Chapter 17

Chemistry and Electricity

To identify reducing agent and oxidizing agent... to construct and balance a complicated redox equation...to navigate a table of standard electrode potentials... to calculate a cell voltage and equilibrium constant...to keep straight, if nothing else, the gain-and-loss terminology of oxidation and reduction—modest but useful goals, facilitated now by a grasp of basic thermodynamic and quantum mechanical principles. Complementing the conceptual emphasis of the white pages and the tutorial approach of the gray pages, the exercises here offer considerable practice in implementing the fundamental equations of electrochemistry:

1. *The relationship between free energy and electrochemical work:* $\Delta G = -n\mathcal{F}\mathcal{E}$

2. *The standard potential of an electrochemical cell:* $\mathcal{E}^\circ = \mathcal{E}^\circ_{red} + \mathcal{E}^\circ_{ox}$

3. *The Nernst equation:* $\mathcal{E} = \mathcal{E}^\circ - \dfrac{RT}{n\mathcal{F}}\ln Q$

4. *The relationship between standard cell potential and the equilibrium constant:*

$$K = \exp\left(-\frac{\Delta G^\circ}{RT}\right) = \exp\left(\frac{n\mathcal{F}\mathcal{E}^\circ}{RT}\right)$$
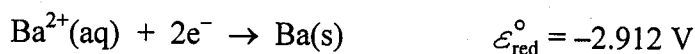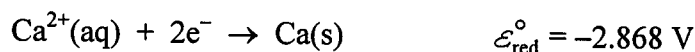
Table C-21 in Appendix C of PoC *(pages A100–A101), containing a selection of standard reduction potentials, will be of constant use throughout. See also Section 3-3, pages R3.2–R3.4, and Examples 3-1 through 3-5 for an earlier (pre-thermodynamic) treatment of oxidation–reduction processes.*

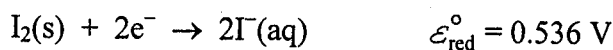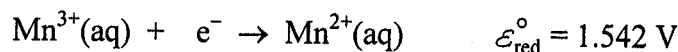*The set begins with a review of the basic mechanics of redox and redox equations.*

1. An oxidizing agent itself undergoes *reduction*. It gains electrons. Of two species, the stronger oxidizing agent has the more positive standard reduction potential. It is better able to induce some other entity to lose electrons and thus undergo oxidation.

See Sections 3-3, 17-3, and 17-7 in *PoC*, as well as Example 17-3 (beginning on page R17.9). Standard reduction potentials are collected in Table C-21 of Appendix C (pages A100–A101).

(a) $Ca^{2+}(aq)$, with a standard reduction potential of -2.868 V, is a stronger oxidizing agent than $Ba^{2+}(aq)$, for which $\varepsilon^{\circ}_{red}$ is equal to -2.912 V (a more negative and hence less positive value). The calcium ion, Ca^{2+}, is more likely than Ba^{2+} to be reduced to its native metal:

$$Ca^{2+}(aq) + 2e^- \rightarrow Ca(s) \qquad \varepsilon^{\circ}_{red} = -2.868 \text{ V}$$
$$Ba^{2+}(aq) + 2e^- \rightarrow Ba(s) \qquad \varepsilon^{\circ}_{red} = -2.912 \text{ V}$$

(b) Gaining *one* electron, $Mn^{3+}(aq)$ is a stronger oxidizing agent than $I_2(s)$:

$$Mn^{3+}(aq) + e^- \rightarrow Mn^{2+}(aq) \qquad \varepsilon^{\circ}_{red} = 1.542 \text{ V}$$
$$I_2(s) + 2e^- \rightarrow 2I^-(aq) \qquad \varepsilon^{\circ}_{red} = 0.536 \text{ V}$$

QUESTION: Suppose that Mn^{3+} is reduced all the way to Mn. Does the reduction potential for

$$Mn^{3+}(aq) + 3e^- \rightarrow Mn(s)$$
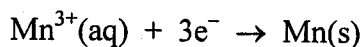
rank higher or lower compared with that for the conversion of $I_2(s)$ into $I^-(aq)$?

ANSWER: Write reaction (3) as the sum of reactions (1) and (2) below:

$$Mn^{3+}(aq) + e^- \rightarrow Mn^{2+}(aq) \qquad \varepsilon^{\circ}_{red}(1) = 1.542 \text{ V}$$
$$\underline{Mn^{2+}(aq) + 2e^- \rightarrow Mn(s) \qquad \varepsilon^{\circ}_{red}(2) = -1.185 \text{ V}}$$
$$Mn^{3+}(aq) + 3e^- \rightarrow Mn(s) \qquad \varepsilon^{\circ}_{red}(3) = \text{ ?}$$
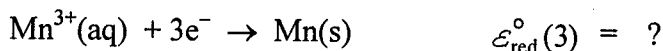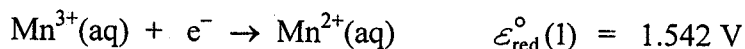
Now determine the net potential for reaction (3)

$$\varepsilon^{\circ}_{red}(3) = -\frac{\Delta G^{\circ}(3)}{n_3 \mathscr{F}}$$

by combining the free energies of reactions (1) and (2):

$$\varepsilon_{red}^{\circ}(3) = -\frac{\Delta G^{\circ}(1) + \Delta G^{\circ}(2)}{n_3 \mathscr{F}} = -\frac{\left[-n_1 \mathscr{F} \varepsilon_{red}^{\circ}(1)\right] + \left[-n_2 \mathscr{F} \varepsilon_{red}^{\circ}(2)\right]}{n_3 \mathscr{F}}$$
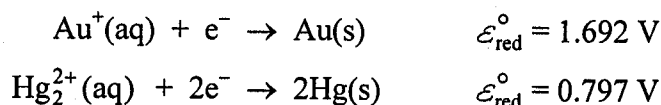
$$= \frac{n_1 \varepsilon_{red}^{\circ}(1) + n_2 \varepsilon_{red}^{\circ}(2)}{n_3} = \frac{1 \times 1.542 \text{ V} + 2 \times (-1.185 \text{ V})}{3}$$

$$= -0.276 \text{ V}$$

The reduction of $I_2(s)$ to $I^-(aq)$, with $\varepsilon_{red}^{\circ} = 0.536$ V, thus is thermodynamically favored over the reduction of $Mn^{3+}(aq)$ to $Mn(s)$—but not over the reduction of $Mn^{3+}(aq)$ to $Mn^{2+}(aq)$.

(c) Au^+ is a stronger oxidizing agent than Hg_2^{2+} :

$$Au^+(aq) + e^- \rightarrow Au(s) \qquad \varepsilon_{red}^{\circ} = 1.692 \text{ V}$$
$$Hg_2^{2+}(aq) + 2e^- \rightarrow 2Hg(s) \qquad \varepsilon_{red}^{\circ} = 0.797 \text{ V}$$

(d) Metallic copper undergoes oxidation to Cu^+, Cu^{2+}, or Cu^{3+}, not reduction to an anionic form. The iron(II) ion, with $\varepsilon_{red}^{\circ} = -0.447$ V, is the stronger oxidizing agent:

$$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s) \qquad \varepsilon_{red}^{\circ} = -0.447 \text{ V}$$
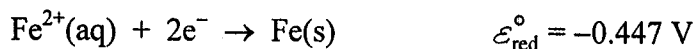
(e) $Al^{3+}(aq)$, which has a less negative (more positive) $\varepsilon_{red}^{\circ}$ than Li^+, is the stronger oxidizing agent of the two:

$$Al^{3+}(aq) + 3e^- \rightarrow Al(s) \qquad \varepsilon_{red}^{\circ} = -1.662 \text{ V}$$
$$Li^+(aq) + e^- \rightarrow Li(s) \qquad \varepsilon_{red}^{\circ} = -3.05 \text{ V}$$
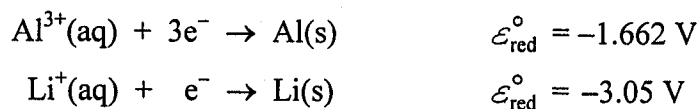
2. A reducing agent itself undergoes *oxidation*. It *loses* electrons. It causes some other entity to gain electrons and thus undergo reduction. Of two species, the stronger reducing agent has the more positive standard *oxidation* potential—hence the more negative standard reduction potential:

$$\varepsilon_{ox}^{\circ} = -\varepsilon_{red}^{\circ} \qquad \text{(for any half-cell reaction)}$$

See Sections 3-3, 17-3, and 17-7 in *PoC*, as well as Example 17-3 (beginning on page R17.9). Standard reduction potentials are provided in Table C-21 of Appendix C (pages A100–A101).

(a) Look up, first, the standard reduction potentials

$$Ca^{2+}(aq) + 2e^- \rightarrow Ca(s) \qquad \mathcal{E}^\circ_{red} = -2.868 \text{ V}$$

$$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s) \qquad \mathcal{E}^\circ_{red} = -0.762 \text{ V}$$
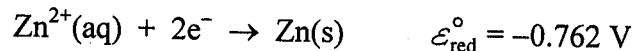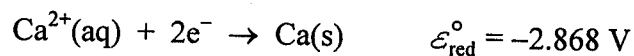
and turn them around to get the corresponding oxidation potentials:

$$Ca(s) \rightarrow Ca^{2+}(aq) + 2e^- \qquad \mathcal{E}^\circ_{ox} = -\mathcal{E}^\circ_{red} = -\left(-2.868 \text{ V}\right) = 2.868 \text{ V}$$

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^- \qquad \mathcal{E}^\circ_{ox} = -\mathcal{E}^\circ_{red} = -\left(-0.762 \text{ V}\right) = 0.762 \text{ V}$$

The voltage in one direction is opposite in sign to the voltage in the other direction.
        Now observe: Metallic calcium ($\mathcal{E}^\circ_{ox} = -\mathcal{E}^\circ_{red} = 2.868$ V) is a stronger reducing
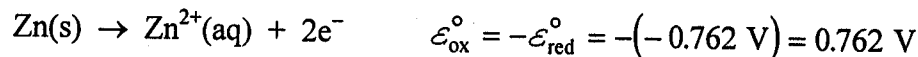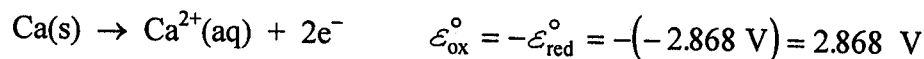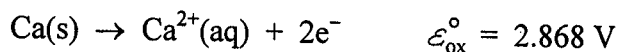agent than metallic zinc ($\mathcal{E}^\circ_{ox} = -\mathcal{E}^\circ_{red} = 0.762$ V). The reaction

$$Ca(s) \rightarrow Ca^{2+}(aq) + 2e^- \qquad \mathcal{E}^\circ_{ox} = 2.868 \text{ V}$$

is thermodynamically favored over the reaction

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^- \qquad \mathcal{E}^\circ_{ox} = 0.762 \text{ V}$$
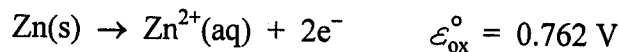
The standard change in free energy ($\Delta G^\circ_{ox} = -n\mathscr{F}\mathcal{E}^\circ_{ox}$) is lower—more negative—for the oxidation of calcium.

(b) $I^-(aq)$ is a stronger reducing agent than $F^-(aq)$:

$$2I^-(aq) \rightarrow I_2(s) + 2e^- \qquad \mathcal{E}^\circ_{ox} = -0.536 \text{ V}$$

$$2F^-(aq) \rightarrow F_2(g) + 2e^- \qquad \mathcal{E}^\circ_{ox} = -2.866 \text{ V}$$
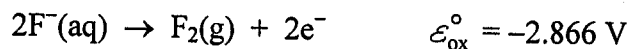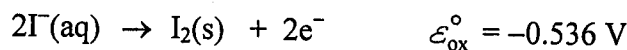
(c) Li(s), the stronger reducing agent, undergoes oxidation more readily than Na(s):

$$Li(s) \rightarrow Li^+(aq) + e^- \qquad \mathcal{E}^\circ_{ox} = 3.05 \text{ V}$$

$$Na(s) \rightarrow Na^+(aq) + e^- \qquad \mathcal{E}^\circ_{ox} = 2.71 \text{ V}$$
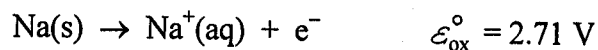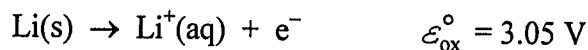
(d) $Zn^{2+}(aq)$ undergoes reduction, not oxidation. Metallic nickel, oxidized to Ni^{2+}, is the stronger reducing agent:

$$Ni(s) \rightarrow Ni^{2+}(aq) + 2e^- \qquad \mathcal{E}^\circ_{ox} = 0.257 \text{ V}$$
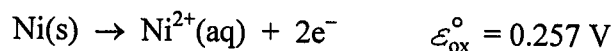
(e) Ag(s), oxidized to Ag^+(aq), is a stronger reducing agent than Mn^{2+}(aq):

$$Ag(s) \rightarrow Ag^+(aq) \ + \ e^- \qquad \mathcal{E}_{ox}^\circ = -0.800 \text{ V}$$

$$Mn^{2+}(aq) \rightarrow Mn^{3+}(aq) + e^- \qquad \mathcal{E}_{ox}^\circ = -1.542 \text{ V}$$
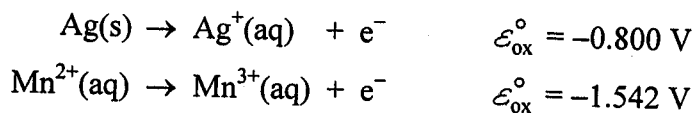
Redox equations of varying complexity are balanced in Exercises 3 through 7. See Section 3-3 and Examples 3-1 through 3-3 in PoC *for additional material on oxidation number and formal charge.*

3. Balance the atoms separately in each half-reaction and then balance the charge, taking the following steps: (1) Add electrons, as needed, to the appropriate sides of the reduction and oxidation equations. (2) If necessary, multiply the separate half-reactions by numerical factors to make the number of electrons lost equal to the number of electrons gained.

For additional practice with simple redox equations, see Example 3-4 and also Exercises 13 through 17 in Chapter 3. For more complicated equations, see Section 17-8, Examples 17-1 and 17-2, and Exercises 4 through 7 in the present chapter.

Remember throughout: The reducing agent is the species that undergoes *oxidation*. The oxidizing agent, partner in the transaction, undergoes *reduction*.

(a) Two iodide ions, I^-, are oxidized to one molecule of I_2, losing two electrons in the process. Iron is reduced from Fe^{3+} to Fe^{2+}, gaining one electron. Multiply the reduction half-reaction by 2 to conserve charge:

$$2I^- \rightarrow I_2 + 2e^- \qquad \text{(oxidation)}$$

$$\underline{2[e^- + Fe^{3+} \rightarrow Fe^{2+}] \qquad \text{(reduction)}}$$

$$2I^-(aq) + 2Fe^{3+}(aq) \rightarrow I_2(s) + 2Fe^{2+}(aq)$$
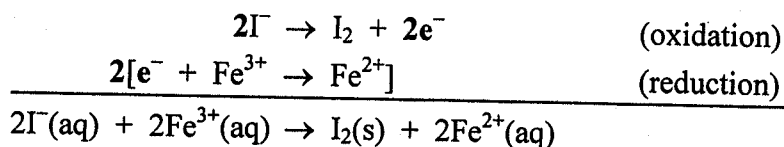
Oxidizing agent (the species that is *reduced*): Fe^{3+}(aq)
Reducing agent (the species that is *oxidized*): I^-(aq)
Moles of electrons transferred: $n = 2$

(b) Chromium is oxidized from Cr^{2+} to Cr^{3+} while thallium is simultaneously reduced from Tl^{3+} to Tl^+. Multiply the oxidation half-reaction by 2 to conserve charge:

$$2[Cr^{2+} \rightarrow Cr^{3+} + e^-] \qquad \text{(oxidation)}$$

$$\underline{2e^- + Tl^{3+} \rightarrow Tl^+ \qquad \text{(reduction)}}$$

$$2Cr^{2+}(aq) + Tl^{3+}(aq) \rightarrow 2Cr^{3+}(aq) + Tl^+(aq)$$
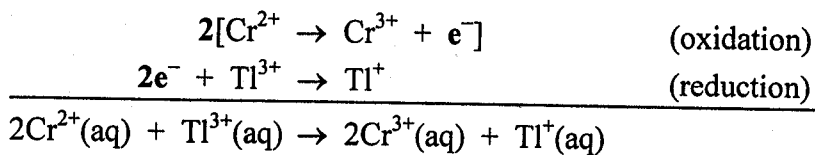
Oxidizing agent: Tl^{3+}(aq)
Reducing agent: Cr^{2+}(aq)
Moles of electrons transferred: $n = 2$

(c) Indium, losing two electrons, is oxidized from In^+ to In^{3+}. A molecule of bromine, Br_2, gains the two electrons and is reduced to two bromide ions:

$$In^+ \rightarrow In^{3+} + 2e^- \qquad \text{(oxidation)}$$

$$\underline{2e^- + Br_2 \rightarrow 2Br^-} \qquad \text{(reduction)}$$

$$In^+(aq) + Br_2(\ell) \rightarrow In^{3+}(aq) + 2Br^-(aq)$$
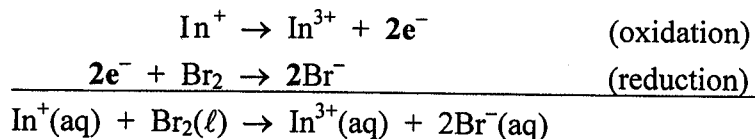
Oxidizing agent: $Br_2(\ell)$
Reducing agent: $In^+(aq)$
Moles of electrons transferred: $n = 2$

4. See pages 633–636 and Example 17-1 in *PoC* for demonstrations of how to balance redox equations in acidic solution. Additional commentary is provided in Exercise 5 below.

(a) Carbon is oxidized from an oxidation state of $+3$ in the oxalate anion to an oxidation state of $+4$ in carbon dioxide. Manganese is reduced from an oxidation state of $+7$ in the permanganate anion to an oxidation state of $+2$ in the Mn^{2+} cation.
  First, balance the oxidation half-reaction:

$$C_2O_4^{2-} \rightarrow CO_2 \qquad \text{(unbalanced)}$$

$$C_2O_4^{2-} \rightarrow 2CO_2 \qquad \text{(C and O are balanced)}$$

$$C_2O_4^{2-} \rightarrow 2CO_2 + 2e^- \qquad \text{(charge is balanced)}$$

Second, balance the reduction half-reaction:

$$MnO_4^- \rightarrow Mn^{2+} \qquad \text{(Mn is balanced)}$$

$$MnO_4^- \rightarrow Mn^{2+} + 4H_2O \qquad \text{(O is balanced)}$$

$$8H^+ + MnO_4^- \rightarrow Mn^{2+} + 4H_2O \qquad \text{(H is balanced)}$$

$$5e^- + 8H^+ + MnO_4^- \rightarrow Mn^{2+} + 4H_2O \qquad \text{(charge is balanced)}$$
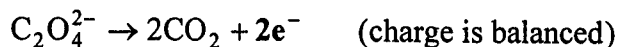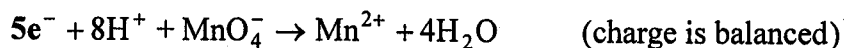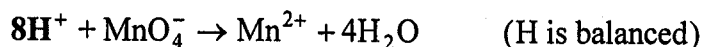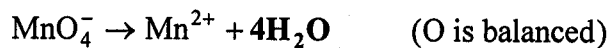
Third, combine the half-reactions and conserve charge:

$$5[C_2O_4^{2-} \rightarrow 2CO_2 + 2e^-] \qquad \text{(oxidation)}$$

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

$$5C_2O_4^{2-}(aq) + 2MnO_4^-(aq) + 16H^+(aq) \rightarrow 10CO_2(g) + 2Mn^{2+}(aq) + 8H_2O(\ell)$$
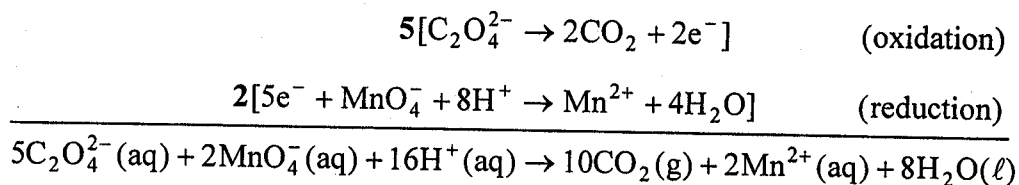
Oxidizing agent: $MnO_4^-(aq)$

Reducing agent: $C_2O_4^{2-}(aq)$

Moles of electrons transferred: $n = 10$

(b) Copper is oxidized from its metallic form to the copper(II) ion, losing two electrons per atom of Cu:

$$Cu \rightarrow Cu^{2+} \qquad \text{(Cu is balanced)}$$

$$Cu \rightarrow Cu^{2+} + \mathbf{2e^-} \qquad \text{(charge is balanced)}$$

The nitrate anion, NO_3^-, is reduced to nitric oxide, NO. Three electrons are gained as nitrogen goes from an oxidation state of +5 to an oxidation state of +2:

$$NO_3^- \rightarrow NO \qquad \text{(N is balanced)}$$

$$NO_3^- \rightarrow NO + \mathbf{2H_2O} \qquad \text{(O is balanced)}$$

$$\mathbf{4H^+} + NO_3^- \rightarrow NO + 2H_2O \qquad \text{(H is balanced)}$$

$$\mathbf{3e^-} + 4H^+ + NO_3^- \rightarrow NO + 2H_2O \qquad \text{(charge is balanced)}$$
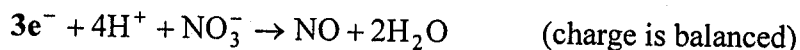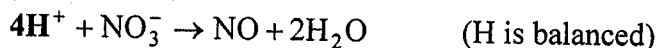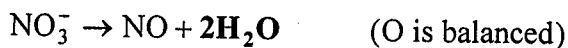
We multiply the oxidation half-reaction by 3 and the reduction half-reaction by 2, thereby coupling giver and taker. Six electrons are transferred in the concerted redox reaction:

$$3[Cu \rightarrow Cu^{2+} + 2e^-] \qquad \text{(oxidation)}$$

$$2[3e^- + NO_3^- + 4H^+ \rightarrow NO + 2H_2O] \qquad \text{(reduction)}$$

$$3Cu(s) + 2NO_3^-(aq) + 8H^+(aq) \rightarrow 3Cu^{2+}(aq) + 2NO(g) + 4H_2O(\ell)$$
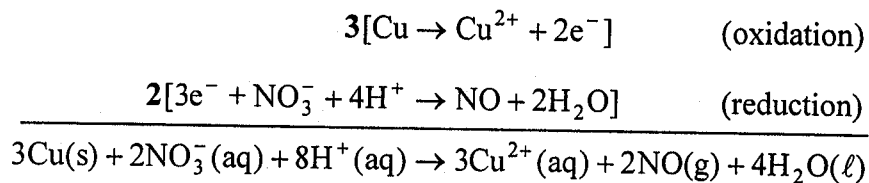
Oxidizing agent: $NO_3^-(aq)$
Reducing agent: $Cu(s)$
Moles of electrons transferred: $n = 6$

