Chapter 1
Structure and Bonding

Organic Chemistry

• What is Organic Chemistry? Why should you study it?

• Every living organism is made of Organic Chemicals
  – Proteins and DNA
  – Foods, medicines and clothes

• “Organic” – until mid 1800’s referred to compounds from living sources (mineral sources were “inorganic”)

• Wöhler in 1828 showed that urea, an organic compound, could be made from a minerals

• Today, organic compounds are those based on carbon structures and organic chemistry studies their structures and reactions
Chemistry of “C” Compounds

• Distinguishing character of Organic chemicals
  – all contain the element CARBON
  – also contain other elements, such as H, N, O, Halogens, P, S etc

• What is special about the element Carbon?
  – belongs to the group 4A
  – four valence electrons
  – four covalent bonds
  – can bond one another to form long chains

• Does not include metal salts and materials (inorganic)
• Does not include materials of large repeating molecules without sequences (polymers)

Atomic Structure

• Atoms consist of
  protons
  neutrons and
  electrons

• Protons have a plus charge, electrons a negative charge, and neutrons have no charge

• Protons and neutrons are found in the nucleus, electrons are outside

• Protons and neutrons account for most of the atom’s mass

• Electrons participate in bonding and reactions
Atomic Structure

- The atomic number (Z) is the number of protons in the atom's nucleus.
- The mass number (A) is the number of protons plus neutrons.
- All the atoms of a given element have the same atomic number.
- Isotopes are atoms of the same element that have different numbers of neutrons and therefore different mass numbers.
Atomic Orbitals

- Electrons reside in distinct regions called orbitals.
- Orbitals represent the area of highest probability of electron location.
- Orbital shape is predicted mathematically by a probability function.
- Four different kinds of orbitals.
- Orbitals are commonly denoted by letters, $s$, $p$, $d$, and $f$.
- $s$ and $p$ orbitals most important in organic chemistry.

Shapes of Atomic Orbitals

- $s$ and $p$ orbitals most important in organic chemistry.
- $s$ orbitals: spherical, nucleus at center.
- $p$ orbitals: dumbbell-shaped, nucleus at middle.

An $s$ orbital

A $p$ orbital
p-Orbitals

- There are three perpendicular \( p \) orbitals, \( px, py, \) and \( pz \), of equal energy.

- Lobes of a \( p \) orbital are separated by region of zero electron density, a node.

Orbitals and Shells

- Orbitals are grouped in shells of increasing size and energy.
- Different shells contain different numbers and kinds of orbitals.
- Each orbital can be occupied by two electrons.
- First shell contains one \( s \) orbital, denoted 1\( s \), holds only 2 electrons.
- Second shell contains one \( s \) orbital (2\( s \)) and three \( p \) orbitals (2\( p \)), 8 electrons.
- Third shell contains an \( s \) orbital (3\( s \)), three \( p \) orbitals (3\( p \)), and five \( d \) orbitals (3\( d \)), 18 electrons.
Electron Configuration of Oxygen (At No: 8)

1st Shell
1s

2nd Shell (Valence Shell)

\{  
2s  

2p

\}

Electron Configurations

- **Aufbau Principle**
  - Places electrons in lowest energy orbitals first

- **Pauli Exclusion Principle**
  - Each orbital can hold two spin-paired electrons

- **Hund’s Rule**
  - When degenerate or equal energy orbitals exist, electrons are added to each orbital unpaired

- **Valence Electrons**
  - Electrons in outermost or highest energy level
  - Electrons involved in bonding and reactions
Electron Configurations

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic number</th>
<th>Configuration</th>
<th>Element</th>
<th>Atomic number</th>
<th>Configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>1</td>
<td>1s</td>
<td>Lithium</td>
<td>3</td>
<td>2s</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1s</td>
</tr>
<tr>
<td>Carbon</td>
<td>6</td>
<td>2p 2s 1s</td>
<td>Neon</td>
<td>10</td>
<td>2p 2s 1s</td>
</tr>
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<td></td>
<td></td>
<td>2p 2s 1s</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sodium</td>
<td>11</td>
<td>3s 2p 2s 1s</td>
<td>Argon</td>
<td>18</td>
<td>3p 2p 2s 1s</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3s 2p 2s 1s</td>
<td></td>
<td></td>
<td>3s 2p 2s 1s</td>
</tr>
</tbody>
</table>

Give the Electron Configuration of

Oxygen (at no: 8) and Chlorine (at no: 17)

\[
\begin{align*}
2p & \quad \uparrow \quad \uparrow \quad \uparrow \\
2s & \quad \uparrow \quad \uparrow \\
1s & \quad \uparrow \quad \uparrow \\
1s^2, 2s^2, 2p^4 & \\
\end{align*}
\]

\[
\begin{align*}
3p & \quad \uparrow \quad \uparrow \quad \uparrow \\
3s & \quad \uparrow \quad \uparrow \\
2p & \quad \uparrow \quad \uparrow \quad \uparrow \\
2s & \quad \uparrow \quad \uparrow \\
1s & \quad \uparrow \quad \uparrow \\
1s^2, 2s^2, 2p^6, 3s^2, 3p^5 & \\
\end{align*}
\]

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**Bond Formation**

- **Octet Rule**
  - Electrons are either transferred or shared in a bond
  - In this way, bonded atoms can achieve a complete octet
  - There are some elements that do not need an octet

- **Ionic Bonds**
  - Usually occur between metals and non-metals
  - Metals usually lose electrons and non-metals usually gain electrons

- **Covalent Bonds**
  - Usually occur between two non-metals
  - Typical type of bond found in most organic molecules

**Lewis Structures**

- **Lewis structures** show valence electrons of an atom as dots
  - Hydrogen has one dot, representing its 1s electron
  - Carbon has four dots (2s² 2p²)

- Stable molecule results at completed shell, octet (eight dots) for main-group atoms (two for hydrogen)

- Atoms with one, two, or three valence electrons form one, two, or three bonds

- Atoms with four or more valence electrons form as many bonds as they need electrons to fill the s and p levels of their valence shells to reach a stable octet
Valency of Carbon in CH₄

- Carbon has four valence electrons (2s² 2p²), forming four bonds (CH₄)

Valences of Nitrogen

- Nitrogen has five valence electrons (2s² 2p³) but forms only three bonds (NH₃)
Non-bonding electrons

- Valence electrons not used in bonding are called **nonbonding electrons**, or **lone-pair electrons**
  - Nitrogen atom in ammonia (NH₃)
    - Shares six valence electrons in three covalent bonds and remaining two valence electrons are nonbonding lone pair

Valences of Oxygen

- Oxygen has six valence electrons (2s² 2p⁴) but forms two bonds (H₂O)

\[
2 \text{H}^- + \cdot\cdot\cdot\cdot - \text{O}^- \rightarrow \text{H}:\cdot\cdot\cdot\cdot - \text{O}^- : \text{H}
\]

**Water (H₂O)**

\[
3 \text{H}^- + \cdot\cdot\cdot\cdot - \cdot\cdot\cdot\cdot - \cdot\cdot\cdot\cdot + \cdot\cdot\cdot\cdot + \text{H}^+ \rightarrow \text{H}:\cdot\cdot\cdot\cdot - \cdot\cdot\cdot\cdot - \cdot\cdot\cdot\cdot - \cdot\cdot\cdot\cdot : \text{H}
\]

**Methanol (CH₃OH)**
### Writing Lewis and Line-Bond Structures of molecules

- Consider CH$_3$NH$_2$
- Calculate electrons each atom needs to be stable
  - C (8) + H 5x(2) + N (8) = 26
- Calculate the number of available electrons (valence)
  - C (4) + H 5x(1) + N (5) = 14
- Calculate the difference or number to be shared
  - 26-14 = 12 electrons or 6 pairs between 7 atoms
  - Atom with highest bonding requirement is in center
  - In organic molecules, carbon is usually in the center

\[
\begin{array}{c}
\text{H} \\
\text{H} \quad \text{C} \quad \text{N} \quad \text{H} \\
\text{H} \quad \text{H}
\end{array}
\]
Problem: Write Lewis and Line-Bond Structures of Chloroform (CHCl₃)

- Molecular formula CHCl₃
- Calculate electrons each atom needs to be stable
  - C (8) + H (2) + Cl (3X8) = 34
- Calculate the number of available electrons (valence)
  - C (4) + H(1) + Cl (3X7) = 26
- Calculate the difference or number to be shared
  - 34-26 = 8 electrons or 4 pairs between 5 atoms
  - Atom with highest bonding requirement is in center

```
: Cl :
H—C—Cl :
: Cl :
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Valence Bond Theory

- Covalent bond forms when two atoms approach each other closely so that a singly occupied orbital on one atom overlaps a singly occupied orbital on the other atom
- Electrons are paired in the overlapping orbitals and are attracted to nuclei of both atoms
  - H–H bond results from the overlap of two singly occupied hydrogen 1s orbitals
Bond Energy & Length

- Reaction $2 \text{H}^+ \rightarrow \text{H}_2$ releases 436 kJ/mol
- Product has 436 kJ/mol less energy than two atoms:
- H–H has bond energy of 436 kJ/mol.
- Bond Length - distance between nuclei that leads to maximum stability
- H–H bond length is 74 pm

Hybridization

- Hybridization theory resulted from refining valence bond theory (VBT)
- Let us look at the structure of methane (CH₄) molecule
- VBT could not account for carbon’s ability to make 4 bonds
- Ground state carbon configuration is $1s^22s^22p_x^12p_y^12p_z^0$
- How does it form four bonds of equal Strength (438kJ/mol)??
- How does it form four bonds of equal length (110pm)??
- How do we explain the H-C-H bond angle of 109.5°??

- 1930’s Linus Pauling proposes electron promotion so now, $1s^22s^12p_x^12p_y^12p_z^1$
- But, orbitals must be of equal energy to allow 4 bonds
- Four new orbitals are formed by hybridizing or mixing the $2s$ and $2p_x$, $2p_y$, & $2p_z$
- Four sp³ hybrid orbitals are created
sp\(^3\) Hybridization

Tetrahedral Geometry

Four C-H sigma (\(\sigma\)) bonds
**Methane, CH\textsubscript{4}**

Four C-H sigma (\(\sigma\)) bonds

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**Ethane, C\textsubscript{2}H\textsubscript{6}**

Six C-H \(\sigma\) bonds and one C-C \(\sigma\) bond
Ammonia, $\text{NH}_3$

Three N-H $\sigma$ bonds

Water, $\text{H}_2\text{O}$

Two O-H $\sigma$ bonds
sp² Hybridization

Side view

Top view

Ethylene, C₂H₄

sp³ carbon

sp³ carbon

Carbon–carbon double bond
Ethylene, $\text{C}_2\text{H}_4$

One C-C $\sigma$ bond, One C-C $\pi$ bond and four C-H $\sigma$ bonds

Non-carbon sp$^2$ hybridized atoms

$\text{H}_2\text{C}^=\text{N} \Rightarrow \text{H}^\bullet\text{C}^\bullet\text{N}$

$\text{sp}^2$ hybridized N

$\text{H}^\bullet\text{C}=\text{O} \Rightarrow \text{H}^\bullet\text{C}^\bullet\text{O}$

$\text{sp}^2$ hybridized O

$\pi$ bond
sp Hybridization

One sp hybrid
Another sp hybrid

Ethyne, C₂H₂

One C-C \( \sigma \) bond, two C-C \( \pi \) bond and two C-H \( \sigma \) bonds
Non-carbon sp hybridized atoms

H₂C·C ≡ N:\nsp hybridized N

Problem

What is the hybridization of each of the indicated atoms in this molecule?