

I. ORBITALS (Section 1.1, 1.2, 1.5)

There are two types of orbitals, atomic and molecular.

A. ATOMIC ORBITALS

1. TYPES OF ATOMIC ORBITALS: There are three types of atomic orbitals that play a role in organic chemistry.
 - a. s-orbitals
 - b. p-orbitals
 - c. d-orbitals
2. ATOMIC SHELLS OR LEVELS
 - a. Atomic orbitals occupy "shells" or "levels", each progressively higher in energy and are designated by number
 - b. The outermost shell is referred to as the "valence shell".
3. DETERMINING ELECTRON CONFIGURATION: Electron configuration (or how electrons "fit" into orbitals and shells) is determined using three basic rules.
 - a. Auf Bau Principle
 - b. Pauli Exclusion Principle
 - c. Hund's Rule

II. CHEMICAL BONDING

A. IONIC BONDS (Section 1.3)

A ionic bond forms between an e- donor atom and an e- acceptor atom.

B. COVALENT BONDS (Section 1.3)

1. TYPES OF COVALENT BONDS
 - a. SIGMA BONDS
 - i. Sigma bonds are often referred to as "single" bonds.
 - ii. Sigma bonds are stronger than pi bonds.
 - iii. Sigma bonds result from "head-on" overlap of atomic orbitals.
 - iv. The two e- involved in a sigma bond reside between the two atoms involved in bonding.
 - b. PI BONDS
 - a. Pi bonds are often referred to as multiple bonds.
 - b. Pi bonds are weaker than sigma bonds.
 - c. Pi bonds result from "sideways" overlap of atomic orbitals.
 - d. The two e- involved in a pi bond reside above and below the line defining the bond.
2. POLAR AND NON-POLAR COVALENT BONDS
 - a. Polar Covalent Bonds
 - i. A polar covalent bond is one in which the e- are unequally shared between two atoms due to differences in electronegativity of those atoms. The more electronegative element has more e-density than the less electronegative element.
 - b. Non-Polar Covalent Bond
 - i. A non-polar covalent bond is one in which the bonding e- are equally shared between two atoms due to differences in electronegativity of those atoms.

C. MOLECULAR STRUCTURE (Section 1.6)

1. Molecular Orbital Theory
 - a. TYPES OF MOLECULAR ORBITALS
 - i. Bonding Molecular Orbitals
 - ii. Anti-Bonding Molecular Orbitals
 - b. Electron Configuration and Lewis Structures in Molecules
2. Valence Bond Theory
A covalent bond forms when two atomic orbitals overlap and share e-

D. NON-COVALENT INTERACTIONS

1. H-bonding
2. Dipole-Dipole Interactions
3. Ion-Dipole Interactions
4. Hydrophobic Interactions

III. HYBRIDIZATION (Sections 1.7-1.14)

Hybridization is the mixing together of "atomic orbitals" (i.e., s-, p-, d-) to form new atomic orbitals. These new, hybridized, atomic orbitals can then overlap to form bonds.

A. CARBON ATOM HYBRIDIZATION: The s- and p-orbitals associated with the valence shell of a carbon atom can mix or "hybridize" in three possible ways. The total number of atomic orbitals always remains constant.

1. Carbon sp^3 hybridization is a result of mixing 1 s-orbital and 3 p-orbitals to get 4 sp^3 orbitals. An sp^3 hybridized carbon atom generally has 4 single (or sigma bonds) associated with it.
2. Carbon sp^2 hybridization is a result of mixing 1 s-orbital and 2 p-orbitals to get 3 sp^2 orbitals and 1 unhybridized p-orbital. An sp^2 hybridized carbon atom generally has 3 single (or sigma bonds) associated with it and one pi bond.
3. Carbon sp hybridization is a result of mixing 1 s-orbital and 1 p-orbital to get 2 sp orbitals and 2 unhybridized p-orbitals. An sp hybridized carbon atom generally has 2 single (or sigma bond) associated with it and 2 pi bonds.

