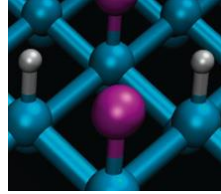
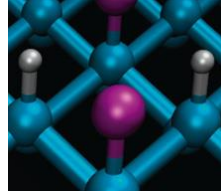


Chapter **7**

# Chemical Bonding and Molecular Structure

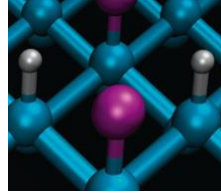
CENGAGE

# The Ionic Bond



- Formed through the electrostatic attraction of two oppositely charged ions
  - Binary ionic compounds form between metals and nonmetals
  - The greater the difference in metallic or nonmetallic properties of elements (more widely separated in the periodic table), the more likely it is that a compound formed from these elements will be ionic

# Formation of Ions

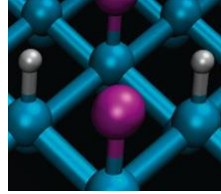


- Forming an ionic bond between a metal and a nonmetal usually requires energy to form the ion pair
  - Ionization energies are positive
  - Electron affinities for nonmetals are negative
- Once an ion pair is formed, the electrostatic force of attraction between the ions significantly lowers their overall energy
    - The potential energy, $V$, for the ion pair where $q_1$ and $q_2$ are the charges, and $r$ is the distance between the nuclei of the two ions can be calculated as follows:

$$V = k\frac{q_1 q_2}{r}$$

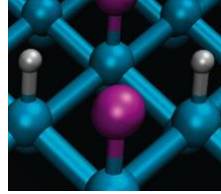
$$k = 1.389 \times 10^5\ KJ\ \text{pm/mol}$$

# Formation of Ions



- The energy released in forming NaF can be calculated as follows:
  - First, the energy change during the formation of the ion pair is calculated
    - The ionization energy for Na is 496 kJ/mol
    - The electron affinity for F is −328 kJ/mol
    - +496 kJ/mol −328 kJ/mol = +168 kJ/mol

# Formation of Ions



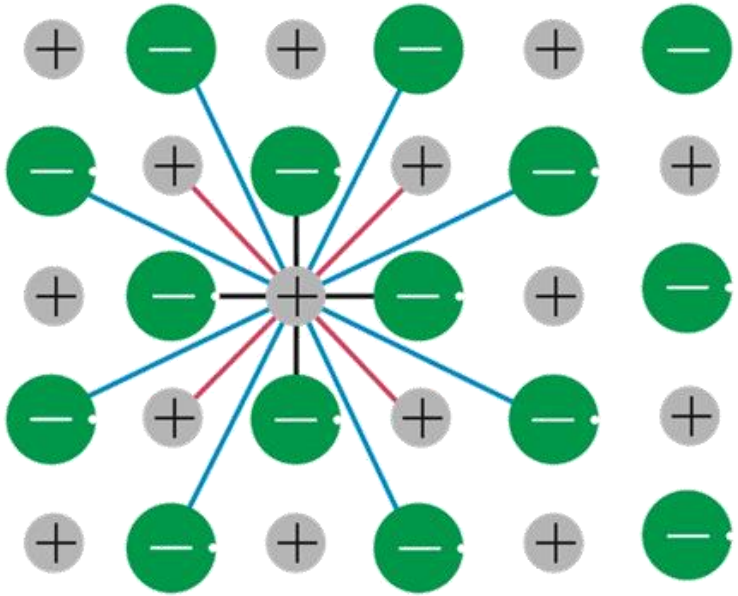
- In a solid lattice, any given ion experiences a large number of attractive and repulsive interactions with other ions

Black lines show attractive forces between (1st) nearest neighbors.

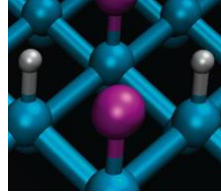
Red lines show repulsive forces with 2nd nearest neighbors.

Blue lines show attractive forces with 3rd nearest neighbors.

Fourth nearest neighbor interactions and higher are not indicated in the figure.

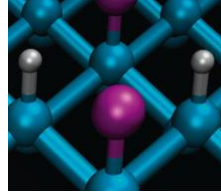


# Formation of Ions



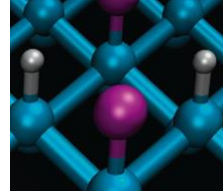
- Lattice energy of a crystal contains contributions from all of the attractions and repulsions
- From the potential energy equation, the observations made are as follows:
  - Small ions with large charges tend to form ionic compounds with large lattice energies
  - Large ions with small charges tend to form ionic compounds with small lattice energies

