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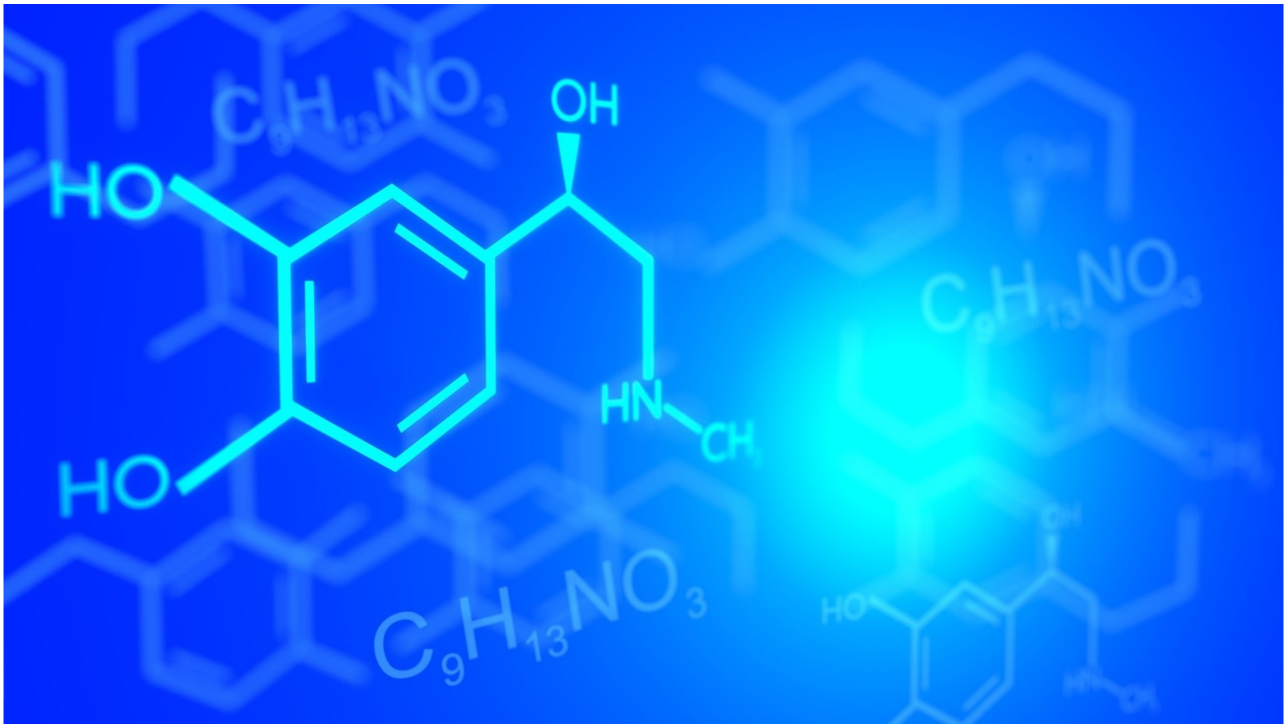
Chemistry 102 - Introduction to General, Organic and Biochemistry II



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> ”You are here to learn the subtle science and exact art of potion-making. As there is little foolish wand-waving here, many of you will hardly believe this is magic. I don't expect you will really understand the beauty of the softly simmering cauldron with its shimmering fumes, the delicate power of liquids that creep through human veins, bewitching the mind, ensnaring the senses. . . . I can teach you how to bottle fame, brew glory, even stopper death — if you aren't as big a bunch of dunderheads as I usually have to teach.”

– J.K. Rowling, Harry Potter and the Sorcerer's Stone

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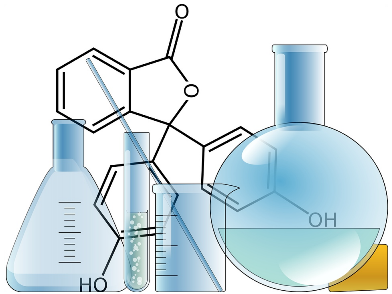
Review of General Chemistry



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1.1 Atoms and Molecules

From a chemistry prospective, all matter that exists is composed of a basic building block the **atom**. The origin of the term atom is the Greek word "atoms" which means indivisible and it was initially thought that atoms could not be divided into more fundamental parts of matter. This is untrue as each individual atom is composed of protons, neutrons and electrons and if one explores further each of those is further composed of other subatomic particles, though that deviates from a study of chemistry to that of physics.

There are a limited number of different types of atoms which we call elements (currently 118 elements have been discovered). Elements can combine together to form an almost unlimited number of compounds/molecules. If we think of atoms as the letters of the alphabet then compounds/molecules are the words formed from them. Just as the limited number of letters in the alphabet can be combined together to form words, sentences and eventually Shakespeare, so to can the elements be combined together to form compounds and molecules which gradually get larger and more complex until they eventually form a living human being.

Three Fundamental Particles

Protons have a relative mass of 1 amu, a positive charge and reside in the nucleus of the atom. The identity of each element on the periodic table is determined by the unique number of protons each has. Hydrogen has one proton, Helium has two and so on.

Neutrons have a relative mass of 1 amu, a neutral charge and also reside in the nucleus of the atom. They are important for the stability of the nucleus and elements which contain different numbers of neutrons are called isotopes. Isotopes are frequently used in many chemical techniques to determine the structure of molecules but have little impact on the physical and chemical properties studied in this book.

Electrons have a relative mass of 1/1832 amu, a negative charge and reside outside the nucleus of the atom. From the perspective of a chemist, electrons are the most important fundamental particle. Electrons

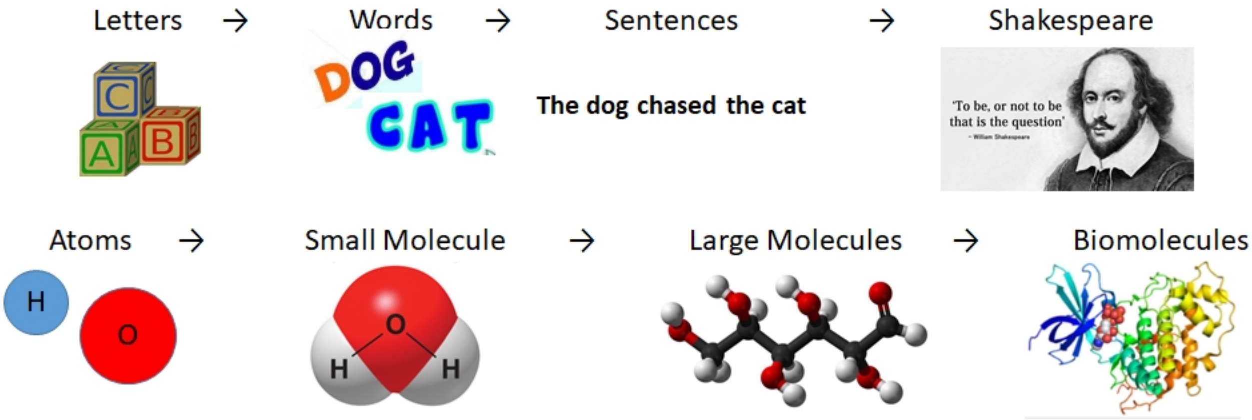


Figure 1.1 An analogy - chemistry (elements) and your english class (letters) are very similar. credit: author

are gained or lost to form ions which react to form ionic compounds. They are shared to form molecular compounds which includes most organic molecules studied in this book. Electrons essentially determine the chemistry we study.

Particle	**Symbol**	**Charge**	**Mass**	**Location**	**Importance**
Proton	p	+	1 amu	Nucleus	determines the element
Neutron	n	0	1 amu	Nucleus	determine the isotope
Electrons	e^-	-1	1/1832 amu	Cloud	determines chemical bonding and reactions

Table 1.1 Important properties of protons, neutrons and electrons

Cations and Anions

A driving force in the discovery of electrons (and protons) was the observation that some substances when dissolved in water conduct electricity and is attracted to the cathode (+) or anode (-) terminals of a battery. Atoms can gain or lose electrons to form charged ions. If an atom loses an electron the resulting ion is positive and called a cation. If an atom gains an electron the resulting ion is negative and called an anion. Multiple electrons can be lost or gained this way.

$$\begin{array}{lll} \text{Cation are positive} & \text{(lose electrons)} & \mathrm{Na} \longrightarrow \mathrm{Na}^{+1} + \mathrm{e}^- \\ \text{Anion are negative} & \text{(gain electrons)} & \mathrm{Cl} + \mathrm{e}^- \longrightarrow \mathrm{Cl}^{-1} \end{array}$$

Chemists represent the charge on an ion using a trailing superscript to denote the number of electrons missing (given a positive sign to indicate the charge on the ion formed), or the number of electrons gained (given a negative sign to indicate the charge on the ion formed). Cations and Anions are important in organic and biochemistry due to the attractive and repulsive forces between the charges as discussed in the next section.

Coulomb's Law Many concepts in chemistry depend on the attractive and repulsive forces between charged (+ and -) or partially charged (δ^+ and δ^-) ions and molecules. The proprieties of charges can be summarized as follows:

1. Two types of charges: positive (+) and negative (-)
2. Opposite charges attract (+/-) and like charges repel (++ or - -)
3. Charges can be transferred. In chemistry this is achieved by gaining or losing electrons.

4. The attractive or repulsive force is directly proportional to the magnitude of the charges and inversely proportional to the distance between them.

$$F = k\frac{q_1 q_2}{r^2}$$

F - force of attraction or repulsion
q_1, q_2 - magnitude of charges
r - distance between charges
k - Coulomb Constant

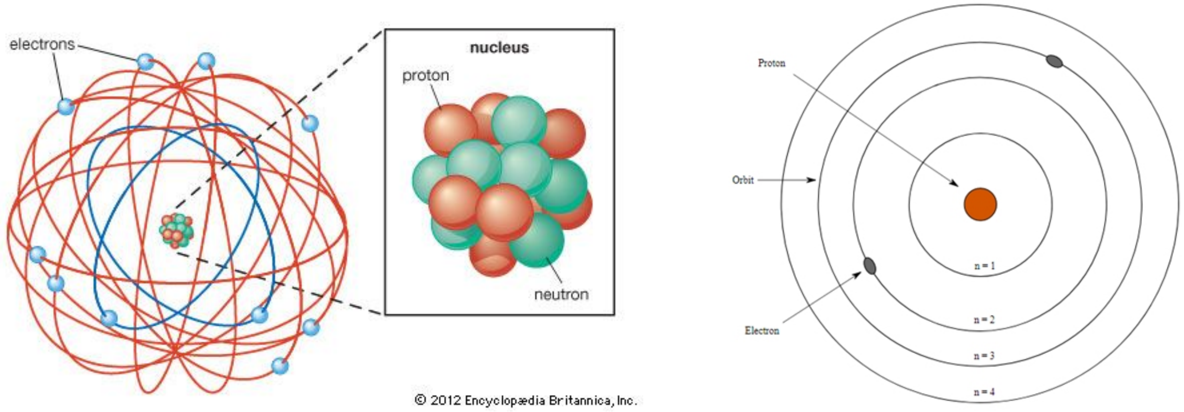
Figure 1.2 Coulomb's Law - describe the attractive or repulsive force between two charged particles. The force is directly proportional to the magnitude of the charges and inversely proportional to the distance between the charges

Coulomb's Law states that the force (F) associated with attraction or repulsion is directly proportional to the magnitude of the charges (q_1 and q_2) and inversely proportional to the distance (r) between the forces. In chemistry Coulomb's law is used to describe the interaction between protons and electrons in an atom, to describe the ionic bond formed between cations and anions (for example in Na^+Cl^-), to understand the sharing of electrons in covalent/molecular compounds, the solubility of compounds in water (and other solvents) and the Intermolecular Forces (IMF's) between molecules that explain many physical properties of compounds.

Models of the Atom

Understanding the structure of an atom, primarily the arrangement of electrons, is key to understanding the rules governing the formation of chemical bonds between atoms to form molecules. Over the course of time many models of the atom have been proposed, several of which will be explored here as each elucidates an important concept.

The **Rutherford Model** of the atom proposed that the protons and neutrons are located in a small, dense, and positively charged nucleus surrounded by a large cloud of negatively charged electrons. The attractive force between the electrons around the nucleus creates a stable atom and the attractive force between electrons to two different atoms nucleus results in the formation of a chemical bond.



(a) (b)

Figure 1.3 (a) Rutherford Model of the Atom (b) Bohr Model of the Atom credit: a: `https://commons.wikimedia.org/wiki/File:22476-004-9B6970F9.jpg` b: `https://commons.wikimedia.org/wiki/File:Bohr's_model.svg`

Bohr Model The next major advance in the understanding of the atom was the Bohr model which placed the electrons in quantized orbitals. The electrons can be pictured like planets orbiting the sun with only certain distances between orbitals allowed. Only the electrons in the outer orbitals are allowed to be lost or gained to form ions and shared to form molecules.

De Broglie Model Electrons are very small, and don't follow the rules of classical mechanics which describes them as particles which orbit the nucleus. Instead we need to think of them as particles and waves (wave/particle duality). Waves can exhibit constructive (waves reinforce) and destructive (waves cancel) interference, this results in forbidden orbitals where destructive interference occurs and allowed orbitals where constructive interference occurs, explaining the quantization of orbitals. This duality also means that a planetary/orbital model is too simple to explain how electrons interact, leading to the development of the Quantum Mechanical model of the atom.

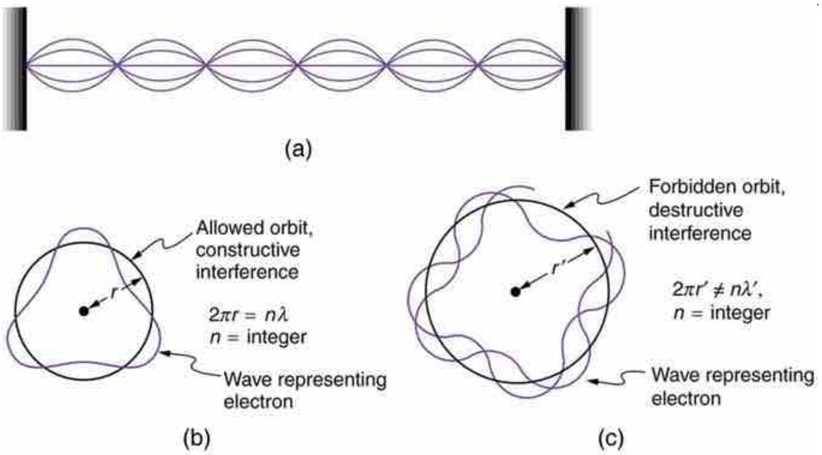


Figure 1.4 De Broglie Model of the atom. (a) electrons have wave and particle properties, specifically a wavelength, if the wavelenth when traced around an orbital results in (b) constructive interference the orbital is allowed and if it results in (c) destructive interference the orbital not allowed. This explains the quantitization of orbitals. credit: c: `http://oer2go.org/mods/en-boundless/www.boundless.com/physics/textbooks/boundless-physics-textbook/atomic-physics-29/the-early-atom-185/de-broglie-and-the-bohr-model-692-6303/index.html`

Model	**Key Aspect**
Rutherford	Nucleus is small, dense, positive charge.
Bohr	Electrons are in quanitized orbitals.
De Broglie	Electrons have properties of waves and particles
Quantum Mechanics	Electron orbitals have different shapes - s, p, d, f.

Table 1.2 Summary - Models of the Atom

1.2 Quantum Mechanic Model of the Atom

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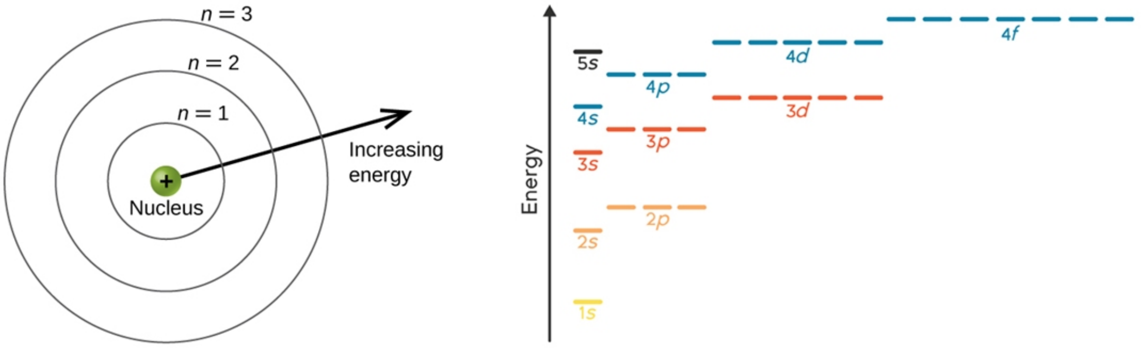
Quantum mechanics uses a mathematical wave-function to describe the location of electrons around an atom. Much like driving a car does not mean you can take one apart and put it back together, one can use Quantum Mechanics to describe electrons without understanding all of the mathematics behind it. Quantum mechanics describes the location of an electron using the four variable given in Table 1.3.

The **principal quantum number** (n) describes the distance an electron is from the nucleus. This also gives the energy of the electron according to Coulomb's Law which says the energy is inversely proportional

Name	**Symbol**	**Importance**
Principal	n	size and energy of (orbital or shell)
Angular Momentum	l	shape of orbital (4 allowed shapes - s,p,d,f)
Magnetic	m_l	orientation of orbital and # of sub-orbitals
Spin	m_2	electron spin - 2 allowed values (+ 1/2 or - 1/2)

Table 1.3 The Four Quantum Numbers, their commonly used symbols and what they describe about an electrons position around the nucleus.

to the distance from the nucleus. Electrons closer to the nucleus have a lower energy (more negative) energy than those further from the nucleus.



(a) (b)

Figure 1.5 (a) The Principal quantum number (n) determines distance the orbital is from the nucleus which using Coulomb's law can also be considered an energy level. The closer to the nucleus the electron is the lower in energy the orbital is. (b) Energy level diagram showing relative energy, orbital shape, and number of suborbital.

The **angular momentum quantum number** (l) describes the shape of orbitals and is normally designated by a letter (s,p,d or f). Unlike the planetary orbitals from the Bohr model of the atom, quantum mechanics predicts more complicated shapes. s-orbitals are spherical in shape, p-orbitals are shaped like dumb-bells d-orbitals and f-orbitals are more complex as shown below in Figure1.6

The **magnetic quantum number** (m_l) describes the orientation in space of each orbital and the number of sub-orbitals in each level (n). For a spherical s-orbital there is a single orientation of the orbital. For the dumb-bell shaped p-orbitals there are three orientations, one along each axis, resulting in 3 separate orbitals. Orientations are noted by a subscript and the axis which the orbital is aligned. For the p-orbitals this results in a p_x, p_y, and p_z orbital. d and f-orbitals are more complex shapes and orientations which we can ignore except for noting that their are 5 d-orbitals and 7 f-orbitals. Figure1.6 show all of the orbital shapes and orientations.

The **spin quantum number (**m_s has two allowed values (+1/2 or -1/2) which also means that each sub-orbital can hold two electrons. Thus an s-orbital with 1 orientation can hold 2 electrons, p-orbitals with 3 orientations each holding 2 electrons holds a total of 6 electrons. d-orbitals hold 10 total electrons and f-orbitals hold 14 electrons. The spin associated with an electron is also important in Nuclear Magnetic Resonance (NMR) which is a technique used in organic chemistry to experimentally determine the structure of molecules.

Electrons are placed in different orbitals according to the Aufbau principals which state that (1) an orbital can hold two electrons (with opposite spin), (2) electrons always fill lower energy orbitals before higher energy orbitals and (3) electrons in degenerate orbitals fill singly and are spin aligned until forced to pair up. The energy level diagram on the right in Figure 1.5 shows the relative energy levels of the orbitals, though

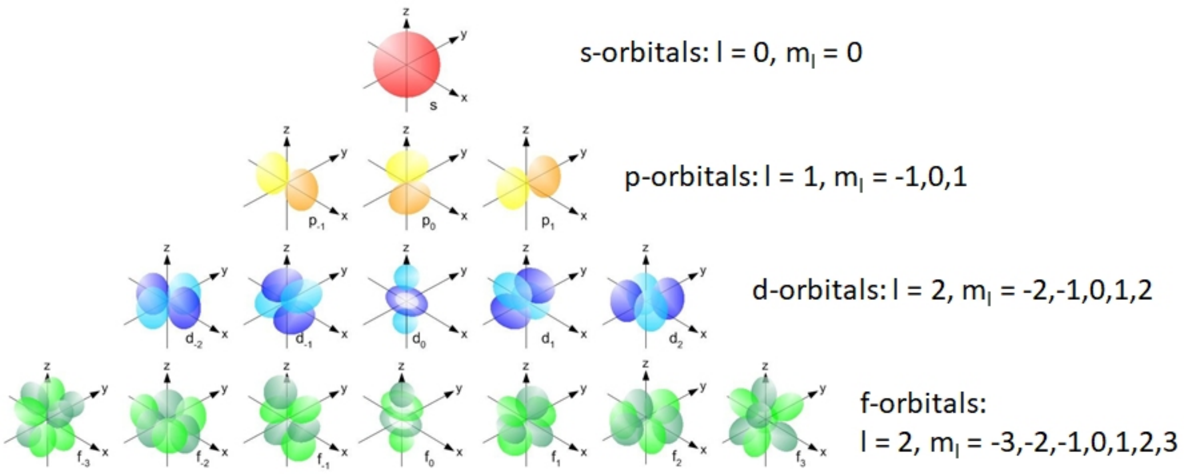
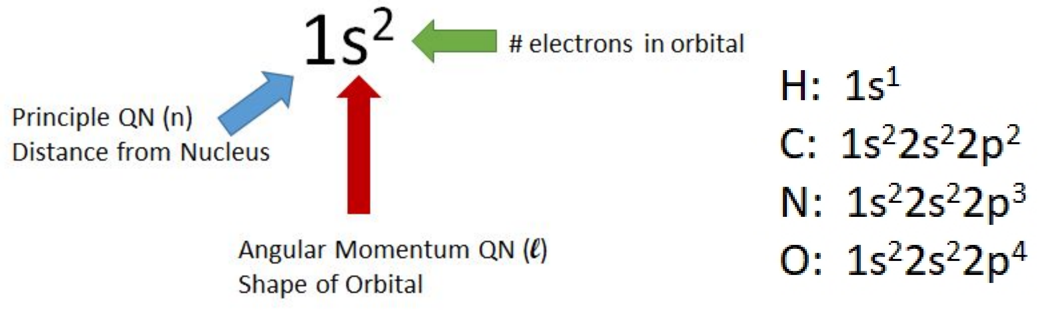


Figure 1.6 The angular momentum (l) quantum number determines the shape of orbitals described by the letters s, p, d, f. The magnetic (m_l) quantum number determines the number of orbitals (1, 3, 5, 7 respectively) and their orientation in space.

more frequently a condensed, shorthand notation is used in which only the principle quantum number, shape and number of electrons are shown.



(a) (b)

Figure 1.7 (a) Electron configuration notation used to show the energy levels of electrons in an atom. (b) Electron configurations for H, C, N, O - the four elements that are most important in organic chemistry. credit: author

The size and shape of the periodic table as shown in Figure 1.8 are reflected by the rules derived from quantum mechanics with the most important concepts being that the rows are related to the principle (n) quantum number, the width of each part of the periodic table reflects the number of electrons that are in a sub-orbital and the columns being associated with the atoms having the same electron configuration in the outermost orbital.

Valence electrons are those electrons found in the outer most orbitals s and p-orbital (orbital with the highest principle quantum number n) of an atom are easily gained or lost to make cations and anions which are attracted to each other by Coulomb's law to form ionic bonds. The same valance electrons can also be shared between atoms to form molecular compounds. Elements in the periodic table were initially placed on columns due to having similar chemical and physical properties, with the discovery of quantum mechanics, it is clear that elements in columns have the same number of valence electrons which is responsible for there similarities.

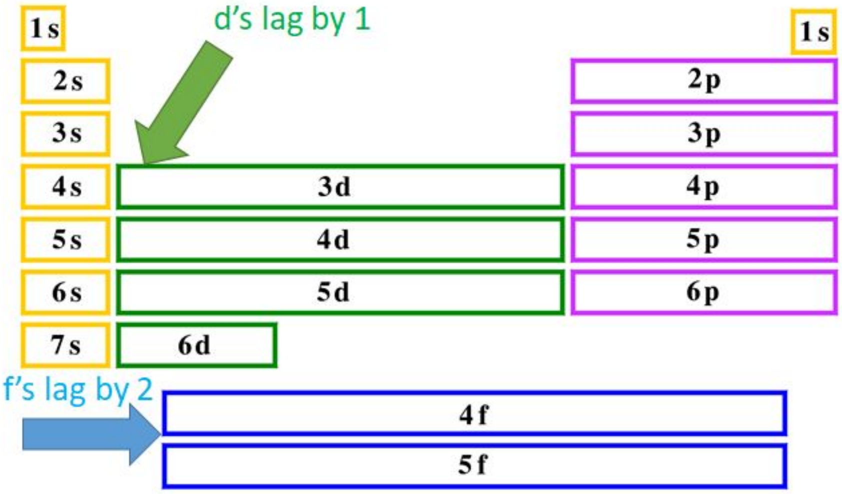


Figure 1.8 Relationship between the periodic table and quantum mechanics. Each row has the same principle (n) quantum number. The designation (s,p,d,f) determines the different sections with the width of each section determined by the number or orientation given by the angular momentum (l) quantum number with each orientation/sub-orbital holding two electrons.

1.3 Lewis Structures

Representing electrons using electron configurations is one way to illustrate what occurs, but another method has also proven quite useful which is commonly called Lewis structures. Gilbert Newton Lewis (1875-1946) developed a model about bonding between atoms to form molecules which he observed to occur such that the electrons in the valence shells add to eight. This is often called the **"octet" rule** and from our knowledge of quantum mechanics reflects having completing filled s and p orbitals (s^2p^6) which represents a stable state. The Lewis model is a simple, yet powerful, model of the atom which allows determination of molecular structure and geometry around a central atom. In most cases it is sufficient for our discussion of organic and biochemistry, though more advanced models based on quantum mechanics will also be examined.

