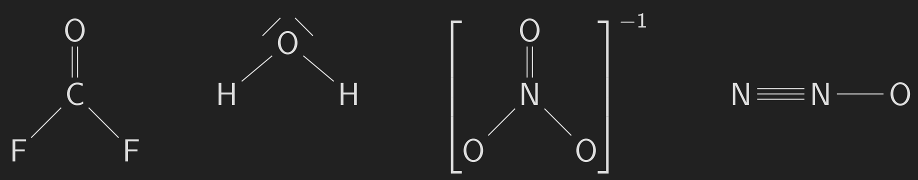
Contents

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 it's 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 represnets covalent bonds as straight lines and lonpairs 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 valance electrons.
- Determing formal charge:
  - Formula: $FC = V - N - \frac{B}{2}$
  - V = valance 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 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 withdrawl of electrons towards to more electronegative atom. δ^+ represnets partial positive charged gained when electrons are pulled away, while δ^- represnets 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 insetsad 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 orbtails 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 descrices 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 produes 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 accroding to MO theory.

▷ Atomic orbitals refer to an individual atom, while molecular orbitals is associated with an entire molecular.

▷ 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 preperties.

Hybridized Atomic Orbitals

▷ **sp^3-hybridized orbitals**: produced by averaging one *s* orbital and three *p* orbitals.

- Hybridized orbitals explains to geomtry of methane, which results form 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 expain geometry of compounds bearing a double bond.
- A double bond if 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. Determin 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 = groups - 1
4. For groups 5-6: sp^{3}d^x; x = 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, sp^3-sp^3 is the weakest.

Molecular Geometry

- **Valence shell electron pair repulsion (VSEPR) theory**: enables the prediction of molecular geometry due to the pressumption 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 tetrahendron 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 H_2O correctly, but for wrong reasons.
    - The lone pairs in H_2O 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 geomterical structure predicted (EDG) by VSEPR using steric number.
     - Octahedral:6, Bipyramid: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 on either end of the dipole multiplied by the distance separtion, 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 determed 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 intereactions 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 restult 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 boling points.
  - Branched hydrocarbons generally have decreased surface area, decreasing boiling point relative to others of similar weight.

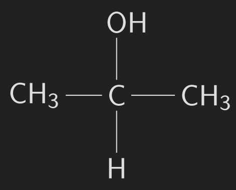
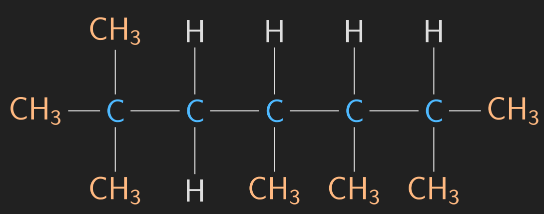
- When comparing boling points of compounds, look for following factors:
  - Any dipole-dipole interactions? Formation of hydrogen bonds?
  - Number of carbon atoms. (surface area)
  - Degree of branching of compound. (surface area)

Structural Theory of Matter

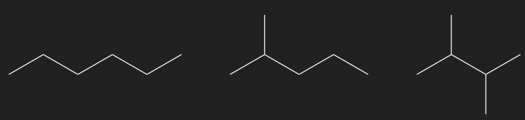
- **Constitutional isomers**: aka structural isomers; same chemical formula, but different in the way the atoms are connect, i.e. their constitution is different.
  - Consistenet with the octet rule.
  - Each element forms a predictable number of bonds, from one to four.
  - The number of possbile constitutional 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 possbile.
  - $CH_3CH_3CHOH \longrightarrow (CH_3)_2CHOH$
- **Molecular formula**: simply shows number of each type of atom with no structural information.
  - C_3H_8O
- Example of converting a condensed structure into a partially condensed structure:
  - $(CH_3)_3CCH_2CH(CH_3)CH(CH_3)CH(CH_3)_2$
  - 
  - This shows just one isomer, more partially condensed structures are possible.

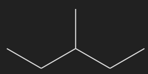
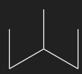
Bond-Line Structures

- **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 posses enough to satisfy octet rule.

Notes on Drawing Bond-Line Structrues

- 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:
  -  = good  = bad
- Direction of a single bond is irrelevant:
  -  is the same as 
- 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 possbile, 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 represnets 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 possbile structures, indicating possible double bounds, triple bounds, rings, or various combinations of each.
  - Only helpful when molecular formula is known for certainty.
- Formula: 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.