B. CARBOCATIONS AND CARBANIONS

1. Carbocations are positively charged (1e- deficient) carbon atoms. They are sp^2 hybridized.
2. Carbanions are negatively charged carbon atoms (1 extra e-). They are sp^3 hybridized.

C. NITROGEN ATOM HYBRIDIZATION

1. Nitrogen atoms that have three sigma bonds and one lone pair are sp^3 hybridized and have tetrahedral geometry.
2. Nitrogen atoms with 2 sigma bonds, one pi bond and a lone pair are sp^2 hybridized.
3. Nitrogen atoms with one sigma bond, two pi bonds and a lone pair are sp hybridized.

D. OXYGEN ATOM HYBRIDIZATION

1. Oxygen atoms that have two sigma bonds and two lone pairs are sp^3 hybridized and have tetrahedral geometry.
2. Oxygen atoms with one sigma bond, one pi bond and two lone pairs are sp^2 hybridized.

IV. DRAWING ORGANIC MOLECULES (Section 1.4)

A. Three basic rules are used for drawing organic molecules.

1. Carbon atoms are assumed to be at the intersection of two lines and at the end of a line.
2. Hydrogen atoms and lone pairs are usually not shown.
3. All other atoms are drawn out using uppercase letters

B. Stereochemistry

The stereochemistry (or 3-dimensional representation) of a carbon atom is indicated in the following ways depending on the hybridization of the carbon atom involved.

1. sp^3 : Bonds show substituents on the C atom as if they were extending from the corners of tetrahedron.
2. sp^2 : Bonds show substituents on the C atom as if they were extending from the corners of a triangle.
3. sp: Bonds show substituents in a straight line.

C. DEGREE OF UNSATURATION (Index of Hydrogen Deficiency) (Section 3.1)

The degree of unsaturation of a molecule is defined as the number of rings and/or pi bonds associated with that molecule. The degree of unsaturation can be determined from molecular formula and can be extremely useful information for determining the structural formula for a molecule when the molecular formula is given.

1. Saturated Hydrocarbons
 - a. The molecular formula for all saturated hydrocarbons (organic molecules which contain only sp^3 C and H) is C_nH_{2n+2}
 - b. Saturated hydrocarbons contain no pi bonds or ring.

2. Calculating the degree of unsaturation
a. The DOU of molecules which contain only carbon and hydrogen or molecules which contain only carbon hydrogen and oxygen can be calculated from the following formula.

$$\left(\begin{array}{l} \# \text{ OF H ATOMS} \\ \text{IN A SATURATED} \\ \text{HYDROCARBON} \\ (\text{C}_n\text{H}_{2n+2}) \end{array} \right) - \left(\begin{array}{l} \# \text{ OF H ATOMS} \\ \text{IN THE} \\ \text{UNKNOWN} \end{array} \right) = \left(\begin{array}{c} \text{DIFFERENCE} \\ 2 \end{array} \right) = \begin{array}{c} \text{DEGREE} \\ \text{OF} \\ \text{UNSATURATIO} \end{array}$$

- b. The DOU of molecules which contain only carbon, hydrogen and nitrogen or molecules which contain only carbon, hydrogen, nitrogen and oxygen can be calculated from the following formula.

$$\left(\begin{array}{l} \# \text{ OF H ATOMS} \\ \text{IN A SATURATED} \\ \text{HYDROCARBON} \\ (\text{C}_n\text{H}_{2n+2}) \end{array} \right) - \left(\begin{array}{l} \# \text{ OF H ATOMS IN THE} \\ \text{UNKNOWN} - \# \text{ OF N} \\ \text{ATOMS IN THE UNKNOWN} \end{array} \right) = \left(\begin{array}{c} \text{DIFFERENCE} \\ 2 \end{array} \right) = \begin{array}{c} \text{DEGREE} \\ \text{OF} \\ \text{UNSATURATION} \end{array}$$

