Petrucci's General Chemistry

PRINCIPLES AND MODERN APPLICATIONS

Twelfth Edition

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The Transition Elements

23

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The Transition Elements

CONTENTS

23-1 General Properties

Atomic (Metallic Radii)

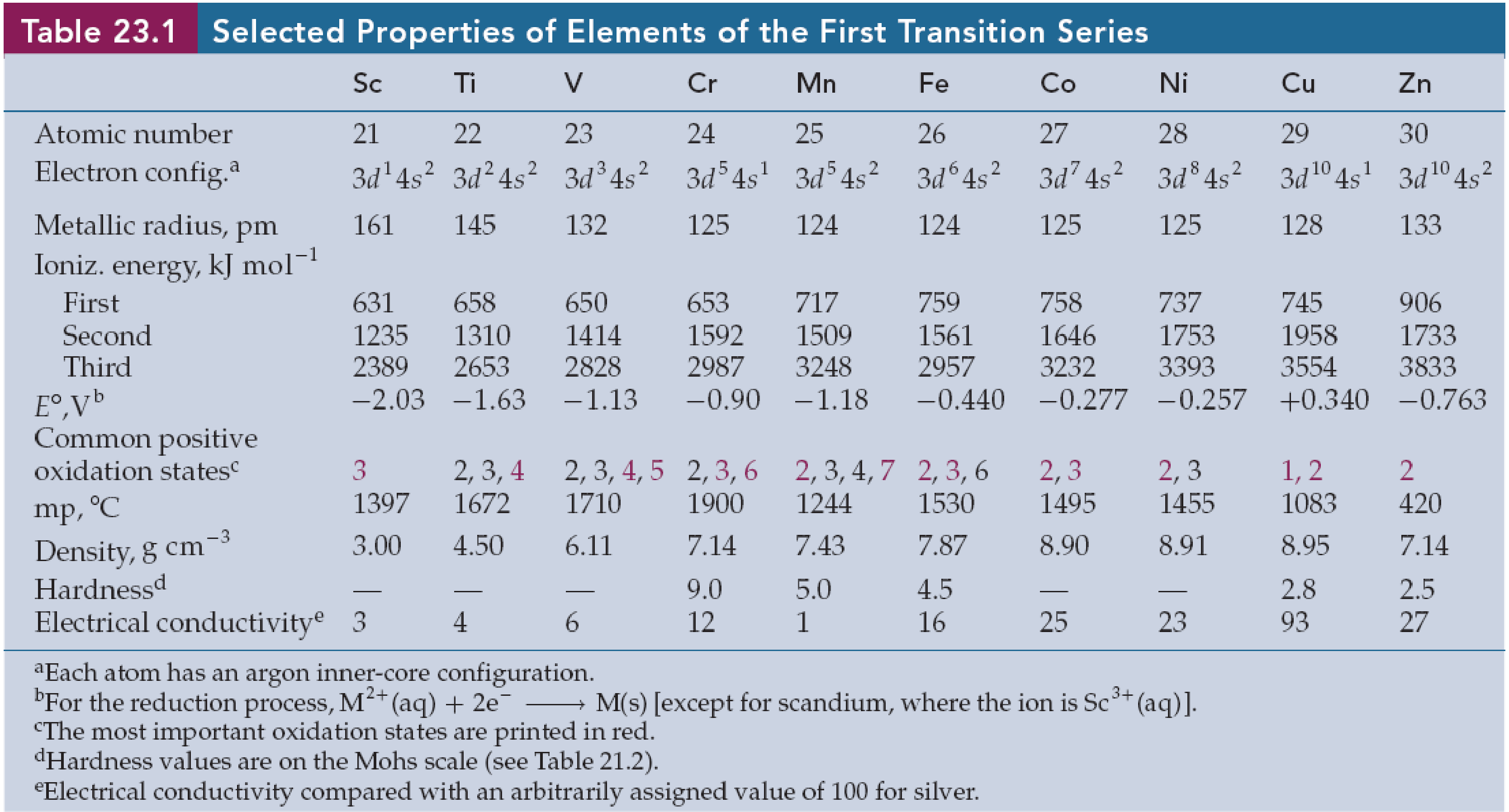

Table 23.1 Selected Properties of Elements of the First Transition Series

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Atomic number	21	22	23	24	25	26	27	28	29	30
Electron config.[a]	$3d^1 4s^2$	$3d^2 4s^2$	$3d^3 4s^2$	$3d^5 4s^1$	$3d^5 4s^2$	$3d^6 4s^2$	$3d^7 4s^2$	$3d^8 4s^2$	$3d^{10} 4s^1$	$3d^{10} 4s^2$
Metallic radius, pm	161	145	132	125	124	124	125	125	128	133
Ioniz. energy, kJ mol^{-1}										
First	631	658	650	653	717	759	758	737	745	906
Second	1235	1310	1414	1592	1509	1561	1646	1753	1958	1733
Third	2389	2653	2828	2987	3248	2957	3232	3393	3554	3833
$E°$, V[b]	−2.03	−1.63	−1.13	−0.90	−1.18	−0.440	−0.277	−0.257	+0.340	−0.763
Common positive oxidation states[c]	3	2, 3, 4	2, 3, 4, 5	2, 3, 6	2, 3, 4, 7	2, 3, 6	2, 3	2, 3	1, 2	2
mp, °C	1397	1672	1710	1900	1244	1530	1495	1455	1083	420
Density, g cm^{-3}	3.00	4.50	6.11	7.14	7.43	7.87	8.90	8.91	8.95	7.14
Hardness[d]	—	—	—	9.0	5.0	4.5	—	—	2.8	2.5
Electrical conductivity[e]	3	4	6	12	1	16	25	23	93	27

[a] Each atom has an argon inner-core configuration.

[b] For the reduction process, $M^{2+}(aq) + 2e^- \longrightarrow M(s)$ [except for scandium, where the ion is $Sc^{3+}(aq)$].

[c] The most important oxidation states are printed in red.

[d] Hardness values are on the Mohs scale (see Table 21.2).

[e] Electrical conductivity compared with an arbitrarily assigned value of 100 for silver.

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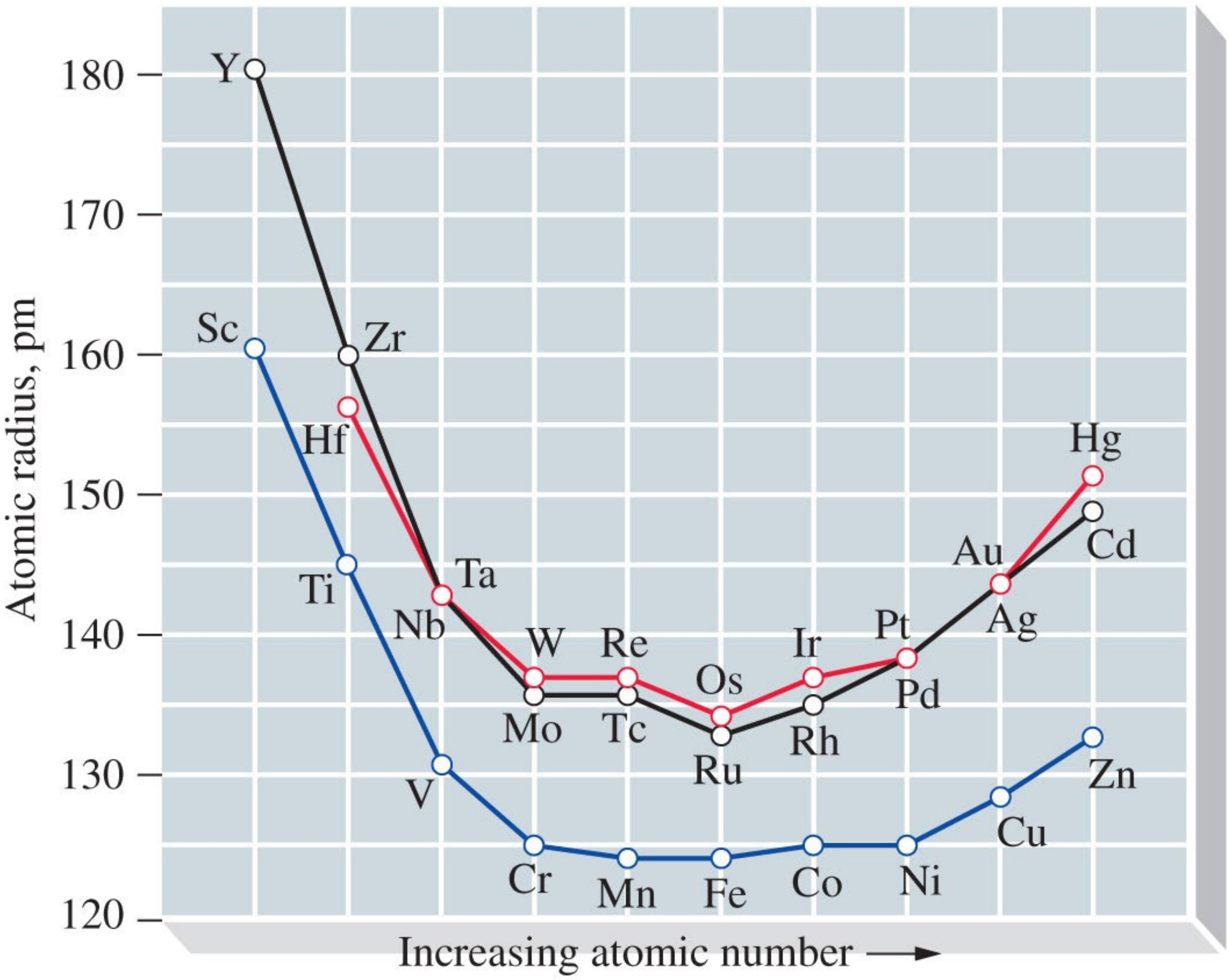

▲ FIGURE 23-1

Atomic radii of the d-block elements

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Electron Configurations and Oxidation States

- an inner core of electrons in the [Ar] configuration
- two electrons in 4*s* for eight members and one 4*s* electron for the remaining two (Cr and Cu)
- 3*d* electrons ranging from one in Sc to ten in Cu and Zn

For Titanium, $[Ar]3d^2 4s^2$, we note several features:

- several possible oxidation states, Ti^{2+}, Ti^{3+} and Ti^{4+}
- maximum oxidation state corresponds to group number (4)

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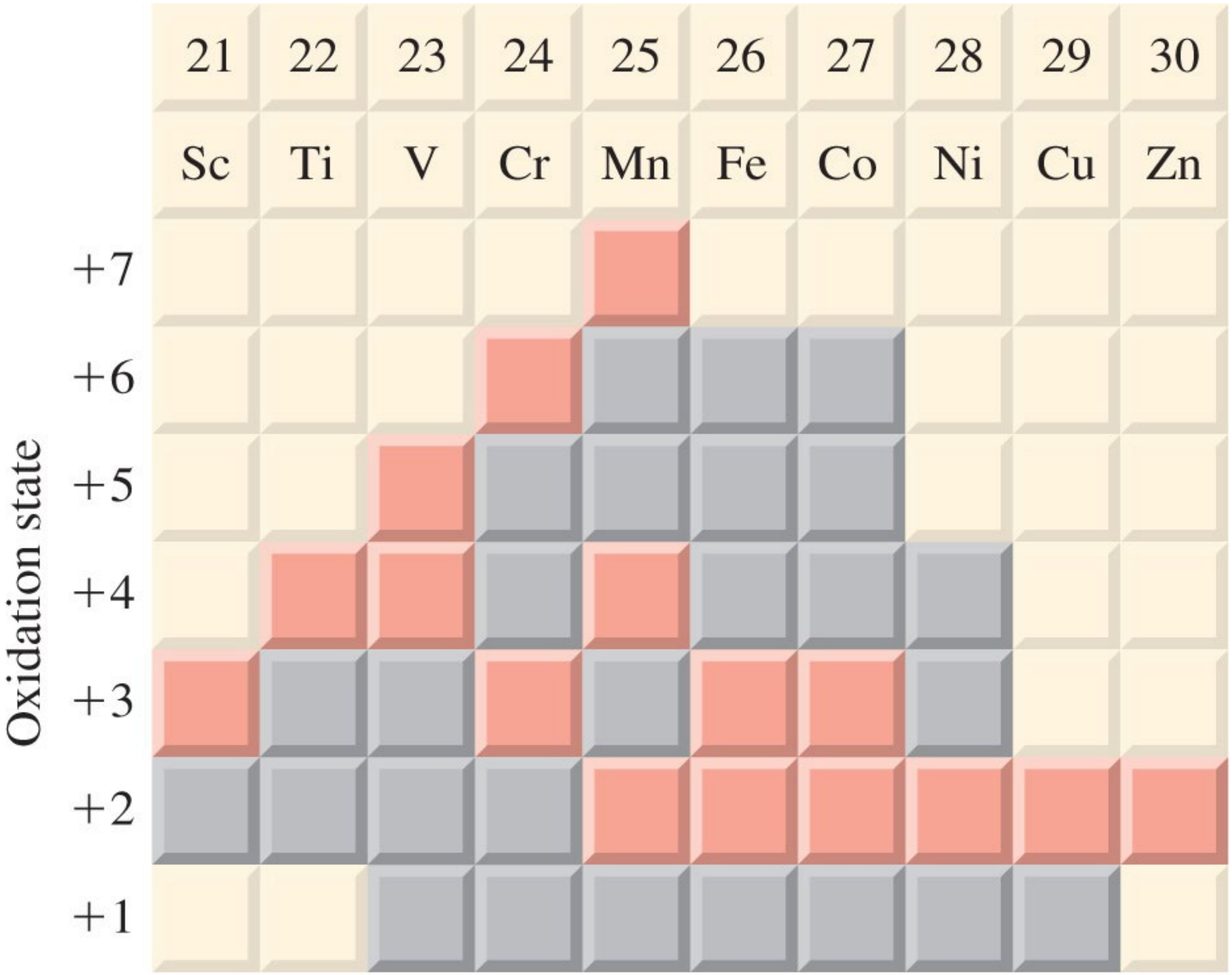

Oxidation state	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn
+7					🟥					
+6				🟥	▨	▨	▨			
+5			🟥	▨	▨	▨	▨			
+4		🟥	🟥	▨	🟥	▨	▨	▨		
+3	🟥	▨	▨	🟥	▨	🟥	🟥	▨		
+2	▨	▨	▨	▨	🟥	🟥	🟥	🟥	🟥	🟥
+1			▨	▨	▨	▨	▨	▨	▨	

▲ FIGURE 23-2

Positive oxidation states of the elements of the first transition series

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Ionization Energies and Electrode Potentials

Ionization energy is fairly constant across the first transition series and are similar to those of group 2 metals.