(c) Three electrons are lost during the oxidation:

$$Bi \rightarrow BiO^+ \qquad \text{(Bi is balanced)}$$

$$\mathbf{H_2O} + Bi \rightarrow BiO^+ \qquad \text{(O is balanced)}$$

$$H_2O + Bi \rightarrow BiO^+ + \mathbf{2H^+} \qquad \text{(H is balanced)}$$

$$H_2O + Bi \rightarrow BiO^+ + 2H^+ + \mathbf{3e^-} \qquad \text{(charge is balanced)}$$

One electron is gained during the reduction:

$$Ce^{4+} \rightarrow Ce^{3+} \qquad \text{(Ce is balanced)}$$

$$\mathbf{e^-} + Ce^{4+} \rightarrow Ce^{3+} \qquad \text{(charge is balanced)}$$
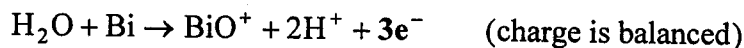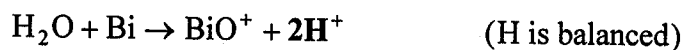
To conserve charge, we multiply the reduction half-reaction by 3:

$$Bi + H_2O \rightarrow BiO^+ + 2H^+ + 3e^- \qquad \text{(oxidation)}$$

$$\underline{\mathbf{3}[e^- + Ce^{4+} \rightarrow Ce^{3+}] \qquad \text{(reduction)}}$$

$$Bi(s) + 3Ce^{4+}(aq) + H_2O(\ell) \rightarrow BiO^+(aq) + 3Ce^{3+}(aq) + 2H^+(aq)$$
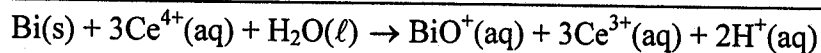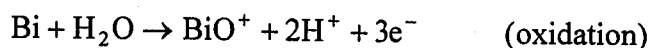
Oxidizing agent: $Ce^{4+}(aq)$
Reducing agent: $Bi(s)$
Moles of electrons transferred: $n = 3$

(d) Losing two electrons, a molecule of carbon monoxide is oxidized to a molecule of carbon dioxide. Carbon goes from C^{2+} in CO to C^{4+} in CO_2:

$$CO \rightarrow CO_2 \qquad \text{(C is balanced)}$$

$$\mathbf{H_2O} + CO \rightarrow CO_2 \qquad \text{(O is balanced)}$$

$$H_2O + CO \rightarrow CO_2 + \mathbf{2H^+} \qquad \text{(H is balanced)}$$

$$H_2O + CO \rightarrow CO_2 + 2H^+ + \mathbf{2e^-} \qquad \text{(charge is balanced)}$$

Gaining four electrons, a molecule of oxygen is reduced to two molecules of water. Oxygen goes from O^0 in O_2 to O^{2-} in H_2O:

$$O_2 \rightarrow 2H_2O \qquad \text{(O is balanced)}$$

$$4H^+ + O_2 \rightarrow 2H_2O \qquad \text{(H is balanced)}$$

$$4e^- + 4H^+ + O_2 \rightarrow 2H_2O \qquad \text{(charge is balanced)}$$
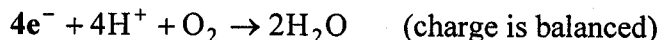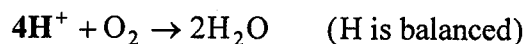
Multiplication of the oxidation equation by 2 ensures the conservation of charge. Note that neither H^+ nor H_2O appears in the net reaction:

$$\mathbf{2}[CO + H_2O \rightarrow CO_2 + 2H^+ + 2e^-] \qquad \text{(oxidation)}$$

$$\underline{4e^- + O_2 + 4H^+ \rightarrow 2H_2O} \qquad \text{(reduction)}$$

$$2CO(g) + O_2(g) \rightarrow 2CO_2(g)$$
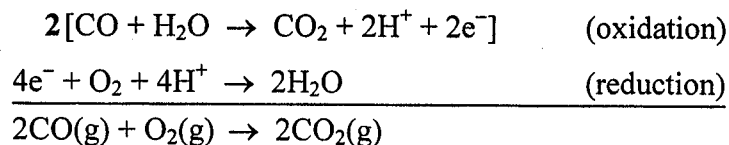
Oxidizing agent: $O_2(g)$
Reducing agent: $CO(g)$
Moles of electrons transferred: $n = 4$

5. Redox equations in acidic solution are balanced using the systematic procedure outlined in Section 17-8 and Example 17-1 of *PoC*:

1. Identify reductant and oxidant by observing which elements undergo a change in oxidation state.

2. Write the half-reactions in raw form.

3. Balance the atoms in each half-reaction, leaving O and H for last. Then:

    i. Balance the oxygen atoms, introducing H_2O molecules where needed.

    ii. Balance the hydrogen atoms, introducing H^+ ions where needed.

4. Balance the charge by adding electrons to the appropriate side, again separately for the half-reactions.

5. Combine the half-reactions into one complete equation, multiplying each half-reaction as needed to conserve charge overall.

(a) First, identify and balance the oxidation half-reaction. Iodine goes from an oxidation state of 0 in molecular iodine to an oxidation state of $+5$ in IO_3^-, losing 10 electrons for every molecule of I_2:

$$I_2 \rightarrow IO_3^-$$ (unbalanced)

$$I_2 \rightarrow 2IO_3^-$$ (I is balanced)

$$6H_2O + I_2 \rightarrow 2IO_3^-$$ (O is balanced)

$$6H_2O + I_2 \rightarrow 2IO_3^- + 12H^+$$ (H is balanced)

$$6H_2O + I_2 \rightarrow 2IO_3^- + 12H^+ + 10e^-$$ (charge is balanced)
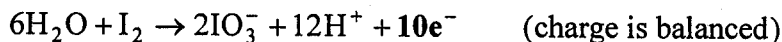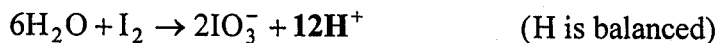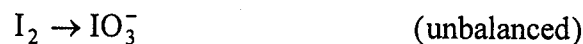
Second, identify and balance the reduction half-reaction (which results in the Cu^{2+} ion gaining two electrons):

$$Cu^{2+} \rightarrow Cu$$ (Cu is balanced)

$$2e^- + Cu^{2+} \rightarrow Cu$$ (charge is balanced)

Third, combine the two half-reactions—multiplying one or the other as needed to balance the total charge. Here, with 10 electrons passing from reducing agent to oxidizing agent, the reduction equation requires a factor of 5:

$$I_2 + 6H_2O \rightarrow 2IO_3^- + 12H^+ + 10e^-$$ (oxidation)

$$5[2e^- + Cu^{2+} \rightarrow Cu]$$ (reduction)

$$I_2(s) + 5Cu^{2+}(aq) + 6H_2O(\ell) \rightarrow 2IO_3^-(aq) + 5Cu(s) + 12H^+(aq)$$
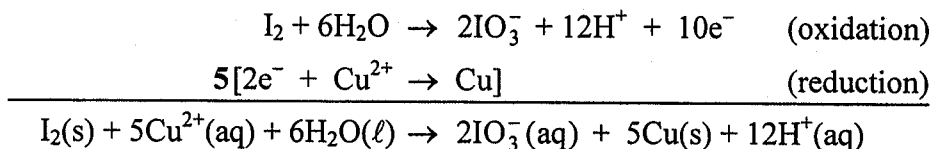
Oxidizing agent: $Cu^{2+}(aq)$
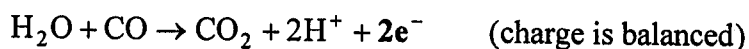Reducing agent: $I_2(s)$
Moles of electrons transferred: $n = 10$

(b) Nickel is oxidized from its metallic form (oxidation number = 0) to the nickel(II) ion. Two electrons are lost:

$$Ni \rightarrow Ni^{2+}$$ (Ni is balanced)

$$Ni \rightarrow Ni^{2+} + 2e^-$$ (charge is balanced)

One electron is gained during the reduction of the pervanadyl ion, VO_2^+, to the vanadyl ion, VO^{2+}. The oxidation number of vanadium decreases from +5 to +4:

$$VO_2^+ \rightarrow VO^{2+}$$ (V is balanced)

$$VO_2^+ \rightarrow VO^{2+} + H_2O$$ (O is balanced)

$$2H^+ + VO_2^+ \rightarrow VO^{2+} + H_2O$$ (H is balanced)

$$e^- + 2H^+ + VO_2^+ \rightarrow VO^{2+} + H_2O$$ (charge is balanced)
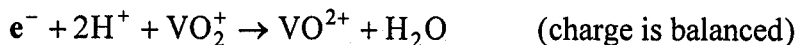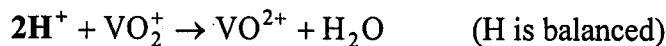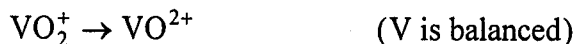
Multiplying the reduction half-equation by 2, we link giver to taker. Two electrons are transferred overall:

$$Ni \rightarrow Ni^{2+} + 2e^- \qquad \text{(oxidation)}$$

$$2[e^- + VO_2^+ + 2H^+ \rightarrow VO^{2+} + H_2O] \qquad \text{(reduction)}$$

$$Ni(s) + 2VO_2^+(aq) + 4H^+(aq) \rightarrow Ni^{2+}(aq) + 2VO^{2+}(aq) + 2H_2O(\ell)$$
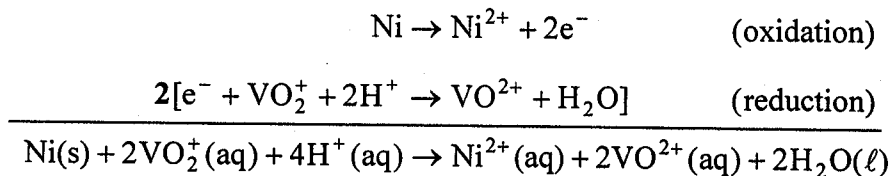
Oxidizing agent: $VO_2^+(aq)$
Reducing agent: $Ni(s)$
Moles of electrons transferred: $n = 2$

(c) Hydrogen sulfide, losing two electrons, is oxidized to elemental sulfur. The oxidation number of sulfur increases from -2 to 0:

$$H_2S \rightarrow S \qquad \text{(S is balanced)}$$

$$H_2S \rightarrow S + 2H^+ \qquad \text{(H is balanced)}$$

$$H_2S \rightarrow S + 2H^+ + 2e^- \qquad \text{(charge is balanced)}$$
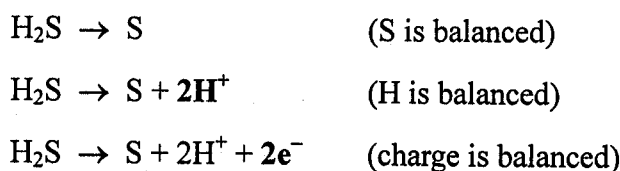
The nitrate anion, gaining three electrons, is reduced to nitric oxide. Nitrogen goes from an oxidation number of $+5$ in NO_3^- to an oxidation number of $+2$ in NO:

$$NO_3^- \rightarrow NO \qquad \text{(N is balanced)}$$

$$NO_3^- \rightarrow NO + 2H_2O \qquad \text{(O is balanced)}$$

$$4H^+ + NO_3^- \rightarrow NO + 2H_2O \qquad \text{(H is balanced)}$$

$$3e^- + 4H^+ + NO_3^- \rightarrow NO + 2H_2O \qquad \text{(charge is balanced)}$$
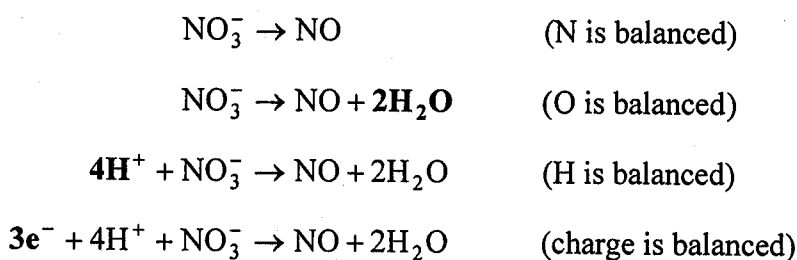
Conservation of charge requires a 3:2 stoichiometric ratio between the oxidation and reduction half-reactions:

$$3[H_2S \rightarrow S + 2H^+ + 2e^-] \qquad \text{(oxidation)}$$

$$2[3e^- + NO_3^- + 4H^+ \rightarrow NO + 2H_2O] \qquad \text{(reduction)}$$

$$3H_2S(aq) + 2NO_3^-(aq) + 2H^+(aq) \rightarrow 3S(s) + 2NO(g) + 4H_2O(\ell)$$
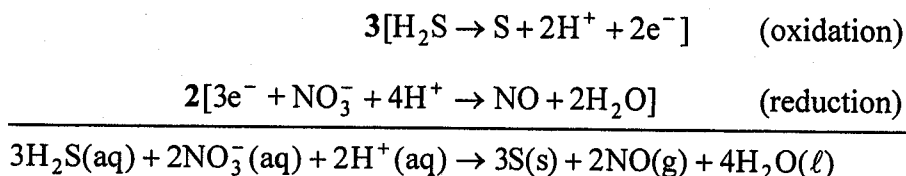
Oxidizing agent: $NO_3^-(aq)$
Reducing agent: $H_2S(aq)$
Moles of electrons transferred: $n = 6$

(d) Two moles of *solid* sodium bromide, NaBr, lose two moles of electrons during the oxidation to one mole of Br_2. Bromine goes from Br^- in NaBr to Br^0 in Br_2:

$$NaBr \rightarrow Br_2 \qquad \text{(unbalanced)}$$

$$2NaBr \rightarrow Br_2 \qquad \text{(Br is balanced)}$$

$$2NaBr \rightarrow Br_2 + 2Na^+ \qquad \text{(Na is balanced)}$$

$$2NaBr \rightarrow Br_2 + 2Na^+ + 2e^- \qquad \text{(charge is balanced)}$$
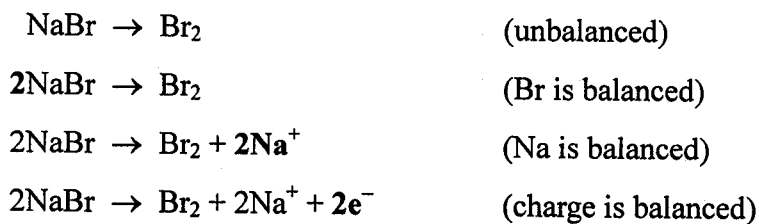
The molecular sulfate ion gains two electrons during its reduction to sulfur dioxide. Sulfur is transformed from an oxidation state of +6 in SO_4^{2-} to an oxidation state of +4 in SO_2:

$$SO_4^{2-} \rightarrow SO_2 \qquad \text{(S is balanced)}$$

$$SO_4^{2-} \rightarrow SO_2 + 2H_2O \qquad \text{(O is balanced)}$$

$$4H^+ + SO_4^{2-} \rightarrow SO_2 + 2H_2O \qquad \text{(H is balanced)}$$

$$2e^- + 4H^+ + SO_4^{2-} \rightarrow SO_2 + 2H_2O \qquad \text{(charge is balanced)}$$
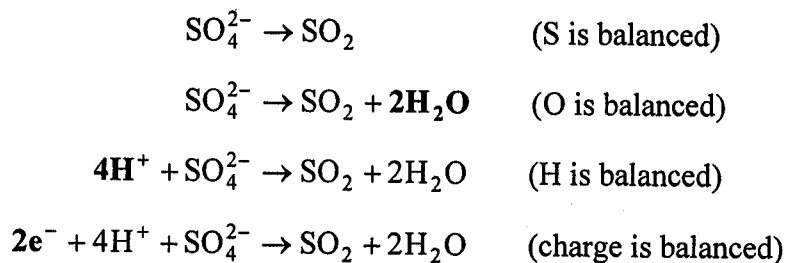
Two electrons are lost, and two electrons are gained:

$$2NaBr \rightarrow Br_2 + 2Na^+ + 2e^- \qquad \text{(oxidation)}$$

$$2e^- + SO_4^{2-} + 4H^+ \rightarrow SO_2 + 2H_2O \qquad \text{(reduction)}$$

$$\overline{2NaBr(s) + SO_4^{2-}(aq) + 4H^+(aq) \rightarrow Br_2(\ell) + SO_2(g) + 2Na^+(aq) + 2H_2O(\ell)}$$
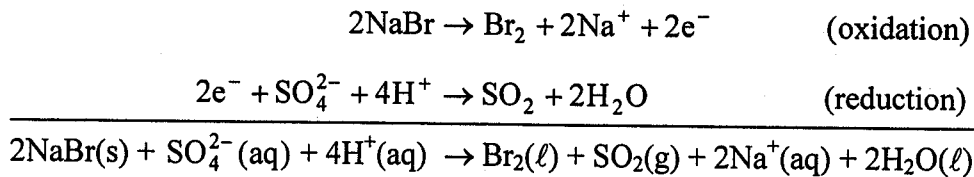
Oxidizing agent: $SO_4^{2-}(aq)$
Reducing agent: NaBr(s)
Moles of electrons transferred: $n = 2$

6. See Section 17-8 and Example 17-2 in *PoC* for demonstrations of how to balance redox equations in basic media. Additional commentary is provided in the solution to Exercise 7.

(a) The bromide ion, Br^-, is oxidized to the bromate ion, BrO_3^-. Six electrons are lost as bromine goes from an oxidation state of −1 in Br^- to an oxidation state of +5 in BrO_3^-:

$$Br^- \rightarrow BrO_3^- \qquad \text{(Br is balanced)}$$

$$\mathbf{3H_2O} + Br^- \rightarrow BrO_3^- \qquad \text{(O is balanced)}$$

$$3H_2O + Br^- \rightarrow BrO_3^- + \mathbf{6H^+} \qquad \text{(H is balanced using } H^+\text{)}$$

$$\mathbf{6OH^-} + 3H_2O + Br^- \rightarrow BrO_3^- + 6H^+ + \mathbf{6OH^-} \qquad \text{(}H^+ \text{ is neutralized by } OH^-\text{)}$$

$$6OH^- + Br^- \rightarrow BrO_3^- + \mathbf{3H_2O} \qquad \text{(}H_2O \text{ is consolidated)}$$

$$6OH^- + Br^- \rightarrow BrO_3^- + 3H_2O + \mathbf{6e^-} \qquad \text{(charge is balanced)}$$
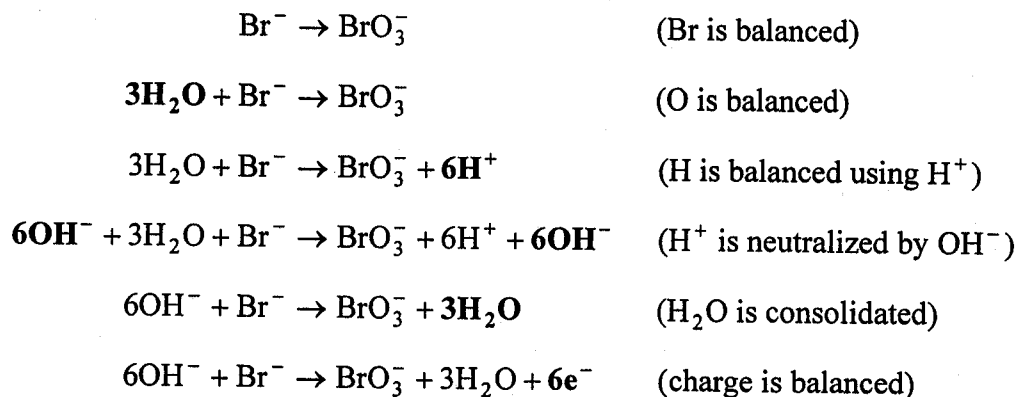
Na^+ is a spectator ion and can be eliminated for simplicity. In the reduction half-reaction that results, the hypochlorite ion (ClO^-) gains two electrons as it becomes the chloride ion, Cl^-. The oxidation number of chlorine decreases from +1 to −1:

$$ClO^- \rightarrow Cl^- \qquad \text{(Cl is balanced)}$$

$$ClO^- \rightarrow Cl^- + \mathbf{H_2O} \qquad \text{(O is balanced)}$$

$$\mathbf{2H^+} + ClO^- \rightarrow Cl^- + H_2O \qquad \text{(H is balanced using } H^+\text{)}$$

$$\mathbf{2OH^-} + 2H^+ + ClO^- \rightarrow Cl^- + H_2O + \mathbf{2OH^-} \qquad \text{(}H^+ \text{ is neutralized by } OH^-\text{)}$$

$$\mathbf{H_2O} + ClO^- \rightarrow Cl^- + 2OH^- \qquad \text{(}H_2O \text{ is consolidated)}$$

$$\mathbf{2e^-} + H_2O + ClO^- \rightarrow Cl^- + 2OH^- \qquad \text{(charge is balanced)}$$
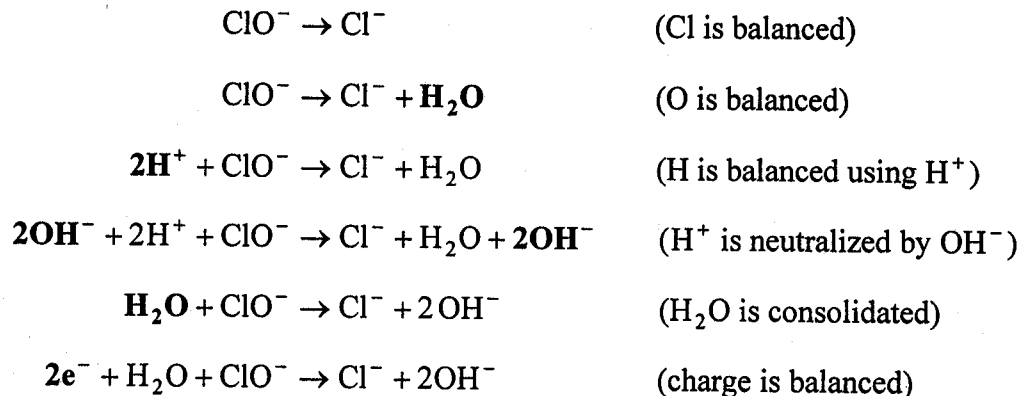
Multiplying the reduction half-reaction by 3, we ensure that the number of electrons lost is equal to the number of electrons gained. In all, six electrons are transferred from giver to receiver:

$$Br^- + 6OH^- \rightarrow BrO_3^- + 3H_2O + 6e^- \qquad \text{(oxidation)}$$

$$\underline{3[2e^- + ClO^- + H_2O \rightarrow Cl^- + 2OH^-]} \qquad \text{(reduction)}$$

$$Br^-(aq) + 3ClO^-(aq) \rightarrow BrO_3^-(aq) + 3Cl^-(aq)$$
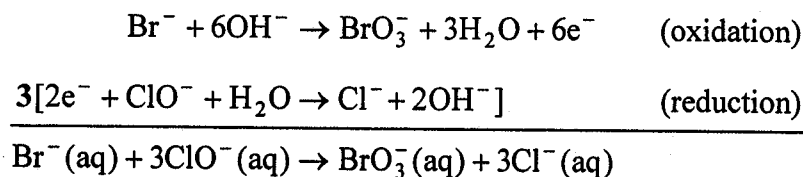
Oxidizing agent: $ClO^-(aq)$
Reducing agent: $Br^-(aq)$
Moles of electrons transferred: $n = 6$

