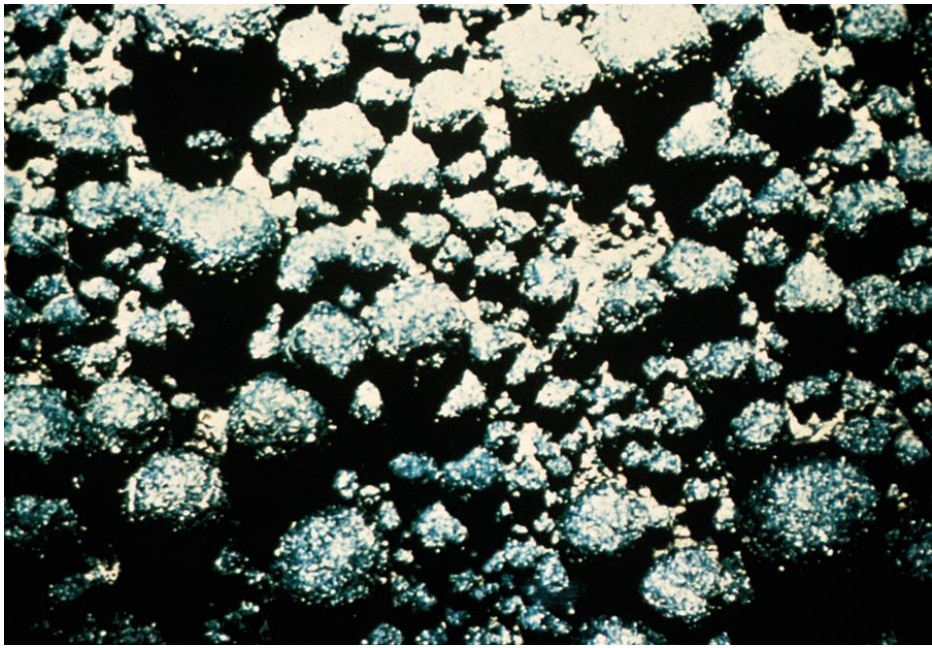
Metallurgy and the Chemistry of Metals

Chapter 20



A ***mineral*** is a naturally occurring substance with a range of chemical compositions.

An ***ore*** is a mineral deposit concentrated enough to allow economical recovery of a desired metal.

Metallurgy is the science and technology of separating metals from their ores and of compounding alloys.

An ***alloy*** is a solid solution either of two or more metals, or of a metal or metals with one or more nonmetals.

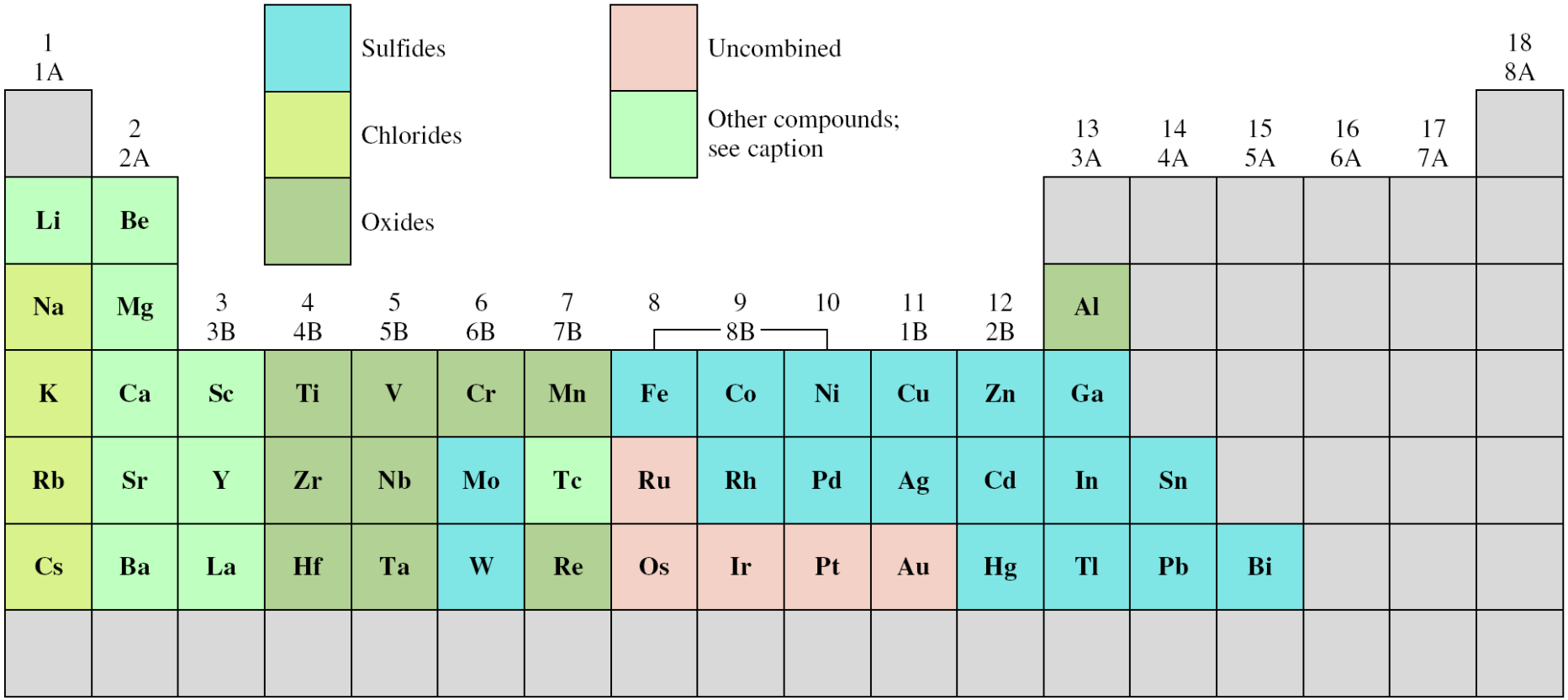
Recovery of a metal from its ore:

1. Preparation of the ore
2. Production of the metal
3. Purification of the metal

TABLE 20.1 Principal Types of Minerals

Type	Minerals
Uncombined metals	Ag, Au, Bi, Cu, Pd, Pt
Carbonates	$BaCO_3$ (witherite), $CaCO_3$ (calcite, limestone), $MgCO_3$ (magnesite), $CaCO_3 \cdot MgCO_3$ (dolomite), $PbCO_3$ (cerussite), $ZnCO_3$ (smithsonite)
Halides	CaF_2 (fluorite), NaCl (halite), KCl (sylvite), Na_3AlF_6 (cryolite)
Oxides	$Al_2O_3 \cdot 2H_2O$ (bauxite), Al_2O_3 (corundum), Fe_2O_3 (hematite), Fe_3O_4 (magnetite), Cu_2O (cuprite), MnO_2 (pyrolusite), SnO_2 (cassiterite), TiO_2 (rutile), ZnO (zincite)
Phosphates	$Ca_3(PO_4)_2$ (phosphate rock), $Ca_5(PO_4)_3OH$ (hydroxyapatite)
Silicates	$Be_3Al_2Si_6O_{18}$ (beryl), $ZrSiO_4$ (zircon), $NaAlSi_3O_8$ (albite), $Mg_3(Si_4O_{10})(OH)_2$ (talc)
Sulfides	Ag_2S (argentite), CdS (greenockite), Cu_2S (chalcocite), FeS_2 (pyrite), HgS (cinnabar), PbS (galena), ZnS (sphalerite)
Sulfates	$BaSO_4$ (barite), $CaSO_4$ (anhydrite), $PbSO_4$ (anglesite), $SrSO_4$ (celestite), $MgSO_4 \cdot 7H_2O$ (epsomite)

Metals and Their Best-Known Minerals



Production of Metals

Roasting

$CaCO_3\ (s) \longrightarrow CaO\ (s) + CO_2\ (g)$

$2PbS\ (s) + 3O_2\ (g) \longrightarrow 2PbO\ (s) + 2SO_2\ (g)$

Chemical Reduction

$TiCl_4\ (g) + 2Mg\ (l) \longrightarrow Ti\ (s) + 2MgCl_2\ (l)$

$Cr_2O_3\ (s) + 2Al\ (s) \longrightarrow 2Cr\ (l) + Al_2O_3\ (s)$

$WO_3\ (s) + 3H_2\ (g) \longrightarrow W\ (s) + 3H_2O\ (g)$

Electrolytic Reduction

$2MO\ (l) \longrightarrow 2M\ \text{(at cathode)} + O_2\ \text{(at anode)}$

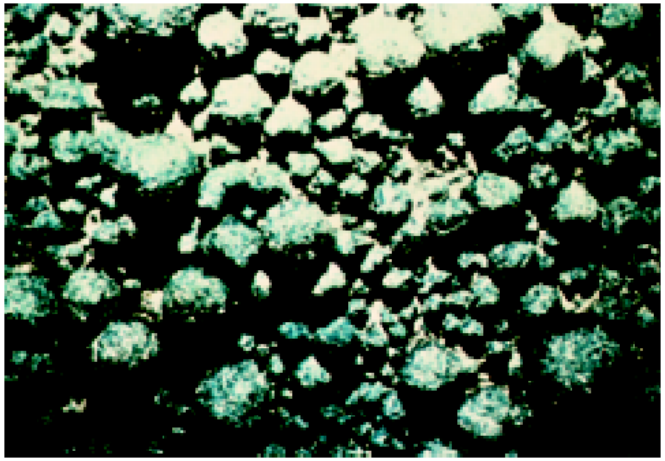
$2MCl\ (l) \longrightarrow 2M\ \text{(at cathode)} + Cl_2\ \text{(at anode)}$

