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Chapter 18 Electrochemistry

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Outline



1. Voltaic cells
2. Standard voltages
3. Relations between E° , ΔG° and K
4. Electrolytic cells
5. Commercial cells

Electrochemistry



- ***Electrochemistry*** is the study of the conversion of electrical and chemical energy
- The conversion takes place in an electrochemical cell, of which there are two main types
 - Voltaic cells
 - Electrolytic cells

Review



- Oxidation
 - Loss of electrons
 - Occurs at electrode called the ***anode***
- Reduction
 - Gain of electrons
 - Occurs at electrode called the ***cathode***
- Redox reactions
 - ***Oxidation and reduction occur together***

Voltaic Cells



- In principle, any spontaneous redox reaction can serve as the source of energy for a voltaic cell
- Cell design
 - Oxidation at one electrode (anode)
 - Reduction at the other electrode (cathode)
 - Electrons move through an external circuit from the anode to the cathode

Mnemonic



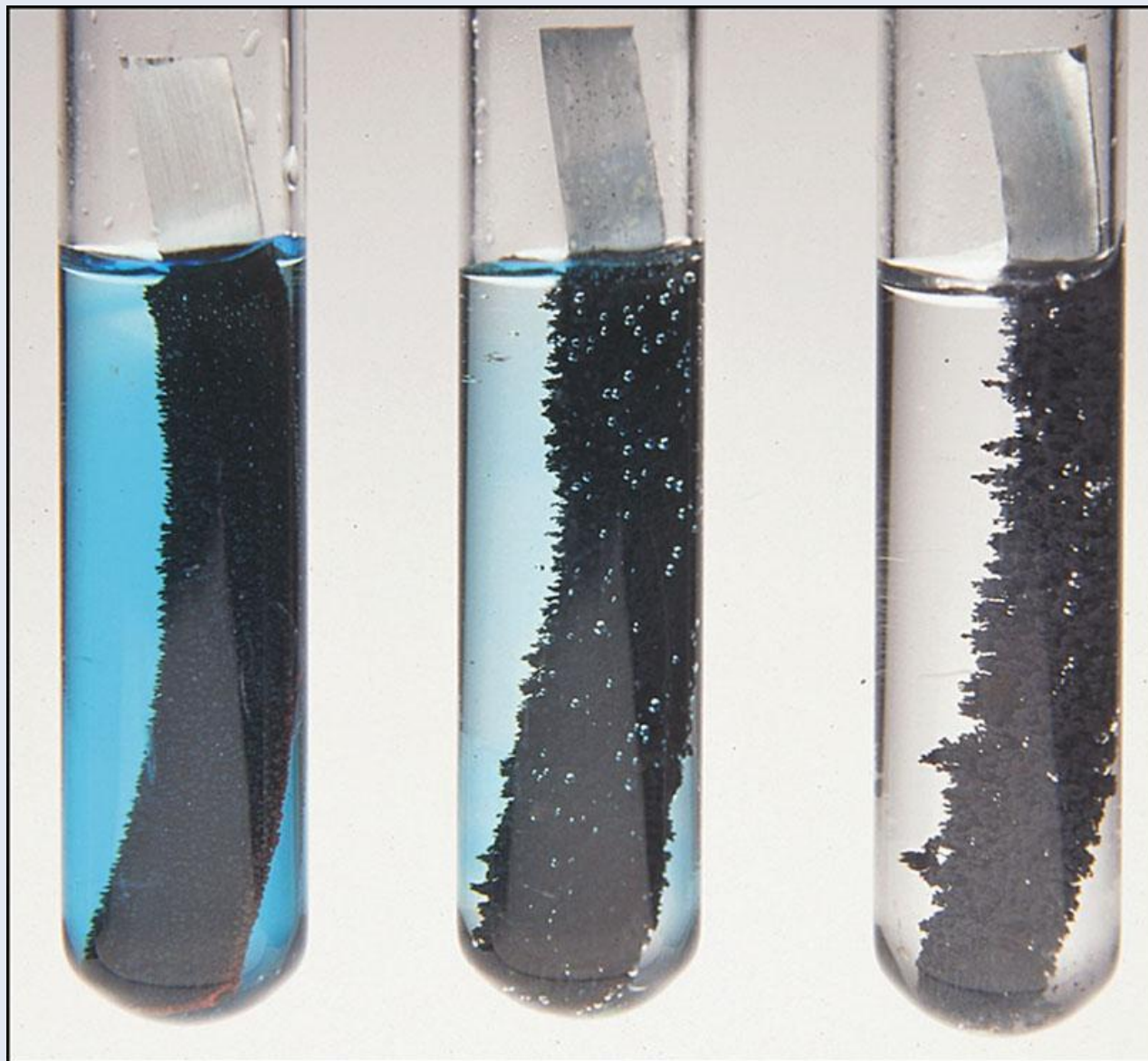
- Oxidation and anode both begin with vowels
- Reduction and cathode both begin with consonants

Zn-Cu²⁺ Reaction



- $\text{Zn (s)} + \text{Cu}^{2+} \text{ (aq)} \rightarrow \text{Zn}^{2+} \text{ (aq)} + \text{Cu (s)}$
 - When run directly in a test tube
 - Cu metal plates out on surface of Zn metal
 - Zn metal enters solution as Zn²⁺ ions
 - Blue color of Cu²⁺ solution fades

Figure 18.1 – Zinc/Copper(II) Reaction



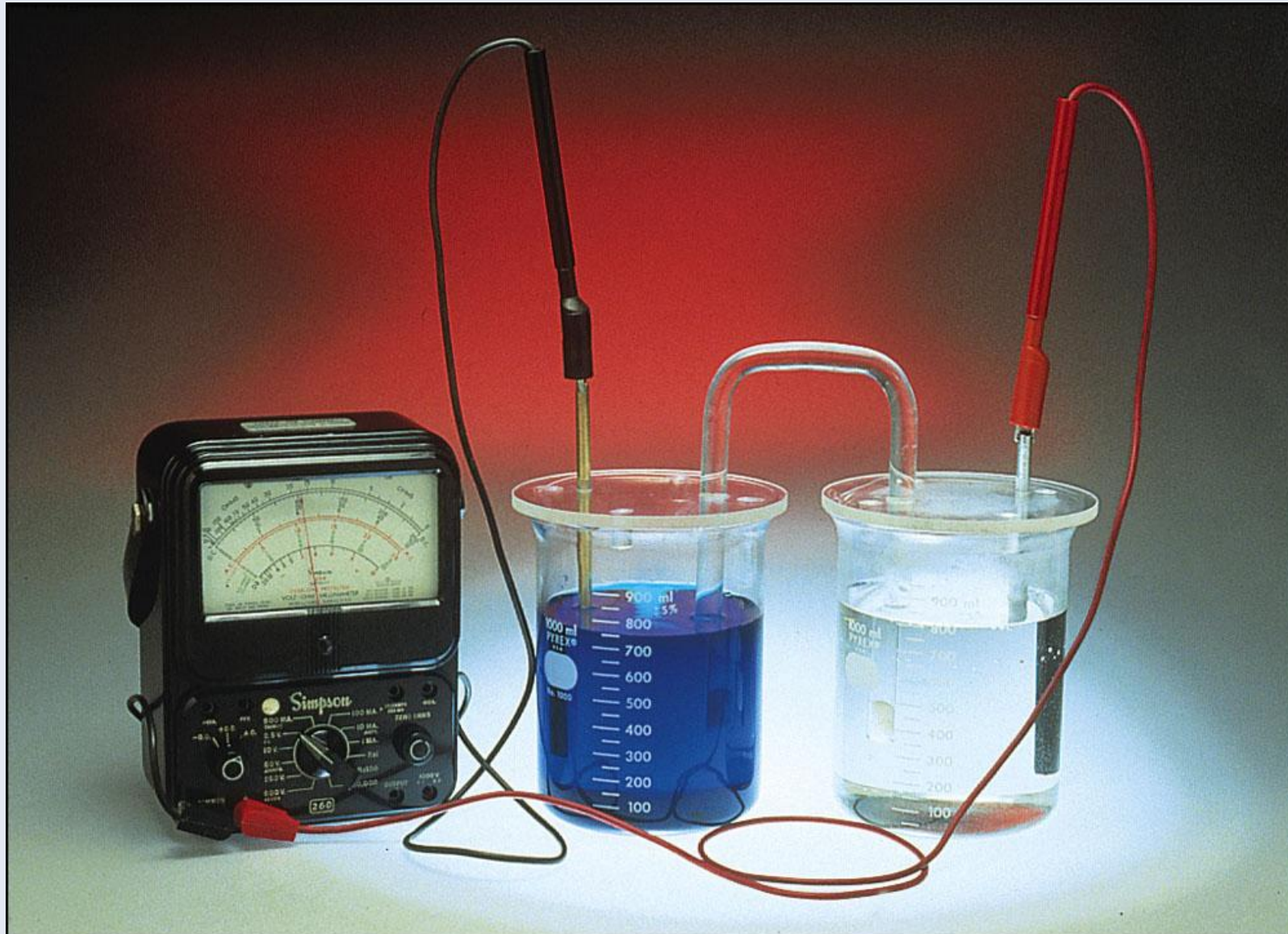
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Zn-Cu²⁺ Cell



- To set up a voltaic cell for the same reaction, we separate the two half-reactions into half cells
 - Zn anode dips into a solution of Zn²⁺ ions
 - Cu cathode dips into a solution of Cu²⁺ ions
 - The external circuit consists of two wires connected to a voltmeter

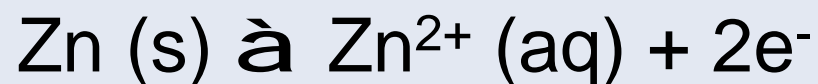
Figure 18.2



Tracing the Flow of Electrons,



1. At the zinc electrode, electrons are produced



The sign of this electrode is (-); think of it as an electron pump

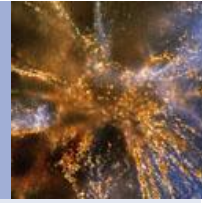
Electrons flow from the red lead, through the voltmeter, to the black lead; the needle deflection indicates the cell voltage

2. The electrons enter the cathode, at which



The sign of this electrode is (+)

Tracing the Flow of Electrons, (Cont'd)



3. As the half reactions occur

A surplus of positive ions builds up at the anode

A surplus of negative ions builds up at the cathode

Anions and cations must flow to balance charge

Salt Bridges

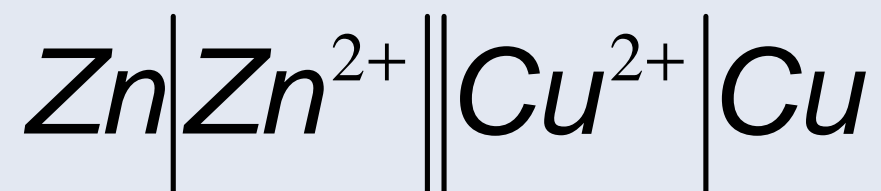


- The salt bridge is a gel-filled U-tube with a solution of a salt containing ions *other than those involved in the redox reaction*
 - KNO_3 is frequently used
 - Cations flow toward the cathode to neutralize the buildup of negative charge
 - Anions flow toward the anode to neutralize the buildup of positive charge

