

CHAPTER 12: CHEMICAL BONDING

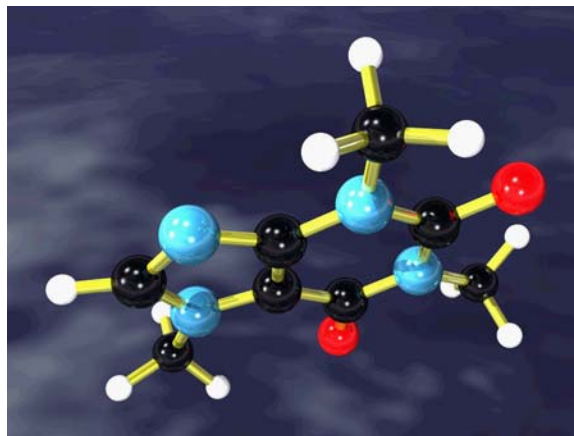
Active Learning Questions: 3-7, 11-19, 21-22
End-of-Chapter Problems: 1-36, 42-62, 65-86, 92-103, 106-109, 115, 117

An American chemist named Gilbert N. Lewis developed the **Lewis bonding theory** in which electrons are represented as dots.

→ The molecules represented are called **Lewis structures** or **Lewis electron-dot formulas**.

Today we use Lewis structures to determine how atoms are arranged in a molecule and to predict the 3D shape of molecules.

- Knowing the shape of a molecule allows us to explain the observed properties and behavior of these substances.
- For example, we can use the structure of the caffeine molecule to explain how the molecule acts as a stimulant.



ball-and-stick model of a caffeine molecule

12.1 TYPES OF CHEMICAL BONDS

chemical bond: what holds atoms or ions together in a compound

The **two types of chemical bonds** are **ionic bonds** and **covalent bonds**.

- **Ionic bonds hold ions** together in **ionic compounds**.
- **Covalent bonds hold atoms** together in **molecules**.

12.5 IONIC BONDING AND STRUCTURES OF IONIC COMPOUNDS

Metals lose electrons from their valence shell

→ **positively charged ions = cations**

Nonmetals gain electrons, adding electrons to their valence shell.

→ **negatively charged ions = anions**

Elements tends to gain or lose electrons, so they will have the same number of electrons as a Noble gas to become more stable.

→ Ions formed by main-group elements are usually **isoelectronic** with—i.e., **have the same number of electrons as**—one of the noble gases!

Recognize the charges formed by the Representative Elements

Group IA elements → +1 charge: Li^+ ("+" = "+1")

Group IIA elements → +2 charge: Mg^{+2}

Group IIIA elements → +3 charge: Al^{+3}

Group VA elements → -3 charge: N^{-3}

Group VIA elements → -2 charge: O^{-2}

Group VIIA elements → -1 charge: F^- ("- = "-1")

IONIC BONDS

Ex. 1 Give the Lewis electron-dot formula below for each of the following **atoms** and **ions**:

| | | | |
|------------|---------------|--------------|-----------|
| sodium | magnesium | chlorine | oxygen |
| sodium ion | magnesium ion | chloride ion | oxide ion |

Example: Draw the electron-dot formulas representing each of the following:

a. sodium atom + chlorine atom react to form sodium chloride (sodium ion + chloride ion)

b. magnesium atom + oxygen atom react to form magnesium oxide

c. aluminum atom + nitrogen atoms react to form aluminum nitride

Thus, in reality, metal atoms **transfer valence electrons** to nonmetal atoms

→ positively charged cations and negatively charged anions

– ions come together → **ionic compound** = 3D network of ions

12.6 LEWIS STRUCTURES

Nonmetal atoms form bonds to achieve a Noble Gas electron configuration.

- However, instead of taking electrons away from one another to form ions, they simply share the electrons in a **covalent bond**.

covalent bond: sharing of a pair of electrons between two nonmetal atoms

- achieved by overlapping outermost subshells that contain the valence electrons

Molecules (or **molecular compounds**) are held together by **covalent bonds**.

molecule: basic unit of a compound of covalently bonded atoms

- Consider the HCl, H₂O, NH₃, and CH₄ molecules below
 - Note how the formula for each gives the actual number of each atom present in the molecule.

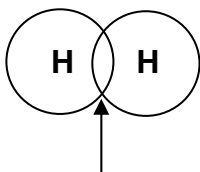


Ex. 1: Use electron dot formulas to represent the reaction described.



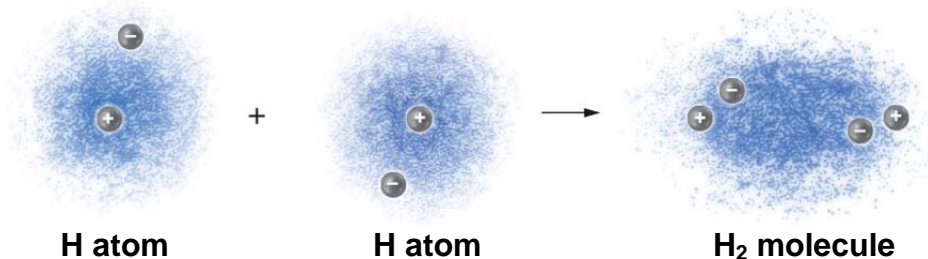
Note in H₂, each H atom now has 2 e⁻ (like He).

