Chapter 9

Models of Chemical Bonding

Periodic Table of the Elements

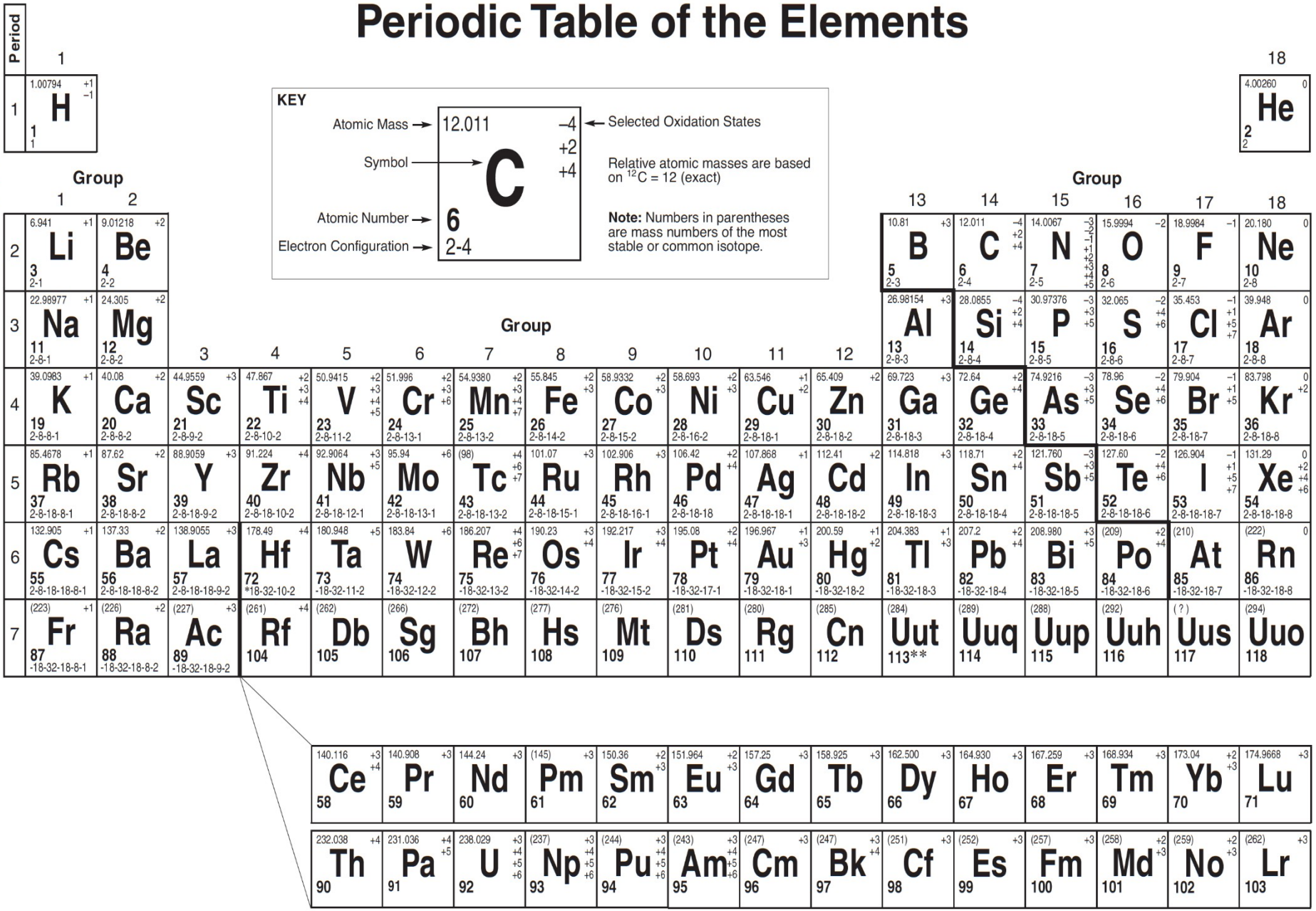


Table of Pauling Electronegativity Values

	IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIII	VIII	VIII	IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA
1	1 H 2.1																	2 He
2	3 Li 1.0	4 Be 1.5											5 B 2.0	6 C 2.5	7 N 3.0	8 O 3.5	9 F 4.0	10 Ne
3	11 Na 0.9	12 Mg 1.2											13 Al 1.5	14 Si 1.8	15 P 2.1	16 S 2.5	17 Cl 3.0	18 Ar
4	19 K 0.8	20 Ca 1.0	21 Sc 1.3	22 Ti 1.5	23 V 1.6	24 Cr 1.6	25 Mn 1.5	26 Fe 1.8	27 Co 1.8	28 Ni 1.8	29 Cu 1.9	30 Zn 1.6	31 Ga 1.6	32 Ge 1.8	33 As 2.0	34 Se 2.4	35 Br 2.8	36 Kr
5	37 Rb 0.8	38 Sr 1.0	39 Y 1.2	40 Zr 1.4	41 Nb 1.6	42 Mo 1.8	43 Tc 1.9	44 Ru 2.2	45 Rh 2.2	46 Pd 2.2	47 Ag 1.9	48 Cd 1.8	49 In 1.8	50 Sn 1.8	51 Sb 1.9	52 Te 2.1	53 I 2.5	54 Xe
6	55 Cs 0.7	56 Ba 0.9	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl 1.8	82 Pb 1.9	83 Bi 1.9	84 Po 2.0	85 At 2.2	86 Rn
7	87 Fr 0.7	88 Ra 0.9	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110	111	112		114		116		

Lanthanides	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
Actinides	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

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***.

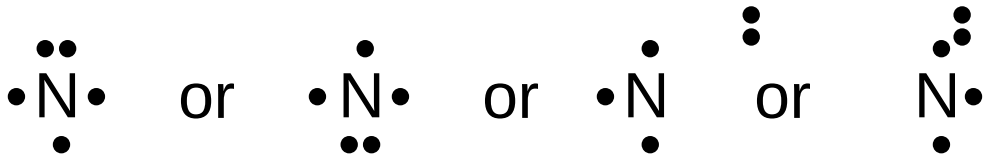
Lewis Electron-Dot Symbols

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.

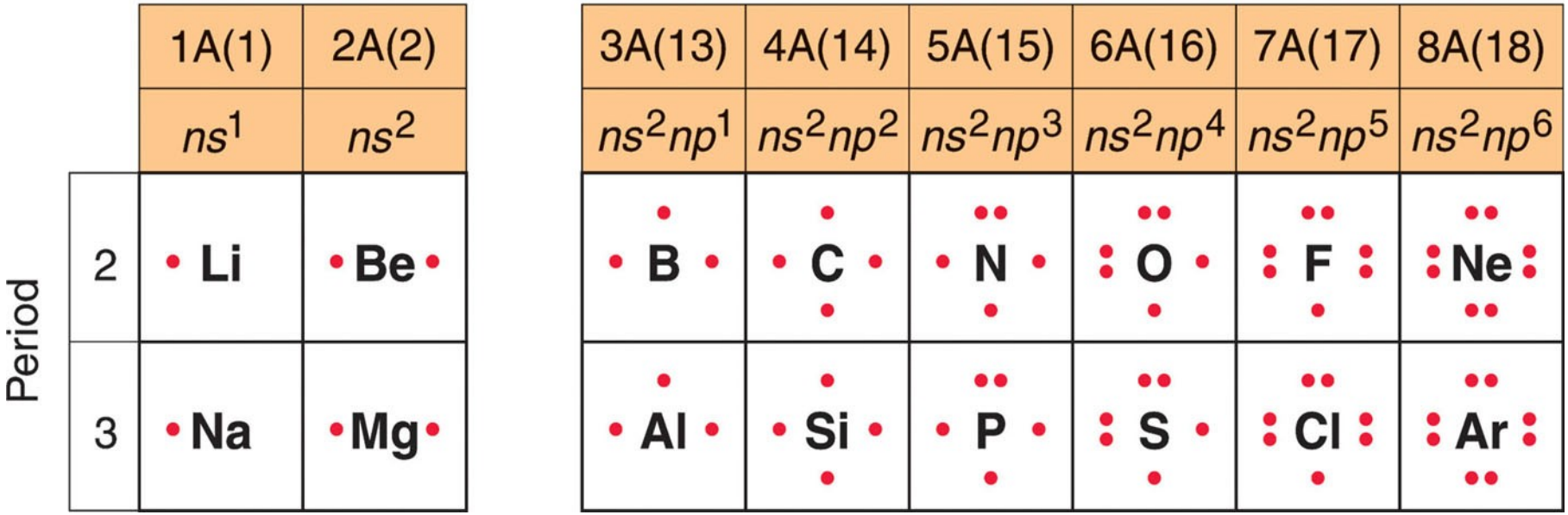
For a ***nonmetal***, the number of unpaired dots equals

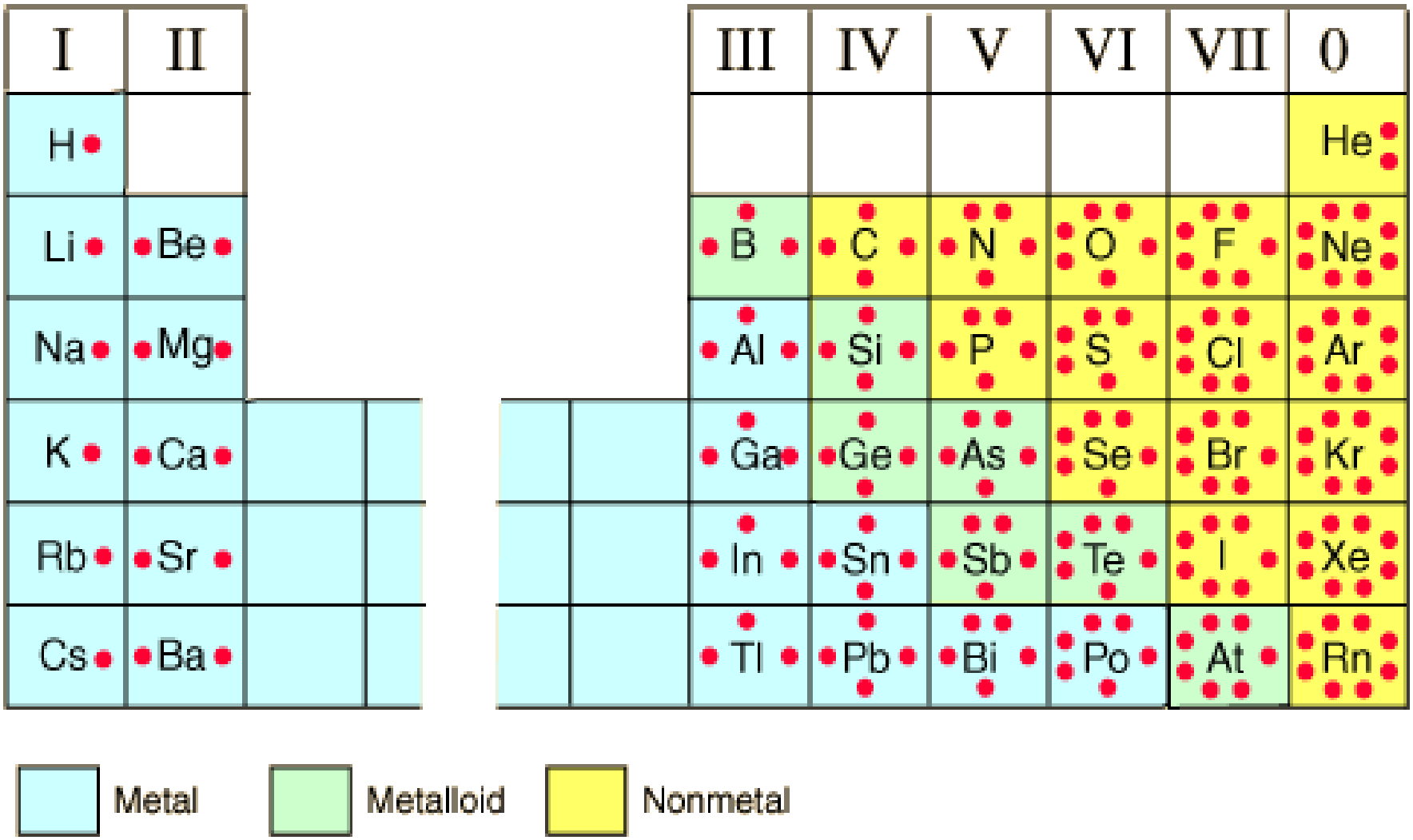
- the number of electrons the atom ***gains*** to form an anion
- or the number it ***shares*** to form covalent bonds.

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.




I
II
III
IV
V
VI
VII
0
H
He
Li
Be
B
C
N
O
F
Ne
Na
Mg
Al
Si
P
S
Cl
Ar
K
Ca
Ga
Ge
As
Se
Br
Kr
Rb
Sr
In
Sn
Sb
Te
I
Xe
Cs
Ba
Tl
Pb
Bi
Po
At
Rn
Metal
Metalloid
Nonmetal

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 atom(s).

