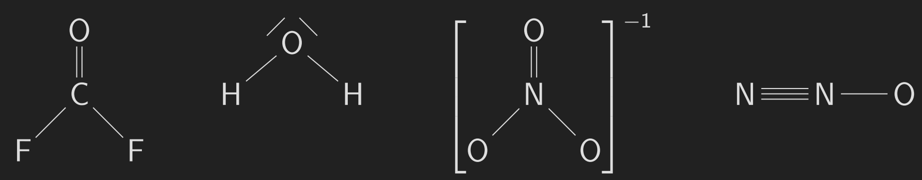
Contents

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.
  - **F, O, N, Cl** (Br, I). Most electronegative elements, from left to right, that are often encountered.
- **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 commoly 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.
    - **Ion-dipole**: electrostatic interaction between an ion and a molecule with a dipole.
  - **Hydrogen bonding**: molecules with a hydrogen attached to an F, O, or N.
    - Not actually a bond, just an interaction.
    - When hydrogen bonds to a electronegative atom, then the hydrogen will have a δ^{+}.
    - 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.
    - Stronger than dipole-dipole interactions.

- **Fleeting dipole-dipole interactions**:
  - Electrons are considered to be in constant motion, which restult in the center of negative charge to vary.
  - **London Dispersion Forces (LDFs)**: On average, the dipole moment is zero, though it can experience transient dipole moments, initiating fleeting attraction/repulsion.
    - All atoms and molecules have LDFs.
    - Weakest, but the dominant force in non-polar molecules.
    - Dispersion forces directly related to molar mass.
  - 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? (increases boiling point)
- Formation of hydrogen bonds? (increase boling point)
- Number of electrons. (more electrons, higher boiling point)
- Number of carbon atoms. (more surface area, higher boiling point)
- Degree of branching of compound. (more branching, more surface area)

Structural Theory of Matter

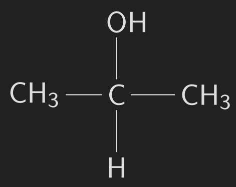
▷ **Constitutional isomers**: aka structural isomers; same chemical formula, but different in the way the atoms are connect, i.e. their constitution is different.
- Consistenet with the octet rule.
- Each element forms a predictable number of bonds, from one to four.
- The number of possbile constitutional isomers increases as the number of carbon atoms increases

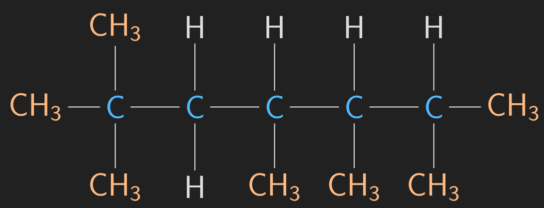
▷ **Stereoisomers**: isomers that differ in spatial arrangement of atoms, rather than connectivity.
- **Geometric isomerism**: aka cis–trans; locked into spatial positions due to double bonds or a ring structure.
  - Cis indicates functional groups that are on the same side of the carbon chain.

    - 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

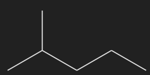
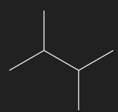
Types of Molecular Representations

- **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:
  - $(CH_3)_3CCH_2CH(CH_3)CH(CH_3)CH(CH_3)_2$
  - 

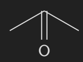
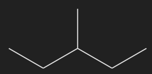
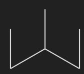
  - This shows just one isomer, more partially condensed structures are possible.

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

- ▷ **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 (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

