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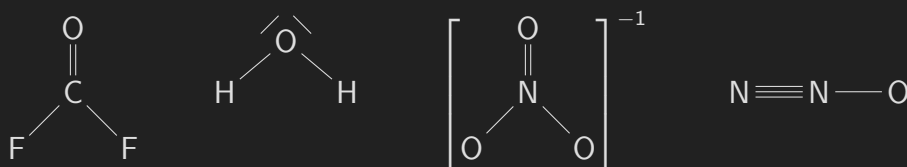
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# 1 General Chemistry Review

## 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.
- ▷ **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.

## 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** 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

- ▷  **$sp^3$ -hybridized orbitals**: produced by averaging one s orbital and **three p** orbitals.
  - Hybridized orbitals explains the geometry of methane, which results from 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 explain 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<sup>3</sup>-sp<sup>3</sup> 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°.
- ▷ **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°.
  - 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°.
  - VSEPR predicts geometry H<sub>2</sub>O correctly, but for wrong reasons.
    - The lone pairs in H<sub>2</sub>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° 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, 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.
  - **Hydrogen bonding:**
    - Not actually a bond, just an interaction.
    - When hydrogen bonds to a electronegative atom, then the hydrogen will have a  $\delta^+$ .
    - **F, O, N, Cl** (Br, I). Most electronegative elements, from left to right, that hydrogen most often bonds too.
    - 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.



- **Fleeting dipole-dipole interactions:**
  - Electrons are considered to be in constant motion, which result in the center of negative charge to vary.
  - On average, the dipole moment is zero, though can experience transient dipole moments, initiating fleeting attraction/repulsion.
  - 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? Formation of hydrogen bonds?
  - Number of carbon atoms. (surface area)
  - Degree of branching of compound. (surface area)

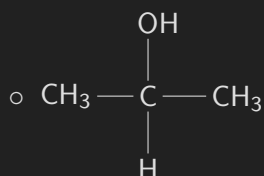
## Structural Theory of Matter

- ▷ **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.*

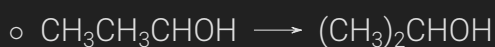
## 2 Molecular Representations

### Molecular Representations

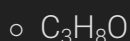
- ▷ **Partially condensed structures:** the C–H bonds are not always drawn, saving space.



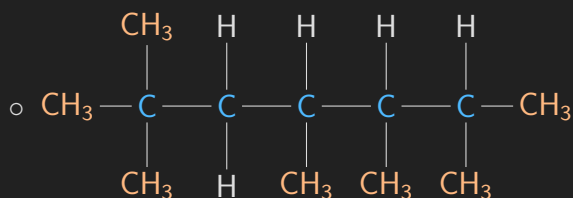
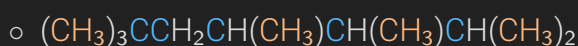
- ▷ **Condensed structures:** single bonds are not drawn and groups of atoms are clustered when possible.



- ▷ **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:

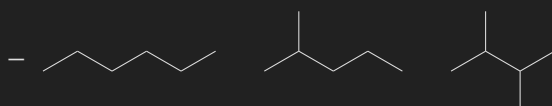


- This shows just one isomer, more partially condensed structures are possible.

### Bond-Line Structures

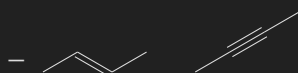
- ▷ **Bond-line structures;** aka skeletal structures; simplify drawing process of chemical structures and are easier to read.

- Each corner or endpoint represents a carbon atom.



- All examples have 6 carbon atoms

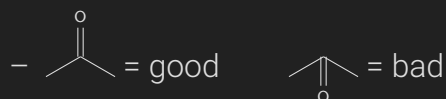
- Double bonds are shown with two lines, triple with three.



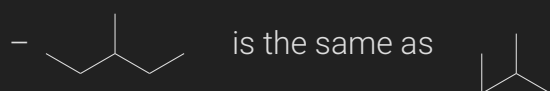
- Triple bonds are drawn linearly due to sp-hybridization
- Hydrogens are not shown; it is assumed that each carbon possesses enough to satisfy octet rule.

### 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 molecular formula:  $C_nH_{2n+2}$   $n$  = carbon atoms
- ▷ **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 HDI of 2.
  - Degrees of freedom help represent possible structures, indicating possible double bonds, triple bonds, rings, or various combinations of each.

### Impact of Other Elements on HDI

- **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.
  - Formula:  $\text{HDI} = \frac{1}{2}(2C + 2 + N - H - X)$ 
    - $X$ : halogen atoms.
- ▷ Calculating HDI provides clues about the structural features of a compound.
- Only helpful when molecular formula is known for certainty.

### Identifying Functional Groups

▷