Chapter 1: Structure Determines Properties
1.1: Atoms, Electrons, and Orbitals

Molecules are made up of atoms

Atoms- protons- (+)-charge, mass = $1.6726 \times 10^{-27}$ kg
neutrons- no charge, mass = $1.6750 \times 10^{-27}$ kg
electrons- (-)-charge, mass= $9.1096 \times 10^{-31}$ kg

Atomic Number ($Z$)= # of protons in the nucleus
nucleus: protons and neutrons- very little volume
but most of the mass

Atomic mass unit (AMU) = $\frac{1}{12}$ mass of $^{12}$C

Electrons: circulate about the nucleus- negligible mass, but the
electron cloud is most of the volume of an atom

Quantum mechanics - electrons have properties of both a particle
and energy. Energy of an electron is given by a wave
function ($\psi$) - electrons have a series of discrete energy
levels.

Schrödinger wave equation ($\psi$) gives the total energy of an
electron at a given point in space (x,y,z)

$\psi^2 = \text{probability of finding an electron at a given point in space}$

Orbital = space where an electron spends ~95% of its time.

Atomic orbitals (AOs)
• electrons are arranged in "shells" at various distances from the
nucleus
• shells are arranged in increasing energy
• within each shell, electrons are paired into orbitals with each
orbital holding two electrons
• paired electrons within an orbital have opposite spins

Pauli exclusion principles
Periodic charts is organized according to the electron shells and AOs

Please review and understand electronic configuration:
Aufbau principle, Pauli exclusion principle, Hund’s rule

Types of AOs
1 s-orbital - spherical (2 e’s)
3 p-orbitals - dumbbell shaped (6 e’s)
5 d-orbitals - four clover leaf and one dumbbell w/ a ring (10 e’s)
7 f-orbitals - (14 e’s)

1st (K) shell: one 1s-orbital
2nd (L) shell: one 2s-orbital and three 2p-orbitals

1s-orbitals: no nodes
2s-orbitals: one nodes
p-orbitals: one node

Nodes: space (points, planes, surfaces) where $\psi^2 = 0$
Valance electrons: electrons in the outermost shell
valance electrons are involved in bonding

Octet rule- atoms will give up, accept, or share electrons in order to achieve a noble gas electronic configuration

1.2: Ionic Bonds - electrostatic attraction between oppositely charged ions
cations - positively (+) charge ions  
anions - negatively (-) charge ions

Na → Na⁺ + e⁻  
1s²2s²2p⁶3s¹ → 1s²2s²2p⁶

Cl + e⁻ → Cl⁻  
1s²2s²2p⁶3s²3p⁵ → 1s²2s²2p⁶3s²3p⁶

Na(0) + Cl(0) → Na⁺ Cl⁻

1.3: Covalent Bonds, Lewis Structures, and the Octet Rule
Covalent bonds result from two atoms sharing a pair or pairs of electrons in order to achieve a noble gas electronic configuration

Each H of H₂ has the electron configuration of He - closed (filled) valance shell

Each atom of F₂ has eight valance electrons and the electron configuration of Ne.

The C of CH₄ has the electron configuration of Ne, while the H's have the electron configuration of He
1.4. Double Bonds and Triple Bonds

\[ \begin{align*}
\text{C}_2\text{H}_6 & \quad \text{C}_2\text{H}_4 & \quad \text{C}_2\text{H}_2 \\
\text{H} & \quad \text{H} & \quad \text{H} \\
\text{H} & \quad \text{C} : \text{C} & \quad \text{H} \\
\text{H} & \quad \text{H} & \quad \text{H} \\
\text{C}_2\text{H}_6 \text{ - ethane} & \quad \text{C}_2\text{H}_4 \text{ - ethylene} & \quad \text{C}_2\text{H}_2 \text{ - acetylene}
\end{align*} \]

1.9: The Shapes of Some Simple Molecules - Molecules are not flat! They are three dimensional.

Valence Shell Electron Pair Repulsion (VSEPR): molecules will adopt a three dimensional geometry so that electron pairs, either in bonds or non-bonding pairs, are as far away from one another as possible.

Atoms in which the number of substituents and/or nonbonding electron pairs is . . .

