Chapter 14

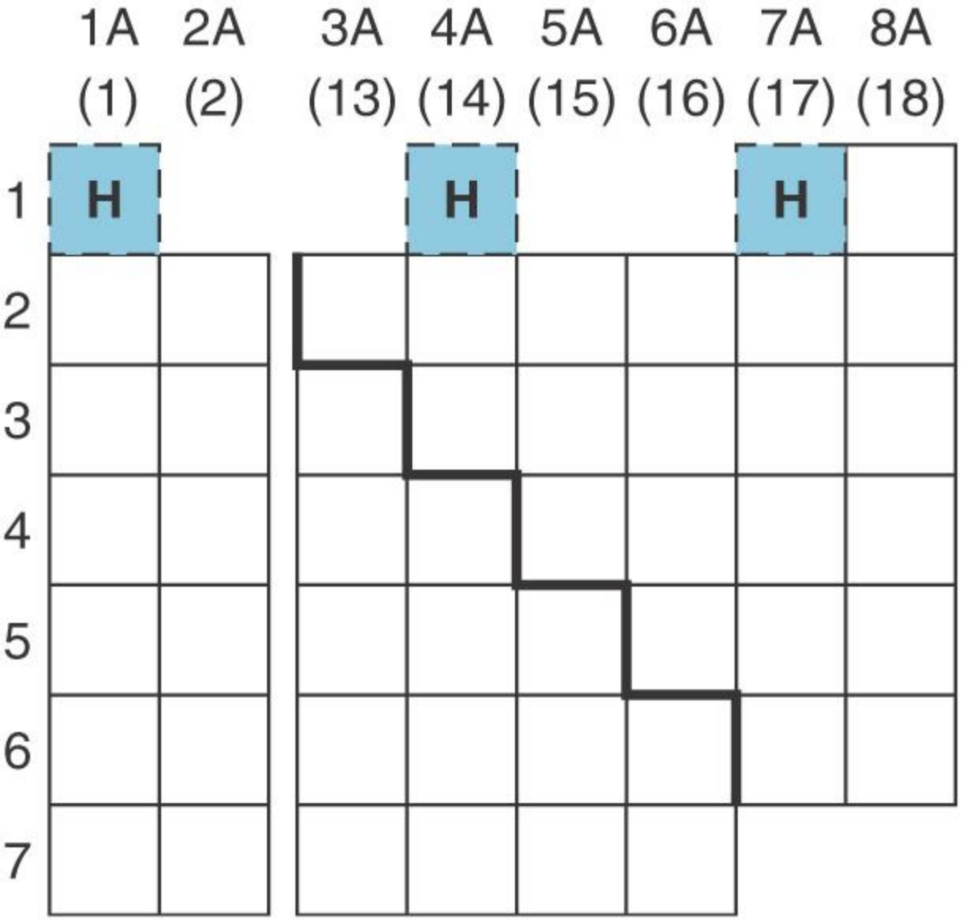
Periodic Patterns in the Main-Group Elements

Periodic Patterns in the Main-Group Elements

Hydrogen

- Hydrogen has a very simple structure:
  - the nucleus has a single positive charge, and has 1 electron.
- Hydrogen is the most abundant element in the universe.
- Hydrogen exists as a diatomic gas, H_2.
  - H_2 is colorless and odorless with very low melting and boiling points.
- H is abundant in combination with oxygen as H_2O.

Figure 14.1 Where does hydrogen belong?



Hydrogen and the Alkali Metals

- Like the Group 1A(1) elements, hydrogen
  - has an outer electron configuration of ns^1,
  - has a single valence electron, and
  - has a common +1 oxidation state.
- Unlike the alkali metals, hydrogen
  - ***shares*** electrons with nonmetals rather than transferring e^- to them.
  - has a much higher ionization energy than any alkali metal, due to its small size.

Hydrogen and Group 4A

- Like the Group 4A(1) elements, H has a half-filled valence level.
- H is similar to the other Group 4A elements in terms of
  - ionization energy,
  - electron affinity,
  - electronegativity, and
  - bond energies.

Hydrogen and the Halogens

- Like the halogens or Group 7A(17), hydrogen
  - exists as a diatomic molecule and
  - needs only 1 electron to fill its valence shell.
- Unlike the halogens
  - H has a much lower electronegativity than any halogen,
  - H lacks the three valence e^- pairs that halogens have, and
  - halide ions (X^-) are common and stable, but the hydride ion (H^-) is rare and reactive.

Highlights of Hydrogen Chemistry

Ionic (saltlike) hydrides form when hydrogen reacts with very reactive metals.

These hydrides are white, crystalline solids.

$$2Li(s) + H_2(g) \rightarrow 2LiH(s)$$

$$Ca(s) + H_2(g) \rightarrow CaH_2(s)$$

Covalent (molecular) hydrides form when hydrogen reacts with nonmetals. In most covalent hydrides, hydrogen has an oxidation number of +1.

$$F_2(g) + H_2(g) \rightarrow 2HF(g) \quad \Delta H^\circ_{rxn} = -546 \text{ kJ}$$

Highlights of Hydrogen Chemistry

Many transition metals form ***metallic (interstitial) hydrides***, in which H_2 molecules and H atoms occupy the holes in the crystal structure of the metal.

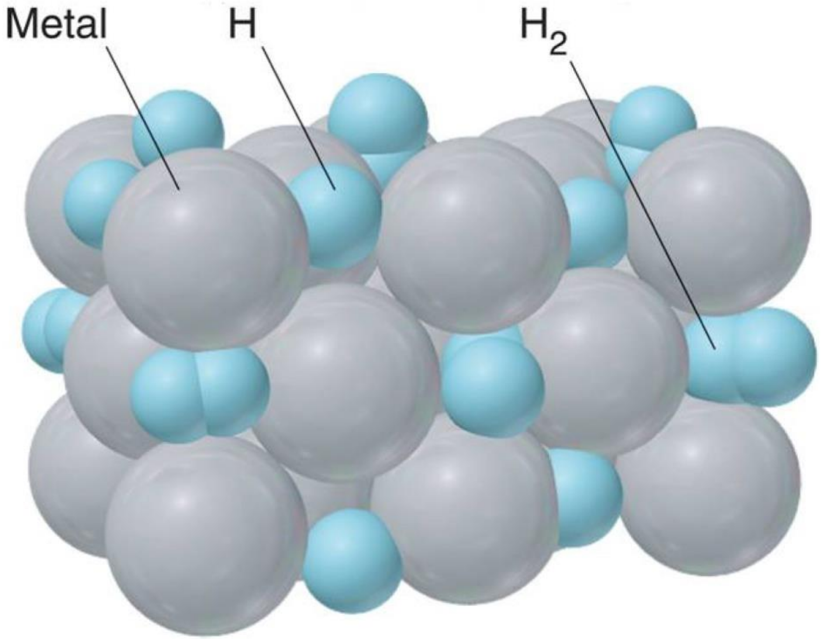


Figure 14.2 **A metallic (interstitial) hydride.**

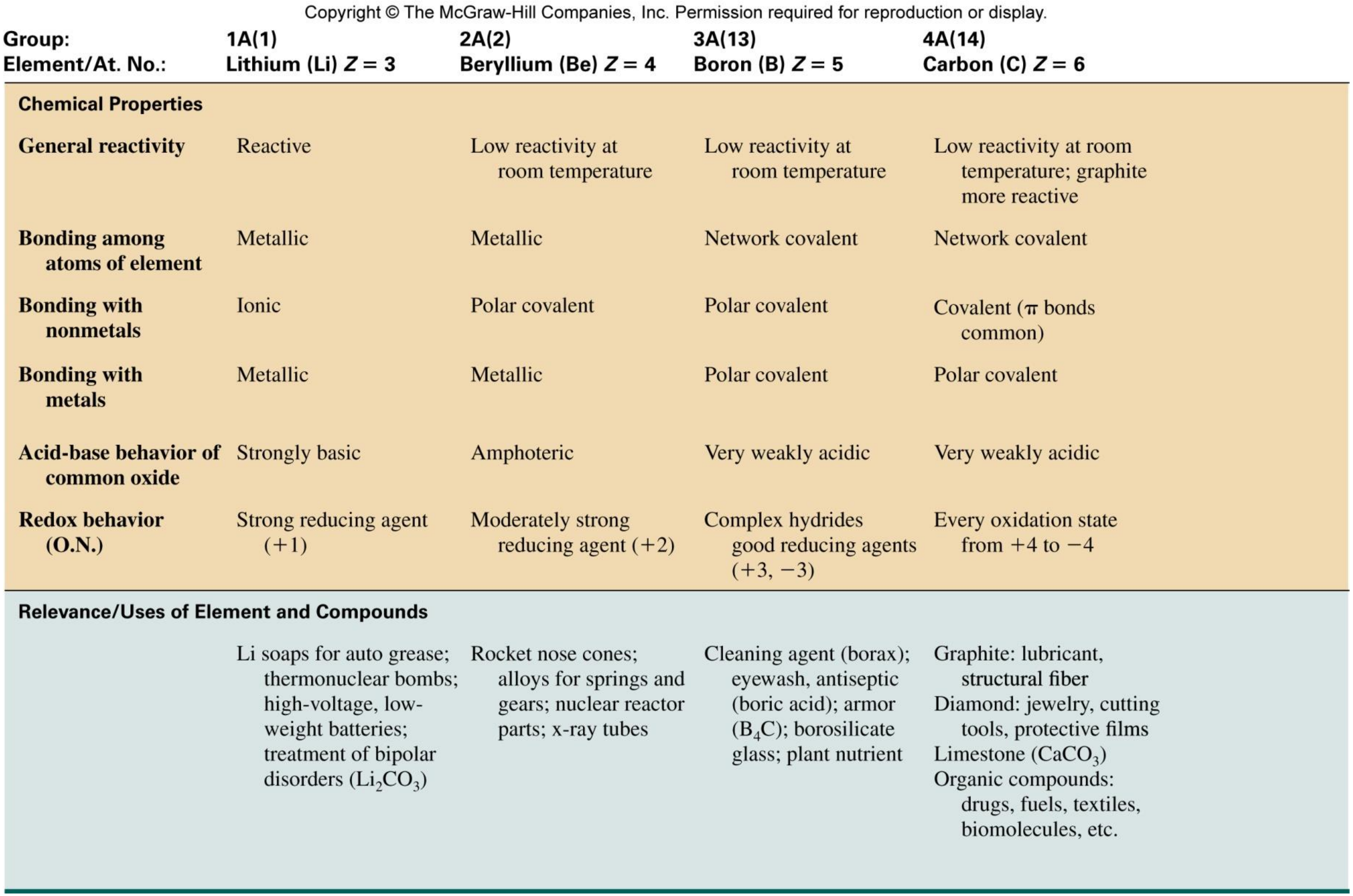
Trends for the Period 2 Elements

- Atomic size generally decreases across the period.
- Ionization energy and electronegativity decrease across the period.
- Metallic character decreases across the period.
    - The type of bonding exhibited changes with metallic character.
- Oxides of the elements become more acidic across the period.
- Reducing strength decreases through the metals, and oxidizing strength increases through the nonmetals.

Table 14.1 Trends in Atomic, Physical, and Chemical Properties of the Period 2 Elements.

Group: **Element/At. No.:**	**1A(1)** **Lithium (Li) $Z = 3$**	**2A(2)** **Beryllium (Be) $Z = 4$**	**3A(13)** **Boron (B) $Z = 5$**	**4A(14)** **Carbon (C) $Z = 6$**
Atomic Properties				
Condensed electron configuration; partial orbital diagram	[He] $2s^1$ [↑] [ ][ ][ ] 2s 2p	[He] $2s^2$ [↑↓] [ ][ ][ ] 2s 2p	[He] $2s^22p^1$ [↑↓] [↑][ ][ ] 2s 2p	[He] $2s^22p^2$ [↑↓] [↑][↑][ ] 2s 2p
Physical Properties				
Appearance				
Metallic character	Metal	Metal	Metalloid	Nonmetal
Hardness	Soft	Hard	Very hard	Graphite: soft Diamond: extremely hard
Melting point/ boiling point	Low mp for a metal	High mp	Extremely high mp	Extremely high mp

Table 14.1 Trends in Atomic, Physical, and Chemical Properties of the Period 2 Elements.



Group: **Element/At. No.:**	**1A(1)** **Lithium (Li) *Z* = 3**	**2A(2)** **Beryllium (Be) *Z* = 4**	**3A(13)** **Boron (B) *Z* = 5**	**4A(14)** **Carbon (C) *Z* = 6**
Chemical Properties				
General reactivity	Reactive	Low reactivity at room temperature	Low reactivity at room temperature	Low reactivity at room temperature; graphite more reactive
Bonding among atoms of element	Metallic	Metallic	Network covalent	Network covalent
Bonding with nonmetals	Ionic	Polar covalent	Polar covalent	Covalent (π bonds common)
Bonding with metals	Metallic	Metallic	Polar covalent	Polar covalent
Acid-base behavior of common oxide	Strongly basic	Amphoteric	Very weakly acidic	Very weakly acidic
Redox behavior (O.N.)	Strong reducing agent (+1)	Moderately strong reducing agent (+2)	Complex hydrides good reducing agents (+3, −3)	Every oxidation state from +4 to −4
Relevance/Uses of Element and Compounds				
	Li soaps for auto grease; thermonuclear bombs; high-voltage, low-weight batteries; treatment of bipolar disorders (Li_2CO_3)	Rocket nose cones; alloys for springs and gears; nuclear reactor parts; x-ray tubes	Cleaning agent (borax); eyewash, antiseptic (boric acid); armor (B_4C); borosilicate glass; plant nutrient	Graphite: lubricant, structural fiber Diamond: jewelry, cutting tools, protective films Limestone ($CaCO_3$) Organic compounds: drugs, fuels, textiles, biomolecules, etc.

Table 14.1 Trends in Atomic, Physical, and Chemical Properties of the Period 2 Elements.

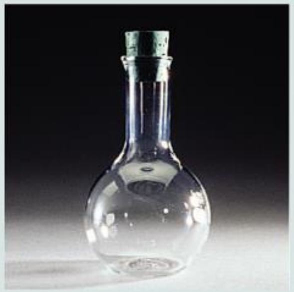
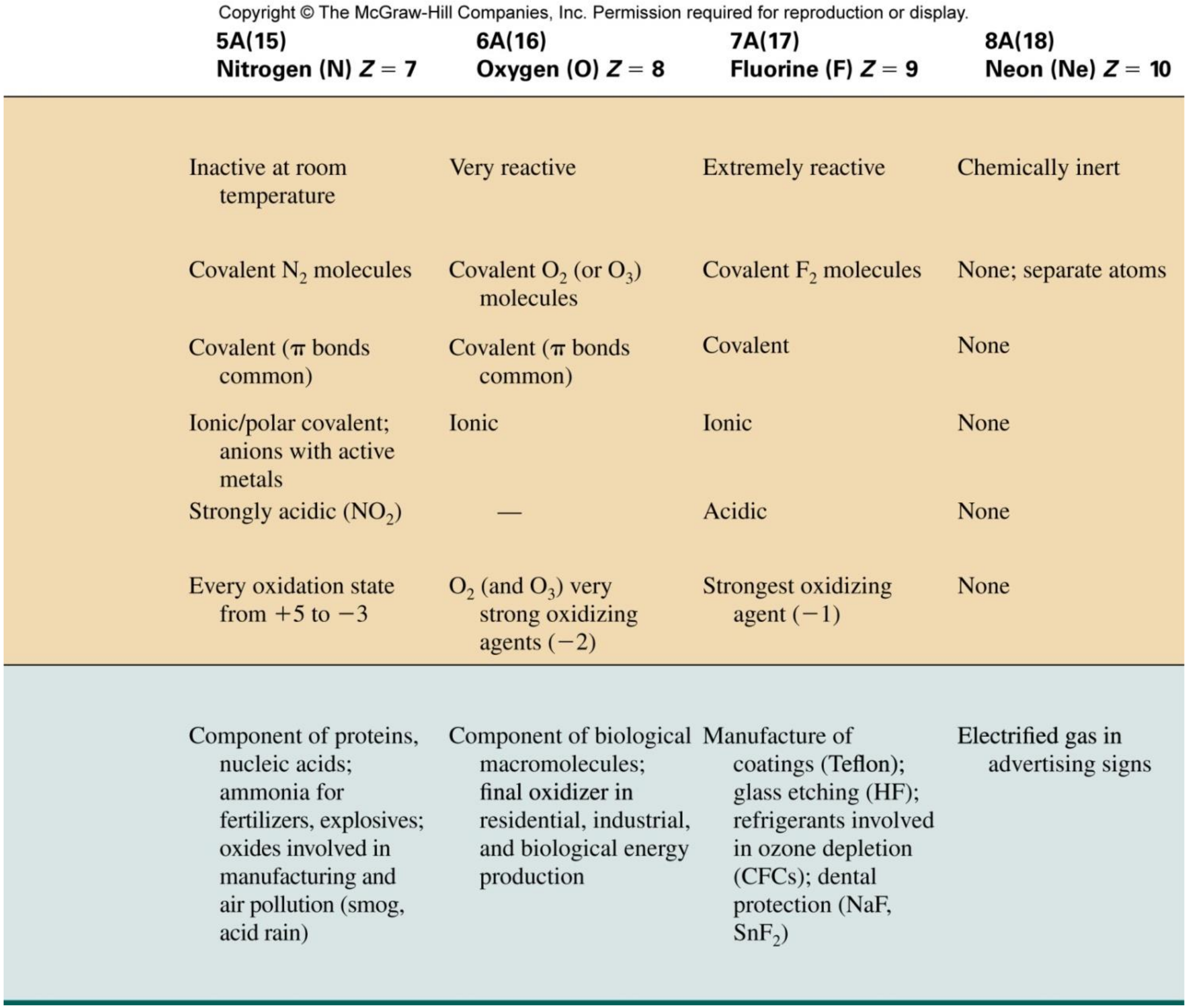
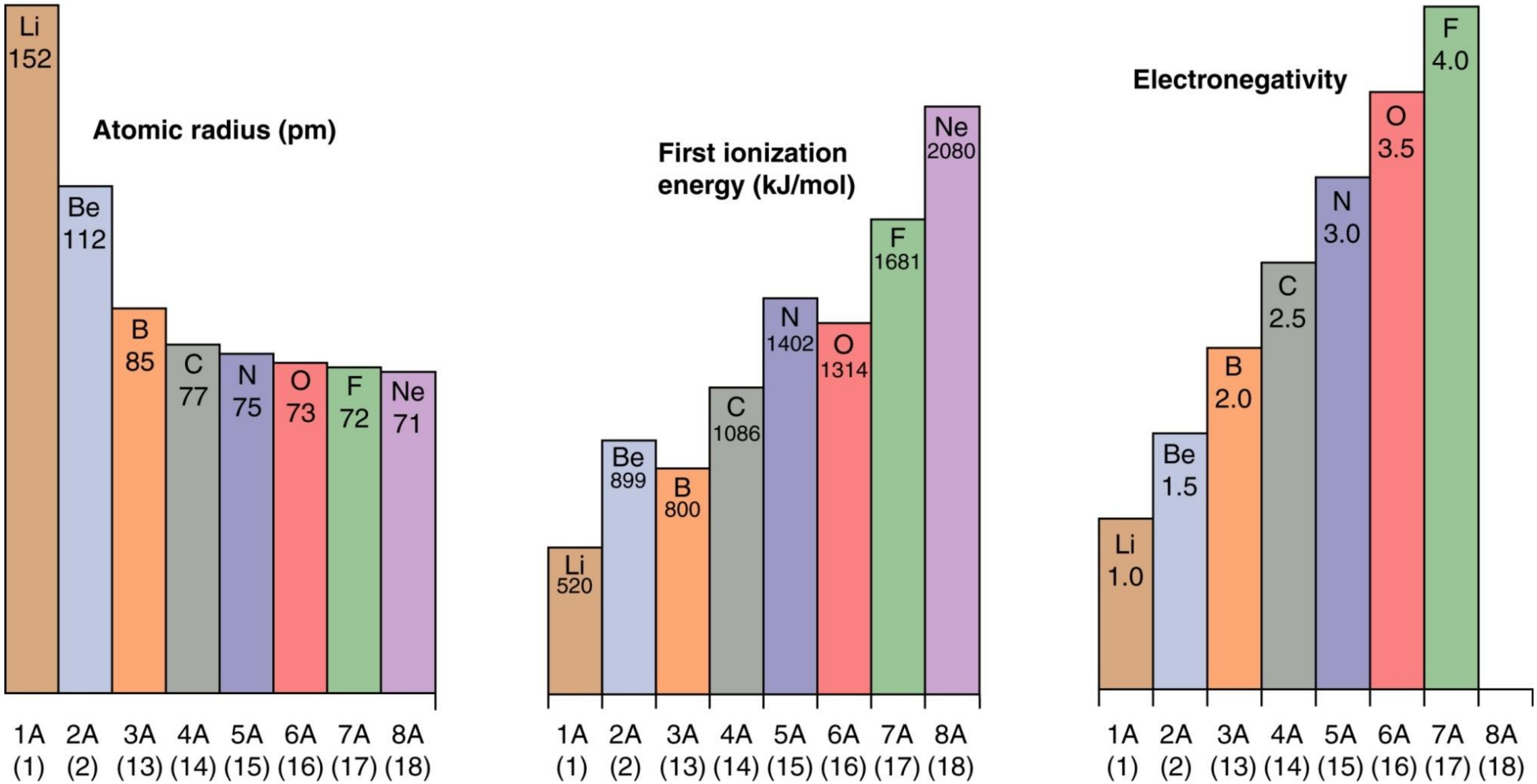
5A(15) **Nitrogen (N) $Z = 7$**	6A(16) **Oxygen (O) $Z = 8$**	7A(17) **Fluorine (F) $Z = 9$**	8A(18) **Neon (Ne) $Z = 10$**
[He] $2s^2 2p^3$ ↑↓ ↑ ↑ ↑ $2s$ $2p$	[He] $2s^2 2p^4$ ↑↓ ↑↓ ↑ ↑ $2s$ $2p$	[He] $2s^2 2p^5$ ↑↓ ↑↓ ↑↓ ↑ $2s$ $2p$	[He] $2s^2 2p^6$ ↑↓ ↑↓ ↑↓ ↑↓ $2s$ $2p$
		**No sample available**	
Nonmetal	Nonmetal	Nonmetal	Nonmetal
—	—	—	—
Very low mp and bp	Very low mp and bp	Very low mp and bp	Extremely low mp and bp

Table 14.1 Trends in Atomic, Physical, and Chemical Properties of the Period 2 Elements.