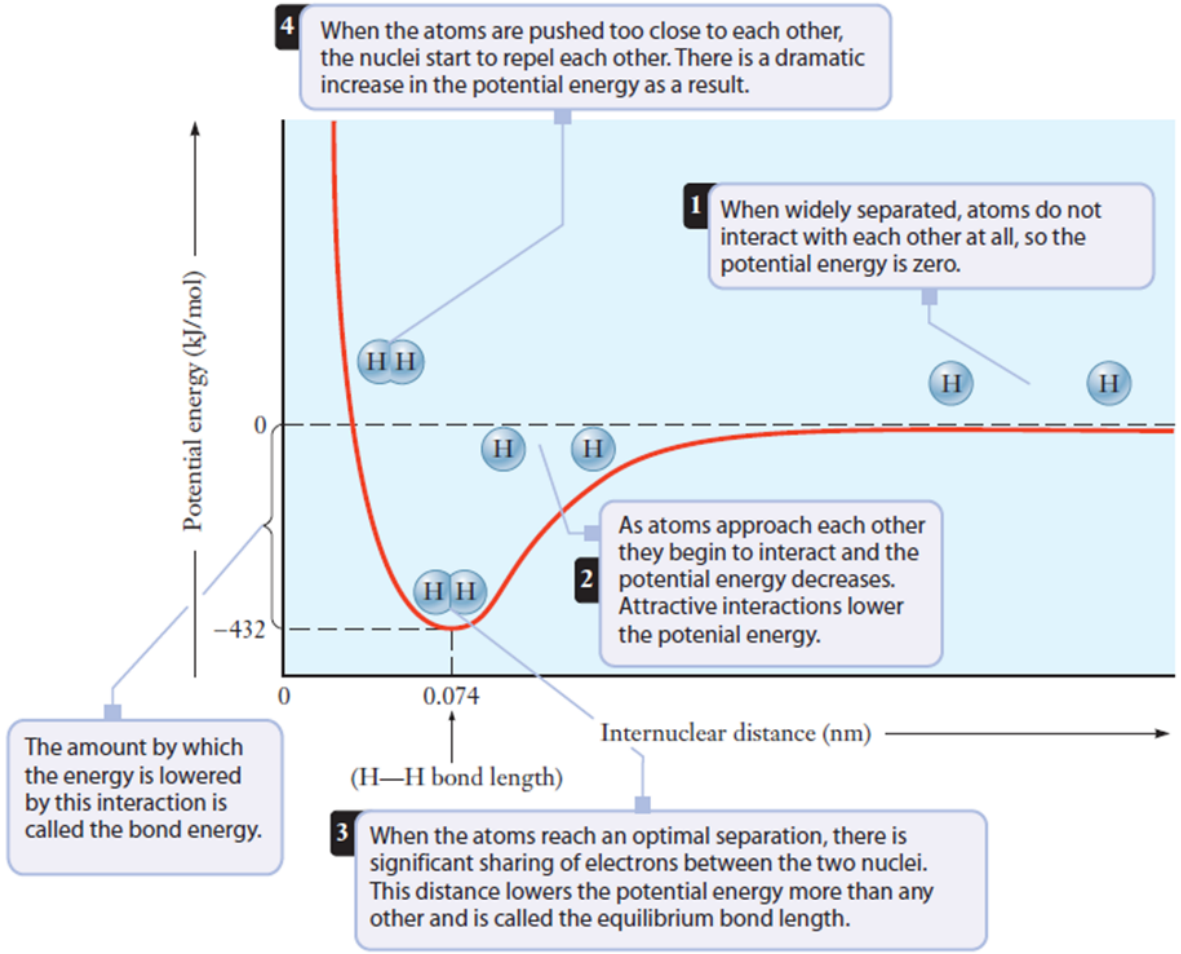
# Covalent Bond



- Based on the sharing of pairs of electrons between two atoms
- Driving force behind bond formation is lowering of overall energy
  - Ionic bonding lowers energy by transferring electrons between a metal and a nonmetal
  - Covalent bonding lowers energy by sharing electrons between two nonmetals

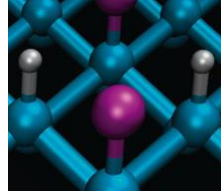
# Chemical Bonds and Energy





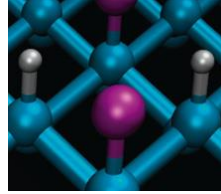

- Nuclei of the bonding atoms repel each other, as do the bonding electrons
- A covalent bond forms when the attractive and repulsive forces balance each other and energy is at a minimum

# Chemical Bonds and Energy



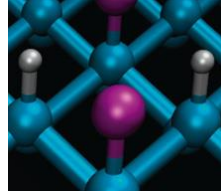
- The point of minimum energy corresponds to the formation of a covalent bond
- Bond energy
  - Energy released when isolated atoms form a covalent bond
- Bond length
  - Distance between the nuclei of the bonded atoms
- Electron density distribution is different for isolated atoms and covalently bonded atoms
  - Isolated atoms have spherical electron density around the nucleus
  - Covalently bonded molecules have a buildup of electron density in the region between the bonded atoms

# Chemical Bonds and Energy



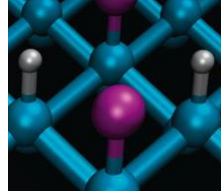
- Formation of chemical bonds always releases energy
  - Once a bond is formed, the same amount of energy (the bond energy) is needed to break the bond apart
  - Bond energies vary depending on the bonding atoms involved
- Chemical reactions involve rearranging bonds, transforming reactants into products
  - Reactions are energetically favored if the energy required to break reactant bonds is less than the energy released in making product bonds