. . . four will adopt a tetrahedral geometry (methane)
. . . three will adopt a trigonal planar geometry (ethylene)
. . . two will adopt a linear geometry (acetylene)

1.5: Polar Covalent Bonds. covalent bonds in which the electrons are not equally shared between the two atoms - there is a net dipole.
Electronegativity: intrinsic ability of an atom to attract electrons. In general, the greater the electronegativity difference between two bonded atoms, the more polar the bond. Electronegativity tends to decrease down a period, and increase across a row (from left to right).

1.10: Molecular Dipole Moments - Dipole moment ($\mu$): molecular property, which is the vector sum of all individual bond dipoles.

$$\mu = e \cdot d$$

$e =$ charge, $d =$ distance; units: Debye (D)

Inductive Effect: atom’s (or group of atoms) ability to polarize a bond through electronegativity differences.

1.6: Structural Formulas of Organic Compounds

Please read, understand, and practice!!

Writing (Drawing) Chemical Structures:
A line between two atoms represents a bond (2 $e^-$)

Skeletal (bond-line) Notation

1. Carbon atoms are at the ends of lines and at the intersection of two lines
2. Hydrogens on carbon atoms are not shown.
3. All non-carbon and non-hydrogen atoms (heteroatoms) are shown.
4. Hydrogens on heteroatoms are shown
5. Formal Charges are shown
1.7: **Formal Charge** - proper Lewis structures must have the proper formal charge

\[
\text{formal charge} = \left( \frac{\text{# of valance } e^-\text{s}}{\text{of the free atom}} \right) - \left( \frac{\text{# of bonding } e^-\text{s}}{2} \right) - \left( \text{# of non-bonding } e^-\text{s} \right)
\]

![Lewis structure](image)

Which is the correct structure?

- Both are correct, and neither is correct.

1.8: **Resonance** - two or more proper Lewis structures can be written for a compounds (or ions).

![Lewis structure for nitromethane](image)

**Nitromethane**

![Lewis structure for benzene](image)

**Benzene**

Which is the correct structure?

- Both are correct, and neither is correct.
Drawing and Interpreting Resonance Forms

1. No one resonance forms accurately depicts the structure of the molecule. The real structure is a composite or hybrid of all resonance forms.

2. Resonance forms differ only by the placement of electrons, usually non-bonding Electron pairs, or the electron pairs of double and triple (π) bonds. Neither the position or hybridization of the atoms can change.

4. Resonance forms are not necessarily equivalent. While all resonance forms contribute to the actual structure (resonance hybrid), some forms may contribute more.

4. All resonance forms must be proper Lewis structures (including formal charges).

6. The actual resonance hybrid is more stable than any single resonance form.

8. In general, the greater the number of resonance forms, the more stable the resonance hybrid.

1.11: Curved Arrows and Chemical Reactions

Curved Arrow Convention

1. Curved arrows show the movement (flow) of electron during bond breaking and/or bond making processes. The foot of the arrow indicates where the electron or electron pair originates, the head of the arrow shows where the electron or electron pair ends up.

A. The movement of a single electron is denoted by a curved single headed arrow (fishhook or hook).

B. The movement of an electron pair is denoted by a curved double headed arrow.

2. If an electron pair moves in on a new atom, another electron pair must leave so that the atom does not exceed a full valance of eight electrons. There are two common exceptions:

A. When an atom already has an incomplete valance (R₂C+).
B. With second row (or below) elements the octet rule may be violated.

3. The arrows completely dictate the Lewis structure of the product.
Arrows in organic chemistry

- Reaction arrow
- Equilibrium arrow
- Resonance arrow

Mechanism arrows

- Double-headed arrow
- Single-headed arrow

1.12: Acids and Bases: The Arrhenius View (please read)
Acid - substance that ionizes to give a proton (H⁺) when dissolved in water
Base - substance that ionizes to give hydroxide (HO⁻) when dissolved in water

1.13: Acids and Bases: The Bronsted-Lowry View
Acid - proton donor
Base - proton acceptor

\[
\begin{array}{c}
B:\quad + \quad H-A & \iff & +B-H & + & :A^- \\
\quad \text{base} & \quad \text{acid} & & \quad \text{conjugate} & \quad \text{conjugate} \\
& & & \quad \text{acid} & \quad \text{base}
\end{array}
\]

\[
\begin{array}{c}
H_2\tilde{\text{O}}:\quad + \quad H-\text{Cl} & \iff & H_2\tilde{\text{O}}\tilde{\text{H}} & + & :\text{Cl}^- \\
& & & \quad \text{hydronium} & \quad \text{ion}
\end{array}
\]
In dilute solution, the $\text{H}_2\text{O}$ concentration is constant (~55.5 M) and is therefore incorporated in the $K_a$ (acid dissociation constant).