Lewis electron dot structures or simply Lewis structures are a useful construct to keep track of valence electrons in representative elements. In this notation the valence electrons are represented by dots surrounding the atomic symbol of an element. Several examples are shown in Figure1.9. Ions are shown in brackets with the corresponding charge as a superscript.

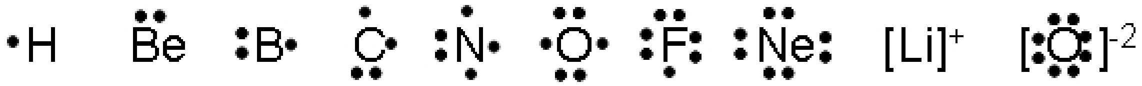


Figure 1.9 Lewis structure examples of the second row elements (Hydrogen to Neon), a cation (Lithium has lost its one valence electron), and an anion (Oxygen has gained two valence electrons). credit: author

Formation of Cations and Anions

Cations and anions form due to the stability gained from having an octet or s^2p^6 configuration in the atoms outermost orbital or valence shell. This explains the common charges that many elements have such as sodium always forming a +1 cation and chlorine always forming a -1 anion. Note that in Lewis structures only the outermost orbital is shown, so the empty outermost orbital around sodium is considered an octet.

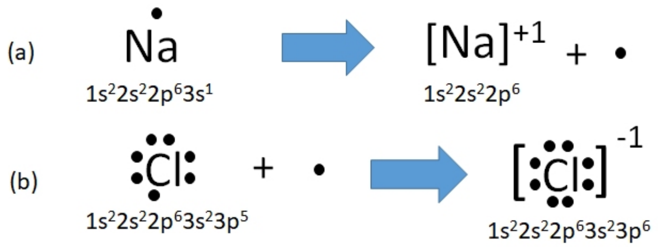


Figure 1.10 Formation of cations and anions using Lewis structures and electron configurations. (a) The sodium atom loses one electron in order to form a +1 sodium cation. (b) The chlorine atom gains one electron in order to form a -1 chlorine anion. Note that in Lewis Structures only the outermost orbital is shown, so the empty outermost orbital around sodium is considered an octet. credit: author

A general rule an which atoms tend to lose electrons (form anions) or gain electrons (form cations) to achieve an octet is an atoms location on the periodic table. The **metalloids** elements - Boron, Silicon, Germanium, Arsenic, Antimony, Tellurium and Polonium separate the **metals** (to the left) which form cations from the **non-metals** (to the right) which form anions. The exception to the rule being Hydrogen which completes an ”octet” with two electrons (due to not having a p-orbital) and is considered a non-metal but typically forms a cation.

1.4 Ionic, Polar Covalent and Covalent Compounds

The **chemical bond** that occurs between atoms to form compounds or molecules minimizes the energy between the charged particles (protons in the nucleus and electron in orbitals) according to Coulomb’s Law. It can occur in two ways, the formation of ionic bonds or the formation of molecular or covalent bonds. If two atoms can lose and gain electrons to complete octets an ionic bond forms between the cation (positive charge) and the anion (negative) charge. If two atoms share electrons to complete octets than a molecular or covalent bond forms due the shared electrons being attracted to protons in both atoms nuclei.

	Ionic Compounds	**Molecular Compounds**
Chemical Bond	Lose/Gain Electrons	Share Electrons
Formed between	metals/non-metals	non-metals/non-metals
Bond Strength	Strong	Weak
Structure	Lattice	Discrete Molecules

Figure 1.11 Key differences between Ionic and Molecular Compounds.

Ionic Compounds

Ionic compounds occur when cations (metals) and anions (non-metals) formed by losing and gaining electrons are then subsequently attracted to each other due to Coulomb’s law. This can be shown using Lewis structures and electron configurations as shown in Figure 1.12. Ionic bonds occur between a full positive and full negative charge and are a strong attraction compared to molecular bonds which share electrons. Ionic compounds generally form lattice structures.

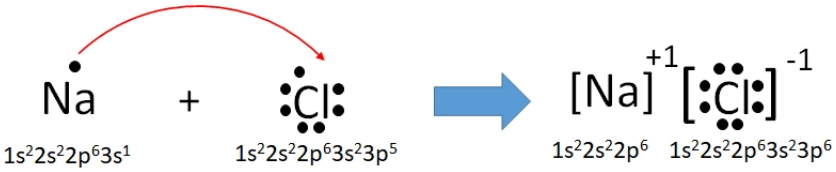


Figure 1.12 Formation of an ionic compound. The sodium atom loses one electron, to chlorine to complete both octets, the resulting cation and anion form an ionic bond due to Coulomb's law. credit: author

Molecular or Covalent Compounds

Molecular compounds (also commonly called **Covalent compounds**) occur when atoms can't form octets by gaining or losing electrons and instead must share electrons to form octets as shown in Figure 1.13. In Lewis Structures shared bonds can be represented in several ways though the most common is a line between two atoms represents a shared pair of electrons. The shared pair of electrons are counted towards each atoms octets.

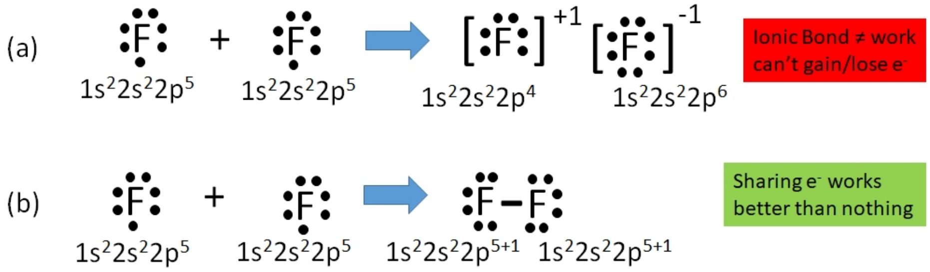


Figure 1.13 (a) Fluorine can't form an ionic bond with itself because only one atom can achieve an octet. (b) Fluorine forms a molecular compound by sharing a pair of electrons (the solid line represents two shared electrons) in order to complete both octets. credit: author

The energy is minimized when forming a molecular bond as the electrons feel the attractive force of both nuclei which reduces the overall energy of the system.

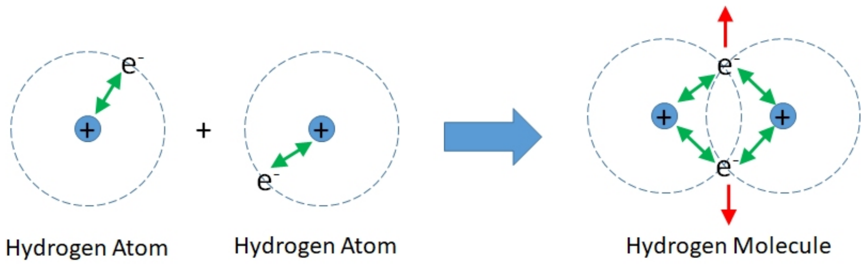


Figure 1.14 Formation of a molecular/covalent bond. On the left is two individual hydrogen atoms, the green arrows represent the attractive forces between the nucleus and the electron. On the right is a hydrogen molecule which allows both electrons to see both nuclei and increases the attractive forces. The red arrows represent electron-electron repulsion which also occur. The net effect is to lower the energy of the system. credit: author

Up to three pairs of electrons can be shared this way forming single (one shared pair of electrons), double (two shared pairs of electrons) and triple (three shared pairs) bonds. **Polyatomic ions** which are part ionic (gain or lose electrons) and part molecular (share electrons) can also be represented by Lewis Structures as a hybrid of both representations.

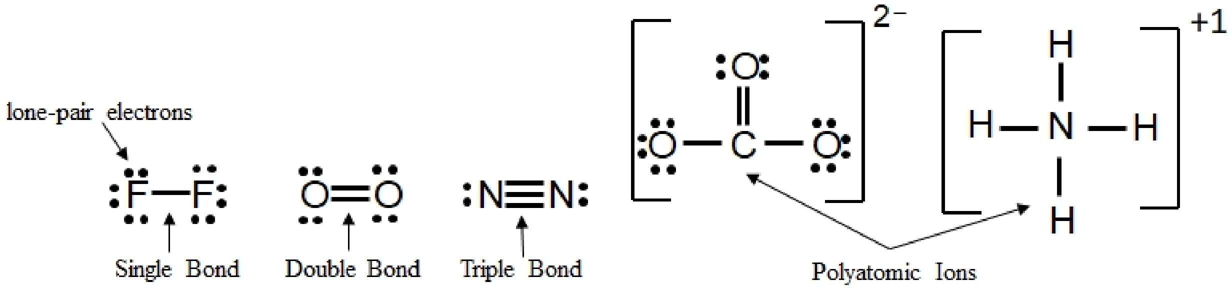
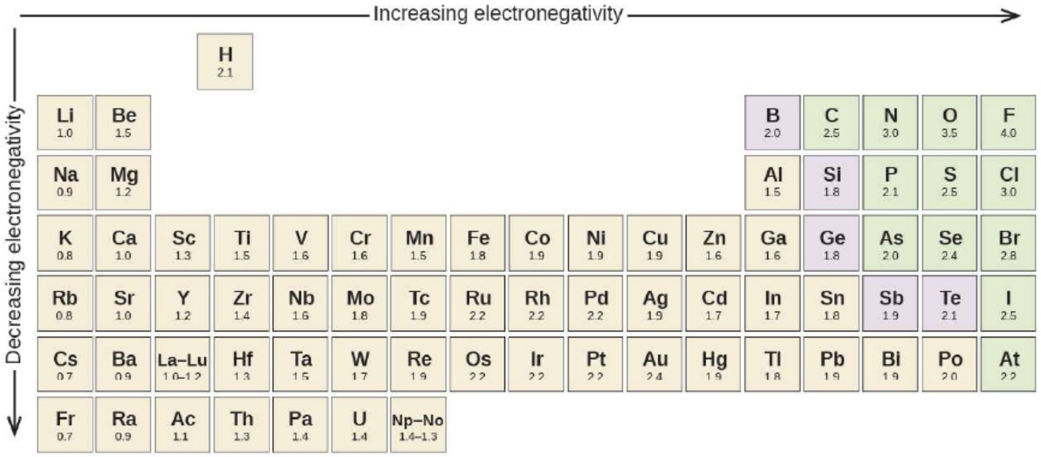


Figure 1.15 Lewis Structures illustrating single, double, triple bonds and polyatomic ions. credit: author

Electronegativity is the attractive force an atom has for the shared electrons in a bond. Electronegativity values are assigned to elements, and can be found in Figure 1.16. In general electronegativity increases across a row (Fluorine is the most electronegative element), and decreases down a column (Francium is the least electronegative element).



			H 2.1														
Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0
Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.9	Ni 1.9	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5
Cs 0.7	Ba 0.9	La–Lu 1.0–1.2	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.9	Bi 1.9	Po 2.0	At 2.2
Fr 0.7	Ra 0.9	Ac 1.1	Th 1.3	Pa 1.4	U 1.4	Np–No 1.4–1.3										

Figure 1.16 Electronegativity values for different elements. The larger the number, the more electronegative the element. credit: ??? (OER Book)

Bond Polarity describes the sharing of electrons between atoms. **Nonpolar Covalent** bonds form between atoms that are alike (ΔEN < 0.5), the shared electrons spend equal amounts of time around each atom and the electron density is symmetrical around the bond. **Polar Covalent** bonds occur between atoms that have different electonegativities ($0.5 < \Delta$EN < 2.0) which results in the electron density between the atoms being unsymmetrical around the bond. The resulting unsymmetrical distribution of electrons is indicated by using the Greek symbols δ^+ to indicate a small excess of positive charge, or δ^- to indicate a small excess of negative charge around an atom. The more electronegative element (larger value) is assigned the symbol (δ^-) the element with the smaller electronegativity value is assigned the symbol (δ^+). Another common method is to use a modified line for the bond with an arrow pointed towards the more electronegative atom, and a small cross towards the more electropositive atom. An example of both labeling methods is shown in Figure 1.17.

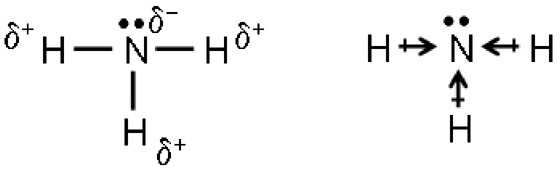


Figure 1.17 In polar bond the unsymmetrical distribution of electrons in a molecular bond between two atoms can be shown different ways. credit: author

In addition to bond polarity, **Molecular Polarity** can also occur when there is an unequal or unsymmetrical distribution of electron density around a molecule (not just between two atoms). **Nonpolar molecules** molecules have a symmetrical distribution of electron density around the entire molecule. **Polar or Dipolar** molecule has an unsymmetrical distribution of electrons around the molecule which results in the molecule being capable of interacting with each other like magnets due to Coulomb's law. The unsymmetrical distribution of electrons across a molecule also uses the (δ^+/δ^-) nomenclature though it is frequently shown pictorially as shown in Figure 1.17. Molecules with nonpolar bonds or with polar bonds that are symmetrical are always nonpolar whereas, molecules with polar bonds that are unsymmetrical are always polar.

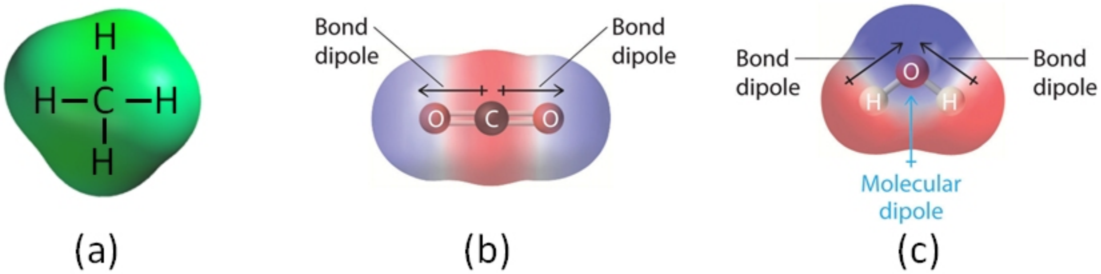


Figure 1.18 (a) A nonpolar molecule with nonpolar bonds and symmetrical distribution of electrons across the molecule. (b) A nonpolar molecule with polar bonds but a symmetrical distribution of electrons across the molecule (c) A polar or dipolar molecule with polar bonds and an unsymmetrical distribution of electrons around the atoms. credit: chemlibre + author

Summary of Ionic, Covalent and Polar Covalent Bonding

As has been discussed above there are three primary types of chemical bonds formed between atoms depending primarily on the electron configuration or Lewis structure and the electronegativity difference between the elements. These differences are summarized in Figure 1.20

As a general rule ionic bonds form when the Lewis structure can from octets by losing and gaining electrons, occurs between metals and non-metals and the elements have large differences in electronegativity ($2.0 < \Delta\text{EN}$). The ionic bond is between a full positive and negative charged cation and anion resulting a strong attraction due to Coulomb's law.

Molecular or covalent bonds form when the Lewis structure has to share electrons to complete octets, occurs between nonmetals and nonmetals and the elements have a small difference in electronegativity. The bond can be either nonpolar or polar. It is nonpolar if the electrons are shared relatively equally between the atoms due to a small difference in electronegativity ($\Delta\text{EN} < 0.5$) between the two atoms. The bond is polar if the electrons are shared unequally between the atoms due to a intermediate difference in electronegativity ($< 0.5\ \Delta\text{EN} < 2.0$) between the atoms. The resulting chemical bond is generally weaker than an ionic bond because no fully positive or negative charges are produced.

	Nonpolar Covalent	Polar Covalent	Ionic
Form between:	nonmetals-nonmetals	nonmetals-nonmetals	metals-nonmetals
ΔEN:	0-0.5	0.2-2.0	2.0-4.0
Electrons are:	shared equally	shared unequally	lost and gained
Bond Strength:	Weaker	Weaker	Stronger
Structure:	Discrete Molecules	Discrete Molecules	Lattice

Figure 1.19 Key differences between nonpolar covalent, polar covalent bonds and ionic bonds.

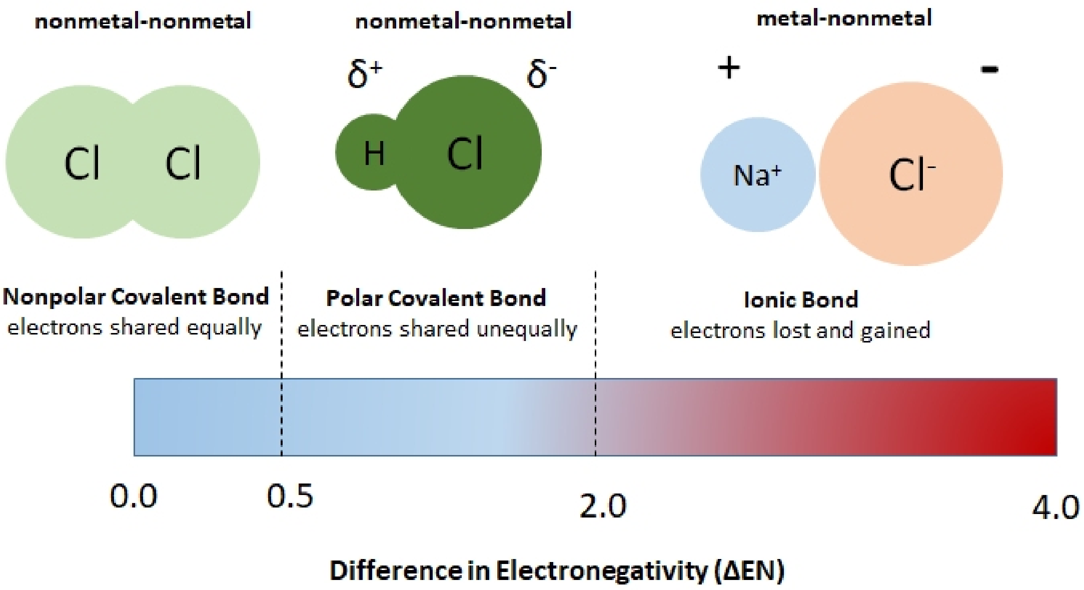


Figure 1.20 Key differences between nonpolar covalent, polar covalent bonds and ionic bonds. credit: author

1.5 Drawing Lewis Structures

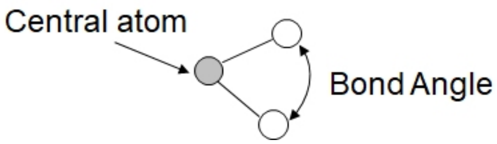
Molecular structure plays a crucial role in organic and biochemistry, the ability to draw Lewis structures, assign geometry, determine molecular polarity are one key to a better understanding of the topics. The following rules represent a good starting point for drawing Lewis structure, assigning geometry and determining the molecular polarity. A detailed example for two molecules is located at the end of this section.

1. Count the valence electrons in the molecule
2. Build a trial structure
3. Distribute electrons to complete octets
4. Finish incomplete octets by making single and double bonds
5. Determine the molecular geometry
6. Determine if the molecule is nonpolar or dipolar.

The geometry around each central atom in a molecule is uniquely determined by a combination of the number of atoms bonded to central atom and the number of lone pair electrons bonded to the central atom. Valence Shell Electron Pair Repulsion Theory (VESPR) states that atoms and lone pair electrons want to remain as far apart as possible due to the repulsive forces between electrons. This results in six primary shapes which obey the octet rule (violations of the octet rule are rare in organic and biochemistry, and will not be required knowledge). For larger molecules there may be more than one central atom and one geometry associated with the molecule. Figure 1.21 and 1.22 defines and gives examples for each geometry.

# atoms bonded	**# lone pairs**	**Geometry**	**Bond Angle**
4	0	Tetrahedral	109.5
3	1	Trigonal Pyramidal	109.5
2	2	Bent	109.5
3	0	Trigonal Planar	120
2	1	Bent	120
2	0	Linear	180

(a)



(b)

Figure 1.21 (a) Six geometries predicted by VSEPR theory. (b) A central atom must be connected to at least two other atoms in order to produce a geometry and bond angle credit: author

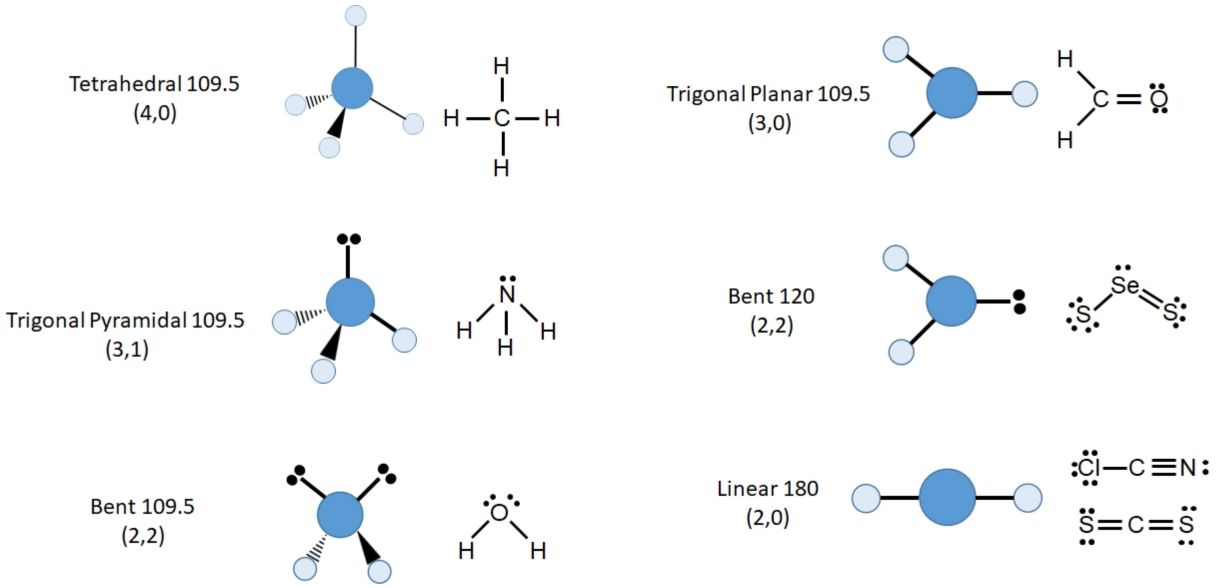


Figure 1.22 A 3D representation of each of the six geometries predicted by VSEPR theory and an example molecule with that geometry. Numbers in parenthesis represent the number of atoms bonded and the number of lone pairs which is unique for each geometry. credit: author

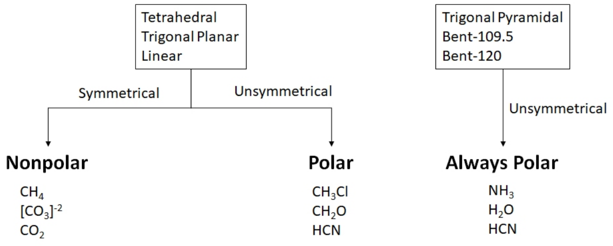
If the molecule is nonpolar or polar will determine how the molecules interact with other molecules and influences physical and chemical properties. More detail is in the next section on Intermolecular Forces (IMF's). In a nonpolar molecule the distribution of electrons around the molecule is symmetrical while in a polar molecule the distribution of electrons is asymmetrical resulting in a polarized molecule where one end has an excess of positive charge and is labeled δ^+) and one end has an excess of negative charge (δ^-). To determine the molecular polarity requires knowing the difference in electronegativity between the atoms (ΔEN) and the molecular geometry.

Organic compounds are mostly composed of C, H, N, and O, Figure 1.23 shows the most common bonds, the difference in electronegativity and whether the bond type is nonpolar or polar using the electronegativity values found in Figure 1.16. The predominant bond type in organic molecules C-H is nonpolar, with C-O, O-H and N-H bonds being very polar.

The geometry of a molecule is also used to determine the molecular polarity, symmetrically shaped molecules are nonpolar, any assymetrical distribution of electrons in a bond cancels out, while in unsymmetrical

Bond	ΔEN	Bond Polarity
C-H	0.4	nonpolar
C-N	0.5	slightly polar
O-N	0.5	slightly polar
N-H	0.9	polar
C-O	1.0	polar
O-H	1.4	polar

(a)



(b)

Figure 1.23 (a) Bond polarity for common organic bonds between C, H, N, and O. (b) Symmetrical geometries always result in nonpolar molecules, Unsymmetrical geometries can results in polar molecules. credit: author

molecules if a polar bond exists than the molecule will also be polar. Molecular geometry's that are symmetrical will be nonpolar if the surrounding atoms are identical whereas if the surrounding atoms are different the molecule will be polar. Any molecular geometry with a lone pair of electrons is unsymmetrical and will result in a polar molecule. There are four potential outcomes when combining bond polarity and molecular geometry are shown Figure 1.24.

