = 0.500 \text{ mol} \times 24.45 \text{ L} \cdot \text{mol}^{-1} = 12.2 \text{ L}$$



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



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

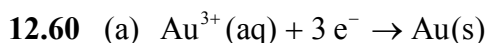
$$\left(\frac{1 \text{ mol e}^{-}}{9.6485 \times 10^4 \text{ C}} \right) = 8.5 \times 10^{-2} \text{ mol e}^{-}$$

$$\begin{aligned} \text{volume of F}_2(\text{g}) &= (8.5 \times 10^{-2} \text{ mol e}^{-}) \left(\frac{1 \text{ mol F}_2(\text{g})}{2 \text{ mol e}^{-}} \right) \left(\frac{24.45 \text{ L F}_2(\text{g})}{1 \text{ mol F}_2(\text{g})} \right) \\ &= 1.0 \text{ L F}_2(\text{g}) \end{aligned}$$

(b) as in part (a),

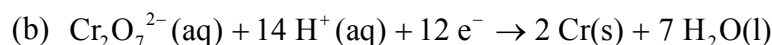
$$\text{volume of O}_2(\text{g}) = (8.5 \times 10^{-2} \text{ mol e}^-) \left(\frac{1 \text{ mol O}_2}{4 \text{ mol e}^-} \right) \left(\frac{24.45 \text{ L}}{1 \text{ mol O}_2} \right) = 0.52 \text{ L}$$

Note: We have assumed that the gases are ideal and so occupy 24.45 L · mol⁻¹ at 298 K and 1.0 atm.



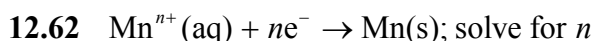
$$\text{current} = (6.66 \mu\text{g Au}) \left(\frac{10^{-6} \text{ g}}{1 \mu\text{g}} \right) \left(\frac{1 \text{ mol Au}}{196.97 \text{ g Au}} \right) \left(\frac{3 \text{ mol e}^-}{1 \text{ mol Au}} \right)$$

$$\left(\frac{9.6485 \times 10^4 \text{ C}}{1 \text{ mol e}^-} \right) \left(\frac{1 \text{ A}}{1 \text{ C} \cdot \text{s}^{-1}} \right) \left(\frac{1}{1800 \text{ s}} \right) = 5.44 \times 10^{-6} \text{ A}$$



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

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

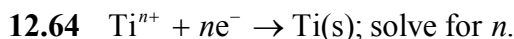
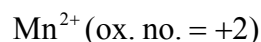


$$\text{moles of Mn} = (4.9 \text{ g Mn}) \left(\frac{1 \text{ mol Mn}}{54.94 \text{ g}} \right) = 0.089 \text{ mol Mn}$$

$$\begin{aligned} \text{total charge used} &= (13.7 \text{ h})(3600 \text{ s} \cdot \text{h}^{-1})(350 \text{ mA}) \left(\frac{10^{-3} \text{ A}}{1 \text{ mA}} \right) \left(\frac{1 \text{ C} \cdot \text{s}^{-1}}{1 \text{ A}} \right) \\ &= 1.73 \times 10^4 \text{ C} \end{aligned}$$

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

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



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

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

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

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

Therefore, the oxidation number is 4, i.e., the species is Ti^{4+} .

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

$$\begin{aligned} \text{charge used} &= (1.0 \text{ mA}) \left(\frac{10^{-3} \text{ A}}{1 \text{ mA}} \right) (31 \text{ d}) \left(\frac{24 \text{ h}}{1 \text{ d}} \right) \left(\frac{3600 \text{ s}}{1 \text{ h}} \right) \\ &= 2.7 \times 10^3 \text{ C} \end{aligned}$$

$$\text{moles of e}^{-} \text{ used} = (2.7 \times 10^3 \text{ C}) \left(\frac{1 \text{ mol e}^{-}}{96\,500 \text{ C}} \right) = 2.8 \times 10^{-2} \text{ mol e}^{-}$$

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

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

(b) Given $2 \text{H}^{+} + 2 \text{e}^{-} \rightarrow \text{H}_2(\text{g})$ (hydrogen reduction), corresponding to

$\text{Zn}^{2+} + 2 \text{e}^{-} \rightarrow \text{Zn(s)}$ (zinc reduction), then 1 mol $\text{H}_2 = 1 \text{ mol Zn}$.