TABLE 20.2 Reduction Processes for Some Common Metals

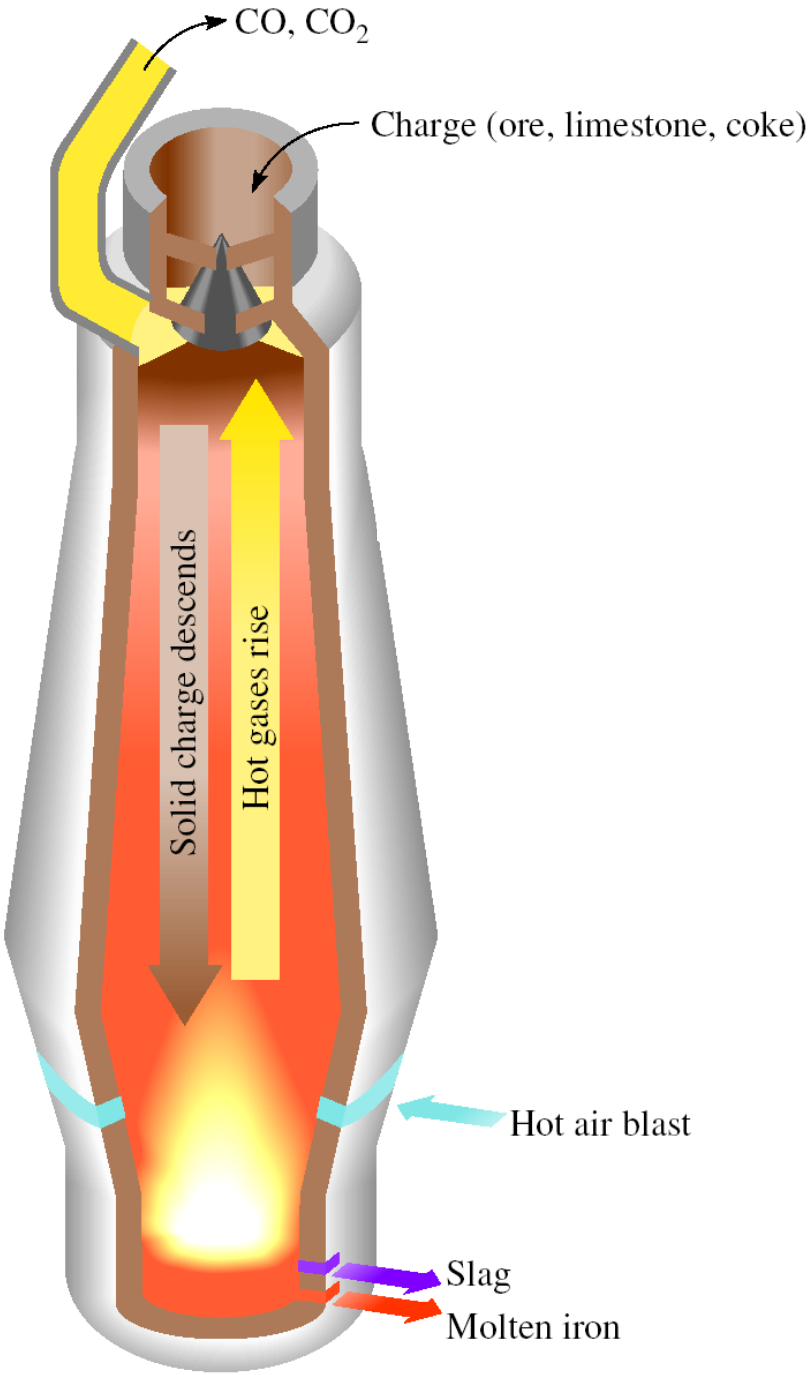
Decreasing activity of metals

Metal	Reduction Process
Lithium, sodium, magnesium, calcium	Electrolytic reduction of the molten chloride
Aluminum	Electrolytic reduction of anhydrous oxide (in molten cryolite)
Chromium, manganese, titanium, vanadium, iron, zinc	Reduction of the metal oxide with a more electropositive metal, or reduction with coke and carbon monoxide
Mercury, silver, platinum, copper, gold	These metals occur in the free (uncombined) state or can be obtained by roasting their sulfides

Mn nodules on the ocean floor



Blast Furnace for Producing Iron (reduction process)



Steel Manufacturing via the Oxygen Process (oxidation process)

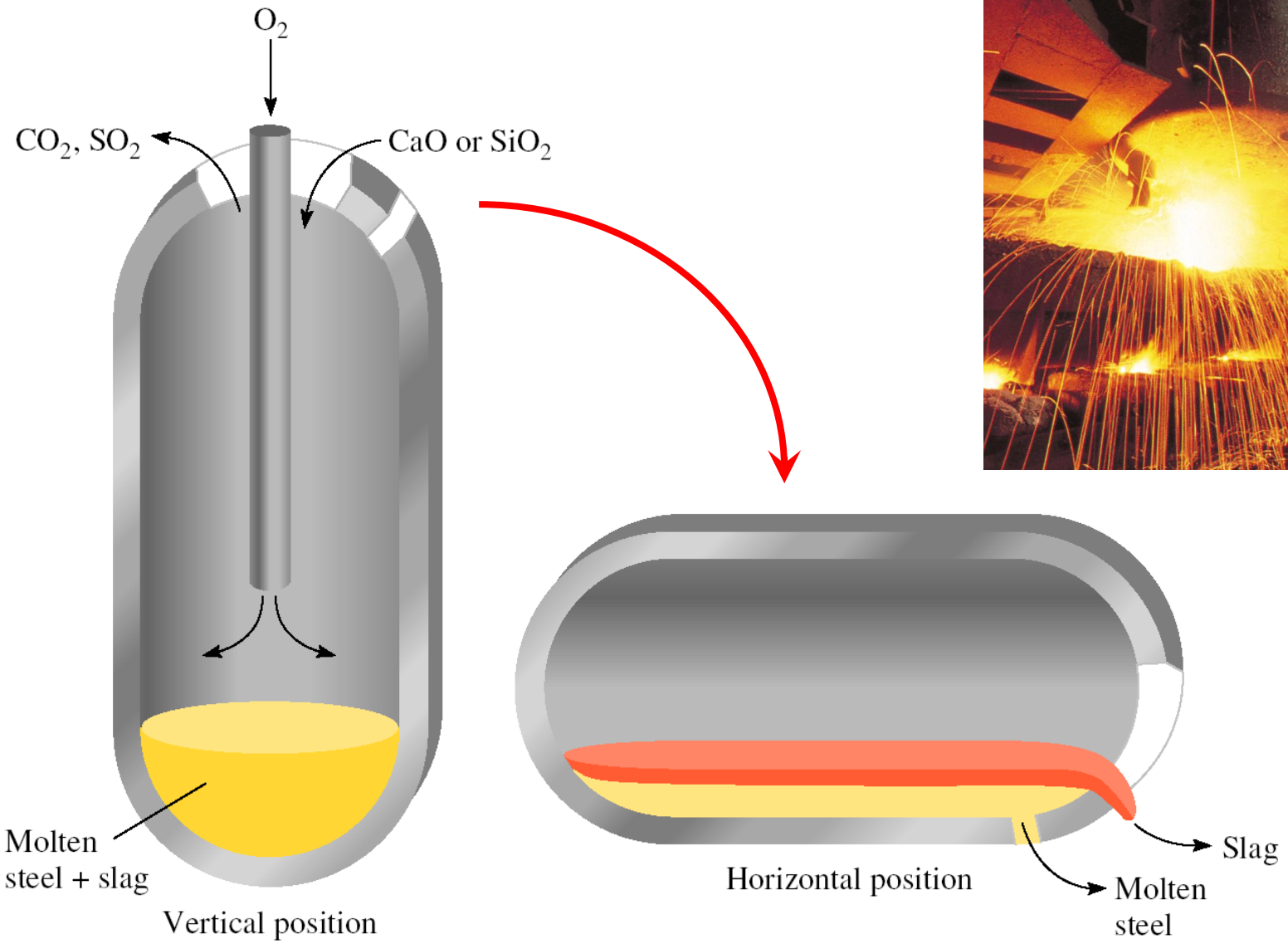


TABLE 20.3 Types of Steel

Type	Composition (Percent by Mass)*								Uses
	C	Mn	P	S	Si	Ni	Cr	Others	
Plain	1.35	1.65	0.04	0.05	0.06	—	—	Cu (0.2–0.6)	Sheet products, tools
High-strength	0.25	1.65	0.04	0.05	0.15–0.9	0.4–1.0	0.3–1.3	Cu (0.01–0.08)	Construction, steam turbines
Stainless	0.03–1.2	1.0–10	0.04–0.06	0.03	1–3	1–22	4.0–27	—	Kitchen utensils, razor blades

*A single number indicates the maximum amount of the substance present.

