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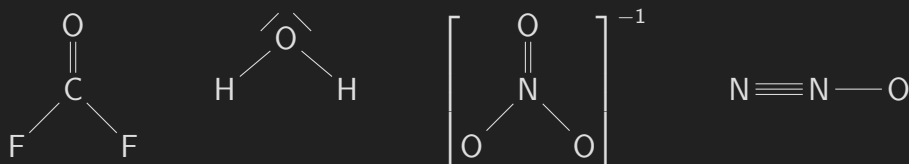
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# 1 General Chemistry Review

## Electrons, Bonds, and Lewis Structures

- ▷ **Covalent bond:** two atoms sharing a pair of electrons.
- ▷ **Octet rule:** *main group elements* that tend to bond in a way that each atom has **eight** electrons in its valence shell.
  - Atoms that do not have eight will share electrons with other elements in order to maintain a stable state.
- ▷ **Main group elements:** sometimes called representative elements, are groups 1, 2 and 13–18 in periodic table.
  - Some elements in group 3 and 12 share properties between transition metals and the main group.
- ▷ The lowest energy (most stable) state of two atoms is determined both by bond length and bond strength.
- ▷ Valence electrons are determined by the group, 1A–8A, of the periodic table.
- ▷ **Lone pair:** unshared, or nonbonding, electrons.
- ▷ **Lewis structures:** 2D model that represents covalent bonds as straight lines and lone pairs as dots.
- ▷ Examples:  $\text{COF}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{NO}_3^-$ ,  $\text{N}_2\text{O}$ :



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

## Identifying Formal Charges

- **Formal charge:** any atom that does not exhibit the appropriate number of valence electrons.
- Determining formal charge:
  - Formula:  $FC = V - N - \frac{B}{2}$
  - V = valence electrons of element
  - N = lone pair electrons
  - B = bonded electrons
- **Less** than expected number of valence electrons results in a **positive** charge.
- **More** than expected number of valence electrons results in a **negative** charge.
- The lower the **magnitude** of formal charge, the **greater the stability** of the whole molecule.
- Atoms that are **more electronegative** hold **negative** formal charges better, which results in **greater stability** vs when the negative charge is spread on less electronegative elements in a polyatomic species.
  - The dominant resonance structure will be that of the greatest stability.

## Induction and Polar Covalent Bonds

- ▷ Bonds can be classified into three categories: covalent, polar covalent, and ionic.
- ▷ The categories emerge from the electronegativity values of the atoms sharing a bond.
- ▷ **Electronegativity:** a measure of the ability of an atom to attract electrons.
  - Electronegativity generally **increases left to right**, and from the **bottom to top** of the periodic table.
  - **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 withdrawal of electrons towards a more electronegative atom.  $\delta^+$  represents partial positive charge gained when electrons are pulled away, while  $\delta^-$  represents the partial negative charge pulled closer.

- ▷ **Ionic bond:** when the difference in electronegativity is **greater than 1.9**.
  - Electrons are not shared in this case, and attraction is instead just the result of oppositely charged ions.

### Dipole Moments and Molecular Polarity

- **Dipole moment ( $\mu$ ):** defined as the amount of partial charge,  $\delta$ , on either end of the dipole multiplied by the distance separation,  $d$ :
  - $\mu = \delta d$
  - $\mu$  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.

### Atomic Orbitals

- ▷ **Atomic orbital (AO):** standing quantum wave (excitation in electron field) around an atom.
  - More energy leads to higher orbital levels.
    - Gives principle quantum number,  $n$ , as is associated with distance from nucleus.
  - Orbital levels: s(1 pair), p(3 pairs), d(5 pairs), f(7 pairs).
    - Angular momentum quantum number that describes three-dimensional region of space that the electron density occupies.
  - Magnetic quantum number describes orientation in space of electron density.
    - $m_l = 0$ ; s orbital
    - $m_l = -1, 0, 1$ ;  $p_x, p_y, p_z$  orbitals.
  - Locations where  $\psi$  (quantum wave function) is zero are called **nodes**.
    - The **more nodes** that an orbital has, the **greater** its energy.
  - *Spin*: allows an orbital to contain only two electrons,  $\pm \frac{1}{2}$
- ▷ **Degenerate orbitals:** orbitals with the same energy level.
- ▷ Order in which orbitals are filled is determined by three principles:

