N5 Chemistry

Gateways to Engineering Studies - Chris Brink

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Chemistry

N5

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Module 1

Organic Chemistry

Learning Outcomes
On the completion of this module the student must be able to:

- Describe organic compounds
- Describe organic chemistry
- Describe hydrocarbons
    - Alkanes
    - Alkenes
    - Alkynes
- Describe hybridization

1.1 Introduction

Organic chemistry is a chemistry sub-discipline involving the scientific study of the structure, properties, and reactions of organic compounds and organic materials, ie, matter in its various forms that contain carbon atoms.

Study of structure includes using physical and chemical methods to determine the chemical composition and constitution of organic compounds and materials.

Study of properties includes both physical properties and chemical properties, and uses similar methods as well as methods to evaluate chemical reactivity, with the aim to understand the behavior of the organic matter in its pure form (when possible), but also in solutions, mixtures, and fabricated forms.

The study of organic reactions includes both their preparation — by synthesis or by other means — as well as their subsequent reactivities, both in the laboratory and via theoretical study.

1.2 Organic compounds

The key rules recommended by the International Union of Pure and Applied Chemistry (HJPAC) are summarized as follows:

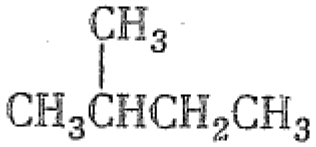
1. Choose as the parent carbon skeleton the longest sequence of C atoms that contains- the principal functional group.

2. Name the parent structure using the name of the alkane that contains the same number of *C* atoms as the chosen structure. Replace *-ane* by *-ene* for double bond or *-yne* for triple bond. If a functional group is present, drop the final *-e* and add suffixes as follows:
   -ol for alcohol (OH)
   -al for aldehyrde (CHO)
   -one for ketone (CO)
   -oic acid for acid (COOH)

3. Use prefixes m alphabetic order to denote other substituents

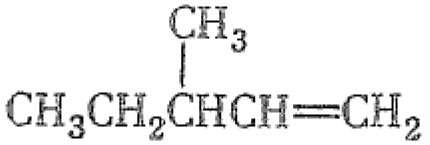
4. Locate substituents and points of unsaturation by number C atoms of the parent skeleton with the following criteria decreasing order of priority:
   (a) Assign the C atom of the principal functional group is number 1 if it is terminal.
   (b) Assign numbers so that the location of the principal functional group is as low as possible if the group is not terminal.
   (c) Assign numbers so that substituents are located lowest possible numbers. If there are two kinds of substituents give low-number preference to the first named.

5. If an attached side chain bears substituents, it too must be numbered starting with the C atom which is attached to the parent carbon skeleton. Names of substituents on the side chain and numbers locating them are enclosed in parentheses with the name of the side chain:



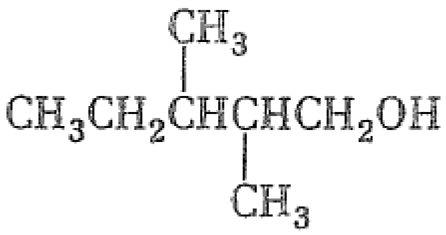
$CH_3\overset{\overset{CH_3}{|}}{C}HCH_2CH_3$

2-*Methylbutane*



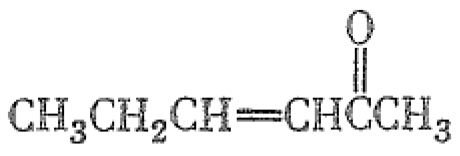
$CH_3CH_2\overset{\overset{CH_3}{|}}{C}HCH{=}CH_2$

