



GENERAL CHEMISTRY

CHE 101

Chemical Bonding I

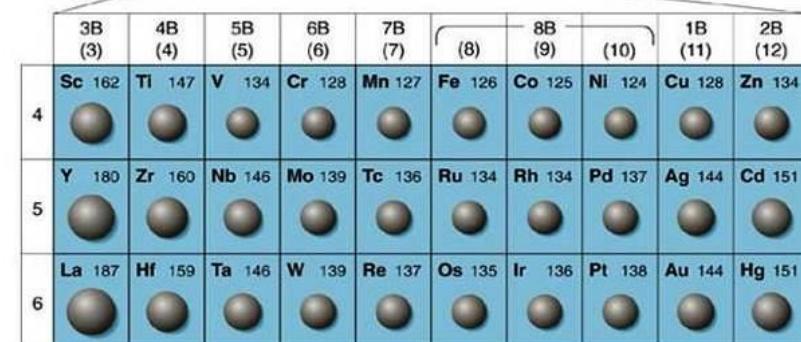
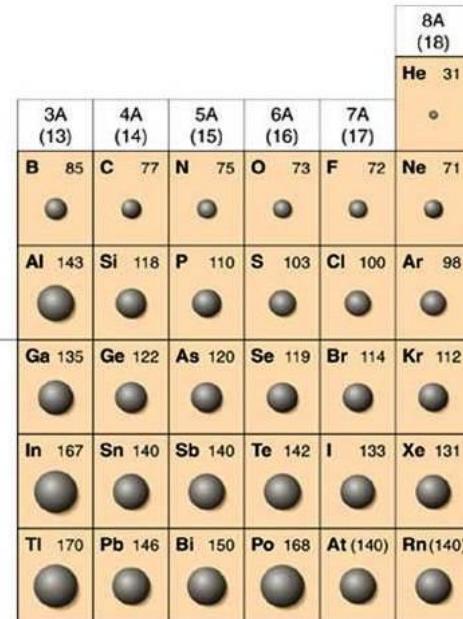
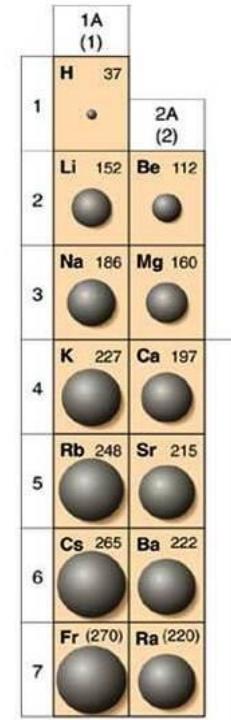
Trends in the Periodic Table

Factors Affecting Atomic Size

- The size of an atom is affected mainly by two factors:
 - 1) Positive Charge in the Nucleus (Z)
 - 2) Number of Shells (n value) around the Nucleus
- A ***higher positive charge*** pulls the electrons closer to the nucleus and ***reduces*** the atomic size.
- The more the number of shells, the greater the ***shielding effect*** from the inner electrons, and this ***increases*** the atomic size.
- The ***net result*** of the above two effects (or the effective nuclear charge, Z_{eff}) determines the final atomic size.

Trends in Atomic Size

- Atomic size **shrinks** across a **period**. The **positive nuclear charge** increases as we move to the right, but the **number of shells (n value)** remains the same.
 - Atomic size **increases** down a **group**. This time we are adding a new shell (**higher n value**) every time we move down the group, and this increases the **shielding effect** by the inner electrons.

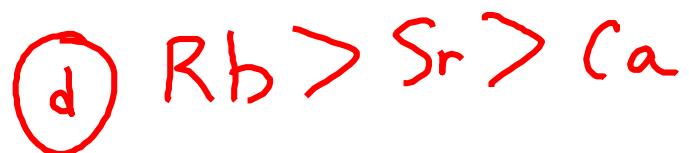
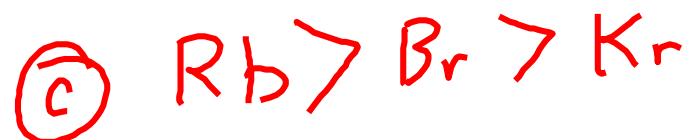
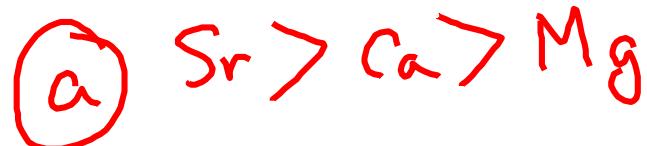


Sample Problem 8.3

Using only the periodic table, rank the following in order of **decreasing** atomic size:



SOLUTION



SAMPLE PROBLEM 8.3

Ranking Elements by Atomic Size

Problem Using only the periodic table (not Figure 8.13), rank each set of main-group elements in order of *decreasing* atomic size:

- (a) Ca, Mg, Sr (b) K, Ga, Ca (c) Br, Rb, Kr (d) Sr, Ca, Rb

Plan To rank the elements by atomic size, we find them in the periodic table. They are main-group elements, so size increases down a group and decreases across a period.

Solution (a) Sr > Ca > Mg. These three elements are in Group 2A(2), and size decreases up the group.

(b) K > Ca > Ga. These three elements are in Period 4, and size decreases across a period.

(c) Rb > Br > Kr. Rb is largest because it has one more energy level (Period 5) and is farthest to the left. Kr is smaller than Br because Kr is farther to the right in Period 4.

(d) Rb > Sr > Ca. Ca is smallest because it has one fewer energy level. Sr is smaller than Rb because it is farther to the right.

Trends in Ionization Energy

- ***Ionization energy (IE)*** is the energy required to **remove** 1 mol of electrons from 1 mol of **gaseous** atoms or ions.
- **Metals** have a ***low IE*** and they form **+ve ions** or **cations**.
- **Non-metals** have a ***high IE*** and they form **-ve ions** or **anions**.
- Ionization energy tends to ***increase*** across a period and ***decrease*** down a group.

Sample Problem 8.4

Using the periodic table only, rank the following in order of **decreasing** IE_1 :

- (a) Kr, He, Ar (b) Sb, Te, Sn (c) K, Ca, Rb (d) I, Xe, Cs

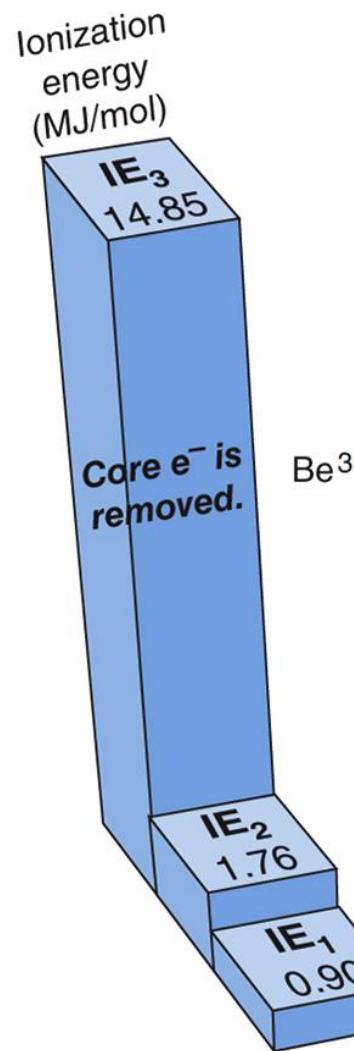
Solution (a) He > Ar > Kr. These are in Group 8A(18), and IE_1 decreases down a group.

(b) Te > Sb > Sn. These are in Period 5, and IE_1 increases across a period.

(c) Ca > K > Rb. IE_1 of K is larger than IE_1 of Rb because K is higher in Group 1A(1). IE_1 of Ca is larger than IE_1 of K because Ca is farther to the right in Period 4.

(d) Xe > I > Cs. IE_1 of I is smaller than IE_1 of Xe because I is farther to the left. IE_1 of I is larger than IE_1 of Cs because I is farther to the right and in the previous period.

The first three Ionization Energies of Beryllium



IE energy drastically increases as we go from outer shells to inner shells.

Sample Problem 8.5

Problem Name the Period 3 element with the following ionization energies (kJ/mol), and write its full electron configuration:

| IE_1 | IE_2 | IE_3 | IE_4 | IE_5 | IE_6 |
|---------------|---------------|---------------|---------------|---------------|---------------|
| 1012 | 1903 | 2910 | 4956 | 6278 | 22,230 |

| IE_1 | IE_2 | IE_3 | IE_4 | IE_5 | IE_6 |
|---------------|---------------|---------------|---------------|---------------|---------------|
| 1012 | 1903 | 2910 | 4956 | 6278 | 22,230 |

\longleftrightarrow 900 \longleftrightarrow 1000 \longleftrightarrow 2000 \longleftrightarrow 1100 \longleftrightarrow 14,000

Plan We look for a large jump in the IE values, which occurs after all valence electrons have been removed. Then we refer to the periodic table to find the Period 3 element with this number of valence electrons and write its electron configuration.

Solution The large jump occurs after IE_5 , indicating that the element has five valence electrons and, thus, is in Group 5A(15). This Period 3 element is phosphorus (P; Z = 15). Its electron configuration is $1s^22s^22p^63s^23p^3$.

Trends in Ionic Size

- Cations are ***smaller*** than their parent atoms while anions are ***larger***.
 - ✓ e.g. Na^+ ion has a smaller radius than Na atom. On the other hand, Cl^- ion has a larger radius than Cl atom.
- Cation size ***decreases*** as the net positive charge ***increases***.
 - ✓ e.g. Mg^{2+} ion has a smaller radius than Na^+ ion.
- Ionic radius ***increases*** down a group since ***n*** value increases.
 - ✓ e.g. K^+ ion has a larger radius than Na^+ ion.

Sample Problem 8.8

Rank each set of ions in order of ***decreasing*** size, and explain your ranking:



SAMPLE PROBLEM 8.8

Ranking Ions by Size

Problem Rank each set of ions in order of *decreasing* size, and explain your ranking:

- (a) Ca^{2+} , Sr^{2+} , Mg^{2+} (b) K^+ , S^{2-} , Cl^- (c) Au^+ , Au^{3+}

Plan We find the position of each element in the periodic table and apply the ideas presented in the text.

Solution (a) Mg^{2+} , Ca^{2+} , and Sr^{2+} are all from Group 2A(2), so their sizes decrease up the group: $\text{Sr}^{2+} > \text{Ca}^{2+} > \text{Mg}^{2+}$.

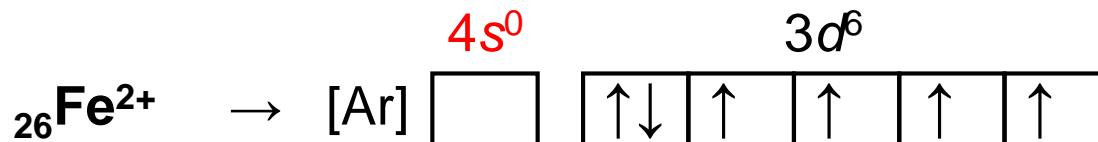
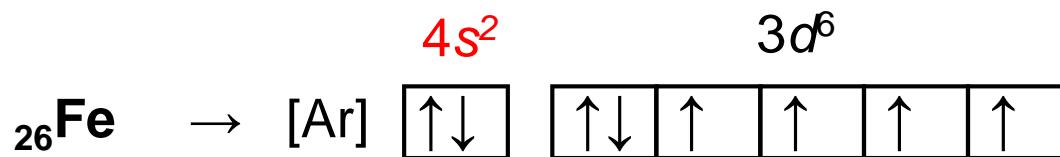
(b) The ions K^+ , S^{2-} , and Cl^- are isoelectronic. S^{2-} has a lower Z_{eff} than Cl^- , so it is larger. K^+ is a cation and has the highest Z_{eff} , so it is smallest: $\text{S}^{2-} > \text{Cl}^- > \text{K}^+$.

(c) Au^+ has a lower charge than Au^{3+} , so it is larger: $\text{Au}^+ > \text{Au}^{3+}$.

Magnetic Properties of Elements

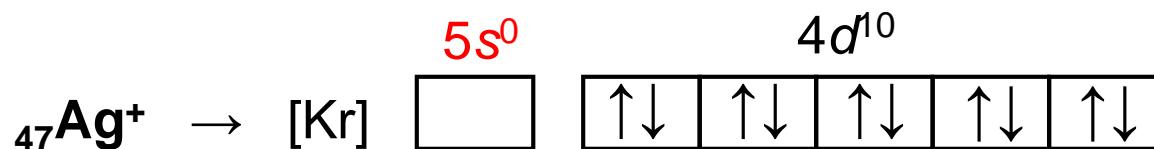
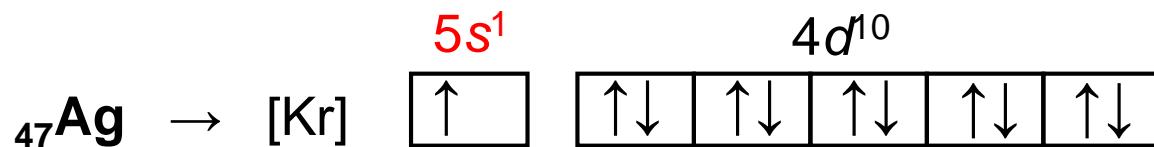
First-In First-Out Principle for forming Ions

- A **4s** subshell is usually lower in energy (more stable) than a **3d** subshell.
- So, while writing the electronic configuration for an atom, the **4s** subshell is filled before a **3d** subshell.
- However, in order to form a positive ion, the electrons are first removed from the **4s** subshell instead of **3d**. That is, **the electrons always come out of the highest *n* value first**.
- Hence, the electrons are put in the **4s** subshell first, but they are taken out of the **4s** subshell first as well (**First-In First-Out Principle**).



Paramagnetic vs Diamagnetic

- A species with any **unpaired** electrons is **paramagnetic**, i.e. it is attracted by a magnetic field.
- A species with all its electrons **paired** is **diamagnetic**, i.e. it is not attracted (and is slightly repelled) by a magnetic field.



- Consistent with the **First-In First-Out Principle**, Ag is **paramagnetic** whereas Ag⁺ turns out to be **diamagnetic**.

Sample Problem 8.7

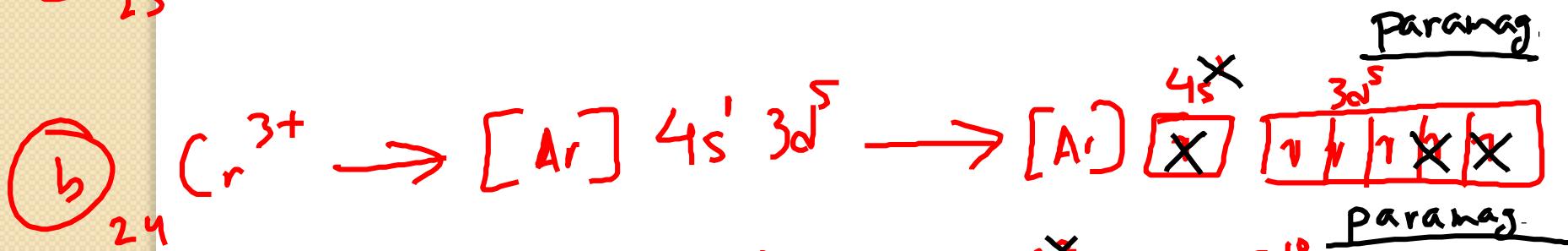
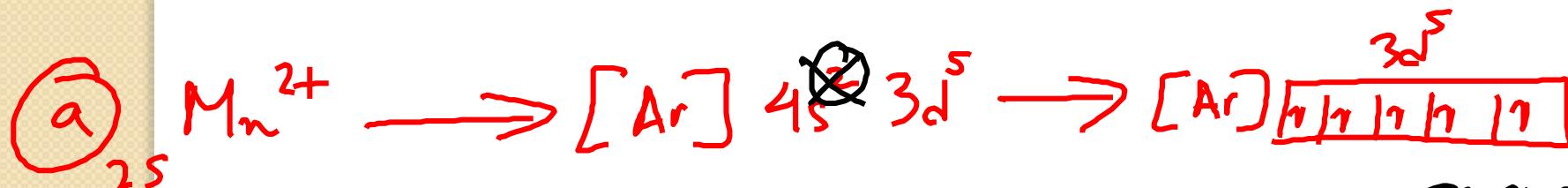
Use condensed electron configurations for each transition metal ion, and predict whether the ion is paramagnetic or diamagnetic.

