



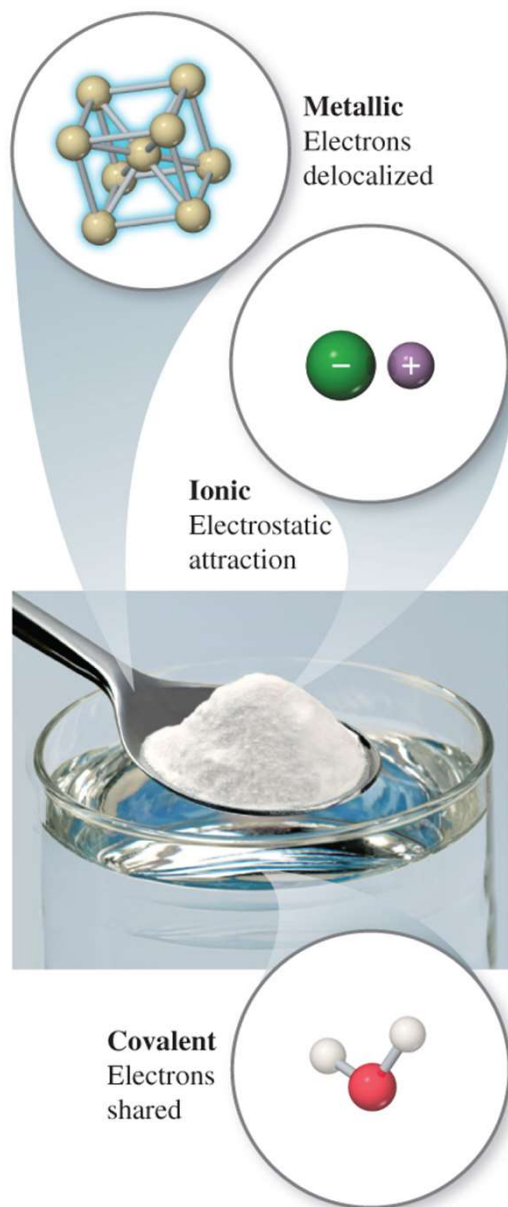
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CHAPTER 7

CHEMICAL BONDING AND MOLECULAR GEOMETRY

Chemical Bonds



- Three basic types of bonds
 - **Ionic**
 - Electrostatic attraction between ions.
 - **Covalent**
 - Sharing of electrons.
 - **Metallic**
 - Metal atoms bonded to several other atoms.

The properties of ionic compounds includes:

Ionic solids exhibit a crystalline structure and tend to be rigid and brittle

They also tend to have high melting and boiling points, which suggests that ionic bonds are very strong.

Ionic solids are also poor conductors of electricity in solid state.

Once dissolved or melted, ionic compounds are excellent conductors of electricity because the ions can move about freely.

The Formation of Ionic Compounds

Binary ionic compounds are composed of just two elements:

metal (which forms the cations) and a nonmetal (which forms the anions)

Many metallic elements have relatively low ionization potentials and lose electrons easily.

Nonmetal atoms have relatively high electron affinities and thus gain electrons.

The net ionic charge of ionic compound is zero. **Eg: Al_2O_3 , Thus, $(2 \times +3) + (3 \times -2) = 0$**

Bond strength and lattice energy

An ionic compound is stable **because** of the electrostatic attraction between its positive and negative ions.

The lattice energy of a compound is a measure of the strength of this attraction.

Lattice energy the energy required to completely separate a mole of a solid ionic compound into its gaseous ions.

Lattice energy, then, increases with the charge on the ions.

It also increases with decreasing size of ions.

Lattice Energies for Some Ionic Compounds

Compound	Lattice Energy (kJ/mol)	Compound	Lattice Energy (kJ/mol)
LiF	1030	MgCl ₂	2326
LiCl	834	SrCl ₂	2127
LiI	730		
NaF	910	MgO	3795
NaCl	788	CaO	3414
NaBr	732	SrO	3217
NaI	682		
KF	808	ScN	7547
KCl	701		
KBr	671		
CsCl	657		
CsI	600		

rk:

the charge of opposite charged ions increases, the electrostatic force of attraction increases and result in high lattice energy.

ionic solid with divalent ions have much larger lattice energy compared to monovalent ionic solid. As ionic radius decreases, ions get closer to each other and increasing the strength of attraction as well as the lattice energy of ionic solid.

Example-1: The lattice energy of LiF (Z^+ and $Z^- = 1$) is **1023 kJ/mol**, Whereas that of MgF₂ ($Z^+ = 2$ and $Z^- = 1$) is **3900 kJ/mol** (r is nearly the same-about 200 pm for both compounds).

Example-2: The lattice energy of MgF₂ (2957 kJ/mol) and that of MgI₂ (2327 kJ/mol). This shows the effect on lattice energy of the smaller ionic size of F⁻ as compared to I⁻.

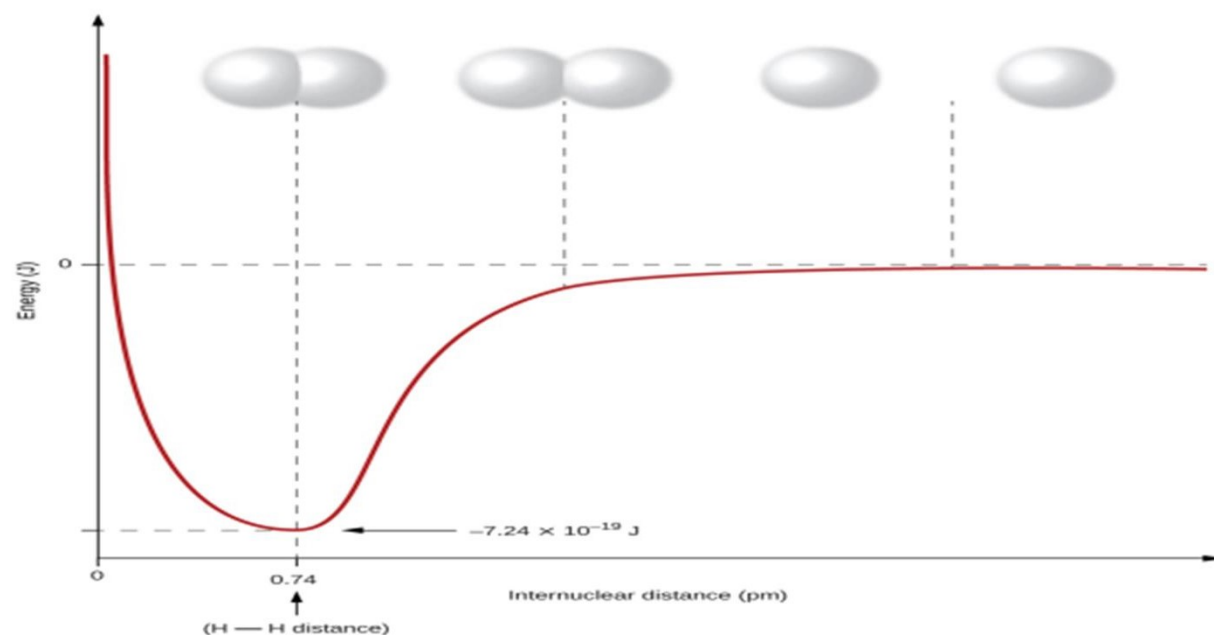
Covalent Bonding

A chemical bond formed by sharing of electron pairs between non-metals.

Formation of Covalent Bonds.

When two nonmetal atoms.

Potential energy decreases as the bond distance decreases.



Potential energy of two separate hydrogen atoms.

Equality of Covalent Bonds.

Electrons in similar diatomic molecule (H_2 , Cl_2) shared equally.

Electrons have an equal probability of being near each nucleus.

We refer to this as a pure covalent bond.