Notice that neither OH^- nor H_2O appears explicitly in the net reaction. An alternative equation, including the Na^+ spectator ions, is written as follows:

$$Na^+(aq) + Br^-(aq) + 3Na^+(aq) + 3ClO^-(aq) \rightarrow$$

$$Na^+(aq) + BrO_3^-(aq) + 3Na^+(aq) + 3Cl^-(aq)$$

$$NaBr(aq) + 3NaClO(aq) \rightarrow NaBrO_3(aq) + 3NaCl(aq)$$
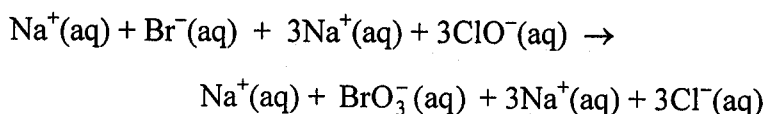
(b) Hydrogen peroxide, H_2O_2, is oxidized to molecular oxygen with a loss of two electrons. The oxidation number of each oxygen atom increases from −1 to 0:

$H_2O_2 \rightarrow O_2$	(O is balanced)
$H_2O_2 \rightarrow O_2 + 2H^+$	(H is balanced using H^+)
$2OH^- + H_2O_2 \rightarrow O_2 + 2H^+ + 2OH^-$	(H^+ is neutralized by OH^-)
$2OH^- + H_2O_2 \rightarrow O_2 + 2H_2O$	(H_2O is consolidated)
$2OH^- + H_2O_2 \rightarrow O_2 + 2H_2O + 2e^-$	(charge is balanced)
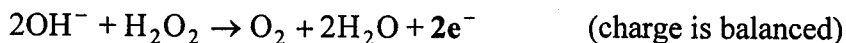
In the reduction half-reaction, aqueous ClO_2 (a neutral molecule in solution, not an ion) is transformed into solid $Ba(ClO_2)_2$ (an ionic compound). The oxidation number of chlorine decreases from +4 in ClO_2 to +3 in ClO_2^-. A total gain of two electrons is reflected in the balanced half-reaction, one electron for each of the two ClO_2 molecules reduced:

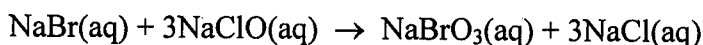|	
$ClO_2 \rightarrow Ba(ClO_2)_2$	(unbalanced)
$2ClO_2 \rightarrow Ba(ClO_2)_2$	(Cl and O are balanced)
$Ba^{2+} + 2ClO_2 \rightarrow Ba(ClO_2)_2$	(Ba is balanced)
$2e^- + Ba^{2+} + 2ClO_2 \rightarrow Ba(ClO_2)_2$	(charge is balanced)
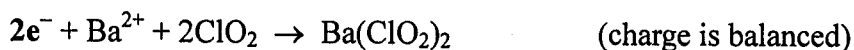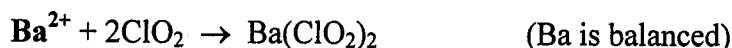
Two electrons thus flow from reducing agent to oxidizing agent:

$$H_2O_2 + 2OH^- \rightarrow O_2 + 2H_2O + 2e^- \quad \text{(oxidation)}$$
$$\underline{2e^- + 2ClO_2 + Ba^{2+} \rightarrow Ba(ClO_2)_2 \quad \text{(reduction)}}$$
$$H_2O_2(aq) + 2ClO_2(aq) + Ba^{2+}(aq) + 2OH^-(aq) \rightarrow O_2(g) + Ba(ClO_2)_2(s) + 2H_2O(\ell)$$
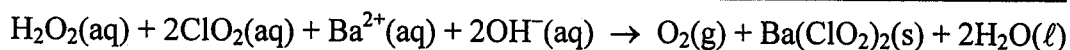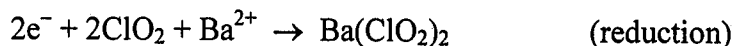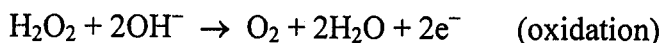
Oxidizing agent: $ClO_2(aq)$
Reducing agent: $H_2O_2(aq)$
Moles of electrons transferred: $n = 2$

Barium is neither oxidized nor reduced. It remains in the +2 oxidation state on both sides of the equation—as the free ion Ba^{2+} and in the ionic compound $Ba(ClO_2)_2$.

(c) Iron is oxidized from Fe^0 in its elemental state to Fe^{2+} in $Fe(OH)_2$:

$$Fe \rightarrow Fe(OH)_2 \qquad \text{(Fe is balanced)}$$

$$\mathbf{2OH^-} + Fe \rightarrow Fe(OH)_2 \qquad \text{(O and H are balanced)}$$

$$2OH^- + Fe \rightarrow Fe(OH)_2 + \mathbf{2e^-} \qquad \text{(charge is balanced)}$$
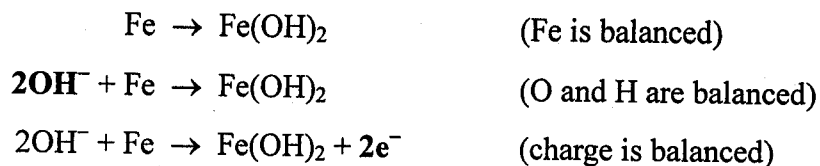
Nickel is reduced from Ni^{4+} in NiO_2 to Ni^{2+} in $Ni(OH)_2$:

$$NiO_2 \rightarrow Ni(OH)_2 \qquad \text{(Ni and O are balanced)}$$

$$\mathbf{2H^+} + NiO_2 \rightarrow Ni(OH)_2 \qquad \text{(H is balanced using } H^+\text{)}$$

$$\mathbf{2OH^-} + 2H^+ + NiO_2 \rightarrow Ni(OH)_2 + \mathbf{2OH^-} \qquad \text{(H is neutralized by } OH^-\text{)}$$

$$\mathbf{2H_2O} + NiO_2 \rightarrow Ni(OH)_2 + 2OH^- \qquad \text{(H}_2\text{O is consolidated)}$$

$$\mathbf{2e^-} + 2H_2O + NiO_2 \rightarrow Ni(OH)_2 + 2OH^- \qquad \text{(charge is balanced)}$$
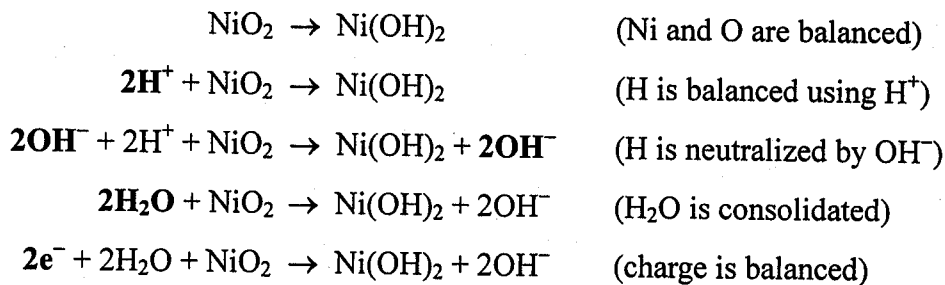
Adding the half-reactions without change, we have the combined redox process:

$$Fe + 2OH^- \rightarrow Fe(OH)_2 + 2e^- \qquad \text{(oxidation)}$$

$$\underline{2e^- + NiO_2 + 2H_2O \rightarrow Ni(OH)_2 + 2OH^- \qquad \text{(reduction)}}$$

$$Fe(s) + NiO_2(s) + 2H_2O(\ell) \rightarrow Fe(OH)_2(s) + Ni(OH)_2(s)$$
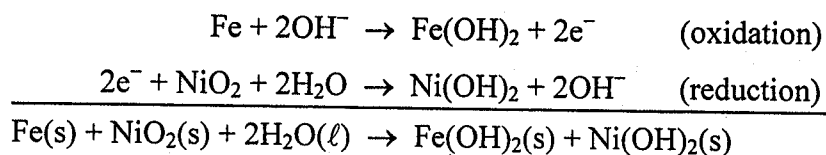
Oxidizing agent: $NiO_2(s)$
Reducing agent: $Fe(s)$
Moles of electrons transferred: $n = 2$

(d) Metallic silver is oxidized to the silver ion, with the loss of one electron:
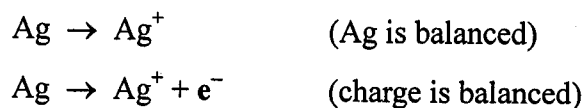
$$Ag \rightarrow Ag^+ \qquad \text{(Ag is balanced)}$$

$$Ag \rightarrow Ag^+ + e^- \qquad \text{(charge is balanced)}$$

One O_2 molecule is reduced to four OH^- ions, gaining four electrons in the process:

$$O_2 \rightarrow \mathbf{2H_2O} \qquad \text{(O is balanced)}$$

$$\mathbf{4H^+} + O_2 \rightarrow 2H_2O \qquad \text{(H is balanced using } H^+\text{)}$$

$$\mathbf{4OH^-} + 4H^+ + O_2 \rightarrow 2H_2O + \mathbf{4OH^-} \qquad \text{(}H^+ \text{ is neutralized by } OH^-\text{)}$$

$$\mathbf{2H_2O} + O_2 \rightarrow 4OH^- \qquad \text{(H}_2\text{O is consolidated)}$$

$$\mathbf{4e^-} + 2H_2O + O_2 \rightarrow 4OH^- \qquad \text{(charge is balanced)}$$

The oxidation half-reaction must be multiplied by 4 to yield a charge-balanced redox equation:
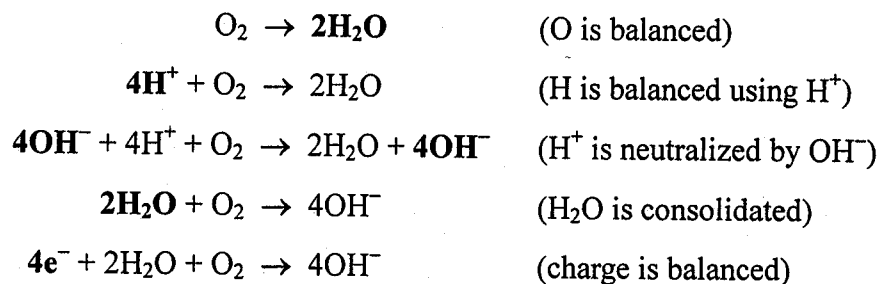
$$4[Ag \rightarrow Ag^+ + e^-] \quad \text{(oxidation)}$$
$$\underline{4e^- + O_2 + 2H_2O \rightarrow 4OH^-} \quad \text{(reduction)}$$
$$4Ag(s) + O_2(g) + 2H_2O(\ell) \rightarrow 4Ag^+(aq) + 4OH^-(aq)$$
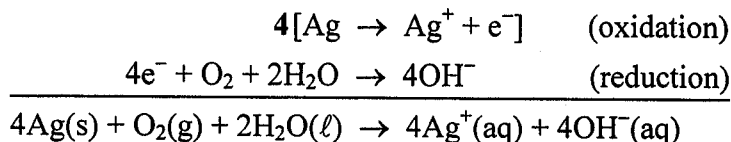
Oxidizing agent: $O_2(g)$
Reducing agent: $Ag(s)$
Moles of electrons transferred: $n = 4$

7. Redox equations in basic solution are balanced using the systematic method outlined in Example 17-2 and Section 17-8 of *PoC* (especially pages 636–637). The general procedure, which sometimes can be simplified, is as follows:

1. Identify reductant and oxidant by observing which elements undergo a change in oxidation state.

2. Write the half-reactions in raw form.

3. Balance the atoms in each half-reaction, leaving O and H for last. Then:

   i. Balance the oxygen atoms, introducing H_2O molecules where needed.

   ii. Balance the hydrogen atoms, introducing H^+ ions where needed.

   iii. Eliminate any dummy H^+ ions by adding the appropriate number of OH^- ions to each side of the equation. Replace every pair of H^+ and OH^- ions by one molecule of H_2O.

4. Balance the charge by adding electrons to the appropriate side, again separately for the half-reactions.

5. Combine the half-reactions into one complete equation, multiplying each half-reaction as needed to conserve charge overall.

(a) First, identify and balance the oxidation half-reaction. Zinc loses two electrons as it goes from Zn^0 in its elemental state to Zn^{2+} in $Zn(OH)_2$:

$$Zn \rightarrow Zn(OH)_2 \qquad \text{(Zn is balanced)}$$
$$2OH^- + Zn \rightarrow Zn(OH)_2 \qquad \text{(O and H are balanced)}$$
$$2OH^- + Zn \rightarrow Zn(OH)_2 + 2e^- \qquad \text{(charge is balanced)}$$
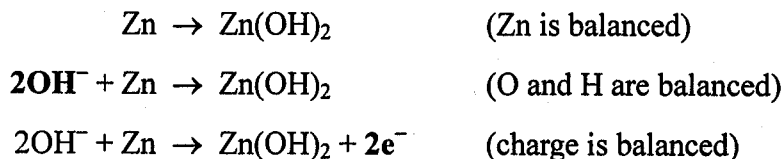
Second, identify and balance the reduction half-reaction. The oxidation number of

manganese drops from $+4$ in MnO_2 to $+3$ in Mn_2O_3. Two moles of electrons are gained for every mole of Mn_2O_3 produced:

$$MnO_2 \rightarrow Mn_2O_3 \qquad \text{(unbalanced)}$$

$$2MnO_2 \rightarrow Mn_2O_3 \qquad \text{(Mn is balanced)}$$

$$2MnO_2 \rightarrow Mn_2O_3 + \mathbf{H_2O} \qquad \text{(O is balanced)}$$

$$\mathbf{2H^+} + 2MnO_2 \rightarrow Mn_2O_3 + H_2O \qquad \text{(H is balanced using } H^+)$$

$$\mathbf{2OH^-} + 2H^+ + 2MnO_2 \rightarrow Mn_2O_3 + H_2O + \mathbf{2OH^-} \qquad \text{(}H^+ \text{ is neutralized by } OH^-)$$

$$\mathbf{H_2O} + 2MnO_2 \rightarrow Mn_2O_3 + 2OH^- \qquad \text{(}H_2O \text{ is consolidated)}$$

$$\mathbf{2e^-} + H_2O + 2MnO_2 \rightarrow Mn_2O_3 + 2OH^- \qquad \text{(charge is balanced)}$$

Third, combine the two half-reactions:
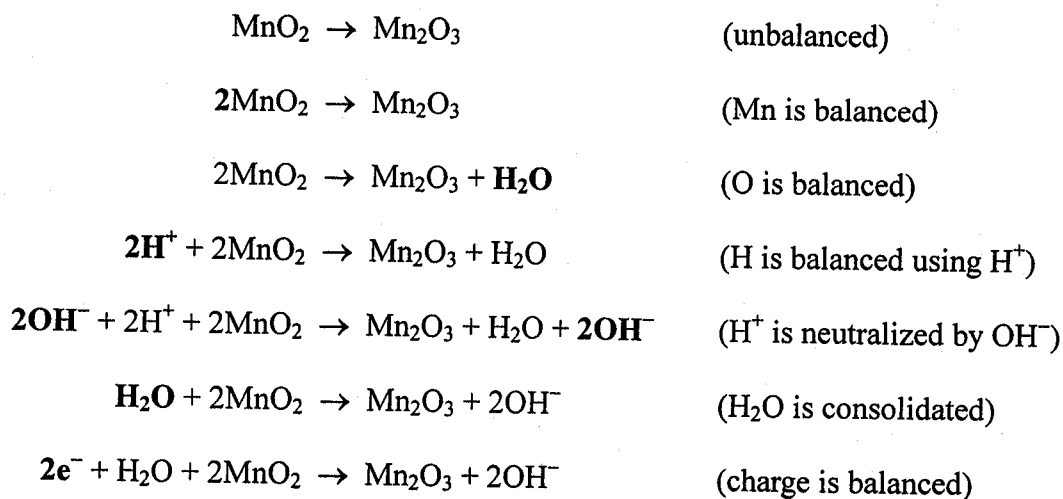
$$Zn + 2OH^- \rightarrow Zn(OH)_2 + 2e^- \qquad \text{(oxidation)}$$
$$\underline{2e^- + 2MnO_2 + H_2O \rightarrow Mn_2O_3 + 2OH^- \qquad \text{(reduction)}}$$
$$Zn(s) + 2MnO_2(s) + H_2O(\ell) \rightarrow Zn(OH)_2(s) + Mn_2O_3(s)$$
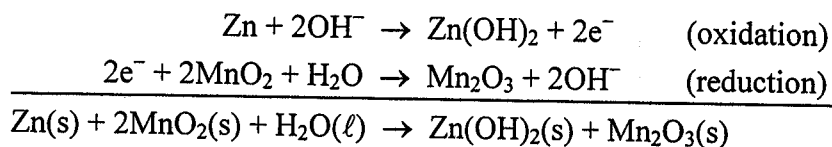
Oxidizing agent: $MnO_2(s)$
Reducing agent: $Zn(s)$
Moles of electrons transferred: $n = 2$

