Unit 8: Ionic/Covalent Bonding and Molecular Geometry

Pre-AP Chemistry

Types of Chemical Bonding

- Ionic Bond:
  - Electrons are transferred forming ions with noble gas configurations.
  - Occurs between atoms with large differences in their tendency to lose or gain electrons.
  - Often occurs between reactive metals (Group 1A and 2A) and nonmetals (Group 7A and the top of 6A).

- Covalent Bond:
  - Electrons are shared.
  - Occurs when atoms have a small difference in their tendency to lose or gain electrons.
  - Commonly occurs between nonmetal atoms.

- Metallic Bond:
  - All metal atoms in a sample pool their valence electrons into an evenly distributed “sea” of electrons that “flows” between and around the metal-ion cores and attracts them
  - Electrons are delocalized moving freely throughout the piece of metal.

Lewis Dot Symbols

- Shorthand way of depicting valence electrons
  - The element symbol represents the nucleus and inner electrons, and the surrounding dots represent the valence electrons
- To draw Lewis symbols for main group elements:
  - The A-group number gives the number of valence electrons.
  - Place one dot at a time on the four sides of the element symbol.
  - Pair up the dots until all are used.

Element	Electron config.	Electron dot symbol
Li	$[He]2s^1$	Li·
Be	$[He]2s^2$	·Be·
B	$[He]2s^22p^1$	·B·
C	$[He]2s^22p^2$	·C·
N	$[He]2s^22p^3$	·N:
O	$[He]2s^22p^4$	:O:
F	$[He]2s^22p^5$	:F:
Ne	$[He]2s^22p^6$	:Ne:

Lewis Dot Symbols

- For a metal: the total number of dots is the maximum number of electrons it loses to form a cation.
- For a nonmetal: the number of unpaired dots is the number of electrons that become paired either through electron gain or through electron sharing

Drawing Lewis Symbols Examples

Draw the Lewis symbols for the following elements

a. Li

b. Ca

c. P

d. Br

e. I

f. C

Covalent Bonding

- A covalent bond is the result of the mutual attraction between the nuclei and an electron pair of two atoms.
- The electrons that are shared between the atoms are called the "shared" or "bonding pair".
- An electron pair that is part of an atom's valence shell but not involved in bonding is called a "lone pair" or "unshared pair".
- Bond order is the number of electron pairs being shared between any two bonded atoms.
  - A single bond consists of a single bonding pair of electrons ($2e^-$) and has a bond order of one.
    - Single bonds are the most common type of bond.
  - A double bond consists of two bonding pairs ($4e^-$) shared between two atoms and has a bond order of two.
  - A triple bond consists of three bonding pairs ($6e^-$) shared between the two atoms and has a bond order of three.

Lewis Structures

- A Lewis structure is a two dimensional structural formula consisting of electron-dot symbols that depict each atom and its neighbors, the bonding pairs that hold them together, and the lone pairs that fill each atom's outer shell.

Lewis Structures of Molecules

- To draw a Lewis structure for molecules, start with the general arrangement of atoms, which is often called the "skeleton".
  - Most molecules consist of a central atom with surrounding atoms bonded to it.
- To determine the skeleton:
  - Carbon is usually a central atom in the structure. In compounds with more than one carbon atom, the carbon atoms are joined in a chain to start the skeleton.
  - Hydrogen is never a central atom because it can form only one covalent bond.
  - Halogens form only a single covalent bond when oxygen is not present and will not generally be a central atom.
  - Oxygen forms only two covalent bonds and is rarely a central atom. However, it may link two carbon atoms in a carbon chain.
  - In simpler molecules, the atom that appears only once in the formula will often be the central atom.

Drawing Lewis Structures

- Once the molecular skeleton is determined, the available valence electrons must be arranged in octets around each atom.
  - Valence electrons of all atoms are added together.
  - If the substance is a polyatomic ion, take into account the electrons used to form the ion.
  - A pair of electrons is placed between each two atoms in the skeletal structure to represent the covalent bond. These electrons are called the **bonding pairs.**
  - The remaining electrons are used to complete the octets of all outer atoms in the skeleton. These electrons are nonbonding pairs (or lone pairs).
  - If any electrons are left over, they are added in pairs to the central atom. These electrons are also lone pairs.

Exceptions to the Octet

- The central atom should have an octet. However, there are a few exceptions to look for.
  - The central atom may have fewer than eight electrons if it is **boron or beryllium**.
  - For other central atoms, double bonds must be constructed to obtain an octet. This is done by taking a nonbonding pair of electrons from an outer atom and placing them as a bonding pair to make a double bond.
  - The central atom may have more than eight electrons if it falls in period 3-7 on the periodic table.

Drawing Lewis Structures Examples

Draw the Lewis structures for the following molecules:

a. Methane	b. Phosphorus trichloride
c. Phosphorus pentachloride	d. Water

Drawing Lewis Structures Examples

Draw the Lewis structures for the following molecules:

e. Methyl chloride	f. Carbon disulfide
g. Silicon tetrafluoride	h. Nitrate

Drawing Lewis Structures Examples

Draw the Lewis structures for the following molecules:

i. Carbonate
j. Boron trifluoride

Coordinate Covalent Bonds

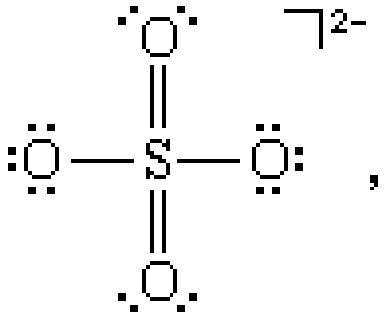
- A coordinate covalent bond is formed when one atom donates both electrons of a bond.
- A common example is ammonia (NH_3) bonding with H^+ to form the ammonium ion (NH_4^+).

