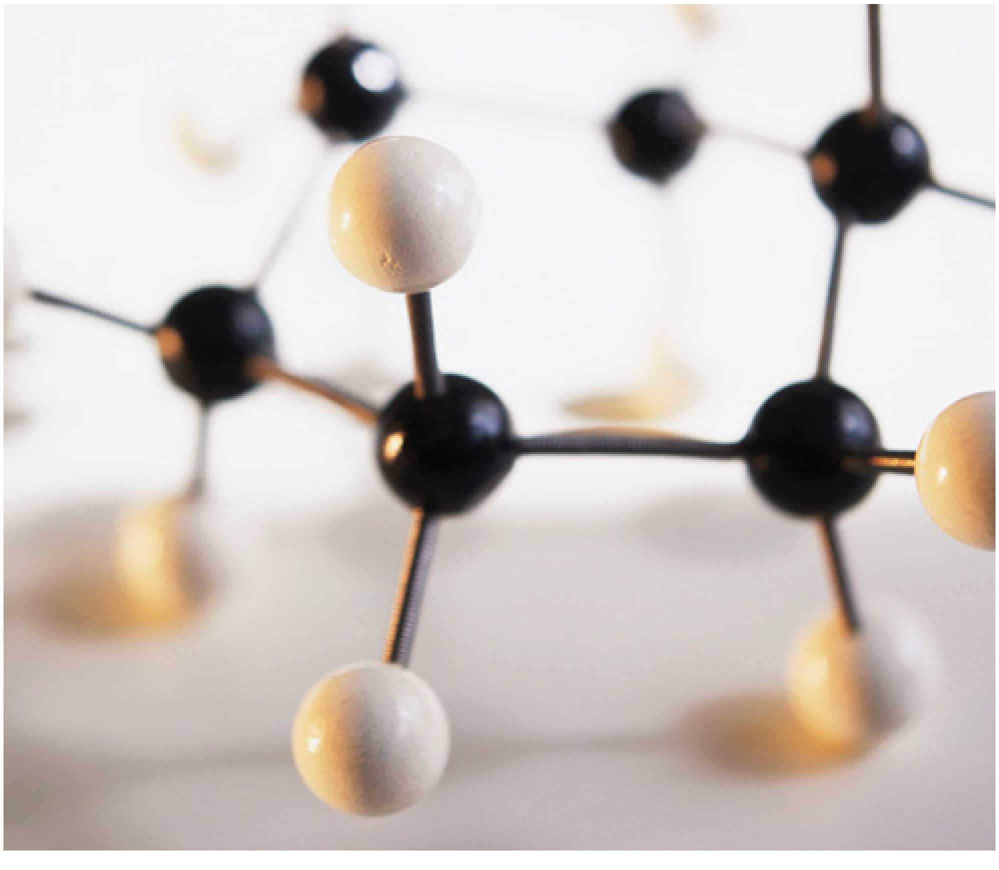
Grossmont College
Chemistry 116
Laboratory Manual



3.1 Edition

Grossmont College
Periodic Table of the Elements

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**
	1A	**2A**											**3A**	**4A**	**5A**	**6A**	**7A**	**8A**
1	**1** H 1.008																	**2** He 4.003
2	**3** Li 6.941	**4** Be 9.012											**5** B 10.811	**6** C 12.011	**7** N 14.007	**8** O 15.999	**9** F 18.998	**10** Ne 20.180
3	**11** Na 22.990	**12** Mg 24.305	**3B**	**4B**	**5B**	**6B**	**7B**	**8B**	**8B**	**8B**	**1B**	**2B**	**13** Al 26.982	**14** Si 28.086	**15** P 30.974	**16** S 32.066	**17** Cl 35.453	**18** Ar 39.948
4	**19** K 39.098	**20** Ca 40.078	**21** Sc 44.956	**22** Ti 47.880	**23** V 50.942	**24** Cr 51.996	**25** Mn 54.938	**26** Fe 55.845	**27** Co 58.933	**28** Ni 58.693	**29** Cu 63.546	**30** Zn 65.410	**31** Ga 69.723	**32** Ge 72.640	**33** As 74.922	**34** Se 78.960	**35** Br 79.904	**36** Kr 83.800
5	**37** Rb 85.468	**38** Sr 87.62	**39** Y 88.906	**40** Zr 91.224	**41** Nb 92.906	**42** Mo 95.95	**43** Tc (98)	**44** Ru 101.07	**45** Rh 102.906	**46** Pd 106.42	**47** Ag 107.868	**48** Cd 112.411	**49** In 114.818	**50** Sn 118.710	**51** Sb 121.760	**52** Te 127.60	**53** I 126.905	**54** Xe 131.29
6	**55** Cs 132.905	**56** Ba 137.327	**57** La 138.906	**72** Hf 178.49	**73** Ta 180.948	**74** W 183.84	**75** Re 186.207	**76** Os 190.23	**77** Ir 192.22	**78** Pt 195.08	**79** Au 196.967	**80** Hg 200.59	**81** Tl 204.38	**82** Pb 207.2	**83** Bi 208.980	**84** Po (209)	**85** At (210)	**86** Rn (222)
7	**87** Fr (223)	**88** Ra (226)	**89** Ac (227)	**104** Rf (261)	**105** Db (262)	**106** Sg (266)	**107** Bh (264)	**108** Hs (269)	**109** Mt (268)	**110** Ds (281)	**111** Rg (272)	**112** Cn (285)	**113** Uut (284)	**114** Uuq (289)	**115** Uup (288)	**116** Uuh (293)	**117** Uus (294)	**118** Uuo (294)

6	**58** Ce 140.115	**59** Pr 140.908	**60** Nd 144.24	**61** Pm (145)	**62** Sm 150.36	**63** Eu 151.965	**64** Gd 157.25	**65** Tb 158.925	**66** Dy 162.50	**67** Ho 164.930	**68** Er 167.26	**69** Tm 168.934	**70** Yb 173.04	**71** Lu 174.967
7	**90** Th 232.038	**91** Pa 231.036	**92** U 238.029	**93** Np (237)	**94** Pu (244)	**95** Am (243)	**96** Cm (247)	**97** Bk (247)	**98** Cf (251)	**99** Es (252)	**100** Fm (257)	**101** Md (258)	**102** No (259)	**103** Lr (262)

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Chemistry 116 Laboratory Manual

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EXPERIMENT 1

Molecular Models of Organic Molecules

Objectives

1. To become familiar with the three-dimensional aspects of molecular structure.
2. To examine the relationship between molecular models and structural formulas.

Introduction

Much of the chemical and biological behavior of molecules is determined by their molecular shape. Organic molecules are three-dimensional. Many people have difficulty visualizing two-dimensional diagrams on paper as three dimensional. The following experiments are designed to help the student of chemistry overcome these problems.

Molecular models are used by practicing chemists at all levels. From the shape of the molecules, the chemist can often see important molecular features that might otherwise escape his or her attention. For example, propane (C_3H_8) looks rather ordinary as a structural formula; but, in three dimensions one can easily see a rich structure even in such a simple molecule. Although the three dimensional structure conveys a lot of information, it is difficult to draw. Chemists must rely on simpler ways to show structures, and structural formulas are often all that are used. We need to fully appreciate the structural details that are understood in the structural formulas. This laboratory exercise is designed to better acquaint you with the relationship of the two dimensional drawings with the three dimensional world of real molecules.

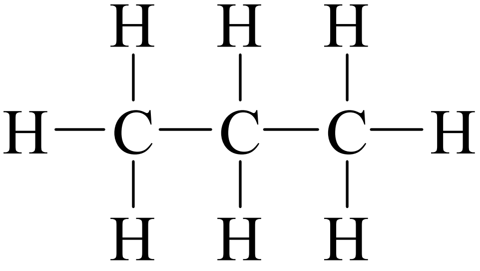
We use several types of drawings to illustrate the structure of molecules. They are as follows.

Chemical formula - A description of the number and types of atoms present in a molecule.

EXAMPLE 1.1 **Propane is C_3H_8.**

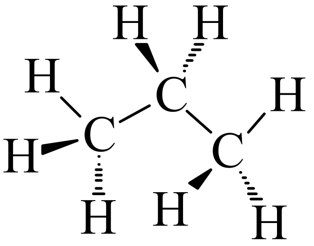
Structural formula - A representation of a structure that emphasizes the bond connection between atoms.

EXAMPLE 1.2



Perspective formula - A representation of a chemical structure that conveys the three dimensional nature of a compound. Solid wedges represent bonds sticking out of the plane of the paper, dashed wedges represent bonds behind the plane of the paper, and straight lines represent bonds in the plane of the paper.

EXAMPLE 1.3

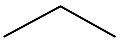


Condensed formula - A condensed representation of a chemical structure that leaves out the vertical bonds and shows the most of structure on one line.

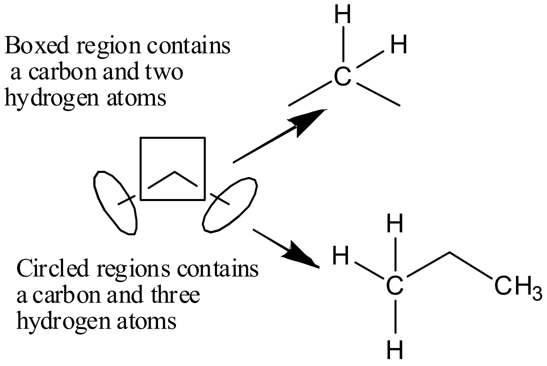
EXAMPLE 1.4 CH_3-CH_2-CH_3 or $CH_3CH_2CH_3$

Line formula - A simplified representation of a structural formula in which only the bonds are drawn. Carbons are located at the junctions of bonds and hydrogens fill all vacant bonding positions.

EXAMPLE 1.5



Line Structure



Boxed region contains a carbon and two hydrogen atoms

Circled regions contains a carbon and three hydrogen atoms

In this laboratory exercise we will build a number of different molecules and draw a variety of different types of formulas for them.

Date Sheet: Organic Molecular Models

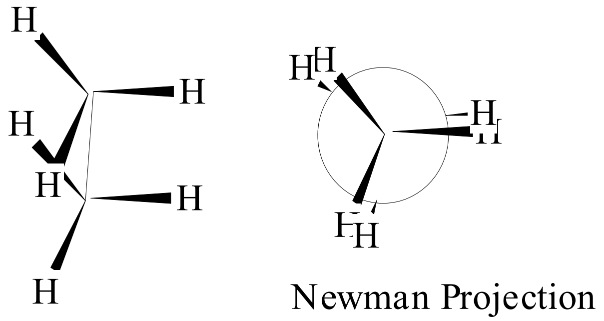
Name: ____ Section: ___________________

Build a model of ethane, C_2H_6, and look at it carefully.

Can you make different conformations of the molecule by twisting any of the bonds? _____

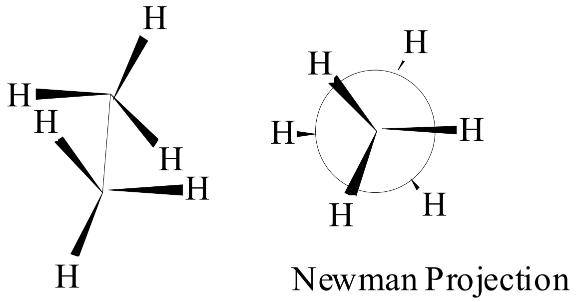
Make the conformation with the hydrogens lined up. This is known as the **eclipsed conformation** and may be represented by a Newman projection as shown below:

FIGURE 1.1



Make the confirmation with the hydrogens as far apart as possible. This is known as the **staggered confirmation** and may represented by a Newman projection as shown below:

FIGURE 1.2



Which of the two conformations of ethane do you think is the most stable?

Replace one of the Hydrogens on each carbon of ethane with a -CH_3. You have now made butane. Rotate around the central C-C bond, and observe the different conformations that are possible.

Draw Newman structures for each of the possible eclipsed and staggered confirmations.

TABLE 1.6

A.	B.	C.	D.	E.	F.

Draw the most stable configuration.

Draw the least stable configuration.

There are at least two structures that are identical to each other. Draw them and explain why they are the same.

Nomenclature

Organic compounds, even the most complex structures, are formally named from simpler pieces. The concept of the alkyl group is very useful in naming organic compounds. Detailed rules are found in your text; however, they can be summarized as:

1. Find the longest continuous chain as you parent hydrocarbon.
2. Identify (with a position number and name) all of the groups attached to the main chain.
3. If two or more names seem possible, the correct name will be that which uses the longest chain for the parent hydrocarbon and whose alkyl groups total the lowest possible position numbers.

Isomers

Isomers are compounds having the same molecular composition (number of atoms), but different arrangements of these atoms. Isomers are really different compounds. They have different solubilities, melting points, boiling points, etc.

With your model of butane rearrange the atoms to make the other isomer of butane. The table below should help you. Fill in the missing information.

TABLE 1.7

Name	Chemical Formula	Structural Formula	Condensed Formula	Line Formula
Butane				
Isobutane or 2-methylpropane				

Make a model of hexane, C_6H_{14}.

How many different isomers of this compound can you make? _____

Fill in the chart on the next page with the 5 isomers of hexane. (See “Nomenclature” on page 5 for nomenclature tips.) Look up the boiling points of each of the isomers in CRC and record them in the table.

TABLE 1.8

IUPAC Name	Condensed Formula	Line Formula	Boiling Point (°C)

The **intermolecular forces** that hold hydrocarbons together are very weak, and require that molecules can interact with one another. The closer they can pack, the stronger the attractive forces. Working with your neighbors stack together several of each isomer.

Which ones fit best? ______________________

We expect that the better stacking models will have stronger intermolecular forces and thus higher boiling points.

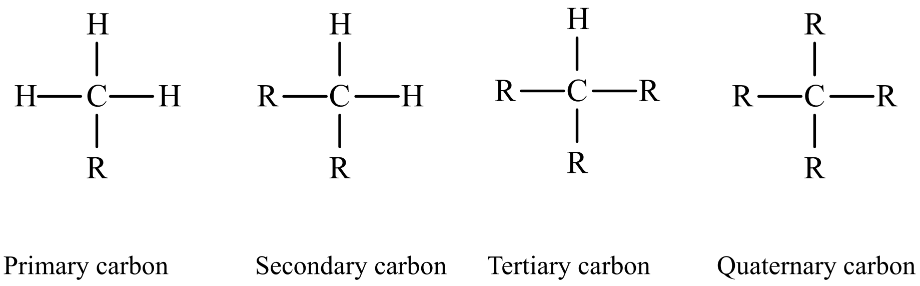
On the basis of your models, which isomer should have the highest boiling point? ______________

Which isomer should have the lowest boiling point? _____________________

Primary, Secondary, and Tertiary Carbons

Carbon atoms may be classified as one of four types depending on the substitution pattern they exhibit. Each type is shown below with its corresponding substitution pattern:

FIGURE 1.3



1° Carbons: Primary carbons have three hydrogen atoms and one other R group attached to the central carbon atom.

2° Carbons: Secondary carbons have two hydrogens and two R groups attached to the central carbon atom.

3° Carbons: Tertiary carbons have only one hydrogen and three R groups attached to the central carbon atom.

4° Carbons: Quaternary carbons have four R groups and no hydrogens attached to the central carbon atom.

R represents any alkyl group.

In Table 1.8 on page 6 put a circle around all primary carbons in red, circle secondary carbons in blue, circle tertiary carbons in green, and circle quaternary carbons in yellow.

Alkyl Groups

The group of atoms that results when a hydrogen atom is removed from an alkane is called an **alkyl group**. The group is named by replacing the -ane suffix of the parent hydrocarbon with -yl. It is important to note that alkyl groups are not independent molecules. Rather, they exist as parts of molecules. Next we will look at the kinds of alkyl groups that can be made from some alkanes.

Make methane and ethane.

How many ways can you remove one hydrogen from each of these molecules to make an alkyl

group? _____

TABLE 1.9 **Draw <u>condensed formulas</u> for the two alkyl groups that are formed.**

Methyl group	
Ethyl group	

Make propane.

How many different ways can you remove a hydrogen from propane? _____

There are two possible propyl groups, they are normal (n-)propyl and iso(i-)propyl.

TABLE 1.10 **Draw <u>condensed formulas</u> for the two isomers and draw them.**

propyl group	
isopropyl group	

Make the two isomers of butane. Identify the alkyl groups that may be derived from these molecules. Use the form R-Cl, where R is the parent chain.

TABLE 1.11 **Draw <u>condensed formulas</u> for these alkyl group.**

n-butyl group	
sec-butyl group	
isobutyl group	
tert-butyl group	

Substituted Alkanes

Make the model of butane again. Remove one hydrogen and substitute a chlorine atom (green).

How many different monosubstituted butanes can you make by substituting different hydrogens for the chlorine atom?__________

Draw condensed formulas for each of these monochlorobutanes below:

Now remove a second hydrogen and replace with a second green chlorine atom.

How many different dichlorobutanes can you make?__________

Draw condensed formulas for each of these molecules in the box below:

Unsaturated Molecules

Alkenes and alkynes are hydrocarbons that have more than a single bond between carbon atoms. **Alkenes** are characterized by double bonds and **alkynes** by triple bonds.

Cis and trans isomers

The ***cis* isomers** have the similar substituents on the same side of the alkene, while the ***trans* isomers** have these groups on opposite sides. As a result of restricted rotation, the *cis* and *trans* isomers do not interconvert.

FIGURE 1.4

More nomenclature

For alkenes the parent hydrocarbon is the longest carbon chain containing the double bond.

The position of the double bond is given by the smaller of the two numbers containing the carbon atoms of the double bond. Cis and trans nomenclature is provided as needed.

Make models of ethene (ethylene) and ethyne (acetylene). (You will use the springs for multiple bonds.) Note the planar nature of these two molecules.

Is there any rotation around the C-C double bond? _____

Replace two of the hydrogen atoms of ethene with methyl groups.

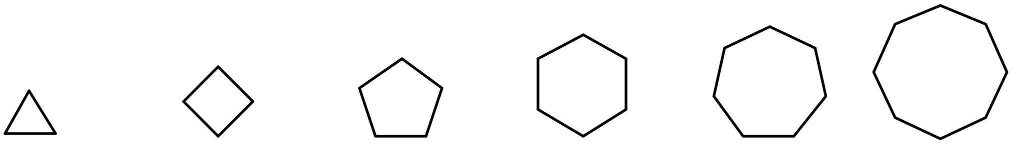
How many different structures can you make? _____

Draw and them in the space below.

Cyclic Compounds

The **cycloalkanes** are hydrocarbons having the general formula, C_nH_{2n}. It is a simple matter to draw all of the ring hydrocarbons as the corresponding geometric figure. It is, of course assume that all of the carbons have hydrogen atoms to fulfill the requirement for every carbon having four bonds. Some of the more common cycloalkanes are represented below:

FIGURE 1.5



cyclopropane cyclobutane cyclopentane cyclohexane cycloheptane cyclooctane

If we assume the rings to be planar, we see that the internal ring angles vary: 60° for cyclopropane, 90° for cyclobutane, 108° for cyclopentane, 120° for cyclohexane, and the bond angles continue to increase as the ring size increases. The stability of the rings seems to correlate with its ability to attain bond angles of 109°. Cyclopropane, which cannot achieve this, is very unstable. Cyclopentane with bond angles of 108° should be the most stable. Cyclohexane however has the ability to bend into a configuration which gives 109° bond angles to all carbons and thus is the most stable compound.

Make models of 3, 4, 5, and 6 carbon rings and study them.

Nomenclature of ring compounds

These are named with the ring as the parent. Other groups are named and numbered so that the total number is as small as possible.

Post Lab Questions

1. What is an alkyl group?

2. How is a primary carbon identified?

3. What is meant by a structural formula?

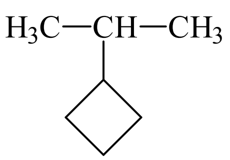
4. Why don't *cis* and *trans* isomers of alkanes exist?

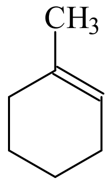
5. How many isomers can you make of C_5H_{12}? __________ Draw and name them.

6. Draw all of the monobromo products of n-propane.

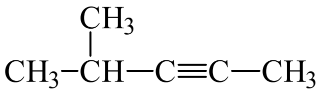
7. Why do alkenes have geometric isomers and alkynes do not?

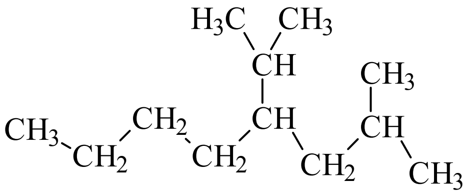
8. Give the names for each of the following compounds:

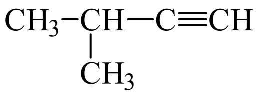
a.


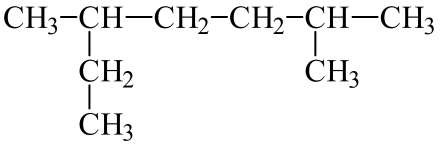
b.


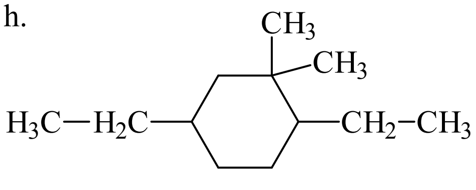
c. $CH_3-CH_2-CH_2-CH=CH_2$

d.

$CH_3-\overset{\substack{CH_3\\|}}{C}H-C\equiv C-CH_3$

e.


f.

$CH_3-\underset{\substack{|\\CH_3}}{C}H-C\equiv CH$

g.

$CH_3-\underset{\substack{|\\CH_2\\|\\CH_3}}{C}H-CH_2-CH_2-\underset{\substack{|\\CH_3}}{C}H-CH_3$

h.


a. ________________________________ e. ________________________________

b. ________________________________ f. ________________________________

c. ________________________________ g. ________________________________

d. ________________________________ h. ________________________________

EXPERIMENT 2

Properties of Hydrocarbons

Objectives

1. To examine the physical characteristics of hydrocarbons.
2. To become familiar with reactions which are characteristic of each of the four principal types of hydrocarbons.
3. To learn to synthesize acetylene.

Introduction

Hydrocarbons are organic compounds which contain only carbon and hydrogen. All organic compounds contain carbon and hydrogen, but many also contain oxygen, nitrogen and other elements. Most organic compounds can be considered to be derivatives of hydrocarbons. The substitution of an organic functional group for a hydrogen atom in a hydrocarbon will produce a compound of that functional class. In this experiment, both aliphatic and aromatic hydrocarbons will be examined. The ***aliphatic* hydrocarbons** contain either straight chains, branched chains and/or certain cyclic arrangements of carbon atoms. The ***aromatic* hydrocarbons** contain at least one aromatic ring, most commonly the benzene ring.

Aliphatic hydrocarbons are divided into three classes: **alkanes**-saturated hydrocarbons which contain only carbon-carbon single bonds; **alkenes**-unsaturated hydrocarbons containing at least one carbon-carbon double bond; and **alkynes**-unsaturated hydrocarbons which contain at least one carbon-carbon triple bond.

Reactions of Hydrocarbons

In today's experiment you will use specific chemical reactions and other simple tests to distinguish between alkanes, alkenes, alkynes, and aromatics.

