- 7. (a) Internal-combustion engines are a major source of pollution and environmental damage. Electric cars powered by hydrogen fuel cells are seen as "pollution free."
 - (b) The number of lead-acid batteries needed to power an electric car would make the car very heavy. Used lead-acid batteries are a major source of lead pollution.
 - (c) Advances in hydrogen fuel cells could make electric cars the "green" solution to pollution from internal-combustion engines.
- 8. Consumer magazines are a good source of information on cells and batteries, regarding their reliability, cost, simplicity of use, safety (leakage), size (volume), shelf life, active life, energy density, power capacity, maintenance, disposal, environmental impact, and ability to be recharged.
- 9. Lithium—iodine batteries are commonly used in pacemakers, but some are powered by radioactive isotopes. Conventional pacemaker batteries last from four to eight years, depending how much the heart uses the pacemaker. A doctor tracks signals from the pacemaker to ascertain when the battery is nearing the end of its life. Rechargeable batteries generally hold less energy, and would need to be replaced more often.

9.5 GALVANIC CELLS

PRACTICE

(Page 700)

Understanding Concepts

1. A galvanic cell is an arrangement of two half-cells that spontaneously produces electricity.

A half-cell is an electrode-electrolyte combination forming one-half of a complete cell.

A porous boundary is a barrier that separates electrolytes while still permitting the movement of ions.

An inert electrode is a solid conductor that serves as an anode or a cathode in a voltaic cell, but is chemically unreactive

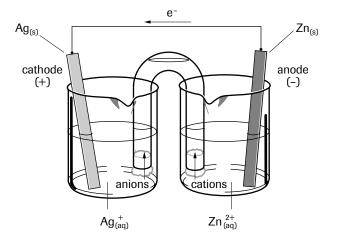
2. A cathode is the electrode where reduction occurs.

An anode is the electrode where oxidation occurs.

- 3. (a) cathode
 - (b) anode
 - (c) anode
 - (d) cathode
- 4. An inert electrode is used in a half-cell where no conducting solid is involved in the half-reaction equation.
- 5. The solution in a salt bridge must be a "spectator" electrolyte chemically; that is, its ions must not react with the half-cell ions that pass through.

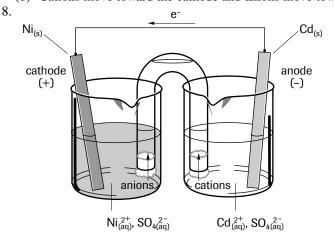
SOA
$$Ag_{(s)} \mid Ag_{(aq)}^{+} \mid Zn_{(aq)}^{2+} \mid Zn_{(s)}$$
 SRA
$$cathode \quad 2 \left[Ag_{(aq)}^{+} + e^{-} \rightarrow Ag_{(s)} \right]$$
 anode
$$Zn_{(s)} \rightarrow Zn_{(aq)}^{2+} + 2 e^{-}$$

$$net \qquad 2 Ag_{(aq)}^{+} + Zn_{(s)} \rightarrow Ag_{(s)} + Zn_{(aq)}^{2+}$$



$$\begin{array}{c} -SOA- \\ Pt_{(s)} \mid Na_{(aq)}^{+}, Cl_{(aq)}^{-}, O_{2(g)}, H_{2}O_{(l)} \parallel Al_{(aq)}^{3+} \mid Al_{(s)} \\ \\ Cathode & 3 \left[O_{2(g)} + 2 H_{2}O_{(l)} + 4 e^{-} \rightarrow 4 OH_{(aq)}^{-} \right] \\ \\ anode & 4 \left[Al_{(s)} \rightarrow Al_{(aq)}^{3+} + 3 e^{-} \right] \\ \\ net & 4 Al_{(s)} + 3 O_{2(g)} + 6 H_{2}O_{(l)} \rightarrow 4 Al_{(aq)}^{3+} + 12 OH_{(aq)}^{-} \right] \\ \\ net & 4 Al_{(s)} + 3 O_{2(g)} + 6 H_{2}O_{(l)} \rightarrow 4 Al(OH)_{3(s)} \\ \\ \\ O_{2(g)} & \\ \\ Cathode \\ (+) & \\ \\ O_{2(g)} & \\ \\ O_$$

- 7. (a) Ions move to maintain electrical neutrality at each electrode. In a simple voltaic (galvanic) cell composed of metals and metal ions, reduction removes positive ions from the solution around the cathode, and oxidation adds positive ions to the solution around the anode. Anions move toward the anode to balance the excess positive charge in the solution around the anode, while cations move toward the cathode to replace the positive charge being removed from the solution around the cathode. Meanwhile, electrons move externally from the anode to the cathode.
 - (b) Cations move toward the cathode and anions move toward the anode.