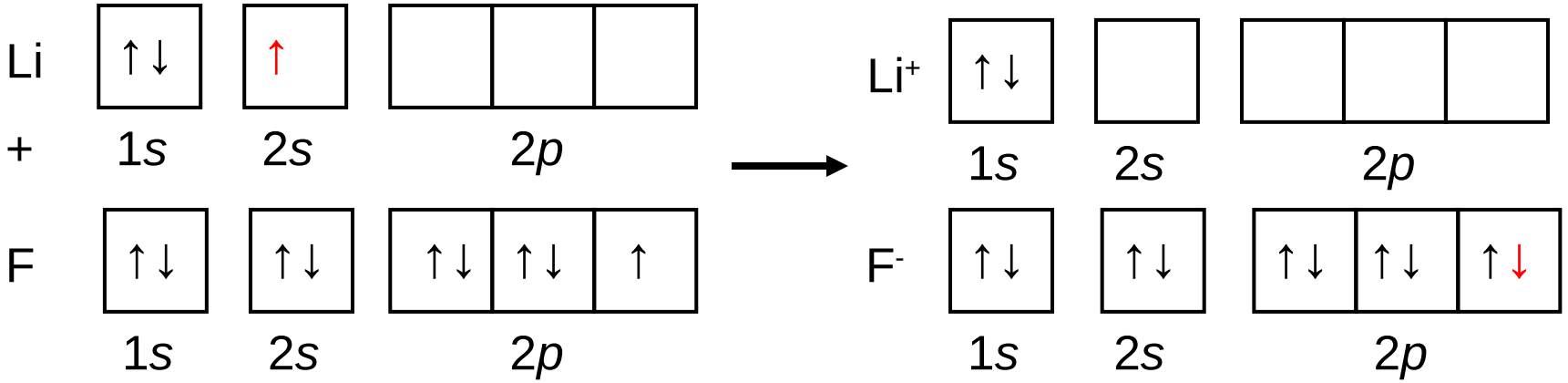
An animation of the formation of Ionic bonds is on the WP site under videos.

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

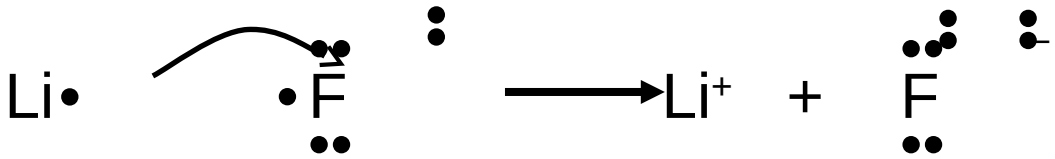
Electron configurations

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

Orbital diagrams



Lewis electron-dot symbols

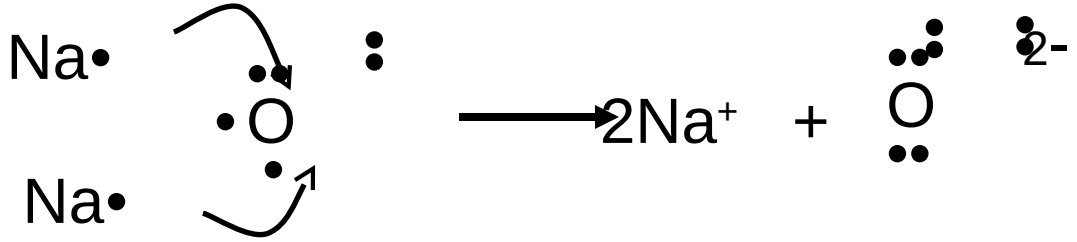


Sample Problem 9.1 Depicting Ion Formation

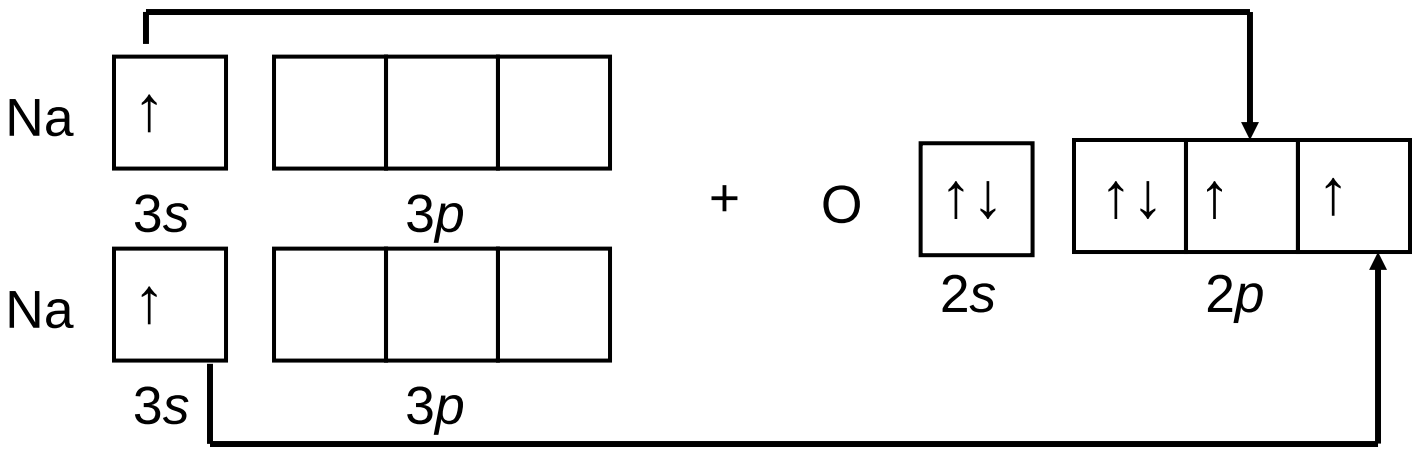
PROBLEM: Use partial orbital diagrams and Lewis symbols to depict the formation of Na^+ and O^{2-} ions from the atoms, and determine the formula of the compound formed.

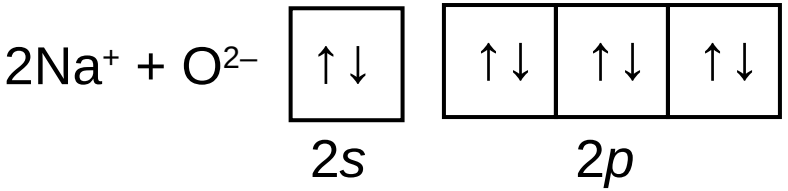
PLAN: Draw orbital diagrams and Lewis symbols for Na and O atoms. To attain filled outer levels, Na loses one electron and O gains two. Two Na atoms are needed for each O atom so that the number of electrons lost equals the number of electrons gained.

SOLUTION:



Sample Problem 9.1





The formula is Na_2O

The Aufbau principle **states that, hypothetically, electrons orbiting one or more atoms fill the lowest available energy levels before filling higher levels (e.g., 1s before 2s). In this way, the electrons of an atom, molecule, or ion harmonize into the most stable electron configuration possible.**

The details of this "building-up" tendency are described mathematically by atomic orbital functions. Electron behavior is elaborated by other principles of atomic physics, such as Hund's rule and the Pauli exclusion principle. Hund's rule asserts that even if multiple orbitals of the same energy are available, electrons fill unoccupied orbitals first, before reusing orbitals occupied by other electrons. But, according to the Pauli exclusion principle, in order for electrons to occupy the same orbital, they must have different spins (−1/2 and 1/2).

From Hund's rules **specify in a simple way how usual energy interactions dictate the ground state term. The rules assume that the repulsion between the outer electrons is much greater than the spin–orbit interaction, which is in turn stronger than any other remaining interactions. This is referred to as the LS coupling regime.**

Full shells and subshells do not contribute to the quantum numbers for total S, the total spin angular momentum and for L, the total orbital angular momentum. Thus when determining the ordering of energy levels in general only the outer valence electrons must be considered.





Hess's law is an expression of the principle of conservation of energy , also expressed in the first law of thermodynamics , and the fact that the enthalpy of a chemical process is independent of the path taken from the initial to the final state.

$$\Delta H^{\ominus}_{reaction} = \sum \Delta H^{\ominus}_{\mathrm{f}\,(products)} - \sum \Delta H^{\ominus}_{\mathrm{f}\,(reactants)}$$

Hess's law allows the ***enthalpy*** change (**ΔH**) for a reaction to be calculated even when it cannot be measured directly. This is accomplished by performing basic algebraic operations based on the chemical equations of reactions using previously determined values for the enthalpies of formation.

The ionization energy (**IE**) is qualitatively defined as the amount of energy required to remove the most loosely bound electron, the valence electron, of an isolated gaseous atom to form a cation. It is quantitatively expressed in symbols as:

$X + \text{energy} \rightarrow X^+ + e^-$

where X is any atom or molecule capable of being ionized, X^+ is that atom or molecule with an electron removed, and e^- is the removed electron. This is an endothermic process.

Comparison of IEs of atoms in the Periodic table reveals two patterns:

- IEs generally increase as one moves from left to right within a period.
- IEs decrease as one moves from down any given group.

TABLE 7.2 **Successive Values of Ionization Energies, *I*, for the Elements Sodium Through Argon (kJ/mol)**

Element	I_1	I_2	I_3	I_4	I_5	I_6	I_7
Na	496	4560					
Mg	738	1450	7730		(Inner-shell electrons)		
Al	578	1820	2750	11,600			
Si	786	1580	3230	4360	16,100		
P	1012	1900	2910	4960	6270	22,200	
S	1000	2250	3360	4560	7010	8500	27,100
Cl	1251	2300	3820	5160	6540	9460	11,000
Ar	1521	2670	3930	5770	7240	8780	12,000

The electron affinity of an atom or molecule is defined as the amount of energy released or spent when an electron is added to a neutral atom or molecule in the gaseous state to form a negative ion.

