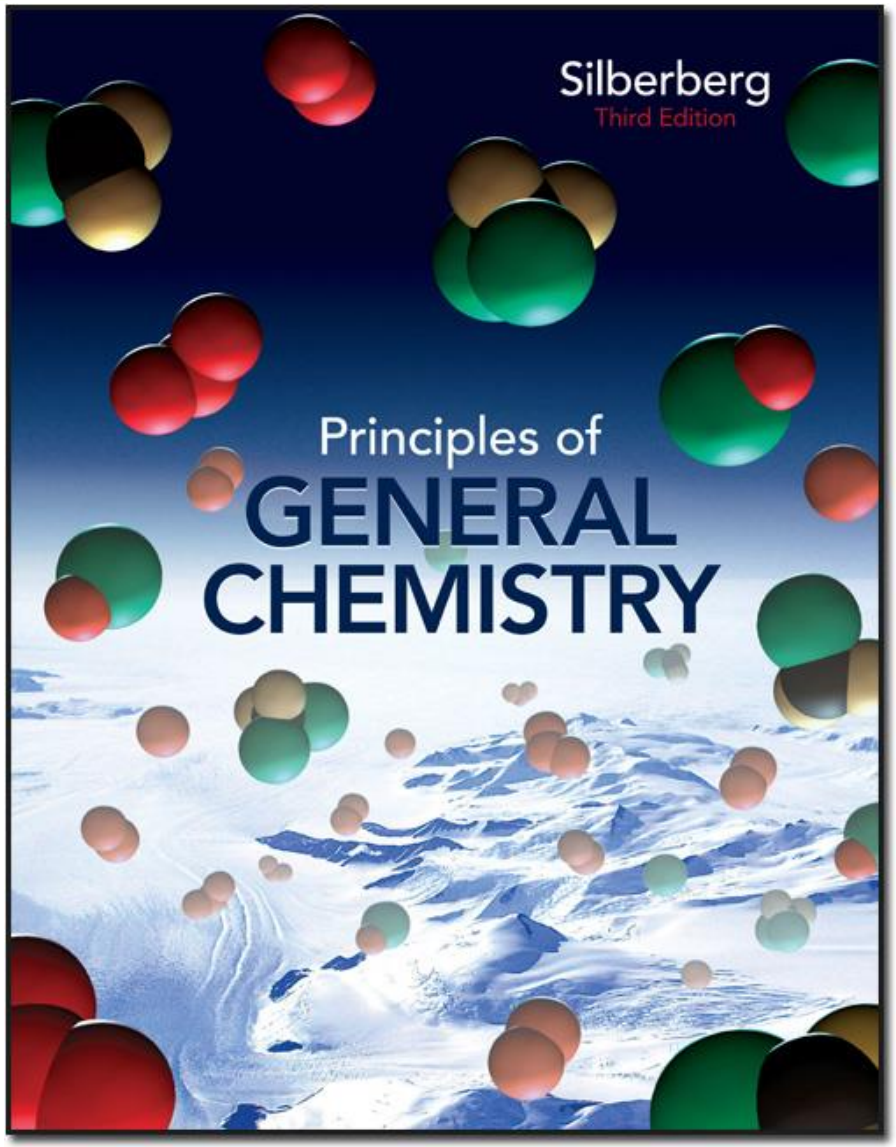

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CHEM 141

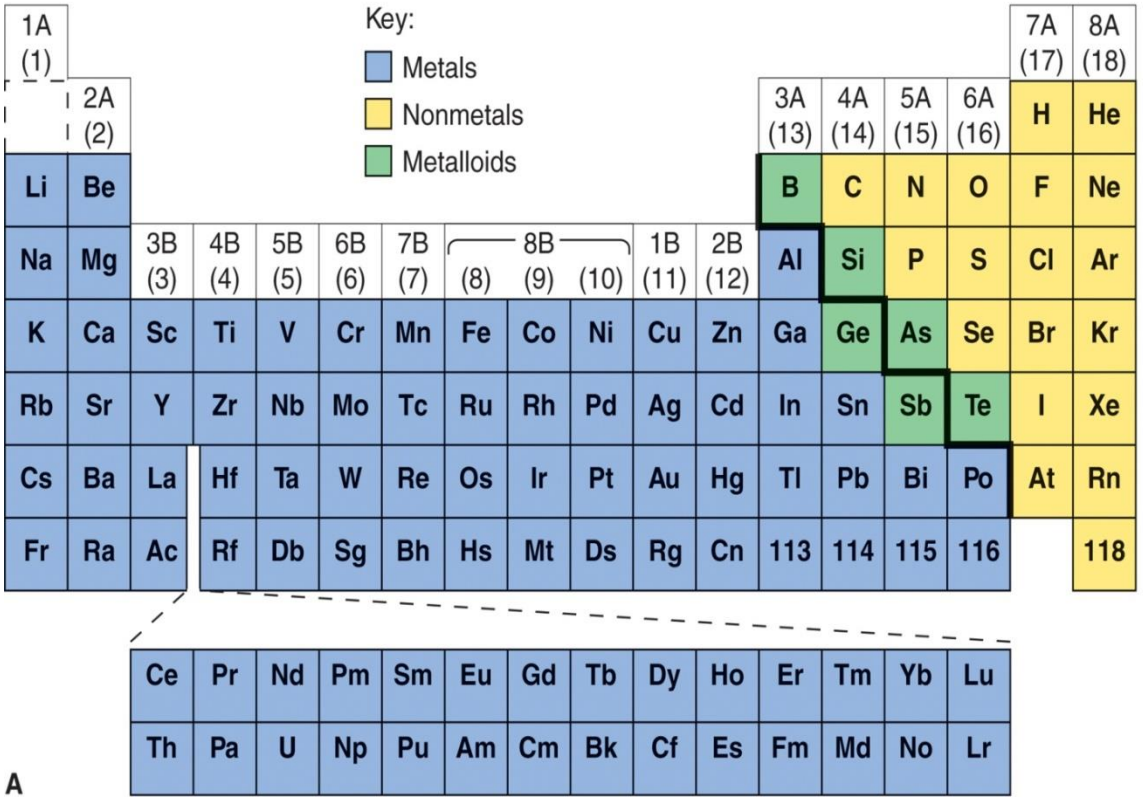
Chapter 9

Chapter 9

Models of Chemical Bonding

Models of Chemical Bonding

Figure 9.1 A comparison of metals and nonmetals.



B

PROPERTY	METAL ATOM	NONMETAL ATOM
Atomic size	Larger	Smaller
Z_{eff}	Lower	Higher
IE	Lower	Higher
EA	Less negative	More negative

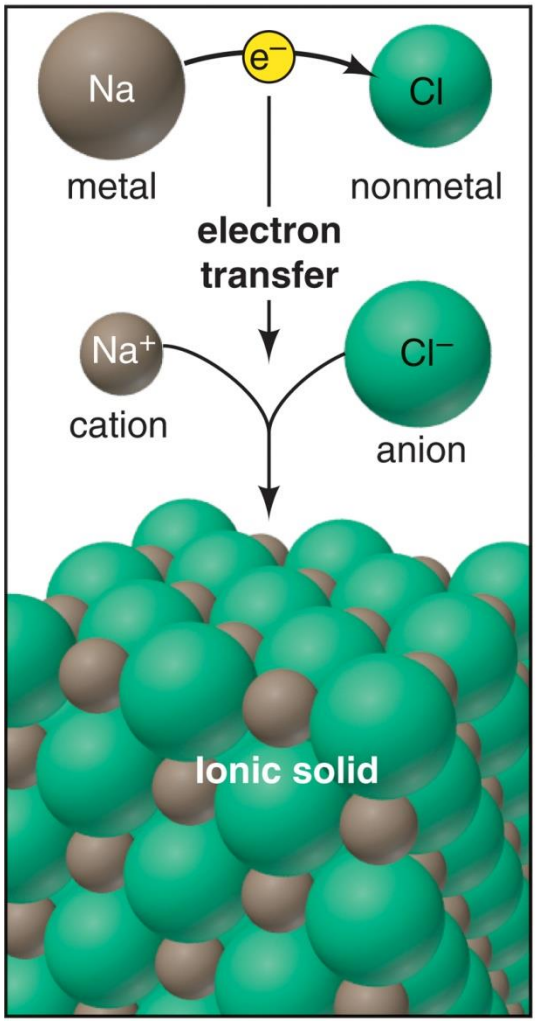
Types of Chemical Bonding

Ionic bonding involves the ***transfer*** of electrons and is usually observed when a ***metal*** bonds to a ***nonmetal***.

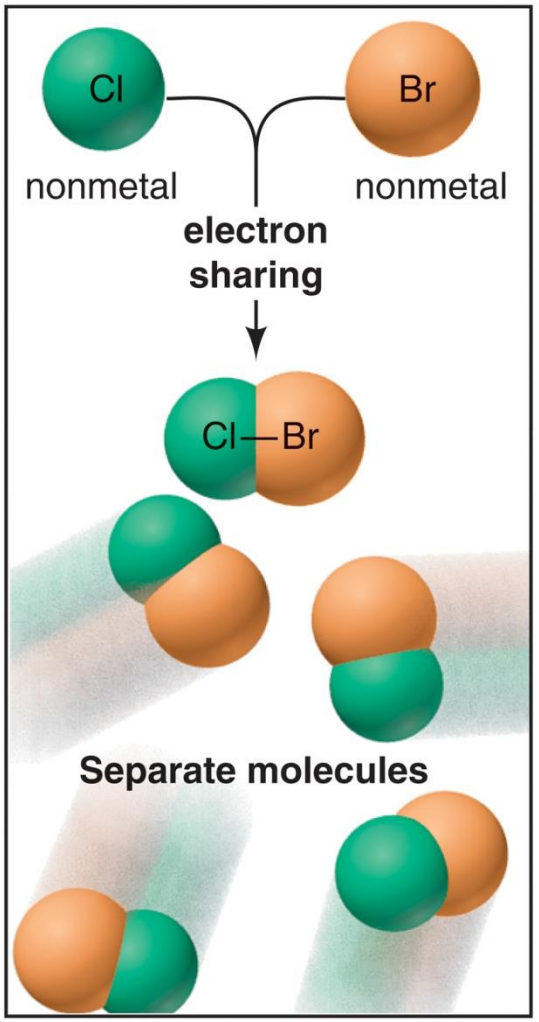
Covalent bonding involves the ***sharing*** of electrons and is usually observed when a ***nonmetal*** bonds to a ***nonmetal***.

Metallic bonding involves ***electron pooling*** and occurs when a ***metal*** bonds to another ***metal***.

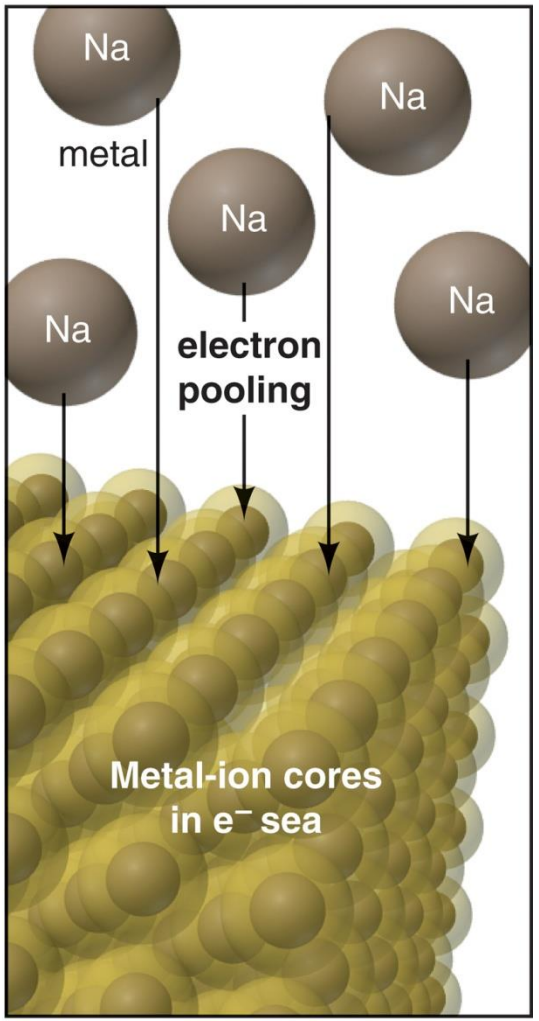
Figure 9.2 Three models of chemical bonding.



