

Faculty of Science

**Unit 4:
Intermolecular Forces
and Organic Chemistry**

CHEM 1503
Chemical Bonding and
Organic Chemistry

Table of Contents

Overview	U4-1
Learning Outcomes	U4-1
Liquids and Solids	U4-2
Intermolecular Attractions	U4-4
The Liquid State	U4-4
Organic Chemistry	U4-7
Introduction to Organic Chemistry	U4-8
Chemical Bonds and Bonding	U4-9
A Quantum Mechanical Approach to Bonding	U4-11
Orbital Hybridization	U4-12
Structural Formulas	U4-12
Bonding in Hydrocarbons	U4-14
Example Problem 1	U4-17
Example Problem 2	U4-17
Functional Groups	U4-17
Acid-Base Theory	U4-20
Physical Properties and Molecular Structure	U4-20
Self-Assessment	U4-23
Practice Exercise 4	U4-24
Suggested Supplementary Exercises	U4-25
Assignment 4	U4-25
Answers to Unit 4 Example Problems	U4-26

Overview

In this unit, you will first study the intermolecular forces that influence the condensed states of matter: liquids and solids. (The other state of matter, gases, is covered in greater depth in CHEM 1523.) This is followed by an introduction to the world of carbon compounds and the field of organic chemistry.

Learning Outcomes

Once you are finished this unit, you should be able to:

- Describe the differences between the liquid and the solid state.
- Explain the terms surface tension, capillary action, meniscus, and viscosity.
- Describe different intermolecular attractions, including the hydrogen bond.
- Discuss the anomalous properties of water.
- Predict the order of melting points between various compounds based on their intermolecular forces.
- Explain different concepts of bonding in organic molecules, including formal charge, hybridization, and multiple bonding.
- Draw Lewis structures and condensed, bond-line, three-dimensional, and dash structural formulas.
- Identify compounds where resonance occurs and draw resonance contributors and hybrids.
- Predict shapes of simple molecules and molecular polarity.
- Identify and name various functional groups.
- Explain how the Brønsted-Lowry and Lewis acid-base theories differ from each other.
- Explain the relationship between intermolecular attractions and the physical properties of organic molecules.
- Using your model kit, build three-dimensional models of simple organic molecules from two-dimensional diagrams and demonstrate isomerism and free rotation.

Liquids and Solids

So far, we have built up our understanding of the behaviour of molecules starting from the electrons, to their orbitals, then to bonding, and finally to molecular shapes and geometries. Now we investigate how molecules interact with each other to give us the three states of matter.

Some properties of liquids and solids are similar to those of gases, while others are quite different. In the condensed states of matter, there is virtually no distance between molecules; whereas in gases, the average distance between molecules is large. It follows that the density of condensed matter is high compared to the density of gases. There are obvious differences between solids and liquids with solids displaying long-range order and liquids having short-range order. (The molecules of gases follow random pathways and display no order.) Solids have a high degree of cohesiveness, liquids have a medium degree of cohesiveness, and there is no cohesiveness in gases.

The average kinetic energy of the molecules of gases, liquids, and solids shows a decrease from large to medium to small, respectively. When the temperature of a gas decreases, the average kinetic energy of the gas molecules also decreases. The molecules no longer have enough energy to overcome intermolecular attractions, and a liquid results. Thus, molecular motion is more restricted in the liquid state. Continued cooling decreases the kinetic energy even further and eventually a solid is formed. Table 4.1 in this unit gives some examples of melting points of various solids to illustrate how molecular mass, size, and extent of intermolecular attractions affect the melting point. Comparing the melting point of nitrogen to water, for instance, should give you the impression that something significant is at play here.

Table 4.1: Melting points of various substances. The following shows how molecular mass, size, and extent of intermolecular attractions raise the melting point.

Substance	Formula	Molecular mass (amu)	Melting point (K)
Hydrogen	H ₂	2	20.3
Nitrogen	N ₂	28	63.1
Methane	CH ₄	16	90
Pentane	C ₅ H ₁₂	72	143
Decane	C ₁₀ H ₂₀	140	243
Hydrogen fluoride	HF	20	181
Ammonia	H ₃ N	17	195
Water	H ₂ O	18	273

The transitions between the distinct states of matter are often easily visualized by considering the large differences in degrees of order of the three phases. Different degrees of order, directly related to intermolecular forces, are consistent with different temperatures—hence the suddenness of melting or boiling.

Finally, both liquids and solids are common states of matter that you see around you every day. Chemists have been able to build an understanding of the properties and structures of solids but the properties of liquids are not as easily defined. Consequently, chemists know less about the character of liquids than they do about solids and gases.

Intermolecular Attractions

Study Sections 11.1 and 11.2 of your textbook. You should note a number of points about these sections.

1. Intermolecular means “between different molecules” and intramolecular means “within the same molecule.” (An easy way to remember this is to think of *international* flights at the airport; travel *between* nations.)
2. The interactions (or attractions or forces) discussed in these sections are just that—they are attractions, *not* bonds. The term “hydrogen bonding,” although accepted and used in chemistry, is misleading. A hydrogen bond is a strong intermolecular attraction. It is not to be confused with the true nonpolar covalent bonding in a hydrogen molecule.
3. Three weak interactions, dipole-dipole, dipole-induced-dipole, and dispersion forces, are known collectively as **van der Waals forces**.

Try Examples 11.1 and 11.2 from your textbook and their practice exercises.