$X + e^- \rightarrow X^- + \text{energy}$

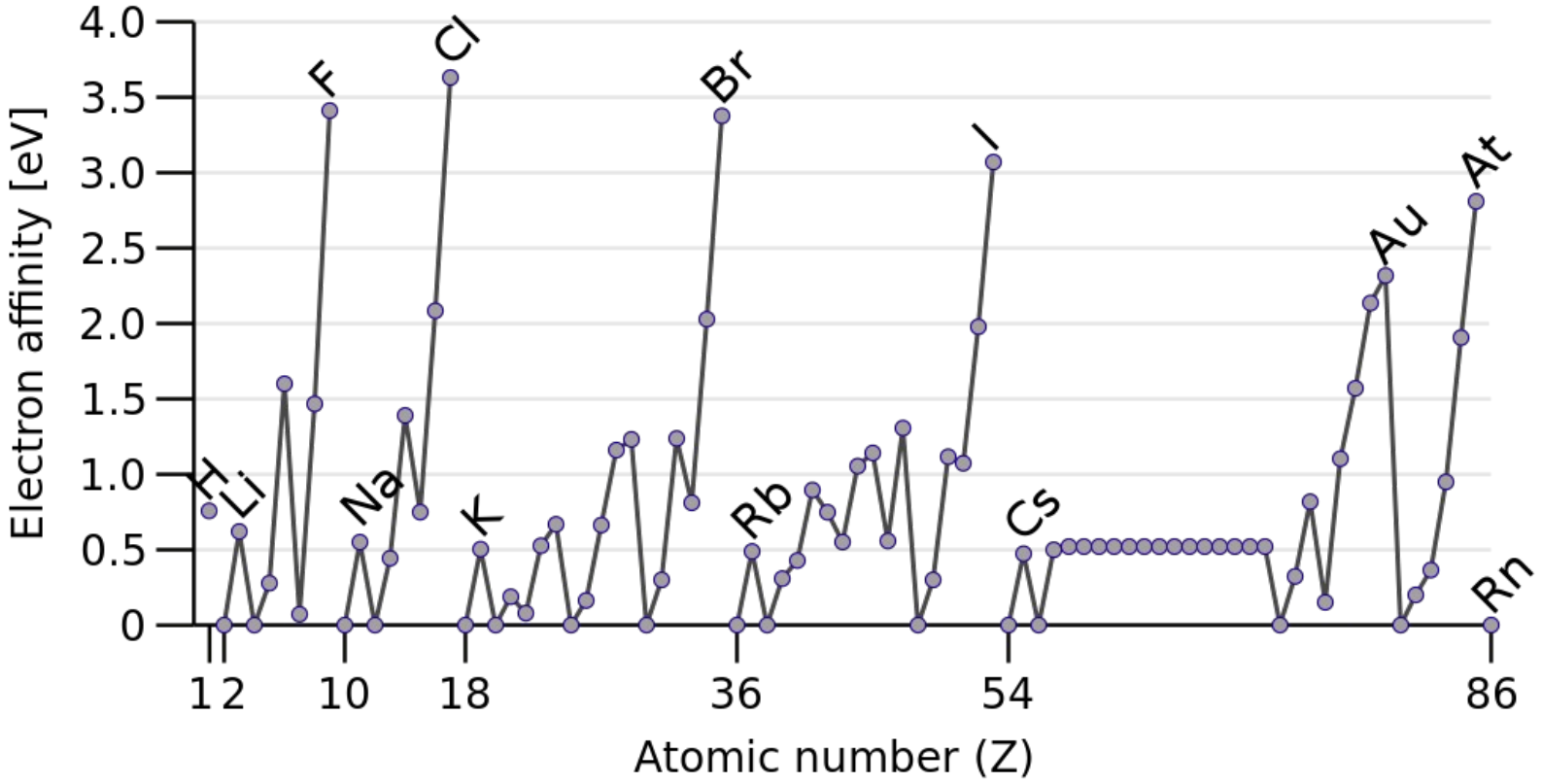
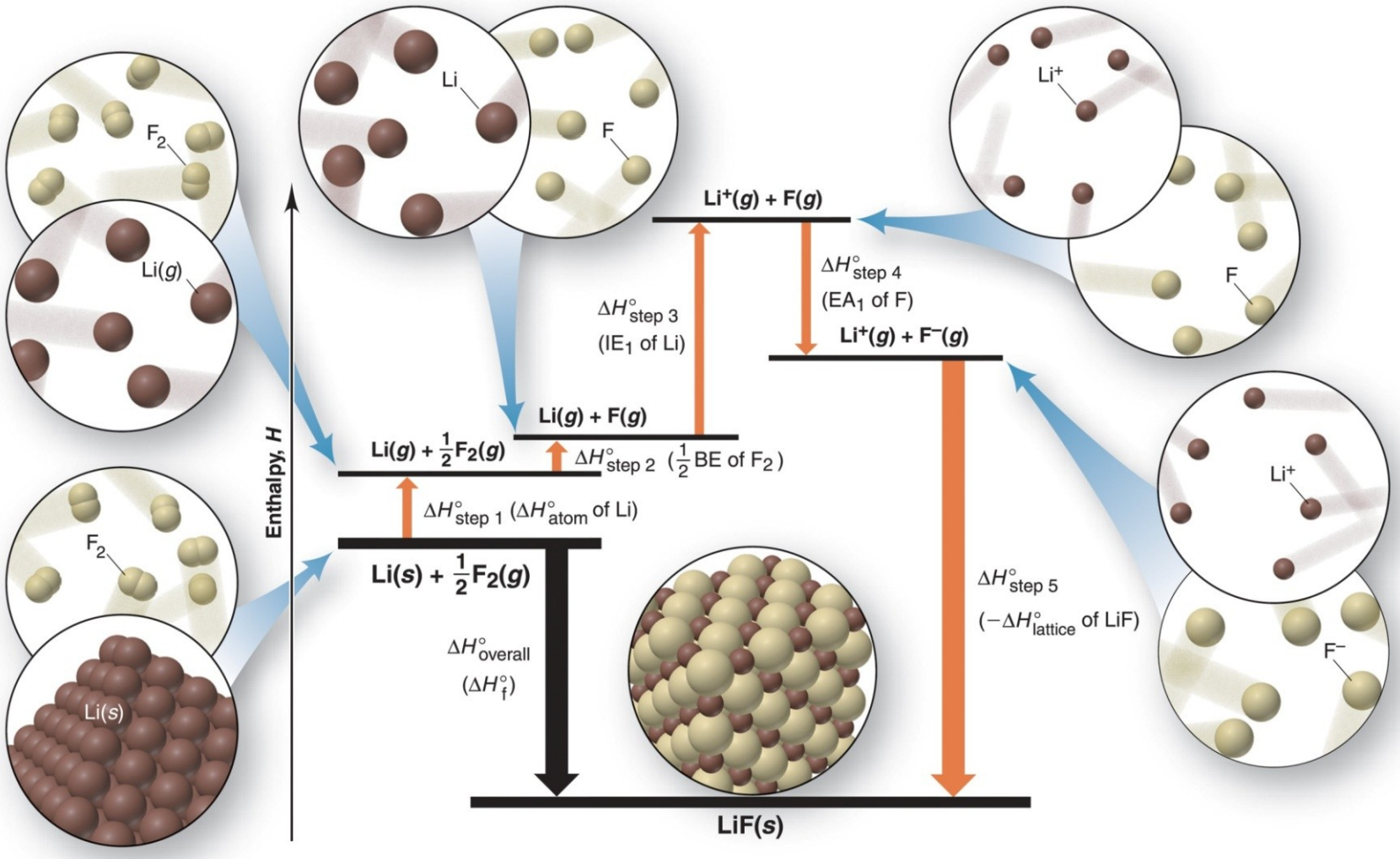
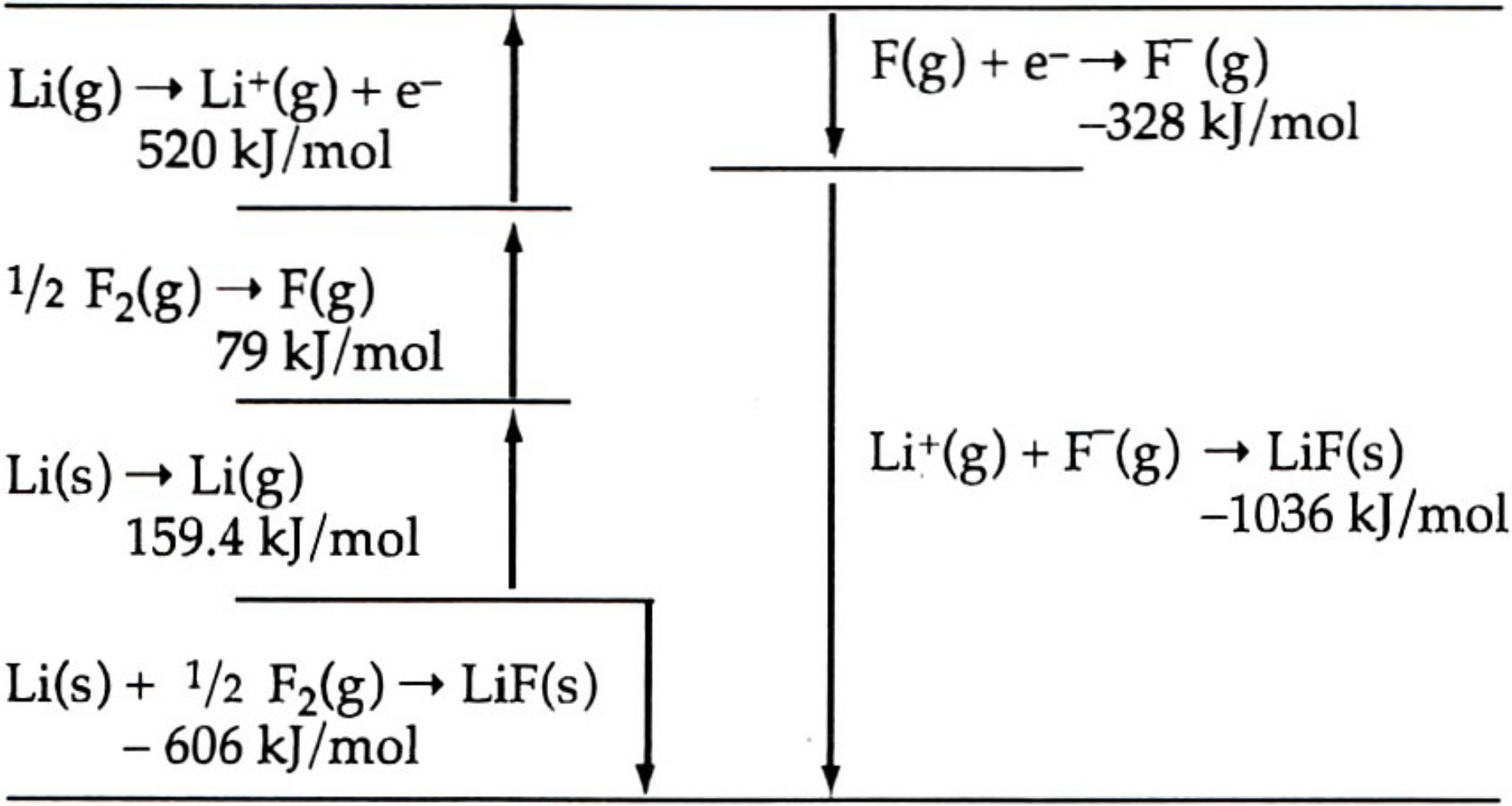


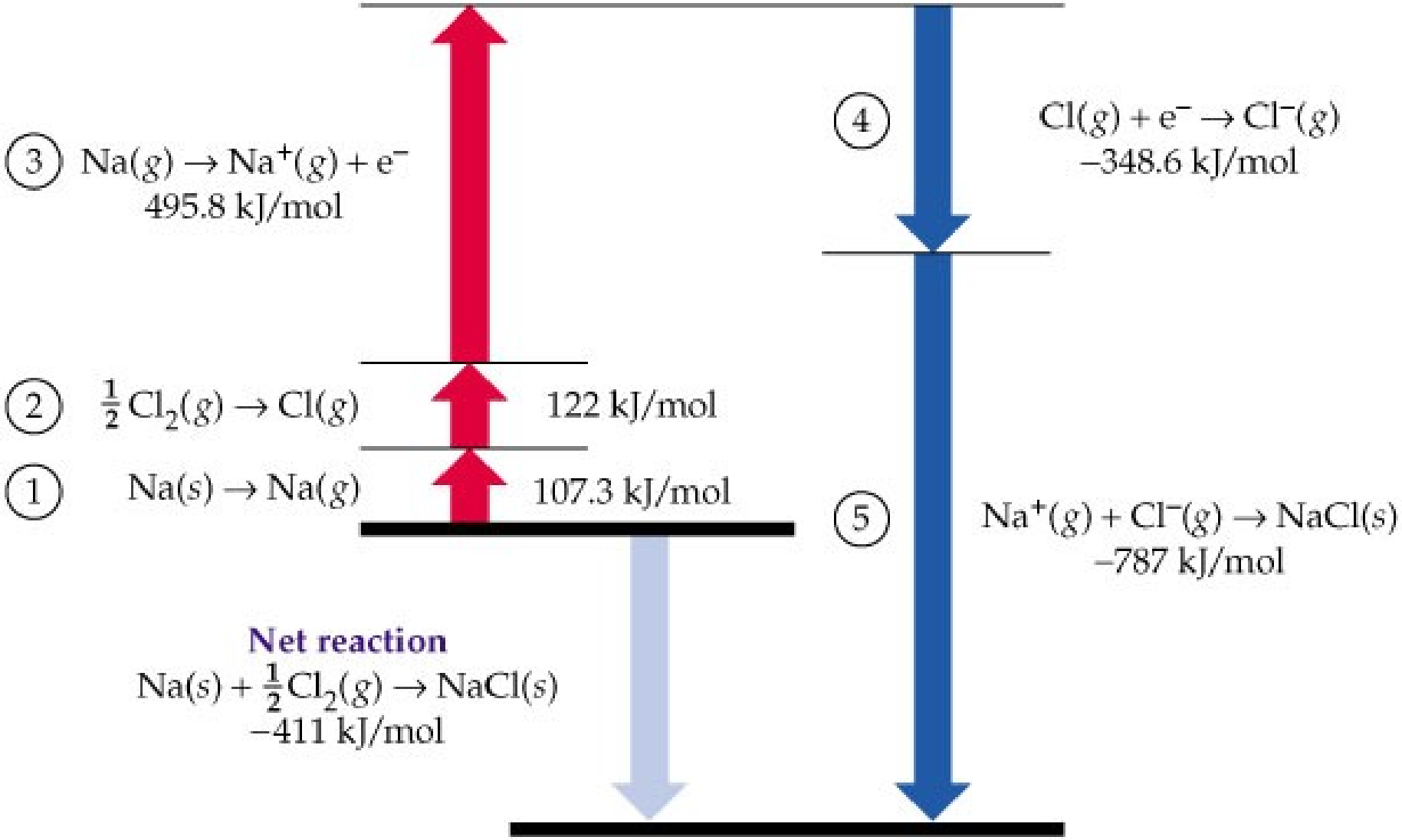
Figure 9.7 The Born-Haber cycle for lithium fluoride.