A Ionic bonding

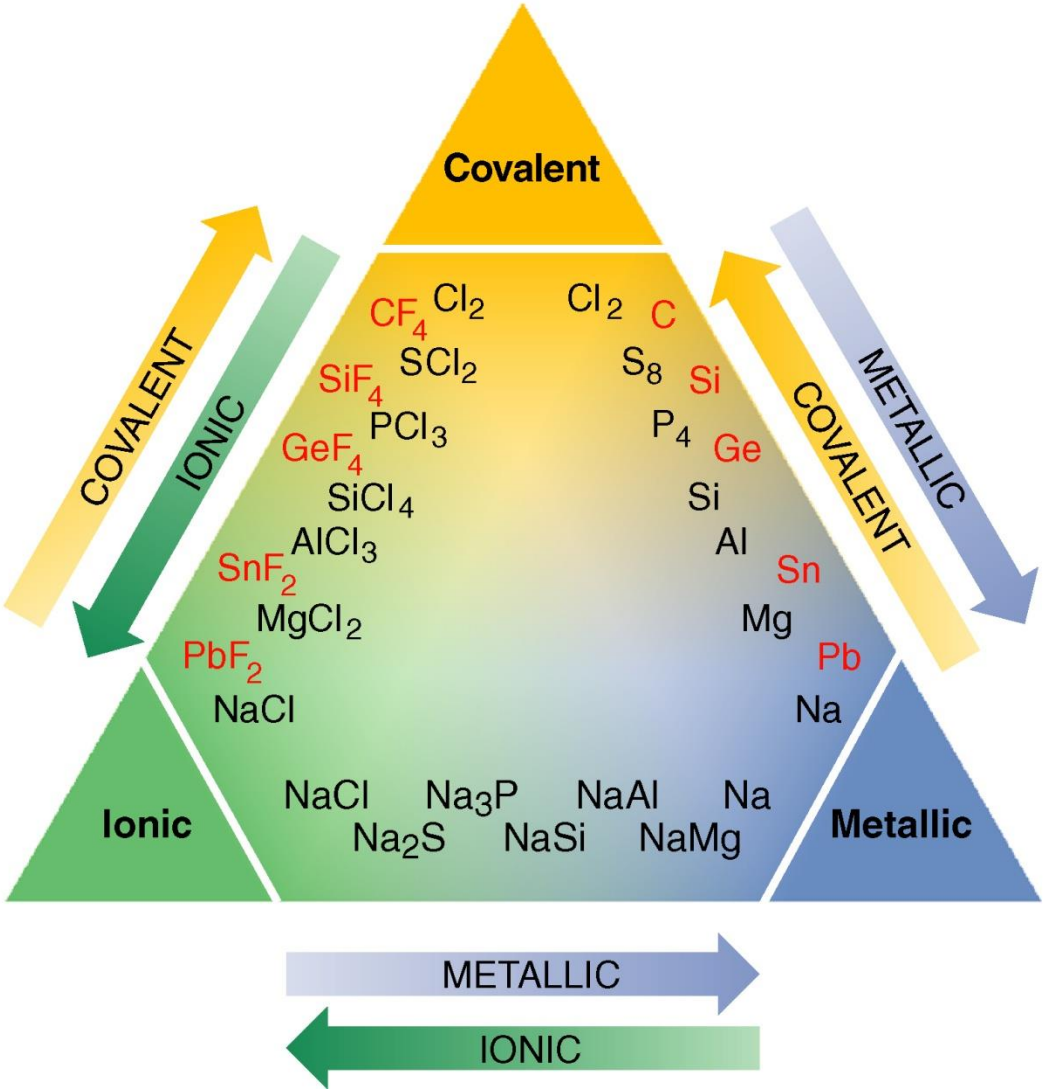


B Covalent bonding



C Metallic bonding

Figure 9.3 **Gradations in bond type among Period 3 (*black type*) and Group 4A (*red type*) elements.**



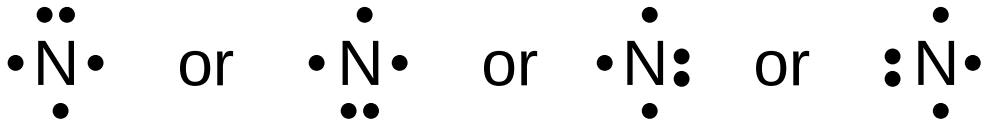
Lewis Electron-Dot Symbols

To draw the Lewis symbol for any main-group element:

- Note the A-group number, which gives the number of valence electrons.
- Place one dot at a time on each of the four sides of the element symbol.
- Keep adding dots, pairing them, until all are used up.

Example:

Nitrogen, N, is in Group 5A and therefore has 5 valence electrons.



Lewis Symbols and Bonding

For a ***metal***, the ***total*** number of dots in the Lewis symbol is the number of electrons the atom loses to form a cation.

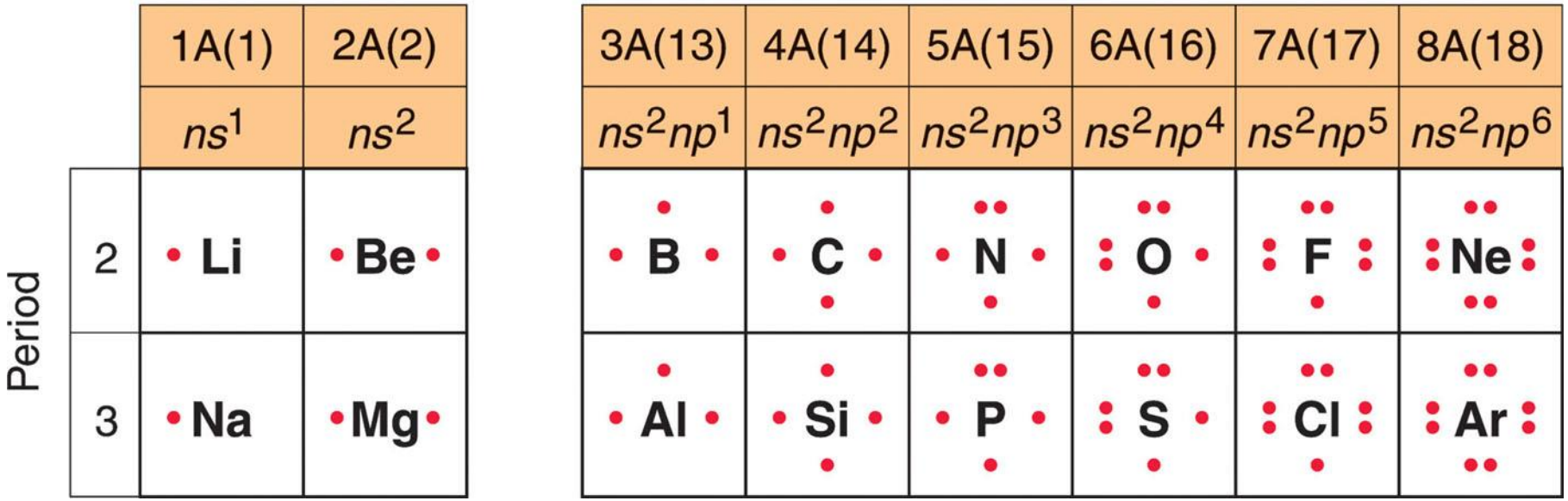
For a ***nonmetal***, the number of unpaired dots equals

- the number of electrons the atom ***gains*** to form an anion
- or the number it ***shares*** to form covalent bonds.

The ***octet rule*** states that when atoms bond, they lose, gain, or share electrons to attain a ***filled outer level of 8 electrons*** (or 2, for H and Li).

Figure 9.4

Lewis electron-dot symbols for elements in Periods 2 and 3.



The Ionic Bonding Model

An ionic bond is formed when a metal ***transfers*** electrons to a nonmetal to form ***ions***, which attract each other to give a solid compound.

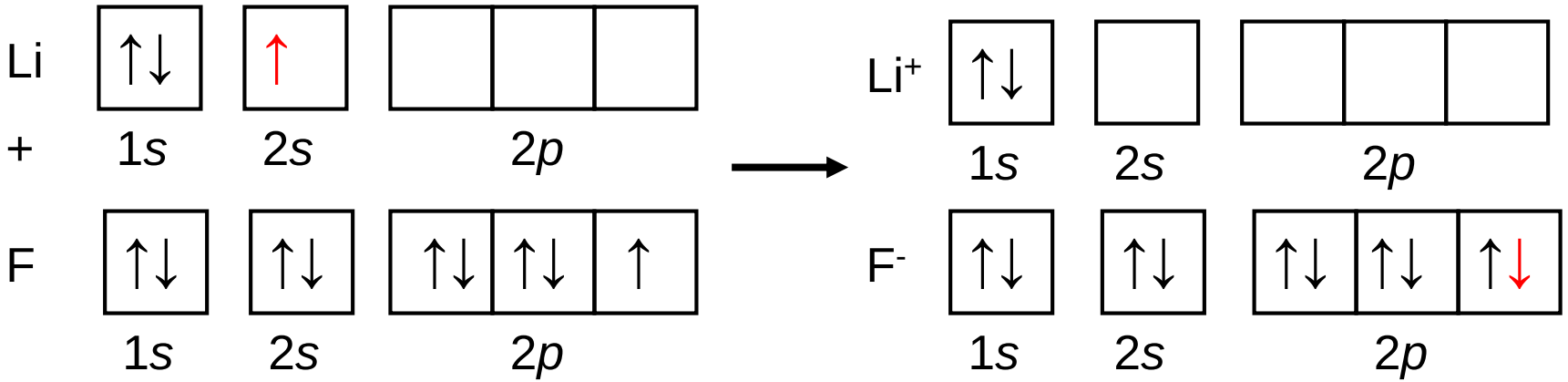
The total number of electrons lost by the metal atom(s) equals the total number of electrons gained by the nonmetal atoms.

Figure 9.5 Three ways to depict electron transfer in the formation of Li^+ and F^-.

Electron configurations

$$Li\ 1s^2 2s^1 + F\ 1s^2 2s^2 2p^5 \longrightarrow Li^+\ 1s^2 + F^-\ 1s^2 2s^2 2p^6$$

Orbital diagrams



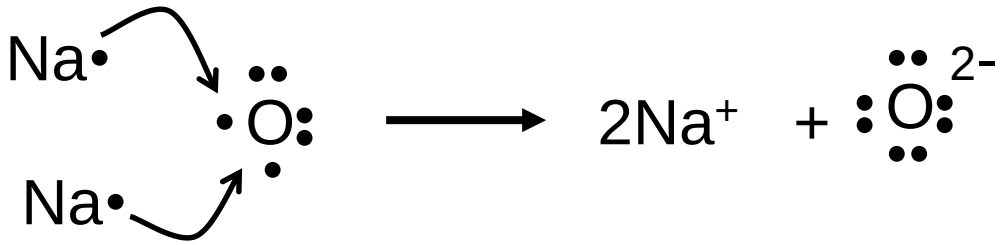
Lewis electron-dot symbols

Sample Problem 9.1 Depicting Ion Formation

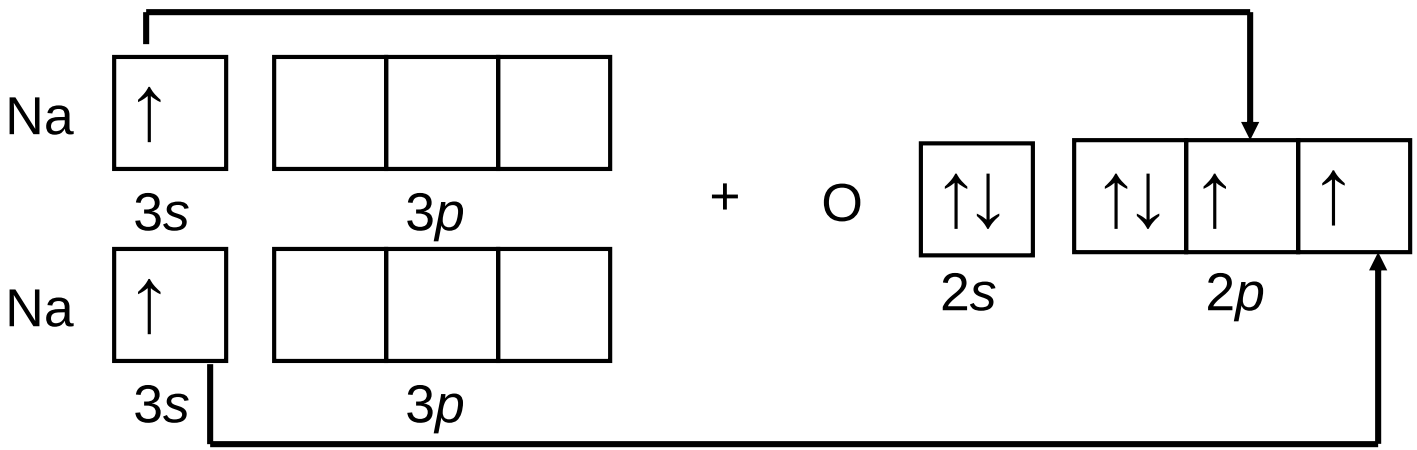
PROBLEM: Use partial orbital diagrams and Lewis symbols to depict the formation of Na^+ and O^{2-} ions from the atoms, and determine the formula of the compound formed.