Purification of Metals

Distillation

$$Ni\ (s) + 4CO\ (g) \xrightarrow{70\ ^oC} NiCO_4\ (g)$$

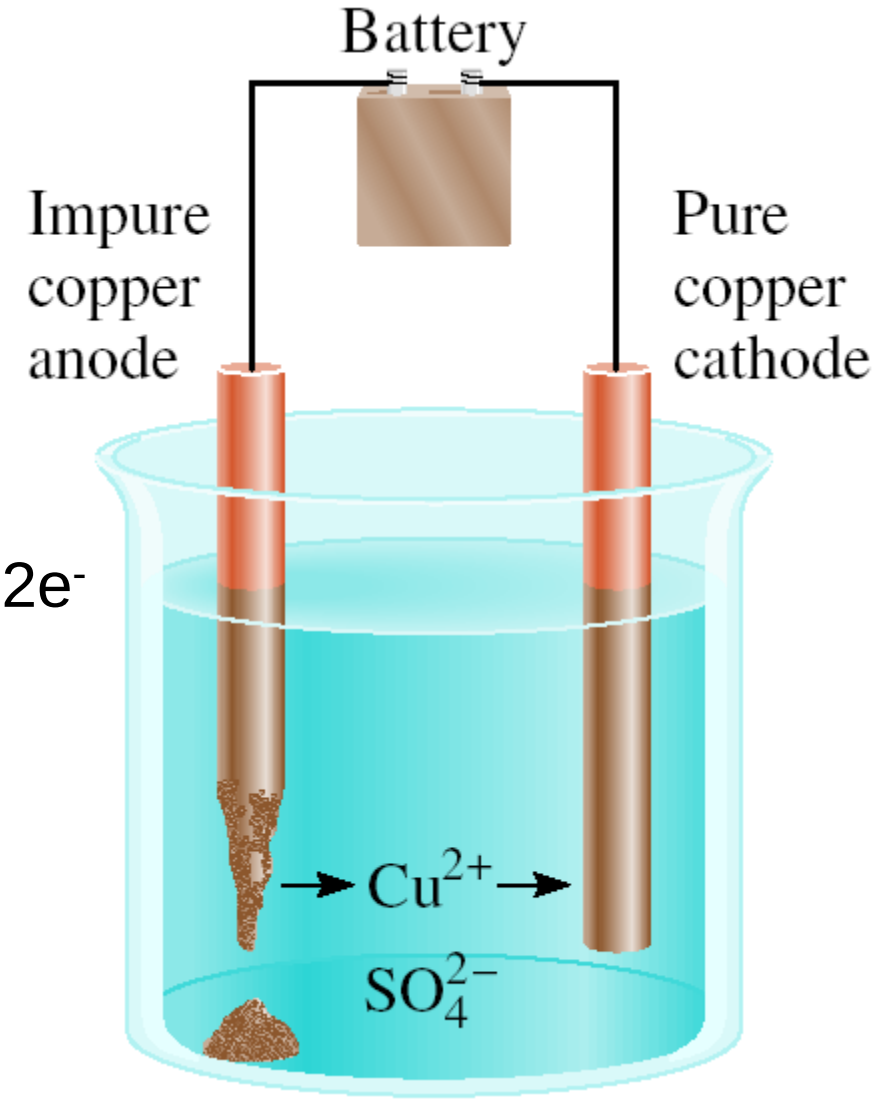
$$NiCO_4\ (g) \xrightarrow{200\ ^oC} Ni\ (s) + 4CO\ (g)$$