The Liquid State

Study Section 11.3 of your textbook. You should understand and be able to explain the phenomena of **surface tension**, **capillary action**, and **viscosity**. You have seen effects of surface tension: some insects can walk across the surface of ponds or puddles. Those of you with steady hands may have been able to float a fine needle on the surface of a glass of water. Such marvels are due to surface tension. Figure 11.8 of your textbook shows how molecules in the interior of a liquid experience equal attractive forces from all directions. Molecules at the surface experience unbalanced forces. They are pulled inwards and sideways so they act as a tight elastic membrane that tries to contract to minimum area. The ratio of surface area to volume is smallest for a sphere, so liquids tend to form drops. In a container, they cannot form drops and instead produce curved surfaces.

In Figure 11.10 in your textbook you can see the shape of the mercury meniscus is rounded upward. You could say that mercury is not “wetting” the glass. What determines whether or not a liquid will wet a surface is the contact angle between the two phases. This in turn depends on the different attractions the liquid molecules have for themselves and for the solid. You may have seen small, almost perfectly spherical droplets of mercury. Usually, water does not form such spherical droplets—it spreads out more. However, given the right surface, mercury and water

can form similar spherical droplets. If you have ever poured a little water into a clean non-stick frying pan or recently waxed surface of a car, you will have seen how the water forms droplets. It could not be said to be wetting the pan or car surface. A detergent is a substance that lowers the surface tension of a liquid by reducing the side-to-side attractions of adjacent surface molecules. If you add a little bit of detergent to the water in the non-stick pan, the spherical droplets collapse. Under such conditions you cannot float a needle on the surface of water, nor can insects walk across it.

Spray-on waterproofing agents for fabrics work by coating the fabric with a substance that has a very low attraction for water molecules. This ensures that water-water attractions predominate rather than water-fabric attractions. The water molecules then retain a spherical shape, even though the actual surface tension of the water has not changed. The water drops remain perched over the openings of the fabric rather than sinking through.

If all molecules experience attractions for each other, why do all surfaces not stick together? The answer to this question is that, given the right conditions, they do. Those conditions depend on the particular surfaces. Very smooth surfaces will stick together. You may have experienced this when trying to separate two very clean, dry microscope slides or slide covers. A good machinist can mill two blocks of steel so well that they can be “twisted” together and broken apart only with difficulty. If surfaces are not smooth and you want them to stick together, you can smooth them out with glue. Glues, cements, and gums are substances that flow into and fill out the holes and imperfections of the surfaces. These substances then harden to become solids with high tensile strengths. The intermolecular attractions between the solid objects and the solidified glue are responsible for holding them together. To hold two metals together, the same principle is used. Solder is a molten metal that solidifies on cooling. Metal surfaces are covered with a thin layer of oxide that the molten solder is not able to wet. A “flux” is used to dissolve away the oxide layer. The molten solder can then “wet” the exposed clean surface of the metal.

What can you do if you want to prevent two surfaces from sticking? When two objects rub together, weak interactions between the surfaces are continually being made and broken. Squeaking noises are due to the vibrations caused by stop-start motions. To stop the squeaking and to prevent wearing of the surfaces, you can apply lubrication. A **lubricant** is a substance that wets the surface efficiently but has enough internal cohesiveness so that it is not squeezed out from between the surfaces. This should explain to you why oil, and not water, is used as a lubricant in machines. Both water and oil are effective wetting agents, but water does not have the cohesiveness of oil. For best results, the lubricant must be designed for the

specific surfaces (to adjust the interfacial forces and wetting power) and for the load (to achieve the right cohesiveness).

An interesting example of the effect of molecular shape on viscosity is found in the protein of egg whites. The mechanical stresses of beating egg whites cause these protein molecules to become partially uncoiled. This increases the viscosity of the whites to the point that they become sufficiently stiff to hold air bubbles. If you beat the egg whites too much, your meringue “falls.” This is because the hydrogen-bonding side groups of the protein become more and more exposed as the chain uncoils; the exposure of the side groups increases surface tension. The bubbles collapse into themselves as the egg whites try to form drops. You should not beat egg whites unless they are at room temperature. When egg whites are cold, the surface tension is too high to stabilize the bubbles—the effect is similar to overheating. You must also ensure that you do not have any egg yolk or oil in your meringue mixture. Both of these substances act as detergents and lower the intermolecular attractions. This reduces the viscosity so much that the air bubbles simply escape and you cannot form a stiff mixture. The best way to completely unwind the egg protein molecules is by heating them. The clear liquid white becomes an opaque gel—a random network of long molecules with voids that are filled with water molecules.

These are just some examples of the importance of intermolecular forces and the properties of liquids. Use the first nine points in the summary at the end of Chapter 11 in your text to help you review the important concepts covered here.

Problem: For each pair, identify the *dominant* intermolecular forces in each substance and select the substance with the *higher* boiling point.

- a. CH_3Br , CH_4
- b. $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$, $\text{CH}_3\text{CH}_2\text{OCH}_3$
- c. CH_3OH , $\text{CH}_3\text{CH}_2\text{OH}$
- d. MgF_2 , PF_3

Solution:

- a. CH_3Br , CH_4

CH_3Br (dipole dipole versus dispersion)

- b. $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$, $\text{CH}_3\text{CH}_2\text{OCH}_3$

$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ (hydrogen bonding versus dipole)

- c. CH_3OH , $\text{CH}_3\text{CH}_2\text{OH}$

$\text{CH}_3\text{CH}_2\text{OH}$ (both can H-bond, but more London forces in $\text{CH}_3\text{CH}_2\text{OH}$)

- d. MgF_2 , PF_3

MgF_2 (ionic bonding, crystalline salt)

Organic Chemistry

The second part of CHEM 1503 deals with organic chemistry, or the study of carbon compounds. Organic chemistry began developing as a science only in the nineteenth century, after the German chemist Friedrich Wöhler synthesized urea (a nitrogen-containing organic molecule found in urine) by heating a solution of ammonium cyanate. Since then its growth has been explosive. Today organic chemistry touches almost all aspects of our lives, giving us some of our most useful materials as well as some of our most harmful ones.