We can also represent the H₂ molecule as follows:



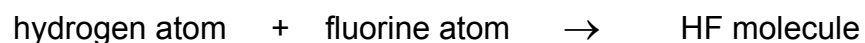
This overlapping region is the covalent bond where electrons are shared.

In terms of quantum mechanics, we can also show the “**electron clouds**” or “**electron density**” for **two H atoms** combining to form the **H₂ molecule**:



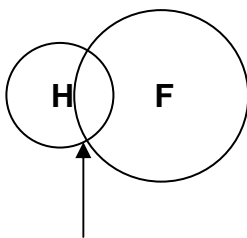
Note: In the H₂ molecule, the electron density is concentrated between the nuclei \oplus because the two H atoms share the electrons equally.

Ex. 2: Use electron dot formulas to represent the reaction described.



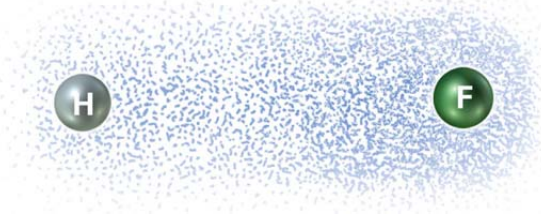
Note in HF, H has 2 e⁻ (like He) and F has 8 valence e⁻ (like other Noble gases).

We can also represent the HF molecule as follows:



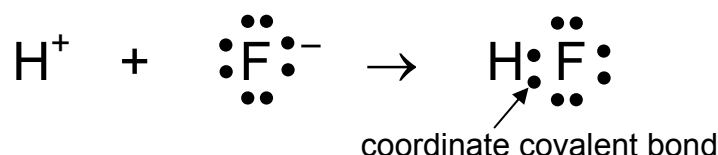
This overlapping region is the covalent bond where electrons are shared.

In terms of quantum mechanics, we can also show the **electron density** in the **HF molecule**:



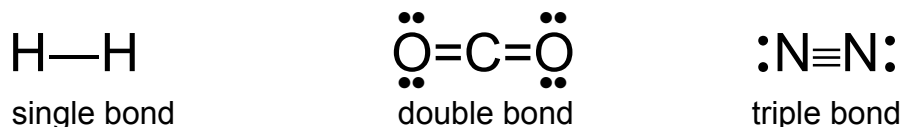
Note: In the HF molecule, the electron density is concentrated between the nuclei but appears more concentrated around the F atom. This is due to a property called **electronegativity**.

Coordinate covalent bond: When one atom donates both electrons to make the bond



MULTIPLE BONDS: Single Bonds, Double Bonds, and Triple Bonds

– Covalent bonds can also be shown as a line to represent the pair of electrons



single bond: the sharing of *one pair of electrons* by two atoms (H—H in H₂)

double bond: the sharing of *two pairs of electrons* by two atoms (O=O in O₂)

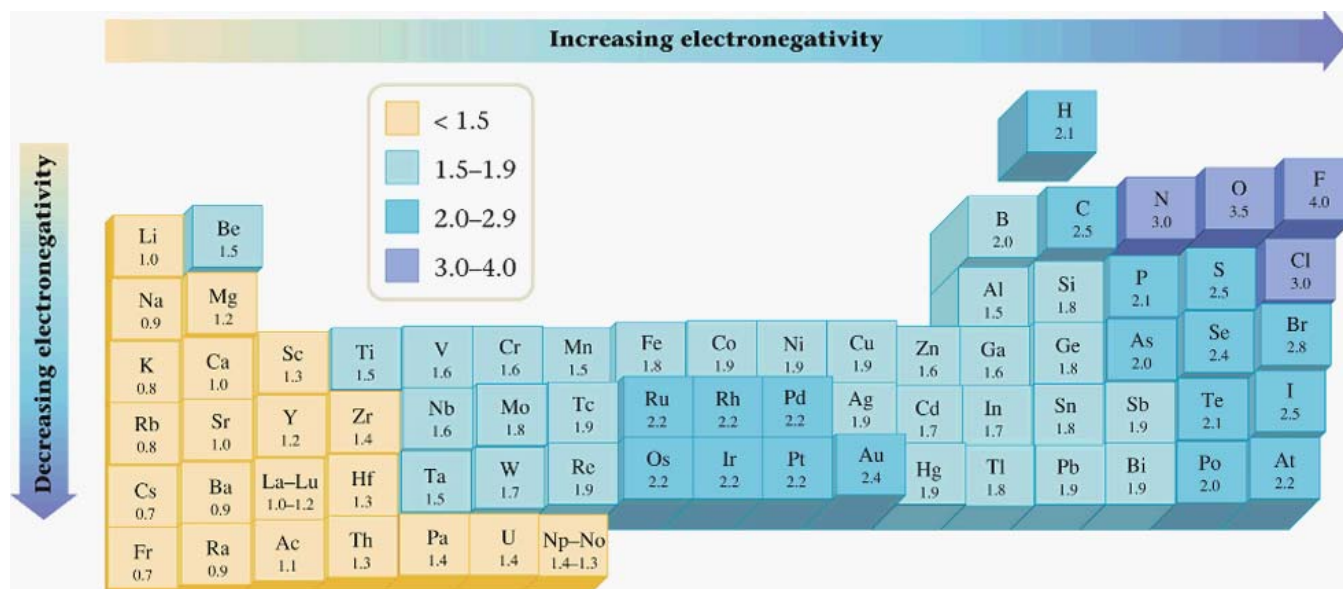
triple bond: the sharing of *three pairs of electrons* by two atoms (N≡N in N₂)

Note: **Single bonds** are the *longest and weakest*, **double bonds** are *shorter and stronger* than single bonds, and **triple bonds** are the *shortest and strongest*.