3-*Methyl*-1-*pentene*



$CH_3CH_2\overset{\overset{CH_3}{|}}{C}H\underset{\underset{CH_3}{|}}{C}HCH_2OH$

2,3-*Dimethyl*-1-*pentanol*



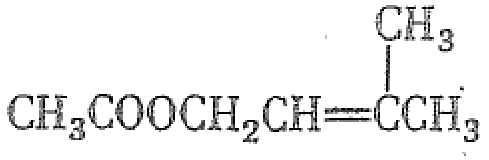
$CH_3CH_2CH{=}CH\overset{\overset{O}{\|}}{C}CH_3$

3-*Hexene*-2-*one*

Esters are named by replacing the suffix of the parent acid –*oic acid* by -*oate*:

$CH_3CH_2CH_2COOCH_3$

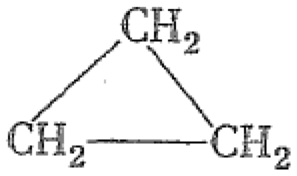
Methylbutanoate



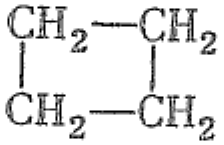
$CH_3COOCH_2CH{=}C(CH_3)CH_3$

3-Methyl-2-butenylethanoate

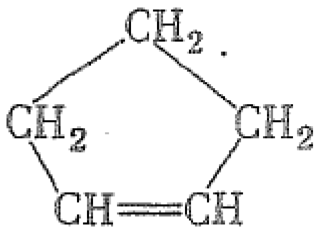
Cyclic aliphatic hydrocarbons are named by prefixing *cyclo-* to the name of the corresponding open-chain hydrocarbon having the same number of C atoms as the ring:



Cyclopropane

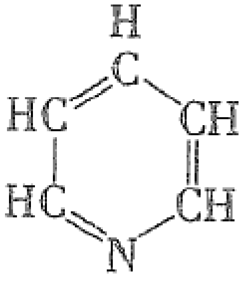


Cyclobutane

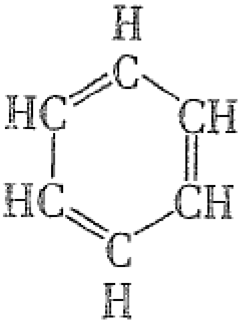


Cyclopentene

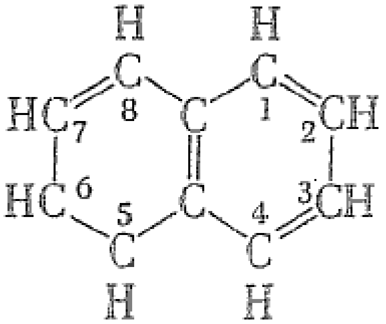
Rings containing atoms other than C (heterocycles) as well as aromatic rings are usually designated by trivial (nonsystematic) names:



Pyridine



Benzene



Naphthalene

To locate substituents, rings are numbered clockwise around the periphery as shown for naphthalene.

1.2.1 Why Carbon?

We begin this discussion of organic chemistry with a question: '"What features of carbon lead to both the abundance and the complexity of organic compounds? Answers fall into two categories: structural diversity and stability.