Standard electrode potentials gradually increase across the series, but all are more readily oxidized than hydrogen.

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Ionic and Covalent Compounds

Significant covalent character when forming compounds with non-metals.

$BeCl_2$, $AlCl_3$ (Al_2Cl_6) are molecular compounds.

Compounds display both ionic and covalent character.

Lower oxidation states are essentially ionic, while thoise in higher oxidation states have covalent character.

MnO	Mn_2O_7
ionic solid mp 1785°C	red, oily, molecular liquid boils at rt

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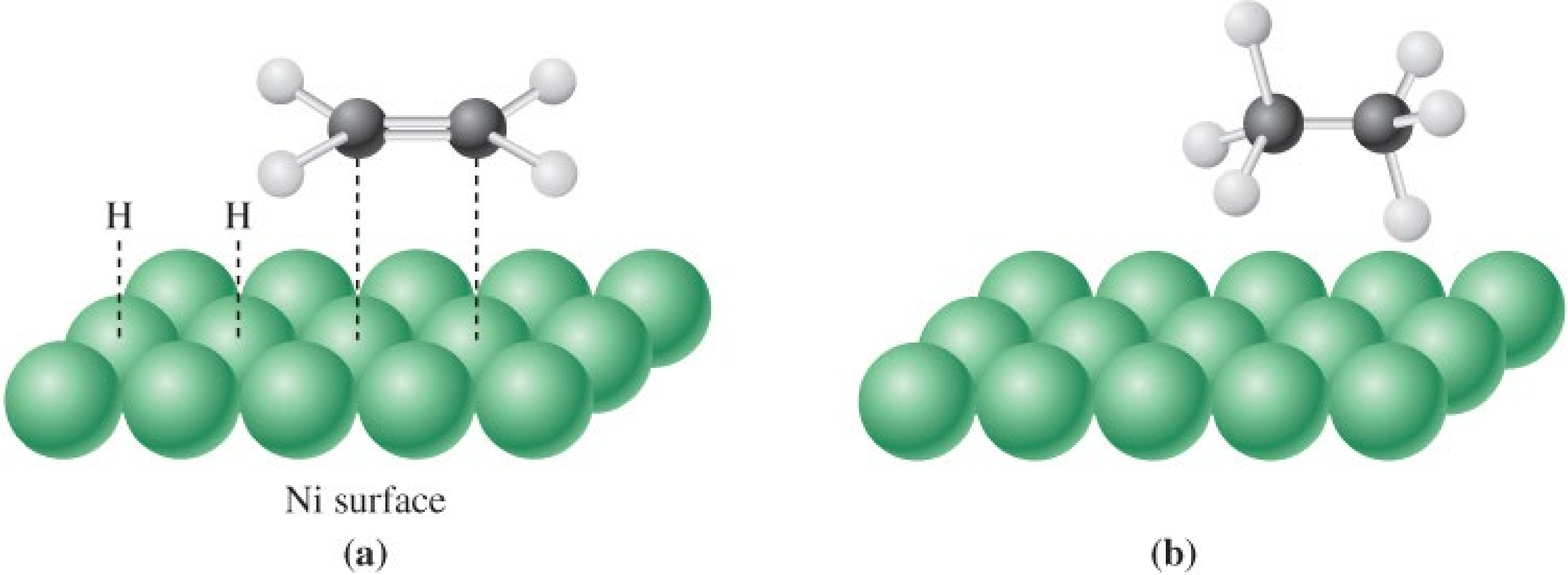
Catalytic Activity



(a)

(b)

▲ FIGURE 23-3

Schematic representation of the metal-catalyzed hydrogenation of C_2H_4

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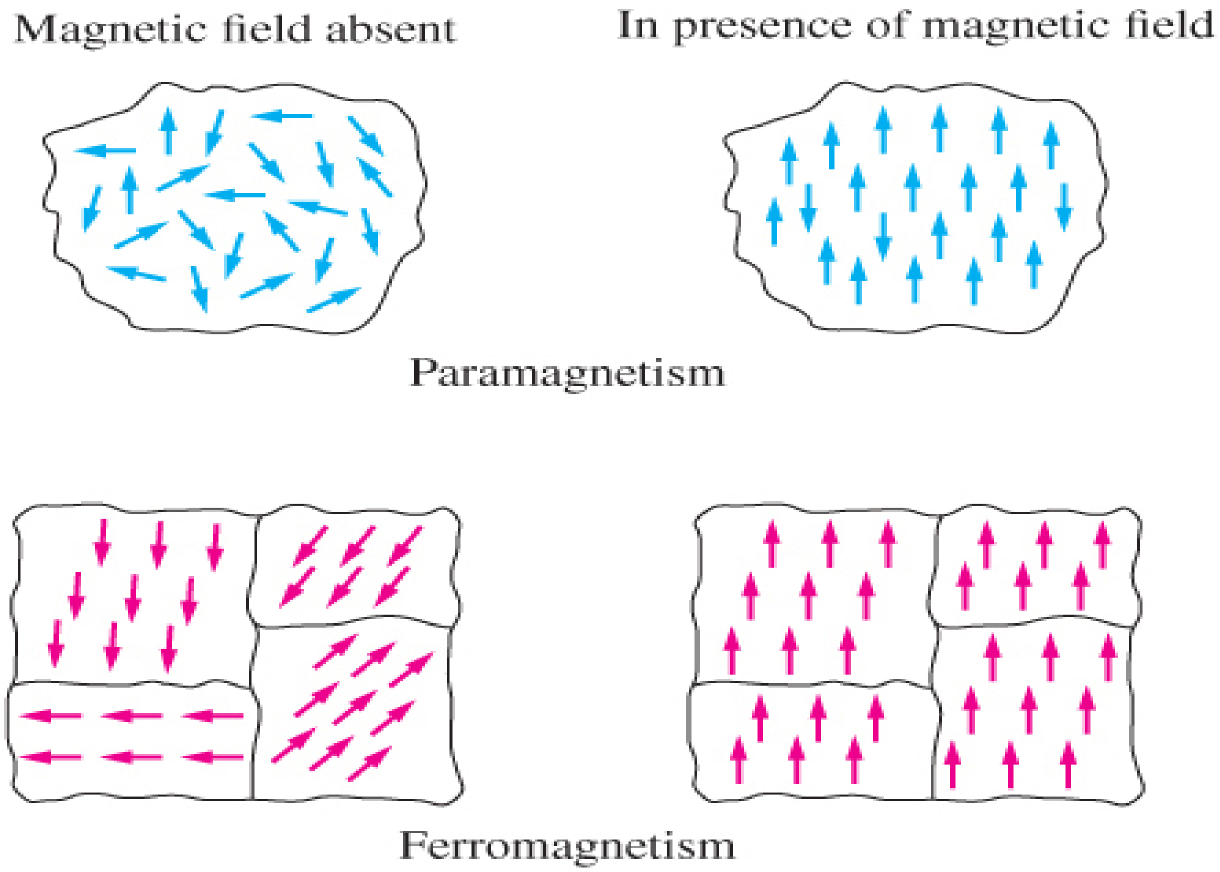
Color and Magnetism



▲ Figure 23-4

Ferromagnetism and paramagnetism compared

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Comparison of Transition and Main-Group Elements

d orbitals are as important as *s* and *p* orbitals giving rise to behavioral differences between transition and main-group elements.

- Multiple versus single oxidation states
- complex-ion formation
- Color
- magnetic properties
- catalytic activity

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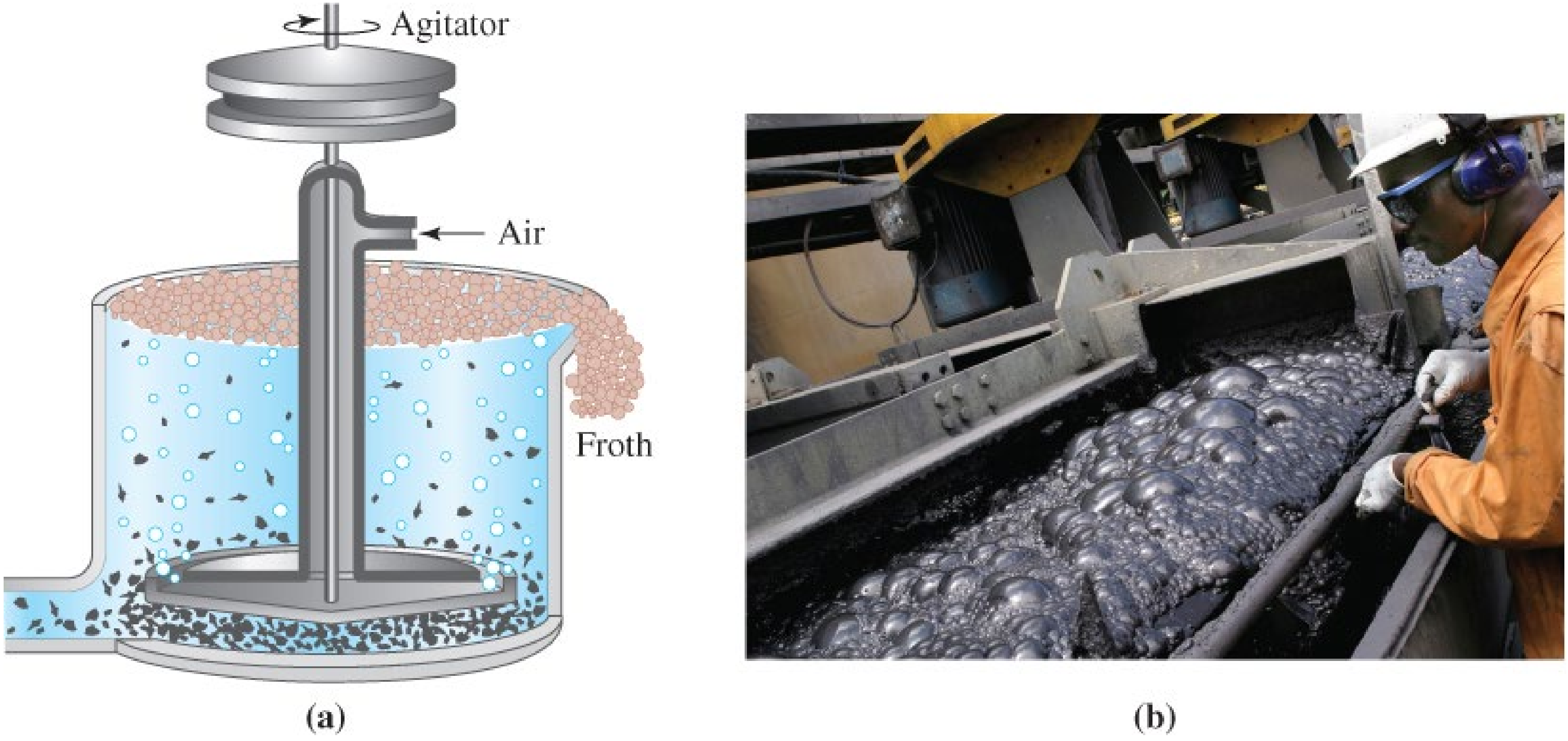
23-2 Principles of Extractive Metallurgy