- **Aufbau principle:** lowest energy orbital is filled first.
- **Pauli exclusion principle:** each orbital can accommodate a maximum of two electrons that have opposite spin.
- **Hund's rule:** electrons are placed in each degenerate orbital before being paired up.
- ▷ Describing the nature of atomic orbital is done with two commonly used theories: *Valence Bond Theory* and *Molecular Orbital Theory*.
- ▷ The commonly used theories give a deeper understanding of covalent bonds, which is essentially just the **overlap of atomic orbitals**.
- ▷ **Constructive/destructive interference:** the result of two waves that approach each other, or overlap.
  - Constructive interference produces a wave with the vector sum of both waves.
  - Destructive interference cancel each other out and produces a node.

### Valence Bond Theory

- **Valence bond theory:** the sharing of electron density between two atoms is a result of the constructive interference of their atomic orbitals.
- *Bond axis:* the line that can be drawn between two hydrogen atoms.
- **Sigma bond ( $\sigma$ ):** a particular type of covalent bond that has circular symmetry with respect to the bond axis.
  - All single bonds are  $\sigma$  bonds.
  - The strongest type of covalent bond.
- **Pi bond ( $\pi$ ):** 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.
  - $\pi$  bonds form double ( $\sigma + \pi$ ) and triple bonds ( $\pi + \sigma + \pi$ ).
  - Individual  $\pi$  bonds are weaker than  $\sigma$  bonds.

## Molecular Orbital Theory

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

## Hybridized Atomic Orbitals

- **$sp^3$ -hybridized orbitals:** produced by averaging one s orbital and **three** p orbitals.
  - Hybridized orbitals explains 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  **$\sigma$  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  $\pi$  bond.
  - This is done to expain geometry of compounds bearing a double bond.

- A double bond is formed from one  $\sigma$  bond and one  $\pi$  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  $\pi$  bonds.
  - A triple bond is formed with the addition of one  $\sigma$  bond due to the overlap of the sp orbitals.
  - Geometry of a triple bond has *linear geometry*.
- Finding the hybridization of any atom can be done simply:
  1. Look at the central item.
  2. Determine groups (number of bonds,  $\pi$  bonds count as 1, and lone pairs attached) of atom.
    - groups aka regions of electron density.
  3. For groups 1-4:  $sp^x$ ;  $x = \text{groups} - 1$
  4. For groups 5-6:  $sp^3d^x$ ;  $x = \text{groups} - 4$
- Bond Strength and Bond Length:
  - Bond length **decreases** with more bonds.
  - Bond strength **increases** with more bonds.
  - The more **s character**, the **shorter** and **stronger** the bond, and the **larger** the bond angle.
    - *s-character*: contribution of the  $\sigma$  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 presumption that all electron pairs repel each other; resulting in a three-dimensional space that maximizes distance from each other.
- ▷ **Steric number:** the total number of electron pairs in a molecule. Can be bonds or lone pairs.
- ▷ **Tetrahedral geometry:** result of four  $\sigma$  bonds and zero lone pairs.
  - produces a tetrahedron with bond angles of  $109.5^\circ$ .
- ▷ **Trigonal pyramidal geometry:** three  $\sigma$  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  $107^\circ$ .
  - The lone pair sits atop the base forming a pyramid like structure.
- ▷ **Bent geometry:** two  $\sigma$  bonds and two lone pairs.
  - VSEPR predicts the lone pairs to be in two corners of the tetrahedral, producing bond angles of  $105^\circ$ .
  - VSEPR predicts geometry  $\text{H}_2\text{O}$  correctly, but for wrong reasons.
    - The lone pairs in  $\text{H}_2\text{O}$  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  $120^\circ$  and lie on the same plan.
- ▷ **Linear geometry:** two electron pairs that oppose each other at  $180^\circ$ , forming a linear structure.
- ▷ General method of determining structure:
  1. Count steric number—the total number of electron pairs in a molecule. Can be bonds or lone pairs.
  2. Determine predicted geometrical structure predicted (EDG) by VSEPR using steric number.
    - Octahedral:6, Bipyrmaid:5, Tetrahedral:4, Trigonal:3, Linear:2
  3. Determin impact (the MG) of lone pairs; more lone pairs results in less space between bonded pairs. Shape depends on EDG.