12.2 ELECTRONEGATIVITY

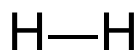
Electronegativity (EN): Ability of an atom in a bond to attract shared electrons to itself

- F is the most electronegative element
- Elements are less electronegative the farther away they are from F.
 - Except for H which has an EN between B and C.
 - Note: This trend mainly applies to elements within the same group or period.



Nonpolar Covalent Bond

- In some covalent bonds, both atoms have equal electronegativity values.
 - The two atoms share the bonding electrons equally.
 - **nonpolar covalent bond**
- Most common example is between two identical atoms: H₂, O₂, N₂, Cl₂, F₂, I₂, Br₂



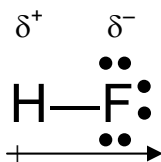
- Nonpolar covalent bonds can also occur between **different** atoms which have identical electronegativity values.

In some covalent bonds, one of the two atoms attracts the bonding electrons more strongly.

- A **polar covalent bond** results between the two atoms.
 - The bond is **polar** because it has two poles, a positive (+) end and a negative (−) end.

Polar Covalent Bond

- Because the electrons spend more time around F, they spend less time around H
 - F gets a partial negative charge (indicated with a δ^-), and H gets partial positive charge (indicated with a δ^+):



Polar molecules will have an **overall dipole** which can be represented with a dipole arrow (pointing to the more electronegative end of the molecule).

- The quantitative measure of a molecule's polarity is called its **dipole moment**,

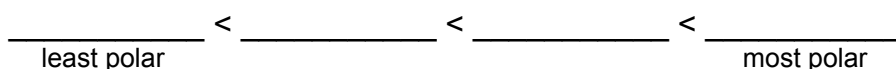
Delta (δ) Notation for polar bonds:

- Electrons concentrate around the more EN atom in a molecule
 - Atom gains a partial negative charge, indicated with δ^- .
- Since electrons spend less time around the other atom
 - Other atom gains a partial positive charge, indicated with δ^+ .

Ex. 1: Use delta notation to indicate which atom in each bond is more electronegative, then use a dipole arrow that points towards the negative pole.



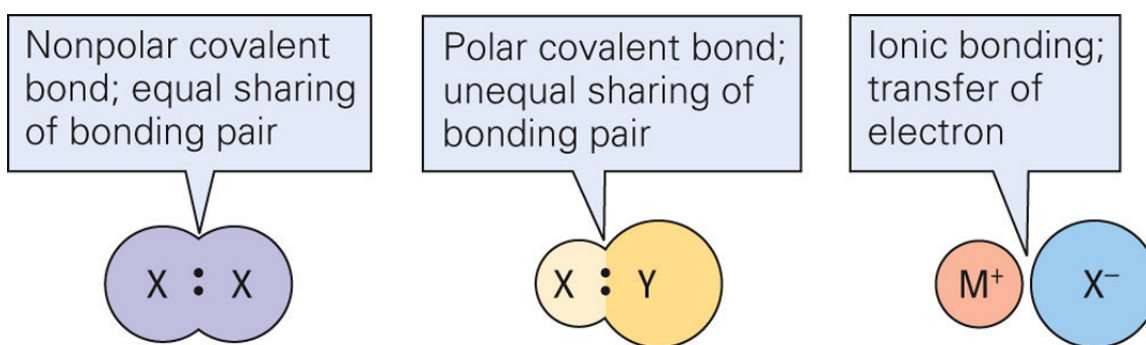
Ex. 2: Use relative electronegativity differences to rank the bonds in Ex. 1 above from least polar to most polar:



Electronegativity Values and Ionic Compounds

Ex. 1: Consider the electronegativity values for sodium and chlorine, and use them to explain why sodium and chlorine react to form an ionic compound rather than a molecule with a covalent bond.

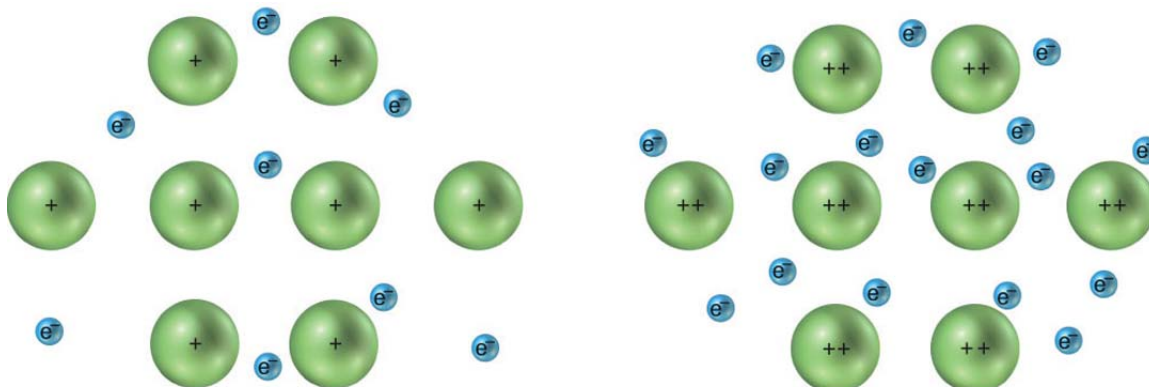
Summary of Nonpolar Covalent Bonds, Polar Covalent Bonds, and Ionic Bonds