Shorthand Cell Notation



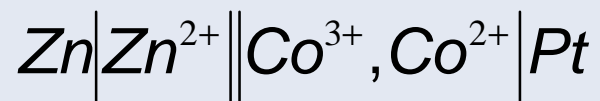
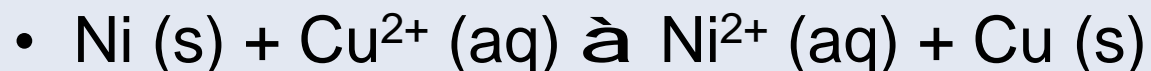
- Oxidation on the left
- Reduction on the right
- Single vertical line represents a phase boundary
 - Liquid-metal or liquid-gas, etc.
- Double line is the salt bridge



Other Salt Bridge Cells

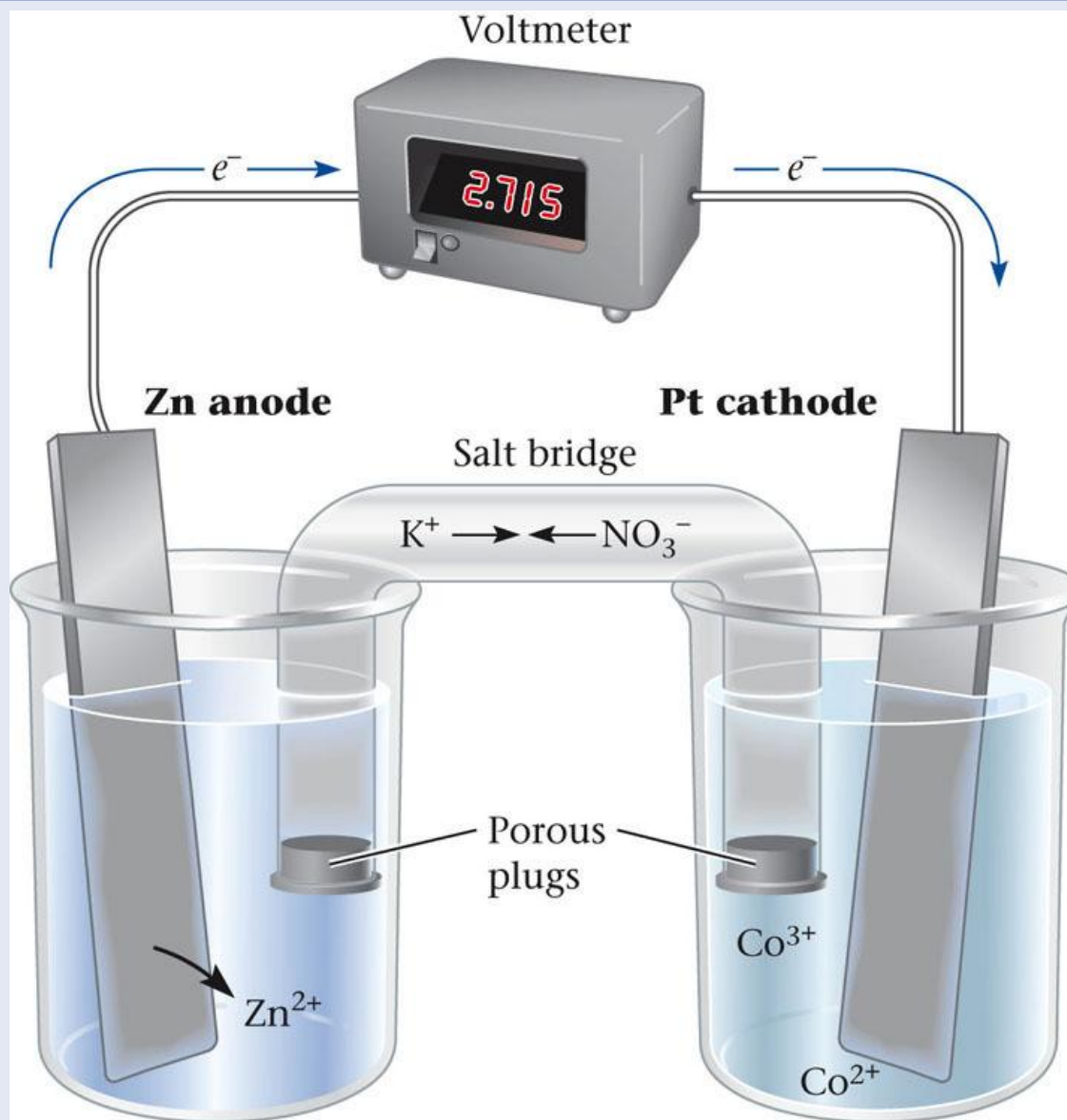


- Many spontaneous redox reactions can be set up as electrochemical cells



- Note that because both species in the reduction are ions, an inert platinum electrode is required

Figure 18.3



Example 18.1



Example 18.1

When chlorine gas is bubbled through an aqueous solution of NaBr, chloride ions and liquid bromine are the products of the spontaneous reaction. For this cell,

- Draw a sketch of the cell, labeling the anode, the cathode, and the direction of electron flow.
- Write the half-reaction that takes place at the anode and at the cathode.
- Write a balanced equation for the cell reaction.
- Write an abbreviated notation for the cell.

Example 18.1, (Cont'd)



Strategy Split the reaction into two half-reactions. Remember that oxidation occurs at the anode, reduction at the cathode. Anions move to the anode, cations to the cathode. Electrons are produced at the anode and transferred through the external circuit to the cathode, where they are consumed.

SOLUTION

(a) Figure 18.4 shows the cell with the appropriate labeled parts and the direction of electron flow indicated.

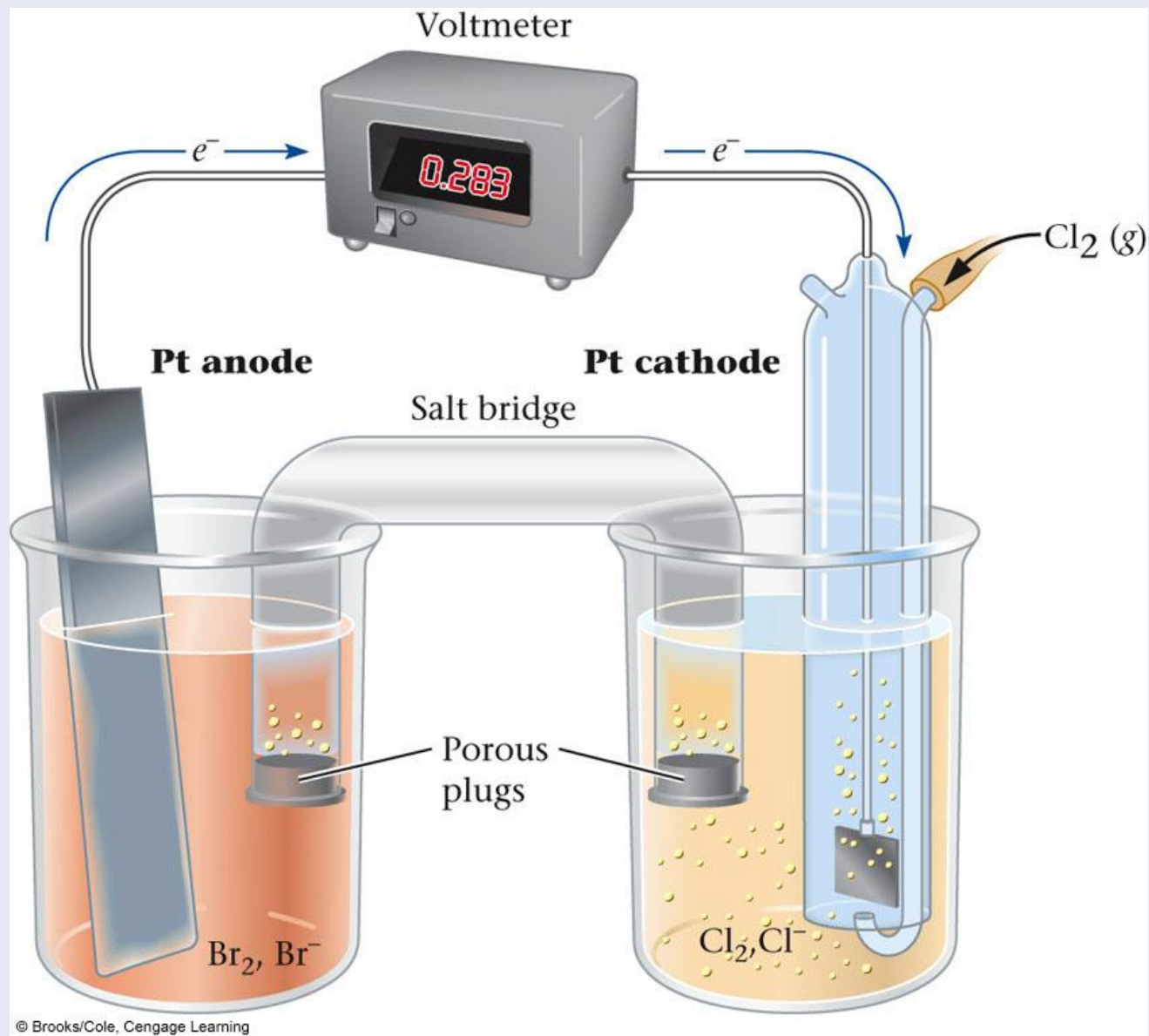
(b) cathode: $\text{Cl}_2(g) + 2e^- \longrightarrow 2\text{Cl}^-(aq)$ (reduction)

anode: $2\text{Br}^-(aq) \longrightarrow \text{Br}_2(l) + 2e^-$ (oxidation)

(c) $\text{Cl}_2(g) + 2\text{Br}^-(aq) \longrightarrow 2\text{Cl}^-(aq) + \text{Br}_2(l)$

(d) $\text{Pt} | \text{Br}_2, \text{Br}^- || \text{Cl}^- | \text{Cl}_2 | \text{Pt}$

Figure 18.4



Voltaic Cell Summary



- A voltaic cell contains two half-cells
- Each half cell consists of an electrode dipping into an aqueous solution
- In one half cell, the anode, oxidation occurs
- In the other half cell, the cathode, reduction occurs

Standard Voltages



- The cell voltage is the driving force for an electrochemical reaction
 - Intensive property; independent of the number of electrons flowing through the cell
 - Depends on the nature of the redox reaction and on the concentration of species involved
- Standard voltages are measured with
 - All aqueous concentrations at 1M
 - The pressure of all gases at 1 atm

E° for a Standard Cell



- $\text{Zn (s)} + 2\text{H}^+ (\text{aq}, 1\text{M}) \rightarrow \text{Zn}^{2+} (\text{aq}, 1\text{M}) + \text{H}_2 (\text{g}, 1 \text{ atm})$
- Temperature is held constant (usually at 25°C)
- $E^\circ = +0.762\text{V}$

E° Oxidation and Reduction



$$E^\circ = E_{red}^\circ + E_{ox}^\circ$$



$$+ 0.762V = E_{red}^\circ (H^+ \rightarrow H_2) + E_{ox}^\circ (Zn \rightarrow Zn^{2+})$$