Concentration



▲ FIGURE 23-5

Concentration of an ore by flotation

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Roasting

$$ZnCO_3(s) \longrightarrow ZnO(s) + CO_2(g) \qquad (23.1)$$

$$2\ ZnS(s) + 3\ O_2(g) \longrightarrow 2\ ZnO(s) + 2\ SO_2(g) \qquad (23.2)$$

Reduction

$$ZnO(s) + C(s) \xrightarrow{\Delta} Zn(g) + CO(g) \qquad (23.3)$$

$$ZnO(s) + CO(s) \xrightarrow{\Delta} Zn(g) + CO_2(g) \qquad (23.4)$$

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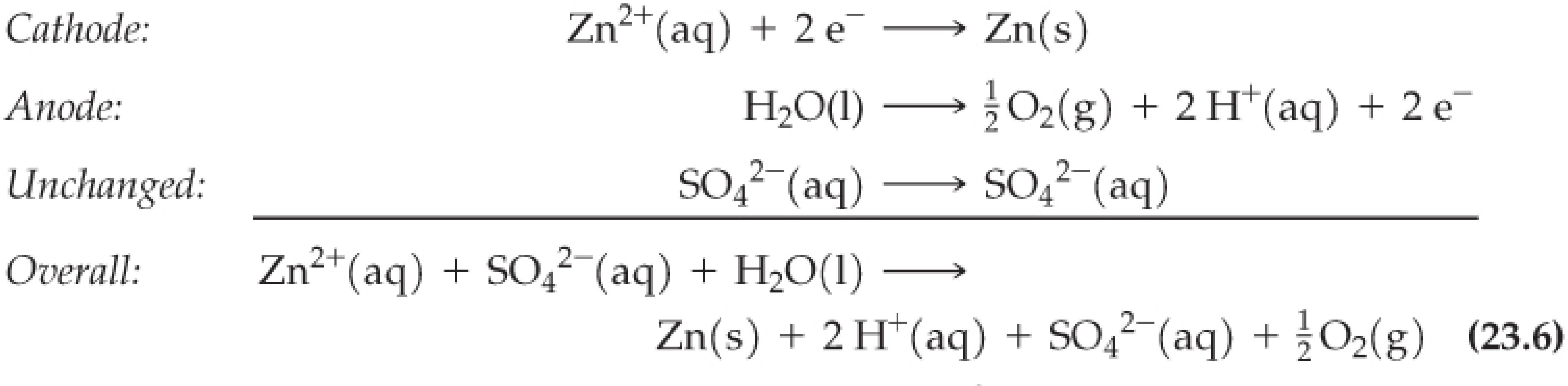
Refining

$$\mathrm{ZnO(s) + 2\,H^{+}(aq) + SO_4{}^{2-}(aq) \longrightarrow Zn^{2+}(aq) + SO_4{}^{2-}(aq) + H_2O(l)} \qquad (23.5)$$



Cathode: $\mathrm{Zn^{2+}(aq) + 2\,e^{-} \longrightarrow Zn(s)}$

Anode: $\mathrm{H_2O(l) \longrightarrow \tfrac{1}{2}O_2(g) + 2\,H^{+}(aq) + 2\,e^{-}}$

Unchanged: $\mathrm{SO_4{}^{2-}(aq) \longrightarrow SO_4{}^{2-}(aq)}$

Overall: $\mathrm{Zn^{2+}(aq) + SO_4{}^{2-}(aq) + H_2O(l) \longrightarrow Zn(s) + 2\,H^{+}(aq) + SO_4{}^{2-}(aq) + \tfrac{1}{2}O_2(g)}$ **(23.6)**

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Zone Refining

▲ FIGURE 23-6
Metallurgy.

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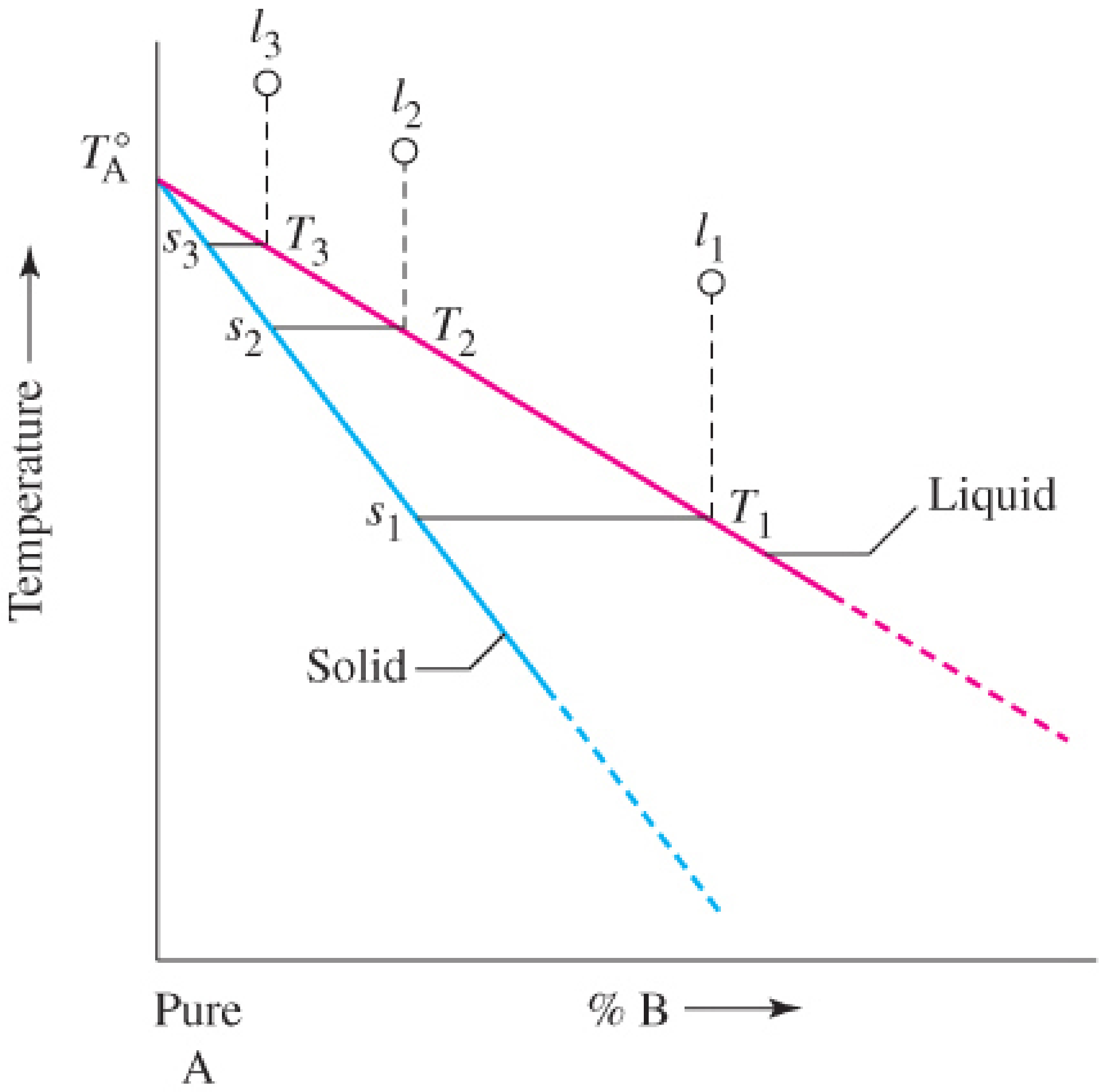

▲ FIGURE 23-7

The principle of zone refining

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Thermodynamics of Extractive Metallurgy

(a) $2\,C(s) + O_2(g) \longrightarrow 2\,CO(g)$ $\Delta_r G°_{(a)}$

(b) $2\,ZnO(s) + O_2(g) \longrightarrow 2\,ZnO(s)$ $\Delta_r G°_{(b)}$

(a) $2\,C(s) + O_2(g) \longrightarrow 2\,CO(g)$ $\Delta_r G°_{(a)}$

−(b) $2\,ZnO(s) \longrightarrow 2\,Zn(s) + O_2(g)$ $-\Delta_r G°_{(b)}$

Overall: $2\,ZnO(s) + 2\,C(s) \longrightarrow 2\,Zn(s) + 2\,CO(g)$ $\Delta_r G° = \Delta_r G°_{(a)} - \Delta_r G°_{(b)}$

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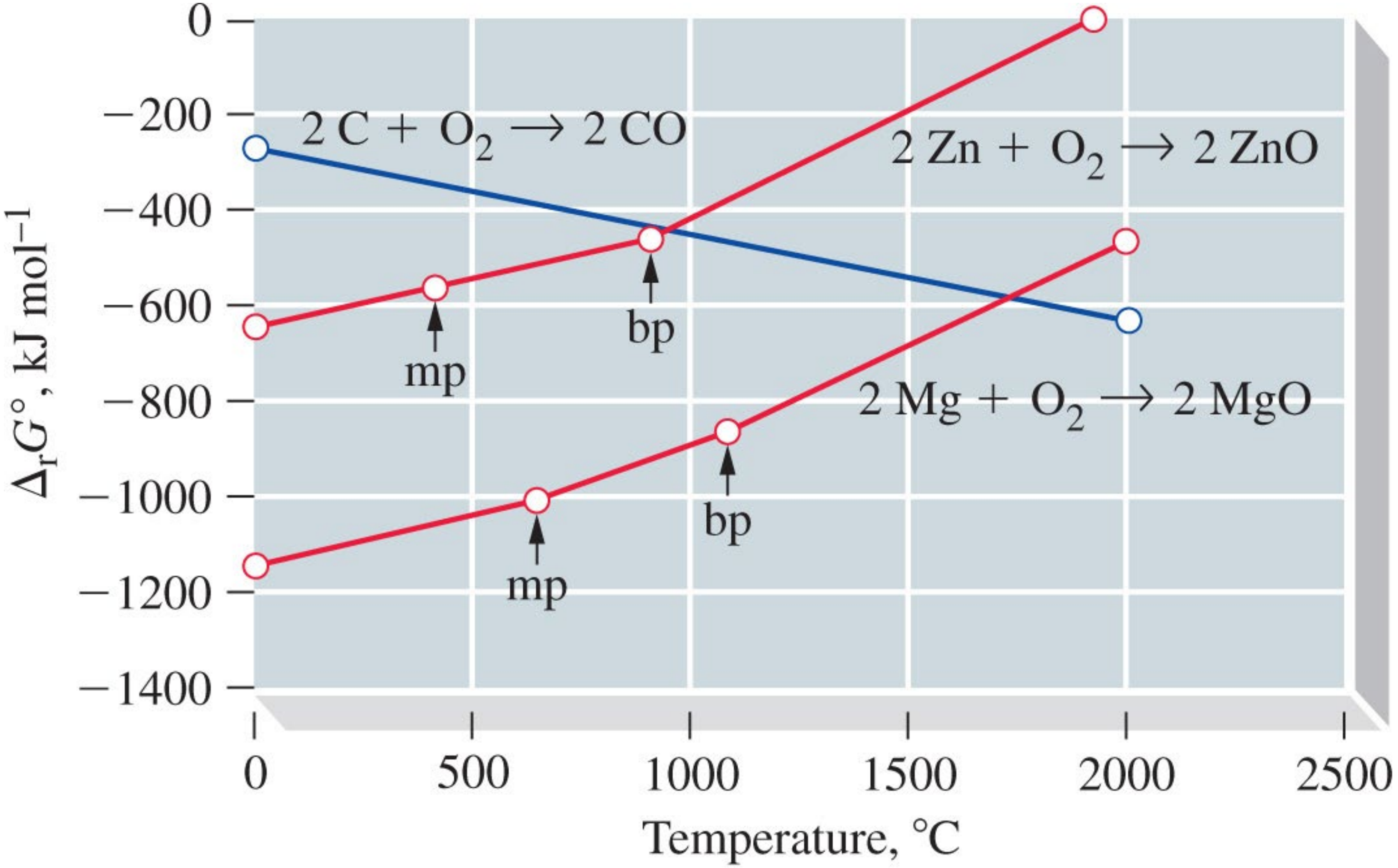

▲ FIGURE 23-8

$\Delta_r G^\circ$ as a function of temperature for some reactions of extractive metallurgy

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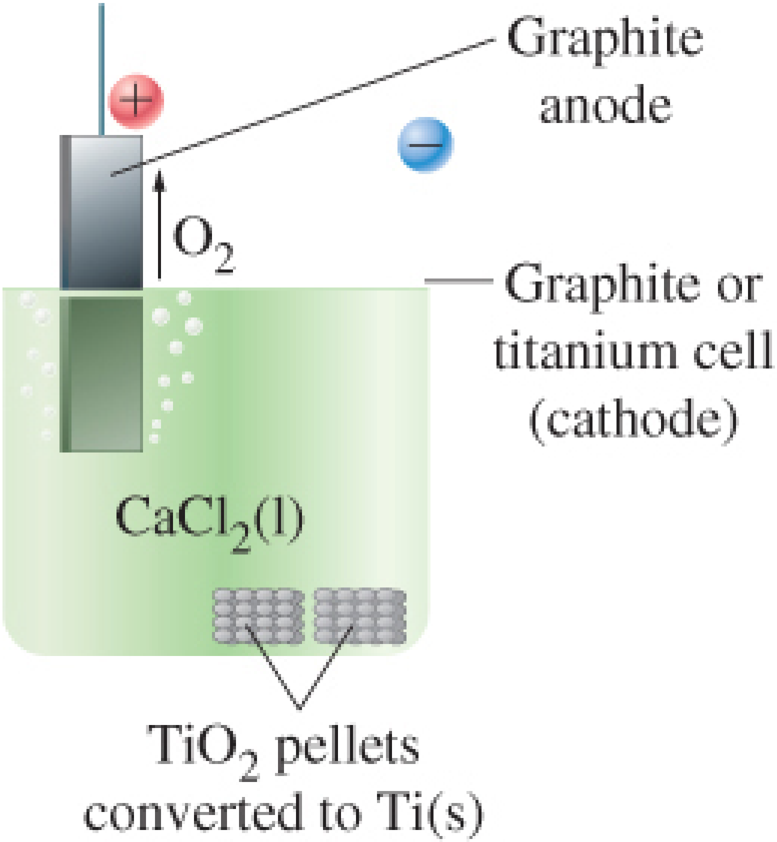
Alternative Methods in Extractive Metallurgy

▲ Vacuum-distilled metallic titanium sponge produced by the Kroll process



▲ Electrolytic production of Ti(s) from $TiO_2(s)$

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Metallurgy of Copper

Concentration of copper is done by floatation and roasting converts iron sulfides to iron oxides. Below 800°C the CuS is not converted to the oxide.