(b) Phosphorus is oxidized from P^{3-} in PH_3 to P^0 in elemental P_4:

$$PH_3 \rightarrow P_4 \qquad \text{(unbalanced)}$$

$$4PH_3 \rightarrow P_4 \qquad \text{(P is balanced)}$$

$$4PH_3 \rightarrow P_4 + \mathbf{12H^+} \qquad \text{(H is balanced using } H^+)$$

$$\mathbf{12OH^-} + 4PH_3 \rightarrow P_4 + 12H^+ + \mathbf{12OH^-} \qquad \text{(}H^+ \text{ is neutralized by } OH^-)$$

$$12OH^- + 4PH_3 \rightarrow P_4 + \mathbf{12H_2O} \qquad \text{(}H_2O \text{ is consolidated)}$$

$$12OH^- + 4PH_3 \rightarrow P_4 + 12H_2O + \mathbf{12e^-} \qquad \text{(charge is balanced)}$$
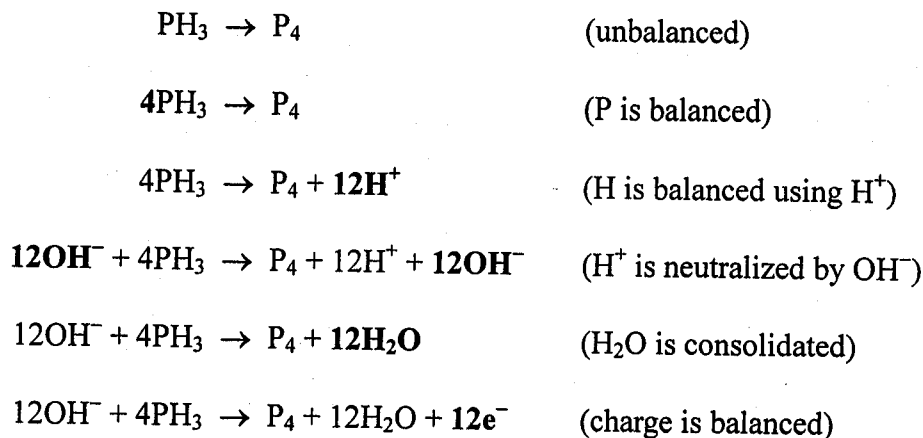
Chromium is reduced from Cr^{6+} in CrO_4^{2-} to Cr^{3+} in $Cr(OH)_4^-$:

$$CrO_4^{2-} \rightarrow Cr(OH)_4^-$$ (Cr and O are balanced)

$$4H^+ + CrO_4^{2-} \rightarrow Cr(OH)_4^-$$ (H is balanced using H^+)

$$4OH^- + 4H^+ + CrO_4^{2-} \rightarrow Cr(OH)_4^- + 4OH^-$$ (H^+ is neutralized by OH^-)

$$4H_2O + CrO_4^{2-} \rightarrow Cr(OH)_4^- + 4OH^-$$ (H_2O is consolidated)

$$3e^- + 4H_2O + CrO_4^{2-} \rightarrow Cr(OH)_4^- + 4OH^-$$ (charge is balanced)
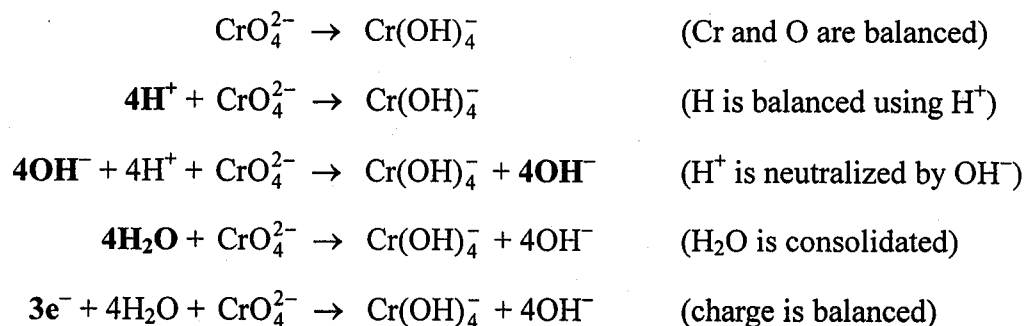
Twelve electrons are lost during oxidation, whereas three electrons are gained during the reduction process as written. To conserve charge, we must multiply the reduction half-reaction by a factor of 4:

$$4PH_3 + 12OH^- \rightarrow P_4 + 12H_2O + 12e^-$$ (oxidation)

$$4[3e^- + CrO_4^{2-} + 4H_2O \rightarrow Cr(OH)_4^- + 4OH^-]$$ (reduction)

$$4PH_3(g) + 4CrO_4^{2-}(aq) + 4H_2O(\ell) \rightarrow P_4(s) + 4Cr(OH)_4^-(aq) + 4OH^-(aq)$$
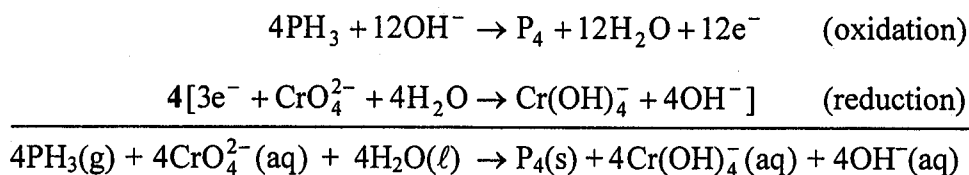
Oxidizing agent: $CrO_4^{2-}(aq)$
Reducing agent: $PH_3(g)$
Moles of electrons transferred: $n = 12$

(c) Gold is oxidized from its elemental state (oxidation number = 0) to Au^+ in the complex $Au(CN)_2^-$, losing one electron:
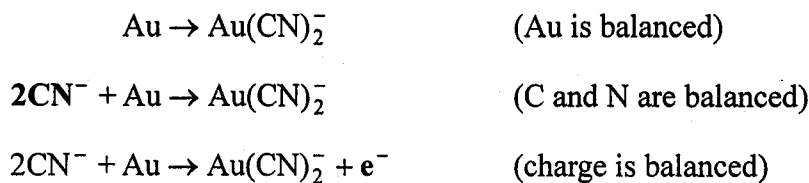
$$Au \rightarrow Au(CN)_2^-$$ (Au is balanced)

$$2CN^- + Au \rightarrow Au(CN)_2^-$$ (C and N are balanced)

$$2CN^- + Au \rightarrow Au(CN)_2^- + e^-$$ (charge is balanced)

One O_2 molecule is reduced to four OH^- ions, gaining four electrons in the process:

$$O_2 \rightarrow 2H_2O$$ (O is balanced)

$$4H^+ + O_2 \rightarrow 2H_2O$$ (H is balanced using H^+)

$$4OH^- + 4H^+ + O_2 \rightarrow 2H_2O + 4OH^-$$ (H^+ is neutralized by OH^-)

$$2H_2O + O_2 \rightarrow 4OH^-$$ (H_2O is consolidated)

$$4e^- + 2H_2O + O_2 \rightarrow 4OH^-$$ (charge is balanced)

The oxidation half-reaction must be multiplied by 4 to yield a charge-balanced redox equation:

$$4[Au + 2CN^- \rightarrow Au(CN)_2^- + e^-] \qquad \text{(oxidation)}$$

$$4e^- + O_2 + 2H_2O \rightarrow 4OH^- \qquad \text{(reduction)}$$

$$4Au(s) + O_2(g) + 8CN^-(aq) + 2H_2O(\ell) \rightarrow 4Au(CN)_2^-(aq) + 4OH^-(aq)$$
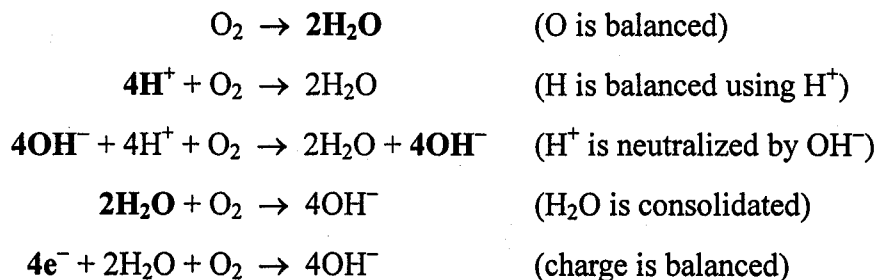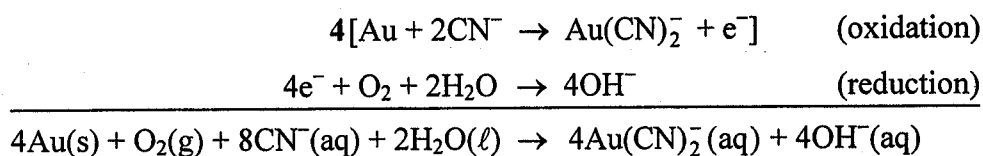
Oxidizing agent: $O_2(g)$
Reducing agent: $Au(s)$
Moles of electrons transferred: $n = 4$

(d) Nitrogen is oxidized from N^- in NH_2OH to N^0 in molecular N_2. Two molecules of NH_2OH lose one electron apiece to produce one molecule of N_2:

$$NH_2OH \rightarrow N_2 \qquad \text{(unbalanced)}$$
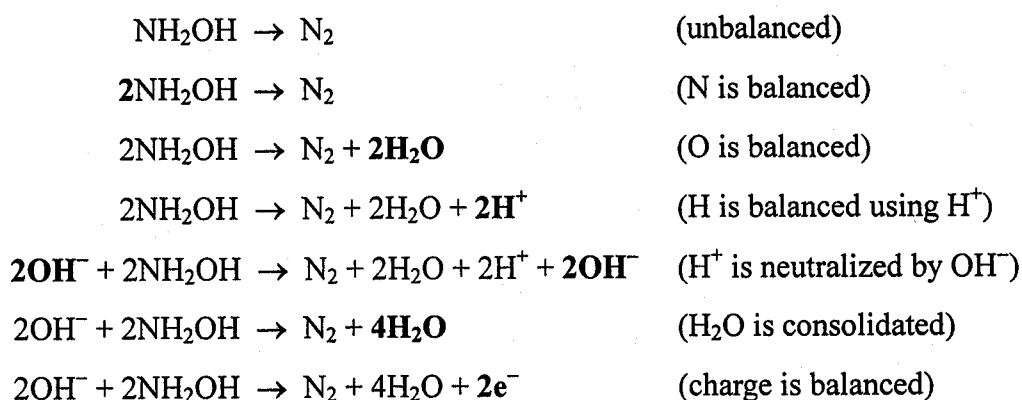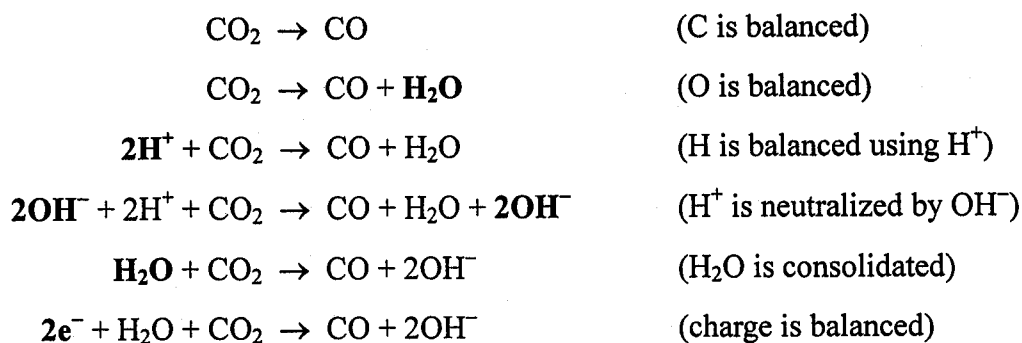
$$2NH_2OH \rightarrow N_2 \qquad \text{(N is balanced)}$$

$$2NH_2OH \rightarrow N_2 + 2H_2O \qquad \text{(O is balanced)}$$

$$2NH_2OH \rightarrow N_2 + 2H_2O + 2H^+ \qquad \text{(H is balanced using } H^+\text{)}$$

$$2OH^- + 2NH_2OH \rightarrow N_2 + 2H_2O + 2H^+ + 2OH^- \qquad \text{(}H^+\text{ is neutralized by } OH^-\text{)}$$

$$2OH^- + 2NH_2OH \rightarrow N_2 + 4H_2O \qquad \text{(}H_2O\text{ is consolidated)}$$

$$2OH^- + 2NH_2OH \rightarrow N_2 + 4H_2O + 2e^- \qquad \text{(charge is balanced)}$$

Gaining the two electrons, carbon is reduced from C^{4+} in CO_2 to C^{2+} in CO:

$$CO_2 \rightarrow CO \qquad \text{(C is balanced)}$$

$$CO_2 \rightarrow CO + H_2O \qquad \text{(O is balanced)}$$

$$2H^+ + CO_2 \rightarrow CO + H_2O \qquad \text{(H is balanced using } H^+\text{)}$$

$$2OH^- + 2H^+ + CO_2 \rightarrow CO + H_2O + 2OH^- \qquad \text{(}H^+\text{ is neutralized by } OH^-\text{)}$$

$$H_2O + CO_2 \rightarrow CO + 2OH^- \qquad \text{(}H_2O\text{ is consolidated)}$$

$$2e^- + H_2O + CO_2 \rightarrow CO + 2OH^- \qquad \text{(charge is balanced)}$$

Coupling reducing agent to oxidizing agent, we obtain the balanced redox equation for the process overall. Note that OH^- does not appear explicitly in the net equation:

$$2NH_2OH + 2OH^- \rightarrow N_2 + 4H_2O + 2e^- \qquad \text{(oxidation)}$$

$$\underline{2e^- + CO_2 + H_2O \rightarrow CO + 2OH^- \qquad \text{(reduction)}}$$

$$2NH_2OH(aq) + CO_2(g) \rightarrow N_2(g) + CO(g) + 3H_2O(\ell)$$
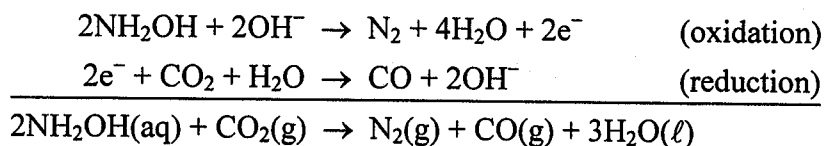
Oxidizing agent: $CO_2(g)$
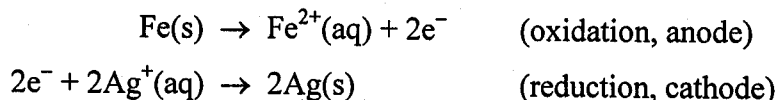Reducing agent: $NH_2OH(aq)$
Moles of electrons transferred: $n = 2$

We now consider the workings of a galvanic cell, using the equation

$$\mathcal{E}^\circ = \mathcal{E}^\circ_{red} + \mathcal{E}^\circ_{ox}$$

to quantify the separate oxidation and reduction half-reactions occurring at anode and cathode. Relevant material is available in Sections 17-4, 17-5, and 17-7.

**8.** We use the same reasoning in both this exercise and the next. See Exercise 9 for additional comments.

(a) Oxidation occurs at the anode, and reduction occurs at the cathode:

$$Fe(s) \rightarrow Fe^{2+}(aq) + 2e^- \qquad \text{(oxidation, anode)}$$

$$2e^- + 2Ag^+(aq) \rightarrow 2Ag(s) \qquad \text{(reduction, cathode)}$$

(b) Given that $\mathcal{E}^\circ_{red} = -0.447$ V for the reduction of Fe^{2+} to Fe,

$$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s) \qquad \mathcal{E}^\circ_{red} = -0.447 \text{ V}$$
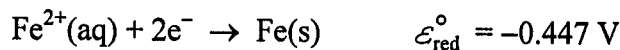
we know immediately that $\mathcal{E}^\circ_{ox} = +0.447$ V for the reverse reaction (the oxidation of Fe to Fe^{2+}):

$$Fe(s) \rightarrow Fe^{2+}(aq) + 2e^- \qquad \mathcal{E}^\circ_{ox} = -(-0.447 \text{ V}) = 0.447 \text{ V}$$
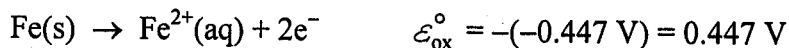
Since the standard cell potential is the sum of the two half-cell voltages,

$$\mathcal{E}^\circ = \mathcal{E}^\circ_{red} + \mathcal{E}^\circ_{ox} = 1.247 \text{ V}$$

we then have
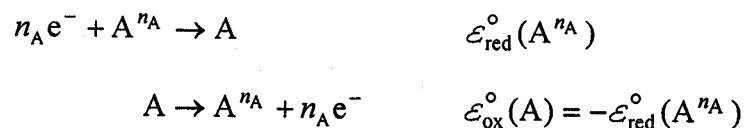
$$\mathcal{E}^\circ_{red} = \mathcal{E}^\circ - \mathcal{E}^\circ_{ox} = 1.247 \text{ V} - 0.447 \text{ V} = 0.800 \text{ V}$$
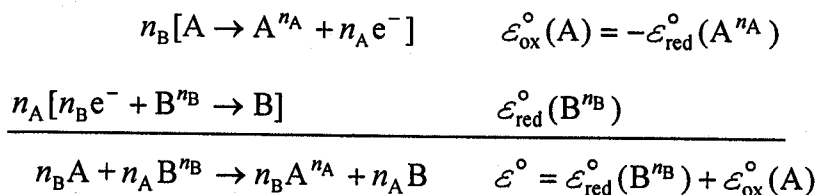
for the cathode reaction.

9. Bear in mind, throughout this entire chapter, the proportionality of free energy (chemical energy) and voltage (electrical potential):

$$\Delta G = -n\mathscr{F}\varepsilon$$

This key relationship ensures that an oxidation potential in one direction is equal in magnitude and opposite in sign to the reduction potential in the other direction. The following symbolic example should serve as a sufficiently general reminder:

$$n_A e^- + A^{n_A} \rightarrow A \qquad \varepsilon_{red}^{o}(A^{n_A})$$

$$A \rightarrow A^{n_A} + n_A e^- \qquad \varepsilon_{ox}^{o}(A) = -\varepsilon_{red}^{o}(A^{n_A})$$
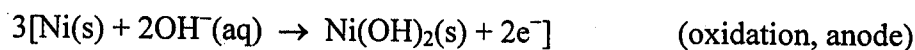
Furthermore, the electrical potential is an intensive property expressed as joules *per coulomb* rather than some total (extensive) number of joules. A cell potential, arising from both an oxidation half-reaction and a reduction half-reaction, is therefore equal to the sum of two fixed voltages—the same for all values of $n = n_A n_B$ in the generic redox reaction below:

$$n_B[A \rightarrow A^{n_A} + n_A e^-] \qquad \varepsilon_{ox}^{o}(A) = -\varepsilon_{red}^{o}(A^{n_A})$$

$$\underline{n_A[n_B e^- + B^{n_B} \rightarrow B] \qquad \varepsilon_{red}^{o}(B^{n_B})}$$

$$n_B A + n_A B^{n_B} \rightarrow n_B A^{n_A} + n_A B \qquad \varepsilon^{o} = \varepsilon_{red}^{o}(B^{n_B}) + \varepsilon_{ox}^{o}(A)$$

See Example 17-4.

(a) By definition, the *oxidation* half-reaction occurs at the *anode*:

$$3[Ni(s) + 2OH^-(aq) \rightarrow Ni(OH)_2(s) + 2e^-] \qquad \text{(oxidation, anode)}$$

The *reduction* half-reaction occurs at the *cathode*:

$$2[CrO_4^{2-}(aq) + 4H_2O(\ell) + 3e^- \rightarrow Cr(OH)_3(s) + 5OH^-(aq)] \qquad \text{(reduction, cathode)}$$
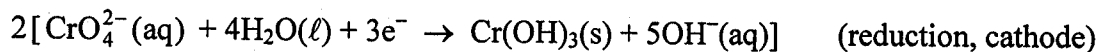
(b) Given that $\varepsilon_{red}^{o} = -0.72$ V for the reduction of $Ni(OH)_2$ to Ni,

$$Ni(OH)_2(s) + 2e^- \rightarrow Ni(s) + 2OH^-(aq) \qquad \varepsilon_{red}^{o} = -0.72 \text{ V}$$
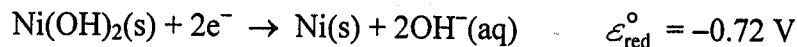
we know immediately that $\varepsilon_{ox}^{o} = +0.72$ V for the reverse reaction [the oxidation of Ni to $Ni(OH)_2$]:

$$Ni(s) + 2OH^-(aq) \rightarrow Ni(OH)_2(s) + 2e^- \qquad \varepsilon_{ox}^{o} = -(-0.72 \text{ V}) = 0.72 \text{ V}$$
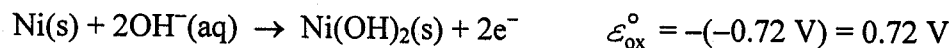
Since the standard cell potential develops as the sum of the two half-cell voltages,

$$\mathcal{E}^{\circ} = \mathcal{E}^{\circ}_{red} + \mathcal{E}^{\circ}_{ox} = 0.59 \text{ V}$$

we then have

$$\mathcal{E}^{\circ}_{red} = \mathcal{E}^{\circ} - \mathcal{E}^{\circ}_{ox} = 0.59 \text{ V} - 0.72 \text{ V} = -0.13 \text{ V}$$

for the cathode reaction.

10. We make use of (1) the relationship between free energy and voltage and (2) the summation of oxidation and reduction half-potentials in an electrochemical cell:

$$\Delta G^{\circ} = -n\mathcal{F}\mathcal{E}^{\circ} \qquad\qquad (1)$$

$$\mathcal{E}^{\circ} = \mathcal{E}^{\circ}_{red} + \mathcal{E}^{\circ}_{ox} \qquad\qquad (2)$$

(a) Insert (2) into (1) and expand:

$$\Delta G^{\circ} = -n\mathcal{F}\mathcal{E}^{\circ} = -n\mathcal{F}\left(\mathcal{E}^{\circ}_{red} + \mathcal{E}^{\circ}_{ox}\right) = -n\mathcal{F}\mathcal{E}^{\circ}_{red} - n\mathcal{F}\mathcal{E}^{\circ}_{ox} = \Delta G^{\circ}_{red} + \Delta G^{\circ}_{ox}$$

(b) Start with the relationship derived in (a),

$$\Delta G^{\circ} = \Delta G^{\circ}_{red} + \Delta G^{\circ}_{ox}$$

and insert the following definitions based on the arguments of Section 14-8:

$$\Delta G^{\circ} = -RT \ln K \qquad \Delta G^{\circ}_{red} = -RT \ln K_{red} \qquad \Delta G^{\circ}_{ox} = -RT \ln K_{ox}$$

The desired result follows straightforwardly from the properties of logarithms (about which, see Appendix B in *PoC*):

$$-RT \ln K = -RT \ln K_{red} - RT \ln K_{ox}$$

$$\ln K = \ln K_{red} + \ln K_{ox}$$

$$\ln K = \ln\left(K_{red} K_{ox}\right)$$

$$K = K_{red} K_{ox}$$

11. In the preceding exercise, we expressed a redox free energy as the sum of contributions from reduction and oxidation half-reactions:

$$\Delta G^\circ = \Delta G^\circ_{red} + \Delta G^\circ_{ox}$$

$$-RT \ln K = -RT \ln K_{red} - RT \ln K_{ox}$$

$$-2.303RT \log K = -2.303RT \log K_{red} - 2.303RT \log K_{ox}$$

$$-\log K = -\log K_{red} - \log K_{ox}$$

If we define

$$pK_{red} = -\log K_{red} \qquad pK_{ox} = -\log K_{ox}$$

by analogy to pK_a (acid) and pK_b (base), then we have the shorthand redox equivalent:

$$pK = pK_{red} + pK_{ox}$$

Recall, in passing, that $\ln A$ is equal to $2.303 \log A$ (*PoC*, pages A45–A47).

12. Decomposing a concerted redox process into reduction and oxidation half-reactions, we obtain the standard cell voltage by adding the two half-potentials:

$$\mathcal{E}^\circ = \mathcal{E}^\circ_{red} + \mathcal{E}^\circ_{ox}$$

See Section 17-7 in *PoC*. Standard reduction potentials are collected in Table C-21 of Appendix C, pages A100–A101.