Before you begin studying the various types of organic molecules and the reactions they undergo, you must have a firm foundation on which to build your new knowledge. In this part of Unit 4, you will review certain topics—bonding, electronegativity, functional groups—from earlier units and see their importance to the study of carbon compounds. Since these topics are fresh in your mind, you may be able to complete this unit quickly. However, you should spend as much time as necessary to understand the material covered here. Although its relevance may not always be obvious, you will need this information in order to tackle the remaining units.

In this part, you will be introduced to some new concepts, such as ways to write or draw organic structures and the idea of thinking in three dimensions while drawing in two dimensions. You will begin to build models of the molecules you draw and visualize different kinds of bonds and their properties. By the time you complete this unit, you should be able to define and explain the terms hybridization, sigma (σ) and pi (π) bonds, electronegativity differences, and resonance contributors for organic molecules. You will be ready to begin your study of organic compounds and their properties and reactions.

Introduction to Organic Chemistry

Turn now to the first chapter of your *Organic Chemistry* supplement, which contains extracts from the book *Organic Chemistry: Structure and Function* by K. Peter C. Vollhardt and Neil E. Schore. Read Section 1-1.

Also read page 37 of Section 1-9 in your *Organic Chemistry* supplement. On this page, you will review the important distinction between an **empirical formula** and a **molecular formula**, as well as learn the concept of **constitutional** or **structural isomers**. Another important chemical concept is that of **valence**, which can be thought of as the number of bonds an atom can form with other atoms in a compound. Carbon is tetravalent, meaning that it can form four bonds. These may be single, double, or triple bonds, and they may be formed with other carbon atoms or with atoms of other elements.

Just as some compounds may have the same *empirical* formula but different *molecular* formulas, so compounds with the same *molecular* formula may have different *structural* formulas. The same numbers of atoms may be present, but the atoms may be attached in a different order. This phenomenon is called **isomerism**, and the compounds are called **isomers**. In later units, you will learn about the various kinds of isomers found among compounds of carbon.

Now study carefully Sections 1-2 to 1-4 in the *Organic Chemistry* supplement. They deal with these fundamental concepts, which you will see again and again throughout this part of the course.

Chemical Bonds and Bonding

Much of the material you will encounter in this part of the course will build on your understanding of chemical bonding. This section reviews material you have seen in earlier units.

Before looking at the different kinds of bonds, let us recall what happens when bonds are formed. Atoms can be visualized as having an outer shell containing electrons. You can find out how many of these **valence electrons** are present in an atom by checking its group number—1, 2, 3, and so on—in the periodic table found inside the covers of your textbook supplement. For example, hydrogen belongs to group 1 and has one valence electron; carbon belongs to group 14 or 4A and has four valence electrons; oxygen belongs to group 16 or 6A and has six valence electrons. In forming bonds, an atom acquires in its outer shell the same number of electrons found in a noble gas such as helium (with two valence electrons) or neon (with eight valence electrons). This is referred to as the **octet rule**. The atom does this by losing, gaining, or sharing electrons.

Review Sections 1-2 to 1-4 of your *Organic Chemistry* supplement in order to reinforce the concepts presented in these sections (including valence electrons, the octet rule, Lewis structures, dipole moments, formal charges, and the VSEPR model).

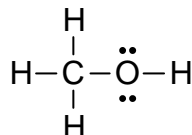
Section 1-3 reviews the VSEPR theory using some examples. The *Organic Chemistry* supplement does not go into as much detail as we saw earlier. This is because most compounds you will encounter in organic chemistry have either a tetrahedral, trigonal planar, or linear shape. Carbon, nitrogen, and oxygen never have an expanded octet or trigonal bipyramidal, octahedral, and related shapes.

Section 1-3 also discusses molecular polarity. In order to be polar, a molecule must have polar bonds and its shape must be such that the polar bonds do not cancel each other. Many molecules made up of atoms with unequal electronegativities have no net dipole moment because the centres of their positive and negative charges coincide.

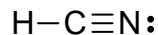
Practise drawing the Lewis structures in the following examples and check the solutions provided, then do Exercises 1-4 to 1-8 in your *Organic Chemistry* supplement.

Example 1: methanol, CH_3OH

Example 2: hydrogen cyanide, HCN

Answers:**Example 1:**

Note, each atom has the electronic structure of a noble gas—two electrons for H and eight each for C and O. For convenience, we generally draw such Lewis structures without showing the lone pairs.

Example 2:

Note that the five pairs of valence electrons are arranged as four bond pairs and one lone pair in the HCN molecule.

Before you leave Section 1-4 of your *Organic Chemistry* supplement, try doing a couple of examples from Problems 25, 26, and 27 at the end of the chapter in the supplement.

In Section 1-5 of the supplement we come to a very important topic in organic chemistry—resonance. Remember, more than one Lewis structure can be drawn for certain compounds simply by changing the positions of the electrons on the atoms. By itself, however, each **resonance structure** or **resonance contributor** does not account for important physical data about the compound. Such data can be explained only if the true structure of the molecule or ion is considered to be a **hybrid** of the different resonance contributors.

You should remember two things about resonance hybrids. First, because they possess **partial double bonds** (bonds that are intermediate between a single and a double bond), you cannot draw complete Lewis structures for them. Your organic supplement shows you how to represent resonance hybrids by using a combination of a solid line and a dashed line and by designating partial charges for certain elements. Second, a resonance hybrid is not a mixture of resonance contributors, and neither does it switch back and forth between two or more resonance contributors. Here's a useful analogy. The mule is a hybrid produced by a horse and a donkey. If you were to see several mules grazing in a field, you would not say that you were seeing equal numbers of horses and donkeys in that field. Nor would you expect a

mule to switch back and forth between a horse and a donkey. Keep this in mind when you think of resonance hybrids. Now look at Figure 4.1 in this unit.