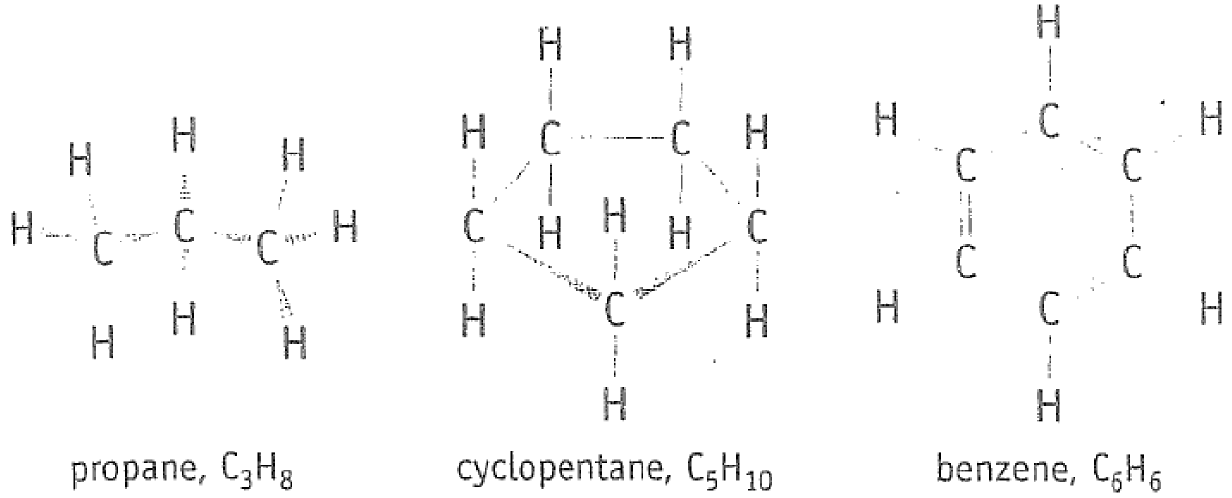
With four electrons in its outer shell, carbon will form four bonds to reach an octet configuration. In contrast, the elements boron and nitrogen form three bonds in molecular compounds, oxygen forms two bonds, and hydrogen and the halogens form one bond.

With a larger number of bonds comes the opportunity to create more complex structures. This will become increasingly evident in this brief tour of organic chemistry.

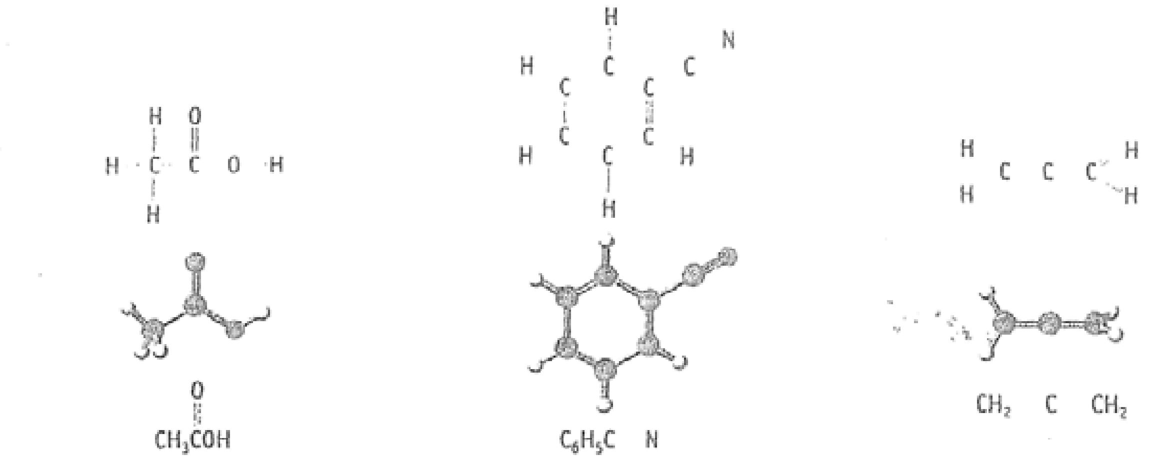
A carbon atom can reach an octet of electrons in various ways (**Figure 1.1**):

- *By forming four single bonds.* A carbon aton1 can bond to four other atoms, which can be either atoms of other elements (often H, N, or O) or other carbon atoms.
- *By forming a double bond and two single bonds.* The carbon atoms in ethylene, $H_2C = CH_2$, are linked to other atoms in this way.
- *By forming two double bonds*, as in carbon dioxide ($O = C = O$).
- *By forming a triple bond and a single bond*, an arrangement seen in acetylene, $HC \equiv CH$.