Although atoms often form compounds by sharing electrons, the electrons are not always shared equally.

When two atoms share electrons unequally, a **bond dipole** results.

The greater the difference in electronegativity, the more polar is the bond.

An unequal distribution of electrons means there is a **polar covalent bond**.

Characterized by **partial +ve** charge & **partial -ve** charge.

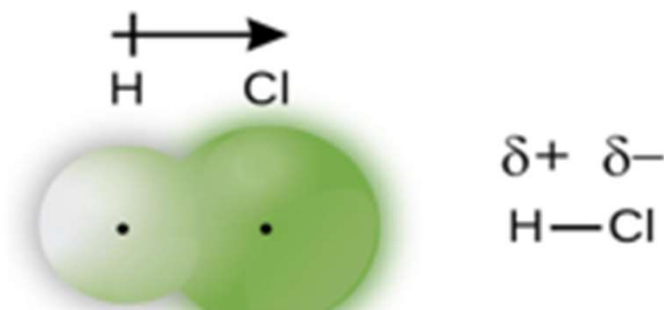
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The atom that attracts the electrons more strongly acquires the partial negative charge and vice versa.

Example: The electrons in the H–Cl bond.

The distribution of electron density in the HCl molecule is uneven.

Symbols δ^+ and δ^- indicate the polarity of the H–Cl bond



Writing Lewis Structures

1. Draw skeletal structure of compound showing what atoms are bonded to each other. Put least electronegative element in the center.
2. Count total number of valence e⁻. Add 1 for each negative charge. Subtract 1 for each positive charge.
3. Complete an octet for all atoms **except** hydrogen
4. If structure contains too many electrons, form double and triple bonds on central atom as needed.

Write the Lewis structure of nitrogen trifluoride (NF₃).

Step 1 – N is less electronegative than F, put N in center

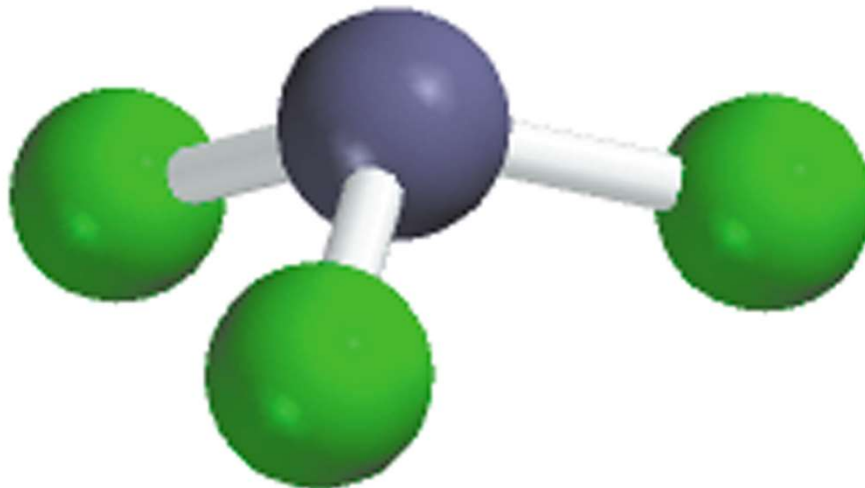
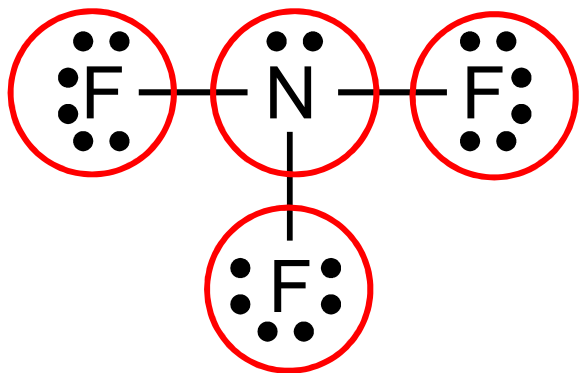
Step 2 – Count valence electrons N - 5 (2s²2p³) and F - 7 (2s²2p⁵)

$$5 + (3 \times 7) = \text{26 valence electrons}$$

Step 3 – Draw single bonds between N and F atoms and complete octets on N and F atoms.

Step 4 - Check, are # of e⁻ in structure equal to number of valence e⁻?

$$3 \text{ single bonds } (3 \times 2) + 10 \text{ lone pairs } (10 \times 2) = \text{26 valence electrons}$$



Write the Lewis structure of the carbonate ion (CO_3^{2-}).

Step 1 – C is less electronegative than O, put C in center

Step 2 – Count valence electrons C - 4 ($2s^2 2p^2$) and O - 6 ($2s^2 2p^4$)
-2 charge – $2e^-$

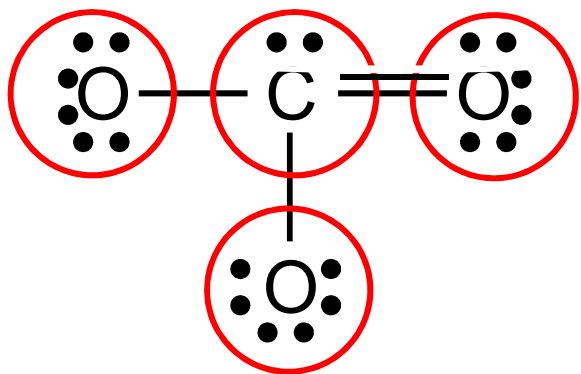
$$4 + (3 \times 6) + 2 = \text{24 valence electrons}$$

Step 3 – Draw single bonds between C and O atoms and complete octet on C and O atoms.

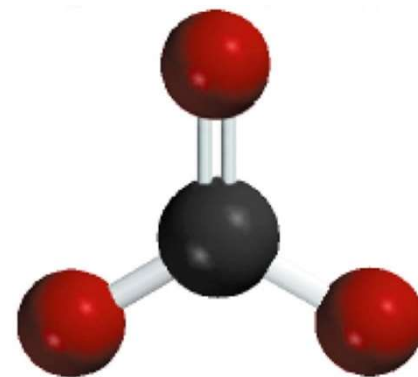
Step 4 - Check, are # of e^- in structure equal to number of valence e^- ?

$$3 \text{ single bonds } (3 \times 2) + 10 \text{ lone pairs } (10 \times 2) = \text{26 valence electrons}$$

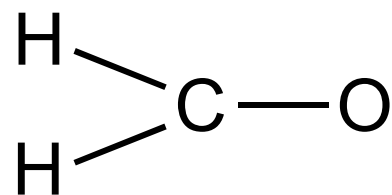
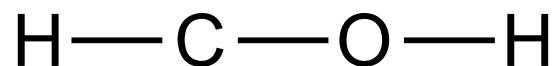
Step 5 - Too many electrons, form double bond and re-check # of e^-



$$\begin{array}{rcl} 2 \text{ single bonds } (2 \times 2) & = & 4 \\ 1 \text{ double bond} & = & 4 \\ 8 \text{ lone pairs } (8 \times 2) & = & 16 \\ \hline \text{Total} & = & 24 \end{array}$$



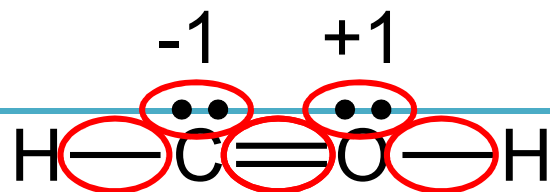
Two possible skeletal structures of formaldehyde (CH₂O)



An atom's **formal charge** is the difference between the number of valence electrons in an isolated atom and the number of electrons assigned to that atom in a Lewis structure.

$$\begin{array}{l} \text{formal charge} \\ \text{on an atom in} \\ \text{a Lewis} \\ \text{structure} \end{array} = \begin{array}{l} \text{total number} \\ \text{of valence} \\ \text{electrons in} \\ \text{the free atom} \end{array} - \begin{array}{l} \text{total number} \\ \text{of nonbonding} \\ \text{electrons} \end{array} - \frac{1}{2} \left(\begin{array}{l} \text{total number} \\ \text{of bonding} \\ \text{electrons} \end{array} \right)$$

The sum of the formal charges of the atoms in a molecule or ion must equal the charge on the molecule or ion.



