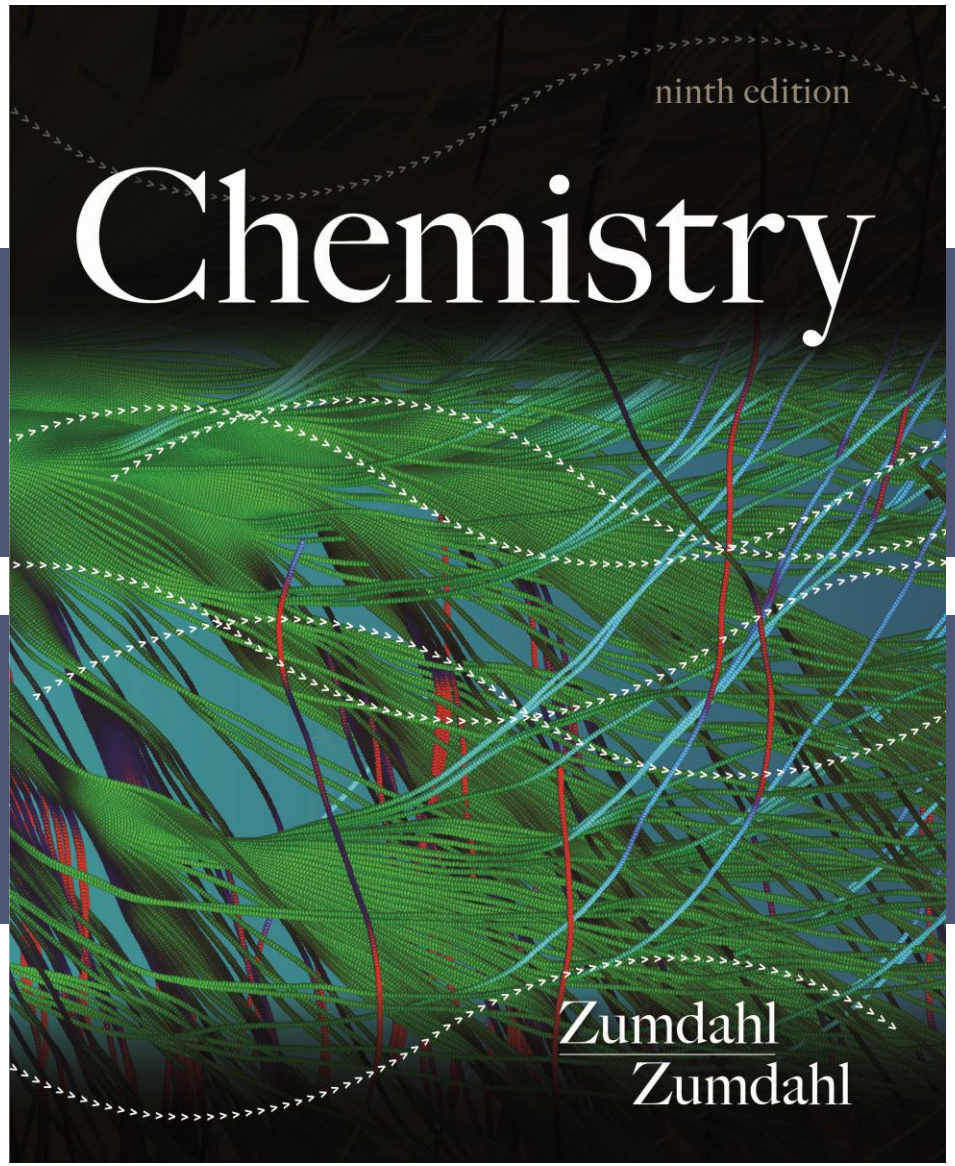

Chapter 18

Electrochemistry

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Chapter 18
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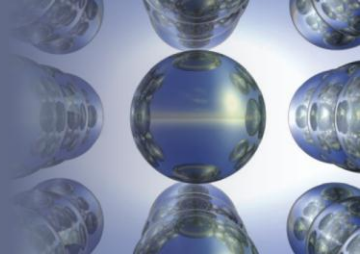

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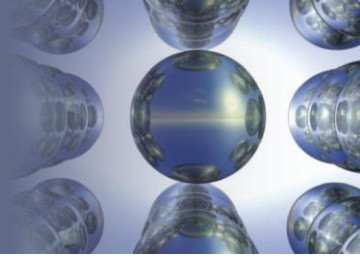

Review of Terms

- Oxidation - Loss of electrons
- Reduction - Gain of electrons
- Reducing agent - Electron donor
- Oxidizing agent - Electron acceptor

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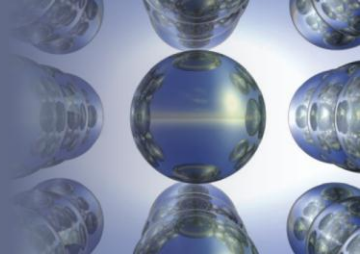

Review of Terms (Continued)

- **Electrochemistry**: Study of the interchange of chemical and electrical energy
- Oxidation–reduction (redox) reaction
  - Involves a transfer of electrons from the reducing agent to the oxidizing agent

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Half-Reaction Method

- Overall reaction is split into two **half-reactions**
  - One involves oxidation, and the other involves reduction

$$Ce^{4+}(aq) + Sn^{2+}(aq) \rightarrow Ce^{3+}(aq) + Sn^{4+}(aq)$$

Unbalanced equation for the oxidation–reduction reaction between cerium(IV) ion and tin(II) ion

$$Ce^{4+}(aq) \rightarrow Ce^{3+}(aq)$$

Reduction

$$Sn^{2+}(aq) \rightarrow Sn^{4+}(aq)$$

Oxidation

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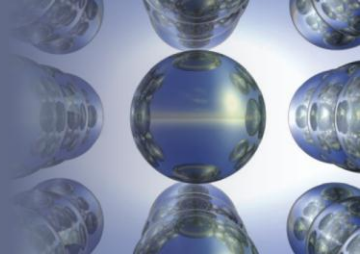

Problem-Solving Strategy - Half-Reaction Method (Acidic Solution)

1. Write separate equations for the oxidation and reduction half-reactions
2. For each half-reaction:
   - Balance all the elements except H and O
   - Balance O using H_2O
   - Balance H using H^+
   - Balance the charge using electrons

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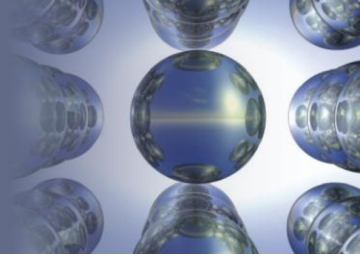

Problem-Solving Strategy - Half-Reaction Method (Acidic Solution) (Continued)

3. If necessary, multiply one or both balanced half-reactions by an integer
   - Helps equalize the number of electrons transferred in the two half-reactions
4. Add the half-reactions, and cancel identical species
5. Check that the elements and charges are balanced

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Interactive Example 18.1 - Balancing Oxidation–Reduction Reactions (Acidic)

- Potassium dichromate ($K_2Cr_2O_7$) is a bright orange compound that can be reduced to a blue-violet solution of Cr^{3+} ions
  - Under certain conditions, $K_2Cr_2O_7$ reacts with ethanol (C_2H_5OH) as follows:

$$H^+(aq) + Cr_2O_7^{2-}(aq) + C_2H_5OH\,(l) \rightarrow Cr^{3+}(aq) + CO_2(g) + H_2O\,(l)$$

  - Balance this equation using the half-reaction method

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Interactive Example 18.1 - Solution

1. The reduction half-reaction is:

$$Cr_2O_7^{2-}(aq) \rightarrow Cr^{3+}(aq)$$

- Chromium is reduced from an oxidation state of +6 in $Cr_2O_7^{2-}$ to one of the +3 in Cr^{3+}

The oxidation half-reaction is:

$$C_2H_5OH\,(l) \rightarrow CO_2\,(g)$$

- Carbon is oxidized from an oxidation state of –2 in C_2H_5OH to +4 in CO_2

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Interactive Example 18.1 - Solution (Continued 1)

2. Balancing all elements except hydrogen and oxygen in the first half-reaction

$$Cr_2O_7^{2-}(aq) \rightarrow 2Cr^{3+}(aq)$$

Balancing oxygen using H_2O

$$Cr_2O_7^{2-}(aq) \rightarrow 2Cr^{3+}(aq) + 7H_2O\,(l)$$

Balancing hydrogen using H^+

$$14H^+(aq) + Cr_2O_7^{2-}(aq) \rightarrow 2Cr^{3+}(aq) + 7H_2O\,(l)$$

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Interactive Example 18.1 - Solution (Continued 2)

2. Balancing the charge using electrons

$$6e^- + 14H^+(aq) + Cr_2O_7^{2-}(aq) \rightarrow 2Cr^{3+}(aq) + 7H_2O\ (l)$$

Next, we turn to the oxidation half-reaction

$$C_2H_5OH\ (l) \rightarrow CO_2\ (g)$$

Balancing carbon

$$C_2H_5OH\ (l) \rightarrow 2CO_2\ (g)$$

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Interactive Example 18.1 - Solution (Continued 3)

2. Balancing oxygen using H_2O

$$C_2H_5OH\,(l) + 3H_2O\,(l) \rightarrow 2CO_2\,(g)$$

Balancing hydrogen using H^+

$$C_2H_5OH\,(l) + 3H_2O\,(l) \rightarrow 2CO_2\,(g) + 12H^+\,(aq)$$

We then balance the charge by adding $12e^-$ to the right side

$$C_2H_5OH\,(l) + 3H_2O\,(l) \rightarrow 2CO_2\,(g) + 12H^+\,(aq) + 12e^-$$

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Interactive Example 18.1 - Solution (Continued 4)

3. In the reduction half-reaction, there are 6 electrons on the left-hand side, and there are 12 electrons on the right-hand side of the oxidation half-reaction
   - Thus, we multiply the reduction half-reaction by 2 to give:

$$12e^- + 28H^+(aq) + 2Cr_2O_7^{2-}(aq) \rightarrow 4Cr^{3+}(aq) + 14H_2O\,(l)$$

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Interactive Example 18.1 - Solution (Continued 5)

4. Adding the half-reactions and canceling identical species

$$12e^- + 28H^+(aq) + 2Cr_2O_7^{2-}(aq) \rightarrow 4Cr^{3+}(aq) + 14H_2O\,(l)$$

$$C_2H_5OH\,(l) + 3H_2O\,(l) \rightarrow 2CO_2\,(g) + 12H^+(aq) + 12e^-$$

$$16H^+(aq) + 2Cr_2O_7^{2-}(aq) + C_2H_5OH\,(l)$$

$$\rightarrow 4Cr^{3+}(aq) + 11H_2O\,(l) + 2CO_2\,(g)$$

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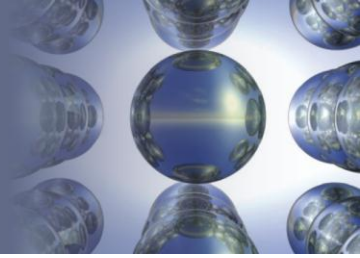

Interactive Example 18.1 - Solution (Continued 6)

5. Check that elements and charges are balanced

Elements balance: $22H, 4Cr, 15O, 2C \rightarrow 22H, 4Cr, 15O, 2C$

Charges balance: $+16 + 2(-2) + 0 = +12 \rightarrow 4(+3) + 0 + 0 = +12$

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Exercise

- Balance the following oxidation–reduction reaction that occurs in acidic solution

$$Br^-(aq) + MnO_4^-(aq) \rightarrow Br_2(l) + Mn^{2+}(aq)$$

$$10Br^-(aq) + 16H^+(aq) + 2MnO_4^-(aq)$$
$$\rightarrow 5Br_2(l) + 2Mn^{2+}(aq) + 8H_2O\,(l)$$

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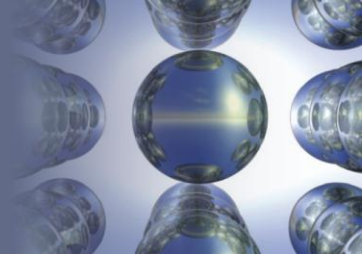

Problem-Solving Strategy - Half-Reaction Method (Basic Solution)

1. Use the half-reaction method as specified for acidic solutions to obtain the final balanced equation as if H^+ ions were present
2. To both sides of the equation obtained above, add a number of OH^- ions that is equal to the number of H^+ ions
   - We want to eliminate H^+ by forming H_2O

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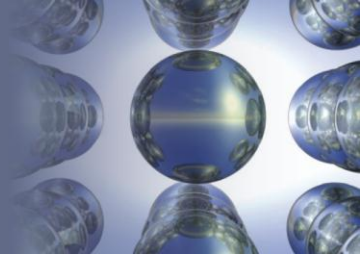

Problem-Solving Strategy - Half-Reaction Method (Basic Solution) (Continued)

3. Form H_2O on the side containing both H^+ and OH^- ions, and eliminate the number of H_2O molecules that appear on both sides of the equation
4. Check that elements and charges are balanced

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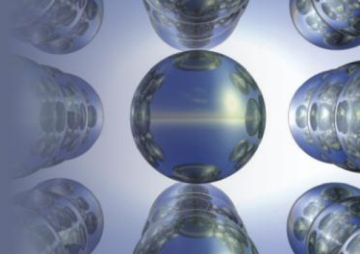

Critical Thinking

- When balancing redox reactions occurring in basic solutions, the text instructs you to first use the half-reaction method as specified for acidic solutions
  - What if you started by adding OH^- first instead of H^+?
  - What potential problem could there be with this approach?