TABLE 2.1

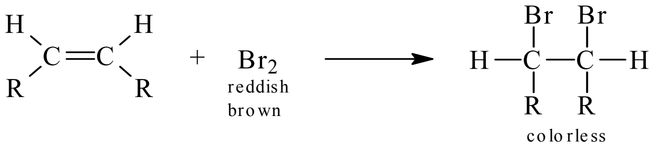
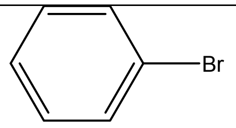
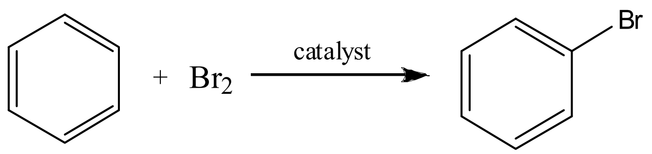
Reaction with Bromine - reaction detected by the disappearance of reddish brown bromine, Br_2	
Alkanes	$R{-}CH_3 + \underset{\text{reddish brown}}{Br_2} \xrightarrow{\text{sunlight}} \underset{\text{colorless}}{R{-}CH_2{-}Br} + HBr$ **(EQ 2.1)**
Alkenes (and Alkynes)	 **(EQ 2.2)**
Aromatics 	**(EQ 2.3)** 

TABLE 2.2

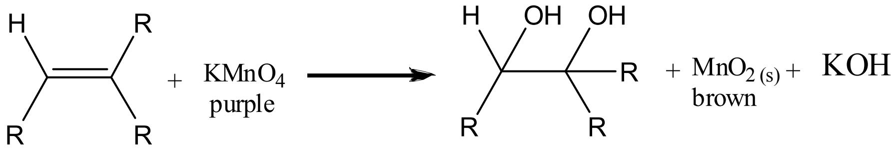
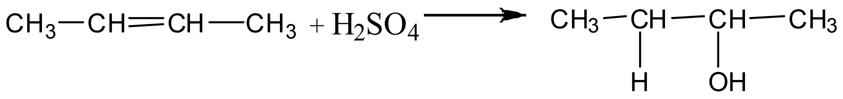
Reaction with Potassium Permanganate - reaction detected by disappearance of purple potassium permangagne, KMnO4 and the formation of brown manganese dioxide MnO2.	
Alkanes	$R{-}CH_3 + KMnO_4 \longrightarrow$ no reaction **(EQ 2.4)**
Alkenes (and Alkynes)	**(EQ 2.5)** 
Aromatics	No reaction

TABLE 2.3

Reaction with Concentrated Sulfuric acid - reaction detected by the evolution of heat and dissolution of organic layer.	
Alkanes	No reaction
Alkenes (and Alkynes)	Unsaturated hydrocarbons react with cold H_2SO_4 by an addition reaction to give alkyl sulfuric acids which dissolve in sulfuric acid. **(EQ 2.6)**  $CH_3{-}CH{=}CH{-}CH_3 + H_2SO_4 \longrightarrow CH_3{-}\underset{H}{CH}{-}\underset{OH}{CH}{-}CH_3$

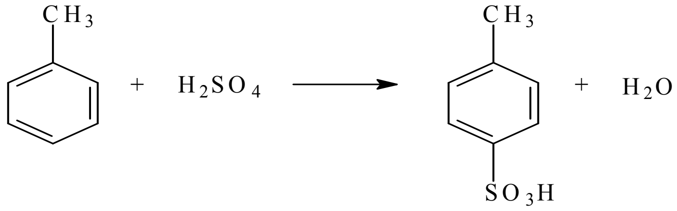
Aromatics	Some activated aromatic hydrocarbons will react slowly with H_2SO_4 by the substitution reaction below:  **(EQ 2.7)**

TABLE 2.4

Reaction with Oxygen (Combustion) - all hydrocarbons react with oxygen to produce carbon dioxide and water. Generally the degree of unsaturation determines the type of flame produced.	
Alkanes	Burn cleanly, producing little or no smoke or soot. The combustion of an alkane produces considerable heat energy thus making excellent fuels.
Alkenes (and Alkynes)	Burn with a luminous yellow flame and produce some smoke and soot. The combustion of an alkene produces slightly less heat energy than the same mass of the corresponding alkane. By general inspection alkenes and alkynes can not be distinguished.
Aromatics	Burn to produce substantial smoke and soot. This is one way to distinguish aromatic compounds from alkanes.

Physical Properties of Hydrocarbons

Alkanes with 1 to 4 carbon atoms are colorless, nearly odorless gases. Alkanes with 5 to 16 carbon atoms are colorless liquids that are less dense than water. Alkanes with 17 or more carbon atoms are waxy, colorless solids.

Alkanes are nonpolar and are not soluble in polar solvents like water. They are very soluble in non-polar solvents.

Alkenes and alkynes have physical properties very similar to those of alkanes.

Experimental Design

A. Combustion

1. Obtain about 1 mL (no more) of heptane in an evaporating dish and start it burning by carefully bringing a lighted match or splint to it.
2. Repeat with equally small volumes of cyclohexene, toluene, and your unknown.
3. Note the amount of smoke and soot.

B. Reaction with Bromine

Caution! Safety Notes:

Dispense bromine solution in the hood, and be especially careful not to spill bromine on your hands.

1. Take three clean, **dry** test tubes.
2. Place about 1 mL of heptane in the first tube, 1mL of cyclohexene in the second, and 1 mL of toluene in the third.
3. Add 3 drops of 5% bromine in acetic acid solution to each sample; stopper the tubes and note the results.
4. Any tube that still shows bromine color after 1 minute should be exposed to sunlight or to a strong electric light for and additional 2 minutes.
5. Perform the same test on your unknown.
6. Containers will be provided for you to dispose of these organic compounds. **DO NOT** pour them down the drain.

C. Reaction with Potassium Permanganate

1. Add 2 drops of KMnO4 solution to about 1mL each of heptane, cyclohexene, toluene and your unknown in test tubes.
2. Mix and note the results.

D. Reaction with Sulfuric Acid

1. Add 2 drops of sulfuric acid, H_2SO_4, solution to about 1 mL each of heptane, cyclohexene, toluene and your unknown in test tubes.
2. Mix and note the results. Does the test tube get warm?

E. Solubility Tests

1. Test the solubility of heptane, cyclohexene, toluene and your unknown in water by adding 1mL (or less) of each hydrocarbon to about 2 mL portions of water.
2. Shake each mixture for a few seconds and note whether they are soluble. For any that are not soluble note the relative density of the hydrocarbon with respect to water.
3. Repeat the test using ligroin in place of water. Ligroin, also known as light naphtha, is a product of the distillation of petroleum which boils between 60 °C and 100 °C and contains hydrocarbon chains of 5-6 carbons.

F. Synthesis of Acetylene

1. Place a small piece (the size of a pea) of calcium carbide, CaC_2, a 20 or 25 cm test tube and add 10 drops of water.
2. After about 30 seconds, thrust a burning splint into the test tube. Record your observations.
3. To confirm by a second method that acetylene is formed in the reaction of water and calcium carbide and that it is unsaturated, prepare a filter-paper stick by folding a piece of filter paper over until it is a stick 5 to 7 cm long and 6 mm wide.
4. Then clean and dry a large test tube and drop in another piece of calcium carbide.
5. Place a *tiny* drop of potassium permanganate on the end of the filter paper stick.
6. Add 10 drops of water to the calcium carbide in the test tube, and put your hand lightly over the test tube to concentrate the acetylene.
7. Now quickly thrust the filter-paper stick into the test tube *without letting it touch the liquid*, and observe what happens to the purple color of the permanganate. Allow 2 or 3 minutes for the reaction to occur.

Prelaboratory Exercises: Hydrocarbons

Name: ____ Section: __________________

1. Name the four types of hydrocarbons and give one example of each type.

2. What solvent should a hydrocarbon dissolve in, a nonpolar or a polar solvent? Justify your answer with an explanation.

3. Write an equation for the reaction of methane with bromine

4. Write the equation for the reaction of ethylene with bromine.

5. What is the evidence for the reaction of potassium permanganate with alkenes?

6. Can the combustion test be used to distinguish between and alkene and an alkyne? Explain your answer.

7. How do we dispose of any organic chemicals we use in the laboratory?

Lab Report: Hydrocarbons

Name: ____ Section: __________________

A. Combustion

TABLE 2.5

Compound	Observation
Heptane	
Cyclohexene	
Toluene	
Unknown	

B, C and D. Reactivities

Unknown Letter _____

TABLE 2.6

Compound	Reaction with Bromine		Reaction with $KMnO_4$	Reaction with H_2SO_4
	room light	bright light	▨	▨
Heptane				
Cyclohexene				
Toluene				
Unknown				

E. Solubilities

TABLE 2.7

	Water	Ligroin
Heptane		
Cyclohexene		
Toluene		
Unknown		

F. Synthesis of Acetylene

Describe what happened when water was added to calcium carbide?

What did you observe when the burning splint was thrust into the test tube?

What did you observe when you put a filter paper stick wet with potassium permanganate into the test tube?

Did the purple color of potassium permanganate disappear? ____________

What color product was formed? ____________

Is Acetylene unsaturated?____________

What is your evidence?

Post Lab Questions

1. Identify your unknown as either an alkane, alkene, or arene. Explain your reasoning.

2. From a chemical standpoint, why is the hydrocarbon mixture called paraffin wax ideally suited for a covering on a jelly jar?

3. Do you expect that acetylene would react with bromine without exposure to light? Explain your answer.

4. On the basis of your experimental results, decide which of the hydrocarbons – saturated, unsaturated, or aromatic – is most reactive. Which is least reactive? Explain your reasoning.

5. Write structural formulas for all of the possible different monobromonation products of the reaction of n-butane with Br_2.

6. Write an equation for the synthesis of acetylene.

7. Draw a scheme to separate the following compounds: 1,4-dimethylbenzene (para-xylene), 2,4-dimethylheptane, and 3-methyl-2-pentene:

8. What will be the product from each of the following reactions:

a. cyclohexane + bromine $\xrightarrow{\text{light}}$

b. cyclohexene + bromine $\longrightarrow$

c. cyclopentane + aqueous potassium permanganate $\longrightarrow$

d. cyclopentene + aqueous potassium permanganate $\longrightarrow$

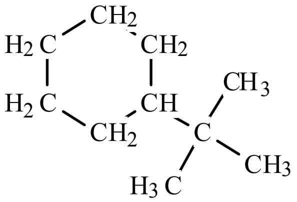
e. 3 hexene + concentrated sulfuric acid $\longrightarrow$

9. Name the following hydrocarbons:

a. $(CH_3)_2CHCH_2CH_2CH{=}C(CH_2CH_3)CH_2CH_2CH_3$ ________________________________

b. $CH_3CH_2CH{=}CHCH(CH_2CH_2CH_3)C(CH_3)_3$ ____________________________________

c. ____



d. $HC{\equiv}CCH_2CH_2C(CH_3)_2CH_2CH_2CH_3$ ____

EXPERIMENT 3

Purification By Crystallization

Objectives

1. To demonstrate the technique of recrystallization.
2. To check the purity of our product using melting points.

Introduction

Part I Recrystallization

Organic compounds usually are more soluble in hot solvents than in cold. An impure solid organic compound, when dissolved in the proper amount of an appropriate solvent at an elevated temperature, will reprecipitate when the solution is cooled. If the hot solution is filtered before being allowed to cool, dirt, lint, or other insoluble impurities will be removed, and the crystals that deposit in the cooled solution usually will be more pure than the starting material. The crystals may be removed from the filtrate by filtration. The soluble impurities and a small amount of the desired substance will stay in solution. This process is called **recrystallization** and is one frequently used for the purification of solid organic compounds.

In this experiment we will purify benzoic acid, an organic compound that is quite insoluble in cold water. The sample is very dirty (floor sweepings have been included with the sample!). A sample will be dissolved in hot water. Avoid using too much water or you may “lose” compound because it will remain in solution. The sample is then filtered by gravity filtration to remove any undissolved impurities. The filtrate is cooled and pure benzoic acid crystallizes from the solution. The pure crystals are collected by vacuum filtration. When the crystals are dry a melting point of the compound is determined.

NOTE: The solubility of pure benzoic acid is 0.2 g/100 mL of water at 4 °C. At 75 °C the solubility is 2.2 g/100 mL of water. The melting point of pure benzoic acid is 122 °C.

Part II - Melting Points

The **melting point** of a solid occurs when the solid and liquid phases are equilibrium, which occurs at a specific temperature. However, the time required to determine a specific melting point can be impractical, so a melting point range of temperatures between the first sign of melting and the complete melting of a solid is found. A *narrow range* of one to two degrees Celsius implies a high degree of purity, while a *broad range* usually implies an impure sample. Thus, the melting point is useful as a means of determining the purity of a compound.

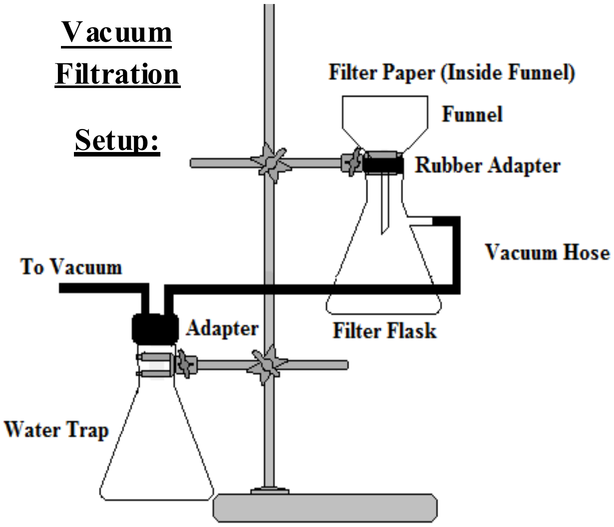
As the thermal energy imparted by the melting point apparatus to the sample become large enough to overcome the intermolecular forces that hold the sample together the sample melts. The temperature recorded is when the first solid begins to melt until the last bit of solid disappears.

Solids often decompose or undergo unusual behavior before melting including changes in appearance such as loss of luster or darkening, softening, shrinking, or appearing moist before melting. These changes are not melting but, sintering; the actual melting point occurs when the first drop of liquid is seen until the last solid liquefies. When a substance melts with decomposition the substance will bubble or form a dark char. In these instances, to observe the melting point or decomposition point is dependent on the rate of heating.

Experimental Design

A. Purification experiment

1. Obtain approximately 2.5 grams of the impure benzoic acid and measure its mass.
2. Place this in a 125 mL Erlenmeyer flask and add about 75 mL of water.
3. Add a boiling chip and heat on a hot plate (swirl the contents regularly) until most of the solid has dissolved. If necessary, add a little more water and continue heating to see if more will dissolve. Do not exceed 100 mL of total solution.
4. Filter the hot solution using a Büchner funnel set-up:



NOTE: To prevent benzoic acid from precipitating in a cold funnel, first pour 100 mL of hot water through the funnel. Then empty the water from the filter flask.

For materials such as benzoic acid, it is often useful to filter into a flask already containing a little water heated to boiling. The water vapor keep the filter funnel hot and helps to prevent premature crystallization

5. Allow the filtrate to cool (do not shake the flask if you want to largest crystals to grow!). When the water has cooled to room temperature (an ice bath helps after most of the crystals have come out of solution) the crystals can be isolated by pouring the solution into a Büchner funnel which is operating properly.

Operating a Vacuum System

- **a.** Set-up a vacuum system by attaching a Büchner funnel to a filter flask.
- **b.** Your filter paper should fit exactly the bottom of the Büchner funnel; it must not extend up the sides of the funnel. You may have to cut the paper to make it fit.
- **c.** Wet the filter paper in the Büchner funnel with water immediately before pouring in the benzoic acid solution.
- **d.** With the aspirator or vacuum on full, pour the crystallized product slowly into the center of the filter paper. Use a spatula to transfer any crystals remaining in the flask.
- **e.** Wash your crystals thoroughly with 10 mL of cold water by pouring the water slowly over the crystals as you stir them. Press the crystals across the bottom of the Büchner funnel with a spatula and dry them by pulling air through the Büchner funnel for a few minutes.
- **f.** Weigh a small glass beaker, transfer the crystals to the beaker and reweigh. Calculate your percent recovery:

$$\%\ \text{recovery} = \frac{\text{mass dry crystals}}{\text{mass sample}} \times 100\% \qquad \textbf{(EQ 3.1)}$$

B. Melting points

The melting point of a substance is the temperature at which the solid crystals of that compound turn to a liquid. This will be a fairly simple measurement.

1. Place just a few small crystals of your unknown acid in the center of the top of your melting point apparatus. Only a very small amount of solid is required to determine a melting point. Insert a thermometer in the appropriate channel in the apparatus.
2. Allow the temperature to increase fairly slowly and record the temperature at which it melts. You should not bother to be extremely careful in this first attempt, as you are just trying to get an approximate melting point the first time around.
3. Once you have an approximate melting point, now you will measure the melting point much more carefully by approaching the melting point very gradually. Clean off the surface of the melting point apparatus and put more crystals on top as before. This time, when you are a few degrees below the melting point, begin to raise the temperature quite slowly. This can be done by turning down the hot plate or by putting a few layers of paper between the hot plate and the melting point apparatus. You may have to use your imagination a bit at this point! The temperature should rise at no more than two degrees per minute at the melting point to measure an accurate melting point.
4. If you have any doubt at all about the melting point, perform the procedure one additional time. If you have two fairly good values which are slightly different, you can take the melting point to be the average of those two values. Record your results in the data section.

Prelab Exercises: Crystallization

Name: ____ Section: __________________

1. Why would a chemist be likely to recrystallize a sample?

2. If 4.4 grams of benzoic acid are dissolved in 200 mL of water at 75 °C and the solution is then cooled to 4 °C, how much recrystallized benzoic acid would be expected to form?

3. Why is the rate of heating a melting point sample limited to 2 °C per minute?

4. A compound is supposed to have a melting point of 120 °C. It has a small amount of an impurity with a very high melting point. What do you think you will note in the melting point of your impure material?

Lab Report: Crystallization

Name: ____ Section: __________________

A. Purification of Benzoic Acid

TABLE 3.1

Data	
Before Purification	
Mass of flask and sample	
Mass of empty flask	
Mass of sample	
After Purification	
Mass of beaker and benzoic acid	
Mass of empty beaker	
Mass of benzoic acid recovered	
Percent Recovery	

Sample Calculations

B. Determination of Melting Point

TABLE 3.2

Data	
Approximate melting point from fist attempt	
Melting point range from second, slower measurement	

Post Lab Questions

1. Why would you use a small amount of water (150 mL) rather than 1 L in purifying a 3 gram sample of benzoic acid?

2. If the benzoic acid was not totally dry when you took the melting point, what effect would this have on the mp? (Hint -- Is melting occurring? or something else?)

3. If you started with 1 gram of the crude benzoic acid mixture, and used 100 mL of water for the crystallization procedure, why don't you expect to obtain <u>all</u> of the benzoic acid in the crude sample? (Hint: How much could you theoretically recover?)

4. A yellow compound is known to have a sharp melting point of 82-83 °C, however, your sample is green colored. What do you think you will observe for the melting point of this sample?

EXPERIMENT 4 *Alcohols*

Objectives

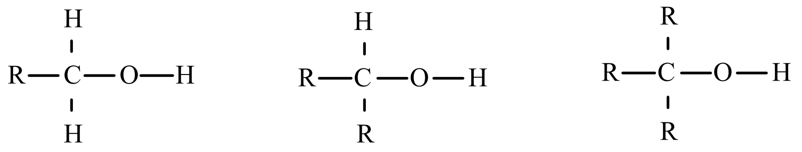
1. To learn about the physical properties of representative alcohols and phenols.
2. To examine reactions of alcohols which are of particular importance in biochemistry and physiology.
3. To become acquainted with some alcohols and phenols which are a part of our everyday life.

Introduction

Methanol or methyl alcohol, CH_3OH, is the simplest member of the alcohol family, but it is not nearly as well known as ethanol, CH_3CH_2OH, the depressant drug in alcoholic beverages. Ethanol (aka ethyl alcohol) is also used as an antiseptic, a solvent for medicines and chemicals, and a preservative.

Methyl alcohol may be viewed as the parent alcohol. If one of the hydrogens in the methyl group of methyl alcohol (a primary alcohol) is replaced us replaced by a carbon group (alkyl or aromatic), the resulting alcohol is still primary; if two hydrogens are replaced, a secondary alcohol is formed; and if all of the methyl hydrogens are replaced, a tertiary alcohol results. R represents the carbon group.

FIGURE 4.1

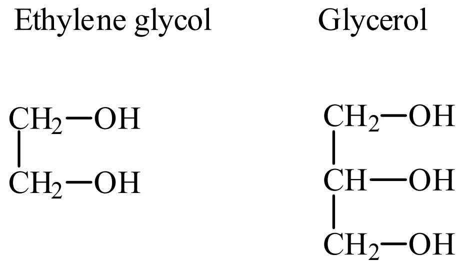


$$R-\overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}-O-H \qquad R-\overset{\displaystyle H}{\underset{\displaystyle R}{\overset{|}{\underset{|}{C}}}}-O-H \qquad R-\overset{\displaystyle R}{\underset{\displaystyle R}{\overset{|}{\underset{|}{C}}}}-O-H$$

A primary alcohol A secondary alcohol A tertiary alcohol

Ethylene glycol and glycerol (glycerin) are examples of alcohols which contain more than one hydroxyl group, -OH. Ethylene glycol is the principal component of antifreeze.

FIGURE 4.2



Physical properties of alcohols

Alcohols can be considered to be derivatives of water with one hydrogen replaced by an alkyl or aromatic group. The hydroxyl group is responsible for many of the physical properties of alcohols. Low molecular weight alcohols are generally water soluble and exhibit strong hydrogen bonding. Higher molecular weight alcohols tend to be insoluble in water as the organic portion of the molecule determines its properties. All alcohols are soluble in organic solvents. Alcohols also tend to have higher melting points and boiling points than hydrocarbons of similar molecular weight due to increased intermolecular H-bonding.

Reactions of alcohols

Reaction of Alcohols with Lucas reagent

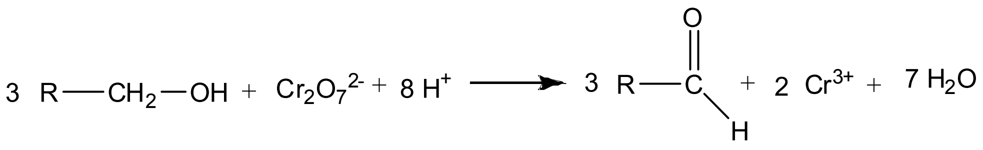
The Lucas test for distinguishing between primary, secondary, and tertiary alcohols is based on the relative rates of reaction of the different classes of alcohol with hydrogen chloride, HCl. The Lucas reagent is a solution of zinc chloride in concentrated hydrochloric acid. A tertiary alcohol reacts rapidly with the reagent to give an insoluble alkyl chloride that appears as a cloudy dispersion or as a separate layer in the solution. A secondary alcohol gives a clear solution at first (as the alcohol dissolves), which becomes cloudy within five minutes. A primary alcohol dissolves to produce a solution that remains clear for several hours. The equation for the reaction which takes place is:

$$\text{R-OH} + \text{HCl} \rightarrow \text{R-Cl} + H_2O_{(l)} \qquad \textbf{(EQ 4.1)}$$

Oxidation

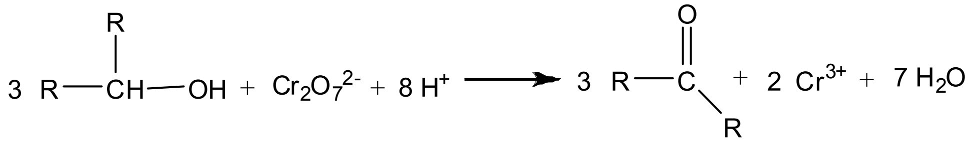
Oxidation of primary and secondary alcohols gives aldehydes and ketones, respectively. (Note: Aldehydes will further oxidize to carboxylic acids unless removed from the reaction mixture.) A common oxidizing agent is potassium dichromate, $K_2Cr_2O_7$, in sulfuric acid, a mild oxidizing agent that will not oxidize tertiary alcohols. A color change from the reddish orange of $K_2Cr_2O_7$–H_2SO_4 to the blue-green of Cr^{3+} confirms oxidation of an alcohol. Chromium is reduced from an oxidation state of +6 in the anhydride to +3 in Cr^{3+}. You will use the oxidation reactions in today's experiment to distinguish tertiary alcohols from primary and secondary alcohols.

primary alcohols **(EQ 4.2)**



$$3\ R-CH_2-OH + Cr_2O_7^{2-} + 8\ H^+ \longrightarrow 3\ R-\overset{\overset{O}{\|}}{C}-H + 2\ Cr^{3+} + 7\ H_2O$$

secondary alcohols **(EQ 4.3)**

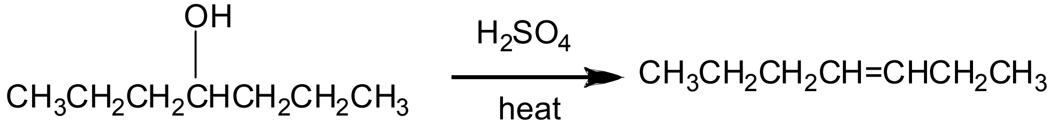


$$3\ R-\overset{\overset{R}{|}}{CH}-OH + Cr_2O_7^{2-} + 8\ H^+ \longrightarrow 3\ R-\overset{\overset{O}{\|}}{C}-R + 2\ Cr^{3+} + 7\ H_2O$$

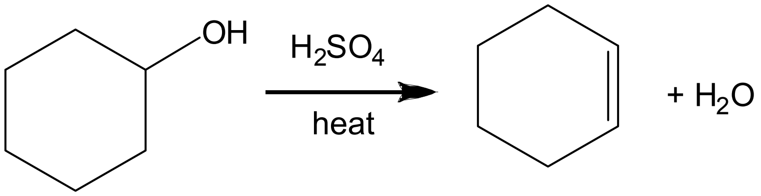
tertiary alcohols - no reaction

Dehydration

Alcohols can be dehydrated to alkenes by heating them with a dehydration agent such as sulfuric acid, H_2SO_4. Dehydration reactions occur with all three types of alcohols: the alcohol loses an -OH group and a hydrogen located on adjacent carbons. These adjacent carbons then form a double bond to produce the alkene product.



$$CH_3CH_2CH_2\overset{\overset{OH}{|}}{C}HCH_2CH_2CH_3 \xrightarrow[heat]{H_2SO_4} CH_3CH_2CH_2CH{=}CHCH_2CH_3$$



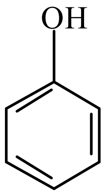
Phenols

Phenols are often classified with alcohols because of the presence of the -OH group. Thus, one might consider phenol as a phenyl alcohol; however, this would not be correct. Phenols are different from alcohols. Phenols are more acidic than alcohols and will not give typical reactions of the alcohols.