Formal Charge

- Formal charge is the difference between the number of electrons an atom has in a Lewis structure and its number of valence electrons.
  - A separation of charge
- To calculate the formal charge, each electron in a Lewis structure is assigned to a specific atom. The number of electrons assigned to an atom is then compared to the number of that atom's valence electrons.
  1. For each atom, count all electrons not used for bonding by the atom.
  2. Count half of the atom's bonding electrons.
  3. Add steps 1 and 2 to obtain the electrons assigned to that atom.
  4. Subtract the assigned electrons from the valence electrons to obtain the formal charge.
     - Formal charge = (Valence e^-) - [Number of nonbonding e^- + ½(Number of bonding e^-]
  - The formal charges on the atoms in a molecule must add up to zero for a neutral compound and add to the charge of the ion in a polyatomic ion.

Calculating Formal Charge Examples

- The Lewis structure with the lowest formal charges on all atoms is the preferred structure.
- Calculate the formal charge of each atom for the sulfate ion, SO_4^{2-} shown below:



Bond Energy and Length

- The strength of a covalent bond depends on the magnitude of the mutual attraction between the bonded nuclei and the shared electrons.
- Bond energy (BE), also called bond strength, is the energy required to overcome this attraction.
  - Bond energy is always positive.
- Bond length is the distance between the nuclei of the two bonded atoms.
- A close relationship exists among bond order, bond length, and bond energy.
  - Two nuclei are more strongly attracted to two shared electron pairs than to one: the atoms are drawn closer together and are more difficult to pull apart
- For a given pair of atoms, a higher bond order results in a shorter bond length and a higher bond energy.
  - A shorter bond is a stronger bond.

Bond Energy

Single Bonds							
C—H	413	N—H	391	O—H	463	F—F	159
C—C	348	N—N	163	O—O	146.		
C—N	293	N—O	201	O—F	190	Cl—F	253
C—O	358	N—F	272	O—Cl	203	Cl—Cl	242
C—F	485	N—Cl	200	O—I	234		
C—Cl	328	N—Br	243			Br—F	237
C—Br	276			S—H	339	Br—Cl	218
C—I	240	H—H	436	S—F	327	Br—Br	193
C—S	259	H—F	567	S—Cl	253		
		H—Cl	431	S—Br	218	I—Cl	208
Si—H	323	H—Br	366	S—S	266	I—Br	175
Si—Si	226	H—I	299			I—I	151
Si—C	301						
Si—O	368						

Multiple Bonds					
C=C	614	N=N	418	O=O	498
C≡C	839	N≡N	945		
C=N	615			S=O	323
C≡N	891			S=S	418
C=O	804*				
C≡O	1076				

Bond Length

Average Bond Lengths for Some Single, Double, and Triple Bonds

Bond	Bond Length (Å)	Bond	Bond Length (Å)
C—C	1.54	N—N	1.47
C=C	1.34	N=N	1.24
C≡C	1.20	N≡N	1.10
C—N	1.43	N—O	1.36
C=N	1.38	N=O	1.22
C≡N	1.16		
		O—O	1.48
C—O	1.43	O=O	1.21
C=O	1.23		
C≡O	1.13		

Comparing Bond Length and Strength

Using only the periodic table, rank the bonds in each set in order of decreasing bond length and decreasing bond strength.

a. S-F, S-Br, S-Cl

b. C=O, C-O, C≡O

c. Si-F, Si-C, Si-O

Resonance Structures

- Often, more than one Lewis structure, each with the same relative placement of atoms, for a molecule or ion with double bonds next to single bonds.
  - Consider ozone (O_3)

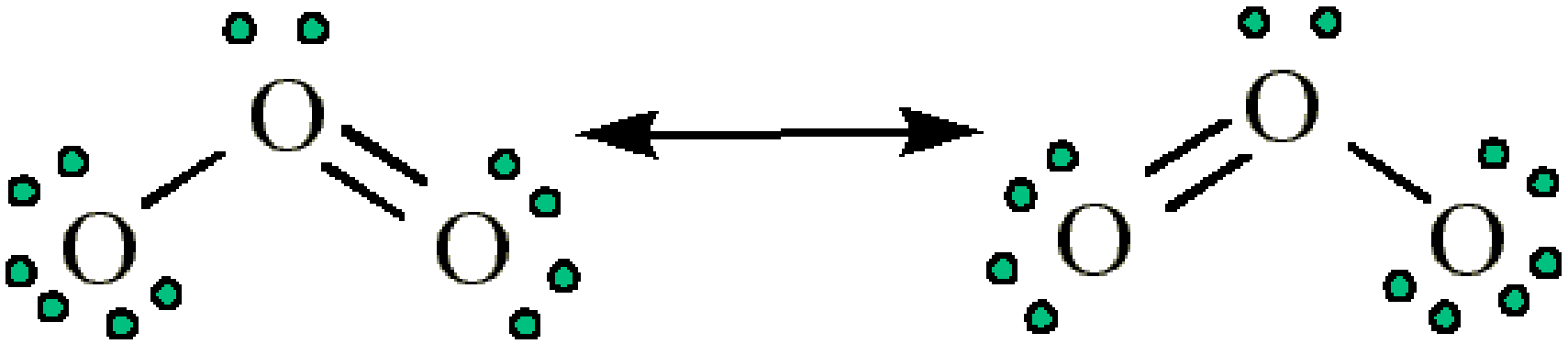


Figure 1: Resonance Structures of Ozone

Resonance Structures

- A molecule shown correctly with two or more Lewis structures, it is said to exhibit resonance.
- Resonance structures have the same relative placement of atoms but different locations of bonding and lone electron pairs.
  - You can convert one resonance form to another by moving lone pairs to bonding positions.
- Resonance structures are not real bonding depictions. (O_3 does not change back and forth from structure to structure. The actual molecule is a resonance hybrid – the average of the resonance forms.

Why Resonance?

- The need for more than one Lewis structure to depict a molecule is the result of electron pair delocalization.
  - In a typical bond, each electron pair is attracted by the nuclei of the two bonded atoms and the density is greatest in the region between the nuclei (each electron pair is localized).
  - In a resonance hybrid, however, two of the electron pairs (one bonding and one non-bonding) are delocalized → their density is "spread" over the entire molecule.
    - Results in two identical bonds, each consisting of a single bond (the localized pair) and a partial bond (the contribution from one of the delocalized electron pairs).
  - Electron delocalization diffuses electron density over a greater volume which reduces electron-electron repulsions, stabilizing the molecule.