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Interactive Example 18.2 - Balancing Oxidation–Reduction Reactions (Basic)

- Silver is sometimes found in nature as large nuggets; more often it is found mixed with other metals and their ores
  - An aqueous solution containing cyanide ion is often used to extract the silver using the following reaction that occurs in basic solution:

$$\mathrm{Ag}(s) + \mathrm{CN}^-(aq) + \mathrm{O}_2(g) \xrightarrow{\text{Base}} \mathrm{Ag(CN)}_2^-(aq)$$

- Balance this equation using the half-reaction method

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Interactive Example 18.2 - Solution

1. Balance the equation as if H^+ ions were present

   Balance the oxidation half-reaction

   $$CN^-(aq) + Ag(s) \rightarrow Ag(CN)_2^-(aq)$$

   Balance carbon and nitrogen

   $$2CN^-(aq) + Ag(s) \rightarrow Ag(CN)_2^-(aq)$$

   Balance the charge

   $$2CN^-(aq) + Ag(s) \rightarrow Ag(CN)_2^-(aq) + e^-$$

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Interactive Example 18.2 - Solution (Continued 1)

1. Balance the reduction half-reaction: $O_2(g) \rightarrow$

   Balance oxygen

   $$O_2(g) \rightarrow 2H_2O(l)$$

   Balance hydrogen

   $$O_2(g) + 4H^+(aq) \rightarrow 2H_2O\ (l)$$

   Balance the charge

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

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Interactive Example 18.2 - Solution (Continued 2)

1. Multiply the balanced oxidation half-reaction by 4

$$8\mathrm{CN}^-(aq) + 4\mathrm{Ag}(s) \rightarrow 4\mathrm{Ag(CN)}_2^-(aq) + 4\mathrm{e}^-$$

Add the half-reactions, and cancel identical species

$$8\mathrm{CN}^-(aq) + 4\mathrm{Ag}(s) \rightarrow 4\mathrm{Ag(CN)}_2^-(aq) + 4\mathrm{e}^-$$

$$4\mathrm{e}^- + \mathrm{O}_2(g) + 4\mathrm{H}^+(aq) \rightarrow 2\mathrm{H}_2\mathrm{O}\ (l)$$

$$8\mathrm{CN}^-(aq) + 4\mathrm{Ag}(s) + \mathrm{O}_2(g) + 4\mathrm{H}^+(aq) \rightarrow 4\mathrm{Ag(CN)}_2^-(aq) + 2\mathrm{H}_2\mathrm{O}\ (l)$$

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Interactive Example 18.2 - Solution (Continued 3)

2. Add OH^- ions to both sides of the balanced equation to eliminate the H^+ ions

   We need to add $4OH^-$ to each side

$$8CN^-(aq) + 4Ag(s) + O_2(g) + \underbrace{4H^+(aq) + 4OH^-}_{4H_2O(l)}(aq) \rightarrow$$

$$4Ag(CN)_2^-(aq) + 2H_2O(l) + 4OH^-(aq)$$

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Interactive Example 18.2 - Solution (Continued 4)

3. Eliminate as many H_2O molecules as possible

$$8CN^-(aq) + 4Ag\,(s) + O_2(g) + 2H_2O\,(l) \rightarrow 4Ag(CN)_2^-(aq) + 4OH^-(aq)$$

4. Check that elements and charges are balanced

Elements balance: 8C, 8N, 4Ag, 4O, 4H $\rightarrow$ 8C, 8N, 4Ag, 4O, 4H

Charges balance: 8(1–) + 0 + 0 + 0 = 8 – $\rightarrow$ 4(1–) + 4(1–) = 8 –

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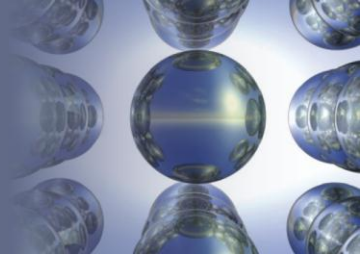

Galvanic Cell

- Device in which chemical energy is changed to electrical energy
- Uses a spontaneous redox reaction to produce a current that can be used to do work
  - Reaction occurs at the interface between the electrode and the solution where electron transfer is facilitated

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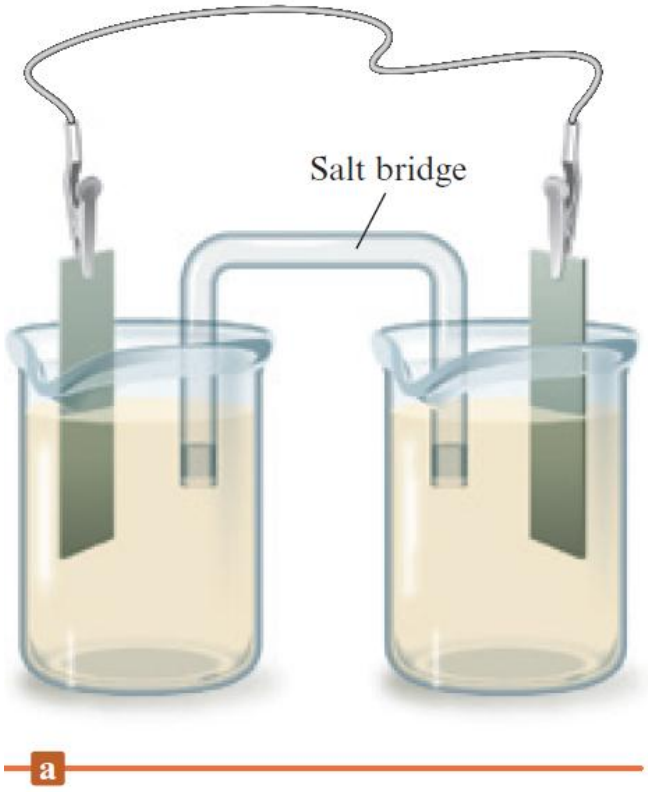
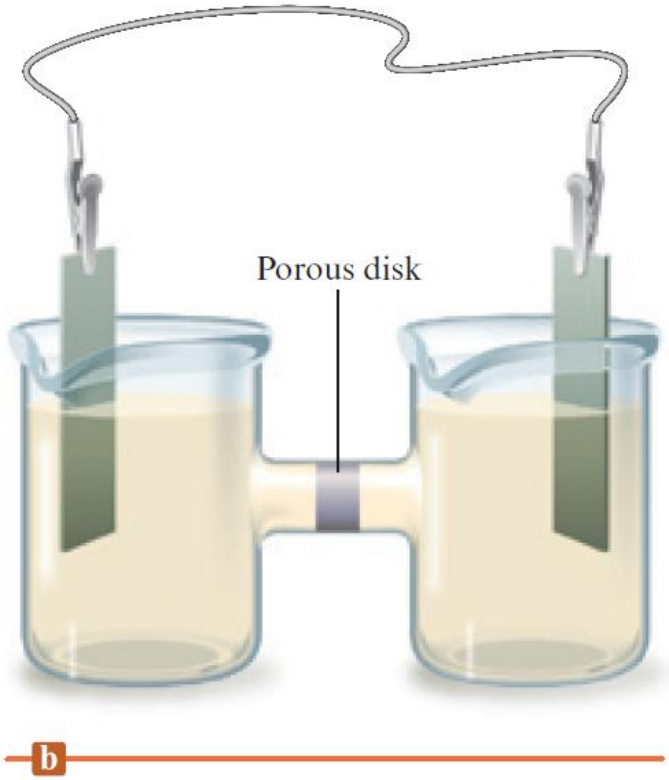
Figure 18.2 - Galvanic Cells



Galvanic cells can contain a salt bridge



Galvanic cells can contain a porous-disk connection

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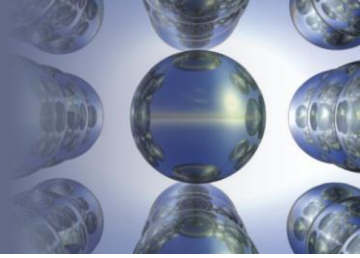

Galvanic Cell - Components

- A salt bridge or a porous disk is used to permit ions to flow without extensive mixing of the solutions
  - **Salt bridge**: Contains a strong electrolyte in a U-tube
  - **Porous disk**: Contains tiny passages that allow hindered flow of ions

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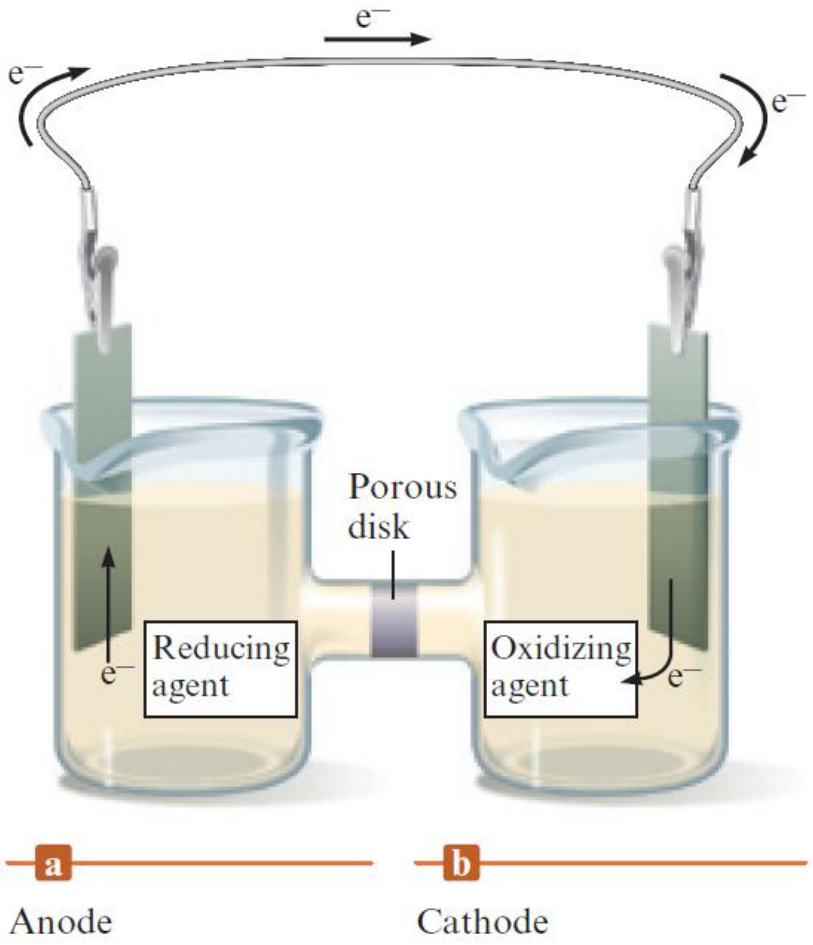
Galvanic Cell - Components (Continued)

- **Anode**: Electrode compartment where oxidation occurs
- **Cathode**: Electrode compartment where reduction occurs



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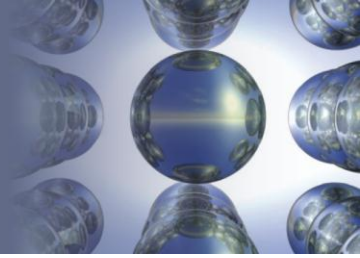

Cell Potential (E_{cell})

- Pull or driving force on electrons
- Termed as the **electromotive force** (emf) of the cell
- **Volt** (V): Unit of electrical potential
  - Defined as 1 joule of work per coulomb of charge transferred

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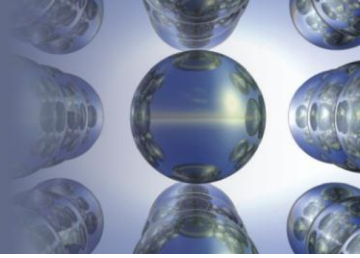

Measuring Cell Potential

- Use a voltmeter
  - **Voltmeter**: Draws current via a known resistance
  - Maximum cell potential can be ascertained by measuring it under zero current
    - **Potentiometer**: Variable voltage device, which is powered by an external source, inserted in opposition to the cell potential

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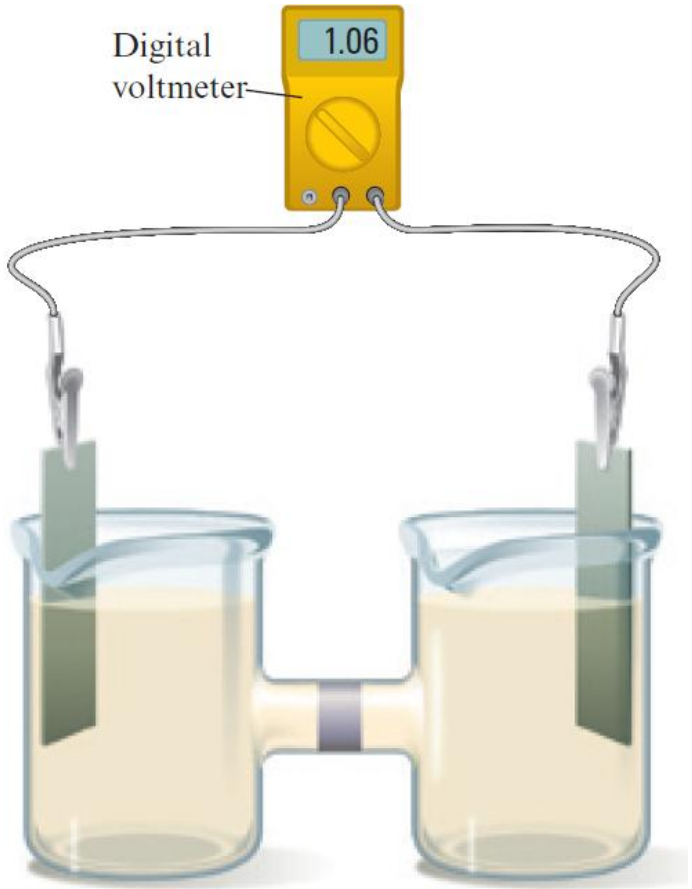
Figure 18.4 - A Digital Voltmeter



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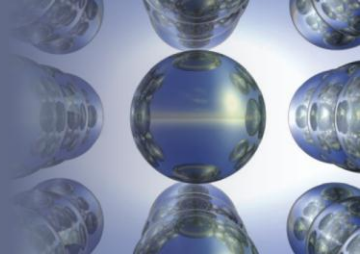

Standard Reduction Potentials

- E° values corresponding to reduction half-reactions with all solutes at 1 *M* and all gases at 1 atm
- All half-reactions are given as reduction processes in standard tables

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Section 18.3
Standard Reduction Potentials