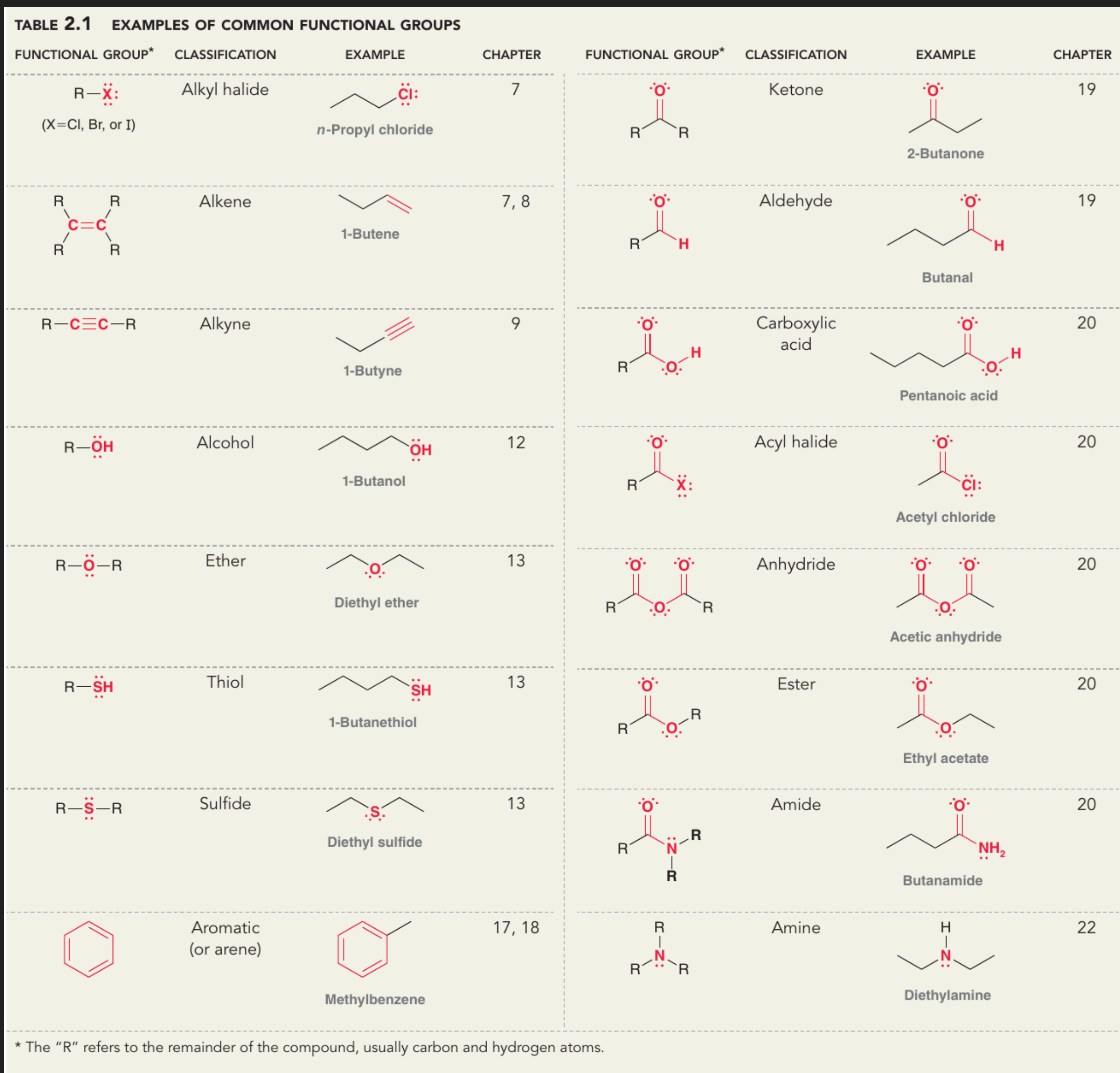


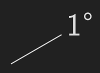
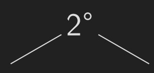
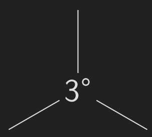
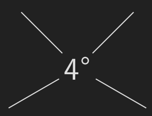
TABLE 2.1 EXAMPLES OF COMMON FUNCTIONAL GROUPS

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.

- **Functional group (R)**: 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.

Characterizing Carbon Centers and Functional Groups

- **Characterizing Carbon Centers**
  - Primary 1°: a carbon with only one carbon-carbon bond.
    - $H_3C{-}CH_3$ 
  - Secondary 2°: a carbon with two carbon-carbon bonds.
    - $H_3C{-}CH_2{-}CH_3$ 
  - Tertiary 3°: a carbon with 3 carbon-carbon bonds.
    - $(CH)_3{-}CH$ 
  - Quaternary 4°: a carbon with four carbon-carbon bonds.
    - $(CH)_4{-}C$ 
- **Characterizing Functional Groups**
  - Certain functional groups can be characters as 1°, 2°, or 3°, based on how many carbon bonds are attached to the carbon with the functional group.