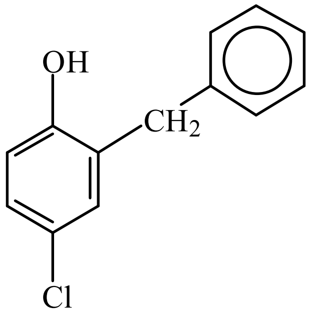
The phenol family includes all compounds which have an -OH group bonded directly to an aromatic ring. Many phenols have strong odors which you may associate with disinfectants. Phenol itself is an important disinfectant.

Lysol cleaner contains a more complex member of the phenol family, 2-benzyl-4-chlorophenol:

FIGURE 4.3



Phenol



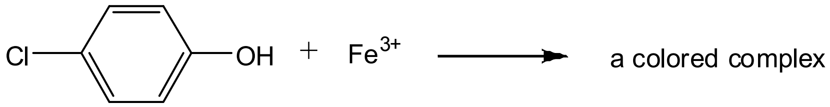
2-benzyl-4-chlorophenol
(Disenfectant in Lysol)

Phenol in concentrated solution is highly toxic to all types of cells. If you spill phenol itself or certain other phenols on your skin, they will burn (kill) the tissue.

Test for Phenols - Ferric Chloride Complex formation

Most phenols react with the ferric ion, Fe^{3+}, in ferric chloride, $FeCl_3$, solution to form complexes varying in color from yellow orange to deep purple. p-Chlorophenol is used to illustrate this reaction:

(EQ 4.4)



Experimental Design

Part I - Alcohols

A. Physical properties of alcohols

1. Describe the color and odor of each of the alcohols.
2. Compare the viscosity of each of the alcohols by letting them drop slowly from a dropper.
3. Assemble an apparatus for determining boiling point:
    a. Using a dry large (2.5-cm diameter) test tube, and a thermometer which reads to 250°C.
    b. Drop a boiling chip into the test tube, and add 2 mL of ethylene glycol.
    c. Adjust the bulb of the thermometer so that it is about 2.5 cm above the surface of the liquid; do not allow the bulb of the thermometer to touch the sides of the test tube.
    d. Heat the glycol with a low flame.
    e. As the liquid boils, you will see the line of condensed vapor creep up the side of the test tube.
    f. Continue to boil the glycol at such a rate that the condensation line remains for a few minutes about 2 cm above the bulb of the thermometer.
    g. When the temperature ceases to rise, you have reached the boiling point of ethylene glycol.
    h. Record this temperature.

B. Reactions of Alcohols

1. Lucas Test
    a. To each of four clean, dry test tubes add 2 mL of Lucas Reagent.
    b. To the first test tube add 4-5 drops of 1-butanol, $CH_3(CH_2)_3OH$; to the second add 4-5 drops of 2-butanol, $CH_3CH_2CH(OH)CH_3$; to the third add 4-5 drops of tert-butyl alcohol, $(CH_3)_3COH$, and to the fourth add 4-5 drops of isobutyl alcohol, $(CH_3)_2CHCH_2OH$.
    c. Shake gently to mix the reagents and then allow the reaction to take place at room temperature. Watch for and time the appearance of cloudiness or a second layer. Record in the data sheet.
2. Oxidation
    a. To each of four clean, dry test tubes add 1 mL of the reagent acetone (acetone is a solvent). To the first test tube add 1 drop of 1-butanol, $CH_3(CH_2)_3OH$; to the second add 1 drop of 2-butanol, $CH_3CH_2CH(OH)CH_3$; to the third add 1 drop of tert-butyl alcohol, $(CH_3)_3COH$ and to the fourth add 1 drop of isobutyl alcohol, $(CH_3)_2CHCH_2OH$.
    b. Then to each test tube add 1 drop of potassium dichromate-sulfuric acid ($K_2Cr_2O_7$–H_2SO_4) oxidizing agent, and mix each solution thoroughly.

Caution! Safety Notes:

Be careful not to get the chromic acid solution on your skin. It will burn and stain your fingers. If you do get it on your skin, rinse off immediately (for at least 15 minutes) as chromium is toxic and can penetrate the skin.

    c. Oxidation is confirmed is the color of the solution changes from reddish orange to blue-green within a few minutes.

3. Dehydration of an Alcohol
    - a. For this experiment you will need a filter-paper stick (roll a piece of filter paper up like a straw to make the filter paper stick), a small test tube in a boiling water bath.
    - b. To the test tube add 10 drops of tert-butyl alcohol and 1 drop of concentrated H_2SO_4.

Caution! Safety Notes:

Concentrated H_2SO_4 is dangerous! If you come in contact with the acid, wash it off immediately for at least 15 minutes.

- c. Put 1 drop of $KMnO_4$ solution on the end of the filter-paper stick, and hold the $KMnO_4$ about 2 or 3 cm above the surface of the alcohol. (Do not let the $KMnO_4$ come in contact with the alcohol at any time.)
- d. Now gently heat the alcohol until it just begins to boil.

What happens to the color on the end of the filter-paper stick?

Record your observations and answer the questions.

Part II - Phenols

A. Physical Properties

Describe the odor and appearance of some common phenols. You will find phenol, p-cresol, vanillin, and thymol to observe.

B. Reactions of Phenols

Formation of Ferric Chloride Complexes

- a. To each of four test tubes add 1 mL of the saturated solutions of phenol, p-cresol, vanillin, and thymol provided.
- b. Now add a drop of 1% ferric chloride solution and note the color of the complex that is formed. With some phenols the color is not permanent, so the solution should be watched closely the instant the ferric chloride is added.
- c. The ingredients on the labels of Lysol cleaner and Chloraseptic mouthwash indicate that each of these products contain a phenol. Confirm the presence of the phenol by using the $FeCl_3$ test.
- d. To 10 drops of each product in a clean test tube, add 5 drops of $FeCl_3$ solution.

Is the presence of a phenol indicated by the formation of a colored complex? (Since Lysol cleaner and Chloraseptic mouthwash are already colored, formation of a complex is indicated by a change in the color of these solutions.)

Prelab Exercises: Alcohols

Name: ____ Section: __________________

1. Draw the structural formula of each of these alcohols and describe each as primary, secondary or tertiary:

TABLE 4.1

Structural formula	2-pentanol	3,3-dimethyl-2-butanol	1-hexanol
Primary, Secondary or Tertiary?			

2. List several alcohols and phenols that are present in consumer products and describe their uses.

Alcohols

a.

b.

c.

Phenols

a.

b.

3. Define the following terms:

TABLE 4.2

viscosity	
oxidation	
hydroxyl group	
hydrogen bonding	

4. In this experiment, what is the evidence for the oxidation of an alcohol?

5. In this experiment what is the evidence for the dehydration of an alcohol? (Describe what you expect to see and what chemical reactions are responsible.)

6. In this experiment what is the evidence for the presence of a phenol?

Lab Report: Alcohols

Name: ____ Section: __________________

Part I - Alcohols

A. Physical Properties

TABLE 4.3 **1 and 2**

Alcohol	color	odor	viscosity
methanol			
ethanol			
2-propanol			
ethylene glycol			
glycerol			

3 Boiling point of ethylene glycol

Observed boiling point: _______________

Literature boiling point: ________________

The molecular weights of isopropyl alcohol and ethylene glycol are very close, 60 g/mol and 62 g/mol, respectively, but their boiling points are far apart (the boiling point of isopropyl alcohol is 82 ^oC). Explain.

Name at least two properties of ethylene glycol which make it an ideal automobile antifreeze.

B. Reactions of Alcohols

1. Lucas Test - Record the time required for each of the following alcohols to react with the Lucas Reagent.

TABLE 4.4

Alcohol	Time for reaction to occur	Description of reaction mixture (Before and after reaction)
n-butanol (1-butanol)		
2-butanol (sec-butanol)		
tert-butanol (tert butyl alcohol)		
2-methyl-1-propanol (iso-butanol)		
unknown		

2. Oxidation - Record your observations for each of the following alcohols and draw the structure of the organic product of the reaction.

TABLE 4.5

Alcohol	Observations	Organic Product
n-butanol (n-butyl alcohol)		
2-butanol (sec-butyl alcohol)		
Tert-butanol (tert-butyl alcohol)		
2-methyl-1-propanol (isobutyl alcohol)		
unknown		

Which of the alcohols were oxidized to aldehydes?

Which of the alcohols are secondary alcohols?

Was your “unknown” alcohol primary, secondary, or tertiary? Explain your reasoning.

3. Dehydration of an Alcohol

Did the potassium permanganate, $KMnO_4$, test prove that dehydration of tert-butyl alcohol occurred to give an alkene? Why or why not?

Could the tert-butyl alcohol have been responsible for reducing the $KMnO_4$? (Hint: Refer data in "B. Reactions of Alcohols" on page 48 "Oxidation") Why or why not?

What is the structure of the alkene formed?

Look up and record the boiling point of the alkene.

Boiling point __________ Reference used _______________

Is the alkene a gas at room temperature? __________

Write an equation for the formation of the alkene.

Part II - Phenols

A. Physical Properties

TABLE 4.6

Compound	Appearance (color, texture, etc.)	Odor
Phenol		
p-cresol		
Vanillin		
Thymol		

B. Reactions of Phenols

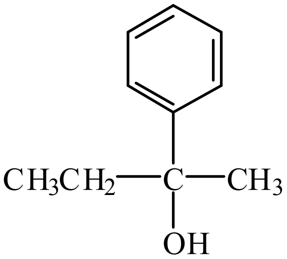
TABLE 4.7

Compound/substance	Observation
Phenol	
p-cresol	
Vanillin	
Thymol	
Chloroseptic	
Lysol	

Post Lab Questions

1. What is the function of phenol in the consumer products you tested?

2. Is the following alcohol primary, secondary, or tertiary? ______________________________

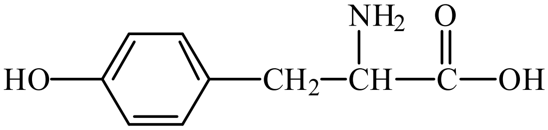


a. Is it a phenol? _________

b. Would $K_2Cr_2O_7$ oxidize this compound? _________

c. Would it undergo dehydration with sulfuric acid? __________

3. The structure of the amino acid tyrosine is:

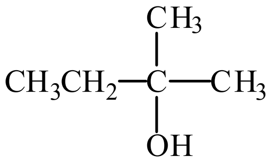


a. Is tyrosine an alcohol? _________

b. A phenol? _________

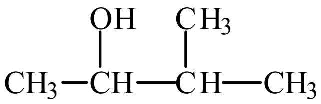
c. On the basis of today's experiment how would you prove whether it is a phenol or an alcohol?

4. Write equations for reactions that could be used to distinguish between the isomeric alcohols:



$$CH_3CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle OH}{C}}-CH_3$$

and



$$CH_3-\overset{\displaystyle OH}{CH}-\overset{\displaystyle CH_3}{CH}-CH_3$$

5. List at least three important uses for glycerol.

6. An unknown compound A is known to be an alcohol with the molecular formula $C_4H_{10}O$. When dehydrated, compound A gave only one alkene product, C_4H_8, compound B. Compound A could not be oxidized. What are the identities of compound A and compound B?

EXPERIMENT 5

Aldehydes and Ketones

Objectives

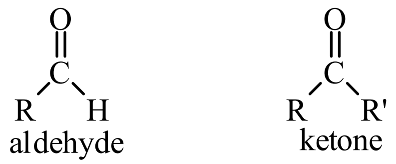
1. To investigate the physical properties and use of some common aldehydes and ketones.
2. To develop familiarity with reactions of aldehydes which are of particular importance in biochemistry.
3. To learn to use characteristic reactions to distinguish between aldehydes and ketones, and between aliphatic and aromatic aldehydes.

Introduction

The **carbonyl group**, like an alkene, has a double bond. Due to electronegativity differences between carbon and oxygen, the double bond is polarized towards the oxygen; in effect causing oxygen to react as though it possessed a negative charge and the carbon a positive charge.

The two major functional group classes that contain the carbonyl are the aldehydes and the ketones

FIGURE 5.1



(Note: An aromatic aldehyde (or ketone) is one in which an aromatic ring is bonded directly to the carbonyl carbon.)

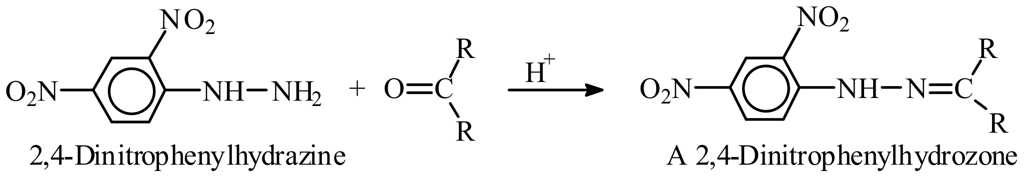
In this experiment you will be introduced to several common aldehydes and ketones. You will compare the physical properties of these substances and also learn chemical tests to distinguish aldehydes from ketones.

Reactions of Aldehydes and Ketones

2,4-Dinitrophenylhydrazone test

Both aldehydes and ketones will react with 2,4-dinitrophenylhydrazine (2,4-DNP) to form a solid 2,4-dinitro-phenylhydrozone. The product is often yellow to orange in color. This test can be easily formed on a spot plate to see whether a carbonyl group is present.

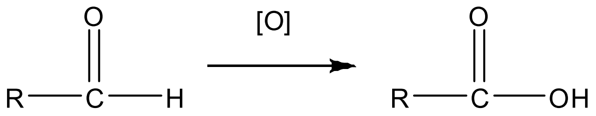
(EQ 5.1)



Oxidation

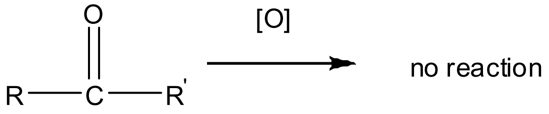
Aldehydes are easily oxidized to carboxylic acids, but ketones are not oxidized at all under ordinary reaction conditions. This difference serves as a convenient way to distinguish between aldehydes and ketones:

Aldehyde Oxidation: **(EQ 5.2)**



$$R-\overset{\overset{\Large O}{\|}}{C}-H \xrightarrow{[O]} R-\overset{\overset{\Large O}{\|}}{C}-OH$$

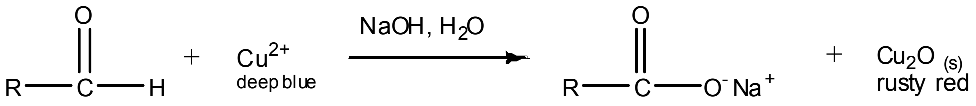
Ketone Oxidation: **(EQ 5.3)**



$$R-\overset{\overset{\Large O}{\|}}{C}-R' \xrightarrow{[O]} \text{no reaction}$$

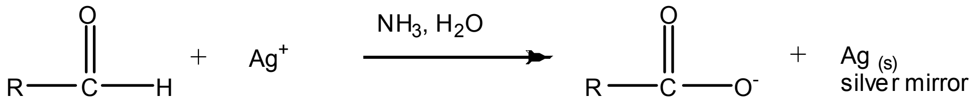
The oxidation can be accomplished by mild oxidizing agents such as cupric ion, Cu^{2+}, in basic solution (Fehling's reagent), or by silver ion, Ag^{+}, in ammonia solution (Tollens' reagent). Net ionic reactions of an aldehyde with Fehling's reagent and with Tollens' reagent, respectively, are:

(EQ 5.4)



$$R-\overset{\overset{\Large O}{\|}}{C}-H + \underset{\text{deep blue}}{Cu^{2+}} \xrightarrow{NaOH,\ H_2O} R-\overset{\overset{\Large O}{\|}}{C}-O^{-}Na^{+} + \underset{\text{rusty red}}{Cu_2O_{(s)}}$$

(EQ 5.5)



$$R\text{—}\overset{\overset{\Large O}{||}}{C}\text{—}H + Ag^+ \xrightarrow{NH_3,\ H_2O} R\text{—}\overset{\overset{\Large O}{||}}{C}\text{—}O^- + Ag_{(s)}$$

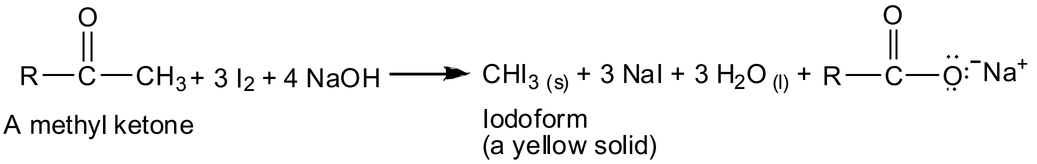
A positive Fehling's test is indicated by the formation of a yellow-red precipitate, which in a blue solution may appear to be greenish. A positive Tollens' test is confirmed by the formation of a silver mirror on the inside of the test tube. Aromatic aldehydes give a weakly positive Fehling's test, so this test can sometimes be used to distinguish between aromatic and aliphatic aldehydes. Both types of aldehydes react with Tollens' reagent.

Students should note that rate and completeness of reactions with aliphatic aromatic aldehydes is different and this will be the basis for deciding if your known is an aliphatic aromatic aldehyde.

Iodoform Reaction of Methyl Ketones

Methyl ketones (ketones which have a methyl group bonded directly to the carbonyl group) react with iodine in basic solution to give iodoform, CHI_3, and other products. (Note: All secondary alcohols, acetaldehyde, and ethanol also give a positive iodoform test.)

(EQ 5.6)



$$R\text{—}\overset{\overset{\Large O}{||}}{C}\text{—}CH_3 + 3\,I_2 + 4\,NaOH \longrightarrow CHI_{3\,(s)} + 3\,NaI + 3\,H_2O_{(l)} + R\text{—}\overset{\overset{\Large O}{||}}{C}\text{—}\ddot{\underset{\cdot\cdot}{O}}{:}^-Na^+$$

Iodoform is a yellow solid with a strong medicinal odor; it is used as an antiseptic. This reaction, known as the iodoform test, can be used to distinguish between methyl and other ketones.

Experimental Design

Part I - Physical properties

A. Odors and Uses

The following common aldehydes and ketones are on the reagent shelf: benzaldehyde, vanillin, camphor, cinnamaldehyde, and formaldehyde solution.

Note the odor of each of them and describe them on Table 5.1 on page 63.

Part II - Chemical properties

A. 2,4-Dinitrophenylhydrazone test

Caution! Safety Notes:

Wear safety glasses. The 2,4-dinitrophenylhydrazine solution is strongly acidic. Avoid getting the reagent on your skin. Handle with care, some phenylhydrazine derivatives are suspected carcinogens!

1. Set out three clean test tubes.
2. To the first add 5 drops of formaldehyde solution, to the second add 5 drops of benzaldehyde, and to the last add 5 drops of reagent-grade acetone.
3. Add several drops of the “2,4-DNP” solution to each test tube.
4. Observe and record your observations. Immediate formation of a precipitate (the color can vary from red to orange to yellow) is indicative of a carbonyl group.

B. Fehling's Test

1. To each of four test tubes add 5 mL of Fehling's reagent.
2. To the first test tube add 6 drops of formaldehyde solution, to the second add 6 drops of benzaldehyde, to the third add 6 drops of reagent-grade acetone, and to the last add 6 drops of the unknown.
3. Stir the solutions thoroughly, and place them in a beaker of boiling water for 10 to 20 minutes.
4. Record your observations in each case. *Formation of trace amounts of* Cu_2O *precipitate is not a confirming test.*

C. Tollens' Test

1. Prepare the Tollens' reagent as follows.
2. To a large clean test tube (if your test tube is not clean and dry the reaction may not work) add 2 mL of a dilute (5%) aqueous silver nitrate, $AgNO_3$, solution, and 1 drop of 10% NaOH solution.
3. Add 2.5 mL of dilute (2%) aqueous ammonia.
4. Then *stir* in additional aqueous ammonia drop by drop until only a few particles of silver oxide remain. *Avoid an excess of aqueous ammonia.*
5. Divide into four test tubes and conduct the Tollens' test on the following aldehydes and ketones.
6. To the first test tube add 2 drops of formaldehyde solution, to the second add 2 drops of benzaldehyde, to the third add 2 drops of reagent-grade acetone, and to the last add 2 drops of the unknown.

7. Stir the solutions thoroughly and let them stand at room temperature for 10 to 15 minutes. (Do not disturb during this time.)
8. Observe whether a mirror forms on the inside of the tube.

Caution! Safety Notes:

Discard the Tollens' test reagents when you have completed this part of the experiment. Explosive compounds may form if the solutions are allowed to stand.

9. The silver mirror can be removed from the test tube by washing it with dilute nitric acid.

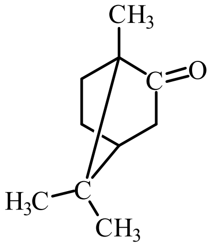
<u>D. Iodoform Test for methyl ketones</u>

1. Stir 10 drops of 10% sodium hydroxide into 2 drops of acetone in 1 mL of water.
2. Then, while shaking the container, add drops of iodine-potassium iodide reagent until the color of the iodine disappears quite slowly. (Approximately 25 drops of iodine-potassium iodide reagent will be required.)
3. Does a precipitate form?
4. Isolate the iodoform by pouring the reaction mixture onto a filter paper in a funnel.
5. Dry the crystals between several pieces of filter paper.
6. Compare the physical properties (odor and color) of your iodoform with the commercial iodoform on the reagent shelf.
7. If your unknown is a ketone, perform the Iodoform test on it as well to determine if it is a methyl ketone.

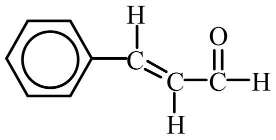
Prelaboratory Exercises: Aldehydes and Ketones

Name: ____ Section: __________________

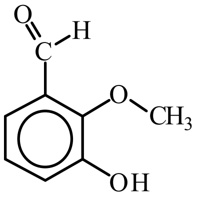
1. Consider the following aldehydes and ketones:



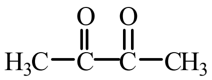
Camphor



Cinnamonaldehyde



Vanillin



$H_3C-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-CH_3$

Diacetal (2,3-butanedione)

a. Which of the compounds are aldehydes?

b. Which of the compounds are ketones?

c. Which compounds would react with Fehling's reagent?

d. Which compounds would react with Tollens' reagent?

e. Which compounds would give a positive iodoform test?

2. What are the similarities and differences in physical and chemical properties between carbonyl group and molecules with an alkene?

3. What reagent reacts with both aldehydes and ketones to give a colored precipitate?

4. Describe a test which can be performed to distinguish between a ketone and an aldehyde? How will each type of compound react?

Lab Report: Aldehydes and Ketones

Name: ____ Section: ___________________

Part I

TABLE 5.1 **A. Odors and uses**

Compound	Appearance	Odor	Uses
Benzaldehyde			
Vanillin			
Camphor			
Cinnamaldehyde			
Formaldehyde			

Draw the structure for acetone and circle the alkyl groups.

Part II - Chemical Properties

TABLE 5.2 **Record your observations from parts A, B, and C.**

Compound	2,4-DNP Test	Fehling's Test	Tollens' Test
Formaldehyde			
Benzaldehyde			
Acetone			
Unknown			

Can 2,4-dinitrophenyl-hydrazine be used to distinguish between an aldehyde and a ketone? Why or why not?

Can Fehling's test be used to distinguish between an aldehyde and a ketone? Why or why not?

Write an equation for the reaction of benzaldehyde with Fehling's reagent.

Can Tollens' test be used to distinguish between an aldehyde and a ketone? Why or why not?

Write an equation for the reaction of formaldehyde with Tollens' reagent.

D. Test for a Methyl Ketone

Describe what happened as you added the iodine solution to acetone.