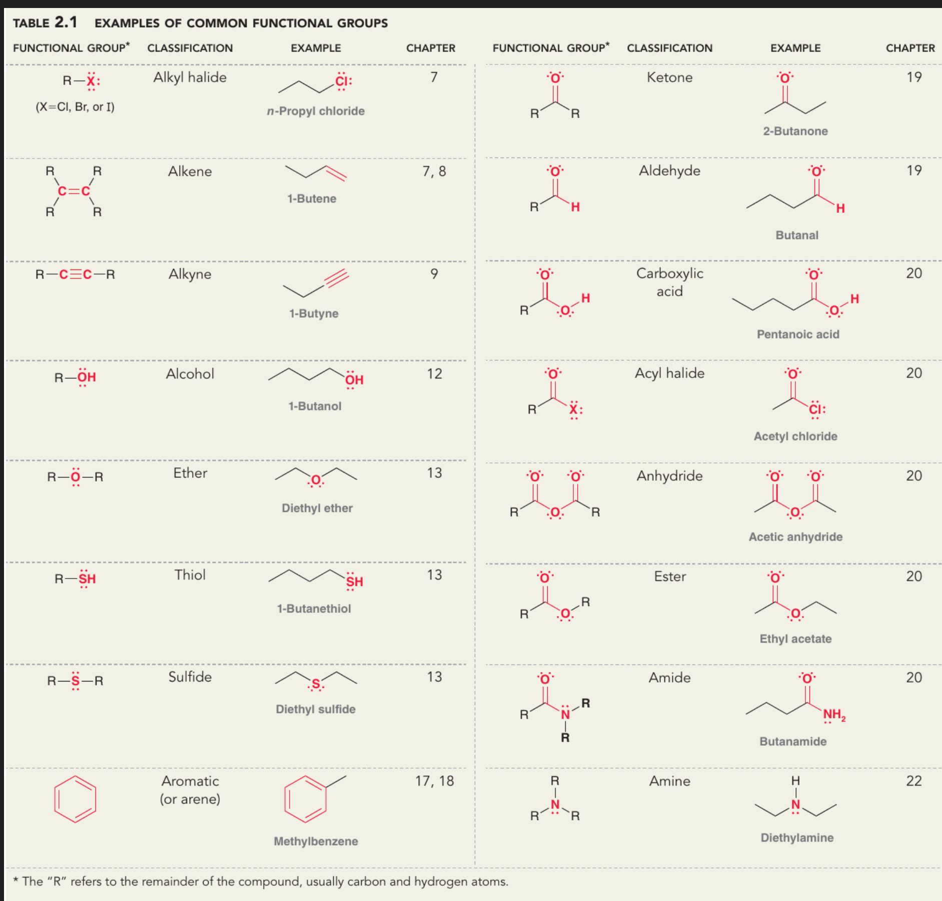


TABLE 2.1 EXAMPLES OF COMMON FUNCTIONAL GROUPS

FUNCTIONAL GROUP*	CLASSIFICATION	EXAMPLE	CHAPTER
R—X: (X=Cl, Br, or I)	Alkyl halide	*n*-Propyl chloride	7
	Alkene	1-Butene	7, 8
R—C≡C—R	Alkyne	1-Butyne	9
R—OH	Alcohol	1-Butanol	12
R—O—R	Ether	Diethyl ether	13
R—SH	Thiol	1-Butanethiol	13
R—S—R	Sulfide	Diethyl sulfide	13
	Aromatic (or arene)	Methylbenzene	17, 18
	Ketone	2-Butanone	19
	Aldehyde	Butanal	19
	Carboxylic acid	Pentanoic acid	20
	Acyl halide	Acetyl chloride	20
	Anhydride	Acetic anhydride	20
	Ester	Ethyl acetate	20
	Amide	Butanamide	20
	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 strcutres would be inferred incorrectly.
- Lone pairs do not have to be drawn and usually are omitted.
- The formal charge allows you to determin lone pairs.
  - Formula: $FC = V - N - \frac{B}{2}$
  - V = valance 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.

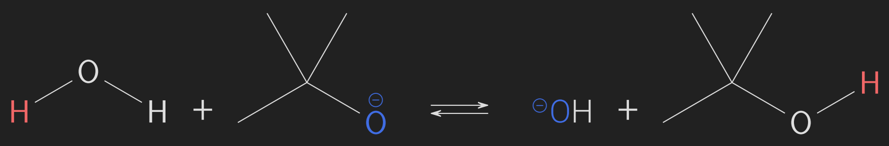
Common Patterns Between Formal Charge and Lone Pairs

- **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 bond 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 Bønsted-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: $HA + B \rightleftharpoons A^- + HB^+$
- 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 ↦

- **Ionic reactions**, aka polar reactions: reactions that involve the particpation 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.

4 Alkanes and Cycloalkanes

Introduction to Alkanes

- ▷

Nomenclature of Alkanes

- ▷