

4.2 The Nature of the Chemical Bond

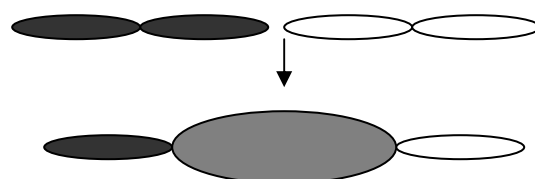
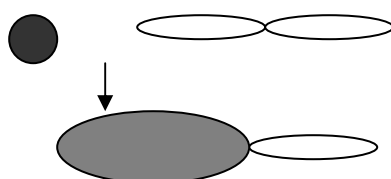
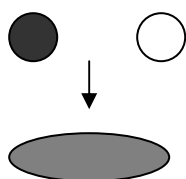
Previously...

Trying to explain how some elements rearranged their valence electrons lead us to assume they moved 2s electrons up to the 2p orbital. (example: boron trifluoride)

Unfortunately we need to realize that in order to move to the 2p orbital the electrons must obtain a higher energy level. This attempt to obtain higher energy would probably discourage bond formation. The valence bond theory provides more information for a better solution.

Valence Bond Theory

- No longer describes bonds as shared electrons
- Includes the concept that an electron is a standing wave and that an electron's position is defined as a cloud with a shape associated with a unique energy level (orbital)
- A half-filled orbital in one atom can overlap with another half-filled orbital of a second atom to form a new, bonding orbital.
- The new, bonding orbital from the overlap of atomic orbitals contains a pair of electrons of opposite spin.
- The total number of electrons in the bonding orbital = 2
- When atoms bond, they arrange themselves in space to achieve the maximum overlap of their half-filled orbitals. Maximum overlap produces a bonding orbital of lowest energy.
- E.g. s-s bond



- Where does it go wrong? When we look at geometry.
- E.g. water (prediction 90° for p shell bonding to s shell but actual bond angle = 104.5°)

Hybrid Orbitals

- Other problems with Lewis Bond Theory
 - Bonding of BeF_2 ; bond dissociation energies; bond lengths
 - Differences in bond energies of "identical" covalent bonds
 - Carbon makes 4 equal strength bonds, as well as double and triple bonds.
- Carbon bonds in a tetrahedron. To get 4 equal bonds from both s and p orbitals you need to promote one of the s electrons and to merge all orbitals to create four equal bonds called sp^3 hybrid orbitals.
- sp^3 refers to 1 s orbital and 3 p orbitals giving 4 hybrid orbitals.
- The hybrid orbital is a mathematical explanation of covalent bonding and is supported by empirical evidence.
- There are several ways to form a hybrid orbital
- See Table 1 on Page 234

Double and Triple Covalent Bonds

- Lewis structures can show the bonds are shared but not how.
- The single bond is created by a sigma (σ) bond. A sigma bond is an end-to-end overlap of atomic orbitals.
- The double bond is created by a sigma (σ) bond and a pi (π) bond. A pi bond is the side-by-side overlap of atomic orbitals (usually p).
- The triple bond is created by a sigma (σ) bond and 2 pi (π) bonds.
- See pages 236 to 239 for diagrams.

Double Bonds

- Using C_2H_4 as an example. The 2 carbons undergo partial hybridization. They form 3 sp^2 hybrid orbitals and keep one of the p orbitals. The hybrid orbitals form sigma bonds: 1 C-C bond and 4 C-H bonds. The remaining p orbitals create a pi bond that exists above and below the sigma bond.
- The extra electrons of the pi bond provide a greater attraction between the two carbon atoms and creates a shorter and stronger bond.

Triple Bonds

- Same premise as double bonds but an sp hybrid is formed along with 2 pi bonds.