Write an equation for the reaction that occurred.

If you did the iodoform test on your unknown, record your observations here. Is it a methyl ketone?

E. Identify the functional group of your unknown

Is it an aliphatic aldehyde, aromatic aldehyde, “regular” ketone or methyl ketone? Explain your reasoning.

Post Lab Questions

1. A compound gives a positive test with 2,4-dinitrophenyl-hydrazine, but does not produce a silver mirror with Tollens' reagent. Based on this information to what class of compounds does it belong? (i.e. alkane, amine, carboxylic acid, etc.)

2. Methyl nonyl ketone is an active ingredient in certain commercial cat and dog repellents.
   - a. Draw the structure for this ketone.
   - b. Would this ketone undergo the iodoform test? Why or why not?
   - c. If so, write an equation for this reaction.

3. Based on information from this experiment and the tests for alcohols (previous experiment) find a solution for this problem. The store room had a flood. Most things didn't get damaged by the water; however, a few bottles of unknowns for the organic lab had the labels come off. The labels read: t-butyl alcohol, n-propanol, pentanal, acetone, and 3-hexanone. What tests could you perform on the contents of the unlabeled bottles to put the correct label on each bottle? (Hint: Draw a flow chart.)

4. Compound A ($C_5H_{10}O$) contains a C=O but gives a negative Tollens' test. Compound A cannot be oxidized with $KMnO_4$ or $K_2Cr_2O_7$. Reduction of A gives B ($C_5H_{11}OH$). Compound B is a secondary alcohol. Dehydration of B gives two alkenes, C and D (both C_5H_{10}). Compound C is a terminal alkene, but D contains an internal double bond. C does not exist as a *cis-/trans-* isomer but D does. Give structures and names for A-D. Show your logic in determining answer.

EXPERIMENT 6

Carboxylic Acid and Ester Chemistry - Synthesis of Aspirin

Objectives

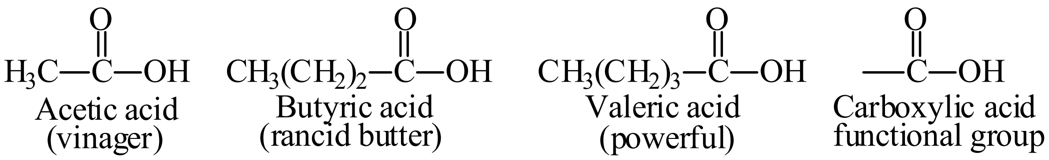
1. Observe the physical and chemical characteristics of carboxylic acids and esters.
2. Study the structure and synthesis of esters.
3. Study aspirin's physiological properties.
4. Prepare the common drug aspirin (acetyl salicylate) from salicylic acid and acetic anhydride.

Introduction

Carboxylic acids

Carboxylic acids are generally recognizable by their sharp and frequently disagreeable odors. Some common carboxylic acids along with their sources follows:

FIGURE 6.1



$H_3C-\overset{\overset{O}{\parallel}}{C}-OH$ Acetic acid (vinager)

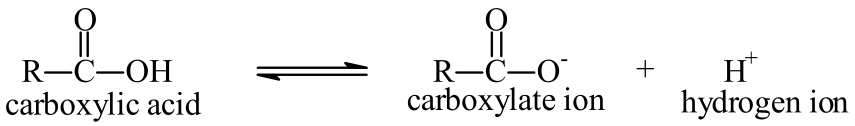
$CH_3(CH_2)_2-\overset{\overset{O}{\parallel}}{C}-OH$ Butyric acid (rancid butter)

$CH_3(CH_2)_3-\overset{\overset{O}{\parallel}}{C}-OH$ Valeric acid (powerful)

$-\overset{\overset{O}{\parallel}}{C}-OH$ Carboxylic acid functional group

Carboxylic acids are weak acids and ionize only slightly in aqueous solution to give a hydrogen ion and a carboxylate anion (where R- is a hydrogen, alkyl, or aromatic group).

(EQ 6.1)



$$\mathrm{R-\overset{O}{\overset{\|}{C}}-OH} \rightleftharpoons \mathrm{R-\overset{O}{\overset{\|}{C}}-O^-} + \mathrm{H^+}$$

At equilibrium, most of the acid is present in water as the unionized molecular acid. Only a few of the lower-molecular-weight acids (up to four carbons) are soluble in water.

Esters

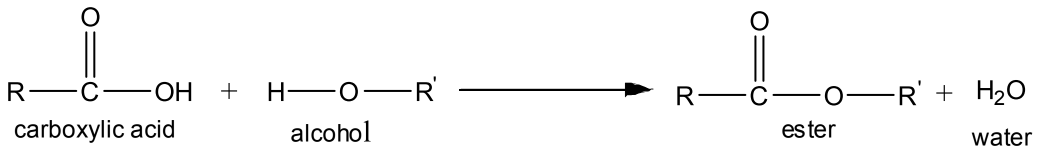
Esters generally have very pleasant odors which are associated with a variety of fruits and flowers. Some of the more common esters and their sources are listed below:

- Isobutyl formate (raspberries)
- *n*-octyl acetate (oranges)
- Methyl salicylate (oil of wintergreen)
- Isoamyl acetate (banana)
- Isobutyl propionate (rum)
- Benzyl acetate (peach)
- Methyl butyrate (apple)

Triglycerides (fats and oils) are some important esters biochemically. We will be studying them in more detail later.

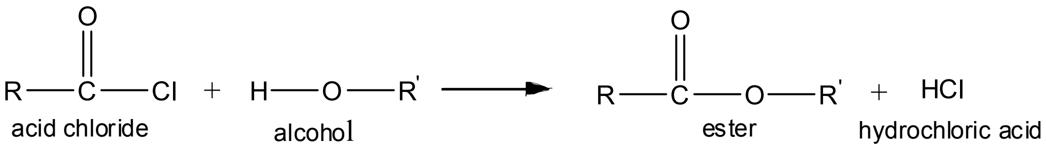
Esters may be synthesized from the reaction of a carboxylic acid (or derivative) and an alcohol as shown below:

(EQ 6.2)



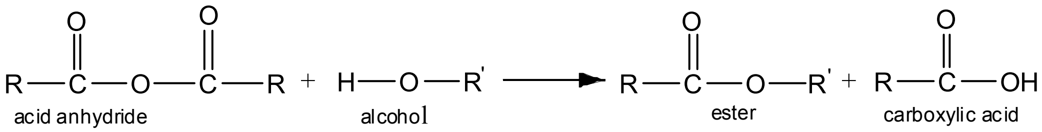
$$\mathrm{R-\overset{O}{\overset{\|}{C}}-OH} + \mathrm{H-O-R'} \longrightarrow \mathrm{R-\overset{O}{\overset{\|}{C}}-O-R'} + \mathrm{H_2O}$$

(EQ 6.3)



$$\mathrm{R-\overset{O}{\overset{\|}{C}}-Cl} + \mathrm{H-O-R'} \longrightarrow \mathrm{R-\overset{O}{\overset{\|}{C}}-O-R'} + \mathrm{HCl}$$

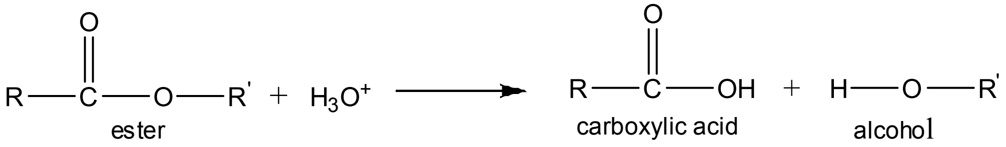
(EQ 6.4)



$$\mathrm{R-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R} + \mathrm{H-O-R'} \longrightarrow \mathrm{R-\overset{O}{\overset{\|}{C}}-O-R'} + \mathrm{R-\overset{O}{\overset{\|}{C}}-OH}$$

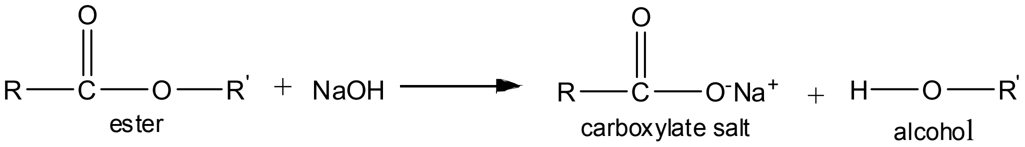
Esters may be hydrolyzed in either acid or basic solution. When the hydrolysis takes place in base it is known as saponification. You will be saponifying the esters in a triglyceride in "Saponification: Soaps and Detergents" on page 111 when you make soap. The reactions for both acid and base hydrolysis of an ester are shown below:

Acid Hydrolysis: **(EQ 6.5)**



$$R-\overset{\overset{O}{\|}}{C}-O-R' + H_3O^+ \longrightarrow R-\overset{\overset{O}{\|}}{C}-OH + H-O-R'$$

Base Hydrolysis (Saponification) **(EQ 6.6)**



$$R-\overset{\overset{O}{\|}}{C}-O-R' + NaOH \longrightarrow R-\overset{\overset{O}{\|}}{C}-O^-Na^+ + H-O-R'$$

Aspirin

Aspirin is one of the most widely used drugs available on the market. It is an analgesic (relieves minor pain of headaches etc.), and antipyretic (reduces fever), and an anti-inflammatory agent.

The medicinal properties of aspirin and some related compounds have been exploited for a very long time. Salicylic acid, a compound found in Salix (willows), has the same basic set of medicinal properties. Native Americans used willow roots and bark as a drug long before Europeans reached this continent. By 16th century the medicinal properties were well documented. By the century it was known that the active ingredient in willow extracts was the salicylic acid. Unfortunately, salicylic acid was too acidic for most people to take orally. Several attempts were made to improve upon the delivery system, among these were:

1875 - Salicylic acid was neutralized with base. This proved easier to swallow, but irritating to the stomach lining.

1886 - Phenol salicylate or Salol was synthesized. This is widely used as an intestinal antiseptic because in is not hydrolyzed by acids and passes through to the intestines where it is hydrolyzed to its active form.

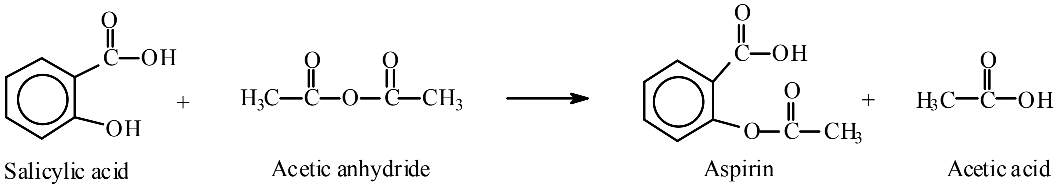
1899 - Acetylsalicylic acid or aspirin was first introduced by the Bayer chemical company. This has become the preferred delivery system.

Methyl salicylate, an oil, found in many plants, has a fragrance associated with wintergreen. When rubbed on the skin this oil penetrates it and is hydrolyzed to salicylic acid which relieves pain and soreness. Thus oil of wintergreen is used widely in liniments such as Ben-Gay.

The mechanism by which salicylic acid works is not well understood. Presently it is thought that it inhibits the synthesis of one or more prostaglandins in the body. Prostaglandins are mediators of several physiological events in the body. Alterations in the concentrations of prostaglandins thus alter certain physiological events and reductions in pain, inflammation and fever appear to be among those physiological events altered.

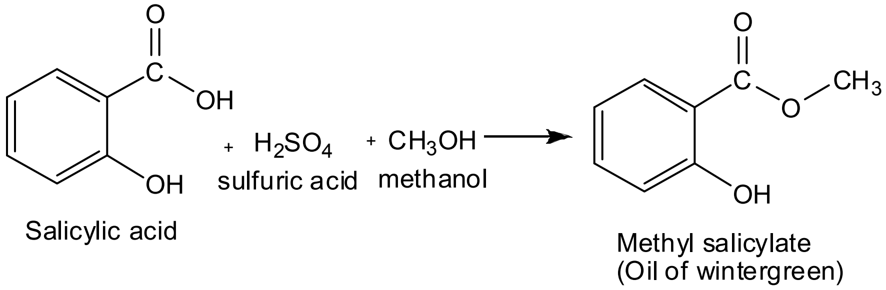
In today's experiment you will make some derivatives of salicylic acid including aspirin and oil of wintergreen. You will also study some of the properties of your aspirin and compare it to commercial aspirin. The reactions you will perform are shown below:

Synthesis of aspirin **(EQ 6.7)**



Notice we will use acetic anhydride here instead of acetic acid. This method is much more efficient than using acetic acid.

Synthesis of oil of wintergreen **(EQ 6.8)**



You must also determine the efficiency of your synthesis (%yield) and the purity of your aspirin. The **percent yield** may be calculated using the equation:

$$\%\text{ yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100\% \qquad \textbf{(EQ 6.9)}$$

where actual yield is the amount of product isolated and theoretical yield is the amount that should have been formed if all of the reactants formed products (remember your limiting reagent stoichiometry from Chemistry 115). For this experiment salicylic acid is the limiting reagent and we do the stoichiometry as follows:

(EQ 6.10)

$$\underset{\text{salicylic acid}}{C_7H_6O_3} + \underset{\text{acetic anhydride}}{C_4H_6O_3} \longrightarrow \underset{\text{aspirin}}{C_9H_8O_4} + \underset{\text{acetic acid}}{C_2H_4O_2}$$

Theoretical yield

$$4.0\text{ g } C_7H_6O_3 \times \frac{1\text{ mol } C_7H_6O_3}{138\text{ g } C_7H_6O_3} \times \frac{1\text{ mol } C_9H_8O_4}{1\text{ mol } C_7H_6O_3} \times \frac{180\text{ g } C_9H_8O_4}{1\text{ mol } C_9H_8O_4} = 5.2\text{ g } C_9H_8O_4 \qquad \textbf{(EQ 6.11)}$$

You can determine purity in several ways.

What are some of these?

What is the most likely contaminant in your aspirin?

Acetic anhydride should all be converted to acetic acid in aqueous solution. Acetic acid is water soluble and thus should be washed away.

What is the solubility of the salicylic acid?

Could it be present in your aspirin sample?

How can you test for its presence?

Experimental Design

A. Physical properties of some carboxylic acids and esters

Several carboxylic acids and esters will be available for you to observe: isoamyl acetate, methyl butyrate, methyl salicylate, isobutyl formate, and valeric acid. Note their appearance, color, physical state, and odors.

B. Synthesis of Aspirin

1. Weigh out approximately 3 g of salicylic acid and place it in a 125 mL Erlenmeyer flask.
2. Add 8 mL of acetic anhydride and 8 drops of 85% phosphoric acid.

> **Caution! Safety Notes:**
>
> Do this step in the hood since acetic anhydride is irritating. Phosphoric acid is also a skin and eye irritant, in addition to being corrosive. Wash for at least 15 minutes if you spill any on yourself.

3. Stir the reaction mixture thoroughly and heat in a boiling water bath for 5 minutes while continuing to stir.
4. Remove the flask from the waterbath, and stir 3 mL of water into the hot mixture immediately.
5. Continue to stir for several more minutes to react any excess acetic anhydride.
6. While continuing to stir add another 60 mL of water.
7. You should begin to see aspirin precipitate out of solution at this point.
8. To precipitate out the remainder of the aspirin, immerse the Erlenmeyer flask in an ice bath for about 5 minutes while continuing to stir.
9. You will now collect the aspirin you have synthesized by vacuum filtration. (Remember your recrystallization experiment.)
10. Collect, dry, and weigh your aspirin crystals. Save some crystals for use later in the experiment.

C. Synthesis of Methyl Salicylate, Isoamyl Acetate, and Ethyl Acetate

1. Take three test tubes and mix the following reagents in them:
2. Tube 1: 3 mL ethyl alcohol, 0.5 mL glacial acetic acid, and 10 drops of concentrated sulfuric acid.
3. Tube 2: 3 mL isoamyl alcohol (also known as isopentyl alcohol, $(CH_3)_2CHCH_2CH_2OH$, 0.5 mL glacial acetic acid, and 10 drops of concentrated sulfuric acid.
4. Tube 3: Salicylic acid crystals (about 1 cm deep in the tube), 2 mL methyl alcohol, and 10 drops concentrated sulfuric acid.
5. Heat the tubes by placing them in boiling water for 3 minutes.
6. After heating, pour a small amount of each product onto a piece of filter paper, carefully smell it by wafting the scent. Describe the odor.

D. Contaminants in aspirin

The presence of unreacted salicylic acid in the synthesized aspirin can be detected with the ferric chloride (aka iron(III) chloride) test.

1. Add about 2 mL of 1% ferric chloride to each of 4 test tubes.
2. Using a clean stirring rod add a few crystals of salicylic acid to the first tube, a few crystals of your aspirin to the second tube, and some crushed commercial aspirin to the third tube.
3. Add nothing to the fourth tube; this will serve as a blank control.
4. Stir each solution thoroughly and observe the colors produced.

The presence of starch in commercial aspirin can be detected with the starch test.

1. Add about 2 mL of deionized water to each of three test tubes.
2. To the first add a few crystals of your aspirin, to the second add some crushed commercial aspirin, and use the third as a control.
3. To each test tube add one drop of iodine solution. A blue-black color will indicate the presence of starch.
4. Record your observations.

Why might starch be added to commercial aspirin preparations?

Prelaboratory Exercises: Aspirin

Name: ______________________________ Section: ______________

1. Write an equation for the acid hydrolysis of aspirin.

2. Give the molecular formula and mass of the following compounds:

TABLE 6.1

	benzene	benzoic acid	phenol
molecular formula			
molecular mass			

3. Draw the structure of *n*-butyl benzoate and label the “acid” and “alcohol” portions of this ester.

4. Write the reaction for the acid hydrolysis of *n*-butyl benzoate.

5. Write the reaction for the saponification of *n*-butyl benzoate.

Lab Report: Aspirin

Name: ____ Section: __________________

A. Physical Properties of Carboxylic Acids and Esters

TABLE 6.2

Compound	Physical description	Odor
isoamyl acetate		
methyl butyrate		
methyl salicylate		
isobutyl formate		
valeric acid		

B. Synthesis of Aspirin

TABLE 6.3

Before reaction	
Mass of weighing paper + salicylic acid	
Mass of weighing paper	
Mass of salicylic acid	
After reaction	
Mass of dry filter paper + aspirin	
Mass of dry filter paper	
Mass of aspirin	

Calculate the mass of aspirin that should have been obtained. Show all work.

Calculate the percent-yield of your synthesis. Show all work.

C. Synthesis of Esters

TABLE 6.4 Name and describe the esters made in each of the test tubes.

Tube Number	Ester Name	Description
1		
2		
3		

Write an equation for the reaction that occurred in test tube 1.

Write an equation for the reaction that occurred in test tube 2.

Write an equation for the reaction that occurred in test tube 3.

D. Contaminants in aspirin

TABLE 6.5 **Ferric Chloride Test**

Test Tube	Observation	Phenol Present?
blank		
salicylic acid		
commercial aspirin		
your aspirin		

TABLE 6.6 **Starch test**

Test Tube	Observation	Starch present?
blank		
commercial aspirin		
your aspirin		

Why might starch be added to commercial aspirin preparation?

Post Lab Questions

1. Sodium salicylate has been used as an analgesic.
   a. Draw the structure of this compound.

   b. Show how you could prepare it from salicylic acid.

2. Isopentyl pentanoate (aka isopentyl valerate) is associated with the smell of ripe apples.
   a. Write the structure for this ester.

   b. Write an equation for its saponification.

3. What mass of aspirin can be prepared by reacting 3.00 g of salicylic acid with an excess of acetic anhydride? Show your work.

4. If 3.16 g of aspirin were recovered from the synthesis in question 3 what would be the percent yield?

5. Aspirin that has been stored for a long time may give a vinegar-like odor. If this aspirin is tested with ferric chloride it will give a purple colored solution. Explain the results.

6. Draw each of the following esters

Isobutyl formate (raspberries)

n-octyl acetate (oranges)

Methyl salicylate (oil of wintergreen)

Isoamyl acetate (banana)

Isobutyl propionate (rum)

Benzyl acetate (peach)

Methyl butyrate (apple)

EXPERIMENT 7

Amines, Amides and Amino Acids

Objective

1. To learn about the physical and chemical properties of some of the common members of the amine and amide families.
2. To recognize the commercial and physiological value of some amines and amides.
3. To examine those reactions of amines and amides that are important in physiology and biochemistry, particularly in the hydrolysis of proteins.

Introduction

Amines

Amines may be viewed as derivatives of ammonia that are formed by successive replacement is the hydrogens of ammonia with alkyl or aromatic groups.

EXAMPLE 7.1

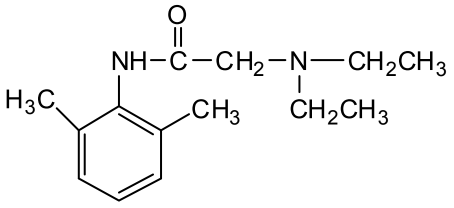
NH_3	CH_3NH_2	$(CH_3)_2NH$	$(CH_3)_3N$
ammonia	methylamine	diethylamine	triethylamine
	primary amine	secondary amine	tertiary amine

As you will observe in today's lab amines and ammonia share many chemical and physical properties in particular their odors. Amines may be classified as primary, secondary or tertiary based upon the number of alkyl groups attached (like alcohols). Molecules with multiple amino groups are classed as diamines or triamines. Other classes of amines include aromatic amines in which one of the alkyl groups is replaced by an aromatic group, and heterocyclic amines in which the nitrogen is found in a ring. Examples of these amines follow.

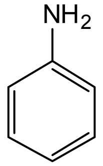
EXAMPLE 7.2 **Some common diamines are:**

1,6-diaminohexane	1,5-diaminopentane
$NH_2(CH_2)_6NH_2$	$NH_2(CH_2)_5NH_2$
precursor to nylon	cadaverine

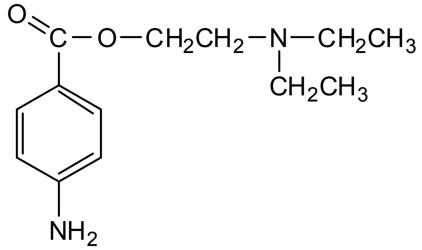
EXAMPLE 7.3 **Some common aromatic amines are:**



Lidocaine (Xylocaine)

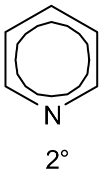


Aniline

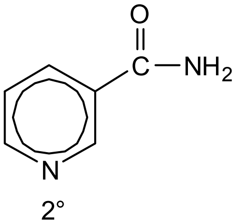


Procaine (Novocaine)

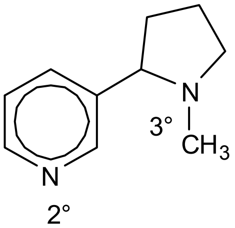
EXAMPLE 7.4 **Some common heterocyclic amines are:**



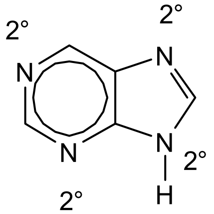
Pyridine



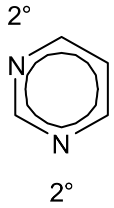
Nicotinamide (niacin)



Nicotine



Pyrimidine



Purine

Reactions of amines with water

All types of amine react with water similarly to ammonia to form an ammonium ion (or substituted ammonium ion) and the hydroxide ion. General equations for this reaction follow:

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$ **(EQ 7.1)**

ammonia + water →ammonium ion + hydroxide ion

$$NR_3 + H_2O \rightleftharpoons R_3NH^+ + OH^-$$ **(EQ 7.2)**

tertiary amine + water → substituted ammonium ion + hydroxide ion

The amines form solutions which are weakly basic to litmus. Substitutes amines are generally slightly more basic than ammonia and aromatic amines are slightly less basic than ammonia.