# Chemical Bonds and the Structure of Molecules

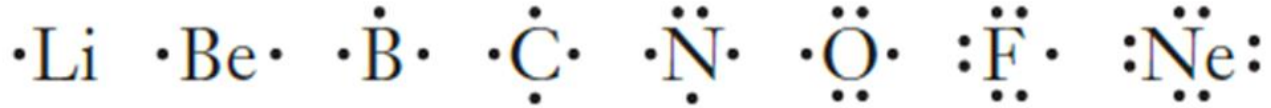


- During ionic bond formation, the cations and anions achieve $np^6$ electronic configurations (noble gas configuration)
  - Metals lose electrons
  - Nonmetals gain electrons
- Octet rule
  - An atom will form covalent bonds to achieve a complement of eight valence electrons
  - The valence shell electronic configuration is $ns^2np^6$ for a total of eight electrons
  - For the $n = 1$ valence shell, hydrogen is an exception to the octet rule and shares only two electrons

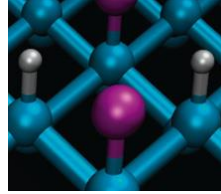
# Chemical Bonds and the Structure of Molecules



- Lewis dot symbols keep track of valence electrons, especially for compounds of main group elements, allowing prediction of bonding in molecules
  - To draw a Lewis dot symbol, the valence electrons are represented by dots and are placed around the element symbol
    - The first four dots are placed singly
    - Starting with the fifth dot, they are paired
    - The Lewis symbols for the second period are shown below



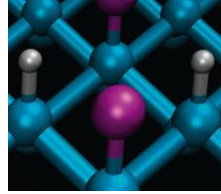
# Chemical Bonds and the Structure of Molecules



| Group | 1 | 2 | 13 | 14 | 15 | 16 | 17 | 18 |
|---|---|---|---|---|---|---|---|---|
| Number of electrons in valence shell | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 (except He) |
| Period 1 | H· | | | | | | | He |
| Period 2 | Li· | ·Be· | ·B· | ·C· | ·N· | ·O· | :F· | :Ne: |
| Period 3 | Na· | ·Mg· | ·Al· | ·Si· | ·P· | ·S· | :Cl· | :Ar: |
| Period 4 | K· | ·Ca· | ·Ga· | ·Ge· | ·As· | ·Se· | :Br· | :Kr: |
| Period 5 | Rb· | ·Sr· | ·In· | ·Sn· | ·Sb· | ·Te· | :I· | :Xe: |
| Period 6 | Cs· | ·Ba· | ·Tl· | ·Pb· | ·Bi· | ·Po· | :At· | :Rn: |
| Period 7 | Fr· | ·Ra· | | | | | | |

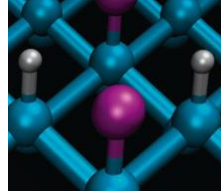
- Lewis dot symbols for main group elements
  - Elements within a group have the same number of valence electrons and identical Lewis dot symbols

# Chemical Bonds and the Structure of Molecules



- Lewis structures show how electrons are shared in a molecule
  - A pair of shared electrons between two atoms is a bonding pair
  - Pairs of electrons associated with one atom are nonbonding or lone pair electrons

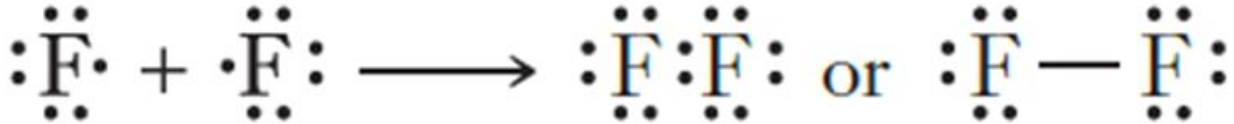
# Chemical Bonds and the Structure of Molecules



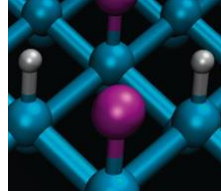
- By sharing an electron from each atom, two hydrogen atoms can form a covalent bond
  - Hydrogen is an exception to the octet rule as it shares only two electrons

$$H\cdot + \cdot H \longrightarrow H:H \quad \text{or} \quad H{-}H$$

- When two fluorine atoms combine, they form a stable covalent bond
  - By sharing a pair of electrons, each atom is surrounded by eight valence electrons



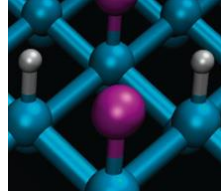
# Bonding Atoms in Molecules



- Multiple bonding results from the sharing of more than one electron pair
  - A double bond results when two bonding pairs are shared
  - A triple bond results when three bonding pairs are shared
  - Strength of the covalent bond increases as the number of bonding pairs increases