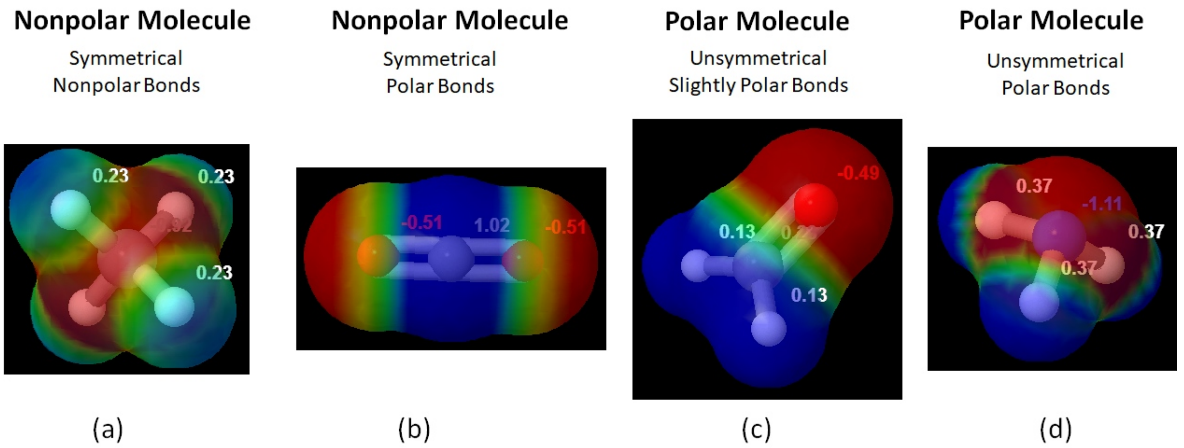


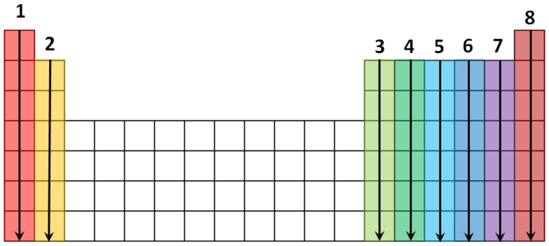
Figure 1.24 Four possible combinations of geometry and bond polarity resulting in nonpolar or polar molecules. Red indicates areas of excess positive charge, blue represents area's of excess negative charge. Values indicate relative amounts of excess charge (red = positive, white = negative). Models constructed using: `http://www.chemeddl.org/resources/models360/models.php`. credit: author

Step 1: Calculate the number of valence electrons

a. Add up valence electrons for all atoms

b. Cation - lose electrons; <u>subtract</u> the charge

c. Anions - gain electrons; <u>add</u> the charge



Ex: NH_4^+

N = 5

4 (H) = 4(1)

Charge = -1

Valence e^- = 8

Ex: CO_3^{-2}

C = 4

3 (O) = 3(6)

Charge = +2

Valence e^- = 24

Step 2: Build a trial structure

a. Place the least electronegative (EN) element in the middle

b. Arrange other atoms around it to make molecules as symmetrical as possible

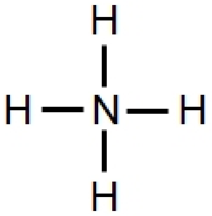
c. Draw one bond connecting atoms together

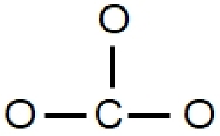
d. H makes 1 bond (never in middle)

e. F, Cl, Br, and I generally form 1 bond

f. Oxygen rarely bonds to oxygen

g. Typical Bonding Patterns – H = 1 bond , O = 1 or 2 bonds, C = 4 bonds, N = 1,2,3 and rarely 4 bonds if it is part of a polyatomic ion.





Step 3: Distribute electrons

a. Count the electrons left after making the trial structure

Remaining e- = Valence e- - 2 × (# of Bonds)

b. Distribute remaining electrons to complete octets (noble gas configurations)

c. Start with the most electronegative (EN) element first

d. Remember H has an "octet" with 2 electrons

Valence e^-: 8

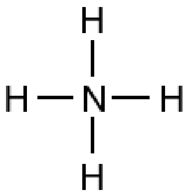
- 2 (# of Bonds): – 2·(4)

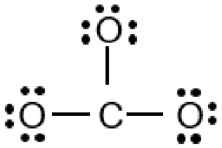
Remaining e^-: 0

Valence e^-: 24

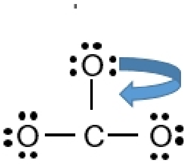
- 2 (# of Bonds): – 2·(3)

Remaining e^-: 18





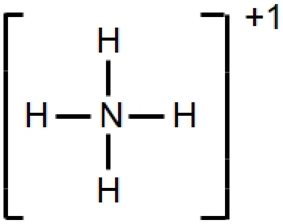
Step 4: Finish any incomplete octets by sharing electrons

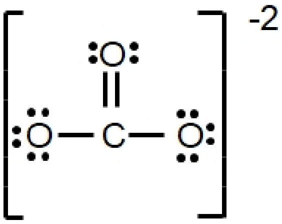

Share the lone pair of electrons on oxygen with the carbon to complete carbons octet.

a. If some atoms can't complete octets remove unshared electron pairs and form double or triple bonds.

b. If all atoms have complete octets the Lewis structure is done

c. Remember to put cations and anions in brackets and include the charge

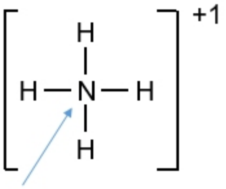




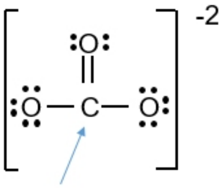
Step 5: Determine the geometry of each Lewis structure

a. Count the number of atoms bonded to the central atom and the number of lone pairs around each central atom.

b. Use Figure 1.21 to determine the geometry



4 atoms, 0 lone pair
Tetrahedral – 109.5



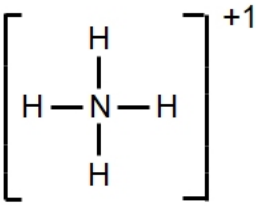
3 atoms, 0 lone pair
Trigonal Planar – 120

Step 6: Determine the polarity of the molecule

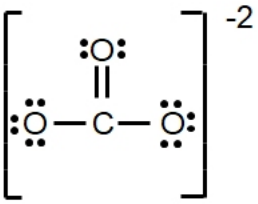
a. Refer to Figure 1.24

b. Nonpolar molecule - symmetrical or nonpolar bonds

c. Polar Molecule - unsymmetrical + polar bonds



Symmetrical
Nonpolar



Symmetrical
Nonpolar

1.6 Intermolecular Forces (IMF's)

While organic and biological chemistry is a very diverse field of study, one fundamental question that interests all organic chemists is how the structure of an organic molecule determines its physical properties. To understand why sperm oil has properties that made it both a useful industrial lubricant for humans and an effective buoyancy control and/or sonic lens for a hunting sperm whale, we first have to understand the nature of both the forces holding each wax molecule together – the covalent single and double bonds between atoms – and also the forces governing the noncovalent interactions between one wax molecule and all the others around it – the so-called 'intermolecular forces' which determine physical properties such as viscosity, melting point, and density.

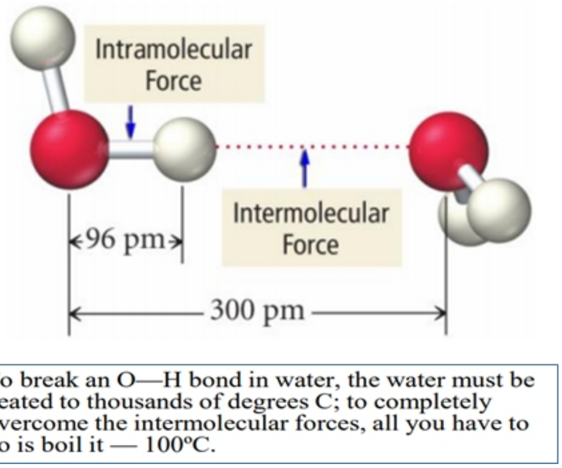
Soderberg

Chemical Bonds occur when electrons are gained or lost to form ionic bonds or shared between atoms to form molecular bonds. Chemical bonds are responsible for the chemical properties of a compound. Chemical bonds are a strong attractive force due to Coulomb's law, ionic bonds are very strong and occur between a cation (full + charge) and an anion (full - charge), while molecular bonds are strong and occur when atoms share electrons.

Intermolecular Forces (IMF's) occur between molecules and are responsible for the physical properties of molecules. Intermolecular forces are primarily due to Coulomb's law but are much weaker than a chemical bond as the attraction is between molecules with partial positive (δ^{+}) and negative (δ^{-}) charges due to the asymmetric distribution of electrons around the molecule.

	Chemical Bond	**Intermolecular Force's**
Between	atoms	molecules
Strength	Strong	Weak
Properties	Chemical	Physical
Types	Ionic	LDF
	Molecular	DD
		HB
		ID
Drawn as	Solid Line	Dashed Line

(a)



To break an O—H bond in water, the water must be heated to thousands of degrees C; to completely overcome the intermolecular forces, all you have to do is boil it — 100°C.

(b)

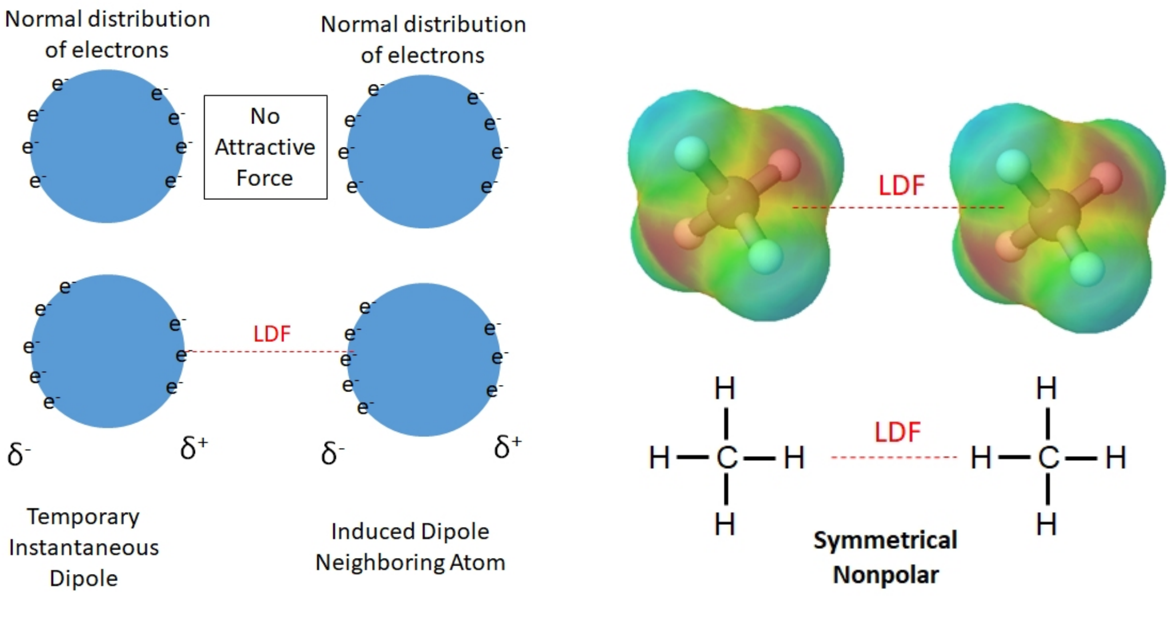
Figure 1.25 (a) Summary of the differences between chemical bonds and intermolecular forces. (b) Lewis structure showing the difference between a chemical bond and an intermolecular force. credit: unknown

London Dispersion Forces (LDF)

London Dispersion Forces (LDF's) also known as **Dispersion Forces** occur between nonpolar molecules due to the formation of temporary, instantaneous dipoles. These temporary dipoles form because the electrons around a molecule are constantly in motion, at some point even in nonpolar molecules there will be a instantaneous moment (like a snapshot of a movie) in which the normally symmetrical distribution of electrons will be unsymmetrically distributed. The resulting dipole can induce a similar, though opposite, distribution of electrons in a nearby molecule resulting in a small electrostatic attractive force between the molecules due to Coulomb's law. This is illustrated in Figure 1.26 between two atoms and between two molecules. The attractive force is very weak as the dipoles are only temporary, however, the attractive forces between two molecules is directly proportional to the size electron cloud around the molecule, becoming very large for large molecules. Often molecular weight is used as an estimate of the size of the molecule. Molecular shape also plays a role as will be seen later.

Dipole-Dipole(DD) Forces

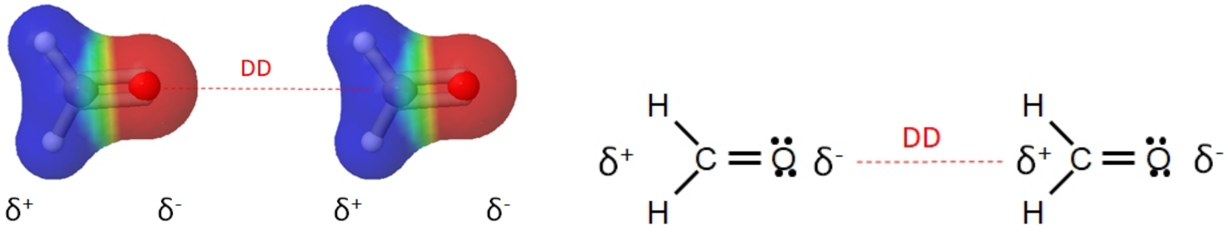
Dipole-Dipole attractions occur between two polar or dipolar molecules due to the electrostatic attraction between the partial charges. The attractive force is directly proportional to how assymetrically the electrons are distributed which can be approximated by the difference in electronegativity (ΔEN) between the atoms



(a) (b)

Figure 1.26 (a) Top: No attractive forces between nonpolar atoms. Bottom: Attractive force between two atoms due to temporary instantaneous dipoles creating a very small difference in the electron distribution. (b) London Dispersion forces between two different representations of methane (CH_4). Methane model constructed using: `http://www.chemeddl.org/resources/models360/models.php` credit: author

in the molecule or more formally by calculating the dipole moment (beyond the scope of this class). Dipole-Dipole attractions are slightly stronger than London Dispersion Forces. Figure 1.27 illustrates a dipole-dipole attraction between two methanal molecules (CH_2O also known as formaldehyde).

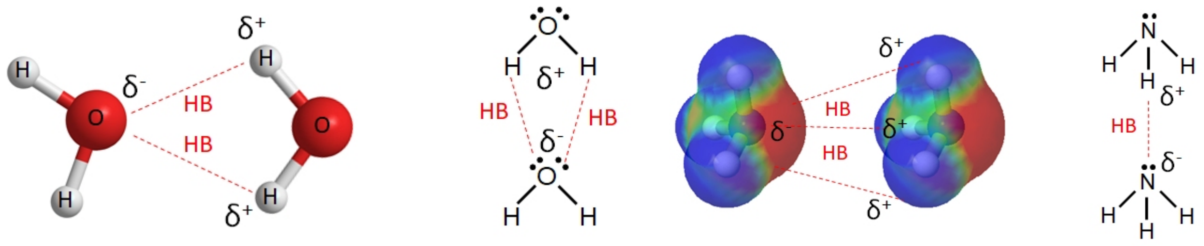


(a) (b)

Figure 1.27 (a) Dipole-Dipole attraction between two methanal (CH_2O) molecules showing the electron density. Methanal model constructed using: `http://www.chemeddl.org/resources/models360/models.php` (b) Dipole-Dipole interaction shown using Lewis structures. credit: author

Hydrogen Bonding (HB)

Hydrogen Bonding is a special case of dipole-dipole interactions that is considerably stronger due to Hydrogen only having one electron, resulting in any dipoles being significantly larger than for other atoms. For a Hydrogen Bond to occur Hydrogen must be bonded to a small highly electronnegative atom (Oxygen, Nitrogen or Fluorine) producing a large dipole due to the combination of hydrogen having a single electron and oxygen, nitrogen and fluorine producing a very polar bond. The hydrogen atom is attracted to a lone pair of electrons on another molecule or to a partial negative charge (δ^-) on another molecule. The resulting electrostatic attraction is approximately ten times stronger than a normal dipole-dipole attraction. The most common source of hydrogen bonding is of course water (H_2O) which can form two hydrogen bonds. Figure 1.28 illustrates this for several molecules. The term Hydrogen Bond is misleading, it is an intermolecular force (IMF), not a chemical bond.

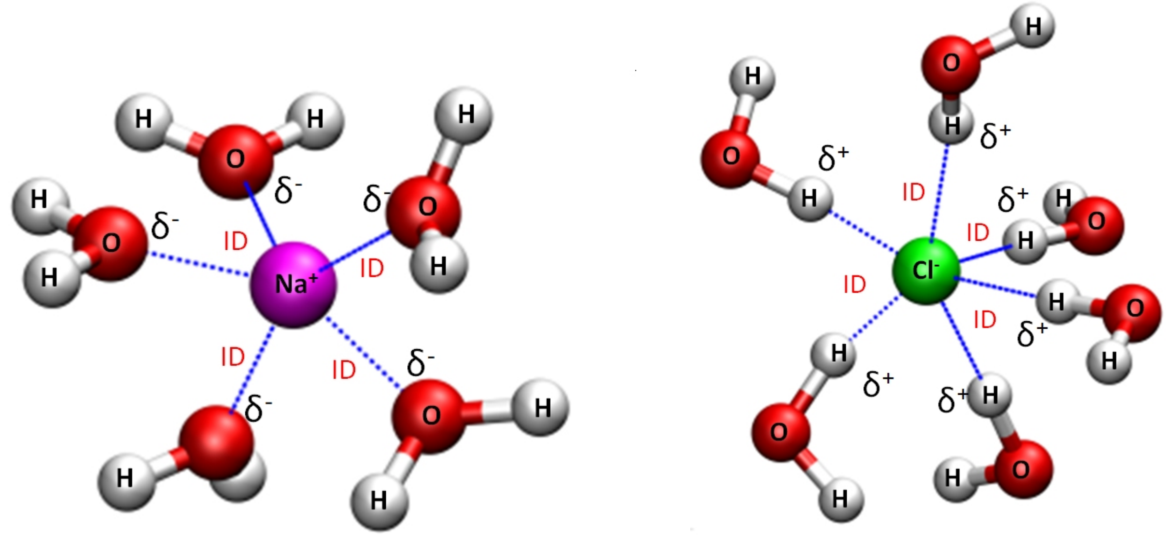


(a) (b)

Figure 1.28 (a) Hydrogen bonding between two water molecules (H_2O). (b) Hydrogen bonding between two ammonia molecules (NH_3). Ammonia model constructed using: `http://www.chemeddl.org/resources/models360/models.php` credit: author

Ion-Dipole (ID)

Ion-Dipole (ID) interactions occur between an ion (cation or anion) and a dipolar molecule. The resulting electrostatic attraction between a full charge (+/-) and a partial charge (δ^+/δ^-) is the strongest intermolecular force. It is proportional to the charge on the ions and the size of the dipole moment, both of which will be ignored in this course.



(a) (b)

Figure 1.29 (a) Ion-Dipole attraction (blue dotted line) between a cation (Na^+) and water molecules (H_2O), note that the water molecules orient with the oxygen (δ^-) towards the cation. (b)Ion-Dipole attraction (blue dotted line) between an anion (Cl^-) and water molecules (H_2O), note that the water molecules orient with the hydrogen (δ^+) towards the anion. credit: author

Summary - Chemical Bonds and Intermolecular Forces

The relative strengths of chemical bonds intermolecular forces can vary greatly depending on the atoms bonded and molecular geometry. Figure 1.30 provides a brief summary of the forces and provides some numbers to give the reader a relative idea of how they compare.

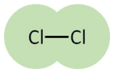
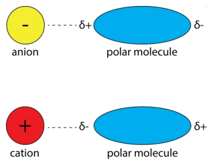
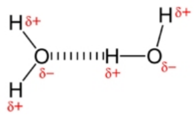
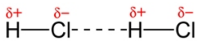
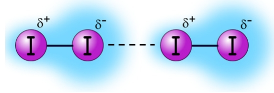
Interaction	Attraction between	Strength kJ/mol	Model	Example Compound
Ionic Bond	Cation-Anion	400-4000		NaCl, $Mg(NO_3)_3$
Molecular Bond	Atoms share e^-	150-1100		Cl_2, CH_4
Ion-Dipole (ID)	Cation and Polar Molec. Anion and Polar Molec.	40-600		$Na^+ \cdots H_2O$ $Cl^- \cdots H_2O$
Hydrogen Bond (HB)	H bonded to O, N, F attracted to lone pair e^-	10-40		$H_2O \cdots H_2O$
Dipole-Dipole (DD)	2 polar molecules	2-25 $\propto$ ΔEN		$HCl \cdots HCl$
London Dispersion Forces (LDF)	2 nonpolar molecules	0.05-40 $\propto$ Size		$I_2 \cdots I_2$

Figure 1.30 Summary of Attractive Forces between atoms (ionic and chemical bonds) and between molecules (intermolecular forces - ID, HD, DD, LDF). credit: NaCl - `https://commons.wikimedia.org/wiki/File:Sodium-chloride-unit-cell-3D-ionic.png`, Cl_2 - Author, Ion-Dipole - `https://www.ck12.org/book/ck-12-chemistry-basic/section/9.4/` Dipole-Dipole - `https://en.wikipedia.org/wiki/File:Dipole-dipole-interaction-in-HCl-2D.png`, London Dispersion Forces - `www.dlt.ncssm.edu`

1.7 Physical Properties and Intermolecular Forces

Physical properties of molecules are inherent characteristics of a molecule that can be determined without changing its composition (ie breaking and making chemical bonds) and are determined by the intermolecular forces between molecules. Physical properties include easily measured properties like melting points, boiling points, states of matters (solid, liquid, gas), density, solubility, vapor pressure and harder to measure properties such as color, taste and odor.

Melting and Boiling Points

The state of matter at a particular temperature, melting points and boiling points are all a measure of how attracted individual molecules are to each other compared to the kinetic energy (temperature) of the molecules. Three molecules can be used to illustrate this, methane (CH_4), water (H_2O), and sodium chloride (NaCl) shown below in Figure 1.31. Methane is a nonpolar molecule and only has weak London Dispersion Forces trying to hold molecules together, at room temperature the molecules have enough kinetic energy to overcome the attractive forces. Water is a polar molecule capable of forming two strong hydrogen bonds between molecules, at room temperature the molecule is a liquid, the kinetic energy is similar in strength to the attractive forces, the molecules cohere but can move. Sodium Chloride forms a rigid lattice held together by ionic bonds which are much stronger than the average intermolecular force, at room temperature the kinetic energy is less than the strong attractive holding the lattice together, thus sodium chloride is a solid at room temperature.

Property	**CH_4**	**H_2O**	**NaCl**
IMF	LDF	HB	IB
MP (℃)	-182	0.0	801
BP (℃)	-164	100.	1413
State (20℃)	gas	liquid	solid

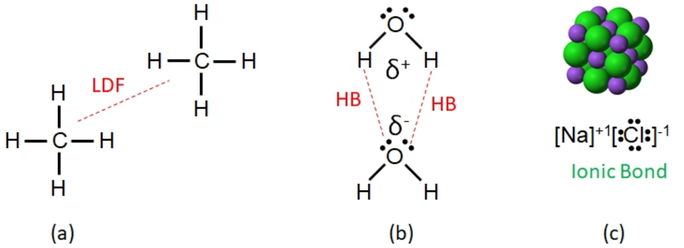


Figure 1.31 Table showing relationship between boiling point, melting point and strength of the attractive forces between three molecules. (a) Methane is nonpolar, has weak London Dispersion Forces holding the molecules together and is a liquid at room temperature. (b) Water is polar and forms two strong hydrogen bonds, it is a liquid at room temperature. (c) Sodium chloride is held together by ionic bonds and is a solid at room temperature. credit: author

The transition from solid to liquid happens at the melting point of a substance, molecules have enough kinetic energy to overcome the attractive forces between the molecules allowing the molecules to move and become liquid. The transition from liquid to gas happens at the boiling point of a substance, molecules have enough kinetic energy to completely overcome the attractive forces holding the molecules together, the molecules move far apart and no longer interact with each other. Both melting point and boiling point are directly dependent on the strength of the attractive forces, weak intermolecular forces like London Dispersion Forces (LDF) lead to low values, while strong intermolecular forces like hydrogen bonds (HB) lead to high values as illustrated in Figure 1.31

Vapor Pressure

Other physical properties like vapor pressure which measure the relative number of molecules in the gas phase compared to the liquid phase are inversely proportional to the strength of the attractive forces. Molecules with strong attractive forces like hydrogen bonds (HB) have low vapor pressures because the molecules lack the kinetic energy to escape the liquid. Molecules with weak attractive forces like London Dispersion Forces (LDF) have high vapor pressures because it takes very little energy for a molecule to go from the liquid phase to the gas phase. This is illustrated for several molecules in Figure 1.32.

Solubility

Solubility is best summarized by two statements which mean much the same thing, “like dissolves like” or “oil and water don’t mix”. Molecules with similar intermolecular forces interact with each other and will dissolve easily or make miscible solutions. Molecules that do not have similar intermolecular forces will not dissolve

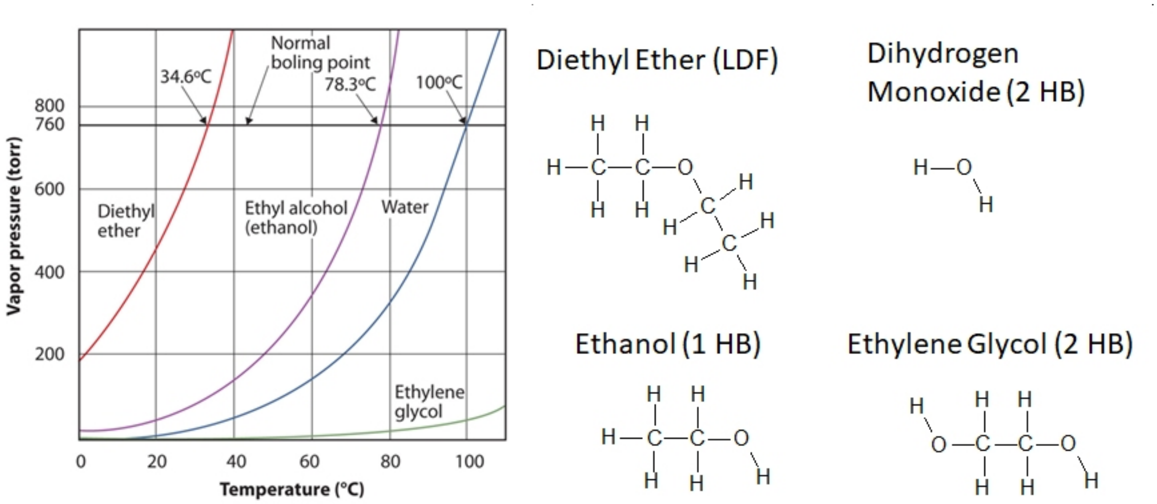
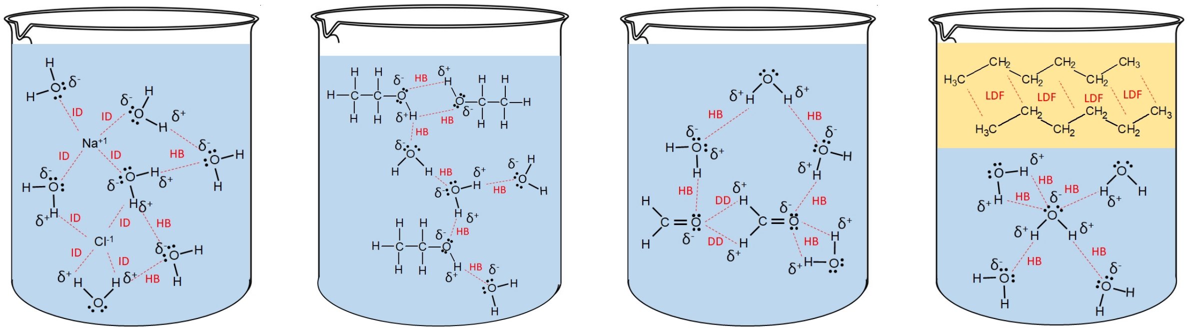


Figure 1.32 Graph showing vapor pressure of several compounds. Note that diethyl ether with only London Dispersion Forces has the highest vapor pressure while Ethalene Glycol which can form two hydrogen bonds (HB) has the lowest vapor pressure. credit: Graph `https://opentextbc.ca/introductorychemistry/`, Lewis Structure - author

or make immiscible solutions. "Like dissolve like" illustrates that nonpolar molecules with only London Dispersion Forces (LDF) will dissolve or are miscible with other nonpolar molecules. Polar molecules with Dipole-Dipole (DD), Hydrogen Bonds (HB) or ionic substances that can form Ion-Dipole (ID) interactions with each other will dissolve or be miscible with each other. "Oil and water don't mix" highlights that nonpolar (LDF) and polar molecules (DD, HB, ID) will generally not dissolve or be immiscible. Figure 1.33 illustrates the solubility of four different compounds in water. Sodium Chloride, ethanol and methanal (acetone) are soluble in water while hexane is not.