(a) Mn^{2+} ($Z = 25$)

(b) Cr^{3+} ($Z = 24$)

(c) Hg^{2+} ($Z = 80$)

SOLUTION



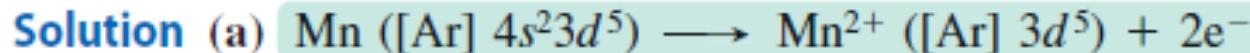
SAMPLE PROBLEM 8.7

Writing Electron Configurations and Predicting Magnetic Behavior of Transition Metal Ions

Problem Use condensed electron configurations to write an equation for the formation of each transition metal ion, and predict whether it is paramagnetic:

- (a) Mn^{2+} ($Z = 25$) (b) Cr^{3+} ($Z = 24$) (c) Hg^{2+} ($Z = 80$)

Plan We first write the condensed electron configuration of the atom, recalling the irregularity for Cr. Then we remove electrons, beginning with ns electrons, to attain the ion charge. If unpaired electrons are present, the ion is paramagnetic.



There are five unpaired e^- , so Mn^{2+} is paramagnetic.



There are three unpaired e^- , so Cr^{3+} is paramagnetic.



The $4f$ and $5d$ sublevels are filled, so there are no unpaired e^- : Hg^{2+} is *not* paramagnetic.

Check We removed the ns electrons first, and the sum of the lost electrons and those in the electron configuration of the ion equals Z .

Chemical Bonding

Types of Chemical Bonding

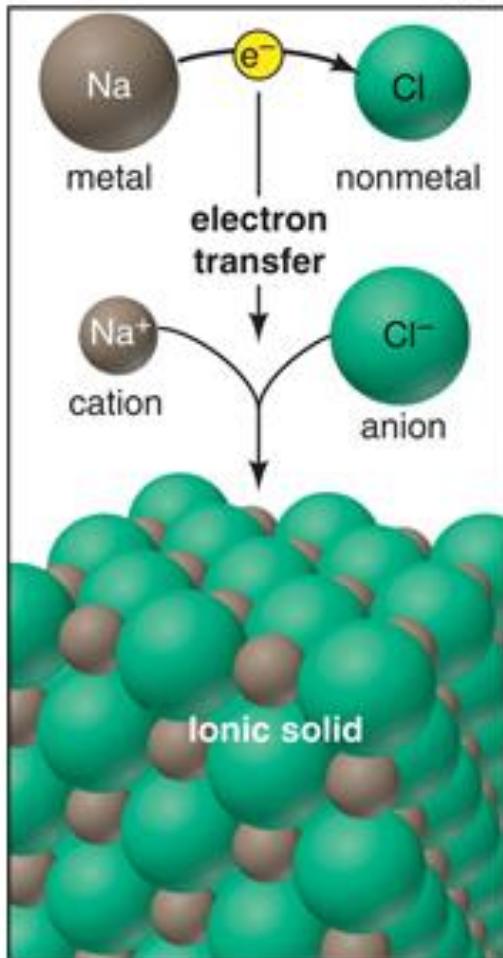
Ionic bonding involves the **transfer** of electrons and is usually observed when a **metal** bonds to a **nonmetal**.

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

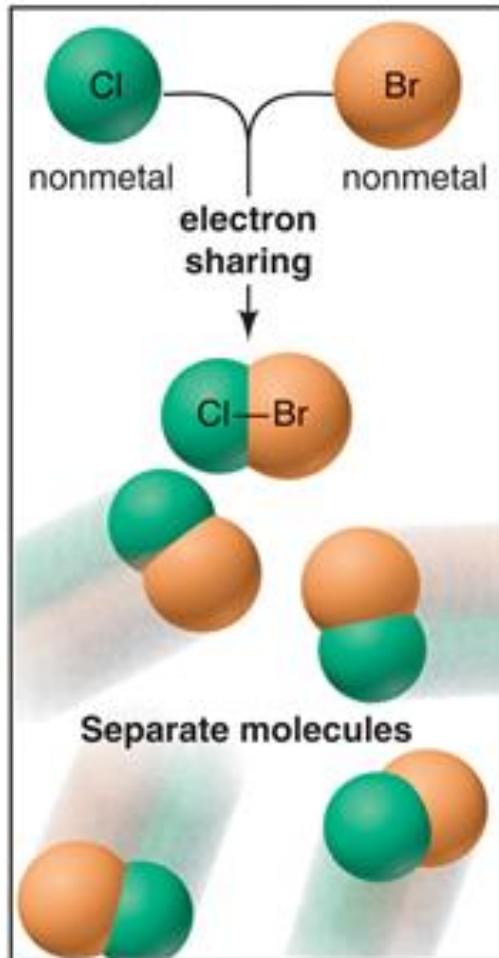
Metallic bonding involves **electron pooling** and occurs when a **metal** bonds to another **metal**.

Three models of chemical bonding

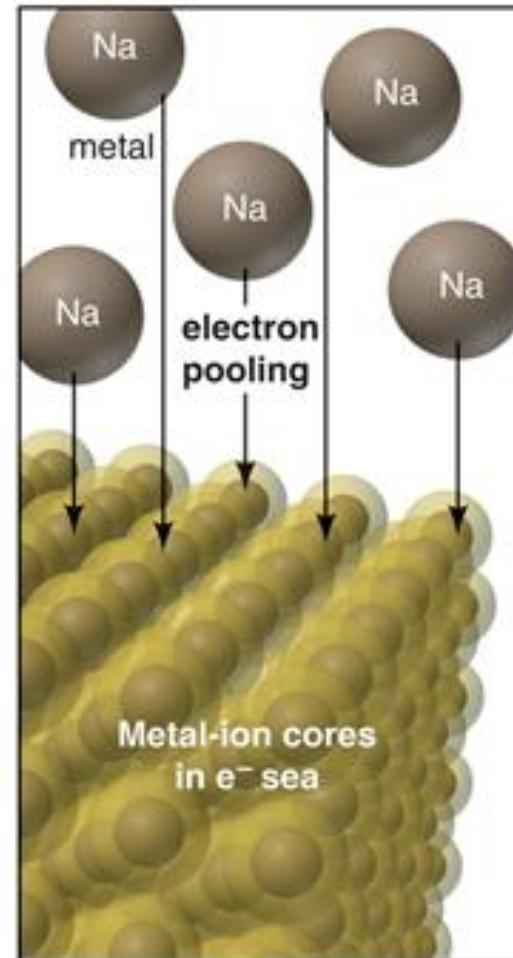
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A Ionic bonding



B Covalent bonding



C Metallic bonding

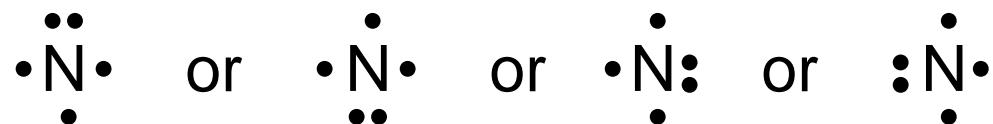
Lewis Electron-Dot Symbols

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.

| | 1A(1) | 2A(2) | 3A(13) | 4A(14) | 5A(15) | 6A(16) | 7A(17) | 8A(18) |
|--------|--------|--------|------------|------------|------------|------------|------------|------------|
| | ns^1 | ns^2 | ns^2np^1 | ns^2np^2 | ns^2np^3 | ns^2np^4 | ns^2np^5 | ns^2np^6 |
| Period | | | | | | | | |
| 2 | • Li | • Be • | • B • | • C • | • N • | • O • | • F • | • Ne • |
| 3 | • Na | • Mg • | • Al • | • Si • | • P • | • S • | • Cl • | • Ar • |

The Ionic Bonding Model

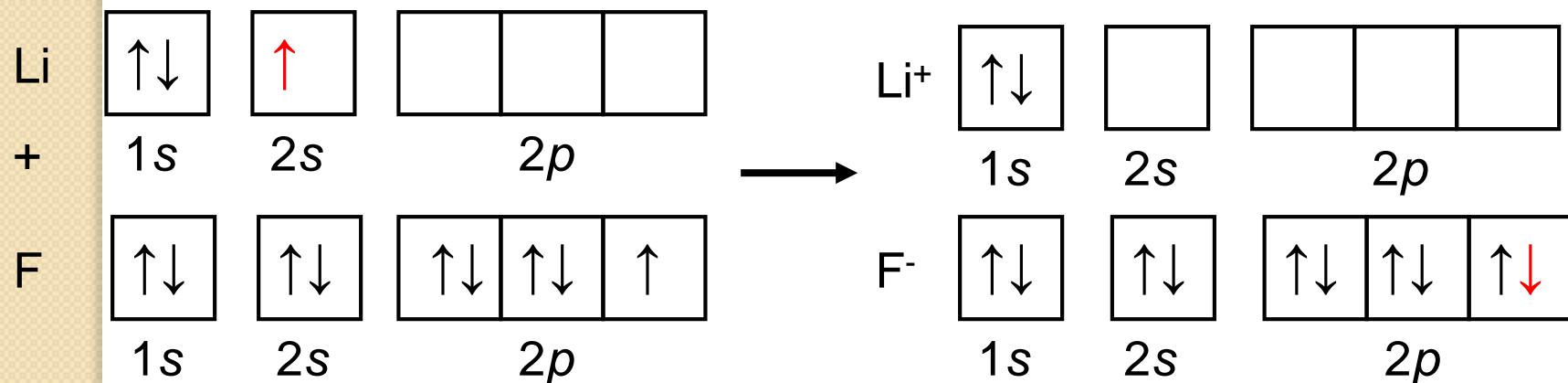
An ionic bond is formed when a metal *transfers* electrons to a nonmetal to form *ions*, which attract each other to give a solid compound.

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

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

Electron configurations $\text{Li } 1s^2 2s^1 + \text{F } 1s^2 2s^2 2p^5 \rightarrow \text{Li}^+ 1s^2 + \text{F}^-$
 $1s^2 2s^2 2p^6$

Orbital diagrams



Lewis electron-dot symbols



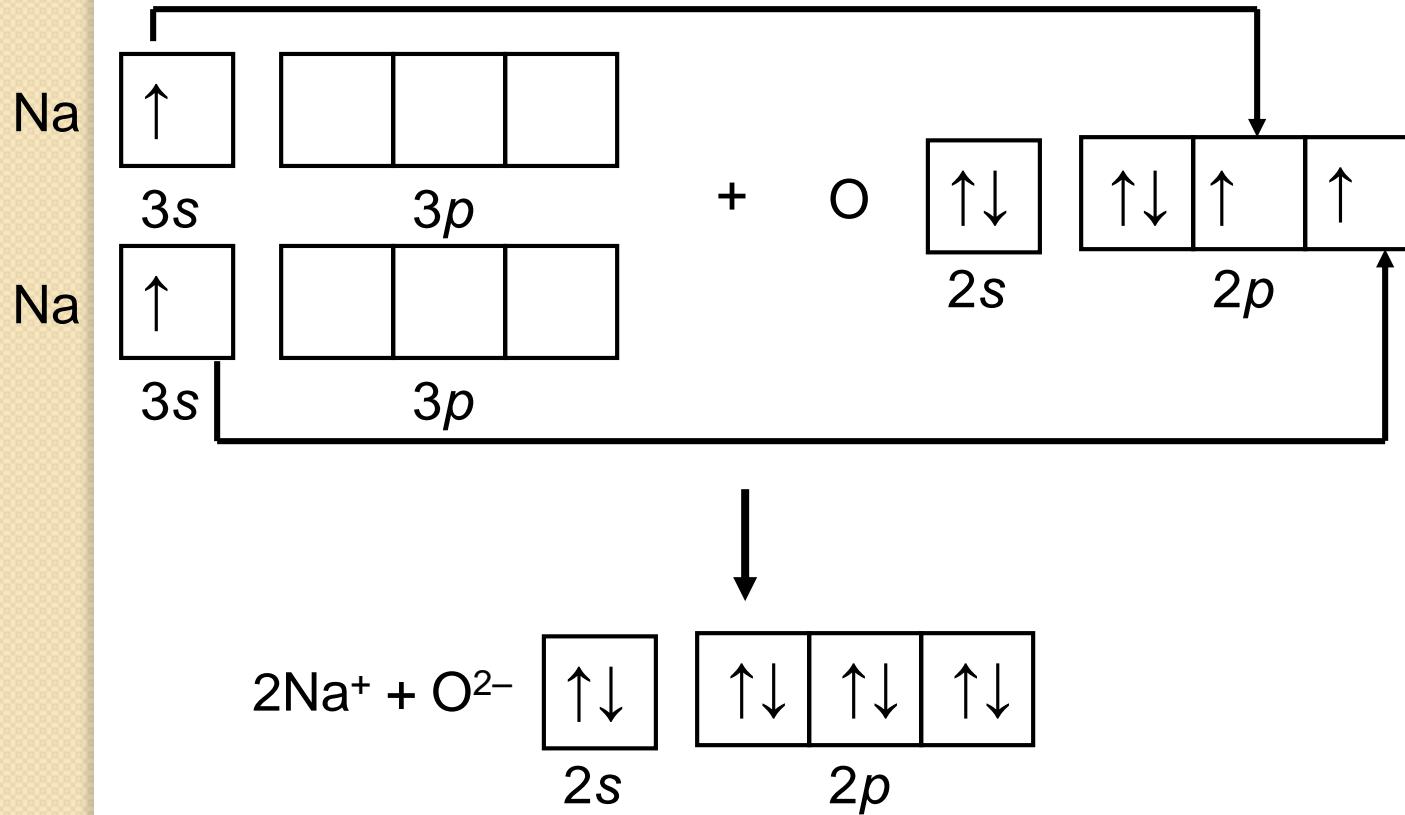
Sample Problem 9.1

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.

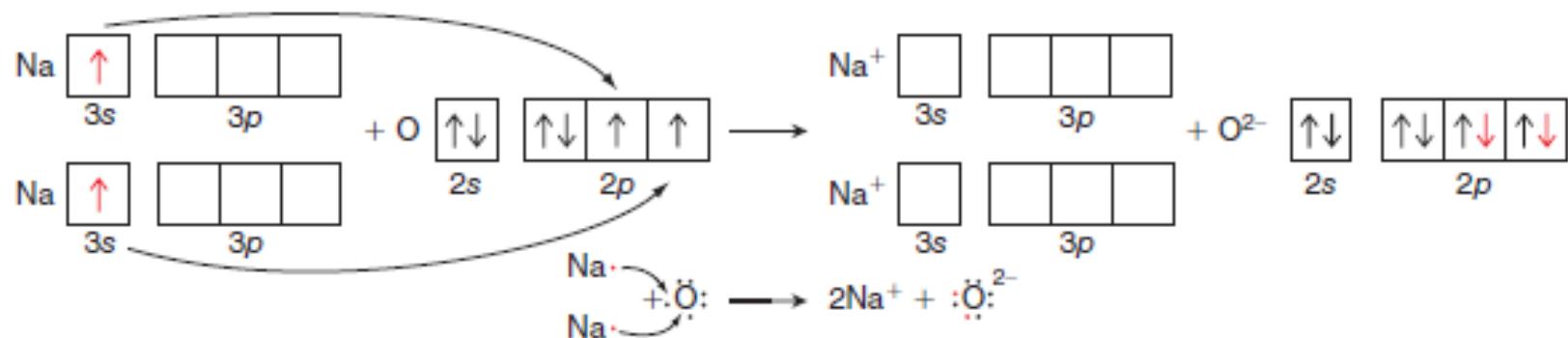
PLAN: Draw orbital diagrams and Lewis symbols for Na and O atoms. To attain filled outer levels, Na loses one electron and O gains two. Two Na atoms are needed for each O atom so that the number of electrons lost equals the number of electrons gained.