(a) Zinc, losing two electrons, is oxidized from its elemental state (oxidation number = 0) to Zn^{2+} in $Zn(OH)_2$. Mercury, gaining two electrons, is reduced from Hg^{2+} in HgO to its elemental state Hg^0.

First, reconstruct the oxidation half-reaction from the overall cell equation:

$$Zn \rightarrow Zn(OH)_2 \qquad \text{(Zn is balanced)}$$

$$2OH^- + Zn \rightarrow Zn(OH)_2 \qquad \text{(O and H are balanced)}$$

$$2OH^- + Zn \rightarrow Zn(OH)_2 + 2e^- \qquad \text{(charge is balanced)}$$
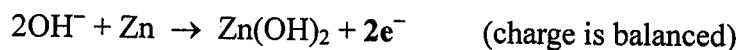
Similarly, reconstruct the reduction half-reaction:

$$HgO \rightarrow Hg \qquad\qquad \text{(Hg is balanced)}$$

$$HgO \rightarrow Hg + \mathbf{H_2O} \qquad\qquad \text{(O is balanced)}$$

$$\mathbf{2H^+} + HgO \rightarrow Hg + H_2O \qquad\qquad \text{(H is balanced using } H^+\text{)}$$

$$\mathbf{2OH^-} + 2H^+ + HgO \rightarrow Hg + H_2O + \mathbf{2OH^-} \qquad\qquad \text{(}H^+\text{ is neutralized by } OH^-\text{)}$$

$$\mathbf{H_2O} + HgO \rightarrow Hg + 2OH^- \qquad\qquad \text{(H}_2\text{O is consolidated)}$$

$$\mathbf{2e^-} + H_2O + HgO \rightarrow Hg + 2OH^- \qquad\qquad \text{(charge is balanced)}$$

Next, combine the half-reactions:

$$Zn + 2OH^- \rightarrow Zn(OH)_2 + 2e^- \qquad \text{(oxidation)}$$

$$\underline{2e^- + HgO + H_2O \rightarrow Hg + 2OH^- \qquad \text{(reduction)}}$$

$$Zn(s) + HgO(s) + H_2O(\ell) \rightarrow Zn(OH)_2(s) + Hg(\ell)$$
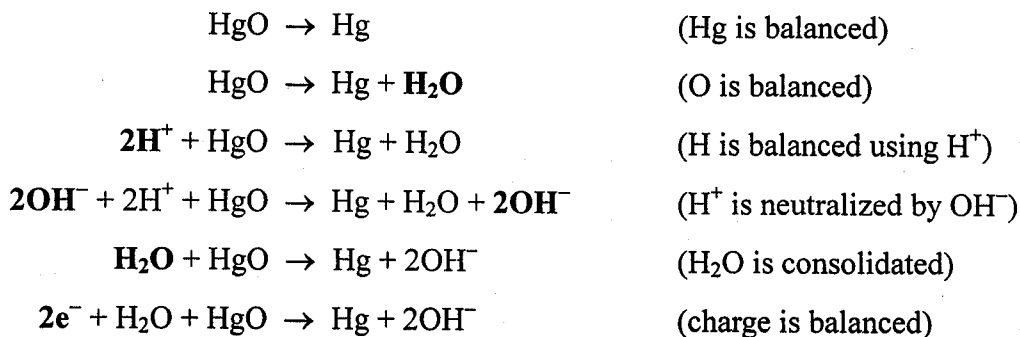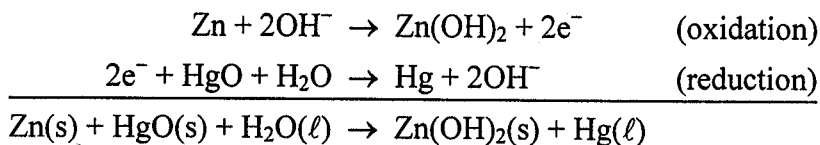
Oxidizing agent: HgO(s)
Reducing agent: Zn(s)
Moles of electrons transferred: $n = 2$

Note how OH^-, although present in both half-reactions, does not appear in the net equation for the cell.

(b) The oxidation half-reaction

$$Zn(s) + 2OH^-(aq) \rightarrow Zn(OH)_2(s) + 2e^-$$
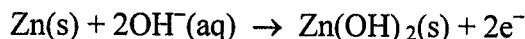
occurs at the anode. The reduction half-reaction

$$HgO(s) + H_2O(\ell) + 2e^- \rightarrow Hg(\ell) + 2OH^-(aq)$$
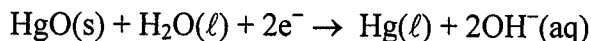
occurs at the cathode.

(c) The reduction half-reaction is listed in the table of standard reduction potentials (Table C-21 in *PoC*):

$$HgO + H_2O + 2e^- \rightarrow Hg + 2OH^- \qquad \varepsilon^\circ_{red} = 0.0977 \text{ V}$$

The oxidation half-reaction

$$Zn + 2OH^- \rightarrow Zn(OH)_2 + 2e^- \qquad \varepsilon^\circ_{ox} = 1.249 \text{ V}$$
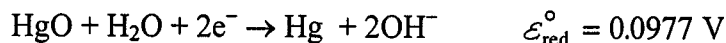
is the reverse of the reduction half-reaction

$$Zn(OH)_2 + 2e^- \rightarrow Zn + 2OH^- \qquad \varepsilon^{\circ}_{red} = -1.249 \text{ V}$$

given in Table C-21. The cell potential is therefore 1.347 V:

$$\varepsilon^{\circ} = \varepsilon^{\circ}_{red} + \varepsilon^{\circ}_{ox} = 0.0977 \text{ V} + 1.249 \text{ V} = 1.347 \text{ V}$$

Exercises in the next large group (13 through 24) deal with the relationships that connect standard cell potential, free energy, and the equilibrium constant. See Sections 17-4, 17-6, and 17-7 in PoC, as well as Examples 17-4 through 17-7.
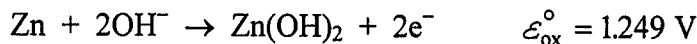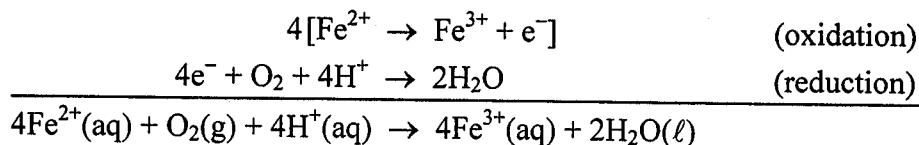
Exercise 13, immediately following, sets the stage for subsequent calculations of ε° and ΔG° in Exercise 14.

13. The oxidizing agent, which *gains* electrons, is *reduced.* Its oxidation number becomes more negative.

The reducing agent, which *loses* electrons, is *oxidized.* Its oxidation number becomes more positive.

(a) Here we can decompose the cell equation into half-reactions merely by inspection:

$$
\begin{array}{ll}
4[Fe^{2+} \rightarrow Fe^{3+} + e^-] & \text{(oxidation)} \\
\underline{4e^- + O_2 + 4H^+ \rightarrow 2H_2O} & \text{(reduction)} \\
4Fe^{2+}(aq) + O_2(g) + 4H^+(aq) \rightarrow 4Fe^{3+}(aq) + 2H_2O(\ell) &
\end{array}
$$

Oxidizing agent: $O_2(g)$
Reducing agent: $Fe^{2+}(aq)$
Moles of electrons transferred: $n = 4$

(b) Elemental hydrogen is oxidized to an oxidation state of +1 in H_2O, losing two electrons per molecule of H_2:

$$H_2 \rightarrow 2H^+ \qquad \text{(H is balanced using } H^+)$$

$$2OH^- + H_2 \rightarrow 2H^+ + 2OH^- \qquad \text{(}H^+ \text{ is neutralized by } OH^-)$$

$$2OH^- + H_2 \rightarrow 2H_2O \qquad \text{(}H_2O \text{ is consolidated)}$$

$$2OH^- + H_2 \rightarrow 2H_2O + 2e^- \qquad \text{(charge is balanced)}$$
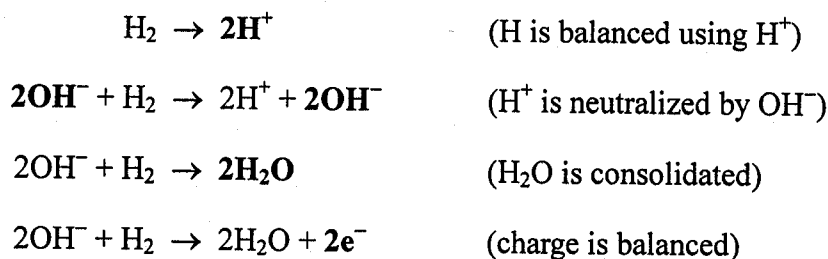
Elemental oxygen is reduced to an oxidation state of −2 in the hydroxide ion, gaining four electrons per molecule of O_2:

$$O_2 \rightarrow 2H_2O \qquad \text{(O is balanced)}$$

$$4H^+ + O_2 \rightarrow 2H_2O \qquad \text{(H is balanced using } H^+\text{)}$$

$$4OH^- + 4H^+ + O_2 \rightarrow 2H_2O + 4OH^- \qquad \text{(} H^+ \text{ is neutralized by } OH^-\text{)}$$

$$2H_2O + O_2 \rightarrow 4OH^- \qquad \text{(} H_2O \text{ is consolidated)}$$

$$4e^- + 2H_2O + O_2 \rightarrow 4OH^- \qquad \text{(charge is balanced)}$$
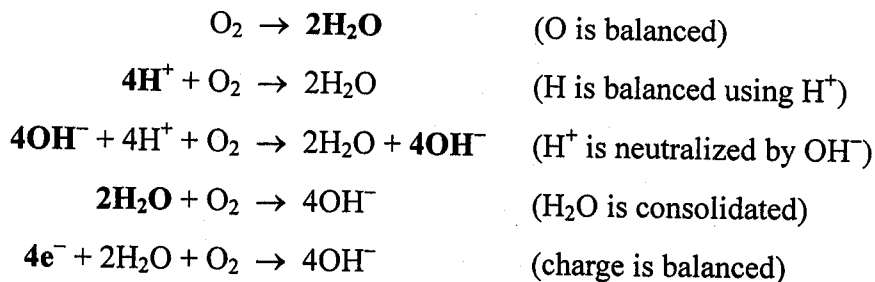
Multiplying the oxidation half-reaction by 2 to conserve charge, we recover the combined redox process:

$$2[H_2 + 2OH^- \rightarrow 2H_2O + 2e^-] \qquad \text{(oxidation)}$$

$$\underline{4e^- + O_2 + 2H_2O \rightarrow 4OH^- \qquad \text{(reduction)}}$$

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(\ell)$$
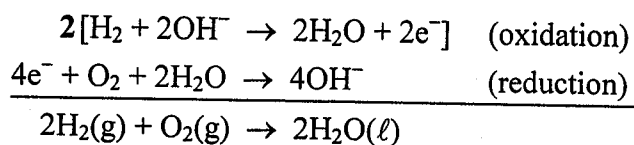
Oxidizing agent: $O_2(g)$
Reducing agent: $H_2(g)$
Moles of electrons transferred: $n = 4$

(c) In acidic solution, water is oxidized to O_2 and H^+. Oxygen goes from an oxidation state of −2 in H_2O to an oxidation state of 0 in O_2:

$$H_2O \rightarrow O_2 \qquad \text{(unbalanced)}$$

$$2H_2O \rightarrow O_2 \qquad \text{(O is balanced)}$$

$$2H_2O \rightarrow O_2 + 4H^+ \qquad \text{(H is balanced)}$$

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \qquad \text{(charge is balanced)}$$
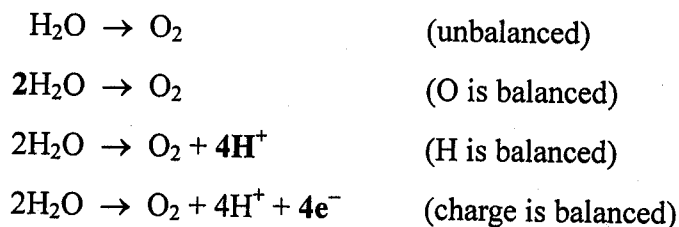
The hydrogen cation, meanwhile, is reduced to molecular hydrogen, gaining two electrons per molecule of H_2:

$$2H^+ + 2e^- \rightarrow H_2 \qquad \text{(balanced)}$$

Charge conservation is enforced when the reduction half-reaction is multiplied by 2:

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \qquad \text{(oxidation)}$$
$$\underline{2\left[2e^- + 2H^+ \rightarrow H_2\right] \qquad\qquad \text{(reduction)}}$$
$$2H_2O(\ell) \rightarrow 2H_2(g) + O_2(g)$$
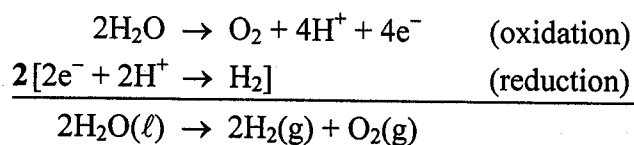
Oxidizing agent: $H^+(aq)$
Reducing agent: $H_2O(\ell)$
Moles of electrons transferred: $n = 4$

14. The standard cell potential

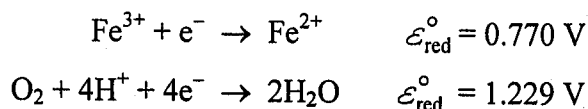$$\mathcal{E}^\circ = \mathcal{E}^\circ_{red} + \mathcal{E}^\circ_{ox}$$

is related to the standard change in free energy by n (the moles of electrons transferred) and the Faraday constant $\mathcal{F}$ (the charge per mole of electrons):

$$\Delta G^\circ = -n\mathcal{F}\mathcal{E}^\circ$$

Reactions with positive $\mathcal{E}^\circ$ and negative ΔG° are spontaneous. Reactions with negative $\mathcal{E}^\circ$ and positive ΔG° are not. See Sections 17-6 and 17-7 in *PoC*, as well as Examples 17-4 through 17-6.

(a) Look up the pertinent standard reduction potentials,

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \qquad \mathcal{E}^\circ_{red} = 0.770 \text{ V}$$

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \qquad \mathcal{E}^\circ_{red} = 1.229 \text{ V}$$

and note that $\mathcal{E}^\circ_{ox} = -\mathcal{E}^\circ_{red}$ for any half-reaction:

$$Fe^{2+} \rightarrow Fe^{3+} + e^- \qquad \mathcal{E}^\circ_{ox} = -\mathcal{E}^\circ_{red} = -0.770 \text{ V}$$

The standard cell potential in this system is thus 0.459 V:

$$4\left[Fe^{2+} \rightarrow Fe^{3+} + e^-\right] \qquad\qquad \mathcal{E}^\circ_{ox} = -0.770 \text{ V}$$
$$\underline{4e^- + O_2 + 4H^+ \rightarrow 2H_2O \qquad\qquad\qquad \mathcal{E}^\circ_{red} = 1.229 \text{ V}}$$
$$4Fe^{2+}(aq) + O_2(g) + 4H^+(aq) \rightarrow 4Fe^{3+}(aq) + 2H_2O(\ell) \qquad \mathcal{E}^\circ = 0.459 \text{ V}$$

$$\mathcal{E}^\circ = \mathcal{E}^\circ_{red} + \mathcal{E}^\circ_{ox} = 1.229 \text{ V} + \left(-0.770 \text{ V}\right) = 0.459 \text{ V}$$
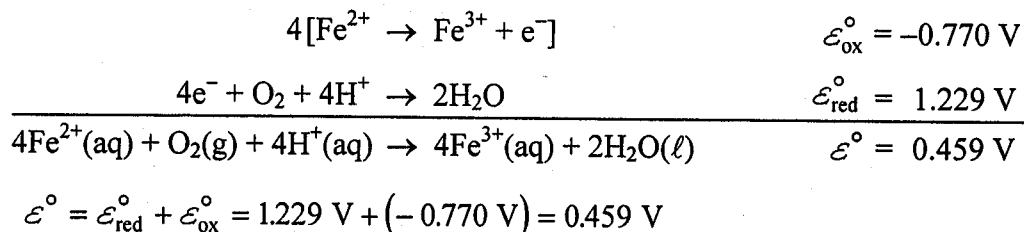
With $n = 4$, the associated change in free energy is -177 kJ:

$$\Delta G^\circ = -n\mathscr{F}\varepsilon^\circ$$

$$= -4 \text{ mol e}^- \times \frac{96{,}485 \text{ C}}{\text{mol e}^-} \times \frac{0.459 \text{ J}}{\text{C}} = -1.77 \times 10^5 \text{ J}$$
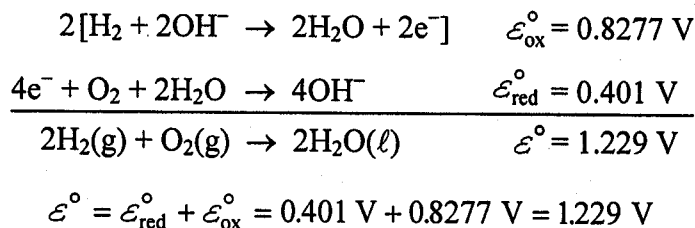
$$= -177 \text{ kJ} \quad \text{(spontaneous)}$$

Recall that the volt is a unit of electric potential, a measure of the work needed to move an electric charge in an electric field:

$$1 \text{ V} = 1 \text{ J C}^{-1}$$

We make use of this defining relationship throughout the chapter, henceforth with no explicit comment.

(b) Use the same method as in (a) above. The calculated values of ε° and ΔG° are 1.229 V and -474.3 kJ, respectively.

Standard cell potential:

$$2[H_2 + 2OH^- \rightarrow 2H_2O + 2e^-] \qquad \varepsilon^\circ_{ox} = 0.8277 \text{ V}$$

$$\underline{4e^- + O_2 + 2H_2O \rightarrow 4OH^- \qquad \varepsilon^\circ_{red} = 0.401 \text{ V}}$$

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(\ell) \qquad \varepsilon^\circ = 1.229 \text{ V}$$

$$\varepsilon^\circ = \varepsilon^\circ_{red} + \varepsilon^\circ_{ox} = 0.401 \text{ V} + 0.8277 \text{ V} = 1.229 \text{ V}$$

Standard free energy ($n = 4$):

$$\Delta G^\circ = -n\mathscr{F}\varepsilon^\circ$$

$$= -4 \text{ mol e}^- \times \frac{96{,}485 \text{ C}}{\text{mol e}^-} \times \frac{1.229 \text{ J}}{\text{C}} = -4.743 \times 10^5 \text{ J}$$

$$= -474.3 \text{ kJ} \quad \text{(spontaneous)}$$

(c) The overall reaction here is the reverse of the one just considered in (b), although arrived at by a different combination of half-reactions. The thermodynamic separations remain fixed in magnitude, however, regardless of the path of reaction. Both ε° and ΔG° change signs—but not magnitudes—and the reverse process becomes nonspontaneous.

Standard cell potential:

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \qquad \mathcal{E}_{ox}^\circ = -1.229 \text{ V}$$

$$\underline{2[2e^- + 2H^+ \rightarrow H_2]} \qquad\qquad \mathcal{E}_{red}^\circ = 0.000 \text{ V}$$

$$2H_2O(\ell) \rightarrow 2H_2(g) + O_2(g) \qquad \mathcal{E}^\circ = -1.229 \text{ V}$$

$$\mathcal{E}^\circ = \mathcal{E}_{red}^\circ + \mathcal{E}_{ox}^\circ = 0.000 \text{ V} + \left(-1.229 \text{ V}\right) = -1.229 \text{ V}$$
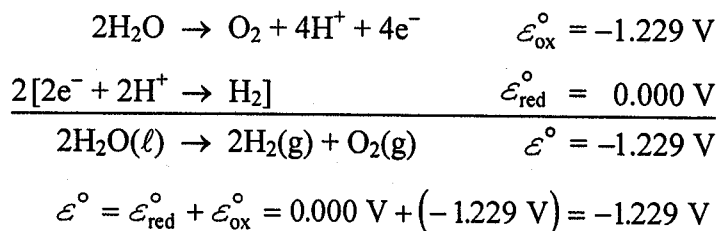
Standard free energy ($n = 4$):

$$\Delta G^\circ = -n\mathscr{F}\mathcal{E}^\circ$$

$$= -4 \text{ mol e}^- \times \frac{96,485 \text{ C}}{\text{mol e}^-} \times \left(-\frac{1.229 \text{ J}}{\text{C}}\right) = 4.743 \times 10^5 \text{ J}$$

$$= 474.3 \text{ kJ} \quad \text{(nonspontaneous)}$$

15. We are given the following reaction, nonspontaneous under standard conditions:

$$2Ag + 2OH^- \rightarrow Ag_2O + H_2O + 2e^- \qquad \mathcal{E}_{ox}^\circ = ?$$

$$\underline{2e^- + Zn^{2+} \rightarrow Zn} \qquad\qquad\qquad \mathcal{E}_{red}^\circ = -0.7618 \text{ V}$$

$$2Ag(s) + Zn^{2+}(aq) + 2OH^-(aq) \rightarrow Ag_2O(s) + Zn(s) + H_2O(\ell) \qquad \mathcal{E}^\circ = -1.104 \text{ V}$$
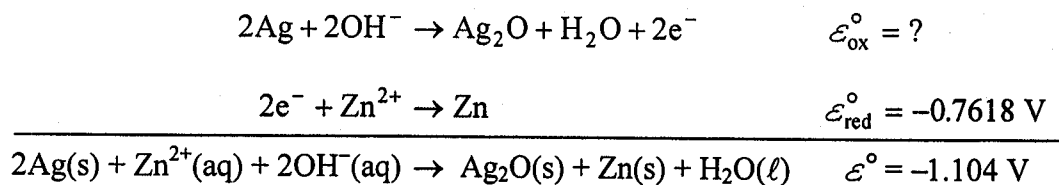
(a) Suppose, for the sake of the exercise, that we know both $\mathcal{E}_{red}^\circ$ for Zn^{2+} (familiar from previous examples) and $\mathcal{E}^\circ$ for the cell (stated in the problem). If so, then we can immediately calculate $\mathcal{E}_{ox}^\circ$ for the oxidation of Ag to Ag_2O:
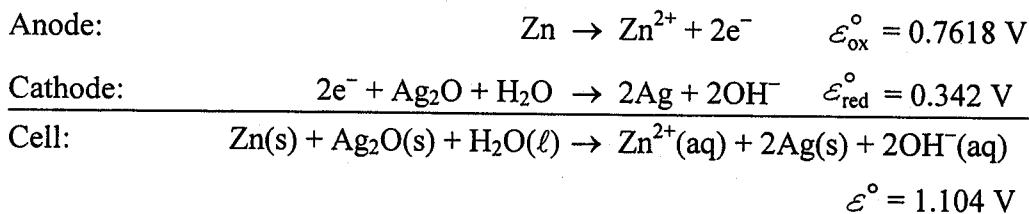
$$\mathcal{E}^\circ = \mathcal{E}_{red}^\circ + \mathcal{E}_{ox}^\circ = -1.104 \text{ V}$$

$$\mathcal{E}_{ox}^\circ = \mathcal{E}^\circ - \mathcal{E}_{red}^\circ = -1.104 \text{ V} - \left(-0.7618 \text{ V}\right) = -0.342 \text{ V}$$

The standard *reduction* potential for the half-reaction

$$Ag_2O(s) + H_2O(\ell) + 2e^- \rightarrow 2Ag(s) + 2OH^-(aq) \qquad \mathcal{E}_{red}^\circ = -\mathcal{E}_{ox}^\circ = 0.342 \text{ V}$$
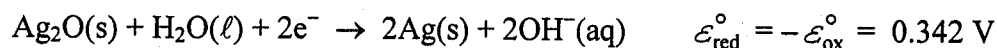
is therefore 0.342 V, consistent with the value listed in Table C-21. Note the sign reversal when the half-reaction is taken in the opposite direction.