Metallic Bonds

- Metallic bonds follow the “electron sea model” in which the valence electrons are shared among all the atoms in the substance.
  - Metals do not often form purely metallic compounds. Rather, they typically form alloys which are solid mixtures with variable composition.
    - Coins, jewelry, steel, etc.
- The “electron sea” is responsible for the properties of metals.
  - Conductivity is a result of the mobility of the electrons.
  - Malleability (the ability to be flattened into sheets) and ductility (the ability to be pulled into wires) are a result of the regularity but not rigidity of the metal ions and the mobility of the valence electrons.

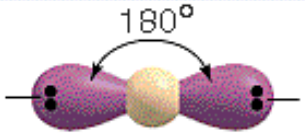
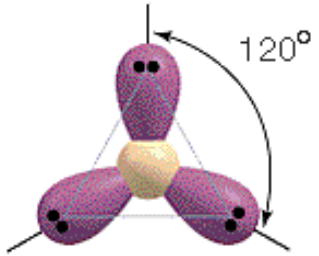
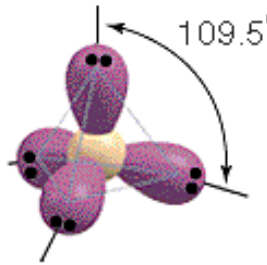
VSEPR Theory

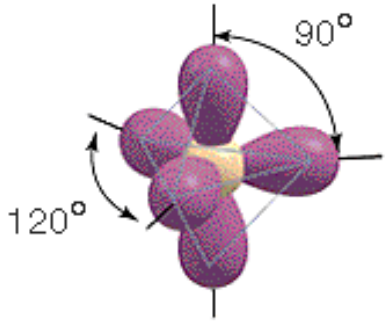
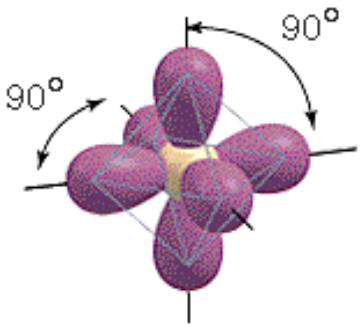
- **Valence Shell Electron Pair Repulsion** theory states that each group of valence electrons around a central atom is located as far away as possible from the others in order to minimize repulsions.
  - A “group” is any number of electrons that occupy a localized region around an atom.
    - May consist of a single bond, double bond, triple bond, lone pair, or even a lone electron.
- Valence electrons repel each other to maximize the angles between them.
- The arrangement of nuclei joined by these groups gives rise to the molecular shape.

Molecular Shape and Bond Angle

- Molecular shape is affected by both bonding and non-bonding groups.
- Bond angle is the angle formed by the nuclei of two surrounding atoms with the nucleus of the central atom at the vertex.
- There are five basic molecular shapes. Each one has identical bonding electron groups around a central atom, creating ideal bond angles.
- To classify molecular shapes, assign a specific AX_mE_n designation.
  - A is the central atom
  - X is a surrounding atom
  - E is a non-bonding valence electron group (usually a lone pair)
  - m and n are integers

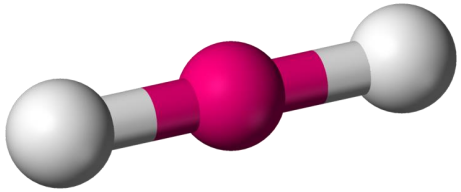
Basic Molecular Shapes

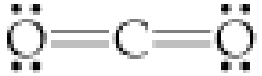
Arrangement of Electron Pairs	Electron-Pair Geometry	Predicted Bond Angles
	Linear	180°
	Trigonal planar	120°
	Tetrahedral	109.5°

Arrangement of Electron Pairs	Electron-Pair Geometry	Predicted Bond Angles
	Trigonal bipyramidal	120° 90°
	Octahedral	90° 180°

Molecular Shapes with 2 Electron Groups (Linear Arrangement)

- When two electron groups attached to a central atom are oriented as far apart as possible, they point in opposite directions.
- The linear molecular shape has a bond angle of 180°.
- Designation: AX_2
- Examples: $BeCl_2$, CO_2



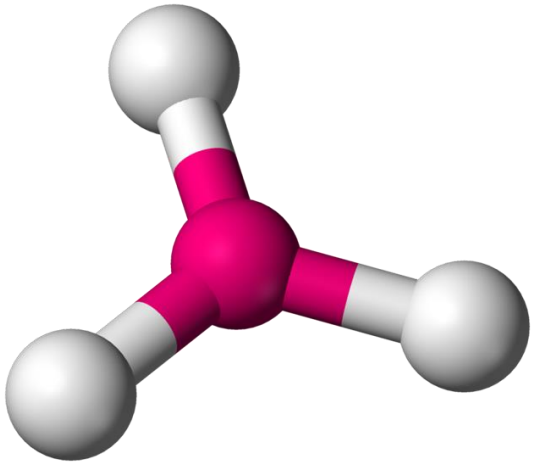
Total Electron Domains	Electron-Domain Geometry	Bonding Domains	Non-bonding Domains	Molecular Geometry	Example
2 pairs	Linear	2	0	Linear	

Molecular Shapes with 3 Electron Groups (Trigonal Planar Arrangement)

- Three electron groups around a central atom repel each other to the corners of an equilateral triangle, giving a trigonal planar arrangement.
- Trigonal planar molecules have an ideal bond angle of 120°.
- This arrangement has two possible molecular shapes, one with three surrounding atoms (AX_3) and the other with two atoms and one lone pair (AX_2E_1)