5A(15) **Nitrogen (N) *Z* = 7**	**6A(16)** **Oxygen (O) *Z* = 8**	**7A(17)** **Fluorine (F) *Z* = 9**	**8A(18)** **Neon (Ne) *Z* = 10**
Inactive at room temperature	Very reactive	Extremely reactive	Chemically inert
Covalent N_2 molecules	Covalent O_2 (or O_3) molecules	Covalent F_2 molecules	None; separate atoms
Covalent (π bonds common)	Covalent (π bonds common)	Covalent	None
Ionic/polar covalent; anions with active metals	Ionic	Ionic	None
Strongly acidic (NO_2)	—	Acidic	None
Every oxidation state from +5 to −3	O_2 (and O_3) very strong oxidizing agents (−2)	Strongest oxidizing agent (−1)	None
Component of proteins, nucleic acids; ammonia for fertilizers, explosives; oxides involved in manufacturing and air pollution (smog, acid rain)	Component of biological macromolecules; final oxidizer in residential, industrial, and biological energy production	Manufacture of coatings (Teflon); glass etching (HF); refrigerants involved in ozone depletion (CFCs); dental protection (NaF, SnF_2)	Electrified gas in advertising signs

Table 14.1 Trends in Atomic, Physical, and Chemical Properties of the Period 2 Elements.



Trends in atomic radius, ionization energy, and electronegativity across Period 2.

Anomalous Behavior in Period 2

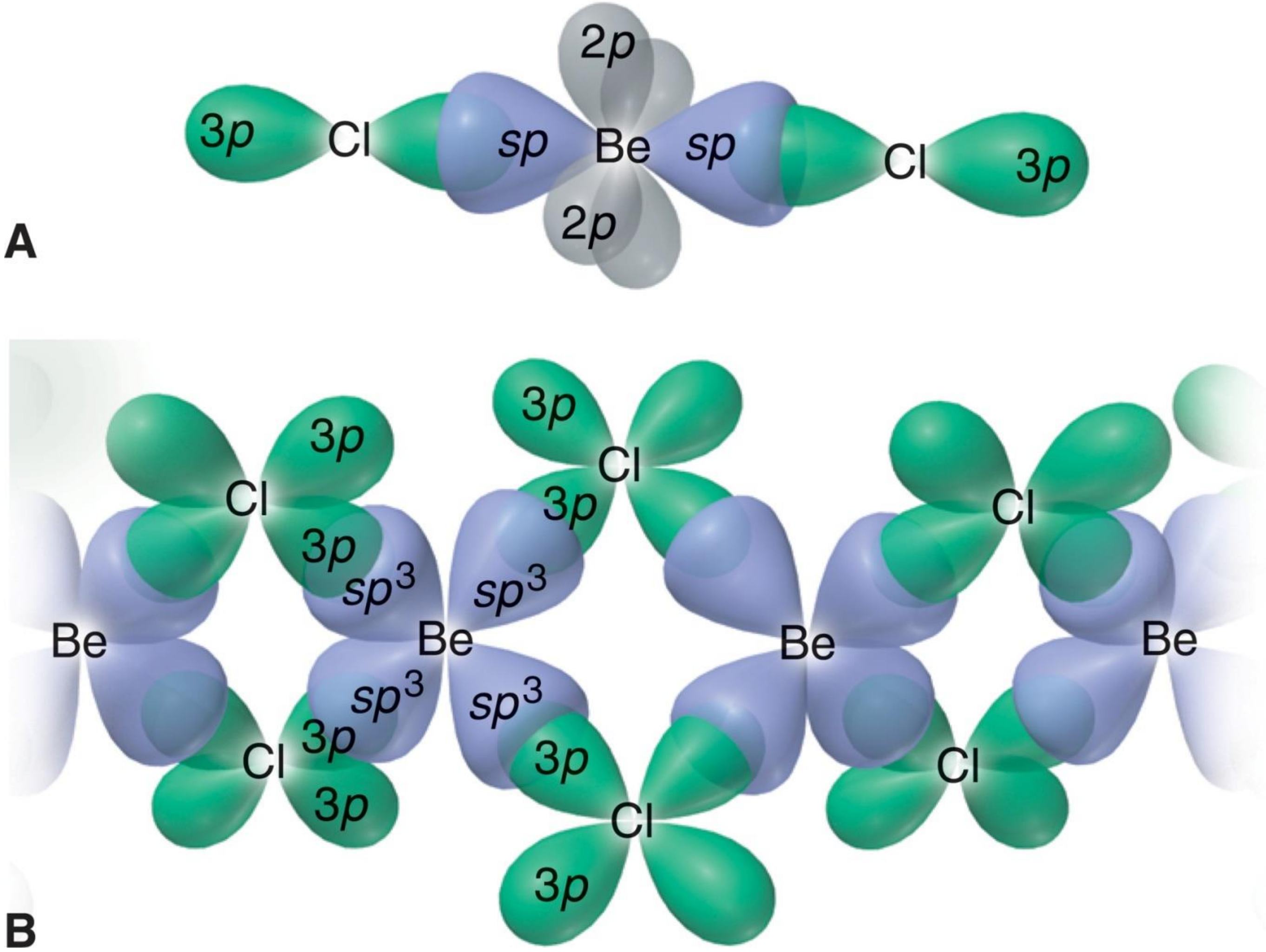
Anomalous behavior in some Period 2 elements is due to their relatively small size and small number of valence orbitals.

Lithium is the only element in Period 2 that forms a simple oxide and nitride.

All ***beryllium*** compounds exhibit ***covalent*** bonding. This is due to the high charge density of Be^{2+}.

Boron forms a complex family of compounds with metals, and covalent compounds with hydrogen called ***boranes***.

Figure 14.3 Overcoming electron deficiency in beryllium chloride.



Anomalous Behavior in Period 2

Carbon bonds to itself extensively and gives rise to organic compounds.

Nitrogen is a triple-bonded, unreactive gas and is very different from the other Group 5A elements, which are reactive solids.

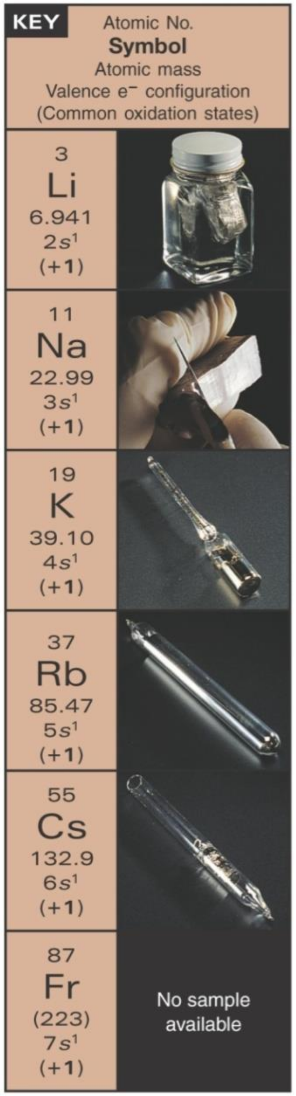
Oxygen is the only gas in Group 6A and is much more reactive than the other members of its group.

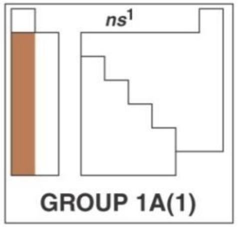
Fluorine is much more electronegative than the other halogens. It reacts violently with water, and HF is a ***weak*** acid where other hydrohalic acids are strong.

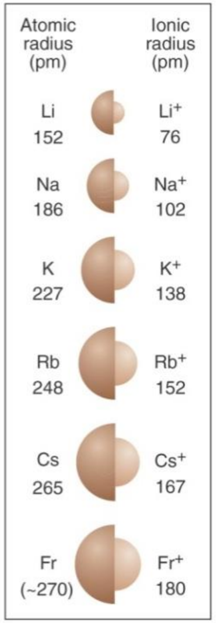
Group 1A(1): The Alkali Metals

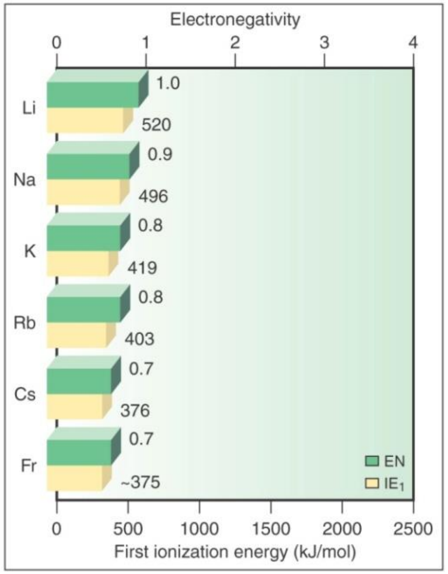
Family Portrait

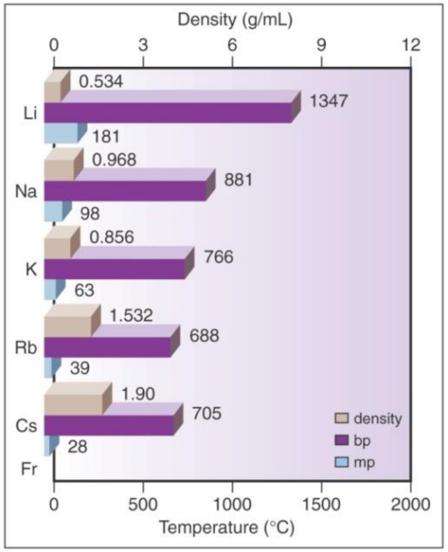
KEY ATOMIC PROPERTIES, PHYSICAL PROPERTIES, AND REACTIONS











GROUP 1A(1): REACTIONS

- Alkali metals are ***powerful reducing agents***.
  - They always occur in nature as +1 cations rather than as free metals.
- Alkali metals reduce halogens to form ionic solids:
  - $2E(s) + X_2 \rightarrow 3EX(s)$ (X = F, Cl, Br, I and E is the alkali metal).
- Alkali metals react vigorously with H_2O:
  - $2E(s) + H_2O(l) \rightarrow 2E^+(aq) + 2OH^-(aq) + H_2(g)$
- Alkali metals reduce H_2 to form ionic hydrides.
  - $2E(s) + H_2(g) \rightarrow 2EH(s)$
- Alkali metals reduce O_2 in air, and tarnish rapidly.

Properties of the Alkali Metals

- Alkali metals are the largest elements in their respective periods and their valence electron configuration is ns^1.
  - The valence e^- is relatively far from the nucleus, resulting in weak metallic bonding.
- Alkali metals are unusually soft for metals. They can be cut easily with a knife.
- Alkali metals have lower melting and boiling points than any other group of metals.
- Alkali metals have lower densities than most metals.

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Lithium floating in oil floating on water. Alkali metals have low densities.

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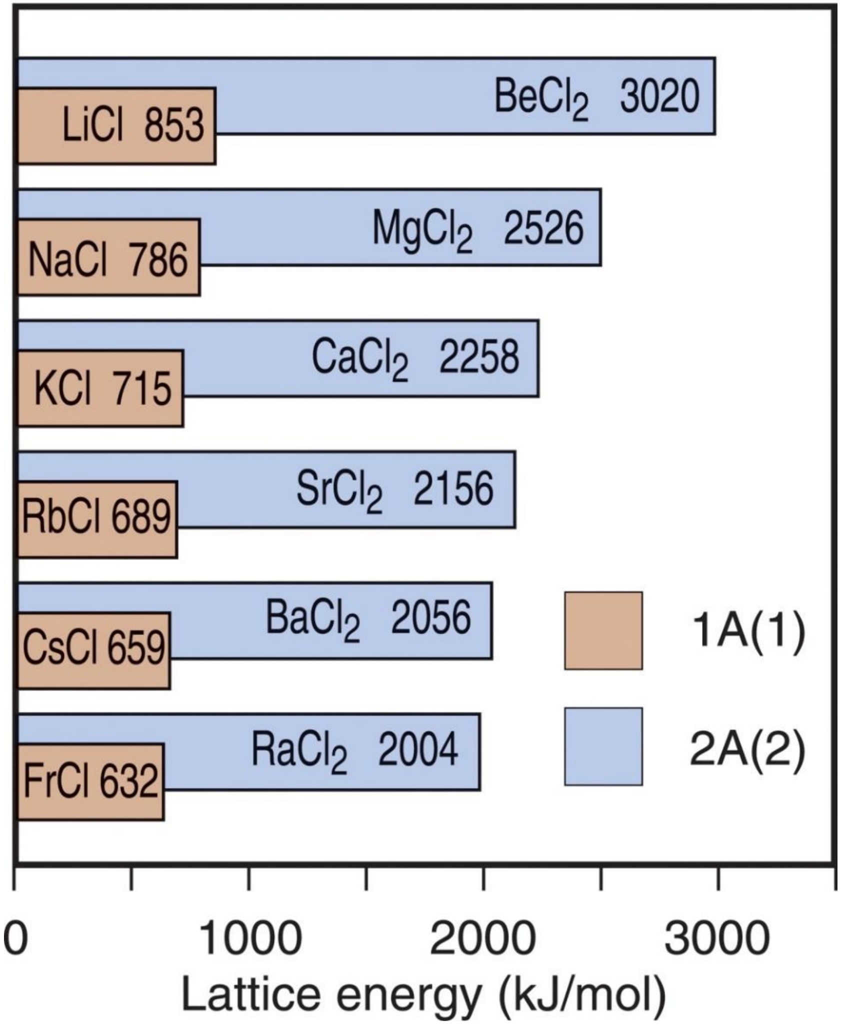
Potassium reacting with water. Alkali metals are very reactive.

Figure 14.4 Lattice energies of the Group 1A(1) and 2A(2) chlorides.

Lattice energy increases as the size of the cation decreases and its charge increases.



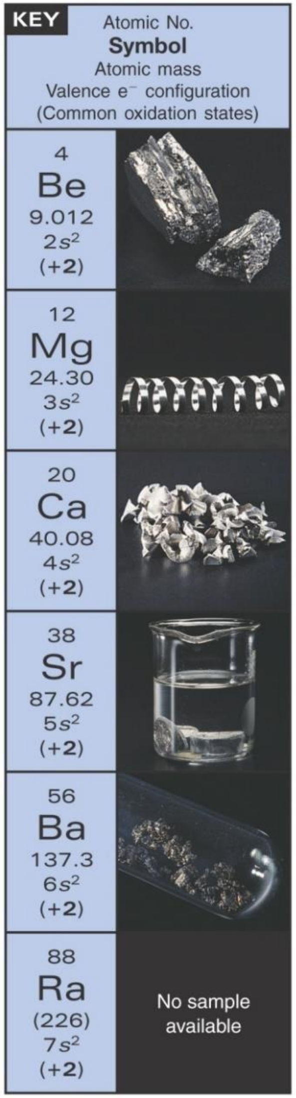
Group 2A(2): The Alkaline Earth Metals

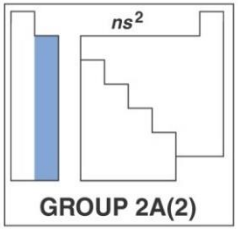
- The oxides of Group 2A(2) elements form basic solutions and melt at extremely high temperatures.
- Group 2A(2) elements have higher ionization energies than Group 1A(1) elements
  - due to their higher effective nuclear charge and smaller size.
- Group 2A(2) elements are strong reducing agents.