Electrolysis

$$Cu\ (s)\ (\text{impure}) \longrightarrow Cu^{2+}\ (aq) + 2e^-$$

$$Cu^{2+}\ (aq) + 2e^- \longrightarrow Cu\ (s)\ (\text{pure})$$

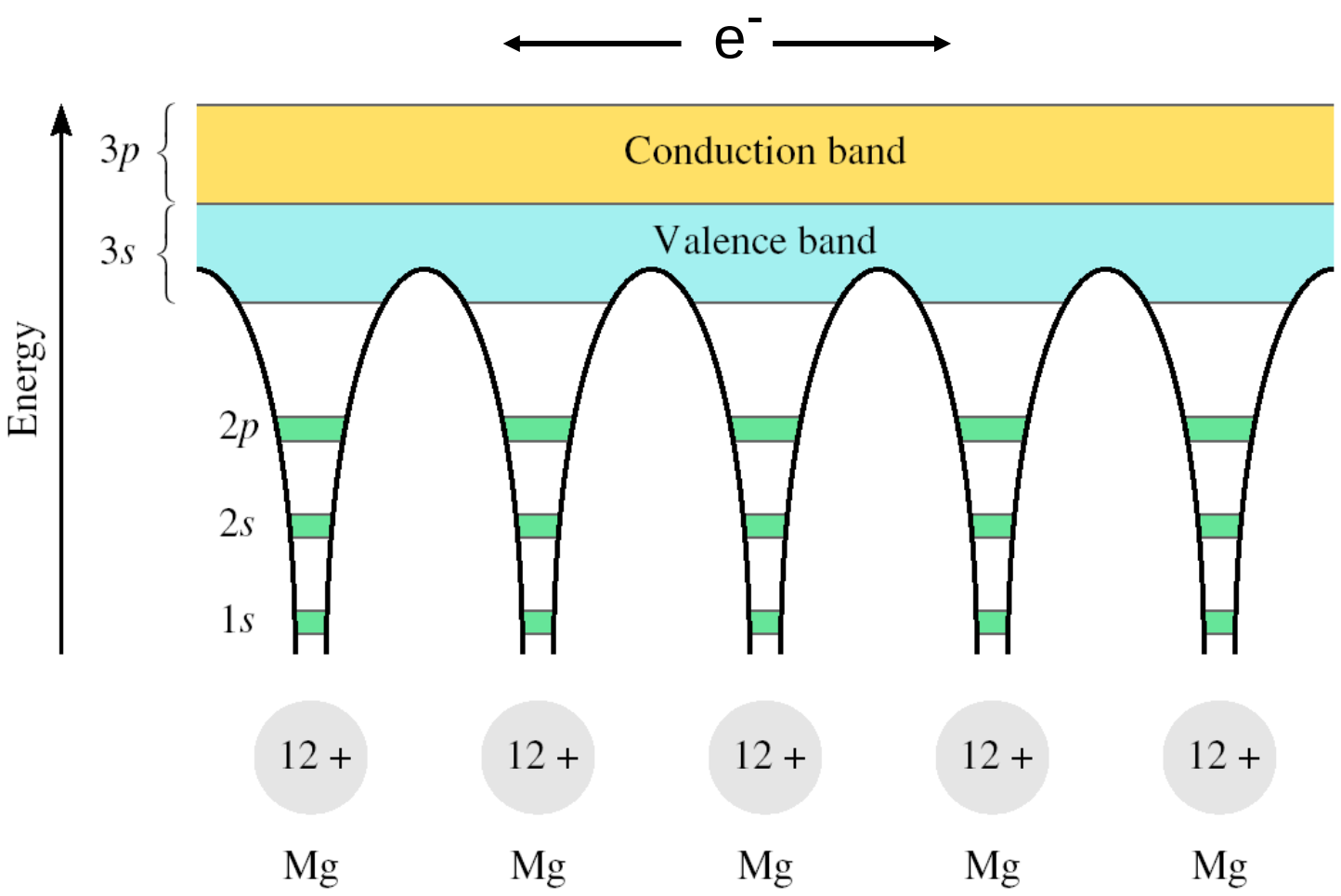
Zone refining



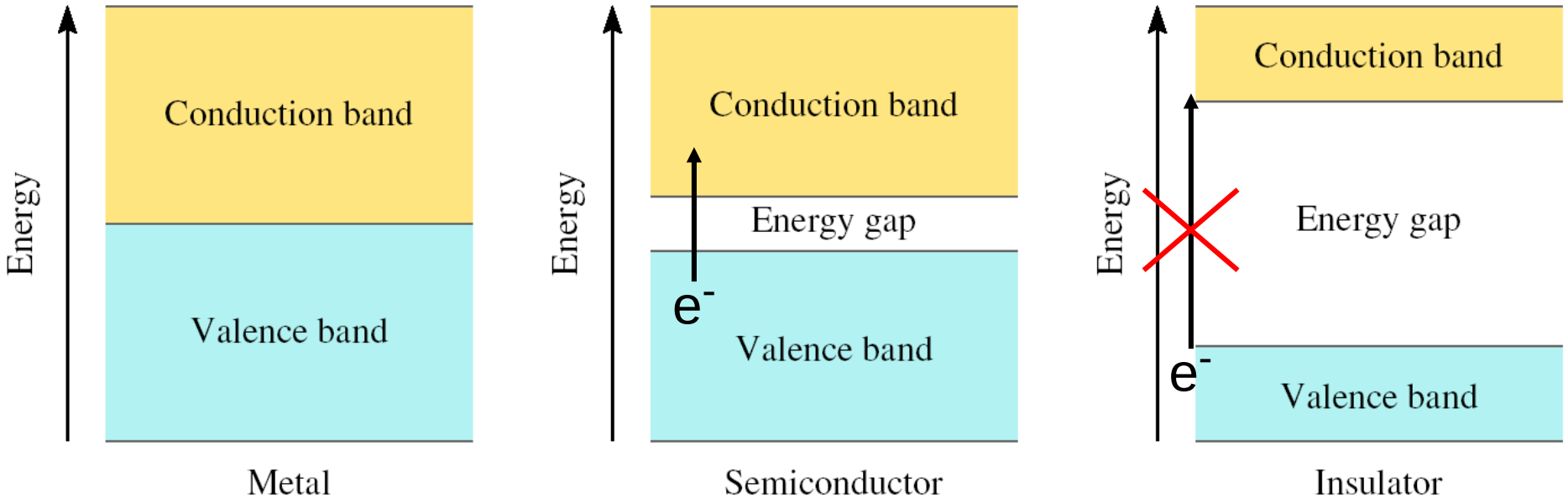
Zone Refining of Metals

In ***band theory of conductivity***, delocalized electrons move freely through “bands” formed by overlapping molecular orbitals.

Mg $1s^2 2s^2 2p^6 3s^2$ or $[Ne]3s^2$



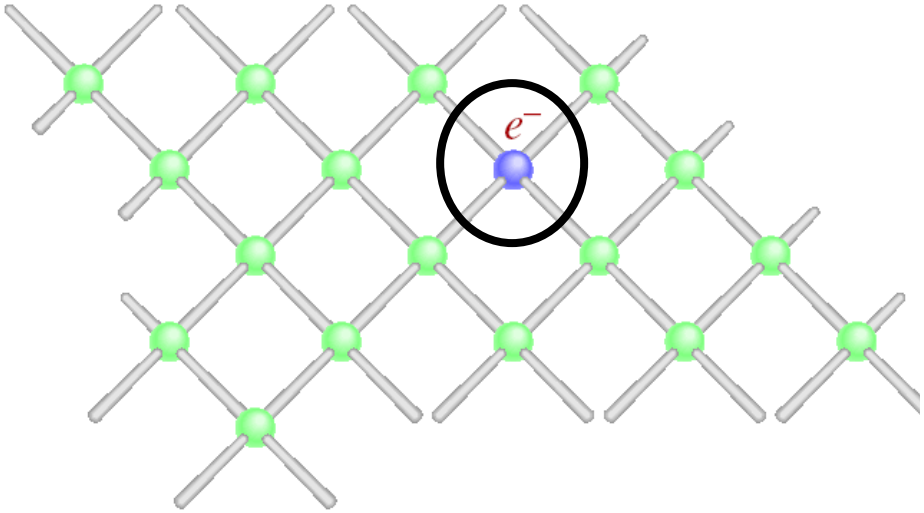
Energy Gaps Between Valence and Conduction Bands in Metals, Semiconductors and Insulators