## Intermolecular Forces and Physical Properties

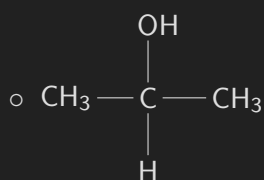
- ▷ **Intermolecular forces:** the attractive forces between individual molecules that determined the physical properties of a compound.
- ▷ *Electrostatic:* forces that occur as a result of the attraction between opposite charges.
- ▷ Electrostatic interactions for neutral molecules (no formal charge) are often classified as into the following categories:
  - **Dipole-dipole interaction:** Compounds with **net dipole** moments.
    - In **solid** space these interactions either **repel or attract** each other.
    - In **liquid** space these interactions tend to **attract more often**, raising melting/boiling point.
    - **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  $\delta^+$ .
    - 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 result 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 boiling points.
    - Branched hydrocarbons generally have decreased surface area, decreasing boiling point relative to others of similar weight.

- ▷ When comparing boiling points of compounds, look for following factors:
  - Any dipole-dipole interactions? (increases boiling point)
  - Formation of hydrogen bonds? (increase boiling 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)

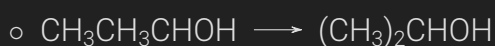
## 2 Molecular Representations

### Types of Molecular Representations

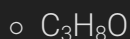
- ▷ **Partially condensed structures:** the C–H bonds are not always drawn, saving space.



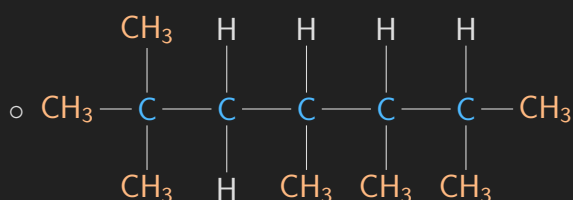
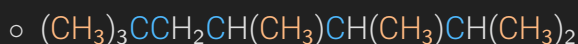
- ▷ **Condensed structures:** single bonds are not drawn and groups of atoms are clustered when possible.



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



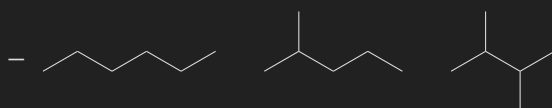
- ▷ Example of converting a condensed structure into a partially condensed structure:



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

### Bond-Line Structures

- **Bond-line structures;** aka skeletal structures; simplify drawing process of chemical structures and are easier to read.
- Each corner or endpoint represents a carbon atom.



- All examples have 6 carbon atoms

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

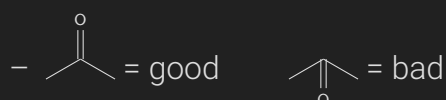


- Triple bonds are drawn linearly due to sp-hybridization

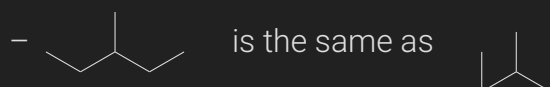
- Hydrogens are not shown; it is assumed that each carbon possesses enough to satisfy octet rule.

### Notes on Drawing Bond-Line Structures

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



- Direction of a single bond is irrelevant:



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

### Hydrogen Deficiency Index: Degrees of Unsaturation

*Excerpt from Chapter 14: Infrared Spectroscopy and Mass Spectrometry*

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

- Degrees of freedom help represent possible structures, indicating possible double bonds, triple bonds, rings, or various combinations of each.
- Only helpful when molecular formula is known for certainty.
- Formula:  $\text{HDI} = \frac{1}{2}(2C + 2 + N - H - X)$ 
  - $X$ : halogen atoms.