METALLIC BONDS

Metals exist as nuclei surrounded by a sea of electrons

- The electrons in a metal are shared among all the nuclei, so the electrons are **delocalized** (i.e., they are not fixed to a specific atom)
- The electrons can shift throughout the entire metal.
 - Electrons are free to move throughout the solid → metals' unique properties
 - e.g. metals conduct heat and electrical because electrons flow through the metal; metals are malleable and ductile because electrons act as a glue, holding the positively charged nuclei together



Example: Identify the bonds in the following by circling one for each:

| | | | | |
|------------------------------------|-------|----------------|-------------------|----------|
| a. The bonds in HF. | ionic | polar covalent | nonpolar covalent | metallic |
| b. The bond in F ₂ . | ionic | polar covalent | nonpolar covalent | metallic |
| c. The bonds in K ₂ O. | ionic | polar covalent | nonpolar covalent | metallic |
| d. The bonds in Cu. | ionic | polar covalent | nonpolar covalent | metallic |
| e. The bonds in CO. | ionic | polar covalent | nonpolar covalent | metallic |
| f. The bonds in O ₂ . | ionic | polar covalent | nonpolar covalent | metallic |
| g. The bond in MgCl ₂ . | ionic | polar covalent | nonpolar covalent | metallic |
| h. The bonds in NO. | ionic | polar covalent | nonpolar covalent | metallic |
| i. The bonds in Br ₂ . | ionic | polar covalent | nonpolar covalent | metallic |
| k. The bonds in NiO. | ionic | polar covalent | nonpolar covalent | metallic |

12.6 and 12.7 LEWIS STRUCTURES (FOR COVALENT COMPOUNDS)

octet rule (rule of eight): atoms bond in a way that each atom has eight electrons (an octet) in its outer shell, *except* hydrogen which only needs 2 electrons

- Atoms will bond to have the same # of valence electrons as the Noble gas in its period.

GUIDELINES for Lewis Structures (or Electron Dot Diagrams) of Molecules

1. Count the total number of valence electrons present
 - from atoms
2. Write the skeleton structure of the compound
 - Put **least electronegative atom as central atom** and surround it with the other atoms.
 - **Note: H and F atoms will always be outer atoms.**
3. Connect all atoms by drawing single bonds between all atoms, then distribute the remaining valence electrons as lone pairs around outer atoms then around the central atom so each has an octet
4. If there are not enough electrons for each atom to have an octet, make **double** or **triple bonds** between central atom and surrounding atoms
 - **BUT fluorine (F) is so electronegative, it will only form a single bond!**

bonding electrons: electron pairs shared between two atoms

nonbonding (lone pair) electrons: unshared electron pairs belonging to a single atom

Ex. 1: Draw the Lewis Diagram for each of the following molecules:

a. H_2O :

b. CH_2O

Ex. 2: Draw the Lewis Structure for each of the following molecules:

| | |
|--------------------------|-----------------------------|
| a. NH_3 | e. CH_2Br_2 |
| b. SOCl_2 | f. PCl_3 |
| c. CF_4 | e. COF_2 |
| d. Cl_2O | f. HCN |

Lewis Structures (or Electron Dot Diagrams) for POLYATOMIC IONS—GUIDELINES

A **polyatomic ion** consists of covalently bonded atoms with an overall charge.

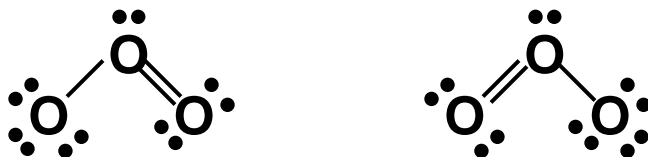
1. Calculate the total number of electrons (e^- s) for all **atoms**
2. Account for # of e^- s associated with charge:
 - If ion is **positively charged**, **subtract** # of electrons from total
 - If ion has +2 charge → subtract 2 electrons from total to get the total # of electrons
 - If ion is **negatively charged**, **add** # of electrons from total
 - If ion has –3 charge → add 3 electrons to get the total # of electrons
3. Divide new total by 2 to get total # of electron pairs
4. Surround central atom (will be indicated) with 4 e^- pairs, then distribute outer atoms around central atom.
5. If any atom (except H) does not have an octet, move nonbonding e^- s from central atom to a position b/w atoms, forming double and triple bonds until all atoms have an octet.
6. Put brackets around all the atoms, and put charge on upper right-hand side
 - This indicates the charge belongs to entire entity rather than to a single atom in the ion.