(a) (b) (c) (d)

Figure 1.33 Solubility - "Like dissolves like" (a-c), and "Oil and water don't mix" (d). (a) Ionic compounds - NaCl dissolve in water through Ion-Dipole (ID) interactions. (b) Ethanol - CH_3CH_2OH dissolves in water through Hydrogen Bond (HB) interactions. (c) Dipolar molecules - CH2O dissolve in water through Dipole-Dipole (DD) and Hydrogen Bond (HB) interactions. (d) Hexane - $CH_3(CH_2)_4CH_3$ will not dissolve in water, London Dispersion forces and Hydrogen bonds can't interact. credit: author

A more detailed rule ranks the IMF's from most polar to least polar and suggests that molecules can interacts (can dissolve or are miscible) with the intermolecular force directly above or below it. This rule is sometimes referred to as the +/- one rule, shown in Figure 1.34. Water is a common solvent for polar molecules, hexane is a good solvent for nonpolar molecules, intermediate between the two is acetone (CH_2O) which can form weak Dipole-Dipole (DD) interactions with polar molecules, but is weak enough that it can also have

London-Dispersion Forces (LDF) with nonpolar molecules.

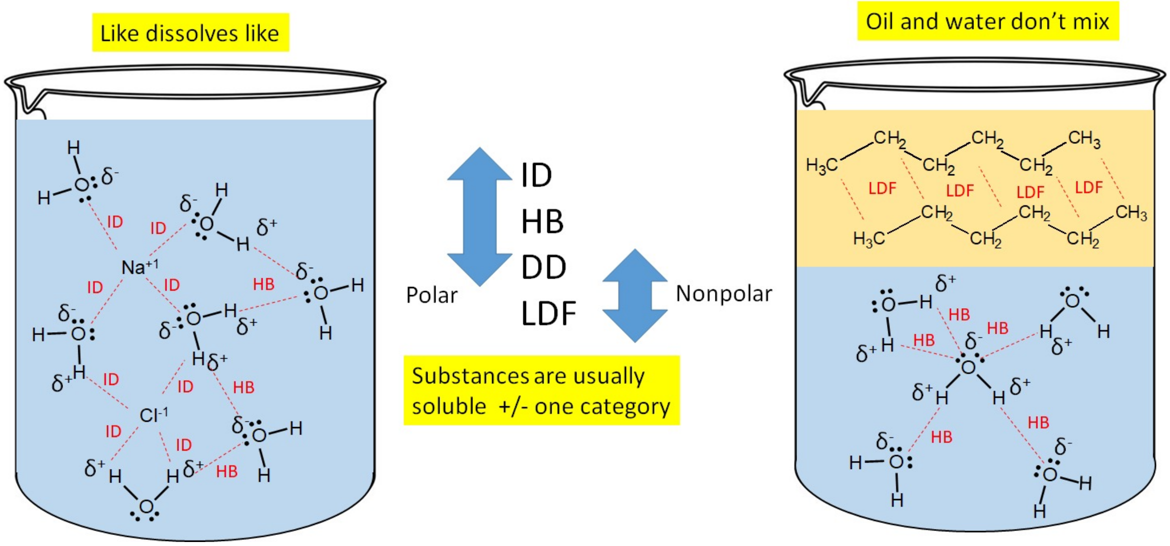


Figure 1.34 Molecules are generally soluble with +/- one category. credit: author

Key Idea: IMF and Physical Properties

1. Intermolecular forces are a measure of the attractive forces between molecules and determine many physical properties.
2. Melting points and boiling points are directly proportional to the strength of the IMF
3. Vapor pressure is inversely proportional to the strength of the IMF
4. Solubility is determine by like dissolves like, which means molecules with similar IMF wll dissolve in each other.

Chapter 2

Alkanes

Oil is primarily composed of alkanes
credit: `https://en.wikipedia.org/wiki/Alkane`

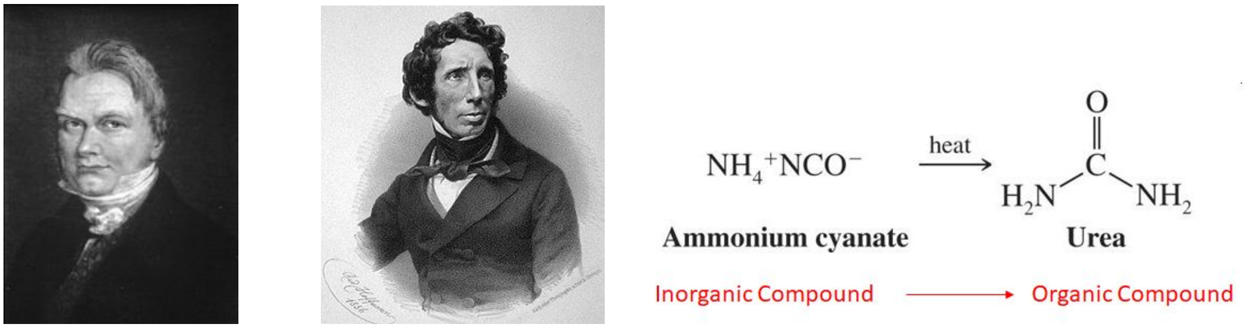
2.1 Historical Perspective

Historically chemistry has been divided into several categories including inorganic chemistry (the focus of first semester), organic chemistry (focus of the first half of this semester), biochemistry (the focus of the second half of this semester), physical chemistry, analytical chemistry and many others. These divisions are artificial and there is considerable overlap between them and between chemistry and the fields of biology and physics. This should be unsurprising as chemistry is usually defined as the science that studies the composition, properties and reactions of matter which makes up everything.

The major branches of **inorganic** chemistry and **organic** chemistry was initially based on the whether the compounds studied came from non-living or living organisms. In 1810, J.J. Berzelius stated that living things work by some mysterious “vital force”, a hypothesis called **vitalism**. Berzelius believed that compounds could be distinguished by whether they required a living organism to produce (organic compounds) or whether they did not (inorganic compounds).

In 1828 Friedrich Wöhler synthesized urea a known organic compound Urea which is a product of protein metabolism in animals without use of a living organism by decomposing ammonium cyanate. In addition to disproving vitalism theory, Wöhler is credited with introducing the concept of a **Functional Group** which are specific parts of a molecule which are responsible for the characteristic physical and chemical properties of those molecules. Functional Groups have similar physical and chemical characteristics across a wide range of molecules.

While the historical perspective does provide some context for what organic chemistry is,it can perhaps be best defined as the study of carbon containing compounds. This classification highlights the fact that the primary component of most organic molecules is a chain of carbon atoms bonded to each other. Other important elements include hydrogen, oxygen and nitrogen and to a lesser extent phosphorus, sulfur and halogen atoms.



(a) (b) (c)

Figure 2.1 (a) J.J. Berzelius - Vitalism Theory (b) Friedrich Wöhler - Urea Synthesis and (c) Urea Synthesis Reaction which disproved the vitalism theory. credit: a: `https://en.wikipedia.org/wiki/Jons_Jacob_Berzelius` b: `https://en.wikipedia.org/wiki/Friedrich_Wohler`

2.2 Functional Groups

Organic chemistry can be organized by many different methods, the easiest is by functional groups, as can be seen by examining the table of contents this book. **Functional Groups (FG)** are specific molecular structures that are responsible for a molecules unique chemical and physical properties. Figure 2.2 lists all functional groups covered in this book along with the general formula, condensed formula, Lewis structure, Line structure and the IUPAC (International Union of Pure and Applied Chemists) name ending. Each of the columns will be discussed in next few sections, and the table should also serve as a road map for the next six chapters on organic chemistry and will be refereed back to frequently. In the biochemistry chapters, macromolecules are associated with one or more functional groups, and to understand the reactions occurring in metabolism one will have to identify the functional groups and the reactions they commonly undergo.

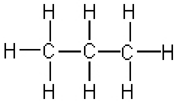
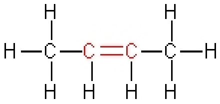
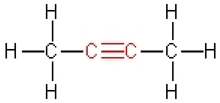
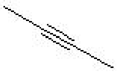
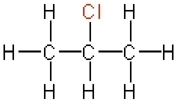
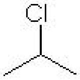
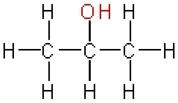
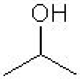
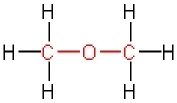
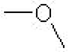
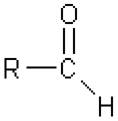
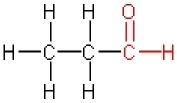
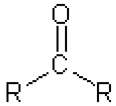
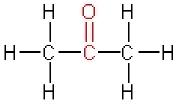
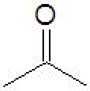
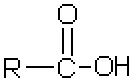
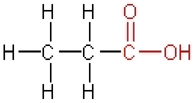
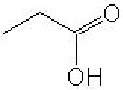
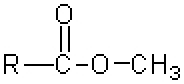
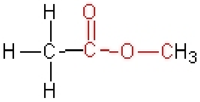
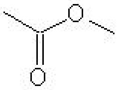
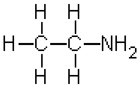
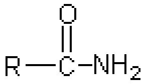
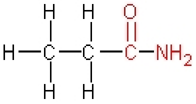
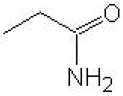
Class	Functional Group	General Formula	Condensed Formula	Lewis Structure	Line Structure	IUPAC Naming
Alkane	C-C	C_nH_{2n+2}	$CH_3CH_2CH_3$			-ane
Alkene	C=C	C_nH_2n	$CH_3CH{=}CHCH_3$			-ene
Alkyne	C≡C	C_nH_{2n-2}	$CH_3C{\equiv}CCH_3$			-yne
Alkyl Halide Haloalkane	C−X X=halogen	$C_nH_{2n+1}X$	$CH_3CHClCH_3$			*-o -ane
Alcohol	C−OH	$C_nH_{2n+2}O$	$CH_3CHOHCH_3$			-ol
Ether	C−O−C	$C_nH_{2n+2}O$	CH_3OCCH_3			*-oxy -ane
Aldehyde		$C_nH_{2n}O$	CH_3CH_2CHO			-al
Ketone		$C_nH_{2n}O$	CH_3COCH_3			-one
Carboxylic acid	 or RCOOH	$C_nH_{2n}O_2$	CH_3CH_2COOH			-oic acid
Ester		$C_nH_{2n}O$	CH_3COOCH_3			-oate
Amine	$R{-}CH_2{-}NH_2$	C,H,N - varies	$CH_3CH_2NH_2$			-amine
Amide		C,H,N,O - varies	$CH_3CH_2CONH_2$			-amide

Figure 2.2 List of all functional groups covered in this textbook. R=any alkane, *special naming rule, named as a side-chain. credit: Lewis structures drawn with ACD/Chemsketch - `https://www.acdlabs.com/resources/freeware/chemsketch/index.php` Line structures - author.

2.3 Lewis Structures of Organic Molecules

The Lewis structure representation of organic molecules gives considerable insight into the bonding patterns seen inorganic molecules. From quantum mechanics, having 8 electrons in the outer orbital of an atom results in the most stable structures, this means that atoms with different numbers of valence electrons form different structures. Organic chemistry focus's on carbon and hydrogen containing compounds with oxygen and nitrogen having an important role and rarely a halogen (Cl, F, Br, I). The typical bonding patterns for each element is shown in Figure 3.1.

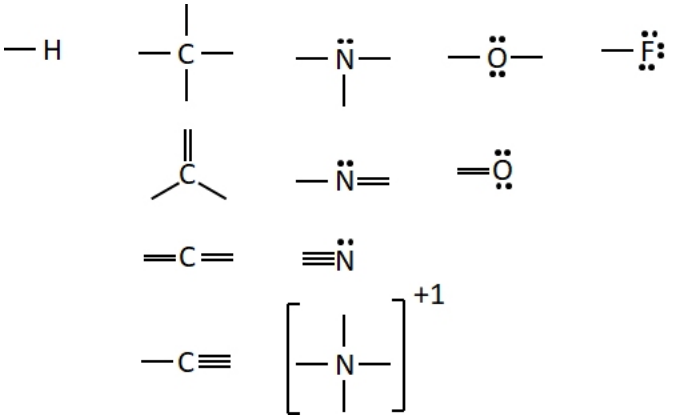


Figure 2.3 Bonding patterns for the most common atoms found in organic molecules. credit: author.

Hydrogen ($1s^1$) has the simplest bonding pattern as it only has one valence electron, and therefore forms only one bond to complete its outermost orbital. Note, hydrogen is an exception to the octet rule in that its outer orbital is a single 1s orbital, there are no 1p orbitals, thus, its "octet" is only two electrons in its outer shell.

Carbon($1s^2, 2s^2, 2p^2$) has four valence electrons, to complete its octet carbon makes four covalent bonds with 2-4 different atoms. The relatively low electronegativity of carbon means that carbon-carbon bonds are nonpolar and carbon readily forms long chains of carbon frequently referred to as a **carbon backbone**.

Nitrogen ($1s^2, 2s^2, 2p^3$) has five valence electrons and typically forms three bonds in a several different ways. Nitrogen will occasionally donate an electron to a chemical bond, forming a polyatomic cation with four bonds. Due to its high electronegativity nitrogen rare bonds with nitrogen except in its elemental state N_2. The exceptionally strong nitrogen-nitrogen triple bond plays an important role in the biochemistry of nitrogen.

Oxygen ($1s^2, 2s^2, 2p^4$) has six valence electrons and can from two bonds to different atoms or one double bond to an atom. Due to its high electronegativity oxygen rarely bonds to oxygen with only a few important exception like its elemental state O_2, ozoneO_3, and hydrogen peroxide H_2O_2.

Halogens (F, Cl, Br, I) are rare in organic molecules, but frequently used in synthesis so are included here. Halogens all share an outer shell electron configuration of s^2, p^5 therefore only form one bond in organic molecules.

2.4 Introduction to Hydrocarbons

Hydrocarbons are compounds containing only carbon and hydrogen atoms bonded together. Hydrocarbons can be broken into several categories based on the bonding patterns. **Aliphatic** compounds include **alkanes** which contain only C-C single bonds, **alkenes** which contain at least one C=C, **alkynes** which contain at least one C≡C bond, and **cycloalkanes and cycloalkenes** which form a ring structure. **Aromatic** compounds contain a unique **benzene** ring structure. Hydrocarbons are also classified as either **saturated** containing only C-C single bonds or **unsaturated** if it contains at least one C=C or C≡C.

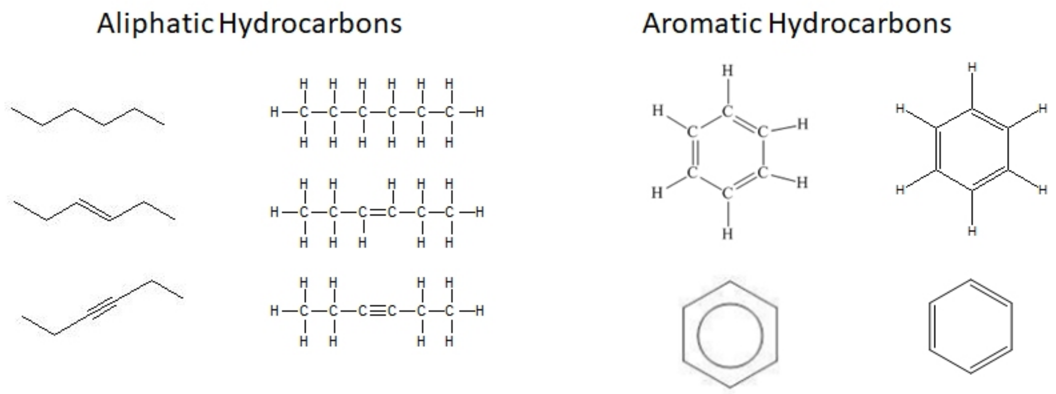


Figure 2.4 Examples of aliphatic and aromatic compounds. Three different examples of aliphatic compounds are given (both Lewis and Line structures). Four different representations are shown for the benzene ring, all are the same molecule. credit: author

2.5 Representations of Organic Molecules

There are many ways to represent and visualize organic molecules, with each style having its advantages and disadvantages. Familiar with all the methods used (especially Line structures) and the flexibility to shift from one representation to another is required to fully understand the physical and chemical properties, reactions, and biological activity. The most common representations used in this book are Lewis structure, Line structures and to a lesser extent condensed structural formulas and 3D models. A brief note on terminology, the longest chain of carbons is often called the **main chain** while any smaller chains branching off are called **side chains**.

Often when drawing organic structures, chemists find it convenient to use the letter 'R' to designate part of a molecule outside of the region of interest. If we just want to refer in general to a functional group without drawing a specific molecule, for example, we can use 'R' groups to focus attention on the group of interest:

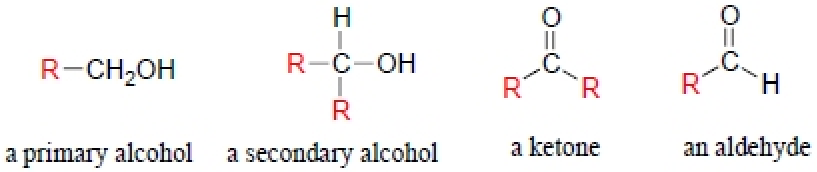


Figure 2.5 The letter 'R' represents the "rest" of of the molecule that just composed of any alkane. credit: Organic Chemistry With a Biological Emphasis - Tim Soderberg

The R group is a convenient way to abbreviate the structures of large biological molecules, especially when we are interested in something that is occurring specifically at one location on the molecule. For example, in Chapter **??** when we look at biochemical oxidation-reduction reactions involving the flavin molecule, we will abbreviate a large part of the flavin structure which does not change at all in the reactions of interest:

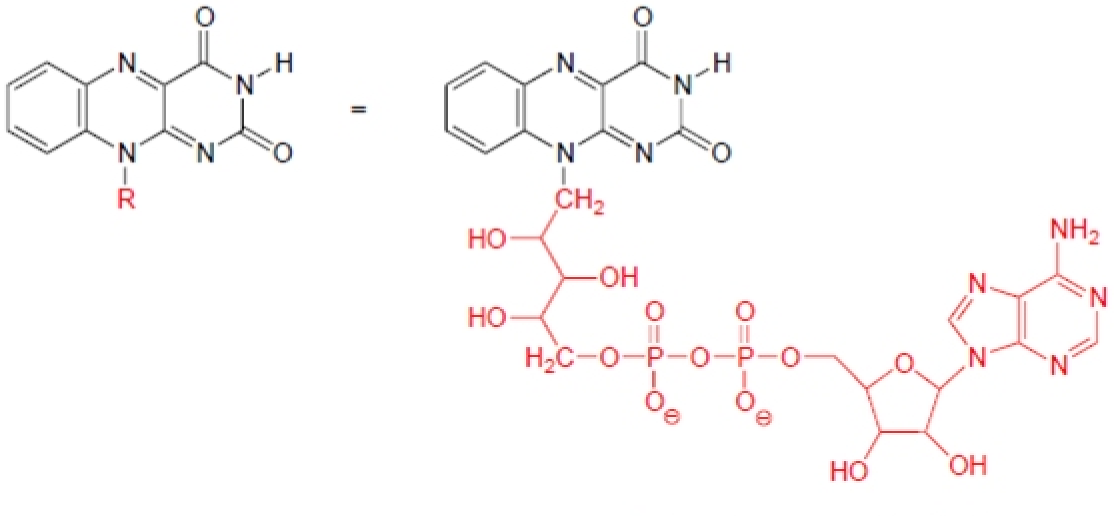
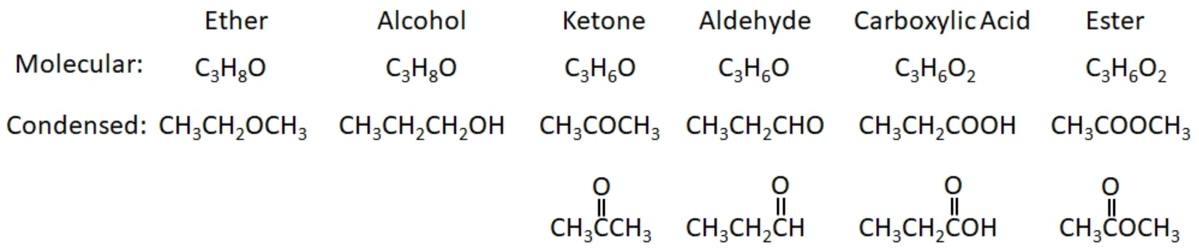


Figure 2.6 The letter 'R' can also represent the "rest" of the molecule that does not change or is not the focus of a chemical or biochemical reaction. credit: Organic Chemistry With a Biological Emphasis - Tim Soderberg

Molecular formulas convey the least amount of information, only providing the number and type of atom present in a compound. It is simple and compact but contains no structural information, and does not even contain enough information to unambigiously determin the functional groups present in a molecule. Many organic molecules share the same molecular formula but have different structures and funtional groups. Note in Figure 2.2 that from the molecular formula there is no way to differentiate between alochols and ethers or aldehydes and ketones, nor can it differentiate between isomers which will be discussed soon.

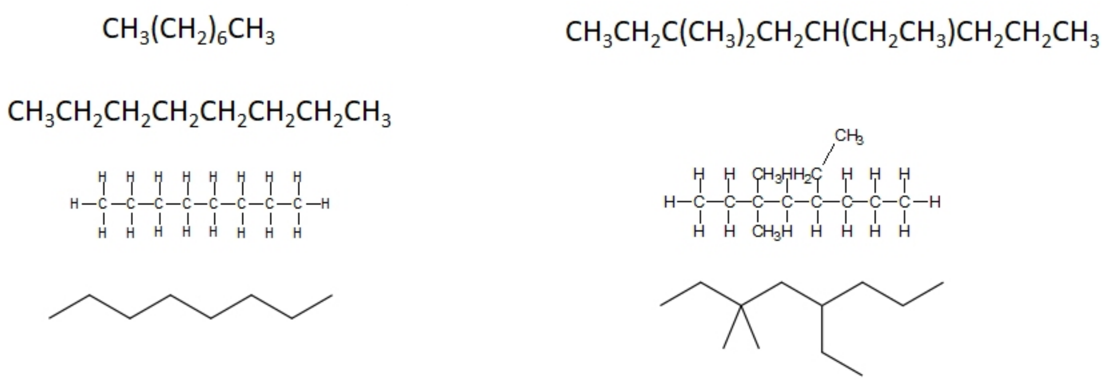


	Ether	Alcohol	Ketone	Aldehyde	Carboxylic Acid	Ester
Molecular:	C_3H_8O	C_3H_8O	C_3H_6O	C_3H_6O	$C_3H_6O_2$	$C_3H_6O_2$
Condensed:	$CH_3CH_2OCH_3$	$CH_3CH_2CH_2OH$	CH_3COCH_3	CH_3CH_2CHO	CH_3CH_2COOH	CH_3COOCH_3
			$CH_3\overset{\overset{O}{\|}}{C}CH_3$	$CH_3CH_2\overset{\overset{O}{\|}}{C}H$	$CH_3CH_2\overset{\overset{O}{\|}}{C}OH$	$CH_3\overset{\overset{O}{\|}}{C}OCH_3$

Figure 2.7 Molecular and condensed structures for several functional groups. credit: author

Condensed structural formulas contain the same information as a molecular formula but attempt to add some structural information by showing how the atoms are connected. It does allow differentiation between different functional groups and isomer. The main advantage might be that the information fits on one line of text, thus works well when using the formula in sentences and paragraphs. Disadvantages are the formula can be confusing for larger molecules. A variation that is sometimes used is the **modified or hybrid condensed formula** which attempts to give more structural information by functional explicitly showing double and triple bonds and functional groups.

For large molecules condensed structures can be tedious and there are several conventions taken to shorten the notation and make it more readable. The first is to use parenthesis to indicate a group is repeated many times.



(a) (b)

Figure 2.8 (a) Example of using parenthesis to represent a long chain of carbons. (b) Example of parenthesis representing side-chains. Note that the Lewis structure is difficult to read and the line structure is a much cleaner. credit: author

The second convention is to use parenthesis to indicate side chains or functional groups in a molecule. The parenthesis show the group attached to the carbon to the left. The use of parenthesis in two different ways can be confusing and requires a good knowledge or Lewis structures and the bonding patterns that complete an atoms octets to determine the correct structure. An excellent guide to condensed structures is linked at `www.chemhaven.org/che102` from the web-site Mastering Organic Chemisry `https://www.masterorganicchemistry.com/2011/06/20/deciphering-what-the-brackets-mean/`.