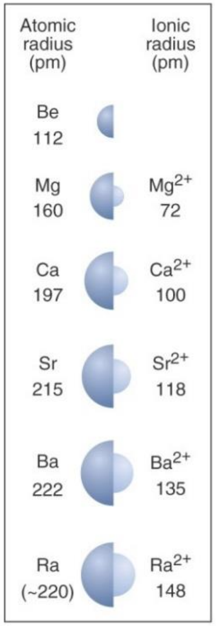
Group 2A(2): The Alkaline Earth Metals

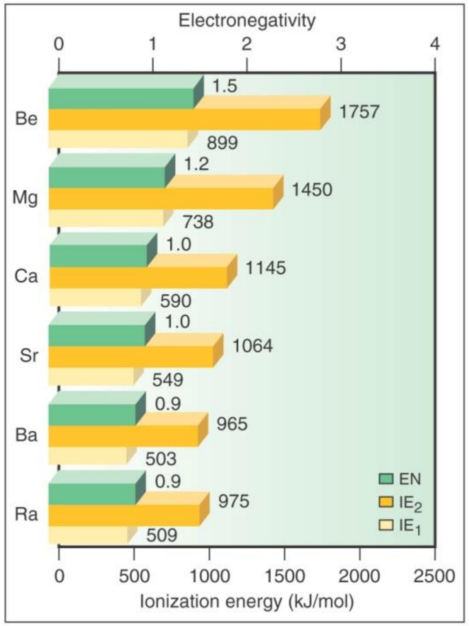
Family Portrait

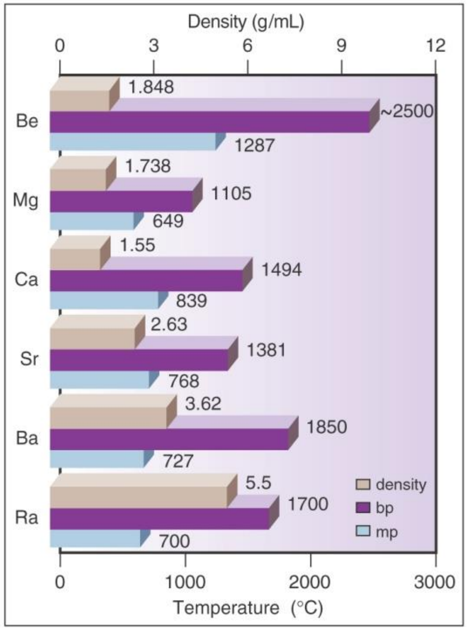
KEY ATOMIC PROPERTIES, PHYSICAL PROPERTIES, AND REACTIONS











GROUP 2A(2) REACTIONS

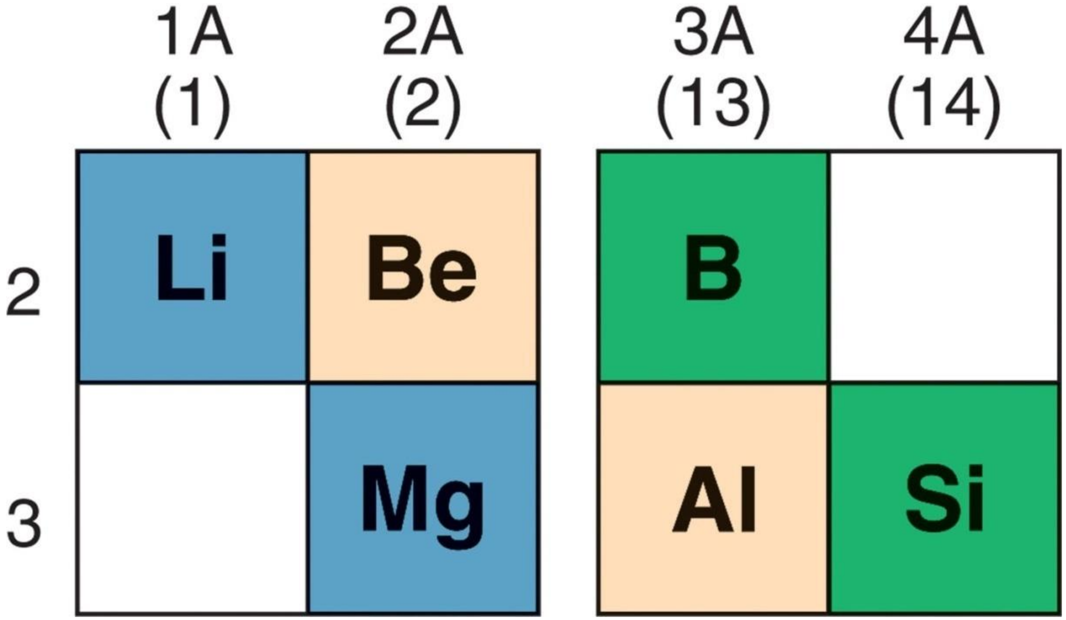
- The metals reduce O_2 to form oxides:
  - $3E(s) + O_2(g) \rightarrow 3EO(s)$
- The larger metals reduce water to form H_2 gas:
  - $2E(s) + H_2O(l) \rightarrow 2E^{2+}(aq) + 2OH^{-}(aq) + H_2(g)$ (E = Ca, Sr, Ba)
- The metals reduce halogens to form ionic halides:
  - $E(s) + X_2 \rightarrow EX_2(s)$ [X = F (not with Be), Cl, Br, I]
- Most of the elements reduce H_2 to form ionic hydrides:
  - $E(s) + H_2(g) \rightarrow EH_2(s)$ (E = all except Be)

GROUP 2A(2) REACTIONS

- The elements reduce nitrogen to form ionic nitrides:
  - $3E(s) + N_2(g) \rightarrow E_3N_2(s)$
- Except for BeO, the element oxides are basic:
  - $EO(s) + H_2O(l) \rightarrow E^{2+}(aq) + 2OH^-(aq)$
- All carbonates undergo thermal decomposition:

$$ECO_3(s) \xrightarrow{\Delta} EO(s) + CO_2(g)$$

Figure 14.5 Three diagonal relationships in the periodic table.

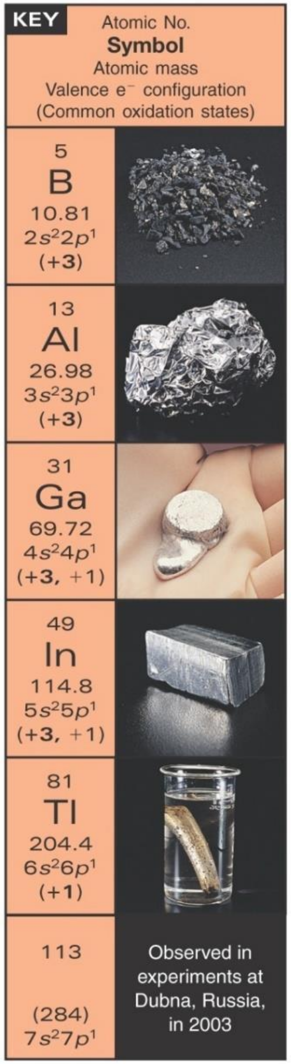


	1A (1)	2A (2)	3A (13)	4A (14)
2	**Li**	**Be**	**B**	
3		**Mg**	**Al**	**Si**

Group 3A(13): The Boron Family

Family Portrait

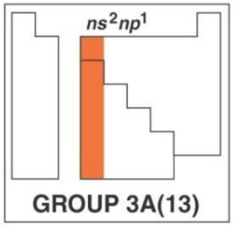
KEY ATOMIC PROPERTIES, PHYSICAL PROPERTIES, AND REACTIONS

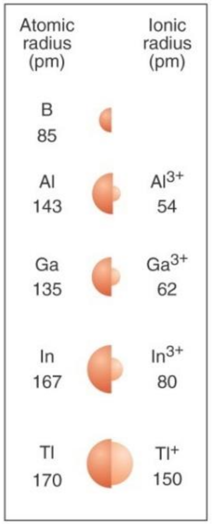


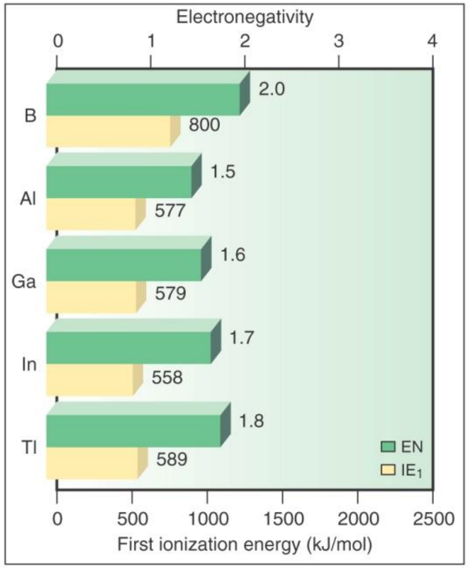
KEY: Atomic No. / **Symbol** / Atomic mass / Valence e^- configuration / (Common oxidation states)

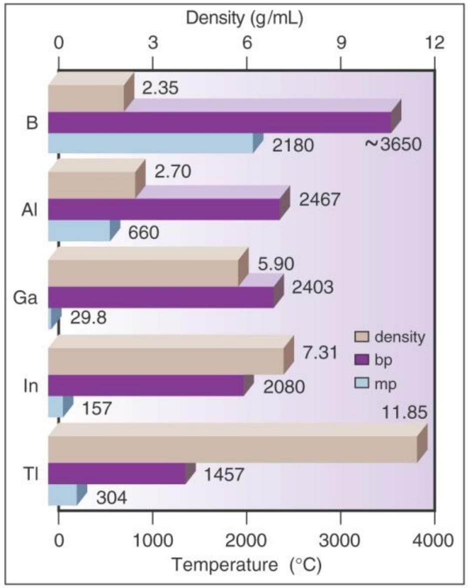
Atomic No.	Symbol	Atomic mass	Valence e^- configuration	Common oxidation states
5	B	10.81	$2s^22p^1$	(+3)
13	Al	26.98	$3s^23p^1$	(+3)
31	Ga	69.72	$4s^24p^1$	(+3, +1)
49	In	114.8	$5s^25p^1$	(+3, +1)
81	Tl	204.4	$6s^26p^1$	(+1)
113		(284)	$7s^27p^1$	

Observed in experiments at Dubna, Russia, in 2003









GROUP 3A(13) REACTIONS

- The elements react sluggishly, if at all, with water:
  - $2Ga(\textit{s}) + 6H_2O(\textit{hot}) \rightarrow 2Ga^{2+}(\textit{aq}) + 6OH^-(\textit{aq}) + 3H_2(\textit{g})$
  - $2Tl(\textit{s}) + 2H_2O(\textit{steam}) \rightarrow 2Ga^+(\textit{aq}) + 2OH^-(\textit{aq}) + H_2(\textit{g})$
- When strongly heated in pure O_2, all members form oxides:

$$4E(\textit{s}) + 3O_2(\textit{g}) \xrightarrow{\Delta} 2E_2O_3(\textit{s}) \quad (E = B, Al, Ga, In)$$

  - Tl forms Tl_2O
- All members reduce halogens (X_2)
  - $2E(\textit{s}) + 3X_2 \rightarrow 2EX_3$ (E = B, Al, Ga, In)
  - $2Tl(\textit{s}) + X_2 \rightarrow 2TlX(\textit{s})$

Influence of Transition Elements on Group 3A(13)

Z_{eff} ***increases*** for the larger 3A elements due to poor shielding by *d* and *f* electrons.

The larger 3A elements have ***smaller*** atomic radii and ***larger*** ionization energies than electronegativities than expected.

These properties influence the physical and chemical behavior of these elements.

Features of Group 3A(13) Elements

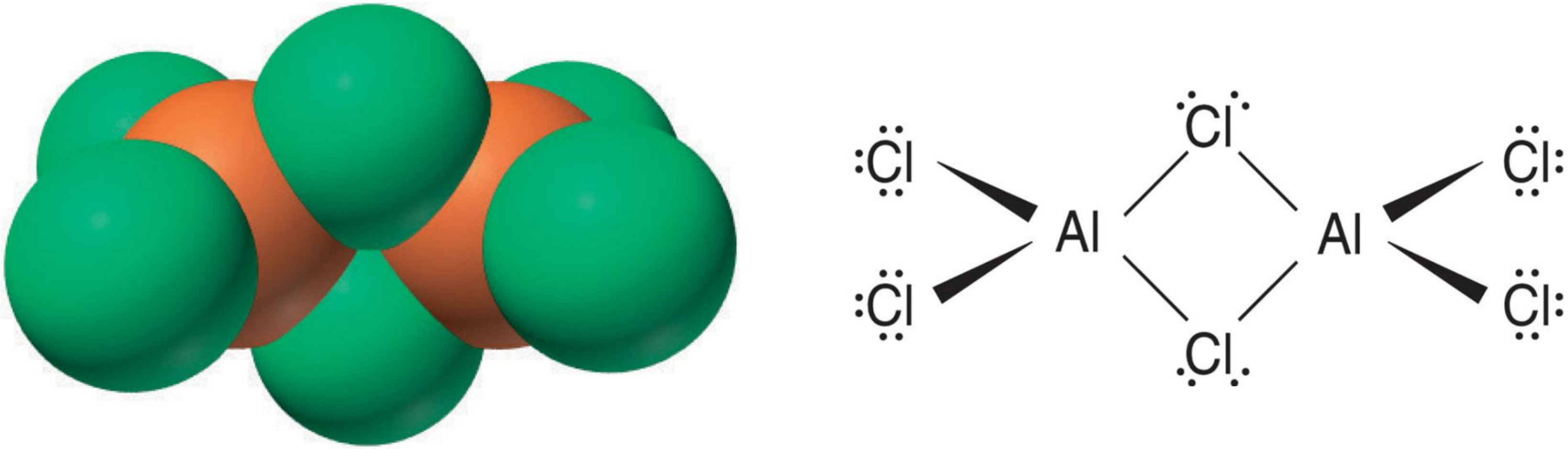
Larger Group 3A elements exhibit ***multiple oxidation states***. They may lose either the *np* electron only, or both the *np* and *ns* electrons.

The ***lower*** oxidation state becomes increasingly prominent down the group, since the ns^2 electrons form an ***inert pair.***

Oxides of the element in the ***lower*** oxidation state are ***more basic*** than oxides in the higher oxidation state.

In_2O is more basic than In_2O_3.

Figure 14.6 The dimeric structure of gaseous aluminum chloride.



Compounds of 3A elements have more covalent character than similar 2A compounds.

Aluminum has the physical properties of a metal, but its halides exist as covalent ***dimers***.

Highlights of Boron Chemistry

All boron compounds are ***covalent***, and B forms a variety of network covalent compounds with other elements.

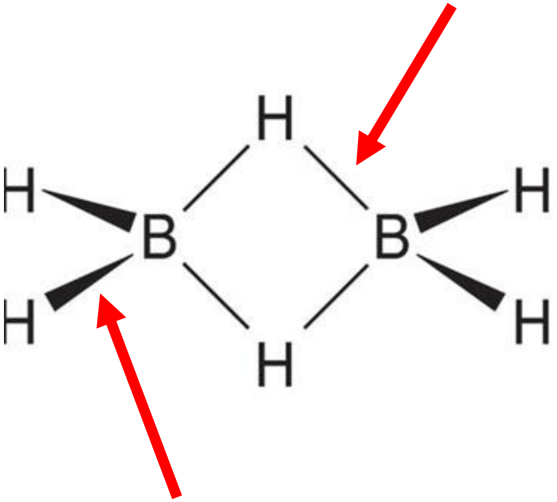
Boron is often electron-deficient in compounds, and acts effectively as a ***Lewis acid*** since it can accept an e$^-$ pair.

$$BF_3(g) + :NH_3(g) \rightarrow F_3B\text{–}NH_3(g)$$

Boron forms ***bridge bonds***, in which ***one pair*** of electrons is shared between ***three*** atoms. This type of bonding is common between B and H.

Figure 14.7 The two types of covalent bonding in diborane.

Hydride *bridge bond* , or three-center, two-electron bond.



Normal covalent bond formed by overlap of *sp*^{3} hybrid orbital from B with *s* orbital from H.

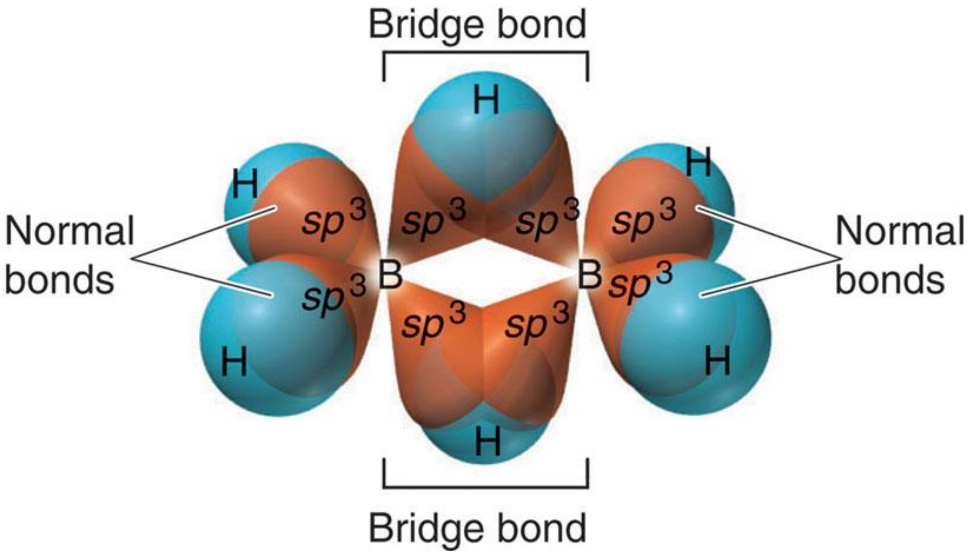
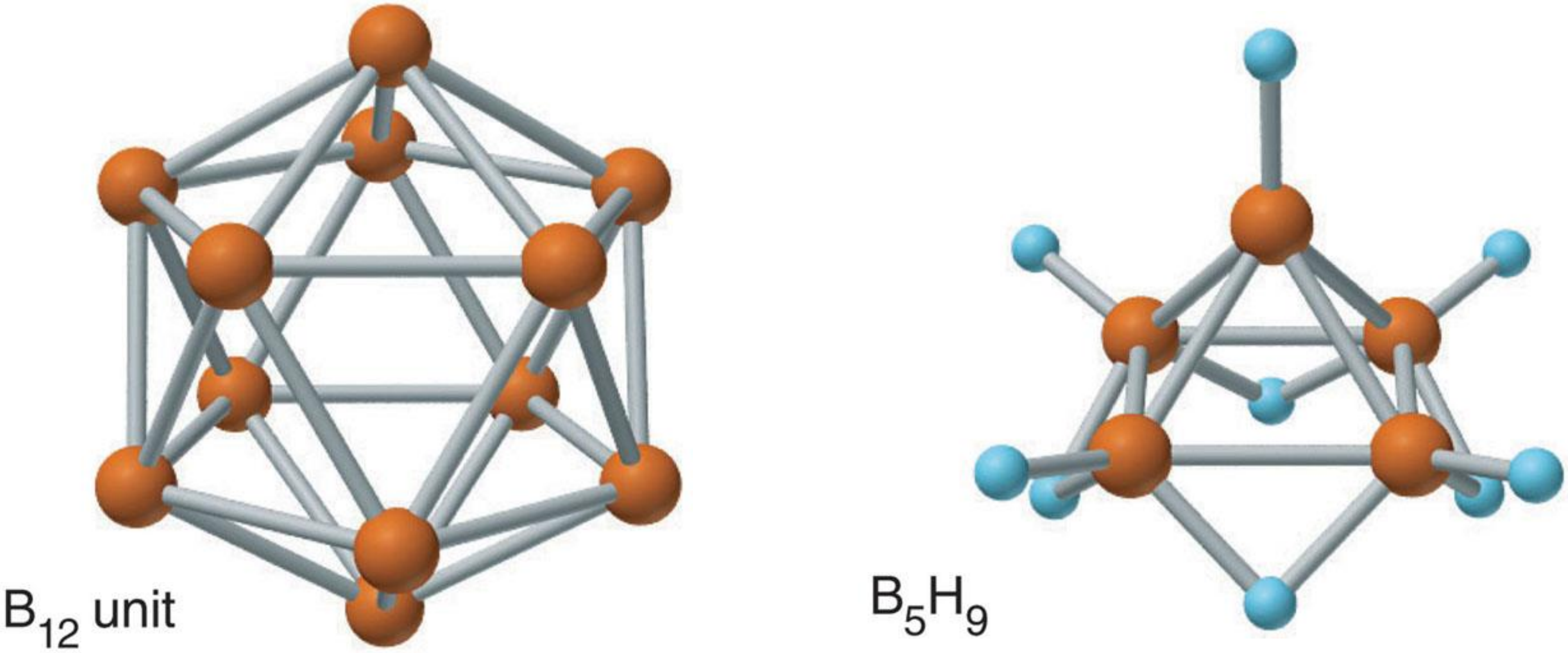


Figure 14.8 The boron icosahedron and one of the boranes.