Recognize, with each of these arrangements, the various possible geometries around carbon: tetrahedral, trigonal planar, and linear. Carbon's tetrahedral geometry is of special significance because it leads to three-dimensional chains and rings of carbon atoms, as in propane and cyclopentane. The ability to form multiple bonds leads to whole families of compounds based on structures such as ethylene, acetylene, and benzene.



propane, C_3H_8 cyclopentane, C_5H_{10} benzene, C_6H_6



(a) Acetic acid. One carbon atom in this compound is attached to 4 other atoms by single bonds and has tetrahedral geometry. The second carbon atom, connected by a double bond to one oxygen, and by single bonds to the other oxygen and to carbon, has trigonal planar geometry.

(b) Benzonitrile. Six trigonal planar carbon atoms make up the benzene ring. The seventh C atom, bonded by a single bond to carbon and a triple bond to nitrogen, has a linear geometry.

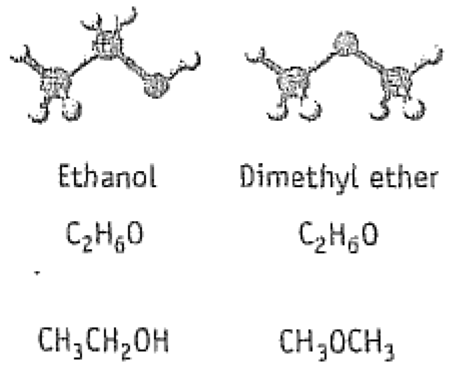
(c) Carbon is linked by double bonds to two other carbon atoms in C_3H_4, a linear molecule commonly called allene.

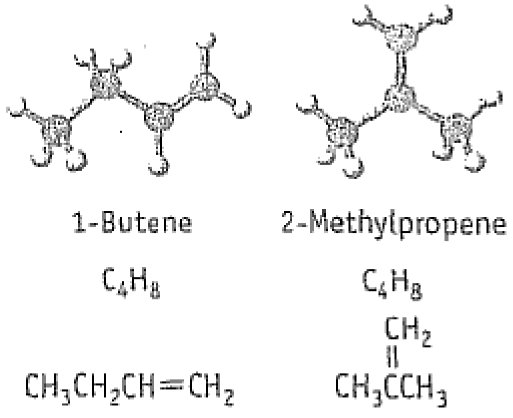
Figure 1.1 Ways that carbon atoms bond

1.2.2 Isomers

A hallmark of carbon chemistry is the remarkable array of isomers that can exist. Isomers are compounds that have identical composition but different structures. Two broad categories of isomers exist: structural isomers and stereoisomers.

Structural isomers are compounds having the same elemental composition, but in which the atoms are linked together in different ways. Ethanol and dimethyl ether are structural isomers, as are l-butene and 2-methylpropene.

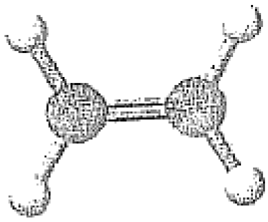




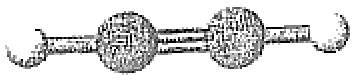
Stereoisomers are compounds with the same formula and in which there is a similar attachment of atoms. However, the atoms have different orientations in space. Two types of stereoisomers exist: geometric isomers and optical isomers.

Cis- and *trans*-2-butene are geometric isomers. Geometric isomerism in these compounds occurs as a result of the C=C double bond. Recall that the carbon atom and the attached groups cannot rotate around a double bond.

Thus, the geometry around the C=C double bond is fixed in space. If two groups occur on the adjacent carbon atoms and on the same side of the double bond, a *cis* isomer is produced. If groups appear on opposite sides, a *trans* isomer is produced.



Ethylene, $H_2C{=}CH_2$



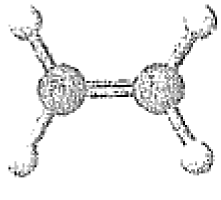
Acetylene, $HC{\equiv}CH$

Figure 1.2 Ethylene and acetylene. These two-carb hydrocarbons can be the building blocks of more complex molecules. These are their common names, but their systematic names are ethene and ethyne.