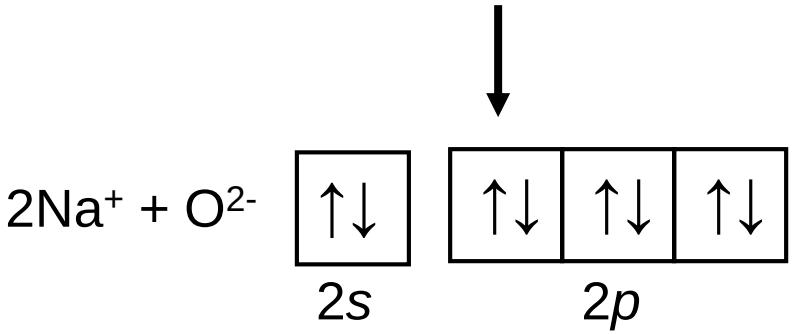
PLAN: Draw orbital diagrams and Lewis symbols for Na and O atoms. To attain filled outer levels, Na loses one electron and O gains two. Two Na atoms are needed for each O atom so that the number of electrons lost equals the number of electrons gained.

SOLUTION:



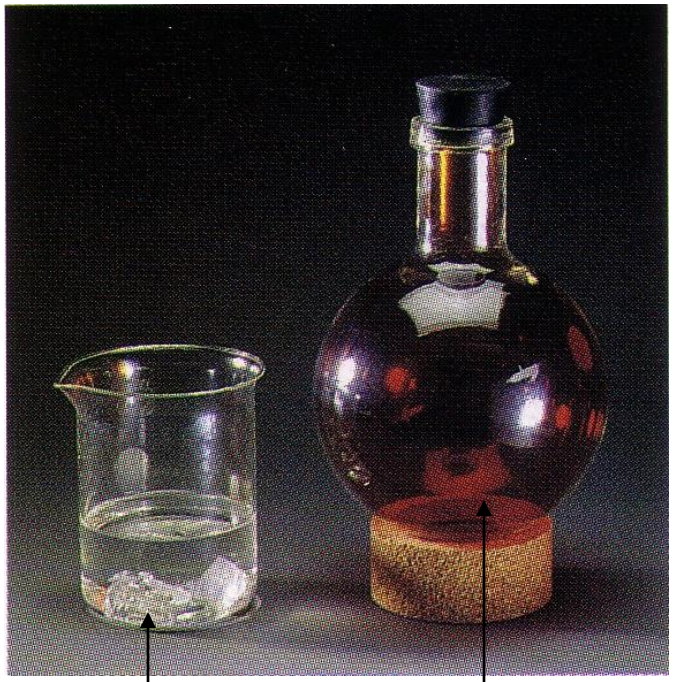
Sample Problem 9.1



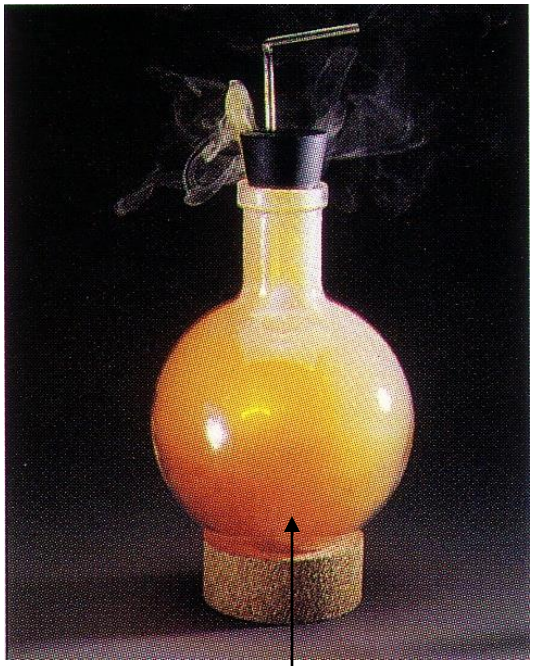


The formula is Na_2O

Figure 9.6 The exothermic formation of sodium bromide.



Na(*s*) $Br_2(l)$



NaBr(*l*)

Periodic Trends in Lattice Energy

Lattice energy is the energy required to separate 1 mol of an ionic solid into gaseous ions.

Lattice energy is a measure of the strength of the ionic bond.

Coloumb's Law

$$\text{Electrostatic energy} \propto \frac{\text{charge A x charge B}}{\text{distance}}$$

$$\text{Electrostatic energy} \propto \frac{\text{cation charge x anion charge}}{\text{cation radius + anion radius}} \propto \Delta H^{o}_{\text{lattice}}$$

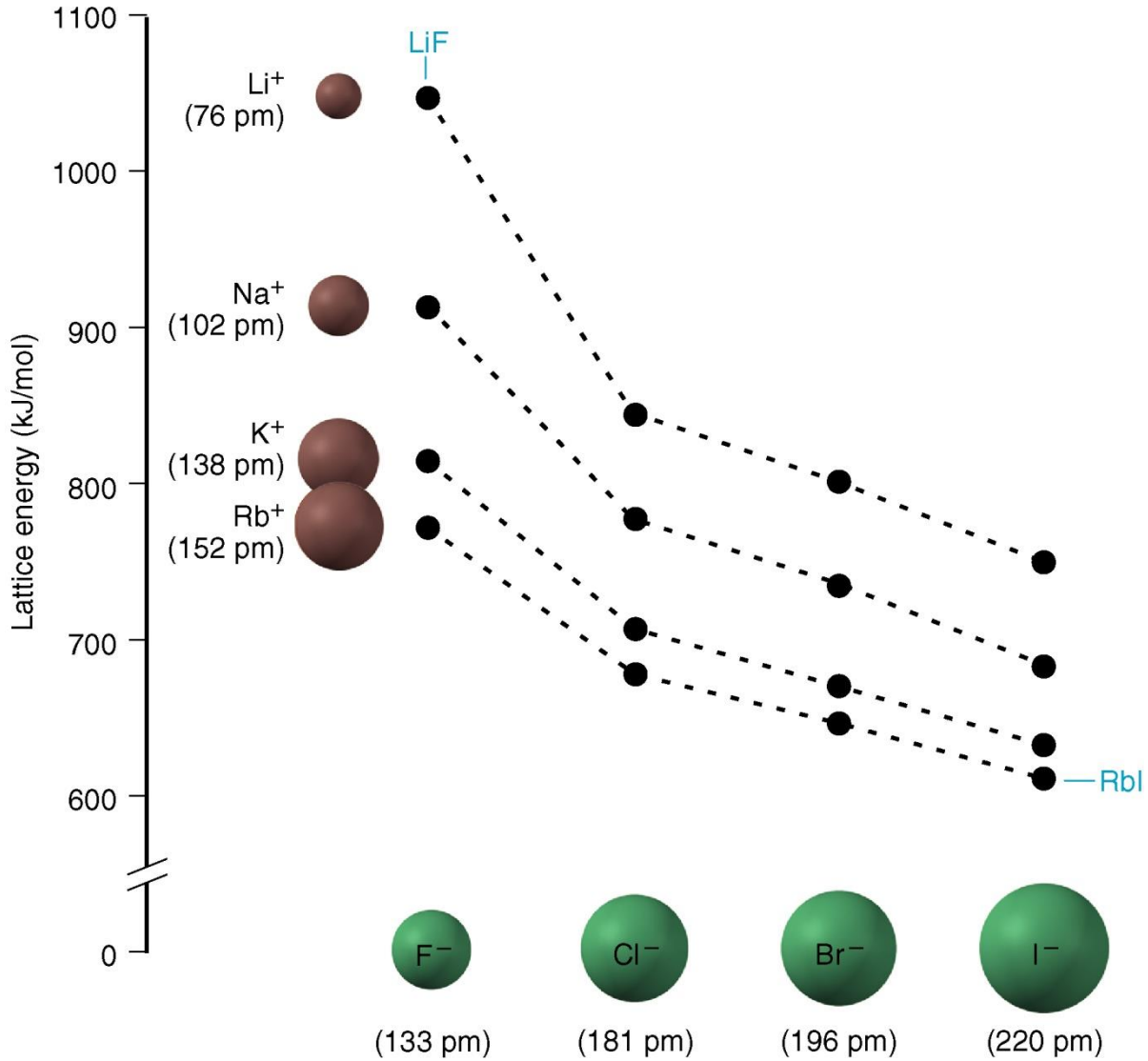
Periodic Trends in Lattice Energy

Lattice energy is affected by ***ionic size*** and ***ionic charge***.

As ionic size ***increases***, lattice energy ***decreases***.
Lattice energy therefore decreases down a group on the periodic table.

As ionic charge ***increases***, lattice energy ***increases***.

Figure 9.7 Trends in lattice energy.

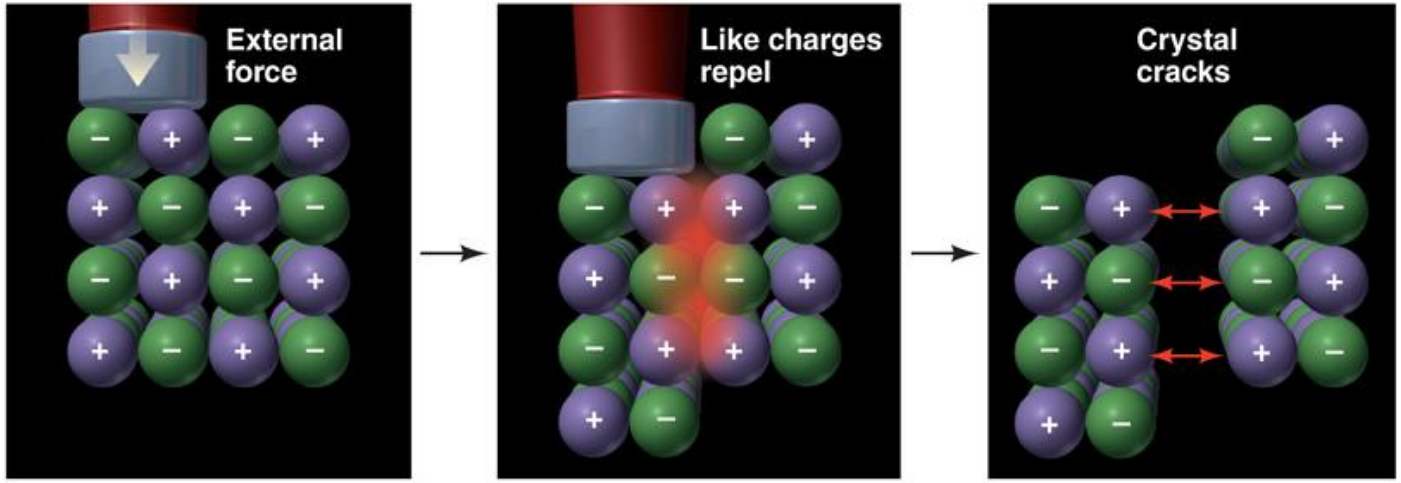


Properties of Ionic Compounds

- Ionic compounds tend to be hard, rigid, and brittle, with high melting points.
- Ionic compounds do not conduct electricity in the solid state.
  - In the solid state, the ions are fixed in place in the lattice and do not move.
- Ionic compounds conduct electricity when melted or dissolved.
  - In the liquid state or in solution, the ions are free to move and carry a current.