## Identifying Functional Groups

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

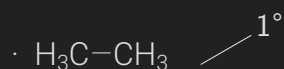
\* The "R" refers to the remainder of the compound, usually carbon and hydrogen atoms.

- ▷ **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.

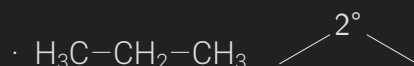
## Characterizing Carbon Centers and Functional Groups

### Characterizing Carbon Centers

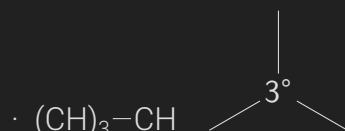
- Primary  $1^\circ$ : a carbon with only one carbon-carbon bond.



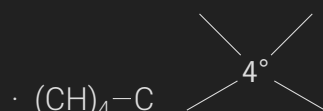
- Secondary  $2^\circ$ : a carbon with two carbon-carbon bonds.



- Tertiary  $3^\circ$ : a carbon with 3 carbon-carbon bonds.



- Quaternary  $4^\circ$ : a carbon with four carbon-carbon bonds.



### Characterizing Functional Groups

- Certain functional groups can be characters as  $1^\circ$ ,  $2^\circ$ , or  $3^\circ$ , 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 structures would be inferred incorrectly.
- ▷ Lone pairs do not have to be drawn and usually are omitted.
- ▷ The formal charge allows you to determine lone pairs.
  - Formula:  $FC = V - N - \frac{B}{2}$
  - $V$  = valence electrons of element
  - $N$  = lone pair electrons
  - $B$  = bonded electrons
  - Solve for lone pairs:  $N = V - FC - \frac{B}{2}$
- ▷ Frequent usage will allow for intuition for lone pairs.

### Common Patterns Between Formal Charge and Lone Pairs

- **Associated Patterns for Oxygen**

- A **negative** ( $\ominus$ ) charge corresponds with **1 bond** and **3 lone pairs**.
- The absence of charge corresponds with **2 bonds** and **2 lone pairs**.
- A **positive** ( $\oplus$ ) 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 structures.
- **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.

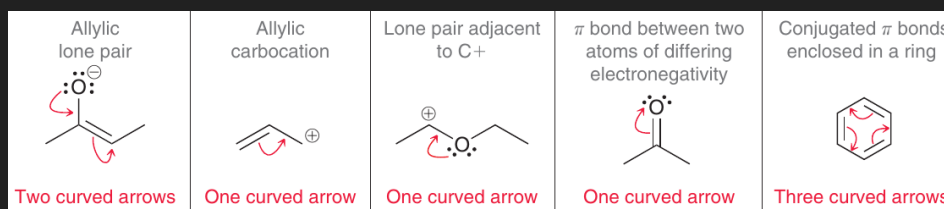


### Resonance: Curved Arrows

- **Curved arrows:** a tool used to help draw resonance structures by representing electrons as if they were moving.
  - Somewhat different from curved arrow notation in reactions, which actually represent the flow of electron density.
  - Can help show 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 adjacent atoms, though the electrons can be pushed multiple times.
- "Legal" moves:
  - $\pi$  bond  $\rightarrow$  lone pair.
  - Lone pair  $\rightarrow \pi$  bond.
  - $\pi$  bond  $\rightarrow \pi$  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:** represents 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 **stabilized** by the delocalization of electrons.
  - Plays a major role in the outcome of many reactions.
- When a lone pair participates in resonance, it will occupy a *p* orbital rather than hybridized; important for 3d shapes of proteins.
- **Localized lone pair:** when a lone pair is not allylic to a  $\pi$  bond.
  - Whenever an atom possesses both a  $\pi$  bond and a lone pair, they will not both participate in resonance.
  - Usually  $\pi$  bonds participate first.