9. The nickel cathode could be replaced by any inert conducting material such as carbon or platinum. The anode solution could be replaced with an inert aqueous electrolyte such as aqueous potassium sulfate.

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PRACTICE

(Page 708)

Understanding Concepts

10. (a) cathode
$$\operatorname{Sn_{(aq)}^{2+}} + 2e^- \to \operatorname{Sn_{(s)}} \qquad E_r^\circ = -0.14 \, \mathrm{V}$$
 anode $\operatorname{Cr_{(s)}} \to \operatorname{Cr_{(aq)}^{2+}} + 2e^- \qquad E_r^\circ = -0.91 \, \mathrm{V}$ net $\operatorname{Sn_{(aq)}^{2+}} + \operatorname{Cr_{(s)}} \to \operatorname{Sn_{(s)}} + \operatorname{Cr_{(aq)}^{2+}}$ $\Delta E^\circ = E_r^\circ_{(cathode)} - E_r^\circ_{(anode)} = -0.14 \, \mathrm{V} - (-0.91 \, \mathrm{V})$ $\Delta E^\circ = +0.77 \, \mathrm{V}$

The standard cell potential is +0.77 V.

(b) cathode
$$SO_{4(aq)}^{2-} + 4 H_{(aq)}^{+} + 2 e^{-} \rightarrow H_{2}SO_{3(aq)} + H_{2}O_{(l)} E_{r}^{\circ} = +0.17 \text{ V}$$
 anode $Co_{(s)} \rightarrow Co_{(aq)}^{2+} + 2e^{-} E_{r}^{\circ} = -0.28 \text{ V}$ net $Co_{(s)} + SO_{4(aq)}^{2-} + 4 H_{(aq)}^{+} \rightarrow H_{2}SO_{3(aq)} + H_{2}O_{(l)} + Co_{(aq)}^{2+}$ $\Delta E^{\circ} = E_{r}^{\circ}_{(cathode)} - E_{r}^{\circ}_{(anode)}$ $= +0.17 \text{ V} - (-0.28 \text{ V})$ $\Delta E^{\circ} = +0.45 \text{ V}$

The standard cell potential is +0.45 V.

(c) cathode
$$O_{2(g)} + 2 H_2 O_{(l)} + 4 e^- \rightarrow 4 OH_{(aq)}^ E_r^{\circ} = +0.40 \text{ V}$$
 anode $E_r^{\circ} = +0.40 \text{ V}$ $E_r^{\circ} = -0.83 \text{ V}$ net $E_r^{\circ} = -0.83 \text{ V}$ $E_r^{\circ} = -0.83 \text{ V}$

The standard cell potential is +1.23 V.

11. (a)
$$Cu_{(s)} \mid Cu_{(aq)}^{2+} \parallel Pb_{(aq)}^{2+} \mid Pb_{(s)}$$
 cathode anode
$$\Delta E^{\circ} = E_{r \text{ (cathode)}}^{\circ} - E_{r \text{ (anode)}}^{\circ}$$

$$= +0.34 \text{ V} - (-0.13 \text{ V})$$

$$\Delta E^{\circ} = +0.47 \text{ V}$$

The standard cell potential is +0.47 V.

$$\begin{array}{lll} \text{(b)} & & \text{Ni}_{(s)} \mid \text{Ni}_{(aq)}^{2+} \parallel Zn_{(aq)}^{2+} \mid Zn_{(s)} \\ & \text{cathode} & \text{anode} \\ & \Delta E^{\circ} & = E_{r}^{\circ}_{(\text{cathode})} - E_{r}^{\circ}_{(\text{anode})} \\ & = -0.26 \text{ V} - (-0.76 \text{ V}) \\ & \Delta E^{\circ} & = +0.50 \text{ V} \end{array}$$

The standard cell potential is +0.50 V.

(c)
$$\begin{aligned} & \text{Pt}_{(\text{s})} \mid \text{Fe}_{(\text{aq})}^{2+}, \text{Fe}_{(\text{aq})}^{3+} \parallel \text{H}_{(\text{aq})}^{+}, \text{H}_{2(\text{g})} \mid \text{Pt}_{(\text{s})} \\ & \text{cathode} & \text{anode} \end{aligned}$$

$$\Delta E^{\circ} = E_{\text{r}}^{\circ}_{(\text{cathode})} - E_{\text{r}}^{\circ}_{(\text{anode})}$$

$$\Delta E^{\circ} = +0.77 \text{ V} - (0.00 \text{ V})$$

$$\Delta E^{\circ} = +0.77 \text{ V}$$

The standard cell potential is +0.77 V.