Trigonal Planar

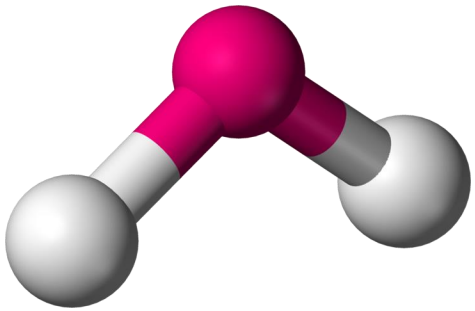
- AX_3 has a molecular shape of trigonal planar with a bond angle of 120°.
- Examples: BF_3, NO_3^-



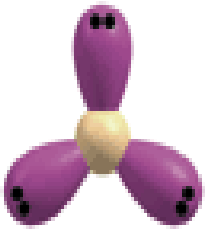
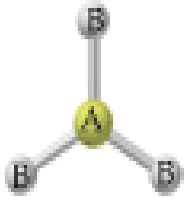
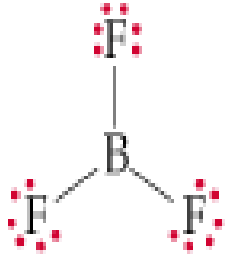
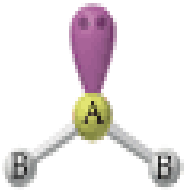
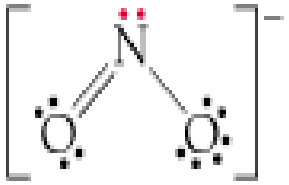
- Double bonds cause a deviation from ideal bond angles because the greater electron density of the double bond repels the single bonds more strongly than they repel each other.

Bent

- AX_2E has a “bent” or “V-shaped” molecular shape.
- The lone pair has a major effect on bond angle. Because a lone pair is held by only one nucleus, it is less confined and exerts stronger repulsions than a bonding pair.
- A lone pair repels bonding pairs more strongly than bonding pairs repel each other, decreasing the bond angle between bonding pairs.
- Examples: NO_2, $SnCl_2$



Trigonal Planar

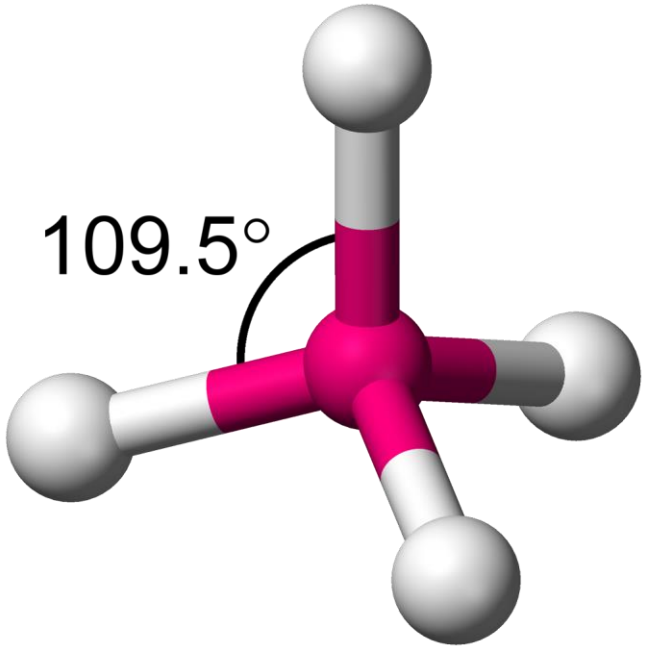
Total Electron Domains	Electron-Domain Geometry	Bonding Domains	Non-bonding Domains	Molecular Geometry	Example
3 pairs	 Trigonal planar	3	0	 Trigonal planar	
		2	1	 Bent	

Molecular Shapes with 4 Electron Groups (Tetrahedral Arrangement)

- Four electron groups around a central atom repel each other to the vertices of a tetrahedron.
- Tetrahedral molecules have an ideal bond angle of 109.5°.
- This arrangement has three possible arrangements:
  - All four electron groups are bonding groups – AX_4
  - One of the 4 groups is a lone pair – AX_3E
  - Two of the 4 groups are lone pairs – AX_2E_2

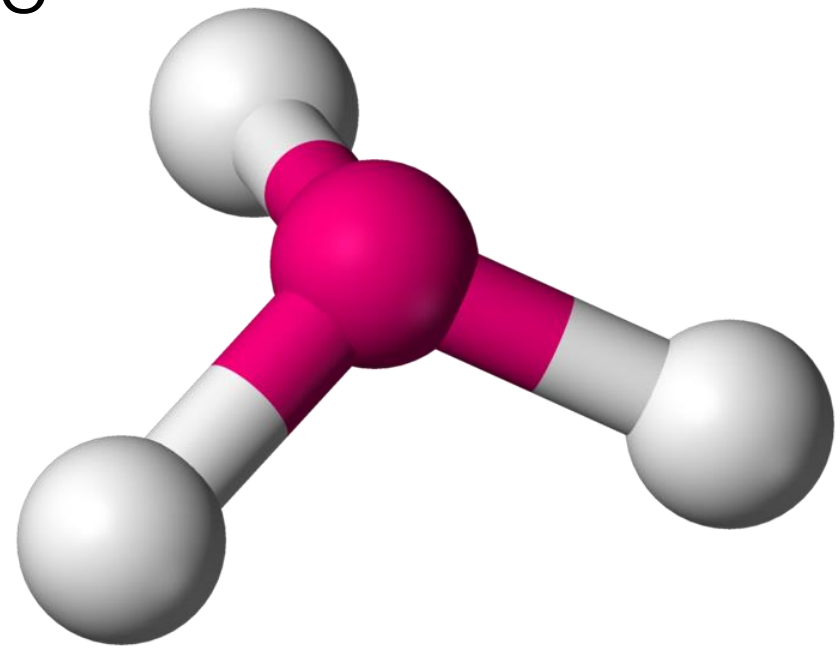
Tetrahedral

- AX4 has a molecular shape of tetrahedral with bond angles of 109.5°.
- Examples: CH_4 (methane), $SiCl_4$, SO_4^{2-}



