

# Contents

## General Chemistry Review

Electrons, Bonds, and Lewis Structures . . . . .	2
Identifying Formal Charges . . . . .	3
Induction and Polar Covalent Bonds . . . . .	3
Atomic Orbitals. . . . .	4
Valence Bond Theory. . . . .	5
Molecular Orbital Theory . . . . .	5
Hybridized Atomic Orbitals. . . . .	6
Molecular Geometry . . . . .	7
Dipole Moments and Molecular Polarity . . . . .	8
Intermolecular Forces and Physical Properties . . . . .	8
Structural Theory of Matter . . . . .	9

## Molecular Representations

Types of Molecular Representations . . . . .	11
Bond-Line Structures . . . . .	11
Notes on Drawing Bond-Line Structures . . . . .	12
Hydrogen Deficiency Index: Degrees of Unsaturation . . . . .	12
Identifying Functional Groups . . . . .	13
Characterizing Carbon Centers and Functional Groups . . . . .	14
Identifying Lone Pairs . . . . .	14
Common Patterns Between Formal Charge and Lone Pairs . . . . .	15
Resonance. . . . .	15
Resonance: Curved Arrows . . . . .	16
Common Patterns of Resonance Structures . . . . .	17
Resonance Hybrid . . . . .	17
Delocalization . . . . .	17
Contributor Significance . . . . .	18

## Acids and Bases

Bønsted-Lowry Acids and Bases . . . . .	19
Quantitative Perspective . . . . .	19
Qualitative Perspective . . . . .	20
Lewis Acids and Bases . . . . .	20
Nucleophiles and Electrophiles . . . . .	21
Flow of Electron Density: Curved-Arrow Notation . . . . .	21
Notes on Drawing Curved Arrows. . . . .	22

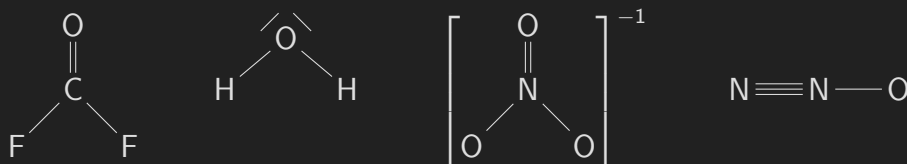
## Alkanes and Cycloalkanes

Introduction to Alkanes . . . . .	23
Nomenclature of Alkanes. . . . .	23

# 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 to 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.

## Atomic Orbitals

- ▷ **Atomic orbital (AO):** standing quantum wave (excitation in electron field) around an atom.
  - More energy leads to higher orbitals 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** it's energy.
  - *Spin*: allows an orbital to contain only two electrons,  $\pm\frac{1}{2}$
- ▷ **Degenerate orbitals:** orbitals with the same energy level.
- ▷ Order in which orbitals are filled is determined by three principles:
  - **Aufbau principle:** lowest energy orbital is filled first.
  - **Pauli exclusion principle:** each orbital can accommodate a maximum of two electrons that have opposite spin.
  - **Hund's rule:** electrons are placed in each degenerate orbital before being paired up.
- ▷ Describing the nature of atomic orbital is done with two commonly used theories: *Valence Bond Theory* and *Molecular Orbital Theory*.
- ▷ The commonly used theories give a deeper understanding of covalent bonds, which is essentially just the **overlap of atomic orbitals**.
- ▷ **Constructive/destructive interference:** the result of two waves that approach each other, or overlap.
  - Constructive interference produces a wave with the vector sum of both waves.
  - Destructive interference cancel each other out and produces a node.

## Valence Bond Theory

- ▷ **Valence bond theory**: the sharing of electron density between two atoms is a result of the constructive interference of their atomic orbitals.
- ▷ *Bond axis*: the line that can be drawn between two hydrogen atoms.
- ▷ **Sigma bond ( $\sigma$ )**: 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<sup>3</sup>-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<sup>2</sup>-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<sup>x</sup>; x = groups - 1
  4. For groups 5-6: sp<sup>3</sup>d<sup>x</sup>; 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  $\sigma$  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  $H_2O$  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  $120^\circ$  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.

## 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.

## 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)

## Structural Theory of Matter

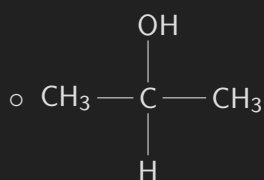
- ▷ **Constitutional isomers:** aka structural isomers; same **chemical formula**, but different in the way the **atoms are connect**, i.e. their constitution is different.
  - Consistent with the octet rule.
  - Each element forms a predictable number of bonds, from one to four.
  - The number of **possible constitutional isomers increases** as the number of **carbon atoms increases**
- ▷ **Stereoisomers:** isomers that differ in **spatial arrangement** of atoms, rather than connectivity.
  - **Geometric isomerism:** aka cis–trans; **locked into spatial positions** due to double bonds or a ring structure.
    - Cis indicates functional groups that are on the same side of the carbon chain.

- Trans indicates functional groups on opposite sides of the carbon chain.
  - **Enantiomers:** aka optical isomers; mirror images of each other that are non-superposable.
    - Human hands are a macroscopic analogy.
- ▷ *More detail will be covered in later sections.*

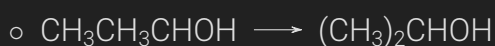
## 2 Molecular Representations

### Types of Molecular Representations

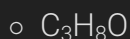
- ▷ **Partially condensed structures:** the C–H bonds are not always drawn, saving space.