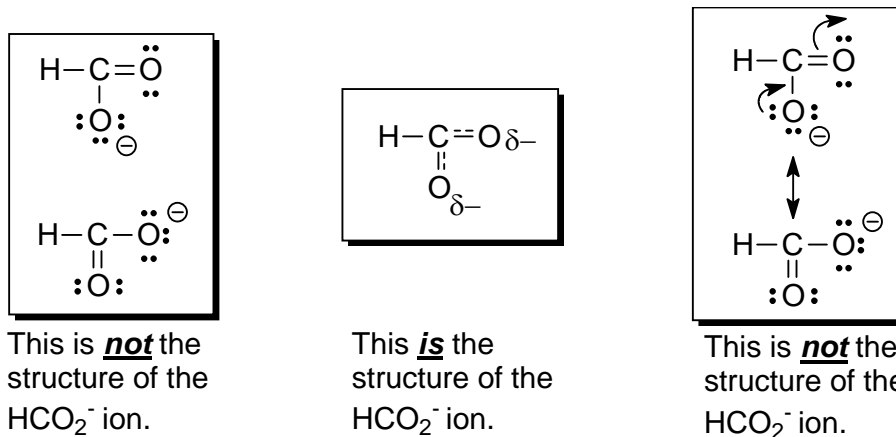


Figure 4.1: Hybrids

Resonance hybrids have structures distinct from but somewhere between the extremes of the resonance *contributors*. Chemists, however, normally draw one of the extreme forms, a resonance contributor, unless they specifically want to show the resonance *hybrid*.

Carefully study Section 1-5 of the *Organic Chemistry* supplement, and then work on Exercises 1-9, and 1-10, and 1-11 .

A Quantum Mechanical Approach to Bonding

Read Sections 1-6 to 1-8 in your *Organic Chemistry* supplement for a review of the quantum mechanical approach.

As you may recall from Unit 1, quantum mechanics takes a more sophisticated approach to atomic and molecular structure with electrons considered as three-dimensional standing waves. Like most chemists, you will not need to follow the math involved, but you should be able to explain the models that are derived from these mathematical expressions.

Orbital Hybridization

The concept of **orbital hybridization** is an extension of the quantum mechanical approach to bonding. In Unit 3, we imagined that *s* and *p* orbitals combine with each other to form hybrid orbitals that are then involved in bonding. An *sp* hybrid orbital results when one *s* combines with one *p* orbital; *sp*² and *sp*³ hybrids result when an *s* orbital combines with two and three *p* orbitals, respectively.

Hybridization is very important in organic chemistry. You must be able to describe how and why hybrid orbitals are formed in order to understand different kinds of organic reactions. Some people like to say that hybridization is not what atoms do; it is what chemists do. Or rather, it is what chemists say atoms do! There is some truth to this: hybridization, after all, is just a model for what chemists think happens when certain molecules are formed. However, this model *does* explain such things as why there are four bonds of equal energy in methane and why boron trifluoride (BF₃) has a bond angle of 120°. Because explanations and predictions from hybridization theory fit so well with experimental facts, organic chemists tend to speak of hybridization as though it were something real rather than a model.

Study Section 1-8 of the *Organic Chemistry* supplement, which covers the quantum mechanical approach to orbital hybridization.

Now that you have a grasp of the ideas behind hybridization, there is a way to quickly identify the hybridization state (*sp*, *sp*², or *sp*³) of a carbon, nitrogen, or oxygen atom in a molecule using a set of simple rules:

- If the atom has only single bonds to other atoms, it is *sp*³ hybridized.
- If the atom has one double bond to another atom (in addition to any single bonds), it is *sp*² hybridized.
- If the atom has two double bonds to two other atoms *or* if the atom has one triple bond to another atom (in addition to any single bonds), it is *sp* hybridized.

Structural Formulas

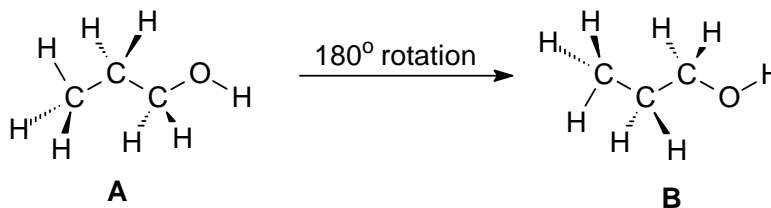
We come now to one of the most important topics for a beginning organic chemistry student—how to write various organic structures. There are several ways to represent molecules, and you will probably often wonder which one you should use.

As time goes by, however, you will learn how to select the logical method for the task at hand. Most of the time, drawing the simplest structure will do the job.

Study Section 1-9 in the *Organic Chemistry* supplement.

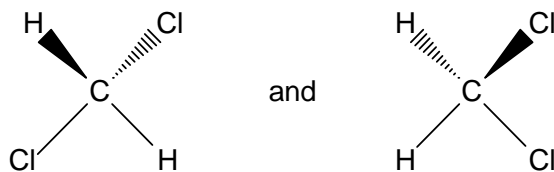
At this point, you will need the model kit that came with your CHEM 160 course package. Read the instruction booklet that accompanies the kit, and then construct a model for propyl alcohol, $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$.