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 (⊖) charge corresponds with 1 bond and 3 lone pairs.
  - The absence of charge corresponds with 2 bonds and 2 lone pairs.
  - A positive (⊕) charge corresponds with 3 bonds and 1 lone pair.
- **Associated Patterns for Nitrogen**
  - A negative charge corresponds with 2 bonds and 2 lone pairs.
  - The absence of charge corresponds with 3 bonds and 1 lone pair.
  - A positive charge corresponds with 4 bonds and 0 lone pairs.

Resonance

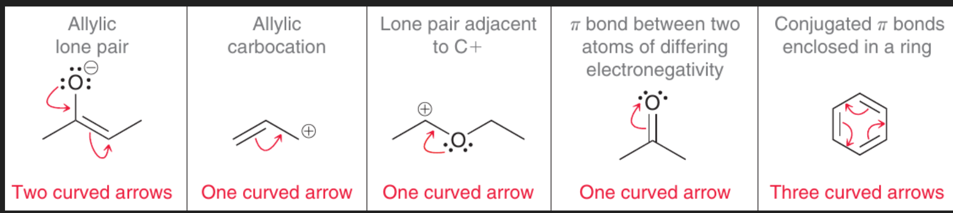
- **Resonance**: description of bonding in molecules or ions by the combination of multiple contributing strcutres.
  - **Resonance structures**: each contributing structure of the resonance hybrid.
    - Formal charges are important to include when drawing resonance structures as it clarifies where locations of lone pairs and movement of electrons.
    - Total charge must remain the same between structures.
- Resonance does not describe any real process, rather it's a method to overcome inadequacy of bond-line drawings.
- Different from isomerism, which differs in arrangements of atomic nuclei in space, rather than how the electrons are assigned to the depictions.

Resonance: Curved Arrows

- **Curved arrows**: a tool used to help draw resonance strcutres by representing electrons as if they were moving.
  - Somwhat different from curved arrow notation in reactions, which actually represent the flow of electron density.
  - Can help shows how to change the formal charge:
    - Formal charges at the tail become more positive, since it's losing an electron.
    - Formal charges at the head more negative, since it's gaining an electron.
- Avoid breaking a single bond.
  - Structures must have atoms connected in same order, though there are minor exceptions that *will be discussed later*.
  - This rule affects the placement of the tail of the arrow, as it represents distribution of previous electrons.
- Never exceed an octet for second-row elements.
  - Not a violation to have less than an octet.
  - This rule affects the placement of the head of the arrow, as it represents sharing of new electrons.
- Can only be used on adjcent atoms, though the electrons can be pushed multiple times.
- "Legal" moves:
  - π bond $\rightarrow$ lone pair.
  - Lone pair $\rightarrow$ π bond.
  - π bond $\rightarrow$ π bond.
  - Every resonance structure can be built through a combination of above three moves.

Common Patterns of Resonance Structures

- **Vinylic**: the two carbon atoms bearing the double bond of a carbon-carbon double bond.
- **Allylic**: atoms connected directly to vinylic positions.



Resonance Hybrid

- **Resonance hybrid**: respresents the *average* of the contributing structures, with bond lengths and partial charges taking on intermediate values.
- No matter how many resonance structures are drawn, they collectively represent one entity.
- Drawn partial bonds and charges to illustrate the delocalization of electrons.

Delocalization

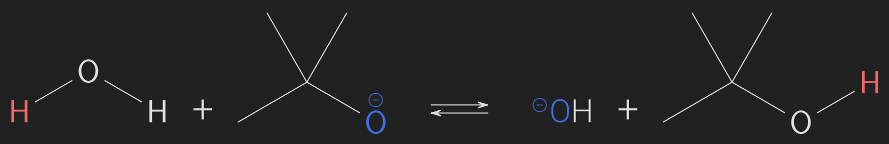
- **Delocalization**: the spreading of electrons between multiple atoms or covalent bonds.
  - **Resonance stabilization**: molecules and ions that are stabalized by the delocalization of electrons.
  - Plays a major role in the outcome of many reactions.
- When a lone pair particpates in resonance, it will occupy a *p* orbtail rather than hybridized; important for 3d shapes of proteins.
- **Localized lone pair**: when a lone pair is not allylic to a π bond.
  - Whenever an atom posses both a π bond and a lone pair, they will not both participate in resonance.
  - Usually π bonds participate first.