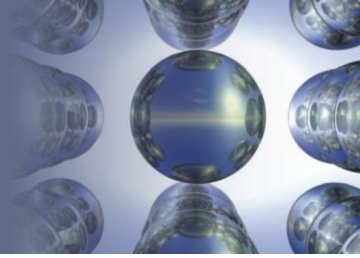

Table 18.1 - Standard Reduction Potentials at 25° C (298 K) for Many Common Half-Reactions

Half-Reaction	$\mathscr{E}°$ (V)	Half-Reaction	$\mathscr{E}°$ (V)
$F_2 + 2e^- \rightarrow 2F^-$	2.87	$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	0.40
$Ag^{2+} + e^- \rightarrow Ag^+$	1.99	$Cu^{2+} + 2e^- \rightarrow Cu$	0.34
$Co^{3-} + e^- \rightarrow Co^{2-}$	1.82	$Hg_2Cl_2 + 2e^- \rightarrow 2Hg + 2Cl^-$	0.27
$H_2O_2 + 2H^- + 2e^- \rightarrow 2H_2O$	1.78	$AgCl + e^- \rightarrow Ag + Cl^-$	0.22
$Ce^{4+} + e^- \rightarrow Ce^{3+}$	1.70	$SO_4^{2-} + 4H^+ + 2e^- \rightarrow H_2SO_3 + H_2O$	0.20
$PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4 + 2H_2O$	1.69	$Cu^{2+} + e^- \rightarrow Cu^+$	0.16
$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$	1.68	$2H^+ + 2e^- \rightarrow H_2$	0.00
$2e^- + 2H^+ + IO_4^- \rightarrow IO_3^- + H_2O$	1.60	$Fe^{3+} + 3e^- \rightarrow Fe$	−0.036
$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$	1.51	$Pb^{2+} + 2e^- \rightarrow Pb$	−0.13
$Au^{3+} + 3e^- \rightarrow Au$	1.50	$Sn^{2+} + 2e^- \rightarrow Sn$	−0.14
$PbO_2 + 4H^+ + 2e^- \rightarrow Pb^{2+} + 2H_2O$	1.46	$Ni^{2+} + 2e^- \rightarrow Ni$	−0.23
$Cl_2 + 2e^- \rightarrow 2Cl^-$	1.36	$PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-}$	−0.35
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$	1.33	$Cd^{2+} + 2e^- \rightarrow Cd$	−0.40
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	1.23	$Fe^{2+} + 2e^- \rightarrow Fe$	−0.44

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Section 18.3
Standard Reduction Potentials

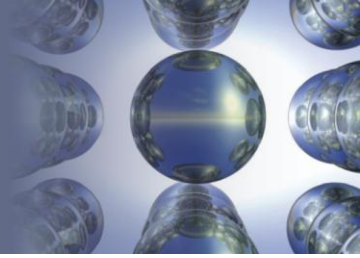

Table 18.1 - Standard Reduction Potentials at 25° C (298 K) for Many Common Half-Reactions (Continued)

Half-Reaction	$\mathscr{E}^\circ$ (V)	Half-Reaction	$\mathscr{E}^\circ$ (V)
$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$	1.21	$Cr^{3+} + e^- \rightarrow Cr^{2+}$	−0.50
$IO_3^- + 6H^+ + 5e^- \rightarrow \frac{1}{2}I_2 + 3H_2O$	1.20	$Cr^{3+} + 3e^- \rightarrow Cr$	−0.73
$Br_2 + 2e^- \rightarrow 2Br^-$	1.09	$Zn^{2+} + 2e^- \rightarrow Zn$	−0.76
$VO_2^+ + 2H^+ + e^- \rightarrow VO^{2+} + H_2O$	1.00	$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	−0.83
$AuCl_4^- + 3e^- \rightarrow Au + 4Cl^-$	0.99	$Mn^{2+} + 2e^- \rightarrow Mn$	−1.18
$NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O$	0.96	$Al^{3+} + 3e^- \rightarrow Al$	−1.66
$ClO_2 + e^- \rightarrow ClO_2^-$	0.954	$H_2 + 2e^- \rightarrow 2H^-$	−2.23
$2Hg^{2+} + 2e^- \rightarrow Hg_2^{2+}$	0.91	$Mg^{2+} + 2e^- \rightarrow Mg$	−2.37
$Ag^+ + e^- \rightarrow Ag$	0.80	$La^{3+} + 3e^- \rightarrow La$	−2.37
$Hg_2^{2+} + 2e^- \rightarrow 2Hg$	0.80	$Na^+ + e^- \rightarrow Na$	−2.71
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	0.77	$Ca^{2+} + 2e^- \rightarrow Ca$	−2.76
$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$	0.68	$Ba^{2+} + 2e^- \rightarrow Ba$	−2.90
$MnO_4^- + e^- \rightarrow MnO_4^{2-}$	0.56	$K^+ + e^- \rightarrow K$	−2.92
$I_2 + 2e^- \rightarrow 2I^-$	0.54	$Li^+ + e^- \rightarrow Li$	−3.05
$Cu^+ + e^- \rightarrow Cu$	0.52		

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Obtaining a Balanced Oxidation–Reduction Reaction - Manipulations

- When a half-reaction is reversed, the sign of E° is reversed

$$E°_{cell} = E°(cathode) - E°(anode)$$

- When a half-reaction is multiplied by an integer, E° remains the same
  - Standard reduction potential is an intensive property

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Standard Reduction Potentials - Example

- Redox reaction

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

- Half-reactions

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \qquad E° = 0.77\ V \qquad (1)$$

$$Cu^{2+} + 2e^- \rightarrow Cu \qquad E° = 0.34\ V \qquad (2)$$

- To balance the cell reaction and calculate the standard cell potential, reverse reaction (2)

$$Cu \rightarrow Cu^{2+} + 2e^- \qquad -E° = -0.34\ V$$

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Standard Reduction Potentials - Example (Continued 1)

- Each Cu atom produces two electrons but each Fe^{3+} ion accepts only one electron
  - Therefore, reaction (1) must be multiplied by 2

$$2Fe^{3+} + 2e^- \rightarrow 2Fe^{2+} \quad E° = 0.77\ V$$

$$2Fe^{3+} + 2e^- \rightarrow 2Fe^{2+} \qquad E(\text{cathode}) = -0.77\ V$$

$$Cu \rightarrow Cu^{2+} + 2e^- \qquad -E\ (\text{anode}) = -0.34\ V$$

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Standard Reduction Potentials - Example (Continued 2)

- Balanced cell reaction

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

- Cell potential
  - $E°_{cell} = E°\ (\text{cathode}) - E°\ (\text{anode})$
  - $E°_{cell} = 0.77\ V - 0.34\ V$
  - $E°_{cell} = 0.43\ V$

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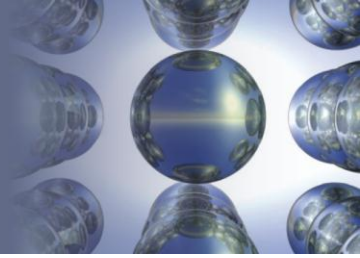

Critical Thinking

- What if you want to "plate out" copper metal from an aqueous Cu^{2+} solution?
  - Use Table 18.1 to determine several metals you can place in the solution to plate copper metal from the solution
  - Defend your choices
  - Why can Zn not be plated out from an aqueous solution of Zn^{2+} using the choices in Table 18.1?

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Interactive Example 18.3 - Galvanic Cells

- Consider a galvanic cell based on the following reaction:

$$Al^{3+}(aq) + Mg(s) \rightarrow Al(s) + Mg^{2+}(aq)$$

  - The half-reactions are:

$$Al^{3+} + 3e^- \rightarrow Al \qquad E° = -1.66\ V\ (1)$$

$$Mg^{2+} + 2e^- \rightarrow Mg \qquad E° = -2.37\ V\ (2)$$

  - Give the balanced cell reaction, and calculate $E°$ for the cell

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Interactive Example 18.3 - Solution

- The half-reaction involving magnesium must be reversed and since this is the oxidation process, it is the anode

$$\mathrm{Mg} \rightarrow \mathrm{Mg^{2+}} + 2\mathrm{e^-} \qquad -\mathrm{E^\circ(anode)} = -\left(-2.37\ \mathrm{V}\right) = 2.37\ \mathrm{V}$$

  - Also, since the two half-reactions involve different numbers of electrons, they must be multiplied by integers

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Interactive Example 18.3 - Solution (Continued)

$$2(Al^{3+} + 3e^- \rightarrow Al) \qquad E°(\text{cathode}) = -1.66\ \text{V}$$

$$3(Mg \rightarrow Mg^{2+} + 2e^-) \qquad E°(\text{anode}) = 2.37\ \text{V}$$

$$2Al^{3+}(aq) + 3Mg(s) \rightarrow 2Al(s) + 3Mg^{2+}(aq) \qquad E°_{\text{cell}} = E°(\text{cathode}) - E°(\text{anode})$$

$$= -1.66\ \text{V} + 2.37\ \text{V} = 0.71\ \text{V}$$

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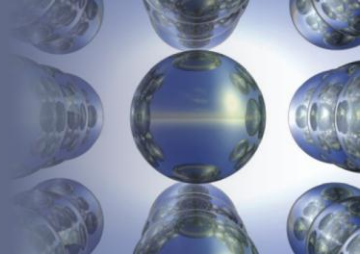

Line Notations

- Describe electrochemical cells
- Anode components are listed on the left
- Cathode components are listed on the right
- Anode and cathode components are separated by double vertical lines
  - The lines indicate a salt bridge or a porous disk

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Line Notations (Continued)

- Phase difference (boundary) is indicated by a single vertical line
- Example
  - $Mg(s)|Mg^{2+}(aq)||Al^{3+}(aq)|Al(s)$
    - $Mg \longrightarrow Mg^{2+} + 2e^-$ (anode)
    - $Al^{3+} + 3e^- \longrightarrow Al$ (cathode)

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Components in the Description of a Galvanic Cell

- Cell potential and the balanced cell reaction
  - Cell potential is always positive for a galvanic cell
    - $E°_{cell} = E°\ (\text{cathode}) - E°\ (\text{anode})$
- Direction of electron flow
  - Obtained by inspecting the half-reactions and using the direction that gives a positive $E°_{cell}$
- Designation of the anode and cathode

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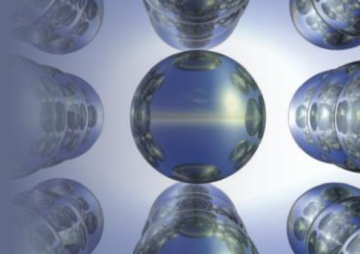

Components in the Description of a Galvanic Cell (Continued)

- Nature of each electrode and the ions present in each compartment
  - If none of the substances participating in the half–reaction are conducting solids, a chemically inert conductor is required

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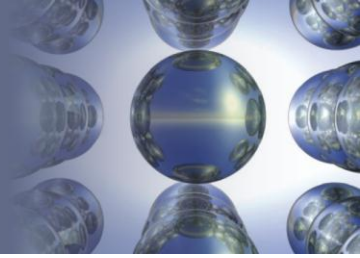

Example 17-4 - Description of a Galvanic Cell

- Describe completely the galvanic cell based on the following half-reactions under standard conditions:

$$Ag^+ + e^- \rightarrow Ag \qquad E^\circ = 0.80\ V \qquad (1)$$

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \qquad E^\circ = 0.77\ V \qquad (2)$$

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Example 17-4 - Solution

- Since a positive E°_{cell} value is required, reaction (2) must run in reverse

$$Ag^+ + e^- \rightarrow Ag \qquad E^\circ \text{ (cathode)} = 0.80 \text{ V}$$

$$Fe^{2+} \rightarrow Fe^{3+} + e^- \qquad -E^\circ \text{ (anode)} = -0.77 \text{ V}$$

$$Ag^+(aq) + Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + Ag(s) \qquad E^\circ_{cell} = 0.03 \text{ V}$$

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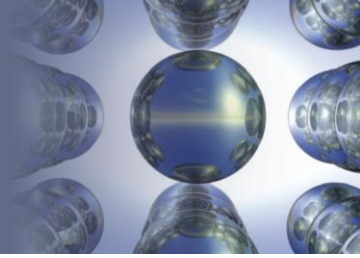

Example 17-4 - Solution (Continued 1)

- Ag^+ receives electrons, and Fe^{2+} loses electrons in the cell reaction
  - The electrons will flow from the compartment containing Fe^{2+} to the compartment containing Ag^+
- Oxidation occurs in the compartment containing Fe^{2+} (electrons flow from Fe^{2+} to Ag^+)
  - Hence this compartment functions as the anode
  - Reduction occurs in the compartment containing Ag^+, so this compartment functions as the cathode

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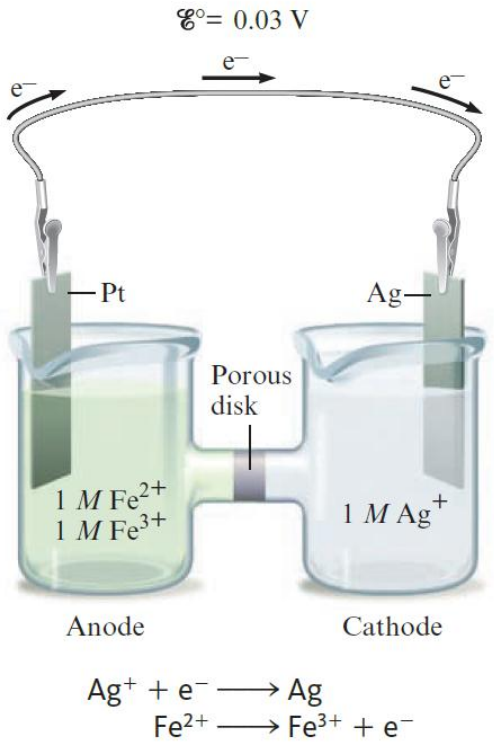
Example 17-4 - Solution (Continued 2)

- The electrode in the Ag/Ag^+ compartment is silver metal, and an inert conductor, such as platinum, must be used in the Fe^{2+}/Fe^{3+} compartment
  - Appropriate counterions are assumed to be present
  - Line notation