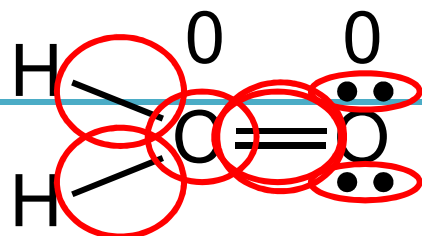
$$\begin{array}{r}
 \text{C} - 4 \text{ e}^- \\
 \text{O} - 6 \text{ e}^- \\
 \hline
 2\text{H} - 2 \times 1 \text{ e}^- \\
 \hline
 12 \text{ e}^-
 \end{array}$$

$$\begin{array}{r}
 2 \text{ single bonds } (2 \times 2) = 4 \\
 1 \text{ double bond} = 4 \\
 2 \text{ lone pairs } (2 \times 2) = 4 \\
 \hline
 \text{Total} = 12
 \end{array}$$

$$\begin{array}{l}
 \text{formal charge} \\
 \text{on an atom in} \\
 \text{a Lewis} \\
 \text{structure}
 \end{array}
 =
 \begin{array}{l}
 \text{total number} \\
 \text{of valence} \\
 \text{electrons in} \\
 \text{the free atom}
 \end{array}
 -
 \begin{array}{l}
 \text{total number} \\
 \text{of nonbonding} \\
 \text{electrons}
 \end{array}
 -
 \frac{1}{2}
 \left(
 \begin{array}{l}
 \text{total number} \\
 \text{of bonding} \\
 \text{electrons}
 \end{array}
 \right)$$

$$\begin{array}{l}
 \text{formal charge} \\
 \text{on C}
 \end{array}
 = 4 - 2 - \frac{1}{2} \times 6 = -1$$

$$\begin{array}{l}
 \text{formal charge} \\
 \text{on O}
 \end{array}
 = 6 - 2 - \frac{1}{2} \times 6 = +1$$



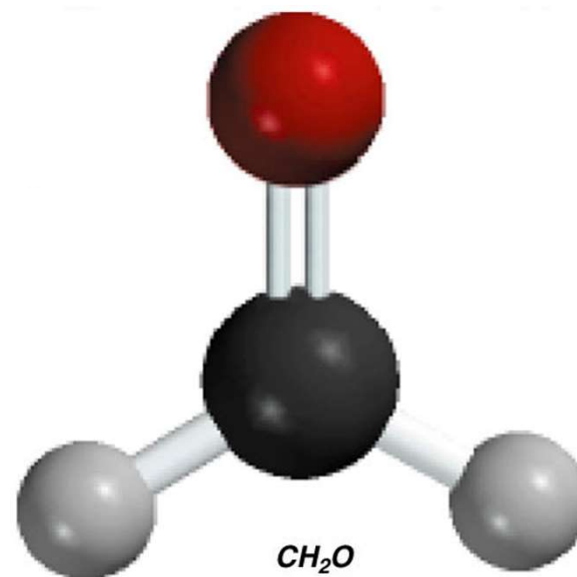
$$\begin{array}{r}
 \text{C} - 4 \text{ e}^- \\
 \text{O} - 6 \text{ e}^- \\
 2\text{H} - 2 \times 1 \text{ e}^- \\
 \hline
 12 \text{ e}^-
 \end{array}$$

$$\begin{array}{r}
 2 \text{ single bonds } (2 \times 2) = 4 \\
 1 \text{ double bond} = 4 \\
 2 \text{ lone pairs } (2 \times 2) = 4 \\
 \hline
 \text{Total} = 12
 \end{array}$$

$$\begin{array}{l}
 \text{formal charge} \\
 \text{on an atom in} \\
 \text{a Lewis} \\
 \text{structure}
 \end{array}
 =
 \begin{array}{l}
 \text{total number} \\
 \text{of valence} \\
 \text{electrons in} \\
 \text{the free atom}
 \end{array}
 -
 \begin{array}{l}
 \text{total number} \\
 \text{of nonbonding} \\
 \text{electrons}
 \end{array}
 -
 \frac{1}{2} \left(\begin{array}{l} \text{total number} \\ \text{of bonding} \\ \text{electrons} \end{array} \right)$$

$$\begin{array}{l}
 \text{formal charge} \\
 \text{on C}
 \end{array}
 = 4 - 0 - \frac{1}{2} \times 8 = 0$$

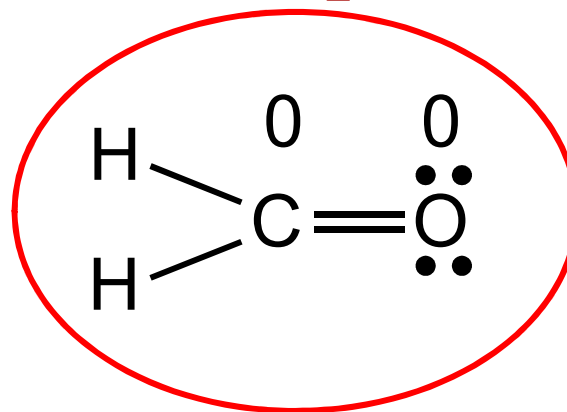
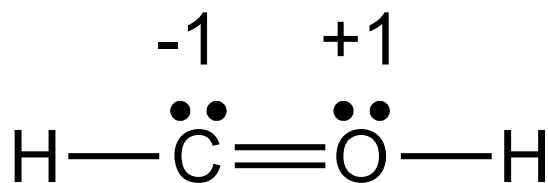
$$\begin{array}{l}
 \text{formal charge} \\
 \text{on O}
 \end{array}
 = 6 - 4 - \frac{1}{2} \times 4 = 0$$



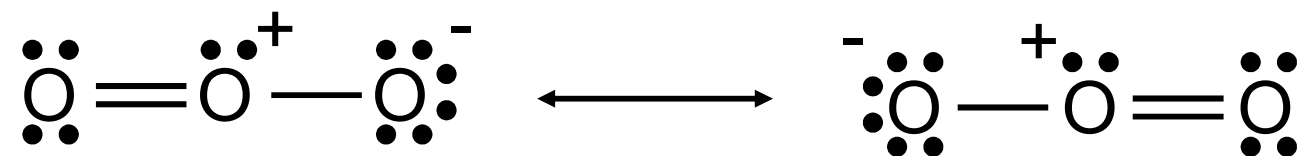
Formal Charge and Lewis Structures

1. For neutral molecules, a Lewis structure in which there are no formal charges is preferable to one in which formal charges are present.
2. Lewis structures with large formal charges are less plausible than those with small formal charges.
3. Among Lewis structures having similar distributions of formal charges, the most plausible structure is the one in which negative formal charges are placed on the more electronegative atoms.