Sample Problem 9.1



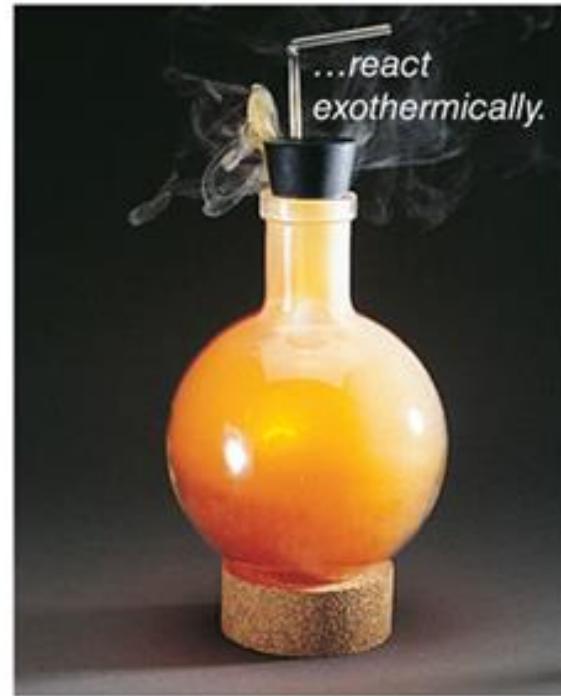
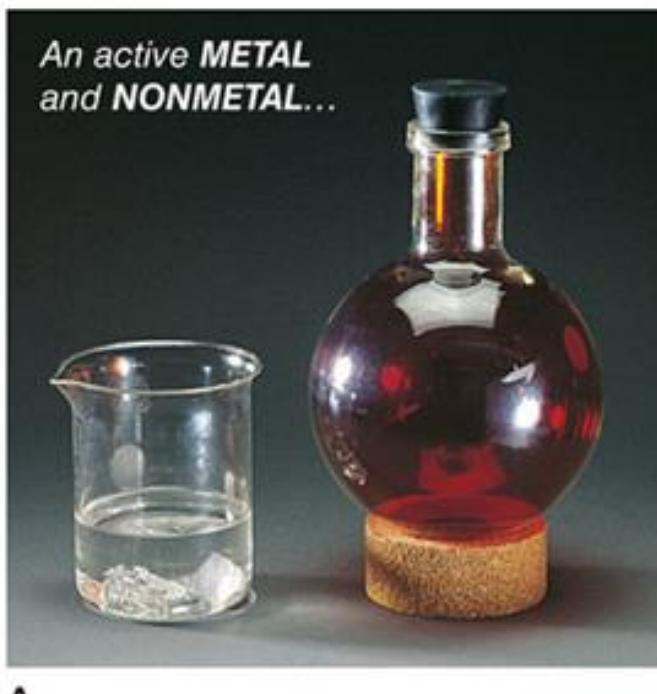
The formula is Na_2O

SOLUTION:



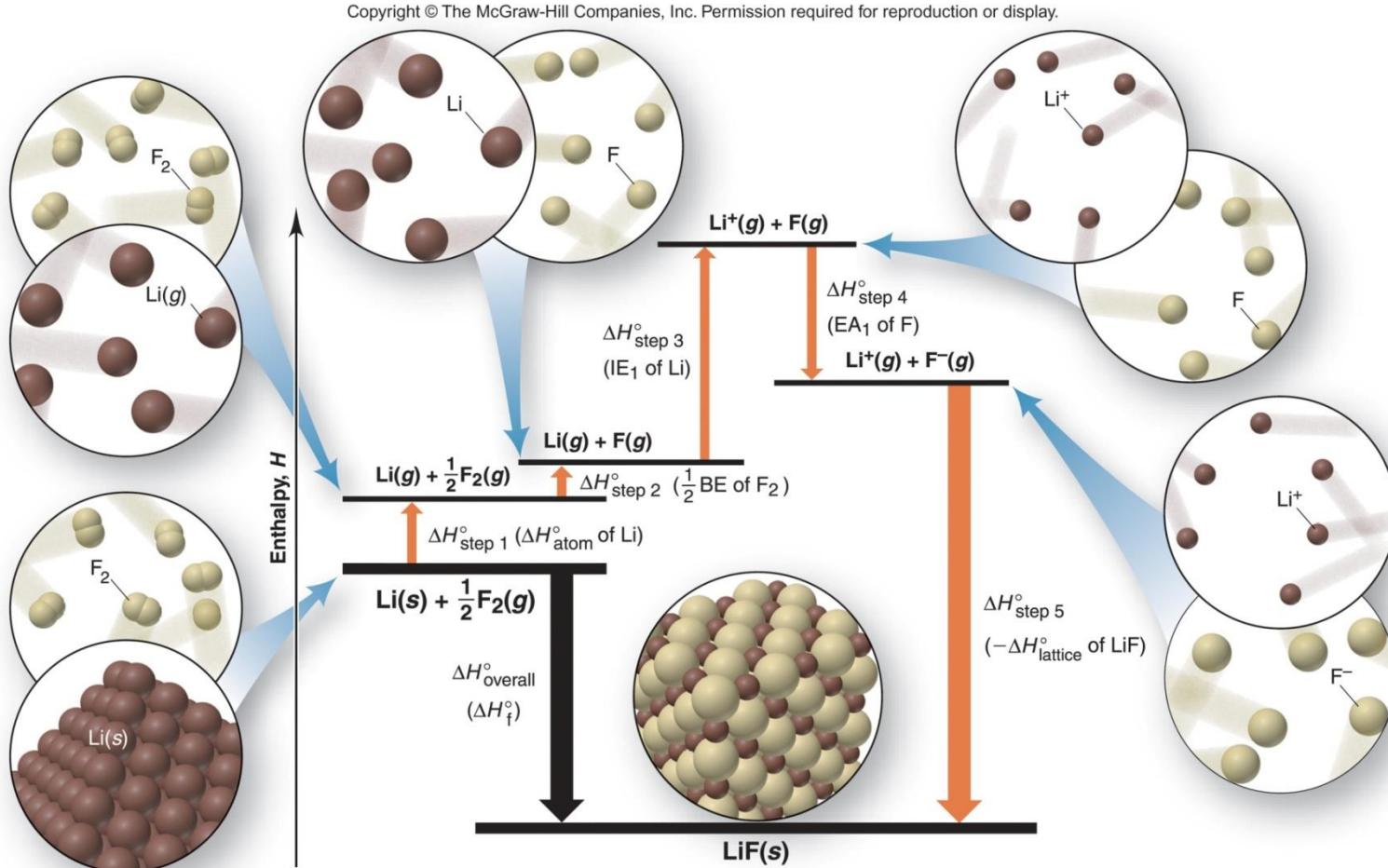
The formula is Na_2O .

Figure 9.6 The exothermic formation of sodium bromide.



Formation of NaBr is one of typical reactions between active metals and nonmetals: ionic solids form readily.

Figure 9.7 The Born-Haber cycle for lithium fluoride.



Periodic Trends in Lattice Energy

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

The magnitude of the lattice energy is a measure of the strength of the ionic interactions and influences macroscopic properties, such as melting point, hardness, and solubility.

Coloumb's Law

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

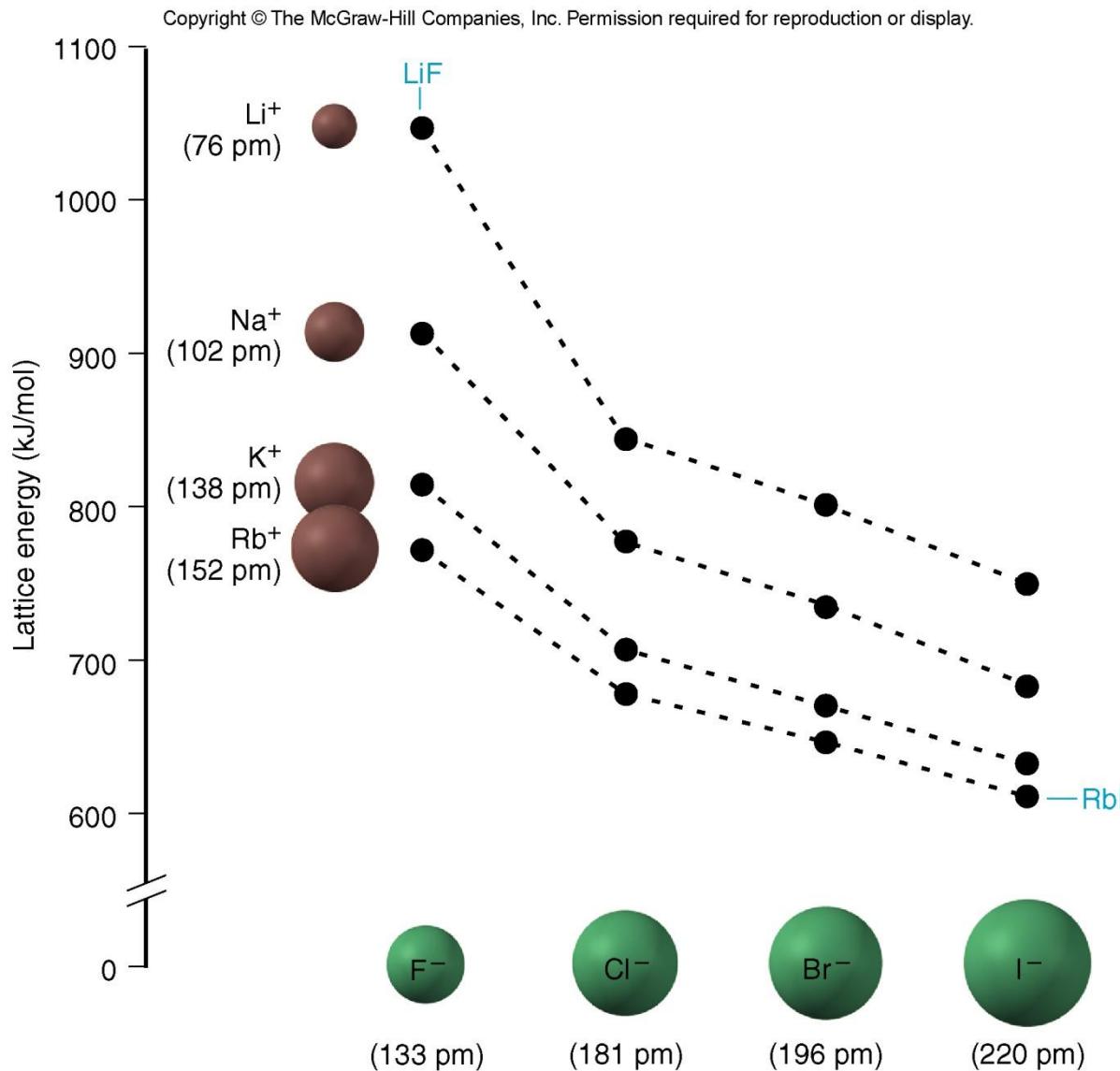
$$\text{Electrostatic energy} \propto \frac{\text{cation charge} \times \text{anion charge}}{\text{cation radius} + \text{anion radius}} \propto \Delta H^\circ_{\text{lattice}}$$

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.



Sample Problem 9.2

Predicting Relative Lattice Energies from Ionic Properties

PROBLEM:

Use ionic properties to choose the compound in each pair with the larger lattice energy: (a) Rbl or NaBr; (b) KCl or CaS.

PLAN:

To choose the compound with the larger lattice energy, we apply Coulomb's law and periodic trends in ionic radius and charge. We examine the ions in each compound: for ions of similar size, higher charge leads to a larger lattice energy; for ions with the same charge, smaller size leads to larger lattice energy because the ions can get closer together.

Sample Problem 9.2

SOLUTION:

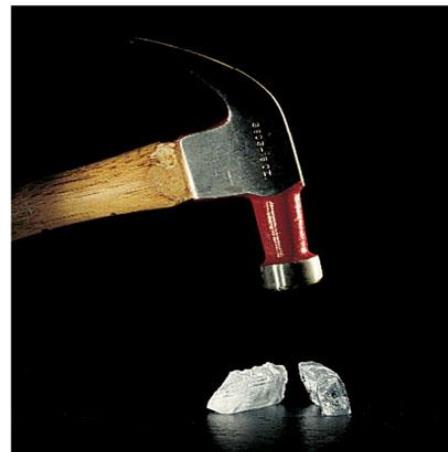
- (a) NaBr. All the ions have single charges, so charge is not involved. Size increases down a group, so Rb^+ is larger than Na^+ , and I^- is larger than Br^- . Therefore, NaBr has the larger lattice energy because it consists of smaller ions.
- (b) CaS. Size decreases from left to right, so K^+ is slightly larger than Ca^{2+} , and S^{2-} is slightly larger than Cl^- . However, these small differences are not nearly as important as the charges: Ca^{2+} and S^{2-} have twice the charge of K^+ and Cl^- , so CaS has the larger 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 9.9