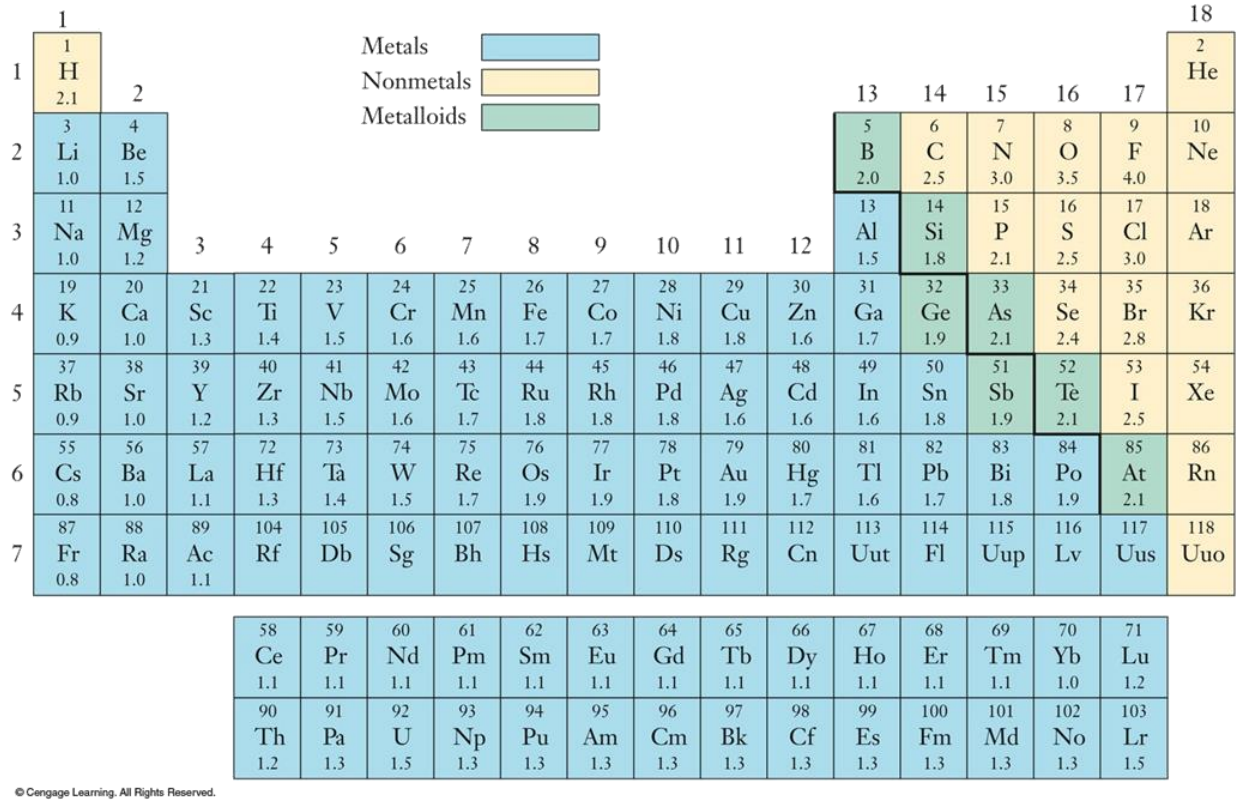
| Type of Bond | Bond Energy (kJ/mol) |
|---|---|
| C—C | 346 |
| C═C | 602 |
| C≡C | 835 |

# Electronegativity and Bond Polarity



- Electronegativity and bond polarity are used to describe compounds whose bonding falls in the middle of this continuum
- Electronegativity is the attraction of an atom for the shared electrons in a covalent bond
  - Electronegativities are not measured quantities
  - Electronegativities are assigned based on factors such as atomic size, electron affinity, and ionization energy
  - The higher the electronegativity value, the more likely an element will attract extra electron density during compound formation

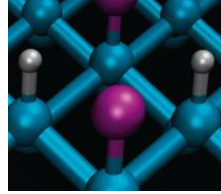
# Electronegativity





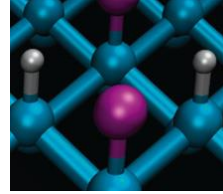
- Electronegativities increase from left to right across a period and from bottom to top for a group
- Fluorine is the most electronegative element, with an electronegativity of 4.0

# Bond Polarity

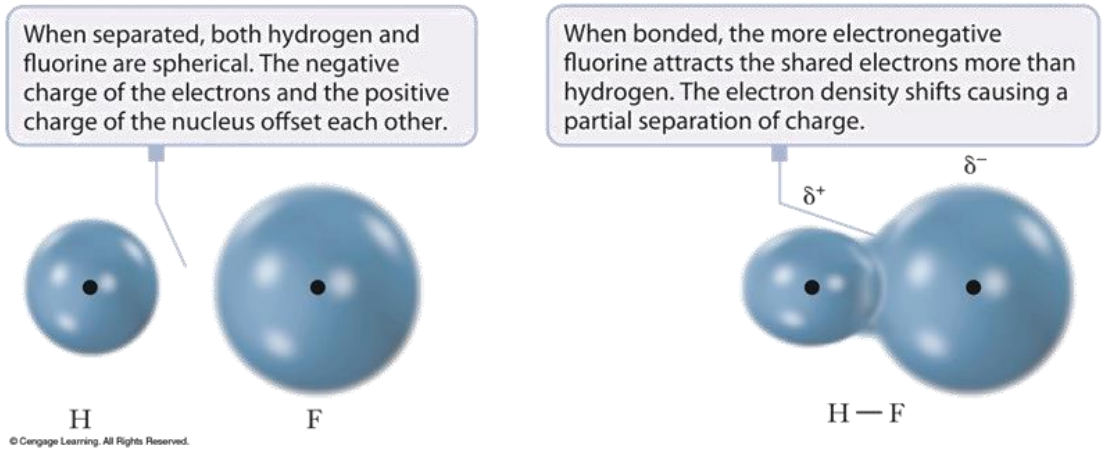


- Electron density is not shared equally when elements with different electronegativities bond
  - More than half of the electron density is associated with the more electronegative element
  - The more electronegative element experiences an increase in electron density and attains a partial negative charge
  - The electronegative element on the other end of the bond experiences a decrease in electron density and attains a partial positive charge
  - The two points of positive and negative charge constitute a dipole
    - The bond has an electric field associated with it and is known as a polar bond