After you have your model, hold it up and turn it around so that you can look at it from a number of different angles and see the various 3-D aspects of the molecule. For example, hold the model in front of you and make it correspond to **drawing A below**. Study your model so that you can begin to easily see in your mind's eye that bonding lines are on the same plane as the paper, dashed lines are bonds that point behind the plane of the paper, and wedges point in front of the plane. Take your model in the orientation of **drawing A** and rotate it 180° top to bottom in order to transform it into **drawing B**. As you rotate the molecule, watch carefully those atoms that are pointing behind the paper in **A** transition to being in front of the paper in **B**.

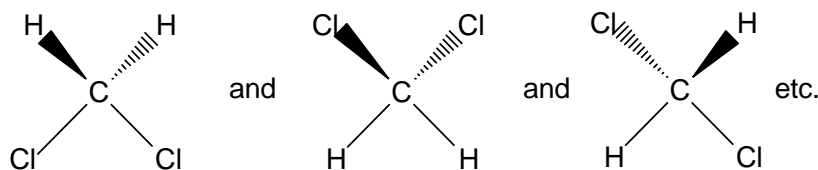


Models can also help you draw three-dimensional formulas like the ones described in Figures 1-22 and 1-23 of your *Organic Chemistry* supplement. It is good practice to build the models of a variety of different molecules as they are presented in this course.

Note that:



represent the same molecule. Make a model of CH_2Cl_2 . Turn it around and assure yourself that all of the following also represent this same compound:



Do Exercises 1-19 to 1-22 in your *Organic Chemistry* supplement. Use your model kit whenever you find it necessary.

Being able to draw and interpret structural formulas is extremely important. Do not continue with new material until you feel confident about this topic. If you need more practice, do the additional problems from Chapter 1 of your *Organic Chemistry* supplement that are recommended later in this unit under the heading Suggested Supplementary Exercises.

Study Section 2-1 of your *Organic Chemistry* supplement, which deals with rates of reactions (kinetics) and the energy changes associated with chemical reactions (thermodynamics). Many of the terms discussed here may be familiar to you from other chemistry or physics courses. Be sure you can define **kinetic and potential energy, stability, enthalpy, endothermic** and **exothermic**, and **bond energy**. It may not be immediately obvious from this section that enthalpy is an energy term. It is the heat energy lost or gained in a process occurring at constant pressure. Chemists use the term **bond energy** for the amount of heat required to break a chemical bond at constant pressure. Strictly speaking, it should be called "bond enthalpy." Note that breaking a bond always requires energy (an endothermic process), while making one releases energy (an exothermic process).

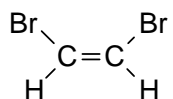
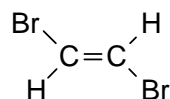
Bonding in Hydrocarbons

Hydrocarbons are compounds with just two elements: carbon and hydrogen. The only bonds they contain are single bonds between carbon and hydrogen, and single, double, or triple bonds between two carbon atoms. Carbon is unique because it can form multiple bonds and bond with many different atoms. Thus, organic chemistry is the only major field of chemistry devoted to the study of the compounds of a single element.

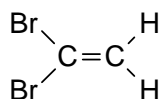
Alkanes are hydrocarbons with only single bonds between carbon atoms. **Alkenes** have carbon-carbon double bonds and **alkynes** have carbon-carbon triple bonds. Earlier, you saw a sigma (σ) bond formed from the head-on overlap of an sp^3 -hybridized orbital of carbon and the s orbital of hydrogen (from Figure 1-18 of your *Organic Chemistry* supplement and the hybridization section in Unit 3). In Figure 1-21 of your supplement, you saw how the double and triple bonds of alkenes and

alkynes are made up of pi (π) bonds as well as sigma bonds. Remember, pi bonds prevent the free rotation of atoms around multiple bonds because the overlap of the *p*-orbitals cannot be broken (see the ethene molecule in Figure 1-21 of the supplement). This restriction results in **cis-trans isomerism** or **stereoisomerism**. Stereoisomers have the same connectivity but differ in the *spatial orientation* of their atoms.

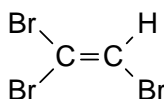
For example, the alkene *cis*-1,2-dibromoethene cannot be converted to *trans*-1,2-dibromoethene, and the two molecules are different compounds. If you make a model of each of these two compounds, you will be able to see that they are not identical. The term **cis** refers to two groups that are attached to each end of a carbon-carbon double bond and that are on the *same* side of the bond. The term **trans** refers to two groups attached to each end of a carbon-carbon double bond and that are on *opposite* sides of the double bond.

*cis*-1,2-dibromoethene*trans*-1,2-dibromoethene

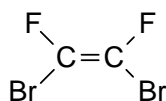
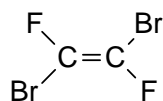
Note that 1,1-dibromoethene and 1,1,2-tribromoethene do not show *cis-trans* isomerism, but 1,2-dibromo-1,2-difluoroethene does.



1,1-dibromoethene



1,1,2-tribromoethene

*cis*-1,2-dibromo-1,2-difluoroethene*trans*-1,2-dibromo-1,2-difluoroethene

Study Sections 2-3, 2-4, and 11-2 of your *Organic Chemistry* supplement. Make sure you can define the following terms:

Hydrocarbon

Alkane

Alkene

Alkyne

Restricted rotation

Cis-trans isomerism

Stereoisomers

Aromatic hydrocarbons

Sigma bonds

Pi bonds

Homologs

Homologous series

Section 11-2 in your supplement describes the formation of sp^2 and sp hybrid orbitals in carbon atoms and of pi bonds in compounds with double and triple bonds. Let's summarize for you six important points about sigma and pi bonds:

- A sigma bond results from a maximum or head-on overlap of orbitals. The orbitals can be pure s or pure p orbitals or any hybridized combination. All of the following pairs of orbitals overlap to produce a sigma bond:

s and s

s and p

sp^3 and s

sp^3 and p

sp^3 and sp^3

sp^3 and sp^2

sp^3 and sp

sp^2 and s

sp^2 and p

sp^2 and sp^2

sp^2 and sp

sp and s

sp and p

sp and sp

- A pi bond is formed only by the sideways overlap of parallel-unhybridized p orbitals.
- A single bond is always a sigma bond.
- A double bond consists of one sigma and one pi bond, and a triple bond consists of one sigma and two pi bonds.
- A pi bond is never found between two atoms without a sigma bond also being present.
- Two sigma bonds cannot be formed between the same atoms.