(b) Reverse each half-reaction to make the process spontaneous:

Anode:		$Zn \rightarrow Zn^{2+} + 2e^-$	$\mathcal{E}^{\circ}_{ox} = 0.7618 \text{ V}$
Cathode:	$2e^- + Ag_2O + H_2O \rightarrow 2Ag + 2OH^-$		$\mathcal{E}^{\circ}_{red} = 0.342 \text{ V}$

Cell: $Zn(s) + Ag_2O(s) + H_2O(\ell) \rightarrow Zn^{2+}(aq) + 2Ag(s) + 2OH^-(aq)$

$$\mathcal{E}^{\circ} = 1.104 \text{ V}$$

(c) The standard cell potential, shown above in (b), is 1.104 V for the spontaneous reaction:
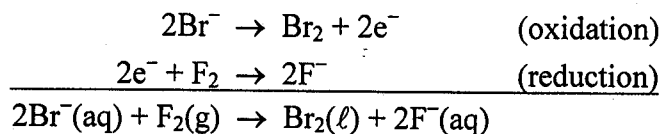
$$\mathcal{E}^{\circ} = \mathcal{E}^{\circ}_{red} + \mathcal{E}^{\circ}_{ox} = 0.342 \text{ V} + 0.7618 \text{ V} = 1.104 \text{ V}$$

The corresponding change in free energy is an extensive property, determined by the molar amount of electrons transferred—in this system, $n = 2$:

$$\Delta G^{\circ} = -n\mathcal{F}\mathcal{E}^{\circ}$$

$$= -2 \text{ mol } e^- \times \frac{96,485 \text{ C}}{\text{mol } e^-} \times \frac{1.104 \text{ J}}{\text{C}} = -2.130 \times 10^5 \text{ J}$$

$$= -213.0 \text{ kJ}$$

16. The reactions are simple enough to analyze by inspection.

(a) Bromine is oxidized from a −1 oxidation state in the bromide ion to a 0 oxidation state in the bromine molecule. Similarly, but in the other direction, fluorine is reduced from 0 in F_2 to −1 in F^-. Two electrons are transferred:
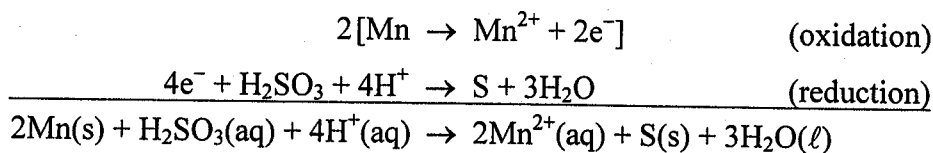
$2Br^- \rightarrow Br_2 + 2e^-$	(oxidation)
$2e^- + F_2 \rightarrow 2F^-$	(reduction)
$2Br^-(aq) + F_2(g) \rightarrow Br_2(\ell) + 2F^-(aq)$	

Oxidizing agent: $F_2(g)$
Reducing agent: $Br^-(aq)$
Moles of electrons transferred: $n = 2$

(b) Manganese is oxidized from its elemental state (oxidation number = 0) to Mn^{2+}. Sulfur is reduced from an oxidation number of +4 in SO_3^{2-} to an oxidation number of 0 in its elemental state. In all, four electrons are transferred from giver to receiver:

$$2[Mn \rightarrow Mn^{2+} + 2e^-] \qquad \text{(oxidation)}$$

$$\underline{4e^- + H_2SO_3 + 4H^+ \rightarrow S + 3H_2O \qquad \text{(reduction)}}$$

$$2Mn(s) + H_2SO_3(aq) + 4H^+(aq) \rightarrow 2Mn^{2+}(aq) + S(s) + 3H_2O(\ell)$$
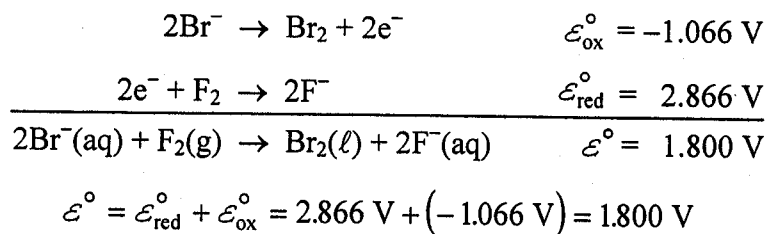
Oxidizing agent: $H_2SO_3(aq)$

Reducing agent: $Mn(s)$

Moles of electrons transferred: $n = 4$

17. The method is the same as in Exercise 14. Consult Table C-21 in *PoC* for values of $\mathcal{E}_{red}^\circ$, and remember that

$$\mathcal{E}_{ox}^\circ = -\mathcal{E}_{red}^\circ$$

for any individual half-reaction.

(a) Carrying over the half-reactions from Exercise 16(a), we calculate a standard cell potential of 1.800 V:
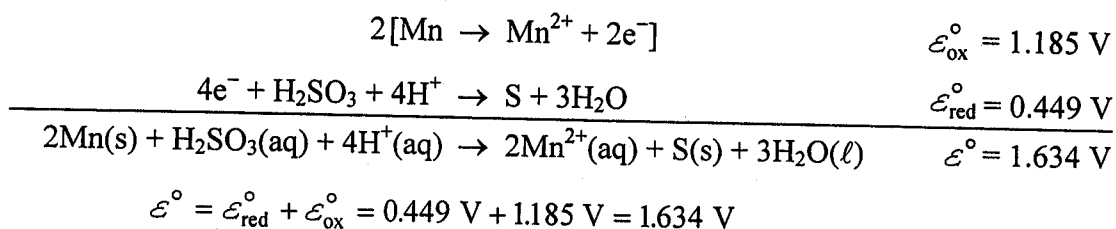
$$2Br^- \rightarrow Br_2 + 2e^- \qquad \mathcal{E}_{ox}^\circ = -1.066 \text{ V}$$

$$\underline{2e^- + F_2 \rightarrow 2F^- \qquad \mathcal{E}_{red}^\circ = 2.866 \text{ V}}$$

$$2Br^-(aq) + F_2(g) \rightarrow Br_2(\ell) + 2F^-(aq) \qquad \mathcal{E}^\circ = 1.800 \text{ V}$$

$$\mathcal{E}^\circ = \mathcal{E}_{red}^\circ + \mathcal{E}_{ox}^\circ = 2.866 \text{ V} + (-1.066 \text{ V}) = 1.800 \text{ V}$$

With $n = 2$, the associated change in free energy is -347.3 kJ:

$$\Delta G^\circ = -n\mathcal{F}\mathcal{E}^\circ$$

$$= -2 \text{ mol } e^- \times \frac{96{,}485 \text{ C}}{\text{mol } e^-} \times \frac{1.800 \text{ J}}{\text{C}} = -3.473 \times 10^5 \text{ J}$$

$$= -347.3 \text{ kJ} \quad \text{(spontaneous)}$$

(b) Use the same method as in (a) above. The calculated values of $\mathcal{E}^\circ$ and ΔG° are 1.634 V and -630.6 kJ, respectively. See the next page for details.

Standard cell potential:

$$2[Mn \rightarrow Mn^{2+} + 2e^-] \qquad \varepsilon^\circ_{ox} = 1.185 \text{ V}$$

$$\frac{4e^- + H_2SO_3 + 4H^+ \rightarrow S + 3H_2O \qquad \varepsilon^\circ_{red} = 0.449 \text{ V}}{2Mn(s) + H_2SO_3(aq) + 4H^+(aq) \rightarrow 2Mn^{2+}(aq) + S(s) + 3H_2O(\ell) \qquad \varepsilon^\circ = 1.634 \text{ V}}$$

$$\varepsilon^\circ = \varepsilon^\circ_{red} + \varepsilon^\circ_{ox} = 0.449 \text{ V} + 1.185 \text{ V} = 1.634 \text{ V}$$

Standard free energy ($n = 4$):

$$\Delta G^\circ = -n\mathscr{F}\varepsilon^\circ$$

$$= -4 \text{ mol } e^- \times \frac{96{,}485 \text{ C}}{\text{mol } e^-} \times \frac{1.634 \text{ J}}{\text{C}} = -6.306 \times 10^5 \text{ J}$$

$$= -630.6 \text{ kJ} \quad \text{(spontaneous)}$$

18. The standard cell potential and difference in free energy are calculated as in Exercise 14:

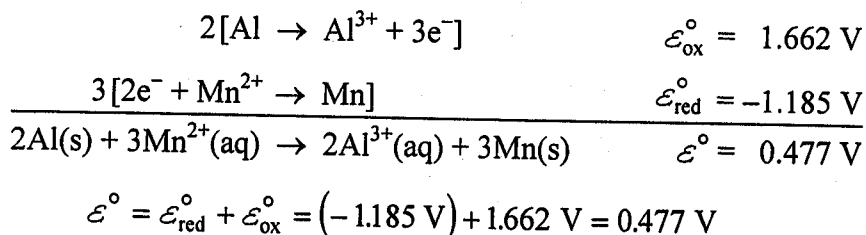$$\varepsilon^\circ = \varepsilon^\circ_{red} + \varepsilon^\circ_{ox}$$

$$\Delta G^\circ = -n\mathscr{F}\varepsilon^\circ$$

The equilibrium constant is determined from the relationship

$$K = \exp\left(-\frac{\Delta G^\circ}{RT}\right) = \exp\left(\frac{n\mathscr{F}\varepsilon^\circ}{RT}\right)$$

first introduced in Section 14-8 and extended now to incorporate the proportionality of ΔG° and ε°. See Sections 17-4, 17-6, and 17-7 in *PoC*, together with pages R17.3–R17.5 and Examples 17-4 through 17-7.
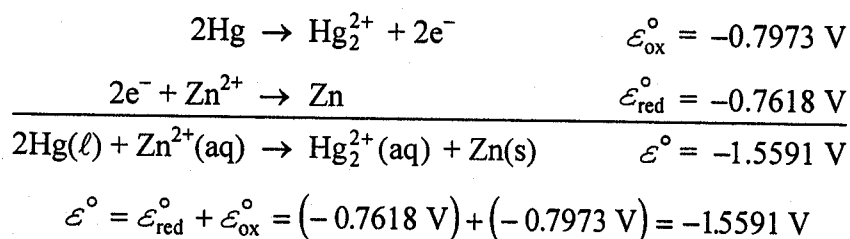
(a) Standard cell potential:

$$2[Al \rightarrow Al^{3+} + 3e^-] \qquad \varepsilon^\circ_{ox} = 1.662 \text{ V}$$

$$\frac{3[2e^- + Mn^{2+} \rightarrow Mn] \qquad \varepsilon^\circ_{red} = -1.185 \text{ V}}{2Al(s) + 3Mn^{2+}(aq) \rightarrow 2Al^{3+}(aq) + 3Mn(s) \qquad \varepsilon^\circ = 0.477 \text{ V}}$$

$$\varepsilon^\circ = \varepsilon^\circ_{red} + \varepsilon^\circ_{ox} = \left(-1.185 \text{ V}\right) + 1.662 \text{ V} = 0.477 \text{ V}$$

Standard free energy ($n = 6$):

$$\Delta G^\circ = -n\mathcal{F}\varepsilon^\circ$$

$$= -6 \text{ mol e}^- \times \frac{96{,}485 \text{ C}}{\text{mol e}^-} \times \frac{0.477 \text{ J}}{\text{C}} = -2.76 \times 10^5 \text{ J}$$

$$= -276 \text{ kJ} \quad \text{(spontaneous)}$$

Equilibrium constant:

$$K = \exp\left(\frac{n\mathcal{F}\varepsilon^\circ}{RT}\right) = \exp\left[\frac{(6)(96{,}485 \text{ C mol}^{-1})(0.477 \text{ J C}^{-1})}{(8.3145 \text{ J mol}^{-1} \text{ K}^{-1})(298.15 \text{ K})}\right] \approx 2 \times 10^{48}$$

$$\text{(effectively } \infty)$$

(b) Standard cell potential:

$$2\text{Hg} \rightarrow \text{Hg}_2^{2+} + 2\text{e}^- \qquad \varepsilon_{ox}^\circ = -0.7973 \text{ V}$$

$$\underline{2\text{e}^- + \text{Zn}^{2+} \rightarrow \text{Zn} \qquad\qquad \varepsilon_{red}^\circ = -0.7618 \text{ V}}$$

$$2\text{Hg}(\ell) + \text{Zn}^{2+}(aq) \rightarrow \text{Hg}_2^{2+}(aq) + \text{Zn}(s) \qquad \varepsilon^\circ = -1.5591 \text{ V}$$

$$\varepsilon^\circ = \varepsilon_{red}^\circ + \varepsilon_{ox}^\circ = \left(-0.7618 \text{ V}\right) + \left(-0.7973 \text{ V}\right) = -1.5591 \text{ V}$$

Standard free energy ($n = 2$):

$$\Delta G^\circ = -n\mathcal{F}\varepsilon^\circ$$

$$= -2 \text{ mol e}^- \times \frac{96{,}485 \text{ C}}{\text{mol e}^-} \times \left(-\frac{1.5591 \text{ J}}{\text{C}}\right) = 3.0086 \times 10^5 \text{ J}$$

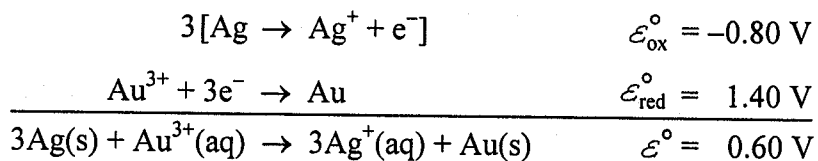$$= 300.86 \text{ kJ} \quad \text{(nonspontaneous)}$$

Equilibrium constant:

$$K = \exp\left(\frac{n\mathcal{F}\varepsilon^\circ}{RT}\right) = \exp\left[\frac{(2)(96{,}485 \text{ C mol}^{-1})(-1.5591 \text{ J C}^{-1})}{(8.3145 \text{ J mol}^{-1} \text{ K}^{-1})(298.15 \text{ K})}\right] \approx 2 \times 10^{-53}$$

$$\text{(effectively } 0)$$

Copper, silver, and gold (the "coinage metals") are used in Exercises 19 through 21 to illustrate the competitive nature of redox processes. The roles of giver and taker are often reversed, and a reducing agent in one reaction may well be an oxidizing agent in another. The outcome depends on the relative electrochemical standing of the two partners.

19. Use the same methods as in Exercises 14 and 18.

(a) Ag is oxidized to Ag^+ at the anode (site of oxidation in any cell), and Au^{3+} is reduced to Au at the cathode. Three electrons pass from reducing agent to oxidizing agent:

$$3[Ag \rightarrow Ag^+ + e^-] \qquad \mathscr{E}^\circ_{ox} = -0.80 \text{ V}$$

$$\underline{Au^{3+} + 3e^- \rightarrow Au \qquad \mathscr{E}^\circ_{red} = 1.40 \text{ V}}$$

$$3Ag(s) + Au^{3+}(aq) \rightarrow 3Ag^+(aq) + Au(s) \qquad \mathscr{E}^\circ = 0.60 \text{ V}$$

Oxidizing agent: $Au^{3+}(aq)$
Reducing agent: $Ag(s)$
Moles of electrons transferred: $n = 3$

(b) See (a) above for the cell equation.

(c) Standard cell potential:

$$\mathscr{E}^\circ = \mathscr{E}^\circ_{red} + \mathscr{E}^\circ_{ox} = 1.40 \text{ V} + (-0.80 \text{ V}) = 0.60 \text{ V}$$

Standard free energy ($n = 3$):

$$\Delta G^\circ = -n\mathscr{F}\mathscr{E}^\circ$$

$$= -3 \text{ mol } e^- \times \frac{96,485 \text{ C}}{\text{mol } e^-} \times \frac{0.60 \text{ J}}{\text{C}} = -1.7 \times 10^5 \text{ J}$$

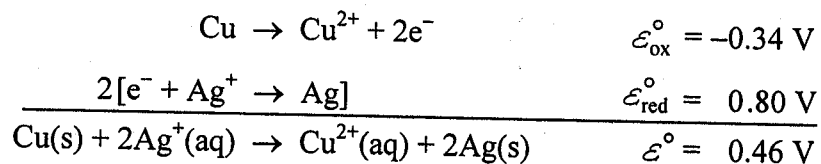$$= -1.7 \times 10^2 \text{ kJ} \quad \text{(spontaneous)}$$

Equilibrium constant:

$$K = \exp\left(\frac{n\mathscr{F}\mathscr{E}^\circ}{RT}\right) = \exp\left[\frac{(3)(96,485 \text{ C mol}^{-1})(0.60 \text{ J C}^{-1})}{(8.3145 \text{ J mol}^{-1} \text{ K}^{-1})(298.15 \text{ K})}\right] \approx 3 \times 10^{30}$$

(effectively ∞)

20. The arithmetic is similar to that used in Exercise 19, but now silver takes on a different role: Electrons in the Cu/Ag cell flow from Cu to Ag^+, not from Ag to Au^{3+} as they do in the Ag/Au cell.

(a) Cu is oxidized to Cu^{2+} at the anode, and Ag^+ is reduced to Ag at the cathode. Two electrons are transferred:

$$Cu \rightarrow Cu^{2+} + 2e^- \qquad\qquad \mathcal{E}^\circ_{ox} = -0.34 \text{ V}$$

$$\underline{2[e^- + Ag^+ \rightarrow Ag] \qquad\qquad \mathcal{E}^\circ_{red} = 0.80 \text{ V}}$$

$$Cu(s) + 2Ag^+(aq) \rightarrow Cu^{2+}(aq) + 2Ag(s) \qquad \mathcal{E}^\circ = 0.46 \text{ V}$$

Oxidizing agent: $Ag^+(aq)$
Reducing agent: $Cu(s)$
Moles of electrons transferred: $n = 2$

(b) See (a) above for the cell equation.

(c) Standard cell potential:

$$\mathcal{E}^\circ = \mathcal{E}^\circ_{red} + \mathcal{E}^\circ_{ox} = 0.80 \text{ V} + \left(-0.34 \text{ V}\right) = 0.46 \text{ V}$$

Standard free energy ($n = 2$):

$$\Delta G^\circ = -n\mathcal{F}\mathcal{E}^\circ$$

$$= -2 \text{ mol } e^- \times \frac{96,485 \text{ C}}{\text{mol } e^-} \times \frac{0.46 \text{ J}}{\text{C}} = -8.9 \times 10^4 \text{ J}$$
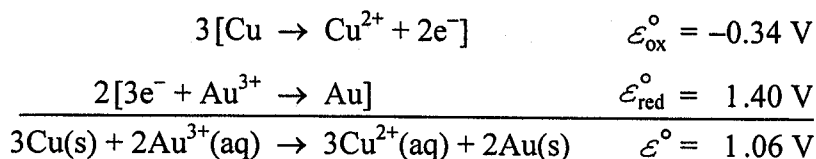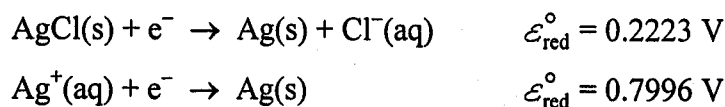
$$= -89 \text{ kJ} \quad \text{(spontaneous)}$$

Equilibrium constant:

$$K = \exp\left(\frac{n\mathcal{F}\mathcal{E}^\circ}{RT}\right) = \exp\left[\frac{(2)(96,485 \text{ C mol}^{-1})(0.46 \text{ J C}^{-1})}{(8.3145 \text{ J mol}^{-1} \text{ K}^{-1})(298.15 \text{ K})}\right] \approx 4 \times 10^{15}$$

(effectively ∞)

21. Similar to the two preceding exercises.

(a) Cu is oxidized to Cu^{2+} at the anode, and Au^{3+} is reduced to Au at the cathode. Six electrons are transferred:

$$3[Cu \rightarrow Cu^{2+} + 2e^-] \qquad\qquad \varepsilon^\circ_{ox} = -0.34 \text{ V}$$

$$\underline{2[3e^- + Au^{3+} \rightarrow Au] \qquad\qquad \varepsilon^\circ_{red} = 1.40 \text{ V}}$$

$$3Cu(s) + 2Au^{3+}(aq) \rightarrow 3Cu^{2+}(aq) + 2Au(s) \qquad \varepsilon^\circ = 1.06 \text{ V}$$

Oxidizing agent: $Au^{3+}(aq)$
Reducing agent: $Cu(s)$
Moles of electrons transferred: $n = 6$

(b) See (a) above for the cell equation.