- The value of E° cannot be measured for a half-cell
- The value of E° for the hydrogen reduction is assigned to be 0.000 V
- Therefore, the E° for the oxidation of zinc is +0.762

Standard Potentials



- Once the hydrogen half cell has been assigned a voltage of 0.000 V, other half cells can be measured relative to it
- Tables of ***standard potentials*** can be prepared
 - These are always ***reduction*** potentials, i.e., E_{red}°
 - To obtain the oxidation potential, simply reverse the sign:
 - $\text{Zn}^{2+} (\text{aq}) + 2\text{e}^{-} \rightarrow \text{Zn} (\text{s}) \quad E_{red}^{\circ} = -0.762\text{V}$
 - $\text{Zn} (\text{s}) \rightarrow \text{Zn}^{2+} (\text{aq}) + 2\text{e}^{-} \quad E_{ox}^{\circ} = +0.762\text{V}$
- Standard voltages for oxidation and reduction are ***equal in magnitude and opposite in sign***

Strengths of Oxidizing and Reducing Agents



- In a table of reduction potentials
- Oxidizing agents are located on the left side
 - The more positive E_{red}^0 is, the stronger the oxidizing agent
 - The strong oxidizing agents are on the bottom left of the table
- Reducing agents are located on the right side
 - The more negative E_{red}^0 is, the stronger the reducing agent
 - The strong reducing agents are on the top right of the table

Table 18.1



Table 18.1 Standard Potentials in Water Solution at 25°C

Acidic Solution, $[H^+] = 1 M$

	E°_{red} (V)
$Li^+(aq) + e^- \longrightarrow Li(s)$	-3.040
$K^+(aq) + e^- \longrightarrow K(s)$	-2.936
$Ba^{2+}(aq) + 2e^- \longrightarrow Ba(s)$	-2.906
$Ca^{2+}(aq) + 2e^- \longrightarrow Ca(s)$	-2.869
$Na^+(aq) + e^- \longrightarrow Na(s)$	-2.714
$Mg^{2+}(aq) + 2e^- \longrightarrow Mg(s)$	-2.357
$Al^{3+}(aq) + 3e^- \longrightarrow Al(s)$	-1.68
$Mn^{2+}(aq) + 2e^- \longrightarrow Mn(s)$	-1.182
$Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s)$	-0.762
$Cr^{3+}(aq) + 3e^- \longrightarrow Cr(s)$	-0.744
$Fe^{2+}(aq) + 2e^- \longrightarrow Fe(s)$	-0.409
$Cr^{3+}(aq) + e^- \longrightarrow Cr^{2+}(aq)$	-0.408
$Cd^{2+}(aq) + 2e^- \longrightarrow Cd(s)$	-0.402
$PbSO_4(s) + 2e^- \longrightarrow Pb(s) + SO_4^{2-}(aq)$	-0.356
$Tl^+(aq) + e^- \longrightarrow Tl(s)$	-0.336
$Co^{2+}(aq) + 2e^- \longrightarrow Co(s)$	-0.282
$Ni^{2+}(aq) + 2e^- \longrightarrow Ni(s)$	-0.236
$AgI(s) + e^- \longrightarrow Ag(s) + I^-(aq)$	-0.152
$Sn^{2+}(aq) + 2e^- \longrightarrow Sn(s)$	-0.141
$Pb^{2+}(aq) + 2e^- \longrightarrow Pb(s)$	-0.127
$2H^+(aq) + 2e^- \longrightarrow H_2(g)$	0.000
$AgBr(s) + e^- \longrightarrow Ag(s) + Br^-(aq)$	0.073

oxidizing agents

reducing agents

Table 18.1, (Cont'd)




Increasing strength of oxidiz	$\text{AgBr}(s) + e^-$	$\longrightarrow \text{Ag}(s) + \text{Br}^-(aq)$	Increasing strength of red 	0.073
	$\text{S}(s) + 2\text{H}^+(aq) + 2e^-$	$\longrightarrow \text{H}_2\text{S}(aq)$		0.144
	$\text{Sn}^{4+}(aq) + 2e^-$	$\longrightarrow \text{Sn}^{2+}(aq)$		0.154
	$\text{SO}_4^{2-}(aq) + 4\text{H}^+(aq) + 2e^-$	$\longrightarrow \text{SO}_2(g) + 2\text{H}_2\text{O}$		0.155
	$\text{Cu}^{2+}(aq) + e^-$	$\longrightarrow \text{Cu}^+(aq)$		0.161
	$\text{Cu}^{2+}(aq) + 2e^-$	$\longrightarrow \text{Cu}(s)$		0.339
	$\text{Cu}^+(aq) + e^-$	$\longrightarrow \text{Cu}(s)$		0.518
	$\text{I}_2(s) + 2e^-$	$\longrightarrow 2\text{I}^-(aq)$		0.534
	$\text{Fe}^{3+}(aq) + e^-$	$\longrightarrow \text{Fe}^{2+}(aq)$		0.769
	$\text{Hg}_2^{2+}(aq) + 2e^-$	$\longrightarrow 2\text{Hg}(l)$		0.796
	$\text{Ag}^+(aq) + e^-$	$\longrightarrow \text{Ag}(s)$		0.799
	$2\text{Hg}^{2+}(aq) + 2e^-$	$\longrightarrow \text{Hg}_2^{2+}(aq)$		0.908
	$\text{NO}_3^-(aq) + 4\text{H}^+(aq) + 3e^-$	$\longrightarrow \text{NO}(g) + 2\text{H}_2\text{O}$		0.964
	$\text{AuCl}_4^-(aq) + 3e^-$	$\longrightarrow \text{Au}(s) + 4\text{Cl}^-(aq)$		1.001
	$\text{Br}_2(l) + 2e^-$	$\longrightarrow 2\text{Br}^-(aq)$		1.077
	$\text{O}_2(g) + 4\text{H}^+(aq) + 4e^-$	$\longrightarrow 2\text{H}_2\text{O}$		1.229
	$\text{MnO}_2(s) + 4\text{H}^+(aq) + 2e^-$	$\longrightarrow \text{Mn}^{2+}(aq) + 2\text{H}_2\text{O}$		1.229
	$\text{Cr}_2\text{O}_7^{2-}(aq) + 14\text{H}^+(aq) + 6e^-$	$\longrightarrow 2\text{Cr}^{3+}(aq) + 7\text{H}_2\text{O}$		1.33
	$\text{Cl}_2(g) + 2e^-$	$\longrightarrow 2\text{Cl}^-(aq)$		1.360
	$\text{ClO}_3^-(aq) + 6\text{H}^+(aq) + 5e^-$	$\longrightarrow \frac{1}{2}\text{Cl}_2(g) + 3\text{H}_2\text{O}$		1.458
	$\text{Au}^{3+}(aq) + 3e^-$	$\longrightarrow \text{Au}(s)$		1.498
	$\text{MnO}_4^-(aq) + 8\text{H}^+(aq) + 5e^-$	$\longrightarrow \text{Mn}^{2+}(aq) + 4\text{H}_2\text{O}$		1.512
	$\text{PbO}_2(s) + \text{SO}_4^{2-}(aq) + 4\text{H}^+(aq) + 2e^-$	$\longrightarrow \text{PbSO}_4(s) + 2\text{H}_2\text{O}$		1.687
	$\text{H}_2\text{O}_2(aq) + 2\text{H}^+(aq) + 2e^-$	$\longrightarrow 2\text{H}_2\text{O}$		1.763
$\text{Co}^{3+}(aq) + e^-$	$\longrightarrow \text{Co}^{2+}(aq)$	1.953		
$\text{F}_2(g) + 2e^-$	$\longrightarrow 2\text{F}^-(aq)$	2.889		

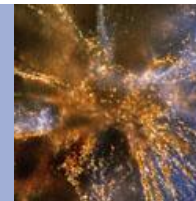
Table 18.1, (Cont'd)



Basic Solution, $[\text{OH}^-] = 1 \text{ M}$

			E_{red}° (V)
$\text{Fe}(\text{OH})_2(\text{s}) + 2e^-$	\longrightarrow	$\text{Fe}(\text{s}) + 2\text{OH}^-(\text{aq})$	-0.891
$2\text{H}_2\text{O} + 2e^-$	\longrightarrow	$\text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq})$	-0.828
$\text{Fe}(\text{OH})_3(\text{s}) + e^-$	\longrightarrow	$\text{Fe}(\text{OH})_2(\text{s}) + \text{OH}^-(\text{aq})$	-0.547
$\text{S}(\text{s}) + 2e^-$	\longrightarrow	$\text{S}^{2-}(\text{aq})$	-0.445
$\text{NO}_3^-(\text{aq}) + 2\text{H}_2\text{O} + 3e^-$	\longrightarrow	$\text{NO}(\text{g}) + 4\text{OH}^-(\text{aq})$	-0.140
$\text{NO}_3^-(\text{aq}) + \text{H}_2\text{O} + 2e^-$	\longrightarrow	$\text{NO}_2^-(\text{aq}) + 2\text{OH}^-(\text{aq})$	0.004
$\text{ClO}_4^-(\text{aq}) + \text{H}_2\text{O} + 2e^-$	\longrightarrow	$\text{ClO}_3^-(\text{aq}) + 2\text{OH}^-(\text{aq})$	0.398
$\text{O}_2(\text{g}) + 2\text{H}_2\text{O} + 4e^-$	\longrightarrow	$4\text{OH}^-(\text{aq})$	0.401
$\text{ClO}_3^-(\text{aq}) + 3\text{H}_2\text{O} + 6e^-$	\longrightarrow	$\text{Cl}^-(\text{aq}) + 6\text{OH}^-(\text{aq})$	0.614
$\text{ClO}^-(\text{aq}) + \text{H}_2\text{O} + 2e^-$	\longrightarrow	$\text{Cl}^-(\text{aq}) + 2\text{OH}^-(\text{aq})$	0.890

Trends in the Table



- Reducing agent strength decreases down the table
- Oxidizing agent strength increases down the table

Example 18.2



Example 18.2 Conceptual

Consider the following species in acidic solution: MnO_4^- , I^- , NO_3^- , H_2S , and Fe^{2+} . Using Table 18.1,

- classify each of these as an oxidizing and/or reducing agent.
- arrange the oxidizing agents in order of increasing strength.
- do the same with the reducing agents.

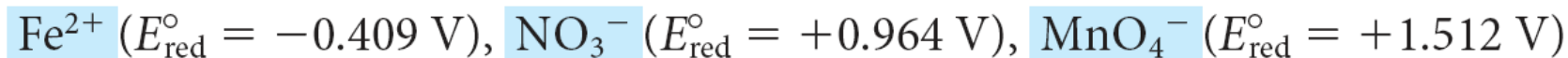
Strategy Remember that oxidizing agents are located in the left column of Table 18.1, reducing agents in the right column. Large positive values of E_{red}° and E_{ox}° are associated with strong oxidizing and reducing agents, respectively.

Example 18.2, (Cont'd)

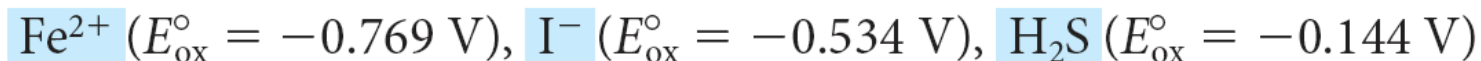


SOLUTION

(a) Oxidizing agents:

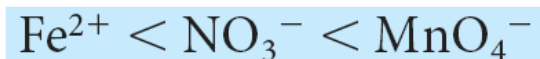


Reducing agents:



Note that Fe^{2+} can act either as an oxidizing agent, in which case it is reduced to Fe, or as a reducing agent, in which case it is oxidized to Fe^{3+} .

