Molecular Geometry

Chapter 9

Limitations of Lewis Dot

Lewis Dot structures tell us how the atoms of a compound bond to one another, but they do not tell us the shape of the molecule.

In order to demonstrate the bonding of atoms in molecules, we shall use the ball and stick models.

VSEPR Theory

Atoms and electrons within a molecule will repel one another. Therefore, scientists developed the VSEPR Theory:

In a small molecule, the pairs of valence electrons are arranged as far apart from each other as possible.

This theory does not work for all elements (esp. the transition metals), but is a good basis for understanding

Electron Domains & Shapes

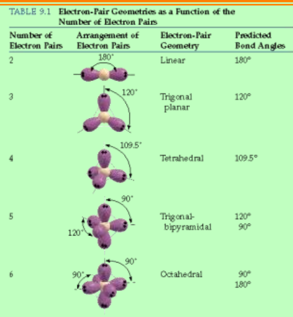


TABLE 9.1 Electron-Pair Geometries as a Function of the Number of Electron Pairs

Number of Electron Pairs	Arrangement of Electron Pairs	Electron-Pair Geometry	Predicted Bond Angles
2	180°	Linear	180°
3	120°	Trigonal planar	120°
4	109.5°	Tetrahedral	109.5°
5	90° 120°	Trigonal-bipyramidal	120° 90°
6	90° 90°	Octahedral	90° 180°

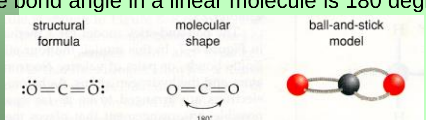
Linear

All molecules that contain 2 atoms are linear. (Ex. HCl)

Some 3 atom molecules are also linear. (Ex. CO_2)

Central atoms with one or two electron domains will be linear.

The bond angle in a linear molecule is 180 degrees.

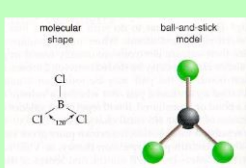


Trigonal Planar

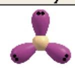
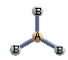
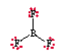
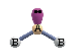
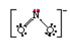
Trigonal means triangular and planar means flat.

A trigonal planar molecule has a central atom bonded with three electron domains. (Ex. BCl_3)

The bond angle is 120 degrees.

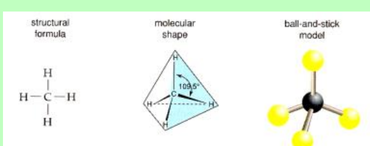


Variations on Trigonal Planar

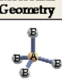
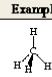
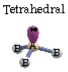
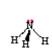
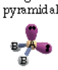
Total Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
3 domains	 Trigonal planar	3	0	 Trigonal planar	
		2	1	 Bent	

Tetrahedral

- Tetra means 4 and hedral means surface. A tetrahedral has four electron domains.
- The tetrahedral is 3 dimensional not 2 dimensional. Therefore, the bond angle is not 90 degrees.
- Bond angle is 109.5 degrees.

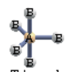


Variations on Tetrahedral

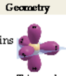
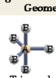
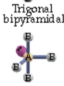
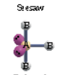
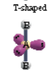
Total Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
4 domains	 Tetrahedral	4	0	 Tetrahedral	
		3	1	 Trigonal pyramidal	
		2	2	 Bent	

Trigonal Bipyramidal

- Trigonal bipyramidal have five electron domains with two geometrically distinct positions: axial and equatorial
- Axial angles are 90º from the equatorial positions, and the equatorial bonds are 120º from one another.
- The equatorial domains become nonbonding domains before the axial.

Total Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
5 domains	 Trigonal bipyramidal	5	0	 Trigonal bipyramidal	PCl_5

Variations on Trigonal Bipyramidal

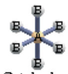
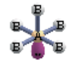
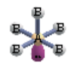
Total Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
5 domains	 Trigonal bipyramidal	5	0	 Trigonal bipyramidal	PCl_5
		4	1	 Seesaw	SF_4
		3	2	 T-shaped	ClF_3
		2	3	 Linear	XeF_2

Octahedral

- When the central atom of a molecule has 6 electron domains, the shape is octahedral, with a bond angle of 90º.

Number of Electron Pairs	Electron-Pair Geometry	Bonding Pairs	Nonbonding Pairs	Molecular Geometry	Example
6 pairs	 Octahedral	6	0	 Octahedral	SF_6

Variations on Octahedral

Total 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

Molecule Polarity & Dipoles

A molecule, just like bonds, can be polar or nonpolar. It depends on the bonds and the shape of the molecule.

A polar molecule (dipole) has one end of the molecule with a positive charge and one end with a negative charge.

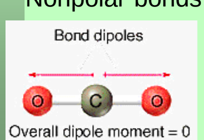
A nonpolar molecule has no charged ends or the same charged ends.