    $Pt(s)|\ Fe^{2+}(aq), Fe^{3+}(aq)||\ Ag^+(aq)|Ag(s$



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Work and Cell Potential

- Cell potential (E) and work (*w*) have opposite signs

$$\mathrm{E} = \frac{-w}{q} \text{ or } -w = q\mathrm{E} \qquad w_{\max} = -q\mathrm{E}_{\max}$$

- In any real, spontaneous process some energy is always wasted
  - Actual work realized is always less than the calculated maximum

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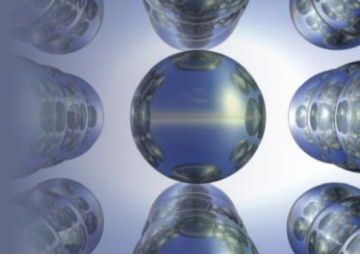

Work and Cell Potential (Continued)

- Actual work done is given by the following equation:

$$w = -qE$$

  - E - Actual potential difference at which current flows
  - q - Quantity of charge in coulombs transferred
- **Faraday** (F): Charge on 1 mole of electrons
  - F = 96,485 C/mol e^-

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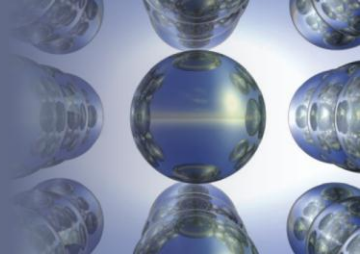

Cell Potential and Free Energy

- Change in free energy equals the maximum useful work that can be obtained from a process
  - $w_{max} = \Delta G$
- For a galvanic cell
  - $w_{max} = -qE_{max} = \Delta G$
- Since $q = nF$
  - Therefore, $\Delta G = -qE_{max} = -nFE_{max}$

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Maximum Cell Potential

- Directly related to the free energy difference between the reactants and the products in the cell

$$\Delta G^\circ = -nF\mathrm{E}^\circ$$

- Galvanic cell will run in the direction that provides a positive E_{cell} value
  - Positive E_{cell} value implies negative ΔG value, which is the condition for spontaneity

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Interactive Example 18.5 - Calculating ΔG° for a Cell Reaction

- Using the data in Table 18.1, calculate ΔG° for the following reaction:

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

  - Is this reaction spontaneous?

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Interactive Example 18.5 - Solution

- The half-reactions are:

$$\mathrm{Cu^{2+} + 2e^- \rightarrow Cu} \qquad \mathrm{E^\circ(cathode)} = 0.34\ \mathrm{V}$$

$$\mathrm{Fe \rightarrow Fe^{2+} + 2e^-} \qquad -\mathrm{E^\circ(anode)} = 0.44\ \mathrm{V}$$

$$\mathrm{Cu^{2+} + Fe \rightarrow Fe^{2+} + Cu} \qquad \mathrm{E^\circ_{cell}} = 0.78\ \mathrm{V}$$

- We can calculate ΔG° from the equation

$$\Delta G^\circ = -nF\mathrm{E}^\circ$$

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Interactive Example 18.5 - Solution (Continued 1)

- Since two electrons are transferred per atom in the reaction, 2 moles of electrons are required per mole of reactants and products
  - Thus, n = 2 mol e^-, F = 96,485 C/mol e^-, and E° = 0.78 V = 0.78 J/C

$$\Delta G^\circ = -\left(2 \text{ mol } e^-\right)\left(96{,}485 \frac{\text{C}}{\text{mol } e^-}\right)\left(0.78 \frac{\text{J}}{\text{C}}\right)$$

$$= -1.5 \times 10^5 \text{ J}$$

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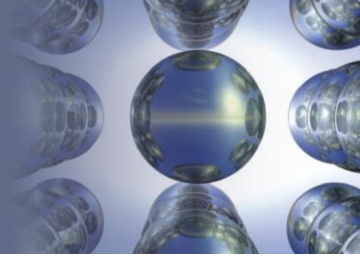

Interactive Example 18.5 - Solution (Continued 2)

- The process is spontaneous, as indicated by both the negative sign of ΔG° and the positive sign of E°_{cell}
  - This reaction is used industrially to deposit copper metal from solutions resulting from the dissolving of copper ores

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Interactive Example 18.7 - The Effects of Concentration on E

- For the cell reaction

$$2\mathrm{Al}(s) + 3\mathrm{Mn}^{2+}(aq) \rightarrow 2\mathrm{Al}^{3+}(aq) + 3\mathrm{Mn}(s) \qquad E°_{cell} = 0.48\ \mathrm{V}$$

  - Predict whether E_{cell} is larger or smaller than $E°_{cell}$ for the following case:

a. $[Al^{3+}] = 2.0\ M$, $[Mn^{2+}] = 1.0\ M$

b. $[Al^{3+}] = 1.0\ M$, $[Mn^{2+}] = 3.0\ M$

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Interactive Example 18.7 - Solution

a. A product concentration has been raised above 1.0 M
   - This will oppose the cell reaction and will cause E_{cell} to be less than E°_{cell} ($E_{cell} < 0.48$ V)

b. A reactant concentration has been increased above 1.0 M
   - E_{cell} will be greater than E°_{cell} ($E_{cell} > 0.48$ V)

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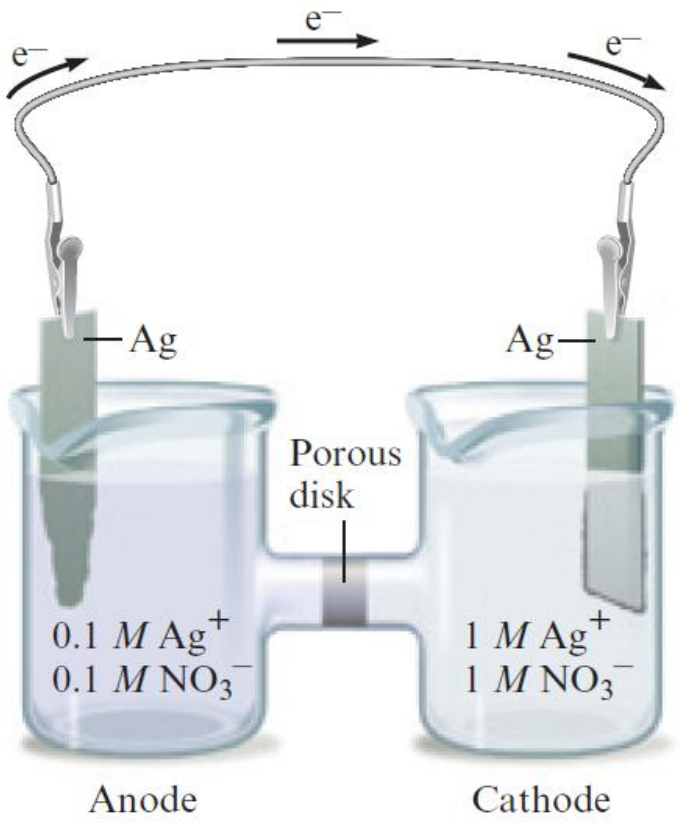
Section 18.5
Dependence of Cell Potential on Concentration

Concentration Cells

- Cells in which both compartments have the same components at different concentrations
  - Cell potential is a factor of difference in concentration
  - Voltages are small



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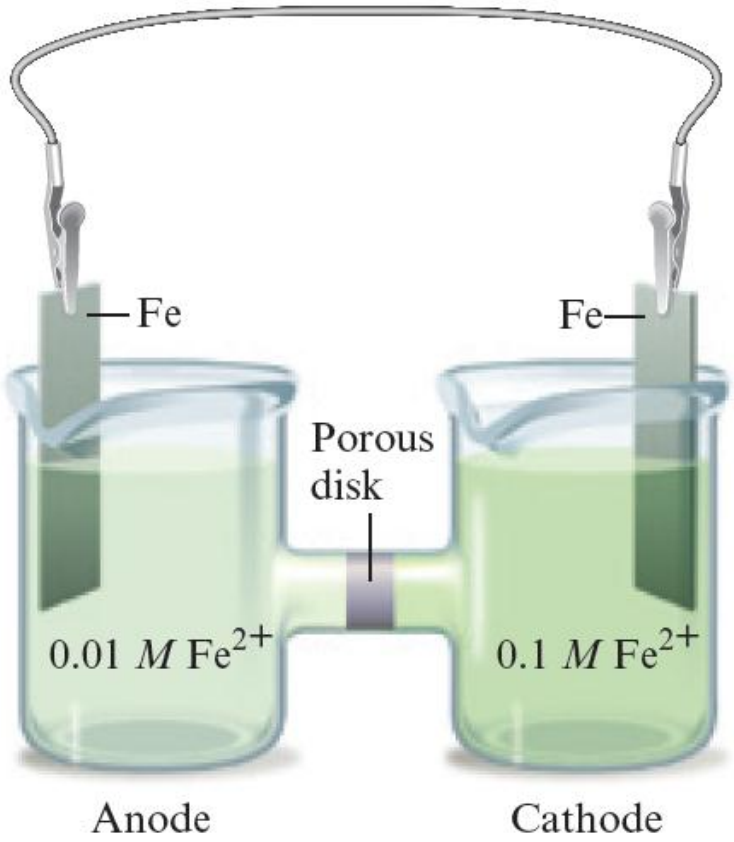
Example 18.8 - Concentration Cells

- Determine the direction of electron flow, and designate the anode and cathode for the cell represented in the figure on the right:



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Example 18.8 - Solution

- The concentrations of Fe^{2+} ion in the two compartments can (eventually) be equalized by transferring electrons from the left compartment to the right
  - This will cause Fe^{2+} to be formed in the left compartment, and iron metal will be deposited (by reducing Fe^{2+} ions to Fe) on the right electrode

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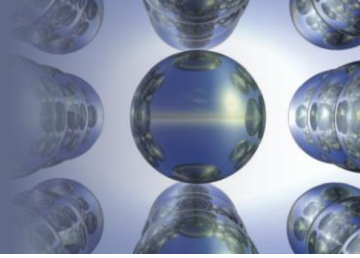

Example 18.8 - Solution (Continued)

- Since electron flow is from left to right, oxidation occurs in the left compartment (the anode) and reduction occurs in the right (the cathode)

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Nernst Equation

- Explains the relationship between cell potential and concentrations of cell components

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

- Given in a form that is valid at 25° C

$$E = E^{\circ} - \frac{0.0591}{n}\log(Q)$$

  - Resulting potential calculated from this equation is the maximum potential before any current flow

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Nernst Equation and Equilibrium

- A cell will spontaneously discharge until it reaches equilibrium
  - Q = K (equilibrium constant)
  - $E_{cell} = 0$

$$E° = \frac{0.0591}{n}\log(K) \quad \left(\text{at equilibrium}\right)$$

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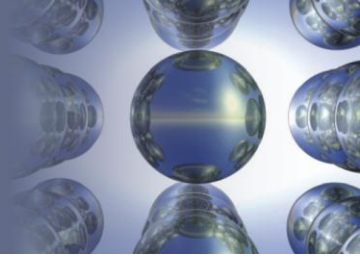

Nernst Equation and Equilibrium (Continued)

- Dead battery
  - Battery in which the cell reaction has reached equilibrium
- At equilibrium:
  - Both cell compartments have the same free energy
  - $\Delta G = 0$
  - Cell can no longer work

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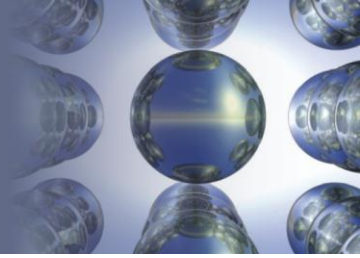

Critical Thinking

- What if you are told that $E^\circ = 0$ for an electrolytic cell?
  - Does this mean the cell is “dead”?
  - What if $E = 0$?
  - Explain your answer in each case

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Example 18.9 - The Nernst Equation

- Describe the cell based on the following half-reactions:

$$VO_2^+ + 2H^+ + e^- \rightarrow VO^{2+} + H_2O \qquad E° = 1.00\ V \qquad (1)$$

$$Zn^{2+} + 2e^- \rightarrow Zn \qquad E° = -0.76\ V \qquad (2)$$

  - Where,
    - T = 25° C
    - $[VO_2^+] = 2.0\ M$ $[H^+] = 0.50\ M$
    - $[VO^{2+}] = 1.0 \times 10^{-2}\ M$ $[Zn^{2+}] = 1.0 \times 10^{-1}\ M$

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Example 18.9 - Solution

- The balanced cell reaction is obtained by reversing reaction (2) and multiplying reaction (1) by 2

2 × reaction (1)

$$2VO_2^+ + 4H^+ + 2e^- \rightarrow 2VO^{2+} + 2H_2O \qquad E°(\text{cathode}) = 1.00\ \text{V}$$

$$Zn \rightarrow Zn^{2+} + 2e^- \qquad -E°(\text{anode}) = 0.76\ \text{V}$$

Reaction (2) reversed

$$\text{Cell reaction: } 2VO_2^+(aq) + 4H^+(aq) + Zn(s) \rightarrow 2VO^{2+}(aq) + 2H_2O(l) + Zn^{2+}(aq) \qquad E°_{cell} = 1.76\ \text{V}$$

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Example 18.9 - Solution (Continued 1)

- Since the cell contains components at concentrations other than 1 *M*, we must use the Nernst equation, where *n* = 2 (since two electrons are transferred), to calculate the cell potential
- At 25° C we can use the following equation:

$$E = E^{\circ}_{cell} - \frac{0.0591}{n}\log(Q)$$

$$= 1.76 - \frac{0.0591}{2}\log\left(\frac{[Zn^{2+}][VO^{2+}]^2}{[VO_2^{+}]^2[H^{+}]^4}\right)$$