(b) Comparing values of E_{red}° ,

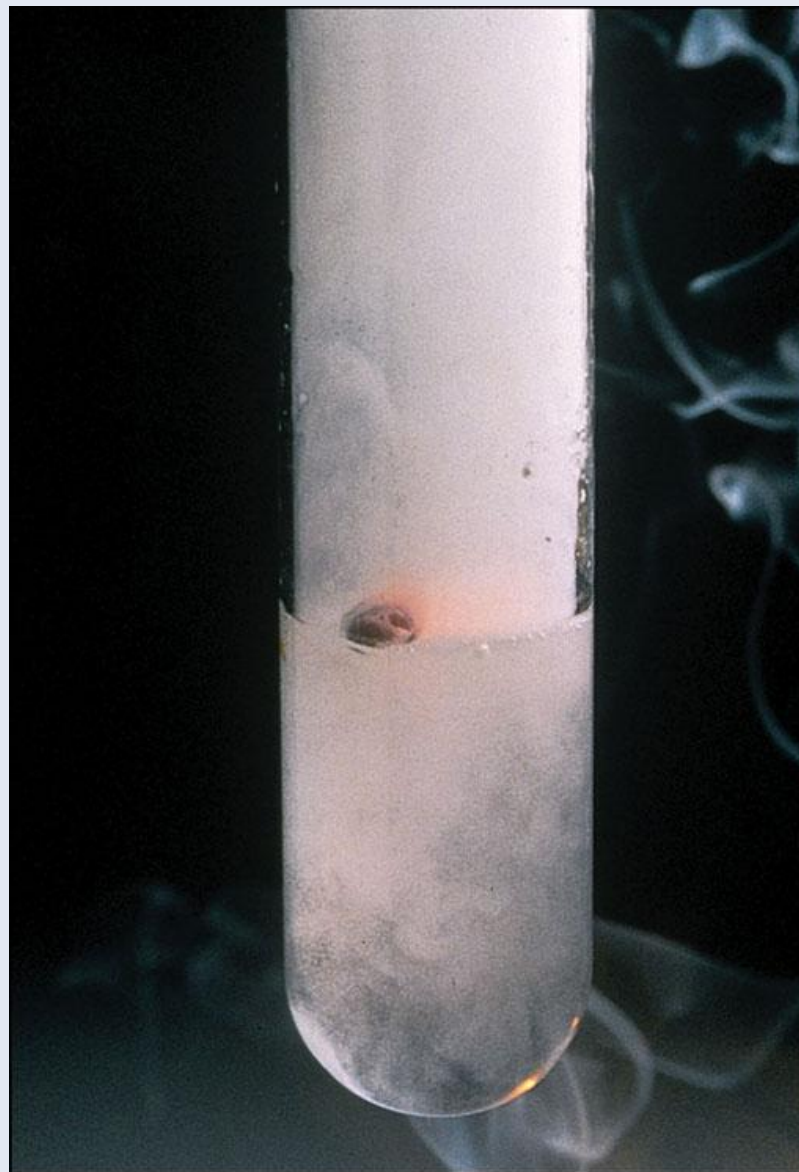


This ranking correlates with the positions of these species in the left column of Table 18.1; MnO_4^{-} is near the bottom, Fe^{2+} closest to the top.

(c) Comparing values of E_{ox}° ,



Lithium as a Reducing Agent



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Calculation of E°



$$E^\circ = E_{red}^\circ + E_{ox}^\circ$$

- Look up the reduction potentials for both half cells
- Change the sign of the oxidation half reaction
- Add the two numbers together
- The resulting E° is always positive for a voltaic cell
- Never multiply E° by any coefficient

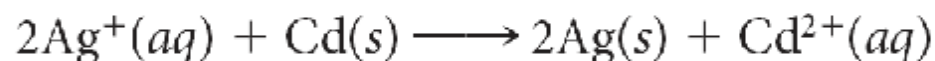
Example 18.3



Example 18.3

Graded

Consider the voltaic cell in which the reaction is



- * (a) Use Table 18.1 to calculate E° for the voltaic cell.
- ** (b) If the value zero is arbitrarily assigned to the standard voltage for the reduction of Ag^+ ions to Ag , what is E_{red}° for the reduction of Cd^{2+} ions to Cd ?

Example 18.3, (Cont'd)

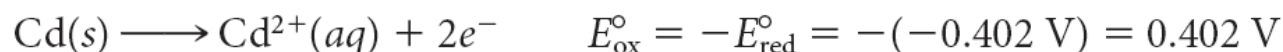


SOLUTION

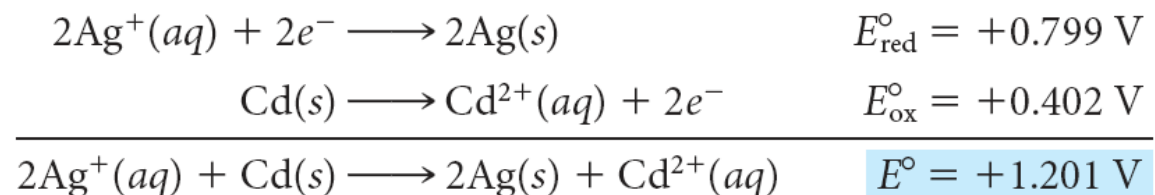
- (a) The oxidation number of silver drops from +1 (Ag^+) to zero (Ag), so the reduction half-reaction with its cell potential is



The oxidation number of cadmium increases from 0 (Cd) to +2 (Cd^{2+}), so the oxidation half-reaction is



We add the half-equations to obtain the overall reaction and add the half-reaction voltages to obtain the overall voltage:

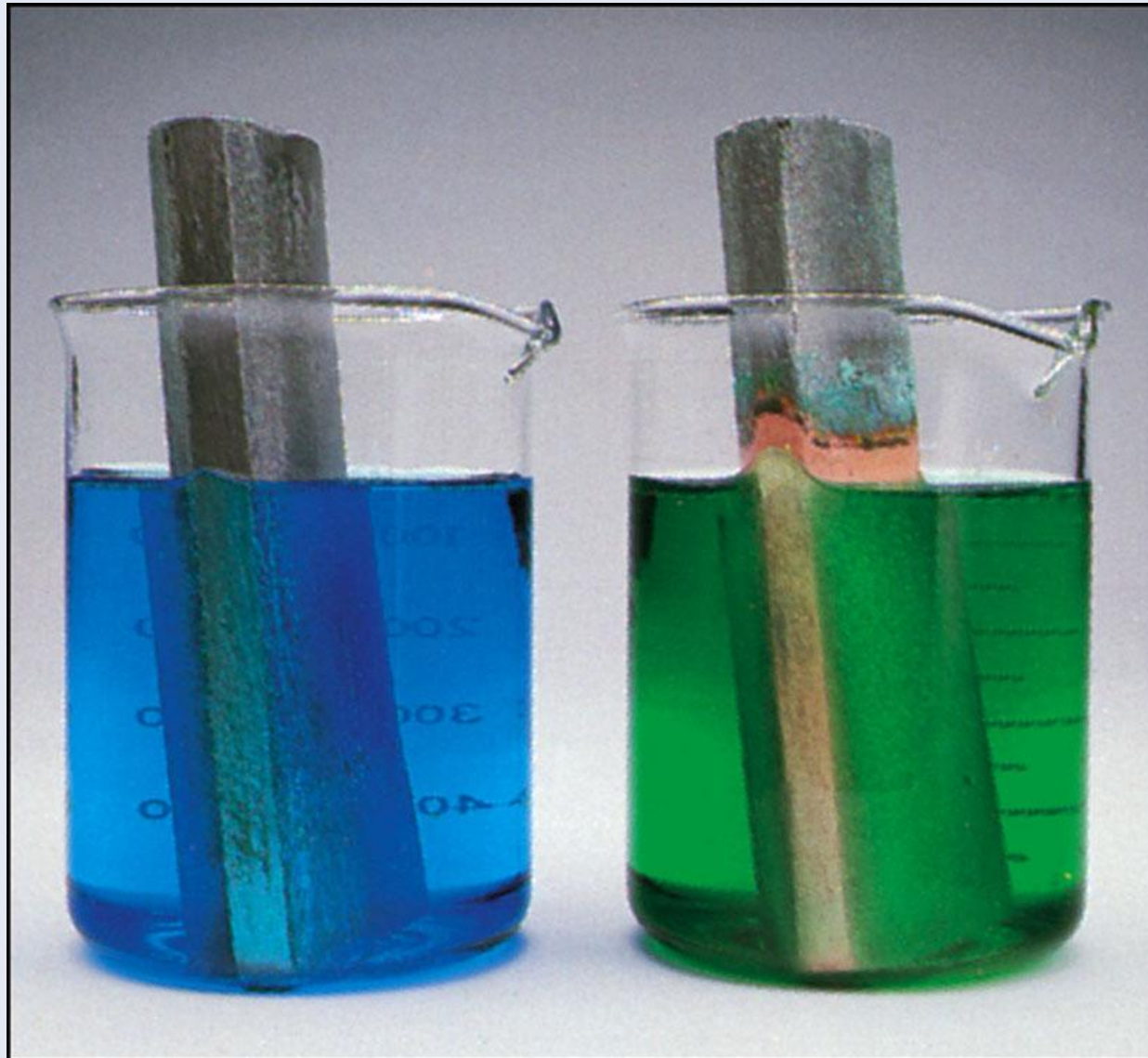


- (b) Recall that $E^\circ = E_{\text{ox}}^\circ + E_{\text{red}}^\circ$. If $E_{\text{red}}^\circ = 0$ for the reduction of silver, then E_{ox}° must satisfy

$$1.201 = 0 + E_{\text{ox}}^\circ \quad E_{\text{ox}}^\circ = 1.201 \text{ V}$$

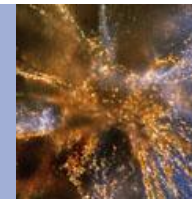
Since E_{red}° for the reduction of Cd^{2+} is asked for, then $E_{\text{red}}^\circ = -E_{\text{ox}}^\circ = -1.201 \text{ V}$.

Figure 18.5



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Spontaneity of Redox Reactions



- If the calculated voltage of a redox reaction is positive, the reaction is spontaneous
- If the calculated voltage of a redox reaction is negative, the reaction is nonspontaneous

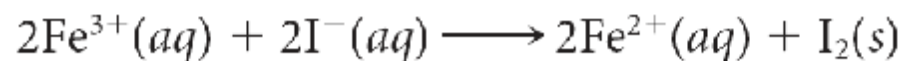
Example 18.4



Example 18.4 Graded

Using standard potentials listed in Table 18.1, decide whether at standard concentrations

- * (a) the reaction



will occur.