After you have studied Sections 2-3, 2-4, and 11-2 in your *Organic Chemistry* supplement and reviewed the points just summarized, take out your model kit again. Many of the concepts you have just seen will become clearer to you after some more practice with molecular structures. First, build models of *ethene* and *ethyne*. The model kit directions explain how to construct sigma and pi bonds. Then try building models of some of the simple examples of molecules containing a functional group, as shown in Table 2-3 in your organic supplement.

Do Exercise 2-16 in the supplement and the following Example Problems in this unit. Answers to *Unit 4 Example Problems* can be found at the very end of this unit.

Example Problem 1

Which of the following alkenes can exist as cis-trans isomers? Write their structures.

- $\text{CH}_2=\text{CHCH}_3$
- $\text{CH}_3\text{CH}=\text{CHCH}_2\text{CH}_3$
- $(\text{CH}_3\text{CH}_2)_2\text{C}=\text{CH}_2$

Example Problem 2

Write structural formulas for all of the alkenes with the formula $\text{C}_2\text{I}_2\text{Br}_2$ and indicate which compounds are cis-trans isomers of each other.

Functional Groups

We mentioned earlier that carbon is unique because it can form multiple bonds and bond with many different atoms. You have just seen how some of these bonds are formed and how they influence a compound's structure.

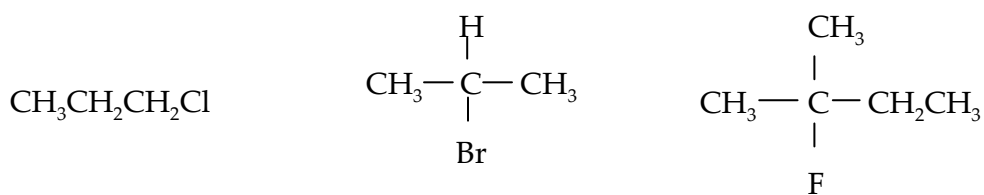
Certain parts of an organic molecule are more chemically reactive than others and are called functional groups. In general, a **functional group** is any part of an organic compound that is not a carbon-carbon single bond or a carbon-hydrogen single bond. Thus alkanes, which have only carbon-carbon and carbon-hydrogen single bonds, have no functional group.

Because compounds with the same functional group have similar properties and undergo similar reactions, they are placed in the same family and are studied together.

To help you remember the different families of organic compounds, make your own chart of functional groups. You can pattern it after the one in Table 2-3 in your *Organic Chemistry* supplement. At this stage, fill in only the family name, the functional group, and the general formula. Don't worry about specific examples and their IUPAC (pronounced I-u-pack; from International Union of Pure and Applied Chemistry) and common names. Use coloured pens and fill your chart with underlining, arrows, or anything that will personalize it and help you remember what it contains. Some people find it useful to go over their chart the last thing at night. Others like to pin it up where they can see it all day. Try different methods until you find the one that works for you. Just like learning a new language, repetition and practice are key. Remember that it is crucial to understand what you are trying to memorize: be sure you study carefully your supplement's section on each family.

Read Sections 8-1 and 8-2 (alcohols). The idea in reading these sections is not to study them intensively at this time. You just want to become familiar with what the structures of the various functional groups are, some of the terminology associated with them, and some of their properties (e.g., the hydrogen bonding of alcohols).

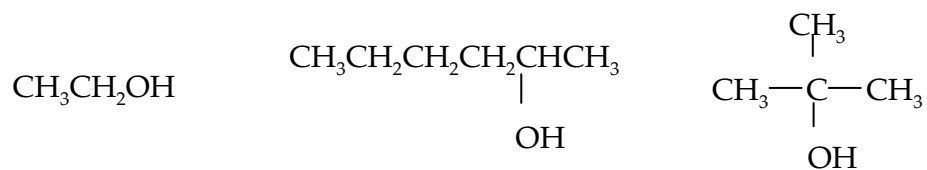
Alkyl halides and alcohols can be classified as primary, secondary, or tertiary (1° , 2° , or 3°), depending on whether one, two, or three carbons are attached to the carbon atom carrying the halogen atom or the hydroxyl ($-\text{OH}$) group. Compounds with only one carbon atom do not fit this classification neatly, but they are usually considered to be primary. Amines are also considered primary, secondary, or tertiary, but this depends on whether one, two, or three organic groups are attached to the *nitrogen atom*. Note the following examples:



a primary
alkyl chloride

a secondary
alkyl bromide

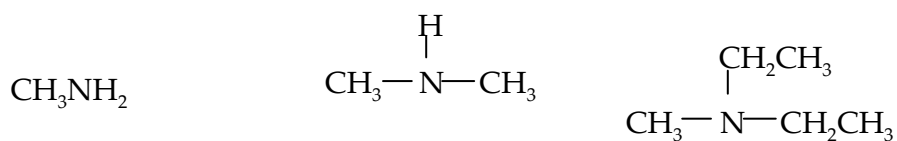
a tertiary
alkyl fluoride



a primary alcohol

a secondary alcohol

a tertiary alcohol



a primary amine

a secondary amine

a tertiary amine

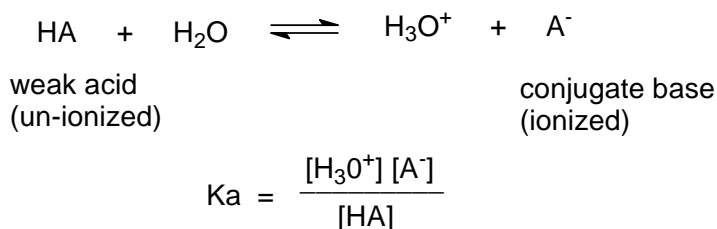
Work on Problems 32 and 45 at the end of Chapter 2 in your *Organic Chemistry* supplement.