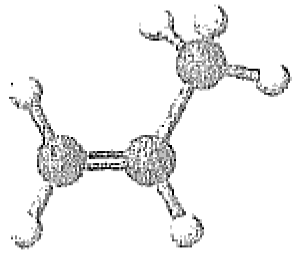
Name	**Boiling point**	**Melting point**	**Dipole Moment (D)**	**ΔH_f^o (gas) (kJ/mol)**
1-butene	-6,26 °C	-185,4 °C	-	-20,5
2-methylpropene	-6,95 °C	-140,4 °C	0,503	-37,5
cis-2-butene	3,71 °C	-138,9 °C	0,253	-29,7
trans-2-butene	0,88 °C	-105,5 °C	0	-33,0

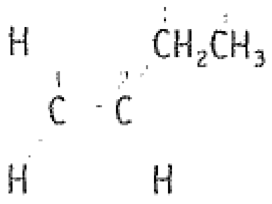
Table 1.1

C_2H_4
Systematic name:
Ethene
Common name:
Ethylene

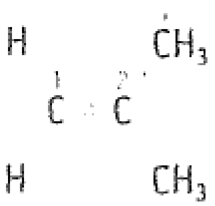


C_3H_6
Systematic name:
Propene
Common name:
Propylene

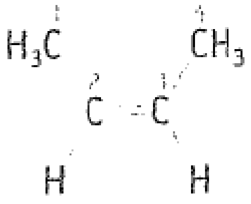




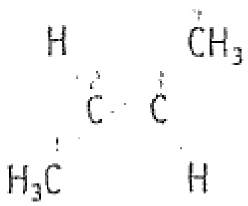
1-butene



2-methylpropene



cis-2-butene



trans-2-butene

Alkene names end in "-ene." As with alkanes, the root name for alkenes is that of the longest carbon chain. The position of the double bond is indicated with number, and, when appropriate, the prefix *cis* or *trans* is added. Three of the C_4H_8 isomers have four-carbon chains and so are butenes.

One has a three-carbon chain and is a propene. Notice that the carbon chain is numbered from the end that gives the double bond the lowest number. In the first isomer at the left, the double bond is between C atoms 1 and 2, so the name is 1-butene and not 3-butene.

Worked Example 1.1

Problem

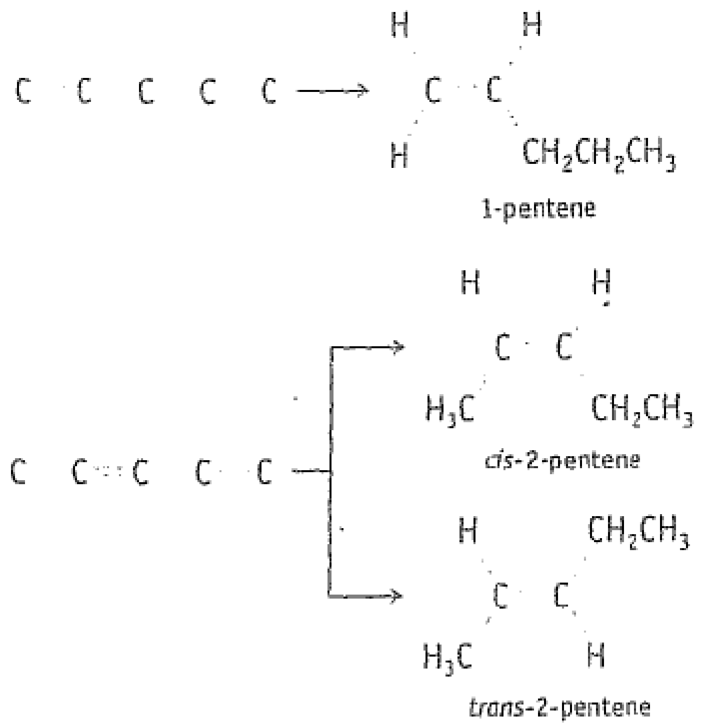
Draw structures for the six possible alkene isomers with the formula C_5H_{10}. Give the systematic name of each.