Reduction of roasted ore at 1400°C causes melting and separation into two layers; the bottom layer is *copper matte* and the top layer is *silicate slag*.

Slag

$$FeO(s) + SiO_2(s) \xrightarrow{\Delta} 2\ FeSiO_3(s) \qquad (23.9)$$

Converstion

$$2\ Cu_2S(l) + 3\ O_2(g) \xrightarrow{\Delta} 2\ Cu_2O(l) + 2\ SO_2(g) \qquad (23.10)$$

$$2\ Cu_2O(l) + Cu_2S(g) \xrightarrow{\Delta} \underset{\textit{blister copper}}{6\ Cu\ (l)} + SO_2(g) \qquad (23.11)$$

Refining

Electrolytically refined to high-purity copper for electrical applications if needed.

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▲ Slag formed during the smelting of copper ore.

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Pyrometallurgical Processes

Any metallurgical method based on roasting an ore, followed by reduction of the oxide to the metal.

- large quantities of waste produced in concentrating low-grade ores
- high energy consumption to maintian temperatures required
- control of gaseous emissions such as SO_2

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Hydrometallurgical Processes

Materials are handled in aqueous solutions at moderate temperature. Three steps are involved.

1. *Leeching:* Extraction of metal ions by a liquid, such as water, acids, bases or salt solutions. Redox processes may be involved.
2. *Purification and concentration:* Separation of impurities by methods such as absorption on charcoal or ion exchange.
3. *Precipitation:* The desired metal is precipitated in an ionic solid, or reduced to the solid (often electrolytically).

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cyanation

$$4\,Au(s) + 8\,CN^-(aq) + O_2(g) + 2\,H_2O(l) \longrightarrow 4\,[Au(CN)_2]^-(aq) + OH^-(aq) \qquad (23.12)$$

displacement

$$2\,[Au(CN)_2]^-(aq) + Zn(s) \longrightarrow 2\,Au(s) + [Zn(CN)_4]^{2-}(aq) \qquad (23.13)$$

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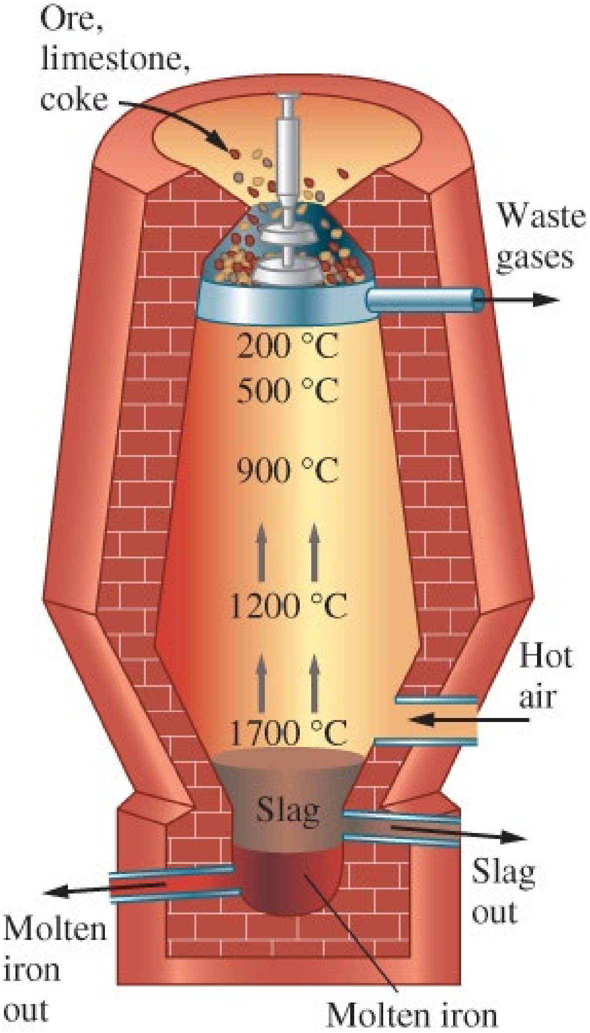
23-3 Metallurgy of Iron and Steel



▲ FIGURE 23-9

Typical blast furnace

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Pig Iron

simplified process in blast furnace:

$$Fe_2O_3(s) + 3\ CO(g) \longrightarrow 2\ Fe(l) + 3\ CO_2(g) \qquad (23.15)$$

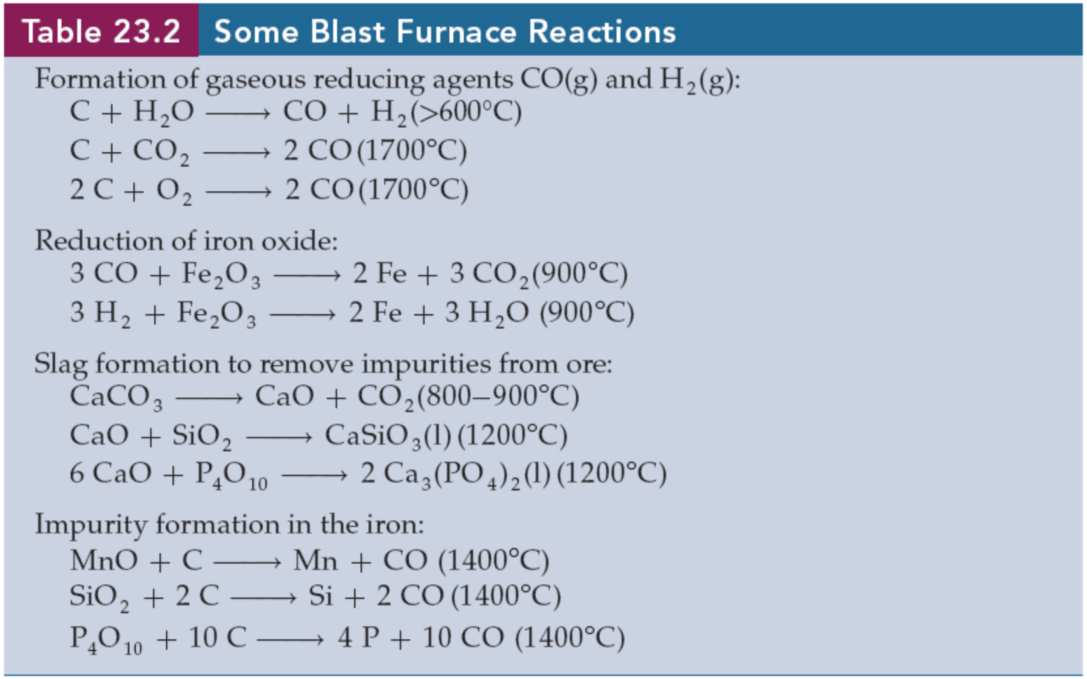

Table 23.2 **Some Blast Furnace Reactions**

Formation of gaseous reducing agents CO(g) and H_2(g):

$C + H_2O \longrightarrow CO + H_2 (>600°C)$

$C + CO_2 \longrightarrow 2\ CO\ (1700°C)$

$2\ C + O_2 \longrightarrow 2\ CO\ (1700°C)$

Reduction of iron oxide:

$3\ CO + Fe_2O_3 \longrightarrow 2\ Fe + 3\ CO_2 (900°C)$

$3\ H_2 + Fe_2O_3 \longrightarrow 2\ Fe + 3\ H_2O\ (900°C)$

Slag formation to remove impurities from ore:

$CaCO_3 \longrightarrow CaO + CO_2 (800\text{–}900°C)$

$CaO + SiO_2 \longrightarrow CaSiO_3(l)\ (1200°C)$

$6\ CaO + P_4O_{10} \longrightarrow 2\ Ca_3(PO_4)_2(l)\ (1200°C)$

Impurity formation in the iron:

$MnO + C \longrightarrow Mn + CO\ (1400°C)$

$SiO_2 + 2\ C \longrightarrow Si + 2\ CO\ (1400°C)$

$P_4O_{10} + 10\ C \longrightarrow 4\ P + 10\ CO\ (1400°C)$

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Steel

Three fundamental changes must be made to convert pig iron to steel:

1)reduction of carbon content from 3-4% to 0-1.5%.

2)removal of Si, Mn, P and other minor impurities through slag formation.

3)addition of alloying elements (Cr, Ni, V, Mo, W) to give steel its desired end properties.

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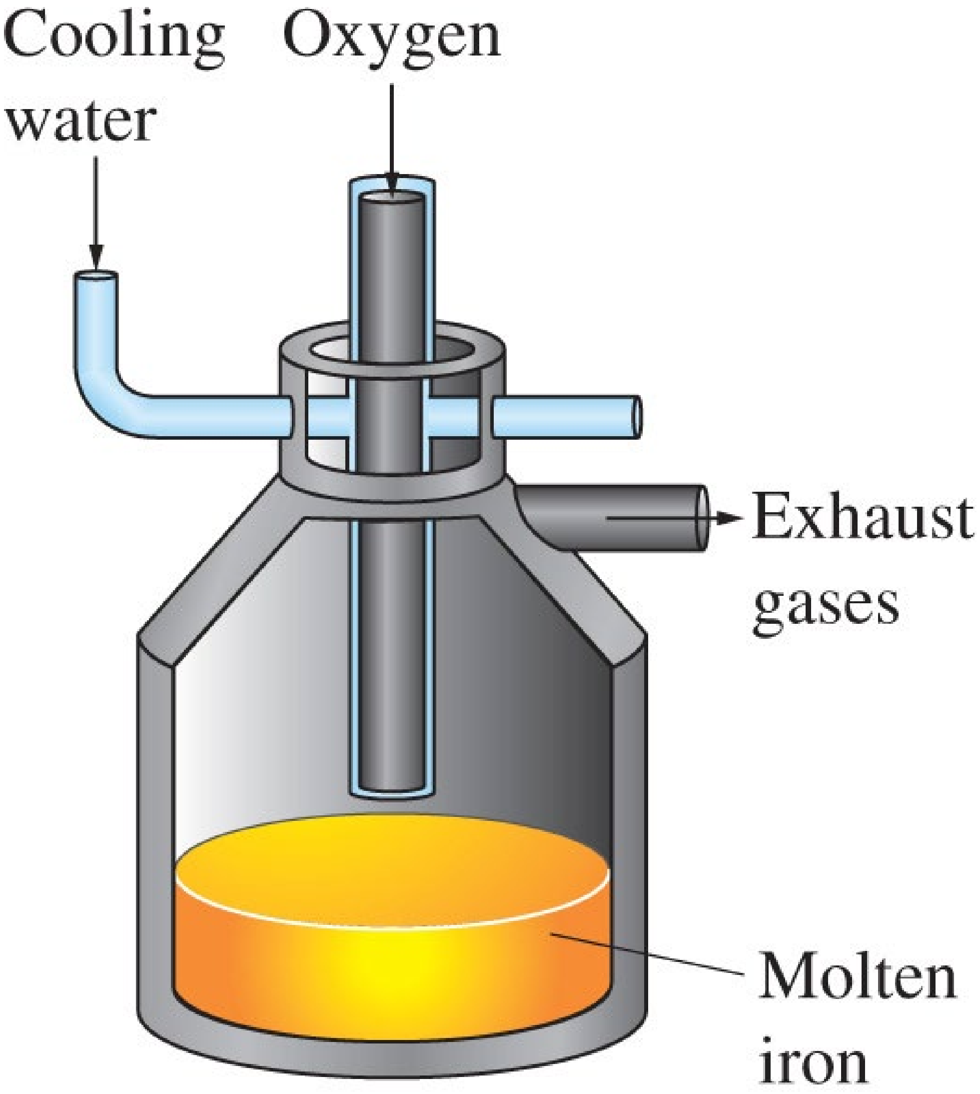

▲ FIGURE 23-10

A basic oxygen furnace

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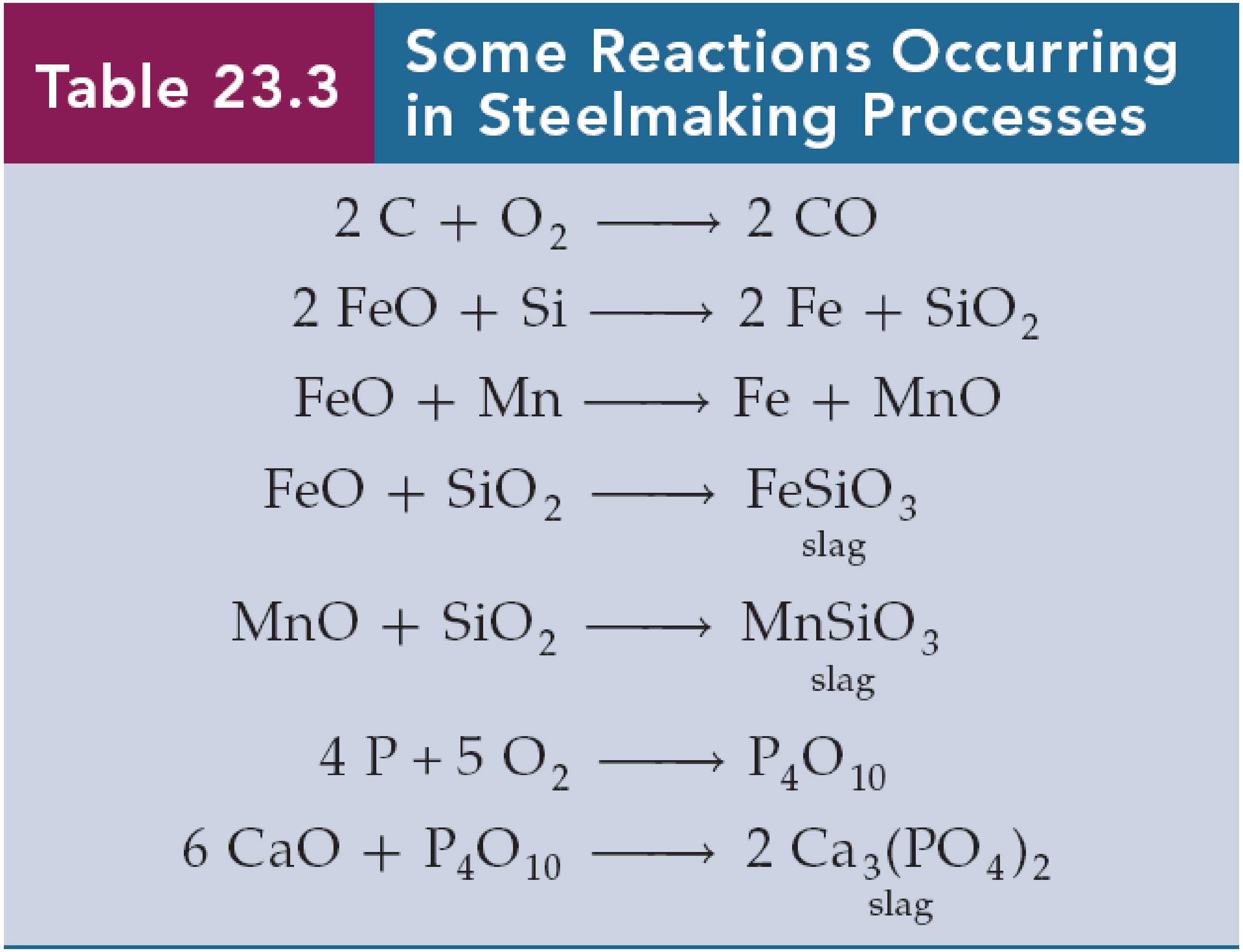