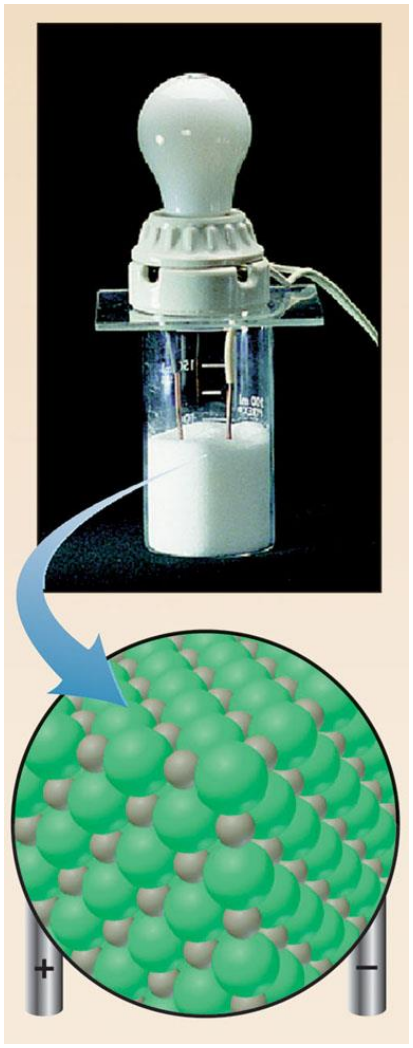
Figure 9.8 Why ionic compounds crack.

A

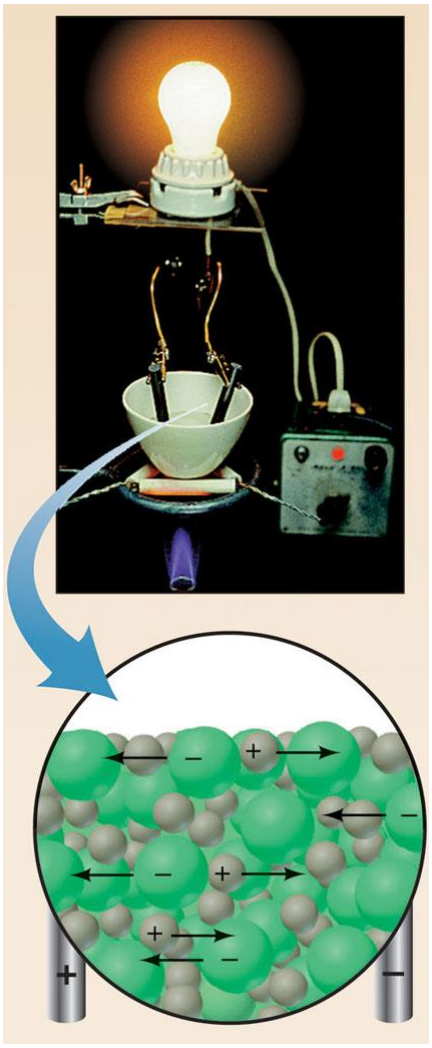


B

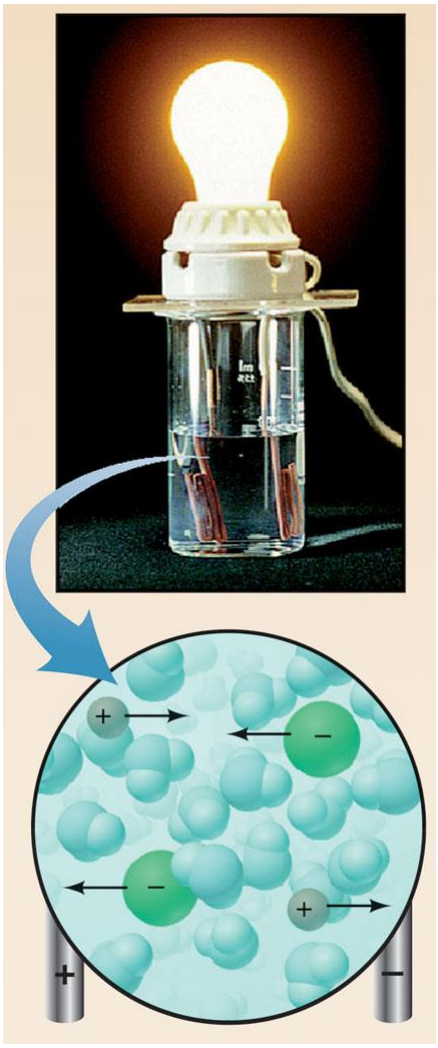
Figure 9.9 **Electrical conductance and ion mobility.**



Solid ionic compound



Molten ionic compound



Ionic compound dissolved in water

Table 9.1 Melting and Boiling Points of Some Ionic Compounds

Compound	mp (°C)	bp (°C)
CsBr	636	1300
NaI	661	1304
$MgCl_2$	714	1412
KBr	734	1435
$CaCl_2$	782	>1600
NaCl	801	1413
LiF	845	1676
KF	858	1505
MgO	2852	3600

Figure 9.10 Covalent bond formation in H_2.

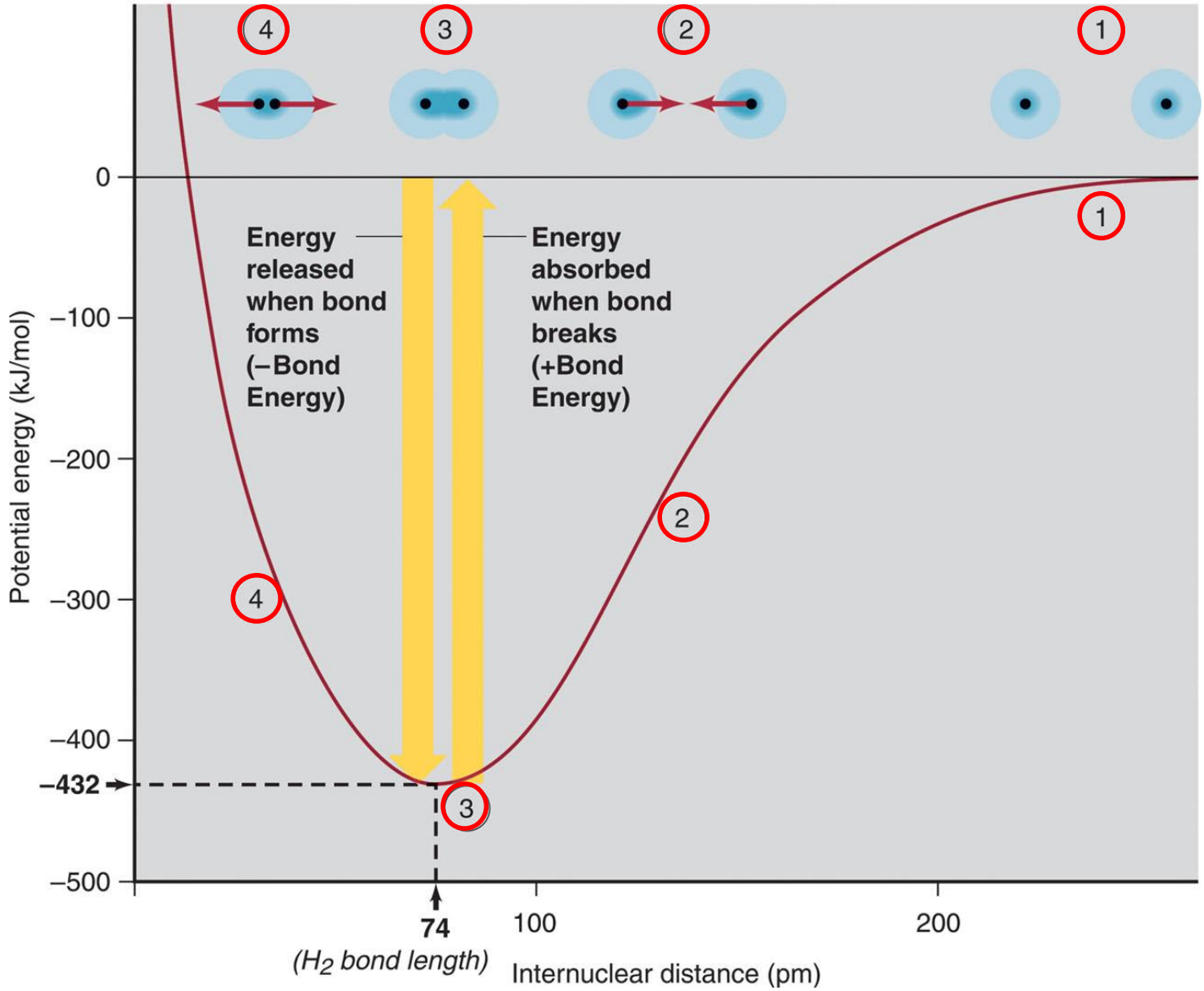
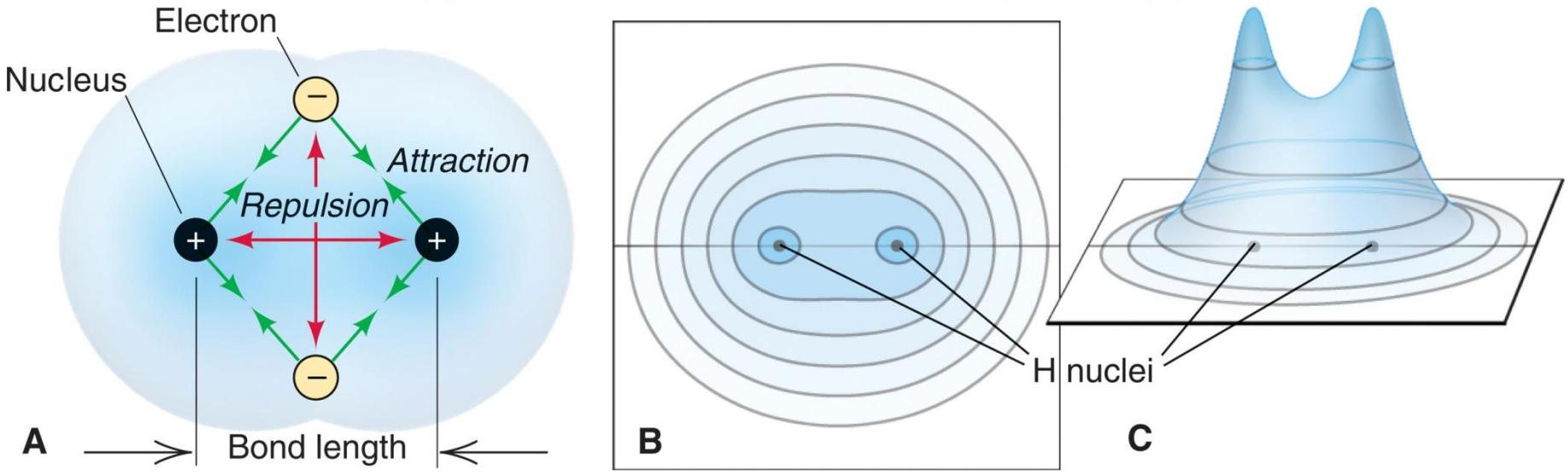


Figure 9.11 Distribution of electron density in H_2.



At some distance (bond length), attractions balance repulsions.

Electron density is high around and between the nuclei.

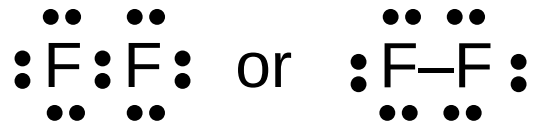
Bonding Pairs and Lone Pairs

Atoms share electrons to achieve a full outer level of electrons. The shared electrons are called a ***shared pair*** or ***bonding pair***.

The shared pair is represented as a pair of dots or a line:

H:H or H–H

An outer-level electron pair that is not involved in bonding is called a ***lone pair***, or ***unshared pair***.



Properties of a Covalent Bond

The ***bond order*** is the number of electron pairs being shared by a given pair of atoms.

A single bond consists of one bonding pair and has a bond order of 1.

The ***bond energy*** (BE) is the energy needed to overcome the attraction between the nuclei and the shared electrons. The ***stronger*** the bond the ***higher*** the bond energy.

The ***bond length*** is the distance between the nuclei of the bonded atoms.

Trends in bond order, energy, and length

For a given pair of atoms, a ***higher bond order*** results in a ***shorter bond length*** and ***higher bond energy***.

For a given pair of atoms, a shorter bond is a stronger bond.

Bond length ***increases*** down a group in the periodic table and ***decreases*** across the period.

Bond energy shows the opposite trend.