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$$\Delta H^{\ominus}_{reaction} = \sum \Delta H^{\ominus}_{\mathrm{f}\,(products)} - \sum \Delta H^{\ominus}_{\mathrm{f}\,(reactants)}$$




3 Na(g) → Na+(g) + e−
495.8 kJ/mol
4 Cl(g) + e− → Cl−(g)
−348.6 kJ/mol
2 ½ Cl2(g) → Cl(g)
122 kJ/mol
1 Na(s) → Na(g)
107.3 kJ/mol
5 Na+(g) + Cl−(g) → NaCl(s)
−787 kJ/mol
Net reaction
Na(s) + ½ Cl2(g) → NaCl(s)
−411 kJ/mol

1. **Conversion of solid sodium to gaseous sodium. This is the enthalpy of sublimation for sodium metal.**

2. Dissociation of gaseous Cl_2 molecules into Cl atoms. This is the bond dissociation energy of Cl_2.

3. Ionization of sodium atoms into ions and electrons. This is the ionization energy of sodium.

4. Formation of Cl^- ions.This is the electron affinity of chlorine.

5. Formation of solid NaCl.This is the (–) lattice energy of sodium chloride

Net reaction: $Na(s) + 1/2\ Cl_2(g) \rightarrow NaCl(s)$

Net energy change: **– 411 kJ/mol**

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 9.8 **Trends in lattice energy.**

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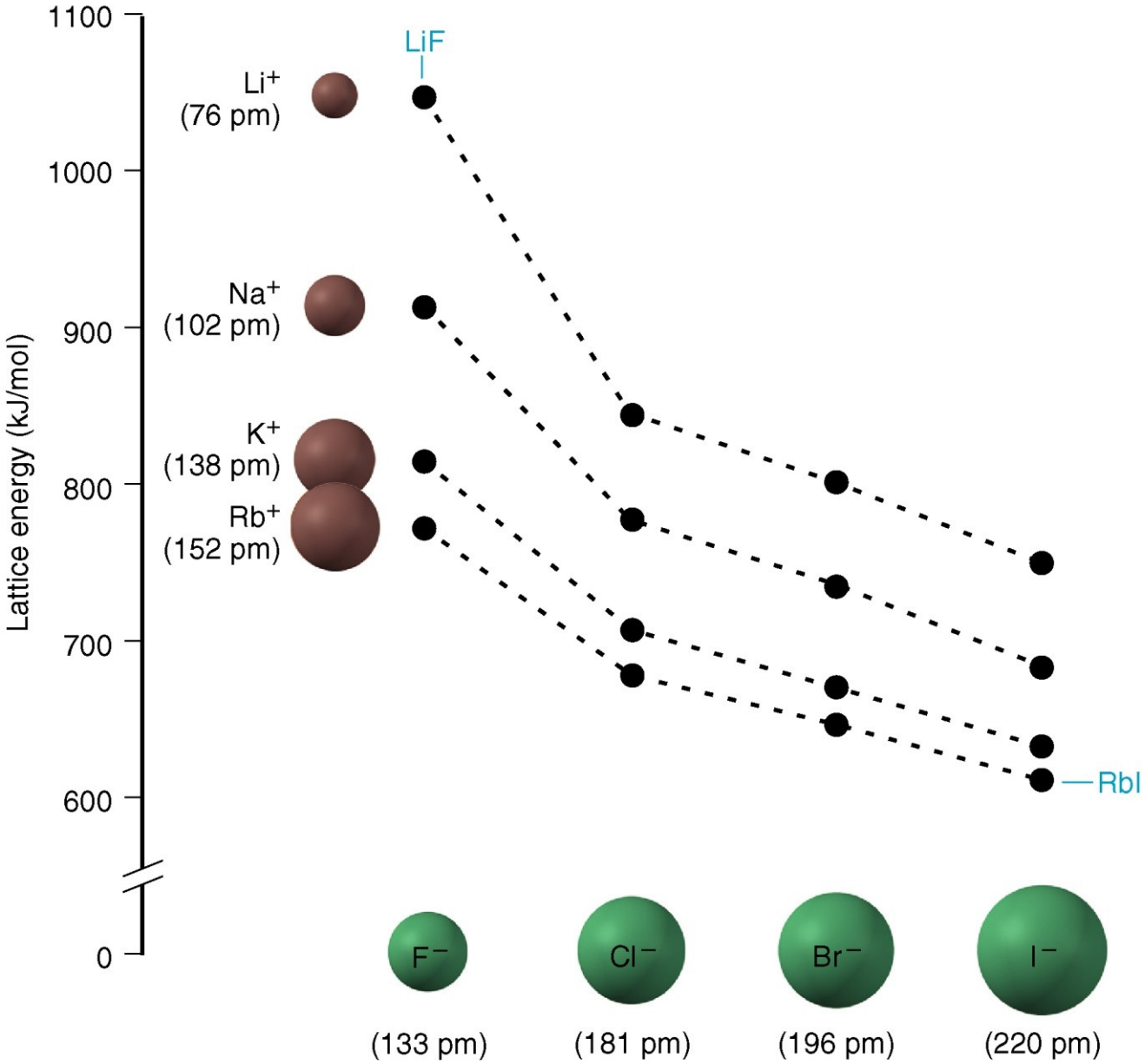


Figure 9.12 Covalent bond formation in H_2.

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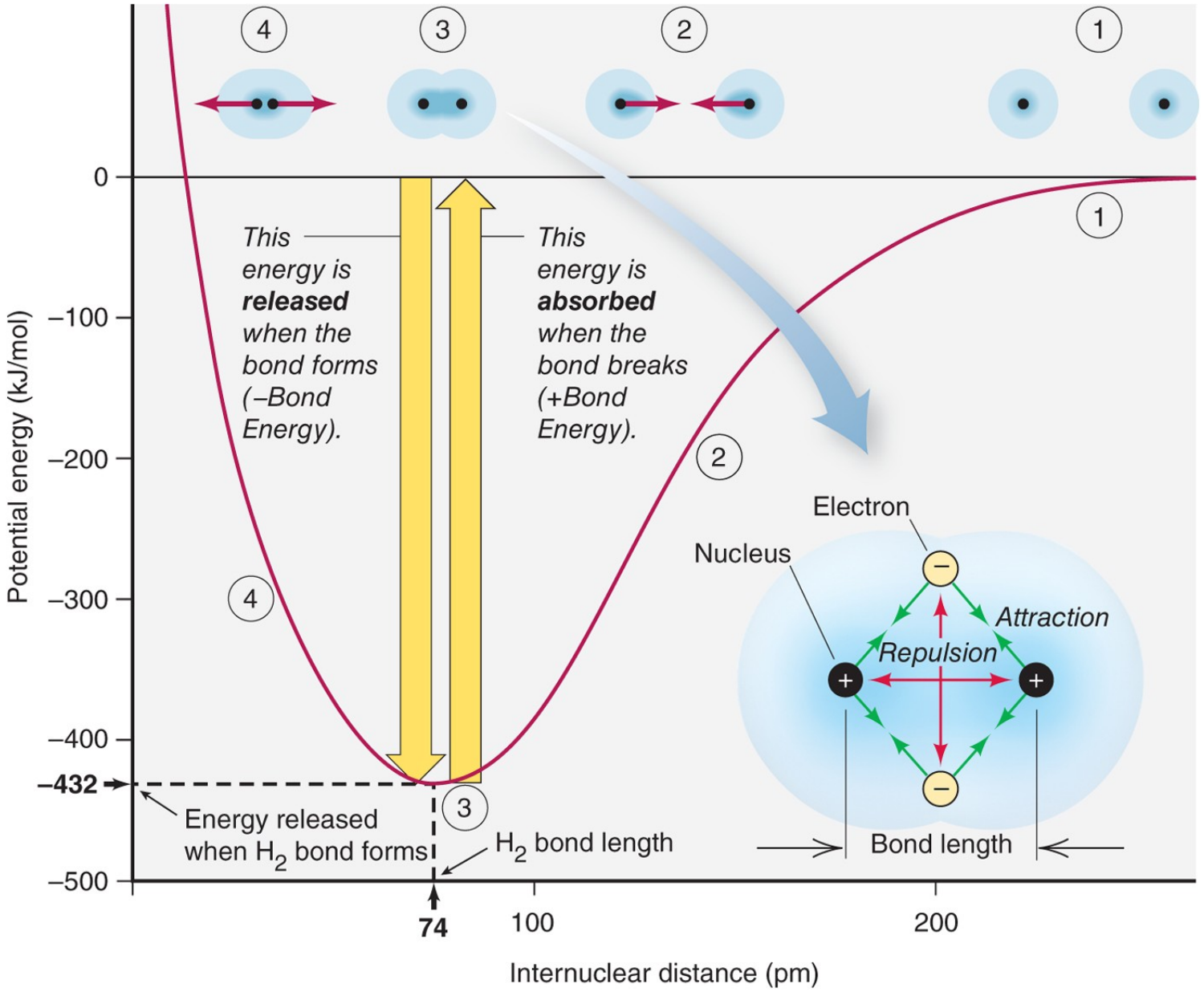
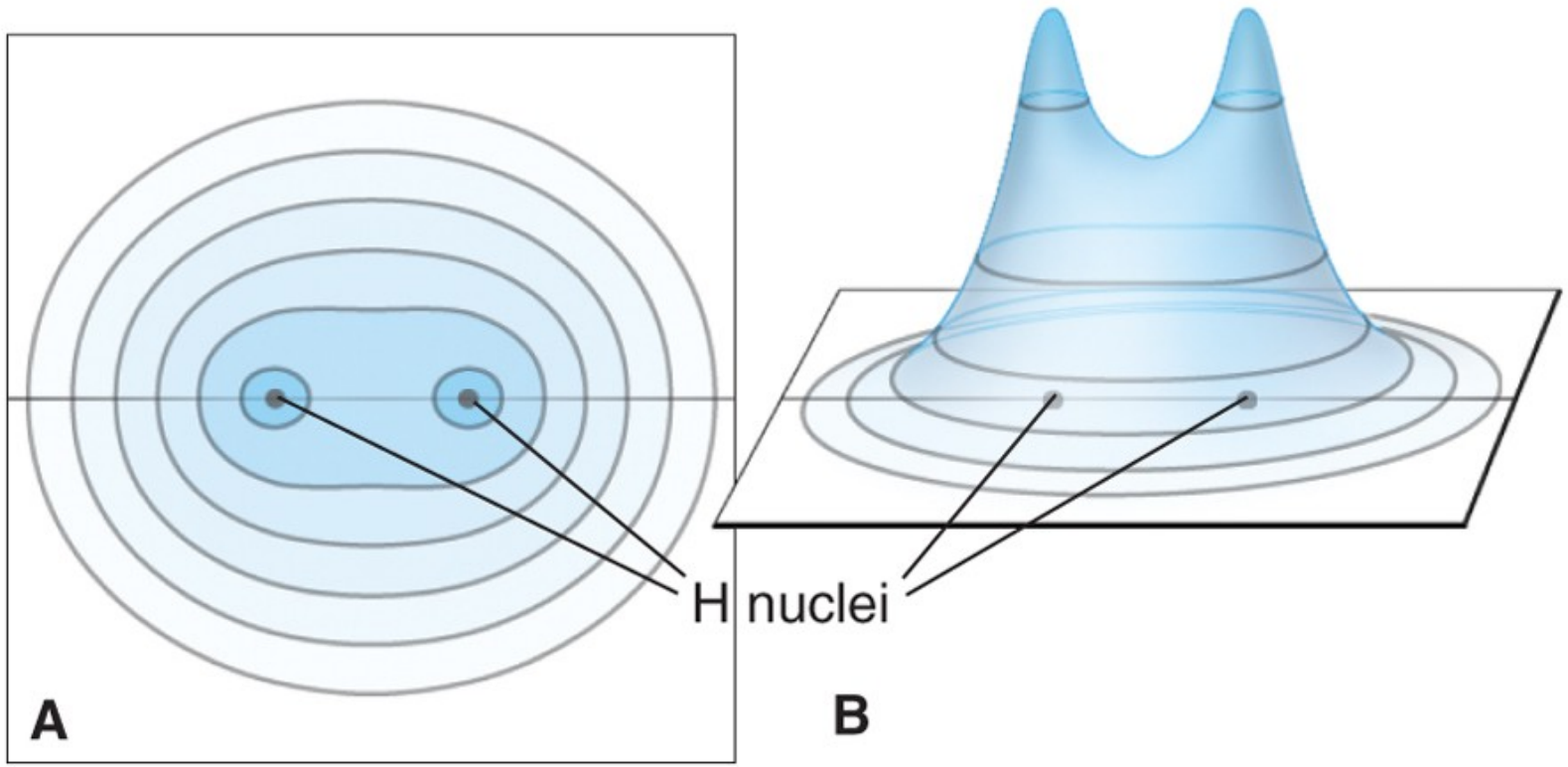


Figure 9.13 Distribution of electron density in H_2.

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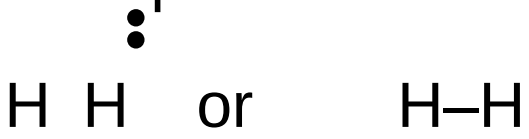
A: Electron density doubles with each concentric curve.

B: The highest regions of electron density are shown as peaks.

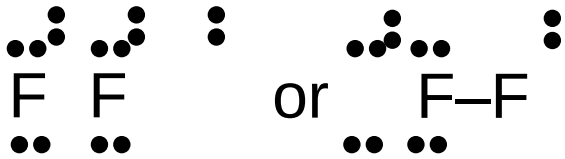
Bonding Pairs and Lone Pairs

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:



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.

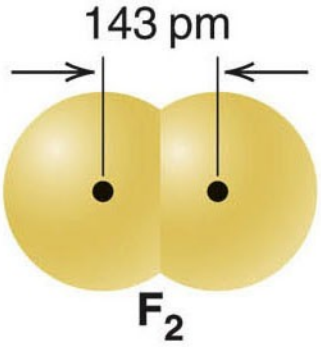
Table 9.2 Average Bond Energies (kJ/mol) and Bond Lengths (pm)

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			

Figure 9.14 **Bond length and covalent radius.**

Internuclear distance (bond length)

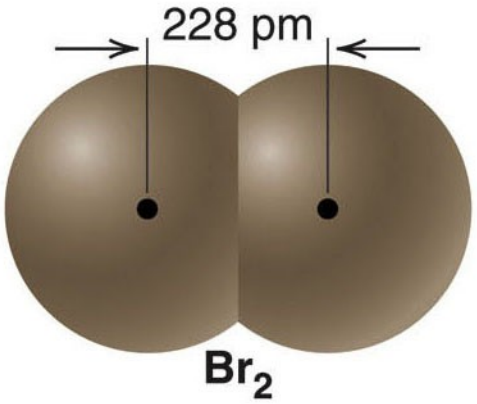
Covalent radius



72 pm

Internuclear distance (bond length)

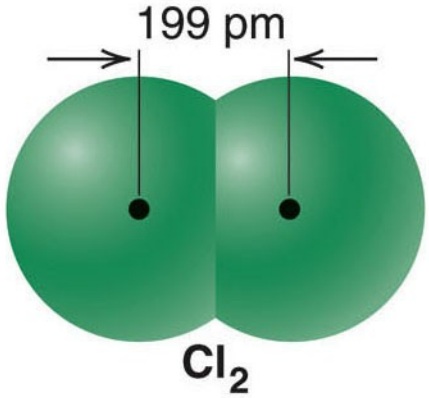
Covalent radius



114 pm

Internuclear distance (bond length)

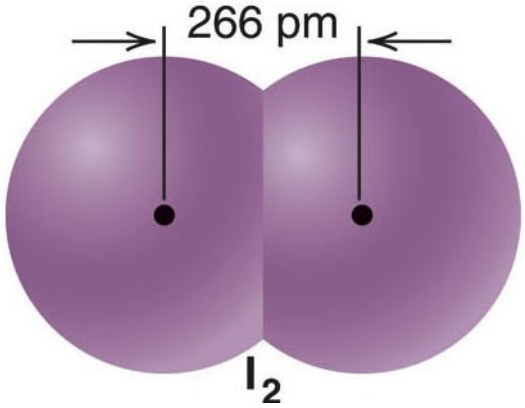
Covalent radius



100 pm

Internuclear distance (bond length)

Covalent radius



133 pm

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 B9.1 Vibrational motions in general diatomic and triatomic molecules.