Table 23.3 Some Reactions Occurring in Steelmaking Processes

$$2\,C + O_2 \longrightarrow 2\,CO$$

$$2\,FeO + Si \longrightarrow 2\,Fe + SiO_2$$

$$FeO + Mn \longrightarrow Fe + MnO$$

$$FeO + SiO_2 \longrightarrow \underset{\text{slag}}{FeSiO_3}$$

$$MnO + SiO_2 \longrightarrow \underset{\text{slag}}{MnSiO_3}$$

$$4\,P + 5\,O_2 \longrightarrow P_4O_{10}$$

$$6\,CaO + P_4O_{10} \longrightarrow \underset{\text{slag}}{2\,Ca_3(PO_4)_2}$$

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23-4 First-Row Transition Metal Elements: Scandium to Manganese

Scandium

- 0.0025% of earths crust, more abundant than many better known metals.
- Mostly obtained from uranium ore.
- Limited commercial use.

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Titanium

- 0.6% of earths crust, 9th most abundant element.
- low density and high structural strength and corrosion resistance.
- extensive use in aircraft and chemical industries, and in bone and dental implants.
- *Titanium tetrachloride,* $TiCl_4$ is commercially important and is used to prepare other titanium compounds.
- *Titanium dioxide,* non-toxic TiO_2 has displaced toxic lead carbonate in paints.

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▲ Titanium joint implants at the hip and knees.

▲ White $TiO_2(s)$, mixed with other components to produce the desired color, is the leading pigment used in paints.

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Vanadium

- 0.02% of earths crust, fairly abundant.
- Several complex ores such as *vanadinite,* $Pb_5(VO_4)_3Cl$.
- *Ferrovanadium* contains 35 to 95% V in Fe.
- 80% of V production is for steel.
- Most important compound is V_2O_5 used as a catalyst for conversion of SO_2 to SO_3 in the contact process for production of sulfuric acid.
- various oxidation states and acid-base characteristics.

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▲ FIGURE 23-11
Some vanadium species in solution

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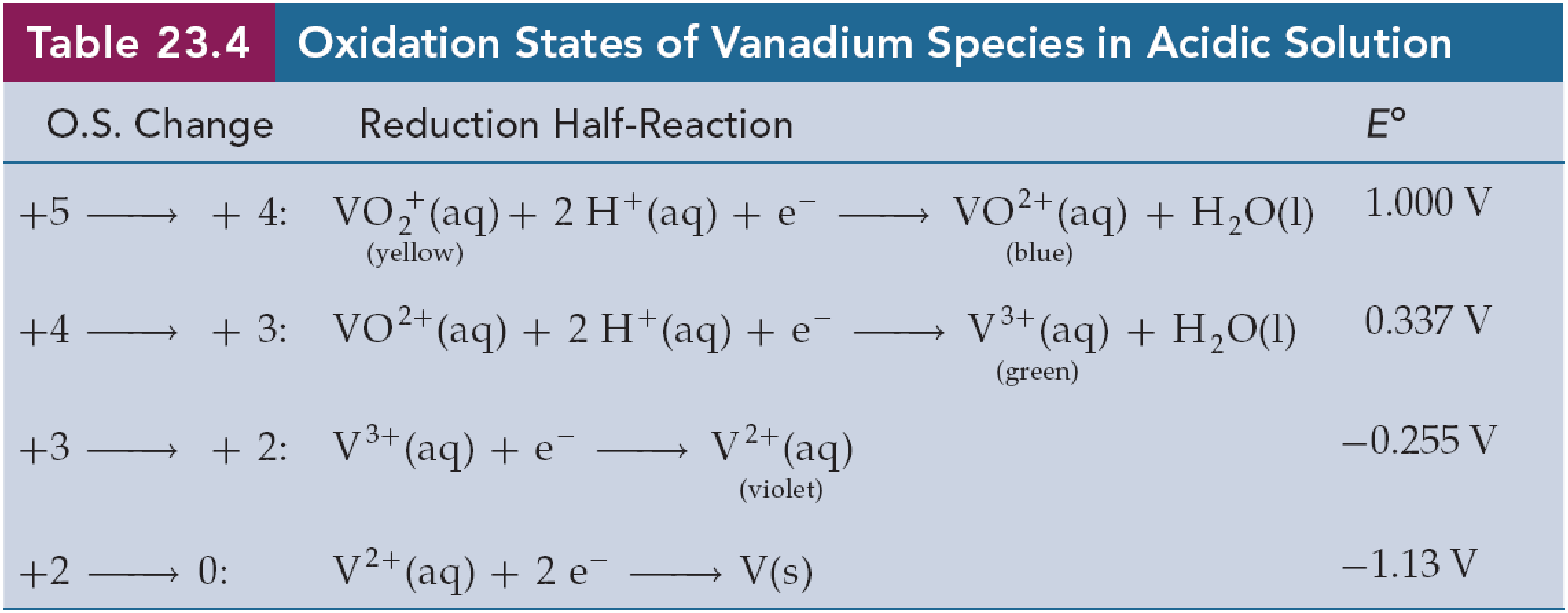

Table 23.4 Oxidation States of Vanadium Species in Acidic Solution

O.S. Change	Reduction Half-Reaction	*E*°
$+5 \longrightarrow +4$:	$\underset{\text{(yellow)}}{VO_2^+(aq)} + 2\,H^+(aq) + e^- \longrightarrow \underset{\text{(blue)}}{VO^{2+}(aq)} + H_2O(l)$	1.000 V
$+4 \longrightarrow +3$:	$VO^{2+}(aq) + 2\,H^+(aq) + e^- \longrightarrow \underset{\text{(green)}}{V^{3+}(aq)} + H_2O(l)$	0.337 V
$+3 \longrightarrow +2$:	$V^{3+}(aq) + e^- \longrightarrow \underset{\text{(violet)}}{V^{2+}(aq)}$	−0.255 V
$+2 \longrightarrow 0$:	$V^{2+}(aq) + 2\,e^- \longrightarrow V(s)$	−1.13 V

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Chromium

- 0.0122% in earths crust and one of the most important industrial chemicals.
- Hard and maintains a bright surface through the action of an invisible oxide coating.
- Resistant to corrosion and used to plate other metals.
- Variety of oxidation states

O.S. + 2: $[Cr(H_2O)_6]^{2+}$, blue

O.S. + 3: (acidic) $[Cr(H_2O)_6]^{3+}$, violet (basic) $[Cr(OH)_4]^{-}$, green

O.S. + 6: (acidic) $Cr_2O_7^{2-}$, orange (basic) CrO_4^{2-}, yellow

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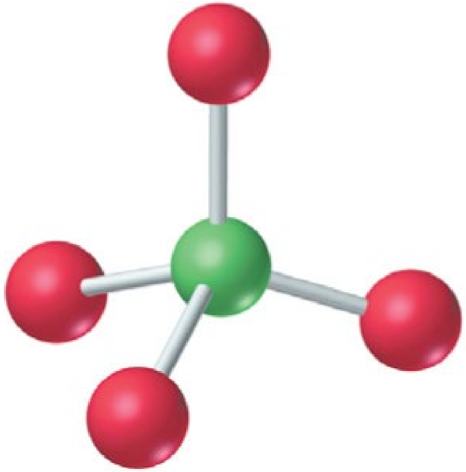
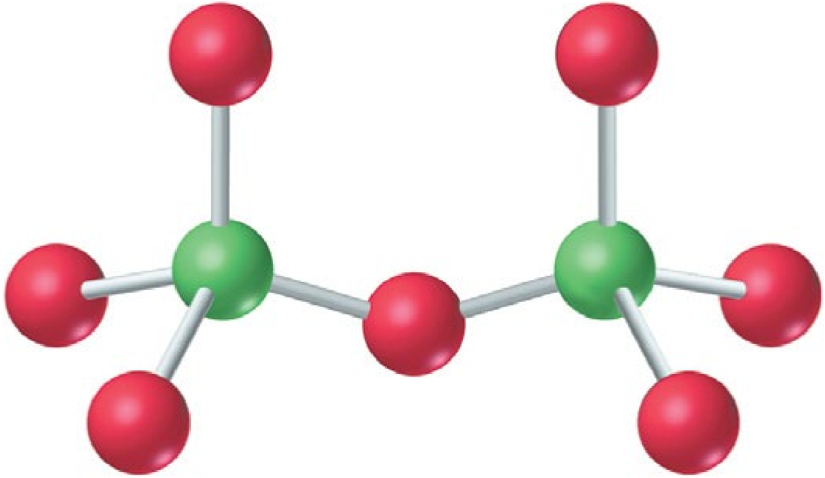


Chromate ion (CrO_4^{2-})



Dichromate ion ($Cr_2O_7^{2-}$)

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▲ FIGURE 23-12

Decomposition of $(NH_4)_2Cr_2O_7$

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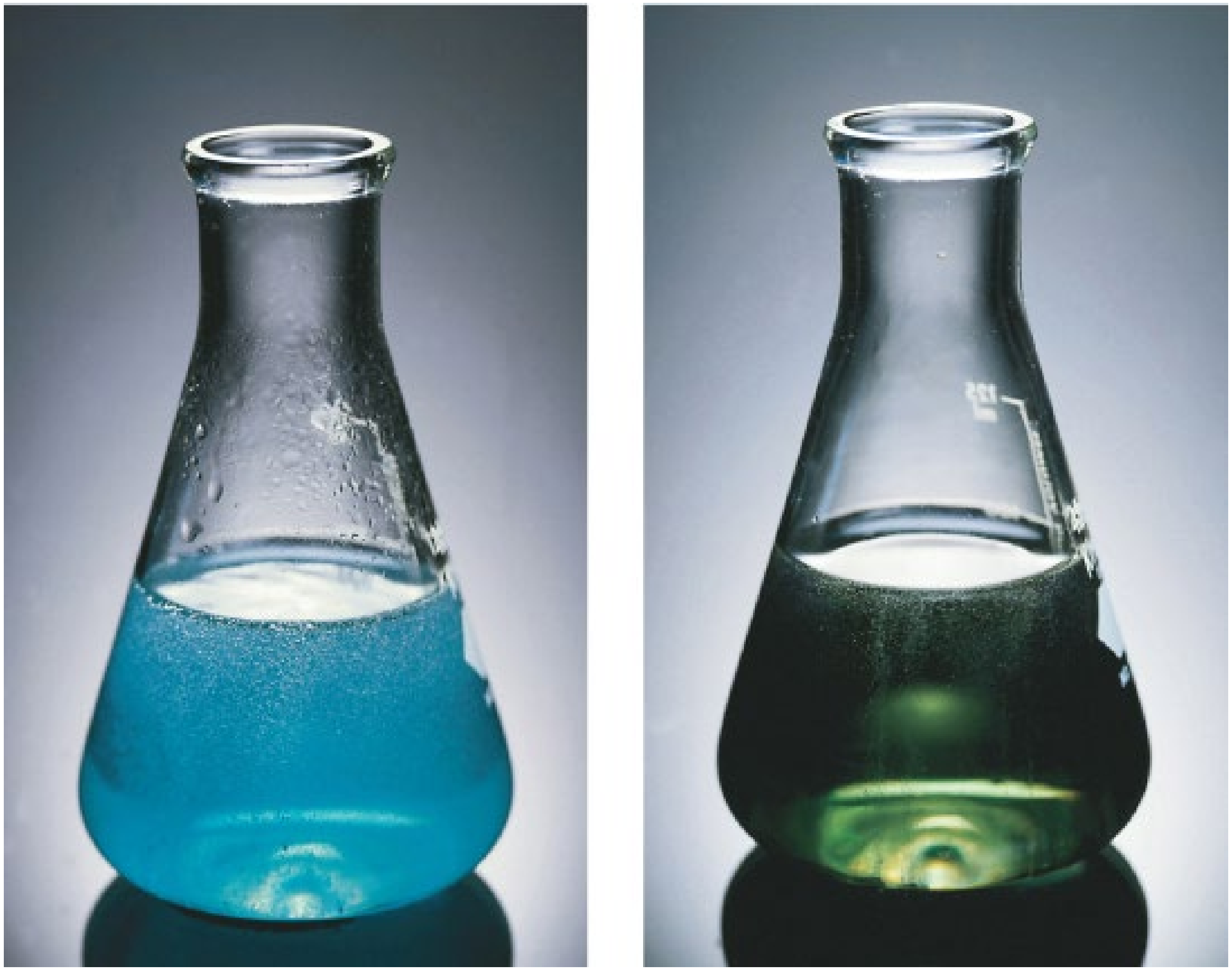

▲ FIGURE 23-13
Relationship between Cr^{2+} and Cr^{3+}

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Manganese

- 1% of earths crust, fairly abundant.
- Important for steel production.
- Exhibits all oxidation states from +2 to +7.