Table 9.2 Average Bond Energies (kJ/mol) and Bond Lengths (pm)

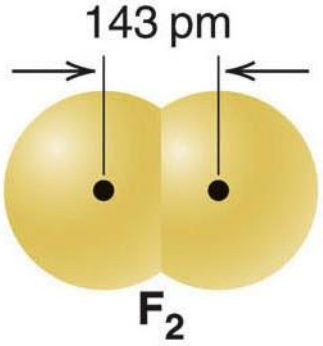
Bond	Energy	Length	Bond	Energy	Length	Bond	Energy	Length	Bond	Energy	Length
Single Bonds											
H—H	432	74	N—H	391	101	Si—H	323	148	S—H	347	134
H—F	565	92	N—N	160	146	Si—Si	226	234	S—S	266	204
H—Cl	427	127	N—P	209	177	Si—O	368	161	S—F	327	158
H—Br	363	141	N—O	201	144	Si—S	226	210	S—Cl	271	201
H—I	295	161	N—F	272	139	Si—F	565	156	S—Br	218	225
			N—Cl	200	191	Si—Cl	381	204	S—I	~170	234
C—H	413	109	N—Br	243	214	Si—Br	310	216			
C—C	347	154	N—I	159	222	Si—I	234	240	F—F	159	143
C—Si	301	186							F—Cl	193	166
C—N	305	147	O—H	467	96	P—H	320	142	F—Br	212	178
C—O	358	143	O—P	351	160	P—Si	213	227	F—I	263	187
C—P	264	187	O—O	204	148	P—P	200	221	Cl—Cl	243	199
C—S	259	181	O—S	265	151	P—F	490	156	Cl—Br	215	214
C—F	453	133	O—F	190	142	P—Cl	331	204	Cl—I	208	243
C—Cl	339	177	O—Cl	203	164	P—Br	272	222	Br—Br	193	228
C—Br	276	194	O—Br	234	172	P—I	184	246	Br—I	175	248
C—I	216	213	O—I	234	194				I—I	151	266
Multiple Bonds											
C=C	614	134	N=N	418	122	C≡C	839	121	N≡N	945	110
C=N	615	127	N=O	607	120	C≡N	891	115	N≡O	631	106
C=O	745 (799 in CO_2)	123	O_2	498	121	C≡O	1070	113			

Table 9.3 The Relation of Bond Order, Bond Length, and Bond Energy

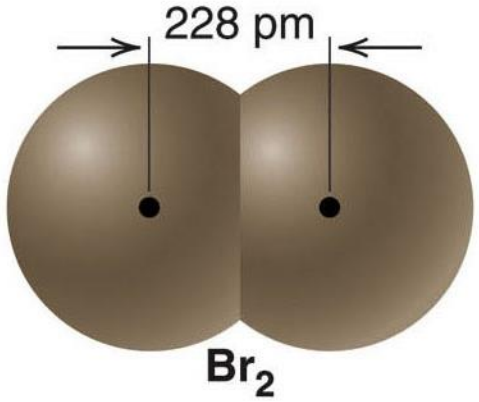
Bond	Bond Order	Average Bond Length (pm)	Average Bond Energy (kJ/mol)
C—O	1	143	358
C═O	2	123	745
C≡O	3	113	1070
C—C	1	154	347
C═C	2	134	614
C≡C	3	121	839
N—N	1	146	160
N═N	2	122	418
N≡N	3	110	945

Figure 9.12 Bond length and covalent radius.

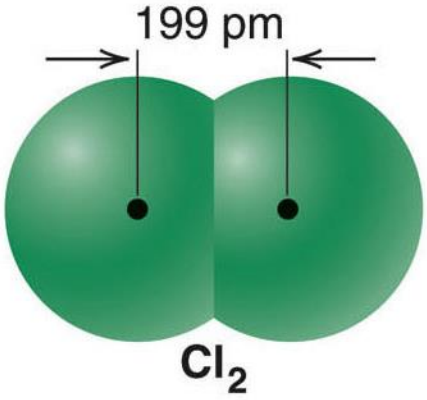
Internuclear distance (bond length)	Covalent radius
143 pm	72 pm



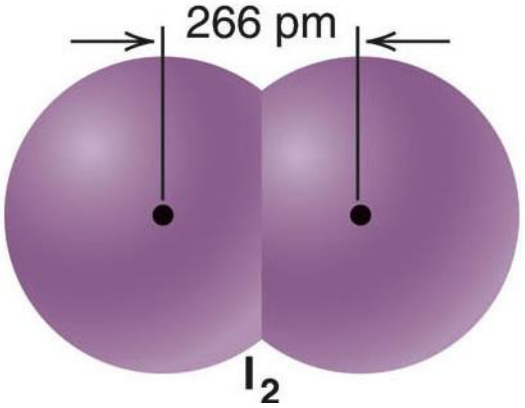
Internuclear distance (bond length)	Covalent radius
228 pm	114 pm



Internuclear distance (bond length)	Covalent radius
199 pm	100 pm



Internuclear distance (bond length)	Covalent radius
266 pm	133 pm



Sample Problem 9.2 Comparing Bond Length and Bond Strength

PROBLEM: Using the periodic table, but not Tables 9.2 or 9.3, rank the bonds in each set in order of *decreasing* bond length and decreasing bond strength:

(a) S–F, S–Br, S–Cl **(b)** C=O, C–O, C≡O

PLAN: (a) S is singly bonded to three different halogen atoms, so the bond order is the same. Bond length increases and bond strength decreases as the atomic radius of the halogen increases.

(b) The same two atoms are bonded in each case, but the bond orders differ. Bond strength increases and bond length decreases as bond order increases.

Sample Problem 9.2

SOLUTION:

(a) Atomic size increases going down a group, so F < Cl < Br.

Bond length: S–Br > S–Cl > S–F

Bond strength: S–F > S–Cl > S–Br

(b) By ranking the bond orders, we get

Bond length: C–O > C=O > C≡O

Bond strength: C≡O > C=O > C–O

Figure 9.13

Strong forces within molecules and weak forces between them.

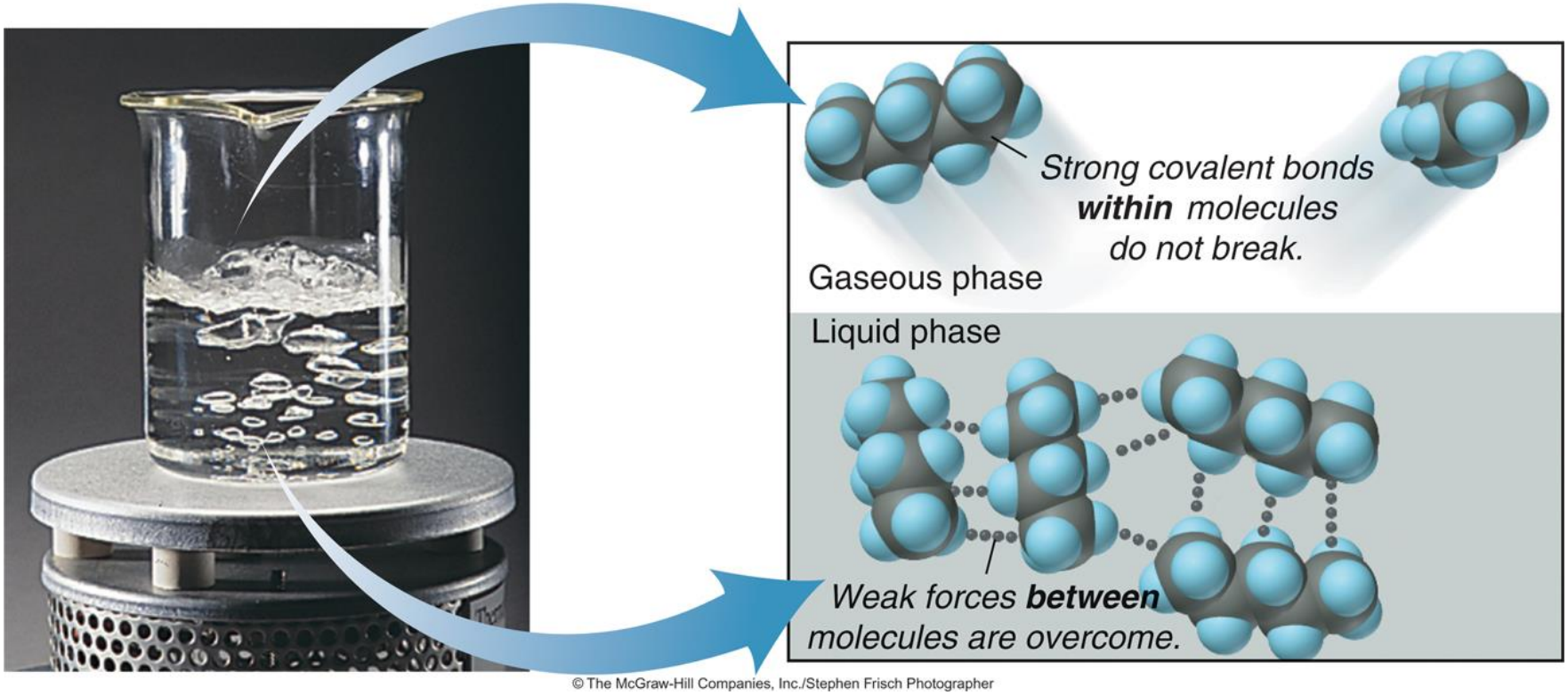


Figure 9.14 **Covalent bonds of network covalent solids: quartz and diamond.**

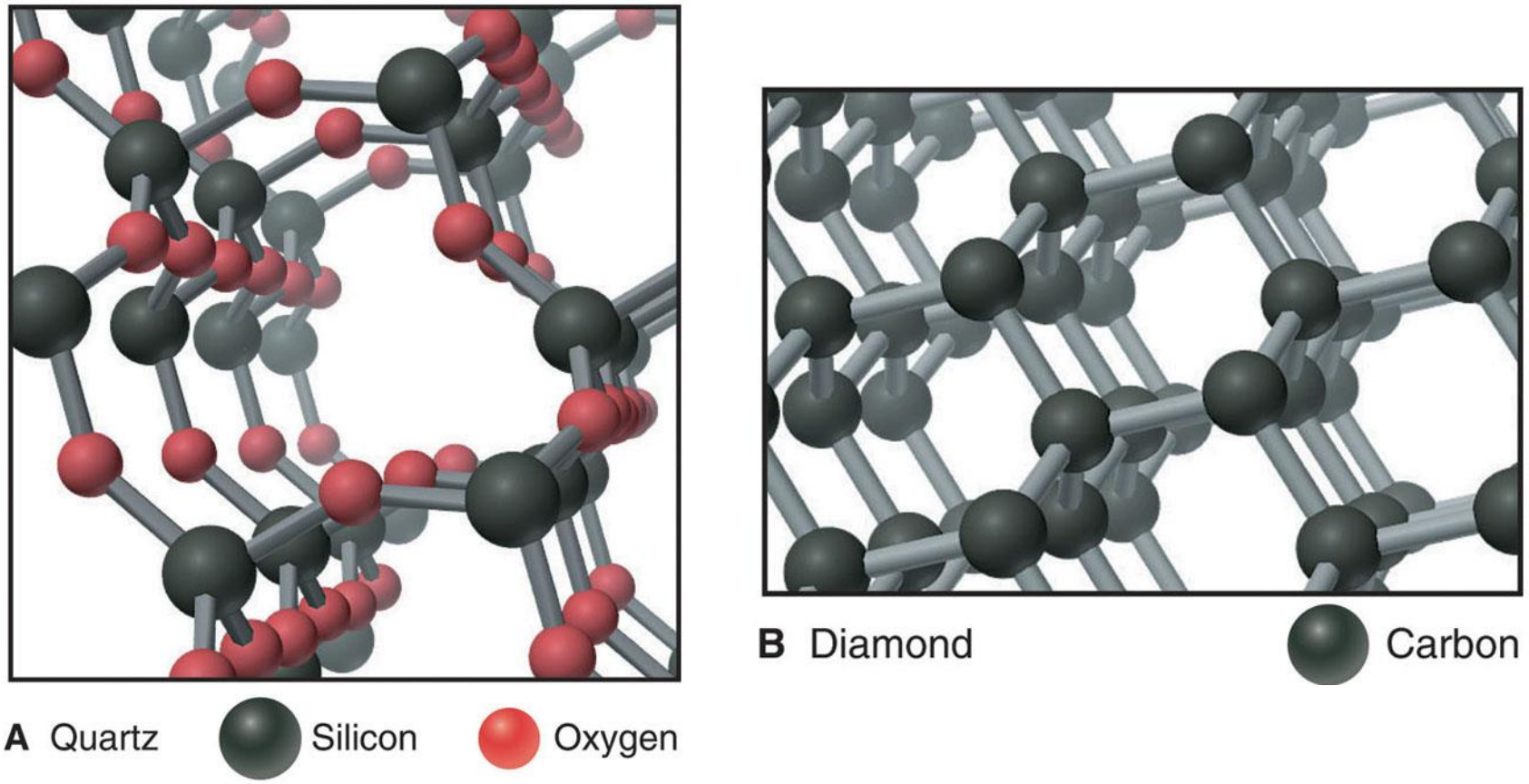
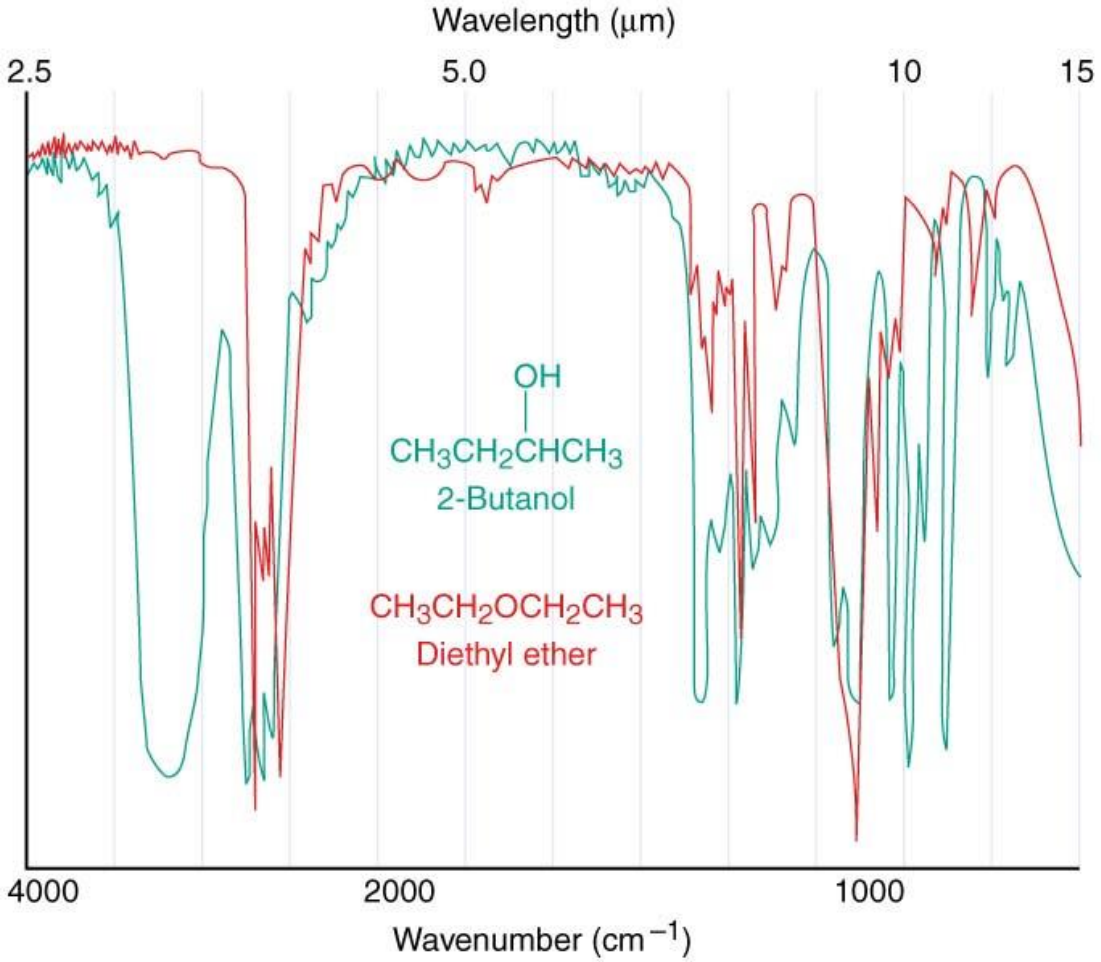