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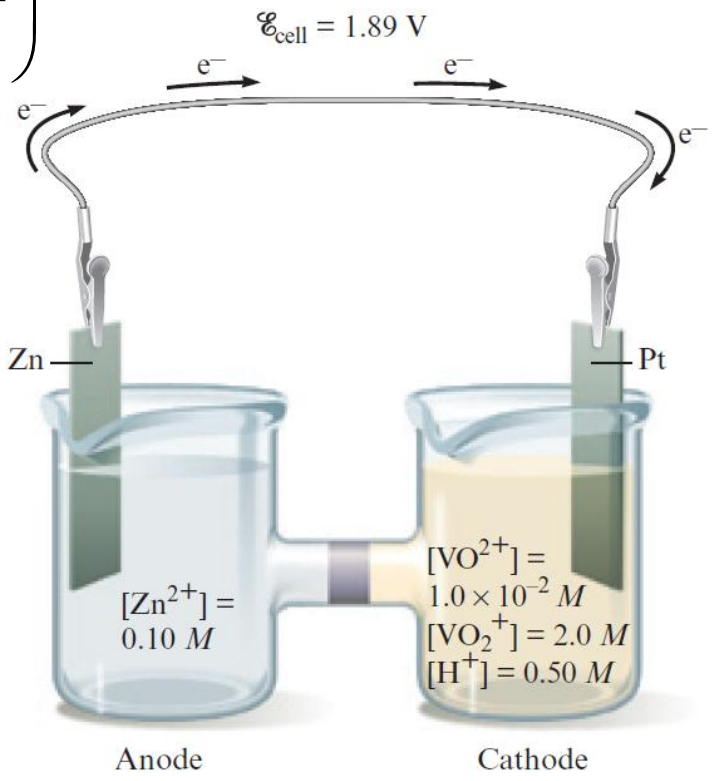
Example 18.9 - Solution (Continued 2)

$$E = 1.76 - \frac{0.0591}{2}\log\left(\frac{(1.0\times10^{-1})(1.0\times10^{-2})^2}{(2.0)^2(0.50)^4}\right)$$

$$= 1.76 - \frac{0.0591}{2}\log(4\times10^{-5})$$

$$= 1.76 + 0.13$$

$$= 1.89\ \text{V}$$



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Exercise

- Consider the cell described below:

$$Zn|Zn^{2+}(1.00\ M)||Cu^{2+}(1.00\ M)|Cu$$

  - Calculate the cell potential after the reaction has operated long enough for the $[Zn^{2+}]$ to have changed by 0.20 mol/L
  - Assume $T = 25^{\circ}$ C

1.09 V

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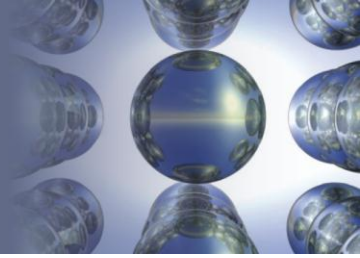

Determining Ion Concentration

- Cell potentials can help determine concentration of an ion
- pH meter - Device used to measure concentration using observed potential
  - Composed of:
    - Standard electrode of known potential
    - **Glass electrode**: Changes potentials based on H^+ ion concentration in a solution
    - Potentiometer

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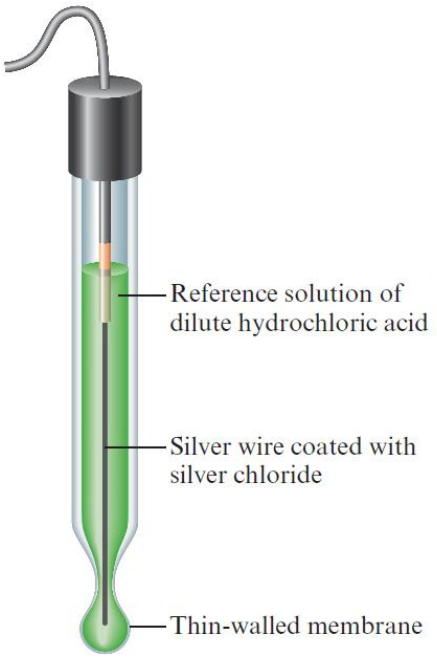
Figure 18.12 - A Glass Electrode

- Electrical potential
  - Depends on the difference in $[H^+]$ between the reference solution and the solution into which the electrode is dipped
  - Varies with the pH of the solution being tested



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Ion-Selective Electrodes

- Electrodes that are sensitive to the concentration of any specific ion
- Examples
  - Using a crystal of lanthanum(III) fluoride (LaF_3) in an electrode to measure [F^-]
  - Using solid sliver sulfide (Ag_2S) to measure [Ag^+] and [S^{2-}]

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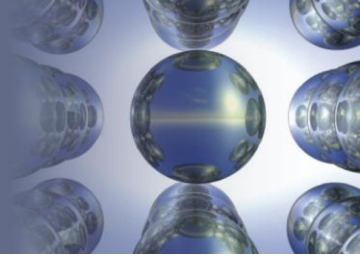

Table 18.2 - Some Ions Whose Concentrations Can Be Detected by Ion-Selective Electrodes

Cations	Anions
H^+	Br^-
Cd^{2+}	Cl^-
Ca^{2+}	CN^-
Cu^{2+}	F^-
K^+	NO_3^-
Ag^+	S^{2-}
Na^+	

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Calculation of Equilibrium Constants for Redox Reactions

- E° and ΔG° have a quantitative relationship
  - At equilibrium, $E_{cell} = 0$ and Q = K

$$E = E° - \frac{0.0591}{n}\log(Q) \qquad 0 = E° - \frac{0.0591}{n}\log(K)$$

$$\log(K) = \frac{nE°}{0.0591} \qquad \text{at } 25°C$$

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Interactive Example 18.10 - Equilibrium Constants from Cell Potentials

- For the oxidation–reduction reaction

$$S_4O_6^{2-}(aq) + Cr^{2+}(aq) \rightarrow Cr^{3+}(aq) + S_2O_3^{2-}(aq)$$

  - The appropriate half-reactions are

$$S_4O_6^{2-} + 2e^- \rightarrow 2S_2O_3^{2-} \qquad E° = 0.17\ V \quad (1)$$

$$Cr^{3+} + e^- \rightarrow Cr^{2+} \qquad E° = -0.50\ V \quad (2)$$

  - Balance the redox reaction, and calculate E° and *K* (at 25° C)

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Interactive Example 18.10 - Solution

- To obtain the balanced reaction, we must reverse reaction (2), multiply it by 2, and add it to reaction (1)

$$S_4O_6^{2-} + 2e^- \rightarrow 2S_2O_3^{2-} \qquad E^\circ\ (\text{cathode}) = 0.17\ \text{V}$$

$$2\left(Cr^{2+} \rightarrow Cr^{3+} + e^-\right) \qquad -E^\circ\ (\text{anode}) = -\left(-0.50\ \text{V}\right)$$

$$\text{Cell reaction: } 2Cr^{2+}(aq) + S_4O_6^{2-}(aq) \rightarrow 2Cr^{3+}(aq) + 2S_2O_3^{2-}(aq) \qquad E^\circ = 0.67\ \text{V}$$

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Interactive Example 18.10 - Solution (Continued 1)

- In this reaction, 2 moles of electrons are transferred for every unit of reaction
  - For every 2 moles of Cr^{2+} reacting with 1 mole of $S_4O_6^{2-}$ to form 2 moles of Cr^{3+} and 2 moles of $S_2O_3^{2-}$
- Thus $n = 2$

$$\log(K) = \frac{n\text{E}^\circ}{0.0591} = \frac{2(0.67)}{0.0591} = 22.6$$

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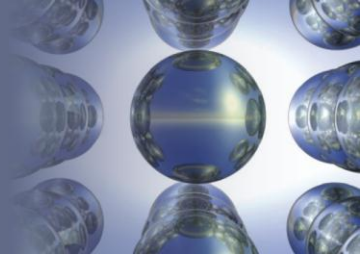

Interactive Example 18.10 - Solution (Continued 2)

- The value of *K* is found by taking the antilog of 22.6

$$K = 10^{22.6} = 4 \times 10^{22}$$

  - This very large equilibrium constant is not unusual for a redox reaction

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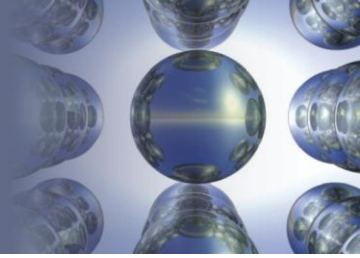
Section 18.6
Batteries



Battery

- Group of galvanic cells that are connected in series
  - Potentials of each individual cell add up to give the total battery potential
- Essential source of portable power in today's society

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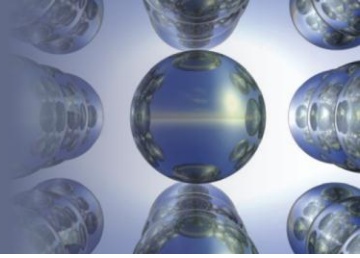

Types of Battery

- Lead storage battery
- Dry cell battery
- Silver cell
- Mercury cell
- Nickel–cadmium battery
- Lithium-ion battery

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Lead Storage Battery

- Components
  - Anode - Lead
  - Cathode - Lead coated with lead dioxide
  - Electrolyte solution - Sulfuric acid
- Electrode reactions

$$\text{Anode reaction: } Pb + HSO_4^- \rightarrow PbSO_4 + H^+ + 2e^-$$

$$\text{Cathode reaction: } PbO_2 + HSO_4^- + 3H^+ + 2e^- \rightarrow PbSO_4 + 2H_2O$$

$$\text{Cell reaction: } Pb(s) + PbO_2(s) + 2H^+(aq) + 2HSO_4^-(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)$$

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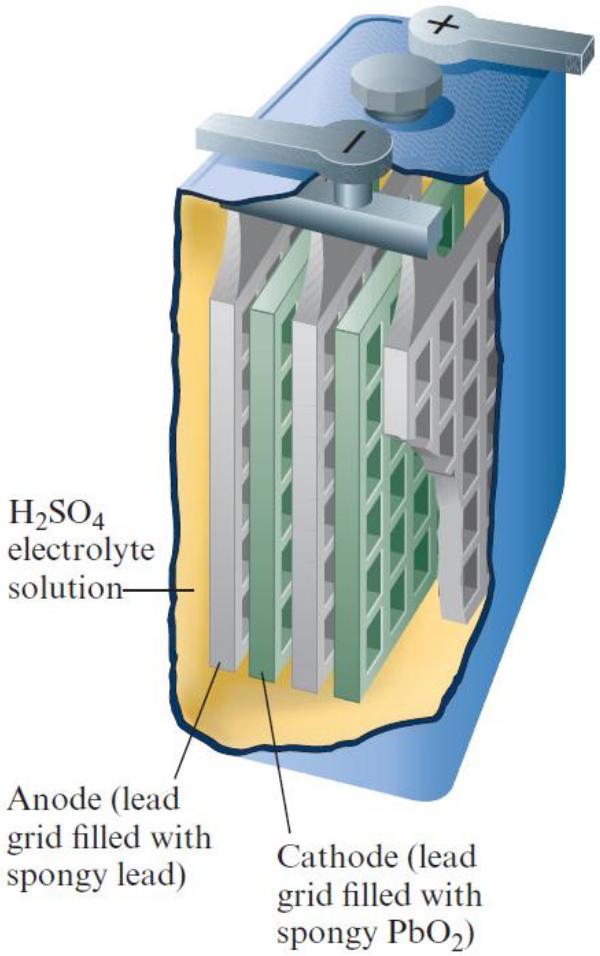
Figure 18.13 - One of the Six Cells in a 12–V Lead Storage Battery



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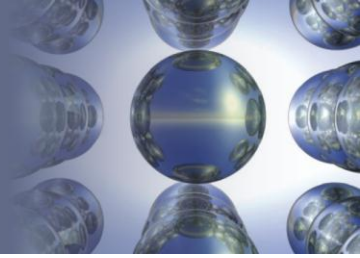

Dry Cell Battery - Acid Version

- Components
  - Zinc inner case that acts as the anode
  - Carbon rod that is in contact with a moist plate of solid MnO_2
  - Solid NH_4Cl and carbon that acts as the cathode

Anode reaction: $Zn \rightarrow Zn^{2+} + 2e^-$

Cathode reaction: $2NH_4^+ + 2MnO_2 + 2e^- \rightarrow Mn_2O_3 + 2NH_3 + H_2O$

cell potential = 1.5 V

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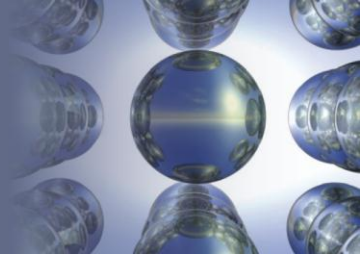

Dry Cell Battery - Alkaline Version

- Components
  - Solid NH_4Cl is replaced with NaOH or KOH

$$\text{Anode reaction: } Zn + 2OH^- \rightarrow ZnO + H_2O + 2e^-$$

$$\text{Cathode reaction: } 2MnO_2 + H_2O + 2e^- \rightarrow Mn_2O_3 + 2OH^-$$

- Lasts for a longer period of time
  - Zinc corrodes less rapidly under basic conditions