Summary of Valence Bond Theory (from textbook pages 240-1)

- Covalent bonds form when atomic or hybrid orbitals with one electron overlap to share electrons.
- Bonding occurs with the highest energy (valence shell) electrons.
- Normally, the s and p orbitals overlap with each other to form bonds between atoms.
- Sometimes s and p orbitals of one atom hybridize to form identical hybrid orbitals that are used to form bonds with other atoms.
- sp^3 , sp^2 , and sp hybrid orbitals are formed from one s orbital and three, two, and one p orbital, respectively.
- There are four sp^3 hybrid orbitals, three sp^2 orbitals, or two sp orbitals when hybridization occurs during bond formation.
- The orientations of sp^3 , sp^2 , and sp hybrid orbitals are tetrahedral (109.5°), trigonal planar (120°), and linear (180°), respectively.
- End-to-end overlap of orbitals (hybrid or not) is called a sigma bond.
- Single covalent bonds are sigma bonds.
- Side-by-side overlap of unhybridized p orbitals is called a pi bond.
- Double bonds have one pi bond, while triple bonds have two pi bonds.
- sp^2 and sp hybrid orbital bonding is usually accompanied by pi bond formation to form double or triple bonds.

Homework

- Practice 1,2,3,4,5,8,9,10,11,12,14,17,18,20,21,26,27,28,29

HYBRIDIZATION

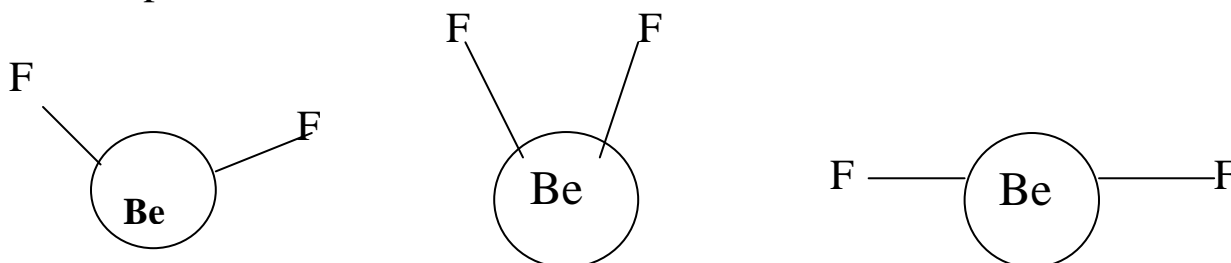
Think of hybrid plants or thoroughbred horses. These things go through a selective breeding or mixing process. Hybrid orbitals are very similar.

VSEPR theory states that the electron clouds arrange themselves so as to be as far apart as possible, but how??

Hybridization – the mathematical mixing of orbitals. Orbitals are mathematical probability equations and equations can be added. This helps to explain how the orbitals arrange themselves when bonding.



The $2s^2$ electrons are already paired and so shouldn't bond or at the very least if they were used to bond, the fluorines should be at any angle apart as the "s" orbital is spherical.



BUT!... We know that all BeF_2 molecules are linear so the "s" orbital can not be the only orbital bonding.

If we mathematically combine the probabilities for the 2s level and one of the 2p levels (the p's are still present even though they are empty) we get orbitals that have both "s" and "p" character called "sp" orbitals.

The "sp" orbitals look like the diagram below and therefore have the proper geometry to account for the linear shape of BeF_2 . The orbitals have 1 small lobe and one large lobe and two of these orbitals together arrange as shown to be 180° apart.



1 “sp” orbital



2 “sp” orbitals

Other hybridizations can occur. Each one has a different amount of “p” character to it depending on the number of “p” orbitals that are added to the “s” orbital

Hybridization	Amount of “p” character	Orbital arrangement	Resultant orbitals
none	none		1 – “s” 3 – “p”
sp	some	linear 	2 – “sp” 2 – “p” - allows for triple bonds
sp ²	more	trigonal planar 	3 – “sp ² ” 1 – “p”(not shown because it comes in and out of page) - allows for double bonds
sp ³	lots	tetrahedral 	4 - “sp ³ ” allows for four equivalent single bonds

Remember the shapes shown above are simply the result of mathematically adding the “s” and 1, 2 or 3 “p” orbital probabilities.

Eg] Carbon – $1s^2 2s^2 2p^2 \rightarrow sp^3$ hybridization $\rightarrow 1s^2 2_{sp^3}^1 2_{sp^3}^1 2_{sp^3}^1 2_{sp^3}^1$
Therefore carbon can make 4 equivalent bonds.