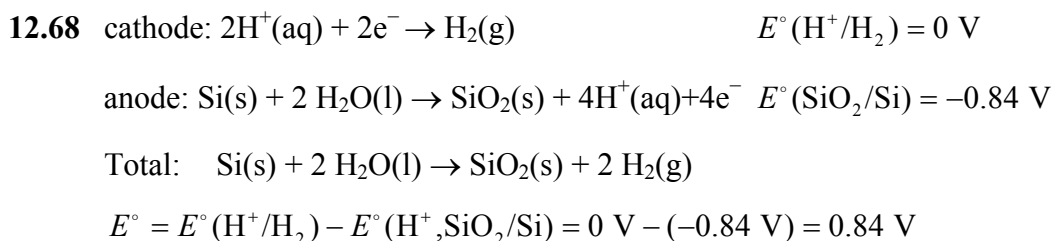
$$\text{moles of Zn} = \frac{0.92 \text{ g Zn}}{65.37 \text{ g} \cdot \text{mol}^{-1} \text{ Zn}} = 1.4 \times 10^{-2} \text{ mol Zn}$$

$1.4 \times 10^{-2} \text{ mol H}_2$ is thus formed.

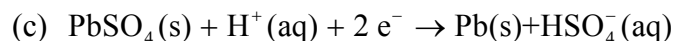
$$\begin{aligned} PV &= nRT \text{ and } V = \frac{nRT}{P} \\ &= \frac{(1.4 \times 10^{-2} \text{ mol H}_2)(0.083\,14 \text{ L} \cdot \text{bar} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298 \text{ K})}{1 \text{ bar}} \end{aligned}$$

$$V = 0.35 \text{ L}$$

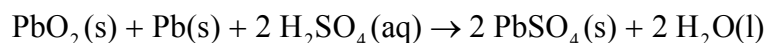
(c) Neither method is ideal for measuring the amount of current compared to today's ammeters. The Zn method has the advantage that the solid zinc is more robust and masses tend to be easier to measure than volumes. Hydrogen, as a gas, is more difficult to keep for long periods of time. It can be readily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



12.70 See Box 12.1 and Table 12.2.



12.72 The overall reaction in discharge is the sum of the anode and cathode reactions in Table 12.2.



So, as the reaction progresses, H₂SO₄ is converted to H₂O. Because the density of H₂SO₄ is greater than that of H₂O, the density of the electrolyte in the battery decreases as the battery is discharged.

- 12.74** (a) Lead-antimony grids have a larger surface area than smooth plates, so the battery can generate large currents (briefly) for starting a car; also, precipitate can adhere to grids better than to a smooth surface.
 (b) $\text{PbSO}_4(\text{s})(\text{Pb}^{2+})$; see the anode reaction in Table 12.2.
 (c) Generally, 6 separate cells are linked in series: $6 \times 2 \text{ V} = 12 \text{ V}$.

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

There are



(a) Metals that have reduction potentials in the range

−0.23 V to +0.34 V will satisfy this requirement. The metals from

Appendix 2B that are appropriate include Sn, In, Pb, Fe, and Bi.

(b) Metals that have reduction potentials in the range +0.34 to +0.80

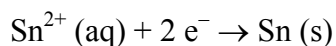
would be appropriate. The only metal in this range that is appropriate is Hg.

(c) Any metal with a reduction potential higher than 0.80 V will leave all three metal ions in solution. These include Au and Pt. Notice that Hg has a potential in this range for oxidation to Hg^{2+} ; however, the reduction potential of the $\text{Hg}_2^{2+}/\text{Hg}$ couple is lower, so that Hg can reduce Ag^+ with the formation of the Hg_2^{2+} ion.

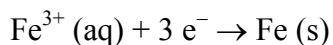
(d) It is not possible to find a metal that will reduce Ag^+ and Ni^{2+} but not Cu^{2+} , as the Cu^{2+} potential lies between those of Ag^+ and Ni^{2+} . Any metal that would not reduce Cu^{2+} would also not reduce Ni^{2+} .