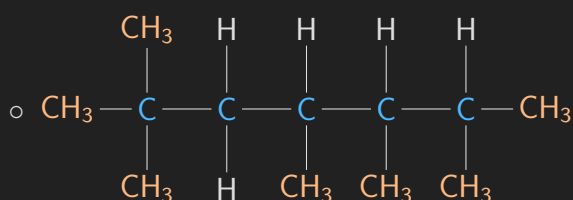
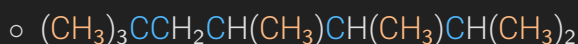
- ▷ **Condensed structures:** single bonds are not drawn and groups of atoms are clustered when possible.



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



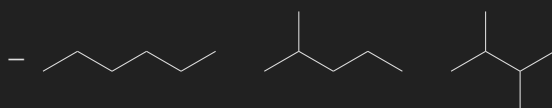
- ▷ Example of converting a condensed structure into a partially condensed structure:



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

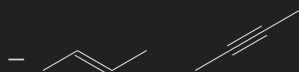
### Bond-Line Structures

- **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.

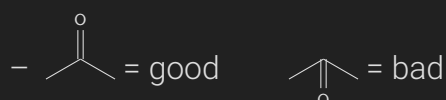


- Triple bonds are drawn linearly due to sp-hybridization

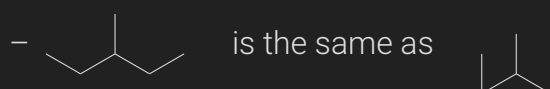
- Hydrogens are not shown; it is assumed that each carbon possesses enough to satisfy octet rule.

### 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	Ketone	 2-Butanone	19
 Alkene	Alkene	 1-Butene	7, 8	 Aldehyde	Aldehyde	 Butanal	19
$\text{R}-\text{C}\equiv\text{C}-\text{R}$	Alkyne	 1-Butyne	9	 Carboxylic acid	Carboxylic acid	 Pentanoic acid	20
$\text{R}-\ddot{\text{O}}\text{H}$	Alcohol	 1-Butanol	12	 Acyl halide	Acyl halide	 Acetyl chloride	20
$\text{R}-\ddot{\text{O}}-\text{R}$	Ether	 Diethyl ether	13	 Anhydride	Anhydride	 Acetic anhydride	20
$\text{R}-\ddot{\text{S}}\text{H}$	Thiol	 1-Butanethiol	13	 Ester	Ester	 Ethyl acetate	20
$\text{R}-\ddot{\text{S}}-\text{R}$	Sulfide	 Diethyl sulfide	13	 Amide	Amide	 Butanamide	20
 Aromatic (or arene)	Aromatic (or arene)	 Methylbenzene	17, 18	 Amine	Amine	 Diethylamine	22

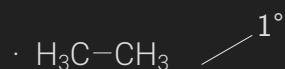
\* The "R" refers to the remainder of the compound, usually carbon and hydrogen atoms.

- ▷ **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.

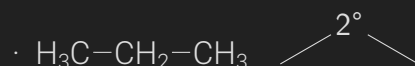
## Characterizing Carbon Centers and Functional Groups

### Characterizing Carbon Centers

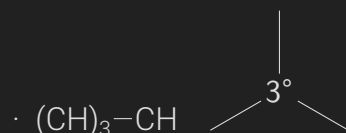
- Primary  $1^\circ$ : a carbon with only one carbon-carbon bond.



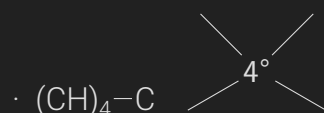
- Secondary  $2^\circ$ : a carbon with two carbon-carbon bonds.



- 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 characterized 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

#### o 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.

#### o 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.
- o **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.

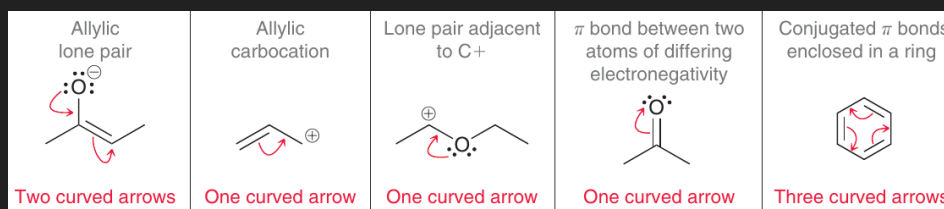
### Resonance: Curved Arrows

- **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.

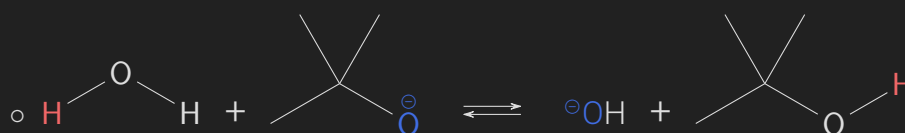
**Contributor Significance**

- 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** 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**.
  - Influences negative charge stability, in relative order of effect.
- **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:**
- **Induction:**
- **Orbitals:**

### 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 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

### Introduction to Alkanes

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### Nomenclature of Alkanes

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