Strategy

A procedure that involved drawing the carbon skeleton and then adding hydrogen atoms served well when drawing structures of alkanes, and a similar approach can be used here. It will be necessary to put one double bond into the framework and to be alert for *cis-trans* isomerism.

Solution

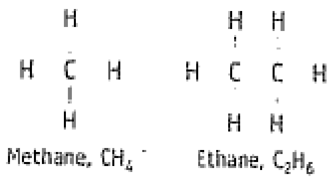
1. A five-carbon chain with one double bond can be constructed in two ways. One gives rise to *cis-trans* isomers.



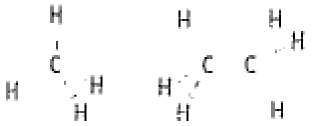
Writing formulae and drawing structures

Previously you learned that there are various ways of presenting structures. It is appropriate to return to that point as we look at organic compounds. Consider methane and ethane, for example. We can represent these molecules in several ways:

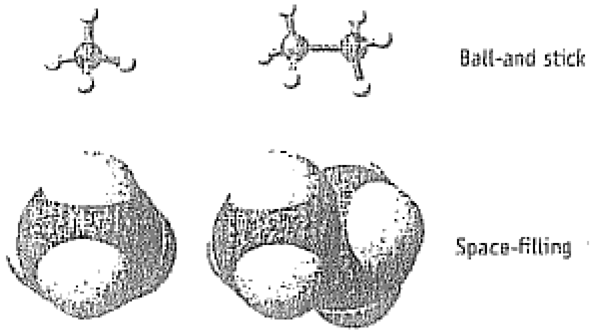
1. *Molecular formula*: CH_4 or C_2H_6. This type of formula gives information only on composition.
2. *Condensed formula*: For ethane this would be written CH_3CH_3 (or as H_3CCH_3). This method of writing the formula gives some information on the way atoms are connected.
3. *Structural formula*: You will recognize this formula as the Lewis structure. An elaboration on the condensed formula in (2), this representation defines more clearly how each atom is connected, but it fails to describe the shapes of molecules.

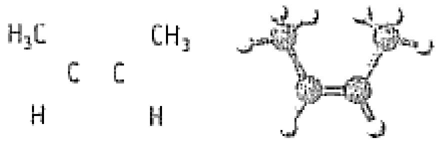


4. *Perspective drawings*: These drawings. are used to convey the three-dimensional nature of molecules. Bonds extending out of the plane of the paper are drawn with wedges, and bonds behind the plane of the paper are represented as dashed wedges. Using these guidelines, the structures of methane and ethane could be drawn as follows:

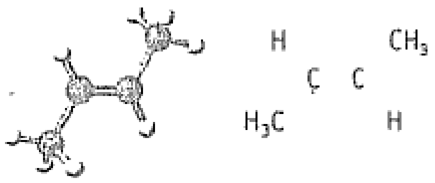


5. Computer-drawn ball-and-stick and space-filling models.



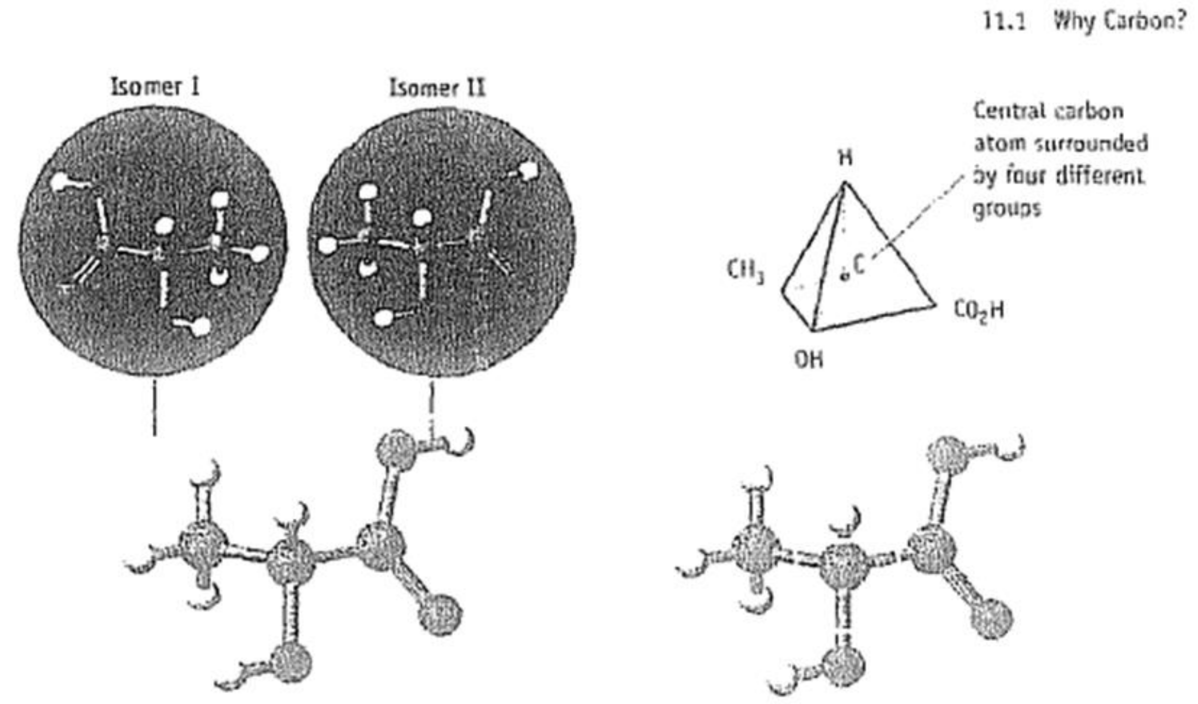


Cis-2-butene, C_4H_8



Trans-2-butene, C_4H_8

Optical isomerism is a second type of stereoisomerism. Optical isomers are molecules that have non-superimposable mirror images (**Figure 1.2**). Molecules (and other objects) that have non-superimposable mirror images are termed chiral. Pairs of non-superimposable molecules are called enantiomers.



(a) Lactic acid isomers are nonsuperimposable

(b) Lactic acid, $CH_3CH(OH)CO_2H$

Figure 1.3 **Optical isomers** (a) Optical isomerism occurs if a molecule and its mirror image cannot be superimposed. The situation is seen if four different groups are attached to carbon. (b) Lactic acid, are attached to the central molecule. Four different groups (H, OH, CH_3, and CO_2H) are attached to the central carbon atom.

Lactic acid is produced from milk when milk is fermented to make cheese. It is also found in other sour foods such as sauerkraut and is a preservative in pickled foods such as onions and olives. In our bodies it is produced by muscle activity and normal metabolism.

See the General Chemistry Now CD-ROM or website: http://www.nbclearn.com/chemistry to explore an interactive version of **Figure 1.4** accompanied by an exercise.

Pure samples of en enantiomers have the same physical properties, such as melting point, boiling point, density and solubility in common solvents.

They differ in one significant way, however, when a beam of plane-polarized light passes through a solution of a pure enantiomer, the plane of polarization rotates. The two enantiomers rotate polarized light to an equal extent, but in opposite directions (**Figure 1.4**).