Acid-Base Theory

In previous chemistry courses, you may have performed many pH calculations, preparations of buffers, titration curves, and so on. You are not expected to do all of these things in this course. For now, it is enough that you can define the various terms referring to acids and bases. This topic is important because acid-base reactions are quite common among organic compounds. You must have some idea of how they occur in order to appreciate reaction mechanisms that you will see later on.

Study Section 2-2 of your *Organic Chemistry* supplement. Make sure that you can define such terms as **conjugate acid** and **conjugate base**, **acidity constant**, **electron-pair acceptor**, **electron-pair donor**, pK_a , pK_b , and pH.

Now work through the following example so that you see why the pH of a half-ionized weak acid equals its pK_a value.



At the half-ionized point, $[\text{HA}] = [\text{A}^-]$. Therefore, $K_a = [\text{H}_3\text{O}^+]$ and $pK_a = \text{pH}$. Put another way, at the mid-neutralization point of a weak acid, the pH will equal the pK_a of the acid.

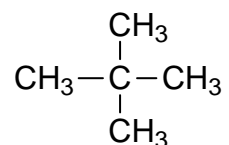
Do Exercises 2-8 and 2-10 and Problem 29 from Chapter 2 of your *Organic Chemistry* supplement. Make sure that you use the curved arrow notation to show the direction of the electron-pair flow. This is important because we will use curved arrows to discuss mechanisms later and so you will need to be familiar with them.

Physical Properties and Molecular Structure

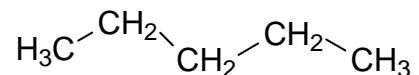
Physical properties of compounds can be measured or observed without changing the compounds' chemical composition. Melting point, boiling point, vapour pressure, smell, colour, viscosity, shape, refractive index, density, and solubility—all of these are examples of physical properties that you will come across, especially in your laboratory course. Some of them, such as melting and boiling points and

solubility, can be explained on the basis of molecular structure and the intermolecular attractive forces among molecules.

As we saw earlier in this unit, ion-ion forces, hydrogen bonds, and van der Waals forces keep molecules together, thereby preventing them from melting or boiling at lower temperatures. Molecular structure affects the boiling point, even when hydrogen bonds are not involved. Continuous-chain molecules can get closer to each other than branched-chain molecules with the same molecular formula. This makes the van der Waals forces between them more efficient. Because more energy is required to overcome these intermolecular attractions, continuous-chain molecules boil at higher temperatures. For example, the C_5H_{12} branched alkane with the structure



has a boiling point of 9.5°C , while its continuous chain counterpart



boils at 36°C .

Most physical properties can be measured, but two can only be observed. These are *smell* and *taste*. Do not taste any chemicals in the laboratory and be sure to carefully follow your lab instructor's guidelines for smelling them safely! But think for a moment about the organic chemicals you smell and taste in everyday life. Millions of dollars are spent annually to develop new fragrances and flavours, and we are constantly bombarded with commercials for new perfumes, outdoor-scented detergents, and artificial sweeteners. Throughout the remainder of this course, we will call your attention to tastes and smells. Unfortunately, we cannot include samples for you to smell. "Scratch'n Sniff" strips would be wonderful for a distance-learning chemistry course, but they wouldn't be very economical!

An organic chemist's nose can be a valuable tool. Unfortunately, not all organic chemicals are pleasing. Some of them give off truly repulsive smells. A famous example is the smell of skunk, produced by a mixture of the two simple organic sulphur compounds shown in Figure 4.2b in this unit. Various reference books call this odour nauseous, evil, and truly appalling. Perhaps it's just as well that we cannot send "smellies" to you in your course package!

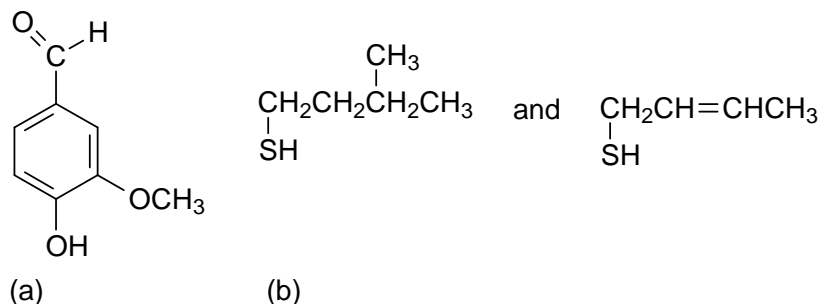


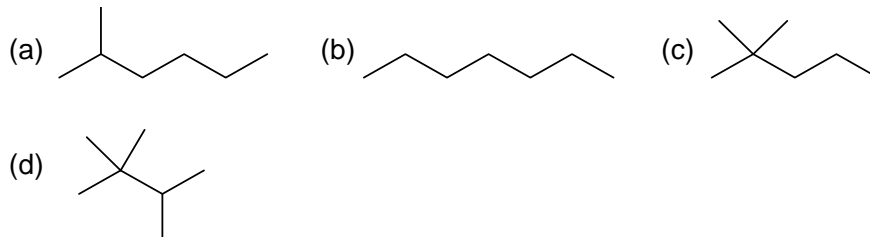
Figure 4.2: Structural formulas of vanillin, 3-methyl-1-butanethiol, and 2-butene-1-thiol

1. Vanillin, found in vanilla beans
2. 3-methyl-1-butanethiol and 2-butene-1-thiol, the major components of skunk juice

Sections 2-6 and 8-2 of your *Organic Chemistry* supplement review material presented earlier in this unit. Study these concepts carefully. Make sure you understand and can define such terms as **permanent dipole moment**, **hydrogen bonding**, **van der Waals forces**, **polarizability**, **hydrophobic**, and **hydrophilic**. You do not have to memorize the data in Table 8-1 of your supplement, but you should be able to explain why certain compounds are water-soluble or have higher melting and boiling points than other compounds.