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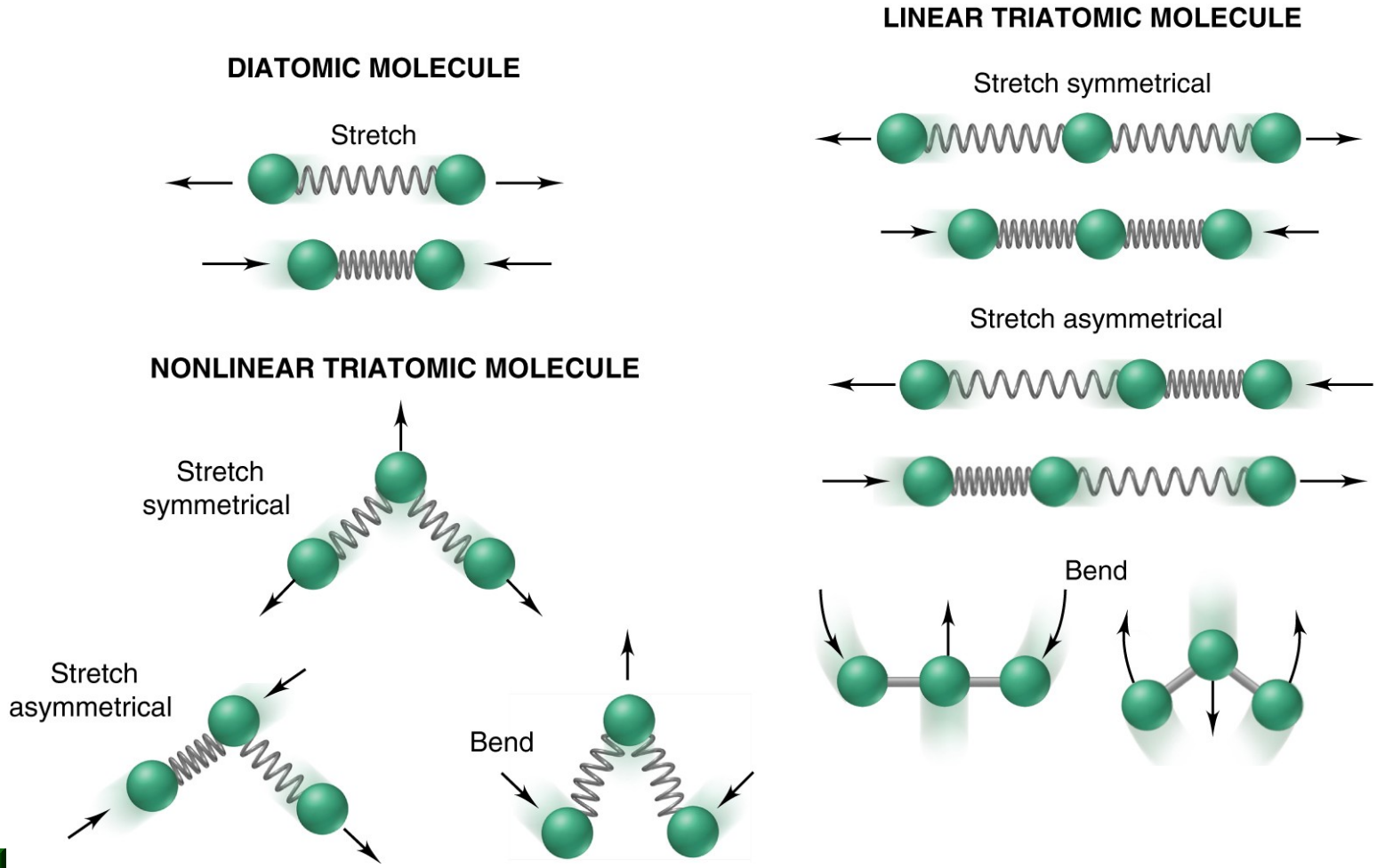


Figure B9.2 **The infrared (IR) spectrum of acrylonitrile.**

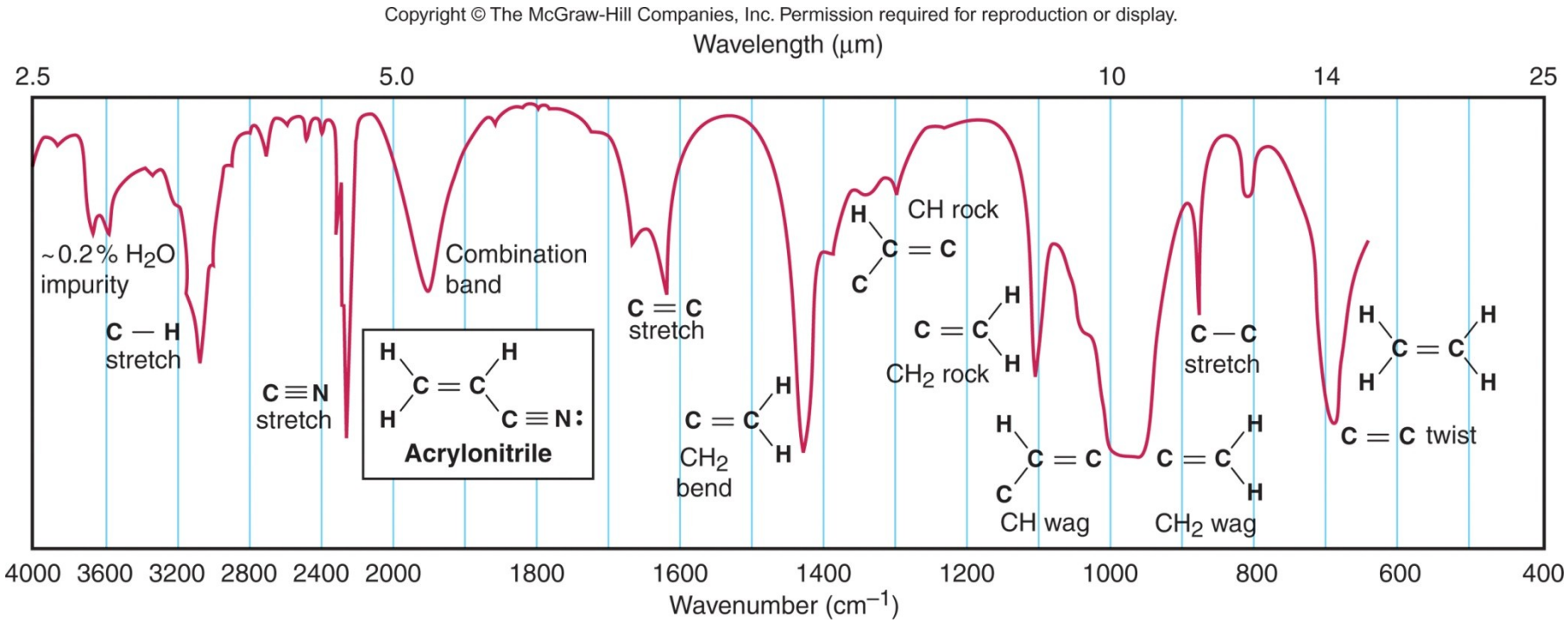


Figure B9.3 **The infrared (IR) spectra of 2-butanol (*green*) and diethyl ether (*red*).**

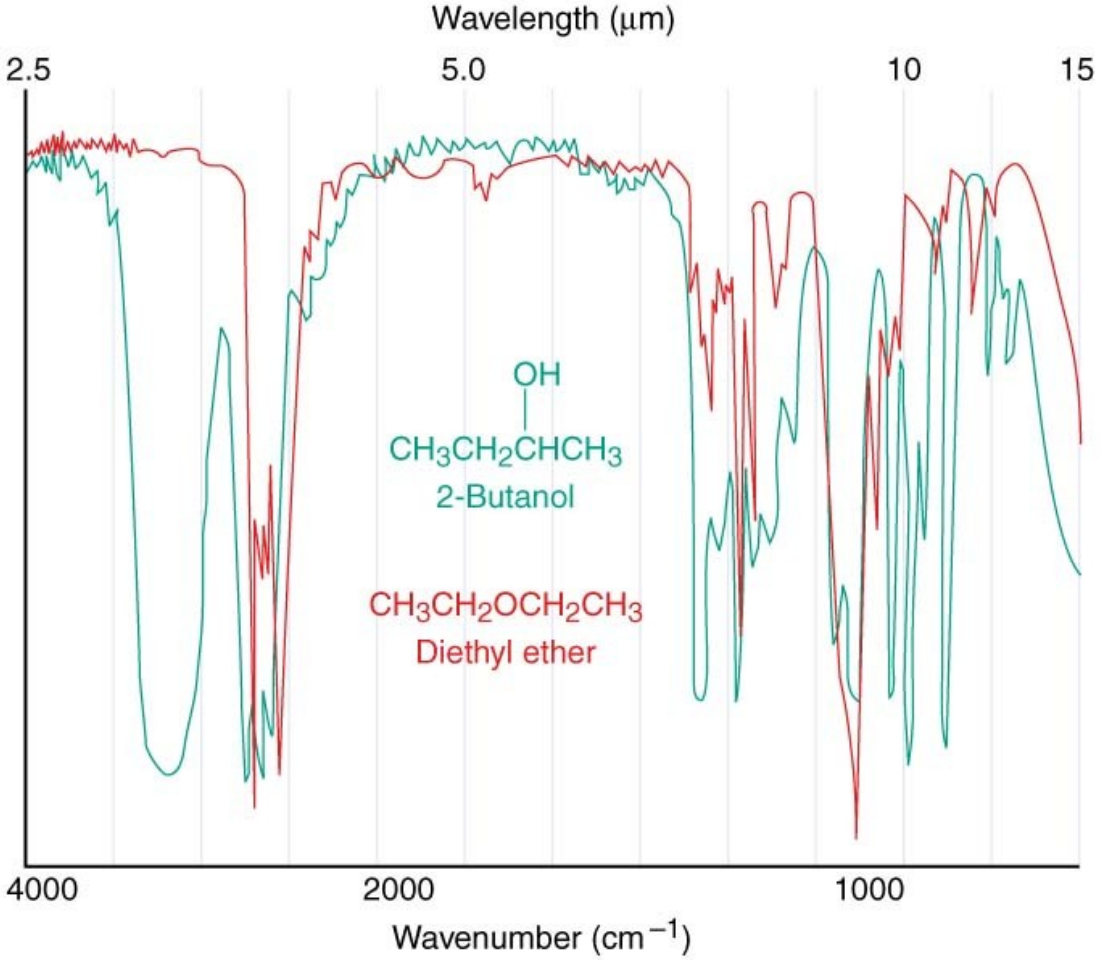
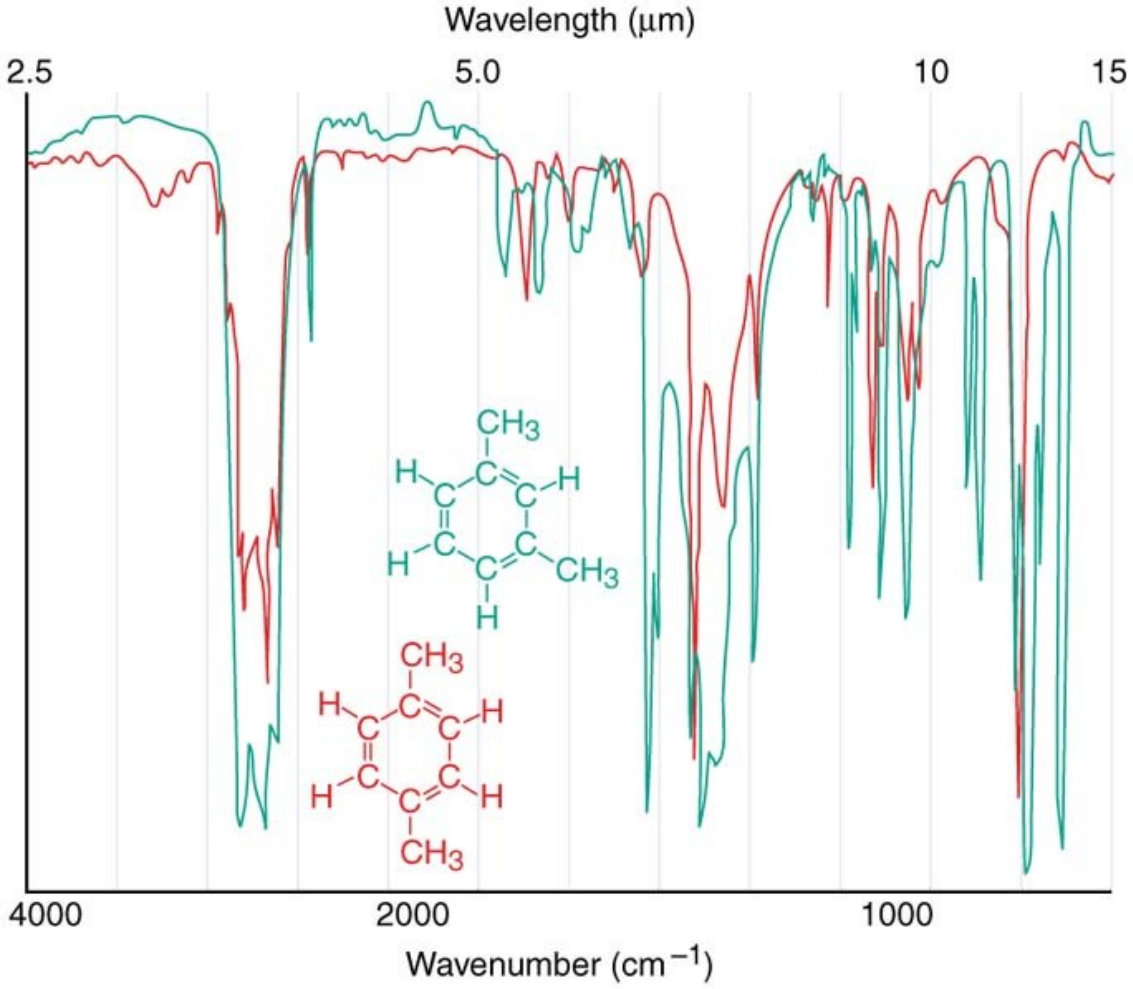


