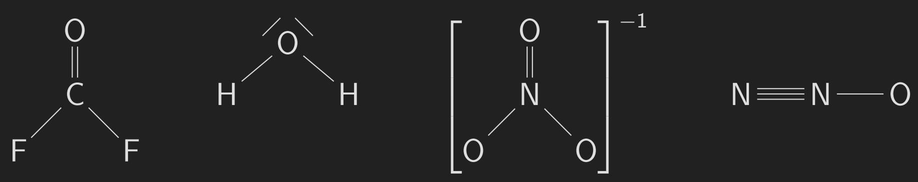
Contents

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

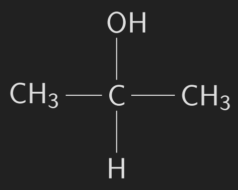
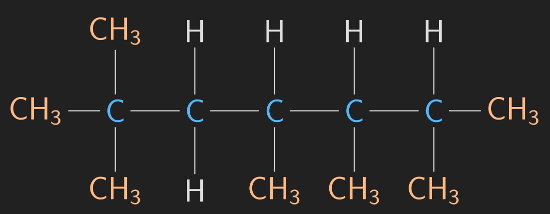
▷ **Constitutional isomers**: aka structural isomers; same chemical formula, but different in the way the atoms are connect, i.e. their constitution is different.
- Consistenet with the octet rule.
- Each element forms a predictable number of bonds, from one to four.

- The number of possbile constitutional isomers increases as the number of carbon atoms increases

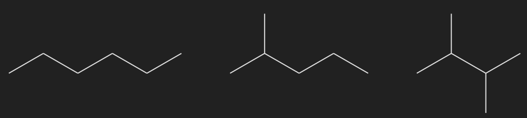
- **Stereoisomers**: isomers that differ in spatial arrangement of atoms, rather than connectivity.
    - **Geometric isomerism**: aka cis–trans; locked into spatial positions due to double bonds or a ring structure.
        - Cis indicates functional groups that are on the same side of the carbon chain.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

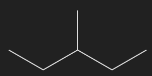
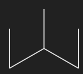
- **Partially condensed structures**: the C−H bonds are not always drawn, saving space.
  - 
- **Condensed structures**: single bonds are not drawn and groups of atoms are clustered when possbile.
  - $CH_3CH_3CHOH \longrightarrow (CH_3)_2CHOH$
- **Molecular formula**: simply shows number of each type 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