Reactions of amines with acids

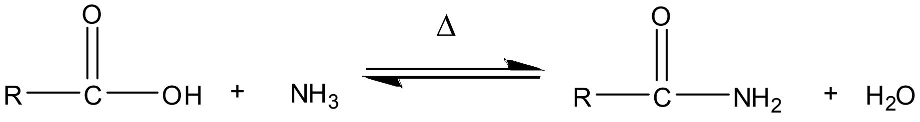
Amines (insoluble bases) react with acids to form soluble salts as shown:

$$HCl \;+\; R_3N \rightarrow R_3NH^+\,Cl^-$$ **(EQ 7.3)**

hydrochloric acid + water soluble 3° amine → water soluble amine hydrochloride

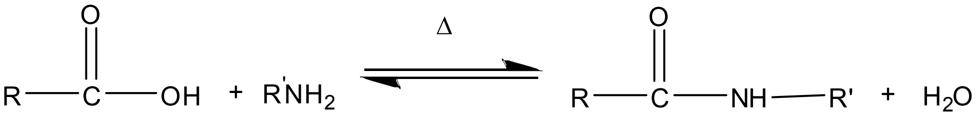
Amines react with carboxylic acids to form amides as shown:

(EQ 7.4)



$$R-\overset{O}{\overset{\|}{C}}-OH + NH_3 \overset{\Delta}{\rightleftharpoons} R-\overset{O}{\overset{\|}{C}}-NH_2 + H_2O$$

(EQ 7.5)

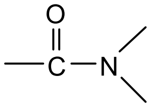


$$R-\overset{O}{\overset{\|}{C}}-OH + R'NH_2 \overset{\Delta}{\rightleftharpoons} R-\overset{O}{\overset{\|}{C}}-NH-R' + H_2O$$

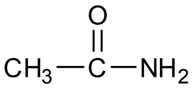
Notice that tertiary amine do not form amides. Why?

Amides

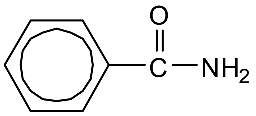
Amides are composed of a carbonyl (C=O) which is bonded to both an alkyl (or aromatic) group and an amine group. Some common amides follow:



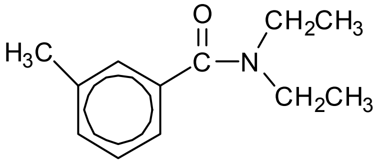
Amide group



Acetamide
(a primary amide)



Benzamide
(a primary aromatic amide)



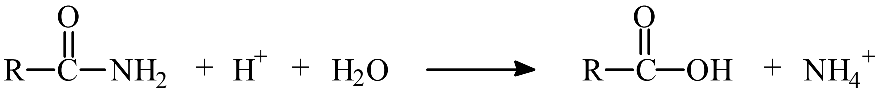
N,N-diethyl-m-toluamide
Off insect repellent
(a tertiary amide)

Reactions of amides

Acid hydrolysis - amides decompose to carboxylic acids and ammonium salts when heated in acid solution

.

(EQ 7.6)

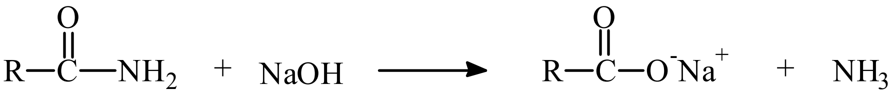


$$R-\overset{O}{\overset{\|}{C}}-NH_2 + H^+ + H_2O \longrightarrow R-\overset{O}{\overset{\|}{C}}-OH + NH_4^+$$

Upon reaction with base ammonia will be liberated and will be detected by its characteristic odor.

Base hydrolysis - amides decompose to carboxylate salts and amines when heated in basic solution.

. **(EQ 7.7)**

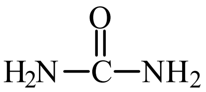


$$R-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2 + NaOH \longrightarrow R-\overset{\overset{\displaystyle O}{\|}}{C}-O^-Na^+ + NH_3$$

Ammonia will be detected as hydrolysis proceeds.

Urea (methanediamide using IUPAC nomenclature), a diamide, will undergo hydrolysis in both acid and base solutions:

FIGURE 7.1



$$H_2N-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2$$

Urea

In acid solution carbonic acid, H_2CO_3, is formed which decomposes further to water and carbon dioxide:

$$H_2CO_{3\,(aq)} \rightarrow H_2O_{(l)} + CO_{2\,(g)} \quad \textbf{(EQ 7.8)}$$

In basic solution ammonia, NH_3, and sodium carbonate, Na_2CO_3, are formed.

A **salt** is an ionic compound, which is composed of cations and anions that are held together by electrostatic forces.

EXAMPLE 7.5 sodium chloride, NaCl, or carboxylate salts, RCO_2Na.

A **molecular compound** is a compound in which atoms are held together by covalent bonds.

EXAMPLE 7.6 carbon dioxide, CO_2, water, H_2O.

A **colloid** is a suspension of tiny particles (20-100 μm in diameter) in a gas, liquid, or solid. Colloids are often classified between homogeneous and heterogeneous mixtures. The small particles give the colloid the appearance of being homogeneous, but are large enough to scatter light.

EXAMPLE 7.7 milk, mayonnaise, whipped cream, orange juice, gelatin desserts, and marshmallows.

Experimental Design

A. Comparison of some common amines and amides

1. Several common amines and amides are located in the hood.
2. Compare the odors of these compounds.

   Can you make any hypotheses regarding their relative volatilities?

   What structural features might contribute to differences in volatility?

   Note the odor of acetamide.

   Does it smell like ammonia?
3. Test the solubility of *n*-butylamine in water by stirring 6 drops of amine into 1 mL of water.
4. Note the odor of the aromatic amine aniline and of the heterocyclic amine pyridine.
5. Examine the insect repellent Off, noting the odor of the amide N,N-diethyl-*m*-toluamide.

B. Amines and amides as bases-Reactions of amines with acids: Salt formation

1. Obtain a drop of butylamine on a dry clean stirring rod and hold the amine close to the open mouth of a bottle of concentrated hydrochloric acid, HCl. Watch what happens.
2. Stir an amount of benzoic acid the size of a pea into 2 mL of distilled water. Does the benzoic acid dissolve?
3. Next stir in drops of butylamine until the solution is strongly basic to litmus. Note any change in the solubility of benzoic acid.
4. Add 10 drops of aniline to 5 mL of water and stir. Does the aniline dissolve?
5. Now add drops of concentrated hydrochloric acid, while stirring, until the solution is strongly acidic to litmus. Does the aniline dissolve?

C. Hydrolysis of amides

Acidic hydrolysis

1. Dissolve about 1 g of acetamide in 5 mL of 10% sulfuric acid in a test tube and heat in a boiling water bath.
2. Identify the odor of the compound that is formed and use moist blue litmus paper to confirm its presence in the vapor.
3. Record your observations.
4. Now add concentrated sodium hydroxide solution by drops to the cooled hydrolysis solution until it is basic.

   What gas do you smell?

Basic Hydrolysis

1. Dissolve 1 g of urea in 2 mL of 10% sodium hydroxide in a test tube.
2. Heat the solution in a boiling water bath and note the odor of the escaping gas.
3. Now make the solution acidic to litmus by adding drops of 10% sulfuric acid solution.

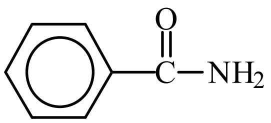
   Is a gas formed?

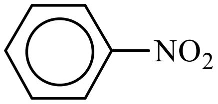
   What is it?

Prelaboratory Exercise: Amines, Amides, and Amino Acids

Name: ____________________________________ Section: ________________

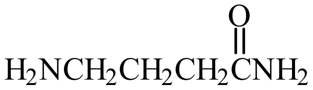
1. Classify each of the following as an amine, an amide, both, or neither:

a  ______________________________

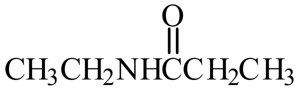
b  ______________________________

c $CH_3CH_2NHCH_2CH_3$ ______________________________

d $(CH_3)_4N^+I^-$ ______________________________

e 

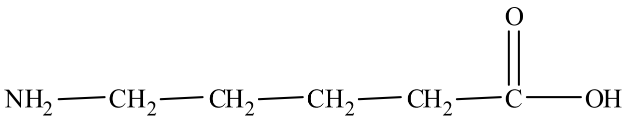
$\mathrm{H_2NCH_2CH_2CH_2\overset{O}{\overset{\|}{C}}NH_2}$ ______________________________

f 

$\mathrm{CH_3CH_2NH\overset{O}{\overset{\|}{C}}CH_2CH_3}$ ______________________________

2. Write an equation for the reaction between aniline and nitric acid.

3. Draw the cyclic amide product of:



$$\mathrm{NH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OH}$$

4. Write equation for the hydrolysis of urea in acidic solution.

5. Write equation for the hydrolysis of urea in basic solution.

Lab Report: Amines, Amides, and Amino Acids

Name: ____ Section: __________________

A. Some common Amines and Amides

TABLE 7.8

Compound	Structure	Primary, secondary, or tertiary	Odor
ammonia			
butyl amine			
pyridine			
aniline			
N,N-diethyl-*m*-toluamide (Off)			
dibutyl amine			
tributyl amine			

Draw the structure of an amine which is an isomer of butylamine.

Is *n*-butyl amine soluble in water? _________

B. Amines as Bases-Reactions of Amines with Acids: Salt Formation

1. What happens when butylamine is held close to the mouth of a bottle of concentrated hydrochloric acid?

   What is the structure of the compound formed which looks like smoke?

What kind of compound is it? (Molecular? Salt? Colloidal?) ___________________________

Write an equation for the reaction that takes place.

2. Does benzoic acid dissolve in pure water? __________

Does it dissolve when butylamine is added? __________

Write an equation for the reaction that takes place.

Suppose the solution containing the products of the reaction between butylamine and benzoic acid was evaporated to dryness and then heated to form an amide. What would be the structure of the amide?

3. Does aniline dissolve in water? _________

Does it dissolve in concentrated hydrochloric acid? __________

If so, why?

C. Hydrolysis of Amides

Acidic Hydrolysis

Give the name and structure of the volatile compound that you smelled when acetamide was hydrolyzed in acidic solution.

Write an equation for the reaction that takes place.

What is the name of the gas you smelled when the hydrolysis was made basic?

Write an equation for the reaction.

Basic Hydrolysis

What gas did you smell when urea was hydrolyzed in basic solution?

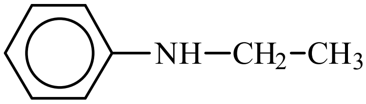
Write an equation for the reaction.

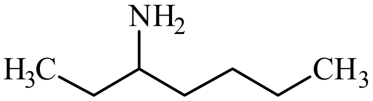
Was a gas formed when the solution was made acidic?

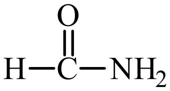
If so, write an equation for the formation of this gas.

Post Lab Questions

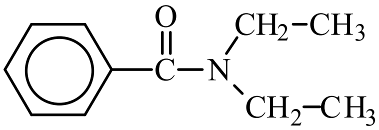
1. Name the following compounds.

a. 

b. 

c. 

$\mathrm{H-\overset{\overset{O}{\|}}{C}-NH_2}$

d. 

a. ______________________________

b. ______________________________

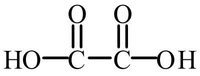
c. ______________________________

d. ______________________________

2. Is niacin a primary, secondary, or tertiary amide? ____________________

3. Write a complete equation for the formation of benzamide from benzoic acid and ammonia.

4. Oxalic acid is a dicarboxylic acid found in rhubarb and oxalis.



$HO-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle O}{\|}}{C}-OH$

Oxalic acid

Draw a structural formula for the diamide of this acid.

EXPERIMENT 8 *Carbohydrates*

Objectives

1. To become familiar with several of the common carbohydrates.
2. To learn the significant differences in the physical and chemical properties of monosaccharides, disaccharides and polysaccharides.
3. To learn some of the important metabolic reactions of carbohydrates.

Introduction

Carbohydrates are the principal components of plants (60-90% by weight). They are also the primary source of energy for animals. Carbohydrates can be classed into three main groups:

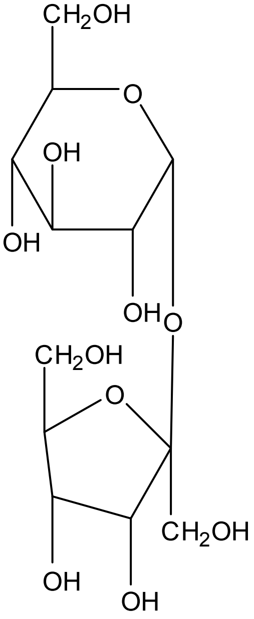
1. **Monosaccharides**-Not broken down into simpler carbohydrates by hydrolysis. These are the simple sugars.
   EXAMPLE 8.1 glucose, fructose
2. **Disaccharides** -Composed of two monosaccharides, may be broken down into simpler sugars by acid hydrolysis.
   EXAMPLE 8.2 sucrose, lactose
3. **Oligosaccharide** -A carbohydrate containing from three to ten monosaccharide units, each joined to the next by a glycoside bond.
   EXAMPLE 8.3 Fructooligosaccharide consist of short chain of fructose joined together by glycosidic bonds. Are found in many vegetables.
4. **Polysaccharides**-Composed of more than two monosaccharides, may be broken down into simpler sugars by acid hydrolysis.
   EXAMPLE 8.4 starch, cellulose

Physical Properties of Carbohydrates

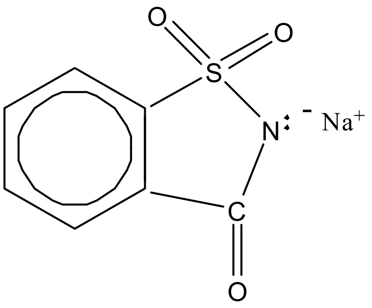
All monosaccharides and disaccharides, and some polysaccharides, are soluble in water but insoluble in organic solvents. Carbohydrates, which are actually polyalcohols, form hydrogen bonds with water. Concentrated sugar solutions (for example, honey) are viscous syrups which are supersaturated and which crystallize slowly.

Sucrose (table sugar) and many other members of the family have a sweet taste. The degree of sweetness depends on the particular structure. Some compounds with unrelated structures (for example saccharin) are far sweeter than sugar.

FIGURE 8.1



Sucrose



Saccharine
(an artificial sweetner)

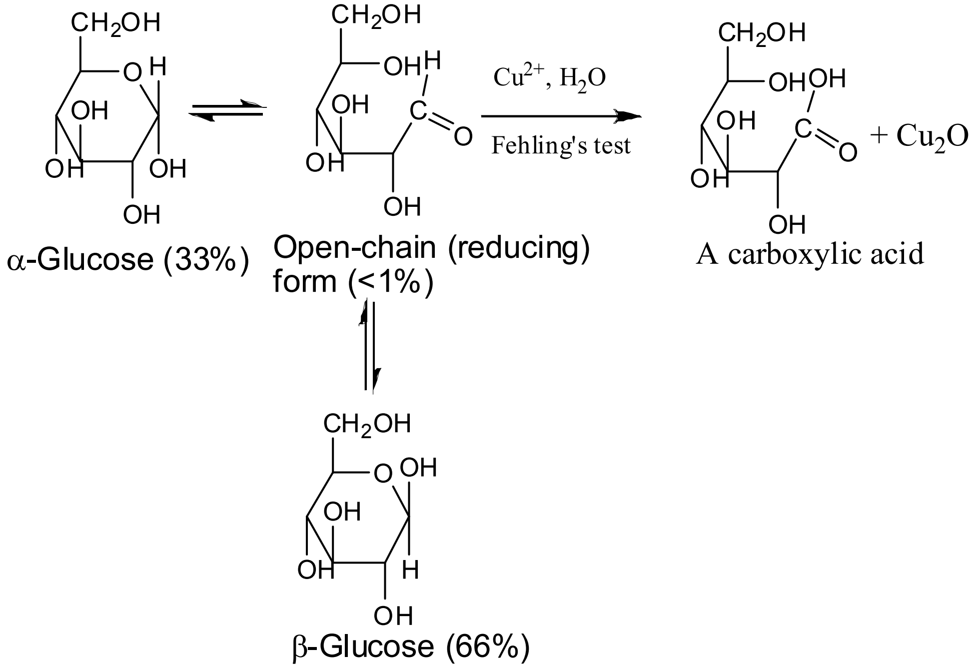
TABLE 8.5 **Some Common Carbohydrates:**

Carbohydrate	Class	Source	Composition
Glucose	mono	honey	
Fructose	mono	honey	
Galactose	mono		
Mannose	mono		
Xylose	mono		
Maltose	di	corn syrup	glucose
Sucrose	di	sugarcane, sugar beets, maple sap, etc	fructose and glucose
Lactose	di	milk	glucose and galactose
Starch (amylose and amylopectin)	Poly	seeds, tubers	glucose
Glycogen	poly	Liver tissue, muscle tissue	glucose
Cellulose	poly	plant cells, wood, cotton, paper	glucose
Inulin	poly	artichokes, dahlias	fructose
xylans	poly	wood, straw, corncobs, grain hulls	

Reducing sugars

All monosaccharides and many disaccharides reduce weak oxidizing agents such as the cupric ion, Cu^{2+}, in Fehling's reagent. These carbohydrates are called reducing sugars. To function as a reducing sugar, a carbohydrate must have an aldehyde functional group or a hemiacetal functional group, which can open to become an aldehyde. For the three forms of glucose, only the open-chain (acyclic form) is oxidized by Fehling's reagent. You will test the reducing ability of several carbohydrates in today's experiment.

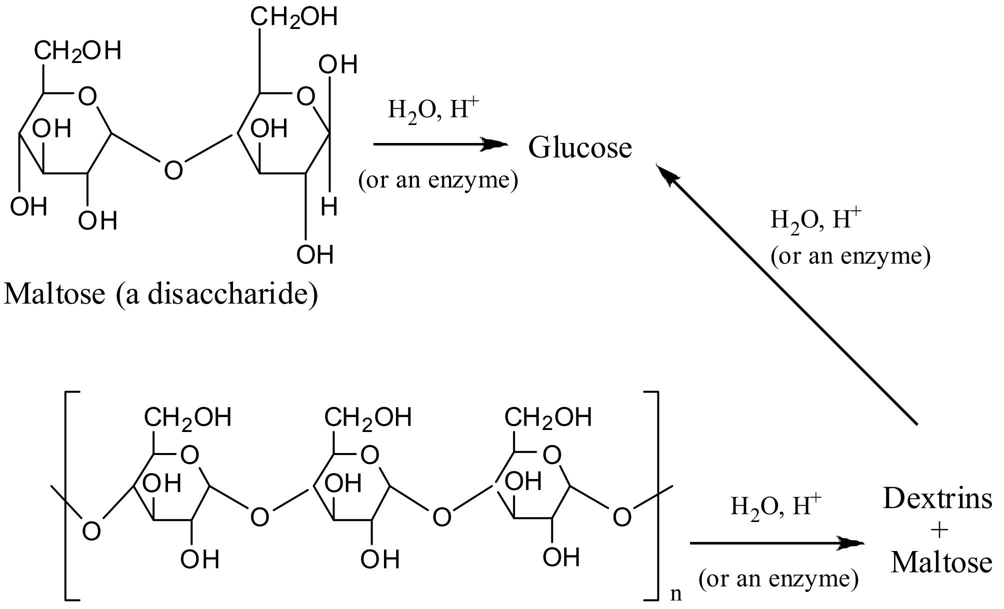
FIGURE 8.2



Hydrolysis of disaccharides and Polysaccharides

Hydrolysis of the acetal bonds in disaccharides (see maltose) gives monosaccharides. Hydrolysis of polysaccharides such as amylose and amylopectin proceeds in stages and yields several products. Cleavage of all of the acetal bonds (complete hydrolysis) produces only glucose. Partial hydrolysis of a few random bonds gives many shortened starch molecules, called dextrins, and some maltose. Maltose molecules result whenever an acetal bond remains between two glucose units.

FIGURE 8.3



Corn syrup, a mixture obtained form the partial hydrolysis of corn starch, contains considerable maltose.

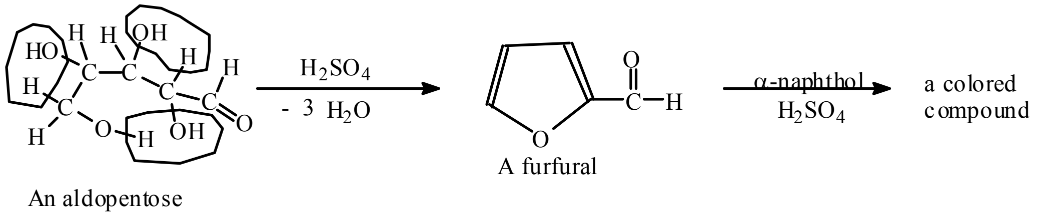
In this experiment, you will determine the effect of hydrolysis in the reducing capability of carbohydrates.

What do you predict the effect will be?

Dehydration of Carbohydrates: The Molisch Test

Carbohydrates, like most alcohols, undergo dehydration reactions in the presence of concentrated sulfuric acid. Pentoses (five carbon sugars) give furfural, and ketohexoses and aldohexoses give substituted furfurals. This is the basis of the Molisch test, a general carbohydrate test in which furfural and the substituted furfurals formed by dehydration of monosaccharides with sulfuric acid react with α-naphthol to form colored compounds.

(EQ 8.1)



You will use the Molisch test to detect carbohydrates in several common foods.

The Starch-Iodine Complex

Starches consist of a mixture of amylose and amylopectin. Potato starch, for example, is 90% amylopectin and 10% amylose. Amylose reacts with iodine, I2, to give an intense blue-black complex, and amylopectin and iodine form a red-purple complex. The color is due to weak bonds between the starch and iodine molecules. Large starch molecules are necessary for the complex to form. Partial hydrolysis of the starch molecules gives dextrins which do not undergo this reaction.

Experimental Design

A. Carbohydrates as Reducing sugars

1. Perform Fehling's test on 2% solutions of the following carbohydrates: lactose, sucrose, glucose, fructose, and starch. Also test solutions of honey and corn syrup.
2. Prepare 50:50 mixtures of each with water. Proceed as follows.
3. To each clean, dry test tube add 10 drops of the carbohydrate solution and 5 mL of Fehling's reagent.
4. Stir thoroughly.
5. Place the test tubes in a boiling water bath for 10 minutes.
6. Record your observations.

B. Hydrolysis of Disaccharides and Polysaccharides

You will study the hydrolysis of starch and sucrose by testing for the formation of reducing sugar with Fehling's reagent. You will use the iodine test to provide further conformation of the hydrolysis of starch.

1. Refresh your memory of the color of the starch-iodine complex by adding 1 drop of dilute iodine to 10 drops of the 2% starch solution of a watch glass.

   What is the color of the complex?
2. Now perform the hydrolysis in the following manner.
3. Stir 2 drops of concentrated hydrochloric acid into 2 mL of the 2% starch solution and into 1 mL of the 2% sucrose solution in a second test tube.
4. Label the test tubes and place them in a boiling water bath for 10 minutes.
5. Next, carry out the iodine test on 10 drops of the hydrolyzed starch solution on a watch glass.

   Has hydrolysis of the starch occurred?
6. Test further for hydrolysis of the starch and the sucrose solutions by neutralizing the acid in each solution with 10% sodium hydroxide (add drop by drop, stirring, until the solution is just basic to litmus) and adding 5 mL of Fehling's reagent.
7. Heat in the water bath for 10 minutes.

   Does Fehling's test indicate that hydrolysis has occurred?

C. The Molisch Test: A General Carbohydrate Test

1. First conduct the Molisch test with glucose to serve as a point of reference. Into 10 drops of a 2% glucose solution in a small test tube, stir 1 drop of Molisch reagent (5% -naphthol in ethanol).
2. Now tilt the test tube and carefully drop 10 drops of concentrated sulfuric acid down the side of the test tube, so that the sulfuric acid forms a layer on the bottom.

Caution! Safety Notes:

Concentrated H_2SO_4 is dangerous! If you come in contact with the acid, wash it off immediately.

3. Note the color at the interface between the acid ant the aqueous solutions.
4. Now perform the Molisch test on 10 drops of each of the following solutions: a nonreducing disaccharide (2%), a ketose (2%), honey (50%), corn syrup (50%), and flour (suspension made by mixing a pea-sized amount with 10 drops of water).

D. Tests for Starch in Food Products

1. Place a few drops of the iodine test solution on the following food products: a slice of potato, a piece of white bread, powdered celery, powdered onion, and some powered macaroni
2. Report your observations.

Prelaboratory Exercise: Carbohydrates

Name: ____ Section: __________________

1. Draw and give the names of a common aldohexose and a common ketohexose.

2. Do you predict that maltose will reduce cupric ion in Fehling's reagent in today's experiment? Why or why not?

3. Describe the structures of dextrin, maltose and amylose. How do they differ?

4. Draw structures for the molecules present in an equilibrium mixture of glucose in water solution.

Lab Report: Carbohydrates

Name: ______________________________ Section: ______________

A. Carbohydrates as Reducing sugars

Classify the sugars tested as reducing or nonreducing.

TABLE 8.6

Carbohydrate	Reducing sugar	Non-reducing sugar
Lactose		
Sucrose		
Glucose		
Fructose		
Starch		
Honey		
Corn syrup		

TABLE 8.7 Explain why two of the carbohydrates are non-reducing. Why were they unable to reduce the Fehling's Reagent and be oxidized? (The reasons of the failure are different for the two carbohydrates.)