Lewis structures provide the most information about a molecule though frequently lone pair electrons and the geometry is not drawn correctly. It conveys structural information in enough detail to determine the geometry around atoms and the functional groups are very apparent. Lewis structures are also used often for chemical reactions because it is easy to see which bonds are broken and made during the reaction. One disadvantages is size, it takes up multiple lines, thus only works well in figures (not normal text). Another disadvantage is they are tedious to draw and contain some unnecessary information like the number and location of hydrogen atoms.

Line structures represent carbons as the ends or vertex of the lines used to draw the molecule and will omit hydrogen atoms as it is assumed that any bond not drawn are to a hydrogen atom. They represent a quick and efficient way to draw molecules, remove the unnecessary hydrogenous and make functional groups easily seen. The main disadvantage of line structures is they assume a lot of structural information and take some practice to get used too.

Ball and stick models is a three dimensional representation of a molecule, atoms are shown as balls and chemical bonds as sticks connecting them together. Molecular model kits represent molecules in this manner and many computer programs allow them to be drawn and rotated in space to give a complete view of the structure. Atoms are distinguished mainly by color with carbon-black, oxygen-red, nitrogen-blue and hydrogen-white. The disadvantage to this representation is that the atoms are drawn to small and the bonds to big to emphasize the geometry of the molecules.

Space filling models are also three dimensional but the chemical atoms and bonds are drawn to scale. The structure represents the best model, but makes it difficult to see geometry around the atoms. The requirement to be drawn using a computer also limits their usefulness.

Other ways to represent organic molecules exist, most specifically made to be computer readable and are not as useful for humans. Knowing they exist is sufficient, they will not be used in this book. The **SMILES** format is similar to the condensed structure but leaves off all the hydrogen atoms. **StdInChI** stands for

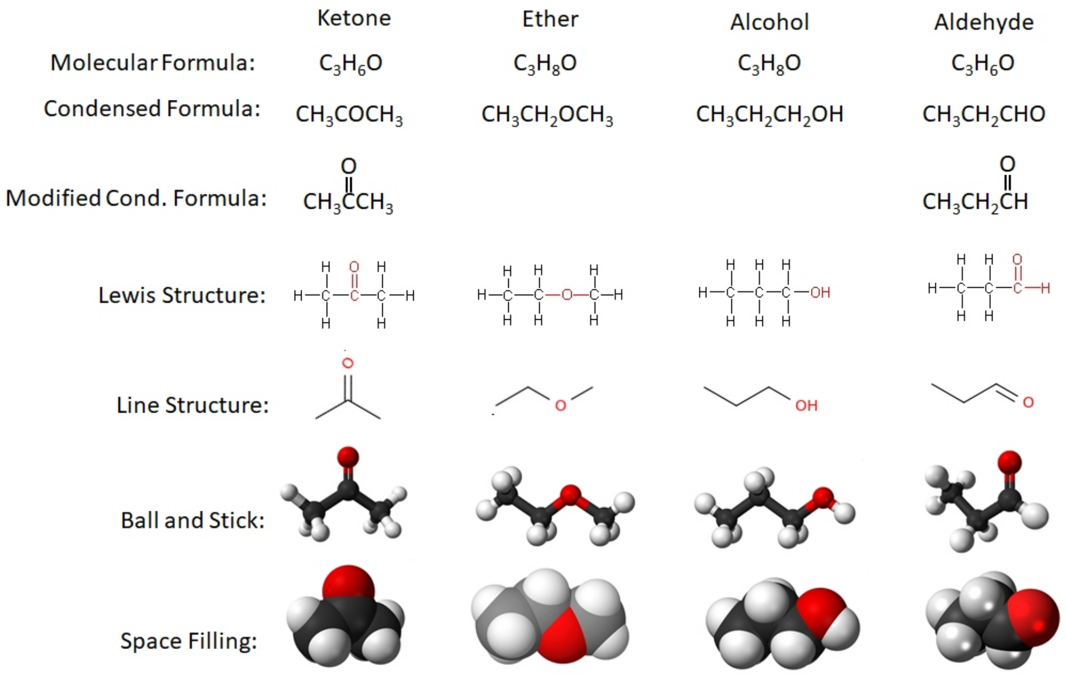
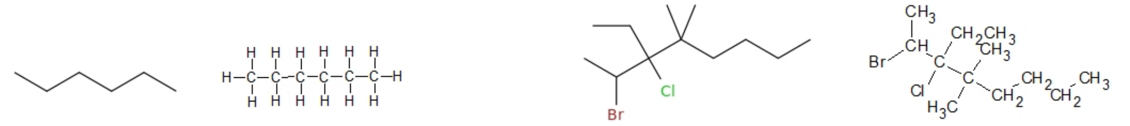


Figure 2.9 Different representations of four molecules, (a) propanone (a ketone) (b) methoxymethane (an ether), (c) 1-propanol (an alcohol) and (d) propanal (an aldehyde). Note that the molecular formula is the same for aldehydes/ketones and alcohols/ethers but the structures are quite different. Also note the differences in how the condensed formulas are writen. credit: author

Standard International Chemical Identifier (`https://en.wikipedia.org/wiki/International_Chemical_Identifier` which was designed to provide a standard way to encode molecular information and to facilitate the search for such information in databases and on the web. Some STDInChI representations become excessively long and are converted to the **StdInChIKey** which provides a "unique" name with only a 1 in 80 billion chance of two molecules having he same representation. Many other possibilities exist. A few examples are given in Figure 2.10.



StdInChI: 1S/C6H14/c1-3-5-6-4-2/h3-6H2,1-2H3

StdInChIKey: VLKZOEOYAKHREP-UHFFFAOYSA-N

SMILES: CCCCCC

(a)

StdInChI: 1S/C12H24BrCl/c1-6-8-9-11(4,5)12(14,7-2)10(3)13/h10H,6-9H2,1-5H3

StdInChIKey: BKAZXIAOJDNQEL-UHFFFAOYSA-N

SMILES: BrC(C)C(C(CCCC)(C)C)(CC)Cl

(b)

Figure 2.10 Several machine readable methods for identifying molecules. (a) Hexane - a relatively simple molecule (b) 2-bromo-3-chloro-3-ethyl-4,4-dimethyloctane - a more complex molecule. credit: author

Exercise 2.1

Question:

For each of the following condensed structures draw the corresponding Lewis structure and Line structure:

(a) $CH_3CHBrCH_2CH_3$

(b) $CH_3(CH_2)_6CH_3$

(c) CH_3CH_2COCHO

(d) $CH_3CH_2OCH_2OH$

(e) $CH_3(CH_2)_3CH(CH_3)_2CH_2CH_3$

Solution:

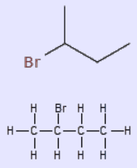
(a) The bromine is not part of the main chain since it can only make one bond, therefore it is a side chain.

(b) The parenthesis represent repeated units because the atoms in the parenthesis CH_2 need two bonds to complete octets.

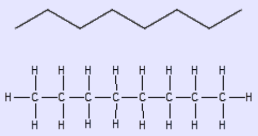
(c) The first CH_2O must be a C−O to complete octets, the last CHO must be a C=O to complete octets.

(d) The first CO must be a C=O to complete octets, the last CH_2OH must be a single bond to C to complete octets.

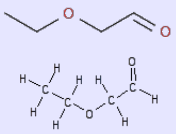
(e) The first set of parenthesis is a continuous chain of CH_2, while the second set of parenthesis must be side chains.



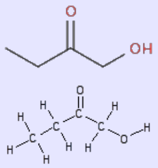
(a)



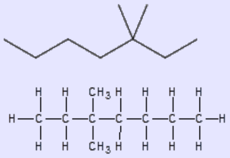
(b)



(c)



(d)



(e)

2.6 Naming Organic Compounds - Alkanes

In 1892 in Geneva the International Union of Pure and Applied Chemists (IUPAC) developed a systematic naming system for organic molecules. The system is quite complex in that it must be able to name millions of compounds uniquely, however, we will limit ourselves to naming compounds with less than ten carbons and one functional group only. IUPAC nomenclature is based on naming a molecule's longest or **main chain (MC)** comprised of carbon-carbon single bonds that contain a functional group, and treating all other atoms as **side chains (SC)**. Each functional group is given a unique suffix (Figure 2.2), the number of carbons in the longest chains (and side chains) is given a unique prefix (Figure 2.11) and all side chains are identified how many there are (Table 2.11)and by location.

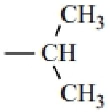
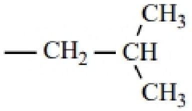
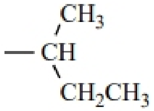
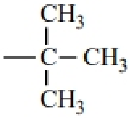
The general process for naming organic molecules is outlined below. These basic rules will be extended as each new functional group is introduced in upcoming chapters. The next several examples should help you

# of C	prefix	# of C	prefix
1	meth-	6	hex-
2	eth-	7	hept-
3	prop-	8	oct-
4	but-	9	non-
5	pent-	10	dec-

# of SC	Prefix
1	no prefix needed
2	di-
3	tri-
4	tetra -

Halogen SC	prefix
fluorine	fluoro-
chlorine	chloro-
bromine	bromo-
iodine	iodo-

(a)

Special SC	IUPAC Prefix	Common Name
	1-methylethyl	isopropyl
	2-methylpropyl	isobutyl
	1-methylpropyl	sec-butyl
	1,1-dimethylethyl	tert-butyl (t-butyl)

(b)

Figure 2.11 (a-upper) Prefix's for number of carbons in a chain for organic molecules. (a-middle) Prefix's for multiple side chains. (a-lower) Prefix's for halogen side chains. (b) Side chains that are often given their common name instead of IUPAC name.

to learn the rules. Study each example carefully and note what new rule each introduces.

IUPAC Naming Rules

Numbering the Longest or Main Chain (MC)

1. Determine the longest continuous chain of carbon atoms that contains the most important functional group.
2. Number the carbon atoms to give the functional group the lowest number.
3. If no functional group takes precedence, number the longest chain to give the side chains (SC) the lowest possible number.
4. If a tie exists break it by giving the lowest number to the side chain that appears first alphabetically (ignore any side chain modifiers).

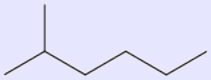
Naming the Compound

1. Start naming the side chains in alphabetical order.
2. Give the location of the side chain(s) separated by a comma. Then a dash, then either the prefix for multiple side chains and/or length of side chains ending in-yl.
3. Location of functional group (if needed) dash length of the main chain then suffix of the main chain.
4. Remember numbers are separated by commas (,). Numbers and letters are separated by a dash (-)

Exercise 2.2 - SC is given the lowest number

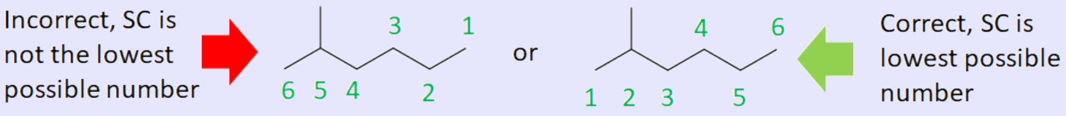
Question:

Give the IUPAC name of the following molecule:

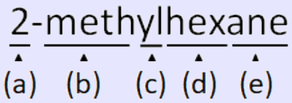


Solution:

1. Number the longest carbon chain. There are two possible ways to number the molecule left to right or right to left.
2. The correct numbering goes from left to right so that the side chain (SC) is given the lowest possible number.



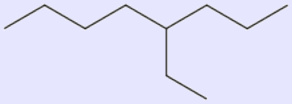
3. Naming the molecule
   a) Begin with the location of the side chain (SC) - 2
   b) Length of the side chain, 1 carbon = meth-
   c) Side chains (SC) are give the suffix -yl
   d) Length of main chain (MC), 6 carbons = hex-
   e) The functional group is an alkane (all C-C single bond), the suffix is -ane
4. Remember dash's (-) separate numbers and letters.



Exercise 2.3 - SC is given the lowest number

Question:

Give the IUPAC name of the following molecule:



Solution:

1. Number the longest carbon chain. There are four possible ways to number the molecule.

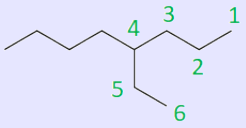
Attempt 1 - Longest chain is only 6 carbons

Attempt 2 - Longest chain is only 7 carbons

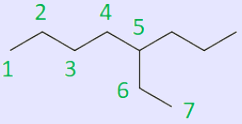
Attempt 3 - Longest chain is 8 carbons, SC is on carbon 5

Attempt 4 - Longest chain is 8 carbons, SC is on carbon 4

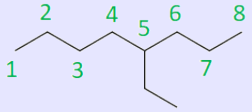
Attempt 1



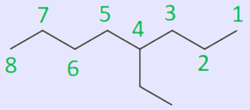
Attempt 2



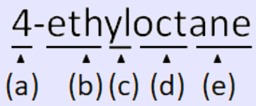
Attempt 3



Attempt 4



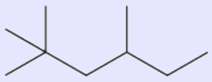
2. The correct choice is attempt 4, the numbering goes from right to left so that the side chain (SC) is given the lowest possible number.
3. Naming the molecule
   a) Begin with the location of the side chain (SC) - 4
   b) Length of the side chain, 2 carbons = eth-
   c) Side chains (SC) are give the suffix -yl
   d) Length of main chain (MC), 8 carbons = oct-
   e) The functional group is an alkane (all C-C single bond), the suffix is -ane
4. Remember dash's (-) separate numbers and letters.



Exercise 2.4 - Multiple side chains (SC)

Question:

Give the IUPAC name of the following molecule:

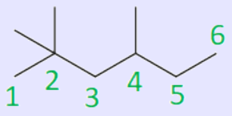


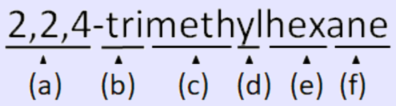
Solution:

1. Number the longest carbon chain. In this case numbering left to right gives 2,2,4 as the location of the methyl side chains. (Starting on the right would give 2,4,4)
2. If there are several side chains it is useful to list them off to the side to aid in alphabetization.
3. Naming the molecule
   a) Begin with the location of the side chains (SC) - 2,2,4

   - b) If there are multiple side chains (SC) of the same length group them together and use prefix given in Figure 2.11 (a) - lower table. In this case there are three methyl groups therefore tri-
   - c) Length of the side chain, 1 carbon = meth-
   - d) Side chains (SC) are give the suffix -yl
   - e) Length of main chain (MC), 6 carbons = hex-
   - f) The functional group is an alkane (all C-C single bond), the suffix is -ane

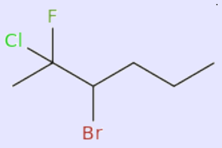
4. Remember comma's (,) separate numbers and dash's (-) separate numbers and letters.





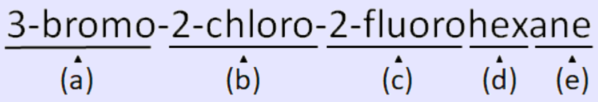
Exercise 2.5 - Alphabetize side chains

Question: Give the IUPAC name of the following molecule:



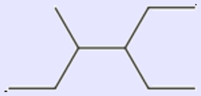
Solution:

1. Number the longest carbon chain. In this case numbering left to right gives 2,2,3 as the location of the halogen side chains. (Starting on the right would give 4,5,5)
2. If there are several side chains it is useful to list them off to the side to aid in alphabetization.
3. Naming the molecule
   - a) Begin with the location of the side chains (SC) in **alphabetical** order, thus 3-bromo goes first.
   - b) Alphabetically 2-chloro is next
   - c) Next is 2-fluoro
   - d) Length of main chain (MC), 6 carbons = hex-
   - e) The functional group is an alkane (all C-C single bond), the suffix is -ane
4. Remember comma's (,) separate numbers and dash's (-) separate numbers and letters.



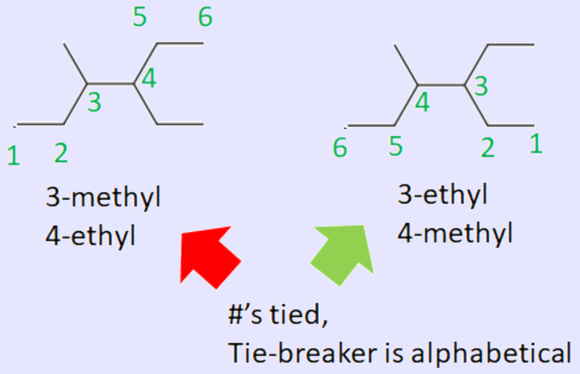
Exercise 2.6 - Alphabetical tie-breaker

Question: Give the IUPAC name of the following molecule:



Solution:

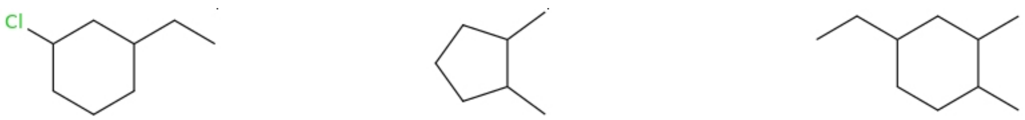
1. Number the longest carbon chain. In this case numbering from either end gives side chains at carbon 3 and 4.
2. If there is a tie in numbering side chains it is broken by giving the lower number to the side chain that comes first alphabetically, i.e. 3-ethyl-4-methyl is better than 3-methyl-4-ethyl.



3. Naming the molecule
    a) Begin with the location of the side chains (SC) in **alphabetical** order, thus 3-ethyl
    b) Then 4-methyl
    c) Length of main chain (MC), 6 carbons = hex-
    d) The functional group is an alkane (all C-C single bond), the suffix is -ane
4. Remember comma's (,) separate numbers and dash's (-) separate numbers and letters.

$$\underset{(a)}{\underline{\text{3-ethyl}}}\text{-}\underset{(b)}{\underline{\text{4-methyl}}}\underset{(c)}{\underline{\text{hex}}}\underset{(d)}{\underline{\text{ane}}}$$

Cycloalkanes, sometimes referred to as cyclic or closed-chain alkanes can occur if the longest chain wraps back on itself to form a closed loop. This results in two fewer hydrogen's in the molecular formula of the compound C_nH_2n. Three and four carbon rings are relatively unstable due to the strained bonds (60° and 90° respectively) compared to the normal bond angle of 109.5° in a normal tetrahedral carbon. When naming cyclic hydrocarbons closed loop is considered the the longest chain and the suffix "cyclo-" is placed in front of the length of the main chain. All other aliphatic chains are considered side chains and follow the normal rules. Several examples are shown in in Figure **??**.



1-chloro-3-ethylcyclohexane 1,2-dimethylcyclopentane 4-ethyl-1,2-dimethylcyclohexane

Figure 2.12 Examples for naming cycloalkanes.

2.7 Isomerism

Isomerism is the relationship between compounds with the same molecular formula but a different structural arrangement of atoms. There are several types of isomers important in organic and biochemistry, structural isomers will be detailed here, cis/trans isomers in Chapter **??** and stereoisomers in Chapter **??**.

Structural or Constitutional isomers have the same molecular formula but the atoms are connected together differently (different structure). While isomers have the same chemical formula, their physical and chemical properties are different. Figure 2.13 shows two isomers of butane (C_4H_{10}) along with how the physical properties can differ due to structure. Butane has a boiling point of -0.5 °C while 2-methylpropane has a boiling point of -11.5 °C . The difference is due to how the molecules interact with each other, butane has a long linear structure, the molecule is more easily polarizable, the resulting London Dispersion Forces between the molecules is stronger, thus a higher boiling point. In 2-methyl propane the molecule is more globular, less polarizable and the London Dispersion Forces are weaker since the molecules can't interact with each other as easily. The small difference in structure and physical properties means that butane is used in cigarette lighters or torch's while 2-methylpropane is used in spray cans or as a refrigerant.

Key Idea: Structural Isomers

Structural Isomers - Same chemical formula, different chemical structure, physical and chemical properties.

When drawing isomers it is important to remember that molecules can be drawn many different ways but be the same molecule. One method to help determine if two structures are the same or different is to name them. If the names are different than the structures are different. Figure 2.14 provides several examples.

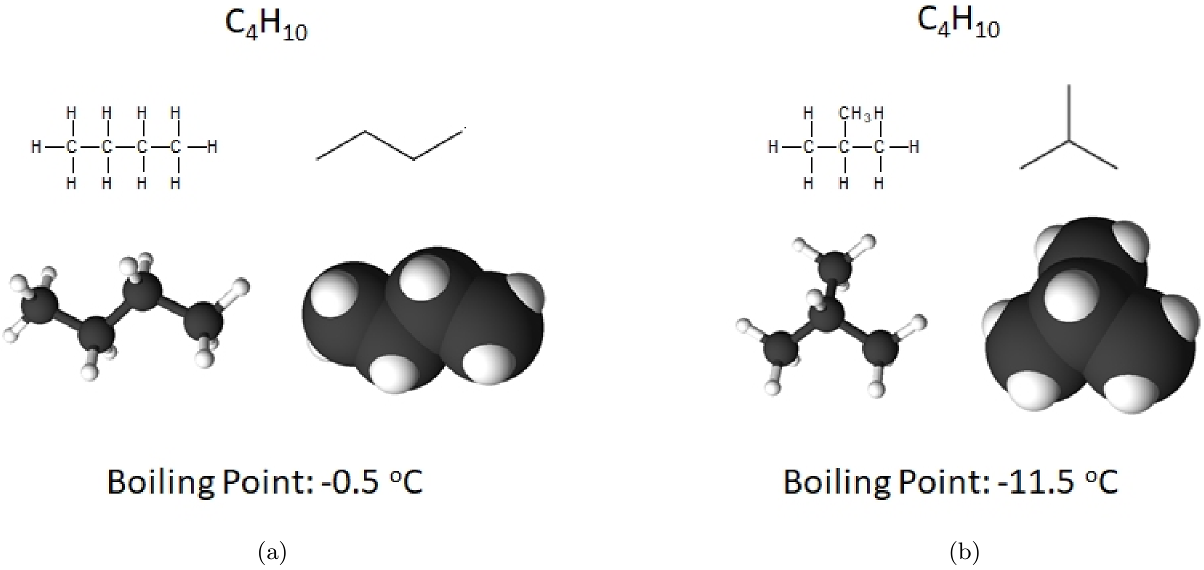


Figure 2.13 Example of structural isomers shown in a number of different structural formats. (a) butane and (b) 2-methylpropane. Note the differences in physical properties of each molecule due to the differences in structure.

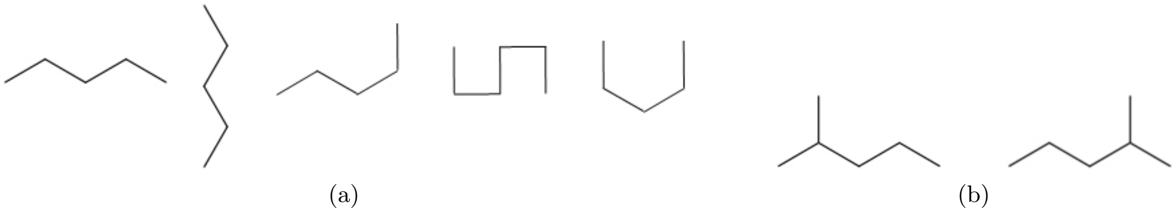


Figure 2.14 (a) Five different ways to draw pentane, they are not isomers, they have the same structure just drawn differently. Rotating, bending, twisting do not change the connectivity of the atoms. If named each would be pentane. (b) Two different ways to draw 2-methylpentane, though they may look different, the molecule is the same just rotated differently. If not careful one could incorrectly name the molecule on the right 4-methylpentane . credit: author

Exercise 2.7

Question: Isomers of pentane (C_5H_{12}):

(a) Draw all possible isomers (3 exist)

(b) Name each isomer

(c) Which isomer will have the lowest boiling point?

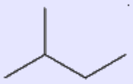
Solution:

(a) The first isomer is always the easiest, draw all the carbons in one chain. The second isomer can be drawn by shortening the length of the main chain by one carbon and using that carbon as a side chain. Move the side chain until all possible positions have been utilized, in this example there is only one allowed position. Repeat these steps to make the last isomer.

(b) In order from left to right: pentane, 2-methylbutane, and 2,2-dimethylpropane

(c) 2,2-dimethylpropane - The most globular/compact structure will likely have the lowest boiling point because the London Dispersion Forces will be the least polarized, and the molecules have least least amount of surface area to interact.

pentane



2-methylbutane

2,2-dimethylpropane

Exercise 2.8

Question: Draw **and** name all the isomers of $C_4H_{11}Cl$. There are four possible isomers.

Solution:

(a) The first isomer is always the easiest, draw all the carbons in one chain and add a chlorine on the first carbon atom to make 1-chlorobutane.

(b) To make further isomers move the chlorine other carbons in the molecule. If the chlorine is moved to the second carbon it makes 2-chlorobutane.

(c) If the chlorine is moved to the third carbon it might appear different but it is really just the second isomer. Remember you always name the molecule to give the smallest number to the side chain (in this case chlorine).

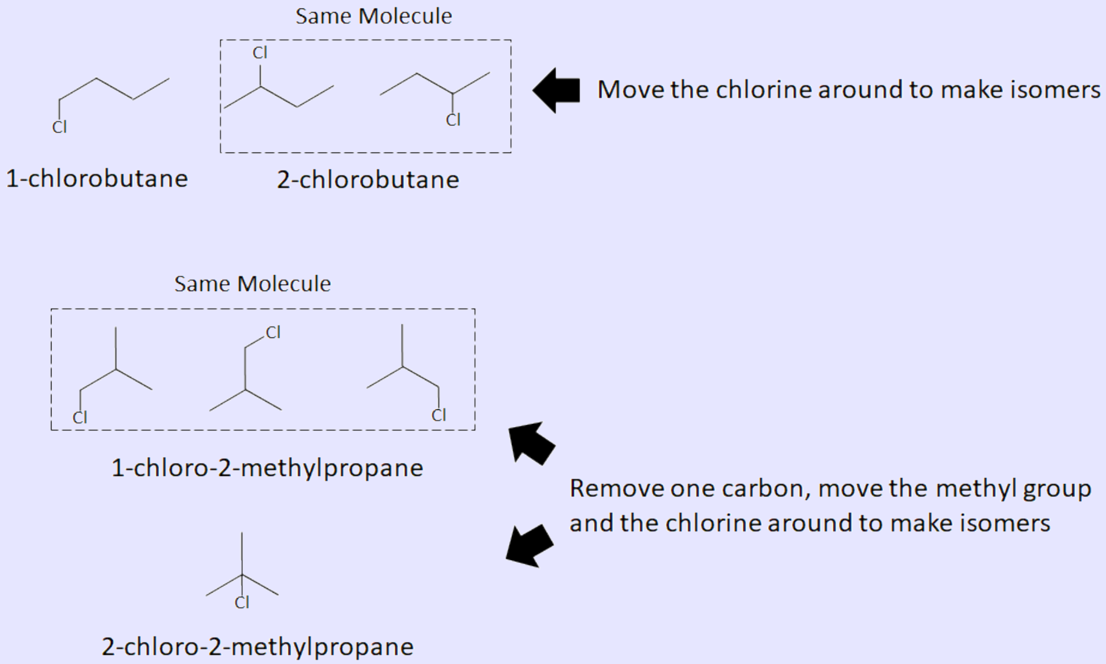
(d) Note that butane is symmetrical between the second and third carbons, thus the first and fourth carbon are the same as are the second and third.