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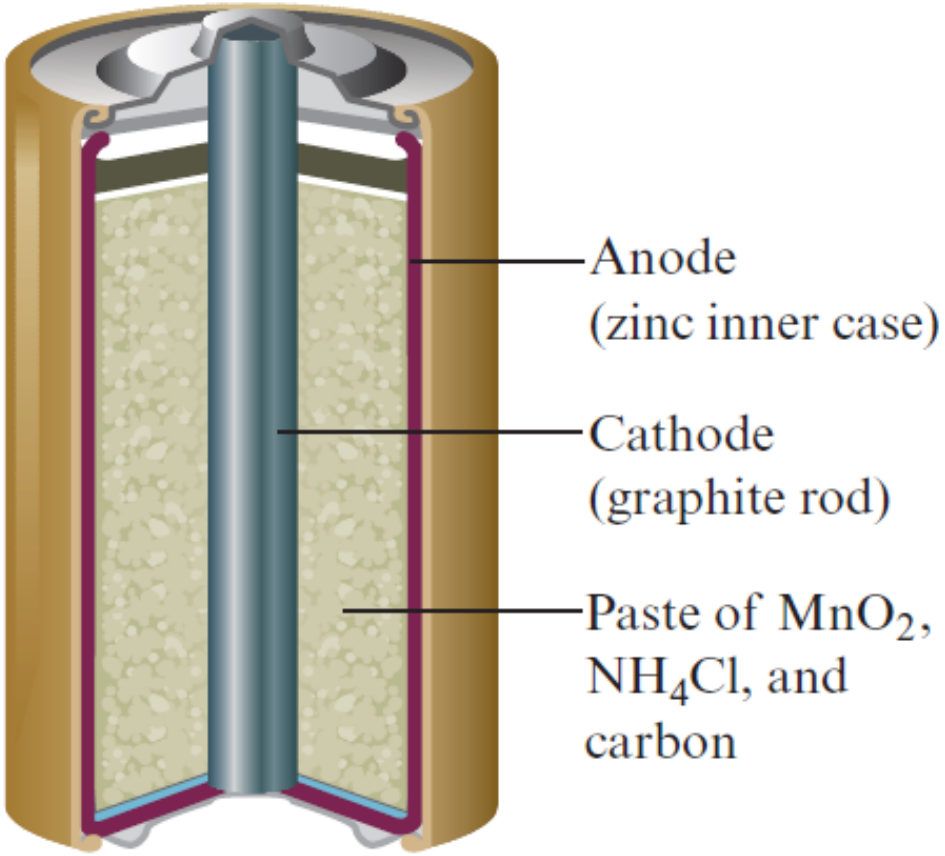
Figure 18.14 - A Common Dry Cell Battery



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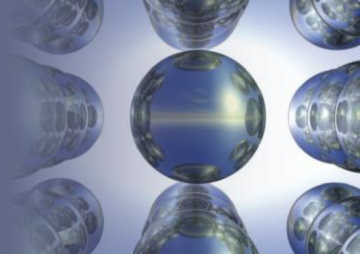

Silver Cell and Mercury Cell Batteries

- Silver cell
  - Contains a Zn anode and a cathode that uses Ag_2O as the oxidizing agent
- Mercury cell
  - Contains a Zn anode and a cathode that uses HgO as the oxidizing agent

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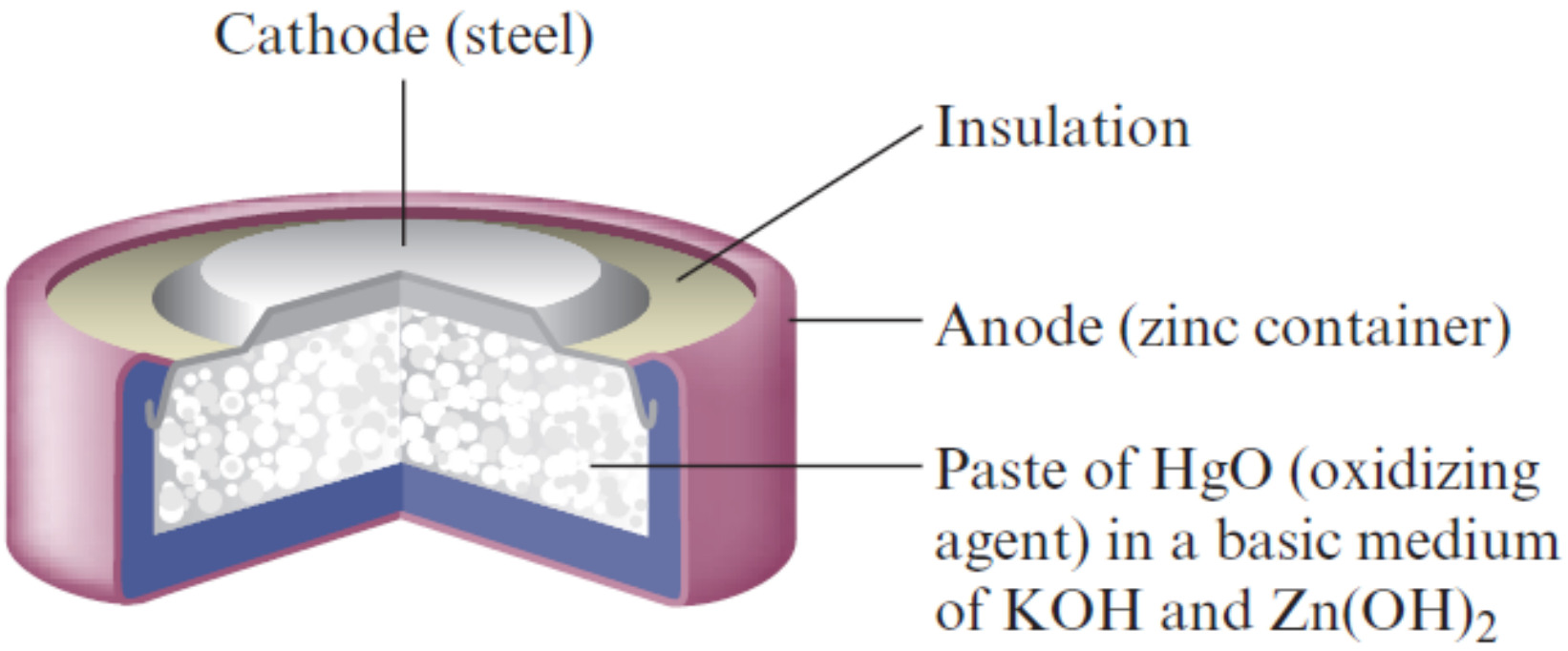
Figure 18.15 - A Mercury Battery



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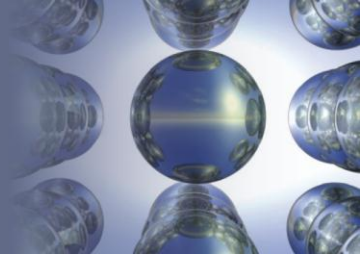

Nickel–Cadmium and Lithium-Ion Batteries

- Nickel–cadmium battery

$$\text{Anode reaction: } Cd + 2OH^- \rightarrow Cd(OH)_2 + 2e^-$$

$$\text{Cathode reaction: } NiO_2 + 2H_2O + 2e^- \rightarrow Ni(OH)_2 + 2OH^-$$

- Lithium-ion batteries
  - Li^+ ions migrate from the cathode to the anode and enter the interior as the battery is charged
  - Charge-balancing electrons travel to the anode through the external circuit in the charger
    - The opposite process occurs on discharge

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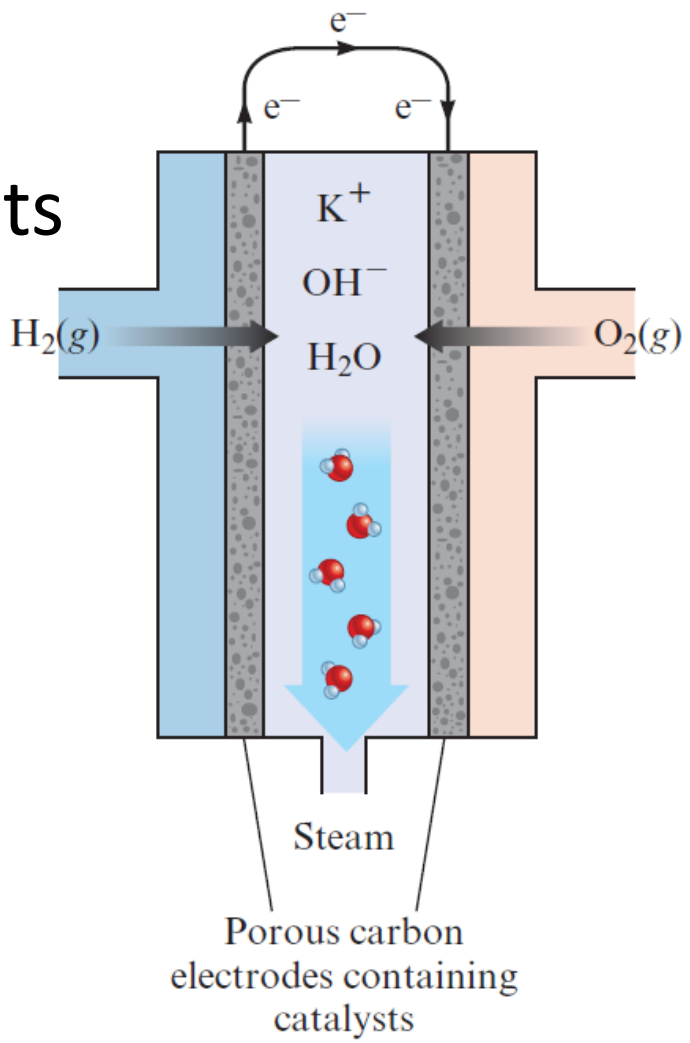
Fuel Cells

- Galvanic cells for which reactants are continuously supplied
- The image depicts a hydrogen–oxygen fuel cell
  - Anode reaction

$$2H_2 + 4OH^- \rightarrow 4H_2O + 4e^-$$

  - Cathode reaction

$$4e^- + O_2 + 2H_2O \rightarrow 4OH^-$$



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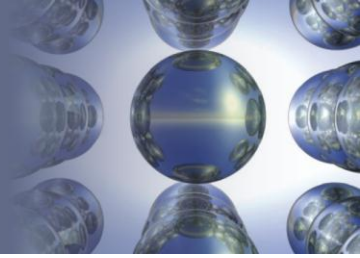

Process of Corrosion

- Can be viewed as the method of returning metals to their natural state
  - Natural state - Ores from which metals are originally obtained
- Involves the oxidation of a metal
  - Spontaneous process

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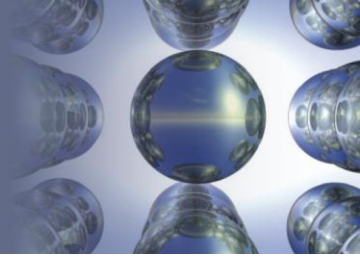

Process of Corrosion (Continued)

- Some metals tend to develop a thin oxide coating to protect against further oxidation
  - Aluminum forms a thin layer of aluminum oxide ($Al_2(OH)_6$)
  - Copper forms an external layer of greenish copper carbonate called patina
  - Silver sulfide forms silver tarnish

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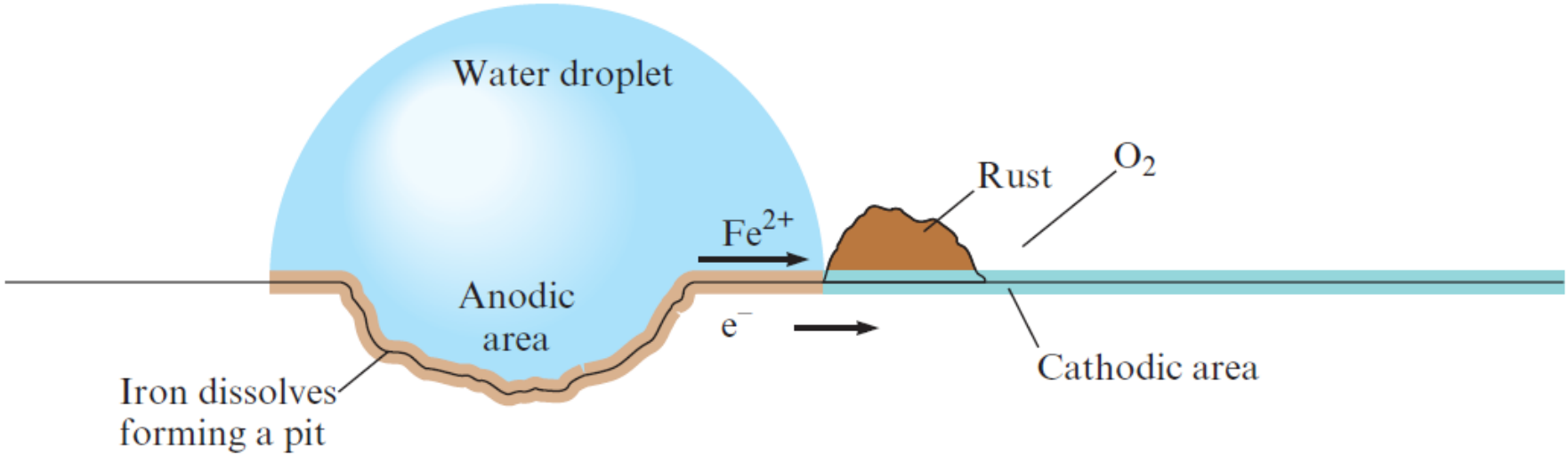
Figure 18.17 - The Electrochemical Corrosion of Iron



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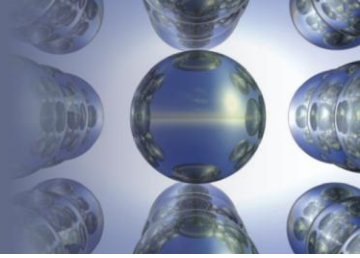

Corrosion Prevention

- Application of paint or metal plating
  - **Galvanizing**: Process in which steel is coated with zinc to prevent corrosion
- Alloying
- **Cathodic protection**
  - Protects steel in buried fuel tanks and pipelines