B_{12} unit

B_5H_9

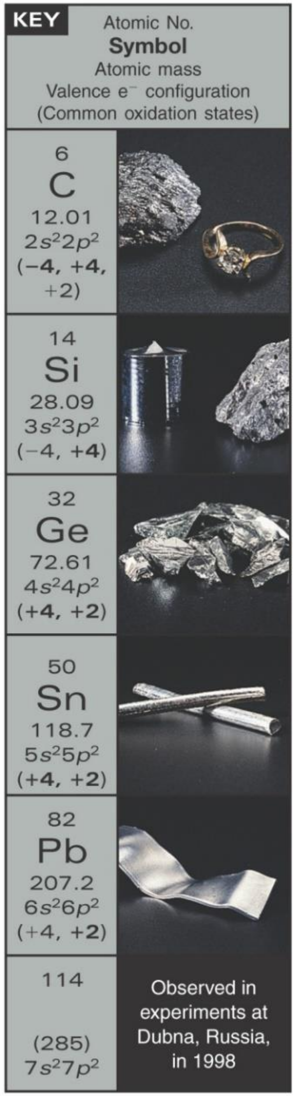
Beryllium and Aluminum

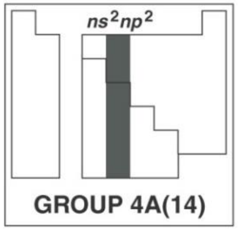
- There is a ***diagonal relationship*** between Be and Al.
- Both form oxoanions in strong base:
  - beryllate, $Be(OH)_4^{2-}$ and aluminate, $Al(OH)_4^{-}$.
- Both have bridge bonds in their hydrides and chlorides.
- Their oxides are
  - coatings that are impervious to water,
  - amphoteric, and
  - extremely hard with high melting points.
- ***Some*** Al and ***all*** Be compounds have significant covalent character.

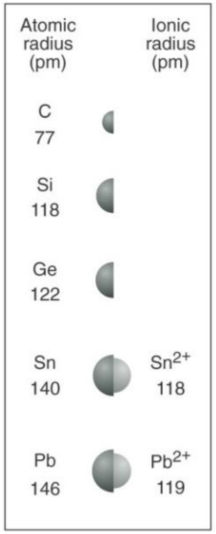
Group 4A(14): The Carbon Family

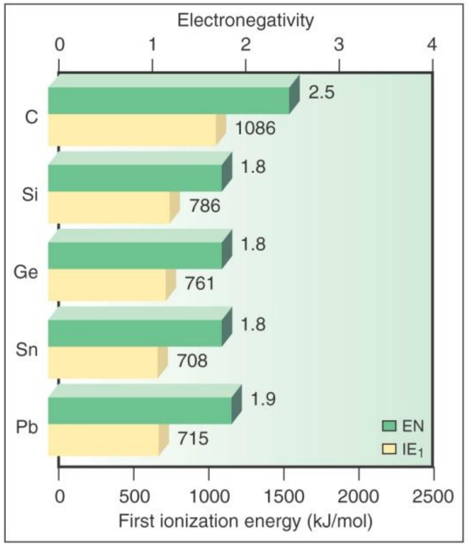
Family Portrait

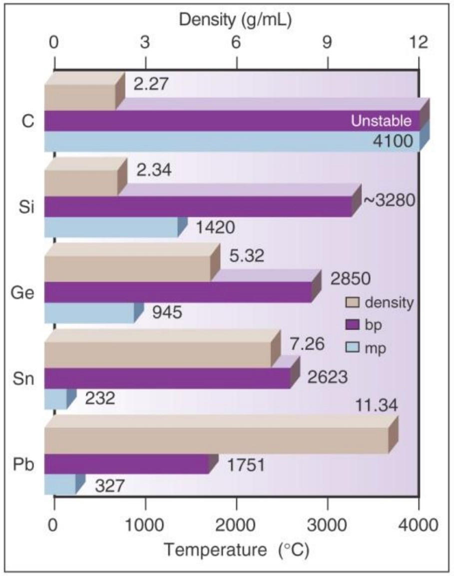
KEY ATOMIC PROPERTIES, PHYSICAL PROPERTIES, AND REACTIONS







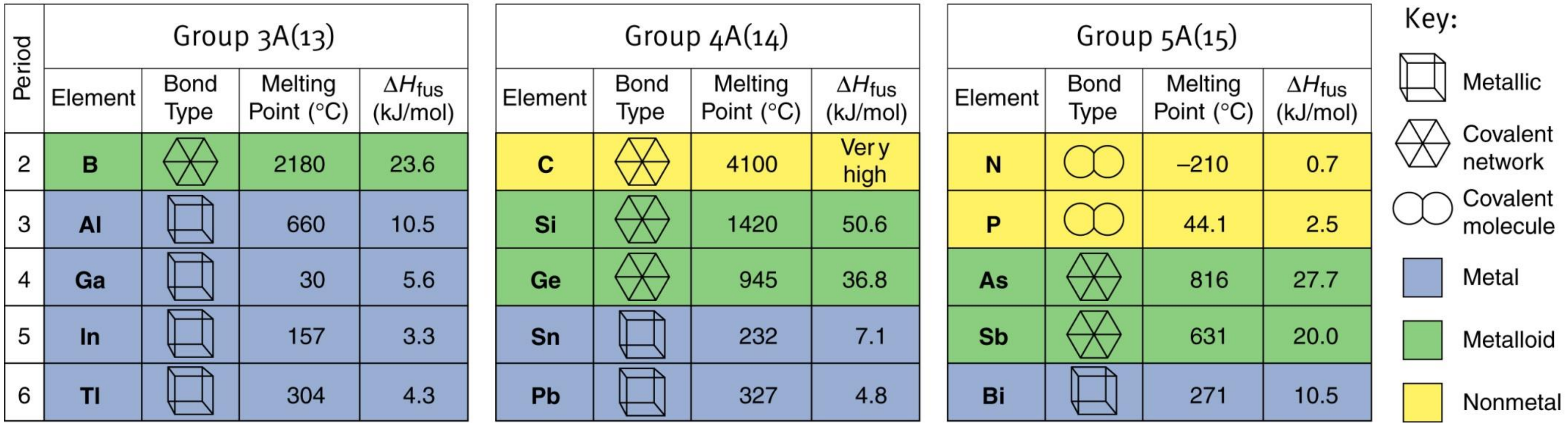




GROUP 4A(14): REACTIONS

- The Group 4A(14) elements are oxidized by halogens:
  - $E(s) + 2X_2 \rightarrow EX_4$ (E = C, Si, Ge)
  - The +2 halides are more stable for tin and lead, SnX_2 and PbX_2.
- The elements are oxidized by O_2:
  - $E(s) + O_2(g) \rightarrow EO_2$ (E = C, S, Ge, Sn)
  - Pb forms the +2 oxide, PbO.
- Oxides become more basic down the group.
- Hydrocarbons react with O_2:
  - $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$
- Silica is reduced to form elemental silicon:
  - $SiO_2(s) + 2C(s) \rightarrow Si(s) + 2CO(g)$

Table 14.2 Bond Type and the Melting Process in Groups 3A(13) to 5A(15)



Period	Group 3A(13)				Group 4A(14)				Group 5A(15)			
	Element	Bond Type	Melting Point (°C)	ΔH_{fus} (kJ/mol)	Element	Bond Type	Melting Point (°C)	ΔH_{fus} (kJ/mol)	Element	Bond Type	Melting Point (°C)	ΔH_{fus} (kJ/mol)
2	🟩 **B**	⬡	2180	23.6	🟨 **C**	⬡	4100	Very high	🟨 **N**	○○	–210	0.7
3	🟦 **Al**	◻	660	10.5	🟩 **Si**	⬡	1420	50.6	🟨 **P**	○○	44.1	2.5
4	🟦 **Ga**	◻	30	5.6	🟩 **Ge**	⬡	945	36.8	🟩 **As**	⬡	816	27.7
5	🟦 **In**	◻	157	3.3	🟦 **Sn**	◻	232	7.1	🟩 **Sb**	⬡	631	20.0
6	🟦 **Tl**	◻	304	4.3	🟦 **Pb**	◻	327	4.8	🟦 **Bi**	◻	271	10.5

Key:

◻	Metallic
⬡	Covalent network
○○	Covalent molecule
🟦	Metal
🟩	Metalloid
🟨	Nonmetal

Allotropes

Allotropes are different crystalline or molecular forms of the same element.

One allotrope of a particular element is usually more stable than another at a particular temperature and pressure.

Carbon has several allotropes, including graphite, diamond, and fullerenes.

Tin exhibits two allotropes; white β-tin and gray α-tin.

Figure 14.9 **Phase diagram of carbon.**

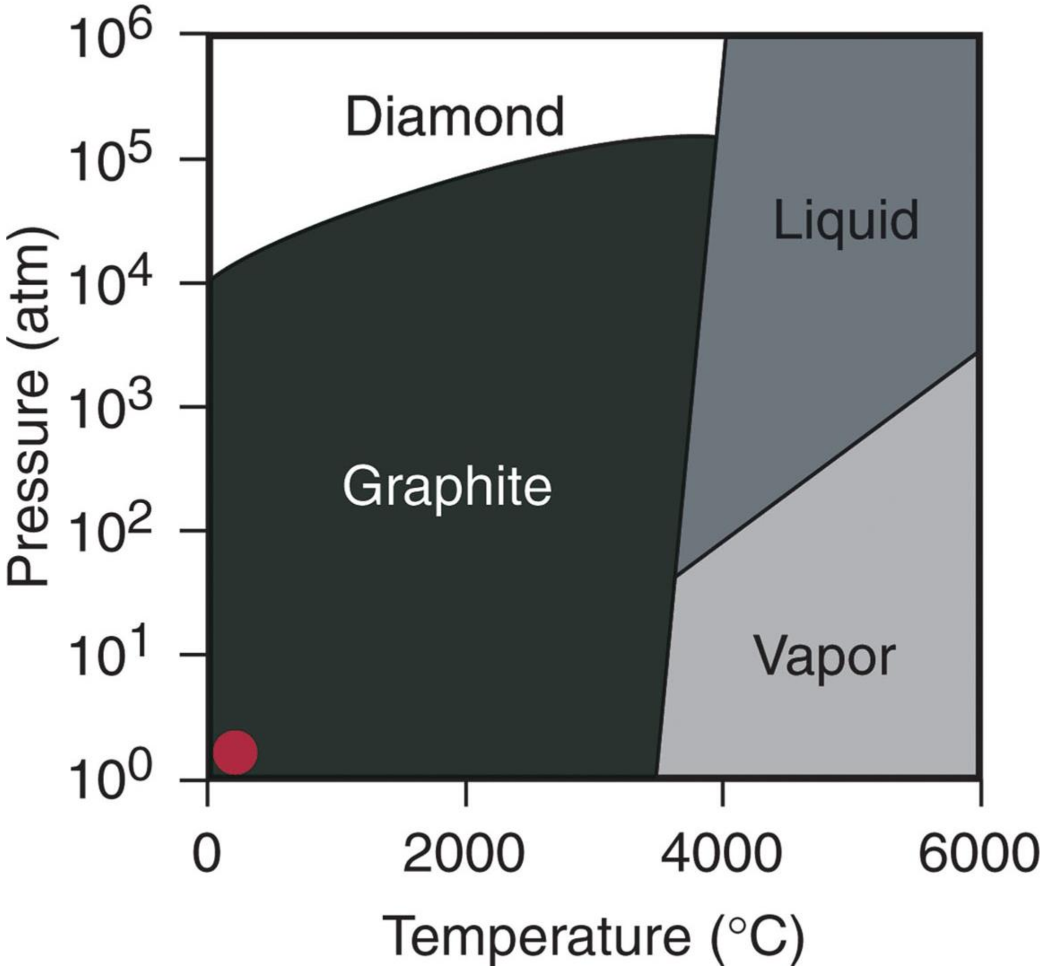
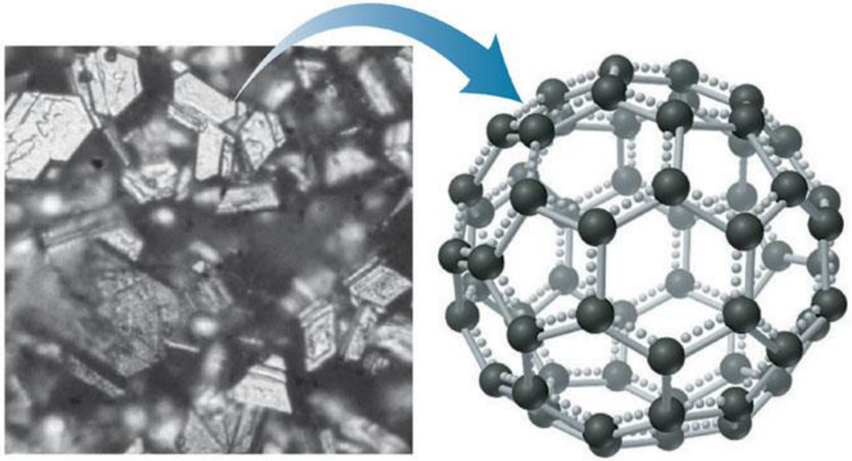
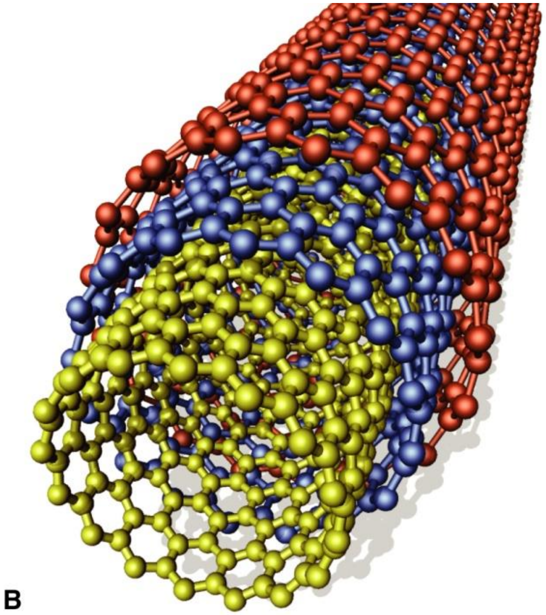


Figure 14.10 Crystalline buckminsterfullerene and a buckyball (A) and nanotubes (B).



Crystals of buckminsterfullerene (C_{60})

Nanotubes



Bonding in Group 4A(14) Compounds

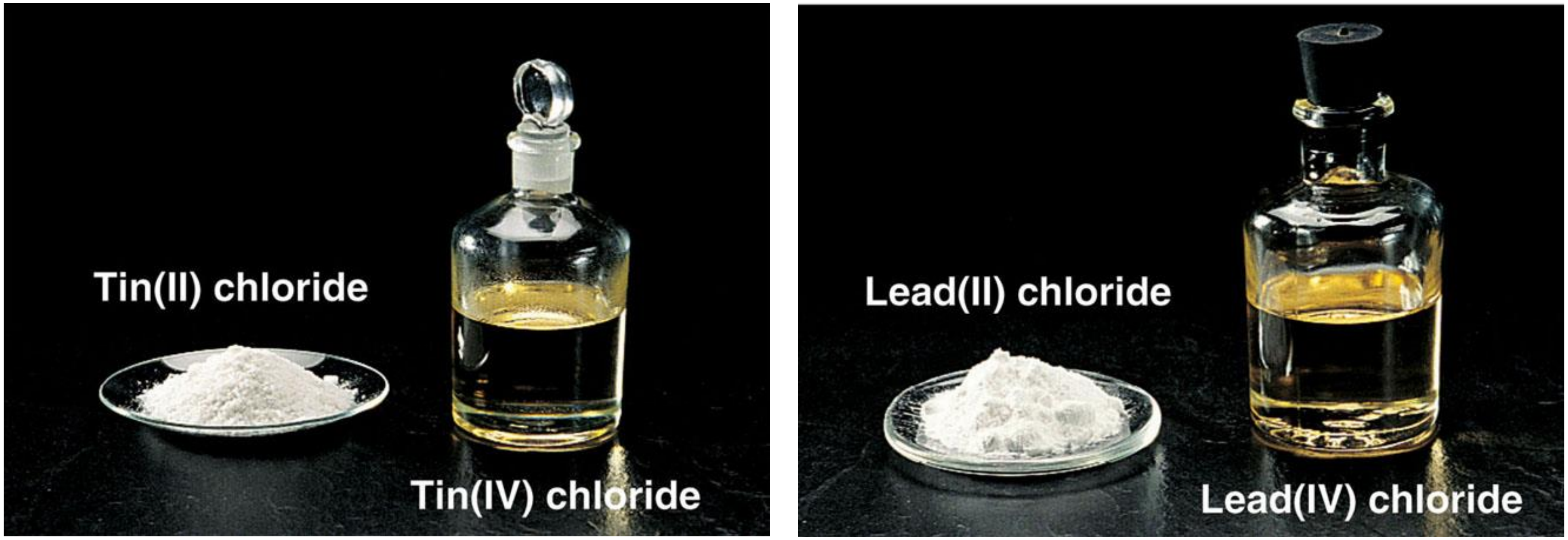
Carbon forms predominantly covalent bonds, but the larger members of the group form bonds with increasing ionic character.

Elements of this group also exhibit multiple oxidation states. ***Lower*** oxidation states become more prominent down the group.

Pb and Sn show more metallic character in their lower oxidation states.

$SnCl_2$ and $PbCl_2$ are white, crystalline solids with high melting points. $SnCl_4$ is a volatile, benzene-soluble liquid.

Figure 14.11 Salt-like +2 chlorides and oily +4 chlorides show greater metallic character of tin and lead in the lower oxidation state.



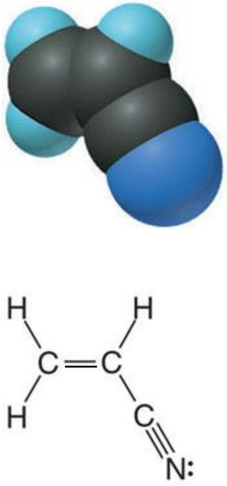
Carbon in Organic Chemistry

The large number and wide variety of ***organic*** compounds is due to the ability of C to bond to itself, and to form multiple bonds.

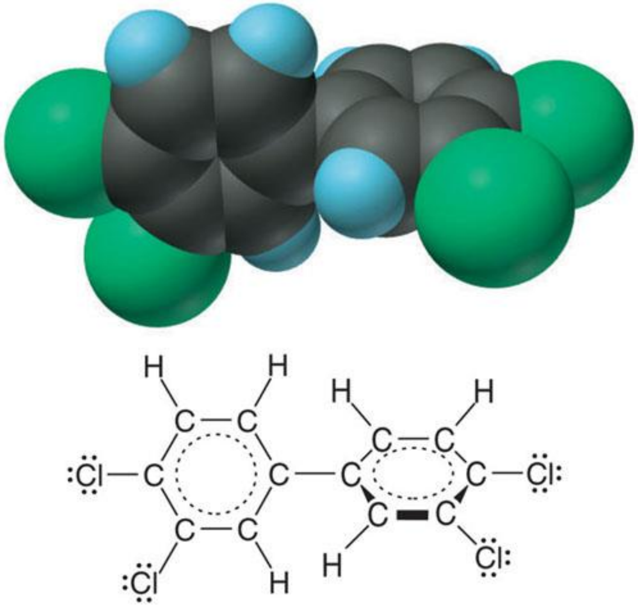
Catenation is the process whereby carbon bonds to itself to form stable chains, branches, and rings.

Since C is small, the C-C bond is short enough to allow effective side-to-side overlap of *p* orbitals. C readily forms double and triple bonds.