Contributor Significance

- Some resonance structures may resemble the actual molecule more than another, in regards to energy and stability.
- Strcures with low potential energy are more stable compared to those of higher values and resemble the actual structure more.
- **Major contributors**: the most stable contributing structures.
- **Minor contributors**: less favorable contributing strcutres.
- Rules for contributing significance, descending:
  - The greatest number of filled octets.
  - The greatest number of covalent bonds.
  - Minimize formally charged atoms.
  - Separation of unlike and like charges, minimized and maximized respectively.
  - Negative charges placed on the most electronegativity atoms, positive charges placed on the less electronegative atoms.
  - Do not deviate substantially from idealized bond lengths and angles.
  - Maintain aromatic substructures locally while avoiding anti-aromatic ones.

3 Acids and Bases

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: $HA + B \rightleftharpoons A^- + HB^+$
  - The strength of the acid/base is inversley proportional to the strength of the conjugate acid/base.
- Most acid-base reactions are reversible.
  - Strong acids tend to be less reversible.
- Example using bond-line structures:
  - 

Quantitative Perspective

- **Equilibrium**: when there is no longer an observable change in concentrations of reactants and products.
  - $K_{eq} = \frac{[H_3O^+][A^-]}{[HA][H_2O]}$
  - Water concentration is fairly constant and can be removed, giving K_a.
    - $K_a = K_{eq}[H_2O] = \frac{[H_3O^+][A^-]}{[HA]}$
  - K_a tends to be large, so it's converted to pK_a.
    - $pK_a = -\log K_a$
    - Generally ranges from -10 (strong acid) to 50 (strong base).
  - pK_a (H^+) can be easily converted to pK_b (OH^-):
    - $pK_b = 14 - pK_a$
- Equilibrium favors formation of the weaker (higher pK_a) acid.
  - Reactions with vastly different pK_a values make the reverse proccess is negligible.
  - Can ignore the reverse reaction in such cases and treat it as a reaction in one direction.

Qualitiative Perspective

- Relative acid strength can be determind by comparing conjugate bases.
  - The more stable (weaker) the conjugate base, the stronger the acid.
  - Does not predict pK_a, just a means of comparing relative acid strenghts with out known pK_a
- **Stabilization factors**: (1) atom bearing the charge, (2) resonance, (3) induction, and (4) orbitals.
  - Generally follow decending order of significance; absence of difference in earlir factors allow for later factors to express more significance.
- **Atom bearing the charge**: Compare atoms bearing negative charge in each conjugate base after deprotonation.
  - First determin if atoms are in same row or column in the periodic table.
  - Row comparison: electronegativity is the dominant effect; stability is greater when the negative charge is on the more electronegative element.
  - Column comparsion: size is the dominant effect; stability is greater when the negative charge is on the larger element.
- **Resonance**: charge that is delocalized across multiple atoms will lead to more stable structures comapred to molecules with no resonance.
  - Helps determing relative stability when both molecules bare the same elements that have a difference in charge.
  - Again, more stability means it's the weaker conjugate base, meaning the proton removed from the atom creating the resonance hybrid will be more acidic.
- **Induction**: induction of other atoms can act to withdraw the negative charge away from the new electronegatively charged atom due to deprotonation.
  - Inductive effect diminishes the further the electronegative atom is away from the depronated atom.
- **Orbitals**: negative charges on atoms with lower hybridization result in greater stability due to proximity to positive nucleus, i.e., $sp > sp^2 > sp^3$
  - sp = triple bond, sp^2 = double bond, sp^3 = three σ bonds.

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.
- All Bønsted-Lowry acids and bases are Lewis acid and bases, but the inverse is not always true.
- 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.

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 meachanisms, 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

Nomenclature of Alkanes

- **Alkane**: acyclic (linear structure) saturated hydrocarbons (no π bonds).
  - General chemical formula: C_nH_{2n+2}
- **Substituents**: branches connected to the parent chain.

Selecting the Parent Chain

- **Parent chain**: the longest carbon chain in an alkane.

Parent Names for Alkanes

Number of Carbons	Parent	Name
1	meth	methane
2	eth	ethane
3	pro	propane
4	but	butane
5	pent	pentane
6	hex	hexane
7	hept	heptane
8	oct	octane
9	non	nonane
10	dec	decane
11	undec	undecane
12	dodec	dodecane
13	tridec	tridecane
14	tetradec	tetradecane
15	pentadec	pentadecane
20	eicos	eicosane
30	triacont	triacontane
40	tetracont	tetracontane
50	pentacont	hectane
100	hect	hectane

- **Substituents**: branches connected to the parent chain, can be a single atom, groups of atoms, that replace one or more hydrogen atoms.
  - If there is competition between chains of equal length, then choose the chain with greatest number of substituents.
- **Cycloalkanes (cyclo)**: presence of a ring in an alkane.