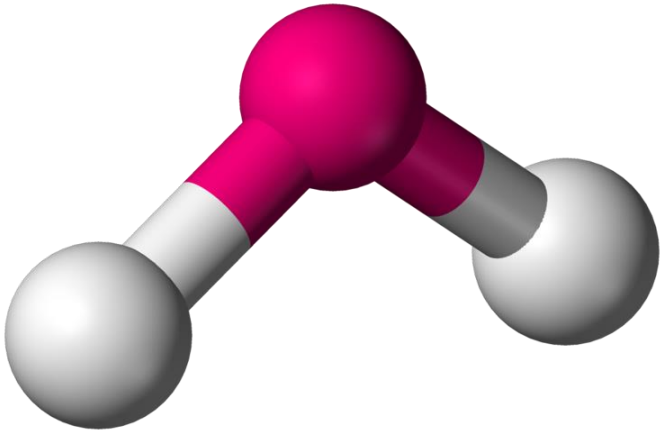
Trigonal Pyramidal

- AX_3E has a molecular shape of trigonal pyramidal (a tetrahedron with one vertex “missing”)
- The stronger repulsions of the lone pair result in the measured bond angles being slightly less than the ideal 109.5°.
- Examples: NH_3, PF_3, H_3O^+

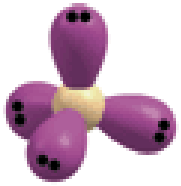
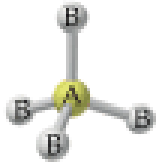
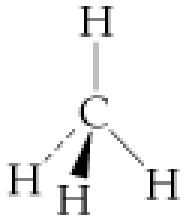
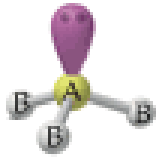
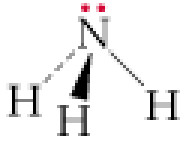
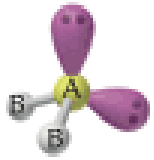


Bent (Tetrahedral)

- AX_2E_2 has a molecular shape of bent or V-shaped.
- The repulsions from the two lone pairs have a greater effect on the bond angle than the repulsions from a single lone pair, reducing the bond angle further.
- Examples: H_2O, SCl_2



Tetrahedral

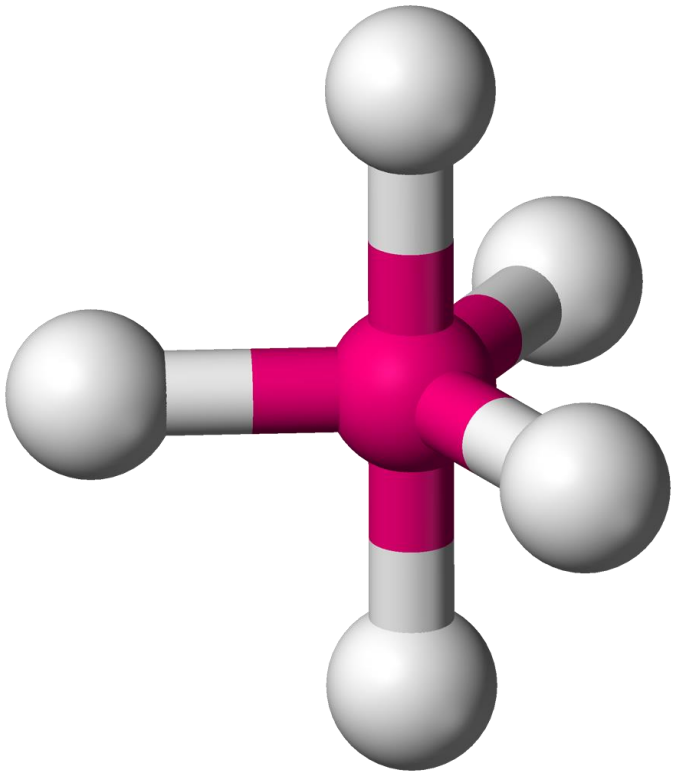
Total Electron Domains	Electron-Domain Geometry	Bonding Domains	Non-bonding Domains	Molecular Geometry	Example
4 pairs	 Tetrahedral	4	0	 Tetrahedral	
		3	1	 Trigonal pyramidal	
		2	2	 Bent	

Molecular Shapes with 5 Electron Groups (Trigonal Bipyramidal Arrangement)

- When five electron groups maximize their separation, they form a trigonal bipyramidal arrangement.
- This arrangement has two types of positions for surrounding electron groups and two ideal bond angles.
  - Three equitorial groups lie on a trigonal plane that includes the central atom with a 120° bond angle.
  - Two axial groups lie above and below this plane with a 90° bond angle.
  - The greater the bond angle, the weaker the repulsions so the 120° repulsions are weaker than the 90° repulsions.
    - The tendency of the electron groups to occupy equitorial positions and, thus, minimize the stronger 90° repulsions governs the four shapes of the trigonal bipyramidal arrangement
- There are four possible arrangements for 5 electron groups
  - AX_5
  - AX_4E
  - AX_3E_2
  - AX_2E_3

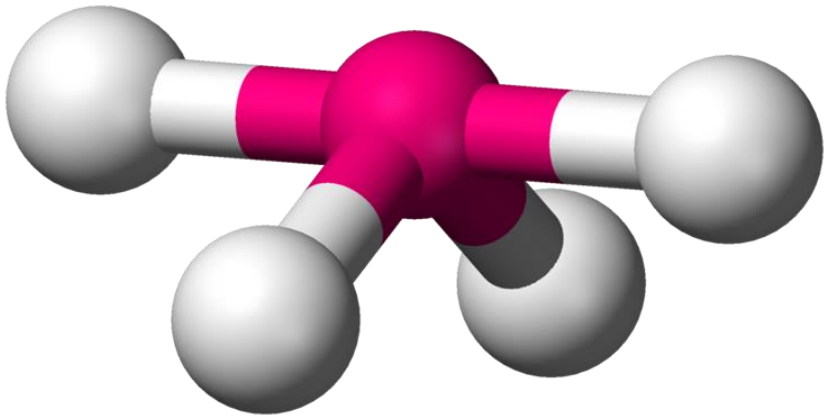
Trigonal Bipyramidal

- AX_5 has a trigonal bipyramidal shape.
- Bond angles are 120° and 90°.
- Examples: PF_5, AsF_5, SOF_4