Carbohydrate	Why non-reducing?

B. Hydrolysis of Disaccharides and Polysaccharides

What was the color of the initial iodine test on the starch solution?

After the starch solution was heated in the water bath for 10 minutes, did the iodine test indicate that hydrolysis had occurred? Why or why not?

Did the Fehling's test confirm that the starch had been hydrolyzed? Why or why not?

Did Fehling's test indicate that hydrolysis of sucrose had occurred after 10 minutes? Why or why not?

Give the names of the product(s) that were formed upon hydrolysis of sucrose.

Give the names of the product(s) that were formed upon hydrolysis of starch.

C. The Molisch Test: A General Carbohydrate Test

TABLE 8.8 Give the types of the monosaccharides contained in each carbohydrate and the color obtained for each in the test.

Type of Carbohydrate	Types of monosaccharides	Color
A nonreducing disaccharide Name		
A ketose Name		
Honey		
Corn Syrup		
Flour		

What type of reaction occurs with each carbohydrate in the Molisch test?

What type of organic product is formed?

D. Tests for starch in Food products

TABLE 8.9

Food	Color	positive	negative
Slice of potato			
Piece of white bread			
Powdered Celery			
Powdered Onion			
Powdered macaroni			

Post Lab Questions

1. Suggest how you might make “honey” from table sugar.

2. Draw the structure of a segment of an amylose molecule, and then show the reaction with water to break the acetal bonds.

3. What type of monosaccharide polymerizes to form inulin?

4. On the basis of today's experiment, suggest a way to determine whether a compound is amylose or inulin.

5. Compare the product that would be obtained from hydrolysis of a 50:50 mixture of inulin and amylose with the hydrolysis product of sucrose.

EXPERIMENT 9

Saponification: Soaps and Detergents

Objectives

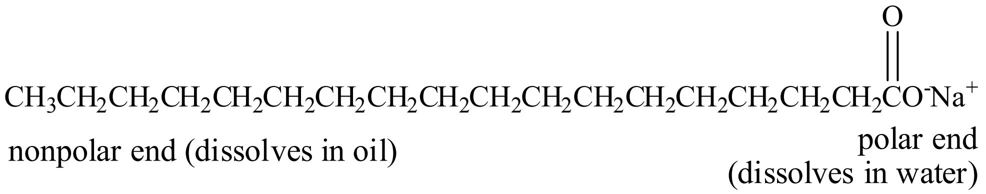
1. To carry out and make observations on the saponification of a triglyceride (a fat).
2. To prepare a soap and examine its properties.
3. To isolate a mixture of fatty acids obtained by acidification of a soap solution.
4. To gain an understanding of the cleansing action of soaps and detergents in hard and soft water.

Introduction

Soap is the salt of a long-chain fatty acid (generally sodium or potassium salts). The fatty acid usually contains 12 to 18 carbon atoms. Solid soaps usually consist of sodium salts of fatty acids, whereas liquid soaps consist of the potassium salts of fatty acids. Potassium soaps are more soluble than sodium soaps and readily produce a lather. Therefore, potassium soaps are used to make liquid soap and shaving cream. Soaps formed from highly saturated, solid fats, such as tallow, lard, or shortening, are hard. Saponification of an unsaturated oil, such as olive oil, gives a soft soap.

A soap, such as sodium stearate, consists of a nonpolar ion (the hydrocarbon chain of the fatty acid) and a polar end (the ionic carboxylate).

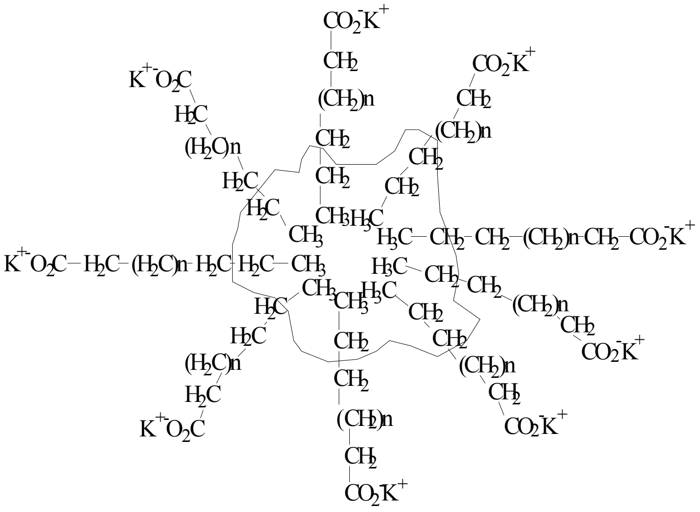
FIGURE 9.1



$$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2\overset{\overset{\displaystyle O}{\|}}{C}O^-Na^+$$

Since “like dissolves like,” the nonpolar end (**hydrophobic** or water hating) of the soap molecule can dissolve the greasy dirt, and the polar or ionic end (**hydrophilic** or water loving) of the molecule is attracted to water molecules; therefore, the dirt from the surface cleaned will be pulled away and suspended in water. Thus, soap acts as an emulsifying agent, a substance used to disperse one liquid (oil molecules) in the form of finely suspended particles or droplets in another liquid (water molecules). The soaps emulsify the fats by forming micelles as pictured in the figure below:

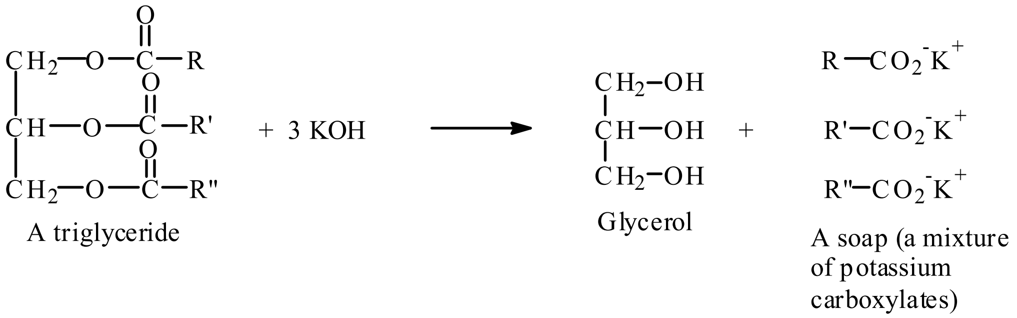
FIGURE 9.2 A Soap Micelle. Soap molecules surround an oil droplet and stick their hydrocarbon tails into it, thus making the entire micelle soluble.



Saponification of Triglycerides

Treatment of fats or oils with strong bases such as lye (NaOH) or potash (KOH) causes them to undergo hydrolysis (saponification) to form glycerol and the salt of a long-chain fatty acid (soap).

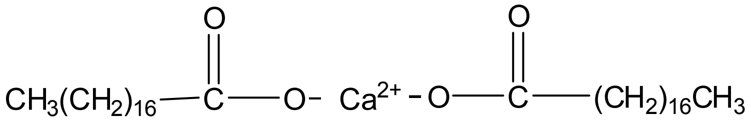
(EQ 9.1)



Salts are made from strong bases and weak acids, they form weakly basic compounds. It is important to test the basicity of soaps because any alkali remaining from the saponification reaction can damage skin, and fabrics. You will test the soap you make for bacisity.

Soaps do not work will in hard water, because the divalent cations of dissolved minerals (Ca^{2+}, Mg^{2+}, and Fe^{2+}) form precipitates with the carboxylate (fatty acid anions of soaps. Consequently, a scum of calcium stearate (and other slightly soluble soaps) is typically found as a ring in the bathtub or as a dingy film on clothes, hair, or skin.

FIGURE 9.3

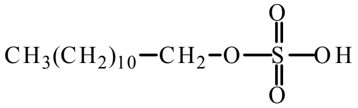


$$CH_3(CH_2)_{16}-\overset{\overset{\displaystyle O}{\|}}{C}-O^- \; Ca^{2+} \; {}^-O-\overset{\overset{\displaystyle O}{\|}}{C}-(CH_2)_{16}CH_3$$

Calcium stearate (a scum in hard water)

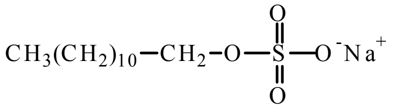
One way to avoid the formation of scum is to precipitate the Ca^{2+} ions from the solution before adding the soap using baking soda for example. Detergents are often mixtures that may contain fillers (to generate bulk), foam-reducing agents, and bleach. Sometimes the additional additives fluoresce (absorb ultraviolet rotation and then produce visible light) to give the appearance of better cleaning power. Their most important component is a **surfactant**, or surface active agent, that takes the place of soap. Synthetic detergents differ from soaps in that they are salts of long-chain alkyl sulfuric acids or alkylbenzenesulfonic acids, rather than carboxylic acids. They also have a hydrophilic head group and a hydrophobic tail and act similarly.

FIGURE 9.4



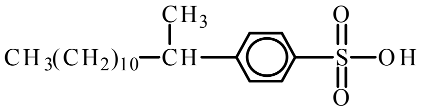
$$CH_3(CH_2)_{10}-CH_2-O-\underset{\underset{\displaystyle O}{\|}}{\overset{\overset{\displaystyle O}{\|}}{S}}-OH$$

An alkyl sulfuric acid

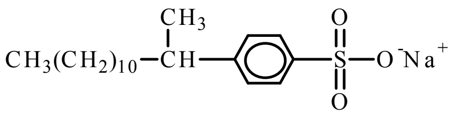


$$CH_3(CH_2)_{10}-CH_2-O-\underset{\underset{\displaystyle O}{\|}}{\overset{\overset{\displaystyle O}{\|}}{S}}-O^-Na^+$$

An alkyl sulfate salt
(a detergent)



An alkylbenzenesulfonic acid

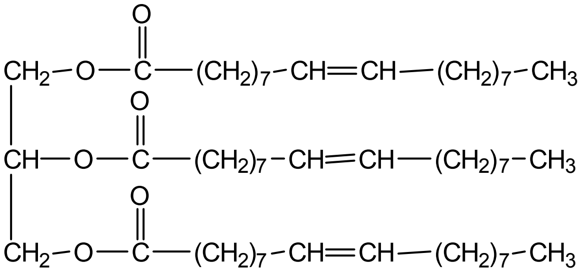


An alkylbenzenesulfonate salt
(a detergent)

These alkyl sulfate and alkyl sulfonate anions of detergents do not form precipitates with these cations as do soaps and therefore are much more effective in hard water.

Olive oil contains mostly triolein, which has three oleic acids. Oleic acid, a monounsaturated fatty acid, is a component of all fats and oils, but is especially abundant in olive and peanut oils.

FIGURE 9.5 Olive Oil



Experimental Design

A. Saponification of a Fat: Preparation of a Potassium Soap

1. Measure 1.5 g (≅ 1 mL) of lard or 5 mL of corn oil into a 125 mL Erlenmeyer flask.
2. Add10 mL of a 10% potassium hydroxide/ ethanol solution.
3. Place the flask in a a boiling hot water bath (a 400 mL beaker containing about 200 mL of water and a few boiling chips) and clamp to the ring stand.
4. While stirring the mixture constantly, the flask with is contents is heated gently for about 20 minutes.

> ⚠ **Caution! Safety Notes:**
>
> If the ethanol/soap mixture ignites, cover the flask with a watch glass to extinguish the flames.

5. After heating, add 30 mL of deionized water.
6. The flask now contains a mixture of the soap, glycerol, and any excess potassium hydroxide. Stir the mixture well to dissolve the soap you have formed.
7. When soap is dissolved cool the mixture in an ice bath and divide into two equal parts.
8. You will precipitate a sodium soap from one half and *save* the other half for later tests.

B. Formation of a Sodium Soap

A sodium soap is prepared from a potassium salt by a process known as “salting out”.

1. To *half* of the potassium soap add 15 mL of a saturated sodium chloride solution.

> **NOTE:** Remember to keep the other half for parts C and D!

2. Stir and let the sodium soap that precipitates out settle for about 10 minutes.
3. Collect the sodium soap by gravity filtration.
4. Set the soap aside to dry until needed in part 4.

C. Preparation of Fatty Acids from a Soap

1. Acidify 3 mL of the potassium soap solution you set aside in part A by adding dilute hydrochloric acid, drop by drop, until the solution is acidic to litmus.

   Does the mixture suds like soap when you shake it?

2. Remove a little of the precipitate with a spatula and try to dissolve it in an organic solvent such as acetone.

   Does it dissolve?

   Try some of the vegetable oil, is it soluble in acetone?

D. Properties of Soaps and Detergents

1. Test a 10% solution your potassium soap, a 10% solution of your sodium soap, Ivory soap, and a 10% solution of detergent as outlined below:
   a. Sudsing action - Shake a 1 mL sample with water and observe whether it forms suds.
   b. Cleansing action - Smear some vegetable oil on a watch glass. Which of the soaps ad detergents remove the oil residue?
   c. Precipitation in hard water - Hard water contains calcium, magnesium, and or iron. To three 1 mL samples of each sample add 10 drops of calcium chloride (0.1%), magnesium chloride (0.1%), and ferrous chloride (0.1%), respectively.

   Do precipitates form?

   Try mixing each with a sample of tap water?

   What does this tell you about the tap water in El Cajon?

   d. Basicity - Test each of the samples with pH paper and record the approximate acidity of each.

Prelaboratory Exercises: Saponification: Soap and Detergents

Name: ____ Section: __________________

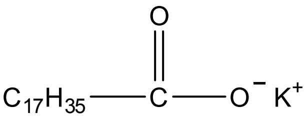
1. Define the following terms:

  a. Hydrophobic

  b. Hydrophilic

  c. Saponification

2. The chemical formula of a soap is



$$C_{17}H_{35}-\overset{\displaystyle O}{\overset{\|}{C}}-O^{-}\ K^{+}$$

Indicate which end of the soap molecule is nonpolar and which end is polar.

3. Why is the use of a soap in hard water impractical? Explain with a chemical equation.

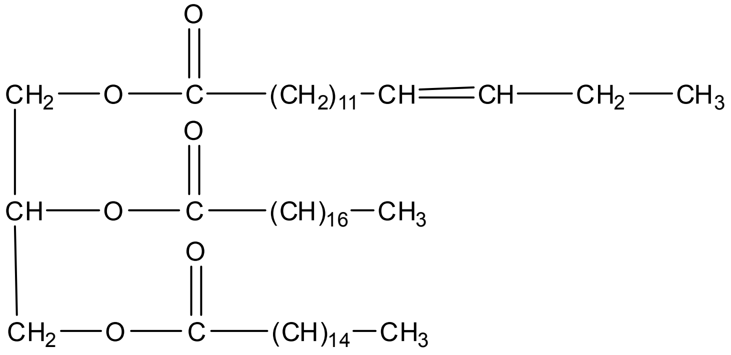
4. Explain why oils and fats (lipids) and greases (hydrocarbons) are insoluble in water.

Observations and Results

Name: ____ Section: __________________

A. Saponification of a Fat: Preparation of a Potassium Salt

Write an equation for the saponification of the fat below:



Explain on the basis of structure why the products of your saponification reaction are soluble in water whereas the starting fat is insoluble.

B. Formation of a Sodium Soap

Write an equation for the conversion of your potassium soap (use one of the fatty acid residues from part A) to a sodium soap, showing condensed structures of the reactants and products.

Describe the texture of your sodium soap.

Is the sodium soap a salt?

Explain.

C. Preparation of Fatty Acids from a Soap

Write an equation for the reaction of the potassium soap (a typical molecule) with hydrochloric acid, showing the structures of reactants and products.

Did the solution show sudsing action after addition of acid?

Explain the behavior.

Describe the texture of your fatty acid preparation.

Did you isolate a single type of fatty acid, or a mixture of fatty acids?

Explain.

D. Properties of Soaps and Detergents

TABLE 9.1

	Potassium Soap	Sodium Soap	Ivory Soap	Detergent
Sudsing action				
Cleansing ability				
addition of Ca^{2+}				
addition of Mg^{2+}				
addition of Fe^{2+}				
addition of tap water				
pH				

Draw pictures to explain how the soap molecules functioned to remove the grease spot.

Write equations for any reactions that occurred between the soap solution (use a typical fatty acid residue) and the metal ions:

How do sodium, potassium, and calcium soaps compare in solubility?

What ions are responsible for the qualities of “hard water”?

Did the metal ions form precipitates with the detergent molecules?

If not, why not?

Is the tap water in your laboratory “hard”?

What is your evidence?

Post Lab Questions

1. In what ways does a sodium soap differ from a potassium soap?

2. Draw the structure of calcium stearate. Is this salt soluble in water?

3. The structure of a sodium sulfonate is shown in the discussion section of this experiment. Draw the structure of the calcium salt of this detergent. Is this salt soluble in water?

4. A water softener is an ion-exchange unit which replaces calcium, magnesium, and ferrous ions with sodium ions. How is a water softener important in increasing the effectiveness of soap?

5. Describe how you could make a hard soap, starting with olive oil.

6. Suppose that the lipid which you used in today's experiment was a mixture of triglyceride and a cholesterol. How could you use the saponification process to separate the cholesterol from the triglyceride?

EXPERIMENT 10

Lipids - Determination of the Iodine Number

Objectives

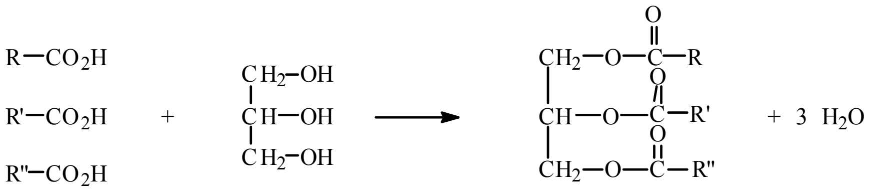
1. To observe the physical properties of some common lipids.
2. To make quantitative comparisons of the extent of unsaturation of some fats.
3. To establish the relationship between the structures of the fatty acid residue in the lipid and the chemical and physical properties of the lipid.

Introduction

Lipids are a broad class of biological compounds that are identified only by their solubility characteristics. Compounds isolated from body tissues are classified as lipids if they are more soluble in organic solvents than in water. Included in this category are esters of glycerol and the fatty acids, steroids such as cholesterol, compounds that incorporate sugar units or a complicated amino alcohol called sphingosine, and compounds called prostaglandins. In this experiment we will identify several of these types of lipids and learn more about their properties.

Fats and oils are the most abundant lipids found in nature. Both types of compounds are called **triacylglycerols** because they are esters composed of three fatty acids joined to glycerol, a trihydroxy alcohol. **Fatty acids** are long-chained organic acids having an even number of carbon atoms. A fatty acid may contain only carbon-carbon single bonds (a saturated fatty acid), or it may contain one or more carbon-carbon double bonds (an unsaturated fatty acid).

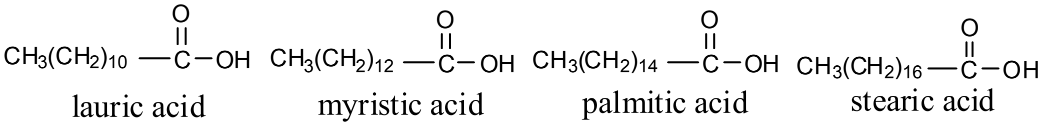
FIGURE 10.1



As the R-groups imply, there may be as many as three different fatty acid residues within a triglyceride molecule; hence the name mixed glyceride. Since the fatty acid residues vary somewhat from one molecule to another, each particular fat or oil is a mixture.

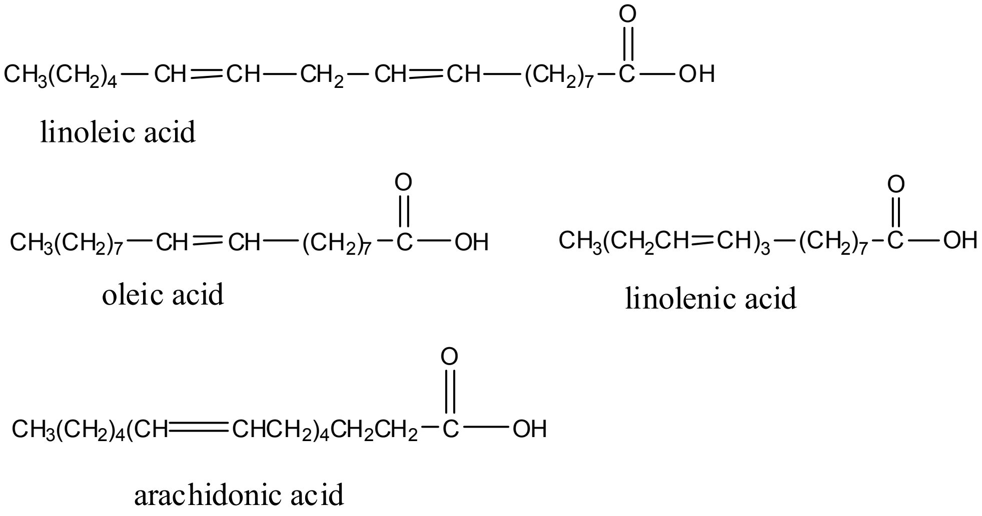
FIGURE 10.2 **Some common fatty acids:**

Saturated fatty acids



$CH_3(CH_2)_{10}-\overset{O}{\overset{\|}{C}}-OH$ $CH_3(CH_2)_{12}-\overset{O}{\overset{\|}{C}}-OH$ $CH_3(CH_2)_{14}-\overset{O}{\overset{\|}{C}}-OH$ $CH_3(CH_2)_{16}-\overset{O}{\overset{\|}{C}}-OH$

Unsaturated fatty acids

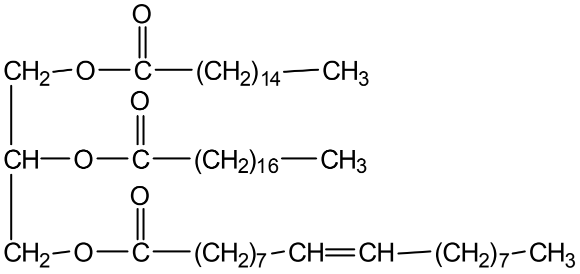


$CH_3(CH_2)_4-CH{=}CH-CH_2-CH{=}CH-(CH_2)_7-\overset{O}{\overset{\|}{C}}-OH$

$CH_3(CH_2)_7-CH{=}CH-(CH_2)_7-\overset{O}{\overset{\|}{C}}-OH$ $CH_3(CH_2CH{=}CH)_3-(CH_2)_7-\overset{O}{\overset{\|}{C}}-OH$

$CH_3(CH_2)_4(CH{=}CHCH_2)_4CH_2CH_2-\overset{O}{\overset{\|}{C}}-OH$

FIGURE 10.3 **Typical lard molecule contains palmitic, stearic, and palmitic acids:**



The saturated fatty acids are solids at room temperature, whereas the unsaturated acids are liquids. The same general relationship between unsaturation and the melting points holds for the triglycerides: the melting points decrease as the proportion of unsaturated fatty acid residues in the triglyceride increases. We find, therefore, that a triglyceride such as tallow, which is rich in saturated fatty acid residues (approximately 90%), is a solid. On the other hand, olive oil, containing approximately 86% oleic and linoleic acid residues, is a liquid. We can conclude that the physical state of the fat, whether liquid or solid, provides a rough idea of the of fatty acid residues that are present. It has become customary to call solid triglycerides fat and liquid ones oils.

Reactions of the Triglycerides

The two functional groups present in triglycerides are esters and alkenes. Esters are capable of undergoing hydrolysis and saponification. See "Saponification: Soaps and Detergents" on page 111. In today's lab we wish to examined the reactivity of the alkene group. The reactions of the alkene group include hydrogenation (addition of H_2), oxidation (responsible for rancidity), and halogenation (addition of a halogen). We will determine the relative saturation of several fats and oils today by reaction them with bromine.

The Iodine Number

A convenient measure of the degree of unsaturation is given by the iodine number. We define the iodine number of a fat as the weight of iodine which reacts with 100 g of fat. Because the reaction with iodine is very slow and often incomplete, actual measurement is made with a more reactive reagent such as BrI, BrCl, or Br_2, dissolved in acetic acid (a 5% solution). The amount of bromine which reacts can then be expressed as an iodine equivalent. The equation that follows shows how to convert you results into an iodine number.

