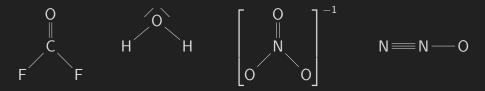
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1 General Chemistry Review

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 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 represents covalent bonds as straight lines and lonpairs as dots.
- \triangleright Examples: COF₂, H₂O, NO₃, N₂O:



▶ **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: $FC = V N \frac{B^1}{2}$
 - ∘ 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, CI** (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^+ represents partial positive charged gained when electrons are pulled away, while δ^- 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 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
 - $-m_{I}=-1,0,1; p_{x}, p_{y}, p_{z} \text{ orbitals.}$
 - \circ 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.
- \triangleright **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.
- \triangleright **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.
 - \circ π bonds form double $(\sigma + \pi)$ and triple bonds $(\pi + \sigma + \pi)$.
 - \circ 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.
- \triangleright 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.
 - o Describes strength, order, and polarity of bonds.
 - Allows for the presence of paired or unpaired electrons.
 - Has spectroscopic preperties.

Hybridized Atomic Orbitals

- \triangleright **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.
 - \circ All bonds in are σ bonds, and thus can be individually represented by the overlap of atomic orbitals.
- \triangleright **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.
 - o 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.
 - o 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^3d^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 =
$$50\%$$
, sp² = 33% , sp³ = 25%

sp-sp bond is the strongest, sp³-sp³ 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.
- \triangleright **Tetrahedral geometry**: result of four σ bonds and zero lone pairs.
 - o produces a tetrahendron with bond angles of 109.5°.
- \triangleright **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.
- \triangleright **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 H₂O 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 geometrical 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

- \triangleright **Dipole moment** (μ): defined as the amount of partial charge, δ , on on either end of the dipole multiplied by the distance separtion, d:
 - $\circ \mu = \delta d$
 - \circ μ generally has an order of magnitude of $10^{-18}\,\mathrm{esu}\cdot\mathrm{cm}$ due to general partial charge (esu) and distance (cm) values.
 - \circ 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.
 - o 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)
 - o 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.
 - o 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.
 - CH₃CH₃CHOH → (CH₃)₂CHOH
- ▶ **Molecular formula**: simply shows number of each type of atom with no structural information.
 - o C₃H₈O
- Example of converting a condensed structure into a partially condensed structure:
 - (CH₃)₃CCH₂CH(CH₃)CH(CH₃)₂
 CH₃ H H H H
 CH₃ C C C C C CH₃
 CH₃ H CH₃ CH₃ CH₃
 - 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

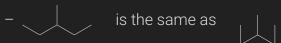
• Hydrogens are not shown; it is assumed that each carbon posses enough to satisfy octet rule.

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

o 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.

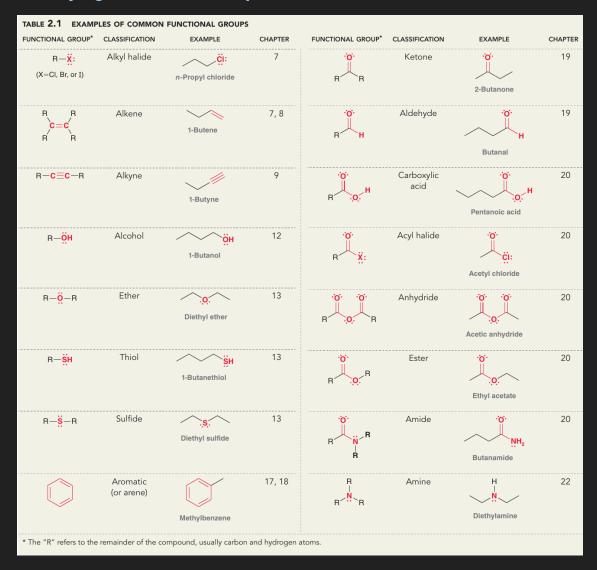
Hydrogen Deficiency Index: Degrees of Unsaturation

Excerpt from Chapter 14: Infrared Spectroscopy and Mass Spectrometry

- ▶ **Saturated compounds**: the maximum number of hydrogen atoms possbile, relative to number of carbon present.
 - o 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.
- \triangleright **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 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 possbile structures, indicating possible double bounds, triple bounds, rings, or various combinations of each.
- o Only helpful when molecular formula is known for certainty.
- Formula: HDI = $\frac{1}{2}(2C + 2 + N H X)$
 - X: halogen atoms.

Identifying Functional Groups



- ▶ **Functional group (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.

- Secondary 2°: a carbon with two carbon-carbon bonds.

- Tertiary 3°: a carbon with 3 carbon-carbon bonds.

- Quaternary 4°: a carbon with four carbon-carbon bonds.

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 structures would be inferred incorrectly.
- ▶ Lone pairs do not have to be drawn and usually are omitted.
- ▶ The formal charge allows you to determin lone pairs.

• Formula:
$$FC = V - N - \frac{B}{2}$$

- V = valance electrons of element
- N = lone pair electrons
- B = bonded electrons

• Solve for lone pairs:
$$N = V - FC - \frac{B}{2}$$

▶ Frequent usage will allow for intuition for lone pairs.

Common Patterns Between Formal Charge and Lone Pairs

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

Resonance

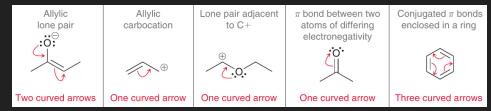
- ▶ **Resonance**: description of bonding in molecules or ions by the combination of multiple contributing strcutres.
 - **Resonance structures**: each contributing structure of the resonance hybrid.
 - Formal charges are important to include when drawing resonance structures as it clarifies where locations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

Resonance: Curved Arrows

- **Curved arrows**: a tool used to help draw resonance structres 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:
 - $-\pi$ bond \rightarrow lone pair.
 - Lone pair $\rightarrow \pi$ bond.
 - $-\pi$ bond $\to \pi$ 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.
- o Allylic: atoms connected directly to vinylic positions.



Resonance Hybrid

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

Delocalization

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

Contributor Significance

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

Midterm 1 3 Acids and Bases

3 Acids and Bases

Bønsted-Lowry Acids and Bases

- ▶ Acid: a proton donor; i.e., a H⁺ donor.
- **Base**: a proton acceptor; i.e., a OH^- (hydroxide ion), which wants a H^+ to form the more stable H_2O .
- Symbolically: HA + B

 A⁻ + HB⁺
- ▷ Example using bond-line structures:



Quantitative Perspective

0

Qualitiative Perspective

0

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.

Midterm 1 3 Acids and Bases

Nucleophiles and Electrophiles

Excerpt from Chapter 6: Chemical Reactivity and Mechanisms \mapsto

▶ **Ionic reactions**, aka polar reactions: reactions that involve the participation of ions as reactants, intermediates, or products.

- o Most cases ions act as intermediates.
- Radical reactions and pericyclic reactions are also major categories, but are typically not discussed in undergraduate courses.
- lonic 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.
 - \circ 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).

Midterm 1 3 Acids and Bases

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

 \triangleright

Nomenclature of Alkanes

 \triangleright