Figure B9.4 **The infrared (IR) spectra of 1,3-dimethylbenzene (*green*) and 1,4-dimethylbenzene (*red*).**



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.

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

Figure 9.17 **Using bond energies to calculate ΔH^{o}_{rxn} for HF formation.**

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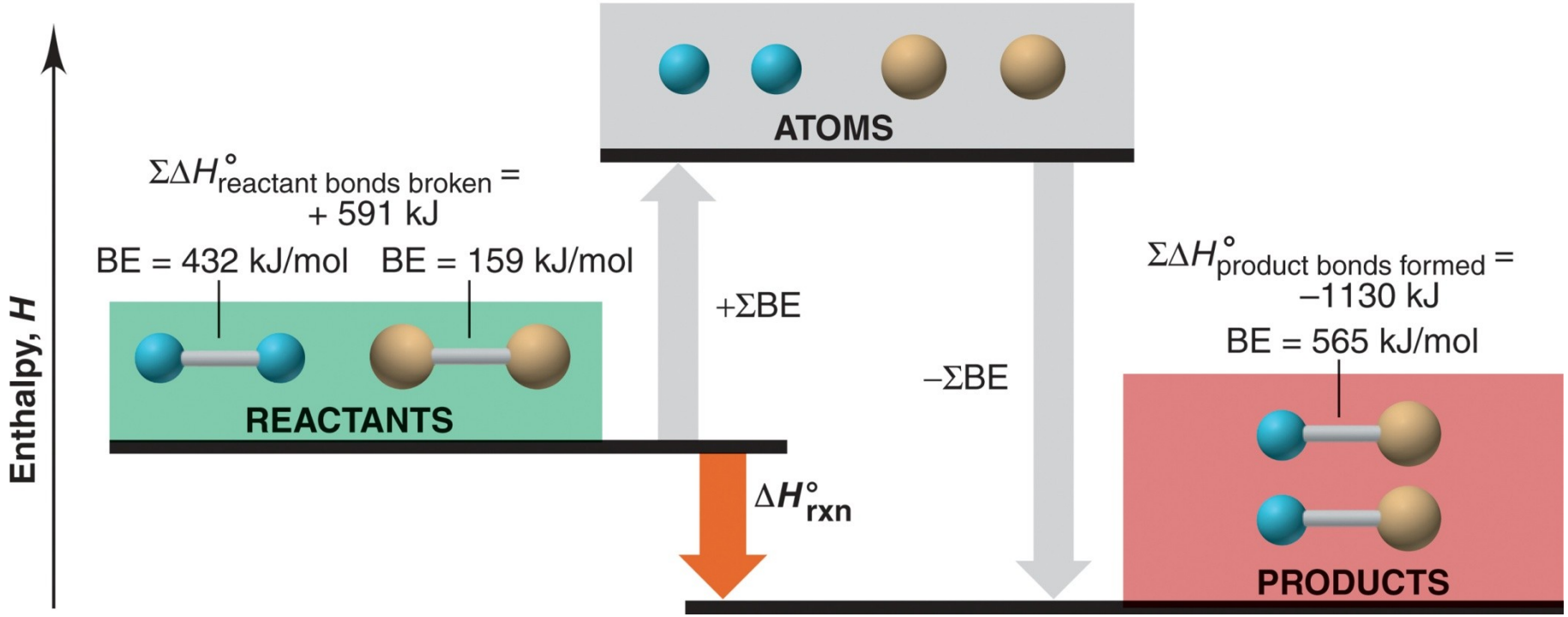
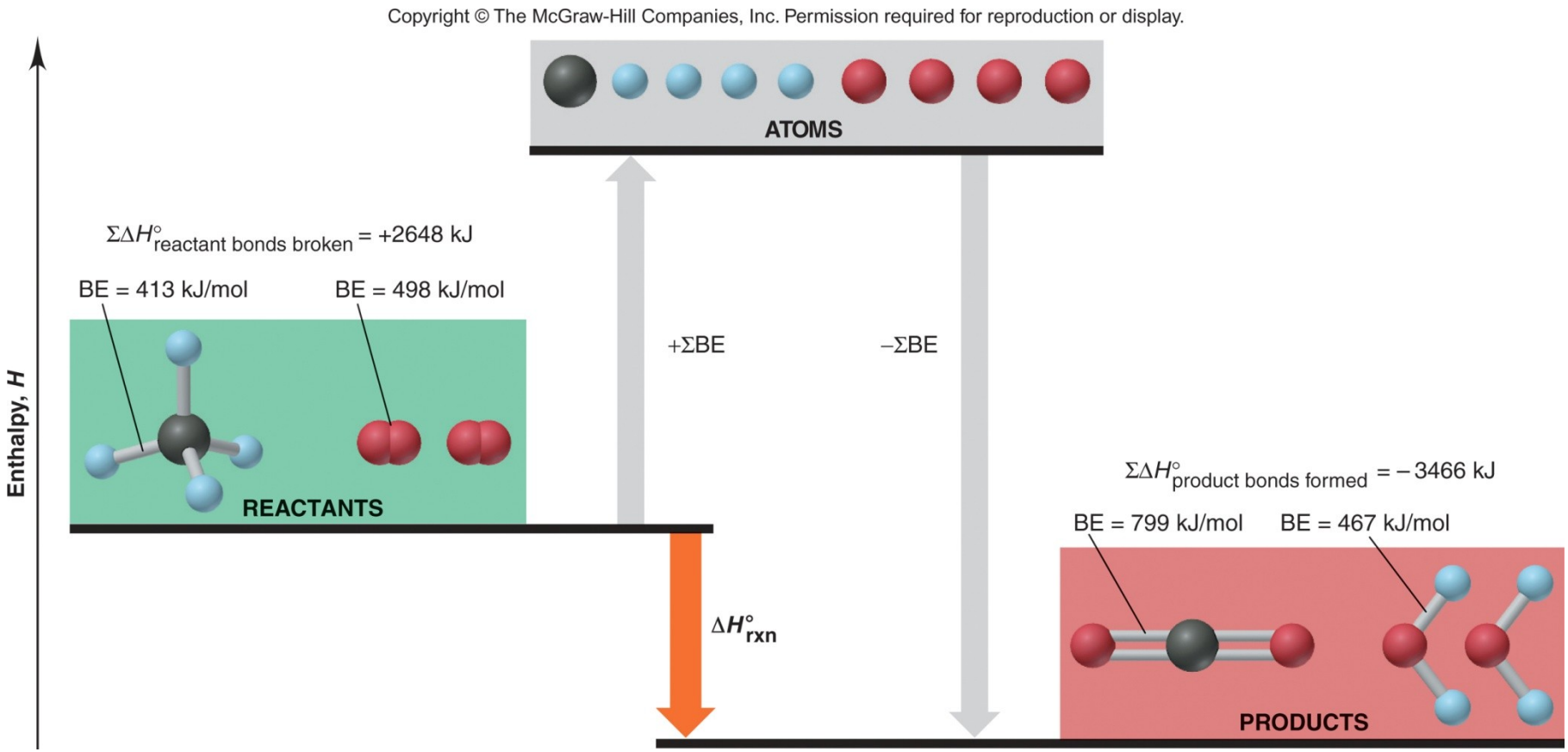
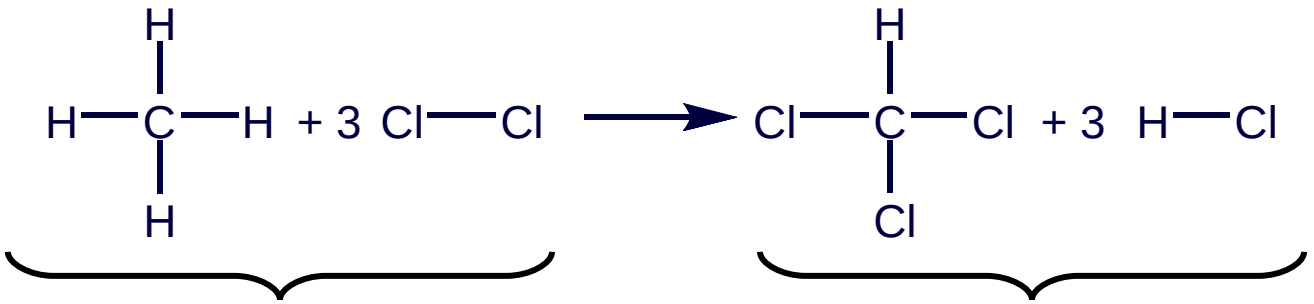


Figure 9.18 **Using bond energies to calculate ΔH^{o}_{rxn} for the combustion of methane.**



Sample Problem 9.4 Using Bond Energies to Calculate ΔH^o_{rxn}

PROBLEM: Calculate ΔH^o_{rxn} for the chlorination of methane to form chloroform.



bonds broken
$\Sigma\Delta H^o$ positive

bonds formed
$\Sigma\Delta H^o$ 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 9.4

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

$\Sigma\Delta H^{o}_{\text{bonds broken}} = 2381$ 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

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

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

$$= 2381 \text{ kJ} + (-2711 \text{ kJ}) = -330 \text{ kJ}$$





Figure 9.19 **Relative bond strength and energy from fuels.**

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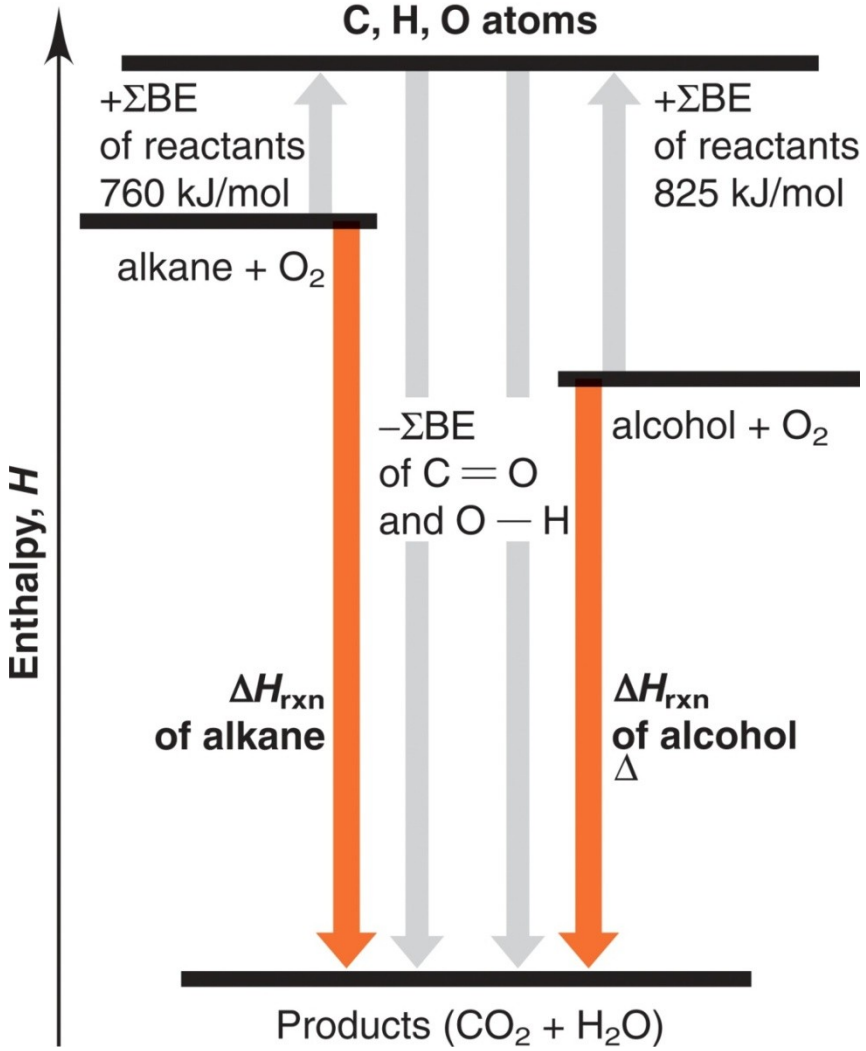


Table 9.4 Enthalpies of Reaction for Combustion of Some Foods

Substance	ΔH_{rxn} (kJ/g)
Fats	
vegetable oil	–37.0
margarine	–30.1
butter	–30.0
Carbohydrates	
table sugar (sucrose)	–16.2
brown rice	–14.9
maple syrup	–10.4

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***.