EXAMPLE 10.1

Data:

Mass of fat = 1.606 g

Mass Br_2 solution used =15.721 g

Mass of Br_2 solution in blank = 10.587 g

$$\text{Mass } Br_2 \text{ reacted} = (\text{mass } Br_2 \text{ solution used - mass } Br_2 \text{ solution blank}) \times \frac{5\ g\ Br_2}{100\ g\ solution} \quad \textbf{(EQ 10.1)}$$

$$\text{Mass } Br_2 \text{ reacted} = (15.721 \text{ g} - 10.587 \text{ g}) \times \frac{5\ g\ Br_2}{100\ g\ solution} = 0.257 \text{ g} \quad \textbf{(EQ 10.2)}$$

$$\text{Mass } I_2 = \text{mass } Br_2 \text{ reacted} \times \frac{1\ mol\ Br_2}{160\ g\ Br_2} \times \frac{1\ mol\ I_2}{1\ mol\ Br_2} \times \frac{254\ g\ I_2}{1\ mol\ I_2} \quad \textbf{(EQ 10.3)}$$

$$\text{Mass } I_2 = 0.257 \text{ g} \times \frac{1\ mol\ Br_2}{160\ g\ Br_2} \times \frac{1\ mol\ I_2}{1\ mol\ Br_2} \times \frac{254\ g\ I_2}{1\ mol\ I_2} = 0.408 \text{ g } I_2 \quad \textbf{(EQ 10.4)}$$

$$\text{Iodine Number} = \frac{mass\ I_2}{mass\ of\ fat} \times 100 \quad \textbf{(EQ 10.5)}$$

$$\text{Iodine Number} = \frac{0.408\ g\ I_2}{1.606\ g\ fat} \times 100 = 25.4 \quad \textbf{(EQ 10.6)}$$

So the fat is probably butter see Table 10.2 .

If a fat contains fatty acid residues with no double bones, its iodine number is 0. Fats with high iodine numbers contain mostly polyunsaturated fatty acids. The table below shows the iodine numbers for some common fats and oils.

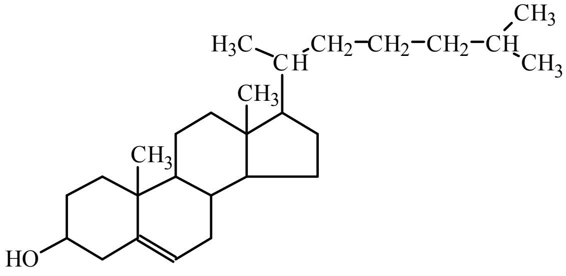
TABLE 10.2

Fat or Oil	Iodine Number	Fat or Oil	Iodine Number
Coconut	8-10	Olive	75-95
Palm	56-60	Peanut	84-100
Butter	25-45	Corn	115-130
Tallow	30-48	Cottonseed	105-115
Lard	45-65	Soybean	125-135
Sardine	120-190	Safflower	130-150

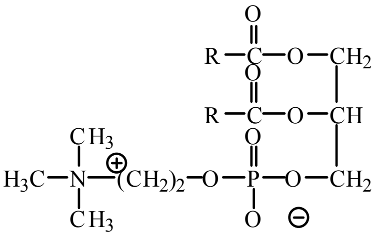
Other Lipids

Triglycerides are the most common members of the lipid family, but they are not the only important ones. Others are the steroids and the lecithins. Still another, lanolin (used as a base for salves and ointments), is a complex mixture of esters, steroids, hydrocarbons, and other compounds.

FIGURE 10.4



Cholesterol (a steroid)



A lecithin (a phospholipid)

A colorimetric test, the Lieberman-Burchard reaction, gives a characteristic green color in the presence of cholesterol. This color is due to the -OH group and the unsaturation of the fused ring. The color change is gradual -- first it appears as a pink coloration, changing later to lilac, and finally to deep green.

Experimental Design

A. Observation of some Lipids and Fatty Acids

1. Observe the appearance, consistency, and odors of the following lipids and fatty acids: cholesterol, lecithin, coconut or palm oil, beef fat (tallow), corn oil, cottonseed oil, stearic acid, oleic acid, and lanolin.
2. Answer the questions which relate to these compounds.

B. Lieberman-Burchard Test for Cholesterol

1. Place a few crystals of cholesterol in a labeled test tube.
2. Add about the same amount of lecithin to a second test tube.
3. Transfer 3 mL of cyclohexane and 1 mL of acetic anhydride to each test tube.
4. Carefully, add one drop of concentrated sulfuric acid to each mixture.
5. Mix the contents and record color changes, if any.
6. Wait 5 minutes. Again record the color of your solutions.

C. Determination of Iodine Numbers of Fats and Oils

Many common household fats and oils claim to be high in polyunsaturated fat. The iodine number of these fats and oils will allow us to compare the degree of unsaturation. In this part of the experiment we will determine the iodine numbers of fat and oil.

To ascertain the iodine number of a substance will require the use of three flasks. *A reagent flask*, from which we will draw our reagent (bromine), a *reaction flask* where we will combine our reagent with a fat or oil, and a *blank flask* containing a solution of known concentration, which we will use for comparison. Keep in mind that as the bromine from the reagent flask is added to the reaction flask a color change will occur. This color change is not a sharp end point, so it is more accurate to add bromine slightly past the end point until the color exactly matches the color of our solution in the blank flask.

Preparation of Flasks

Reagent Flask

1. Prepare a bromine reagent flask from a 25 mL Erlenmeyer flask.
2. Fit the flask with a medicine dropper by means of a one-hole cork or stopper.
3. Fill the flask 3/4 full with the 5% bromine acetic acid solution.
4. Weigh the flask and solution and record the mass on Table 10.4 on page 136 in the results section.

Caution! Safety Notes:

Do not get the bromine-acetic acid solution on your skin. If this happens, wash it off immediately for at least 15 minutes.

Blank Flask

1. In a second Erlenmeyer flask place 10 drops of bromine acetic acid solution from the reagent flask.
2. Add 10 mL of cyclohexane to the blank flask and close with a stopper.
3. Set this blank flask aside on a piece of white paper.
4. Reweigh the reagent flask and record the new mass on Table 10.4 on page 136.

Reaction Flask

1. In the third Erlenmeyer flask we will react bromine with a fat or oil.
2. Weigh the third flask and record its mass on Table 10.5 on page 137.
3. To the empty flask add 0.2-0.3 g of fat or a small drop of oil. (Liquids may be added with a dropper and solids with a spatula. Try to get all of your sample on the bottom of the flask.)
4. Reweigh the flask containing the fat or oil and record its mass on Table 10.5 on page 137.
5. Calculate and record the mass of the fat or oil.
6. Now add 5 mL of cyclohexane to dissolve your fat or oil and place this flask next to your blank flask on the white sheet of paper.

Reaction of Reagent with the Fat or Oil

1. When all of the fat or oil is dissolved in the cyclohexane, you are ready to add the reagent and determine the iodine numbers.
2. Weigh the reagent flask and record the mass on Table 10.4 on page 136.
3. Now add bromine from the reagent flask to the dissolved fat in the reaction flask.
4. Start with approximately 10 drops at a time and swirl until the bromine color dissipates, then as the color approaches the color of the blank flask, add bromine more slowly.
5. Continue to add bromine from the reagent flask until the color of the reaction flask matches the color of the blank flask. The color should persist for about 10 seconds.
6. When the colors of both flasks are the same stop.
7. Weigh the reagent flask and record the new mass on Table 10.5 on page 137.
8. Pour the contents of the reaction flask into the container provided in the hood.
9. Clean the reaction flask well and repeat the experiment.
10. Determine the iodine number of both a fat and oil using the calculations discussed earlier.

Prelaboratory Exercise: Iodine Number

Name: ____ Section: __________________

1. Is the "alcohol portion" of all triglycerides the same? Explain.

2. What is a fatty acid residue?

3. For myristic acid, linolenic acid, and lauric acid:
    - **a.** Write the complete condensed structure for a triglyceride composed of the following acids:
    - **b.** Which of the fatty acid residues is unsaturated?

4. What is the difference (physically and structurally), if any, between a fat and an oil?

5. Which fat or oil in Table 10.2 on page 128 is most unsaturated?

Lab Report: Iodine Number

Name: ____ Section: __________________

Part A- Observations of some Lipids and Fatty Acids

Describe the structure and texture of the compounds examined is a pure steroid.

Describe the structure and texture of the compound(s) that is a phospholipid?

Based on your observations of the physical properties of the compounds, which has the higher melting point, stearic acid or oleic acid?

What is your evidence?

Give the names of the lipids which are primarily triglycerides, and indicate which of these triglycerides contains the most saturated fatty acid residues.

Part B- Lieberman-Burchard Test for Cholesterol

TABLE 10.3

	Initial color	Color after addition of H_2SO_4	Color after 5 minutes
Cholesterol			
Lecithin			

Part C - Determination of the iodine numbers of Fats and oils

TABLE 10.4

Mass of reagent flask (3/4 full of bromine)	
Mass of reagent flask less 10 drops to blank	
Mass of bromine used (in blank)	

Sample Calculations

TABLE 10.5

Mass of fat /Oil calculations	Lard	Tallow	Safflower Oil	Corn Oil
Mass of reaction flask with fat/oil				
Mass of empty reaction flask				
Mass of fat used				
Mass of Bromine Calculations				
Mass of reagent flask (before titration)				
Mass of reagent flask (after titration)				
Mass of Bromine used				
Iodine number				

Sample Calculations

Which of your lipids did you find to be most unsaturated? Why?

Based on the data which you obtained in this experiment and on information in the discussion section, can you make the statement that vegetable fats are more unsaturated than animal fats? Explain your answer using your data.

According to your experimental data, which contains the most unsaturated fatty acid residues, a molecule of corn oil or a molecule of lard?

Fatty acid residues which are typical of a butter molecule are myristic, palmitic, and oleic. Draw the structure of a molecule of this triglyceride, and show its reaction with bromine.

Post Lab Questions

1. One triglyceride contains two stearic acid residues and one linoleic acid residue: another has two oleic acid residues and one stearic acid residue. Would the triglycerides have identical iodine numbers? Explain.

2. A 4.92 g sample of oil requires 3.2 g of bromine-acetic acid solution to react with all of the alkene residues. What is the iodine number of the oil?

3. Answer the following questions about myristic acid, oleic acid, and linolenic acid
   a. Draw the structure of a triglyceride molecule which contains the above acids:

   b. What is the iodine number of this triglyceride?

4. Using the triglyceride of question 3, which is an oil:
    - a. Write a reaction showing the conversion of this oil to a solid shortening.
    - b. What is the name of this type of reaction?

EXPERIMENT 11

General Organic Unknown Lab: How Good a Detective are You?

Objective

The purpose of this lab is to bring together all the different tools you have used in the previous organic chemistry labs in the course. You will be generating your own flow chart style qualitative, “qual”, scheme which you will use to identify an unknown molecule both by its chemical and physical properties.

Introduction

In your previous organic chemistry labs you have experimented on a number of qualitative tests for organic functional groups. Some of the qual tests work as a stand-alone (for example the bromine test for alkenes and alkynes) and some tests must be done in tandem to make a choice of functional group (for example both Lucas and potassium dichromate to determine primary, secondary and tertiary alcohol). A list of the available tests are below:

1. Bromine test for alkenes.
2. Burning test to distinguish alkene, alkane and aromatic.
3. Potassium Permanganate test for alkenes.*
4. Lucas reagent test for alcohols.
5. Potassium dichromate/H_sSO_4 test for alcohols.
6. 2,4 Dinitrophenylhydrazine test for ketones/aldehydes.
7. Tollens’ reagent test for aldehydes.
8. Fehling’s reagent test for aldehydes.
9. Sodium hydroxide/solubility test for phenols and carboxylic acids.**
10. Sodium bicarbonate/solubility test for carboxylic acids only.**
11. Hydrochloric acid solubility test for amines.
12. $FeCl_3$ test for phenols.
13. Melting point: a general qual technique for any solid.

14. Boiling point: a general qual technique for any liquid.

[*]A test you did but which you will not be using in this experiment.

[**]A test you did not actually do in the lab, but which was mentioned in lecture and which you may be using in this lab.

If one is given a generic organic compound which has only one important major functional group, one can develop a “qual scheme,” using the above tests, to identify the functional group in the molecule. That, combined with either a boiling point or a melting point will allow you to determine the actual identity of your unknown amongst a longer list of possible candidate compounds.

LIST OF POTENTIAL UNKNOWN MOLECULES:

TABLE 11.1

Alkanes:

octane
2,2-dimethylhexane
cyclohexane
methylcyclopentane
hexane

Arenes:

benzene
toluene
p-anisole
ethyl benzene
t-butyl benzene
naphthalene

Ketones:

acetone
2-pentanone
butanone
2,3-butanedione
cyclohexanone
2-methylcyclopentanone

Phenols:

phenol
p-cresol (4-methyl phenol)
thymol (2-methyl-5-isopropyl phenol)
p-t-butyl phenol
m-ethyl phenol (3-ethyl phenol)

Amines:

triethylamine
n-hexylamine
aminocyclohexane
n-butylamine
t-butylamine

Alkenes:

trans-2-butene
1-pentene
trans-2-hexene
cyclohexene
1,2-dimethylcyclopentene

Aldehydes:

hexanal
acetaldehyde
butanal
benzaldehyde
formaldehyde
heptanal

Carboxylic Acids:

pentanoic acid
benzoic acid
lactic acid
3-phenyl propanoic acid
p-chloro benzonic acid
heptanoic acid

Alcohols: (note a mixture or 1°, 2°, and 3°)

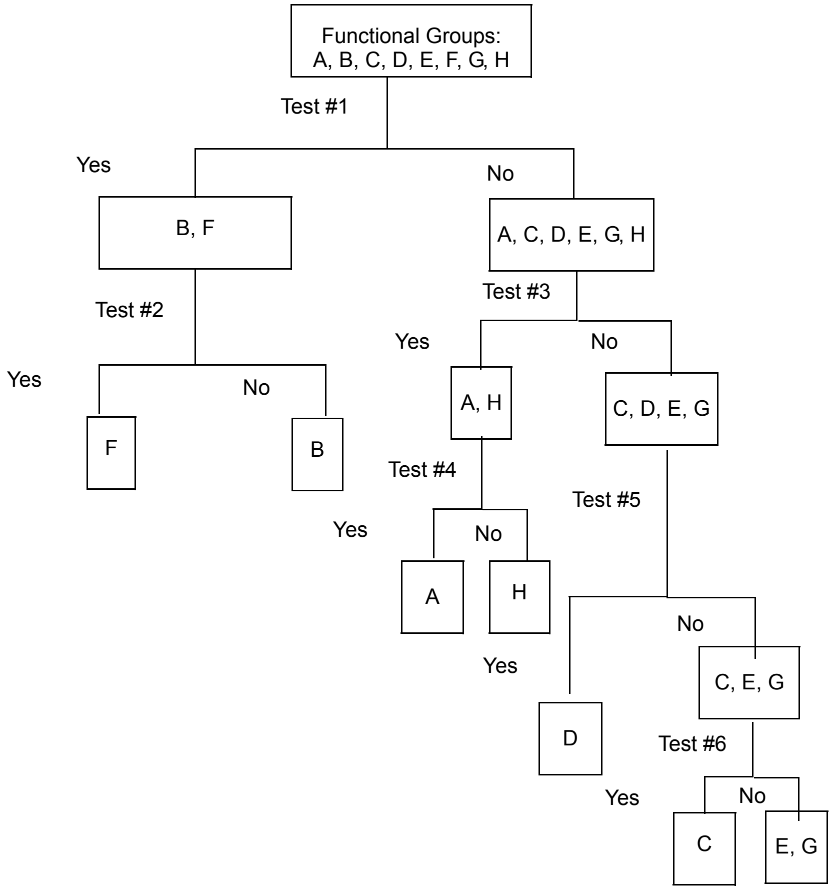
t-butyl alcohol
2-methyl-2-butanol
cyclopentanol
n-pentanol
ethanol

isopropanol
2-methyl-2-butanol
3-pentanol
2-methyl-1-propanol
2-butanol

Qual Schemes

Before doing your experiment, you will be required to come up with a qual scheme. This will be a flow chart which, if applied to any of the compounds in the list above could be used to determine the functional group on an unknown molecule. It is suggested that you begin by using qual tests which could separate two functional groups from the rest, rather than separating out one functional group at a time, as this will, in the end, require less tests to finally determine for sure what your functional group is. A schematic for a functional group is drawn below:

FIGURE 11.1



And so forth.

Once you have created a qual scheme which is signed and approved by your instructor, you can proceed to apply your qual scheme to your compound. After identifying your functional group, you will either do a melting point or a boiling point to identify the actual compound you were given.

Experimental Design

Perform your qual scheme on your unknown compound, using the techniques described in the relevant labs you have already done. There will be some things that are not exactly as seen before. For example, you may be trying a test on a solid when in the past; you only did the test on a liquid. Apply common sense on how to do such tests, but if in doubt, ask your instructor to help you devise directions. The two tests you have not yet done are described below. Also, we will change the test for solubility of an amine somewhat, so the method is described below:

1. Test for solubility with sodium bicarbonate.
    - a. Take one gram (or one milliliter if it is a liquid) of the unknown compound and attempt to dissolve it in 10 mL of deionized water in a large test tube.

  - **b.** If it does not dissolve, add 10 mL of the sodium bicarbonate solution supplied for the lab.
  - **c.** Use a stirring rod for two or three minutes if it does not dissolve immediately.
  - **d.** If the compound dissolves at this point, the test is positive.

2. Test for solubility with sodium hydroxide.
   - **a.** Take one gram (or one milliliter if it is a liquid) of the unknown compound.
   - **b.** Attempt to dissolve it in 10 mL of deionized water in a large test tube.
   - **c.** If it does not dissolve, add 10 mL of 6.0 M sodium hydroxide.
   - **d.** Use a stirring rod for a couple of minutes to see if you can make the compound dissolve.
   - **e.** If it dissolves, the test is positive.
3. Test for solubility with hydrochloric acid.
   - **a.** Take one gram (or one milliliter if it is a liquid) of the unknown compound.
   - **b.** Attempt to dissolve it in 10 mL of deionized water in a large test tube.
   - **c.** If it does not dissolve, add 10 mL of 6.0 M hydrochloric acid.
   - **d.** Use a stirring rod for a couple of minutes to see if you can make the compound dissolve.
   - **e.** If it does dissolve, the test is positive.

If you have identified your functional group through only a couple of tests, you do not have to complete the entire qual scheme you have devised. Consider yourself lucky! Record your observations for each of the tests you have done in the observation sheet supplied.

4. Melting Point or Boiling Point
   - **a.** Once you have identified the functional group for your compound, either take a boiling point (see “Alcohols” on page 39) or a melting point (see “Purification By Crystallization” on page 29), depending on which is appropriate in your case.
   - **b.** Record the result in the appropriate space on the observation sheet.

Observations Sheet

Name: ____ Section: __________________

Based on these results, after looking up the melting or boiling points of the appropriate compounds with the same functional group in the CRC Handbook or any other reference you can find. Determine the identity of your unknown compound. At every point where it is appropriate, state your reasoning.

TESTS:

Test #1 ____________________________________

Observations:

Conclusion:

Test #2____________________________________

Observations:

Conclusion:

Test #3____________________________________

Observations:

Conclusion:

Test #4____

Observations:

Conclusion:

Test #5____

Observations:

Conclusion:

Test #6____

Observations:

Conclusion:

Test #7____

Observations:

Conclusion:

Test #8________________________________

Observations:

Conclusion:

Test #9________________________________

Observations:

Conclusion:

CONCLUSION:

What is the functional group on your unknown compound?

MELTING OR BOILING POINT:

Observations:

FINAL IDENTIFICATION OF YOUR UNKNOWN COMPOUND:

Melting or boiling points of the potential candidate compounds: (state the reference you took the values from).

What compound were you given as your unknown?

EXPERIMENT 12

Enzyme Isolation and Kinetics

Introduction

Enzymes are an integral part of biological systems. They function as catalysts for many chemical reactions that would occur either very slowly or infrequently in nature. They perform a myriad of functions, including aiding in digestion, communication between cells, synthesis of DNA and other biomolecules and respiration.

The study of enzymes and their activity is important in understanding how normal cellular processes take place and how diseases may be influenced by the irregular activity of these proteins. In order to understand how enzymes function, it is first necessary to isolate them from all other enzymes in an organism. Once this is accomplished, it is then possible to examine chemical reactions catalyzed by the enzyme and how other molecules may inhibit the enzyme function.

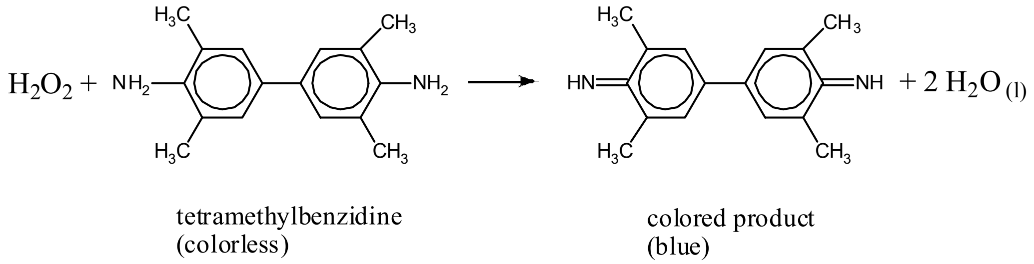
In this lab we will be purifying a protein from California giant kelp *Macrocystis pyrferia* and examining its catalytic properties.

The algae off the coast of California (and many other areas as well) have been shown to produce volatile halogenated hydrocarbons such as tribromomethane. The estimated annual worldwide production of these gasses by algae has been estimated to be in the gigatons (10^9 tons)/year. The halogenated hydrocarbons are known to be “greenhouse gasses” (they are similar to the “freon” compounds) and this natural source is thought to be a significant proportion of the total amount released by all sources. There is no known reason for the biological production of these compounds, but some have speculated that they have anti-microbial properties. The enzyme believed to be responsible for the production of these halogenated hydrocarbons by algae is vanadium bromoperoxidase. Vanadium bromoperoxidase is named for the facts that it contains the metal vanadium as a cofactor, and that it uses hydrogen peroxide to add bromine to organic molecules according to the following reaction:

$$H_2O_2 + Br^- + H^+ + HA \rightarrow Br\text{-}A + 2\,H_2O \qquad \textbf{(EQ 12.1)}$$

However if there is no bromine present, an oxidation reaction can take place, and it is this reaction that we will be using in our experiments:

(EQ 12.2)



We are able to watch the progress of the reaction visually as the clear solution turns blue with the production of the oxidized produce. We will quantitate the reaction by measuring the intensity of the color using a spectrophotometer.

Prior to studying the chemical properties of vanadium bromoperoxidase, we need to separate it from the other components in the algae. Separation is accomplished by taking advantage of differing chemical properties associated with different molecules.

In this lab we will focus on three purification processes: differential solubility, hydrophobicity and total net charge.

Differential solubility - One of the major classes of biomolecules in kelp is the alginates. These are sulfated polysaccharides and are what give the plant it's mucous like feel. Alginates are the molecules commercially extracted from kelp and used in a variety of consumer products from ice cream to cosmetics to beer. The barium ion (Ba^{2+}) when mixed with sulfate ions, or molecules containing sulfate ions, will form insoluble salts. Since the alginates contain sulfate groups while proteins do not, we are able to use this phenomenon to selectively remove the alginates from our solution.

$$\text{Protein-}SO_4^{2-} + Ba^{2+} \rightarrow \text{Protein-}BaSO_{4\,(s)} \qquad \textbf{(EQ 12.3)}$$

Hydrophobicity ("water hating")- Proteins are composed of strings of amino acids. Amino acids can, due to their particular atomic and molecular composition, be ionic, polar or nonpolar under normal conditions. The relative proportions of these three types of amino acids in a protein will therefore have a profound effect on its solubility. Proteins rich in charged and polar amino acids will be very water-soluble while those containing a large percentage of nonpolar amino acids will be less soluble. We can magnify this effect by the addition of salts to a solution. The increase in the amount of total charge in the environment surrounding the proteins will cause the more nonpolar (or hydrophobic) ones to want to stick together (it is the old "like dissolves like" the non-polar molecules would rather associate with each other than the highly ionic water/salt solution. Furthermore, the more non-polar the protein, the less salt required to cause it to aggregate. As scientists we can use this phenomenon to our advantage. By adding salt to a protein solution in batches, we can precipitate some of the proteins while others remain in the solution. Adding more salt will then cause a different group of proteins to precipitate. By careful manipulation we can then selectively remove the protein of interest while leaving others in solution. In our experiment, we will be using the salt ammonium sulfate to accomplish this type of separation.