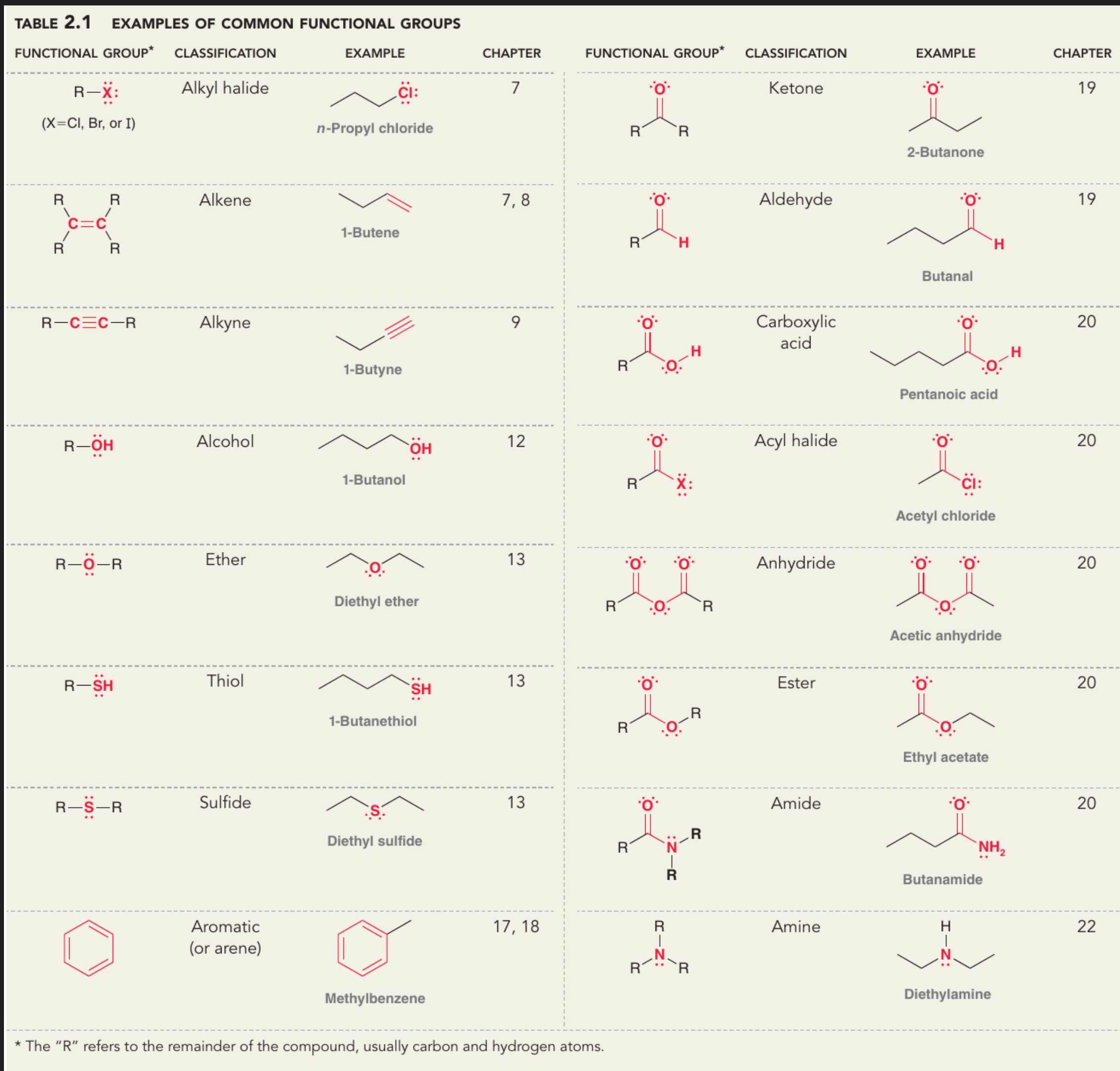


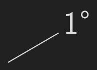
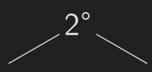
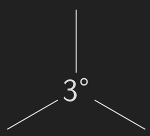
TABLE 2.1 EXAMPLES OF COMMON FUNCTIONAL GROUPS

FUNCTIONAL GROUP*	CLASSIFICATION	EXAMPLE	CHAPTER
R—X: (X=Cl, Br, or I)	Alkyl halide	*n*-Propyl chloride	7
$R_2C=CR_2$	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 one bond and three lone pairs.
- The absence of charge corresponds with two bonds and two lone pairs.
- A positive (⊕) 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

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 about three moves.

Patterns in Drawing Resonance Structures

- **Vinylic**: two carbon atoms bearing the double of a carbon-carbon double bond.
- **Allylic**: atoms connected directly to vinylic positions.
- **Allylic lone pair**: an atom that contains lone pairs and adjacent to a carbon-carbon double bond.
  - Any lone pair next to a π bond can serve the same function for the purposes of drawing resonance structures.
  - Two pushes of electrons will be ultimately be needed.
- **Allylic carbocation**: a positive charge located in an allylic position.
  - Only one arrow required, represents the π bond $\rightarrow$ π bond push.
  - **Conjugated**: when two π bonds are separated by a single π bond.
-

Contributor Significance

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Resonance Hybrid

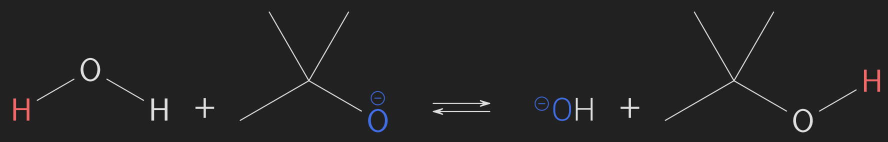
- **Resonance hybrid**: respresents the *average* of the contributing structures, with bond lengths and partial charges taking on intermediate values.

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.

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.

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

Introduction to Alkanes

- ▷

Nomenclature of Alkanes

- ▷