Why ionic compounds crack



A

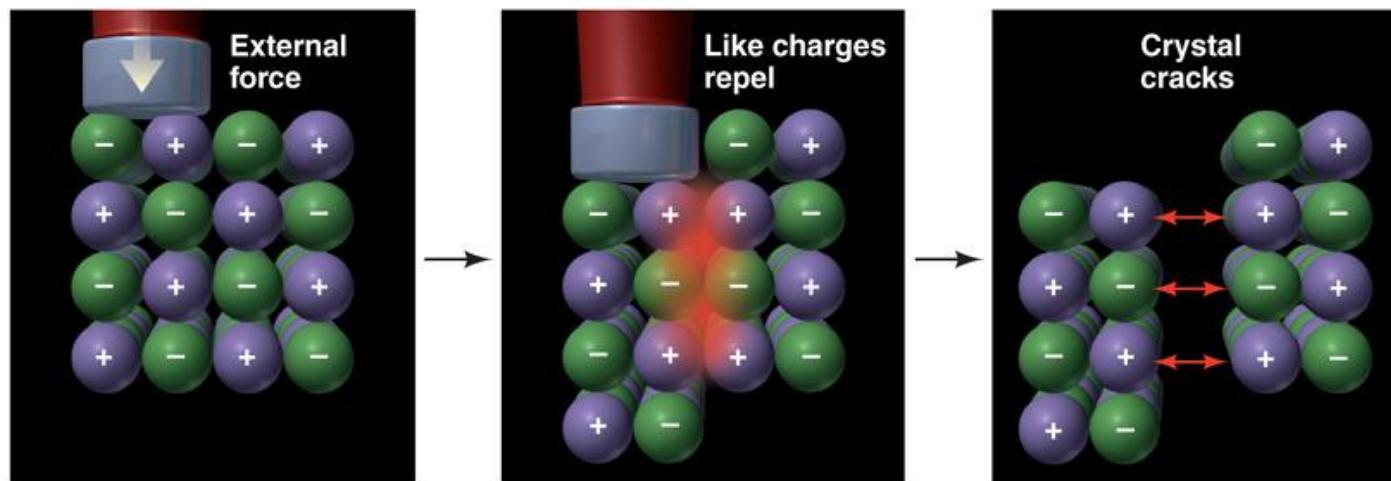
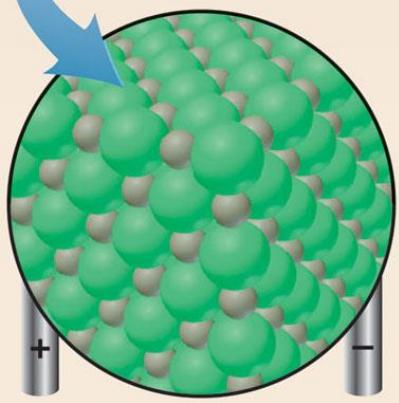
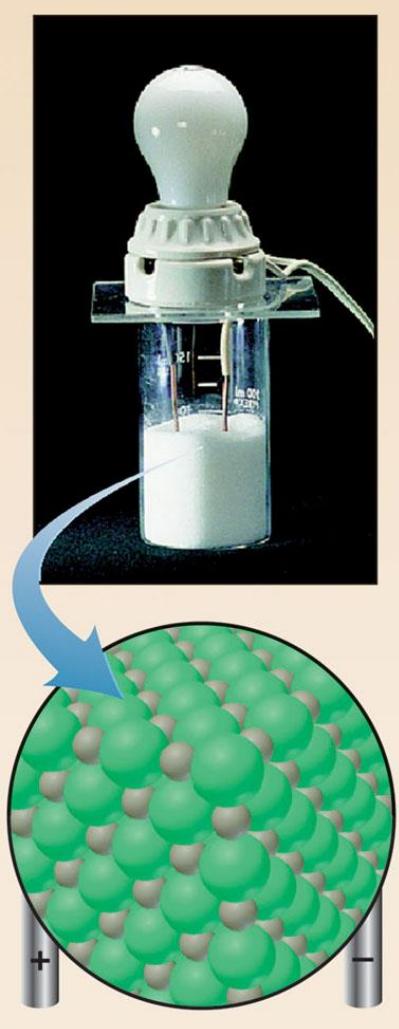
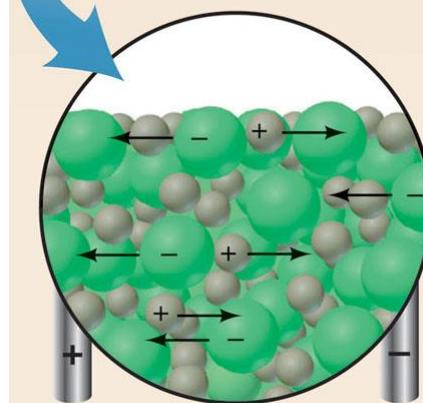
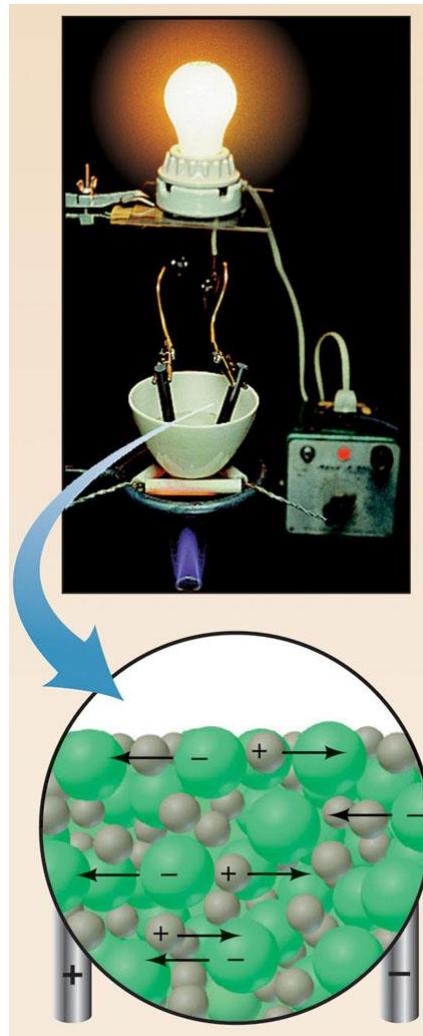


Figure 9.10

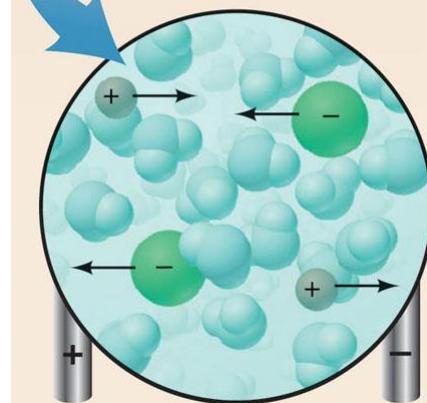
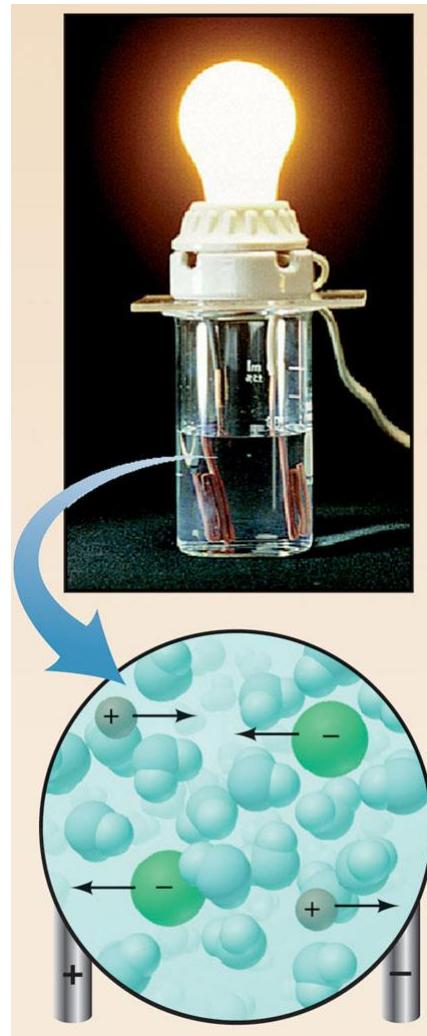
Electrical conductance and ion mobility



Solid ionic compound



Molten ionic compound



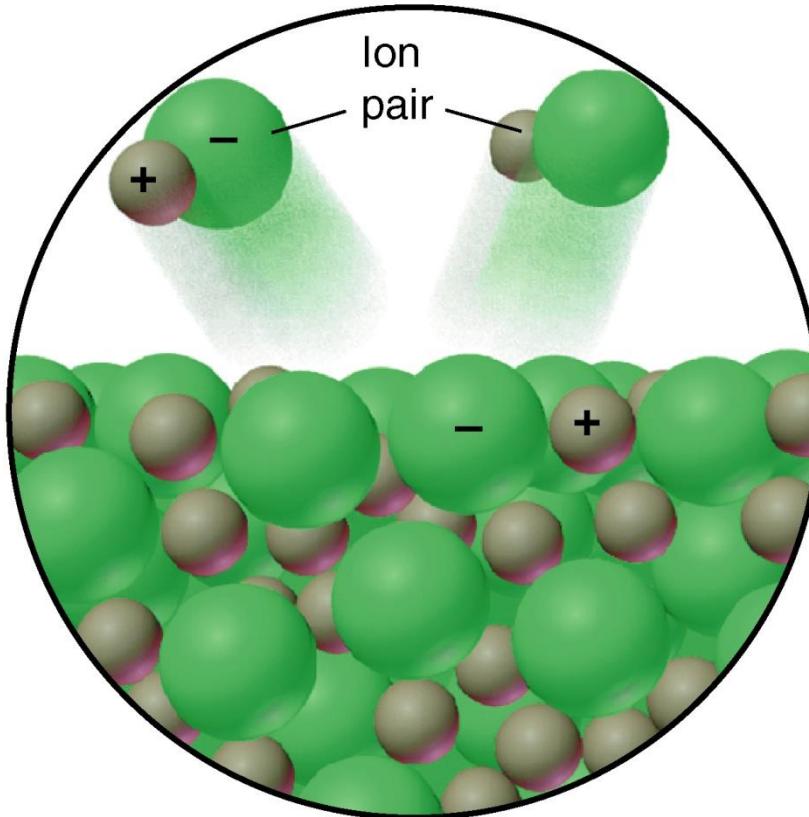
Ionic compound dissolved in water

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 9.11 Ion pairs formed when an ionic compound vaporizes

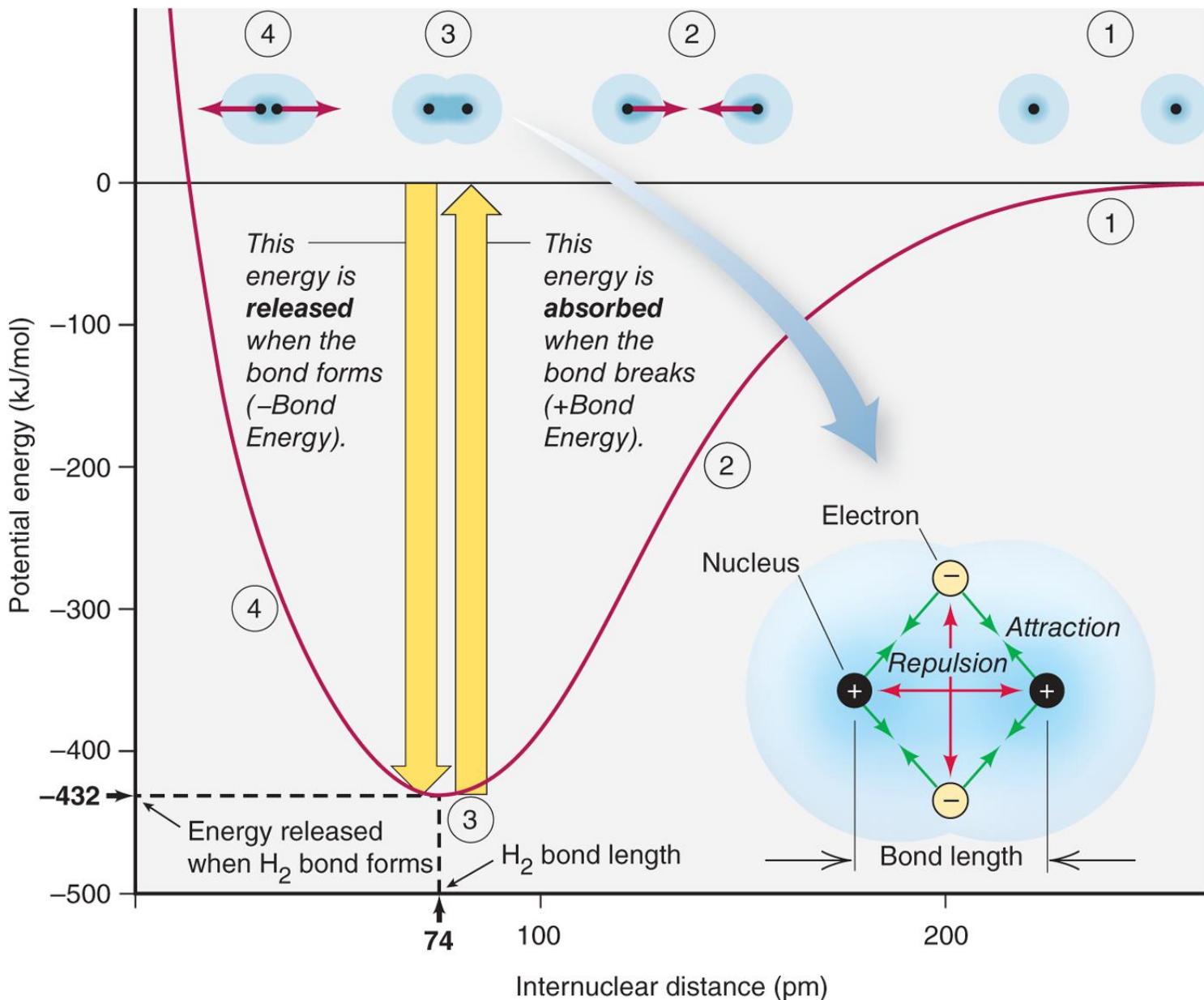
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Interionic attractions are so strong that when an ionic compound is vaporized, ion pairs are formed

Figure 9.12 Covalent bond formation in H₂

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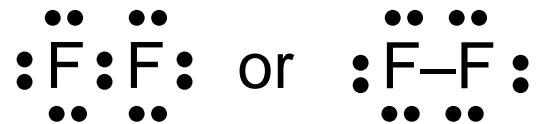
Bonding Pairs and Lone Pairs

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.

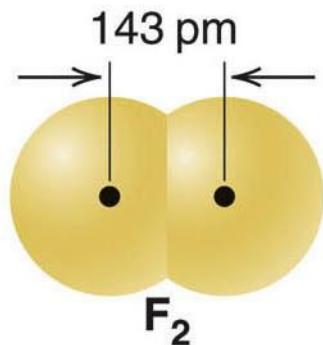
Bond energy shows the opposite trend.

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

Figure 9.14

Bond length and covalent radius

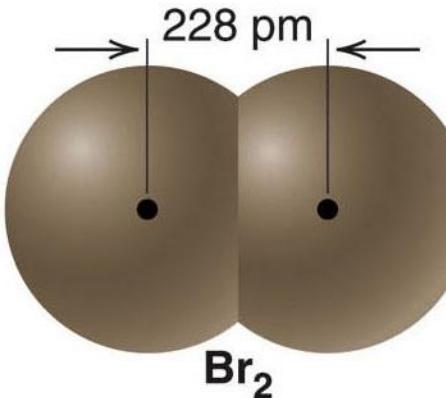
Internuclear distance
(bond length)



Covalent
radius

72 pm

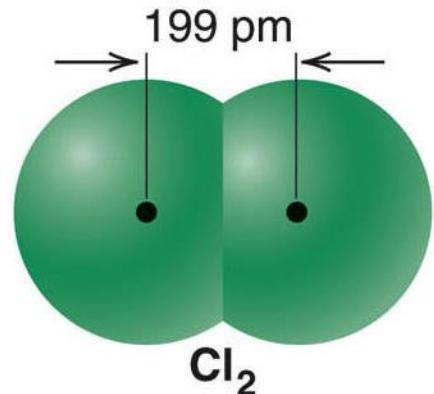
Internuclear distance
(bond length)



Covalent
radius

114 pm

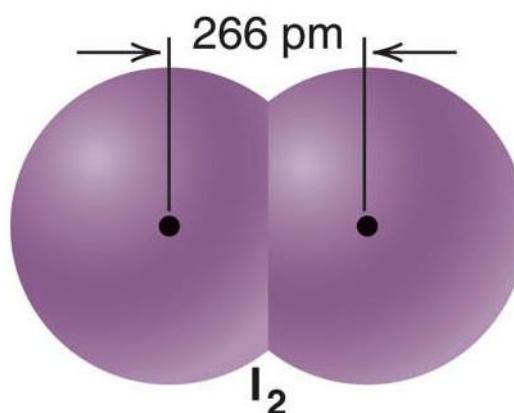
Internuclear distance
(bond length)



Covalent
radius

100 pm

Internuclear distance
(bond length)



Covalent
radius

133 pm

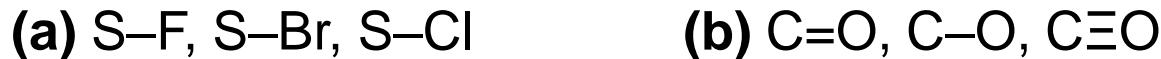
Table 9.3 The Relation of Bond Order, Bond Length, and Bond Energy

| 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 |

Sample Problem 9.3

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:



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 9.3

SOLUTION:

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

Bond length: S–Br > S–Cl > S–F

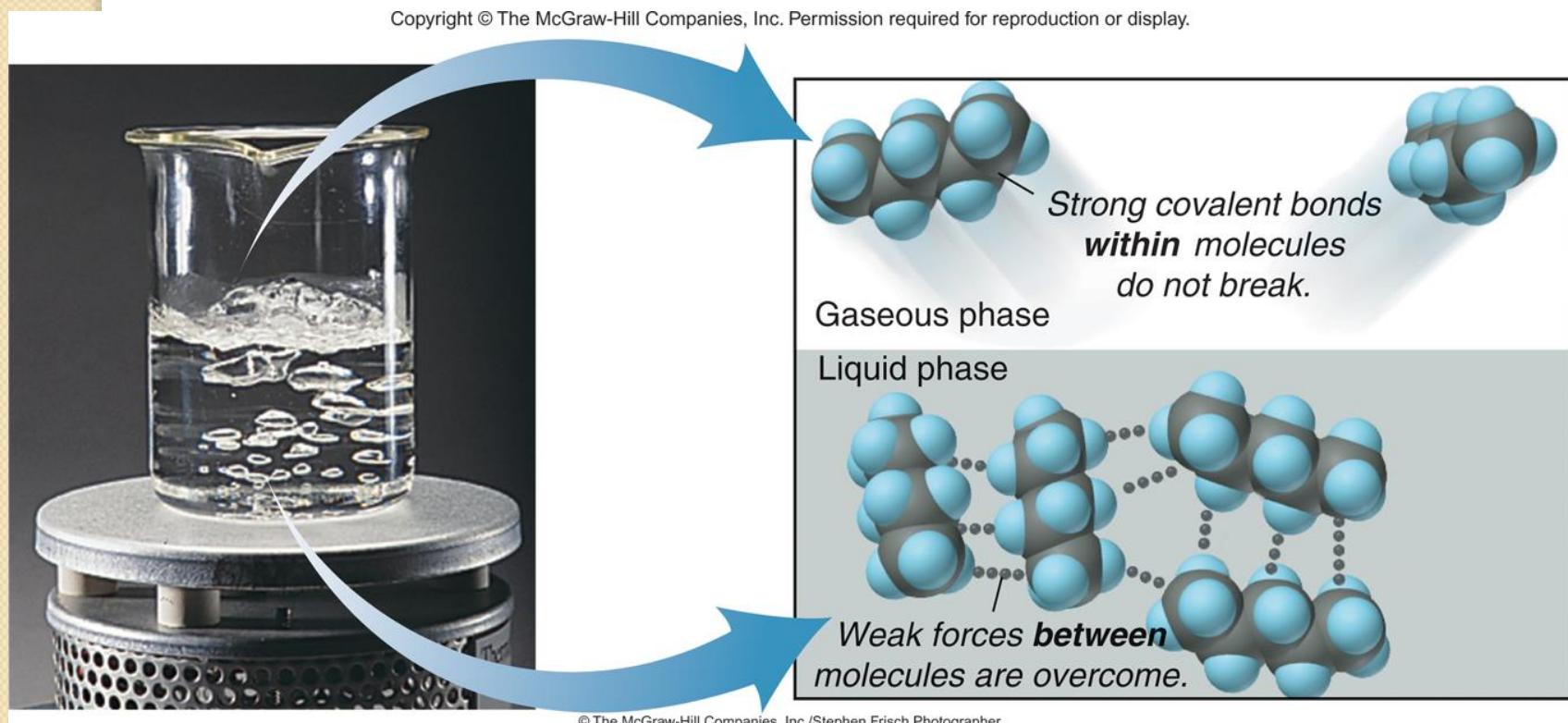
Bond strength: S–F > S–Cl > S–Br

- (b) By ranking the bond orders, we get

Bond length: C–O > C=O > C≡O

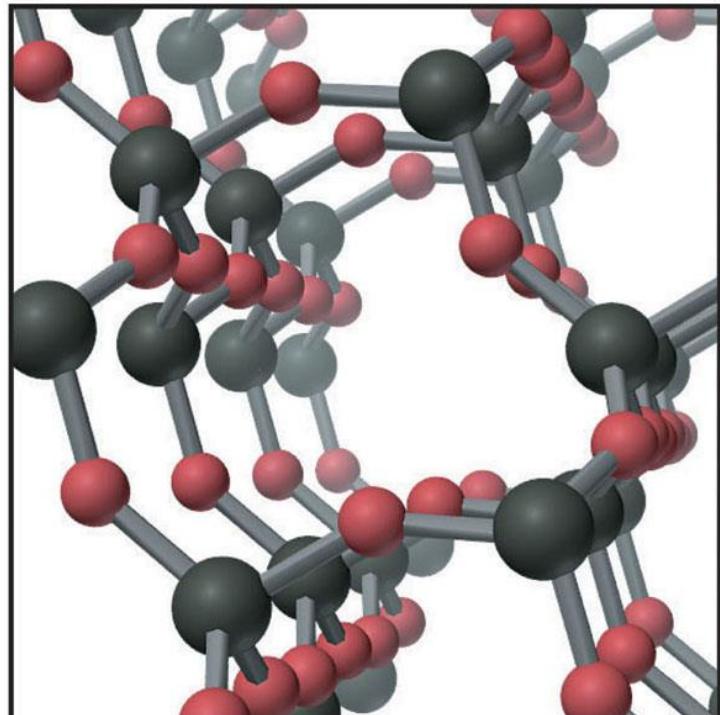
Bond strength: C≡O > C=O > C–O

Figure 9.15: Strong forces within molecules and weak forces between them

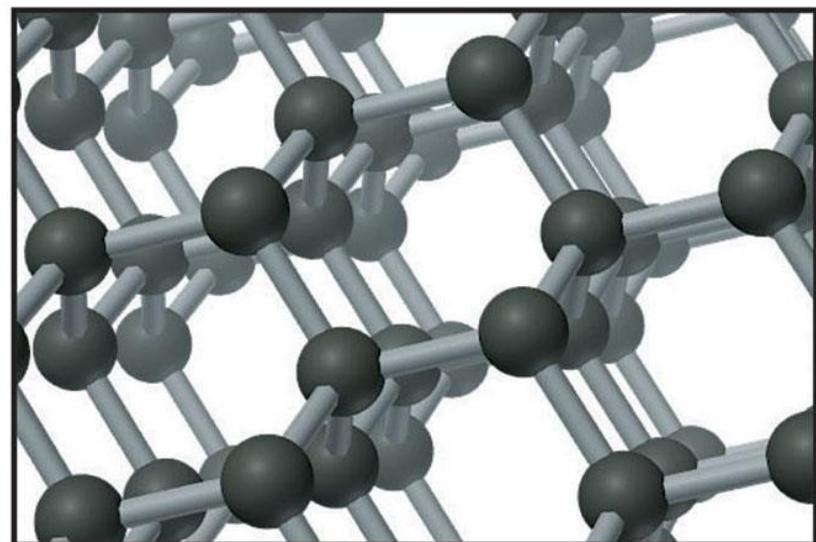


Strong bonding forces hold the atoms together within the molecule, and **Weak intermolecular forces** act between separate molecules in the sample. It is the weak forces between molecules that account for the physical properties of molecular covalent substances. For example, look what happens when pentane (C_5H_{12}) boils (Figure 9.15): weak forces between pentane molecules are overcome, not the strong $C\text{-}C$ and $C\text{-}H$ bonds within each pentane molecule.

Figure 9.16 Covalent bonds of network covalent solids: quartz and diamond



A Quartz



B Diamond



Bond Energies and $\Delta H^\circ_{\text{rxn}}$

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

$$\Delta H^\circ_{\text{rxn}} = \sum \Delta H^\circ_{\text{reactant bonds broken}} + \sum \Delta H^\circ_{\text{product bonds formed}}$$

Figure 9.17

Using bond energies to calculate $\Delta H^\circ_{\text{rxn}}$ for HF formation

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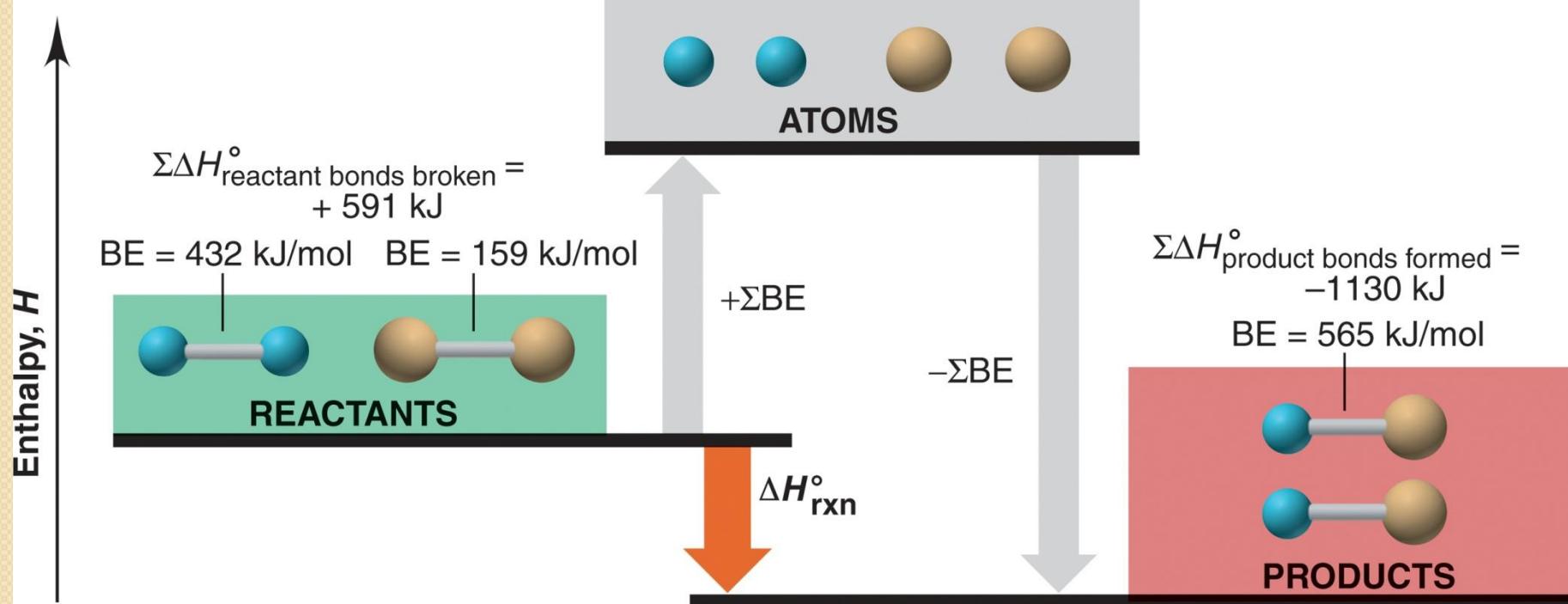
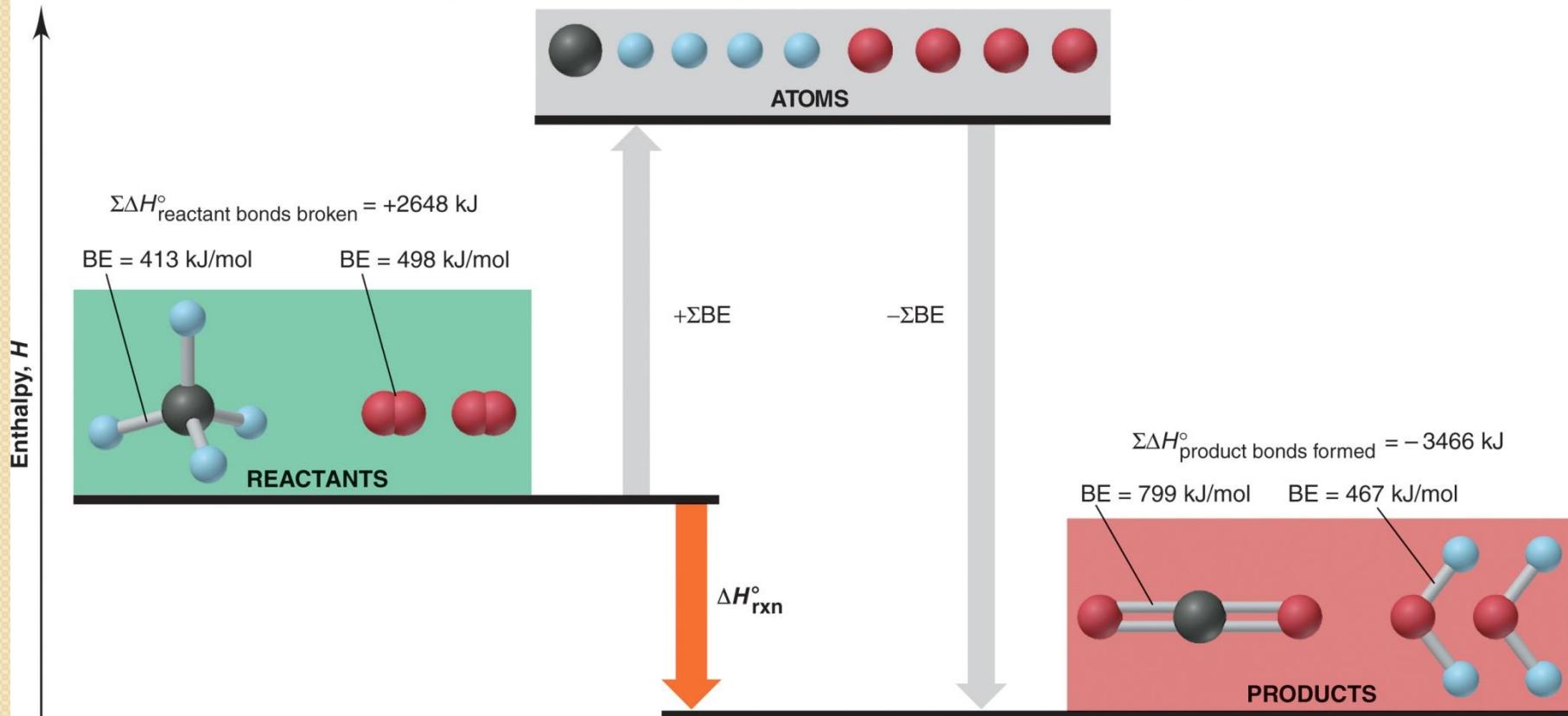


Figure 9.18 Using bond energies to calculate $\Delta H^\circ_{\text{rxn}}$ for the combustion of methane

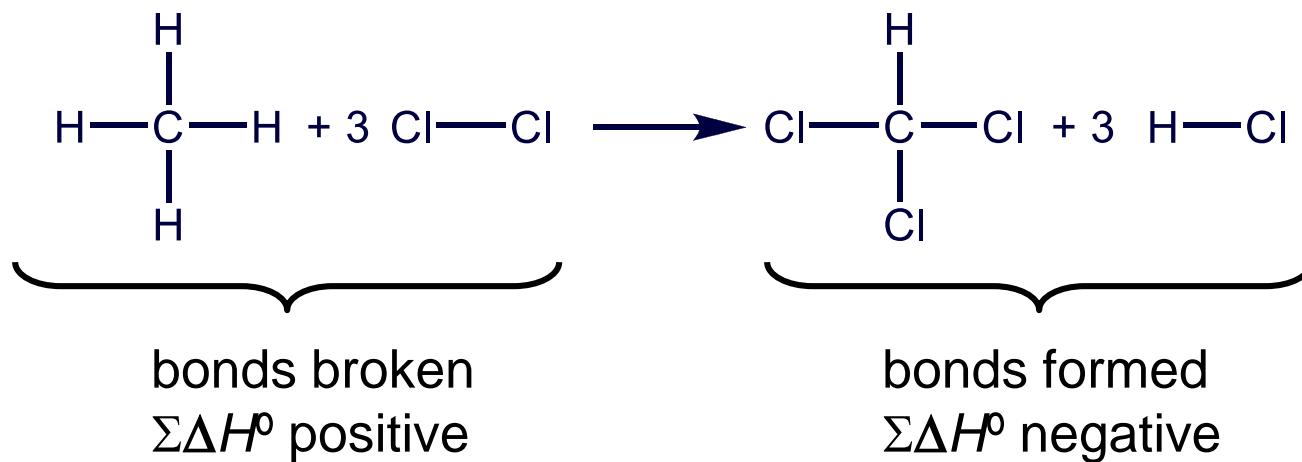
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Sample Problem 9.4

Using Bond Energies to Calculate $\Delta H^\circ_{\text{rxn}}$

PROBLEM: Calculate $\Delta H^\circ_{\text{rxn}}$ for the chlorination of methane to form chloroform.