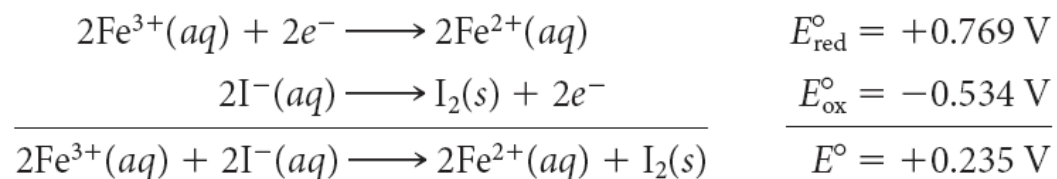
- ** (b) Fe(s) will be oxidized to Fe²⁺ by treatment with hydrochloric acid.
- *** (c) a redox reaction will occur when the following species are mixed in acidic solution: Cl⁻, Fe²⁺, Cr²⁺, I₂.

Example 18.4, (Cont'd)



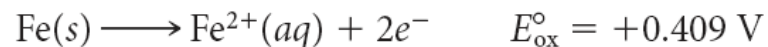
SOLUTION

(a) Breaking up the reaction into two half-reactions:

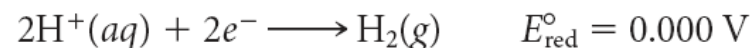


Since E° is positive, we conclude that the reaction is spontaneous at standard concentrations.

(b) The oxidation half-reaction is



Hydrochloric acid consists of H^{+} and Cl^{-} ions. Of these two ions, only H^{+} is listed in the left column of Table 18.1; the Cl^{-} ion cannot be reduced. The reduction half-reaction must be



Because the calculated voltage is positive,

$$E^{\circ} = +0.409 \text{ V} + 0.000 \text{ V} = +0.409 \text{ V}$$

The following redox reaction, obtained by summing the half-reactions,



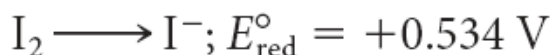
should and does occur (Figure 18.6).

Example 18.4, (Cont'd)

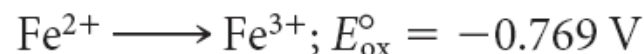
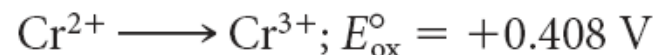
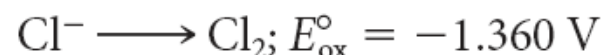


- (c) The most straightforward way to solve this problem is to start by listing all the possible half-reactions of these species as given in Table 18.1. Then see if you can combine an E_{red}° with an E_{ox}° to give a positive E° .

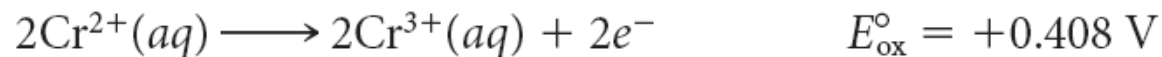
Possible Reductions



Possible Oxidations



The only combination that gives a positive E° is the reaction of iodine with chromium(II):



Relations Between E , ΔG° and K



- There is a relationship between the spontaneity of the reaction in a voltaic cell, the free energy change, and therefore the equilibrium constant
- E° and ΔG°

$$\Delta G^\circ = -nFE^\circ$$

- ΔG° is the standard free energy change (gases, 1 atm; solutions, 1 M)
- E° is the standard cell voltage
- n is the number of moles of electrons transferred in the reaction
- F is called the Faraday constant, the charge on a mole of electrons

E° and K



- Recall that

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

- So

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

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

- We can combine R , T , and F to $0.0257V$

E° and K , (Cont'd)



$$E^\circ = \frac{0.0257V}{n} \ln K$$

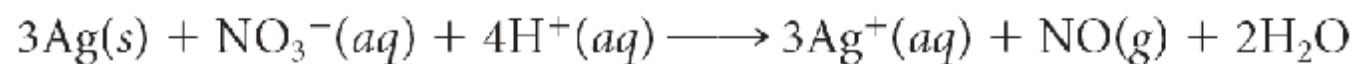
- The equation applies at 25°C
- Note that
 - If E° is positive, K is greater than 1
 - If E° is negative, K is less than 1

Example 18.5



Example 18.5

For the reaction



use Table 18.1 to calculate, at 25°C,

- (a) ΔG° (b) K

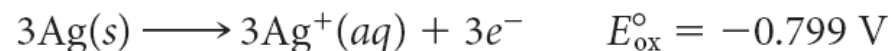
Example 18.5, (Cont'd)



Strategy Split the redox equation into two half-equations (oxidation and reduction). This enables you to calculate both E° and n . Then use Equations 18.2 and 18.3 to find ΔG° and K .

SOLUTION

(a) Ag is oxidized to Ag^+ ; NO_3^- is reduced to NO. The half-equations are



Clearly, $n = 3$



$$E^\circ = +0.165 \text{ V}$$

$$\Delta G^\circ = -nFE = -3 \text{ mol} \times 9.648 \times 10^4 \frac{\text{J}}{\text{mol} \cdot \text{V}} \times 0.165 \text{ V} = -4.78 \times 10^4 \text{ J} = -47.8 \text{ kJ}$$

$$(b) \ln K = \frac{nE^\circ}{(0.0257 \text{ V})} = \frac{3(0.165)}{0.0257} = 19.3$$

$$K = e^{19.3} = 2.4 \times 10^8$$

Reality Check The answers to (a) and (b) are related through the equation $\Delta G^\circ = -RT \ln K$. If you carry out the calculation, you will find that ΔG° and K are indeed consistent with one another.

Table 18.2



Table 18.2 Relation Between E° , K , and ΔG° ($n = 2$)

E° (V)	K	ΔG° (kJ)	E° (V)	K	ΔG° (kJ)
+2.00	4×10^{67}	-400	-2.00	3×10^{-68}	+400
+1.00	6×10^{33}	-200	-1.00	2×10^{-34}	+200
+0.50	8×10^{16}	-100	-0.50	1×10^{-17}	+100
+0.25	3×10^8	-50	-0.25	4×10^{-9}	+50
+0.10	2×10^3	-20	-0.10	0.0004	+20
+0.05	50	-10	-0.05	0.02	+10
0.00	1	0			

E° and Extent of Reaction



- As there is with ΔG° , there is clearly a connection between E° and the position of equilibrium
 - If E° is greater than 0.10 V, the reaction goes largely to completion (K is large)
 - If E° is less than -0.10 V, the reaction does not proceed to any appreciable extent (K is small)

Effect of Concentration on Voltage



- Since there is clearly an effect of concentration on ΔG° , there is a concentration effect on E° as well
- Voltage will increase if
 - The concentration of reactant is increased
 - The concentration of product is reduced
- Voltage will decrease if
 - The concentration of reactant is decreased
 - The concentration of product is increased

Voltaic Cell and Equilibrium



- As a voltaic cell operates, the concentration of reactant decreases and the concentration of product increases
 - Eventually the forward and reverse reactions come to equilibrium
 - Once equilibrium is reached, there is no net driving force

The Nernst Equation



- Recall that

$$\Delta G = \Delta G^{\circ} + RT \ln Q$$

- We can substitute for E° and obtain

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

$$E = E^{\circ} - \frac{0.0257V}{n} \ln Q$$

Interpreting Q in the Nernst Equation



- If $Q > 1$, product concentrations are higher than those of reactants
 - E is less than E°
- If $Q < 1$, reactant concentrations are higher than those of products
 - E is greater than E°
- If $Q = 1$, standard conditions prevail
 - $E = E^\circ$

Example 18.6



Example 18.6 Graded

Consider a voltaic cell in which the following reaction occurs



- * (a) Calculate E for the cell at 25°C .
- ** (b) When the voltaic cell is at 35°C , E is measured to be 0.039 V . What is E° at 35°C ?

Example 18.6, (Cont'd)



Strategy

- (a) Find (1) Q , Then (2) n , (3) E° and finally (4) substitute those values into the Nernst equation to find E .
- (b) Use the same values for Q and n obtained in (a). Use the Nernst equation for any temperature T , *not* equation 18.4.

Example 18.6, (Cont'd)



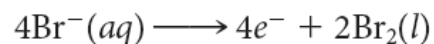
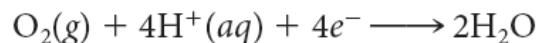
SOLUTION

(a) (1) $1.24 = -\log_{10}[\text{H}^+] \quad [\text{H}^+] = 0.058 \text{ M}$

$$Q = \frac{1}{[\text{H}^+]^4 (P_{\text{O}_2}) [\text{Br}^-]^4} = \frac{1}{(0.058)^4 (0.98) (0.15)^4}$$

(2) $= 1.8 \times 10^8$

To find n , break the reaction down into two half-reactions:



Clearly then, $n = 4$.

(3) $E^\circ = E_{\text{red}}^\circ \text{O}_2 + E_{\text{ox}}^\circ \text{Br}^- = +1.229 \text{ V} - 1.077 \text{ V} = 0.152 \text{ V}$

(4) Substituting into the Nernst equation,

$$E = 0.152 \text{ V} - \frac{0.0257 \text{ V}}{4} \ln(1.8 \times 10^8) = 0.030 \text{ V}$$

(b) We solve for the standard voltage E° by substituting into the equation

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

That gives

$$E^\circ = 0.039 \text{ V} + \left[\frac{8.31 \text{ J/mol} \cdot \text{K} \times (273 + 35) \text{ K}}{4 \times 9.648 \times 10^4 \text{ J/mol} \cdot \text{V}} \right] \ln(1.8 \times 10^8) = 0.165 \text{ V}$$

Example 18.7



Example 18.7

Consider a voltaic cell at 25°C in which the reaction is



It is found that the voltage is +0.560 V when $[\text{Zn}^{2+}] = 0.85 \text{ M}$ and $P_{\text{H}_2} = 0.988 \text{ atm}$.
What is the pH in the $\text{H}_2\text{-H}$ half-cell?

Example 18.7, (Cont'd)



Strategy This example is handled exactly like Example 18.6 except that you cannot obtain a numerical value for Q and in the last step you solve for $[H^+]$ instead of for E .