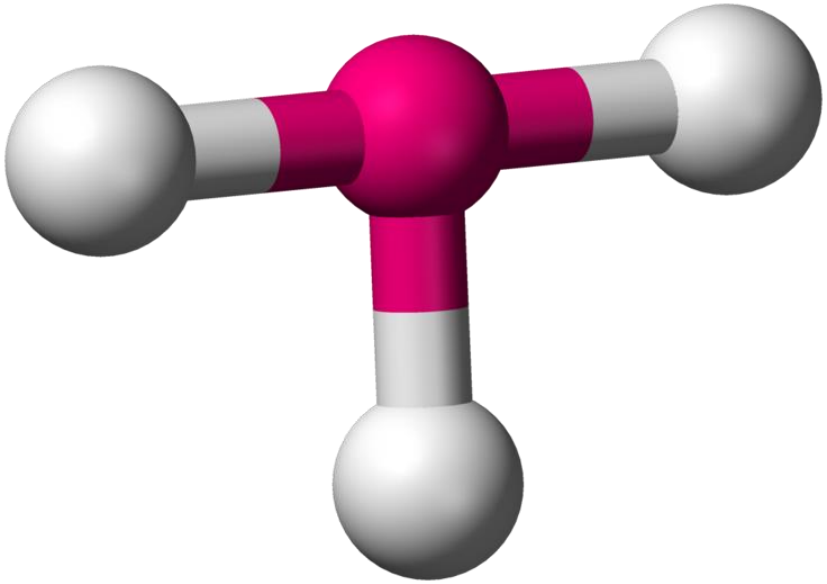
Seesaw

- AX_4E has a seesaw shape.
- Since lone pairs exert stronger repulsions than bonding pairs, lone pairs occupy equitorial positions.
- Lone pairs reduce bond angles.
- Examples: SF_4, XeO_2F_2, IF_4^+



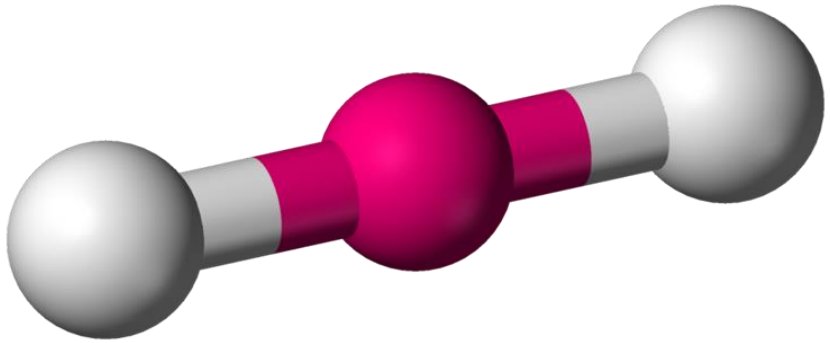
T-Shape

- AX_3E_2 has a molecular shape of T-Shape.
- Lone pairs occupy equitorial positions.
- Examples: ClF_3, BrF_3

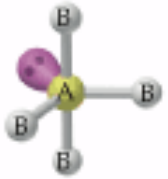
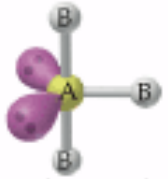
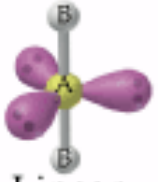


Linear (Trigonal Bipyramidal)

- AX_2E_3 has a molecular shape of linear with a bond angle of 180°.
- Lone pairs occupy all three equitorial positions, leaving both bonding groups in the axial positions.
- Examples: XeF_2, I_3^-, IF_2^-



Trigonal Bipyramidal

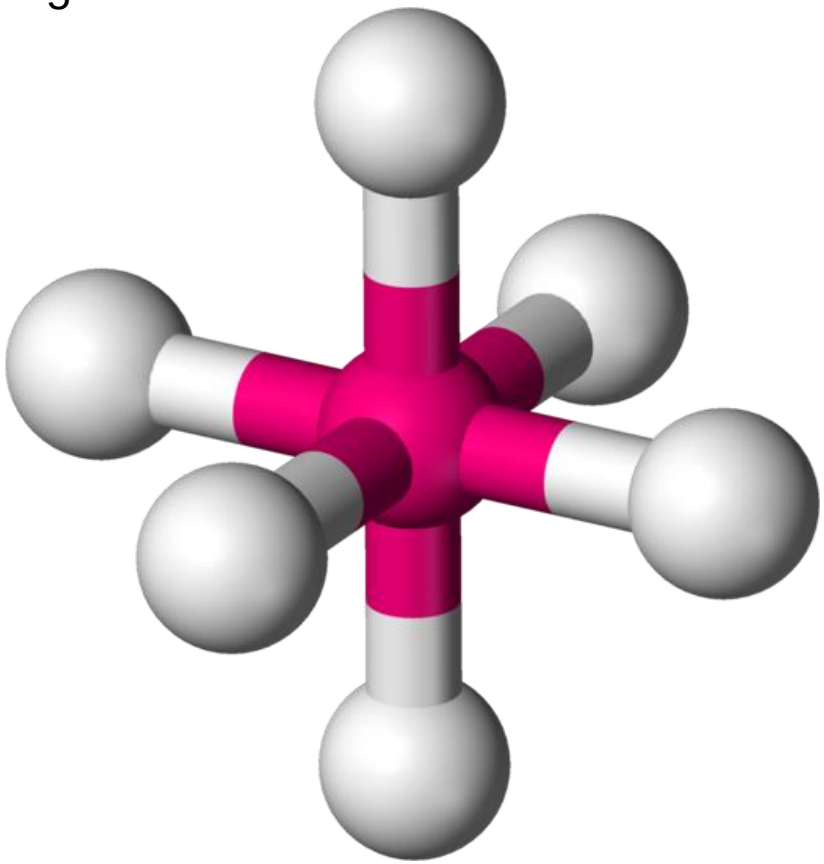
Number of Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
5 domains	Trigonal bipyramidal	5	0	Trigonal bipyramidal	PCl_5
		4	1	 Seesaw	SF_4
		3	2	 T-shaped	ClF_3
		2	3	 Linear	XeF_2