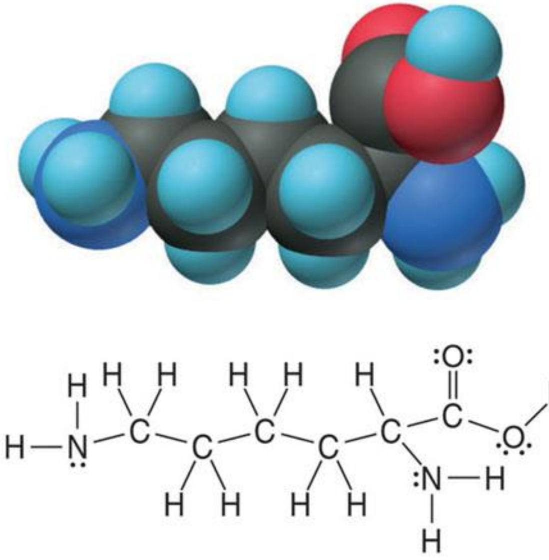
Figure 14.12 Three of the several million known organic compounds of carbon.



Acrylonitrile



PCB



S

Lysine

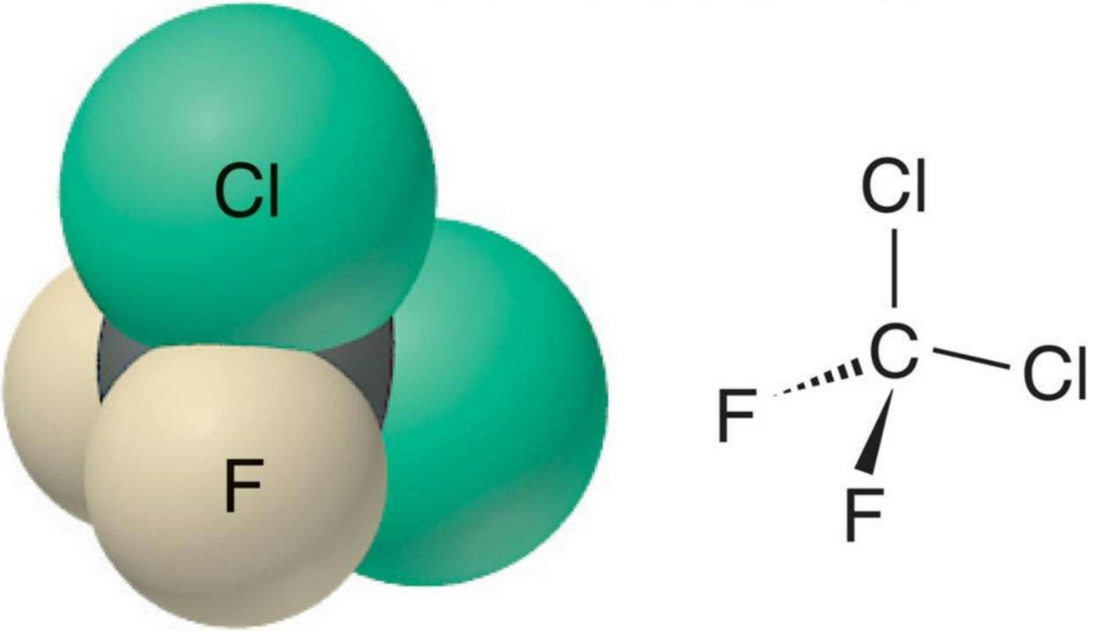
Inorganic Compounds of Carbon

Carbon bond with oxygen to form ***carbonates***. Metal carbonates such as $CaCO_3$ are abundant in minerals.

Carbon forms two common gaseous oxides, CO and CO_2, which are molecular. Other Group 4A(14) elements form network-covalent or ionic oxides.

Carbon halides have major uses as solvents and in structural plastics.

Figure 14.13 Freon-12 (CCl_2F_2), a chlorofluorocarbon.



Chlorofluorocarbons (CFC's or Freons) are chemically and thermally stable, nontoxic, and nonflammable. They are excellent cleaners, refrigerants, and propellants, but they decompose extremely slowly near the Earth's surface. They readily enter the stratosphere, where UV radiation causes them to release free Cl atoms that damage the ozone layer.

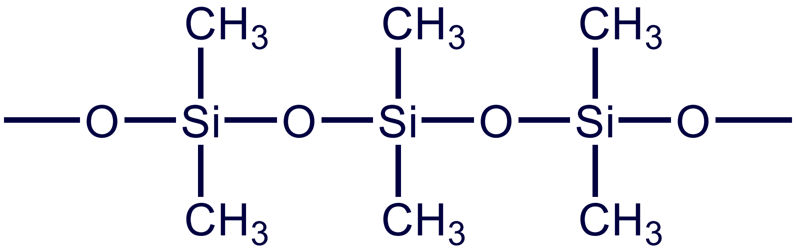
Highlights of Silicon Chemistry

Silicon bonds to oxygen to form repeating –Si–Oi– units, which are found in ***silicates*** and ***silicones***.

The silicate building unit is the ***orthosilicate grouping***, $–SiO_4–$, which has a tetrahedral arrangement.

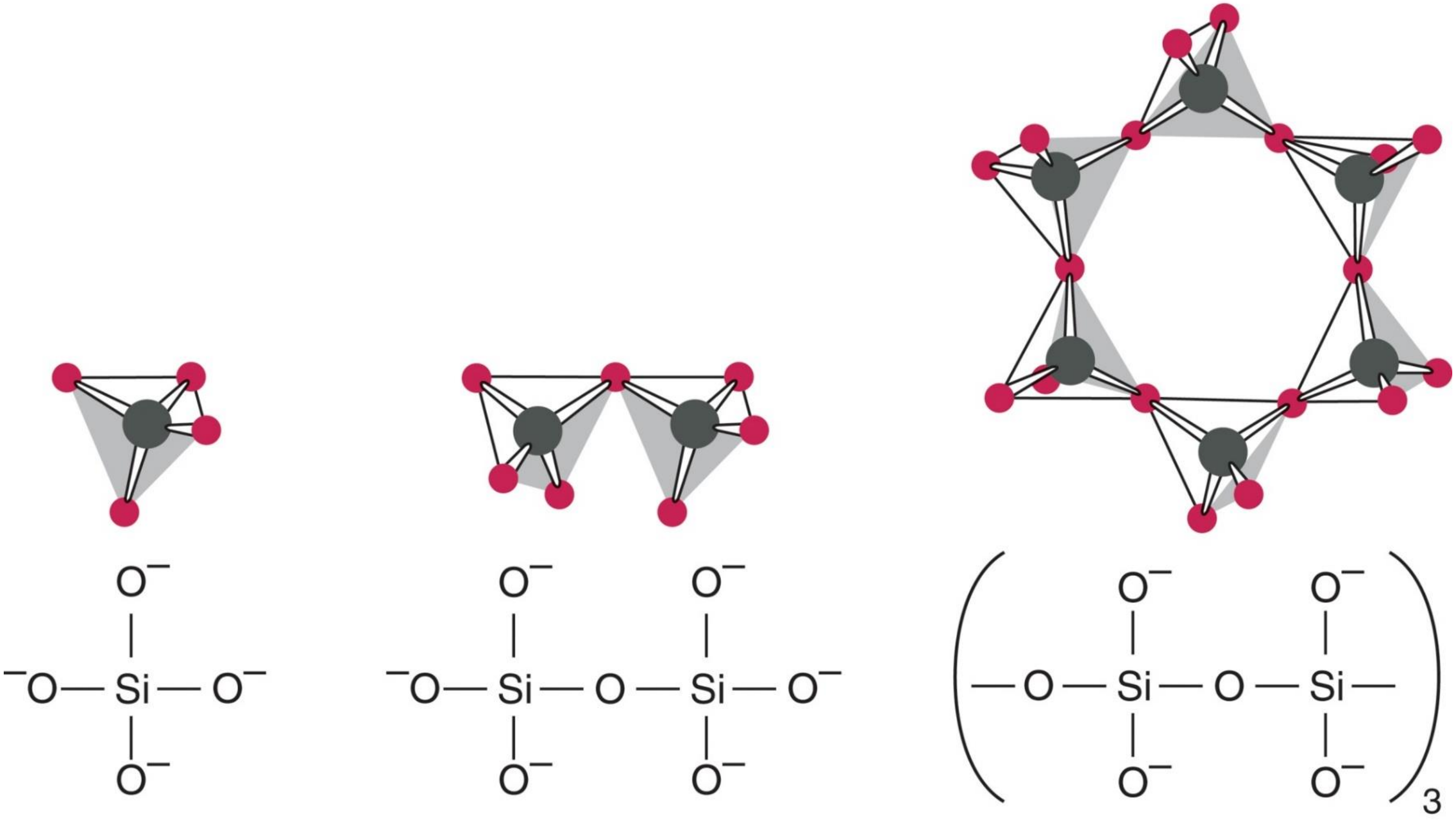
Silicate minerals are the dominant form of matter in the nonliving world. They include clay, sand, and semiprecious stones.

Silicone polymers are synthetic substances consisting of alternating Si and O atoms. They are used in a wide variety of applications.



$$—O—\underset{CH_3}{\overset{CH_3}{Si}}—O—\underset{CH_3}{\overset{CH_3}{Si}}—O—\underset{CH_3}{\overset{CH_3}{Si}}—O—$$

Figure 14.14 Structures of the silicate anions in some minerals.



SiO_4^{4-}

Silicate ion in zircon

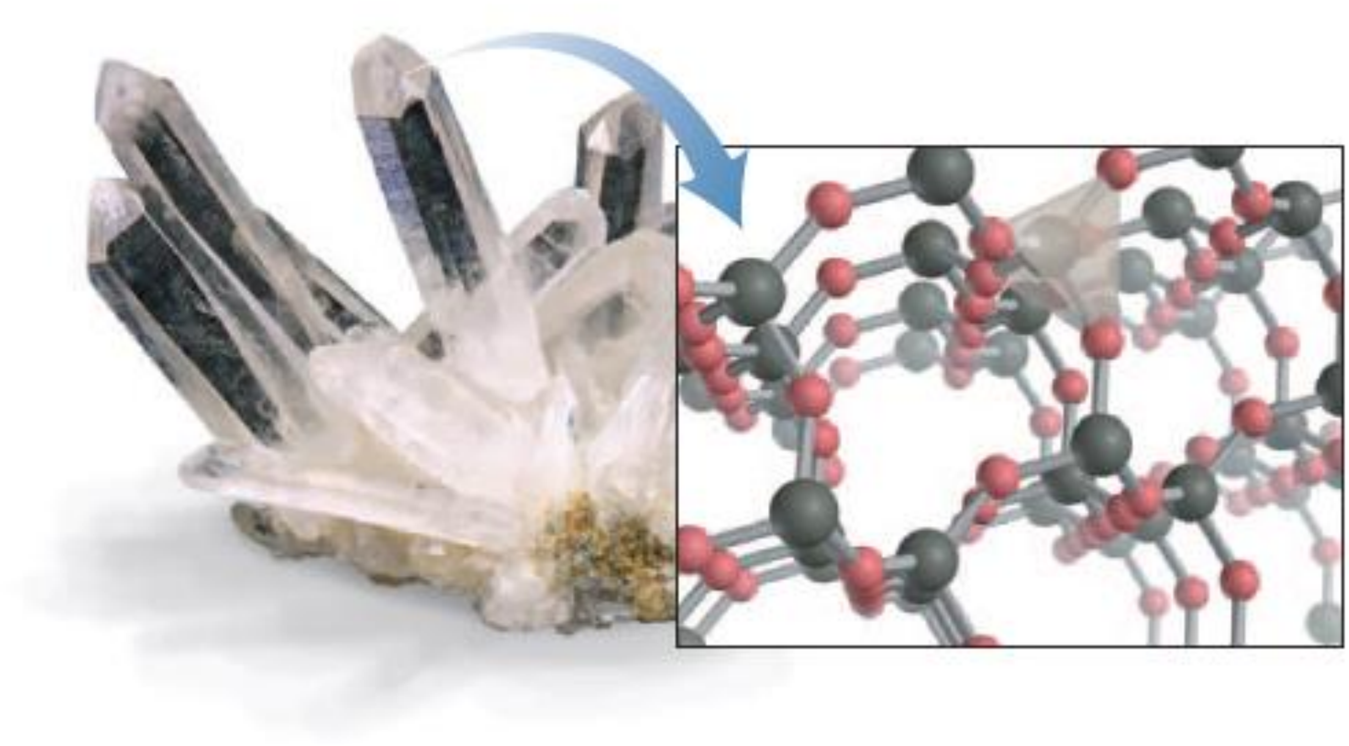
$Si_2O_7^{6-}$

Silicate ion in hemimorphite

$Si_6O_{18}^{12-}$

Silicate ion in beryl

Figure 14.15 Quartz is a three-dimensional framework silicate.



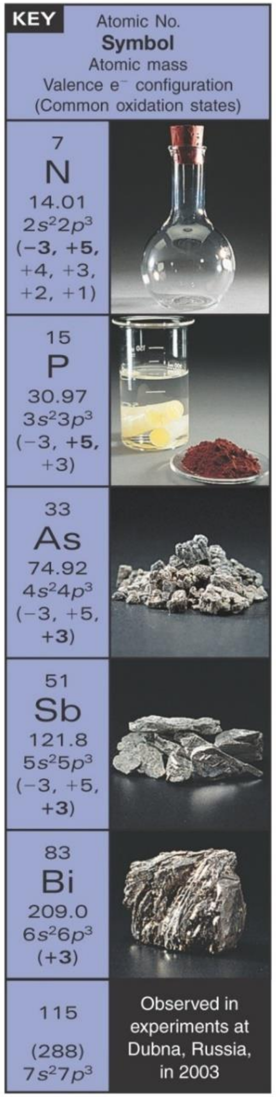
Group 5A(15) Elements

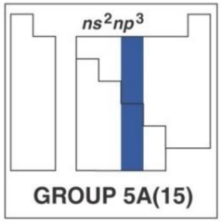
- ***Nitrogen*** is a diatomic gas (N_2) with a very low boiling point, due to its very weak intermolecular forces.
- ***Phosphorus*** exists most commonly as tetrahedral P_4 molecules. It has stronger dispersion forces than N_2.
- ***Arsenic*** exists as extended sheets of As atoms covalently bonded together. The covalent network structure gives it a high melting point.
- ***Antimony*** also has a covalent network structure.
- ***Bismuth*** has metallic bonding. Its melting point is lower than that of As or Sb.

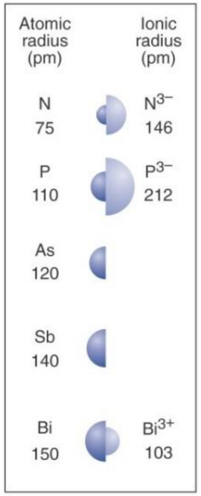
Group 5A(15): The Nitrogen Family

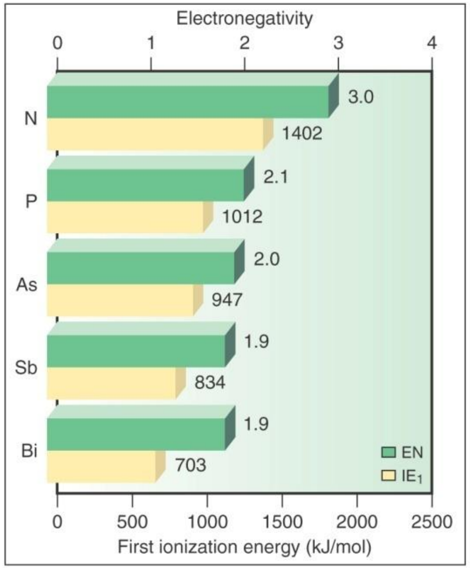
Family Portrait

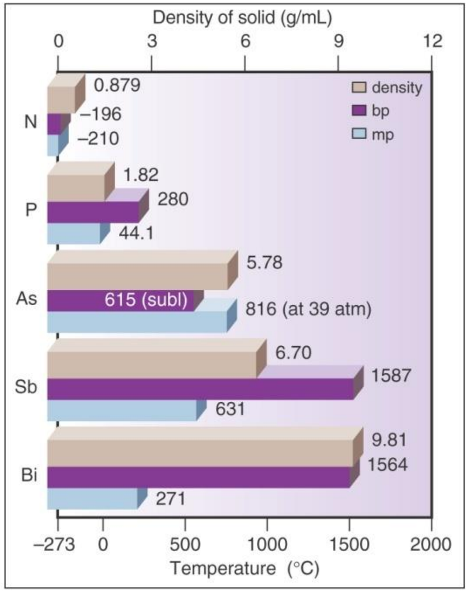
KEY ATOMIC PROPERTIES, PHYSICAL PROPERTIES, AND REACTIONS











GROUP 5A(15) REACTIONS

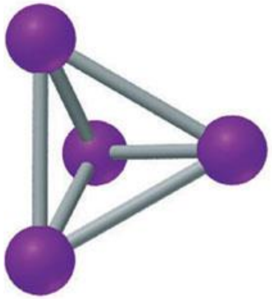
- Nitrogen is “fixed” industrially in the Haber process:
  - $N_2(g) + 3H_2(g) \rightleftarrows 2NH_3(g)$
- Hydrides of other group members are formed by reaction in water or acid of a metal phosphide, arsenide, etc.
  - $Ca_3P_2(s) + 6H_2O(l) \rightarrow 2PH_3(g) + 3Ca(OH)_2(aq)$
- Halides are formed by direct combination of the elements:
  - $2E(s) + 3X_2 \rightarrow 2EX_3$ (E = all except N)
  - $EX_3 + X_2 \rightarrow EX_5$ (E = all except Ni and Bi with X = F and Cl, but no $BiCl_5$; E = P for X = Br)

Family Portrait

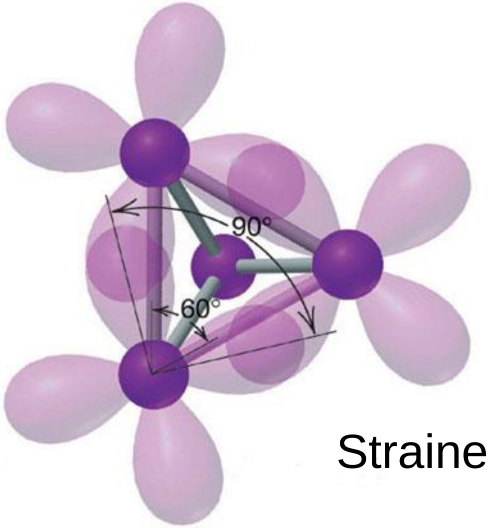
GROUP 5A(15) REACTIONS

- Oxoacids are formed from the halides in a reaction with water:
  - $EX_3 + 3H_2O(l) \rightarrow H_3EO_3(aq) + 3HX(aq)$ (E = all except N)
  - $EX_5 + 4H_2O(l) \rightarrow H_3EO_4(aq) + 5HX(aq)$ (E = all except N and Bi)

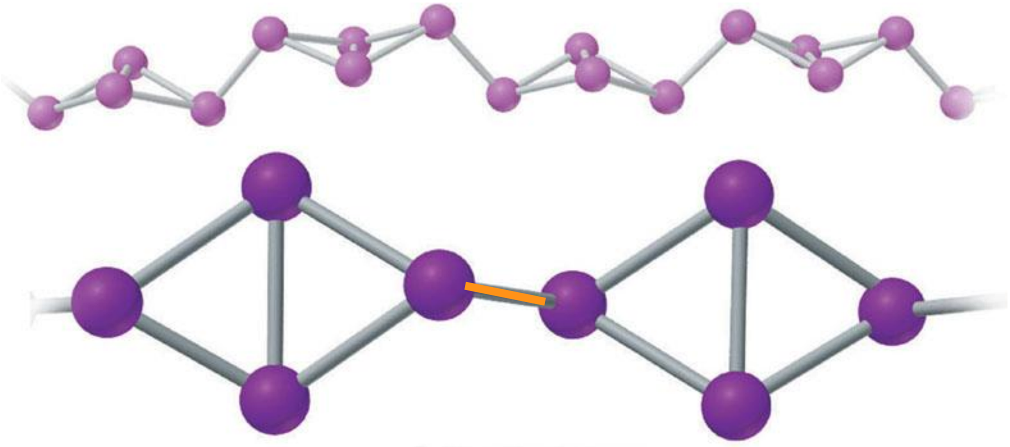
Figure 14.16 Two allotropes of phosphorous.