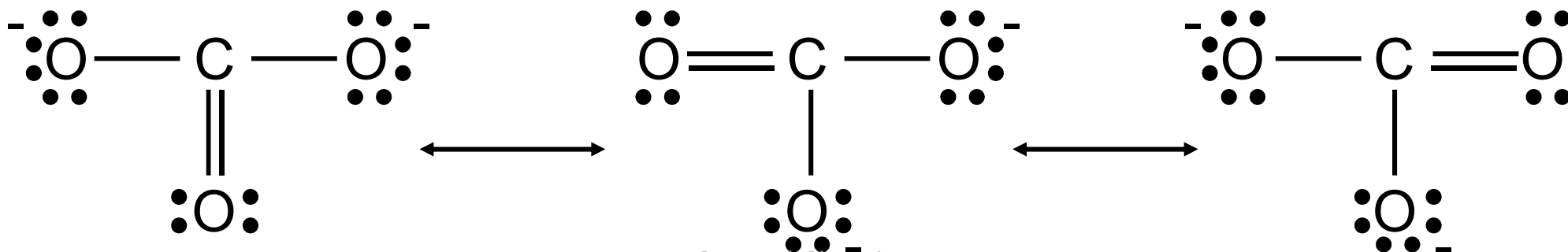
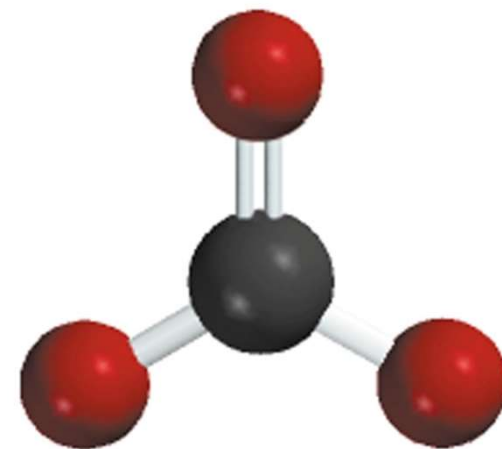
Which is the most likely Lewis structure for CH_2O ?



A **resonance structure** is one of two or more Lewis structures for a single molecule that cannot be represented accurately by only one Lewis structure.



What are the resonance structures of the carbonate (CO_3^{2-}) ion?



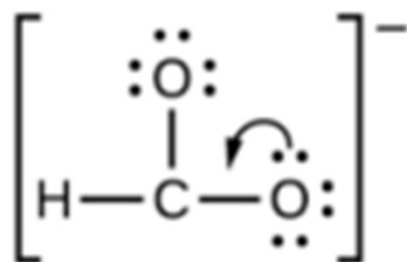
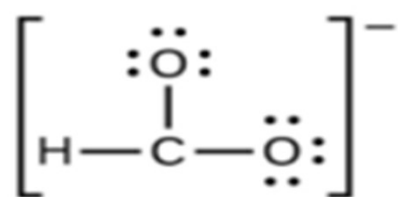
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le: Draw the Lewis formula of the following molecules or Polyatomic ions

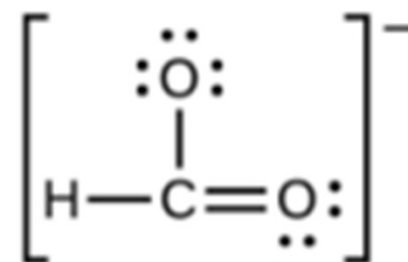
a) CHO_2^- b) CF_4 c) PH_4^+ d) SO_4^{2-} e) CoCl_2

Valence electrons/atom $\times$ 1 atom = 4, H: 1 valence electron/atom $\times$ 1 atom = 1, O: 6

Valence electrons/atom $\times$ 2 atoms = 12, **+1** additional electron **=18 valence electrons**



gives



Exceptions to the Octet Rule

Many covalent molecules have central atoms that do not have eight electrons in their Lewis structures. These molecules fall into **three** categories.

Odd-electron

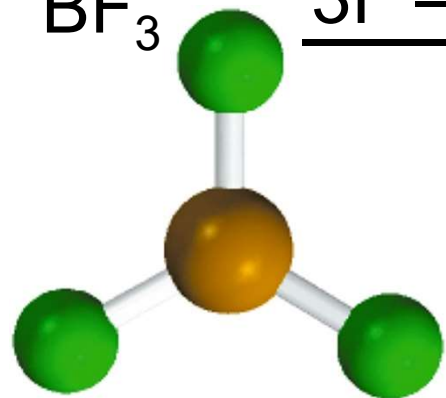
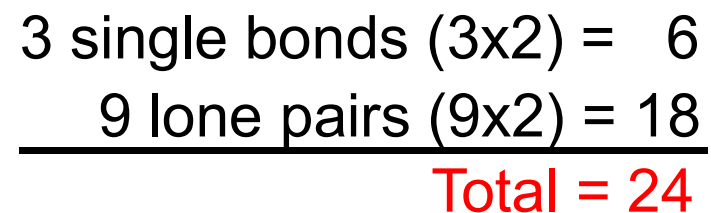
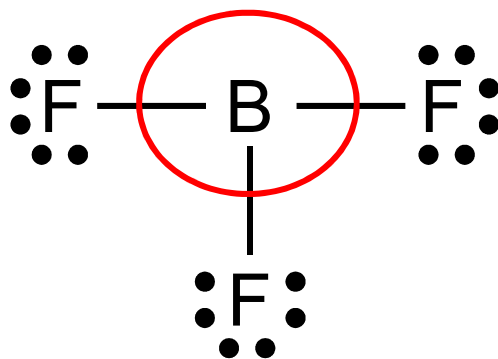
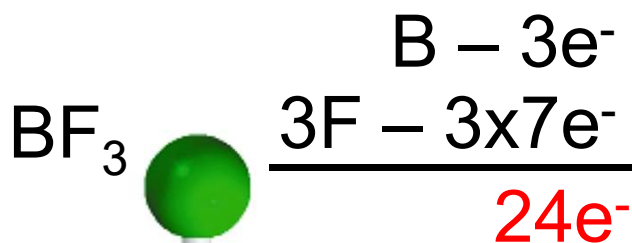
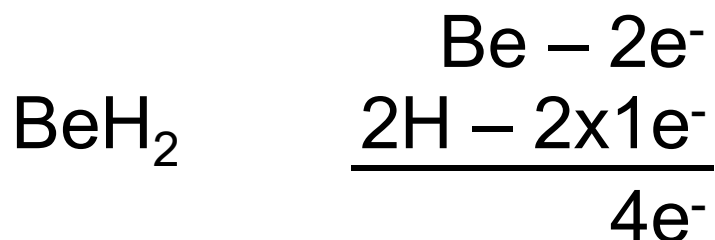
Electron-deficient

Hypervalent

Transition elements and inner transition elements also do not follow the octet rule.