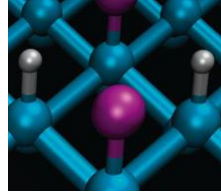
# Bond Polarity



- Also referred to as a polar covalent bond since electrons are still being shared
- The greater the electronegativity difference, the more polar the bond
- When the electronegativity difference is zero, the bond is classified as nonpolar covalent
- When the electronegativity difference exceeds 2.0, the bond is classified as ionic

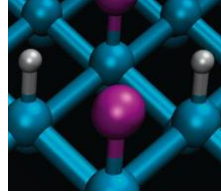


# Keeping Track of Bonding: Lewis Structures



- Lewis structures indicate how many bonds are formed and between which elements in a compound
- Step 1: Count the total valence electrons in the molecule or ion
  - Sum the number of valence electrons for each element in a molecule
  - For ions, add or subtract valence electrons to account for the charge

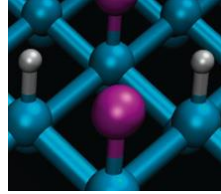
# Keeping Track of Bonding: Lewis Structures



- For the compound $OF_2$, the number of valence electrons is 20

$$\begin{aligned} \text{F} \quad & 2 \times 7 = 14 \\ \text{O} \quad & \underline{1 \times 6 = 6} \\ & \text{Total} = 20 \end{aligned}$$

# Keeping Track of Bonding: Lewis Structures

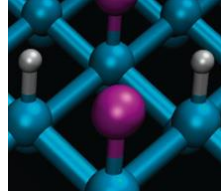


- Step 2: Draw the skeletal structure of the molecule
  - The element written first in the formula is usually the central atom, unless it is hydrogen
  - Usually, the central atom is the least electronegative

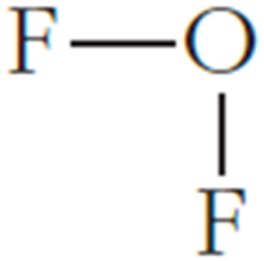
F O

F

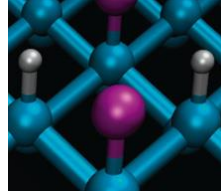
# Keeping Track of Bonding: Lewis Structures



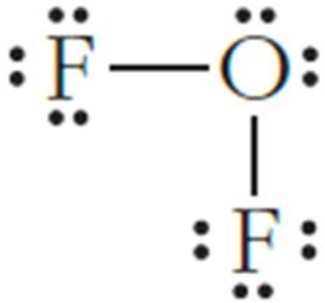
- Step 3: Place single bonds between all connected atoms in the structure by drawing lines between them
  - A single line represents a bonding pair
  - Four electrons are placed in bonds
  - 16 electrons are left to place



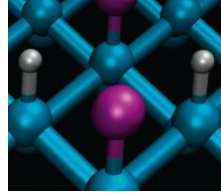
# Keeping Track of Bonding: Lewis Structures



- Step 4: Place the remaining valence electrons not accounted for on individual atoms until the octet rule is satisfied
- Place electrons as lone pairs whenever possible
  - Place electrons first on outer atoms, then on central atoms
    - Six electrons are placed as lone pairs on each F to satisfy the octet rule for each F
    - The four remaining electrons are placed on the O to satisfy its octet

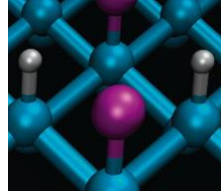


# Keeping Track of Bonding: Lewis Structures

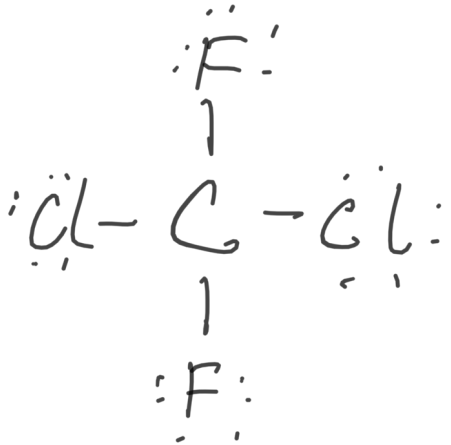


- Step 5: Create multiple bonds by shifting lone pairs into bonding positions as needed for any atoms that do not have a full octet of valence electrons
  - With experience, you will be able to correctly choose atoms between which multiple bonds can be formed
  - Multiple bonds are not required for $OF_2$, as the octet rule is satisfied for each atom