Molecular Shapes with 6 Electron Groups (Octahedral Arrangement)

- When six electron groups maximize their separation, they form an octahedral arrangement.
  - An octahedron is a polyhedron with eight faces made of identical equilateral triangles and six identical vertices.
- All groups have a 90° ideal bond angle.
- Three important molecular shapes occur with this arrangement:
  - AX_6
  - AX_5E
  - AX_4E_2

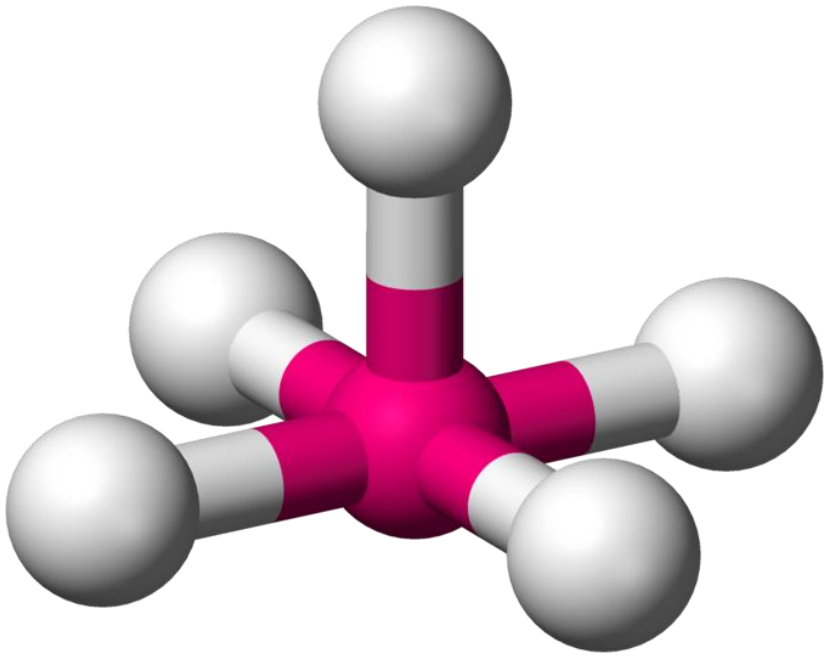
Octahedral

- With six bonding groups, AX_6 has a molecular shape of octahedral with bond angles of 90°.
- Examples: SF_6, IOF_5



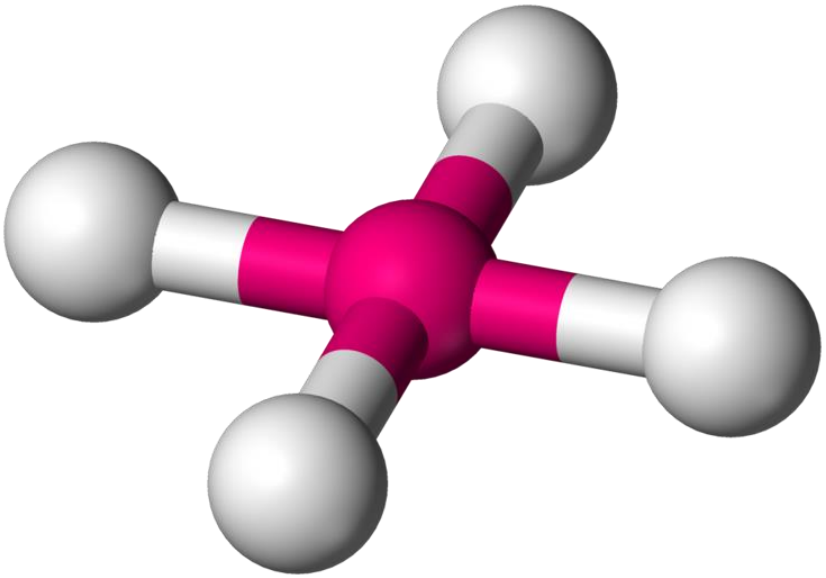
Square Pyramidal

- AX_5E has a molecular shape of square pyramidal.
  - Because there is only one ideal bond angle, it makes no difference which position one lone pair occupies.
- Examples: BrF_5, TeF_5^-, $XeOF_4$

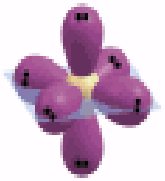
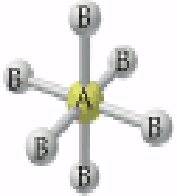
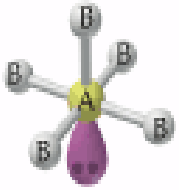
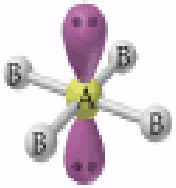


Square Planar

- AX_4E_2 has a molecular shape of square planar.
- The two lone pairs lie at opposite vertices to avoid the stronger lone pair-lone pair repulsions at 90°
- Examples: XeF_4, ICl_4^-



Octahedral

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

Using the VSEPR Theory to Determine Molecular Shape

1. Write the Lewis structure from the molecular formula to see the relative placement of atoms and number of electron groups.
2. Assign an electron-group arrangement by counting all electron groups around the central atom, bonding plus non-bonding.
3. Predict the ideal bond angle from the electron group arrangement and the direction of any deviation caused by lone pairs or double bonds.
4. Draw and name the molecular shape by counting bonding groups and non-bonding groups separately.