Example 18.7, (Cont'd)



SOLUTION

$$(1) \quad Q = \frac{[\text{Zn}^{2+}](P_{\text{H}_2})}{[\text{H}^+]^2} = \frac{(0.85)(0.988)}{[\text{H}^+]^2}$$

$$(2) \quad n = 2 \quad \text{since } 2e^- \text{ are exchanged}$$

$$(3) \quad E^\circ = E_{\text{ox}}^\circ \text{ Zn} + E_{\text{red}}^\circ \text{ H}^+ = +0.762 \text{ V}$$

(4) Substituting into the Nernst equation, we have

$$E = E^\circ - \frac{0.0257}{n} \ln Q$$

That gives

$$0.560 \text{ V} = +0.762 \text{ V} - \frac{0.0257}{2} \ln \frac{(0.85)(0.988)}{[\text{H}^+]^2}$$

$$\ln \frac{(0.84)}{[\text{H}^+]^2} = (0.762 - 0.560) \left(\frac{2}{0.0257} \right) = 15.7$$

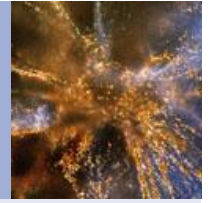
$$\frac{0.84}{[\text{H}^+]^2} = 6.7 \times 10^6$$

$$[\text{H}^+] = 3.5 \times 10^{-4}$$

$$\text{pH} = 3.45$$

Reality Check E is less than E° because the concentration of reactants, H^+ and Br^- , are less than 1 M .

pH and Specific Ion Electrodes



- Glass electrodes can be constructed such that the difference in concentration of ion inside and outside the electrode may be measured
 - pH meter electrodes
 - Specific ion electrodes

Electrolytic Cells



- In an ***electrolytic cell***, a nonspontaneous reaction may be caused to occur by the application of an external voltage
 - In essence, this means pumping electrons into the reaction
 - The process is called ***electrolysis***

Quantitative Relationships



- $\text{Ag}^+ (\text{aq}) + \text{e}^- \rightarrow \text{Ag} (\text{s})$
 - 1 mol $\text{e}^- \rightarrow$ 1 mol Ag
- $\text{Cu}^{2+} (\text{aq}) + 2\text{e}^- \rightarrow \text{Cu} (\text{s})$
 - 2 mol $\text{e}^- \rightarrow$ 1 mol Cu
- $\text{Au}^{3+} (\text{aq}) + 3\text{e}^- \rightarrow \text{Au} (\text{s})$
 - 3 mol $\text{e}^- \rightarrow$ 1 mol Au

Figure 18.8

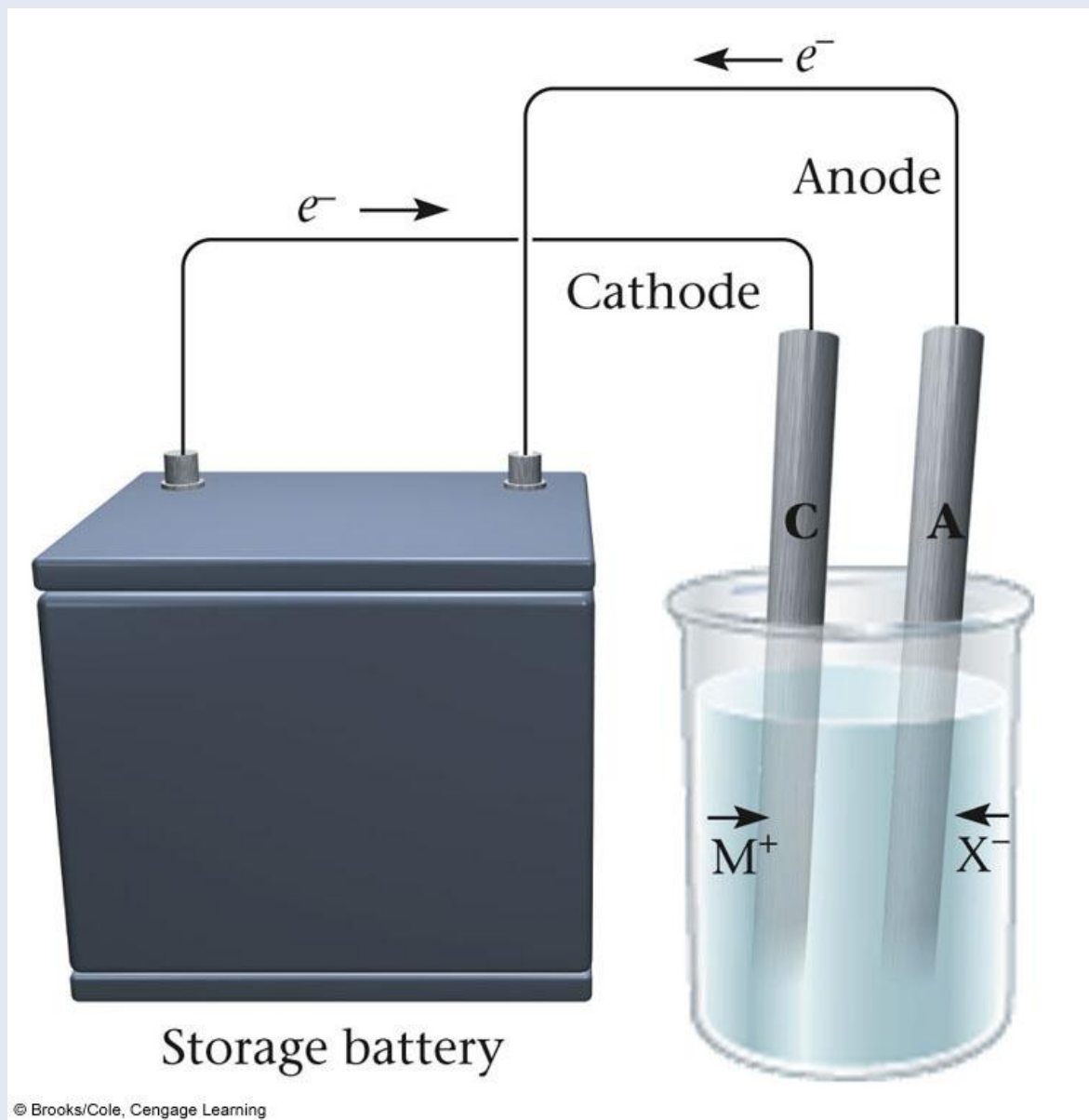
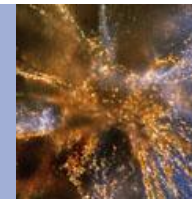


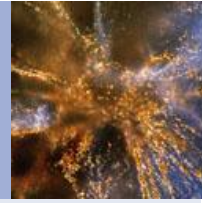
Table 18.3



Table 18.3 Electrical Units

Quantity	Unit	Defining Relation	Conversion Factors
Charge	coulomb (C)	$1 \text{ C} = 1 \text{ A} \cdot \text{s} = 1 \text{ J/V}$	$1 \text{ mol } e^- = 9.648 \times 10^4 \text{ C}$
Current	ampere (A)	$1 \text{ A} = 1 \text{ C/s}$	
Potential	volt (V)	$1 \text{ V} = 1 \text{ J/C}$	
Power	watt (W)	$1 \text{ W} = 1 \text{ J/s}$	
Energy	joule (J)	$1 \text{ J} = 1 \text{ V} \cdot \text{C}$	$1 \text{ kWh} = 3.600 \times 10^6 \text{ J}$

Electrical Units



- Charge
 - 1 mol electrons = 96,480 coulombs (of charge)
- Current
 - 1 ***ampere*** = 1 coulomb/sec
- Electrical energy
 - 1 joule = 1 C·V
 - 1 kWh = 3.600×10^6 J = 3.600×10^3 kJ

Example 18.8



Example 18.8

Chromium metal can be electroplated from an aqueous solution of potassium dichromate. The reduction half-reaction is



A current of 6.00 A and a voltage of 4.5 V are used in the electroplating.

- How many grams of chromium can be plated if the current is run for 48 minutes?
- How long will it take to completely convert 215 mL of 1.25 M $\text{K}_2\text{Cr}_2\text{O}_7$ to elemental chromium?
- How many kilowatt hours of electrical energy are required to plate 1.00 g of chromium?

Example 18.8, (Cont'd)



SOLUTION

(a) Use a conversion-factor approach:

ampere \longrightarrow coulomb \longrightarrow mol e^- \longrightarrow mol Cr \longrightarrow grams Cr

Remember that 1 A = 1 C/s.

$$\begin{aligned} 6.00 \text{ A} \times \frac{1 \text{ C/s}}{1 \text{ A}} \times 48 \text{ min} \times \frac{60 \text{ s}}{1 \text{ min}} \times \frac{1 \text{ mol } e^-}{9.648 \times 10^4 \text{ C}} \times \frac{2 \text{ mol Cr}}{12 \text{ mol } e^-} \times \frac{52.00 \text{ g Cr}}{1 \text{ mol Cr}} \\ = 1.55 \text{ g} \end{aligned}$$

(b) This time, we start by finding the number of moles of $\text{Cr}_2\text{O}_7^{2-}$.

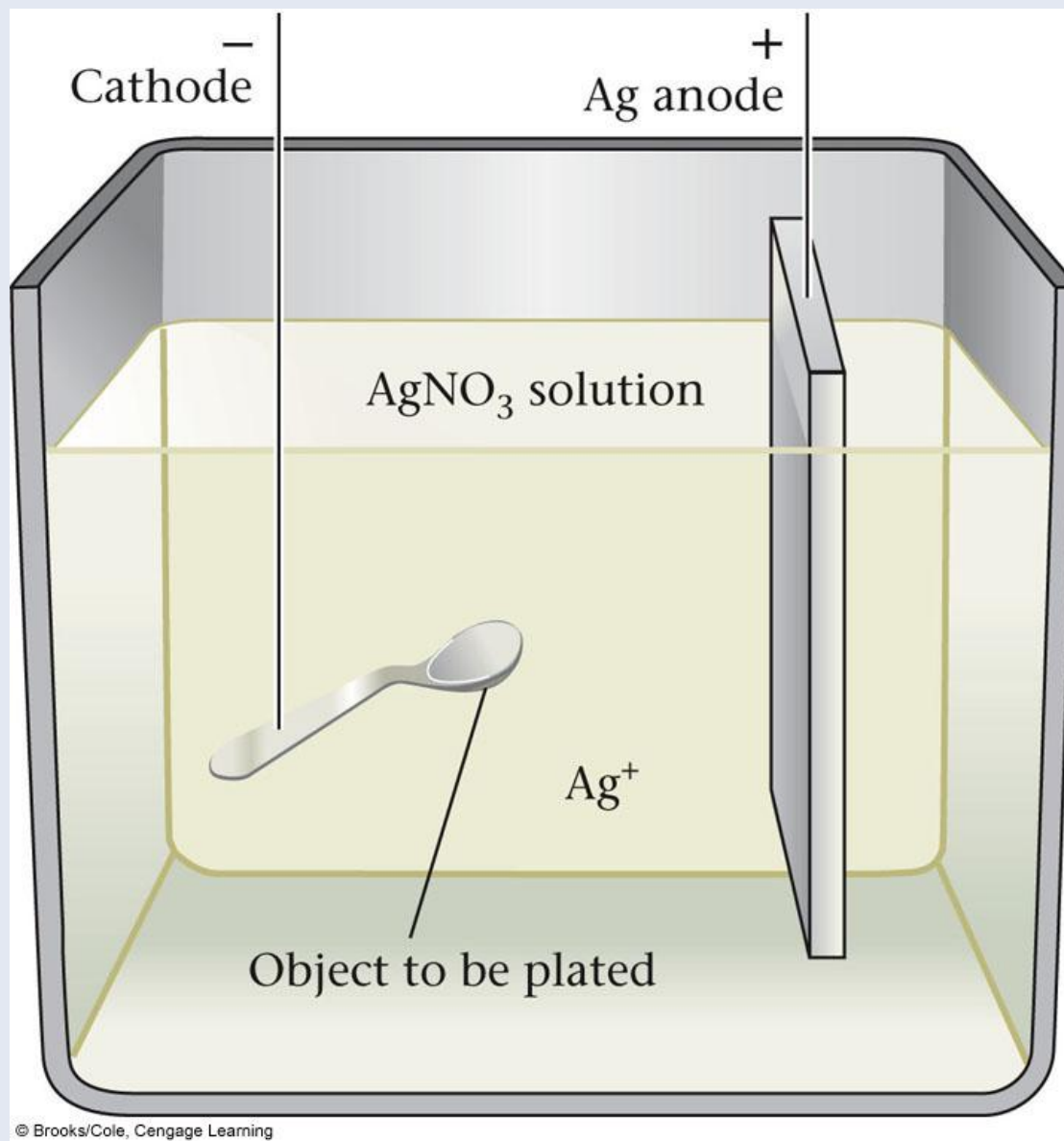
$$\begin{aligned} n_{\text{Cr}_2\text{O}_7^{2-}} \longrightarrow n_{e^-} \longrightarrow \text{C} \longrightarrow \text{s} \\ 0.215 \text{ L} \times \frac{1.25 \text{ mol Cr}_2\text{O}_7^{2-}}{1 \text{ L}} \times \frac{12 \text{ mol } e^-}{1 \text{ mol Cr}_2\text{O}_7^{2-}} \times \frac{9.648 \times 10^4 \text{ C}}{1 \text{ mol } e^-} \times \frac{1 \text{ A}}{1 \text{ C/s}} \times \frac{1}{6 \text{ A}} \\ = 5.19 \times 10^4 \text{ s} = 14.4 \text{ h} \end{aligned}$$