12. cathode
$$Au_{(aq)}^{3+} + 3 e^- \rightarrow Au_{(s)}$$
 $E_r^{\circ} = +1.50 \text{ V}$ anode $In_{(s)} \rightarrow In_{(aq)}^{3+} + 3 e^ E_r^{\circ} = ?$

net $Au_{(aq)}^{3+} + In_{(s)} \rightarrow Au_{(s)} + In_{(aq)}^{3+}$ $\Delta E^{\circ} = +1.84 \text{ V}$
 $\Delta E^{\circ} = E_r^{\circ}_{(cathode)} - E_r^{\circ}_{(anode)}$
 $E_r^{\circ}_{(anode)} = E_r^{\circ}_{(cathode)} - \Delta E^{\circ}$
 $= +1.50 \text{ V} - (+1.84 \text{ V})$
 $E_r^{\circ}_{(anode)} = -0.34 \text{ V}$

The standard reduction potential for the $In_{(aa)}^{3+}$ | $In_{(s)}$ half-cell is -0.34 V.

- 13. If the standard lithium cell is chosen as the reference half-cell with its reduction potential defined as 0.00 V, then 3.04 V must be added to each reduction potential in the table. Therefore, the reduction potential for the copper half-cell becomes +3.38 V and the reduction potential for the zinc half-cell becomes +2.28 V.
- 14. The chemical system has come to equilibrium.

Applying Inquiry Skills

15. Analysis

cathode anode
$$C_{(s)} \mid Cr_2O_{7(aq)}^{2-}, Cr_{(aq)}^{3+} \parallel Pd_{(aq)}^{2+} \mid Pd_{(s)}$$

$$\Delta E^{\circ} = +1.23 \text{ V} \qquad E_{r}^{\circ} = ?$$

$$\Delta E^{\circ} = E_{r \text{ (cathode)}}^{\circ} - E_{r \text{ (anode)}}^{\circ}$$

$$E_{r \text{ (anode)}}^{\circ} = E_{r \text{ (cathode)}}^{\circ} - \Delta E^{\circ}$$

$$= +1.23 \text{ V} - (+0.28 \text{ V})$$

$$E_{r \text{ (anode)}}^{\circ} = +0.95 \text{ V}$$

The standard reduction potential for the $Pd_{(aq)}^{2+}\mid Pd_{(s)}$ half-cell is +0.95 V.

cathode anode
$$\begin{array}{lll} {\rm Pd}_{(\rm s)} \mid {\rm Pd}_{(\rm aq)}^{2+} \parallel {\rm Tl}_{(\rm aq)}^+ \mid {\rm Tl}_{(\rm s)} \\ & E_{\rm r}^{\,\circ} \, = \, +0.95 \, {\rm V} \quad E_{\rm r}^{\,\circ} = ? \\ & E_{\rm r}^{\,\circ}_{\,\, (\rm anode)} \, = \, E_{\rm r}^{\,\circ}_{\,\, (\rm cathode)} \, - \, \Delta E^{\circ} \\ & = \, +0.95 \, {\rm V} \, - \, (\, +1.29 \, {\rm V}) \\ & E_{\rm r}^{\,\circ}_{\,\, (\rm anode)} \, = \, -0.34 \, {\rm V} \end{array}$$

The standard reduction potential for the $Tl_{(aq)}^+ \mid Tl_{(s)}$ half-cell is -0.34 V.

cathode anode
$$Tl_{(s)} \mid Tl_{(aq)}^{+} \parallel Ti_{(aq)}^{2+} \mid Ti_{(s)}$$

$$\Delta E^{\circ} = +1.29 \text{ V}$$

$$E_{r}^{\circ} = -0.34 \text{ V} \quad E_{r}^{\circ} = ?$$

$$E_{r \text{ (anode)}}^{\circ} = E_{r \text{ (cathode)}}^{\circ} - \Delta E^{\circ}$$

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=
$$-0.34 \text{ V} - (+1.29 \text{ V})$$

 $E_{\text{r (anode)}}^{\circ} = -1.63 \text{ V}$

The standard reduction potential for the $Ti^{2+}_{(aq)}\mid Ti_{(s)}$ half-cell is –1.63 V.