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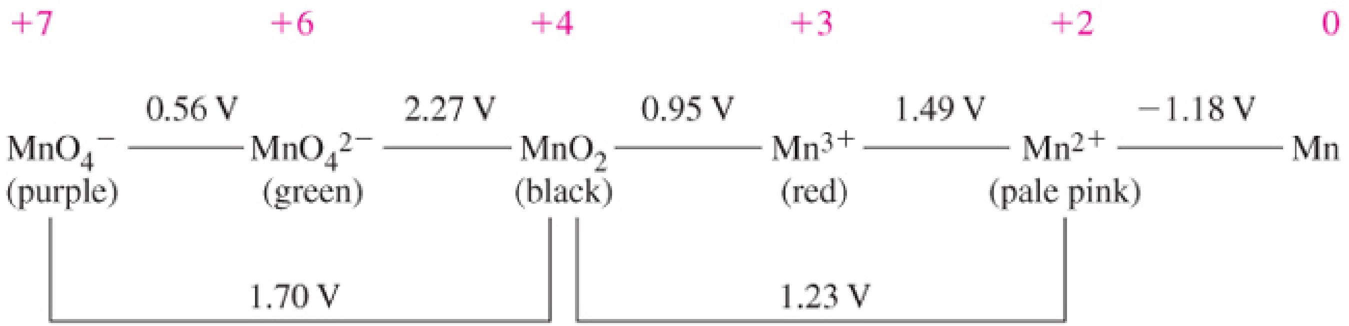
Acidic solution ($[H^+] = 1$ M):



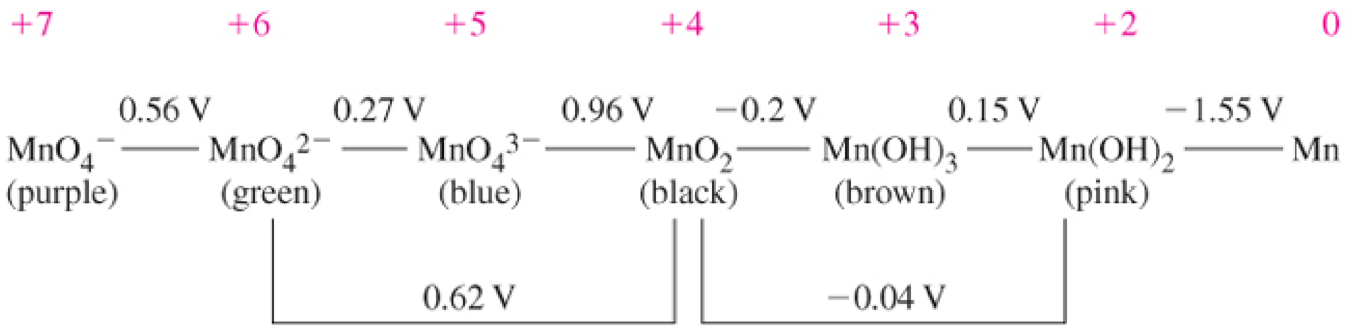
+7 +6 +4 +3 +2 0

$$\underset{\text{(purple)}}{MnO_4^-} \xrightarrow{0.56\ V} \underset{\text{(green)}}{MnO_4^{2-}} \xrightarrow{2.27\ V} \underset{\text{(black)}}{MnO_2} \xrightarrow{0.95\ V} \underset{\text{(red)}}{Mn^{3+}} \xrightarrow{1.49\ V} \underset{\text{(pale pink)}}{Mn^{2+}} \xrightarrow{-1.18\ V} Mn$$

1.70 V

1.23 V

Basic solution ($[OH^-] = 1$ M):



+7 +6 +5 +4 +3 +2 0

$$\underset{\text{(purple)}}{MnO_4^-} \xrightarrow{0.56\ V} \underset{\text{(green)}}{MnO_4^{2-}} \xrightarrow{0.27\ V} \underset{\text{(blue)}}{MnO_4^{3-}} \xrightarrow{0.96\ V} \underset{\text{(black)}}{MnO_2} \xrightarrow{-0.2\ V} \underset{\text{(brown)}}{Mn(OH)_3} \xrightarrow{0.15\ V} \underset{\text{(pink)}}{Mn(OH)_2} \xrightarrow{-1.55\ V} Mn$$

0.62 V

−0.04 V

▲ FIGURE 23-14

Electrode potential diagrams for manganese

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23-5 The Iron Triad: Iron, Cobalt, and Nickel

▲ Cobalt-samarium magnets are used in high-efficiency motors

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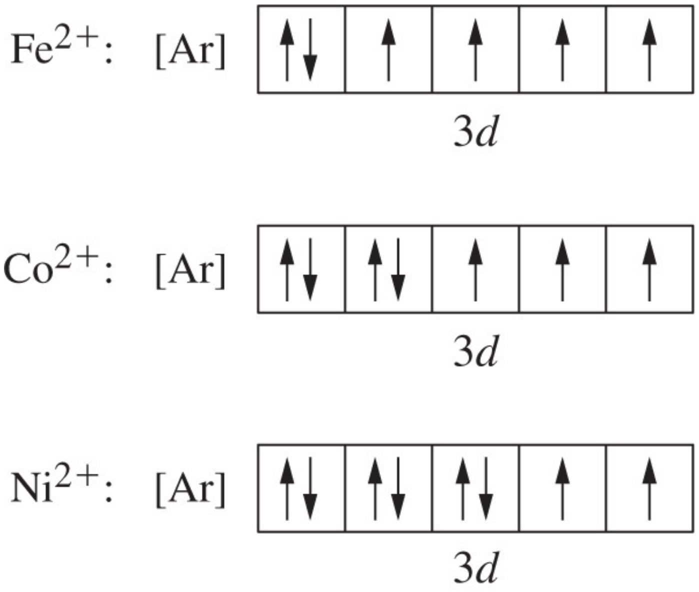
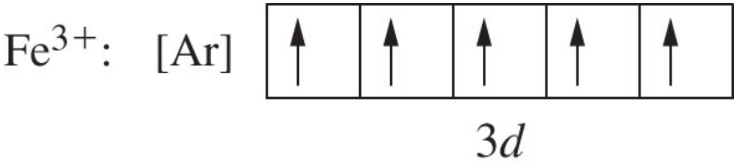
Oxidation States

The +2 oxidation state is commonly encountered in all three metals



For Co and Ni the +2 state is most stable, but for Fe it is +3



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Some Reactions of the Iron Triad Elements

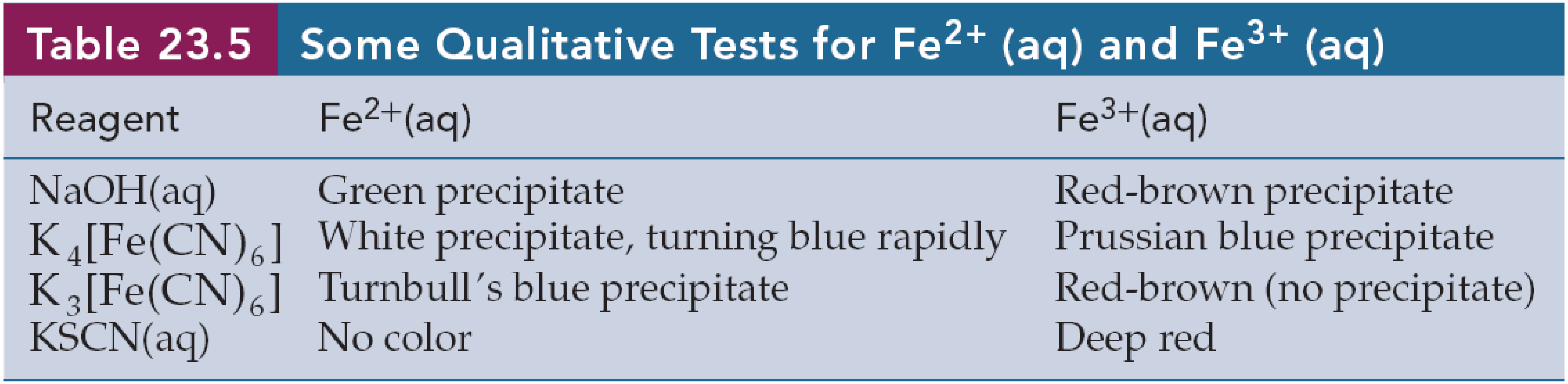

Table 23.5 Some Qualitative Tests for Fe^{2+} (aq) and Fe^{3+} (aq)

Reagent	Fe^{2+}(aq)	Fe^{3+}(aq)
NaOH(aq)	Green precipitate	Red-brown precipitate
$K_4[Fe(CN)_6]$	White precipitate, turning blue rapidly	Prussian blue precipitate
$K_3[Fe(CN)_6]$	Turnbull's blue precipitate	Red-brown (no precipitate)
KSCN(aq)	No color	Deep red

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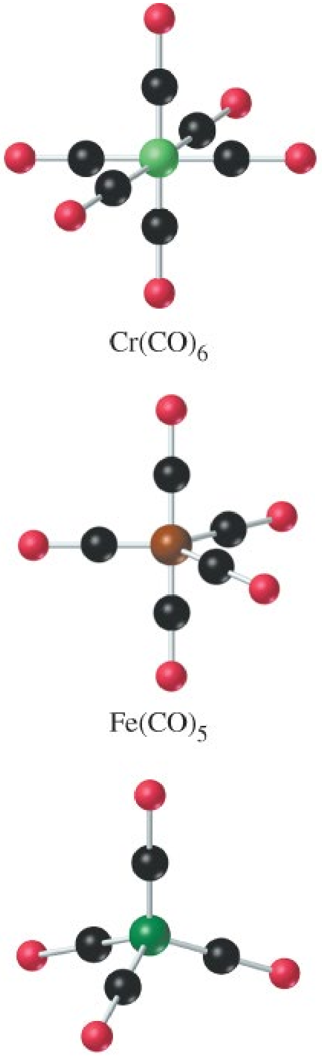

$Cr(CO)_6$

$Fe(CO)_5$

$Ni(CO)_4$

▲ FIGURE 23-15

Structure of some simple carbonyls

Table 23.6 Three Metal Carbonyls

	Number of e^-		
	From Metal	From CO	Total
$Cr(CO)_6$	24	12	36
$Fe(CO)_5$	26	10	36
$Ni(CO)_4$	28	8	36

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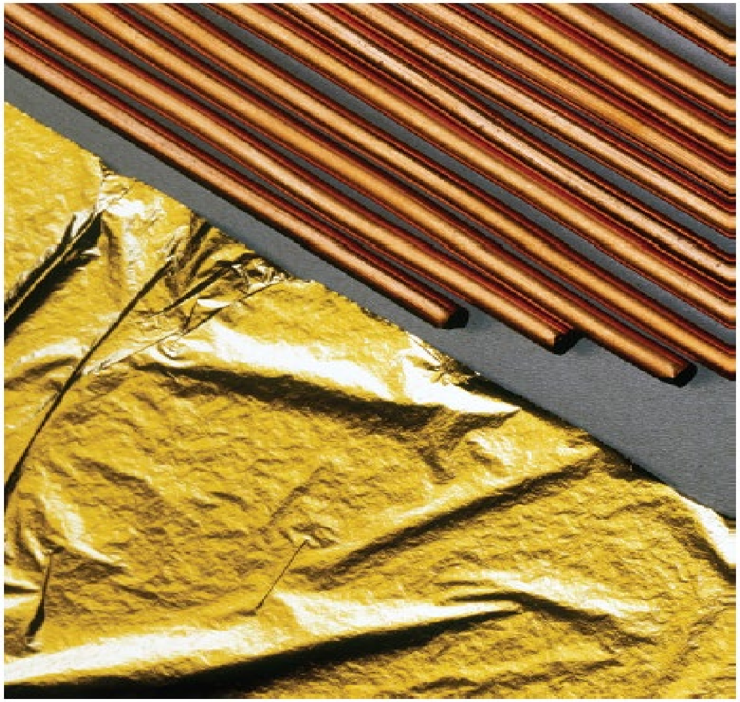
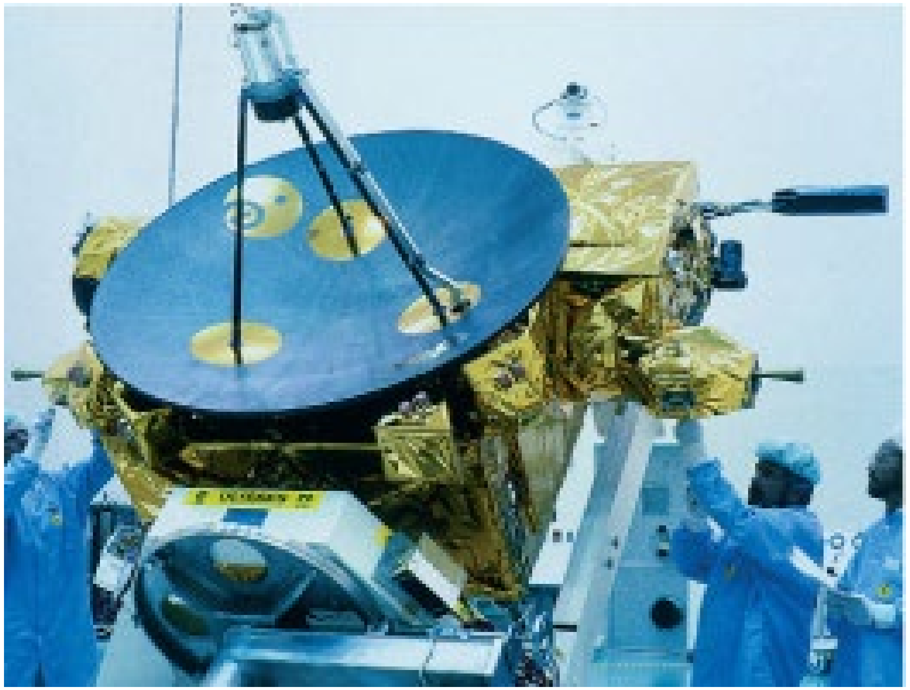
23-6 Group 11: Copper, Silver, and Gold