Example: Draw the Lewis Diagram for each of the following polyatomic ions:

| | |
|-----------------------|-----------------------|
| a. NH_4^+ | c. BrO_3^- |
| b. SO_4^{2-} | d. PO_4^{3-} |

12.7 LEWIS STRUCTURES OF MOLECULES WITH MULTIPLE BONDS (RESONANCE)

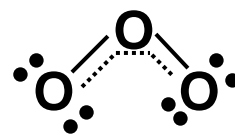
Given the Lewis structure for ozone, we expect either of the following structures:



so one bond (O—O) bond should be longer than the other (O=O).

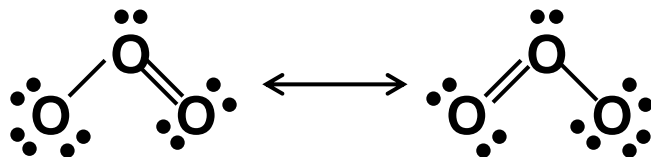
BUT experimental evidence indicates that both oxygen-oxygen bonds in ozone are identical, so neither of the structures accurately represents the molecule.

The actual structure is a cross between the two structures, where the electron pair is actually spread over all three atoms:



These electrons are considered **delocalized electrons** because they are spread between more than two atoms.

To correctly represent such delocalized electrons using Lewis formulas we show all the Lewis formulas with a double-arrow between each:



where each of these structures is called a **resonance structure**.

resonance structure: one of two or more Lewis structures representing a single molecule with bonding that cannot be described fully with only one Lewis structure

resonance: The use of two or more Lewis structures to represent one molecule

- The real ozone molecule does not oscillate between the two resonance structures but is a unique, stable structure that cannot be adequately represented with one Lewis structure.

Ex. 1 Give the resonance structures for NO_2^- :

Ex. 2 Give the resonance structures for the carbonate ion, CO_3^{2-} :

Lewis Electron-Dot Formulas for Ternary Oxyacids (e.g. HNO_3 , H_2SO_4 , etc.)

- Ternary oxyacids are molecules that contain hydrogen, oxygen, and one other element.
 - Ternary oxyacids are essentially a polyatomic ion with each hydrogen in the acid bonded to a different oxygen atom.
- In ternary oxyacids, the central atom is the "other element" which is surrounded by oxygen, and the hydrogen atoms are bonded directly to the oxygen atoms.
 - more than one central atom in the molecule

Example: Draw the Lewis electron-dot formula for each of the following:

| | |
|----------------------------|----------------------------|
| a. HClO_3 | b. H_2SO_4 |
| c. H_2SO_3 | d. H_2CO_3 |

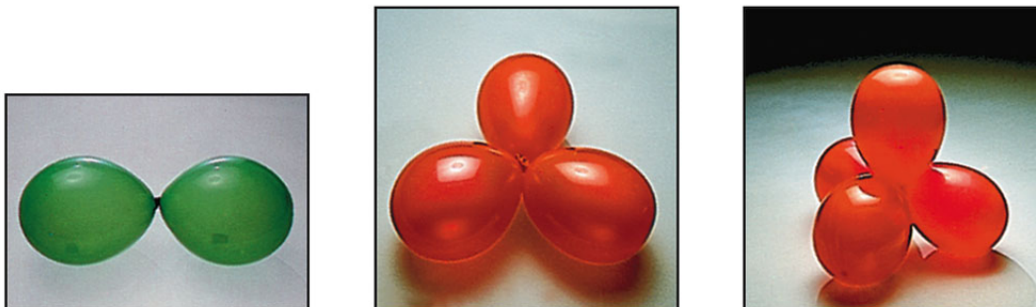
12.8 MOLECULAR STRUCTURE

12.9 MOLECULAR STRUCTURE: THE VSEPR MODEL

Repulsion between electrons causes them to be as far apart as possible

→ **Valence Shell Electron Pair Repulsion (VSEPR) Model**

- **repulsion** between **electron pairs** around a *central atom* → the **shape of molecule**
- For example, consider the following shapes resulting from balloons tied together are the same shapes that molecules will achieve.



Molecular geometry refers to three-dimensional arrangement of atoms in molecule

- responsible for many physical and chemical properties (boiling point, density, etc.)

Determining the Shapes of Molecules

- If there are **only two atoms**, the molecule must be **linear**.
- If there are **more than two atoms** in the molecule
 - **the shape depends** on **number of electrons around the central atom**
 - The electrons orient themselves to maximize the distance between them.



Ex. 1: a. Draw the Lewis structure for **CO₂**, where both carbon-oxygen bonds are equivalent.

Lewis structure

3D sketch of molecule w/ bond angle

- b. What shape maximizes the distance between the two sets of electrons around carbon? Sketch the molecule, and indicate the bond angles above.

Thus, the two outer atoms are **180°** from each other → the shape = **linear (AB₂)**.

Ex. 2: Draw the Lewis structure for CH_2O then determine the shape and the bond angles.

Lewis structure

3D sketch of molecule w/ bond angle

- The three outer atoms are 120° from one another
 - shape = **trigonal planar** (AB_3)
 - three outer atoms at the corners of an equilateral triangle
- Each outer atom is 120° from the other two outer atoms.