Predicting Molecular Shapes Examples

Draw the Lewis structure, give the molecular shape, and predict the bond angles (relative to ideal) of the following:

Molecule	Lewis Structure	Molecular Shape
a. PF_3		
b. $COCl_2$		
c. CS_2		

Predicting Molecular Shapes Examples

Draw the Lewis structure, give the molecular shape, and predict the bond angles (relative to ideal) of the following:

Molecule	Lewis Structure	Molecular Shape
d. CBr_4		
e. SF_2		
f. SbF_5		

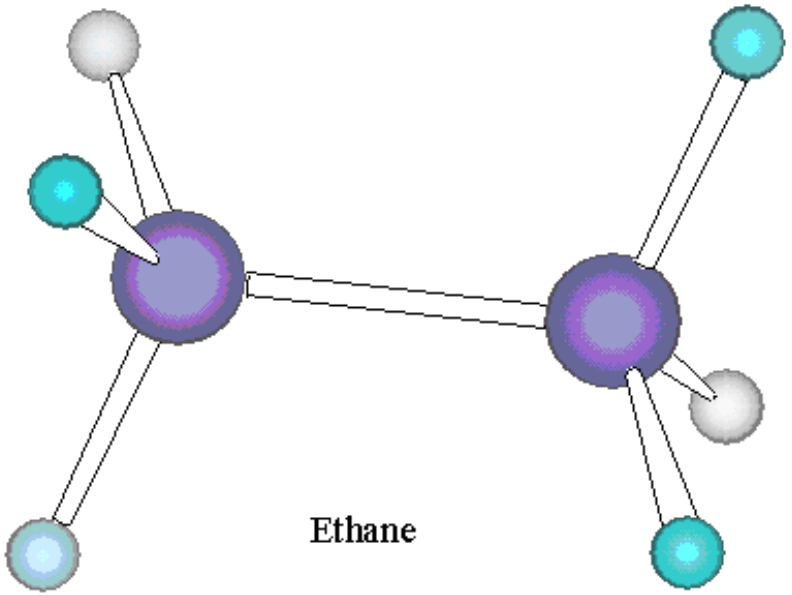
Predicting Molecular Shapes Examples

Draw the Lewis structure, give the molecular shape, and predict the bond angles (relative to ideal) of the following:

Molecule	Lewis Structure	Molecular Shape
g. BrF_5		
h. NO_3^-		

Molecular Shapes with More Than One Central Atom

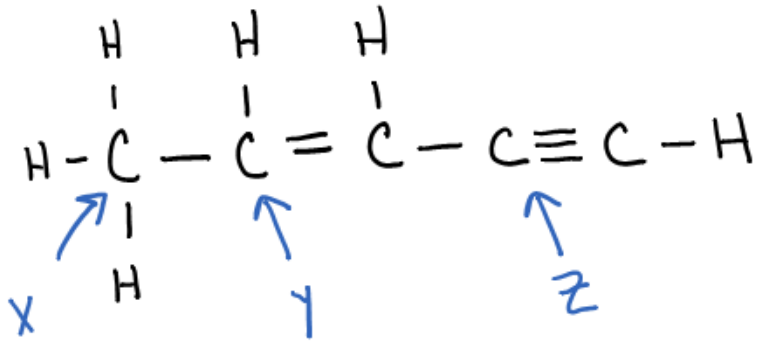
- Many molecules have more than one central atom. The shapes of these molecules are combinations of the molecular shapes with a single central atom.
- Example: Ethane (C_2H_6)



Ethane

Molecular Shapes with More than One Central Atom Examples

For the Lewis structure shown below, identify the molecular shape and ideal bond angle for each labeled carbon.

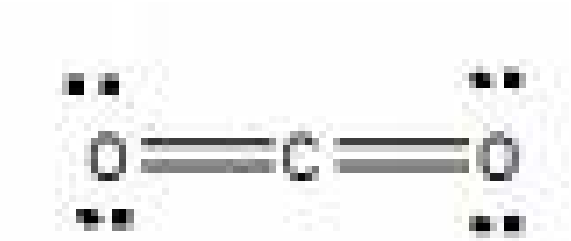


Bond Polarity

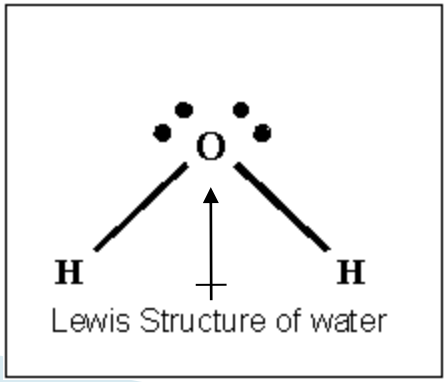
- Covalent compounds can have polarity as a result of atoms sharing electrons unequally.
- Partial charges (δ+, δ-) develop from the imbalance.
- The dipole moment is the product of partial charges and the distance between them.
- Molecules with a net imbalance of charge have a molecular polarity.
  - In molecules with more than two atoms, both shape and bond polarity determine molecular polarity.

Molecular Polarity

- The presence of polar bonds does not always lead to a polar molecule.
  - Carbon dioxide has two polar bonds. However, CO_2 is linear with each bond 180° from the other. The two identical bond polarities are counterbalanced and give the molecule no net dipole moment.



  - Water has two polar V-shaped with the lone pairs reinforcing the partial negativity of the oxygen end.



Lewis Structure of water

Predicting Molecular Polarity

- There are four general rules for determining whether a molecule is polar.
  1. A molecule that is symmetrical is nonpolar. It does not matter how polar the individual bonds are.
  2. A nonsymmetrical molecule is polar if the bonds are polar.
  3. A molecule with more than one type of atom attached to the central atom is often nonsymmetrical and therefore polar.
  4. A central atom with nonbonding electron pairs is often nonsymmetrical and polar.

Predicting Polarity Examples

- Predict whether each of the following molecules will exhibit molecular polarity:
  a. Ammonia

  b. Boron trifluoride

  c. Methyl chloride (CH_3Cl)

  d. Carbonyl sulfide (SCO)

  e. H_2S

Predicting Polarity Examples

- Predict whether each of the following molecules will exhibit molecular polarity:

f. PH_3

g. SiF_4

h. CS_2

i. NO_3^-