## Shapes of Molecules and Hybridization

## A. Molecular Geometry

- Lewis structures provide us with the number and types of bonds around a central atom, as well as any NB electron pairs. They do not tell us the 3-D structure of the molecule.

$\mathrm{CH}_{4}$ as drawn conveys no 3-D information (bonds appear like they are $90^{\circ}$ apart)
- The Valence Shell Electron Pair Repulsion Theory (VSEPR), developed in part by Ron Gillespie at McMaster in 1957, allows us to predict 3-D shape. This important Canadian innovation is found worldwide in any intro chem course.
- VSEPR theory has four assumptions

1. Electrons, in pairs, are placed in the valence shell of the central atom
2. Both bonding and non-bonding (NB) pairs are included
3. Electron pairs repel each other $\rightarrow$ maximum separation.
4. NB pairs repel more strongly than bonding pairs, because the NB pairs are attracted to only one nucleus

- To be able to use VSEPR theory to predict shapes, the molecule first needs to be drawn in its Lewis structure.
- VSEPR theory uses the AXE notation ( $m$ and $n$ are integers), where $\mathrm{m}+\mathrm{n}=$ number of regions of electron density (sometimes also called number of charge clouds).


1. Molecules with no NB pairs and only single bonds

- We will first consider molecules that do not have multiple bonds nor NB pairs around the central atom ( $\mathrm{n}=0$ ).
- Example: $\mathrm{BeCl}_{2}$
o Molecule is linear $\left(180^{\circ}\right)$
- Example: $\mathrm{BF}_{3}$
- Example: $\mathrm{CH}_{4}$
o Molecule is tetrahedral ( $109.5^{\circ}$ )
- Example: $\mathrm{PF}_{5}$
o Molecule is trigonal bipyramidal ( $90^{\circ}$ and $120^{\circ}$ ). There are three X atoms in a planar triangle and two axial atoms, one above and one below the central atom.
- Example: $\mathrm{SF}_{6}$


## 2. Molecules with $\geq 1$ NB pairs and only single bonds

- The geometry of the regions of electron density is roughly the same as what we see when no NB pairs are involved.
- However, the shape of the molecule is determined by looking at only the bonding pairs, NOT the non-bonding pairs.
- Example: $\mathrm{NH}_{3}$
o There are four regions of electron density ( $m+n=4$ ), and the electronic arrangement is still tetrahedral.
o Yet, the shape of the molecule (look at bonding pairs only) is trigonal pyramidal. Angles < $109.5^{\circ}$ (why?)
- Example: $\mathrm{H}_{2} \mathrm{O}$
o Electronic arrangement is tetrahedral. Shape of molecule = bent
- Example: NF
o Electronic arrangement is trigonal planar. Shape of molecule = linear
- Example: $\mathrm{SF}_{4}$
o Electronic arrangement is trigonal bipyramidal. Shape of molecule = see saw
- Example: $\mathrm{XeF}_{3}{ }^{+}$
o Electronic arrangement is trigonal bipyramidal. Shape of molecule $=$ T-shaped
- Example: $\mathrm{XeF}_{5}{ }^{+}$


## o Electronic arrangement is octahedral. Shape of molecule = Square pyramidal

- Example: $\mathrm{ICl}_{4}{ }^{-}$
o Electronic arrangement is octahedral. Shape of molecule = Square planar
- Example: the amino acid alanine
o There can be more than one "central atom"


## 3. Molecules with double or triple bonds

- These are quite simple: treat them as single bonds, and the AXE system still works. i.e. a multiple bond is still considered to be one region of electron density.
- Examples: predict the shapes of $\mathrm{CO}_{2}, \mathrm{C}_{2} \mathrm{H}_{4}$, and $\mathrm{NO}_{2}{ }^{-}$


## B. Molecular Polarity

- Recall that electronegativity is a relative measurement of an atom's ability to attract a bonding electron pair to itself.

- Differences in electronegativity between two covalently bonded atoms result in a polar covalent bond, and atoms have a partial negative or partial positive charge.
- These bonds are said to have dipole moments, which can be experimentally quantified. If placed in an electric field, the molecule will rotate and line up to the field.
- The greater the bond polarity, the greater the dipole moment. However, can we say that a molecule with a polar bond must also be a polar molecule? Not necessarily!
- Note: The overall polarity of a molecule depends on its geometry and the presence of polar bonds.
o The presence of polar bonds does not necessarily imply that the molecule is polar. This is because the bond dipole moments can cancel out (no net dipole moment).
o Think of the bond dipoles as vectors, and if the sum of all of the vectors is zero, the molecule is not polar.
- Examples:
$\mathrm{CO}_{2}$
$\mathrm{H}_{2} \mathrm{O}$
$\mathrm{BF}_{3}$
$\mathrm{NH}_{3}$
- Notice that non-polar molecules are highly symmetrical, allowing the bond dipole moments to cancel out.
- In a set of resonance structures, the overall polarity is averaged out over the resonance structures. For example, $\mathrm{CO}_{3}{ }^{2-}$ and $\mathrm{SO}_{4}{ }^{2-}$ are non-polar (no net dipole moment).