White phosphorous (P_4)



Strained bonds in P_4



Red phosphorous

Patterns of Behavior in Group 5A(15)

- N gains 3 electrons to form the anion N^{3-}, but only in compounds with active metals.
- The higher elements in the group are ***metallic*** and ***lose*** electrons to form cations.
- Oxides change from acidic to amphoteric to basic as you move down the group.
- All Group 5A(15) elements form gaseous hydrides with the formula EH_3.
  - All except NH_3 are extremely reactive and toxic.

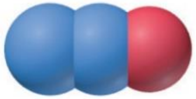
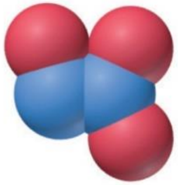
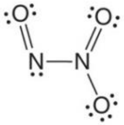
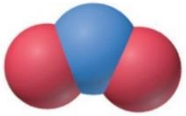
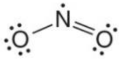
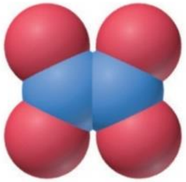
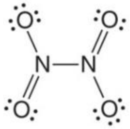
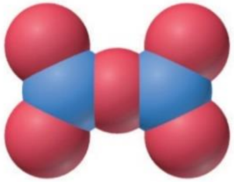
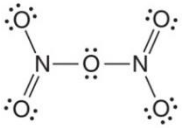
Oxides of Nitrogen

- Nitrogen forms six stable oxides. ΔH_f for all six oxides is ***positive*** because of the great strength of the NΞN bond.
- NO is produced by the oxidation of ammonia:
  - $4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g)$
  - This is the first step in the production of nitric acid.
- NO is converted to 2 other oxides by heating:

$$3NO(g) \xrightarrow{\Delta} N_2O(g) + NO_2(g)$$

  - This type of redox reaction is called ***disproportionation***.
- NO_2 is a component of photochemical smog.

Table 14.3 Structures and Properties of the Nitrogen Oxides

Formula	Name	Space-filling Model	Lewis Structure	Oxidation State of N	ΔH_f° (kJ/mol) at 298 K	Comment
N_2O	Dinitrogen monoxide (dinitrogen oxide; nitrous oxide)		:N≡N—Ö:	+1 (0, +2)	82.0	Colorless gas; used as dental anesthetic ("laughing gas") and aerosol propellant
NO	Nitrogen monoxide (nitrogen oxide; nitric oxide)		:Ṅ=Ö:	+2	90.3	Colorless, paramagnetic gas; biochemical messenger; air pollutant
N_2O_3	Dinitrogen trioxide			+3 (+2, +4)	83.7	Reddish brown gas (reversibly dissociates to NO and NO_2)
NO_2	Nitrogen dioxide			+4	33.2	Orange-brown, paramagnetic gas formed during HNO_3 manufacture; poisonous air pollutant
N_2O_4	Dinitrogen tetraoxide			+4	9.16	Colorless to yellow liquid (reversibly dissociates to NO_2)
N_2O_5	Dinitrogen pentaoxide			+5	11.3	Colorless, volatile solid consisting of NO_2^+ and NO_3^-; gas consists of N_2O_5 molecules

Nitrogen Oxoacids and Oxoanions

- ***Nitric acid*** (HNO_3) is produced by the Ostwald process:
  - The third step is $3NO_2(g) + H_2O(l) \rightarrow 2HNO_3 + NO(g)$
- Nitric acid is a strong oxidizing agent as well as a strong acid.
- The nitrate (NO_3^-) also acts as an oxidizing agent.
  - All nitrate salts are water soluble.
- ***Nitrous acid*** (HNO_2) is a much weaker acid than nitric acid.
  - This follows the general pattern for oxoacids – the more O atoms bonded to the central nonmetal, the stronger the acid.

Figure 14.17 The structures of nitric and nitrous acids and their oxoanions.

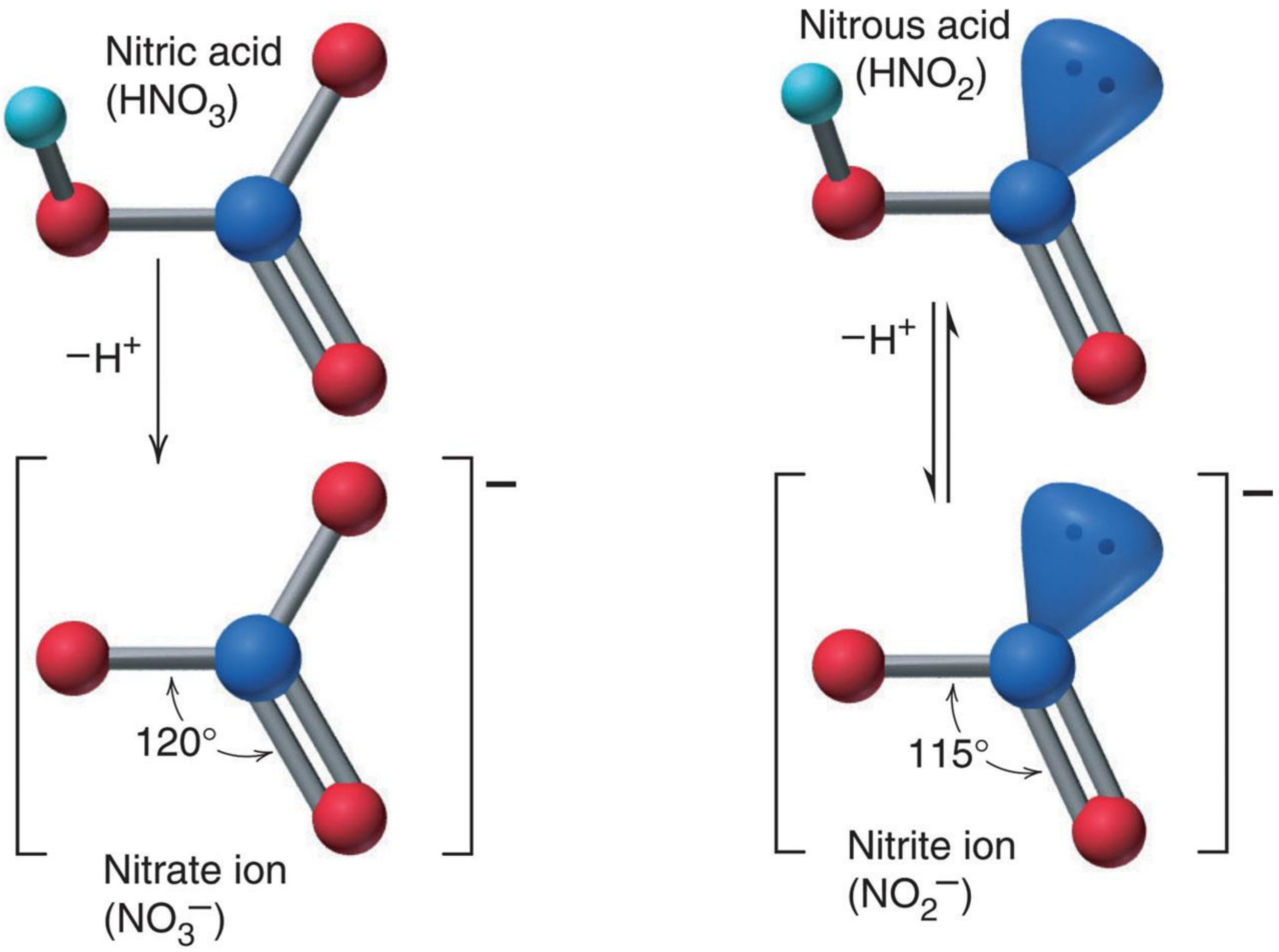
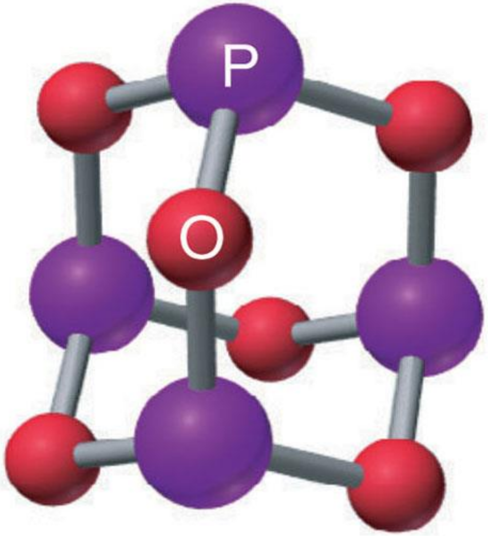
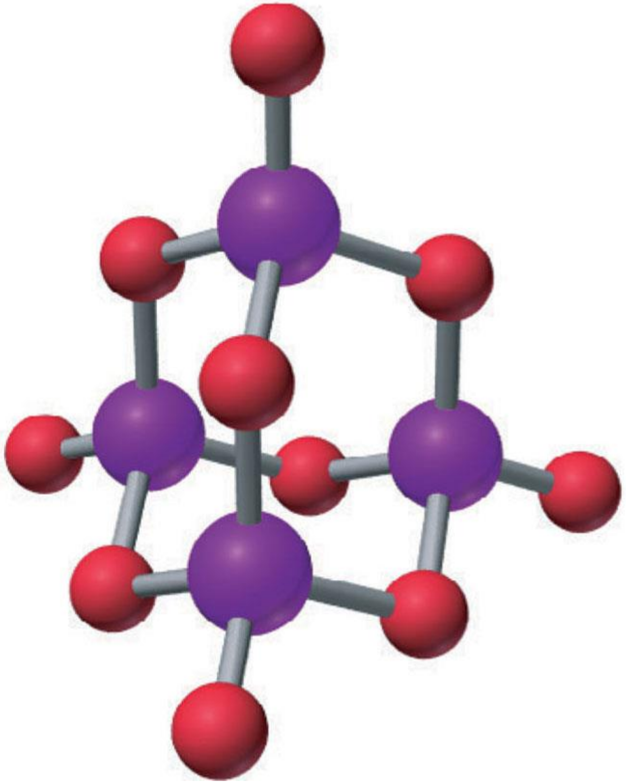


Figure 14.18 Important oxides of phosphorous.

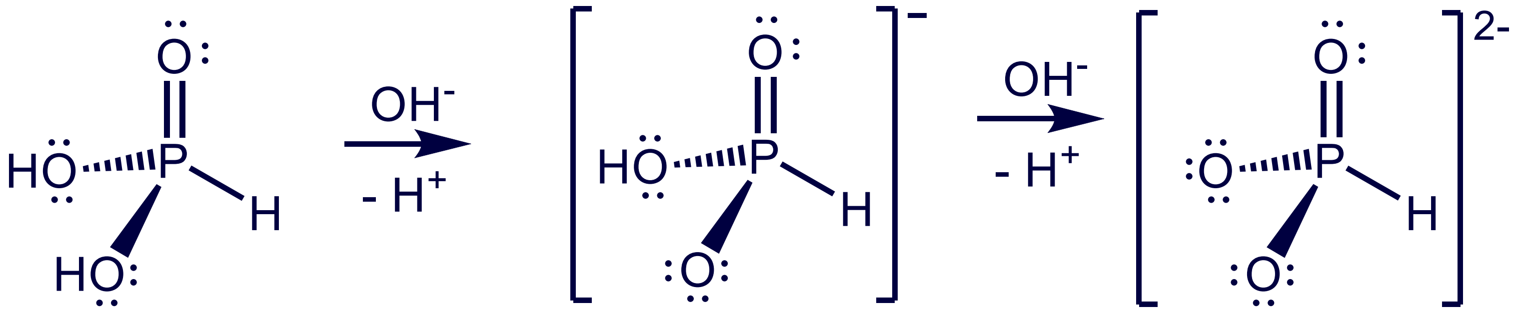


P_4O_6 has P in its +3 oxidation state.

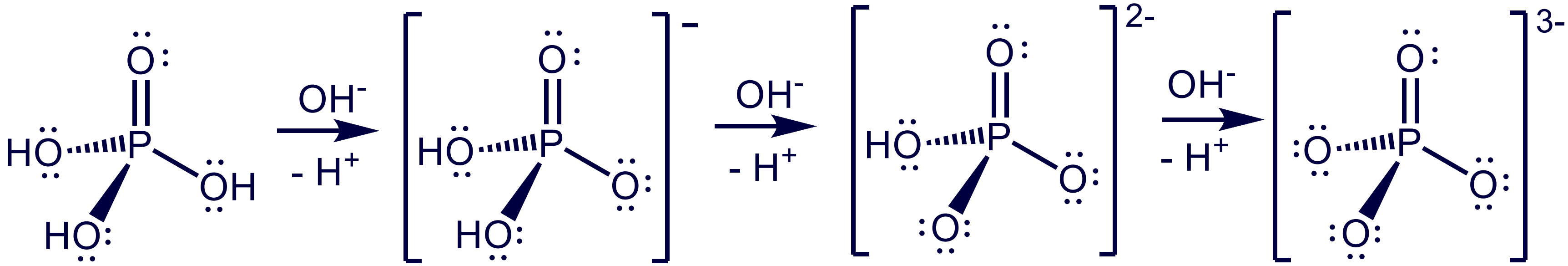


P_4O_{10} has P in its +5 oxidation state.
This compound is a powerful drying agent.

Oxoacids of Phosphorus

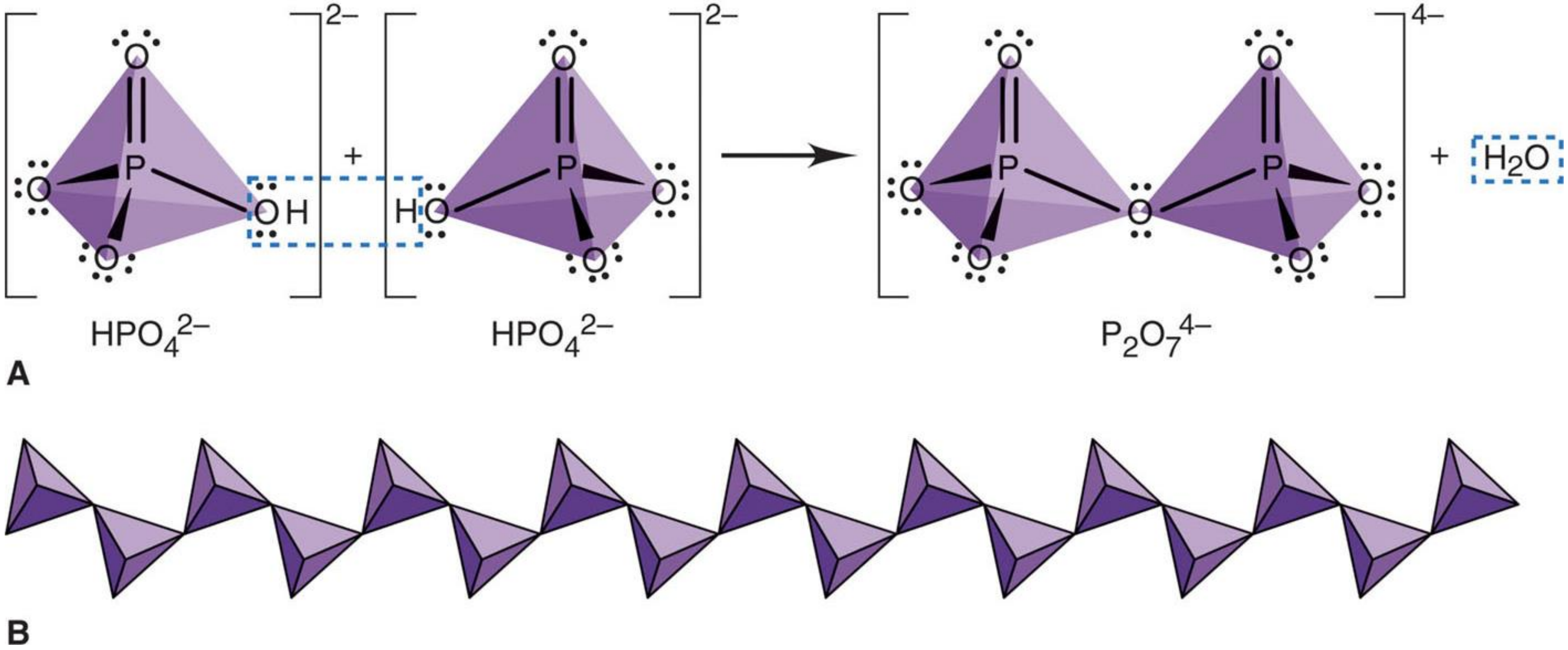


H_3PO_3 has only ***two*** acidic H atoms; the third is bonded to the central P and does not dissociate.



H_3PO_4 has ***three*** acidic H atoms. It is a weak acid, but in strong base all three H^+ are lost to give the phosphate anion.

Figure 14.19 **The diphosphate ion and polyphosphates.**



Hydrogen phosphates lose water when heated to give polyphosphates, which contain P–O–P linkages.

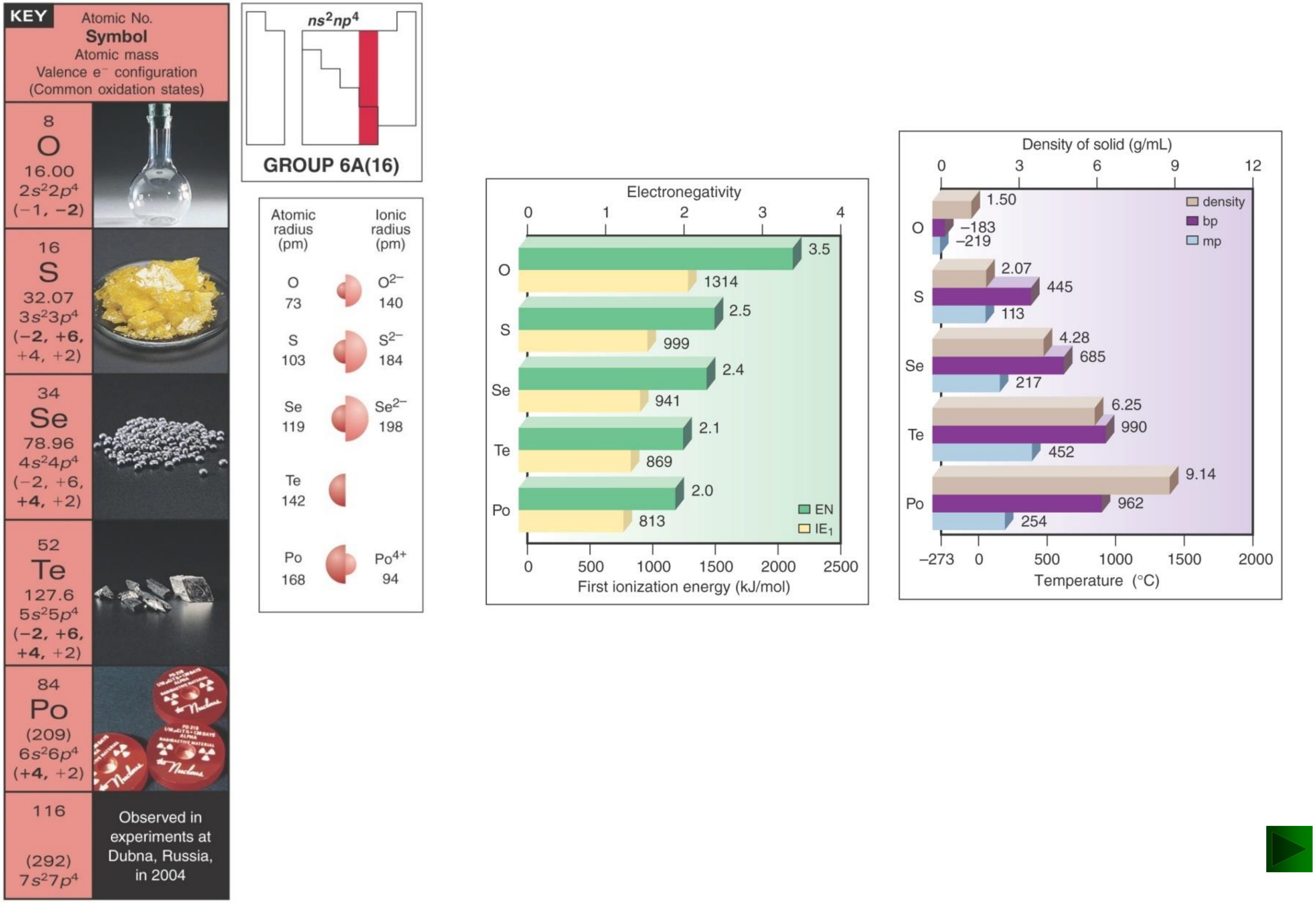
Group 6A(16) Elements

- ***Oxygen***, like nitrogen, occurs as a low-boiling diatomic gas, O_2.
- ***Sulfur***, like phosphorus, occurs as a polyatomic molecular solid.
- ***Selenium***, like arsenic, commonly occurs as a gray metalloid.
- ***Tellurium***, like antimony, displays network covalent bonding.
- ***Polonium***, like bismuth, has a metallic crystal structure.