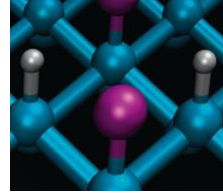
# Example Problem 7.4



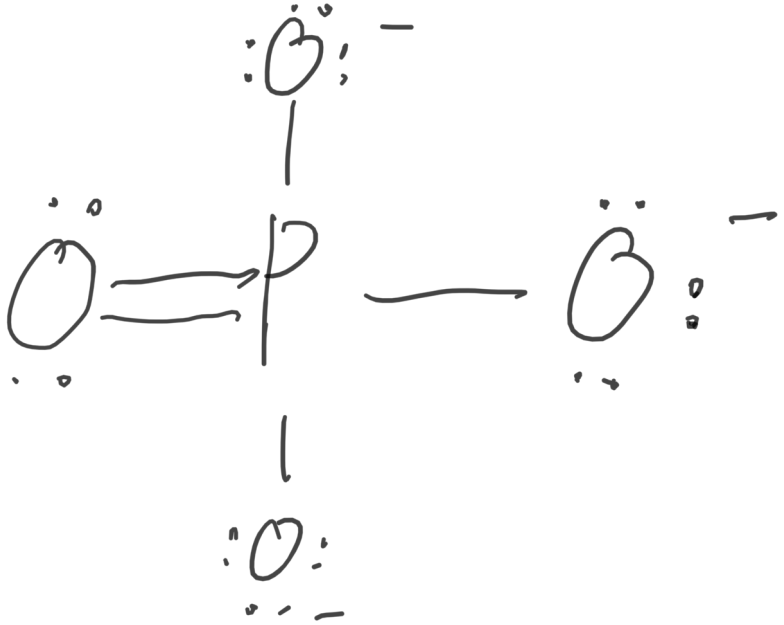
- Draw the Lewis structure of dichlorodifluoromethane, $CF_2Cl_2$, also known as DuPont's Freon-12



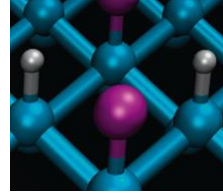
# Example Problem 7.5



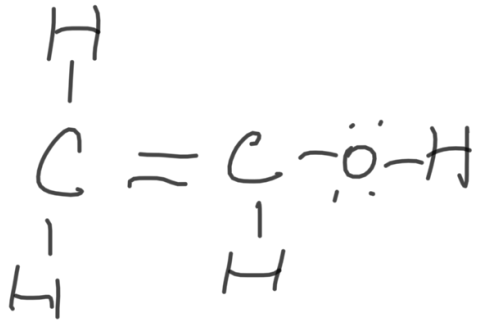
- Draw the Lewis structure of the phosphate ion, $PO_4^{3-}$



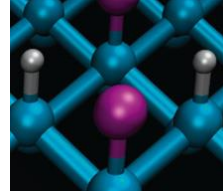
# Example Problem 7.6



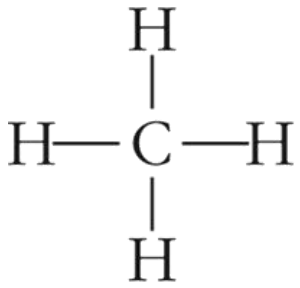
- Draw the Lewis structure of vinyl alcohol, $CH_2CHOH$, the monomer from which poly(vinyl alcohol) is made

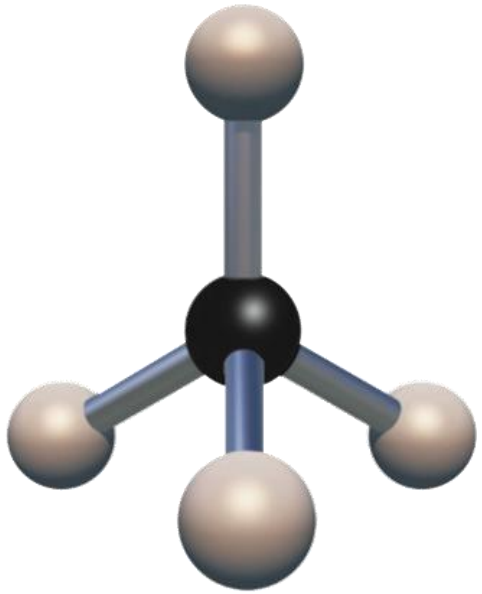


# Hybrid Orbitals



- During orbital hybridization, the repulsion between electrons in bonding atoms can be strong enough to reshape the orbitals of the atoms
  - The angles between the reshaped orbitals must match observed bond angles.