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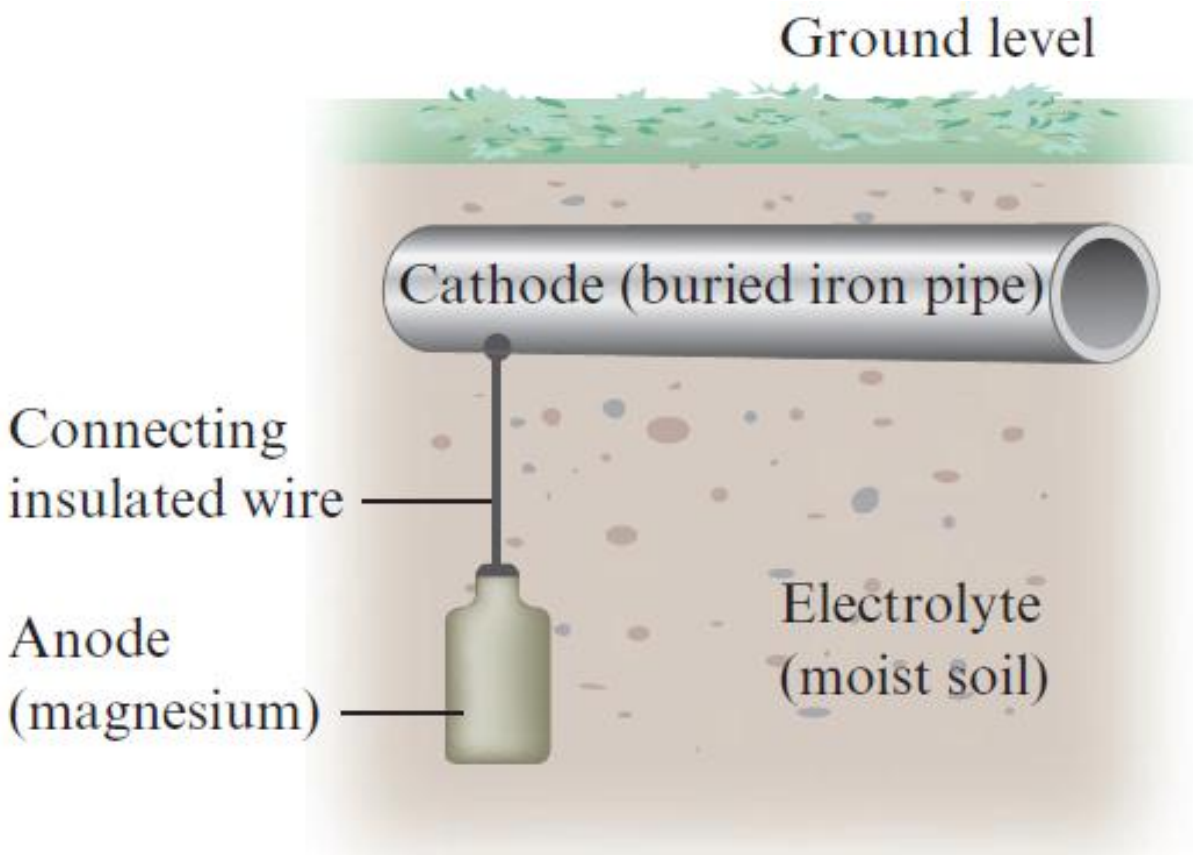
Figure 18.18 - Cathodic Protection of an Underground Pipe



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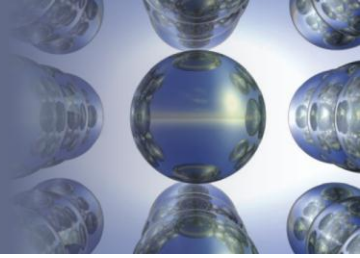

Electrolysis

- Forcing a current through a cell to produce a chemical change for which the cell potential is negative
- **Electrolytic cell**: Device that uses electrical energy to produce a chemical change

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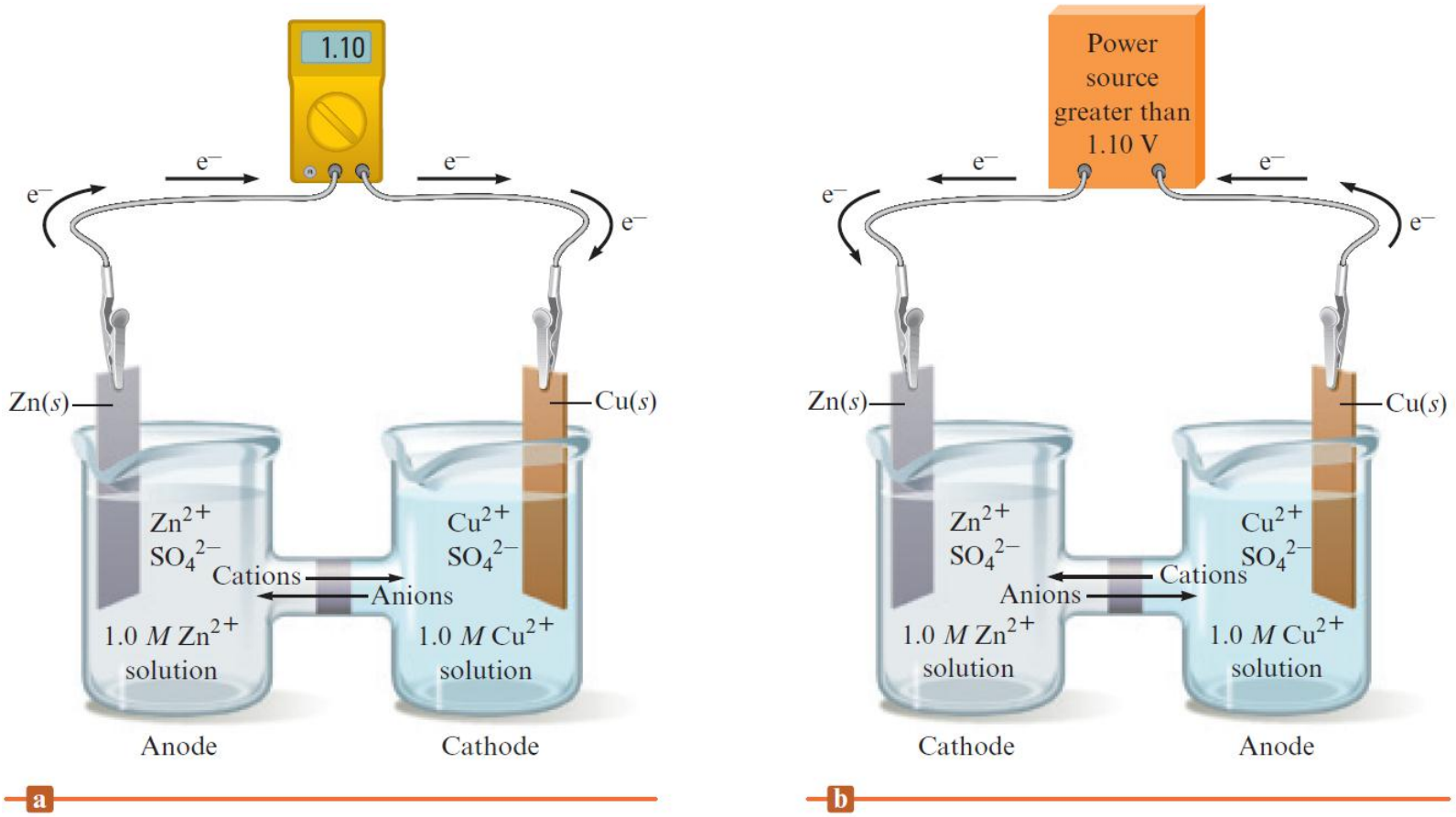
Figure 18.19 - A Galvanic Cell and an Electrolytic Cell



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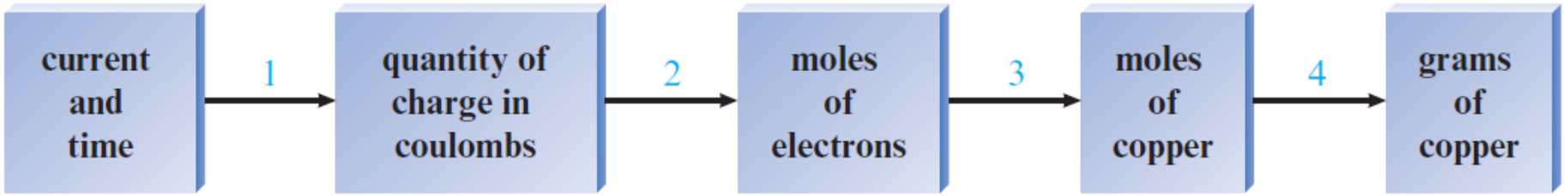
Stoichiometry of Electrolysis

- Refers to determining how much chemical change occurs with the flow of a given current for a specified time
- Steps to solve a stoichiometry problem



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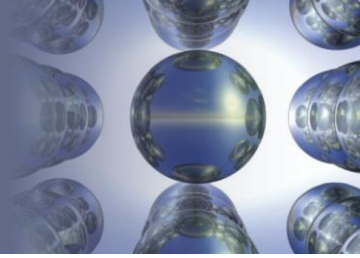

Interactive Example 18.11 - Electroplating

- How long must a current of 5.00 A be applied to a solution of Ag^+ to produce 10.5 g silver metal?

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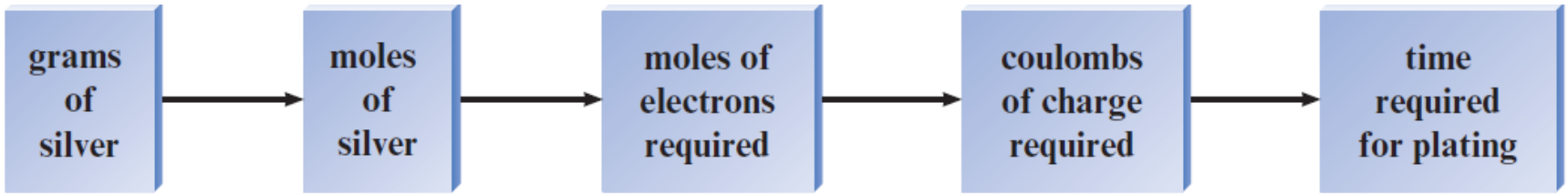
Interactive Example 18.11 - Solution

- In this case, we must use the steps given earlier in reverse



$$10.5\,\text{g Ag} \times \frac{1\,\text{mol Ag}}{107.868\,\text{g Ag}} = 9.73 \times 10^{-2}\,\text{mol Ag}$$

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Interactive Example 18.11 - Solution (Continued 1)

- Each Ag^+ ion requires one electron to become a silver atom

$$Ag^+ + e^- \rightarrow Ag$$

  - Thus 9.73×10^{-2} mole of electrons is required, and we can calculate the quantity of charge carried by these electrons

$$9.73 \times 10^{-2}\ \text{mol}\ e^- \times \frac{96,485\ \text{C}}{\text{mol}\ e^-} = 9.39 \times 10^3\ \text{C}$$

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Interactive Example 18.11 - Solution (Continued 2)

- The 5.00 A (5.00 C/s) of current must produce 9.39×10^3 C of charge
  - Thus,

$$\left(5.00\,\frac{\text{C}}{\text{s}}\right) \times (\text{time, in s}) = 9.39 \times 10^3\,\text{C}$$

$$\text{Time} = \frac{9.39 \times 10^3}{5.00}\,\text{s} = 1.88 \times 10^3\,\text{s} = 31.3\,\text{min}$$

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Electrolysis of Water - Nonspontaneous Reaction

Anode reaction: $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ $\quad -E° = -1.23\ V$

Cathode reaction: $4H_2O + 4e^- \rightarrow 2H_2 + 4OH^-$ $\quad E° = -0.83\ V$

Net reaction: $6H_2O \rightarrow 2H_2 + O_2 + \underbrace{4(H^+ + OH^-)}_{4H_2O}$ $\quad E° = -2.06\ V$

Or

$2H_2O \rightarrow 2H_2 + O_2$

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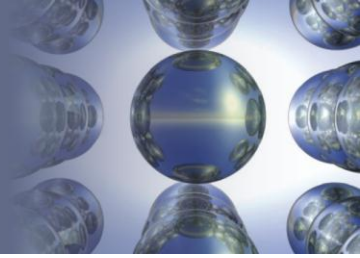

Interactive Example 18.12 - Relative Oxidizing Abilities

- An acidic solution contains the ions Ce^{4+}, VO_2^+, and Fe^{3+}
  - Using the E° values listed in Table 18.1, give the order of oxidizing ability of these species, and predict which one will be reduced at the cathode of an electrolytic cell at the lowest voltage

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Interactive Example 18.12 - Solution

- The half-reactions and E° values are as follows:

$$Ce^{4+} + e^- \rightarrow Ce^{3+} \qquad E° = 1.70\ V$$

$$VO_2^+ + 2H^+ + e^- \rightarrow VO^{2+} + H_2O \qquad E° = 1.00\ V$$

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \qquad E° = 0.77\ V$$

  - The order of oxidizing ability is therefore:

$$Ce^{4+} > VO_2^+ > Fe^{3+}$$

  - The Ce^{4+} ion will be reduced at the lowest voltage in an electrolytic cell

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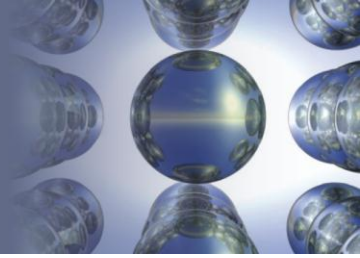

Production of Aluminum

- Aluminum is extracted from bauxite
  - Not pure aluminum oxide
  - Bauxite is treated with aqueous sodium hydroxide to obtain pure hydrated alumina
    - Alumina dissolves in the basic solution
    - Other metals remain as solids
  - Extraction of purified alumina

$$2CO_2(g) + 2AlO_2^-(aq) + (n + 1)H_2O(l) \rightarrow 2HCO_3^-(aq) + Al_2O_3 \cdot nH_2O(s)$$

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Production of Aluminum (Continued)

