4.2 The Nature of the Chemical Bond

Valence Bond Theory

- 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 must be two.
- 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 s-p bond p-p bond

- Where does it go wrong? When we look at geometry.
- E.g. water (prediction 109.5º, actual 104.5º)

Repulsion of the electrons needs to be considered.

Hybrid Orbitals

- Problem with Lewis Bond Theory → 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 to create four sp^3 hybrid orbitals.
- sp^3 refers to 1 s orbital and 3 p orbitals giving 4 hybrid orbitals.

- The hybrid orbital only exists when bonding occurs.
- 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