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:

$$4 \times \text{C-H} = (4 \text{ mol})(413 \text{ kJ/mol}) = 1652 \text{ kJ}$$

$$3 \times \text{Cl-Cl} = (3 \text{ mol})(243 \text{ kJ/mol}) = 729 \text{ kJ}$$

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

For bonds formed:

$$3 \times \text{C-Cl} = (3 \text{ mol})(-339 \text{ kJ/mol}) = -1017 \text{ kJ}$$

$$1 \times \text{C-H} = (1 \text{ mol})(-413 \text{ kJ/mol}) = -413 \text{ kJ}$$

$$3 \times \text{H-Cl} = (3 \text{ mol})(-427 \text{ kJ/mol}) = -1281 \text{ kJ}$$

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

$$\begin{aligned}\Delta H^\circ_{\text{reaction}} &= \Sigma \Delta H^\circ_{\text{bonds broken}} + \Sigma \Delta H^\circ_{\text{bonds formed}} \\ &= 2381 \text{ kJ} + (-2711 \text{ kJ}) = -330 \text{ kJ}\end{aligned}$$

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***.

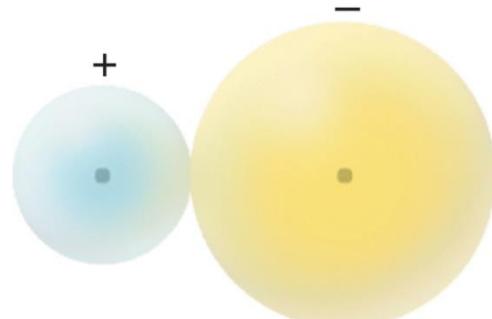
The ability of an atom in a covalent bond to attract the shared electron pair is called its ***electronegativity***.

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*.

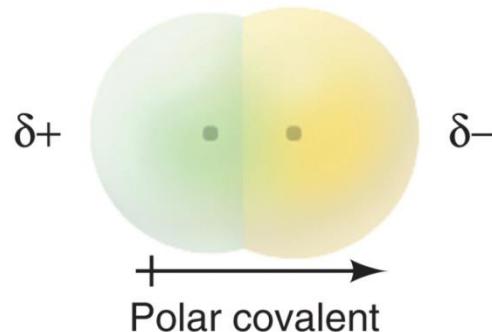
Figure 9.20

Bonding between the models

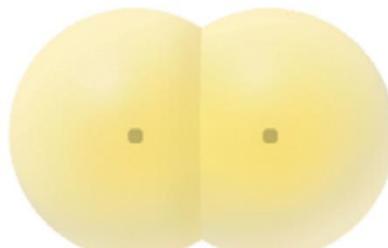
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Pure ionic



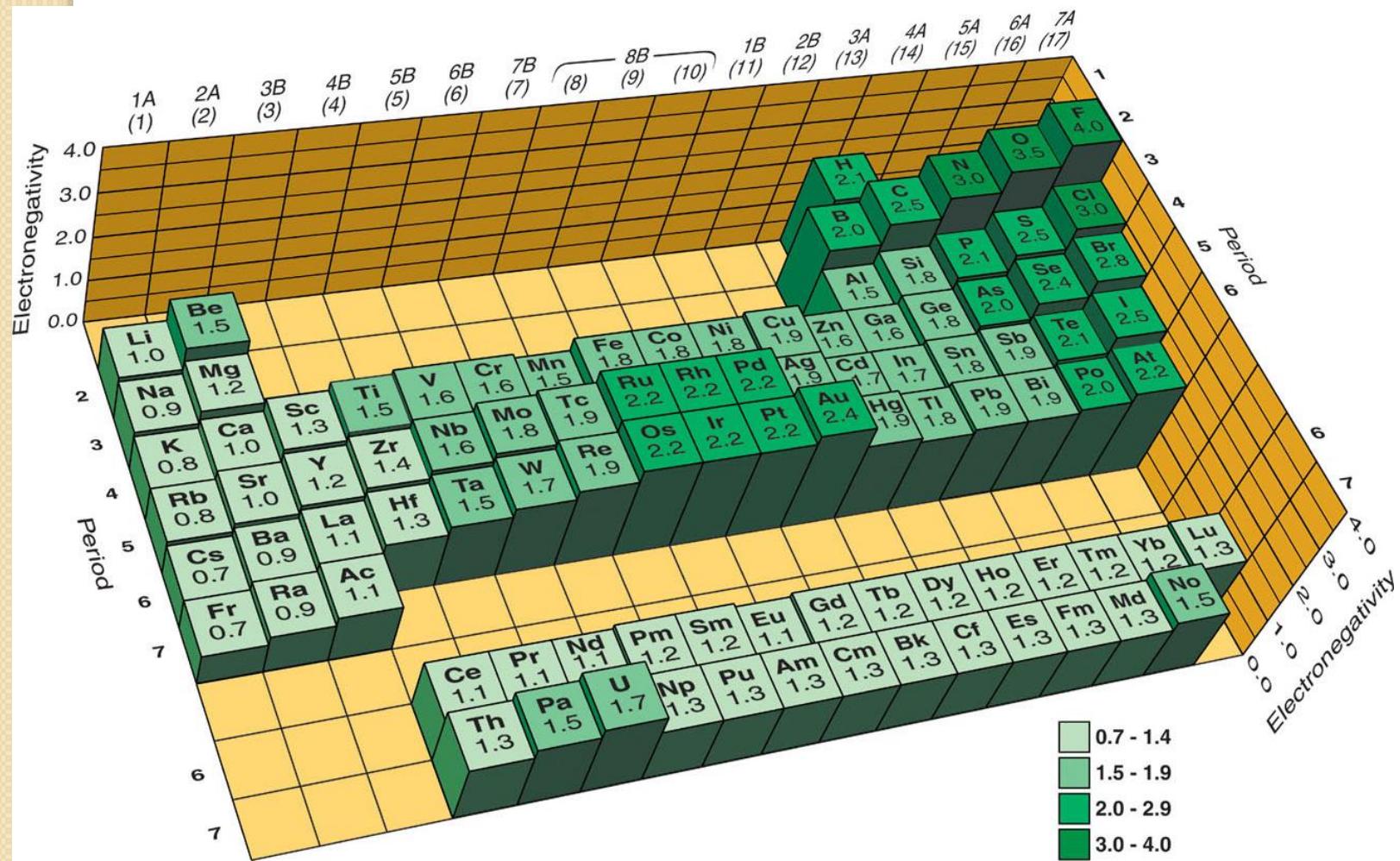
Polar covalent



Pure covalent

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**.

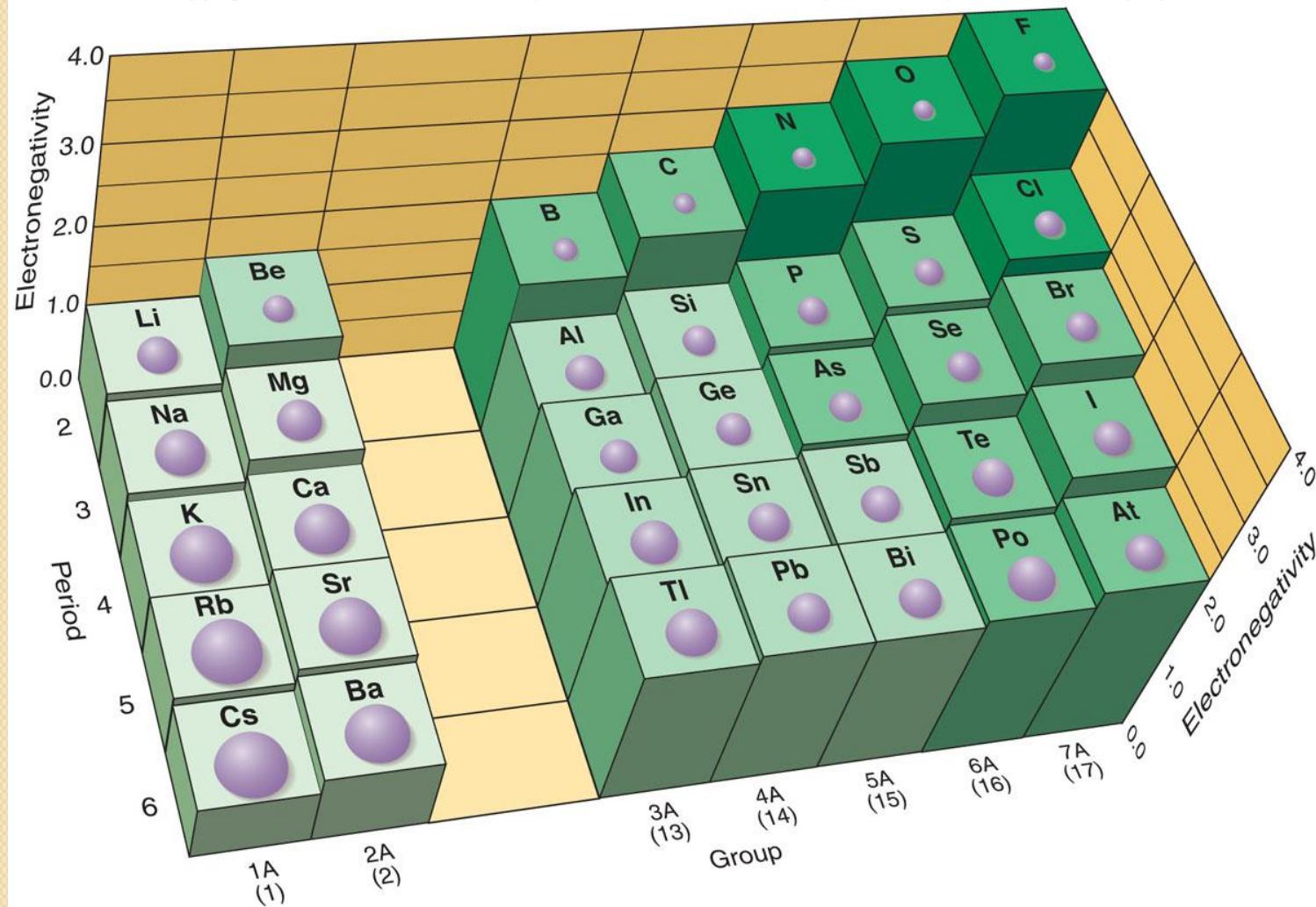
In general electronegativity **decreases** down a group as atomic size **increases**.

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

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

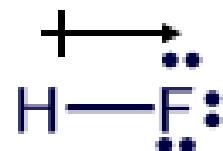
Figure 9.22 Electronegativity and atomic size

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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 $\delta+$ and $\delta-$ symbols.

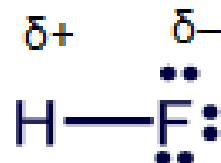
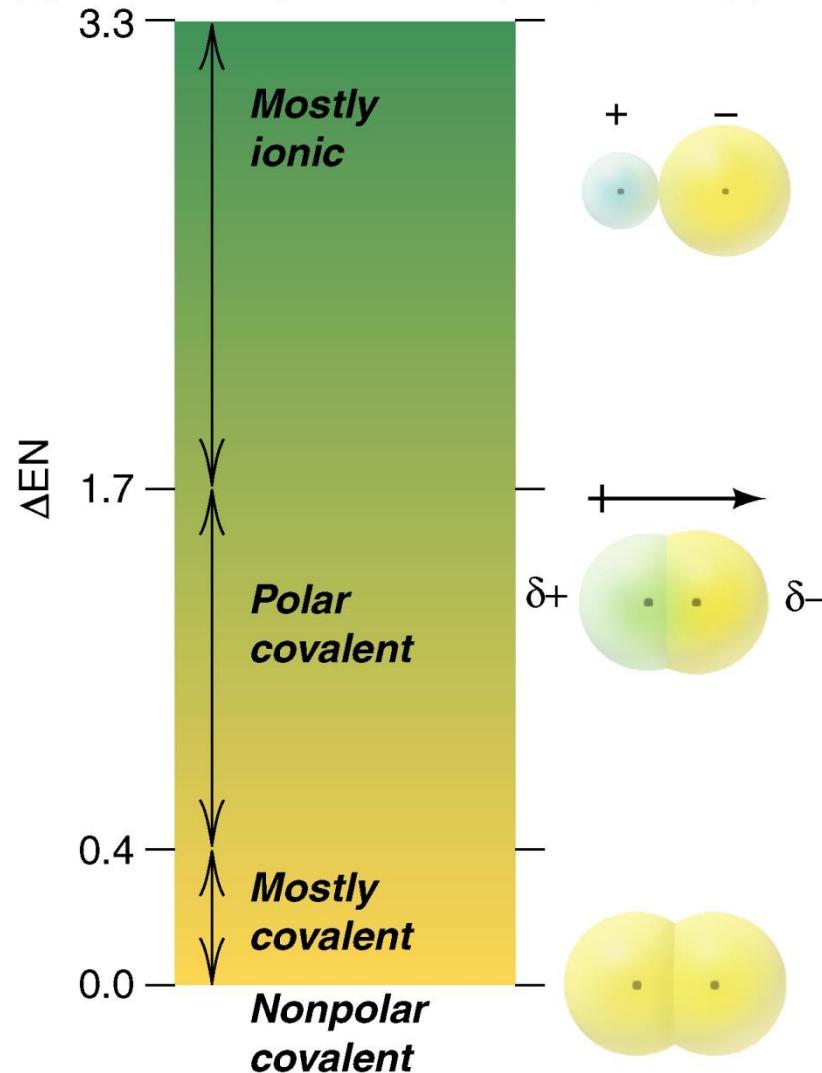


Figure 9.24 ΔEN ranges for classifying the partial ionic character of bonds

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Sample Problem 9.5

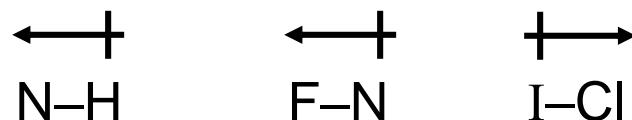
Determining Bond Polarity from EN Values

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:

$$\text{N} = 3.0, \text{H} = 2.1; \text{F} = 4.0; \text{I} = 2.5, \text{Cl} = 3.0$$



Sample Problem 9.5

(b) The EN values are:

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

$$\Delta EN \text{ for } H-N = 3.0 - 2.1 = 0.9$$

$$\Delta EN \text{ for } H-O = 3.5 - 2.1 = 1.4$$

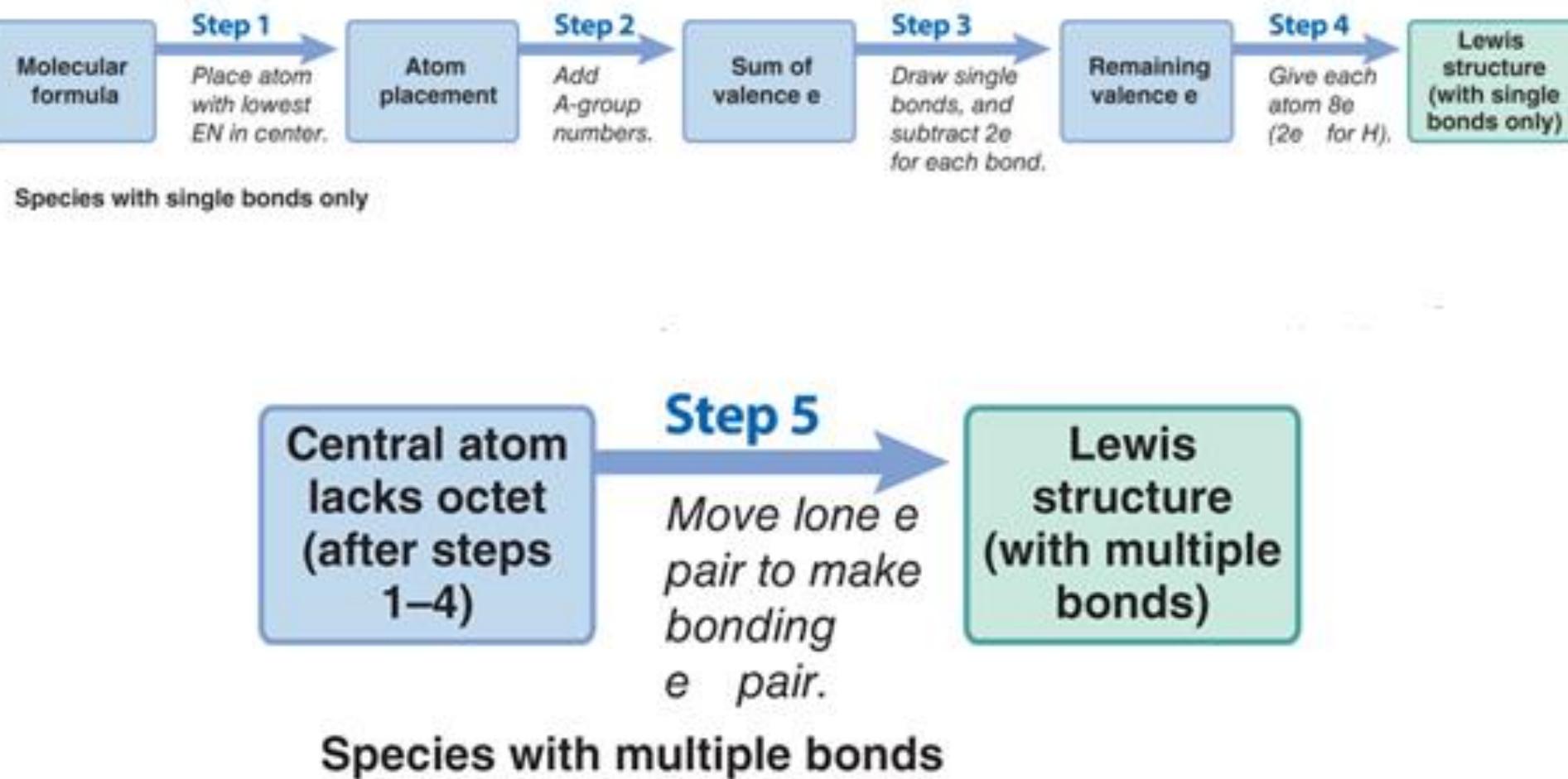
$$\Delta EN \text{ for } H-C = 2.5 - 2.1 = 0.4$$

In order of polarity:
 $H-C < H-N < H-O$

Chapter 10

The Shapes of Molecules

Figure 10.1 The steps in converting a molecular formula into a Lewis structure



Example: NF₃

Molecular Formula

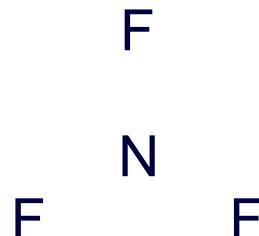
Atom placement

Sum of valence e⁻

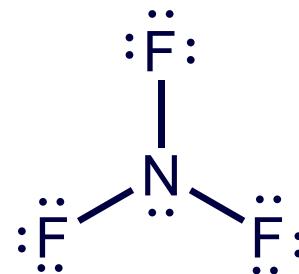
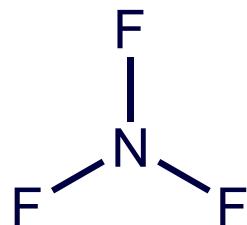
Remaining valence e⁻

Lewis structure

N has a lower EN than F, so N is placed in the center.



$$\begin{aligned}1 \times N &= 1 \times 5 = 5e^- \\3 \times F &= 3 \times 7 = 21 e^- \\ \hline \text{Total} &= 26 e^-\end{aligned}$$



Sample Problem 10.1

Writing Lewis Structures for Species with One Central Atom

PROBLEM: Write a Lewis structure for (a) CCl_2F_2 ; and (b) PCl_2^- .

SOLUTION:

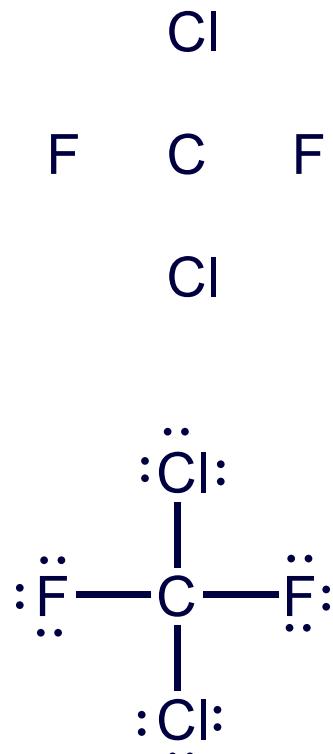
(a) CCl_2F_2

Step 1: Place the atoms relative to each other. Carbon has the lowest EN and is the central atom. The other atoms are placed around it.

Step 2: $[1 \times \text{C}(4e^-)] + [2 \times \text{F}(7e^-)] + [2 \times \text{Cl}(7e^-)]$
= 32 valence e^-

Steps 3-4: Add single bonds, then give each atom a full octet.

CHECK: Confirm that each atom has an octet and your Lewis structure accounts for 32 valence electrons.



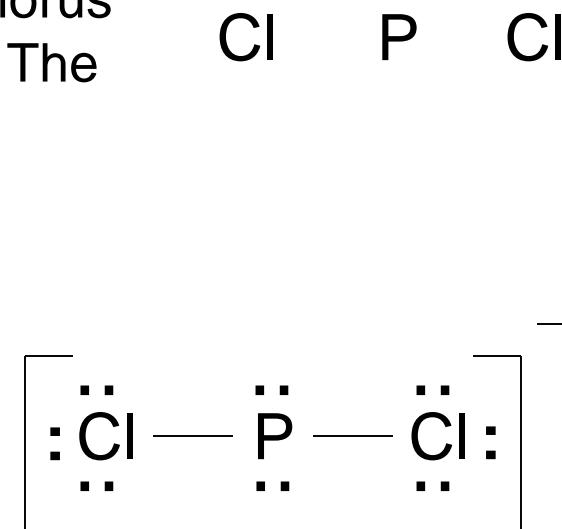
Sample Problem 10.1

(b) PCl_2^-

Step 1: Place atoms relative to each other. Phosphorus has the lower EN and is the central atom. The other atoms are placed around it.

Step 2: $[1 \times \text{P}(5\text{e}^-)] + [2 \times \text{Cl}(7\text{e}^-)] + [1 \text{ negative charge } (1\text{e}^-)] = 20 \text{ valence e}^-$

Steps 3-4: Add single bonds, then give each atom a full octet.



Step 5: Since PCl_2^- is an ion, draw square brackets as shown and add the negative sign at the top (outside the brackets).

CHECK: Confirm that all atoms have octets and your Lewis structure accounts for 20 valence electrons.

Sample Problem 10.2

Writing Lewis Structures for Molecules with More than One Central Atom

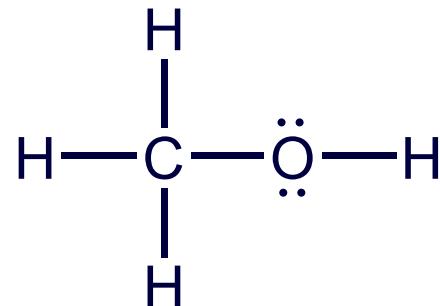
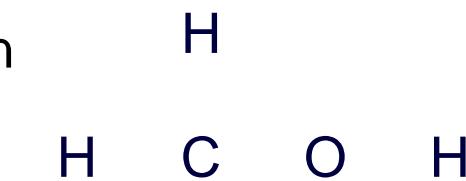
PROBLEM: Write the Lewis structure for methanol (molecular formula CH_4O), an important industrial alcohol that is being used as a gasoline alternative in car engines.

SOLUTION:

Step 1: Place the atoms relative to each other. H can only form one bond, so C and O must be central and adjacent to each other.

Step 2: $[1 \times \text{C}(4e^-)] + [1 \times \text{O}(6e^-)] + [4 \times \text{H}(1e^-)]$
 $= 14$ valence e^-

Step 3-4: Add single bonds, then give each atom (other than H) a full octet.



Multiple Bonds

If there are not enough electrons for the ***central*** atom to attain an octet, a multiple bond is present.

Step 5: If the central atom does not have a full octet, change a lone pair on a surrounding atom into another bonding pair to the central atom, thus forming a multiple bond.

Sample Problem 10.3

Writing Lewis Structures for Molecules with Multiple Bonds

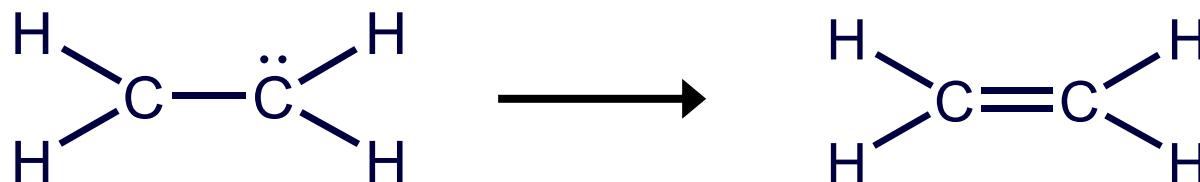
PROBLEM: Write Lewis structures for the following:

- (a) Ethylene (C_2H_4), the most important reactant in the manufacture of polymers
- (b) Nitrogen (N_2), the most abundant atmospheric gas

PLAN: After following steps 1 to 4 we see that the central atom does not have a full octet. We must therefore add step 5, which involves changing a lone pair to a bonding pair.

SOLUTION:

- (a) C_2H_4 has $2(4) + 4(1) = 12$ valence e^- . H can have only one bond per atom.



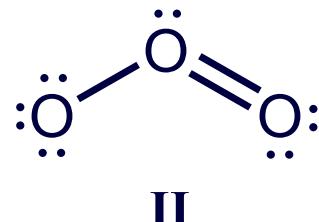
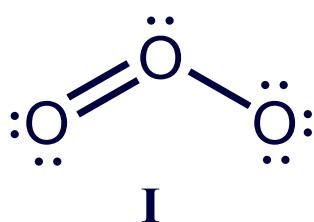
Sample Problem 10.3

(b) N₂ has 2(5) = 10 valence e⁻.



Resonance Structures

O_3 can be drawn in 2 ways:

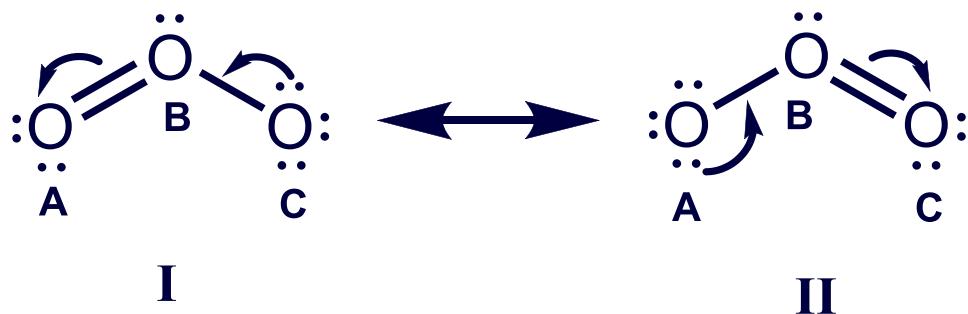


These are two different reasonable Lewis structures for the **same** molecule.

Neither structure depicts O_3 accurately, because in reality the O-O bonds are identical in length and energy.

Resonance Structures

The structure of O_3 is shown more correctly using both Lewis structures, called **resonance structures**. A two-headed resonance arrow is placed between them.



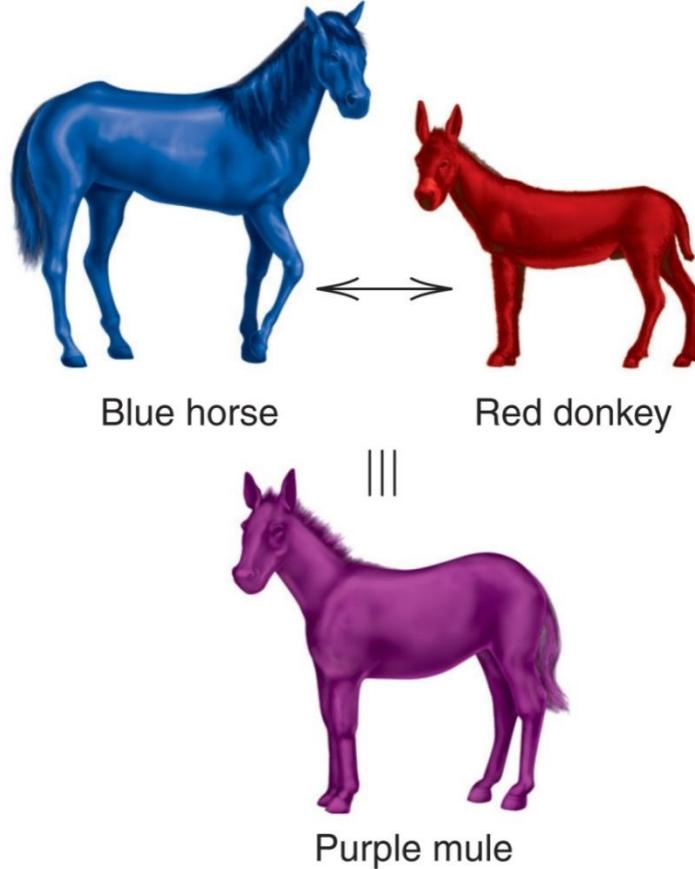
Resonance structures have the *same relative placement of atoms but different locations of bonding and lone electron pairs*.

The Resonance Hybrid

A species like O_3 , which can be depicted by more than one valid Lewis structure, is best represented as a ***resonance hybrid***.

Resonance forms ***are not real bonding depictions***.
 O_3 does ***not*** change back and forth between its two resonance forms.

The ***real structure*** of the resonance hybrid for O_3 is an ***average*** of its contributing resonance forms.

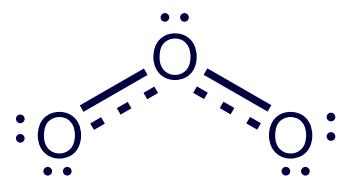


A mule is a genetic mix, a hybrid, of a horse and a donkey. It is not a horse one instant and a donkey the next. Likewise, a resonance hybrid has a **single** structure although it retains characteristics of its resonance forms.

Electron Delocalization

Lewis structures depict electrons as **localized** either on an individual atom (lone pairs) or in a bond between two atoms (shared pair).

In a resonance hybrid, electrons are **delocalized**: their density is “spread” over a few adjacent atoms.

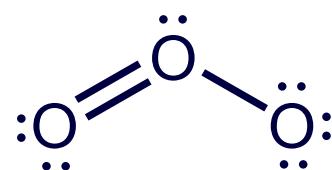


Dotted lines are used to show delocalized electrons.

Fractional Bond Orders

Resonance structures often have *fractional bond orders* due to partial bonding.

For O₃, bond order = $\frac{3 \text{ electron pairs}}{2 \text{ bonded-atom pairs}} = 1\frac{1}{2}$



Sample Problem 10.4

Writing Resonance Structures

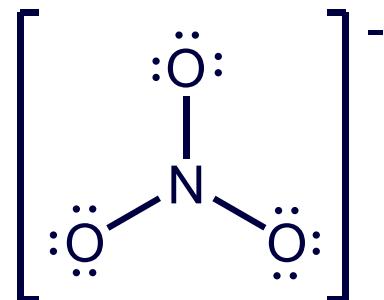
PROBLEM: Write resonance structures for the nitrate ion, NO_3^- , and find the bond order.

PLAN: Write the Lewis structure, remembering to add 1e^- to the total number of valence e^- for the -1 charge. We apply Step 5 to form multiple bonds. Since multiple bonds can be formed in more than one location, there are resonance forms.