Acid strength is often given by $pK_a$ values:

$$pK_a = -\log_{10} K_a$$

The lower the $pK_a$ value, the stronger the acid strength.

*Conjugate bases of strong acids are weak bases*

*Conjugate bases of weak acids are strong bases*

### Table 1.8 (p. 38-9): Acidity constants ($pK_a$) of acids

<table>
<thead>
<tr>
<th>weaker acid</th>
<th>Acid</th>
<th>$pK_a$</th>
<th>conjugate base</th>
<th>stronger base</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$CH$_2$OH</td>
<td>16.0</td>
<td>CH$_3$CH$_2$O$^-$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H$_2$O</td>
<td>15.7</td>
<td>HO$^-$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HCN</td>
<td>9.2</td>
<td>$^-$CN</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH$_3$CO$_2$H</td>
<td>4.7</td>
<td>CH$_3$CO$_2$$^-$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HF</td>
<td>3.2</td>
<td>F$^-$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H$_2$NO$_3$</td>
<td>-1.3</td>
<td>HNO$_3$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H$_3$O$^+$</td>
<td>-1.7</td>
<td>H$_2$O</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HCl</td>
<td>-7.0</td>
<td>Cl$^-$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
1.14: What Happened to $pK_b$? (Please read) A separate basicity constant $K_b$ is not necessary because of the relationships between acid strength ($K_a$) and the conjugate base strength; acid-base reactions can be described exclusively using $pK_a$ values.

1.15: How Structure Affects Acid Strength

\[ \text{H-A} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{A}^- \]

1. The H-A bond strength- the weaker the H-A bond, the more readily it is broken (more acidic)

<table>
<thead>
<tr>
<th></th>
<th>H-F</th>
<th>H-Cl</th>
<th>H-Br</th>
<th>H-I</th>
</tr>
</thead>
<tbody>
<tr>
<td>$pK_a$</td>
<td>3.1</td>
<td>-3.9</td>
<td>-5.8</td>
<td>-10.4</td>
</tr>
</tbody>
</table>

2. The electronegativity of A – inductive effects

\[
\begin{align*}
\text{H}_3\text{C}-\text{H}_2\text{C}-\text{O}-\text{H} & \quad pK_a = -16 \\
\text{F}_3\text{C}-\text{H}_2\text{C}-\text{O}-\text{H} & \quad pK_a = -11.3 \\
\text{H}_3\text{C}-\text{C}-\text{O}-\text{H} & \quad pK_a = -4.7 \\
\text{F}_3\text{C}-\text{C}-\text{O}-\text{H} & \quad pK_a = -0.5
\end{align*}
\]

3. Electron delocalization in the conjugate base (A$^-$)

\[
\begin{align*}
\text{H}_3\text{C}-\text{H}_2\text{C}-\text{O}^- & \quad + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{C}-\text{H}_2\text{C}-\text{O}^- & \quad + \text{H}_3\text{O}^+ \\
pK_a = 4.7
\end{align*}
\]

1.16: Acid-Base Equilibria

\[
\begin{align*}
\text{H}_3\text{C}-\text{C}-\text{O}^- & \quad + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{C}-\text{C}-\text{O}^- & \quad + \text{H}_3\text{O}^+ \\
pK_a = 4.7 \\
\text{H}_3\text{C}-\text{C}-\text{O}^- & \quad + \text{Na}_2\text{H} \rightleftharpoons \text{H}_3\text{C}-\text{C}-\text{O}^- & \quad + \text{Na}_2\text{H} \\
pK_a = 4.7
\end{align*}
\]

The equilibrium favors the side of the weaker acid and weaker base.
A strong acid is one that is stronger than $\text{H}_3\text{O}^+$ ($pK_a \sim -1.7$)
A weak acid is one that is weaker than $\text{H}_3\text{O}^+$
A strong base is one that is stronger than $\text{HO}^-$
A weak base is one that is weaker than $\text{HO}^-$

1.17: Lewis Acids and Lewis Bases

Acid - an electron pair acceptor
Base - an electron pair donor.