Figure 9.15 **The infrared (IR) spectra of 2-butanol (*green*) and diethyl ether (*red*).**



Bond Energies and ΔH^{o}_{rxn}

The heat released or absorbed during a chemical change is due to differences between the bond energies of reactants and products.

$$\Delta H°_{rxn} = \Sigma \Delta H°_{\text{reactant bonds broken}} + \Sigma \Delta H°_{\text{product bonds formed}}$$

Figure 9.16 **Using bond energies to calculate $\Delta H°_{rxn}$ for HF formation.**

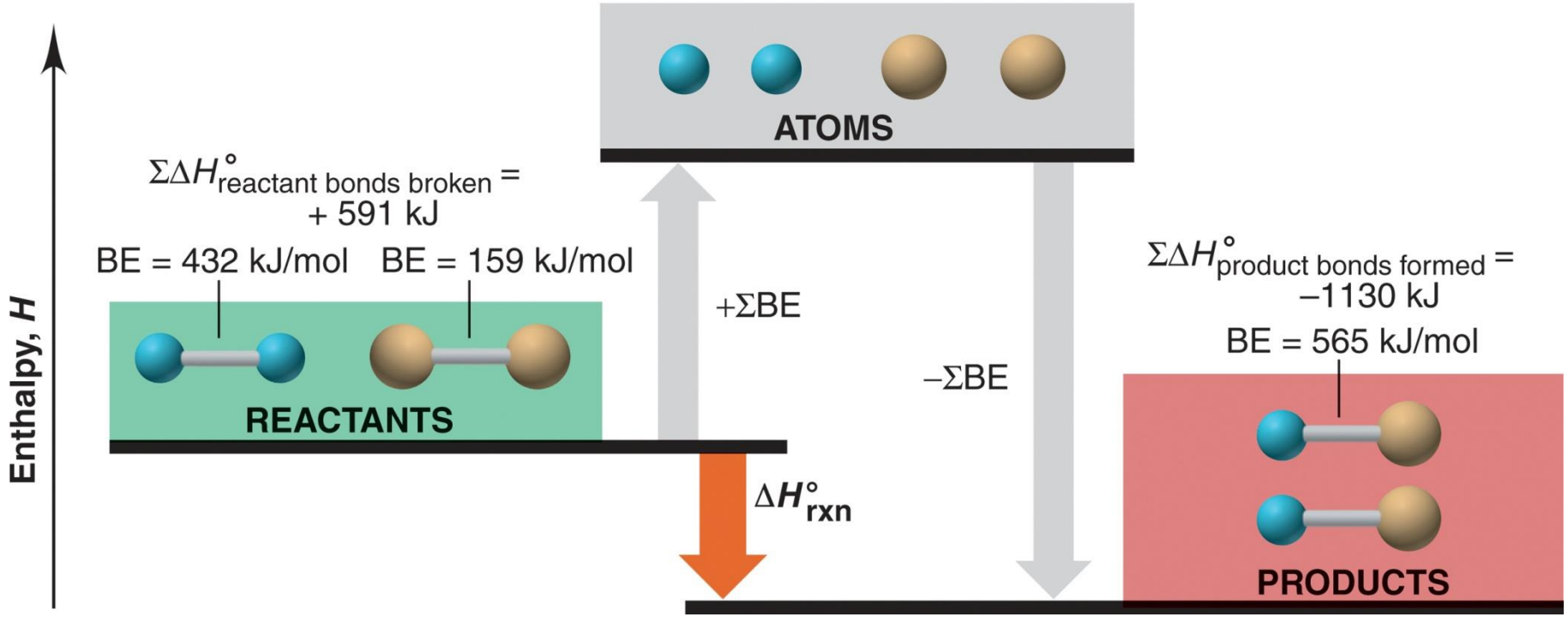
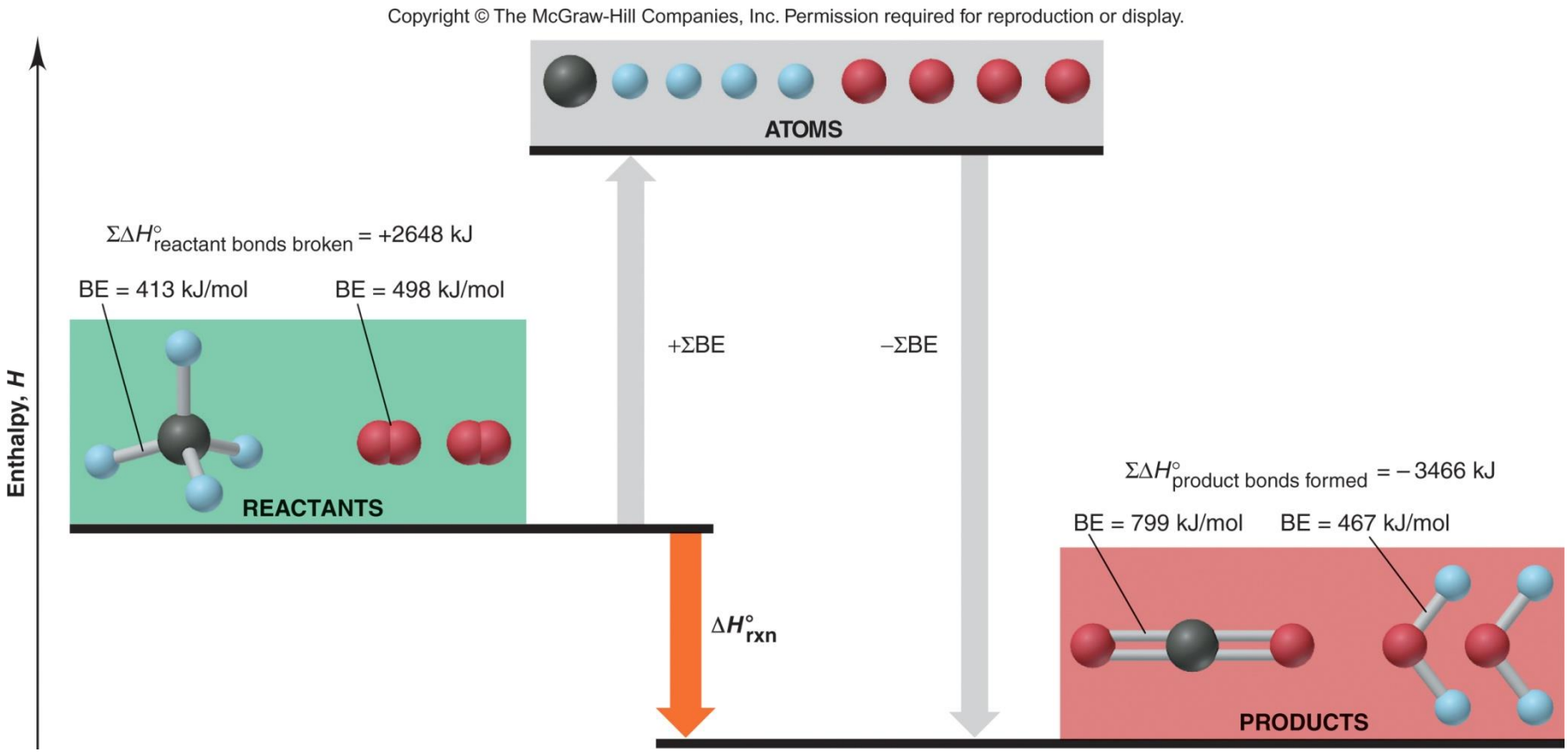


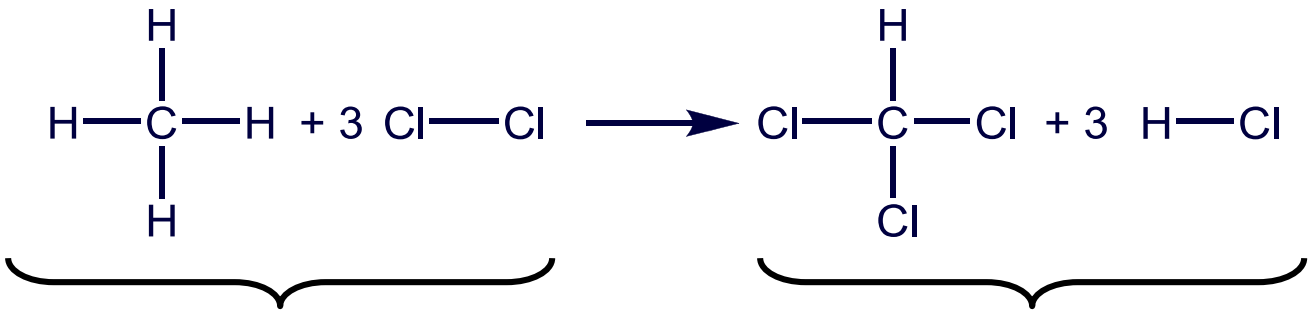
Figure 9.17 **Using bond energies to calculate ΔH°_{rxn} for the combustion of methane.**



Sample Problem 9.3

Using Bond Energies to Calculate $\Delta H°_{rxn}$

PROBLEM: Calculate $\Delta H°_{rxn}$ for the chlorination of methane to form chloroform.



bonds broken
$\Sigma\Delta H°$ positive

bonds formed
$\Sigma\Delta H°$ negative

PLAN: All the reactant bonds break, and all the product bonds form. Find the bond energies in Table 9.2 and substitute the two sums, with correct signs, into Equation 9.2.