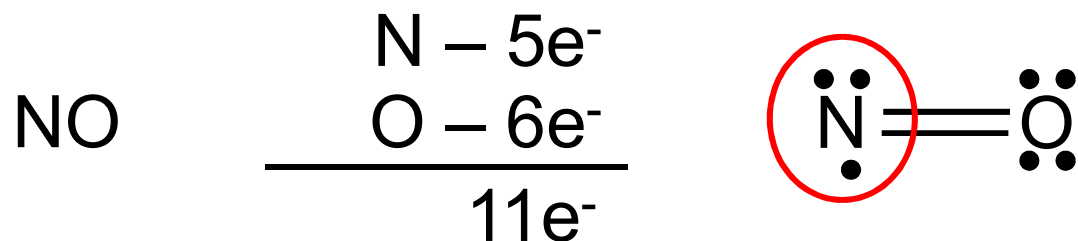
Exceptions to the Octet Rule

The Incomplete Octet

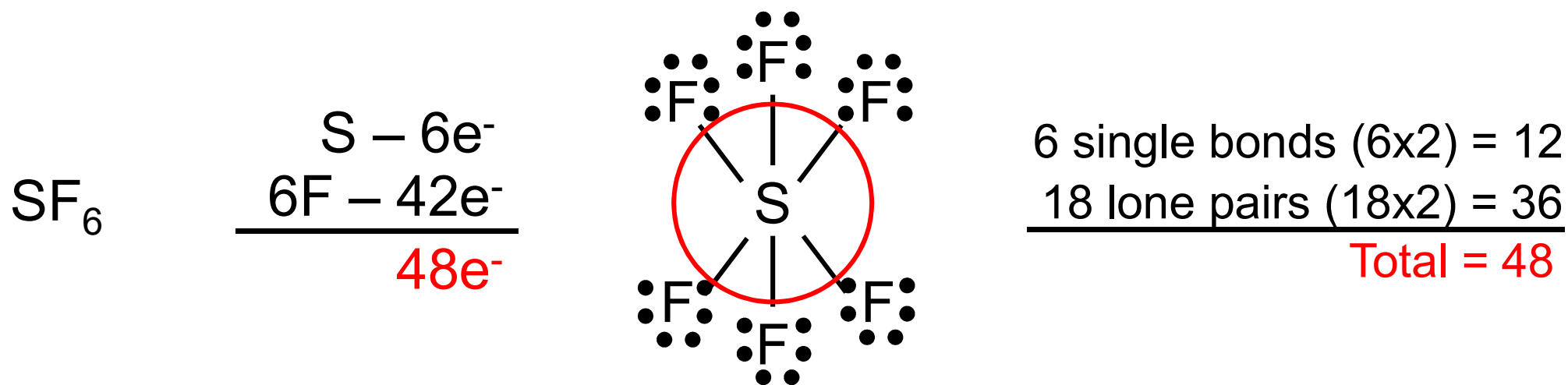


Exceptions to the Octet Rule

Odd-Electron Molecules



The Expanded Octet (central atom with principal quantum number $n > 2$)



$$\begin{array}{r} 6 \text{ single bonds } (6 \times 2) = 12 \\ 18 \text{ lone pairs } (18 \times 2) = 36 \\ \hline \text{Total} = 48 \end{array}$$

Bond Strength Of Covalent Bond

Most simply, the strength of a bond is measured by determining how much energy is required to break the bond.

This is the **bond enthalpy**.

The bond enthalpy for a Cl—Cl bond, $D(\text{Cl}—\text{Cl})$, is measured to be 242 kJ/mol.

Stable molecules exist because covalent bonds hold the atoms together.

We measure the strength of a covalent bond by the energy required to break it.

The energy necessary to separate the bonded atoms.

The stronger a bond, the greater the energy required to break it.

The energy required to break a specific covalent bond in one mole of gaseous molecules.

Called the bond energy or the bond dissociation energy.



Bond energy for a diatomic molecule, $\text{DX}-\text{Y}$, is defined as the standard enthalpy change for the endothermic reaction.

As the number of bonds between two atoms increases, the bond length decreases.

Table: Average Bond Lengths and Bond Energies for Some Common Bonds

Bond	Bond Length (Å)	Bond Energy (kJ/mol)
C–C	1.54	345
C=C	1.34	611
C≡C	1.20	837
C–N	1.43	290
C=N	1.38	615
C≡N	1.16	891
C–O	1.43	350
C=O	1.23	741
C≡O	1.13	1080

VSEPR Theory

Valence shell electron-pair repulsion theory (VSEPR theory).

enables us to predict the **molecular structure**, including approximate **bond angles** around the central atom

by examination of the number of bonds and lone electron pairs in its Lewis structure. It focuses on the position taken by the groups of **electrons** on the central atoms of a molecule.

VSEPR theory predicts the arrangement of electron pairs around each central atom.

It usually corrects the arrangement of atoms in a molecule.

We should understand, however, that the theory only considers **electron-pair repulsion**.

In general, according to the VSEPR model, the repulsive force decrease in the following order: **Lone pair-lone pair > lone pair-bonding pair > bonding pair-bonding pair**

The best arrangement of a given number of electron domains is the one that minimizes the repulsions among them."

Electron pair arrangement and molecular shape

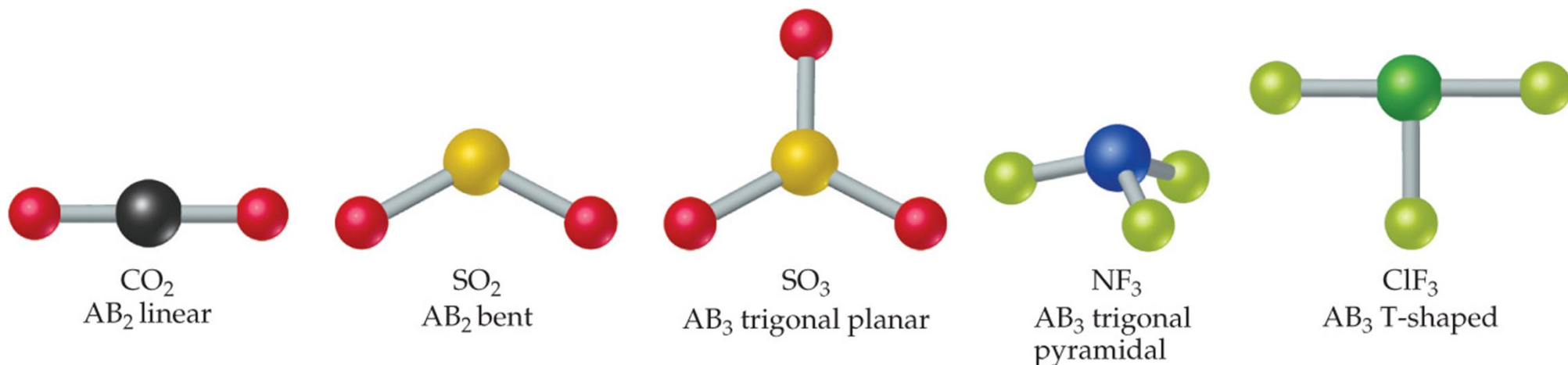
Electron pair arrangement- is defined by the sets of electrons both bonding and non-bonding (lone pairs) around the central atom.

The electron set arrangement can give rise to different molecular shape.

Remark: AX_mE_n

Molecular Shapes

- The shape of a molecule plays an important role in its reactivity.
- By noting the number of bonding and nonbonding electron pairs, we can easily predict the shape of the molecule.



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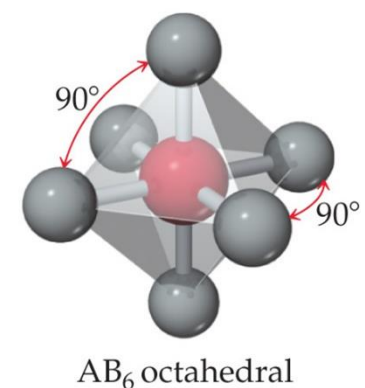
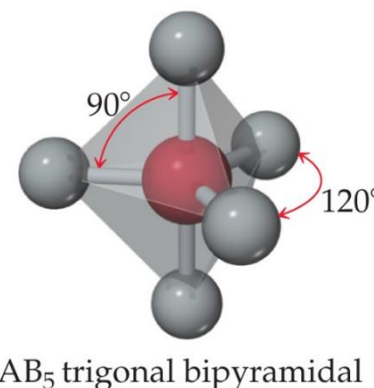
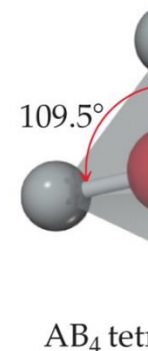
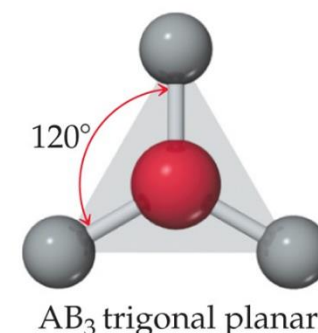
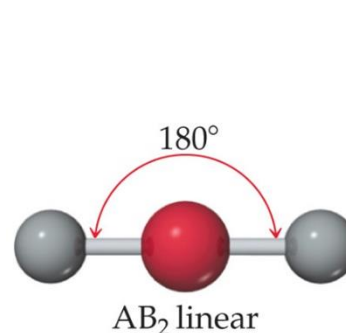
What Determines the Shape of a Molecule?