- Purified alumina is mixed with cryolite and melted
  - Aluminum ion is reduced to aluminum metal in an electrolytic cell
  - Alumina reacts with the cryolite anion

$$Al_2O_3 + 4AlF_6^{3-} \rightarrow 3Al_2OF_6^{2-} + 6F^-$$

  - Overall cell reaction

$$2Al_2O_3 + 3C \rightarrow 4Al + 3CO_2$$

- Aluminum produced is 99.5% pure

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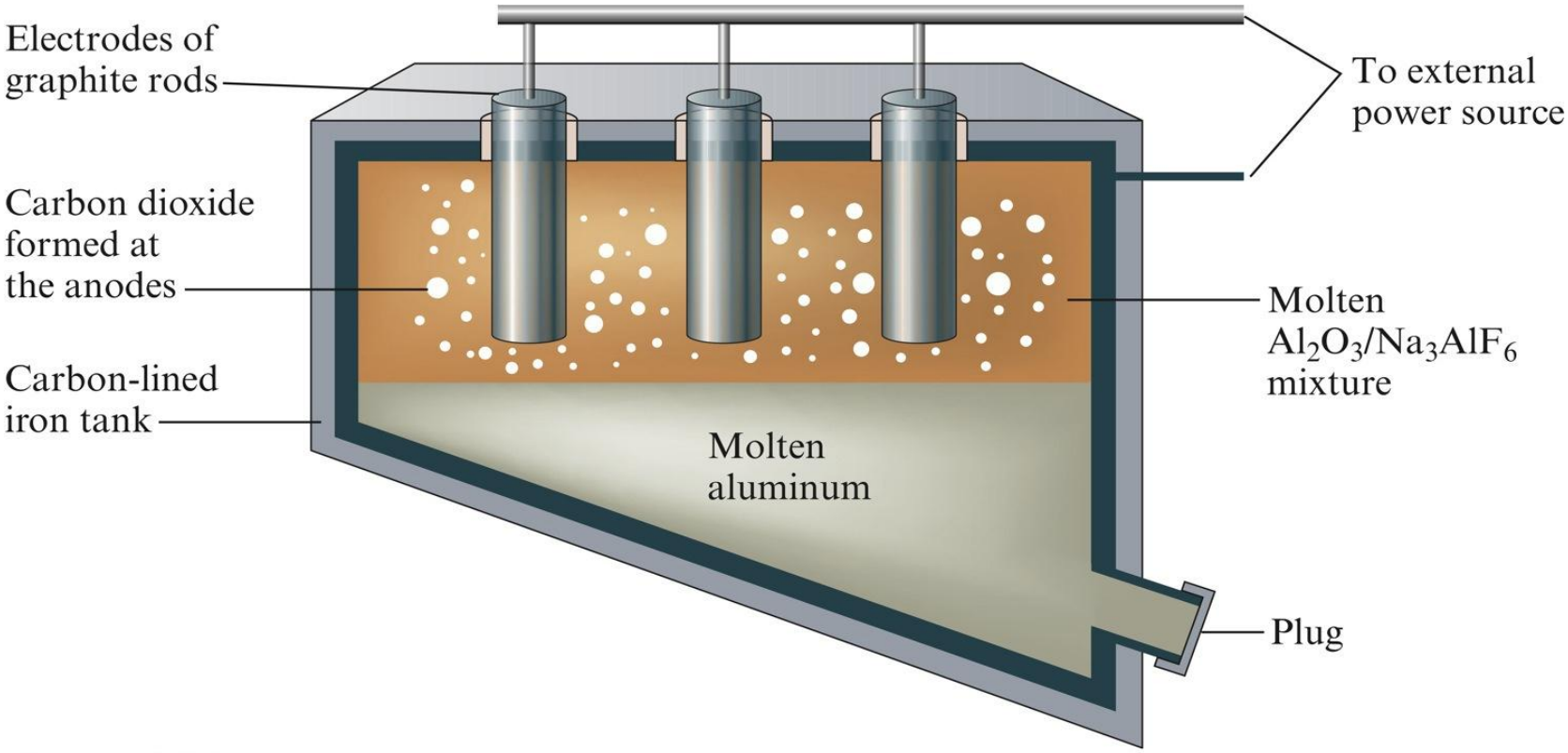
Figure 18.22 - Electrolytic Cell for Producing Aluminum by the Hall–Heroult Process



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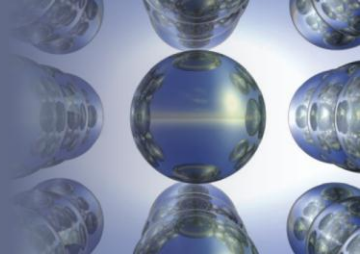

Electrorefining of Metals - Example

- Impure copper that is derived from the reduction of copper ore is cast into large slabs that serve as anodes for electrolytic cells
  - Electrolyte - Aqueous copper sulfate
  - Cathodes - Thin sheets of ultrapure copper

$$\text{Anode reaction: } Cu \rightarrow Cu^{2+} + e^{-}$$

$$\text{Cathode reaction: } Cu^{2+} + 2e^{-} \rightarrow Cu$$

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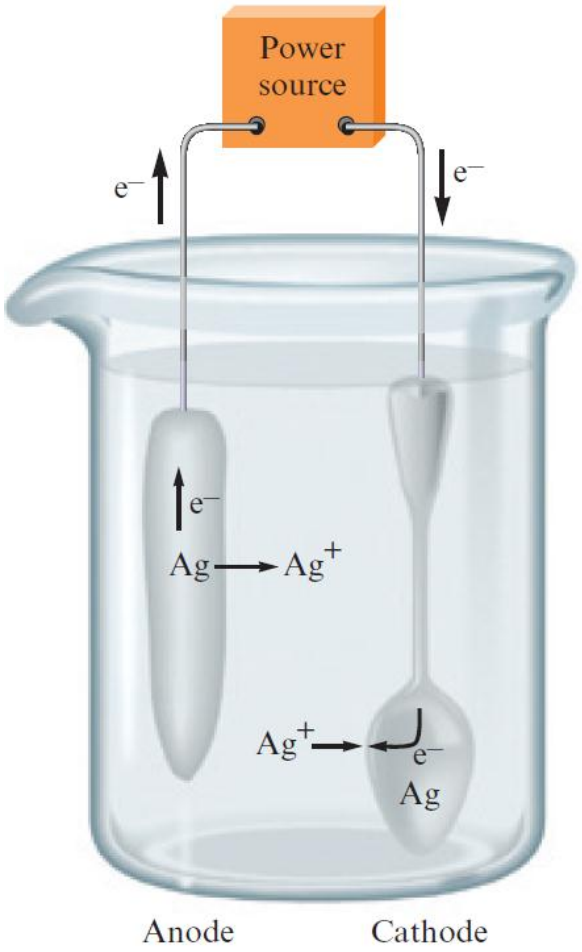
Section 18.9
Commercial Electrolytic Processes

Metal Plating

- Protects metals that corrode easily
- Can be done by making the object as the cathode in a tank containing ions of the plating metal
  - Example - Electroplating of a spoon



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Electrolysis of Sodium Chloride (Brine)

- Process used for the production of sodium metal
- Steps
  - Mix solid NaCl with solid $CaCl_2$ to lower the melting point
  - Electrolyze the mixture in a **Downs cell**

$$\text{Anode reaction: } 2Cl^- \rightarrow Cl_2 + 2e^-$$

$$\text{Cathode reaction: } Na^+ + e^- \rightarrow Na$$

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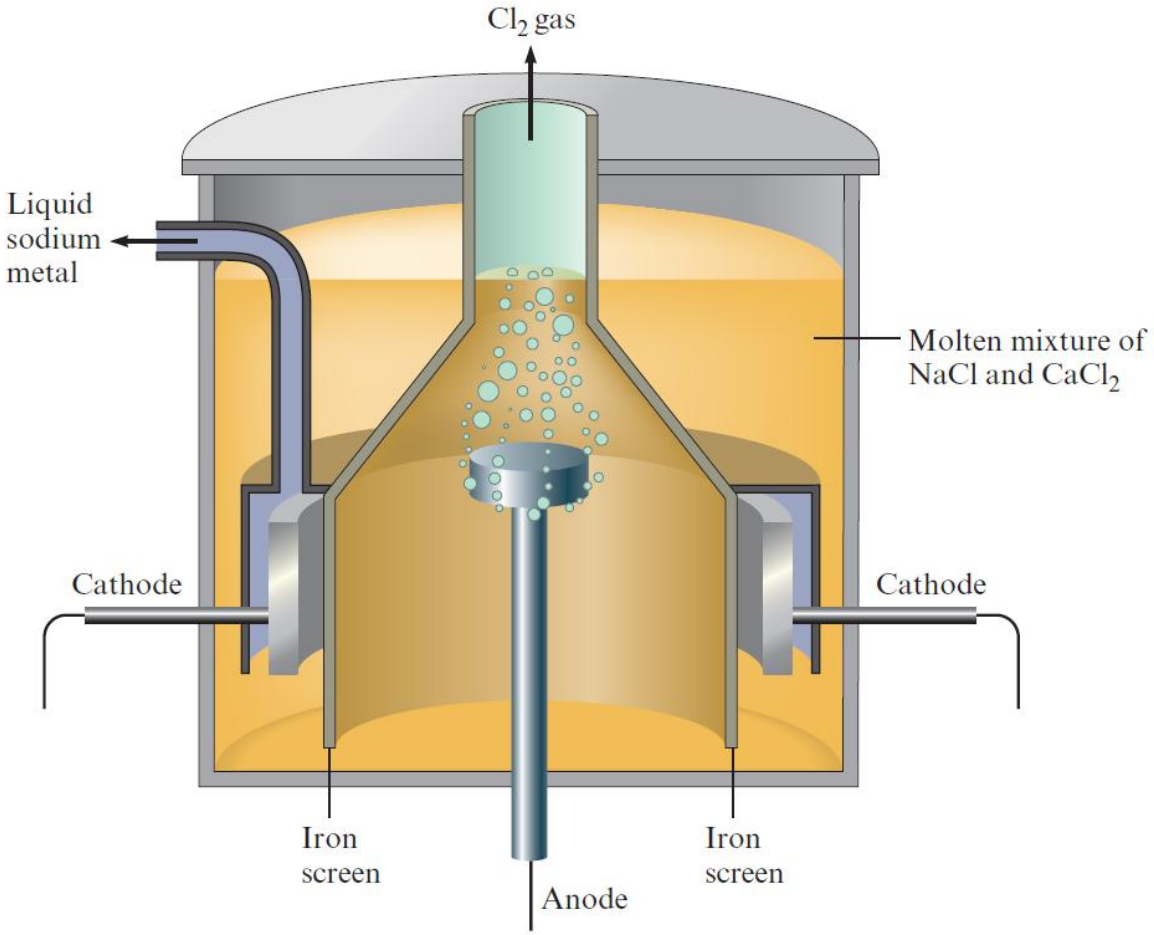
Section 18.9
Commercial Electrolytic Processes

Figure 18.25 - The Downs Cell



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Electrolysis of Sodium Chloride (Brine) (continued)

- The sodium is drained off in the Downs cell
  - Cooled and cast into blocks
  - Stored in an inert solvent, such as mineral oil, to prevent its oxidation
- Produces hydrogen and chlorine gas

$$\text{Anode reaction: } 2Cl^- \rightarrow Cl_2 + 2e^-$$

$$\text{Cathode reaction: } 2H_2O + 2e^- \rightarrow H_2 + 2OH^-$$

- Leaves a solution containing dissolved NaOH and NaCl

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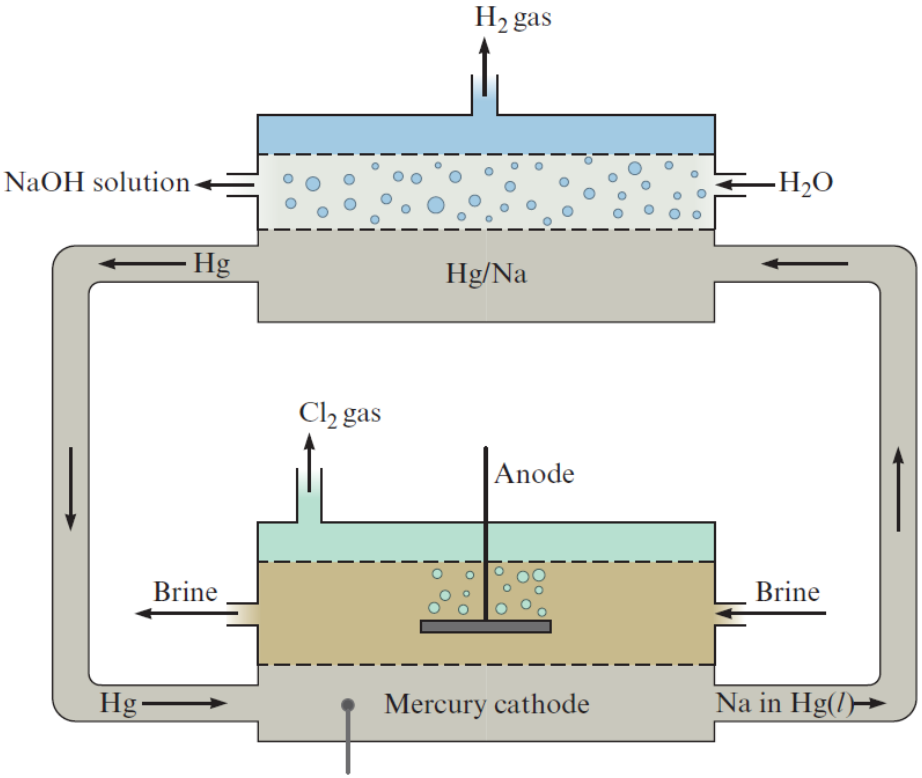
Figure 18.26 - Mercury Cell for Production of Chlorine and Sodium Hydroxide

- Contamination of the sodium hydroxide by NaCl
  - Can be eliminated by electrolyzing the brine in a **mercury cell**
  - Reaction of resulting sodium metal

$$2Na(s) + 2H_2O(l) \rightarrow 2Na^+(aq) + 2OH^-(aq) + H_2(g)$$



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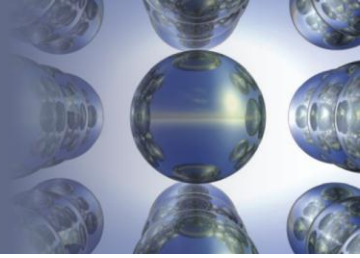

Chlor–Alkali Process

- Involves:
  - Recovering pure NaOH from an aqueous solution
  - Pumping the re-generated mercury into the electrolysis cell
- Currently carried out in diaphragm cells
  - Cathode and anode are separated by a diaphragm
    - Allows passage of water molecules, Na^+ ions, and Cl^- ions
    - Blocks passage of OH^- ions

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Chlor–Alkali Process (Continued)

- Disadvantage
  - The aqueous effluent from the cathode compartment contains a mixture of NaOH and untreated NaCl
    - Needs to be purified to derive pure NaOH
- Advancement in the chlor–alkali industry
  - Uses a membrane to separate the anode and cathode compartments in brine electrolysis cells
    - Membrane is impermeable to anions

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