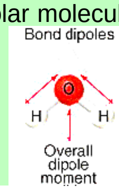
Polarity & Dipoles

Chemists use arrows to represent the polarity of a bond and a molecule.

Polar bonds = polar or nonpolar molecule

Nonpolar bonds = nonpolar molecule





Hybrid Orbitals

Our standard idea of electron orbitals does not explain the VSEPR theory.

To explain this, scientists theorize that when an atom forms bonds, the orbitals promote electrons to higher orbitals and then hybridize the orbitals into hybrid orbitals.

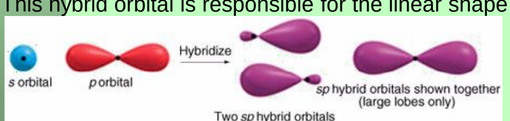
Hybrid orbitals are mixtures of the s, p and d orbitals of atoms.

sp hybrid orbital

When an alkali earth atom bonds, it promotes one of its 2 s-orbital electrons to the p-orbital.

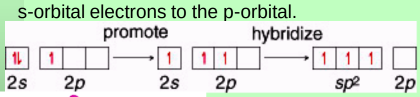
Once promoted, the orbitals hybridize into a new shape, or electron domains, which move as far apart as they can. The new orbital is called the sp hybrid orbital (1 s and 1 p)

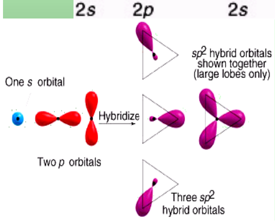
This hybrid orbital is responsible for the linear shape



sp^2 hybrid orbital

When a group 13 atom bonds, it promotes one of it 2 s-orbital electrons to the p-orbital.



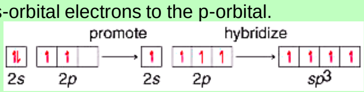


Once promoted, the orbitals hybridize into a new shape, or electron domains, which move as far apart as they can. The new orbital is called the sp^2 hybrid orbital (1 s and 2 p)

This hybrid orbital is responsible for the trigonal planar shape

sp^3 hybrid orbital

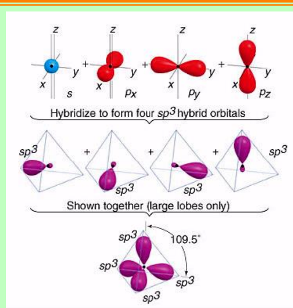
When a group 14 atom bonds, it promotes one of it 2 s-orbital electrons to the p-orbital.



Once promoted, the orbitals hybridize into a new shape, or electron domains, which move as far apart as they can. The new orbital is called the sp^3 hybrid orbital (1 s and 3 p)

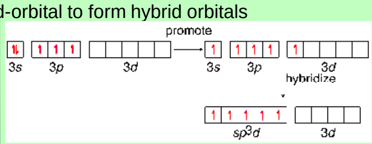
This hybrid orbital is responsible for the tetrahedral shapes

sp^3 hybrid orbital



sp^3d and sp^3d^2 hybrid orbitals

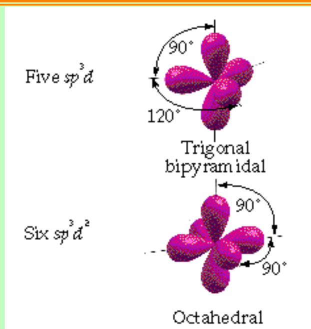
Atoms in the 3rd period and beyond can also use the d-orbital to form hybrid orbitals



Once promoted, the orbitals hybridize into a new shape, or electron domains, which move as far apart as they can. The new orbital is called the sp^3d hybrid orbital (1 s, 3 p and 1 or 2 d)

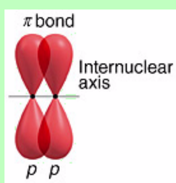
These hybrid orbitals are responsible for the trigonal bipyramidal and octahedral classes of shapes

sp^3d and sp^3d^2 hybrid orbitals



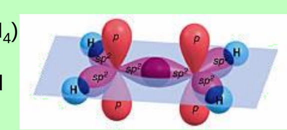
Multiple bonds

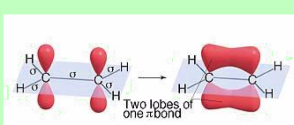
- The single bond between two atoms is formed by a sigma (σ) bond. A σ bond occurs along the internuclear axis.
- Double and triple bonds occur when σ bonds occur at the same time as pi (π) bonds. π bonds occur when the overlap regions occur above and below the internuclear axis.



Multiple Bonds (σand □)

- When ethene (C_2H_4) forms, the carbons are held together by a σ and a π bond.
- The π bond overlap looks like the second picture.





Multiple Bonds (∫ ανδ □)

When a triple bond occurs, one ∫ ανδ τωο □ bonds occur: