1.1 Organic Chemistry

- Why do we distinguish between organic and inorganic compounds?

*Organic compounds* contain carbon atoms

- Why are organic compounds important? Organic compounds make up things like:
  - Food
  - Clothes
  - Pharmaceuticals
  - Plastics

![Reaction: Ammonium cyanate (Inorganic) to Urea (Organic) via heat]

Heat

\[ \text{NH}_4\text{OCN} \xrightarrow{\text{Heat}} \text{H}_2\text{N}+\overset{\text{C}}{\text{C}}+\overset{\text{NH}_2}{\text{NH}_2} \]

Ammonium cyanate (Inorganic)  Urea (Organic)
1.3 Covalent Bonding

- A covalent bond is a PAIR of electrons shared between two atoms. For example...

```
H\cdot + .H → H−H
```

![Graph with energy levels and internuclear distance](image)

- Energy: $−436 \text{ kJ/mol}$
- Internuclear distance: $0.74 \text{ Å}$
1.3 Counting Valence Electrons

• You can always calculate the number of valence electrons by analyzing the e- configuration.

• Or, for Group A elements only, just look at the Group number on the periodic table (Group number = # of valence electrons)

• Practice with SkillBuilder 1.2
1.2 Structural Theory

- Atoms that are most commonly bonded to carbon include N, O, H, and halides (F, Cl, Br, I).
- With some exceptions, each element generally forms a specific number of bonds with other atoms.

<table>
<thead>
<tr>
<th>Tetravalent</th>
<th>Trivalent</th>
<th>Divalent</th>
<th>Monovalent</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="C" /> Carbon generally forms <strong>four</strong> bonds.</td>
<td><img src="image" alt="N" /> Nitrogen generally forms <strong>three</strong> bonds.</td>
<td><img src="image" alt="O" /> Oxygen generally forms <strong>two</strong> bonds.</td>
<td><img src="image" alt="H—X" /> Hydrogen and halogens generally form <strong>one</strong> bond. (where X = F, Cl, Br, or I)</td>
</tr>
</tbody>
</table>

- Practice with SkillBuilder 1.1
1.3 Simple Lewis Structures

• For simple Lewis Structures...
  1. Draw the individual atoms using dots to represent the valence electrons.
  2. Put the atoms together so they **share pairs** of electrons to make complete octets.

• Take NH$_3$, for example...

• Note the nitrogen has a **lone pair** of electrons
1.4 Formal Charge

- Consider the formal charge on the atoms in the structure below, and determine if any of the atoms should have a formal charge.

- **Carbon** needs 4 valence electrons to be neutral (Group IV).
- Carbon is surrounded by 8 electrons here, but it only owns 4 of them (1 from each of the bonds).
- Since carbon owns 4 electrons, and needs 4 electrons to be neutral, it does not have a formal charge.
Now determine if the oxygen atom has a formal charge here.

- **Oxygen** needs **6 valence electrons** to be neutral (Group VI)
- Oxygen is surrounded by 8 electrons here, but it **only owns 7 of them** (1 from the bond, plus 3 lone pairs).
- Since oxygen owns 7 electrons here, and needs 6 electrons to be neutral, it **has an extra electron**, and therefore has a **-1 charge**.

Practice with SkillBuilder 1.4
1.5 Polar Covalent Bonds

- **Electronegativity** - how strongly an atom attracts shared electrons

<table>
<thead>
<tr>
<th>Element</th>
<th>Electronegativity</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>2.1</td>
</tr>
<tr>
<td>Li</td>
<td>1.0</td>
</tr>
<tr>
<td>Be</td>
<td>1.5</td>
</tr>
<tr>
<td>B</td>
<td>2.0</td>
</tr>
<tr>
<td>C</td>
<td>2.5</td>
</tr>
<tr>
<td>N</td>
<td>3.0</td>
</tr>
<tr>
<td>O</td>
<td>3.5</td>
</tr>
<tr>
<td>F</td>
<td>4.0</td>
</tr>
<tr>
<td>Na</td>
<td>0.9</td>
</tr>
<tr>
<td>Mg</td>
<td>1.2</td>
</tr>
<tr>
<td>Al</td>
<td>1.5</td>
</tr>
<tr>
<td>Si</td>
<td>1.8</td>
</tr>
<tr>
<td>P</td>
<td>2.1</td>
</tr>
<tr>
<td>S</td>
<td>2.5</td>
</tr>
<tr>
<td>Cl</td>
<td>3.0</td>
</tr>
<tr>
<td>K</td>
<td>0.8</td>
</tr>
<tr>
<td>Br</td>
<td>2.8</td>
</tr>
</tbody>
</table>

If you remember that F is the most electronegative atom, then you can always remember the relative electronegativity of the atoms in the same column or the same row of the PTE.
1.5 Polar Covalent Bonds

- There are three types of bonds:

**COVALENT BOND:** electrons shared between two atoms, where electronegativity difference is less than 0.5

**POLAR COVALENT BOND:** electrons shared between two atoms with electronegativity difference between 0.5 and 1.7

**IONIC BOND:** the electrons are not really shared, the two atoms differ in electronegativity by more than 1.7, and so the more electronegative atom owns the electrons.
1.5 Polar Covalent Bonds

- Some bonds are acceptable to write as a covalent bond or an ionic bond, as in the following example:

- The electronegativity difference is 1.5, so it is on the cusp of polar covalent and ionic, according to just one method used for determining electronegativity values. So, the \textit{absolute} difference in electronegativity is to be taken with a grain of salt.

- \textbf{Practice with SkillBuilder 1.5}
1.10 Molecular Geometry

• Valence shell electron pair repulsion (VSEPR theory)

Valence electrons (shared and lone pairs) repel each other

• To determine molecular geometry, start with the steric number... which gives us a quick prediction

\[
\begin{align*}
\text{H--C--H} & \quad \text{H--N--H} & \quad \text{H--O--H} \\
\text{H} & \quad \text{H} & \quad \text{H} \\
\text{Steric number} = 4 & \quad \text{Steric number} = 4 & \quad \text{Steric number} = 4 \\
\# \text{ of } \sigma \text{ bonds} = 4 & \quad \# \text{ of } \sigma \text{ bonds} = 3 & \quad \# \text{ of } \sigma \text{ bonds} = 2 \\
\# \text{ of lone pairs} = 0 & \quad \# \text{ of lone pairs} = 1 & \quad \# \text{ of lone pairs} = 2
\end{align*}
\]
1.10 Molecular Geometry

- The steric number translates to the hybridization of the central atom
  - If the Steric number is 4, then it is \( sp^3 \)
  - If the Steric number is 3, then it is \( sp^2 \)
  - If the Steric number is 2, then it is \( sp \)
1.10 Molecular Geometry – $sp^3$

- For any $sp^3$ hybridized atom, the 4 valence electron pairs will form a **tetrahedral electron group geometry**

- Methane has 4 equal bonds, so the bond angles are equal

- The bond angles in ammonia are a little smaller

- The bond angles in oxygen are even smaller still
1.10 Molecular Geometry – \( sp^3 \)

- The **molecular geometry** is described for only the atoms bonded to the central atom; **electron group geometry** includes lone pairs.

<table>
<thead>
<tr>
<th>TABLE 1.3</th>
<th>COMMON MOLECULAR SHAPES THAT CAN BE PREDICTED WITH VSEPR THEORY</th>
</tr>
</thead>
<tbody>
<tr>
<td>EXAMPLE</td>
<td>BONDING ELECTRON PAIRS (BONDS)</td>
</tr>
<tr>
<td>CH(_4)</td>
<td>4</td>
</tr>
<tr>
<td>NH(_3)</td>
<td>3</td>
</tr>
<tr>
<td>H(_2)O</td>
<td>2</td>
</tr>
<tr>
<td>BF(_3)</td>
<td>3</td>
</tr>
<tr>
<td>BeH(_2)</td>
<td>2</td>
</tr>
</tbody>
</table>

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1.10 Molecular Geometry – \( sp^2 \)

- Calculate the steric number for BF\(_3\)

- The electron pairs in \( sp^2 \) hybridized orbitals (either bonded electrons or lone pairs) will form a **trigonal planar electron group geometry** (steric number = 3 = trigonal planar)
1.10 Molecular Geometry – $sp^2$

- Realize that the boron atom, in BF$_3$, is $sp^2$ hybridized. The three bonds are made with $sp^2$ orbitals, and the unhybridized $p$ orbital remains empty.
1.10 Molecular Geometry – *sp*

- When *steric number* = 2, the geometry will be **linear** and the atom will be *sp*-hybridized.

- Consider BeH₂

- Draw a Lewis structure for CO₂. Are the *p* orbitals on the C atom also empty in this compound, like they are with Be in the previous example?
1.10 Molecular Geometry – Summary

- Practice with SkillBuilder 1.8

If steric number = 4
- $sp^3$
  - Tetrahedral arrangement of electron pairs
    - No lone pairs
    - One lone pair
    - Tetrahedral
    - Trigonal pyramidal

If steric number = 3
- $sp^2$
  - Trigonal planar arrangement of electron pairs
    - Two lone pairs
    - One lone pair
    - Bent
    - Trigonal planar

If steric number = 2
- $sp$
  - Linear arrangement of electron pairs
    - No lone pairs
    - Linear
1.6 Atomic Orbitals = Electron Density

- The type of orbital is identified by its shape (s, p)

- **Electron density**: term used to refer to probability of finding an electron (the orbital shape is 90-95% of the space where an electron “probably” is)

- We think of an **atomic orbital** as a cloud of **electron density**
1.6 Phases of Atomic Orbitals

- Electrons behave as both particles and waves. How can they be BOTH? Maybe the theory is not yet complete.
- The theory does match experimental data, and it has predictive capability.
  - Like a wave on a lake, an electron’s wavefunction can have a positive (+) value, a negative (−) value, or zero (a node).
1.6 Atomic Orbitals

- Because they are generated mathematically from wavefunctions, orbital regions can also be (−), (+), or ZERO.

  - The sign of the wave function has nothing to do with electrical charge.

- In this p-orbital, there is a nodal plane. The sign of the wavefunction will be important when we look at orbital overlapping in bonds.
1.7 Valence Bond Theory

- A bond occurs when atomic orbitals overlap. Overlapping orbitals is like overlapping waves.

- Only constructive interference results in a bond.
1.7 Valence Bond Theory

- The bond for a H₂ molecule results from constructive interference.

The bonded electrons spend most of their time in the overlapping atomic orbital space... which is called a **sigma (σ) bond**.
1.9 Hybridized Atomic Orbitals

- The ground state electron configuration for carbon can’t explain how carbon makes four bonds.

  ![Energy Diagram](Image)

  Only two orbitals have unpaired electrons to be shared in the ground state.

  There are 4 unpaired electrons here, but 4 equal bonds cannot be made with two different types of orbitals (s vs p).

- If considering the excited state, it still doesn’t explain how carbon makes 4 equivalent bonds, like the 4 bonds to H in a methane molecule.

  ![Methane](Image)
1.9 Hybridized Atomic Orbitals

- The carbon must undergo hybridization to form 4 equal atomic orbitals, with symmetrical geometry.

- The atomic orbitals must be equal in energy to form four equal-energy symmetrical C-H bonds.
1.9 Hybridized Atomic Orbitals

- the shape of an $sp^3$ orbital results from having 25% s-character, and 75% p-character
To make CH$_4$, the 1s atomic orbitals of four H atoms will overlap with the four $sp^3$ hybrid atomic orbitals of C.
1.9 Hybridized Atomic Orbitals

- Consider ethene (ethylene).

- Each carbon in ethene must bond to three other atoms, so only three hybridized atomic orbitals are needed.
1.9 Hybridized Atomic Orbitals

- An $sp^2$ hybridized carbon will have three equal-energy $sp^2$ orbitals and one unhybridized $p$ orbital.

- The shape of an $sp^2$ orbital results from having 33% $s$-character and 67% $p$-character.
1.9 Hybridized Atomic Orbitals

- The $sp^2$ atomic orbitals overlap to form sigma ($\sigma$) bonds

- The $p$ orbitals, here, overlap to form a pi bond
1.9 Hybridized Atomic Orbitals

- The pi (\(\pi\)) bond is formed by SIDE-BY-SIDE overlap of the \(p\) orbitals. The electron density of the pi bond is spread out above and below the plane of the molecule, as shown below.

- Pi bonds are weaker than sigma bonds.
1.9 Hybridized Atomic Orbitals

- Consider ethyne (acetylene).

\[ \text{H} \equiv \text{C} \equiv \text{C} \equiv \text{H} \]

- Each carbon in ethyne must bond to **two** other atoms, so only **two** hybridized atomic orbitals are needed.

These orbitals are not affected

Two degenerate sp orbitals

Energy
1.9 Hybridized Atomic Orbitals

- The sp atomic orbitals overlap HEAD-ON to form sigma (σ) bonds while the unhybridized p orbitals overlap SIDE-BY-SIDE to form pi (π) bonds.

- Practice with Skillbuilder 1.7
1.9 Bond Strength and Length

• Which should be stronger, a pi bond or a sigma bond?

*The sigma bond is considered stronger as it requires almost twice the bond energy of a pi bond to break it.*

• Which should be longer, an $sp^3$ – $sp^3$ sigma bond overlap or an $sp$ – $sp$ sigma bond overlap? Realize the more s-character in the orbitals, the shorter they will be.

*$sp^3$ bond lengths are the longest, followed by $sp^2$, and then $sp$ bonds.*
1.9 Bond Strength and Length

- Rationalize the bond strengths and lengths below

<table>
<thead>
<tr>
<th>TABLE 1.2</th>
<th>COMPARISON OF BOND LENGTHS AND BOND ENERGIES FOR ETHANE, ETHYLENE, AND ACETYLENE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ETHANE</td>
</tr>
<tr>
<td>Structure</td>
<td></td>
</tr>
<tr>
<td>C—C bond length</td>
<td>1.54 Å</td>
</tr>
<tr>
<td>Bond energy</td>
<td>368 kJ/mol</td>
</tr>
</tbody>
</table>
Consider the dipole for CH₃Cl

Dipole moment (μ) = charge (e) x distance (d)

- Plug in the charge and distance

\[ \mu = (1.056 \times 10^{-10} \text{ esu}) \times (1.772 \times 10^{-8} \text{ cm}) \]

- Note that the amount of charge separation is less than what it would be if it were a full charge separation (4.80 \times 10^{-10} \text{ esu})

\[ \mu = 1.87 \times 10^{-18} \text{ esu} \cdot \text{cm} \]

- Convert to debye

\[ \mu = 1.87 \text{ D} \]
What would the dipole moment be if CH₃Cl were 100% ionic?

\[ \mu = \text{charge (e)} \times \text{distance (d)} \]

- Plug in the charge and distance, using the full charge of an electron

\[ \mu = (4.80 \times 10^{-10} \text{ esu}) \times (1.772 \times 10^{-8} \text{ cm}) \]

\[ \mu = 8.51 \times 10^{-18} \text{ esu} \cdot \text{cm} = 8.51 \text{ D} \]

What % of the C-Cl bond is ionic?

22% ionic character means the C-Cl bond is mostly covalent

\[ \frac{1.87 \text{ D}}{8.51 \text{ D}} \times 100\% = 22\% \]
1.11 Molecular Polarity & Dipoles

- The polarity of some other common bonds

<table>
<thead>
<tr>
<th>Bond</th>
<th>Bond Length ($\times 10^{-8}$ cm)</th>
<th>Observed $\mu$ (D)</th>
<th>Percent Ionic Character</th>
</tr>
</thead>
<tbody>
<tr>
<td>C—O</td>
<td>1.41</td>
<td>0.7 D</td>
<td>$\frac{(0.7 \times 10^{-18} \text{ esu} \cdot \text{cm})}{(4.80 \times 10^{-10} \text{ esu})(1.41 \times 10^{-8} \text{ cm})} \times 100% = 10%$</td>
</tr>
<tr>
<td>O—H</td>
<td>0.96</td>
<td>1.5 D</td>
<td>$\frac{(1.5 \times 10^{-18} \text{ esu} \cdot \text{cm})}{(4.80 \times 10^{-10} \text{ esu})(0.96 \times 10^{-8} \text{ cm})} \times 100% = 33%$</td>
</tr>
<tr>
<td>C==O</td>
<td>1.227</td>
<td>2.4 D</td>
<td>$\frac{(2.4 \times 10^{-18} \text{ esu} \cdot \text{cm})}{(4.80 \times 10^{-10} \text{ esu})(1.23 \times 10^{-8} \text{ cm})} \times 100% = 41%$</td>
</tr>
</tbody>
</table>
1.11 Molecular Polarity & Dipoles

Why is the C=O double bond so much more polar than the C-O single bond?

<table>
<thead>
<tr>
<th>TABLE 1.4</th>
<th>PERCENT IONIC CHARACTER FOR SEVERAL BONDS</th>
</tr>
</thead>
<tbody>
<tr>
<td>BOND</td>
<td>BOND LENGTH (x 10^-8 cm)</td>
</tr>
<tr>
<td>C—O</td>
<td>1.41</td>
</tr>
<tr>
<td>O—H</td>
<td>0.96</td>
</tr>
<tr>
<td>C≡O</td>
<td>1.227</td>
</tr>
</tbody>
</table>
1.11 Molecular Polarity & Dipoles

- For molecules with multiple polar bonds, the dipole moment is the vector sum of all of the individual bond dipoles.
1.11 Molecular Polarity & Dipoles

- Electrostatic potential maps are often used to give a visual depiction of polarity.
1.12 Intermolecular Forces

- Many properties such as solubility, boiling point, density, state of matter, melting point, etc. are affected by the attractions between separate molecules.

- Neutral molecules (polar and nonpolar) are attracted to one another through...
  - Dipole-dipole interactions
  - Hydrogen bonding
  - Dispersion forces (a.k.a. London forces or fleeting dipole-dipole forces)
1.12 Dipole-Dipole Attractions

- Dipole-dipole forces result when polar molecules line up their opposite charges.

- Note acetone’s permanent dipole results from the difference in electronegativity between C and O

- The dipole-dipole attractions BETWEEN acetone molecules increases acetone’s boiling and melting points while similar molecules without dipole-dipole interactions, such as isobutylene, have lower boiling and melting points.
1.12 Dipole-Dipole Attractions

- Isobutylene and acetone have such different MP and BPs because of dipole-dipole interactions. Isobutylene lacks a significant dipole moment.

Isobutylene
Melting point = $-140.3^\circ$C
Boiling point = $-6.9^\circ$C

Acetone
Melting point = $-94.9^\circ$C
Boiling point = $56.3^\circ$C

isobutylene is less polar, has weaker dipole-dipole attractions and therefore a lower BP

Acetone is more polar, and so it has a higher BP
1.12 Hydrogen Bonding

- Hydrogen bonds are an especially strong type of dipole-dipole attraction
- Hydrogen bonds are strong because the partial + and – charges are relatively large
- **H-bonding** is the **attractive force** between an H bonded to an electronegative atom (N, O and F) and a lone pair on another electronegative atom.

![Hydrogen bond interaction between molecules of water](image)

![Hydrogen bond interaction between molecules of ammonia](image)
1.12 Hydrogen Bonding

- Only when a hydrogen shares electrons with a highly electronegative atom (O, N, F) will it carry a large partial positive charge.

- The large $\delta^+$ on the H atom can attract large $\delta^-$ charges on other molecules.

- Even with the large partial charges, H-bonds are still about 20 times weaker than covalent bonds.
1.12 Hydrogen Bonding

- Solvents that engage in H-bonding are called **protic solvents**. Solvents that do not H-bond are **aprotic**

*acetic acid* *(protic)*

*diethyl ether* *(aprotic)*

*dimethylsulfoxide, called DMSO* *(aprotic)*
1.12 Hydrogen Bonding

- Increasing the amount and extent of hydrogen bonding explains why the following isomers have different boiling points

\[
\begin{align*}
\text{Trimethylamine} & : & \text{Boiling point} &= 3.5^\circ\text{C} \\
\text{Ethylmethylamine} & : & \text{Boiling point} &= 37^\circ\text{C} \\
\text{Propylamine} & : & \text{Boiling point} &= 49^\circ\text{C}
\end{align*}
\]
1.12 London Dispersion Forces

• If two molecules are nonpolar (dipole = 0 D), they still will have an attractive force between them

  – This occurs due to an induced, transient dipole moment, called London Dispersion Forces

• Nonpolar molecules normally have their electrons (−) spread out evenly around the nuclei (+) completely balancing the charge

• However, the electrons are in constant random motion within their MOs
1.12 London Dispersion Forces

- The constant random motion of the electrons in the molecule will sometimes produce an electron distribution that is NOT evenly balanced with the positive charge of the nuclei.

- Such uneven distribution produces a temporary dipole, which can induce a temporary dipole in a neighboring molecule.
1.12 London Dispersion Forces

- The result is a fleeting attraction between the two molecules.

- Such fleeting attractions are generally weak.
- But like any weak attraction, if there are enough of them, they can add up to be significant.
1.12 London Dispersion Forces

- London dispersion forces are the reason why molecules with more mass generally have higher boiling points.

- Practice with SkillBuilder 1.10
1.12 London Dispersion Forces

- The more branching in a molecule, the lower it’s surface area, and the weaker the London dispersion forces.

Pentane
Boiling point = 36°C

2-Methylbutane
Boiling point = 28°C

2,2-Dimethylpropane
Boiling point = 10°C
1.13 Solubility

• As you learned in general chemistry, **like-dissolves-like**

• **Polar compounds** *generally* mix well with other polar compounds
  – If the compounds mixing are all capable of H-bonding and/or strong dipole-dipole, then there is no reason why they shouldn’t mix

• **Nonpolar compounds** *generally* mix well with other nonpolar compounds
  – If none of the compounds are capable of forming strong attractions, then no strong attractions would have to be broken to allow them to mix
1.13 Solubility

• We know it is difficult to get a polar compound (like water) to mix with a nonpolar compound (like oil)
  – We can’t use just water to wash oil off our dirty cloths

• To remove nonpolar oils, and grease, and dirt... we need soap