- c. The DOU of molecules which contain only carbon, hydrogen and a halogen, or molecules which contain only carbon, hydrogen, a halogen and oxygen can be calculated from the following formula.

$$\left(\begin{array}{l} \# \text{ OF H ATOMS} \\ \text{IN A SATURATED} \\ \text{HYDROCARBON} \\ (\text{C}_n\text{H}_{2n+2}) \end{array} \right) - \left(\begin{array}{l} \# \text{ OF H ATOMS} \\ + \\ \# \text{ OF HALOGENS} \\ \text{IN THE} \\ \text{UNKNOWN} \end{array} \right) = \left(\begin{array}{c} \text{DIFFERENCE} \\ 2 \end{array} \right) = \begin{array}{c} \text{DEGREE} \\ \text{OF} \\ \text{UNSATURATION} \end{array}$$

V. ISOMERS

There are four general types of isomers of organic compounds.

- SKELETAL ISOMERS:** Isomers with the same molecular formula but with a different carbon skeleton.
- FUNCTIONAL GROUP ISOMERS:** Isomers with the same molecular formula but with a different functional group.
- POSITIONAL ISOMERS:** Isomers with the same molecular formula, same carbon skeleton but a different position of functional group.
- STEREISOMERS (Cycloalkanes only):** Isomers with the same molecular formula, same chemical connections but different 3-dimensional geometry.

VI. POLARITY IN MOLECULES AND BONDS (Section 1.15)

A. FORMAL ELECTRICAL CHARGES ON ATOMS

The following rules can be used for determining formal charges of atoms.

- Draw the Lewis dot structure of the molecule.
- Use the following "formula" for determining the formal charge of each atom in the molecule.

$$\# \text{ of valence } e^- - \# \text{ of bonding } e^- - \# \text{ of non-bonding } e^- = \text{formal charge}$$

B. DIPOLE MOMENT:

Dipole moment is a measure of charge separation in a molecule. A qualitative determination of the dipole moment of a molecule can be made using the following set of rules.

- Consider all the negatively charged parts of the molecule.
 - Electronegative atoms
 - Lone pair electrons on atoms
 - Negative formal charges
- Consider all the positive parts of the molecule.
 - Electropositive elements
 - Positive formal charges
- Draw out directional arrows indicating the polarity of each bond in the molecule.
- Find a center point of all negative elements and a center point of all positive elements. The dipole moment will be directed from the positive center point toward the negative center point.

VII. NON-COVALENT INTERACTIONS

- A. H-bonding
- B. Dipole-Dipole Interactions
- C. Ion- Dipole Interactions
- D. Hydrophobic Interactions

VIII. RESONANCE (Sections 1.22, 7.1, 7.3-7.7)

- A. Resonance is a phenomena which describes the shared nature of electrons through pi orbitals within the same molecule.
- B. General features of resonance structures and resonance theory
 1. Resonance structures are generally associated with molecules that have pi systems. At least three consecutive atoms with p-orbitals must be available.
 2. All resonance forms of a molecule are included in representing the overall structure.
 3. The most stable resonance forms make the greatest contribution to the overall structure.
 4. Structures with the least charge separation and formal charges are the most stable.
 5. All resonance forms of the same molecule have the same total number of electrons.
 6. Resonance forms exist due to the movement of e- through orbital a pi system.
- C. Examples
 1. Benzene
 2. Allylic carbocations
 3. Allylic carbanions