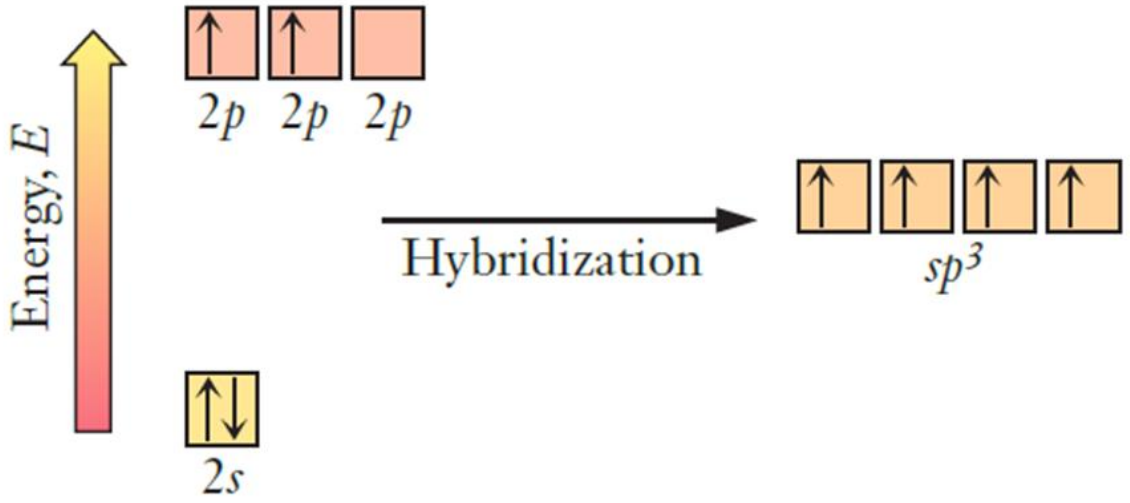




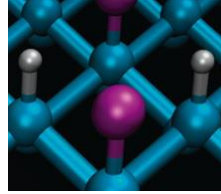
- $CH_4$ is the simplest binary compound of C and H
  - All four bond angles are 109.5°
  - Four identical orbitals with angles of 109.5° between them are needed on C

# Hybrid Orbitals



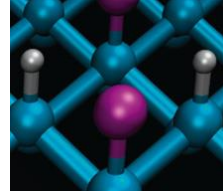

- Hybridization of the *s* and *p* orbitals on carbon
  - The four $sp^3$ hybrid orbitals have equal energy
  - The four valence electrons are distributed evenly across the $sp^3$ hybrid orbitals
  - The angle between the $sp^3$ hybrid orbitals is 109.5°

# Shapes of Molecules



- Molecular shape
  - The way bonded atoms arrange themselves in three dimensions
  - Affects molecular properties, including reactivity
- Valence shell electron pair repulsion (VSEPR) theory
  - Molecules assume a shape that allows them to minimize the repulsions between electron pairs in the valence shell of the central atom
  - Electron pairs include both lone pair electrons and bonding pair electrons

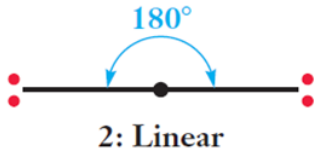
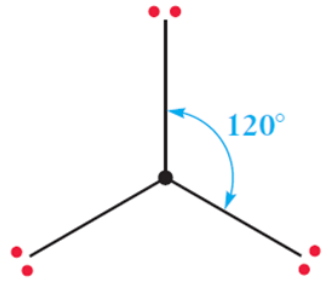
# Shapes of Molecules



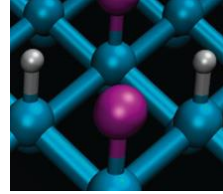
Bond angles and shapes are predicted by electron pair repulsion between valence electron pairs

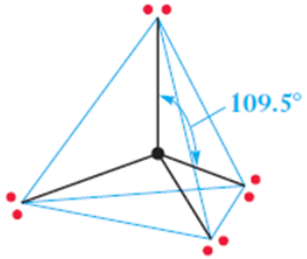
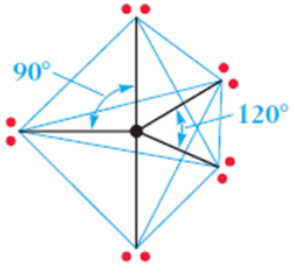
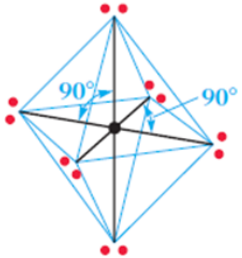
**Table 7.3** Molecular shapes based on VSEPR theory

Each of the geometric arrangements shown in the table minimizes the electron pair repulsions for the indicated number of electron pairs. To visualize the shapes of molecules, it is essential that you have a sound mental picture of each of these geometries.

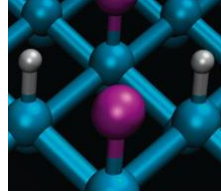
| Number of Electron Pairs | Geometric Name | Bond Angles | Diagram |
|---|---|---|---|
| 2 | Linear | 180° |   2: Linear |
| 3 | Trigonal planar | 120° |   3: Trigonal planar |

# Shapes of Molecules



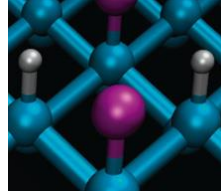
| Number of Electron Pairs | Geometric Name | Bond Angles | Diagram |
|---|---|---|---|
| 4 | Tetrahedral | 109.5° |   4: Tetrahedral |
| 5 | Trigonal bipyramidal | 120°, 90° |   5: Trigonal bipyramidal |
| 6 | Octahedral | 90°, 180° |   6: Octahedral |