(e) To find further isomers make the chain shorter. There is now a methyl group that can be moved around the molecule **and** a chlorine group. Note that the methyl group can't be placed on the ends of the molecule or it becomes part of the longest chain.

(f) The third isomer has a methyl group on the second carbon and a chlorine on the first carbon, 1-chloro-2-methylpropane.

(g) The fourth isomer has the chlorine on the second carbon (same as the methyl group), 2-chloro-2-methylpropane.

(h) It might appear that the chlorine can be placed on the methyl group or at the other end of the molecule but all of those structures are just the third isomer rotated. If you named each of them they would be correctly named as 1-chloro-2-methylpropane.



2.8 Physical Properties of Alkanes

In general alkanes are relatively uninteresting, they are colorless and odorless....should add more here JCM

Melting and Boiling Points

Alkanes are composed of C-C and C-H covalent bonds, the difference in electronegativity in the bonds is small (zero and 0.4 respectively) resulting in nonpolar bonds and nonpolar molecules. Figure 2.15 gives the properties of many alkanes. The attractive forces between molecules that is responsible for physical properties is limited to London Dispersion Forces (LDF). London Dispersion Forces are the weakest intermolecular force (IMF) but is proportional to the size of the molecule. Small alkanes (1-4 carbons) are gases at room temperature, as the size of the molecules increases alkanes become liquids (5-16 carbons) and finally to solids (17+ carbons).

The shapes of molecules effects the intermolecular forces between molecules as shown in Figure **??**. For isomers, the more branched the chain, the lower the melting and boiling points tends to be. London Dispersion Forces only operate over very short distances between one molecule and its neighbors, for more branched, globular molecules they can not get as close together thus the attractions are weaker and the melting and boiling points are lower.

Name	**Formula**	**Melting Point (°C)**	**Boiling Point (°C)**	**Density)**	**Physical State (20°C)**
Methane	CH_4	-182	-164	0.688 g/L	gas
Ethane	C_2H_6	-183	-89	1.256 g/L	gas
Propane	C_3H_8	-190	-42	1.867 g/L	gas
Butane	C_4H_{10}	-138	-1	2.493 g/L	gas
Pentane	C_5H_{12}	-130	36	0.626 g/mL	liquid
Hexane	C_6H_{14}	-95	69	0.659 g/mL	liquid
Octane	C_8H_{18}	-57	125	0.703 g/mL	liquid
Heptadecane	$C_{17}H_{36}$	22	302	0.777 g/mL	solid

Figure 2.15 Physical properties of alkanes. For density, note the change in units going from gases (g/L) to liquids (g/mL).

Solubility

Alkanes which are nonpolar, are insoluble in water, a poloar molecule and when mixing alkanes and water form an immiscible solution. Another term often used to describe the interaction of alkanes and water is hydrophobic ("water fearing"). As will be seen many other functional groups are nonpolar and alkanes (primarily hexane) is frequently used as a solvent or reaction medium for fats, oils and waxes (discussed in Chapter **??**). The old adage oil and water don't mix is a good summation of the solubility of alkanes.

(a)

(b)

Figure 2.16 Alkanes are insoluble in water, as the old adage oil and water don't mix implies. This can prove disastrous in the case of an oil tanker spill and its interaction with the environment and wildlife. (a) Brazil oil spill - 2019 (b) Black Sea oil spill - 2007. credit: (a) `https://commons.wikimedia.org/wiki/File:2019_Northeast_Brazil_oil_spill.png` (b) `https://commons.wikimedia.org/wiki/File:Oiled_Bird_-_Black_Sea_Oil_Spill_111207.jpg`

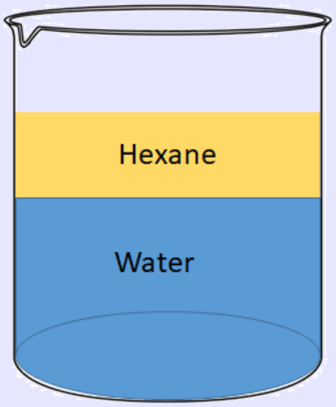
Exercise 2.9 Physical Properties of Alkanes

Question: Without looking at Figure 2.15 answer the following questions. Explain all answers.

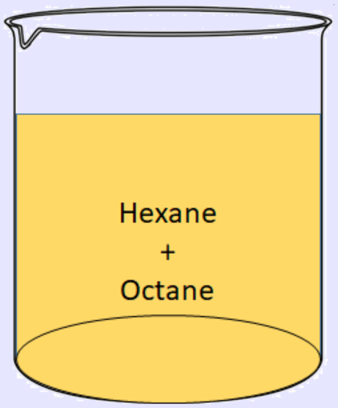
1. Which would have the higher boiling point hexane or nonane?
2. Which would have the lower melting point 2,2-dimethylpentane or heptane?
3. Sketch a picture of what a mixture of 25 mL of hexane and 100 mL of water would look like.
4. Sketch a picture of what a mixture of 25 mL of hexane and 100 mL of octane would look like.

Solution:

1. Nonane would have the higher boiling point because both molecules are nonpolar and only have London Dispersion Forces attractions between the molecule, Nonane is a larger molecule (9 vs. 6 carbons) and the attractive force is directly proportional to the size of the molecule.
2. 2,2-dimethylpentane would have the lower melting point, both molecules are nonpolar and only have LDF attractions. Both molecules are the same size (7 carbons) but 2,2-dimethylpentane is more globular therefore there will be less interaction between molecules than there would be between heptane molecules resulting in 2,2-dimethylpentane having the lower melting point.
3. Hexane (nonpolar, LDF) and Water (polar, HB) will not mix. Hexane is less dense than water and will float on top.
4. Hexane (nonpolar, LDF) and Octane (nonpolar, LDF) will be miscible and form a homogeneous solution.



(3)



(4)

2.9 Overview of Chemical Reactions in Organic Chemistry

One reason organic molecules play a large role in biochemistry is the versatility of carbon. The C-C bond is quite stable in most reactions, at the same time carbon can make a wide variety of bonds to different atoms. There are thousands of different types of reactions in organic chemistry and more are being constantly discovered or invented. One way to begin to make sense of the reactions is to look for similarities and organize them in different ways. Each functional group will also only undergo a limited number of different types of reactions. While you won't have to learn thousands of chemical reactions in this course, you will be responsible for approximately 50 reactions. However, if the reactions are grouped into categories there are perhaps only 15 reactions.

Unlike inorganic chemistry where chemical reactions were carefully balanced to obey Conservation of Mass and included the states of most compounds, in organic chemistry reactions are often left unbalanced and frequently only the main organic compounds are shown. Some states may be included when known, but many times the states of the reactants and products is not easy to determine.

In courses that cover organic chemistry in 2-3 semesters at the 200 course level a great amount of time and detail is put into learning a large number of reaction mechanisms and the many different interactions between molecules. Mechanisms with names like - SN1, SN2, E1, E2 and molecules that are nucleophiles and electrophile are discussed. This book covers organic chemistry in one-half of one semester at a 100 course level and can not go into that level of detail. Certain liberties, simplifications, omissions and perhaps a few white lies will be given in order to focus on how organic chemistry relates to biochemistry.

Reaction mechanisms are the actual physical or chemical processes that occur during a reaction. Understanding the reaction mechanism can lead to a deeper understanding of chemical reactions and many times a common mechanism can be used for a variety of similar chemical reactions. This chapter will focus on learning free-radical mechanisms, other reaction mechanisms will be introduced in future chapters. Some symbols frequently used in reaction mechanisms are shown in Figure 2.17 and are important to understand. Bond breaking is shown as a jagged (red) line through a bond, arrows (blue) are used to show where the electrons go, new bonds being formed are shown as a dashed line (green).

2.10 Free Radical Mechanism

Free radicals are formed when chemical bonds are broken leaving an unpaired electron on each atom or molecule. Free radicals are very reactive and immediately seek to form new chemical bonds. Ultraviolet light is higher in energy than visible light and is often used to generate free radicals in diatomic molecules like the halogens. The light is not strong enough to break a C-C or C-H single bond, thus the organic molecule is unaffected. Free radical reactions can be broken into three steps, initiation, propagation and termination.

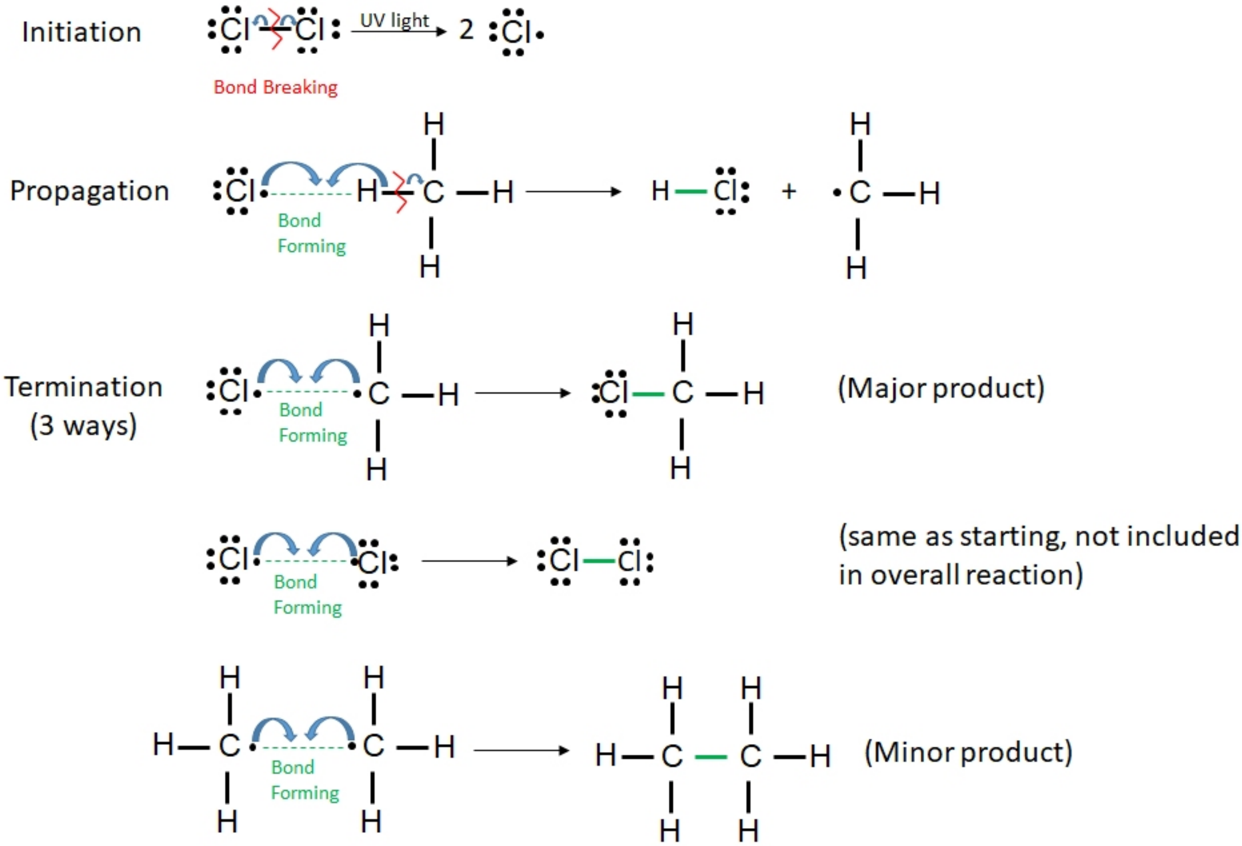


Figure 2.17 Free radical reaction between chlorine and methane illustrating the mechanism of the reaction broken into three steps, initiation, propagation and termination. credit: author.

Initiation occurs when ultraviolet light is used to break the chemical bond in a diatomic molecule forming two free radicals. **Propagation** occurs next a free radical reacts with an organic molecule to produce another free radical, generally breaking a C-H bond. In the example one can picture this as the chlorine free radical approach the C-H bond, chlorine has a higher electronegativity and wants the electrons in a shared bond more than the carbon which is already bonded to the chlorine. The C-H bond is broken and a H-Cl bond is formed. Note in the propagation step a free radical is formed, thus the reaction can keep propagating. The resulting free radicals can react in a number of different ways to produce a variety of products. **Termination** occurs when two free radicals react with each other and don't produce a new free-radical, thus terminating the reaction. In the example given, there are three possible ways for the free radicals to recombine. The first when a chlorine free radical reacts with a methane free radical, this is highly favored. The second reaction between two chlorine free radicals makes the starting material which will undergo initiation to continue the reaction. The last product occurs when two methane free radicals react, but his occurs rarely. Figure 2.17 below shows an example reaction for the reaction of chlorine and methane.

The reaction is rarely drawn out in the detail shown in Figure 2.17 and generally only includes the major products formed in the reaction. Figure 2.18 illustrates the reaction as it will generally be seen.

$$\mathrm{CH_4} + \mathrm{Cl_2(g)} \xrightarrow{\text{UV light}} \mathrm{CH_3Cl} + \mathrm{HCl}$$

Figure 2.18 Reaction from Figure 2.17 written without the mechanism and only showing the major products.

Methane is a simple molecule with one carbon and four identical hydrogens, for larger molecules with more than one carbon, three different types of free radicals can be formed, differentiated by how many carbons are attached to the carbon free radical. Primary (1°) free radical occur at the end of molecules, carbon is boned to one other carbon, secondary (2^circ) free radicals occur in the middle of a molecule, carbon is connected to two other carbons, and tertiary (3°) free radicals where carbon is bonded to three other carbons as shown in Figure 2.19. The stability of the free radicals determine which products in a reaction are the most stable and will form preferentially. Carbons bonded to other carbons are the most stable free radicals therefore primary free radicals are least likely to form and tertiary free radicals most likely to form ($1° < 2° < 3°$).

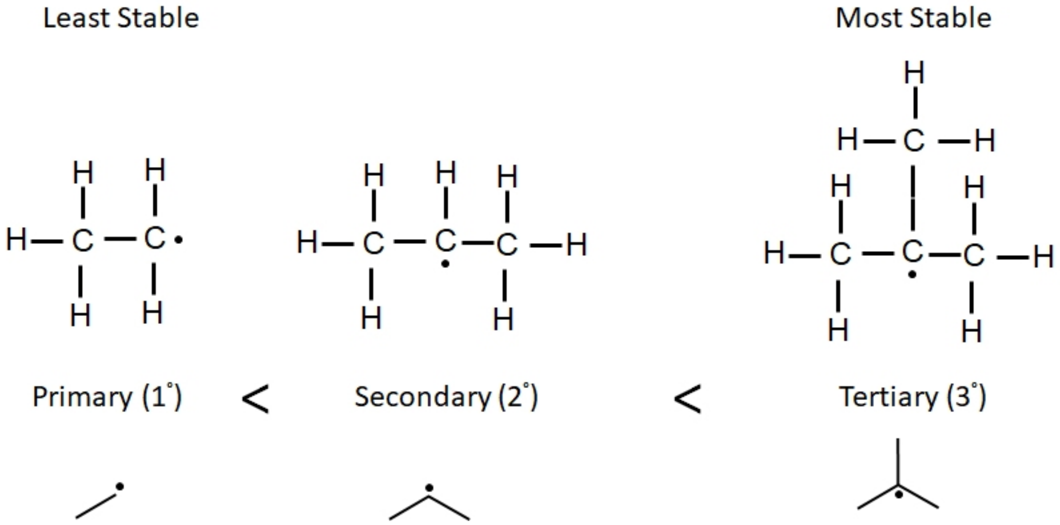


Figure 2.19 Example of each type of free radical in order of stability, $1° < 2° < 3°$. credit: author

For more complicated molecules several different free radicals can be formed leading to multiple products. In Figure 2.20 is an example which will illustrate this for the reaction of 2-methylbutane with chlorine. In the reaction it is important to note that there are four unique locations the free radical may occur resulting in four different products. Position 1 and 4 would produce a primary free radical, position 3 a secondary free radical and position 2 a tertiary free radical. Position 5 is not unique, it is the same as position 1. The product formed from the tertiary free radical will be the most stable and thus favored product in the reaction and is circled. Often in organic chemistry only the important products are written and no attempt to balance the reaction is made.

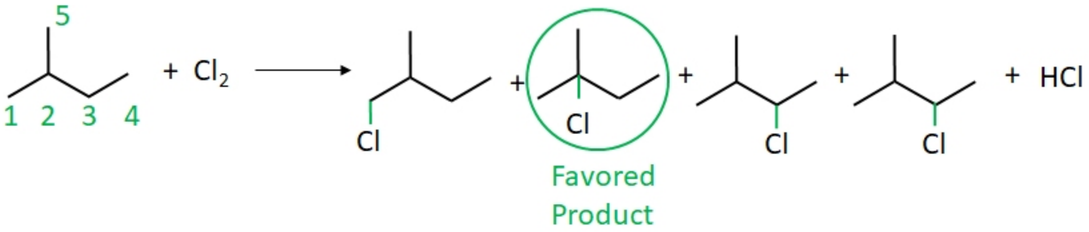


Figure 2.20 Reaction of 2-methylbutane and chlorine illustrating the complexities of organic chemistry reactions when multiple products can occur. credit: author

As is apparent from the reaction in Figure 2.20, organic chemistry reactions can be complex and often result in multiple products. In fact in this reaction the products that could occur when two alkane radicals react together have not been drawn as it is highly unflavored. It is beyond the scope of this class to determine how favored a product is or the percentages of each product made, it will suffice to simply circle the favored product. Separating out multiple products can be costly and time consuming, thus a considerable amount of research occurs attempting to make only one product in a reaction predominately occur.

2.11 Reactions of Alkanes

Alkane reactions can be categorized into four different categories, combustion reactions, substitution reactions, elimination reactions and addition reactions. Each main category of reactions can have several variations.

One method for grouping reactions is to examine how the atoms are rearranged. In a combustion reaction the alkane is completely rearranged by breaking all bonds and reforming them. The other reactions studied are less destructive and result in only minor rearrangement of the atoms in a molecule. These can be broken into three categories - Substitution, Elimination, and Addition reactions depending on how the connectivity between atoms is changed in the reactions.

Careful examination will reveal that alkanes and aromatics only undergo Substitution and Elimination reactions while in the next chapter alkenes and alkynes undergo addition reaction.

Combustion Reactions

There is one reaction that is common to all organic molecules is that they are all combustible and can be burned to release energy. Fossil fuels like methane (commonly called natural gas) is used to produce electricity, cook foods and heat homes. Gasoline (a mixture of alkanes) is used to fuel cars and planes for transportation. Biologically we consume organic molecules (carbohydrates, fats and proteins) which are broken down in a series of steps to supply energy, the the overall reaction is essentially the same as a combustion reaction.

In an ideal **combustion reaction** all of the C, H, and O atoms in a molecule are converted to carbon dioxide and water, the reaction is exothermic, releasing energy as a product. One should always remember Lavosier and Conservation of Mass and balance all combustion reactions. Combustion reactions can also be classified as oxidation/reduction reactions which will be discussed in more detail in later chapters.

Key Idea: Combustion Reactions

$$\_\_\_ \text{ Any C, H, O compound} + \_\_\_\text{O}_2(\text{g}) \longrightarrow \_\_\_\text{CO}_2(\text{g}) + \_\_\_\text{H}_2\text{O}(\text{g}) + \text{energy}$$

Exercise 2.10 Combustion Reactions

Question:

Complete the following reaction: ___  + ___O_2(g) ⟶

Solution:

Combustion reactions can be recognized because they always require oxygen to occur. All combustion reactions result in the formation of carbon dioxide and water and are exothermic,releasing energy. The last step is to balance the reaction, it requires converting the line structure to a molecular formula in order to balance the reaction. The molecule pictures is hexane, counting the ends and vertex's there are 6 carbons, to complete carbons octets the end carbons require 3 more bonds to hydrogen and each other carbon requires 2 more bonds to hydrogen to complete octets, this implies there are 14 hydrogen's on the molecule. Rewrite the reaction as:

$$\_\_\_\text{C}_6\text{H}_{14} + \_\_\_\text{O}_2(\text{g}) \longrightarrow \_\_\_\text{CO}_2(\text{g}) + \_\_\_\text{H}_2\text{O}(\text{g}) + \text{energy}$$

The last step is to balance the reaction.

$$\underline{\ 2\ }\text{C}_6\text{H}_{14} + \underline{\ 19\ }\text{O}_2(\text{g}) \longrightarrow \underline{\ 12\ }\text{CO}_2(\text{g}) + \underline{\ 14\ }\text{H}_2\text{O}(\text{g}) + \text{energy}$$

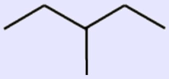
Substitution Reactions

Substitution reactions occur when atoms are exchanged or swapped between two molecules. Alkanes are compromised of only C-C and C-H bonds,of which the C-C bond is very stable and will only break under extreme conditions, therefore the atom that will be exchanged/swapped is a hydrogen atoms. In advanced organic classes there are two types of substitution reactions labeled S_N1 and S_N2 depending on how the reaction occurs, this however is beyond the scope of this book. Instead we will examine the reaction in terms of the free radical mechanism explored in the previous section. Figure 2.21 illustrates a substitution reaction in a number of ways, as a student it is your goal to determine which works best for you, though often it is a combination of explanations that works best.

Substitution reactions like free-radical reactions can result in multiple products depending on which C-H bond is broken. In this course we will assume only mono-substitution occurs and write all possible products produced and circle the most favored products based on free radical stability.

Exercise 2.11 Substitution Reaction - Most Stable Product

Question:

Complete the following reaction:  + Cl_2 ⟶

Solution:

1. First identify the unique carbon-hydrogen bonds that can be broken when forming free radicals. Take careful note of the molecules symmetry as along carbons 3 and 6.

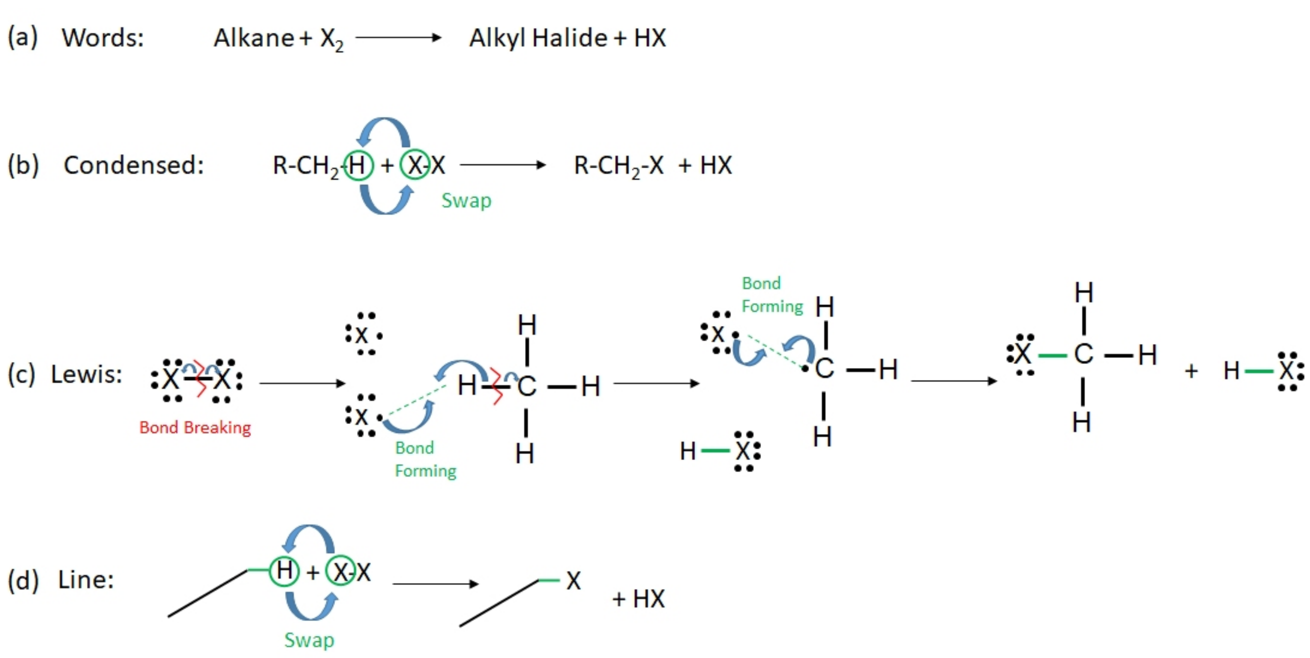
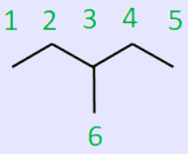
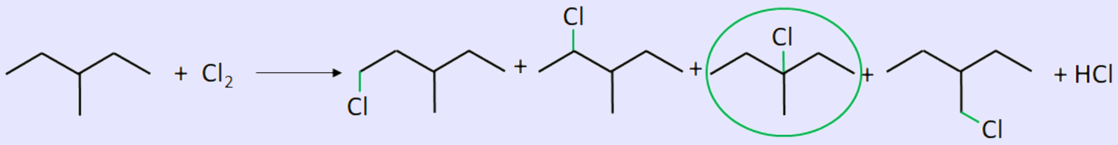


Figure 2.21 Substitution reactions occur when atoms are swapped between two molecules. The reaction can be understood in several different ways. (a) Word reactions focus on the functional group changes, (b) condensed structures can help illustrate a mechanism, (c) Lewis structures give detailed information about the mechanism but are cumbersome, and (d) Line drawing are the most frequently used method due to ease with which they are drawn. credit: author



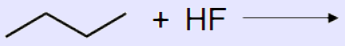
2. The unique positions are 1, 2, 3, and 6. Carbon 5 is the same as carbon 2 and carbon 6 is the same as carbon 1. Four products will be made.
3. Draw each product. Don't forget to include HCl.
4. Determine which product is the most stable and circle it. Remember the order of stability 1° < 2° < 3°. Carbon 3 would form a tertiary free radical and thus form the most stable or favored product.