Group 6A(16): The Oxygen Family

Family Portrait

KEY ATOMIC PROPERTIES, PHYSICAL PROPERTIES, AND REACTIONS



GROUP 6A(16) REACTIONS

- Halides are formed by direct combination:
  - $E(s) + X_2(g) \rightarrow$ various halides (E = S, Se, Te; X = F, Cl)
- The other elements in the group are oxidized by O_2:
  - $E(s) + O_2(g) \rightarrow EO_2$ (E = S, Se, Te, Po)
- SO_2 is oxidized further:
  - $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$
- The thiosulfate ion is formed when an alkali metal sulfite reacts with sulfur:
  - $S_8(g) + 8Na_2SO_3(s) \rightarrow 8Na_2S_2O_3(aq)$

Allotropes in the Oxygen Family

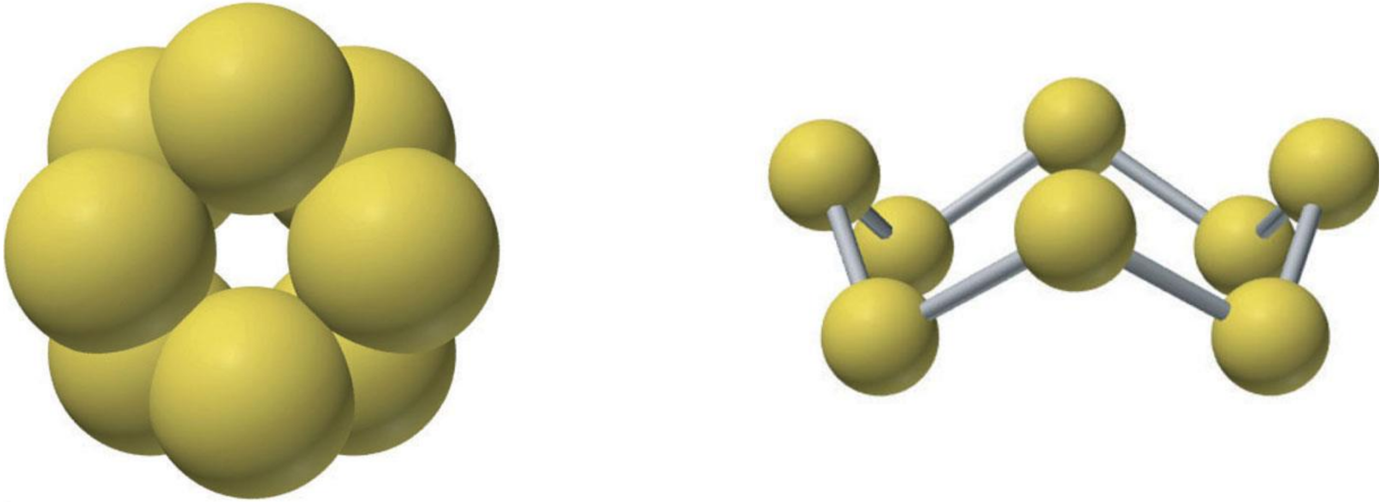
Oxygen has two allotropes:

- O_2, which is essential to life, and
- O_3 or ozone, which is poisonous.

Sulfur has more than 10 different forms, due to the ability of S to catenate. S–S bond lengths and bond angles may vary greatly.

Selenium has several allotropes, some consisting of crown-shaped Se_8 molecules.

Figure 14.20 The cyclo-S_8 molecule.



top view

side view

At room temperature, the sulfur molecule is a crown-shaped ring of eight atoms. The most stable S allotrope is orthorhombic α-S_8, which consists of cyclo-S_8.

Hydrides of the Oxygen Family

- Oxygen forms two hydrides:
  - water (H_2O) and hydrogen peroxide (H_2O_2).
  - H_2O_2 contains oxygen in a -1 oxidation state.
- The hydrides of the other 6A elements are foul-smelling, poisonous gases.
  - H_2S forms naturally in swamps from the breakdown of organic matter and is as toxic as HCN.
- H_2O and H_2O_2 can form H bonds, and therefore have higher melting and boiling points than other H_2E compounds.
- Hydride bond angles decrease and bond lengths increase down the group.

Halides of the Oxygen Family

Except for O, the Group 6A elements form a wide range of halides.

Their structure and reactivity patterns depend on the sizes of the central atom and the surrounding halogens.

As the central atom becomes ***larger***, the halides become more stable.

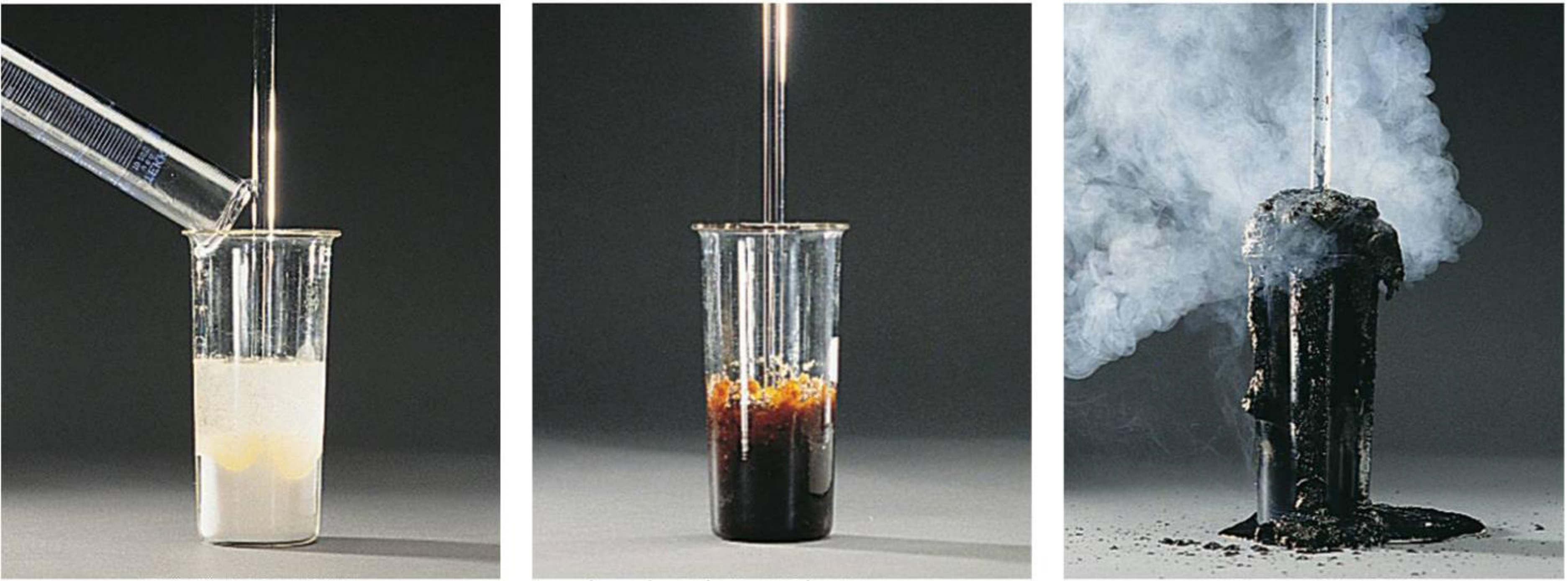
This pattern is related to the effect of electron repulsions due to crowding of lone pairs and halogen atoms around the central atom.

This is opposite to the previously observed bonding patterns, where bond strength decreases as bond length increases.

Highlights of Sulfur Chemistry

- Sulfur forms two important oxides:
  - SO_2 has S in its +4 oxidation state. It is a colorless, choking gas that forms when S, H_2S or a metal sulfide burns in air.
  - SO_3 has S in the +6 oxidation state.
- Sulfur forms two important oxoacids.
  - Sulfurous acid (H_2SO_3) is a weak acid with two acidic protons.
  - Sulfuric acid (H_2SO_4) is a strong acid, and is an important industrial chemical. It is an excellent dehydrating agent.

Figure 14.21 The dehydration of sugar by sulfuric acid.



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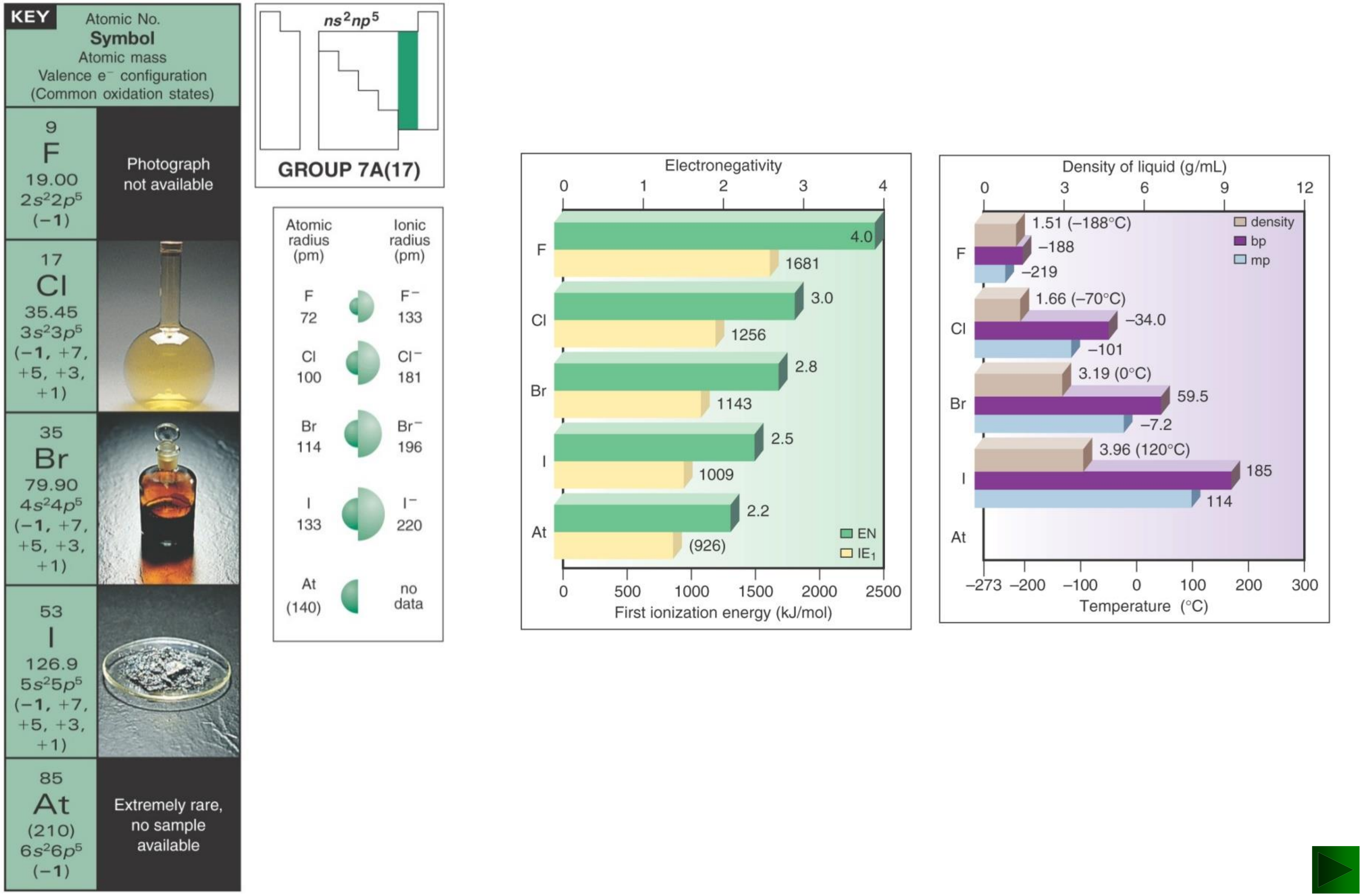
Group 7A(17): The Halogens

Family Portrait

KEY ATOMIC PROPERTIES, PHYSICAL PROPERTIES, AND REACTIONS



GROUP 7A(17) REACTIONS

- The halogens (X_2) oxidize many metals and nonmetals. The reaction with H_2 is characteristic:
  - $X_2 + H_2(g) \rightarrow 2HX(g)$
- The halogens undergo disproportionation in water:
  - $X_2 + H_2O(l) \leftrightarrows HX(aq) + HXO(aq)$ (X = Cl, Br, I)
- In aqueous base, the reaction goes to completion to form hypohalites and, at higher temperatures, halates:

$$3Cl_2(g) + 6OH^-(aq) \xrightarrow{\Delta} ClO_3^-(aq) + 5Cl^-(aq) + 3H_2O(l)$$

Reactivity of the Halogens

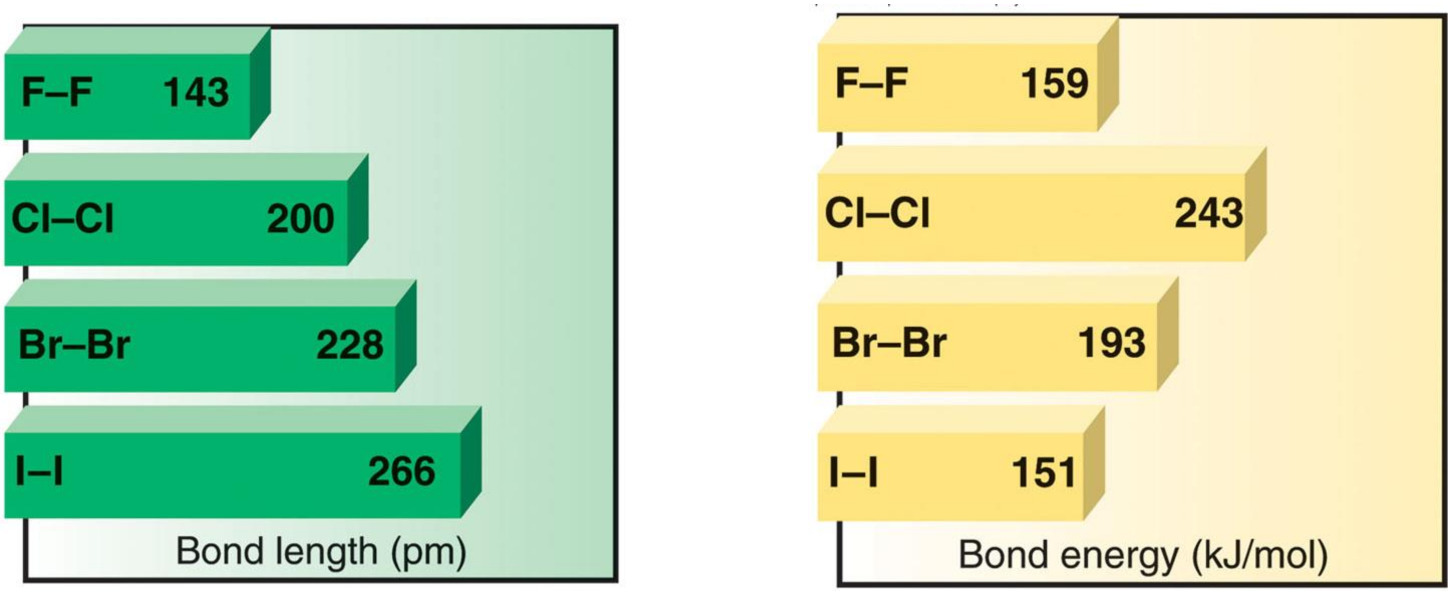
A halogen atom needs only one electron to fill its valence shell. Halogens are therefore very reactive elements.

The halogens display a wide range of electronegativities, but all are electronegative enough to behave as nonmetals.

A halogen will either
- gain one electron to form a halide anion or
- share an electron pair with a nonmetal atom.

The reactivity of the halogens ***decreases*** down the group, reflecting the decrease in electronegativity.

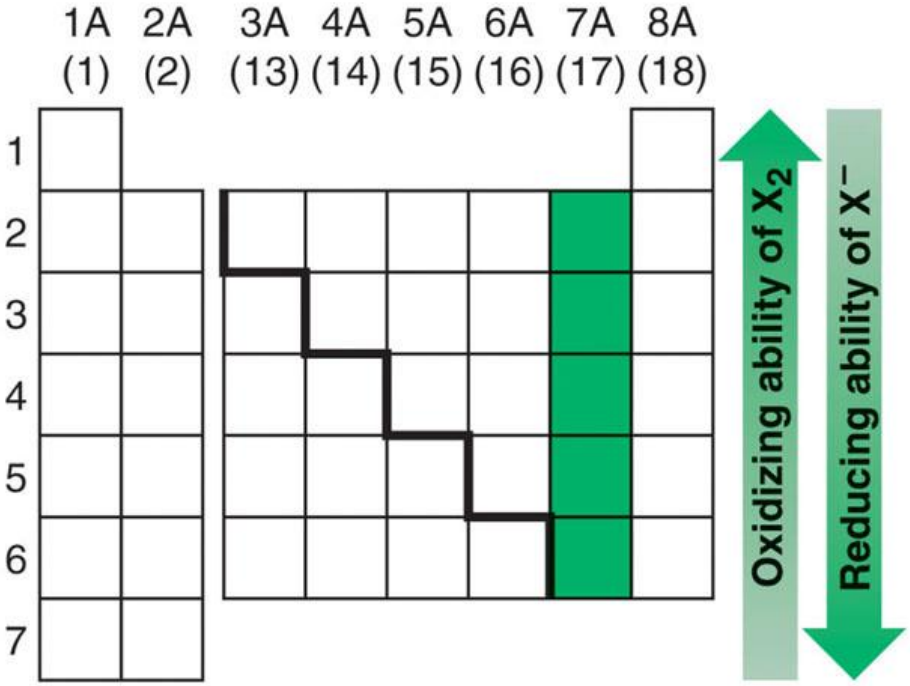
Figure 14.22 Bond energies and bond lengths of the halogens.