Simply put, electron pairs, whether they be bonding or nonbonding, repel each other.

By assuming the electron pairs are placed as far as possible from each other, we can predict the shape of the molecule.

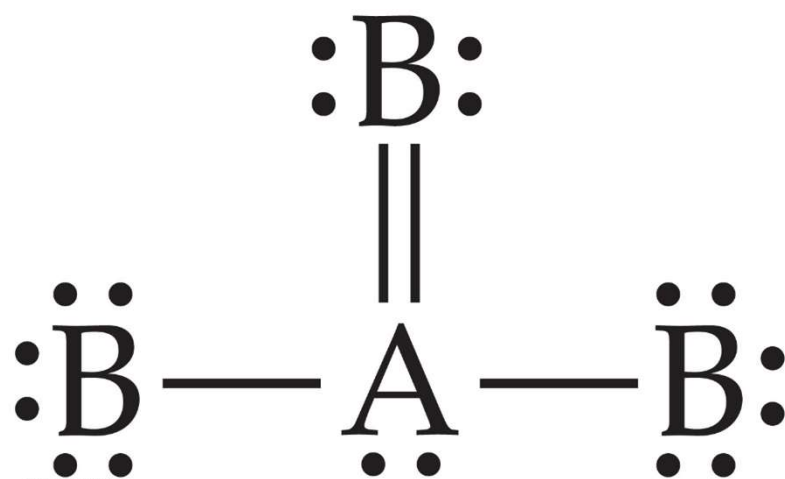
The electron-domain geometry is often *not* the shape of the molecule, however.

The molecular geometry is that defined by the positions of *only* the atoms in the molecules, not the nonbonding pairs.



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Electron Domains

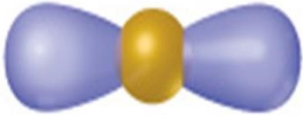
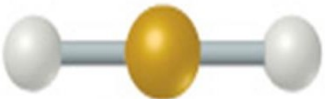


- The central atom in this molecule, A, has four electron domains.

- We can refer to the electron pairs as **electron domains**.
- In a double or triple bond, all the electrons shared between those two atoms are on the same side of the central atom; therefore, they count as one electron domain.

Linear Electron Domain

- Electron-Domain and Molecular Geometries for Two, Three, and Four Electron Domains around a Central Atom

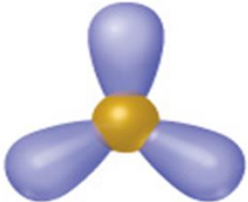
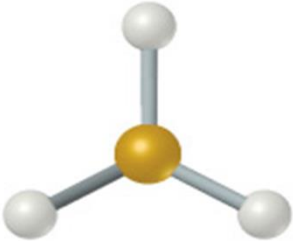
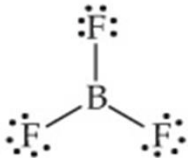
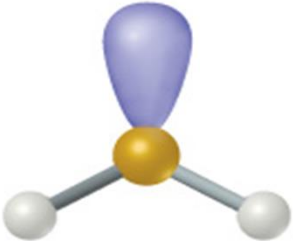
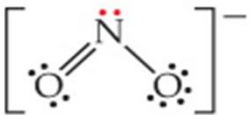
Number of Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
	 Linear	2	0	 Linear	$\ddot{\text{O}}=\text{C}=\ddot{\text{O}}$

- In the linear domain, there is only one molecular geometry: linear.
- NOTE: If there are only two atoms in the molecule, the molecule will be linear no matter what the electron domain is.

Trigonal Planar Electron Domain

• Electron-Domain and Molecular Geometries for Two, Three, and Four

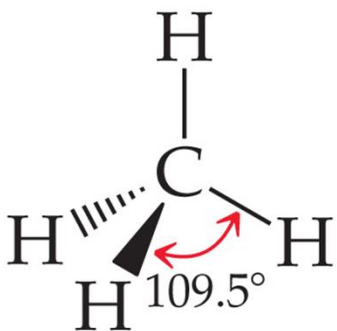
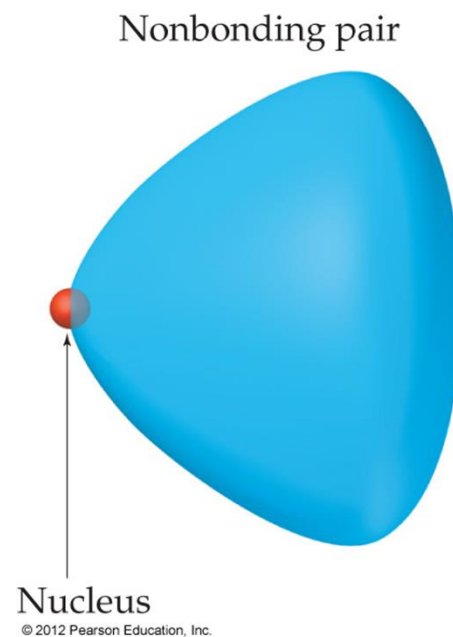
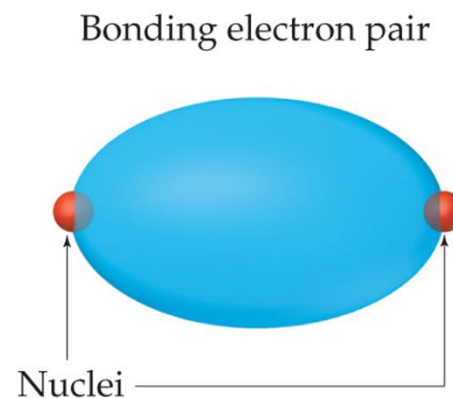
Electron Domains around a Central Atom

Number of Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
3	 Trigonal planar	3	0	 Trigonal planar	
		2	1	 Bent	

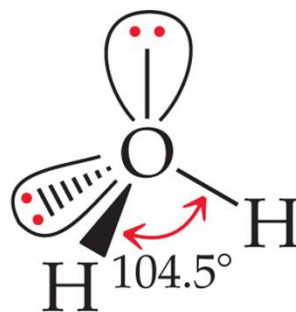
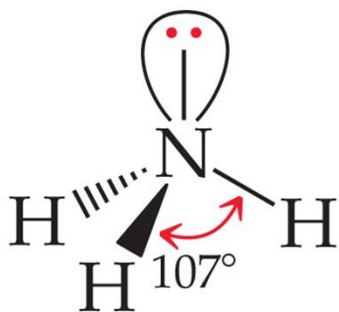
- There are two molecular geometries:
 - Trigonal planar, if all the electron domains are bonding,
 - Bent, if one of the domains is a nonbonding pair.

Nonbonding Pairs and Bond Angle

- Nonbonding pairs are physically larger than bonding pairs.
- Therefore, their repulsions are greater; this tends to decrease bond angles in a molecule.