▲ Gold leaf and copper wire



▲ Gold plating on a space antenna

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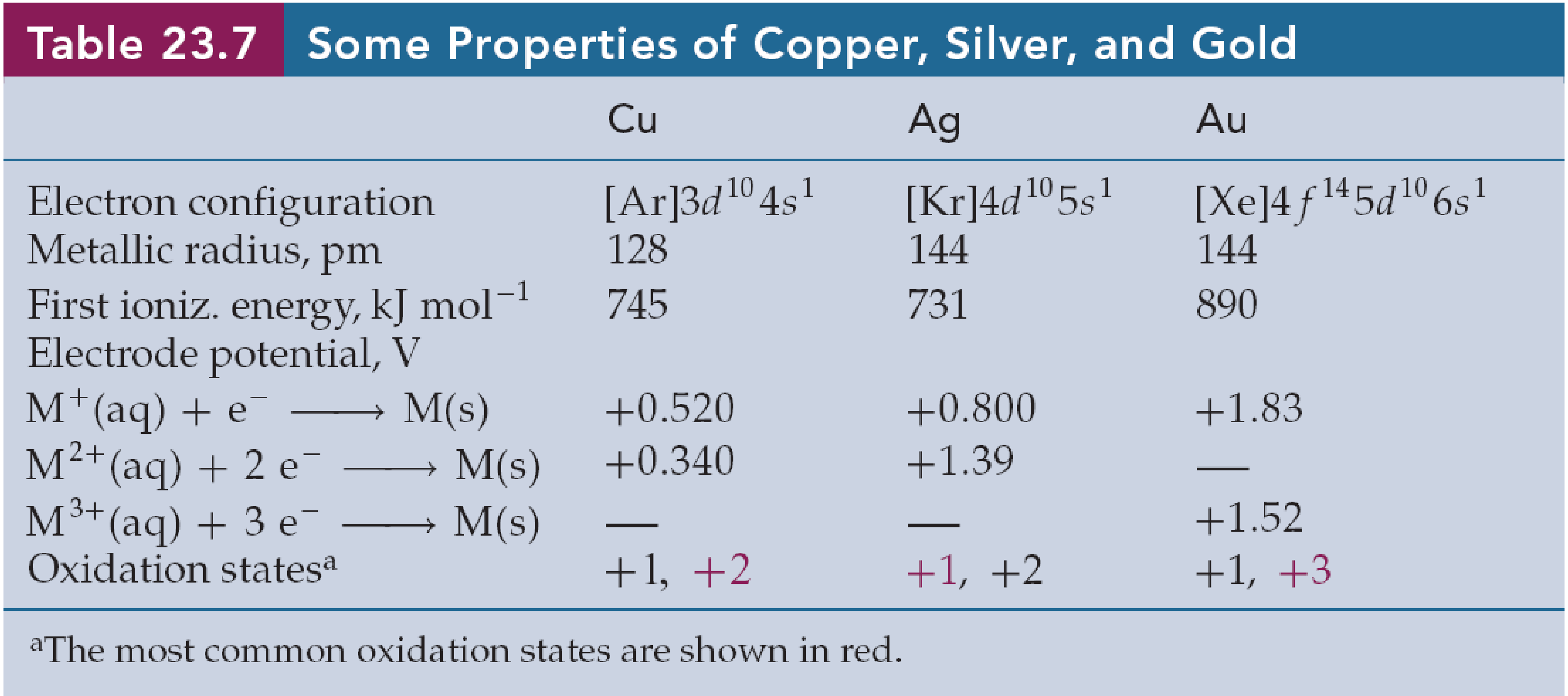

Table 23.7 Some Properties of Copper, Silver, and Gold

	Cu	Ag	Au
Electron configuration	$[Ar]3d^{10}4s^1$	$[Kr]4d^{10}5s^1$	$[Xe]4f^{14}5d^{10}6s^1$
Metallic radius, pm	128	144	144
First ioniz. energy, kJ mol^{-1}	745	731	890
Electrode potential, V			
$M^+(aq) + e^- \longrightarrow M(s)$	+0.520	+0.800	+1.83
$M^{2+}(aq) + 2\,e^- \longrightarrow M(s)$	+0.340	+1.39	—
$M^{3+}(aq) + 3\,e^- \longrightarrow M(s)$	—	—	+1.52
Oxidation states[a]	+1, +2	+1, +2	+1, +3

[a] The most common oxidation states are shown in red.

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23-7 Group 12: Zinc, Cadmium, and Mercury

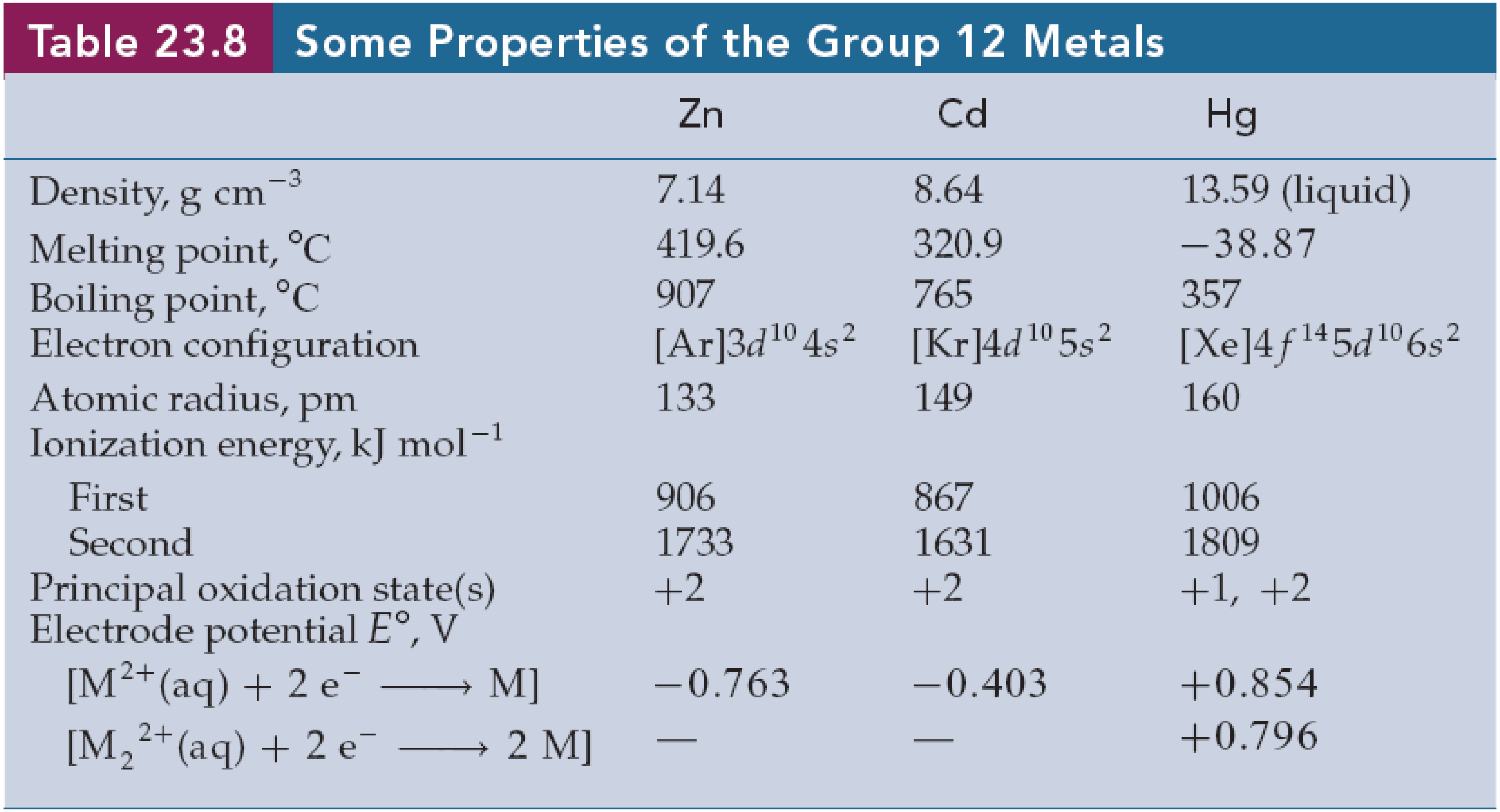

Table 23.8 **Some Properties of the Group 12 Metals**

	Zn	Cd	Hg
Density, g cm^{-3}	7.14	8.64	13.59 (liquid)
Melting point, °C	419.6	320.9	−38.87
Boiling point, °C	907	765	357
Electron configuration	$[Ar]3d^{10}4s^2$	$[Kr]4d^{10}5s^2$	$[Xe]4f^{14}5d^{10}6s^2$
Atomic radius, pm	133	149	160
Ionization energy, kJ mol^{-1}			
First	906	867	1006
Second	1733	1631	1809
Principal oxidation state(s)	+2	+2	+1, +2
Electrode potential $E°$, V			
$[M^{2+}(aq) + 2\,e^- \longrightarrow M]$	−0.763	−0.403	+0.854
$[M_2{}^{2+}(aq) + 2\,e^- \longrightarrow 2\,M]$	—	—	+0.796

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Mercury differs from Zn and Cd in a number of ways in addition to physical appearance.

- little tendency to combine with oxygen, HgO is unstable.
- very few Hg compounds are water soluble or even hydrated.
- many Hg compounds are covalent, and except for HgF_2, the halides are only slightly ionized in aqueous solution.
- Hg(I) forms a common diatomic ion with a metal-metal covalent bond, Hg_2^{2+}.
- Hg will not displace $H_2(g)$ from $H^+(aq)$.