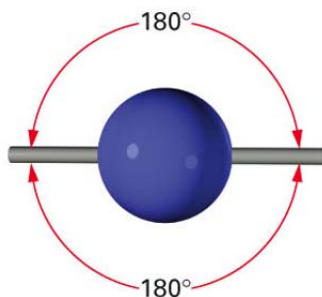
Ex. 3: Draw the Lewis structure for CH_4 then determine the shape and the bond angles.

Lewis structure

3D sketch of molecule w/ bond angle

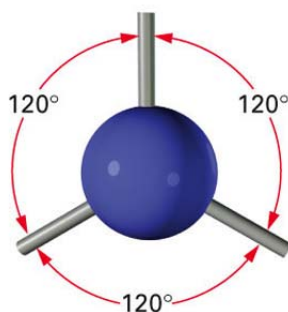
- to maximize the distance between the electrons pairs, the bond angles are 109.5°
 - shape = **tetrahedral** (AB_4)
- *tetra* = four, so “tetrahedral” is used to indicate four sides or four faces
- each outer atom is 109.5° from the other three outer atoms

MOLECULES WHERE CENTRAL ATOM HAS NO LONE PAIRS



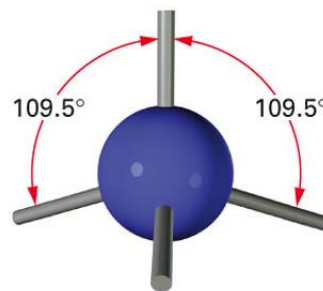
Linear

Two outer atoms around the central atom (AB_2)



Trigonal Planar

Three outer atoms around the central atom (AB_3)



Tetrahedral

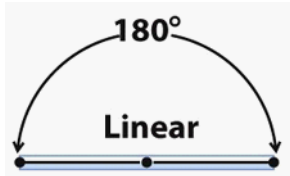
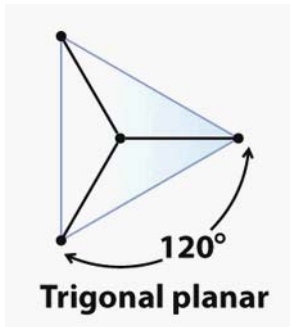
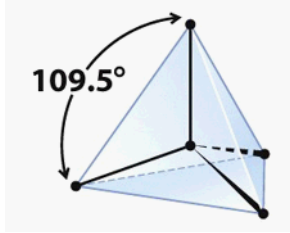
Four outer atoms around the central atom (AB_4)

Molecular Geometries with 2 to 4 Outer Atoms on the Central Atom (where the Central Atom Has No Lone Pairs)

Consider a molecule composed of only two types of atoms, A and B:

A=central atom B=outer atoms

Table I: Molecular Geometries (or Shapes) and Bond Angles

| Steric Number | # of Outer Atoms | # of Lone Pairs on Central Atom | General Formula | MOLECULAR GEOMETRY and NAME |
|---------------|------------------|---------------------------------|-----------------|---|
| 2 | 2 | 0 | AB_2 |  |
| 3 | 3 | 0 | AB_3 |  |
| 4 | 4 | 0 | AB_4 |  |

When there are lone pairs of electrons around the central atom, knowing the **steric number** for the central atoms can help determine the three-dimensional shape.

The **steric number (SN)** of the central atom is determined as follows:

$$\text{steric number} = \left(\begin{array}{l} \# \text{ of atoms bonded} \\ \text{to the central atom} \end{array} \right) + \left(\begin{array}{l} \# \text{ of lone pairs} \\ \text{on the central atom} \end{array} \right)$$

MOLECULES WHERE CENTRAL ATOM HAS ONE OR MORE LONE PAIRS

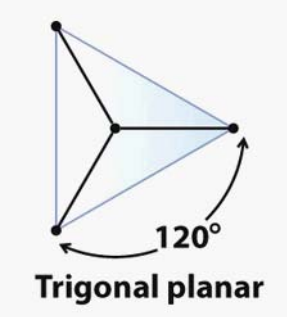
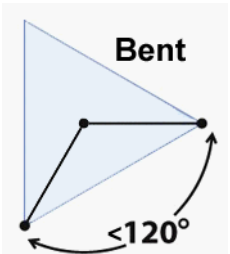
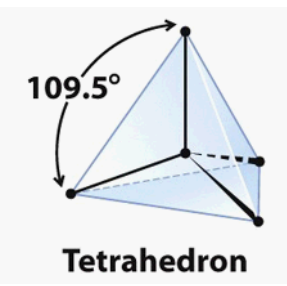
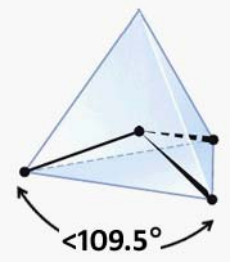
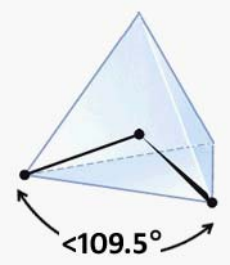
A=central atom B=outer atoms E=lone pairs

A central atom with lone pairs has three types of repulsive forces

lone - pair vs. lone - pair repulsion > lone - pair vs. bonding - pair repulsion > bonding - pair vs. bonding - pair repulsion

- **bonding pairs:** takes up less space than lone pairs since held by attractive forces exerted by nuclei of two bonded atoms
- **lone pairs:** take up more space than bonding electrons