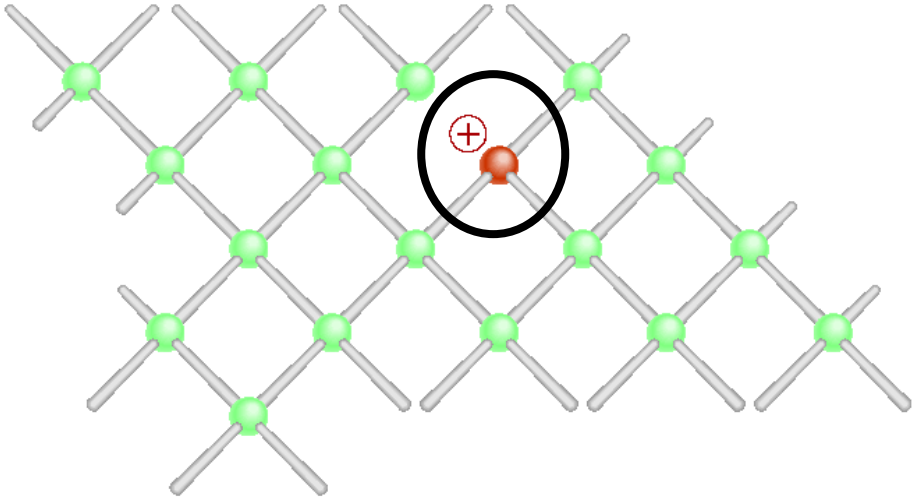


Semiconductors

Si

$[Ne]3s^2 3p^2$





n-type semiconductor

donor impurities

P

$[Ne]3s^2 3p^3$

p-type semiconductor

acceptor impurities

B

$[Ne]3s^2 3p^1$

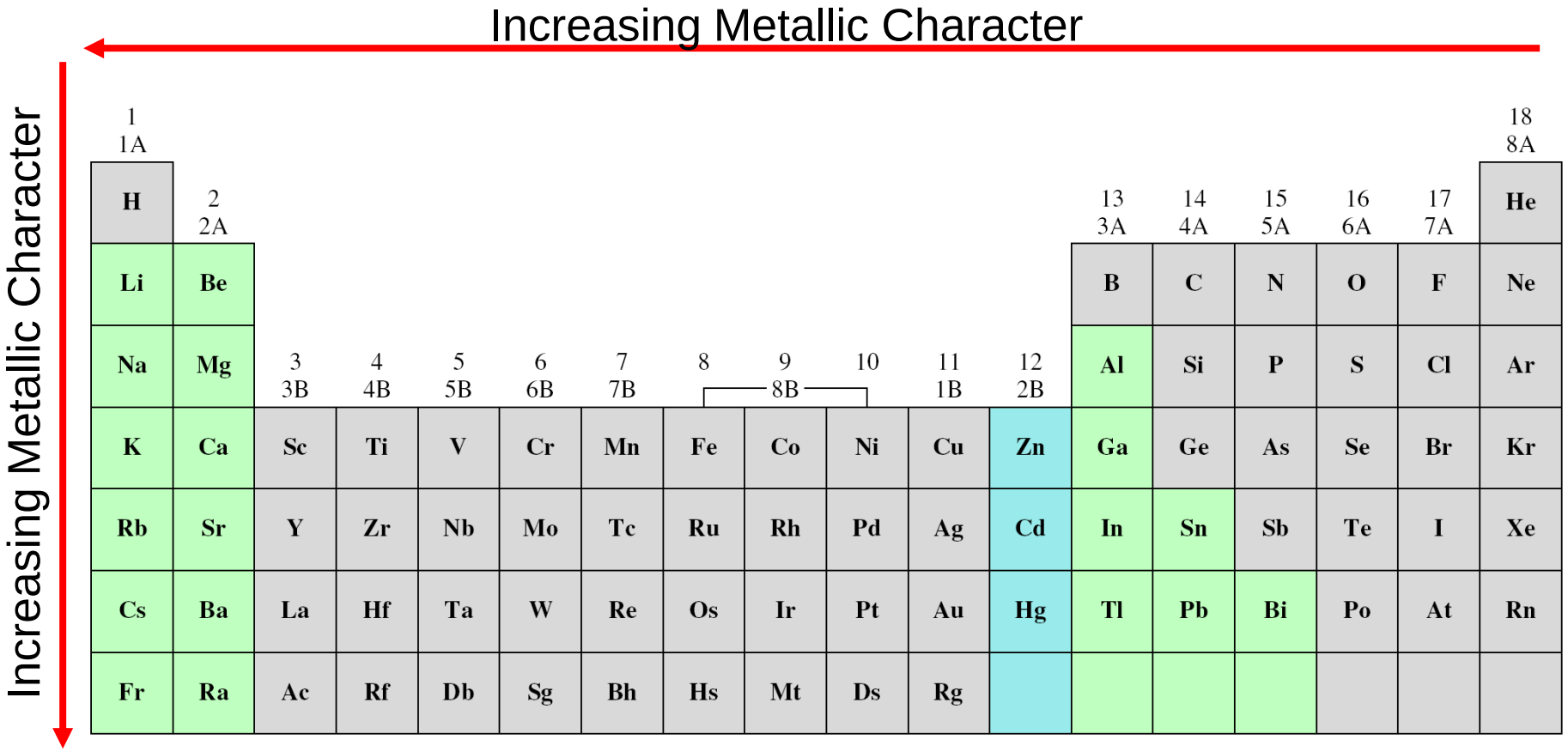

Increasing Metallic Character
Increasing Metallic Character
1 1A
2 2A
3 3B
4 4B
5 5B
6 6B
7 7B
8
9 8B
10
11 1B
12 2B
13 3A
14 4A
15 5A
16 6A
17 7A
18 8A
H
He
Li
Be
B
C
N
O
F
Ne
Na
Mg
Al
Si
P
S
Cl
Ar
K
Ca
Sc
Ti
V
Cr
Mn
Fe
Co
Ni
Cu
Zn
Ga
Ge
As
Se
Br
Kr
Rb
Sr
Y
Zr
Nb
Mo
Tc
Ru
Rh
Pd
Ag
Cd
In
Sn
Sb
Te
I
Xe
Cs
Ba
La
Hf
Ta
W
Re
Os
Ir
Pt
Au
Hg
Tl
Pb
Bi
Po
At
Rn
Fr
Ra
Ac
Rf
Db
Sg
Bh
Hs
Mt
Ds
Rg