Sample Problem 9.3

SOLUTION:

For bonds broken:

4 x C-H = (4 mol)(413 kJ/mol) = 1652 kJ

3 x Cl-Cl = (3 mol)(243 kJ/mol) = 729 kJ

$\Sigma \Delta H^\circ_{\text{bonds broken}}$ = 2381 kJ

For bonds formed:

3 x C-Cl = (3 mol)(-339 kJ/mol) = -1017 kJ

1 x C-H = (1 mol)(-413 kJ/mol) = -413 kJ

3 x H-Cl = (3 mol)(-427 kJ/mol) = -1281 kJ

$\Sigma \Delta H^\circ_{\text{bonds formed}}$ = -2711 kJ

$\Delta H^\circ_{\textbf{reaction}} = \Sigma \Delta H^\circ_{\text{bonds } \textbf{broken}} + \Sigma \Delta H_{\textbf{ bonds formed}}$

= 2381 kJ + (-2711 kJ) = - 330 kJ

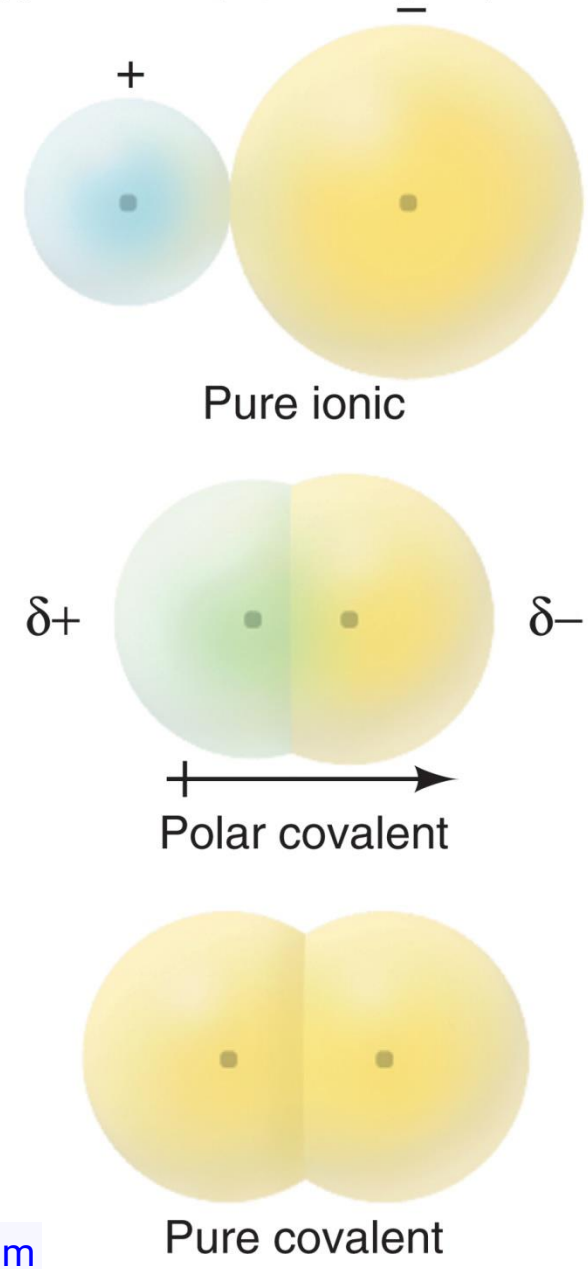
Electronegativity and Bond Polarity

A covalent bond in which the shared electron pair is not shared equally, but remains closer to one atom than the other, is a ***polar covalent bond***.

The ability of an atom in a covalent bond to attract the shared electron pair is called its ***electronegativity***.

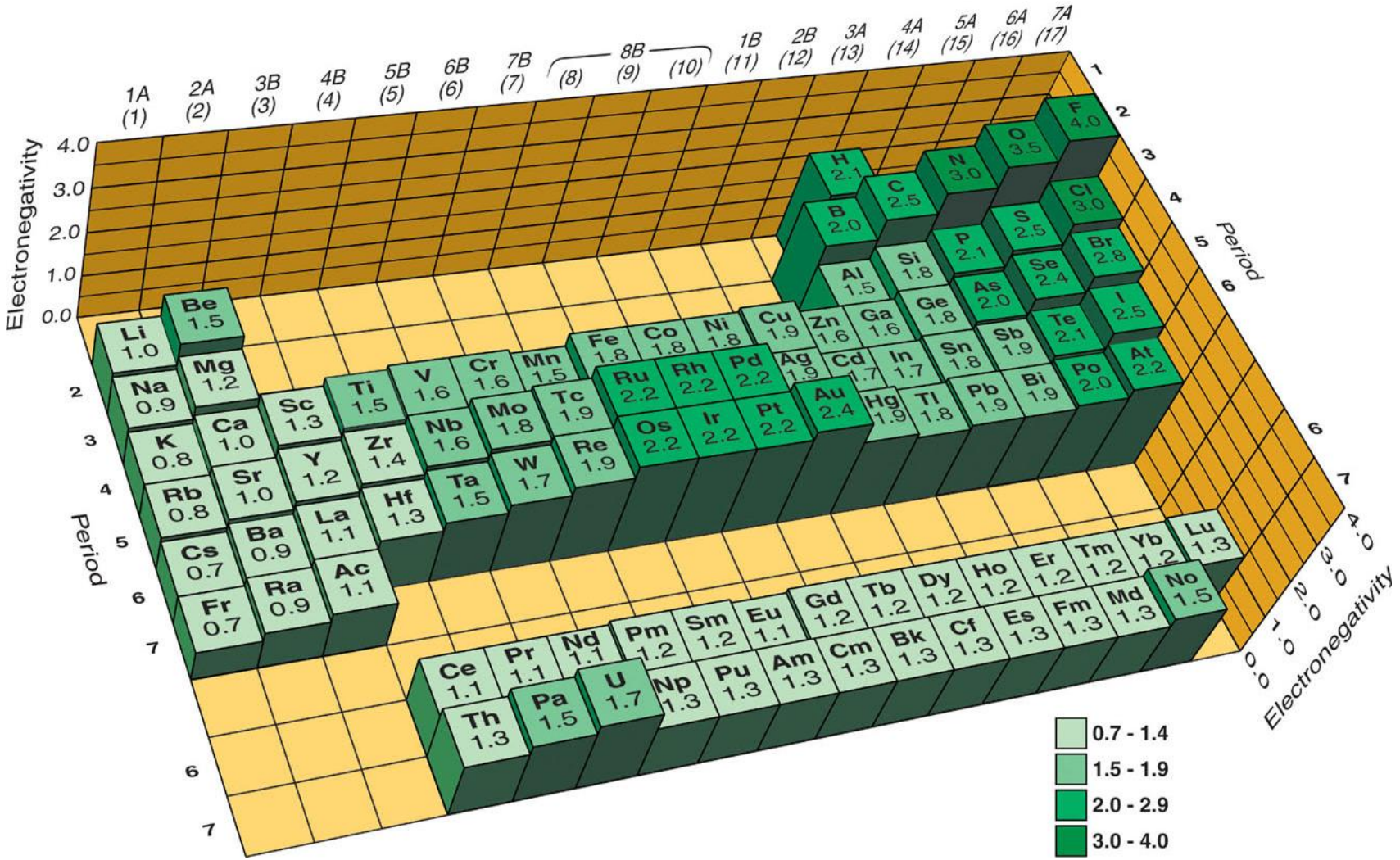
Unequal sharing of electrons causes the more electronegative atom of the bond to be *partially* negative and the less electronegative atom to be *partially* positive.

Figure 9.18 Bonding between the models.



Polar covalent bonds are much more common than either pure ionic or pure covalent bonds.

Figure 9.19 The Pauling electronegativity (EN) scale.



Trends in Electronegativity

The most electronegative element is ***fluorine.***

In general electronegativity ***decreases*** down a group as atomic size ***increases***.

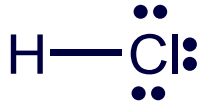
In general electronegativity ***increases*** across a period as atomic size ***decreases***.

Nonmetals are ***more*** electronegative than metals.

Electronegativity and Oxidation Number

Electronegativities can be used to assign oxidation numbers:

- The more electronegative atom is assigned ***all*** the ***shared*** electrons.
- The less electronegative atom is assigned ***none*** of the shared electrons.
- Each atom in a bond is assigned ***all*** of its ***unshared*** electrons.
- O.N. = # of valence e^- – (# of shared e^- + # of unshared e^-)

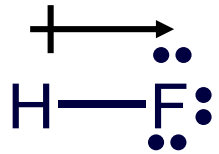
Example: 

Cl is more electronegative than H, so for Cl:
valence e^- = 7
shared e^- = 2
unshared e^- = 6
O.N. = 7 – (2 + 6) = -1

H is less electronegative than Cl, so for H:
valence e^- = 1
shared e^- = 0 (all shared e^- assigned to Cl)
unshared e^- = 0
O.N. = 1 – (0 + 0) = +1

Depicting Polar Bonds

The unequal sharing of electrons can be depicted by a polar arrow. The head of the arrow points to the ***more electronegative element***.



A polar bond can also be marked using δ+ and δ- symbols.

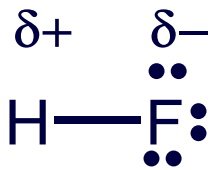
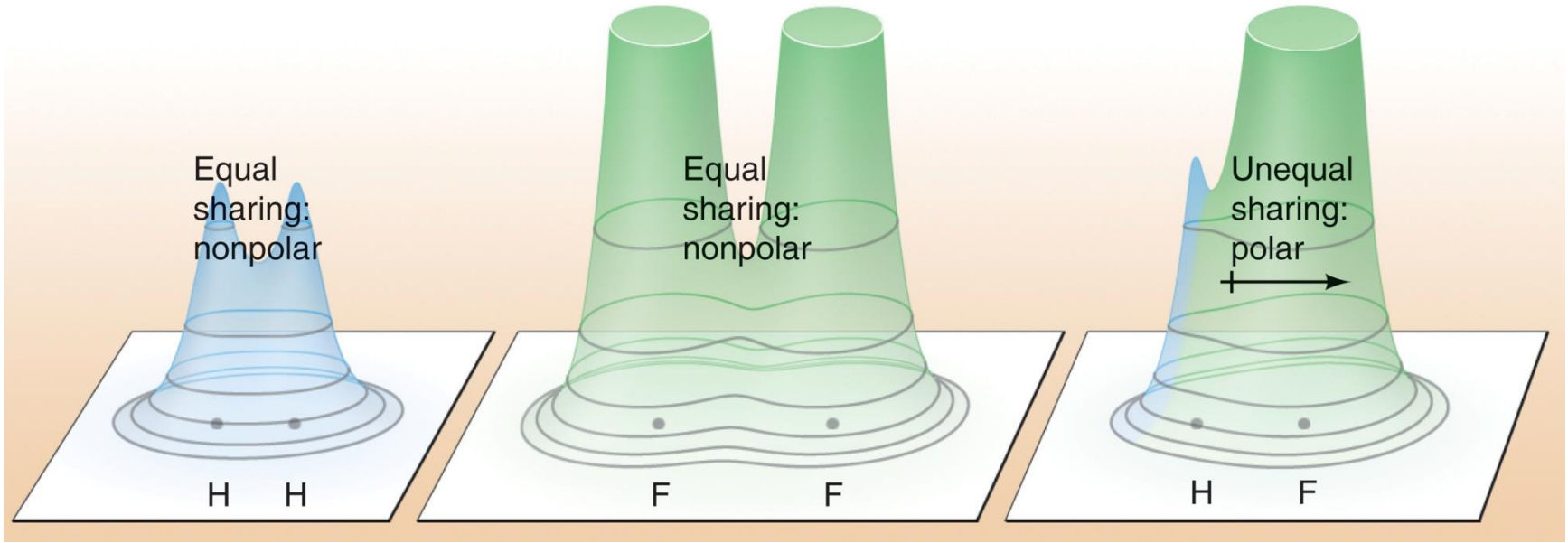


Figure 9.20 Electron density distributions in H_2, F_2, and HF.



In HF, the electron density shifts from H to F.

The H–F bond has partial ionic character.