Table II: Molecular Geometries For a Central Atom With Lone Pairs

| Original Shape | General Formula | # of Outer Atoms | # of Lone Pairs on Central Atom | Molecular Shape and Name |
|--|--------------------------------|------------------|---------------------------------|---|
|  <p>Trigonal planar SN=3</p> | AB ₂ E | 2 | 1 |  <p>Bent <120° bent or angular</p> |
|  <p>Tetrahedron SN=4</p> | AB ₃ E | 3 | 1 |  <p>trigonal pyramidal <109.5°</p> |
| | AB ₂ E ₂ | 2 | 2 |  <p>bent or angular <109.5°</p> |

AB₂E: bent (or angular) (central atom and 2 outer atoms have a bent shape)

– Example: Give the Lewis diagram, shape, and bond angles for **SO₂**.

Lewis structure

3D sketch of molecule w/ bond angles

Steric number (SN) = 3

→ Start with AB₃ molecule and replace one **B atom** w/ a **lone pair of electrons (E)** → **AB₂E**

AB₃E: trigonal pyramid (central atom and 3 outer atoms make a pyramid)

– Example: Give the Lewis structure and shape for **NH₃** (including bond angles).

Lewis structure

3D sketch of molecule w/ bond angles

Steric number (SN) = 4

→ Start with AB₄ molecule and replace one **B atom** with a **lone pair of electrons (E)**

→ **AB₃E**

AB₂E₂: bent (or angular) (central atom and 2 outer atoms have a bent shape)

– Example: Give the Lewis structure and shape for **H₂O** (including bond angles).

Lewis structure

3D sketch of molecule w/ bond angle

Steric number (SN) = 4

→ Start with AB₄ molecule and replace one **B atom** with a **lone pair of electrons (E)**

→ **AB₂E₂**

Given any molecule or polyatomic ion, be able to determine the Lewis Structure, then determine the general formula (e.g. AB_2E_2) to identify the corresponding molecular geometry (or shape) and bond angle(s) for the molecule.

Example: For the following molecules and polyatomic ions:

- Draw the Lewis structure.
- Determine the molecular geometry of the molecule.
- Determine the approximate bond angles.

a. **CH₃F**

Lewis structure

ii. shape of **CH₃F**: _____

iii. bond angles in **CH₃F**: _____

c. **phosphite ion, PO₃⁻³**

Lewis structure

ii. shape of **PO₃⁻³**: _____

iii. bond angles in **PO₃⁻³**: _____

b. **OF₂**

Lewis structure

ii. shape of **OF₂**: _____

iii. bond angles in **OF₂**: _____

d. **azide ion, N₃⁻**

Lewis structure

ii. shape of **N₃⁻**: _____

iii. bond angles in **N₃⁻**: _____

ELECTRONEGATIVITY AND POLARITY

For diatomic molecules:

- **nonpolar molecules:** when the 2 atoms have equal EN values
- **polar molecules:** when the 2 atoms have different EN values
 - have dipole (+ve and –ve ends)

For molecules of three or more atoms:

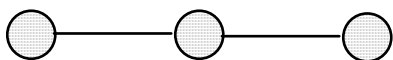
- polarity depend on individual bonds and geometry around central atom
- **Polar molecules** have an **overall dipole** (positive end and negative end)
- In **nonpolar molecules**, all the individual dipoles cancel → **no overall dipole**.

Guidelines for Determining if a Molecule is Polar or Nonpolar

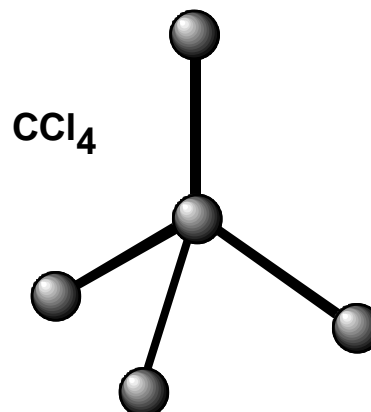
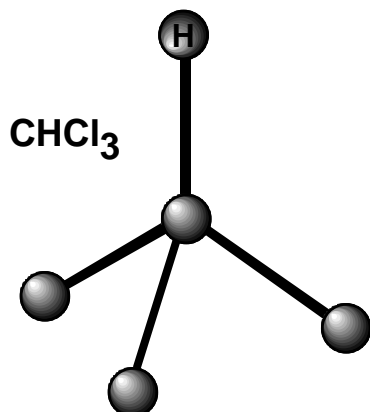
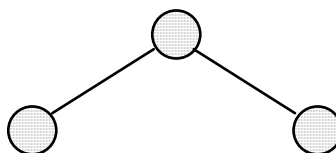
1. Use a dipole arrow to indicate which atom in a nonpolar bond is more electronegative.
2. Determine if there is an overall dipole:
 - If two arrows point in opposite directions, all arrows point in, or all arrows point out, then the dipoles cancel → **nonpolar molecule**.
 - If all arrows point towards the same direction and don't cancel, there is an **overall dipole** for the molecule → **polar molecule**.
 - A **dipole moment** is the quantitative measure of the separation of charges in a molecule → The higher the dipole moment, the more polar the molecule.