Example Problem 3

Rank the following structural isomers in order of increasing boiling point:



And so we come to the end of Unit 4. Turn now to Practice Exercise 4 and follow the directions given there. Organic chemistry continues in Unit 5!

Self-Assessment

Having reached the end of this unit, you should be able to:

- Describe the differences between the liquid and the solid state.
- Explain the terms surface tension, capillary action, meniscus, and viscosity.
- Describe different intermolecular attractions, including the hydrogen bond.
- Discuss the anomalous properties of water.
- Predict the order of melting points between various compounds based on their intermolecular forces.
- Explain different concepts of bonding in organic molecules, including formal charge, hybridization, and multiple bonding.
- Draw Lewis structures and condensed, bond-line, three-dimensional, and dash structural formulas.
- Identify compounds where resonance occurs and draw resonance contributors and hybrids.
- Predict shapes of simple molecules and molecular polarity.
- Identify and name various functional groups.
- Explain how the Brønsted-Lowry and Lewis acid-base theories differ from each other.
- Explain the relationship between intermolecular attractions and the physical properties of organic molecules.
- Using your model kit, build three-dimensional models of simple organic molecules from two-dimensional diagrams and demonstrate isomerism and free rotation.

Practice Exercise 4

Finish working through Unit 4 before starting this practice exercise which is found listed under the Practice Exercises section of course. The solutions to these problems will be provided once you have completed this practice exercise.

You may first want to try some of the supplementary exercises suggested under the next heading. However, if you feel that you have a reasonable understanding of the material, you can start the practice exercise immediately. If you have no difficulties with this practice exercise, begin Assignment 4. If you feel that you need more practice, go to the "Suggested Supplementary Exercises" that follow.

You should make a serious attempt to solve the practice exercise problems by yourself, using as a guide similar examples given in the textbook, the *Organic Chemistry* supplement, and in this unit. If your attempt is serious, you will learn a lot more from the worked solutions.

Suggested Supplementary Exercises

At the end of each chapter in your textbook and your *Organic Chemistry* supplement are further exercises on the material covered. We suggest that you do as many of these exercises as necessary. Doing such problems helps you understand and apply the principles involved from Chapter 11 and the concepts discussed. Fully worked solutions for all even-numbered problems are given in the *Student Solutions Manual* by B. J. Cruickshank and Raymond Chang. Some of the even-numbered exercises at the end of this chapter have their answers in the back of the textbook. If you decide to try the odd-numbered problems and need help, consult your Open Learning Faculty Member.

Important: You should make a serious attempt to solve a problem by yourself before looking at a worked solution.

From Chapter 11 of your textbook:

11.8, 11.10, 11.12, 11.14, 11.16, 11.18, 11.22, 11.28, 11.32, 11.108, 11.112

From Chapter 1 of your *Organic Chemistry* supplement:

25-29, 38-42, 44-46, and 50

From Chapter 2 of your *Organic Chemistry* supplement:

27, 29, 32, 38 (draw the structures only, do not try to name the compounds), and 40 (identify the primary, secondary, and tertiary groups, do not try to name the compounds)

Assignment 4

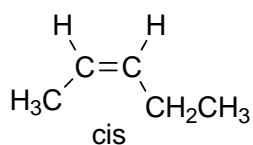
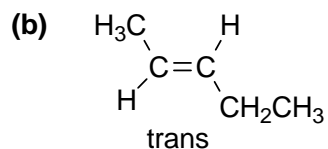
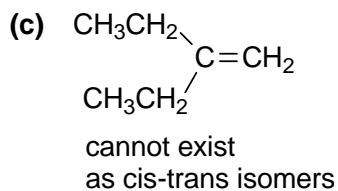
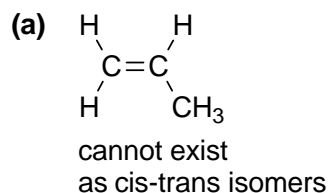
Now refer to your *Assignments* and complete Assignment 4. Consult your Course Guide for the week this assignment is due.

You may send the assignment to your Open Learning Faculty Member using the assignment tool in Blackboard or by mail with a Marked Assignment Form.

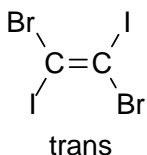
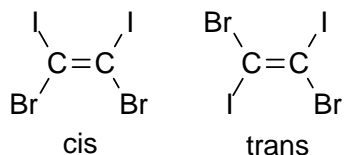
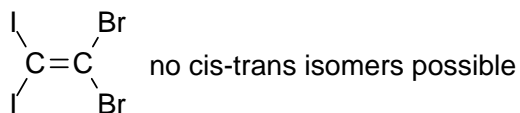
Be sure to keep a copy of the assignment—it will be useful if you wish to discuss your work with your Open Learning Faculty Member.

Answers to Unit 4 Example Problems

1.



2.



3. Increasing boiling point: (d)<(c)<(a)<(b).

Note that all compounds have the same molecular formula, but (d) is the most branched alkane and (b) is the least branched.