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

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



$$\begin{aligned} m(\text{Sn deposited}) &= (4631 \text{ C}) \left(\frac{1 \text{ mol e}^-}{96485 \text{ C}} \right) \left(\frac{1 \text{ mol Sn}}{2 \text{ mol e}^-} \right) \left(\frac{118.7 \text{ g Sn}}{1 \text{ mol Sn}} \right) \\ &= 2.85 \text{ g Sn} \end{aligned}$$



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

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

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

12.80 (a) Water containing dissolved ions.

(b) Galvanizing steel (coating it with a film of zinc) is a form of rust protection. Zinc lies below iron in the electrochemical series, so if a scratch exposes the iron, the more strongly reducing zinc can release electrons to the iron. The zinc, not the iron, is oxidized. A sacrificial anode is one that is more easily oxidized than the metal to be preserved from oxidation. Therefore, it is preferentially oxidized, affording the desired protection.

(c) Elements below iron in the electrochemical series, for example Mg, are used as sacrificial anodes to protect the steel hulls of ships. Pb, below iron in the series, would work but would pose environmental hazards.

12.82 (a) Perhaps. Technically speaking, its potential is below the iron couple. From a practical point of view, however, owing to its passivation, it may not readily interact with its surrounding aqueous medium.

(b) Zn: yes, E° below iron couple.

Ag: no, E° above iron couple.

Cu: no, E° above iron couple.

Mg: yes, E° below iron couple.

(c) the moisture (and its dissolved ions) in the surrounding soil

12.84 The appropriate half-reactions are:



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



In order to calculate the potential of a half-reaction we need to convert the

E° values into ΔG° values:

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

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

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

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

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

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

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

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

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



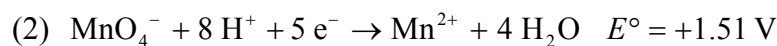
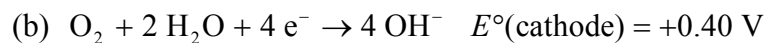
$$\begin{aligned} E^{\circ}(\text{C}) &= \frac{RT \ln K_{\text{sp}}}{nF} \\ &= \frac{(8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298.2 \text{ K}) \ln(6.5 \times 10^{-18})}{2(9.65 \times 10^4 \text{ C} \cdot \text{mol}^{-1})} \\ &= -0.51 \text{ V} \end{aligned}$$

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

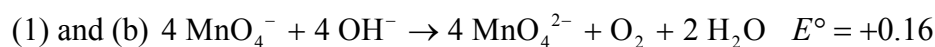
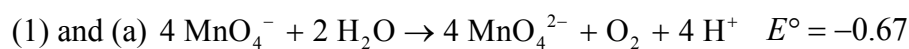
$$E^{\circ}(\text{A}) = -0.74 \text{ V}$$

- 12.88** See Appendix 2B or Table 12.1.





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

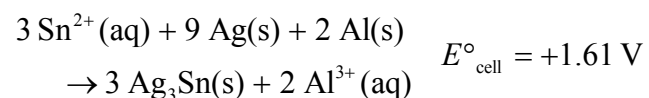
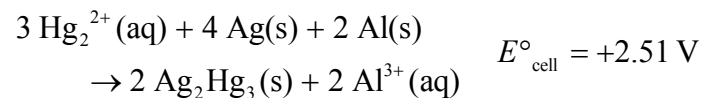


((2) and (b) give the same result as (2) and (a)).

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

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

The two possible cell reactions are



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

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



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

Need $[\text{Cu}^+]$ at equivalence point.



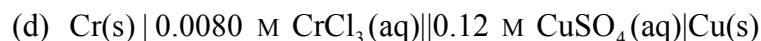
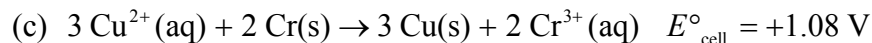
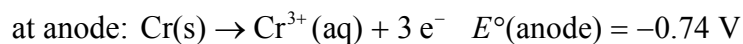
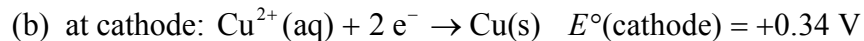
$$K_{\text{sp}} = [\text{Cu}^+][\text{Br}^-] = s^2 = 5.2 \times 10^{-9}$$

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

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

$E = +0.276 \text{ V}$ is the potential at the equivalence point.