F_2 shows an anomalous bond energy. The F-F bond is ***weaker*** than expected since the lone pairs on the small F atom repel each other more than the lone pairs of other halogens.

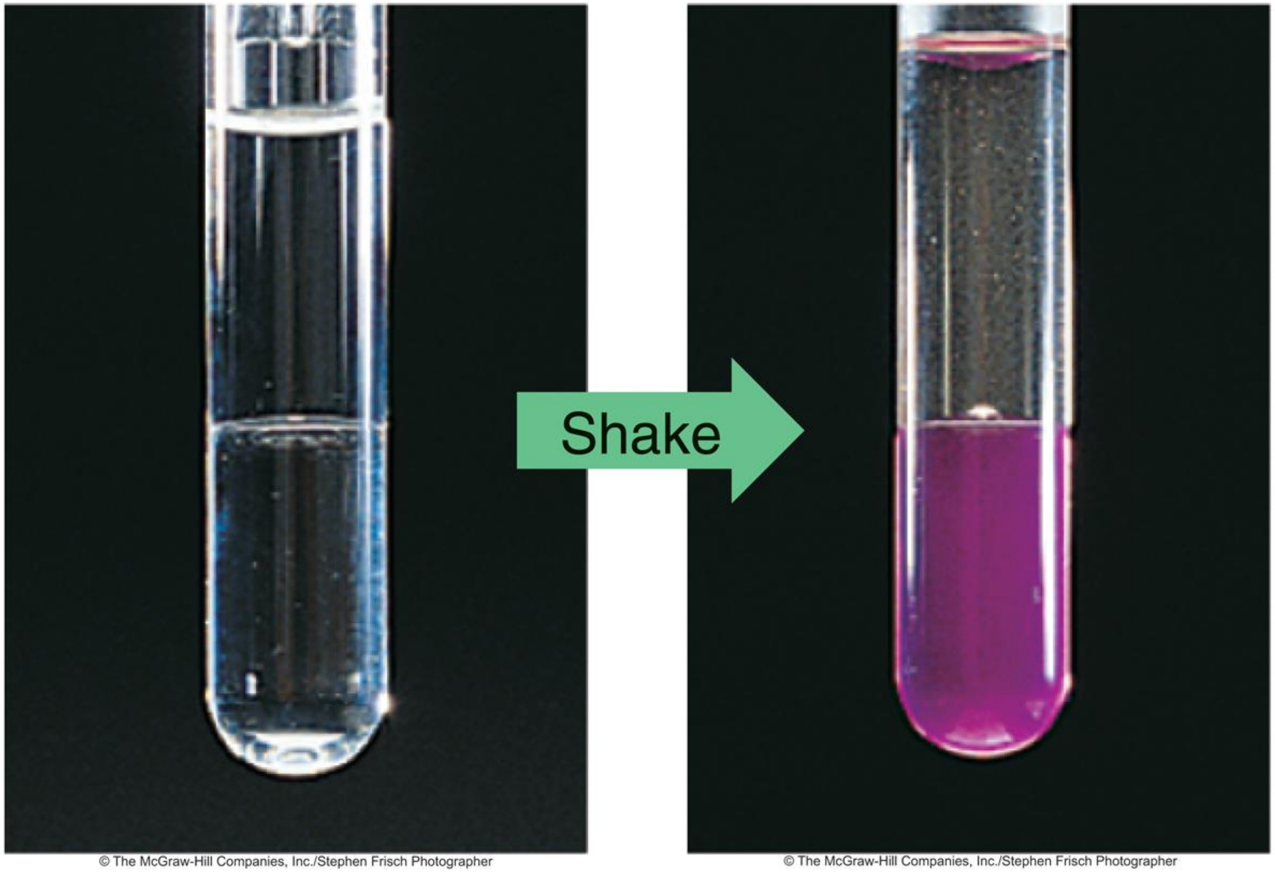
F_2 is the ***most*** and I_2 the ***least*** reactive halogen.

Figure 14.23 The relative oxidizing ability of the halogens.



Halogens are strong ***oxidizing*** agents. The oxidizing ability of X_2 ***decreases*** down the group while the reducing ability of X^- ***increases***.

Figure 14.23 continued



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$$Cl_2(aq) + 2I^-(aq) \rightarrow 2Cl^-(aq) + I_2 \text{ (in } CCl_4)$$

Cl_2 is a ***stronger oxidizing agent*** than I_2. Cl_2 will therefore displace I^- from solution. I_2 will not displace Cl^- ions.

Interhalogen Compounds

Halogens bond with each other to form ***interhalogen compounds***.

The central atom will have the lower electronegativity and a positive oxidation state.

The interhalogens illustrate a general principle of oxidation states: odd-numbered groups exhibit odd-numbered oxidation states while even-numbered groups exhibit even-numbered oxidation states.

When bonds form or break, two electrons are involved, so the oxidation states of the atoms involved commonly change by 2.

Odd-numbered oxidation states:

F and I are both in Group 7A, an odd-numbered group.

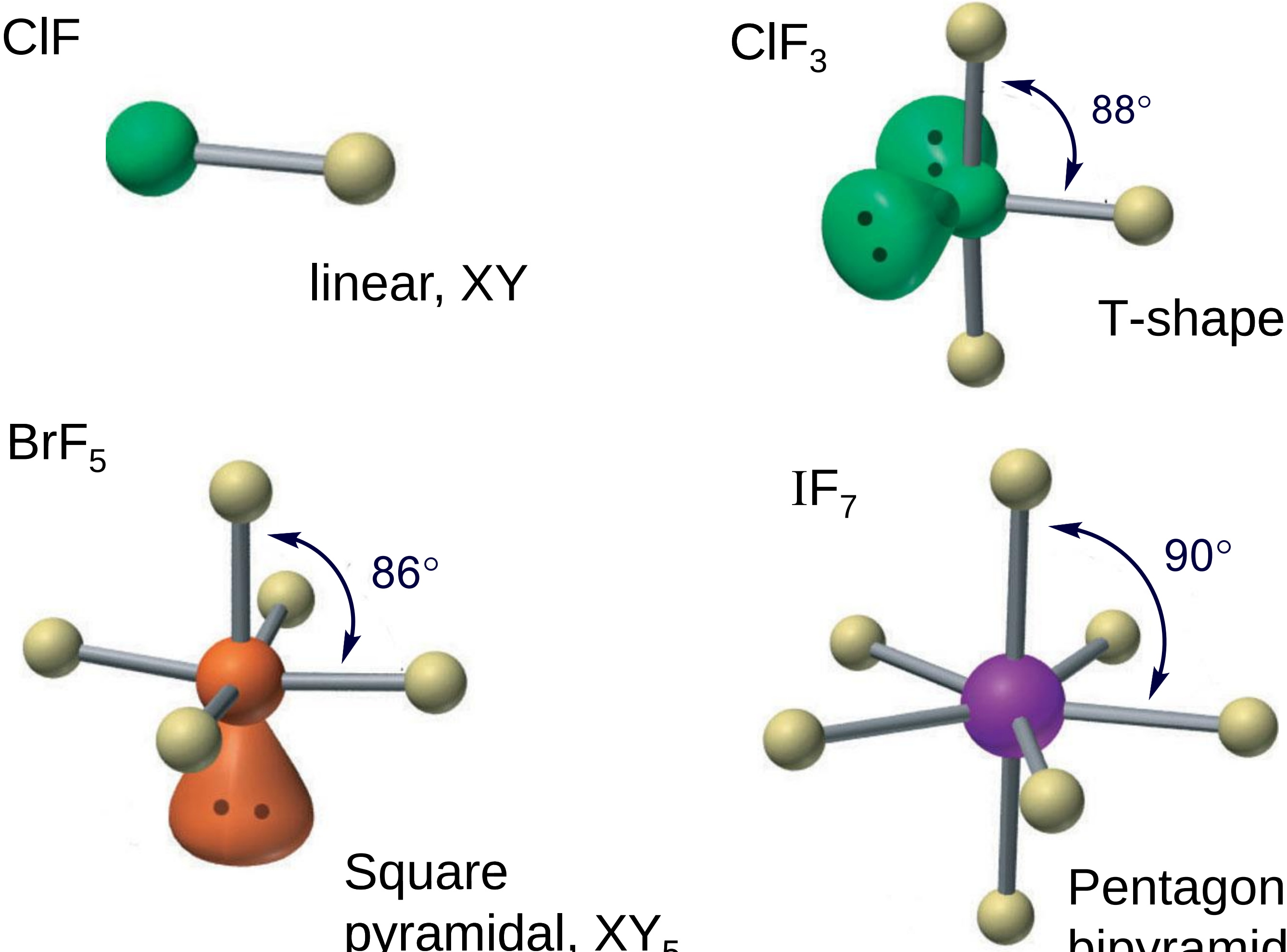
$$\overset{0}{I_2} + \underset{0}{F_2} \rightarrow 2\overset{+1}{I}\underset{-1}{F} \qquad \overset{+1}{I}\underset{-1}{F} + \underset{0}{F_2} \rightarrow \overset{+3}{I}\underset{-1}{F_3}$$

Even-numbered oxidation states:

S is in Group 6A, an even-numbered group.

$$\overset{0}{S} + F_2 \rightarrow \overset{+2}{S}F_2 \qquad \overset{+2}{S}F_2 + F_2 \rightarrow \overset{+4}{S}F_4$$

Figure 14.24 Molecular shapes of the main types of interhalogen compounds.



ClF

linear, XY

ClF_3

T-shaped, XY_3

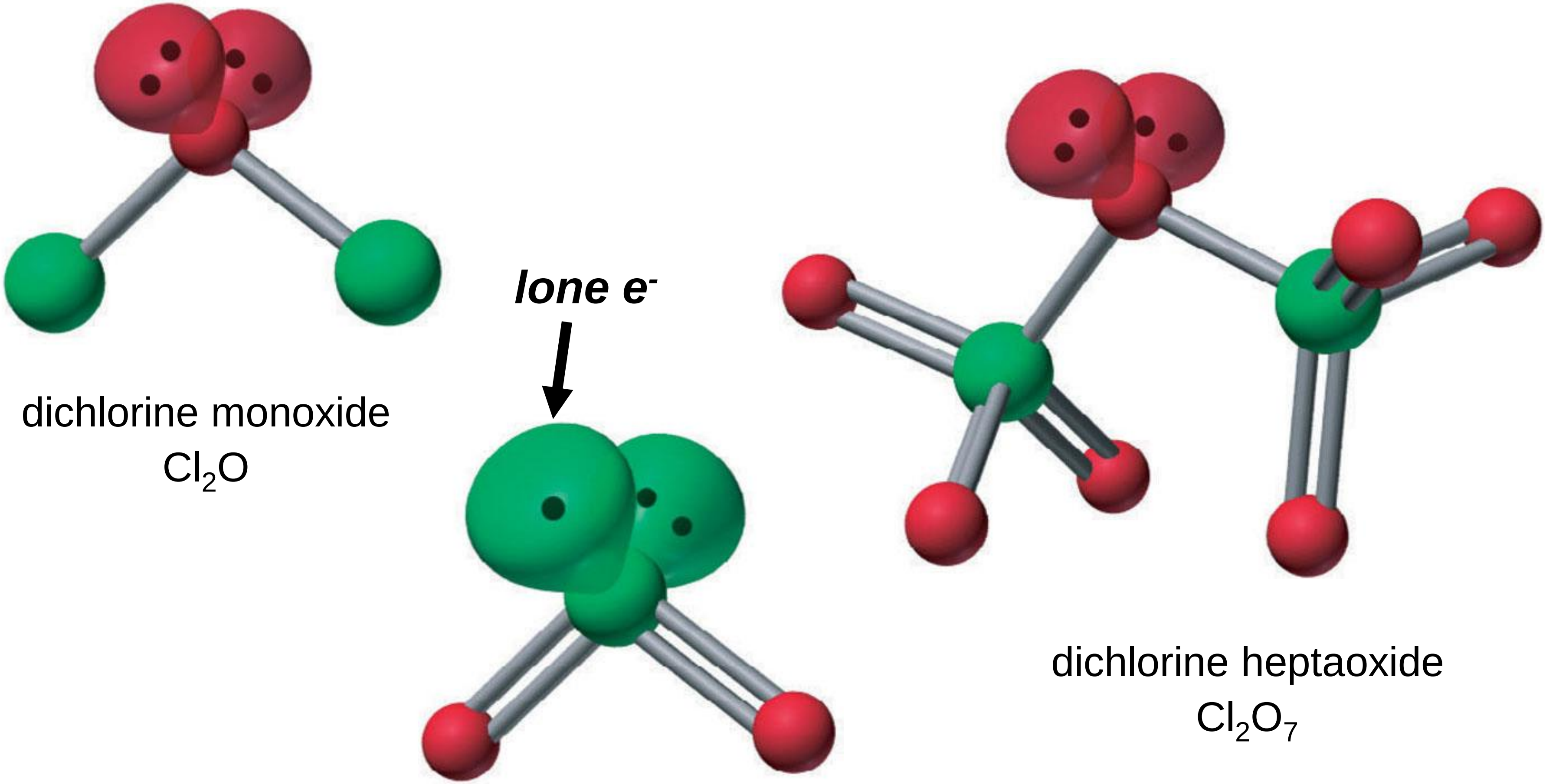
BrF_5

Square pyramidal, XY_5

IF_7

Pentagonal bipyramidal, XY_7

Figure 14.25 Chlorine oxides.

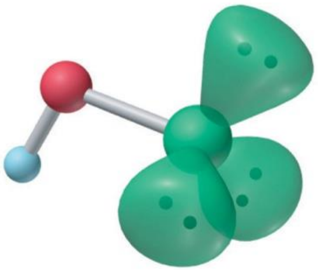
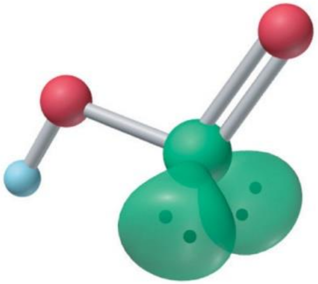
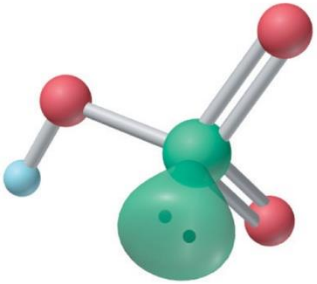
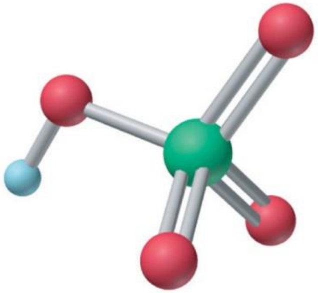


dichlorine monoxide
Cl_2O

chlorine dioxide
ClO_2

dichlorine heptaoxide
Cl_2O_7

Table 14.4 The Known Halogen Oxoacids*

Central Atom	Hypohalous Acid (HOX)	Halous Acid (HOXO)	Halic Acid ($HOXO_2$)	Perhalic Acid ($HOXO_3$)
				
Fluorine	HOF	—	—	—
Chlorine	HOCl	HOClO	$HOClO_2$	$HOClO_3$
Bromine	HOBr	(HOBrO)?	$HOBrO_2$	$HOBrO_3$
Iodine	HOI	—	$HOIO_2$	$HOIO_3$, $(HO)_5IO$
Oxoanion	Hypohalite	Halite	Halate	Perhalate

*Lone pairs are shown only on the halogen atom, and each atom has its lowest formal charge.

Relative Strength of Halogen Oxoacids

The relative strength of halogen oxoacids depends on both the ***electronegativity*** and the ***oxidation state*** of the halogen.

For oxoacids with the halogen in the same oxidation state, acid strength ***decreases*** as the halogen EN ***decreases***.

$$HOClO_2 > HOBrO_2 > HOIO_2$$

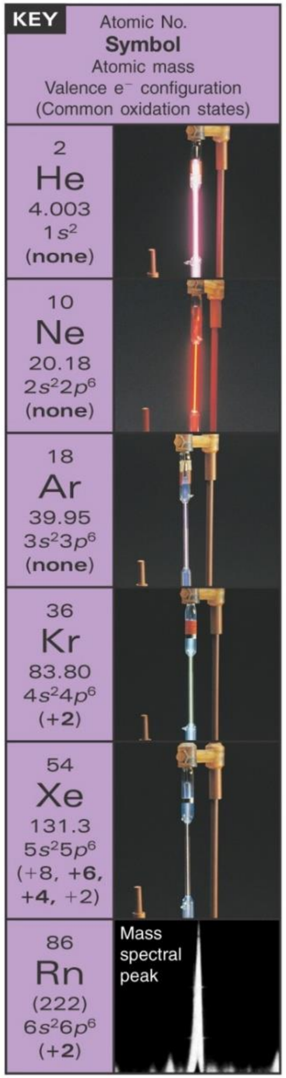
For oxoacids of a given halogen, acid strength ***decreases*** as the oxidation state of the halogen ***decreases.***

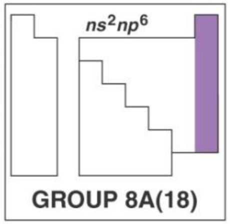
$$HOClO_3 > HOClO_2 > HOClO$$

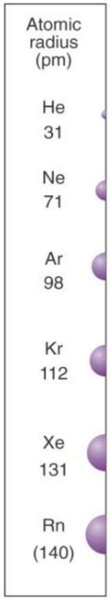
Group 8A(18): The Noble Gases

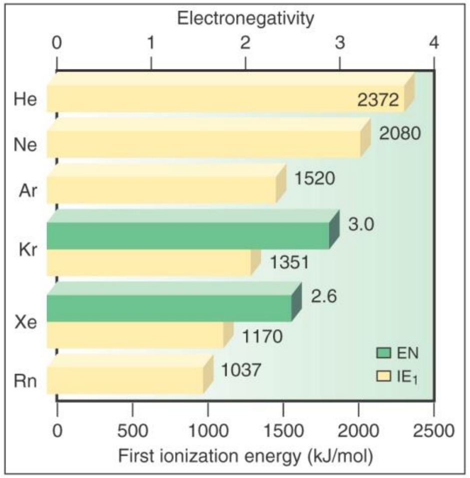
Family Portrait

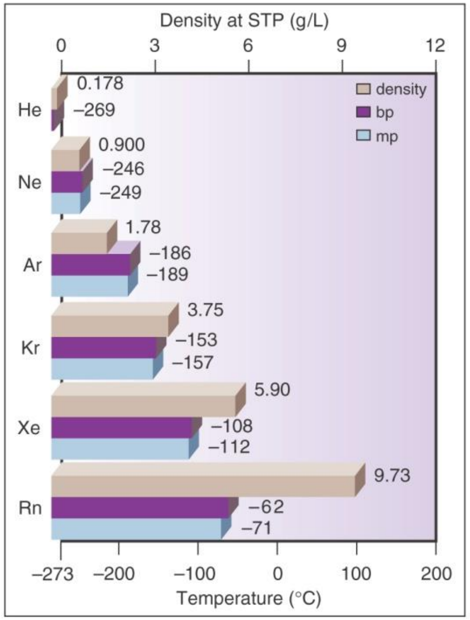
KEY ATOMIC PROPERTIES, PHYSICAL PROPERTIES, AND REACTIONS











Noble Gases

- Noble gases have a full valence shell.
- The noble gases are the smallest elements in their respective periods, with the highest ionization energies.
- Atomic size increases down the group and IE decreases.
- Noble gases have very low melting and boiling points.
- Only Kr, Xe, and Rn are known to form compounds.
  - Xe is the most reactive noble gas and exhibits all even oxidation states from +2 to +8.

Figure 14.26 Crystals of xenon tetrafluoride (Xe(F_4).