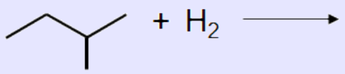


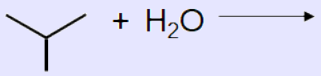
Many different molecules can be substituted onto an alkane, the reaction mechanism is the same in all cases. Molecules which can substitute onto alkanes include the diatomics (X_2 where X = F, Cl, Br or), acids (HX, where X = F, Cl, Br, I), water (H−OH) and technically H_2 though since the products and reactants are the same it results in a no reaction. If one is counting reactions, then it could be considered four separate reactions or if one is counting mechanism than it is one single reaction. Exercise **??** shows several different possibilities for substitution reactions.

Exercise 2.12

Question: Complete the following reactions:

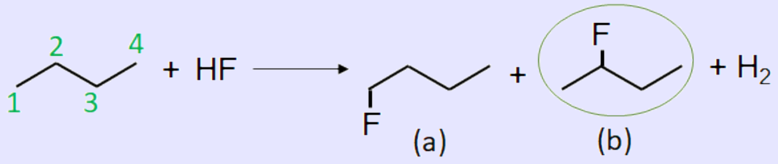
1. 

2. 

3. 

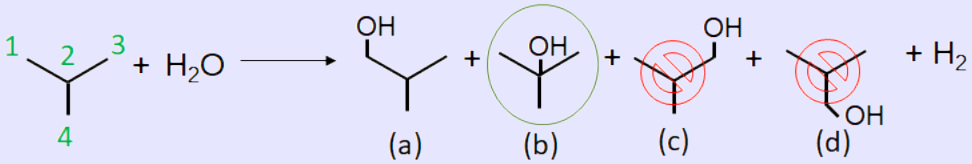
Solution:

1. There are 4 hydrogens that could swap but due to the symmetry of the molecule only hydrogens 1 and 2 will yield unique products. Applying the order of stability for free radicals, the free radical formed on carbon 2 is the most stable, resulting in product (b) being the most stable.



2. Swapping two hydrogens does not change the molecule, thus there is no reaction.

3. There are 4 hydrogens that could swap but due to symmetry the hydrogens on carbon 1,3,4 are all the same. There are two unique products produced. The most stable free radical is formed on the carbon with the most carbons attached, molecule (b)



Key Idea: Substitution Reactions

Mechanism - Swap atoms
Possible Reactants - Diatomics (X_2), Acids (HX), Water (H-OH), and H_2
Recognized by - Alkane + ?
Key aspects - multiple products possible, circle most stable product, free radical stability - $1° < 2° < 3°$

Elimination Reactions

Elimination reactions occur when adjacent atoms are more attracted to each other and form **leaving group** resulting in the elimination or loss of a small molecule from an alkane and the formation of a carbon-carbon double bond C=C) or alkene. In advanced chemistry classes it occurs via two mechanisms E_1 and E_2 but in this book we will use the idea of free radicals to explain it. Elimination reactions generally require high temperatures which is written above the reaction arrow, while below it the Δ symbol represents heat. Another way to recognize elimination reactions is the reaction only has one reactant, the reaction occurs internally between adjacent atoms, this is also called an intramolecular reaction.

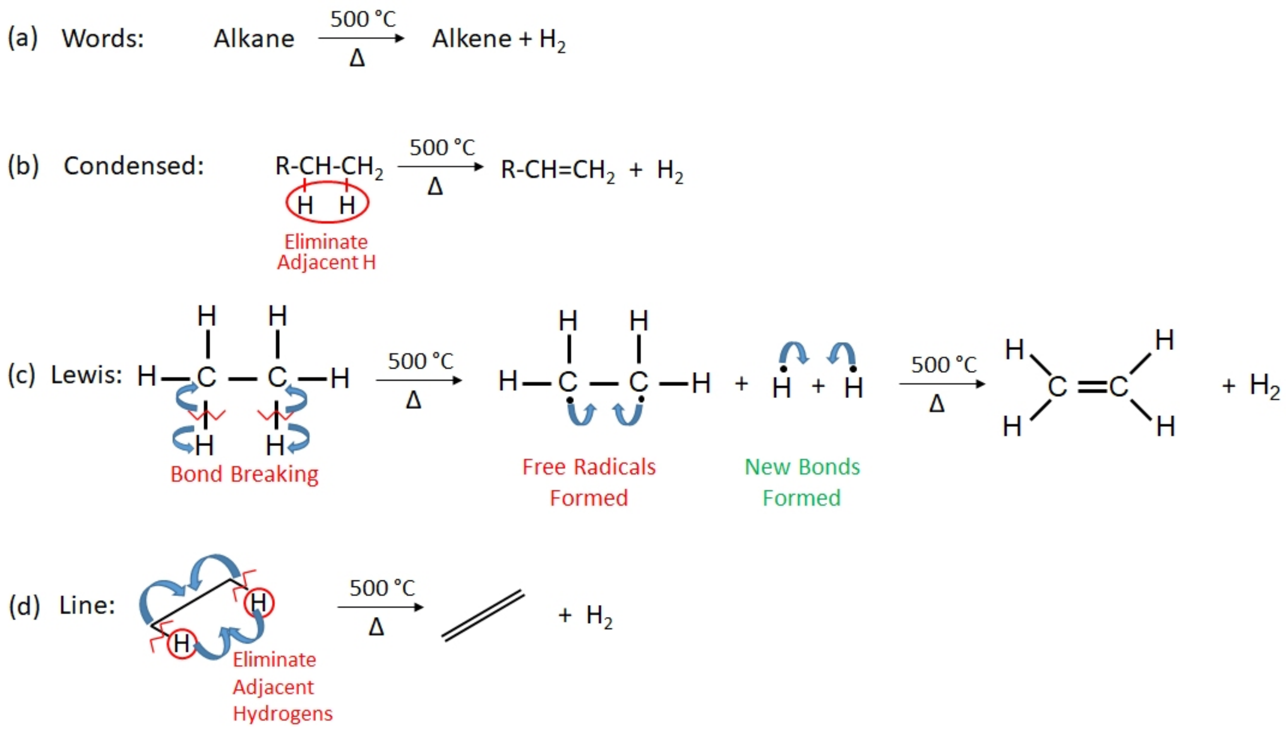


Figure 2.22 Elimination reactions occur when adjacent atoms break away a molecule resulting in the formation of an alkene. The reaction can be understood in several different ways. (a) Word reactions focus on the functional group changes, (b) condensed structures can help illustrate a mechanism, (c) Lewis structures give detailed information about the mechanism but are cumbersome, and (d) Line drawing are the most frequently used method due to ease with which they are drawn. credit: author

Figure 2.22 illustrates the mechanism in four different ways. The key is identifying adjacent atoms that will be eliminated from the molecule forming a C=C double bond and another small molecule. There are many types of leaving groups, in the example given here the leaving group is adjacent hydrogen's. Other good leaving groups are halogens (Cl, F, Br, I) and hydroxy groups (-OH). If the molecule is large enough multiple products are possible. The favored product is given by **Saytzeff's rule**, which states that the most stable product formed will be the more highly substituted alkene. Another way to phrase this is the hydrogen from the carbon with the least number of hydrogen's preferentially leaves.

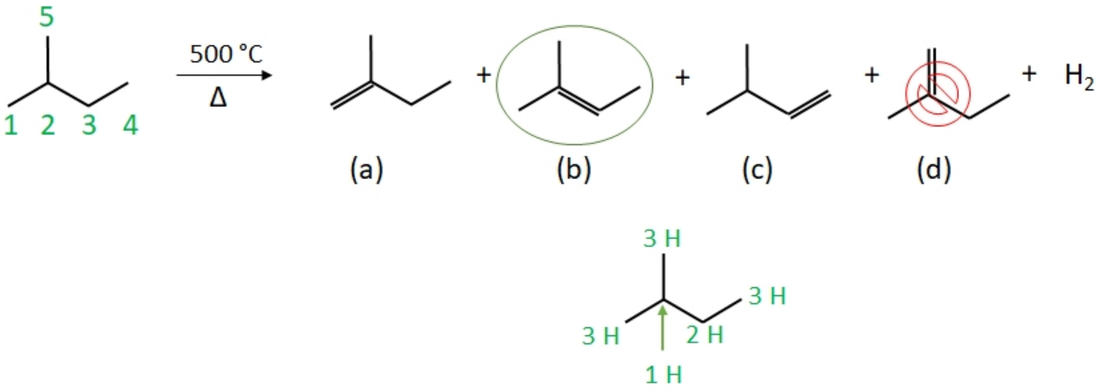


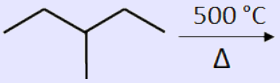
Figure 2.23 Saytzeff's rule states that if more than one product can be formed, the favored product is the most substituted alkene, or lose the hydrogen from the carbon(s) with the least number of hydrogens. credit: author

Saytzeffs rule is illustrated in Figure 2.23 the reaction of 2-methylbutane. The first step is remove hydrogen from all pairs or adjacent carbons, in this case carbon pairs (1-2, 2-3, 2-5, 3-4) which gives four different organic products (a-d). Product (d) is removed from consideration as it is the same molecule as (a). to apply Saytzeff's rule, we need to count the number of hydrogen on each carbon as shown under the reaction. Preferentially the carbon with the least hydrogen's (carbon 2) will form the double bond to the adjacent carbon with the fewest hydrogen's (carbon 3) resulting in molecule (b) being the preferred product which is circled.

Exercise 2.13 Elimination Reaction and Saytzeff's Rule

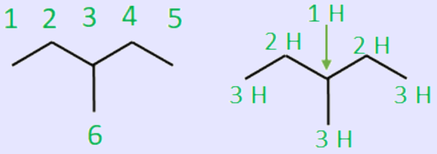
Question:

Complete the following reaction:



Solution:

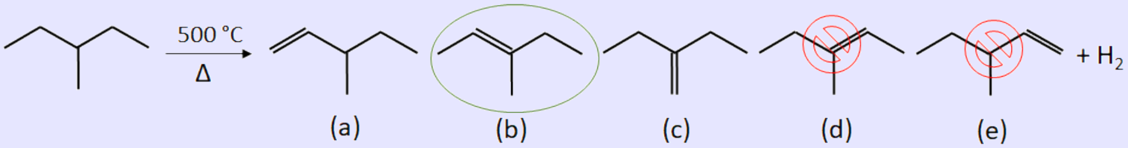
1. Examine the molecule for adjacent pairs of hydrogen to eliminate. Take careful note of the molecules symmetry. It will also be useful to label how many hydrogen's are on each carbon.



2. Elimination can occur between carbons (1,2), (2,3), (3,6). Note that removing hydrogen's from carbons (3,4) results in the same product as removing them from carbons (2,3) and the same applies for carbons (4,5) and (1,2).
3. Draw each product. Don't forget to include the molecule that is eliminated (H_2). Included in the answer are the duplicate molecules (d) and (e) to make it easier to see how they are the

same as already drawn products. Normally they are not included in the answer.

4. Determine which product is the most stable and circle it according to Saytzeff's rule. Carbon 3 has the least H attached so preferentially leaves along with the H on carbon 2 (second least H), thus the most stable molecule is (c).

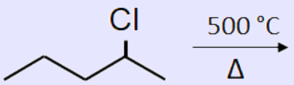


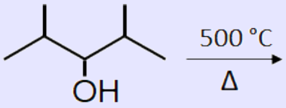
In addition to losing hydrogen, functional groups like halogens (F, Cl, Br, I) and alcohols (OH) can be eliminated from alkanes to produce alkenes. These functional groups are much easier to lose than hydrogen, a fact which organic chemists and biochemists can make use of to control where a carbon-carbon (C=C) is formed. This often simplifies reactions greatly as only one or two products are formed. Exercise 2.11 shows three additional examples of elimination reactions illustrating additional possibilities that need to be studied.

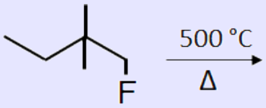
Exercise 2.14 Elimination Reactions - 3 Examples

Question:

Complete the following reactions:

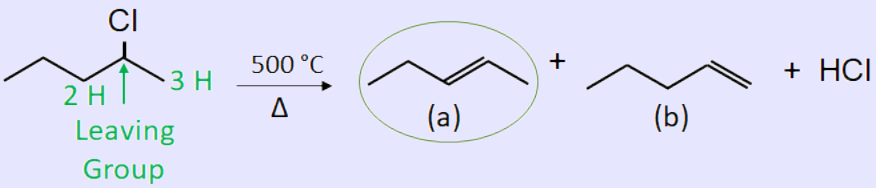
1. 

2. 

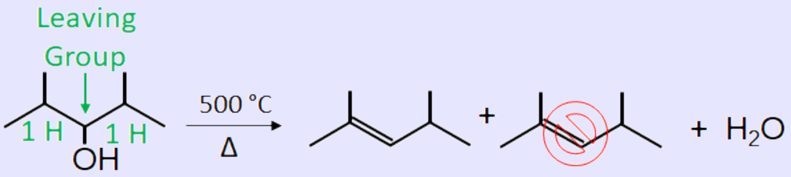
3. 

Solution:

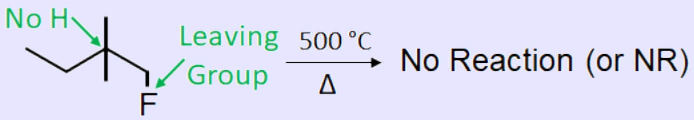
1. The leaving group in the reaction is Cl, only the adjacent hydrogens can leave, limiting the locations the double bond can form. Applying Saytzeff's rule the more stable product is when the H leaves from the carbon in the middle of the compound.



2. The leaving group in the reaction is -OH, only the adjacent hydrogens can leave. Note the symmetry in the molecule, both hydrogens that can leave would result in the identical product. In this case there is only one product (so no need to circle the most stable product). Normally the duplicate product is not drawn.



3. In this example, F is the leaving group, however, there are no hydrogen adjacent to the F, therefore an elimination reaction can not occur. Write No Reaction or NR as the product.



Key Idea: Elimination Reactions

Mechanism - Eliminate adjacent atoms
Possible atoms to eliminate - two adjacent H, or halogen and adjacent hydrogen or hydroxy (-OH) group and adjacent H.
Recognized by - Single reactant (alkane, alkyl halide or alcohol). Reaction arrow is unique.
Key aspects - multiple products possible, Saytzeff's rule - circle most stable product (most substituted or remove H from C with least H.

2.12 Important Alkanes

Alkanes are used widely in our everyday lives for a variety of uses, they are a primary source of energy, they have important medical uses, and impact our global ecology. A few short examples follow illustrating the importance of alkanes.

Fossil Fuels and Energy Generation

Alkanes are the source of a large fraction of energy used in our modern society to heat homes, drive cars and generate electricity shown in Figure 2.24. The top three sources of energy are all alkanes, petroleum at 37%, natural gas at 32% and coal at 11% this accounts for approximately 80% of the energy generated. The energy is generated by simple combustion, an exothermic chemical reaction, as discussed earlier in section 2.11

The petroleum that is pumped out of the ground is a complex mixture of several thousand organic compounds including straight-chain alkanes, cycloalkanes, alkenes, and aromatic hydrocarbons with four to several hundred carbon atoms. Petroleum is separated into different fractions based on vapor pressure into the products used everyday. Natural gas is composed of mostly methane mixed with smaller amounts of ethane, propane and butane. Propane is easily condensed into a liquid and used as as fuel source. The alkanes from pentane

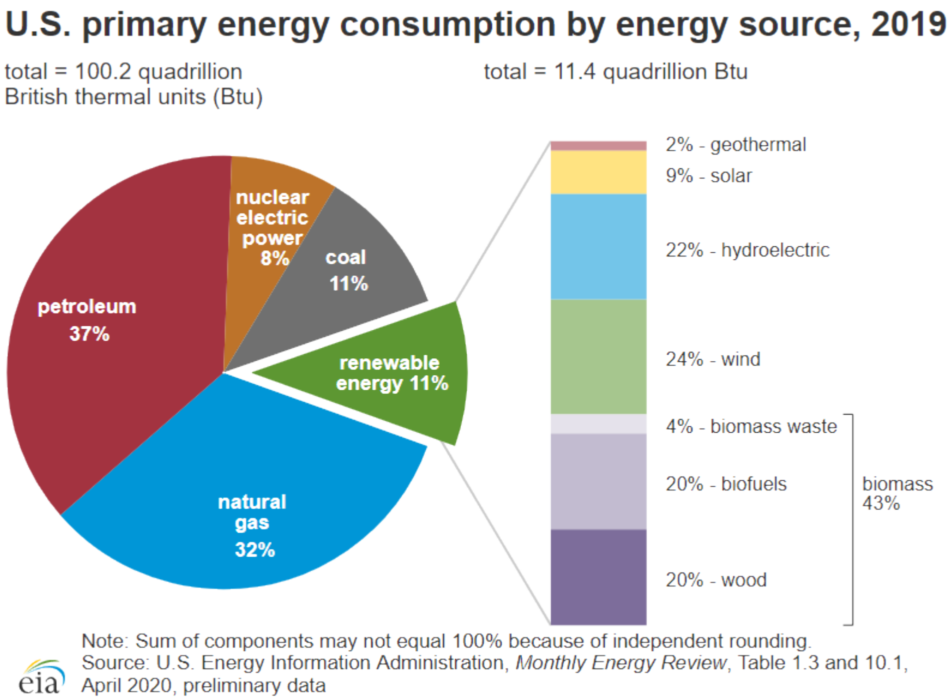


Figure 2.24 United States energy consumption by source in 2019. As shown in the chart, petroleum has the biggest share at 37%, while natural gas is in second place with 32% share. credit: `https://www.eia.gov/energyexplained/us-energy-facts/`

(C_5H_{12}) to octane (C_8H_{18}) are refined into gasoline used to drive cars. Heavier alkanes from nonane (C_9H_{20}) to hexadecane ($C_{16}H_{34}$) are refined into diesel fuel, kerosene and jet fuel.

More Information: `https://en.wikipedia.org/wiki/Petroleum`

Chlorofluorocarbons and the Ozone Layer

Refrigeration is a key technology in modern society from keeping food cold to slow the growth of bacteria to cooling homes during the hot summer months. Many different compounds have been used as refrigerants, with the most successful being various chlorofluorocarbons (or CFC's). The first successful one was dichlorodifluoromethane CCl_2F_2), it and other similar compounds became widespread in the 1970's with over one million tons produced and an industry worth over 500 million dollars. If that were all to the story it would be a successful application of chemistry. The bad news is that CFC's in the upper stratosphere cause ozone depletion, destroying an essential piece of the atmosphere.

The ozone layer is a thin layer (approximately 10 ppm) of O_3 present in the upper stratosphere (9-18 miles) of earths atmosphere that is responsible for absorbing damaging radiation for the sun. Most importantly it absorbs ultrviolet light (UV light) specifically it absorbs 97-98% of the UV-B (200-315 nm) which is linked to many harmful effects. UV-B radiation health effects include being the primary cause of sunburn, excessive exposure leads to cataracts, suppression of the immune system, skin cancer and genetic damage.

CFC's are very stable in the lower atmosphere, and eventually end up in the upper atmosphere where UV light can cause them to form free radicals. Chlorine acts as a catalyst in the destruction of ozone, one chlorine free radical from a CFC can destroy over 100,000 ozone molecules! This lead to the formation of an "ozone hole" where less ozone is concentrated and more dangerous UV radiation is allowed to pass through.

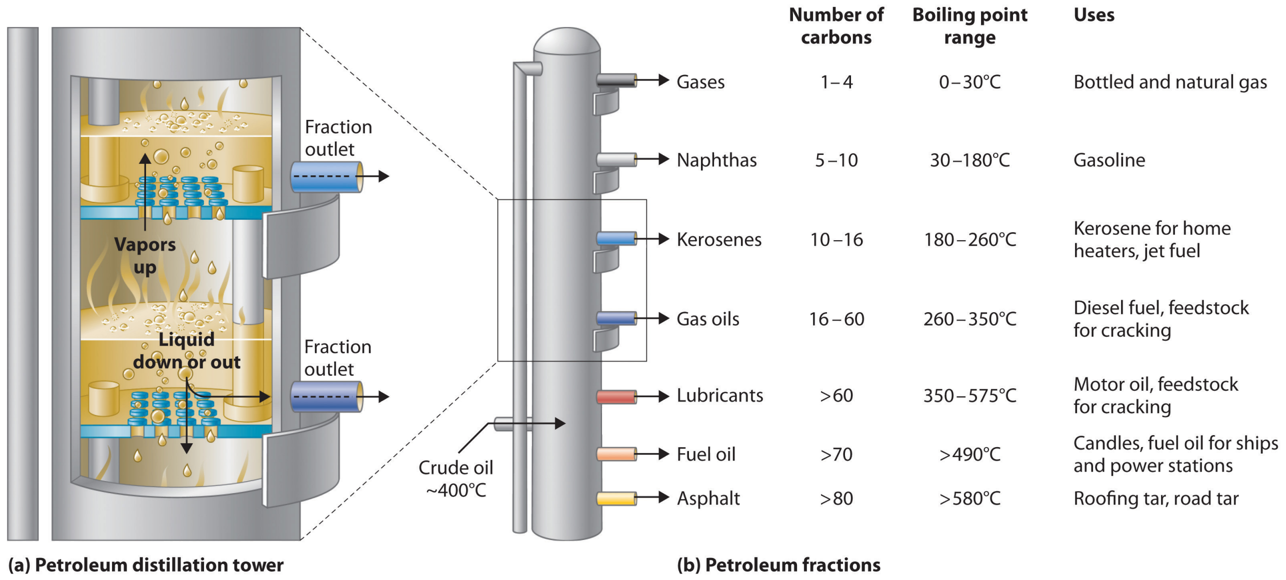


Figure 2.25 (a) Distillation column used for separating petroleum fractions by vapor pressure. (b) Molecules condense at different temperatures, depending on vapor pressure which is inversely proportional to the size of the molecule. The most volatile components (those with the lowest boiling points) condense at the top of the column, and the least volatile (those with the highest boiling points) condense at the bottom. credit: urlt.ly/s9cT

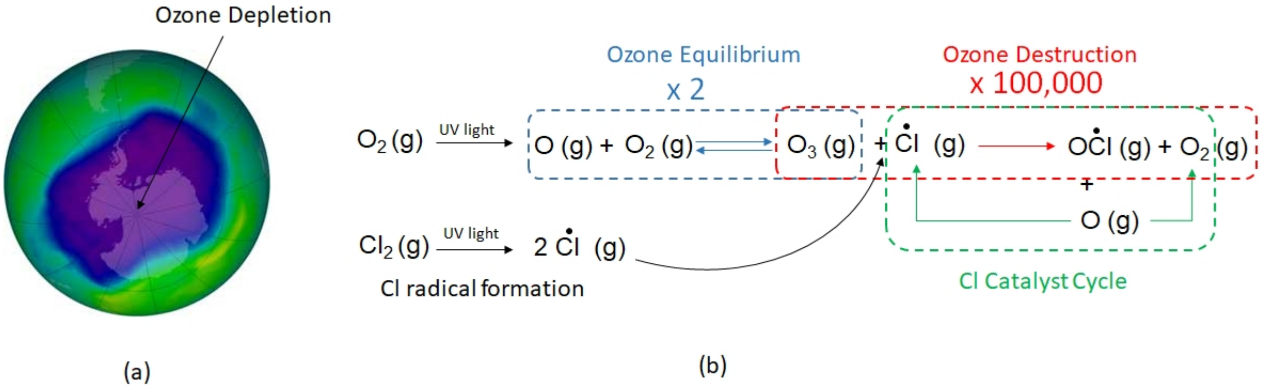


Figure 2.26 (a) Image from NASA showing the ozone hole above Antarctica in 2006. (b) Complex relationship showing ozone formation, destruction, and the radical chlorine catalyst cycles. The rate of destruction is much faster than the rate of creation leading to a net decrease in ozone. credit (a): `http://www.nasa.gov/vision/earth/lookingatearth/ozone_record.html` (b) author

this hole increased in size and duration and lead to laws have been passed limiting the production and use of CFC's and phasing their use out of several industries. Many refridgerants have been replaced by a mixture of propane and butane often called "greenfreeze". The changes have lead to a regeneration of the ozone layer. A 2020 report estimates that full implementation of the Montreal Protocol on Substances the Deplete the Ozone Layer is expected to prevent approximately 443 million cases of skin cancer, 2.3 million skin cancer deaths, and 63 million cases of cataracts for people in the United States born in the years 1890–2100.

More Information: `https://en.wikipedia.org/wiki/Ozone_depletion`
`https://www.epa.gov/ozone-layer-protection`

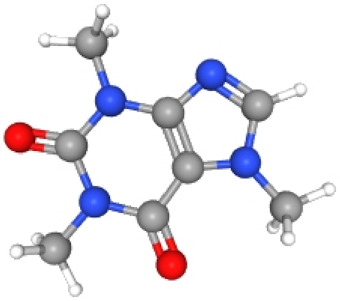
2.13 Review

Key Idea: Reaction Mechanisms

Combustion - occurs for all C,H,O compounds - always produces CO_2(g) + H_2O(g) + energy
Substitution - swap atoms - alkanes and aromatics
Elimination - eliminate a small molecule - alkanes and aromatics
Addition - add a small molecule - alkenes and alkynes

Chapter 3

Alkenes, Alkynes, and Aromatics



1,3,7-Trimethylpurine-2,6-dione
aka caffeine molecule

3.1 Structure of Alkenes and Alkynes

Alkenes and alkynes are hydrocarbons with one or more carbon-carbon double (alkenes) or triple (alkynes) bonds as shown in Figure 3.1. These compounds are often referred to as **unsaturated** hydrocarbons because they have fewer hydrogen atoms than the analogous alkane due to the fomation of the double and triple bond.