# Shapes of Molecules



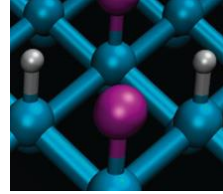
- Molecular geometries are predicted systematically
  - Draw the Lewis dot structure
  - Count the number of bonding and nonbonding electron pairs around the central atom
    - Double and triple bonds count as one bonding pair
  - For zero nonbonding pairs on the central atom, the molecular shape matches the shape predicted by VSEPR
  - For nonbonding pairs on the central atom, a base geometry predicted by VSEPR theory is used

# Example Problem 7.7

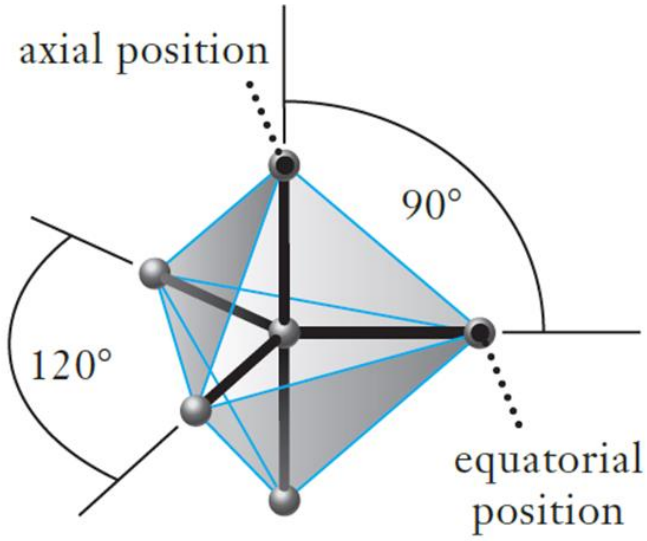


- Determine the shape of each of the following species
  - $PO_4^{3-}$
  - $PCl_5$

# Shapes of Molecules



- Lone pair electrons occupy more space than bonding electrons because they are less tightly localized
  - Example- $SF_4$ has four bonding electron pairs and a lone pair. Because lone pair–bond pair repulsion is larger than bond pair–bond pair repulsion, the lone pair occupies the less repulsive equatorial position



# Shapes of Molecules

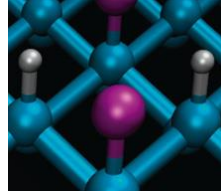
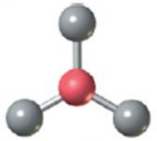
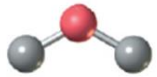
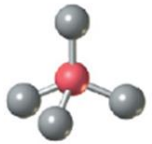
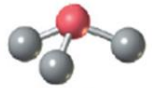
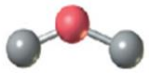
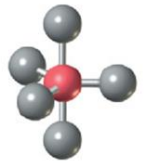
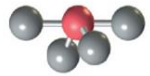
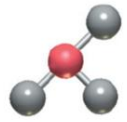


**Table 7.4** Common molecular shapes

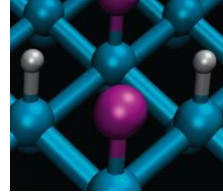
The molecular shapes resulting from various combinations of the total number of electron pairs around the central atom and the number of long pairs

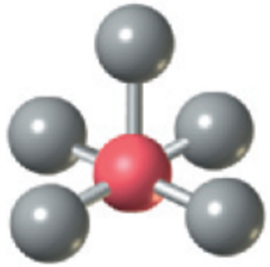
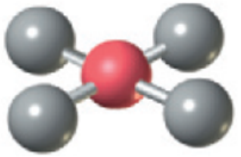
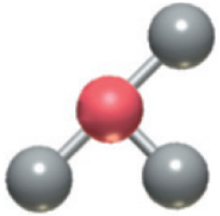
| Number of Electron Pairs | Number of Lone Pairs | Shape | Ball and Stick Model |
|---|---|---|---|
| 3 | 0 | Trigonal planar |  |
| 3 | 1 | Bent (120°) |  |
| 4 | 0 | Tetrahedral |  |
| 4 | 1 | Trigonal pyramidal |  |
| 4 | 2 | Bent (109.5°) |  |

| Number of Electron Pairs | Number of Lone Pairs | Shape | Ball and Stick Model |
|---|---|---|---|
| 5 | 0 | Trigonal bipyramidal |  |
| 5 | 1 | Seesaw |  |
| 5 | 2 | T-shape |  |
| 5 | 3 | Linear |  |
| 6 | 0 | Octahedral |  |

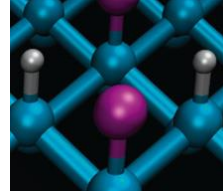
Molecular shapes for various combinations of bonding and nonbonding electron pairs

# Shapes of Molecules



| Number of Electron Pairs | Number of Lone Pairs | Shape | Ball and Stick Model |
|---|---|---|---|
| 6 | 1 | Square pyramidal |  |
| 6 | 2 | Square planar |  |
| 6 | 3 | T-shape |  |
| 6 | 4 | Linear |  |

# Example Problem 7.8



- Determine the shape of the following molecules using VSEPR theory
  - $SF_4$
  - $BrF_5$