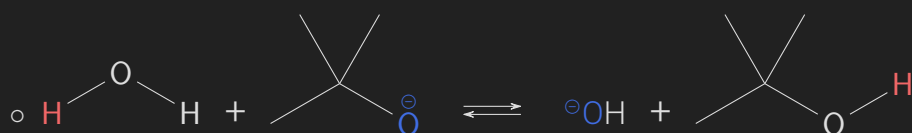
**Contributor Significance**

- Some resonance structures may resemble the actual molecule more than another, in regards to energy and stability.
- Structures 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 structures.
- 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  $\text{H}^+$  donor.
- ▷ **Base:** a **proton acceptor**; i.e., a  $\text{OH}^-$  (hydroxide ion), which wants a  $\text{H}^+$  to form the more stable  $\text{H}_2\text{O}$ .
- ▷ General definition: **acid + base**  $\rightleftharpoons$  **conjugate base + conjugate acid**
  - Symbolically:  $\text{HA} + \text{B} \rightleftharpoons \text{A}^- + \text{HB}^+$
  - 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.
  - $K_{eq} = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}][\text{H}_2\text{O}]}$
  - Water concentration is fairly constant and can be removed, giving  $K_a$ .
    - $K_a = K_{eq} [\text{H}_2\text{O}] = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$
  - $K_a$  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).
  - $pK_a (\text{H}^+)$  can be easily converted to  $pK_b (\text{OH}^-)$ :
    - $pK_b = 14 - pK_a$
- Equilibrium **favors formation** of the **weaker** (higher  $pK_a$ ) acid.
  - Reactions with vastly different  $pK_a$  values make the reverse process is negligible.
  - Can ignore the reverse reaction in such cases and treat it as a reaction in one direction.

### Qualitative Perspective

- Relative acid strength can be determined 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 strengths without known  $pK_a$ .
- **Stabilization factors:** (1) **atom bearing the charge**, (2) **resonance**, (3) **induction**, and (4) **orbitals**.
  - Generally follow descending order of significance; absence of difference in earlier 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 determine 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 comparison:** **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 compared to molecules with no resonance.
  - Helps determine relative stability when both molecules bear 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 deprotonated 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  $\sigma$  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 Brønsted-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 participation of ions as reactants, intermediates, or products.
  - Most cases ions act as intermediates.
  - Radical reactions and pericyclic reactions are also major categories, but are typically not discussed in undergraduate courses.
  - Ionic reactions occur when one reactant has a site of **high electron density** and the other reactant has a site of **low electron density**.
- ▷ **Nucleophiles**: an electron rich atom that is capable of donating a pair of electrons.
  - **Nucleophiles are Lewis bases**.
  - Any atom that possesses a localized lone pair can be nucleophilic.
  - $\pi$  bonds can also function as nucleophiles due to their region of space having high electron density.
  - **Polarizability**: the ability of an atom to distribute its electron density unevenly in response to external influences.
    - Correlated with size of the atom, which increases the number electrons that are distant from the nucleus.
- ▷ **Electrophiles**: an electron-deficient atom that is capable of accepting a pair of electrons.
  - **Electrophiles are Lewis acids**.

## Flow of Electron Density: Curved-Arrow Notation

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

### Notes on Drawing Curved Arrows

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

## 4 Alkanes and Cycloalkanes

### Nomenclature of Alkanes

- ▷ **Alkane:** acyclic (linear structure) saturated hydrocarbons (no  $\pi$  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 **yl**.

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 than the rest of the structure, then it becomes a substituent.



## Naming Complex substituents

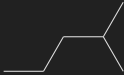

- **Complex substituents:** branched alkyl substituents.
- Begin by numbering carbons going **away** from the parent chain, then name it as if it's a parent chain itself.
  - Complex substituents are placed in parentheses, indicating it as a single substituent of the parent chain.
- Some complex substituents 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 assigning locant:
  - If one substituent is present, then assign the lowest number possible.
  - 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
  - Hyphens 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 increasing molecular size.
- ▷ Determining 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
$C_{40}H_{82}$	4,111,846,763