(EQ 12.4)

$$\text{hydrophobic: Protein}_{(aq)} \xrightarrow{(NH_4)_2SO_4} \text{Protein}_{(l)}$$

Total net charge - As we stated above, certain amino acid side chains are ionic, that means that at a neutral pH they can be either positively or negatively charged. If one were to take a protein and sum up all the charged groups, the imbalance between positive and negative side chains leads to a net charge on the protein (i.e. 5 positive and 12 negative would be a net negative 7 charge). This characteristic can also be exploited for the purification of proteins. If one were to take a solid material that had a positively charged group on it, negatively charged proteins would be attracted to it while positively charged proteins would be repelled. In this experiment, we will use a **positively charged** material (DEAE or diethylaminoethyl in our case) to attract negatively charged proteins (our protein, bromoperoxidase, is very negatively charged).

(EQ 12.5)

$$\text{Protein-DEAE}_{(s)} \xrightarrow{\text{NaCl}} \text{DEAE} + \text{Protein}^{n-}_{(aq)}$$

The ionic interaction between the proteins and the solid material can be broken up by the addition of ions to the solution surrounding the material. The stronger the interaction between the solid material and the protein, the higher the ion concentration required to disrupt it, and separate the protein. This is what we will be doing on day two. We will pass the kelp extract from day 1 over our “column” where many of the proteins will stick. The proteins can then be removed by passing increasing concentrations of a salt solution through the column. Different proteins will come out in the different salt solutions, thereby allowing us to remove many proteins that are of no interest to us from the bromoperoxidase that we are trying to isolate.

Catalytic Properties of Bromoperoxidase

Once we have a relatively pure enzyme, we can study its catalytic properties. The reason for having a pure enzyme is that there are many other proteins in an organism that can catalyze reactions using the same reactants. If these other enzymes are present, we may not be able to observe the particular actions of our enzyme.

There are many conditions that affect the catalytic activity of an enzyme. Among these are temperature, pH, the concentration of the substrates, the presence of inhibitors and cofactors. We will examine many of these parameters in our experiment.

pH. All enzymes have evolved to have a maximal activity at a specific pH. When the pH of a solution is either higher or lower than the optimal value the enzyme will be less active. We will look at the activity of bromoperoxidase at pH 4, 6 and 8 to attempt to determine what the best pH value is for this particular enzyme (Day 2 steps 8-10).

Substrate concentration. In chemical reactions, an increase in the substrates will lead to an increase in the speed of the reaction. With enzymes this is only true to a point. Increasing the substrate will increase the rate of the reaction until the enzyme becomes saturated (it cannot work any faster). After this point, increases in the substrate concentration will have no effect on the speed of the reaction. We will look at three different concentrations of one of the substrates, hydrogen peroxide, to see the effect on the speed of the reaction Day 2 steps 8, 11, and 12.

Inhibitors. Some molecules can affect the catalytic activity of an enzyme. If they decrease the activity, they are called inhibitors. In this experiment, we will look at how the inhibitor sodium thiocyanate blocks the activity of bromoperoxidase. (Day 2 step 13)

Temperature. For most chemical reactions increasing the temperature will increase the speed of the reaction. This is not true with enzymes. The speed of an enzyme catalyzed reaction will increase with increasing temperature to a point, after which the increasing temperature will cause the enzyme to denature (unfold) and its catalytic activity will be lost. In our experiment, we will examine the effect of heating bromoperoxidase on its catalytic activity (Day 2 steps 8 and 14).

Protocol

Day 1

1. Obtain 60 mL of homogenized *Macrocystis pyrifera* (California giant kelp) from the instructor (alternatively, you can do the grinding in the lab). This homogenate contains 5 g of algae/50 mL of buffer (50 mM Tris-HCl, pH 8.0).
2. Centrifuge the material for 10 minutes in the Table-top centrifuge to remove the particulate material. Make sure that the centrifuge is balanced (you should have two tubes with equal amounts of liquid on opposite sides of each other).
3. Decant the liquid into a 100 mL beaker.
4. Add 1 mL of 1 M $BaCl_2$ to the liquid. At this point, a gelatinous precipitate should form. Centrifuge the material for 10 minutes to separate the precipitate from the liquid.
5. Save the liquid and dispose of the precipitate.
6. Determine the volume of the remaining liquid using your graduated cylinder.

Liquid Volume ______________

7. Add 0.07 g $(NH_4)_2SO_4$ for every mL of the liquid (about 3.5 g total).
8. Stir well to dissolve the salt and let stand for 10 minutes.
9. Centrifuge the liquid for 10 minutes, saving the liquid and disposing of the solid material.
10. Measure the volume of the liquid with a graduated cylinder and record the volume

$(NH_4)_2SO_4$ added _____________

Liquid Volume _______________

11. Add 0.5 g $(NH_4)_2SO_4$ per mL to the liquid (about 15-20 g).
12. Stir well to dissolve the salt and let stand for 10 minutes.
13. Centrifuge the liquid for 10 minutes, saving the solid and disposing of the liquid material.

$(NH_4)_2SO_4$ added _____________

14. Add 5 mL of 50 mM Tris buffer to the solid and gently swirl to dissolve.
15. Label a container with your name and give this material to the lab instructor for storage until the next lab period.
16. Purification by column chromatography using DEAE
    a. From your instructor, retrieve your sample and a DEAE column for chromatography.
    b. Wash the column with 15 mL of 50 mM Tris pH 8.0; collect the liquid in a waste container. The purpose of this step is simply to clean the column. You do not need to collect the effluent.
    c. Apply your sample to the column, collect the liquid that flows through into 1 or 2 clean test tubes.

d. Apply to the column 10 mL each of the following, collecting the material that elutes into 2 test tubes. Be sure that all the liquid has run into your column before adding the next salt solution. With each increase in salt, you will be removing different proteins that had initially bound to the positively charged material in the column.

- 50 mM Tris
- 50 mM Tris, 0.2 M NaCl
- 50 mM Tris, 0.4 M NaCl
- 50 mM Tris, 0.6 M NaCl
- 50 mM Tris, 0.8 M NaCl
- 50 mM Tris, 1.2 M NaCl

17. Take 0.1 mL from each of the test tubes and add it to 0.1 mL of reaction solution (containing 1 mM TMB, 1 µM Na_3VO_4. 3 mM H_2O_2, 100 mM phosphate pH 6.0). Look for a colored product to form, and save the tubes that gives the most blue color (you will need about 8 mL of solution for the rest of the experiment).
18. Give your labeled sample to your instructor.

Day 2

1. Warm up your spectrophotometer.
2. Set the wavelength to 655 nm. Have your instructor examine the setup prior to continuing with the experiment. See the handout on the operation of the spectrophotometer for the proper setup and use of the equipment.
3. Put 30 drops of your enzyme into a test tube and heat it at about 70 °C in a water bath.
4. Record the time you put it in as well as the temperature range it was held at.
5. Remove it after 30 minutes.
6. Do this while you are performing the other steps below.
7. We will use this material to examine the effect of heat on bromoperoxidase.

In each of the experiments below, the spectrophotometer will determine the change in absorbance of the solution (the formation of the colored product) per minute.

Record this information on your lab sheet.

8. In a spectrometer cuvette, take 30 drops of your enzyme and add it to 4.0 mL of a solution that is 1 mM TMB, 1 µM Na_3VO_4, 3 mM H_2O_2, 100 mM phosphate pH **6.0**. Quickly mix the solution thoroughly and place it in the spectrophotometer and record the absorbance every sixty seconds for 10 minutes. (Your instructor may have you record % Transmittance instead of absorbance.)
9. Repeat step 8 with a solution that is 1 mM TMB, 1 µM Na_3VO_4, 3 mM H_2O_2, 100 mM phosphate **pH 4.0**.
10. Repeat step 8 with a solution that is 1 mM TMB, 1 µM Na_3VO_4, 3 mM H_2O_2, 100 mM phosphate **pH 8.0**.
11. Repeat step 8 with a solution that is 1 mM TMB, 1 µM Na_3VO_4, **1 mM H_2O_2**, 100 mM phosphate pH 6.0.
12. Repeat step 8 with a solution that is 1 mM TMB, 1 µM Na_3VO_4, **0.1 mM H_2O_2**, 100 mM phosphate pH 6.0.
13. Repeat step 8 with a solution that is 1 mM TMB, **0.1 mM NaSCN**, 1 µM Na_3VO_4, 3 mM H_2O_2, 100 mM phosphate pH 6.0.

14. Repeat step 8 using your **heated enzyme** rather than your normal enzyme sample.

Lab Write-up

Your lab write-up will include a detailed record of your observations, both on day 1 and day 2, including such details as masses and volumes of substances used, colors observed, and generally any observation which was relevant to making a careful record of the experiment and the results you got.

The write-up should also include all the data you recorded on day 2, including the temperature at which you held the sample in the hot water bath.

Prepare a graph of your absorbance (or % transmittance) versus time date for each of the runs you performed. You may want to use the graphing program available through the Chemistry. department. It will be helpful to have a graph of steps 8, 9 and 10. Steps 8, 11 and 12, and so forth to illustrate the trends observed. Determine the **rate** of each of the enzyme catalyzed reactions by measuring the slopes of your graphs. This should be done fairly easily using the graphing program already mentioned.

Using the results obtained from these graphs, answer the four questions. Do not just give an answer to the questions, but **state your reasoning carefully and in detail**.

What is the optimal pH at which the bromoperoxidase functions? Try to estimate your answer to the tenth unit of pH.

Was the bromoperoxidase enzyme saturated at any of the H_2O_2 concentration levels you used? If so, at what concentration level did it appear to have been saturated?

Was the bromoperoxidase enzyme inhibited by NaSCN? If so, to what extent was its action slowed by NaSCN?

Was the bromoperoxidase irreversibly denatured by being kept at an elevated temperature for 30 minutes? If so, to what extent was it irreversibly denatured?

“Dry Lab” Data for Enzyme Isolation and Kinetics Lab

n/a

Temperature 75 ° C put in at 2:25 pm

removed at 2:59 pm temperature 69 °C

Temperature in the room: 22.7 °C

8. The tube acquired strong blue color.		9. The tube got a very light blue-green.		10. The tube turned a bit blue.		11. The tube got quite blue.	
time (min)	absorbance	time (min)	absorbance	time (min)	absorbance	time (min)	absorbance
0	0.040	0	0.029	0	0.034	0	0.041
1	0.089	1	0.032	1	0.058	1	0.079
2	0.128	2	0.036	2	0.075	2	0.131
3	0.189	3	0.035	3	0.099	3	0.175
4	0.258	4	0.040	4	0.109	4	0.249
5	0.299	5	0.043	5	0.133	5	0.301
6	0.360	6	0.044	6	0.150	6	0.352
7	0.411	7	0.049	7	0.168	7	0.403
8	0.449	8	0.053	8	0.185	8	0.438
9	0.528	9	0.055	9	0.199	9	0.498
10	0.560	10	0.055	10	0.221	10	0.545

12. The tube got quite blue.		13. The tube turned a little yellow.		14. The tube got very slightly green.	
time (min)	absorbance	time (min)	absorbance	time (min)	absorbance
0	0.033	0	0.024	0	0.026
1	0.055	1	0.023	1	0.033
2	0.068	2	0.025	2	0.035
3	0.086	3	0.029	3	0.036
4	0.111	4	0.027	4	0.040
5	0.130	5	0.026	5	0.045
6	0.148	6	0.029	6	0.048
7	0.170	7	0.029	7	0.057
8	0.196	8	0.028	8	0.062
9	0.221	9	0.030	9	0.068
10	0.234	10	0.030	10	0.072

EXPERIMENT 13

Molecular Models

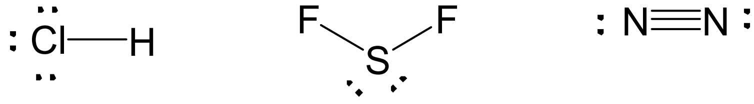
Introduction

Chemists often use models to visualize molecular structures. Molecular geometries can frequently influence chemical and physical properties, thus it is important to begin to recognize the way that atoms bond together and how they orient themselves in a molecule. In this experiment, you will build a variety of molecules using molecular models in order to become familiar with some of the more common geometries.

Lewis Structures

In 1916, G. N. Lewis developed a theory in which he proposed that atoms would bond together to share electrons so that all representative atoms would be surrounded by 8 valence electrons. Hydrogen, H, and helium, He, are exceptions having a maximum of 2 valence electrons surrounding them. Chemists still use that model when drawing **Lewis Electron Dot** structures for molecules. Your textbook outlines the procedure for drawing correct electron dot structures for common compounds. A few examples of correctly drawn Lewis structures are shown in Figure 13.1 on page 159.

FIGURE 13.1



Remember that all non-bonding electron pairs must be shown in a correct Lewis Structure!

Molecular Geometries

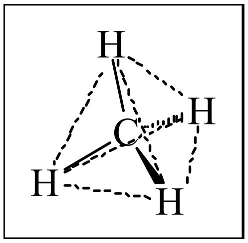
Valence **S**hell **E**lectron-**P**air **R**epulsion theory or **VSEPR** is used to predict molecular geometries. VSEPR theory proposes that the structure of a molecule is determined by the repulsive interaction of electron pairs in the valence shell of its central atom. In other words, the bonding pairs and the non-bonding (lone) pairs around a given atom are as far apart as possible.

EXAMPLE 13.1 Methane, CH_4

has four valence electrons from the carbon atom, and one valence electron from each hydrogen atom.

$$\left(\frac{4VE}{C}\right)(1C)+\left(\frac{1VE}{H}\right)(4H) = 8VE \qquad \textbf{(EQ 13.1)}$$

FIGURE 13.2



Therefore, methane has four bonding electron pairs around the carbon atom. In order to maximize the distance between these bonding electrons (and minimize the repulsive forces) the hydrogen atoms will orient themselves forming a tetrahedron with 109.5° bond angles as shown in.Figure 13.2 .

EXAMPLE 13.2 Ammonia, NH_3, and water, H_2O

If pairs of non-bonding, lone pairs also surround an atom they will also require space. An example of this is shown in both ammonia and water where the angles between the four sets of electron pairs are still approximately 109.5° (experiment shows the angles are about 107° and 104.5° respectively) as seen in Figure 13.3 .

FIGURE 13.3

Orbital geometry is the geometrical arrangement of all electron groups includes bonding and nonbonding electrons. **Molecular geometry** only looks at the shape of the bonding electrons. An incomplete summary of the orbital geometries, molecular geometries, and approximate bond angles is illustrated in the prelab section in Table 13.5 on page 165. You will complete it.

Ions

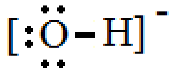
If you need to draw the Lewis Electron Dot structures for ions, add or subtract valence electrons based upon the charge on the molecule.

EXAMPLE 13.3 **Hydroxide ion, OH^-**

would have 6 valence electrons from the oxygen, 1 valence electron from the hydrogen, and 1 extra valence electron due to the charge, giving it a total of 8 valence electrons.:

$$\left(\frac{6VE}{O}\right)(1O)+\left(\frac{1VE}{H}\right)(1H)+1e^{-} \; = \; 8VE \tag{EQ 13.2}$$

FIGURE 13.4



Double and Triple Bonds

Like single bonds and nonbonding electron pairs, double and triple bonds are considered one "cloud" of electron density.

EXAMPLE 13.4 **Hydrogen cyanide, HCN**

FIGURE 13.5

H-C≡N:

One bonding cloud is from the hydrogen-carbon single bond and the other bonding cloud is from the carbon≡nitrogen triple bond.

There are no non-bonding clouds on the carbon atom, which is the central atom.

Therefore, a molecule such as hydrogen cyanide would have two bonding "clouds" and zero non-bonding "clouds" around the central atom.

For molecules that contain double and triple bonds as well as single bonds, you must differentiate between sigma (σ) and pi (π) bonding electrons. **Sigma bonds** are the first bonds formed and **pi bonds** are the second (for double) and third (for triple) bonds formed. Another way to visualize this is to see the bonding and nonbonding electrons as clouds of electron density. So single, double, triple bonds and lone pairs all represent one cloud of electron density. Figure 13.6 on page 161 and Figure 13.7 on page 162 show how to count sigma and pi bonds.

FIGURE 13.6 **Formaldehyde has two single bonds and one double bond.**

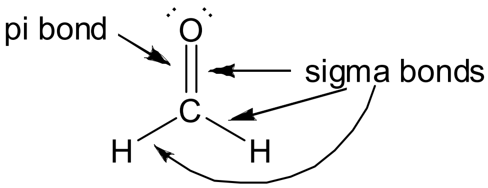
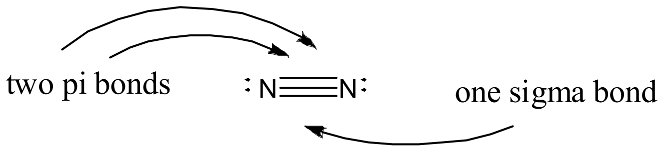
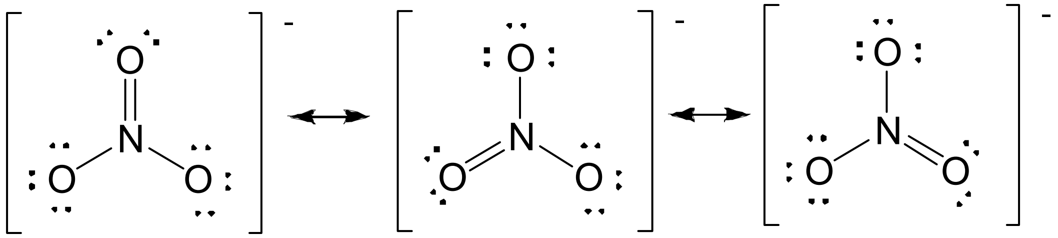


FIGURE 13.7 Nitrogen gas has one triple bond.



Another consideration is resonance. Molecules that have **resonance structures** have a double bond (pi bond) that can move around the central without changing the structure of the molecule. In other words, atoms are not moving, rather an electron pair is moving, so the octet rule is obeyed.

FIGURE 13.8 Try this by drawing the resonance structures for the nitate, NO_3^-, ion.



Formal Charge

- Not all atoms within a neutral molecule need be neutral
- The location of any charges is often important for understanding reactivity.
- Get into the habit of labeling the formal charges on any atoms.

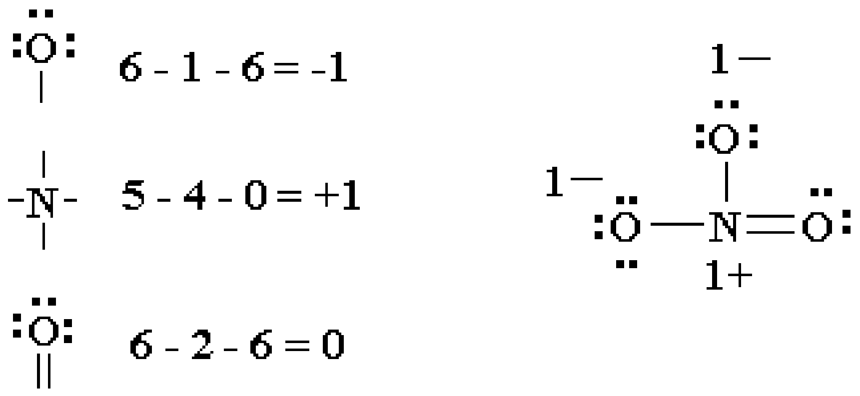
Formal charge is an accounting procedure. It allows chemists to determine the location of charge in a molecule as well as compare how good a Lewis structure might be. The formula for calculating formal charge is shown below:

$$\text{Formal charge} = (\text{valence } e^-) - (1/2 \text{ bonding } e^-) - (\text{lone electrons}). \qquad \textbf{(EQ 13.3)}$$

You should be able to determine which atoms have formal charge based on comparing the structure with common, known neutral structures. To do this you need to recognize the common neutral structures:

- Carbon: 4 bonds;
- Nitrogen: 3 bonds, 1 lone pair;
- Oxygen: 2 bonds, 2 lone pairs
- Fluorine: 1 bond, 3 lone pairs

FIGURE 13.9 **Let's return the nitrate ion, Figure 13.8 on page 162**



The formal charges should add up to the charge of the nitrate ion -1.

$$-1 + -1 + 1 + 0 = -1 \quad \text{(EQ 13.4)}$$

Procedure

Build and draw the molecules and ions listed in the tables on the following pages. Be sure to answer the questions regarding these molecules. Remember, we're counting lone pairs and bonding electrons around the central atom. Your instructor may want to check each model to ensure that you built all of them.

Prelaboratory Exercise: Molecular Models

Name: ____ Section: __________________

1. Complete the following table:

TABLE 13.5

Valence shell electron pairs	Bonding electron “clouds”	Lone pairs		Orbital geometry	Approximate bond angles	Molecular geometry	Hybridization
Diatomic molecule	1	No central		Linear	180°	Linear	sp
2	2	0	AX_2	Linear	180°	Linear	sp
3	3	0	AX_3	Trigonal Planar	120°		sp^2
	2	1	$\ddot{A}X_2$			Bent	sp^2
	4	0	AX_4	Tetrahedral	109.5°	Tetrahedral	sp^3
4	3	1	$\ddot{A}X_3$			Trigonal Pyramidal	sp^3
	2	2	$:\ddot{A}X_2$		<109.5°	Bent	sp^3

2. How many valence electrons does an atom of nitrogen contain? ______

3. How many valence electrons are in a molecule of $C_4H_6Br_2$? ______

4. How many valence electrons are in a $CH_3CO_2^-$ ion?______

5. How many valence electrons are in a $NH_3C_2H_5^+$ ion?______

6. What is the abbreviation for the theory used to determine the geometry of molecules?

7. What is the orbital or electronic geometry of a molecule with 2 nonbonding electron pairs and 2 bonding electron pairs?

8. What is the orbital or electronic geometry of a molecule with 0 nonbonding electron pairs and 2 bonding electron pairs?

9. What is the molecular geometry of a molecule with 1 nonbonding electron pair and 2 bonding electron pairs?

10. What is the molecular geometry of a molecule with 1 nonbonding electron pair and 3 bonding electron pairs?

11. What is the approximate bond angle of a molecule with 1 nonbonding electron pair and 2 bonding electron pairs?

12. What is the approximate bond angle of a molecule with 0 nonbonding electron pair and 4 bonding electron pairs?

Data Sheet: Molecular Models

Name: ____ Section: ____________________

Fill in the sheet below for the molecules you build. You may use pencil to complete this exercise.

TABLE 13.6

Molecule	**CBr_4**	**PH_3**	**SiO_2**
Total # Valence Electrons			
Lewis Structure Draw resonance forms where appropriate and determine all non-zero formal charges.			
Number of Bonding clouds of electrons around central			
Number of Non-bonding Electron pairs on central			
Electronic or Orbital Geometry			
Molecular Geometry (Name)			
Molecule Polarity			
Hybridization			
3-Dimensional Sketch with Bond Angles Noted			
Bond Angles			

TABLE 13.7

Molecule	C_2H_6	C_2H_4	C_2H_2
Total # Valence Electrons			
Lewis Structure Draw resonance forms where appropriate and determine all non-zero formal charges.			
Number of Bonding Electrons clouds on one carbon atom			
Number of Nonbonding Electron Pairs on one carbon atom			
Electronic or Orbital Geometry (both carbons)			
Molecular Geometry (Name) (both carbons)			
Molecule Polarity			
Hybridization			
3-Dimensional Sketch			
Bond Angle H-C-H			

TABLE 13.8

Molecule	**HF**	**C_2H_5OH**	**SO_3**
Total # Valence Electrons			
Lewis Structure Draw resonance forms where appropriate and determine all non-zero formal charges.			
Number of Bonding Electrons clouds on central atom	H F	C O	
Number of nonbonding Electron Pairs on central atom	H F	C O	
Electronic or Orbital Geometry on central atom	H F	C O	
Molecular Geometry (Name) on central atom	H F	C O	
Molecule Polarity			
Hybridization			
3-Dimensional Sketch			
Bond Angle		H-C-H C-O-H	

TABLE 13.9

Molecule	H_3O^+	CO_3^{2-}	NH_2^-
Total # Valence Electrons			
Lewis Structure Draw resonance forms where appropriate and determine all non-zero formal charges.			
Number of Bonding Electrons clouds on central			
Number of Nonbonding Electron Pairs on central			
Electronic or Orbital Geometry			
Molecular Geometry (Name)			
Hybridization			
3-Dimensional Sketch			
Bond Angle			

Post Lab Questions

1. Why are the valence electrons of an atom the only electrons likely to be involved in bonding to other atoms?

2. Why do representative elements tend to form bonds giving them a total of 8 valence electrons?

3. How is the structure around a given atom related to repulsion between valence electron pairs on the atom involved?

4. Why are all diatomic molecules linear, regardless of the number of valence electron pairs on the atoms involved?