Naming Substituents

- **Alkyl groups**: Substituents that are named the same as the parents, but with the added letters ly.

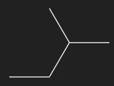
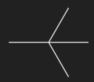
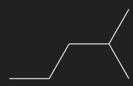
Names of Alkyl Groups

Substituent Carbons	Terminology
1	methyl
2	ethyl
3	propyl
4	butyl
5	pentyl
6	hexyl
7	heptyl
8	octyl
9	nonyl
10	decyl

- When a group is connected to the ring, then the ring is generally treated as the parent.
  - If the ring has fewer atoms the the rest of the structure, then it becomes a substituent.

Naming Complex Subsituents

- **Complex substituents**: branched alkyl substituents.
- Begin by numbering carbons going away from the parent chain, then name it as if its a parent chain itself.
  - Complex substituent are placed in parentheses, indicating it as a single substituent of the parent chain.
- Some complex substituents have common names that are so well established and allowed by IUPAC.
  - An alkyl group bearing three carbon atoms; only one way to branch it.
    - **Isopropyl group**: (1-methylethyl): 
  - Alkyl groups bearing four carbon atoms, which can be branched three different ways:
    - **sec-butyl** (1-methylpropyl): 

        - **isobutyl** (2-methylpropyl): 
        - **tert-butyl** (1,1-dimethylethyl): 
    - Alkyl groups bearing five carbons, which can be branched many more ways. Two common ways:
        - **isopentyl (isoamyl)** (3-methylbutyl): 
        - **neopentyl** (2,2-dimethylpropyl): 

Assembling the Systematic Name

- **Locant**: the location of a carbon numbered parent chain.
- Rules for assinging locant:
    - If one substituent is present, then assign the lowest number possbile.
    - When multiple substituents are present, then the first substituent receives the lowest number.
        - If there is a tie, the second locant should be as low as possible.
        - If tie cannot be broken, then lowest number is assigned alphabetically.
    - Prefixes are used when the same substituent appears more than once.
        - di:2, tri:3, tetra:4, penta:5, 6:hexa
    - Hypens are used to separate numbers from letters, while commas are used to separate numbers from each other.
    - Substituents are alphabeticalized after all locants are correctly assigned.
        - Prefixes are ignored during alphabeticalization.
- Summary of discrete steps:
    1. **Identify parent chain**
    2. **Identify and name substituents**
    3. **Number the parent chain and assign a locant to each substituent**
    4. **Arrange the substituents alphabetically**

Constitutional Isomers of Alkanes

- For an alkane, the number of possible constitutional isomers increases with increaseing molecular size.
- Determing IUPAC name is the best way to tell if two alkanes are constitutional isomers, or just different representations of the same one.

Constitutional Isomers for Various Alkanes

Molecular Formula	Constitutional Isomers
C_3H_8	1
C_4H_{10}	2
C_5H_{12}	3
C_6H_{14}	5
C_7H_{16}	9
C_8H_{18}	18
C_9H_{20}	35
$C_{10}H_{22}$	75
$C_{15}H_{32}$	4,347
$C_{20}H_{42}$	366,319
$C_{40}H_{62}$	4,111,846,763

Newman Projections

- **Conformations**: the variety of possible three-dimensional shapes of a compound that are interchangeable by low energy pathways.
  - Conformations vary in potential energy.
  - Changes due to rotation about σ bonds.
- **Configurations**: refer to different orientations in space that require breaking of bonds (high energy pathway) to change.
  - Cis and trans isomers in alkenes (*discussed later*)
- **Newman projections**: a type of representation of compounds specially designed for showing the conformation of a molecule.
  - Drawn from the angle of the observer, with the front carbon represented in front of the circle, and the back carbon behind the circle.
  - ***Chemmacros package is broken due to font usage, need to figure out how to fix that before inserting drawings***