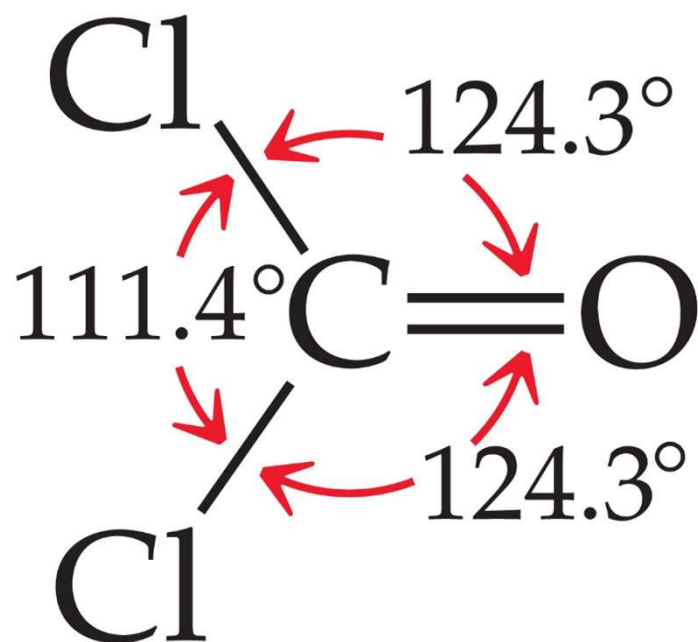


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Multiple Bonds and Bond Angles

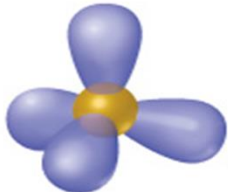
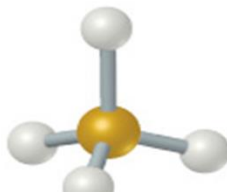
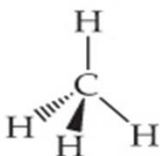
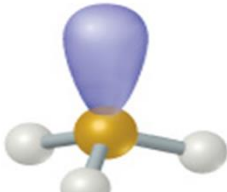
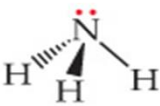
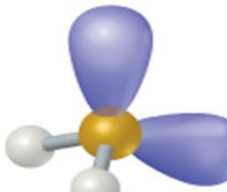


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- Double and triple bonds place greater electron density on one side of the central atom than do single bonds.
- Therefore, they also affect bond angles.

Tetrahedral Electron Domain

Electron-Domain and Molecular Geometries for Two, Three, and Four Electron Domains around a Central Atom

Number of Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
4	 Tetrahedral	4	0	 Tetrahedral	
		3	1	 Trigonal pyramidal	
		2	2	 Bent	

Tetrahedral Electron Domain

There are three molecular geometries:

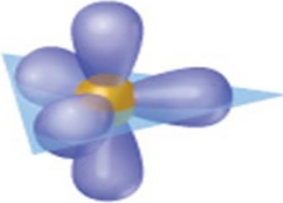
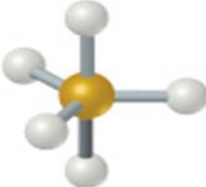
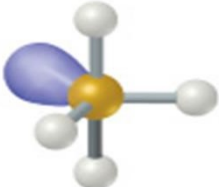
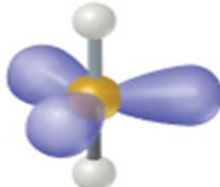
Tetrahedral, if all are bonding pairs,

Trigonal pyramidal, if one is a nonbonding pair,

Bent, if there are two nonbonding pairs.

Trigonal Bipyramidal Electron Domain

Electron-Domain and Molecular Geometries for Five and Six Electron Domains around a Central Atom

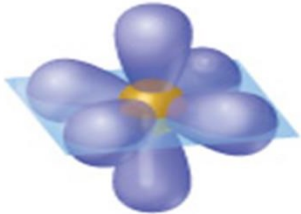
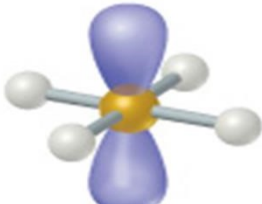
Number of Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
5	 Trigonal bipyramidal	5	0	 Trigonal bipyramidal	PCl ₅
		4	1	 Seesaw	SF ₄
		3	2	 T-shaped	ClF ₃
		2	3	 Linear	XeF ₂

Trigonal Bipyramidal Electron Domain

- There are four distinct molecular geometries in this domain:
 - Trigonal bipyramidal
 - Seesaw
 - T-shaped
 - Linear

Octahedral Electron Domain

Electron-Domain and Molecular Geometries for Five and Six Electron Domains around a Central Atom

Number of Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
6	 Octahedral	6	0	 Octahedral	SF_6
		5	1	 Square pyramidal	BrF_5
		4	2	 Square planar	XeF_4

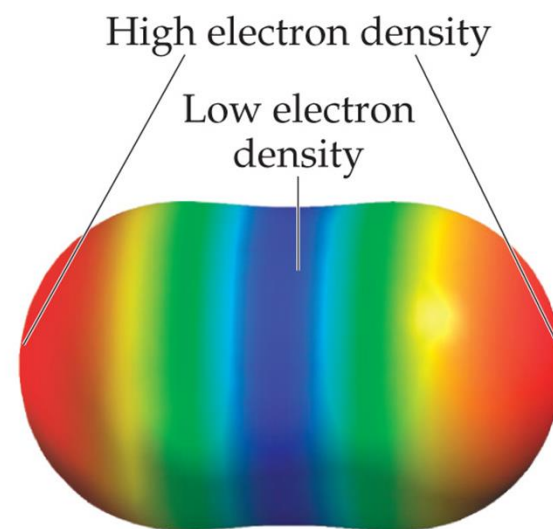
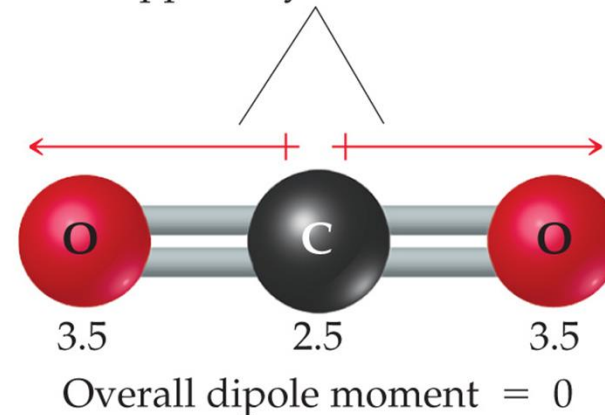
Octahedral Electron Domain

- All positions are equivalent in the octahedral domain.
- There are three molecular geometries:
 - Octahedral
 - Square pyramidal
 - Square planar

Polarity

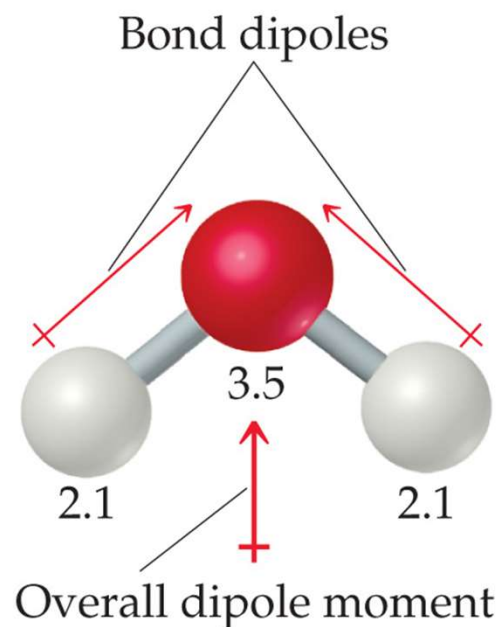
- At the beginning of this chapter, we discussed bond dipoles(polarity).
- But just because a molecule possesses polar bonds does not mean the molecule *as a whole* will be polar.