(c) Standard cell potential:

$$\varepsilon^\circ = \varepsilon^\circ_{red} + \varepsilon^\circ_{ox} = 1.40 \text{ V} + \left(-0.34 \text{ V}\right) = 1.06 \text{ V}$$

Standard free energy ($n = 6$):

$$\Delta G^\circ = -n\mathscr{F}\varepsilon^\circ$$

$$= -6 \text{ mol } e^- \times \frac{96,485 \text{ C}}{\text{mol } e^-} \times \frac{1.06 \text{ J}}{\text{C}} = -6.14 \times 10^5 \text{ J}$$

$$= -614 \text{ kJ} \quad \text{(spontaneous)}$$

Equilibrium constant:

$$K = \exp\left(\frac{n\mathscr{F}\varepsilon^\circ}{RT}\right) = \exp\left[\frac{(6)(96,485 \text{ C mol}^{-1})(1.06 \text{ J C}^{-1})}{(8.3145 \text{ J mol}^{-1} \text{ K}^{-1})(298.15 \text{ K})}\right] \approx \exp 247.5 \rightarrow \infty$$

Extremely large or extremely small equilibrium constants often can be measured to high accuracy by electrochemical methods.
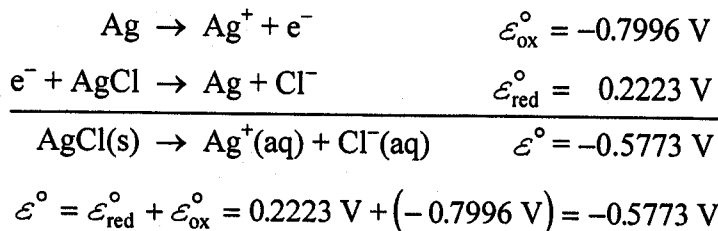
22. We begin with standard electrode potentials for the reduction of AgCl and Ag^+:

$$AgCl(s) + e^- \rightarrow Ag(s) + Cl^-(aq) \qquad \varepsilon^\circ_{red} = 0.2223 \text{ V}$$

$$Ag^+(aq) + e^- \rightarrow Ag(s) \qquad\qquad \varepsilon^\circ_{red} = 0.7996 \text{ V}$$

Since oxidation and reduction are reverse reactions, the potential ε°_{ox} for the oxidation of Ag to Ag^+ is implicit in the value of ε°_{red}:

$$Ag(s) \rightarrow Ag^+(aq) + e^- \qquad \mathcal{E}_{ox}^o = -\mathcal{E}_{red}^o = -0.7996 \text{ V}$$

(a) Combining the oxidation of Ag with the reduction of AgCl, we reconstruct the desired reaction:

$$Ag \rightarrow Ag^+ + e^- \qquad\qquad \mathcal{E}_{ox}^o = -0.7996 \text{ V}$$

$$\underline{e^- + AgCl \rightarrow Ag + Cl^- \qquad\qquad \mathcal{E}_{red}^o = 0.2223 \text{ V}}$$

$$AgCl(s) \rightarrow Ag^+(aq) + Cl^-(aq) \qquad \mathcal{E}^o = -0.5773 \text{ V}$$

$$\mathcal{E}^o = \mathcal{E}_{red}^o + \mathcal{E}_{ox}^o = 0.2223 \text{ V} + \left(-0.7996 \text{ V}\right) = -0.5773 \text{ V}$$

With $\mathcal{E}^o$ in hand, we then go on to calculate K_{sp} at 25°C:

$$K_{sp} = \exp\left(-\frac{\Delta G^o}{RT}\right) = \exp\left(\frac{n\mathscr{F}\mathcal{E}^o}{RT}\right)$$

$$= \exp\left[\frac{(1)\left(96{,}485.309 \text{ C mol}^{-1}\right)\left(-0.5773 \text{ J C}^{-1}\right)}{\left(8.3145 \text{ J mol}^{-1} \text{ K}^{-1}\right)\left(298.15 \text{ K}\right)}\right] = 1.74 \times 10^{-10}$$

(b) Since $\mathcal{E}^o < 0$ and $\Delta G^o > 0$, the reaction is nonspontaneous: $K_{sp} \ll 1$.

23. Use the same method as in Exercise 22, this time coupling the oxidation of Ag with the reduction of Ag_2CrO_4 (see Table C-21 in Appendix C of *PoC*):
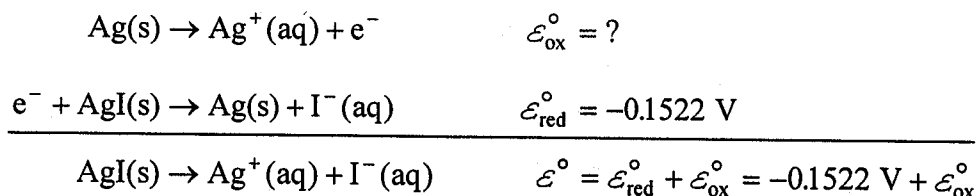
$$2[Ag \rightarrow Ag^+ + e^-] \qquad\qquad \mathcal{E}_{ox}^o = -0.7996 \text{ V}$$

$$\underline{2e^- + Ag_2CrO_4 \rightarrow 2Ag + CrO_4^{2-} \qquad\qquad \mathcal{E}_{red}^o = 0.4470 \text{ V}}$$

$$Ag_2CrO_4(s) \rightarrow 2Ag^+(aq) + CrO_4^{2-}(aq) \qquad \mathcal{E}^o = -0.3526 \text{ V}$$

$$\mathcal{E}^o = \mathcal{E}_{red}^o + \mathcal{E}_{ox}^o = 0.4470 \text{ V} + \left(-0.7996 \text{ V}\right) = -0.3526 \text{ V}$$
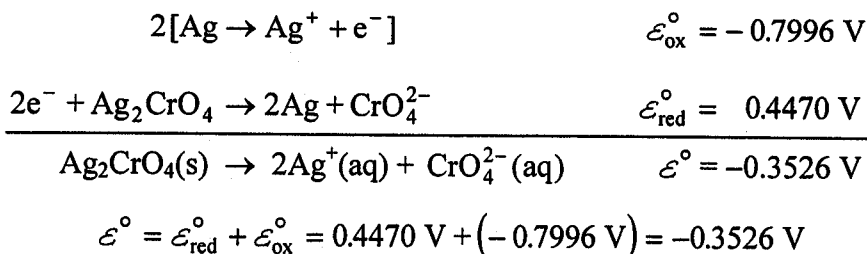
The solubility-product constant is then calculated as follows:

$$K_{sp} = \exp\left(-\frac{\Delta G^o}{RT}\right) = \exp\left(\frac{n\mathscr{F}\mathcal{E}^o}{RT}\right)$$

$$= \exp\left[\frac{(2)\left(96{,}485.309 \text{ C mol}^{-1}\right)\left(-0.3526 \text{ J C}^{-1}\right)}{\left(8.3145 \text{ J mol}^{-1} \text{ K}^{-1}\right)\left(298.15 \text{ K}\right)}\right] = 1.20 \times 10^{-12}$$

24. This problem can be solved even without explicit knowledge of the oxidation potential for silver.

First write the dissolution of AgI as the sum of two half-reactions, just as in the two preceding exercises:

$$Ag(s) \rightarrow Ag^+(aq) + e^- \qquad \mathcal{E}^\circ_{ox} = ?$$

$$e^- + AgI(s) \rightarrow Ag(s) + I^-(aq) \qquad \mathcal{E}^\circ_{red} = -0.1522 \text{ V}$$

$$AgI(s) \rightarrow Ag^+(aq) + I^-(aq) \qquad \mathcal{E}^\circ = \mathcal{E}^\circ_{red} + \mathcal{E}^\circ_{ox} = -0.1522 \text{ V} + \mathcal{E}^\circ_{ox}$$

Now compare with the dissolution of AgCl:

$$Ag(s) \rightarrow Ag^+(aq) + e^- \qquad \mathcal{E}^\circ_{ox} = ?$$

$$e^- + AgCl(s) \rightarrow Ag(s) + Cl^-(aq) \qquad \mathcal{E}^\circ_{red} = 0.2223 \text{ V}$$

$$AgCl(s) \rightarrow Ag^+(aq) + Cl^-(aq) \qquad \mathcal{E}^\circ = \mathcal{E}^\circ_{red} + \mathcal{E}^\circ_{ox} = 0.2223 \text{ V} + \mathcal{E}^\circ_{ox}$$
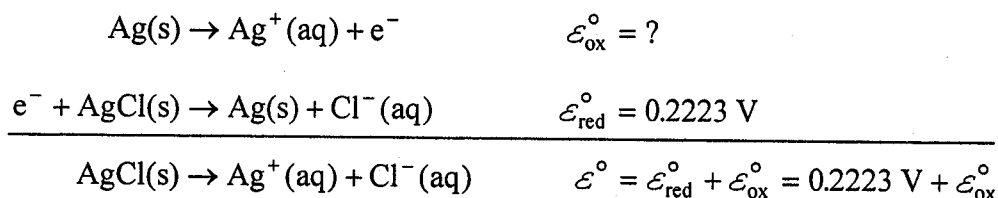
Next, use the relationship

$$\Delta G^\circ = -RT \ln K_{sp} = -n\mathscr{F}\mathcal{E}^\circ$$

to write expressions for the solubility-product constants:

$$K_{sp} = \exp\left(-\frac{\Delta G^\circ}{RT}\right) = \exp\left(\frac{n\mathscr{F}\mathcal{E}^\circ}{RT}\right)$$

$$K_{sp}(AgI) = \exp\left[\frac{n\mathscr{F}}{RT}\left(\mathcal{E}^\circ_{ox} - 0.1522 \text{ J C}^{-1}\right)\right]$$

$$K_{sp}(AgCl) = \exp\left[\frac{n\mathscr{F}}{RT}\left(\mathcal{E}^\circ_{ox} + 0.2223 \text{ J C}^{-1}\right)\right]$$

Note that $\mathcal{E}^\circ_{ox}$ is the same in each reaction: the standard oxidation potential for the oxidation of Ag to Ag$^+$. With $n\mathscr{F}/RT$ identical as well, we have the following ratio at 25°C:

$$\frac{K_{sp}(\text{AgI})}{K_{sp}(\text{AgCl})} = \exp\left[\frac{n\mathscr{F}}{RT}(-0.1522 - 0.2223)\text{ J C}^{-1}\right]$$

$$= \exp\left[\frac{(1)(96{,}485\text{ C mol}^{-1})(-0.3745\text{ J C}^{-1})}{(8.3145\text{ J mol}^{-1}\text{ K}^{-1})(298.15\text{ K})}\right]$$

$$= 4.67 \times 10^{-7}$$

Since both salts have the generic formula AgX, they also share the same algebraic equation for the solubility-product constant and molar solubility x:

$$K_{sp} = [\text{Ag}^+][\text{X}^-] = x^2$$

$$x = \sqrt{K_{sp}}$$

AgI, possessing the smaller value of K_{sp}, is therefore less soluble in water than AgCl. The ratio calculated above is less than one part in 2,000,000:

$$\frac{K_{sp}(\text{AgI})}{K_{sp}(\text{AgCl})} = 4.67 \times 10^{-7}$$

The relationship between cell voltage and concentration is explored in Exercises 25 through 33. See Section 17-6 and Example 17-8 in PoC.

25. Consider the Nernst equation:

$$\mathscr{E} = \mathscr{E}^\circ - \frac{RT}{n\mathscr{F}}\ln Q$$

The symbols $\mathscr{E}^\circ$ and $\mathscr{E}$ denote, respectively, the potential under standard conditions and the potential as a function of T (temperature) and Q (reaction quotient).

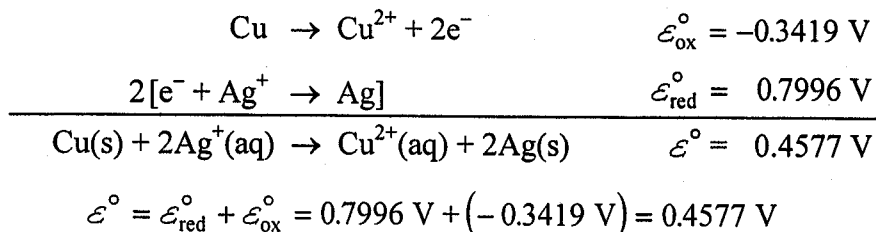**(a)** Observe that $\mathscr{E} = 0$ when $Q = K$, just as $\Delta G = 0$ when $Q = K$:

$$\mathscr{E}^\circ = -\frac{\Delta G^\circ}{n\mathscr{F}} = \frac{RT}{n\mathscr{F}}\ln K$$

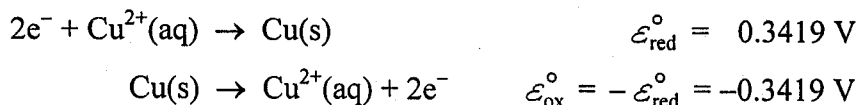The system is at equilibrium, as described in Section 14-8. See also page R17.4.

(b) When $Q = 1$ (and hence $\ln Q = 0$), both the cell potential and the difference in free energy assume their standard values:

$$\varepsilon = \varepsilon^\circ \qquad \Delta G = \Delta G^\circ$$

26. Cu is oxidized to Cu^{2+}, and Ag^+ is reduced to Ag. Two electrons pass from reducing agent to oxidizing agent, falling through a potential of 0.4577 V under standard conditions:

$$Cu \rightarrow Cu^{2+} + 2e^- \qquad\qquad \varepsilon^\circ_{ox} = -0.3419 \text{ V}$$

$$\underline{2[e^- + Ag^+ \rightarrow Ag] \qquad\qquad \varepsilon^\circ_{red} = 0.7996 \text{ V}}$$

$$Cu(s) + 2Ag^+(aq) \rightarrow Cu^{2+}(aq) + 2Ag(s) \qquad \varepsilon^\circ = 0.4577 \text{ V}$$

$$\varepsilon^\circ = \varepsilon^\circ_{red} + \varepsilon^\circ_{ox} = 0.7996 \text{ V} + \left(-0.3419 \text{ V}\right) = 0.4577 \text{ V}$$

Note that the oxidation potential for Cu is obtained as the negative of the corresponding reduction potential (its reverse reaction):

$$2e^- + Cu^{2+}(aq) \rightarrow Cu(s) \qquad\qquad \varepsilon^\circ_{red} = 0.3419 \text{ V}$$

$$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^- \qquad \varepsilon^\circ_{ox} = -\varepsilon^\circ_{red} = -0.3419 \text{ V}$$

Given ε°, n, T, and the concentrations of Cu^{2+} and Ag^+ needed to determine the reaction quotient,

$$Q = \frac{[Cu^{2+}]}{[Ag^+]^2}$$

we then use the Nernst equation to solve for the nonstandard voltage:

$$\varepsilon^\circ = 0.4577 \text{ V} \qquad\qquad n = 2 \qquad\qquad T = 298.15 \text{ K}$$

$$\varepsilon = \varepsilon^\circ - \frac{RT}{n\mathscr{F}}\ln Q = 0.4577 \text{ V} - \frac{0.05916 \text{ V}}{2}\log\frac{[Cu^{2+}]}{[Ag^+]^2}$$

The constant 0.05916 V, equal to $2.3026RT/\mathscr{F}$ at 25°C, is valid only when the base-10 logarithm is substituted for the natural logarithm.

(a) With both $[Cu^{2+}]$ and $[Ag^+]$ equal to 1.000 *M*, the reaction quotient stands at 1.000 and the cell delivers its standard voltage:

$$Q = \frac{[Cu^{2+}]}{[Ag^+]^2} = \frac{1.000}{(1.000)^2} = 1.000$$

$$\log Q = \log 1.000 = 0$$

$$\mathcal{E} = \mathcal{E}^\circ - \frac{0.05916 \text{ V}}{n} \log Q = 0.4577 \text{ V} - \frac{0.05916 \text{ V}}{2} \log 1.000 = 0.4577 \text{ V}$$

(b) The reaction quotient rises to 4.00,

$$Q = \frac{[Cu^{2+}]}{[Ag^+]^2} = \frac{1.000}{(0.500)^2} = 4.00$$

and the voltage drops accordingly:

$$\mathcal{E} = 0.4577 \text{ V} - \frac{0.05916 \text{ V}}{2} \log 4.00 = 0.4399 \text{ V}$$

(c) The reaction quotient falls to 0.500,

$$Q = \frac{[Cu^{2+}]}{[Ag^+]^2} = \frac{0.500}{(1.000)^2} = 0.500$$

and the voltage *rises* accordingly:

$$\mathcal{E} = 0.4577 \text{ V} - \frac{0.05916 \text{ V}}{2} \log 0.500 = 0.4666 \text{ V}$$

(d) The deviation from $\mathcal{E}^\circ$ caused by $Q = 2.00$ is equal in magnitude and opposite in sign to the deviation caused by $Q = 0.500$:

$$Q = \frac{[Cu^{2+}]}{[Ag^+]^2} = \frac{0.500}{(0.500)^2} = 2.00$$

$$\log 2.00 = -\log 0.500 = 0.301$$

The cell potential decreases by 0.0089 V:

$$\mathcal{E} = 0.4577 \text{ V} - \frac{0.05916 \text{ V}}{2} \log 2.00 = 0.4488 \text{ V}$$

27. Carry over the reaction from the preceding exercise:

$$Cu(s) + 2Ag^+(aq) \rightarrow Cu^{2+}(aq) + 2Ag(s) \qquad \varepsilon° = 0.4577 \text{ V}$$
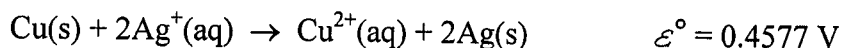
Two moles of electrons are transferred per mole of Cu ($n = 2$).

(a) The difference in standard free energy, $\Delta G° = -88.32$ kJ, is proportional to the standard cell voltage:

$$\Delta G° = -n\mathscr{F}\varepsilon° = -2 \text{ mol } e^- \times \frac{96{,}485 \text{ C}}{\text{mol } e^-} \times \frac{0.4577 \text{ J}}{C} = -8.832 \times 10^4 \text{ J}$$

A large drop in the standard free energy produces an exponentially large equilibrium constant:

$$K = \exp\left(-\frac{\Delta G°}{RT}\right) = \exp\left[-\frac{\left(-8.832 \times 10^4 \text{ J mol}^{-1}\right)}{\left(8.3145 \text{ J mol}^{-1} \text{ K}^{-1}\right)\left(298.15 \text{ K}\right)}\right] = 2.97 \times 10^{15}$$

(b) If $\varepsilon = 0$, then the cell must be at equilibrium ($Q = K$):

$$K = \frac{[Cu^{2+}]}{[Ag^+]^2} = 2.97 \times 10^{15}$$

$$[Ag^+] = \sqrt{\frac{[Cu^{2+}]}{K}} = \sqrt{\frac{1.000}{2.97 \times 10^{15}}} = 1.83 \times 10^{-8} \text{ } M$$

(c) The process is in equilibrium (and $\varepsilon = 0$) whenever $[Cu^{2+}]$ and $[Ag^+]$ satisfy the mass-action expression for K:

$$K = \frac{[Cu^{2+}]}{[Ag^+]^2} = 2.97 \times 10^{15}$$

$$[Ag^+] = \sqrt{\frac{[Cu^{2+}]}{K}} = \sqrt{\frac{5.000}{2.97 \times 10^{15}}} = 4.10 \times 10^{-8} \text{ } M$$

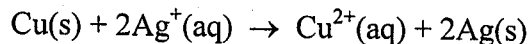**(d)** We calculate the equilibrium concentration of Cu^{2+} in analogous fashion:

$$[Cu^{2+}] = K[Ag^+]^2 = \left(2.97 \times 10^{15}\right)(1.000)^2 = 2.97 \times 10^{15} \text{ } M$$

The equilibrium constant is so large that the reaction goes effectively 100% to the right.

28. Solve the Nernst equation at 25°C,

$$\varepsilon = \varepsilon^\circ - \frac{0.05916 \text{ V}}{n} \log Q \qquad (T = 298.15 \text{ K})$$

for the reaction

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

given the following data:

$$\varepsilon^\circ = 0.4577 \text{ V} \qquad n = 2 \qquad [Cu^{2+}] = 1.000 \ M$$

(a) First, determine Q for $\varepsilon = 0.5000$ V. Then use Q to calculate the corresponding concentration of Ag^+:

$$\log Q = \frac{n\left(\varepsilon^\circ - \varepsilon\right)}{0.05916 \text{ V}} = \frac{2\left(0.4577 \text{ V} - 0.5000 \text{ V}\right)}{0.05916 \text{ V}} = -1.430$$

$$Q = \frac{[Cu^{2+}]}{[Ag^+]^2} = 10^{\log Q}$$

$$[Ag^+] = \sqrt{\frac{[Cu^{2+}]}{10^{\log Q}}} = \sqrt{\frac{1.000}{10^{-1.430}}} = 5.19 \ M \quad (3 \text{ sig fig})$$

The difference between ε° and ε (−0.0423 V) limits the result to three significant figures.