According to the evidence, the relative strength of the four oxidizing agents, in decreasing order of E_r° , is:

SOA
$$\operatorname{Cr_2O_{7(aq)}^{2-}} + 14 \operatorname{H}^+_{(aq)} + 6 \operatorname{e}^- \rightleftharpoons \operatorname{Cr}^{3+}_{(aq)} + 7 \operatorname{H_2O_{(l)}} E_r^{\circ} = +1.23 \operatorname{V}$$

$$\operatorname{Pd}^{2+}_{(aq)} + 2 \operatorname{e}^- \rightleftharpoons \operatorname{Pd_{(s)}} \qquad \qquad E_r^{\circ} = +0.95 \operatorname{V}$$

$$\operatorname{Tl}^+_{(aq)} + \operatorname{e}^- \rightleftharpoons \operatorname{Tl_{(s)}} \qquad \qquad E_r^{\circ} = -0.34 \operatorname{V}$$

$$\operatorname{Ti}^{2+}_{(aq)} + 2 \operatorname{e}^- \rightleftharpoons \operatorname{Ti}_{(s)} \qquad \qquad E_r^{\circ} = -1.63 \operatorname{V}$$

16. Prediction

Since the two cells are connected in series, the total electric potential difference of the two cells is predicted to equal the sum of the ΔE° values of each cell.

copper–silver cell
$$\Delta E^{\circ} = E_{r \text{ (cathode)}} - E_{r \text{ (anode)}}$$

$$= +0.80 \text{ V} - (+0.34 \text{ V})$$

$$\Delta E^{\circ} = +0.46 \text{ V}$$
copper–zinc cell
$$\Delta E^{\circ} = E_{r \text{ (cathode)}}^{\circ} - E_{r \text{ (anode)}}^{\circ}$$

$$= +0.34 \text{ V} - (-0.76 \text{ V})$$

$$\Delta E^{\circ} = +1.10 \text{ V}$$

The predicted voltmeter reading is: +0.46 V + (+1.10 V) = +1.56 V

SECTION 9.5 QUESTIONS

(Page 709)

Understanding Concepts

1. (a) The cell potential is predicted from the standard reduction potential values.

$$\Delta E^{\circ} = E_{\rm r\ (cathode)}^{\circ} - E_{\rm r\ (anode)}^{\circ}$$

- (b) This prediction is restricted to cells containing all entities shown in the half-reaction equations and operating at standard conditions, i.e., SATP using 1.0 mol/L solutions.
- 2. A positive cell potential indicates a spontaneous reaction and a negative cell potential indicates a nonspontaneous reaction.
- 3. Galvanic cells are designed with two different half-cells each containing an electrode and electrolyte. Therefore, a spontaneous combination will always exist.
- 4. The standard hydrogen half-cell is at 25°C and consists of an inert platinum electrode immersed in a 1.00 mol/L solution of hydrogen ions, with hydrogen gas at 100 kPa bubbling over the electrode. Standard reduction potentials for all other half-cells are measured relative to that of the standard hydrogen half-cell, defined as exactly zero volts.
- 5. A reference half-cell is necessary because it is impossible to determine the reduction potential of a single half-cell. A voltmeter can only measure a potential difference, ΔE° .

6. (a)
$$\Delta E^{\circ} = E_{\text{r (cathode)}}^{\circ} - E_{\text{r (anode)}}^{\circ}$$

$$= -0.28 \text{ V} - (-0.76 \text{ V})$$

$$\Delta E^{\circ} = +0.48 \text{ V}$$

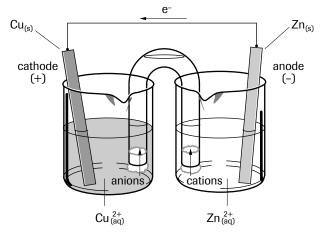
The potential of a standard cobalt–zinc cell is +0.48 V.

(b) The theoretical interpretation of this cell potential is the cobalt(II) ions have a stronger attraction for electrons than zinc ions. The 0.48 V is a measure of the difference in their abilities to attract electrons.