Example: Determine whether the following molecules are polar or nonpolar:

CO₂:



H₂O:



Example: For the following molecules:

- Draw the Lewis structure.
- Determine the shape of the molecule.
- Determine the approximate bond angles.

i. **SO₃**

Lewis structure

ii. shape of **SO₃**: _____

iii. bond angle in **SO₃**: _____

iv. Sketch the 3D shape of the **SO₃** molecule below, then *draw an arrow* to show the dipole on each polar bond.

v. The **SO₃** molecule is _____.

(Circle one) polar nonpolar

- Sketch the molecule to show the dipoles.
- Indicate if the molecule is polar/nonpolar.

i. **CH₂F₂**

Lewis structure

ii. shape of **CH₂F₂**: _____

iii. bond angles in **CH₂F₂**: _____

iv. Sketch the 3D shape of the **CH₂F₂** molecule below, then *draw an arrow* to show the dipole on each polar bond.

v. The **CH₂F₂** molecule is _____.

(Circle one) polar nonpolar

Example: For the following molecules:

- Draw the Lewis structure.
- Determine the shape of the molecule.
- Determine the approximate bond angles.

i. **PF₃**

Lewis structure

ii. shape of **PF₃**: _____

iii. bond angle in **PF₃**: _____

iv. Sketch the 3D shape of the **PF₃** molecule below, then *draw an arrow* to show the dipole on each polar bond.

v. The **PF₃** molecule is _____.

(Circle one) polar nonpolar

- Sketch the molecule to show the dipoles.
- Indicate if the molecule is polar/nonpolar.

i. **COCl₂** (in which the C-Cl bonds are equivalent)

Lewis structure

ii. shape of **COCl₂**: _____

iii. bond angles in **COCl₂**: _____

iv. Sketch the 3D shape of the **COCl₂** molecule below, then *draw an arrow* to show the dipole on each polar bond.

v. The **COCl₂** molecule is _____.

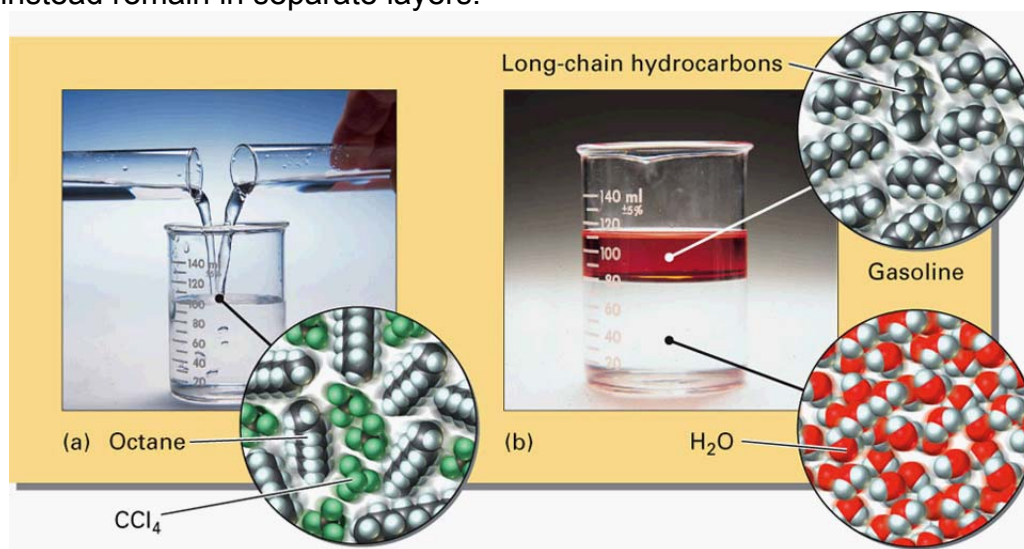
(Circle one) polar nonpolar

"Like dissolves like" rule:

- Polar substances will dissolve in or mix with other polar substances.
- Nonpolar substances will dissolve in mix other nonpolar substances.
- But polar and nonpolar substances don't mix or dissolve in one another.

Consider the images below:

- (a) *Two nonpolar liquids*, $\text{CCl}_4(l)$ and octane (C_8H_{18}) in gasoline, will mix.
(b) *Polar water molecules* do not mix with *nonpolar* gasoline/octane molecules but instead remain in separate layers.



Note: Hydrocarbons are compounds that contain only carbon and hydrogen (e.g. C_8H_{18}).

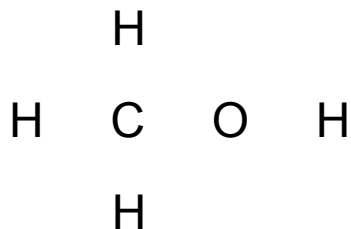
- The symmetrical shape of hydrocarbons results in the dipoles for each C-H bond in the molecule always cancelling—e.g. just like in CH_4 .

→ **Hydrocarbons are always *nonpolar*.**

Ex. 1: a. Draw the Lewis structure for methanol (CH_3OH) using the skeleton structure below, then sketch the 3D shape with dipoles:

Lewis structure

3D shape with dipoles



- b. Is methanol polar or nonpolar? Polar Nonpolar
- c. Would it mix with water? Yes No

Thus, any **alcohol**—a *molecule* with a **hydroxyl (OH) group**—is **polar**, so **liquid alcohols will mix with** and **solid alcohols will dissolve in water**.