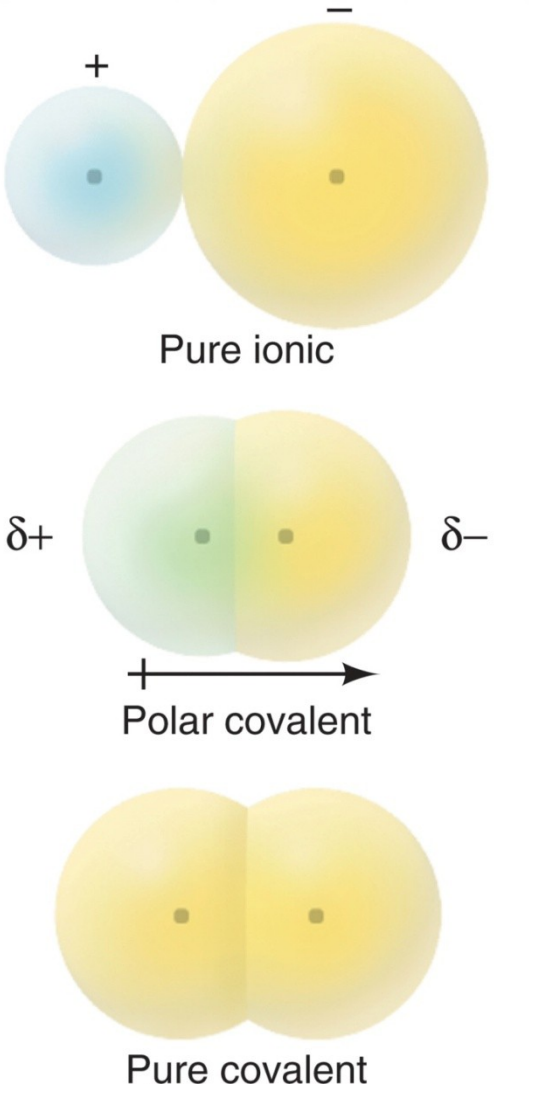
Unequal sharing of electrons causes the more electronegative atom of the bond to be *partially* negative and the less electronegative atom to be *partially* positive.





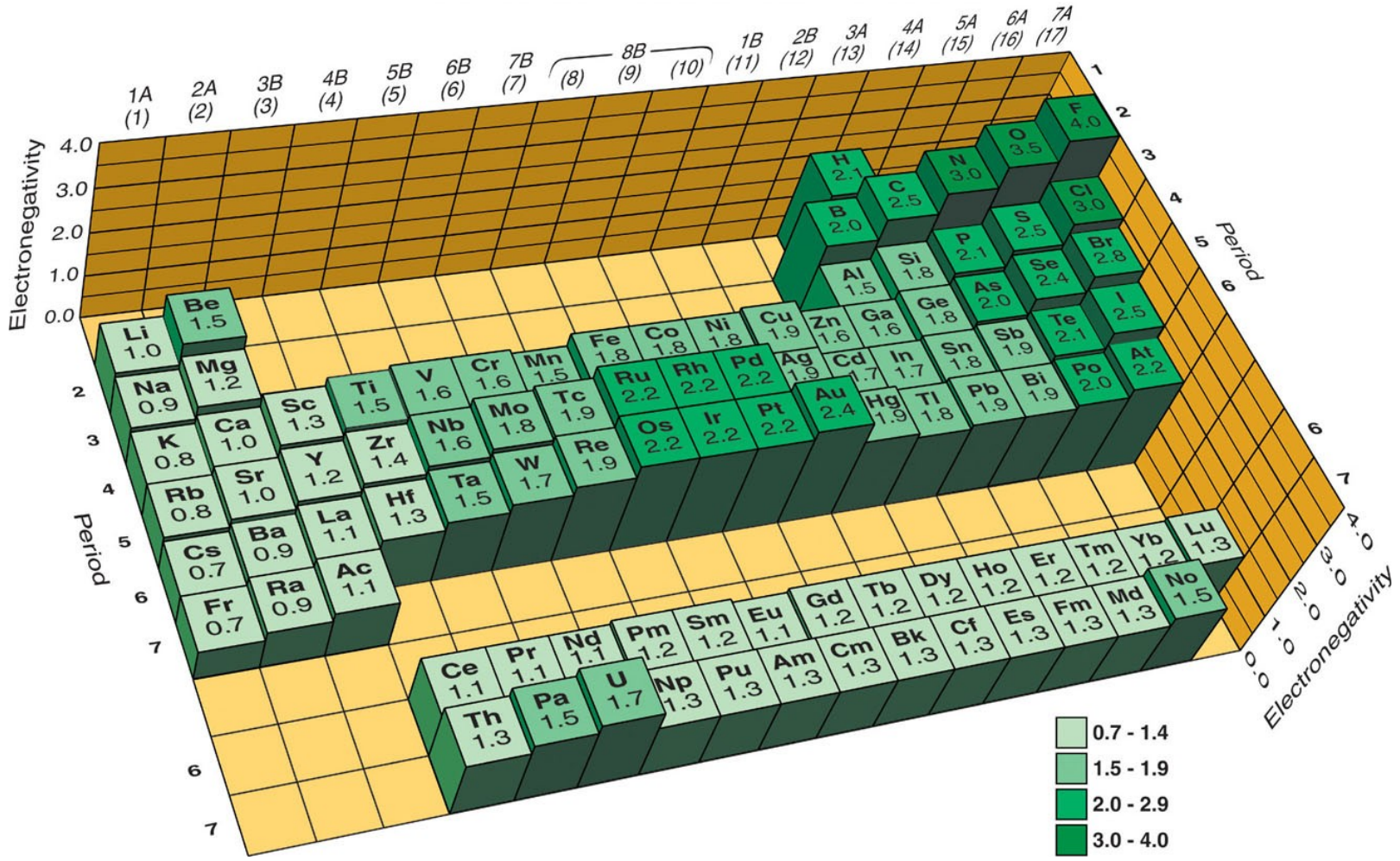
Figure 9.20 Bonding between the models.

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

Figure 9.21 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***.

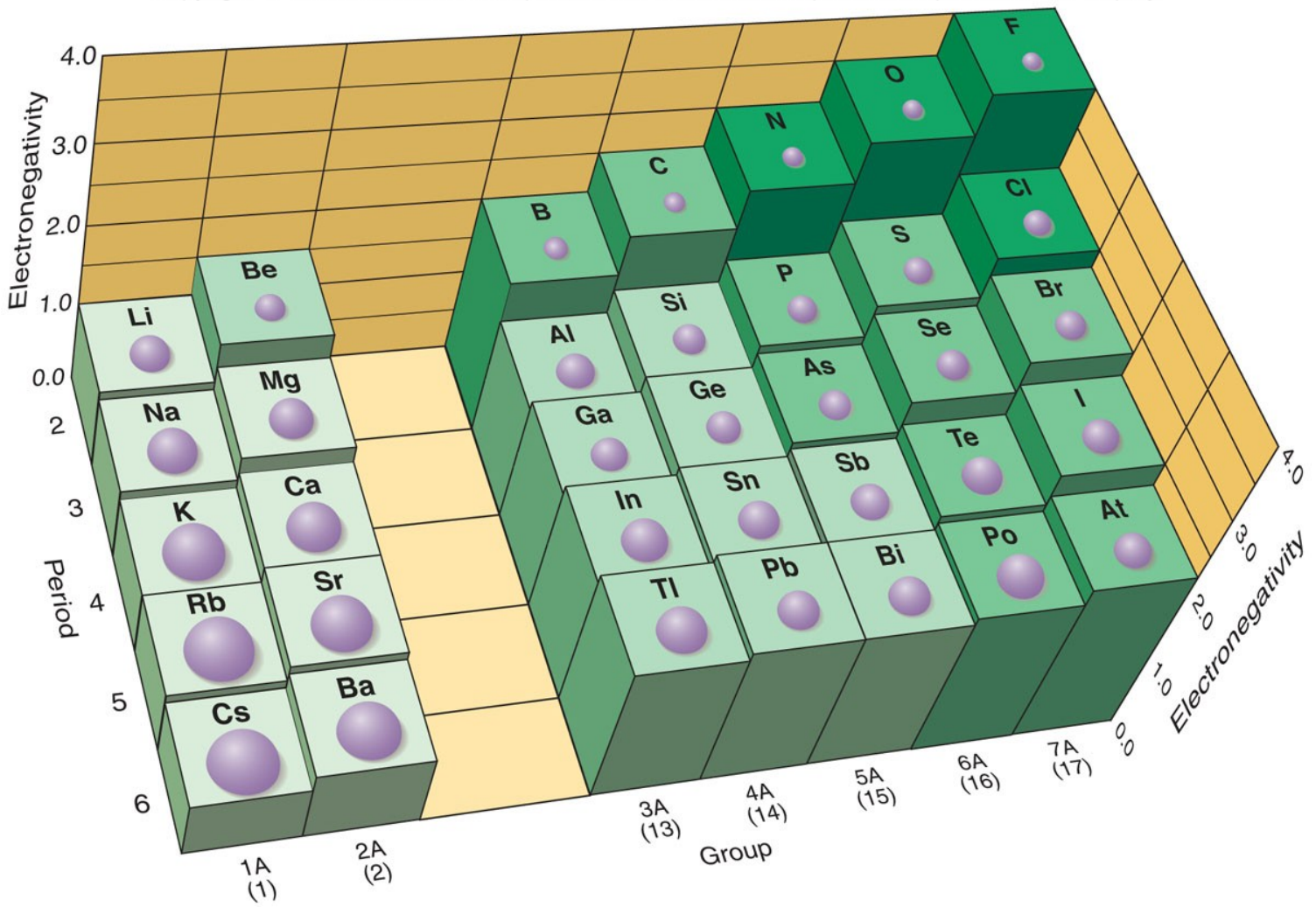
Nonmetals tend to be ***more*** electronegative than metals.





Figure 9.22 Electronegativity and atomic size.

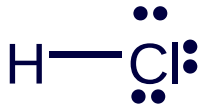
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Electronegativity and Oxidation Number

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

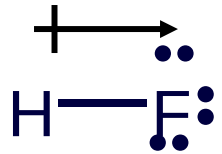
shared e^- = 0 (all shared e^- assigned to Cl)

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.

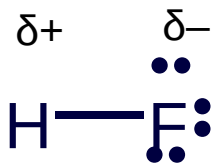
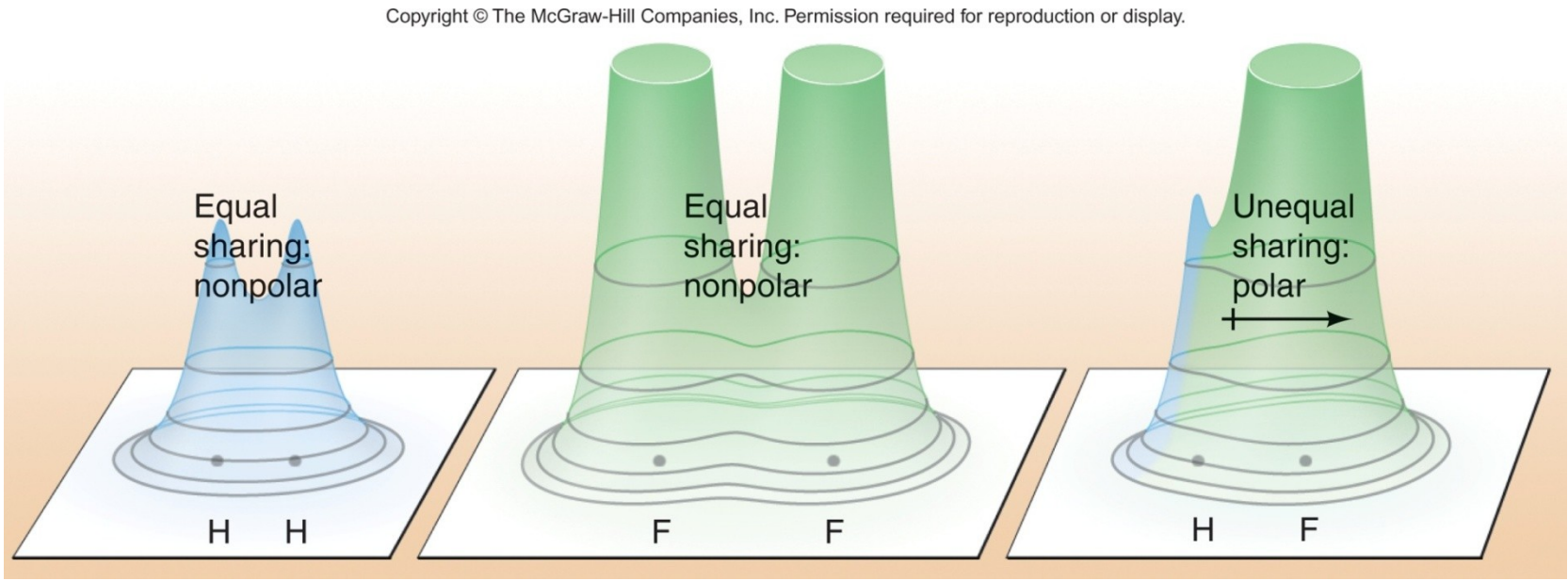


Figure 9.23 Electron density distributions in H_2, F_2, and HF.