(c) Here we start with the grams of chromium plated.

$$\begin{aligned} m_{\text{Cr}} \longrightarrow n_{\text{Cr}} \longrightarrow n_{e^-} \longrightarrow \text{C} \longrightarrow \text{energy(J)} \longrightarrow \text{energy(kWh)} \\ 1.00 \text{ g Cr} \times \frac{1 \text{ mol Cr}}{52.00 \text{ g}} \times \frac{12 \text{ mol } e^-}{2 \text{ mol Cr}} \times \frac{9.648 \times 10^4 \text{ C}}{1 \text{ mol } e^-} \times \frac{1 \text{ J}}{1 \text{ C} \cdot \text{V}} \times 4.5 \text{ V} \times \frac{1 \text{ kWh}}{3.600 \times 10^6 \text{ J}} \\ = 0.014 \text{ kWh} \end{aligned}$$

Reality Check Note that using an applied voltage of 4.5 V is irrelevant to parts (a) and (b).

Application of Electrolysis – Silver Plating



Cell Reactions in Water Solution



- Reactions at the cathode
 - Reduction of a cation to its metal
 - $\text{Ag}^+ (\text{aq}) + \text{e}^- \rightarrow \text{Ag} (\text{s})$ +0.799V
 - Reduction of water to hydrogen gas
 - $2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 (\text{g}) + 2\text{OH}^- (\text{aq})$ -0.828V
- Anode reactions
 - Oxidation of an anion to a nonmetal
 - $2\text{I}^- (\text{aq}) \rightarrow \text{I}_2 (\text{s}) + 2\text{e}^-$ -0.534V
 - Oxidation of water to oxygen gas
 - $2\text{H}_2\text{O} \rightarrow \text{O}_2 (\text{g}) + 4\text{H}^+ (\text{aq}) + 4\text{e}^-$ -1.299V

Which Reaction



- Water will be reduced when a cation is very difficult to reduce
 - K^+ , Na^+ , etc.
- Water will be oxidized when an anion is very difficult to oxidize
 - NO_3^- , SO_4^{2-} , etc.

Table 18.4

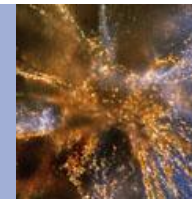


Table 18.4

Electrolysis of Water Solutions

Solution	Cathode Product	Anode Product
$\text{CuBr}_2(aq)$	$\text{Cu}(s)$	$\text{Br}_2(l)$
$\text{AgNO}_3(aq)$	$\text{Ag}(s)$	$\text{O}_2(g)$
$\text{KI}(aq)$	$\text{H}_2(g)$	$\text{I}_2(s)$
$\text{Na}_2\text{SO}_4(aq)$	$\text{H}_2(g)$	$\text{O}_2(g)$

Electrolysis of KI (aq)



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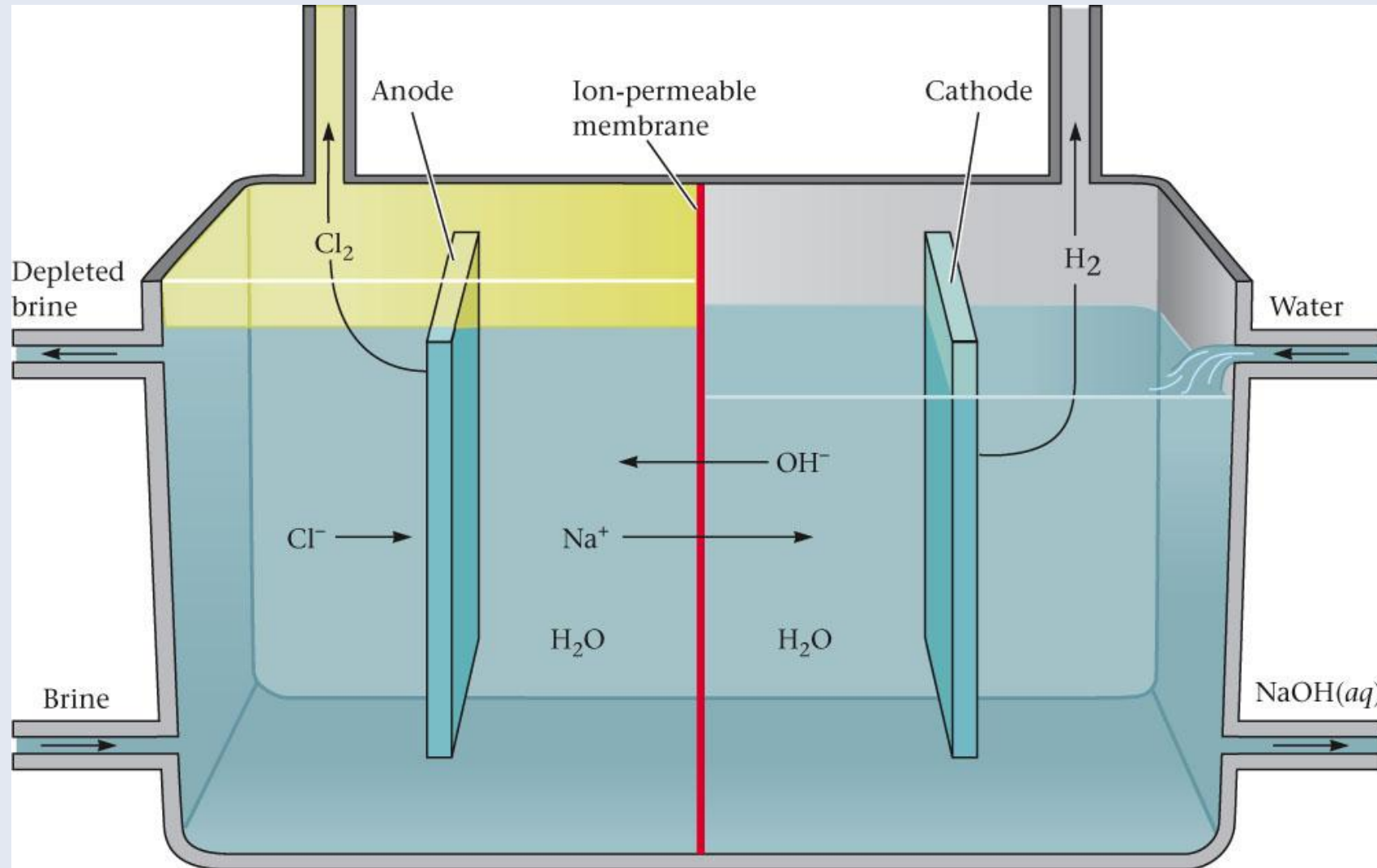
- Hydrogen gas (color from phenolphthalein, indicating the presence of OH^-) is produced at the cathode
- Iodine is produced at the anode

Commercial Cells



- Electrolysis of aqueous NaCl
 - Anode: $2\text{Cl}^- \rightarrow \text{Cl}_2 (\text{g}) + 2\text{e}^-$
 - Cathode: $2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 (\text{g}) + 2\text{OH}^- (\text{aq})$
- Products
 - Chlorine: bleaching agent; used in manufacture of plastics such as PVC
 - Hydrogen: used to produce ammonia
 - NaOH: used to process paper, purify aluminum, manufacture glass

Chlor-Alkali Process

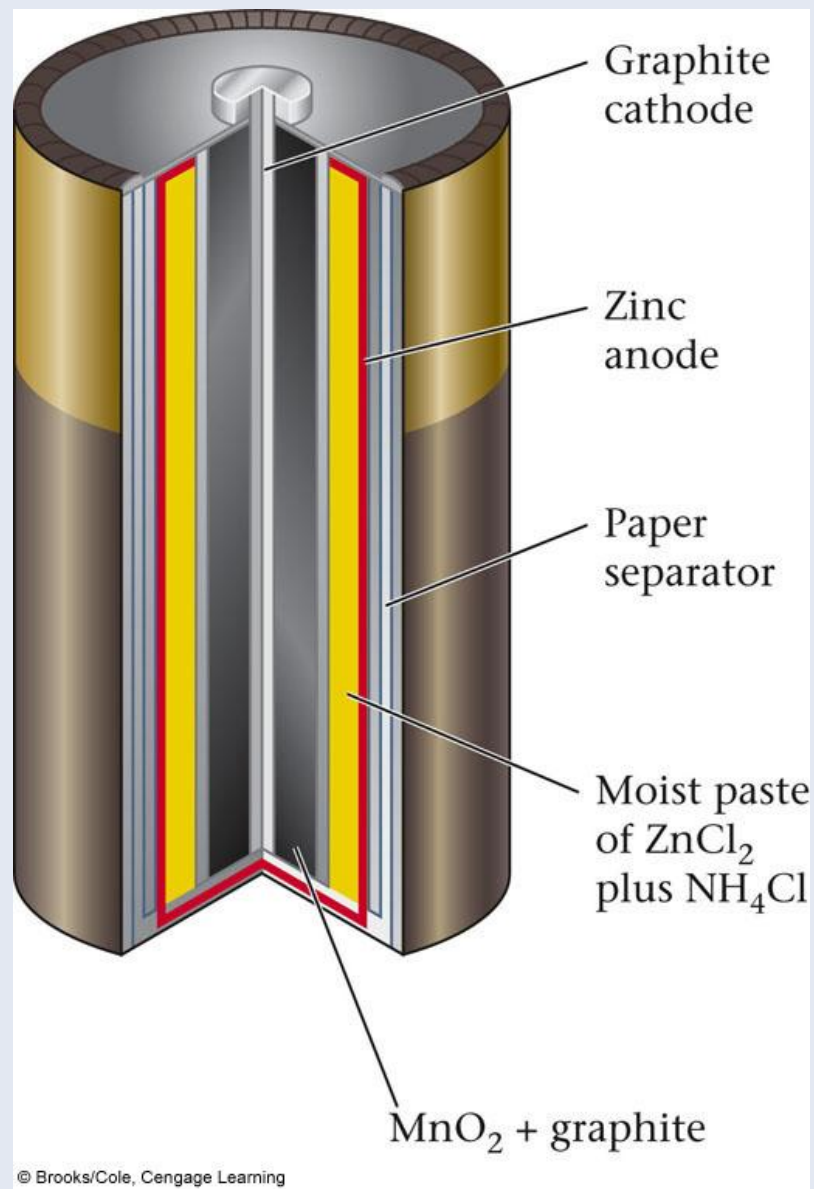


Primary Cells



- Primary cells (batteries) are non-rechargeable
- LeClanché cells
 - $\text{Zn (s)} + 2\text{MnO}_2 \text{ (s)} + 2\text{NH}_4^+ \text{ (aq)} \rightarrow \text{Zn}^{2+} \text{ (aq)} + 2\text{NH}_3 \text{ (aq)} + \text{H}_2\text{O}$
 - Gas is produced (insulator)
- Alkaline batteries
 - Use KOH rather than NH_4Cl electrolyte
 - $\text{Zn(s)} + 2\text{MnO}_2 \text{ (s)} \rightarrow \text{ZnO (s)} + \text{Mn}_2\text{O}_3 \text{ (s)}$
 - No gas is produced

