

Contents

General Chemistry Review

Electrons, Bonds, and Lewis Structures	2
Identifying Formal Charges	2
Induction and Polar Covalent Bonds	3
Atomic Orbitals.	3
Valence Bond Theory.	4
Molecular Orbital Theory	5
Hybridized Atomic Orbitals.	5
Molecular Geometry	7
Dipole Moments and Molecular Polarity	8
Intermolecular Forces and Physical Properties	8
Structural Theory of Matter	9

Molecular Representations

Molecular Representations.	10
Bond-Line Structures.	10
Notes on Drawing Bond-Line Structures	11
Hydrogen Deficiency Index: Degrees of Unsaturation	11
Hydrogen Saturation.	11
Hydrogen Deficiency Index	12
Identifying Functional Groups	12
Identifying Lone Pairs	13
Common Patterns Between Formal Charge and Lone Pairs	13

Acids and Bases

Introduction to Brønsted-Lowry Acids and Bases	14
Lewis Acids and Bases	14
Nucleophiles and Electrophiles	14
Flow of Electron Density: Curved-Arrow Notation	15
Notes on Drawing Curved Arrows.	15

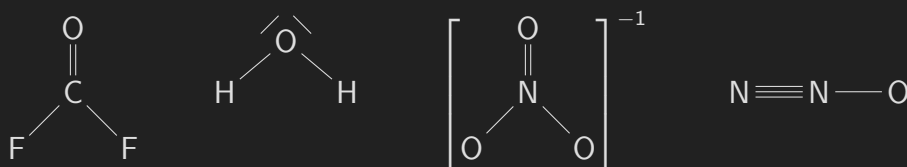
Alkanes and Cycloalkanes

Introduction to Alkanes	16
Nomenclature of Alkanes.	16

1 General Chemistry Review

Electrons, Bonds, and Lewis Structures

- ▷ **Covalent bond:** two atoms sharing a pair of electrons.
- ▷ **Octet rule:** *main group elements* that tend to bond in a way that each atom has **eight** electrons in its valence shell.
 - Atoms that do not have eight will share electrons with other elements in order to maintain a stable state.
- ▷ **Main group elements:** sometimes called representative elements, are groups 1, 2 and 13–18 in periodic table.
 - Some elements in group 3 and 12 share properties between transition metals and the main group.
- ▷ The lowest energy (most stable) state of two atoms is determined both by bond length and bond strength.
- ▷ Valence electrons are determined by the group, 1A–8A, of the periodic table.
- ▷ **Lone pair:** unshared, or nonbonding, electrons.
- ▷ **Lewis structures:** 2D model that represents covalent bonds as straight lines and lone pairs as dots.
- ▷ Examples: COF_2 , H_2O , NO_3^- , N_2O :



- ▷ **Resonance structures:** a set of two or more Lewis structures that collectively describe the electronic bonding of a single polyatomic species, including fractional bonds.

Identifying Formal Charges

- ▷ **Formal charge:** any atom that does not exhibit the appropriate number of valence electrons.
- ▷ Determining formal charge:
 - Formula: $FC = V - N - \frac{B}{2}$
 - V = valence electrons of element
 - N = lone pair electrons

- B = bonded electrons
- ▷ **Less** than expected number of valence electrons results in a **positive** charge.
- ▷ **More** than expected number of valence electrons results in a **negative** charge.
- ▷ The lower the **magnitude** of formal charge, the **greater the stability** of the whole molecule.
- ▷ Atoms that are **more electronegative** hold **negative** formal charges better, which results in **greater stability** vs when the negative charge is spread on less electronegative elements in a polyatomic species.
 - The dominant resonance structure will be that of the greatest stability.

Induction and Polar Covalent Bonds

- ▷ Bonds can be classified into three categories: covalent, polar covalent, and ionic.
- ▷ The categories emerge from the electronegativity values of the atoms sharing a bond.
- ▷ **Electronegativity**: a measure of the ability of an atom to attract electrons.
 - Electronegativity generally **increases left to right**, and from the **bottom to top** of the periodic table.
- ▷ **Covalent bond**: when the difference in electronegativity is **less than 0.5**.
- ▷ **Polar covalent bond**: when the difference in electronegativity is **between 0.5 and 1.9**, then the electrons are not equally shared and become polar.
- ▷ **Induction**: the withdrawal of electrons towards a more electronegative atom. δ^+ represents partial positive charge gained when electrons are pulled away, while δ^- represents the partial negative charge pulled closer.
- ▷ **Ionic bond**: when the difference in electronegativity is **greater than 1.9**.
 - Electrons are not shared in this case, and attraction is instead just the result of oppositely charged ions.

Atomic Orbitals

- ▷ **Atomic orbital (AO)**: standing quantum wave (excitation in electron field) around an atom.
 - More energy leads to higher orbital levels.
 - Gives principle quantum number, n , as is associated with distance from nucleus.
 - Orbital levels: s(1 pair), p(3 pairs), d(5 pairs), f(7 pairs).

- Angular momentum quantum number that describes three-dimensional region of space that the electron density occupies.
- Magnetic quantum number describes orientation in space of electron density.
 - $m_l = 0$; s orbital
 - $m_l = -1, 0, 1$; p_x, p_y, p_z orbitals.
- Locations where ψ (quantum wave function) is zero are called **nodes**.
 - The **more nodes** that an orbital has, the **greater** it's energy.
- *Spin*: allows an orbital to contain only two electrons, $\pm\frac{1}{2}$
- ▷ **Degenerate orbitals**: orbitals with the same energy level.
- ▷ Order in which orbitals are filled is determined by three principles:
 - **Aufbau principle**: lowest energy orbital is filled first.
 - **Pauli exclusion principle**: each orbital can accommodate a maximum of two electrons that have opposite spin.
 - **Hund's rule**: electrons are placed in each degenerate orbital before being paired up.
- ▷ Describing the nature of atomic orbital is done with two commonly used theories: *Valence Bond Theory* and *Molecular Orbital Theory*.
- ▷ The commonly used theories give a deeper understanding of covalent bonds, which is essentially just the **overlap of atomic orbitals**.
- ▷ **Constructive/destructive interference**: the result of two waves that approach each other, or overlap.
 - Constructive interference produces a wave with the vector sum of both waves.
 - Destructive interference cancel each other out and produces a node.

Valence Bond Theory

- ▷ **Valence bond theory**: the sharing of electron density between two atoms is a result of the constructive interference of their atomic orbitals.
- ▷ *Bond axis*: the line that can be drawn between two hydrogen atoms.
- ▷ **Sigma bond (σ)**: a particular type of covalent bond that has circular symmetry with respect to the bond axis.

- All single bonds are σ bonds.
- The strongest type of covalent bond.
- ▷ **Pi bond (π)**: covalent bonds where two lobes of an orbital overlap with two lobes of another atom.
 - Each atomic orbital has zero electron density at a shared nodal plane, passing through the two bonded nuclei.
 - π bonds form double ($\sigma + \pi$) and triple bonds ($\pi + \sigma + \pi$).
 - Individual π bonds are weaker than σ bonds.

Molecular Orbital Theory

- ▷ **Molecular orbital theory (MO)**: uses linear combinations of atomic orbitals to model and explore the consequences of orbital overlap.
 - The newly described orbitals are called **molecular orbitals** according to MO theory.
- ▷ Atomic orbitals refer to an individual atom, while molecular orbitals is associated with an entire molecule.
- ▷ In other words, MO theory states that atomic orbitals cease to exist when they overlap. Instead they are replaced with multiple molecular orbitals which span the entire molecule.
- ▷ Molecular orbitals are more stable (lower energy) since electrons are attracted by both nuclei.
- ▷ When there are **nodes** between the nuclei, then the resulting σ^* orbitals become **antibonding**, as they **destabilize** (increase the energy) of a molecular orbital.
- ▷ Best used to produce a quantitative picture of bonding.
 - Describes strength, order, and polarity of bonds.
 - Allows for the presence of paired or unpaired electrons.
 - Has spectroscopic properties.

Hybridized Atomic Orbitals

- ▷ **sp^3 -hybridized orbitals**: produced by averaging one s orbital and **three p** orbitals.
 - Hybridized orbitals explains the geometry of methane, which results from the **now four degenerate** orbitals pushing apart to achieve tetrahedral

geometry.

- Hybridized orbitals become **unsymmetrical**, producing a larger front lobe that is more efficient than standard p orbitals in the ability to form bonds.
- All bonds in are **σ bonds**, and thus can be individually represented by the overlap of atomic orbitals.
- ▷ **sp^2 -hybridized orbitals**: produced by averaging the s orbital with only **two** of p orbitals.
 - The remaining p orbital is unaffected, and free multiple p orbitals results in a π bond.
 - This is done to explain geometry of compounds bearing a double bond.
 - A double bond is formed from one σ bond and one π bond.
 - Associated with *trigonal planar geometry*.
- ▷ **sp -hybridized orbitals**: produced by averaging of one s orbital and **one** p orbital.
 - Leaves two p orbitals and resulting in two π bonds.
 - A triple bond is formed with the addition of one σ bond due to the overlap of the sp orbitals.
 - Geometry of a triple bond has *linear geometry*.
- ▷ Finding the hybridization of any atom can be done simply:
 1. Look at the central item.
 2. Determine groups (number of bonds, π bonds count as 1, and lone pairs attached) of atom.
 - groups aka regions of electron density.
 3. For groups 1-4: sp^x ; $x = \text{groups} - 1$
 4. For groups 5-6: sp^3d^x ; $x = \text{groups} - 4$
- ▷ Bond Strength and Bond Length:
 - Bond length **decreases** with more bonds.
 - Bond strength **increases** with more bonds.
 - The more **s character**, the **shorter** and **stronger** the bond, and the **larger** the bond angle.
 - *s -character*: contribution of the σ bond in a hybridization.
 - e.g. $sp = 50\%$, $sp^2 = 33\%$, $sp^3 = 25\%$

- sp-sp bond is the strongest, sp³-sp³ is the weakest.

Molecular Geometry

- ▷ **Valence shell electron pair repulsion (VSEPR) theory:** enables the prediction of molecular geometry due to the presumption that all electron pairs repel each other; resulting in a three-dimensional space that maximizes distance from each other.
- ▷ **Steric number:** the total number of electron pairs in a molecule. Can be bonds or lone pairs.
- ▷ **Tetrahedral geometry:** result of four σ bonds and zero lone pairs.
 - produces a tetrahedron with bond angles of 109.5°.
- ▷ **Trigonal pyramidal geometry:** three σ bonds and one lone pair.
 - The lone pair occupy more space than bonded electron pairs, so the remaining angles are slightly less than a tetrahedral, at 107°.
 - The lone pair sits atop the base forming a pyramid like structure.
- ▷ **Bent geometry:** two σ bonds and two lone pairs.
 - VSEPR predicts the lone pairs to be in two corners of the tetrahedral, producing bond angles of 105°.
 - VSEPR predicts geometry H₂O correctly, but for wrong reasons.
 - The lone pairs in H₂O have different energy levels, suggesting one pair occupies a *p* orbital with the other in a lower-energy hybridized orbital.
- ▷ VSEPR theory is best used for a first approximation and is mostly accurate for most small molecules.
- ▷ **Trigonal planar geometry:** three electron pairs forming three bond angles of 120° and lie on the same plan.
- ▷ **Linear geometry:** two electron pairs that oppose each other at 180°, forming a linear structure.
- ▷ General method of determining structure:
 1. Count steric number—the total number of electron pairs in a molecule. Can be bonds or lone pairs.
 2. Determine predicted geometrical structure predicted (EDG) by VSEPR using steric number.
 - Octahedral:6, Bipyrmaid:5, Tetrahedral:4, Trigonal:3, Linear:2

3. Determin impact (the MG) of lone pairs; more lone pairs results in less space between bonded pairs. Shape depends on EDG.

Dipole Moments and Molecular Polarity

- ▷ **Dipole moment (μ):** defined as the amount of partial charge, δ , on either end of the dipole multiplied by the distance separation, d :
 - $\mu = \delta d$
 - μ generally has an order of magnitude of 10^{-18} esu·cm due to general partial charge (esu) and distance (cm) values.
 - 1 debye (D) = 10^{-18} esu·cm
- ▷ **Molecular dipole moment:** the vector sum of the individual dipole moments.
 - Lone pairs have significant effect on the molecular dipole moment.
 - Also called the net dipole moment.

Intermolecular Forces and Physical Properties

- ▷ **Intermolecular forces:** the attractive forces between individual molecules that determined the physical properties of a compound.
- ▷ *Electrostatic:* forces that occur as a result of the attraction between opposite charges.
- ▷ Electrostatic interactions for neutral molecules (no formal charge) are often classified as into the following categories:
 - **Dipole-dipole interaction:** Compounds with net dipole moments.
 - In solid space these interactions either repel or attract each other.
 - In liquid space these interactions tend to attract more often, raising melting/boiling point.
 - **Hydrogen bonding:**
 - Not actually a bond, just an interaction.
 - When hydrogen bonds to a electronegative atom, then the hydrogen will have a δ^+ .
 - **F, O, N, Cl** (Br, I). Most electronegative elements, from left to right, that hydrogen most often bonds too.
 - Hydrogen bonding is strong due to size of hydrogen atom, resulting in very close partial charge interactions.
 - The more hydrogen bonds, the higher the boiling point tends to be.

- **Fleeting dipole-dipole interactions:**
 - Electrons are considered to be in constant motion, which result in the center of negative charge to vary.
 - On average, the dipole moment is zero, though can experience transient dipole moments, initiating fleeting attraction/repulsion.
 - Heavier hydrocarbons generally experience a stronger force due to increased surface area, and thus greater chance for non-zero dipole moments, which results in higher boiling points.
 - Branched hydrocarbons generally have decreased surface area, decreasing boiling point relative to others of similar weight.
- ▷ When comparing boiling points of compounds, look for following factors:
 - Any dipole-dipole interactions? Formation of hydrogen bonds?
 - Number of carbon atoms. (surface area)
 - Degree of branching of compound. (surface area)

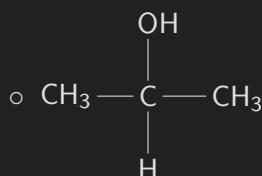
Structural Theory of Matter

- ▷ **Constitutional isomers:** aka structural isomers; same **chemical formula**, but different in the way the **atoms are connect**, i.e. their constitution is different.
 - Consistent with the octet rule.
 - Each element forms a predictable number of bonds, from one to four.
 - The number of **possible constitutional isomers increases** as the number of **carbon atoms increases**
- ▷ **Stereoisomers:** isomers that differ in **spatial arrangement** of atoms, rather than connectivity.
 - **Geometric isomerism:** aka cis–trans; **locked into spatial positions** due to double bonds or a ring structure.
 - Cis indicates functional groups that are on the same side of the carbon chain.
 - Trans indicates functional groups on opposite sides of the carbon chain.
 - **Enantiomers:** aka optical isomers; mirror images of each other that are non-superposable.
 - Human hands are a macroscopic analogy.
- ▷ *More detail will be covered in later sections.*

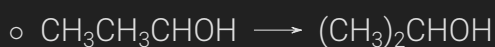
2 Molecular Representations

Molecular Representations

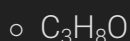
- ▷ **Partially condensed structures:** the C–H bonds are not always drawn, saving space.



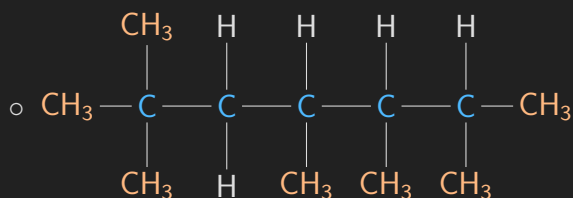
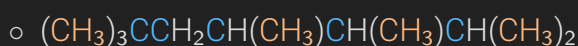
- ▷ **Condensed structures:** single bonds are not drawn and groups of atoms are clustered when possible.



- ▷ **Molecular formula:** simply shows number of each type of atom with no structural information.



- ▷ Example of converting a condensed structure into a partially condensed structure:

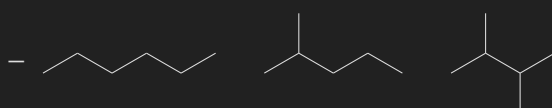


- This shows just one isomer, more partially condensed structures are possible.

Bond-Line Structures

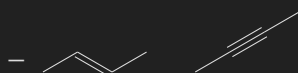
- ▷ **Bond-line structures;** aka skeletal structures; simplify drawing process of chemical structures and are easier to read.

- Each corner or endpoint represents a carbon atom.



- All examples have 6 carbon atoms

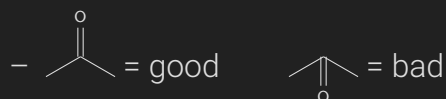
- Double bonds are shown with two lines, triple with three.



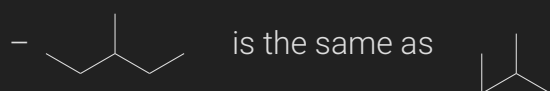
- Triple bonds are drawn linearly due to sp-hybridization
- Hydrogens are not shown; it is assumed that each carbon possesses enough to satisfy octet rule.

Notes on Drawing Bond-Line Structures

- Carbon atoms in a straight chain should be drawn in zigzag format in order to accurately show each carbon.
- Double bonds should be drawn as far apart as possible:



- Direction of a single bond is irrelevant:



- All **heteroatoms** (atoms other than carbon and hydrogen) must be drawn.
 - Hydrogens next to heteroatoms must be shown.
- Carbons cannot have more than four bonds.

Hydrogen Deficiency Index: Degrees of Unsaturation

Excerpt from Chapter 14: Infrared Spectroscopy and Mass Spectrometry

Hydrogen Saturation

































- ▷ **Saturated compounds:** the maximum number of hydrogen atoms possible, relative to number of carbon present.
 - Determining saturation using molecular formula: C_nH_{2n+2} n = carbon atoms
 - **Halogens:** takes the place of a hydrogen atom; **add one H** for each halogen.
 - **Oxygen:** no affect on saturation; **ignore**.
 - **Nitrogen:** needs an extra hydrogen; **subtract one H** for each nitrogen.
- ▷ **Unsaturated compounds:** a compound that contains at least one π bond, resulting fewer than the maximum number of hydrogen atoms.
 - Compounds with rings also result in an unsaturated compound.
 - **Degree of unsaturation:** a number that represents **half** the "missing" number of hydrogen atoms when compared to a saturated compound.

Hydrogen Deficiency Index

- **Hydrogen deficiency index (HDI)**: the measure of degrees of unsaturation.
 - e.g. two degrees of unsaturation results in a HDI of 2.
 - Degrees of freedom help represent possible structures, indicating possible double bonds, triple bonds, rings, or various combinations of each.
 - Only helpful when molecular formula is known for certainty.
- Formula: $\text{HDI} = \frac{1}{2}(2C + 2 + N - H - X)$
 - X: halogen atoms.

Identifying Functional Groups

- ▷ **Functional group**: specific substituents or moieties within molecules that may be responsible for the characteristic chemical reactions.
 - **Substituents**: an atom or group of atoms which replaces one or more hydrogen atoms on the parent hydrocarbon chain.
 - **Moiety**: a part of a molecule which is typically found within other molecules and often given a specific name.

FUNCTIONAL GROUP*	CLASSIFICATION	EXAMPLE	CHAPTER	FUNCTIONAL GROUP*	CLASSIFICATION	EXAMPLE	CHAPTER
 (X=Cl, Br, or I)	Alkyl halide	 n-Propyl chloride	7		Ketone	 2-Butanone	19
	Alkene	 1-Butene	7, 8		Aldehyde	 Butanal	19
	Alkyne	 1-Butyne	9		Carboxylic acid	 Pentanoic acid	20
	Alcohol	 1-Butanol	12		Acyl halide	 Acetyl chloride	20
	Ether	 Diethyl ether	13		Anhydride	 Acetic anhydride	20
	Thiol	 1-Butanethiol	13		Ester	 Ethyl acetate	20
	Sulfide	 Diethyl sulfide	13		Amide	 Butanamide	20
	Aromatic (or arene)	 Methylbenzene	17, 18		Amine	 Diethylamine	22

* The "R" refers to the remainder of the compound, usually carbon and hydrogen atoms.

Identifying Lone Pairs

- ▷ Formal charges must always be drawn on bond line structures, otherwise the resulting bond line structures would be inferred incorrectly.
- ▷ Lone pairs do not have to be drawn and usually are omitted.
- ▷ The formal charge allows you to determine lone pairs.
 - Formula: $FC = V - N - \frac{B}{2}$
 - V = valence electrons of element
 - N = lone pair electrons
 - B = bonded electrons
 - Solve for lone pairs: $N = V - FC - \frac{B}{2}$
- ▷ Frequent usage will allow for intuition for lone pairs.

Common Patterns Between Formal Charge and Lone Pairs

◦ Associated Patterns for Oxygen

- A negative (\ominus) charge corresponds with one bond and three lone pairs.
- The absence of charge corresponds with two bonds and two lone pairs.
- A positive (\oplus) charge corresponds with three bonds and one lone pair

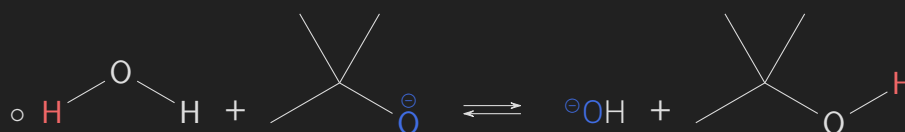
◦ Associated Patterns for Nitrogen

- A negative charge corresponds with two bonds and two lone pairs.
- The absence of charge corresponds with three bonds and one lone pair.
- A positive charge corresponds with four bonds and no lone pairs

3 Acids and Bases

Introduction to Brønsted-Lowry Acids and Bases

- ▷ **Acid:** a proton donor; i.e., a H^+ donor.
- ▷ **Base:** a proton acceptor; i.e., a OH^- (hydroxide ion), which wants a H^+ to form the more stable H_2O .
- ▷ General definition: acid + base \rightleftharpoons conjugate base + conjugate acid
- ▷ Symbolically: $\text{HA} + \text{B} \rightleftharpoons \text{A}^- + \text{HB}^+$
- ▷ Example using bond-line structures:



Lewis Acids and Bases

- ▷ The Lewis definition is more broad than the Brønsted-Lowry definition.
- ▷ Lewis describes acidity in terms of electrons, rather than protons.
- ▷ **Lewis acid:** electron-pair acceptor.
- ▷ **Lewis base:** electron-pair donor.
- ▷ Most reactions are described in terms of Lewis base and acids, since molecules without donatable protons are unable to be described by the Brønsted-Lowry definition.

Nucleophiles and Electrophiles

Excerpt from Chapter 6: Chemical Reactivity and Mechanisms \leftrightarrow

- ▷ **Ionic reactions**, aka polar reactions: reactions that involve the participation of ions as reactants, intermediates, or products.
 - Most cases ions act as intermediates.
 - Radical reactions and pericyclic reactions are also major categories, but are typically not discussed in undergraduate courses.
 - Ionic reactions occur when one reactant has a site of high electron density and the other reactant has a site of low electron density.
- ▷ **Nucleophiles:** an electron rich atom that is capable of donating a pair of electrons.
 - Nucleophiles are Lewis bases.

- Any atom that possesses a localized lone pair can be nucleophilic.
- π bonds can also function as nucleophiles due to their region of space having high electron density.
- **Polarizability**: the ability of an atom to distribute its electron density unevenly in response to external influences.
 - Correlated with size of the atom, which increases the number electrons that are distant from the nucleus.
- ▷ **Electrophiles**: an electron-deficient atom that is capable of accepting a pair of electrons.
 - Electrophiles are Lewis acids.

Flow of Electron Density: Curved-Arrow Notation

- ▷ All reactions are accomplished via a flow of electron density.
- ▷ Electron density flow is illustrated with curved arrows.
 - **Reaction mechanism**: how the reaction occurs in terms of the motion
 - All ionic mechanisms, regardless of complexity, are combinations of four characteristic patterns of electron flow (*discussed later*).

Notes on Drawing Curved Arrows

- **Tails** must be placed on either a bond or a lone pair.
 - Shows the **source**, i.e., the electron donor (base).
 - Electrons can only be found in lone pairs or bonds, so **never place the tail** of a curved arrow on a **positive charge**.
- **Heads** must be placed so that it shows either the formation of a bond or the formation of a lone pair.
 - Shows the **destination**, i.e., the electron acceptor (acid).
 - Avoid drawing an arrow that violates the octet rule, so never draw an arrow that gives more than four orbitals to a second-row element.

4 Alkanes and Cycloalkanes

Introduction to Alkanes



Nomenclature of Alkanes