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

The H–F bond has partial ionic character.

Figure 9.24 **ΔEN ranges for classifying the partial ionic character of bonds.**

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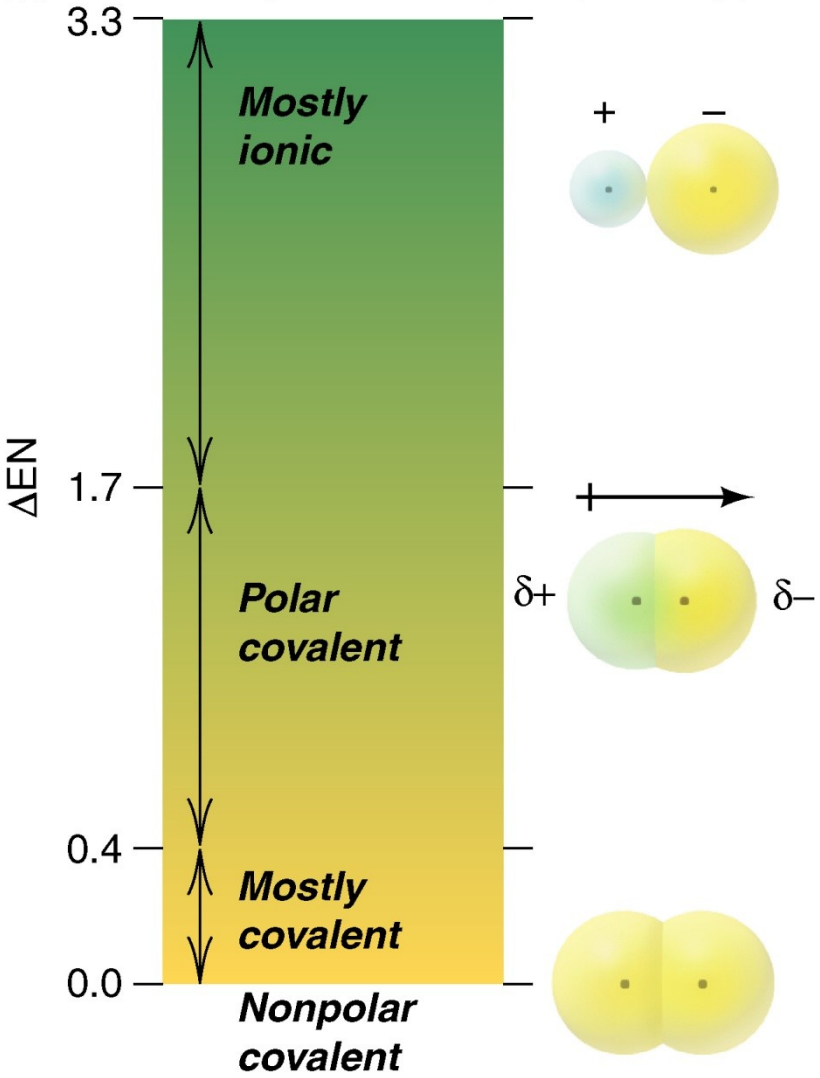
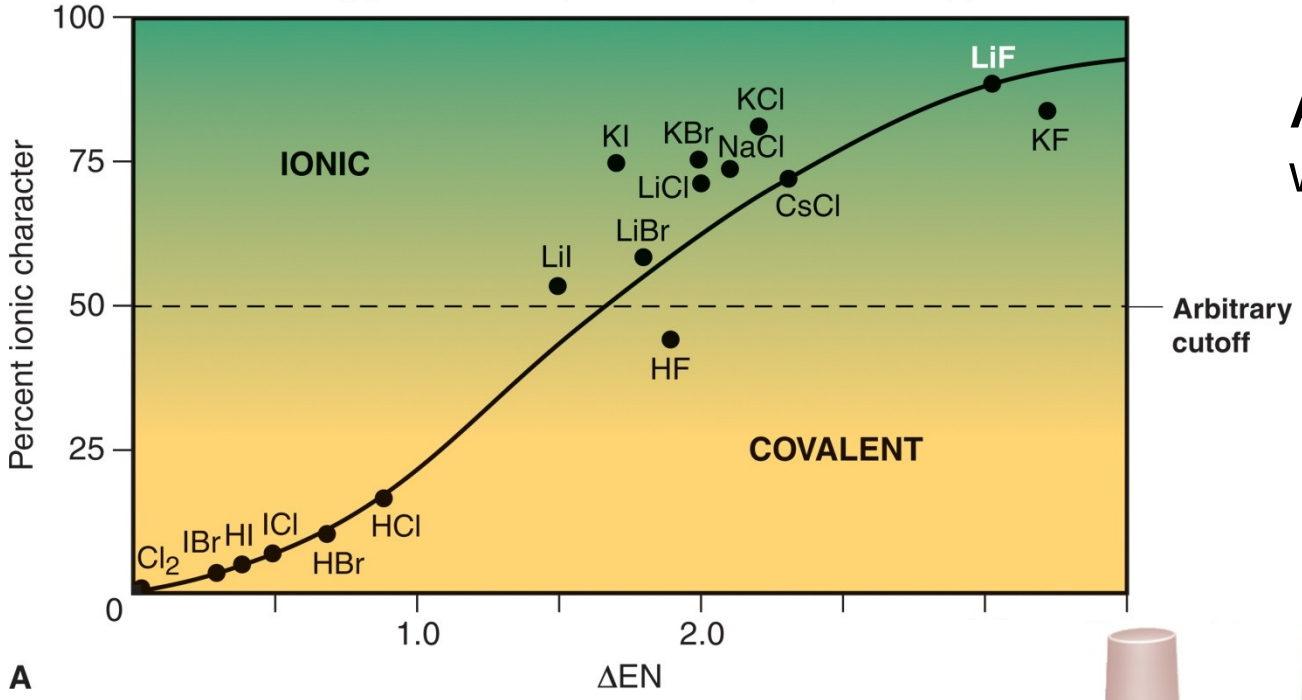


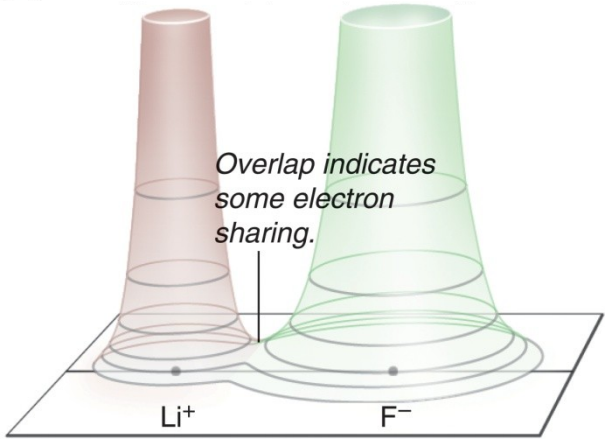
Figure 9.25 Percent ionic character as a function of ΔEN.

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A: ΔEN correlates with ionic character.

B: Even in highly ionic LiF (ΔEN = 3.0) some electron sharing occurs between the ions in the gaseous ion pair.



Sample Problem 9.5 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.

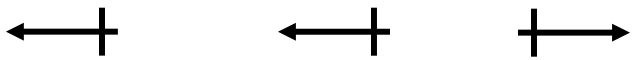
(b) Rank the following bonds in order of increasing polarity: H–N, H–O, H–C.

PLAN: **(a)** We use Figure 9.21 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



N–H F–N I–Cl

Sample Problem 9.5

(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

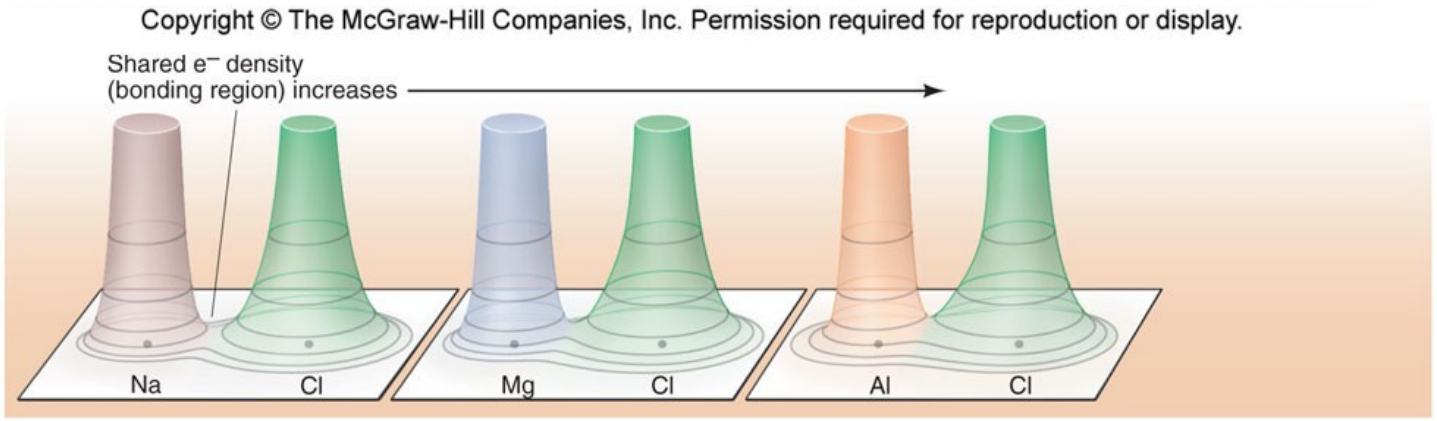
ΔEN for H–O = 3.5 – 2.1 = 1.4

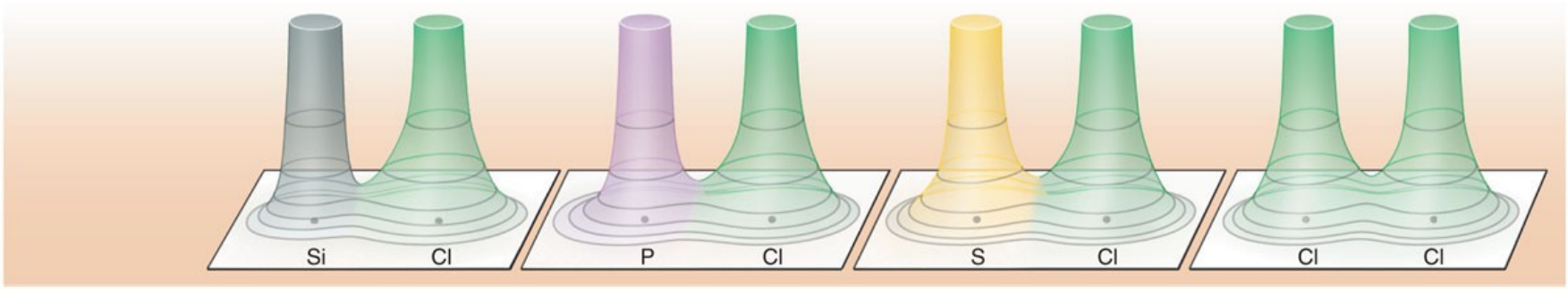
ΔEN for H–C = 2.5 – 2.1 = 0.4

In order of polarity:

H-C < H-N < H-O

Figure 9.26 **Electron density distributions in bonds of the Period 3 chlorides.**





There is a steady increase in electron sharing from left to right.

Metallic Bonding

The ***electron sea*** model of metallic bonding proposes that:

- All metal atoms in the sample contribute their valence electrons to form a delocalized electron “sea”.
- The metal “ions” (nuclei with core electrons) lie in an orderly array within this mobile sea.
- All the atoms in the sample share the electrons.
- The metal is held together by the attraction between the metal “cations” and the “sea” of valence electrons.

Properties of Metals

- Metals are generally solids with moderate to high melting points and much higher boiling points.
  - Melting points decrease down a group and increase across a period.
- Metals can be shaped without breaking.
  - The electron sea allows the metal ions to slide past each other.
- Metals are good conductors of electricity in both the solid and liquid states.
  - The electron sea is mobile in both phases.
- Metals are good conductors of heat.





Table 9.5 Melting and Boiling Points of Some Metals

Element	mp (°C)	bp (°C)
Lithium (Li)	180	1347
Tin (Sn)	232	2623
Aluminum (Al)	660	2467
Barium (Ba)	727	1850
Silver (Ag)	961	2155
Copper (Cu)	1083	2570
Uranium (U)	1130	3930

Figure 9.28

Melting points of the Group 1A(1) and Group 2A(2) metals.

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