7. (a) SOA:
$$Cu_{(aq)}^{2+}$$
, SRA: $Zn_{(s)}$

cathode
$$Cu_{(aq)}^{2+} + 2e^{-} \rightarrow Cu_{(s)}$$
 $E_{r}^{\circ} = +0.34 \text{ V}$ anode $Zn_{(s)} \rightarrow Zn_{(aq)}^{2+} + 2e^{-}$ $E_{r}^{\circ} = -0.76 \text{ V}$ net $Cu_{(aq)}^{2+} + Zn_{(s)} \rightarrow Cu_{(s)} + Zn_{(aq)}^{2+}$ $\Delta E^{\circ} = E_{r}^{\circ} \text{ (cathode)} - E_{r}^{\circ} \text{ (anode)}$ $= +0.34 \text{ V} - (-0.76 \text{ V})$ $\Delta E^{\circ} = +1.10 \text{ V}$

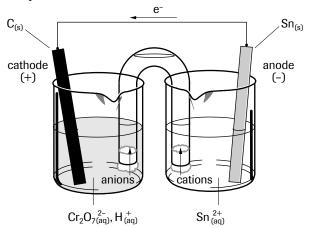
The potential of this cell is +1.10 V.



(b) SOA:
$$\operatorname{Cr_2O_{7(aq)}^{2-}}$$
, SRA: $\operatorname{Sn_{(s)}}$

cathode
$$\operatorname{Cr_2O_{7(aq)}^{2-}} + 14 \operatorname{H_{(aq)}^+} + 6e^- \rightarrow 2 \operatorname{Cr_{(aq)}^{3+}} + 7 \operatorname{H_2O_{(l)}}$$
 $E_r^\circ = +1.23 \operatorname{V}$ anode $\operatorname{SI_{(aq)}^{2-}} + 14 \operatorname{H_{(aq)}^+} + 3 \operatorname{Sn_{(s)}} \rightarrow \operatorname{SR_{(aq)}^{2+}} + 7 \operatorname{H_2O_{(l)}} + 3 \operatorname{Sn_{(aq)}^{2+}}$ $E_r^\circ = -0.14 \operatorname{V}$ net $\operatorname{Cr_2O_{7(aq)}^{2-}} + 14 \operatorname{H_{(aq)}^+} + 3 \operatorname{Sn_{(s)}} \rightarrow 2 \operatorname{Cr_{(aq)}^{3+}} + 7 \operatorname{H_2O_{(l)}} + 3 \operatorname{Sn_{(aq)}^{2+}}$ $\Delta E^\circ = E_r^\circ_{\text{(cathode)}} - E_r^\circ_{\text{(anode)}}$ $= +1.23 \operatorname{V} - (-0.14 \operatorname{V})$ $\Delta E^\circ = +1.37 \operatorname{V}$

The potential of this cell is +1.37 V.



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8.
$$2 Ag_{(aq)}^{+} + X_{(s)} \rightarrow 2 Ag_{(s)} + X_{(aq)}^{2+}$$
 $\Delta E^{\circ} = +1.08 \text{ V}$ $\Delta E^{\circ} = E_{r \text{ (cathode)}}^{\circ} - E_{r \text{ (anode)}}^{\circ}$ $E_{r \text{ (anode)}}^{\circ} = E_{r \text{ (cathode)}}^{\circ} - \Delta E^{\circ}$ $= +0.80 \text{ V} - (+1.08 \text{ V})$ $E_{r \text{ (anode)}}^{\circ} = -0.28 \text{ V}$

The reduction potential for the $X_{(aq)}^{2+} \mid X_{(s)}$ half-cell is -0.28 V, which could represent $Co_{(aq)}^{2+} \mid Co_{(s)}$.

9.6 CORROSION

Try This Activity: Home Corrosion Experiment

(Page 711)

- (a) According to the labels, 7-Up has more kinds of acids and electrolytes (carbonic acid, malic acid, and citric acid) than Coca-Cola (carbonic acid and phosphoric acid). This might suggest that the iron in the steel nail would corrode more in the 7-Up than in the Coca-Cola.
 - After about 20 h, the nail in the 7-Up changed from the initial shiny, silvery-grey metal to a slightly darker grey appearance. The change was uniform and the nail was still smooth.
 - After about 20 h, the nail in the Coca-Cola changed from the initial shiny, silvery-grey metal to a darker grey, speckled appearance throughout the whole nail. Some dark brown blotches were evident on the nail only where it was near the surface of the liquid.
- (b) It appears that the nail in the Coca-Cola corroded more than the one in the 7-Up but a longer observation period would be necessary to confirm this. The concentrations of each of the acids are not given on the label. Qualitatively, it may be possible that phosphoric acid in Coca-Cola has a major effect. The initial prediction appears to be false but the reasons for this are not clear.

SECTION 9.6 QUESTIONS

(Page 714)

Understanding Concepts

- 1. For the corrosion of iron an oxidizing agent, most commonly oxygen and water, must be present and in contact with the iron.
- 2. The presence of acidic solutions, electrolytes, mechanical stresses, and contact with less active metals accelerate the corrosion of iron.