12.94 (a) The chrome-plated piece of metal is the anode. It is immersed in 200 mL of 0.0080 M $\text{CrCl}_3(\text{aq})$ in one of the 250-mL beakers. The copper wire is the cathode in 200 mL of 0.12 M $\text{CuSO}_4(\text{aq})$ in the other beaker. These two electrodes are connected to each other through the voltmeter by clips and wires. Each end of the salt bridge is submerged in one of the two solutions in the beakers to complete the circuit.

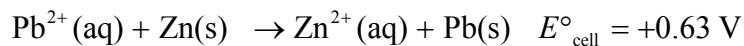
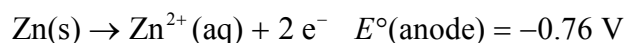
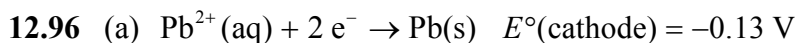


(e) $E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.025693 \text{ V}}{n} \ln \frac{[\text{Cr}^{3+}]^2}{[\text{Cu}^{2+}]^3}$

$$E_{\text{cell}} = 1.08 \text{ V} - \frac{0.025693 \text{ V}}{6} \ln \frac{(0.0080)^2}{(0.12)^3}$$

$$E_{\text{cell}} = 1.08 \text{ V} - 0.00428 \ln 0.037$$

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



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

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

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

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

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

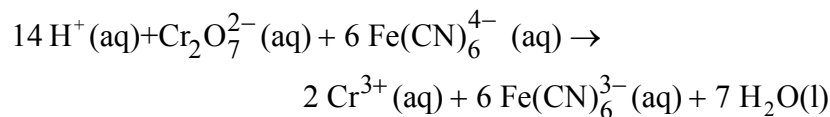
$$E_{\text{cell}} = 0.63 \text{ V} - \left(\frac{0.0257 \text{ V}}{2} \right) \ln \frac{[\text{Zn}^{2+}]}{(0.10)}$$

$$E_{\text{cell}} = 0.63 \text{ V} - (0.0128 \text{ V})[\ln [\text{Zn}^{2+}] - \ln (0.10)]$$

$$E_{\text{cell}} = 0.63 \text{ V} - (0.0128 \text{ V})[\ln [\text{Zn}^{2+}] + 2.30]$$

$$E_{\text{cell}} = 0.60 \text{ V} - 0.0128 \ln [\text{Zn}^{2+}]$$

12.98 Cell reaction:



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

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

We can use the Nernst Equation to get E° .

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

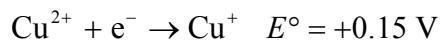
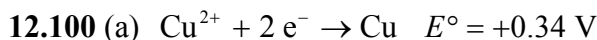
$$1.18 = E^{\circ} - \frac{0.025693 \text{ V}}{6} \ln \frac{(0.01)^2 (1 \times 10^{-4})^6}{(0.1)(1.0)^6}$$

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

$$E^{\circ} = 0.91 \text{ V} = \frac{0.025693 \text{ V}}{6} \ln K$$

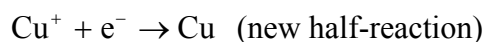
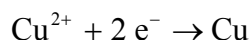
$$\ln K = 2.125 \times 10^2$$

$$K = 2.0 \times 10^{92}$$



Here, we do not combine the half-reactions to obtain an overall cell reaction; instead, we combine them to obtain a new half-reaction.

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



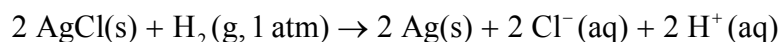
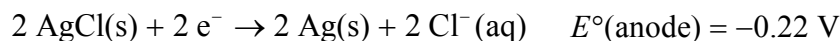
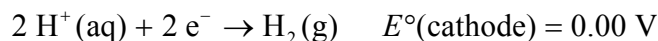
$$\begin{aligned} \text{Cu}^{2+}/\text{Cu}^{+} \quad \Delta G^{\circ}_{\text{r}} &= -nFE^{\circ} = -(2)(9.65 \times 10^4 \text{ C} \cdot \text{mol}^{-1})(+0.34 \text{ J} \cdot \text{C}^{-1}) \\ &= -66 \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$

$$\begin{aligned} \text{Cu}^{+}/\text{Cu} \quad \Delta G^{\circ}_{\text{r}} &= -nFE^{\circ} = -(1)(9.65 \times 10^4 \text{ C} \cdot \text{mol}^{-1})(-0.15 \text{ J} \cdot \text{C}^{-1}) \\ &= +15 \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$