## Newman Projections

- ▷ **Conformations:** the variety of possible three-dimensional shapes of a molecule that are interchangeable by low energy pathways.
  - Conformations vary in potential energy.
  - Changes due to rotation about  $\sigma$  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 substituents of front and back carbons as the  $\sigma$  bonds rotates.
- There are an infinite number of possible conformations, but there are conformations of maximum and minimum energy.
  - **Staggered conformation:** **lowest energy** conformation, when two substituents are at maximum dihedral angle from each other.
  - **Eclipsed conformation:** the **highest energy** conformation, when two substituents are at the minimum dihedral angle from each other.
- **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 overlap is broken.
  - A sample of ethane gas at room temperature will have  $\approx 99\%$  of its molecules staggered.
- Ethane has total cost of 12 kJ/mol (4 kJ/mol/H), while propane has total cost of 14 kJ/mol.
  - Reasonable estimates of energy cost of an H eclipsing a  $\text{CH}_3$  group must be 6 kJ/mol.

### Conformational Analysis of Butane

- Butane has three eclipsed conformations that are **not degenerate**.
  - Dihedral angle of  $0^\circ$  has the highest eclipsed energy, while both conformations at  $\pm 120^\circ$  are second highest in energy and degenerate.
  - Likewise, a dihedral angle of  $180^\circ$  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  $180^\circ$ ; the lowest staggered energy.
  - Occurs when the methyl groups are farthest apart.
- **Steric interaction**: nonbonding interactions that influences energy levels conformations.
- **Gauche interaction**: unfavorable intereaction between substituents, causing an increases in energy due to electron cloud repulsion.
  - Gauche intereaction is a type of steric intereactions present at  $\pm 60^\circ$  of the next eclipsed conformation.
- Costs of butane: 19 kJ/mol, 16 kJ/mol, 3.8 kJ/mol
  - Energy cost of eclipsing  $\text{CH}_3/\text{CH}_3$ : 11 kJ/mol
  - Energy cost for gauche interaction of  $\text{CH}_3/\text{CH}_3$  3.8 kJ/mol for butane.
  - Energy cost of eclipsing  $\text{CH}_3/\text{H}$ : 6 kJ/mol
  - Energy cost of eclipsing  $\text{H}/\text{H}$ : 4 kJ/mol

### Cycloalkanes

- ▷ **Angle strain**: the increases in energy associated with a bond angle that has deviated from the preferred angle of  $109.5^\circ$ .
  - 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 strain 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  $109.5^\circ$ ; 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  $109.5^\circ$ ; 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 interaction**.
- Second highest potential energy.
- **Twisted boat:** second lowest potential energy, a slightly less strained version of boat that avoids some of the flagpole interaction.

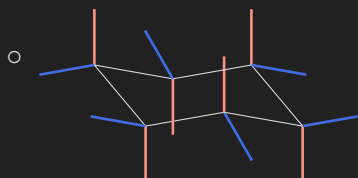
- Majority of cyclohexanes are found in chair form. All other forms are intermediates between alternate chair forms.

### 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.

## 5 Stereoisomerism

### Overview of Stereoisomerism

- ▷ **Constitutional isomers:** aka structural isomers; same **chemical formula**, but different in the way the **atoms are connect**, i.e. their constitution is different.
- ▷ **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:** functional groups that are on the **same side** of the carbon chain.
    - **Trans:** functional groups on **opposite sides** of the carbon chain.
    - *Cis-trans* terminology is used to describe disubstituted alkenes (carbon chain with  $\pi$  bond), even when the the two substituents are different from each other.
      - Does not apply to disubstituted alkenes in which the substituents are connect in the same position.

### Chirality

- **Superimposable (achiral):** when an an object's mirrored version is identical to the actual object.
- **Chiral:** objects that are not superimposable.
- All three-dimensional objects can be classified as either chiral or achiral.
- **Enantiomer:** the nonsuperimposable mirror image of a chiral compound.
  - Can be used in speech the same way **twin** is used.
- The most common source of molecular chirality is the presence of a carbon bearing **four different groups**.
  - **Chirality (chiral) center:** a tetrahedral carbon that bears four different groups.

### Cahn-Ingold-Prelog System

▷

### Optical Activity

▷



## Enantiomers and Diastereoisomers



## Symmetry and Chirality