(b) Apply the same method as in (a) above:

$$\varepsilon = 0.4600 \text{ V} \qquad [Ag^+] = 1.1 \ M$$

(c) Again, use the same method:

$$\varepsilon = 0.4200 \text{ V} \qquad [Ag^+] = 0.231 \ M$$

29. We apply the Nernst equation to the reduction of Fe^{3+} to Fe^{2+} in acidic solution.

Standard voltage:

$$H_2 \rightarrow 2H^+ + 2e^- \qquad\qquad \varepsilon^\circ_{ox} = 0.000 \text{ V}$$
$$\underline{2[e^- + Fe^{3+} \rightarrow Fe^{2+}]} \qquad\qquad \underline{\varepsilon^\circ_{red} = 0.770 \text{ V}}$$
$$2Fe^{3+}(aq) + H_2(g) \rightarrow 2Fe^{2+}(aq) + 2H^+(aq) \qquad \varepsilon^\circ = 0.770 \text{ V}$$
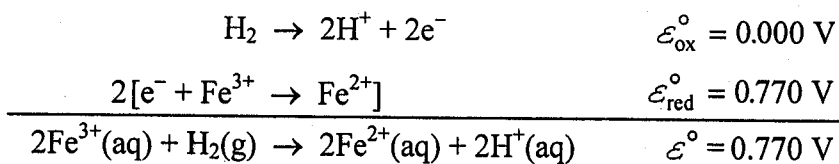
Nernst equation ($n = 2$):

$$\varepsilon = \varepsilon^{\circ} - \frac{0.05916 \text{ V}}{n} \log Q \qquad (T = 298.15 \text{ K})$$

$$Q = \frac{[Fe^{2+}]^2 [H^+]^2}{[Fe^{3+}]^2 \, P_{H_2}}$$

If $Q = 1$, as it does under the conditions specified in (a), then the cell delivers its standard potential of 0.770 V:

$$[H^+] = 10^{-pH} = 10^{-0.000} = 1.00 \text{ } M$$

$$Q = \frac{[Fe^{2+}]^2 [H^+]^2}{[Fe^{3+}]^2 \, P_{H_2}} = \frac{(1.00)^2 (1.00)^2}{(1.00)^2 (1.000)} = 1.00$$

$$\varepsilon = \varepsilon^{\circ} - \frac{0.05916 \text{ V}}{2} \log 1.00 = \varepsilon^{\circ} = 0.770 \text{ V}$$

Under any other conditions (such as those given in part b, for example), the reaction quotient is unequal to 1,

$$[H^+] = 10^{-pH} = 10^{-1.000} = 1.00 \times 10^{-1} \text{ } M$$

$$Q = \frac{[Fe^{2+}]^2 [H^+]^2}{[Fe^{3+}]^2 \, P_{H_2}} = \frac{(1.00)^2 (1.00 \times 10^{-1})^2}{(1.00)^2 (1.000)} = 1.00 \times 10^{-2}$$

and the instantaneous voltage ε differs from the standard value ε°:

$$\varepsilon = 0.770 \text{ V} - \frac{0.05916 \text{ V}}{2} \log(1.00 \times 10^{-2})$$

$$= 0.770 \text{ V} - \frac{0.05916 \text{ V}}{2} (-2.000)$$

$$= 0.829 \text{ V}$$

The remaining calculations are all done in the same way. In each case, the reaction quotient is an even power of 10:

$$Q = 10^{-2m} \qquad -\log Q = 2m \qquad (m = 0, 1, 2, \ldots 7)$$

Results are collected in the following table:

	$[Fe^{3+}]$ (M)	P_{H_2} (atm)	$[Fe^{2+}]$ (M)	pH	Q	ε (V)
(a)	1.00	1.000	1.00	0.000	1.00×10^{0}	0.770
(b)	1.00	1.000	1.00	1.000	1.00×10^{-2}	0.829
(c)	1.00	1.000	1.00	2.000	1.00×10^{-4}	0.888
(d)	1.00	1.000	1.00	3.000	1.00×10^{-6}	0.947
(e)	1.00	1.000	1.00	4.000	1.00×10^{-8}	1.007
(f)	1.00	1.000	1.00	5.000	1.00×10^{-10}	1.066
(g)	1.00	1.000	1.00	6.000	1.00×10^{-12}	1.125
(h)	1.00	1.000	1.00	7.000	1.00×10^{-14}	1.184

30. Use the same method as in the preceding exercise, substituting the appropriate pressure (in atmospheres) into the reaction quotient Q:

$$[H^+] = 10^{-pH} = 10^{-0.000} = 1.00 \ M$$

$$Q = \frac{[Fe^{2+}]^2[H^+]^2}{[Fe^{3+}]^2 \, P_{H_2}} = \frac{(1.00)^2(1.00)^2}{(1.00)^2 \, P_{H_2}} = \frac{1.00}{P_{H_2}}$$

$$\varepsilon = \varepsilon^\circ - \frac{0.05916 \ V}{n} \log Q \qquad (\varepsilon^\circ = 0.770 \ V, \ n = 2, \ T = 298.15 \ K)$$

Results are tabulated below:

	$[Fe^{3+}]$ (M)	P_{H_2} (atm)	$[Fe^{2+}]$ (M)	pH	Q	ε (V)
(a)	1.00	0.250	1.00	0.000	4.00	0.752
(b)	1.00	0.500	1.00	0.000	2.00	0.761
(c)	1.00	0.750	1.00	0.000	1.33	0.766
(d)	1.00	1.000	1.00	0.000	1.00	0.770

31. We continue with the reaction introduced in Exercise 29:

$$2Fe^{3+}(aq) + H_2(g) \rightarrow 2Fe^{2+}(aq) + 2H^+(aq)$$
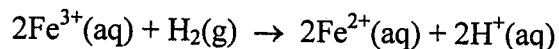
$$\varepsilon^\circ = 0.770 \ V \qquad n = 2 \qquad Q = \frac{[Fe^{2+}]^2[H^+]^2}{[Fe^{3+}]^2 \, P_{H_2}}$$

(a) Given a nonstandard cell potential,

$$\varepsilon = 0.800 \text{ V}$$

we use the Nernst equation to calculate the reaction quotient (Q) and thence the concentration of Fe^{3+}:

$$\log Q = \frac{n\left(\varepsilon^\circ - \varepsilon\right)}{0.05916 \text{ V}} = \frac{2\left(0.770 \text{ V} - 0.800 \text{ V}\right)}{0.05916 \text{ V}} = -1.014$$

$$Q = \frac{(1.00)^2(1.00)^2}{[Fe^{3+}]^2(1.00)} = \frac{1.00}{[Fe^{3+}]^2} = 10^{\log Q}$$

$$[Fe^{3+}] = \sqrt{\frac{1.00}{10^{\log Q}}} = \sqrt{\frac{1.00}{10^{-1.014}}} = 3.2 \text{ } M$$

The subtraction of ε from ε° (to yield -0.030 V) limits the result to two significant figures.

(b) The difference between ΔG and ΔG° is proportional to the difference between ε and ε°:

$$\Delta G - \Delta G^\circ = -n\mathscr{F}\left(\varepsilon - \varepsilon^\circ\right)$$

$$= -2 \text{ mol e}^- \times \frac{96{,}485 \text{ C}}{\text{mol e}^-} \times \frac{(0.800 - 0.770) \text{ J}}{\text{C}} = -5.8 \times 10^3 \text{ J}$$

$$= -5.8 \text{ kJ}$$

Alternatively, we may use Q directly to arrive at the same value (expressed per mole of H_2):

$$\Delta G - \Delta G^\circ = RT \ln Q$$

$$= 2.303RT \log Q$$

$$= (2.303)(8.3145 \text{ J mol}^{-1} \text{ K}^{-1})(298.15 \text{ K})(-1.014)$$
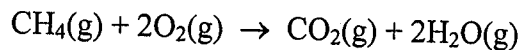
$$= -5.8 \times 10^3 \text{ J mol}^{-1}$$

(c) With a reaction quotient less than 1,

$$Q = 10^{\log Q} = 10^{-1.014} = 0.097$$

the system is overweighted toward reactants. The process will go to the right. See (a) above for the calculation of Q.

32. The reaction quotient and voltage for the process

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$$

are unaffected if all partial pressures are changed simultaneously by the same factor:
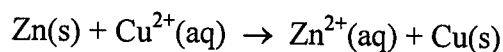
$$Q = \frac{P_{CO_2} P_{H_2O}^2}{P_{CH_4} P_{O_2}^2}$$

$$\varepsilon = \varepsilon^° - \frac{RT}{n\mathscr{F}} \ln Q$$

There are three moles of gaseous reactants and three moles of gaseous products. See Section 12-6 and Example 12-13 in *PoC*.

33. The cell potential

$$\varepsilon = \varepsilon^° - \frac{RT}{n\mathscr{F}} \ln Q$$

for the transformation

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

is determined by a reaction quotient equal to unity in each of the three systems:

$$Q = \frac{[Zn^{2+}]}{[Cu^{2+}]} = \frac{0.50}{0.50} = \frac{1.00}{1.00} = \frac{2.00}{2.00} = 1.00$$

The voltage thus takes on its standard value of 1.10 V, regardless of the separate concentrations $[Zn^{2+}]$ and $[Cu^{2+}]$ that contribute to Q:
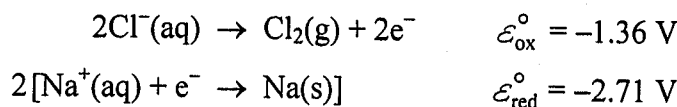
$$\varepsilon = \varepsilon^° - \frac{RT}{n\mathscr{F}} \ln Q = \varepsilon^° - \frac{RT}{n\mathscr{F}} \ln 1.00 = 1.10 \text{ V} - 0 = 1.10 \text{ V}$$

Electrolytic cells are covered in Section 17-9 of PoC *and illustrated further in Examples 17-9 and 17-10. Exercises 36 through 40, in particular, provide illustrations of Faraday's laws: (1) The mass of material consumed or produced at an electrode varies directly with the total amount of electric charge flowing through the cell. (2) For a given amount of charge, the mass of material varies directly with m (the molar mass) and inversely with n (the number of moles of electrons transferred per mole of substance).*

34. The first step is to decompose the process

$$2Na^+(aq) + 2Cl^-(aq) \rightarrow 2Na(s) + Cl_2(g)$$
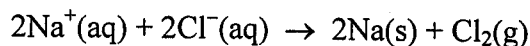
into half-reactions and consult Table C-21 in *PoC*:

$$2Cl^-(aq) \rightarrow Cl_2(g) + 2e^- \qquad \mathcal{E}^o_{ox} = -1.36 \text{ V}$$
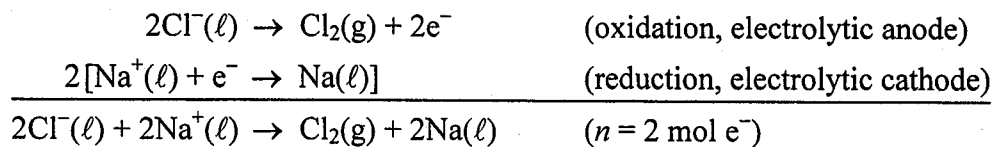
$$2[Na^+(aq) + e^- \rightarrow Na(s)] \qquad \mathcal{E}^o_{red} = -2.71 \text{ V}$$

That done, we note that the reduction of $Na^+(aq)$ is thermodynamically less favored than the reduction of $H_2O(\ell)$. The standard potential for the reduction of water (−0.83 V) is *less negative* than −2.71 V:

$$2H_2O(\ell) + 2e^- \rightarrow H_2(g) + 2OH^-(aq) \qquad \mathcal{E}^o_{red} = -0.83 \text{ V}$$

Electrons therefore will flow to H_2O (not Na^+), and $H_2(g)$ will be produced at the cathode instead of $Na(s)$.
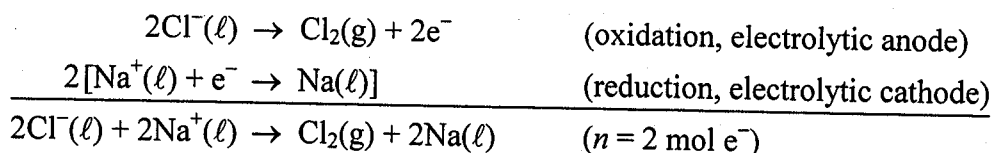
35. See Section 17-9 of *PoC* for a description of an electrolytic cell.

(a) The redox conventions are the same as those for a galvanic cell. Oxidation occurs at the anode; reduction occurs at the cathode:

$$2Cl^-(\ell) \rightarrow Cl_2(g) + 2e^- \qquad \text{(oxidation, electrolytic anode)}$$
$$\underline{2[Na^+(\ell) + e^- \rightarrow Na(\ell)]} \qquad \text{(reduction, electrolytic cathode)}$$
$$2Cl^-(\ell) + 2Na^+(\ell) \rightarrow Cl_2(g) + 2Na(\ell) \qquad (n = 2 \text{ mol } e^-)$$

(b) The anode of an electrolytic cell is held at positive potential. Electrons are withdrawn from the anode and delivered to the external power supply.

36. The half-reactions for this electrolytic cell (see Exercise 35) show that two moles of electrons are delivered for every two moles of sodium produced:

$$2Cl^-(\ell) \rightarrow Cl_2(g) + 2e^- \qquad \text{(oxidation, electrolytic anode)}$$

$$\underline{2[Na^+(\ell) + e^- \rightarrow Na(\ell)]} \qquad \text{(reduction, electrolytic cathode)}$$

$$2Cl^-(\ell) + 2Na^+(\ell) \rightarrow Cl_2(g) + 2Na(\ell) \qquad (n = 2 \text{ mol } e^-)$$

Given a mass of sodium in grams, we first calculate the total number of coulombs required:

$$100.0 \text{ g Na} \times \frac{1 \text{ mol Na}}{22.98977 \text{ g Na}} \times \frac{2 \text{ mol } e^-}{2 \text{ mol Na}} \times \frac{96{,}485 \text{ C}}{\text{mol } e^-} = 4.197 \times 10^5 \text{ C}$$

After that, we determine the time needed for the current to deliver this quantity of charge:
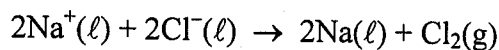
$$4.197 \times 10^5 \text{ C} \times \frac{1 \text{ s}}{10.0 \text{ C}} \times \frac{1 \text{ h}}{3600 \text{ s}} = 11.7 \text{ h}$$

Doing so, we make use of both the Faraday constant ($\mathscr{F}$) and the definition of the ampere (A):

$$\mathscr{F} = 96{,}485 \text{ C mol}^{-1}$$

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

37. Refer to Exercises 35 and 36 for the electrolysis of molten sodium chloride. One mole of chlorine gas is evolved for every two moles of Na^+ reduced:

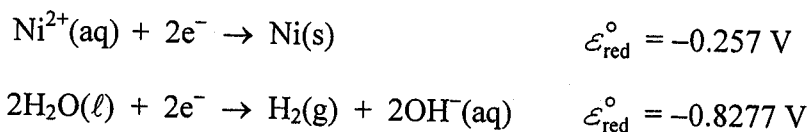$$2Na^+(\ell) + 2Cl^-(\ell) \rightarrow 2Na(\ell) + Cl_2(g)$$

Given 1.000 gram of sodium, we straightforwardly determine the corresponding amount and volume of Cl_2.

$$n = 1.000 \text{ g Na}^+ \times \frac{1 \text{ mol Na}^+}{22.98977 \text{ g Na}^+} \times \frac{1 \text{ mol Cl}_2}{2 \text{ mol Na}^+} = 2.175 \times 10^{-2} \text{ mol Cl}_2$$

$$V = \frac{nRT}{P} = \frac{(2.175 \times 10^{-2} \text{ mol})(0.08206 \text{ atm L mol}^{-1} \text{ K}^{-1})(298.15 \text{ K})}{1.000 \text{ atm}} = 0.5321 \text{ L}$$

See Section 10-2 for a treatment of the ideal gas law.

38. Compare the voltages associated with the competing half-reactions:

$$Ni^{2+}(aq) + 2e^- \rightarrow Ni(s) \qquad\qquad \varepsilon^\circ_{red} = -0.257 \text{ V}$$

$$2H_2O(\ell) + 2e^- \rightarrow H_2(g) + 2OH^-(aq) \qquad \varepsilon^\circ_{red} = -0.8277 \text{ V}$$

The nickel(II) ion, Ni^{2+}, has the more positive (less negative) standard reduction potential. Since the reduction of Ni^{2+} to Ni is more favorable than the reduction of H_2O to H_2, the proposed reaction involving Ni^{2+} can indeed proceed in aqueous solution.

39. The definition of current,

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

enables us to calculate the total charge delivered in the stated time:

$$\text{Current} \times \text{time} = \text{charge}$$

Recalling, specifically, that $1 \text{ A} = 1 \text{ C s}^{-1}$, we multiply amperes (coulombs per second) by the time in seconds to obtain the number of coulombs:

$$\text{Ampere} \times \text{second} = \frac{\text{coulomb}}{\text{second}} \times \text{second} = \text{coulomb}$$

The total charge thus obtained is the same for all three systems:

CURRENT	TIME	CHARGE

$$\frac{35.0 \text{ C}}{\text{s}} \times \left(2.00 \text{ h} \times \frac{3600 \text{ s}}{\text{h}}\right) = 2.52 \times 10^5 \text{ C}$$

Given this amount of charge, we subsequently use $\mathscr{F}$, n, and the molar mass $\mathscr{m}$ to convert coulombs into electrons into grams of metal produced, as shown in the calculations below. See also Example 17-9 in *PoC*, beginning on page R17.18.

(a) Two moles of electrons are needed to transform one mole of Cu^{2+} into one mole of Cu:

$$\text{CHARGE} \times \frac{1}{\mathscr{F}} \times \frac{1}{n} \times \mathcal{m} = \text{MASS}$$

$$2.52 \times 10^5 \text{ C} \times \frac{1 \text{ mol e}^-}{96{,}485 \text{ C}} \times \frac{1 \text{ mol Cu}}{2 \text{ mol e}^-} \times \frac{63.546 \text{ g Cu}}{\text{mol Cu}} = 83.0 \text{ g Cu}$$

(b) A similar calculation, this time for the reduction of Ni^{2+} to Ni. As above, $n = 2$:

$$2.52 \times 10^5 \text{ C} \times \frac{1 \text{ mol e}^-}{96{,}485 \text{ C}} \times \frac{1 \text{ mol Ni}}{2 \text{ mol e}^-} \times \frac{58.693 \text{ g Ni}}{\text{mol Ni}} = 76.6 \text{ g Ni}$$

(c) Again, two moles of electrons are needed to reduce one mole of Fe^{2+} to one mole of Fe:

$$2.52 \times 10^5 \text{ C} \times \frac{1 \text{ mol e}^-}{96{,}485 \text{ C}} \times \frac{1 \text{ mol Fe}}{2 \text{ mol e}^-} \times \frac{55.845 \text{ g Fe}}{\text{mol Fe}} = 72.9 \text{ g Fe}$$

To sum up: Since each of the three reductions here involves the same change in oxidation number,

$$M^{2+}(aq) + 2e^- \rightarrow M(s) \qquad (n = 2 \text{ mol e}^-)$$
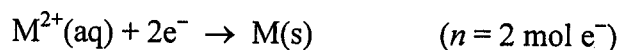
and since the total charge carried by the current is the same throughout, the mass of product is directly proportional to the molar mass.

40. The governing equations with their corresponding units are set forth below:

$$\text{Current} = \frac{\text{charge}}{\text{time}} \qquad \qquad \text{Concentration} \times \text{volume} = \text{amount}$$

$$A = \frac{C}{s} \qquad \qquad \frac{\text{mol}}{L} \times L = \text{mol}$$

(a) First, we apply the relationship between concentration, volume, and amount to establish the quantity of Ag^+ on hand:

$$\frac{0.200 \text{ mol Ag}^+}{L} \times 0.200 \text{ L} = 0.0400 \text{ mol Ag}^+$$

Using the Faraday constant to go from electrons to coulombs,

$$\mathcal{F} = \frac{96,485 \text{ C}}{\text{mol e}^-}$$

we then calculate the total charge and hence the time required for the specified current:

$$\text{Time} = \frac{\text{charge}}{\text{current}} = \frac{0.0400 \text{ mol Ag}^+ \times \dfrac{1 \text{ mol e}^-}{\text{mol Ag}^+} \times \dfrac{96,485 \text{ C}}{\text{mol e}^-}}{3.00 \text{ A} \times \dfrac{1 \text{ C s}^{-1}}{\text{A}}} = 1286 \text{ s} = 21.4 \text{ min}$$

(b) See part (c) below for a more detailed explanation of the following calculation:

$$[\text{Ag}^+(100 \text{ s})] = \frac{\text{original amount} - \text{amount removed}}{\text{volume}}$$

$$= \frac{0.0400 \text{ mol} - \left(3.00 \text{ C s}^{-1}\right)\left(100 \text{ s}\right) \times \dfrac{1 \text{ mol}}{96,485 \text{ C}}}{0.200 \text{ L}}$$

$$= \frac{0.0400 \text{ mol} - 0.00311 \text{ mol}}{0.200 \text{ L}} = 0.184 \ M$$

(c) Given the magnitude and duration of the current, we calculate the total charge delivered:

$$\text{Charge} = \text{current} \times \text{time}$$

The Faraday constant enables us to convert this charge into the amount of Ag^+ ions removed from solution ($n = 1$ mol e$^-$):

$$\overset{\text{CURRENT}}{\left(3.00 \text{ C s}^{-1}\right)} \overset{\text{TIME}}{\left(200 \text{ s}\right)} \times \underset{\underset{\substack{\text{FARADAY} \\ \text{CONSTANT}}}{\uparrow}}{\frac{1 \text{ mol e}^-}{96,485 \text{ C}}} \times \underset{\underset{n}{\uparrow}}{\frac{1 \text{ mol Ag}^+}{1 \text{ mol e}^-}} = 0.00622 \text{ mol Ag}^+$$

The new concentration at $t = 200$ s follows directly:

$$[Ag^+(200 \text{ s})] = \frac{\text{original amount} - \text{amount removed}}{\text{volume}}$$

$$= \frac{0.0400 \text{ mol} - 0.00622 \text{ mol}}{0.200 \text{ L}}$$

$$= 0.169 \; M$$

Observe that the amount of Ag^+ removed is directly proportional to the elapsed time.

(d) Similar:

$$[Ag^+(300 \text{ s})] = \frac{0.0400 \text{ mol} - (3.00 \text{ C s}^{-1})(300 \text{ s}) \times \dfrac{1 \text{ mol}}{96{,}485 \text{ C}}}{0.200 \text{ L}} = 0.153 \; M$$