SOLUTION:

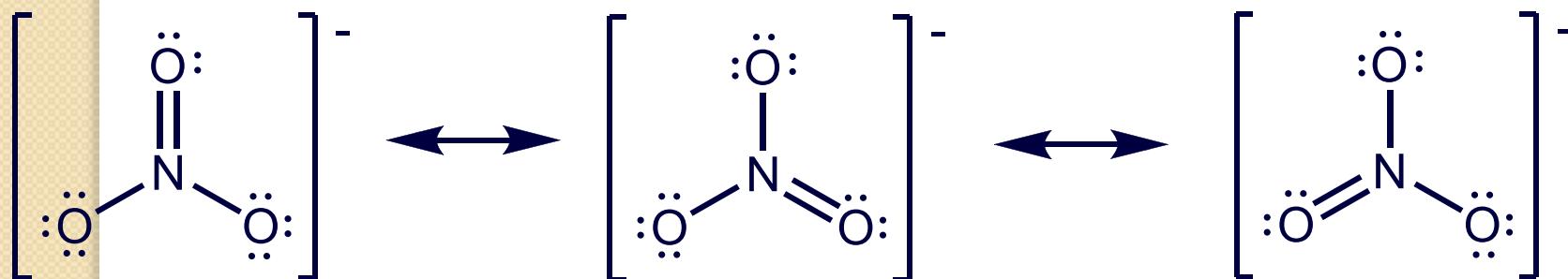
Nitrate has $[1 \times \text{N}(5\text{e}^-)] + [3 \times \text{O}(6\text{e}^-)] + 1\text{e}^- = 24$ valence e^-

After Steps 1-4:



Sample Problem 10.4

Step 5. Since N does not have a full octet, we change a lone pair from O to a bonding pair to form a double bond.



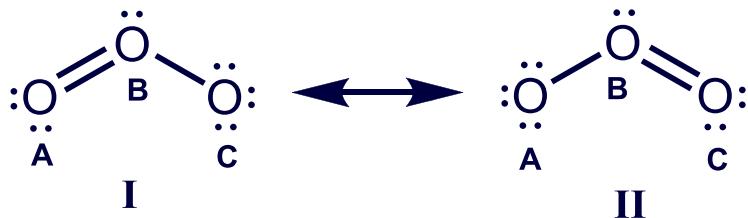
$$\text{Bond order} = \frac{\text{4 shared electron pairs}}{\text{3 bonded-atom pairs}} = 1\frac{1}{3}$$

Formal Charge

Formal charge is the charge an atom would have if all electrons were shared **equally**.

Formal charge of atom =

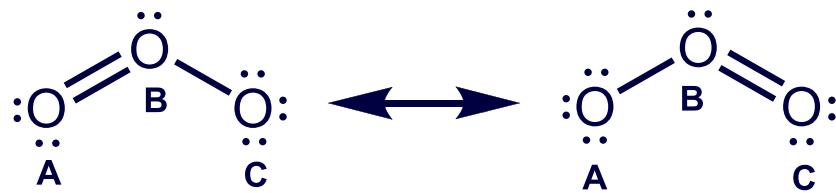
of valence e⁻ - (# of unshared valence e⁻ + ½ # of shared valence e⁻)



For O_A in resonance form I, the formal charge is given by
6 valence e⁻ - (4 unshared e⁻ + ½(4 shared e⁻) = 6 – 4 – 2 = 0

Formal Charge

Formal charges must sum to the actual charge on the species for ***all*** resonance forms.



$$O_A [6 - 4 - \frac{1}{2}(4)] = 0$$

$$O_B [6 - 2 - \frac{1}{2}(6)] = +1$$

$$O_C [6 - 6 - \frac{1}{2}(2)] = -1$$

$$O_A [6 - 6 - \frac{1}{2}(2)] = -1$$

$$O_B [6 - 2 - \frac{1}{2}(6)] = +1$$

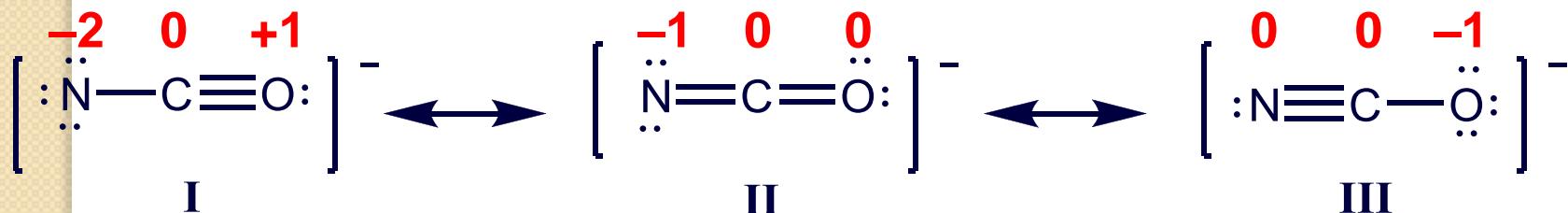
$$O_C [6 - 4 - \frac{1}{2}(4)] = 0$$

For both these resonance forms the formal charges sum to zero, since O_3 is a neutral molecule.

Choosing the More Important Resonance Form

- Smaller formal charges (positive or negative) are preferable to larger ones.
- The **same** nonzero formal charges on adjacent atoms are not preferred.
Avoid like charges on adjacent atoms.
- A more negative formal charge should reside on a more electronegative atom.

Example: NCO⁻ has 3 possible resonance forms:



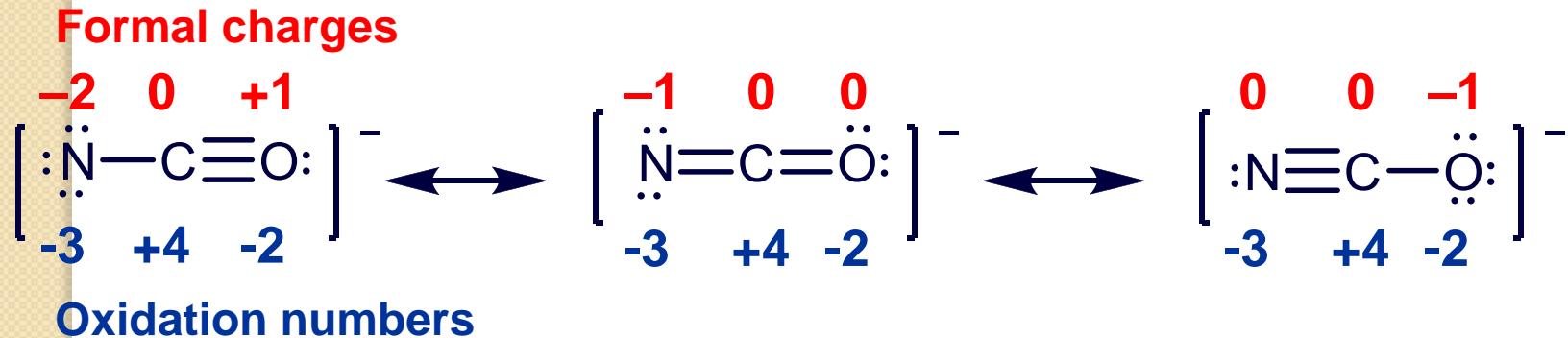
Resonance forms with smaller formal charges are preferred.
Resonance form I is therefore **not** an important contributor.

A negative formal charge should be placed on a more electronegative atom, so resonance form III is preferred to resonance form II.

The overall structure of the NCO⁻ ion is a **weighted average** of all three forms; **resonance forms II and III contribute *more* than I**, and III contributes more than II.

Formal Charge Versus Oxidation Number

For a ***formal charge***, bonding electrons are ***shared equally*** by the atoms.

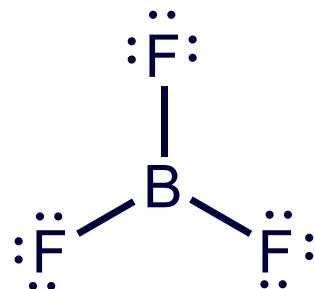


For an ***oxidation number***, bonding electrons are ***transferred*** to the ***more*** electronegative atom.

- The formal charge of an atom may change between resonance forms.
- The oxidation number of an atom is the ***same*** in all resonance forms.

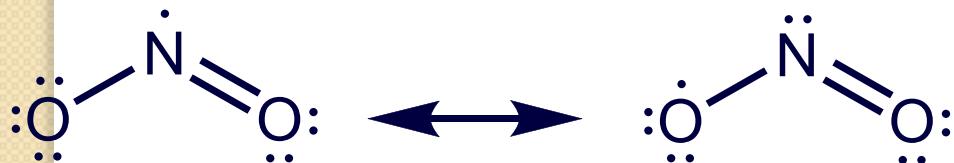
Exceptions to the Octet Rule

Molecules with Electron-Deficient Atoms



B and Be are commonly electron-deficient.

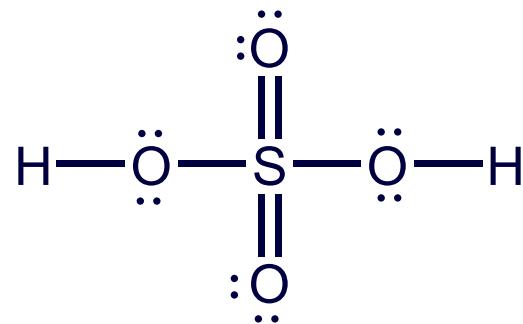
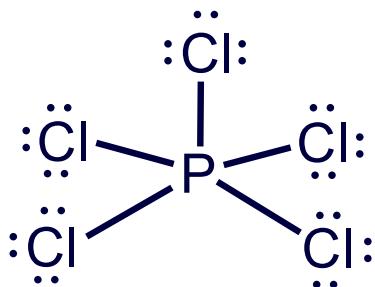
Odd-Electron Species



A molecule with an odd number of electrons on central atom is called a ***free radical***.

Exceptions to the Octet Rule

Expanded Valence Shells



An expanded valence shell is only possible for ***nonmetals from Period 3 or higher*** because these elements have available ***d orbitals***.

Sample Problem 10.5

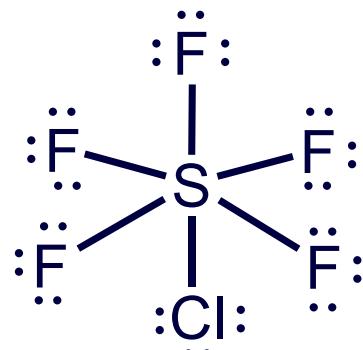
Writing Lewis Structures for Octet-Rule Exceptions

PROBLEM: Write a Lewis structure and identify the octet-rule exception for (a) SClF_5 ; (b) H_3PO_4 (draw two resonance forms and select the more important); (c) BFCl_2 .

PLAN: Draw each Lewis structure and examine it for exceptions to the octet rule. Period 3 elements can have an expanded octet, while B commonly forms electron-deficient species.

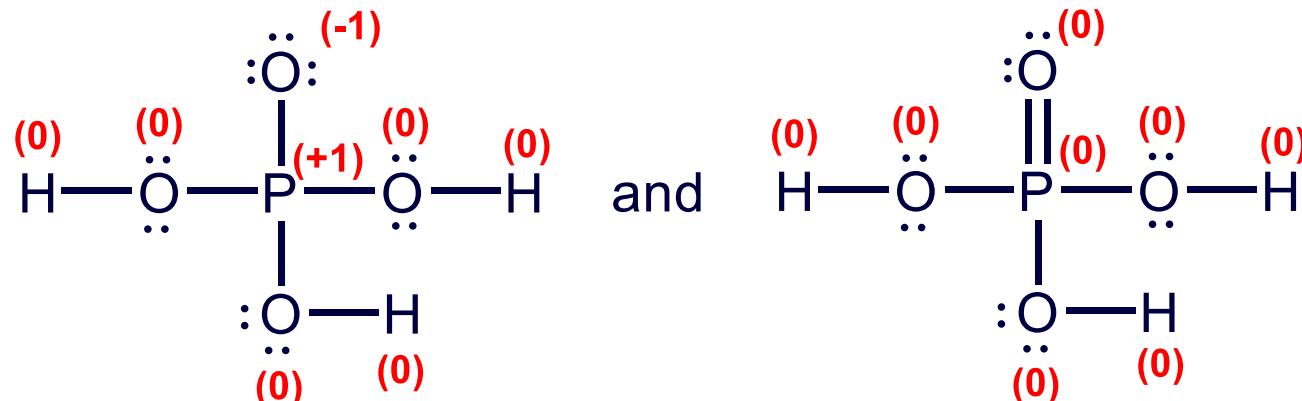
SOLUTION:

(a) The central atom is S, which is in Period 3 and can have an expanded valence shell.



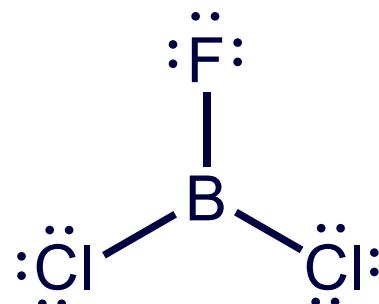
Sample Problem 10.5

(b) H_3PO_4 has two resonance forms and formal charges indicate the more important form.



Structure I obeys the octet rule but has nonzero formal charges. Structure II has an expanded valence shell with zero formal charges. According to formal charge rules, structure II is the more important structure.

(c) BFCl_2 is an electron-deficient molecule. B has only six electrons surrounding it.



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H
1.012
IIA3
Li
6.944
Be
9.0111
Na
22.9912
Mg
24.313
IIIIB4
IVB5
VB6
VIB7
VIIIB8
VIIIB9
VIIIB10
VIIIB11
VIIIB12
VIIIB18
VIIIA2
He
4.00

Periodic Table

| | | | | | |
|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|
| 13 IIIA | 14 IVA | 15 VA | 16 VIA | 17 VIIA | 18 VIIIA |
| 5 B 10.81 | 6 C 12.01 | 7 N 14.01 | 8 O 16.00 | 9 F 19.00 | 10 Ne 20.18 |
| 13 Al 26.98 | 14 Si 28.09 | 15 P 30.97 | 16 S 32.07 | 17 Cl 35.45 | 18 Ar 39.95 |
| 31 Ga 69.72 | 32 Ge 72.61 | 33 As 74.92 | 34 Se 78.96 | 35 Br 79.90 | 36 Kr 83.80 |
| 45 Rh 102.91 | 46 Pd 106.42 | 47 Ag 107.87 | 48 Cd 112.41 | 49 In 114.82 | 50 Sn 118.71 |
| 77 Ir 192.2 | 78 Pt 195.1 | 79 Au 197.0 | 80 Hg 200.6 | 81 Tl 204.4 | 82 Pb 207.2 |
| 109 Ds (271) | 110 Rg (272) | 111 | | | |

87
Fr

(223)

88

Ra

(226)

Ac^A

(227)

Rf

(261)

Db

(262)

Sg

(263)

Bh

(264)

Hs

(265)

Mt

(266)

Ds

(271)

Rg

(272)

| | | | | | | | | | | | | | | |
|---|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|---------------------------|---------------------------|---------------------------|---------------------------|
| * | 58 Ce 140.1 | 59 Pr 140.9 | 60 Nd 144.2 | 61 Pm (145) | 62 Sm 150.4 | 63 Eu 152.0 | 64 Gd 157.3 | 65 Tb 158.9 | 66 Dy 162.5 | 67 Ho 164.9 | 68 Er 167.3 | 69 Tm 168.9 | 70 Yb 173.0 | 71 Lu 175.0 |
| ^ | 90 Th 232.0 | 91 Pa (231) | 92 U 238.0 | 93 Np (237) | 94 Pu (244) | 95 Am (243) | 96 Cm (247) | 97 Bk (247) | 98 Cf (251) | 99 Es (252) | 100 Fm (257) | 101 Md (258) | 102 No (259) | 103 Lr (260) |