Equal and oppositely directed bond dipoles

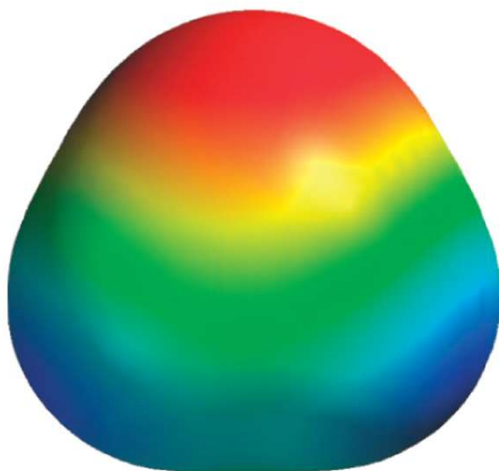


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Polarity

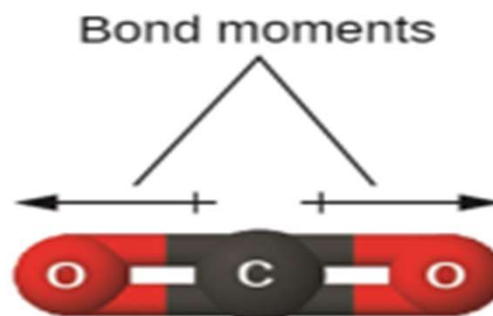


By adding the individual bond dipoles, one can determine the overall dipole moment for the molecule.



their bond moments cancel (vector sum equals zero), then the molecule is **nonpolar**

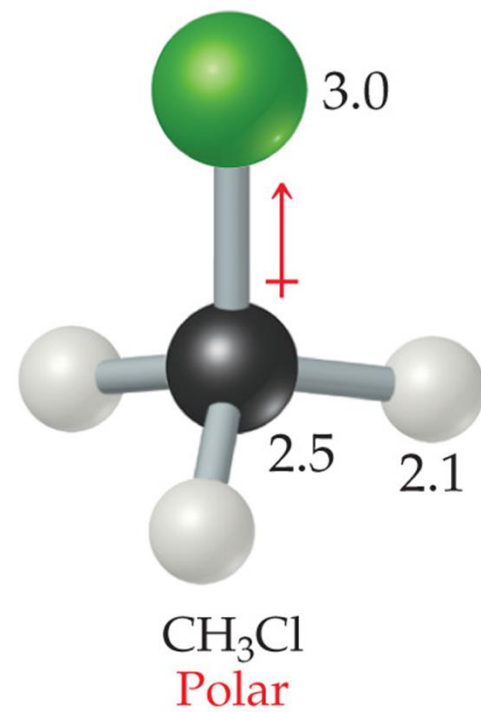
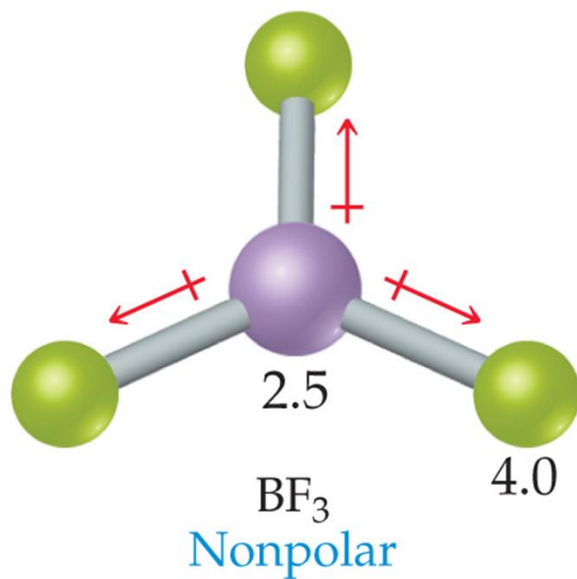
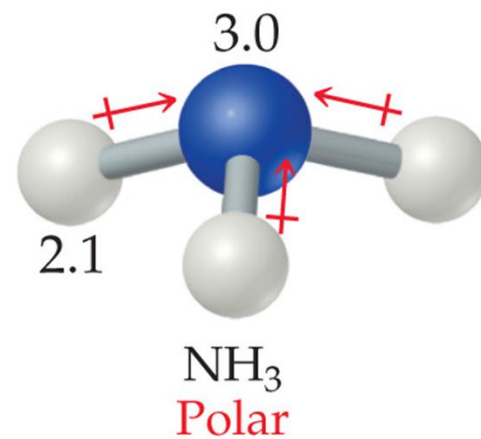
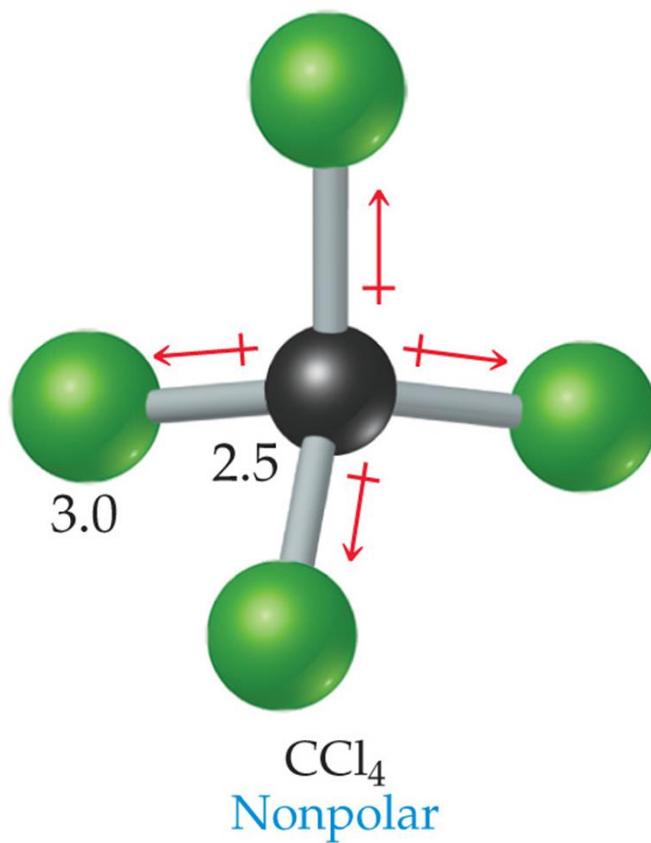
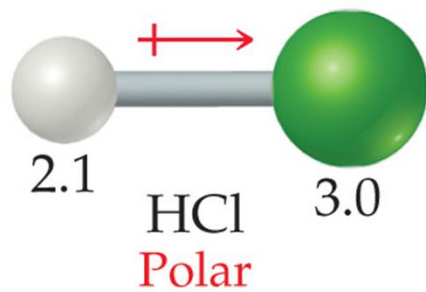
Example: The situation in CO_2



Overall dipole moment = 0

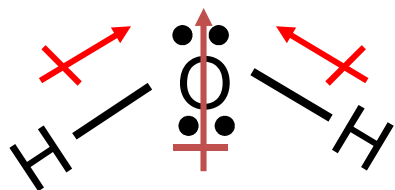
Each of the bonds is **polar**, but the molecule as a whole is **nonpolar**. *Why?*

Polarity

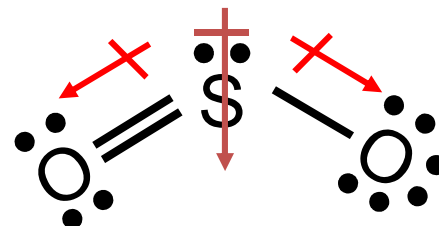


Which of the following molecules have a dipole moment?

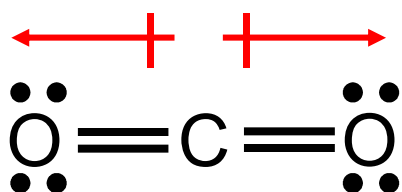
H_2O , CO_2 , SO_2 , and CF_4



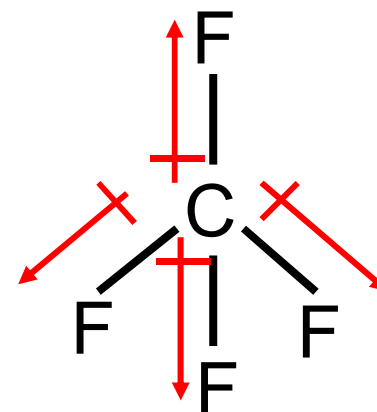
dipole moment
polar molecule



dipole moment
polar molecule



no dipole moment
nonpolar molecule



no dipole moment
nonpolar molecule