3.2 Valence Bond Theory

Key Idea: Review - Quantum mechanics and Lewis Structures

Be sure to review Quantum mechanics in Chapter **??** and Lewis structures in Chapter 1.3.

The Lewis structures of organic molecules provides a simple description of bonding between atoms in organic molecules and has the advantage of being fairly quick, easy to draw, and resulting in the correct shape and bond angles using Valence Shell Electron Pair Repulsion (VSEPR) theory. Lewis structures have some flaws though, (1) they fail to differentiate between single, double and triple bonds, (2) it not explain the different bond lengths (distance between atoms) and (3) different bond strengths (amount of energy to break the bond. Additionally Lewis theory does not take into account quantum mechanics which describes electrons being in orbitals with different shapes and distances from the nucleus.

Quantum mechanics describes bonding between atoms as the result of the overlap between two atomic orbitals, each holding one electron. This is easily illustrated for simpler molecules such as H_2, F_2 and HF as shown in Figure 3.2. The amount of overlap can be calculated and corresponds well with the bond

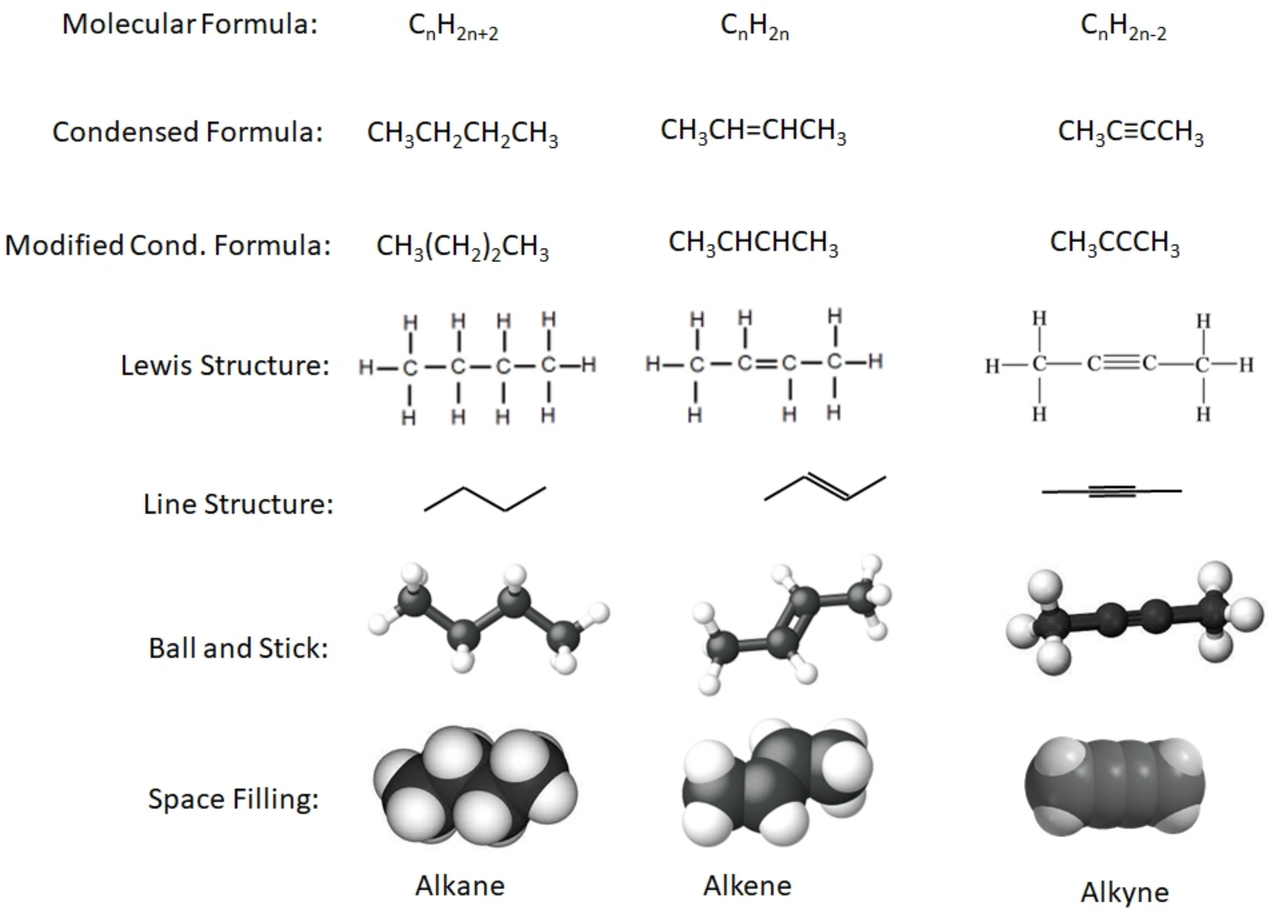


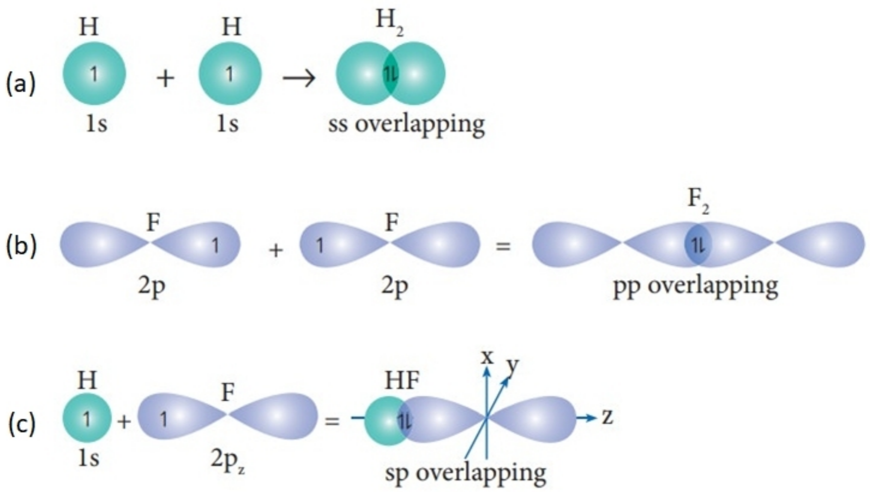
Figure 3.1 Structure of an (a) Alkanes (b) Alkenes and (c) Alkynes. Note that for the alkene shown there are multiple structures that will be discussed in when isomers are discussed. Credit: Author and `https://opentextbc.ca/chemistry/chapter/20-1-hydrocarbons/`

length (distance between atoms) and bond strength (amount of energy to break the bond) determined experimentally.

This model works well for diatomic molecules but begins to fail for even simple molecules like water where quantum mechanics would predict the overlap between oxygen 2p-orbitals and hydrogen 1s orbitals would result in a 90^o bond angle because p-orbitals are orthogonal. In experiments the bond angle in water is slightly smaller than the idealized angle predicted from VESPR theory of 109^o. Quantum Mechanics also has difficulty predicting the shape of methane (CH_4) since carbon would only have 2 unpaired electrons in p-orbital and that 3 of the bonds would be s-p overlaps while the fourth bond would have to be an s-s overlap.

Valence Bond Theory solves many of the problems pure quantum mechanics has describing these molecules by realizing that when the chemical bonds are formed, the wave functions of the different orbitals combine to form new, lower energy orbitals. The process can be broken down into two steps, **promotion** - an electron in a lower energy orbital is promoted to a higher energy orbital and **hybridization** - orbitals mix with each other to create hybrid orbitals. There are three types of orbitals that result from hybridization depending on how many s and p orbitals mix to form new orbitals. Each will be examined in turn.

Figure **??** illustrates the process for sp^3 hybrid orbitals. On top is the energy level diagram showing that promoting an electron increases the energy of the molecule resulting in an excited state denoted by the an



Bond	Length (nm)	Strength (Kj/mol)
H-H	75.1	436
F-F	142	157
H-F	91.7	568

Figure 3.2 (a) Orbital overlap between two 1s orbitals of hydrogen to form H_2, (b) orbital overlap of two 2p orbitals of fluorine to form F_2 and (c) orbital overlap of a 1s and 2p orbitals of H and F to form HF. credit: unknown

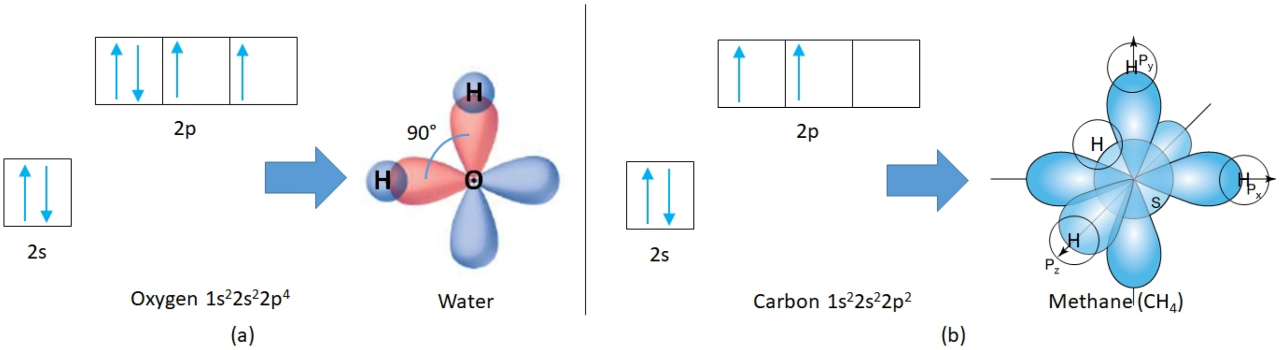


Figure 3.3 (a) The overlap between 2p orbitals from quantum mechanics would result in (a) water having a 90^o bond angle instead of the measured 104.5^o bond angle and (b) would result in two different typs of overlap for CH_4 with 3 bonds forming 2p-1s overlaps and the last bond forming a 2s-1s overalp. credit: author modified version of content from (a) `https://openstax.org/details/books/chemistry-atoms-first-2e` and (b) `https://xaktly.com/OrbitalHybridization.html`

asterisk (*). The resulting orbital wave functions are hybridized to form four new, lower energy orbitals called sp^3 hybrid orbitals. On the bottom this is illustrated using the orbitals from quantum mechanics to produce the new, hybrid orbitals. The resulting orbitals have a tetrahedral geometry with a bond angle of 109.5^o, matching the expected result from Lewis theory, VSEPR theory and the experimentally measured bond angles. The modifications to quantum mechanics made by Valence Bond Theory result in the formation of a methane molecule that now has four equivalent bonds to hydrogen.

In alkanes the carbon-carbon single bonds exhibit **free-rotation** around the bond, while in alkenes (C=C) and alkynes (C≡C) the pi bond prohibit free rotation. T

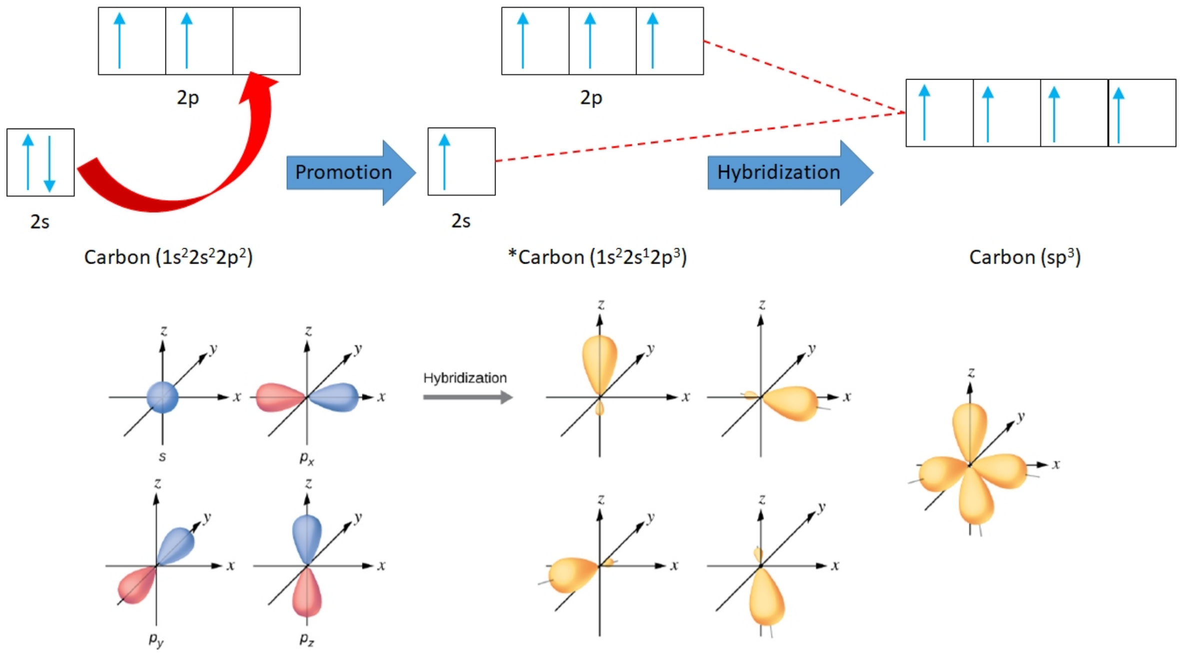


Figure 3.4 (a) Energy level diagram showing: Promotion - an electron in a lower energy level (2s) is placed in a higher energy orbital (2p), the resulting carbon atom is in an excited state denoted by the *, and Hybridization - the 2s and 2p orbitals mix resulting in 3 sp^3 hybrid orbitals that are overall lower in energy than the original orbitals. (b) Mixing of 2s and 2p orbitals to create 4 hybrid orbitals. The resulting orbital correctly predict a tetrahedral shape and 109.5^o bond angle. credit: (a) author (b)

3.3 Geometric Isomers or Cis-Trans Isomers

In Chapter 2.7 we saw that carbon atoms in alkanes can be connected in many different ways for a given chemical formula resulting in the formation of structural isomers. Alkenes and Alkynes can also have the same type of structural isomers but Alkenes due to the rigid C=C they also exhibit Geometric or Cis/Trans iosmerism.

Alkenes can also demonstrate structural isomerism. In alkenes, there are multiple structural isomers based on where in the chain the double bond occurs. The condensed structural formulas of 1-butene ($CH_2{=}CH{-}CH_2{-}CH_3$)and 2-butene ($CH_3{-}CH{=}CH{-}CH_3$)show this. The number in the name of the alkene refers to the lowest numbered carbon in the chain that is part of the double bond, naming will be discussed in detail in the next section..

With a molecule such as 2-butene, a different type of isomerism called geometric isomerism can be observed. Geometric isomers are isomers in which the order of atom bonding is the same but the arrangement of atoms in space is different. The double bond in an alkene is not free to rotate because of the nature of the pi bond. Therefore, there are two different ways to construct the 2-butene molecule. Figure 3.5 shows the two geometric isomers, called cis-2-butene and trans-2-butene.

The cis isomer has the two single hydrogen atoms on the same side of the molecule, while the trans isomer has them on opposite sides of the molecule. In both molecules, the bonding order of the atoms is the same. In order for geometric isomers to exist, there must be a rigid structure in the molecule to prevent free rotation around a bond. If the double bond in an alkene was capable of rotating, the two geometric isomers above would not exist. In addition, the two carbon atoms must each have two different groups attached in order for there to be geometric isomers. Propene has no geometric isomers because one of the carbon atoms has two single hydrogens bonded to it.

Physical and chemical properties of geometric isomers are generally different. While cis -2-butene is a polar molecule, trans -2-butene is nonpolar. Heat or irradiation with light can be used to bring about the conversion of one geometric isomer to another. The input of energy must be large enough to break the pi bond between the two carbon atoms, which is weaker than the sigma bond. At that point, the now single bond is free to rotate and the isomers can interconvert.

As with alkenes, alkynes display structural isomerism beginning with 1-butyne and 2-butyne. However, there are no geometric isomers with alkynes because there is only one other group bonded to the carbon atoms that are involved in the triple bond.

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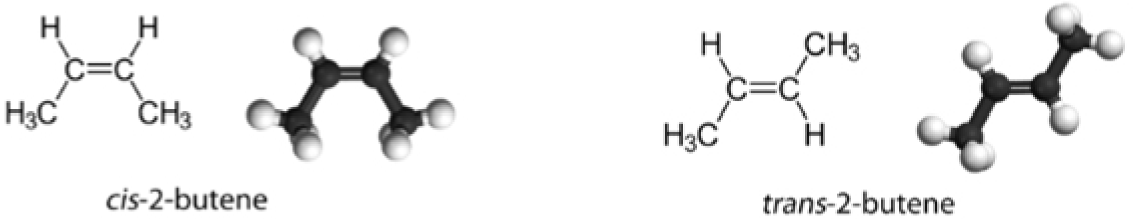


cis-2-butene

trans-2-butene

Figure 3.5 Cis and Trans isomers of 2-butene. credit: `https://courses.lumenlearning.com/cheminter/chapter/organic-chemistry/`

3.4 Naming Alkenes and Alkynes

The naming rules for alkanes discussed in Chapter 2.6 form the basis for naming all organic molecules. For each new functional group, one must learn a new rule or modify an existing rule. For alkenes and alkynes the new rules are:

1. The functional group (alkene or alkyne) is always part of the longest chain and is always given the smallest possible number. (This rule takes priority over the numbering of the sidechains.)
2. If there are four or more carbon atoms in a chain, we must indicate the position of the double or triple bond. The location is placed after any side-chains and before the longest chains.

3. The ending of the molecule is changed from -ane, for a double bond to -ene and for a triple bond to -yne.

Exercise 3.1Naming Simple Alkenes

Question: Question

Solution: Answers

3.5 Physical Properties of Alkenes

3.6 Chemical Reactions - Alkenes and Alkynes

Addition Reactions

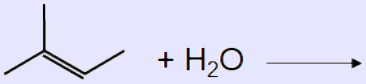
Addition reactions are the opposite of elimination reactions, a small molecule is added to a carbon-carbon double bond (C=C). The electrons in a carbon-carbon double bond are highly reactive, the reason why will be detailed in Chapter **??**. A small molecule approaches the exposed electrons in the double bond, the bond breaks forming a free radical which then reacts with the small molecule.

Similar to elimination reactions, multiple products are possible if an unsymmetrical molecule is added, for example HX where X = halogen or if water (H-OH) is added. The most stable product is given by **Markovnikov's rule** which states that when an unsymmetrical molecule is added to a carbon-carbon double bond the H goes to the C atom that already has the most H atoms attached. An example is shown in Figure 3.7.

Exercise 3.2 Addition Reaction and Markovnikov's Rule

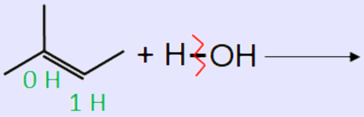
Question:

Complete the following reaction:



Solution:

1. First recognize it is an addition reaction because the reactants include a C=C + small molecule.
2. Count the number of H on each C so you can apply Markovnikov's rule, also recognize that H_2O is better thought of as H-OH highlighting which bond breaks in the reaction.



3. The added molecule H−OH is unsymmetrical, therefore two products can be made. Apply Markovnikov's rule to determine the most stable molecule - H is added to the C with the greater number of H. In this example molecule (a) is the most stable.

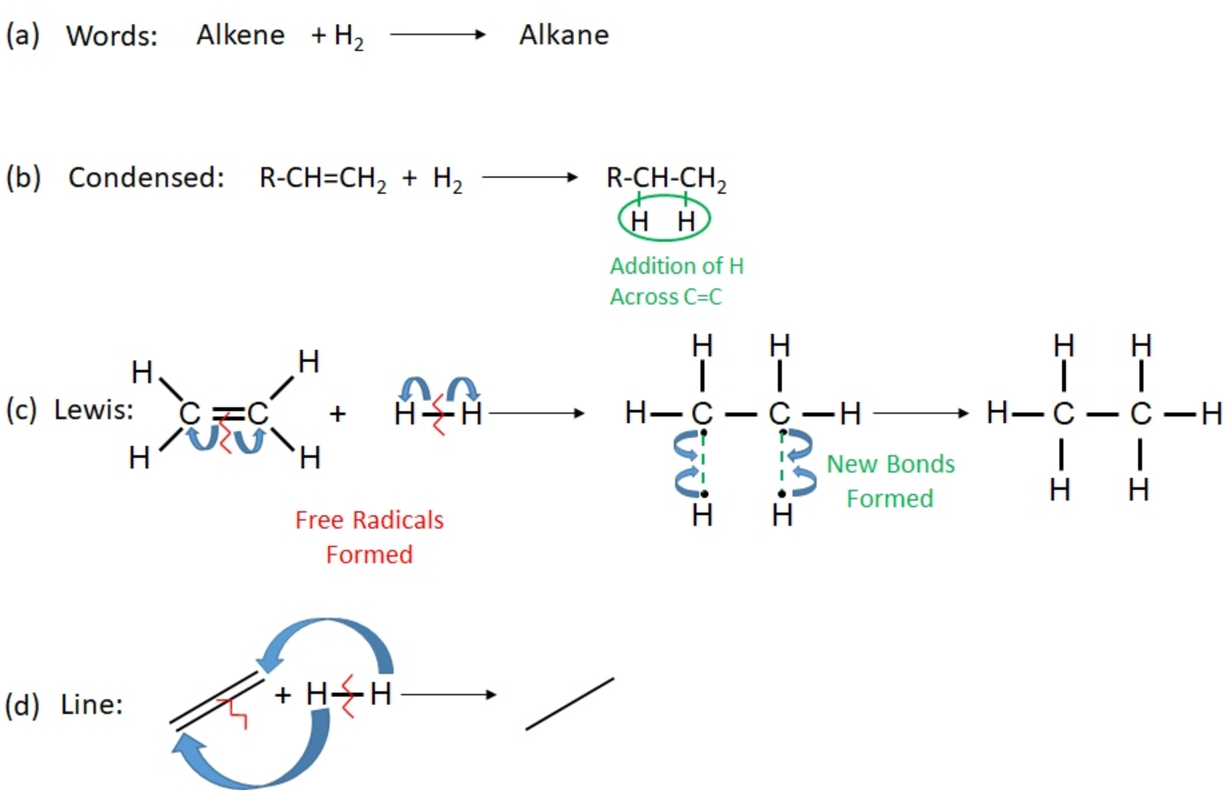


Figure 3.6 Addition reactions occur when a small molecule reacts with the exposed/highly reactive electrons in a carbon-carbon double bond (C=C). The reaction can be understood in several different ways. (a) Word reactions focus on the functional group changes, (b) condensed structures can help illustrate a mechanism, (c) Lewis structures give detailed information about the mechanism but are cumbersome, and (d) Line drawing are the most frequently used method due to ease with which they are drawn. credit: author

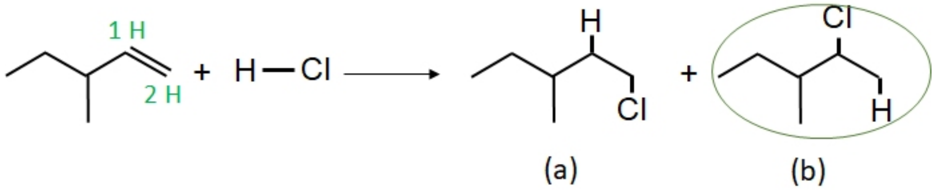
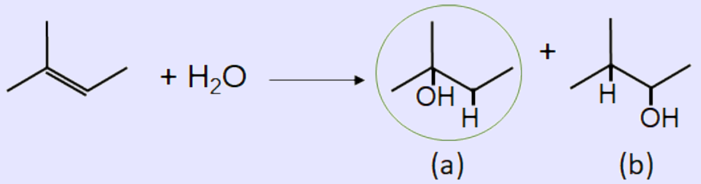


Figure 3.7 Markovnikov's rule states that if an unsymmetrical molecule is added across a carbon-carbon double bond (C=C) the more stable product is the one in which the hydrogen adds to the carbon with the most hydrogen. Therefore molecule (b) is the more stable product and should be circled. credit: author



Key Idea: Addition Reactions

Mechanism - Add a molecule across a C=C
Possible molecules to add: H_2, halogens (X_2), acids (HX), and water (H-OH)
Recognized by - Alkene + ??
Key aspects - multiple products possible if added molecule is unsymmetrical, Markovnikov's rule - circle most stable product (H adds to C with most H).

3.7 Importance Alkanes, Alkynes and Aromatics

The two simplest unsaturated compounds ethene ($CH_2{=}CH_2$) and ethyne (common name - acetelyne) ($CH{\equiv}CH$) were once used as anesthetics and were introduced to the medical field in 1924. However, it was discovered that acetylene forms explosive mixtures with air, so its medical use was abandoned in 1925. Ethylene was thought to be safer, but it too was implicated in numerous lethal fires and explosions during anesthesia. Even so, it remained an important anesthetic into the 1960s, when it was replaced by nonflammable anesthetics such as halothane ($CHBrClCF_3$).

Ball

The first two alkenes in Table 13.1 "Physical Properties of Some Selected Alkenes"—ethene and propene (Figure 13.1 "Ethene and Propene")—are most often called by their common names—ethylene and propylene, respectively. Ethylene is a major commercial chemical. The US chemical industry produces about 25 billion kilograms of ethylene annually, more than any other synthetic organic chemical. More than half of this ethylene goes into the manufacture of polyethylene, one of the most familiar plastics. (For more information about polymers and plastics, see Section 13.5 "Polymers".) Propylene is also an important industrial chemical. It is converted to plastics, isopropyl alcohol, and a variety of other products. (For more information about alcohols, see Chapter 14 "Organic Compounds of Oxygen", Section 14.2 "Alcohols: Nomenclature and Classification".) Chapter 13 Unsaturated and Aromatic Hydrocarbons 13.1

Ball

Alkenes (sometimes called olefins) have carbon-carbon double bonds, and alkynes have carbon-carbon triple bonds. Ethene, the simplest alkene example, is a gas that serves as a cellular signal in fruits to stimulate ripening. (If you want bananas to ripen quickly, put them in a paper bag along with an apple - the apple emits ethene gas, setting off the ripening process in the bananas). Ethyne, commonly called acetylene, is used as a fuel in welding blow torches.

Soderberg

3.8 Review