TABLE 20.4 Properties of Alkali Metals

	Li	Na	K	Rb	Cs
Valence electron configuration	$2s^1$	$3s^1$	$4s^1$	$5s^1$	$6s^1$
Density (g/cm^3)	0.534	0.97	0.86	1.53	1.87
Melting point (°C)	179	97.6	63	39	28
Boiling point (°C)	1317	892	770	688	678
Atomic radius (pm)	152	186	227	248	265
Ionic radius (pm)*	78	98	133	148	165
Ionization energy (kJ/mol)	520	496	419	403	375
Electronegativity	1.0	0.9	0.8	0.8	0.7
Standard reduction potential (V)†	−3.05	−2.71	−2.93	−2.93	−2.92

*Refers to the cation M^+, where M denotes an alkali metal atom.
†The half-reaction $M^+(aq) + e^- \longrightarrow M(s)$.

Halite: NaCl

Alkali Metals (ns^1, $n \geq 2$)

$$M \longrightarrow M^{+1} + 1e^-$$

$$2M_{(s)} + 2H_2O_{(l)} \longrightarrow 2MOH_{(aq)} + H_{2(g)}$$

$$2M_{(s)} + O_{2(g)} \longrightarrow M_2O_{(s)}$$

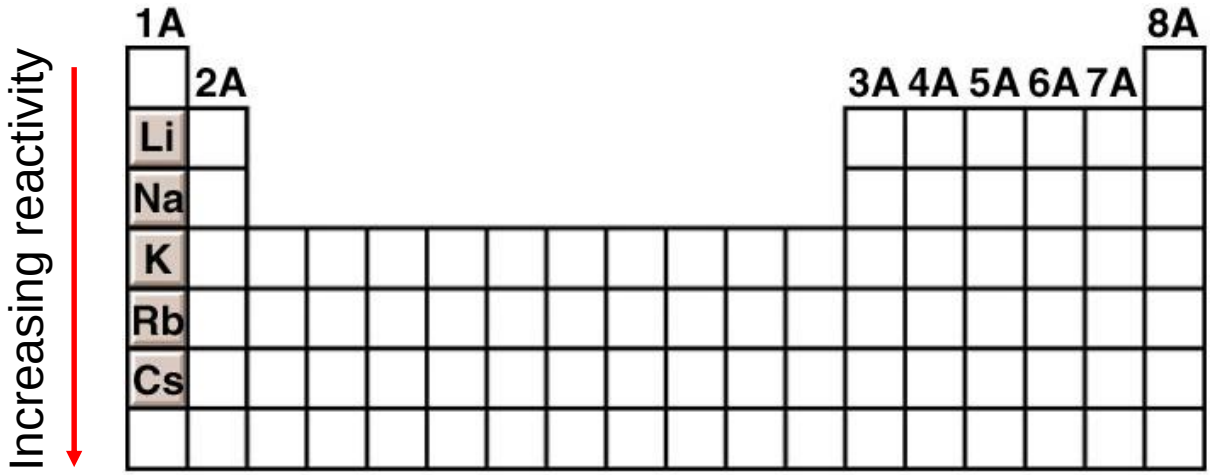


TABLE 20.5 Properties of Alkaline Earth Metals

	Be	Mg	Ca	Sr	Ba
Valence electron configuration	$2s^2$	$3s^2$	$4s^2$	$5s^2$	$6s^2$
Density (g/cm^3)	1.86	1.74	1.55	2.6	3.5
Melting point (°C)	1280	650	838	770	714
Boiling point (°C)	2770	1107	1484	1380	1640
Atomic radius (pm)	112	160	197	215	222
Ionic radius (pm)*	34	78	106	127	143
First and second ionization	899	738	590	548	502
energies (kJ/mol)	1757	1450	1145	1058	958
Electronegativity	1.5	1.2	1.0	1.0	0.9
Standard reduction potential (V)†	−1.85	−2.37	−2.87	−2.89	−2.90

*Refers to the cation M^{2+}, where M denotes an alkali earth metal atom.
†The half-reaction is $M^{2+}(aq) + 2e^- \longrightarrow M(s)$.

Dolomite: $MgCO_3 \cdot CaCO_3$

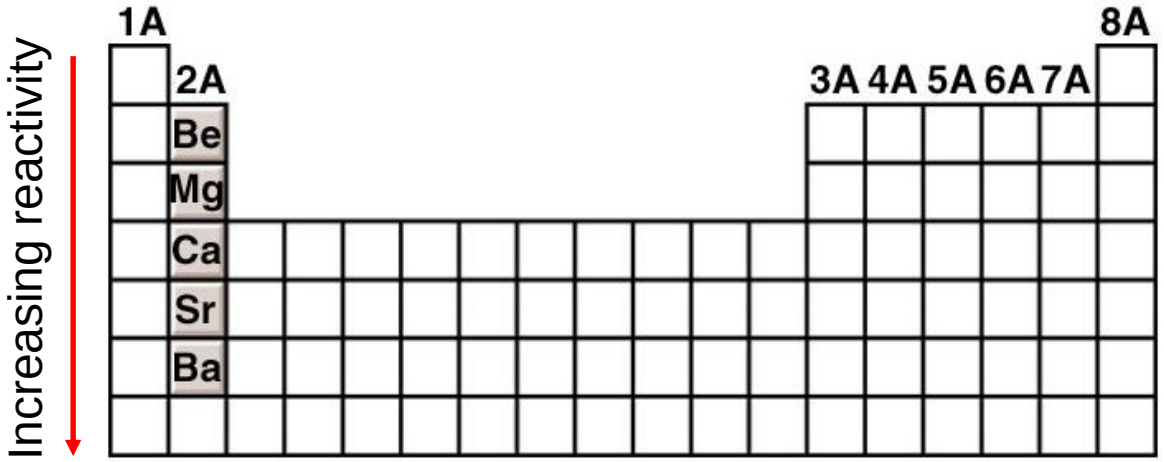
Alkaline Earth Metals (ns^2, $n \geq 2$)