Figure 9.21 **ΔEN ranges for classifying the partial ionic character of bonds.**

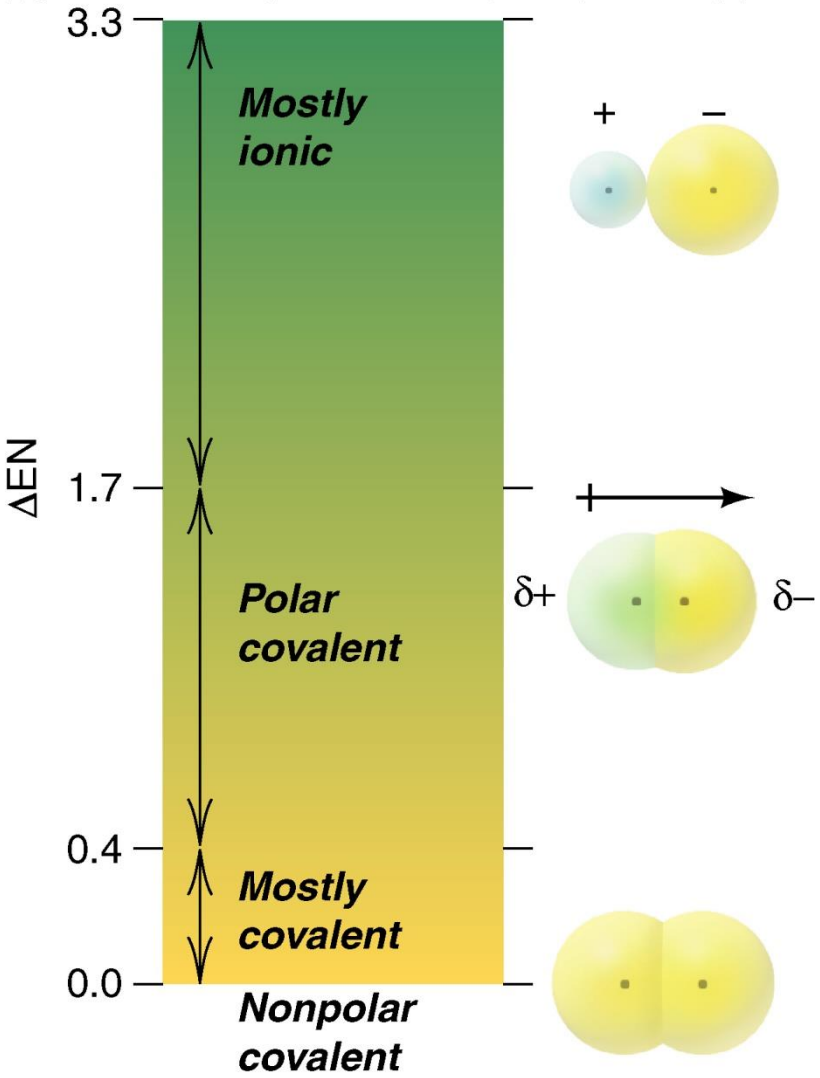
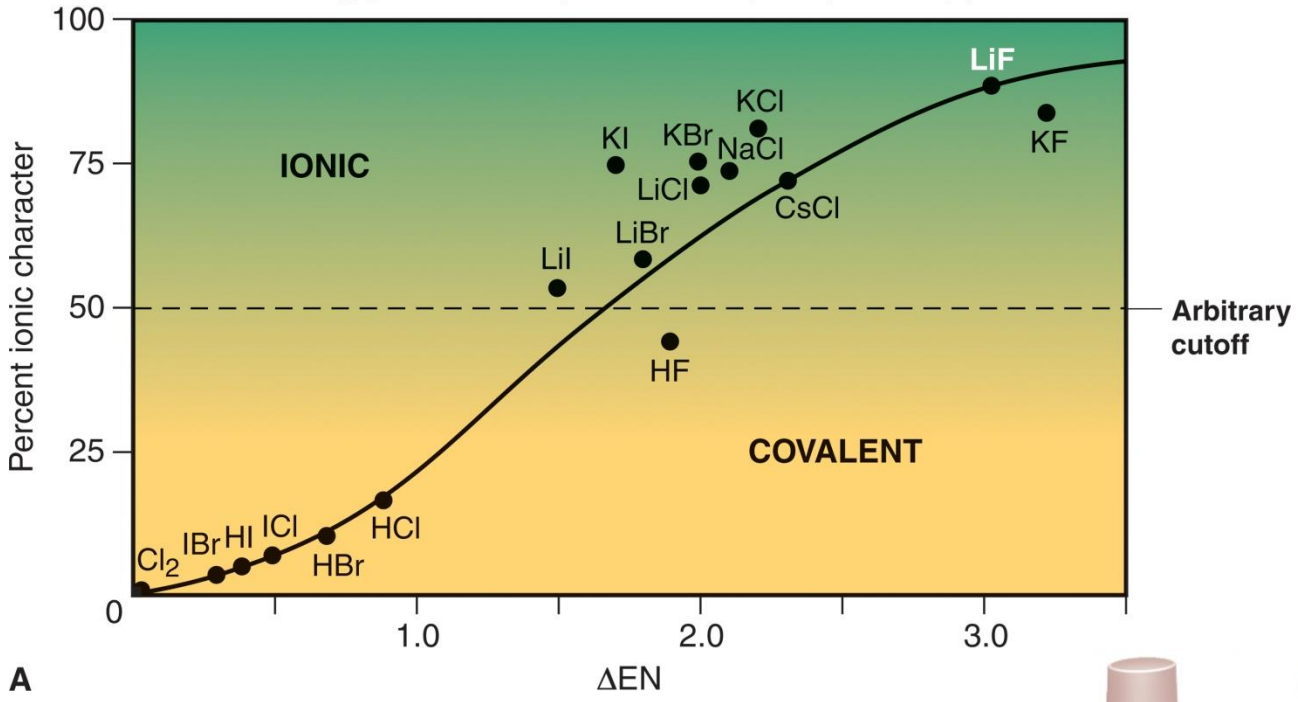
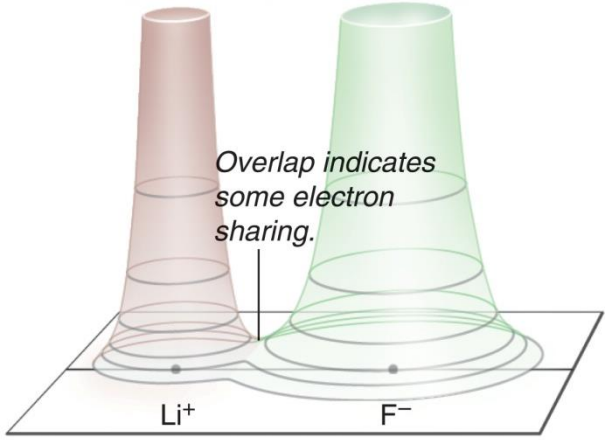


Figure 9.22 Percent ionic character as a function of ΔEN.





Sample Problem 9.4 Determining Bond Polarity from EN Values

PROBLEM: **(a)** Use a polar arrow to indicate the polarity of each bond: N–H, F–N, I–Cl.

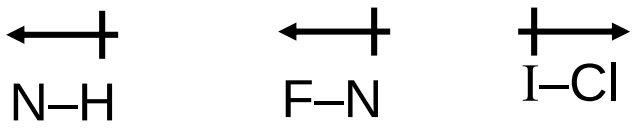
(b) Rank the following bonds in order of increasing polarity: H–N, H–O, H–C.

PLAN: **(a)** We use Figure 9.19 to find the EN values for each element. The polar arrow points toward the more electronegative element.

(b) The greater the ΔEN between the atoms, the more polar the bond.

SOLUTION: **(a)** The EN values are:

N = 3.0, H = 2.1; F = 4.0; I = 2.5, Cl = 3.0



Sample Problem 9.4

(b) The EN values are:

N = 3.0, H = 2.1; O = 3.5; C = 2.5

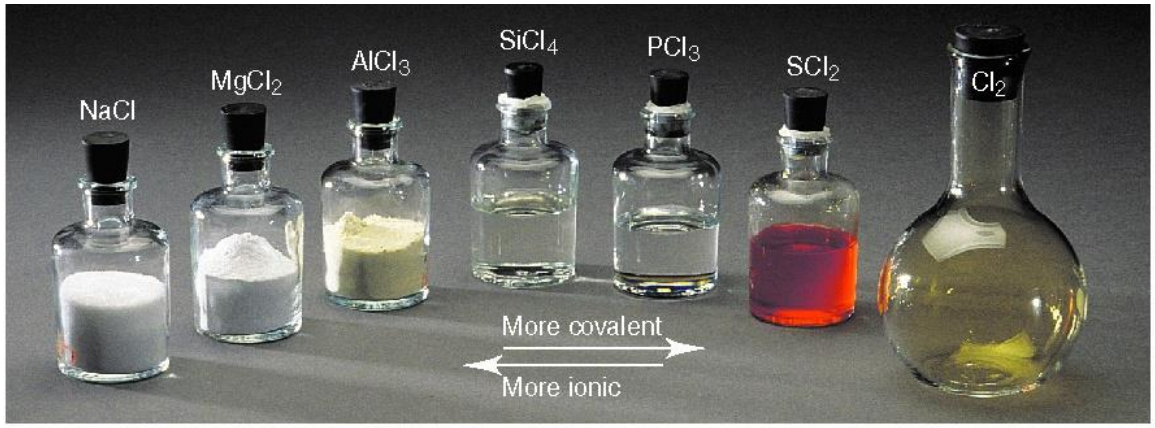
ΔEN for H–N = 3.0 – 2.1 = 0.9

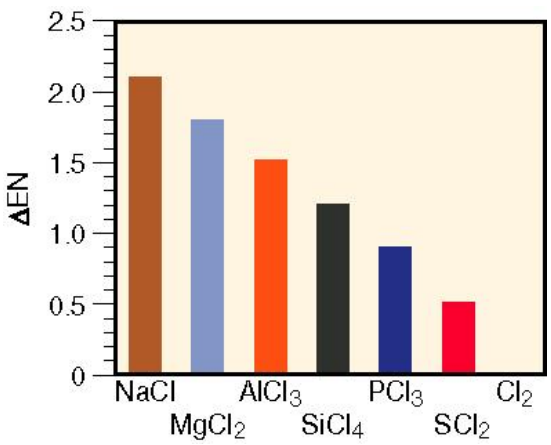
ΔEN for H–O = 3.5 – 2.1 = 1.4

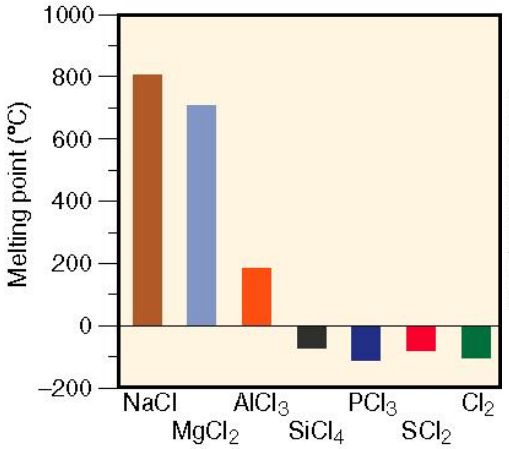
ΔEN for H–C = 2.5 – 2.1 = 0.4

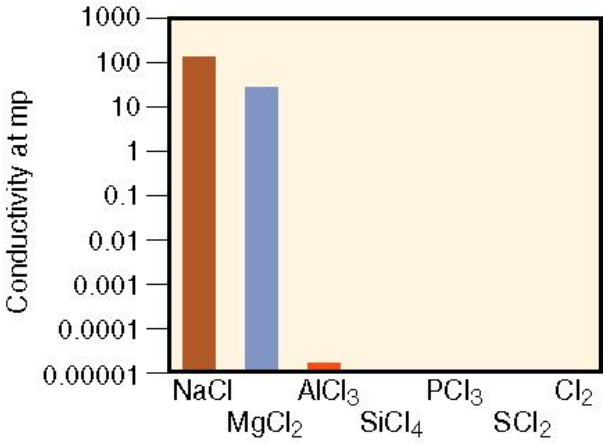
H-C < H-N < H-O

Figure 9.23 Properties of the Period 3 chlorides.









As ΔEN decreases, melting point and electrical conductivity decrease because the bond type changes from ionic to polar covalent to nonpolar covalent.

You tube video

https://www.youtube.com/watch?v=6twRHdevc-A

https://www.youtube.com/watch?v=02Q352-Y7iU