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

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

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



$$E^\circ_{\text{cell}} = 0.22 \text{ V}$$

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

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

$$\ln [\text{H}^+] = 2.303 \log [\text{H}^+] = -2.303(\text{pH}),$$

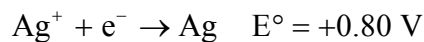
so $E = 0.22 \text{ V} + 0.0592 \text{ V} \times \text{pH}$, and

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

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

(b) $\text{pOH} = 14.00 - \text{pH}$

12.104 (a) The variation of potential for



with Ag^+ concentration is derived from the Nernst equation:

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

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

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

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

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

From the K_{sp} values, we can determine $[Ag^+]$ at 1 M X^- for each:

$[Ag^+] = K_{sp}$ (because $K_{sp} = [Ag^+][X^-]$). If we use these values in the relationship $E = +0.80 \text{ V} + 0.059 16 \log[Ag^+]$, we calculate the following potentials:

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

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

12.106 The potential for electrolyzing a metal cation will change as the concentration of the metal decreases during an electrolysis reaction. This will require increasing the potential across the cell. We do not need to know the actual beginning concentration in order to calculate this answer. The Nernst equation will allow us to calculate the potential difference between E_1 and E_2 :

$$E_1 = E^\circ - \frac{0.059 16}{1} \log \frac{1}{[M^+(1)]}$$

$$E_2 = E^\circ - \frac{0.059 16}{1} \log \frac{1}{[M^+(2)]}$$

Subtracting the first equation from the second gives

$$E_2 - E_1 = -\frac{0.05916}{1} \left\{ \log \frac{1}{[M^+(2)]} - \log \frac{1}{[M^+(1)]} \right\}$$

$$E_2 - E_1 = -\frac{0.05916}{1} \log \frac{[M^+(1)]}{[M^+(2)]}$$

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

$$E_2 - E_1 = -\frac{0.05916}{1} \log \frac{[M^+(1)]}{0.0001 \times [M^+(1)]} = -0.24 \text{ V}$$

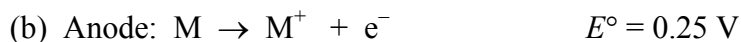
The potential will need to be increased by about 0.24 V in order to plate out 99.99% of the metal.

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

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

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

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



$$\mathbf{12.110} \quad P_{Cl_2} = P_{total} - P_{H_2O}$$

$$= 770. \text{ Torr} - 17.54 \text{ Torr} = 752 \text{ Torr} \left(\frac{1 \text{ atm}}{760 \text{ Torr}} \right)$$

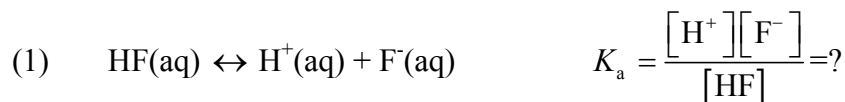
$$= 0.990 \text{ atm}$$

$$n_{Cl_2} = \frac{P_{Cl_2} V}{RT} = \frac{(0.990 \text{ atm})(20.0 \text{ L})}{(0.08206 \text{ atm} \cdot \text{L} \cdot \text{K}^{-1} \text{mol}^{-1})(293.15 \text{ K})} = 0.823 \text{ mol}$$

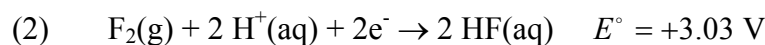
$$Q = (0.823 \text{ mol } Cl_2) \left(\frac{2 \text{ mol } e^-}{1 \text{ mol } Cl_2} \right) \left(\frac{96485 \text{ C}}{\text{mol } e^-} \right) = 1.59 \times 10^5 \text{ C}$$

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

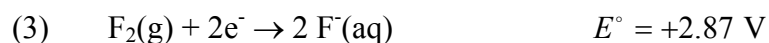
12.112 The reaction of interest is



We have



and from Appendix 2B,



Since combining reactions $(1/2)(3) - (1/2)(2) = (1)$,

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

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

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

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