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Uses of the Group 12 Metals

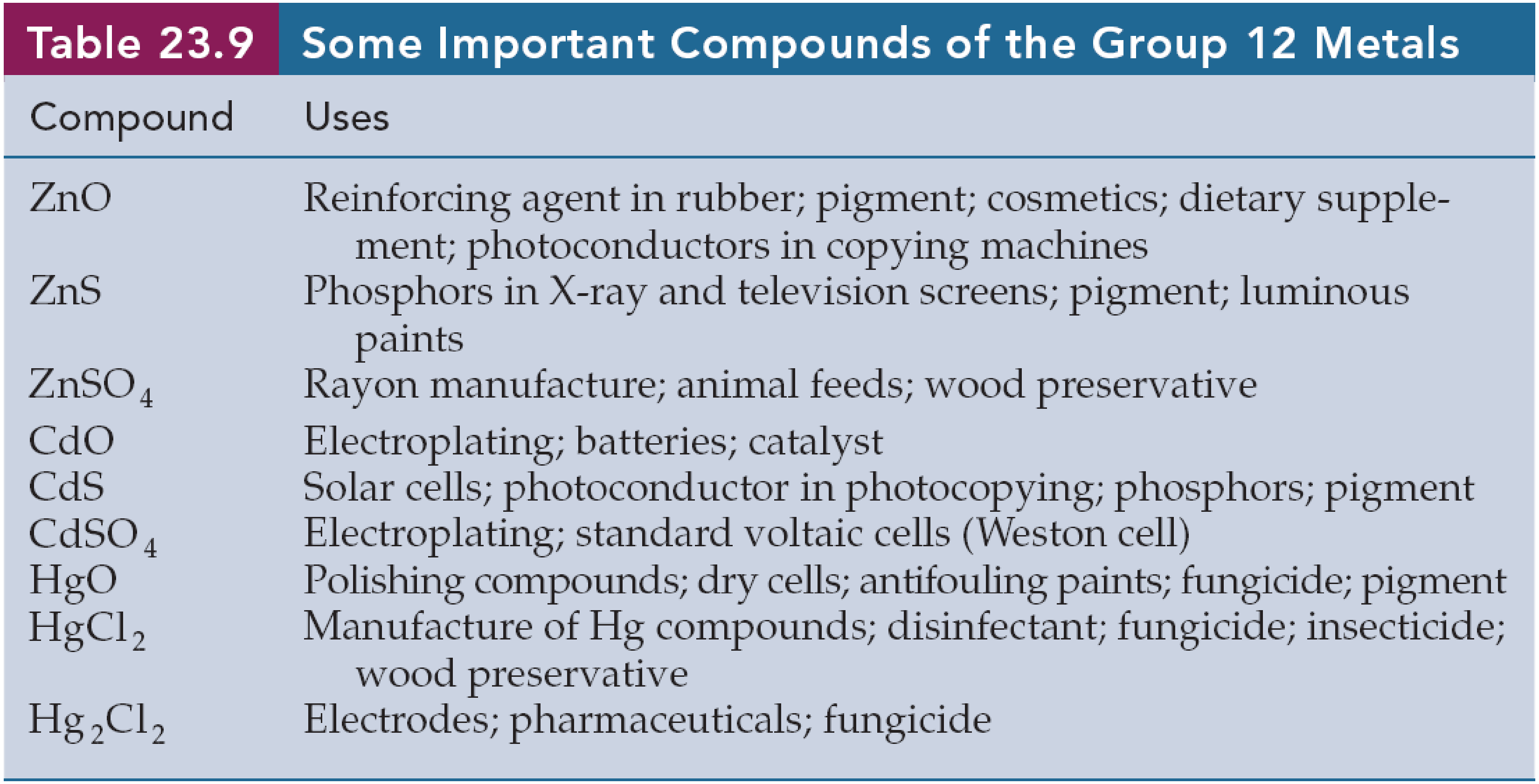

Table 23.9 **Some Important Compounds of the Group 12 Metals**

Compound	Uses
ZnO	Reinforcing agent in rubber; pigment; cosmetics; dietary supplement; photoconductors in copying machines
ZnS	Phosphors in X-ray and television screens; pigment; luminous paints
$ZnSO_4$	Rayon manufacture; animal feeds; wood preservative
CdO	Electroplating; batteries; catalyst
CdS	Solar cells; photoconductor in photocopying; phosphors; pigment
$CdSO_4$	Electroplating; standard voltaic cells (Weston cell)
HgO	Polishing compounds; dry cells; antifouling paints; fungicide; pigment
$HgCl_2$	Manufacture of Hg compounds; disinfectant; fungicide; insecticide; wood preservative
Hg_2Cl_2	Electrodes; pharmaceuticals; fungicide

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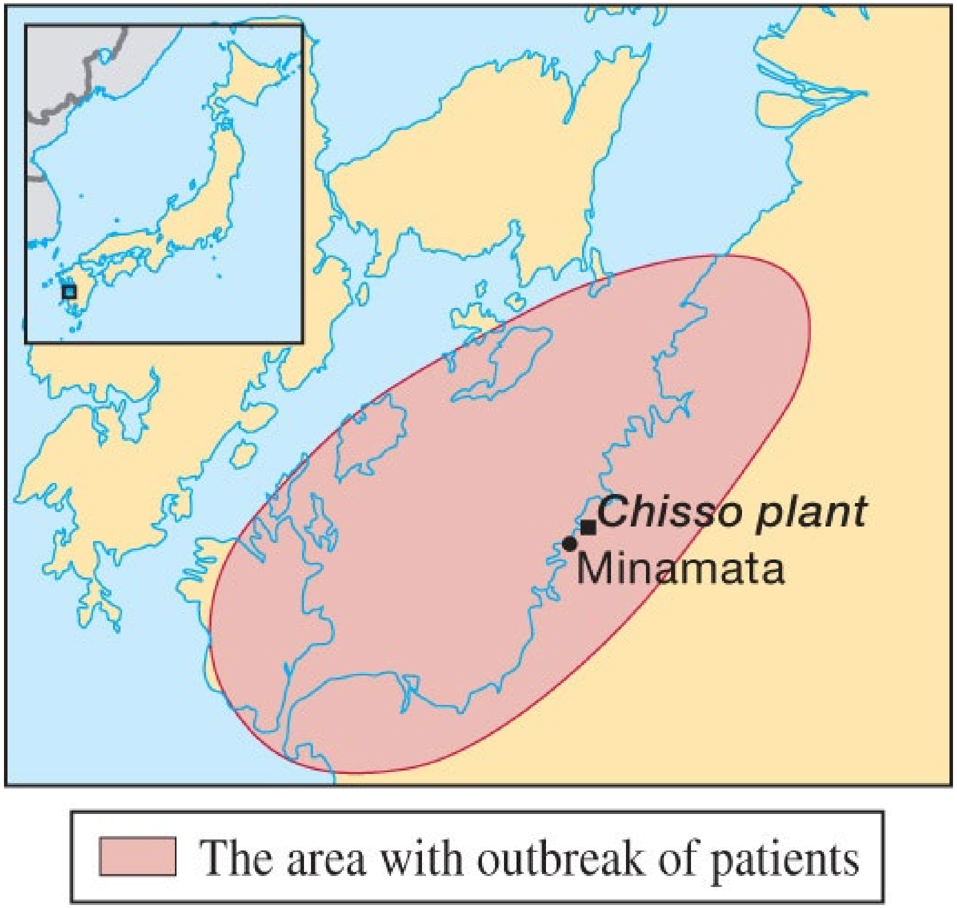
Mercury and Cadmium Poisoning



▲ The area of contamination in Japan where mercury poisoning was observed.

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23-8 Lanthanides

Lanthanum ($Z = 57$) through lutetium ($Z = 71$) are called *lanthanide, lanthanoid or rare earth elements.*

- not very rare.
- occur primarily as oxides.
- mainly 4*f* orbitals, and because 4*f* play a minor role in chemical bonding, similarities are found among the elements.
- very similar properties among the elements.
- +3 is the most common oxidation state.
- difficult to extract fro their natural sources and to separate from one another.

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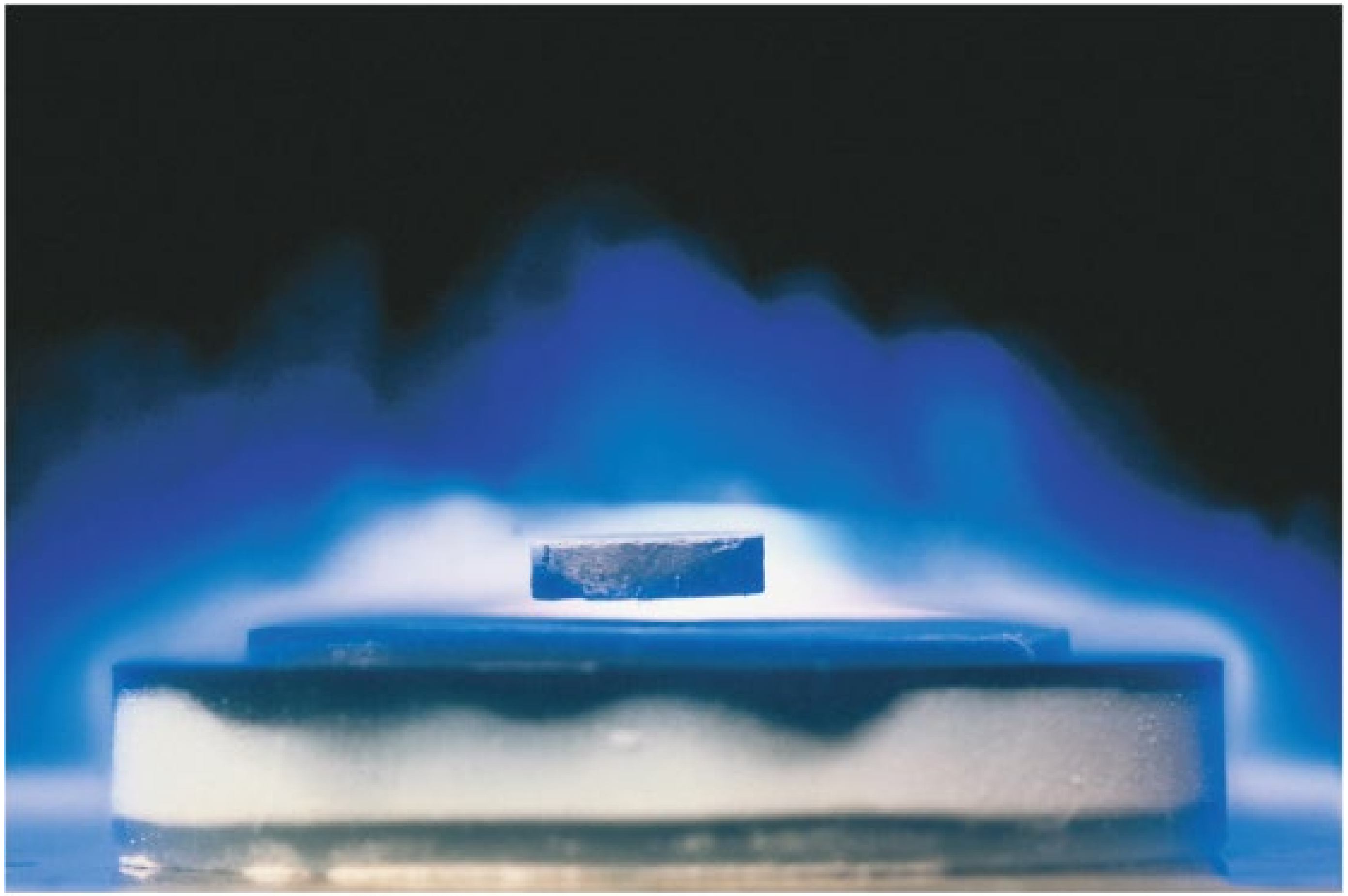
23-9 High-Temperature Superconductors



▲ FIGURE 23-16

Magnetic levitation using a superconductor

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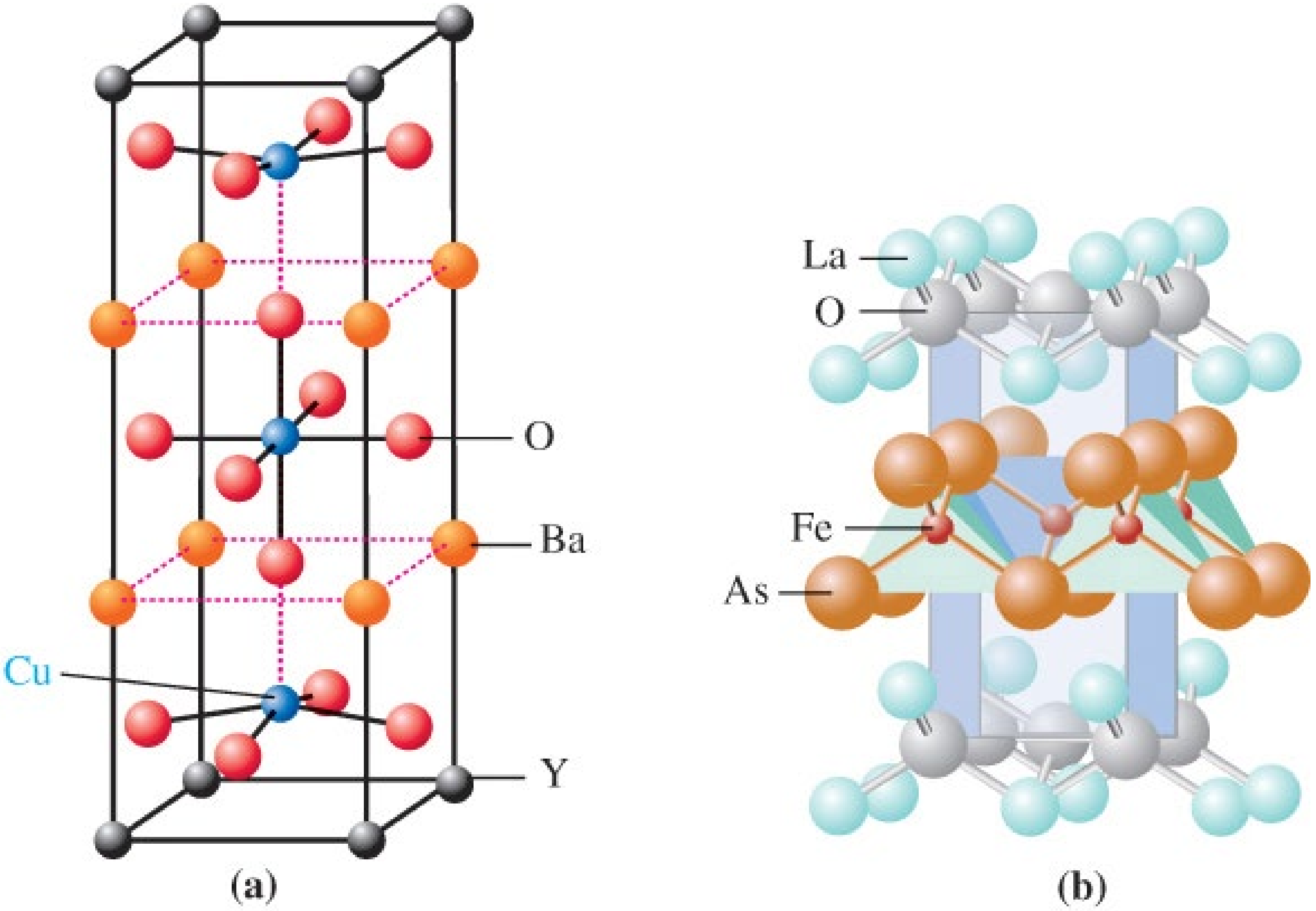

▲ FIGURE 23-17

Structures of $YBa_2Cu_3O_7$ and LOFeAs

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End of Chapter

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