$M \longrightarrow M^{+2} + 2e^-$

$Be_{(s)} + 2H_2O_{(l)} \longrightarrow$ No Reaction

$Mg_{(s)} + H_2O_{(g)} \longrightarrow MgO_{(s)} + H_{2(g)}$

$M_{(s)} + 2H_2O_{(l)} \longrightarrow M(OH)_{2(aq)} + H_{2(g)}$ M = Ca, Sr, or Ba

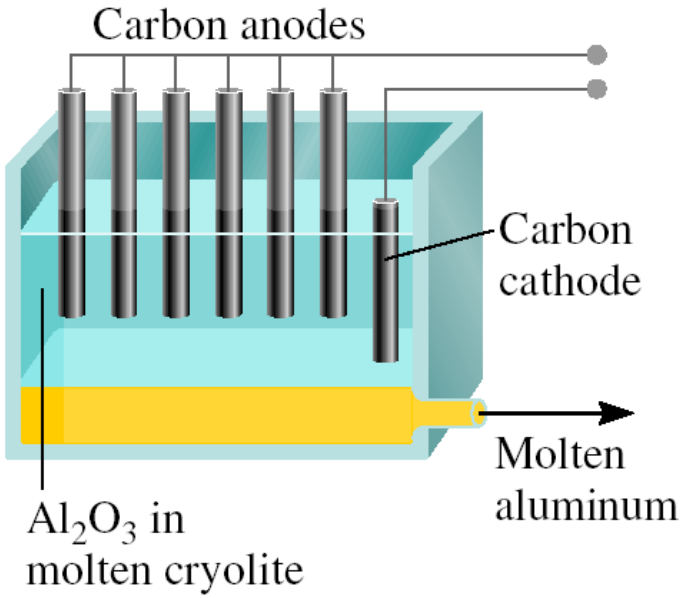


Aluminum

Impure Al_2O_3 (s) + $2OH^-$ (aq) $\longrightarrow$ $2AlO_2^-$ (aq) + H_2O (l)

AlO_2^- (s) + H_3O^+ (aq) $\longrightarrow$ $Al(OH)_3$ (s)

$2Al(OH)_3$ (s) $\xrightarrow{\Delta}$ Al_2O_3 (s) + $3H_2O$ (g)

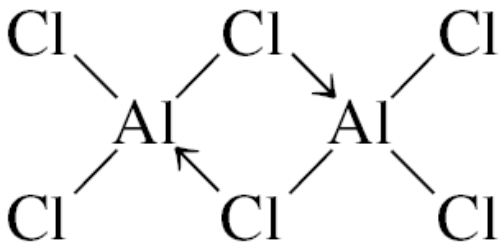


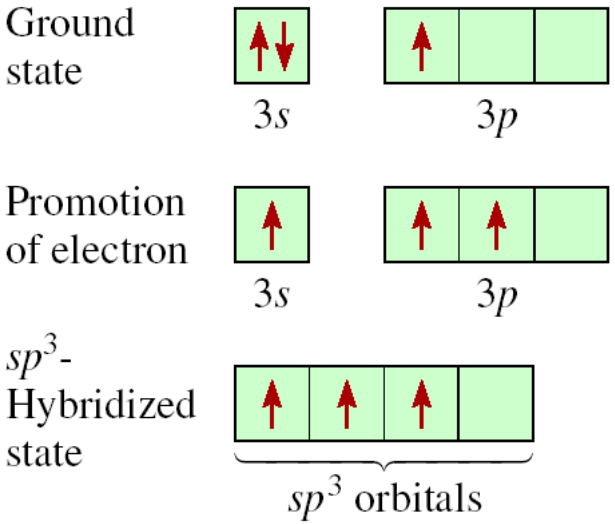
Anode: $3[2O^{2-} \longrightarrow O_2\ (g) + 4e^-]$

Cathode: $4[Al^{3+} + 3e^- \longrightarrow Al\ (l)]$

$2Al_2O_3 \longrightarrow 4Al\ (l) + 3O_2\ (g)$

$AlCl_3$ Dimer



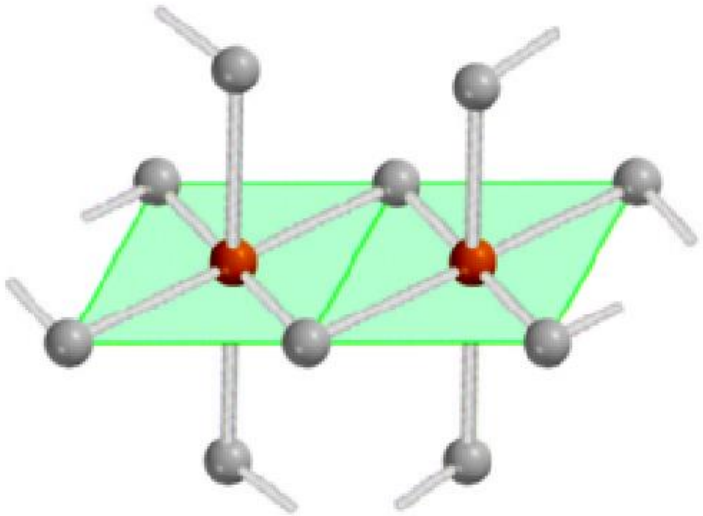


Amphoterism

$$Al(OH)_3(s) + 3H^+(aq) \longrightarrow Al^{3+}(aq) + 3H_2O(l)$$

$$Al(OH)_3(s) + OH^-(aq) \longrightarrow Al(OH)_4^-(aq)$$

Aluminum hydride: a polymer



Double salts

$$M^{+}M^{3+}(SO_4)_2 \cdot 12H_2O$$

M^{+}: K^{+}, Na^{+}, NH_4^{+}
M^{3+}: Al^{3+}, Cr^{3+}, Fe^{3+}

$$KAl(SO_4)_2 \cdot 12H_2O$$

Chemistry In Action: Recycling Aluminum

Collecting

Purifying