IX. ACIDS & BASES: There are two general definitions of acids and bases: Bronsted-Lowry and Lewis

A. BRONSTED LOWRY ACIDS & BASES (Section 1.16, 1.18-1.217.9)

1. A Bronsted Lowry Acid DONATES A PROTON
2. A Bronsted Lowry Base ACCEPTS A PROTON
3. CONJUGATE ACIDS AND BASES
 - a. A conjugate acid results after a Bronsted Lowry base has accepted a proton.
 - b. A conjugate base results after a Bronsted Lowry acid has donated a proton.
4. IDENTIFYING ACIDS AND BASES IN A REACTION
The acid and the base in an acid-base reaction can be identified by "following the proton". Determine where the proton (H⁺) is going to and where it is coming from. The proton comes from the *acid* and goes to the *base*.
5. STRENGTHS OF ACIDS AND BASES
The strength of an acid or a conjugate acid is generally reported as pKa.
The strength of an acid (reported in pKa units) is related to its Ka.
 - a. Ka is the ionization constant (i.e., equilibrium constant) for an acid in water. The Ka is defined by the ratio:

$$K_a = \frac{[A^-][H_3O^+]}{[HA][H_2O]} \quad \begin{array}{l} \text{(Products)} \\ \text{(Reactants)} \end{array}$$

- b. Acid strength is reported as pKas, so the relationship between pKa and Ka must be established. The pKa is the negative log of the Ka.

$$pK_a = -\log K_a$$

Therefore, a strong acid has a large Ka, but a small pKa. A weak acid has a small Ka and a large pKa.

- c. In organic chemistry, the strength of a base is reported as a pKa of the conjugate acid of the base, not as a pKb. The strength of a base can be determined from the pKa of the base's conjugate acid
- d. The more stable the conjugate base of an acid, the larger the Ka and the smaller the pKa. The structure (electronic and steric effects) of the conjugate base influence its stability.
The more stable the base, the smaller the Ka and the larger the pKa of the conjugate acid of the base. The structure (electronic and steric effects) of the base influence its stability. A large pKa of a conjugate acid of a base indicates it is a strong base
- e. Relationship of pKa and pKb

B. pH and pKa: IONIZATION OF ACIDS & BASES / SOLUBILITY (1.24, 7.9)

1. Weak acids ionize in basic aqueous solutions to form salts
2. Weak bases ionize in acidic aqueous solutions to form salts
3. Compounds of similar or like polarity dissolve in each other.
4. Ionized acids and bases are polar and are soluble in water, which is polar.
Therefore, when an acid ionizes in aqueous base, it dissolves, and when a base ionizes in aqueous acid it dissolves. Acids are NOT soluble in acid and bases are NOT soluble in base.
5. The Table 1 lists common functional groups and their acid/base/neutral behavior. Table 2 lists pH values for various compartments of the body.
6. **Hendersohn-Hasselbach Equation**

The Hendersohn-Hasselbach equation describes the mathematical relationship between pH and pKa. It allows for the calculation of exactly how much of an acidic or basic compound is ionized at equilibrium.

$$\text{pH} = \text{pKa} + \log \frac{[\text{Base}]}{[\text{Acid}]} \quad \begin{array}{l} \leftarrow \text{-----could also be conjugate base} \\ \leftarrow \text{-----could also be conjugate acid} \end{array}$$

C. EFFECTS OF SUBSTITUENTS ON pKa

Substituent can influence pKa of carboxylic acids through electronic effects (resonance and induction)

1. **CARBOXYLIC ACIDS (GENERAL)**
 - a. The more stable the carboxylate anion, the stronger the acid.
 - b. Carboxylate anions are stabilized via an electron withdrawing group substituent via an "inductive effect".
 - c. The further away the EWG, the less effect it has on the pKa of the acid.
 - d. Electron donating groups destabilized the carboxylate anion and thus result in a weaker acid (higher pKa).
2. **Electronic Effects on BENZOIC ACIDS**
 - a. EWG on the benzene ring of benzoic acid stabilize the carboxylate anion.
 - b. EWG's on the benzene ring of benzoic acids result in a stronger acid (lower pKa).
 - c. Electron donating groups on the benzene ring of the benzoic acid destabilize the carboxylate anion and thus result in a weaker acid (higher pKa).