## C. Hybridization (Compounds with Single Bonds)

- How does molecular shape relate to the orbitals in the valence shell?
- Consider methane, $\mathrm{CH}_{4}$, which uses the valence electrons in the $2 \mathrm{~s}, 2 p_{\mathrm{x}}, 2 p_{\mathrm{y}}$, and $2 p_{\mathrm{z}}$ orbitals. These electrons must become unpaired prior to making bonds with H .
- Recall the shapes of the $s$ and $p$ orbitals.
- If we used these orbitals to bond with the H atoms, we would get this structure. Yet, we know that the proper structure from VSEPR theory is tetrahedral. This structure shown is clearly incorrect!
- How do we explain this?
- Before bonding to H atoms, the one $2 s$ and three $2 p$ atomic orbitals are mixed and rearranged to give a new set of four equivalent (same energy) "hybrid" atomic orbitals $\left(s p^{3}\right)$ arranged at tetrahedral angles of $109.5^{\circ}$.

- Each new hybrid orbital around the C contains one electron.
- After each pairs up with one electron from H , the orbitals contain an electron pair.

- The single bond formed by the direct, head-on overlap of orbitals is a sigma bond $(\sigma)$.
- Note: hybrid orbitals can also contain NB pairs, for example, in ammonia and water. These also have tetrahedral electronic arrangements and are $s p^{3}$.
- $\mathrm{NH}_{3}$, which has a tetrahedral electronic arrangement, contains three $\sigma$ bonds. Its shape is trigonal pyramidal.

- $s p^{3}$ hybridization is just one possibility. Five major hybridization types form the VSEPR structures, and these types are summarized in this table (details follow).

| Regions of <br> $\mathrm{e}^{-}$density | Atomic <br> orbitals | Hybrid <br> orbitals | Electronic <br> arrangement |
| :---: | :--- | :--- | :--- |
| 2 | one $s$, one $p$ | two $s p$ | linear |
| 3 | one $s$, two $p$ | three $s p^{2}$ | trigonal planar |
| 4 | one $s$, three $p$ | four $s p^{3}$ | tetrahedral |
| 5 | one $s$, three $p$, one $d$ | five $s p^{3} d$ | trigonal bipyramidal |
| 6 | one $s$, three $p$, one $d$ | six $s p^{3} d^{2}$ | octahedral |

o Regions of electron density: an NB pair, a single bond, or a multiple bond each constitute one region.
o Electronic arrangement may not equate to molecular shape if there is at least an NB pair present.

## 1. $s p$ hybridization

- The combination of one $s$ and one $p$ results in the formation of two $s p$ orbitals. These two hybrid orbitals are $180^{\circ}$ apart.

- Where we have used only one of the $p$ orbitals, there must be two $p$ orbitals remaining. (Recall there are three $p$ orbitals). We'll see later on that these leftover orbitals are used when there is multiple bonding.
- The two leftover $p$ are $90^{\circ}$ to each other and the $s p$ hybrids.


## 2. $\boldsymbol{s} \boldsymbol{p}^{2}$ hybridization

- One $s+$ two $p=$ three $s p^{2}$ orbitals $120^{\circ}$ apart.

- There is one leftover $p$ orbital remaining, since we started with three $p$ orbitals and used two of them for hybridization.

3. $\boldsymbol{s p}^{3}$ hybridization

- One $s+$ three $p=$ four $s p^{3}$ orbitals $109.5^{\circ}$ apart.
- There are no leftover $p$ orbitals. Also see diagram on p. 12.


4. Others: $s p^{3} d$ and $s p^{3} d^{2}$ hybridization

- One $s+$ three $p+$ one $d=$ five $s p^{3} d$ orbitals
- One $s+$ three $p+$ two $d=\operatorname{six} s p^{3} d^{2}$ orbitals

$\mathrm{IF}_{5}$ (sq. pyramidal)


## D. Hybridization (Compounds with Multiple Bonds)

- How do we assign hybridization to compounds containing multiple bonds? The same way! We still examine the number of regions of electron density (table on page 13).
- Consider ethene. Each carbon has an $\mathrm{AX}_{3}$ configuration ( $s p^{2}$-hybridized). Remember to count double bonds as one region. Each C also
 has a remaining $p$ orbital (see p. 15).
- Recall that $\sigma$ bonds are formed by the direct overlap of orbitals, which result in single bonds. Where do double bonds come from?
o The first bond in the double bond comes from a regular single bond caused by direct overlap (i.e. a o bond)

o The second bond comes from the sideways overlap of the leftover $p$ orbitals to give a pi $(\pi)$ bond. This is $90^{\circ}$ to the plane defined by the trigonal-planar $\sigma$ bonds. The $\pi$ bond is both above and below the plane (2 lobes).

- The structure therefore appears like this... note that $\pi$ bonds involve a sideways overlap, so bond rotation is not possible.

- How about a triple bond? Example: acetylene $\mathrm{H}-\mathrm{C} \equiv \mathrm{C}-\mathrm{H}$
o Carbon atoms are sp-hybridized, and each has two remaining $p$ orbitals $90^{\circ}$ to each other (see p. 14)
o The first bond in the triple bond originates from the direct overlap of $s p$ orbitals ( $\sigma$ bond)
o Both the second and the third bonds in the triple bond are $\pi$ bonds originating from the sideways overlap of the remaining $p$ orbitals. These two $\pi$ bonds are $90^{\circ}$ apart.

- Example: assign the hybridizations and the number of $\pi$ bonds present in the molecule acetone