Conformational Analysis of Ethane and Propane

- **dihedral (torsional) angle**: the angle between atoms of front and back carbons as the σ bonds rotates.
- There are an infinite number of possbile conformations, but there are conformations of maximum and minium energy.
  - **Staggered conformation**: lowest energy conformation.
  - **Eclipsed conformation**: the highest energy conformation.
- **Degenerate**: when all staggered conformations have the same amount of energy.
  - All staggered and eclipsed conformations of ethanes are degenerate.
- **Torsional strain**: the difference in energy between staggered and eclipsed conformations.
  - Recent quantum methods suggest conformation possesses a favorable interaction between occupied, bonding molecular orbitals and unoccupied, antibonding molecular orbitals.
  - An increase in potential energy occurs when the favorable overalp is broken.
  - A sample of ethane gas at room temperature will have $\approx 99\%$ of its molecules staggered.
- Ethane has total cost of $12\,\mathrm{kJ/mol}$ ($4\,\mathrm{kJ/mol/H}$), while propane has total cost of $14\,\mathrm{kJ/mol}$.
  - Reasonable estimates of energy cost of an H eclipsing a CH_3 group must be $6\,\mathrm{kJ/mol}$.

Conformational Analysis of Butane

- Butane has three eclipsed conformations that are not degenerate.
  - Dihedral angle of 0° has the highest eclipsed energy, while both conformations at $\pm 120^\circ$ are second highest in energy and degenerate.
  - Likewise, a dihedral angle of 180° has the lowest staggered energy, while both conformations at $\pm 60^\circ$ are second lowest in energy and degenerate.
- **Anti conformation**: the conformation with a dihedral angle of 180; the lowest staggered energy.
  - Occurs when the methyl groups are farthest apart.

- **Steric interaction**: nonbonding intereactions that influences energy levels conformations.
- **Gauche interaction**: unfavorable intereaction between methyl groups, causing an increases in energy due to electron cloud repulsion.
  - Gauche intereaction is a type of steric intereactions present at $\pm 60°$.
  - Has an energy cost $3.8\,\mathrm{kJ/mol}$
- Total cost of butane: $19\,\mathrm{kJ/mol}$.
  - Energy cost of eclipsing CH_3: $11\,\mathrm{kJ/mol}$
  - Energy cost of eclipsing CH_3/H: $6\,\mathrm{kJ/mol}$

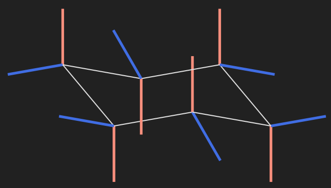
Cycloalkanes

- **Angle strain**: the increases in energy associated with a bond angle that has deviated from the preferred angle of $109.5°$.
  - Cyclic alkanes, excpet cyclopropane, are not planar.
  - Expected angels are different than origanally proposed by Adolph von Baeyer, which assumed rings were planar.
  - Angle strain is only one factor that contributes to the energy of various ring sizes.
- **Cyclopropane**:
  - Under significant angle strain.
  - Locked into an eclipsed conformation due to triangular structure; exhibiting significant torsional strain.
  - Thus highly reactive and very susceptible to ring-opening reactions.
- **Cyclopentane**:
  - Less angle strain than cyclopropane.
  - More torsional strian than cyclopropane due to four sets eclipsing hydrogens.
  - Adopts slightly "puckered" shape, which is the cause of reduced angle strain.
- **Cyclopentane**:
  - Less total strain than both cyclopropane and cyclopentane.
  - Can adopt a relatively low strained conformation.

Conformations of Cyclohexane

- **Chair conformation**:
  - Bond angles close to $109.5°$; little angle strain.
  - No torsional strain; all hydrogens are staggered.
  - Least potential energy of cyclohexane conformations.
  - **Half-chair**: highest potential energy, formed via interchange between alternate chair form; leads into twisted boat.
- **Boat conformation**:
  - Bond angles also close to $109.5°$; little angle strain.
  - Two sources of torsional strain; many of hydrogens are eclipsed.
  - One hydrogen on each side experiences a steric interaction called the flagpole intereaction.
  - Second highest potential energy.
  - **Twisted boat**: second lowest potential energy, a slightly less strained version of boat that avoids some of the flagpole interaction.
- Majority of cyclohexanes are found in chair form. All other forms are intermediates between alternate chair forms.

Drawing Chair Conformations

- 
- **Axial position**: parallel to a vertical axis passing through the center of the ring.
  - less stable than equatorial due to steric strain.
- **Equatorial**: positioned approximately along the equator of the ring.
- 
- The chair is more stable when the methyl (substituent) group is in the equatorial position.
  - The larger the substituent, the more equatorial-substituted conformer is favored.