Figure 18.11 – Dry Cell Battery

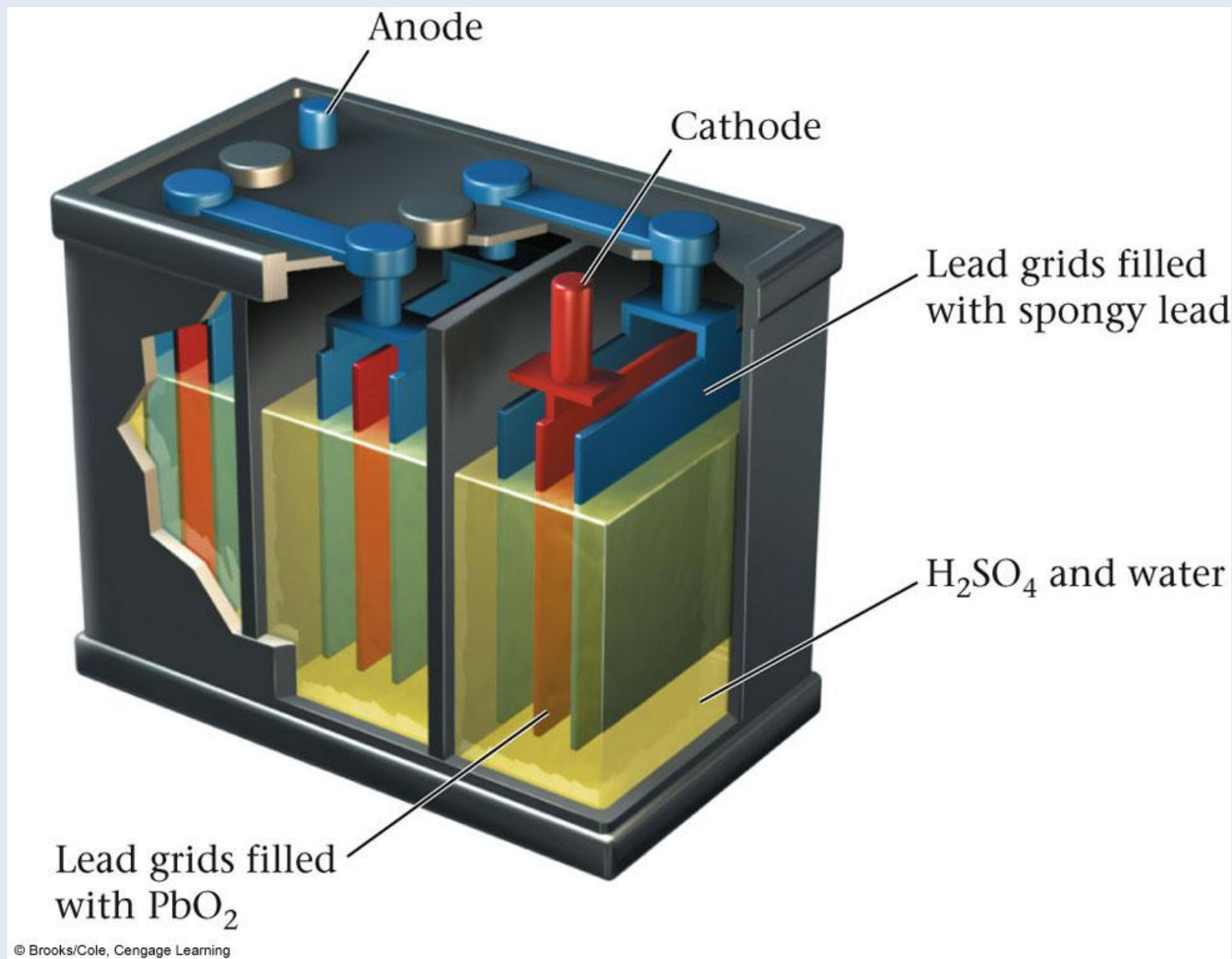


Storage (Rechargeable) Cells

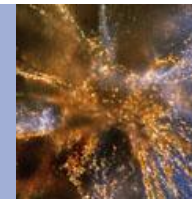


- Secondary battery
- Can be recharged repeatedly
 - Cell is run in reverse (polarity is reversed)
- Examples
 - Lead-acid cell: six, 2.0 V lead cells
 - $\text{Pb (s)} + \text{PbO}_2 \text{ (s)} + 2\text{H}^+ \text{ (aq)} + 2\text{HSO}_4^- \text{ (aq)} \rightarrow 2\text{PbSO}_4 \text{ (s)} + 2\text{H}_2\text{O}$
 - $\Delta G^\circ = -371.4 \text{ kJ at } 25^\circ \text{ C}$

Figure 18.12 – Lead-Acid Auto Battery



Lead Storage Battery



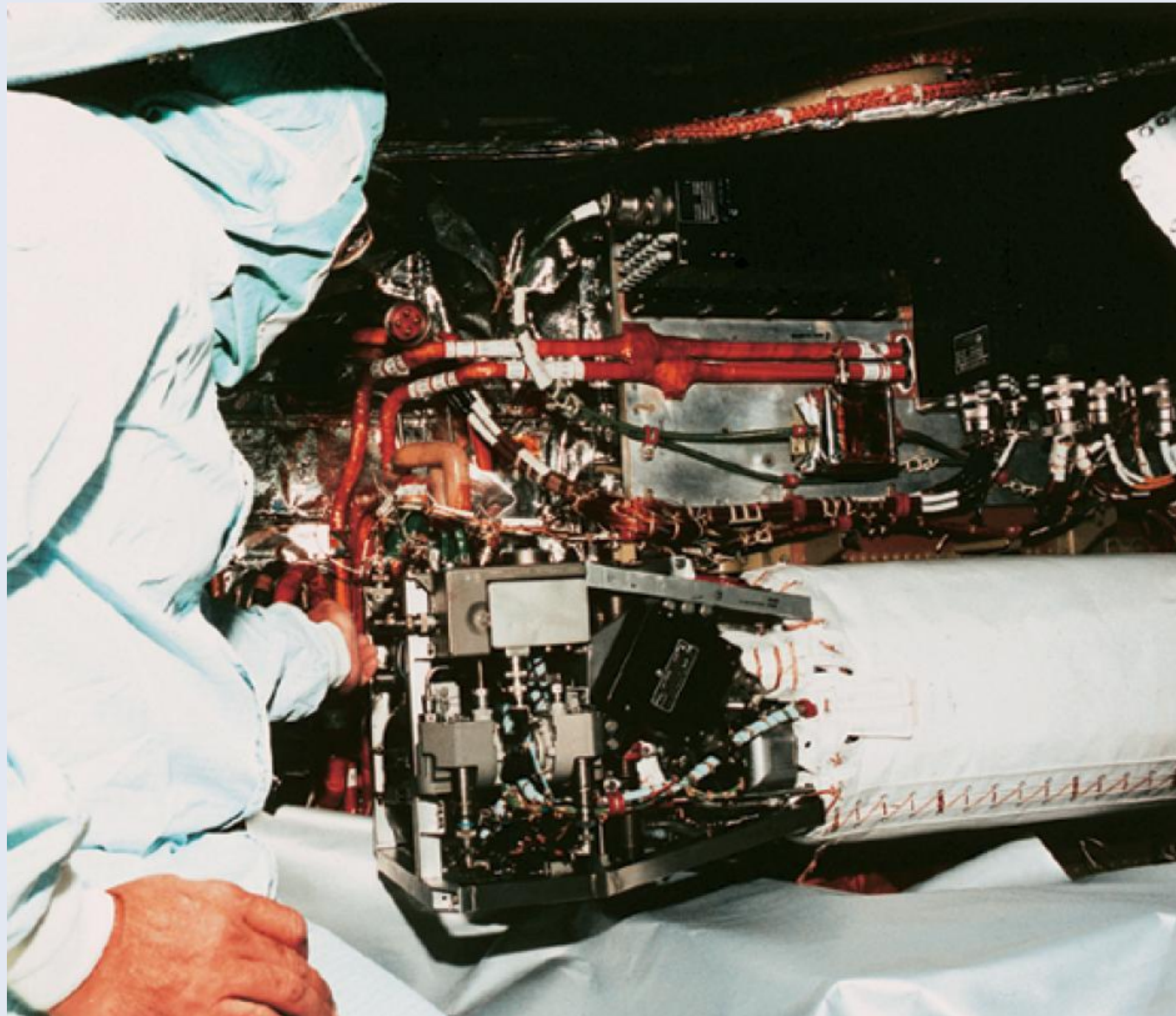
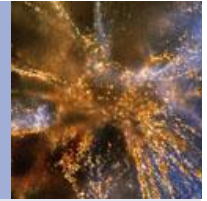
- Disadvantages
 - Relatively low energy density (heavy!)
 - When the battery is recharged, some water may be electrolyzed, producing a safety hazard
 - $2\text{H}_2\text{O} \rightarrow \text{H}_2 (\text{g}) + \text{O}_2 (\text{g}) \quad \Delta G^\circ = +474.4 \text{ kJ at } 25^\circ \text{ C}$

Fuel Cells



- A fuel cell is essentially a battery with continuously supplied reactants
- Anode: $2\text{H}_2 (\text{g}) + 4\text{OH}^- (\text{aq}) \rightarrow 4\text{H}_2\text{O} + 4\text{e}^-$
- Cathode: $\text{O}_2 (\text{g}) + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^- (\text{aq})$
- Net: $2\text{H}_2 (\text{g}) + \text{O}_2 (\text{g}) \rightarrow 2\text{H}_2\text{O} \quad \Delta G^\circ = -474.4 \text{ at } 25^\circ \text{ C}$

Hydrogen-Oxygen Fuel Cell



Fuel Cells in Practice



- Clean, non-polluting
- Cost per kJ is high: chemistry is simple but the engineering is complex
- Storage of hydrogen as a fuel is difficult and potentially dangerous

Key Concepts



1. Draw a diagram for a voltaic cell, labeling the electrodes and diagramming current flow
2. Use standard potentials to
 - Compare relative strengths of oxidizing and reducing agents
 - Calculate E and/or reaction spontaneity
3. Relate E° to ΔG° and K
4. Use the Nernst equation to relate voltage to concentration
5. Relate mass of product to charge, energy or current in electrolysis reactions