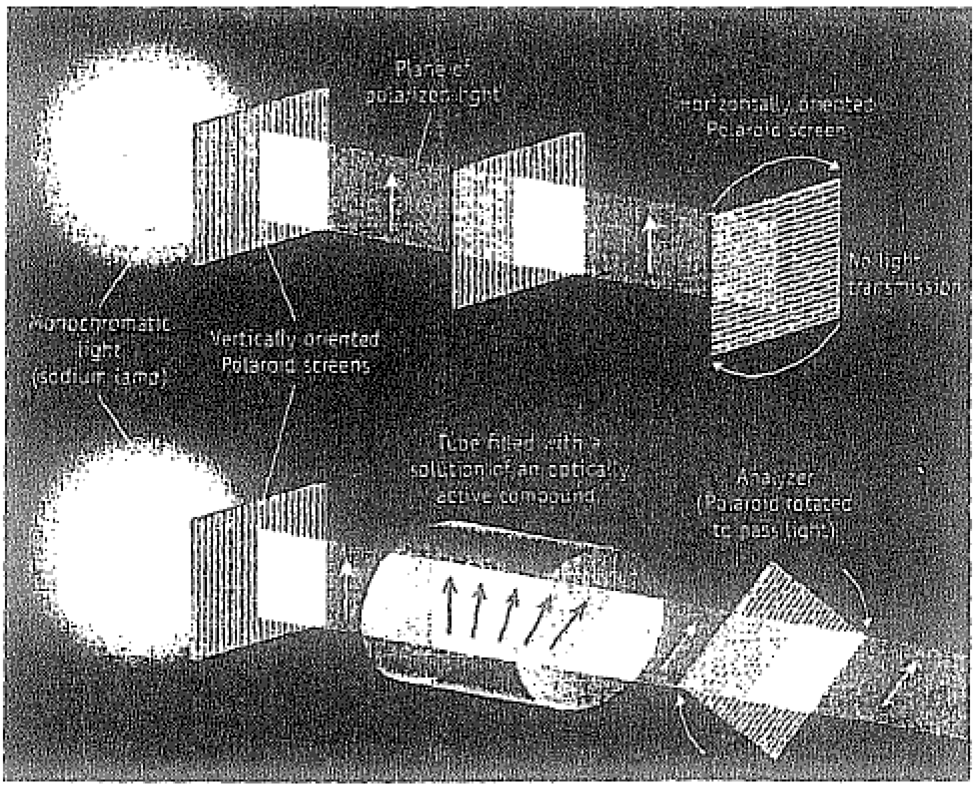


Figure 1.4 **Rotation of plane-polarised light by an optical isomer** (Top) Monochromatic light (light of only one wavelength) is produced by a sodium lamp. After it passes through a polarizing filter, the light vibrates in only one direction – it is polarized. Polarized light will pass through a second polarizing filter if this filter is positioned parallel to the first fitter, but not if the second fitter is perpendicular. (Bottom) A solution of an optical isomer placed between the first and second polarizing fllters causes rotation of the plane of polarized light. The angle of rotation can be determined by rotating the second filter until maximum light transmission occurs. The magnitude and direction of rotation are unique physical properties of the optical isomer being tested.

The term "optical isomerism" is used because this effect involves light (see **"A Closer Look: Optical Isomers"**).

The most common examples of chiral compounds are those in which four different atoms (or groups of atoms) are attached to a tetrahedral carbon atom. Lactic acid, found in milk and a product of normal human metabolism, is an example of one such chiral compound (**Figure 1.3**).

Optical isomerism is particularly important in the amino acids and other biologically important molecules.

A Closer Look: Optical Isomers

Everyone has accidentally put a left shoe on a right foot, or a left-handed glove on a right hand. It doesn't work very well. Even though our two hands and two feet appear generally similar, a very important distinction separates them. Left hands and feet are mirror images of right hands and feet.

Most importantly, these mirror images cannot be superimposed. We describe them as chiral. Many common objects have this property. Some seashells are chiral, for example.

Wood screws and machine bolts are also chiral, being distinguished by left-handed or right-handed threads.

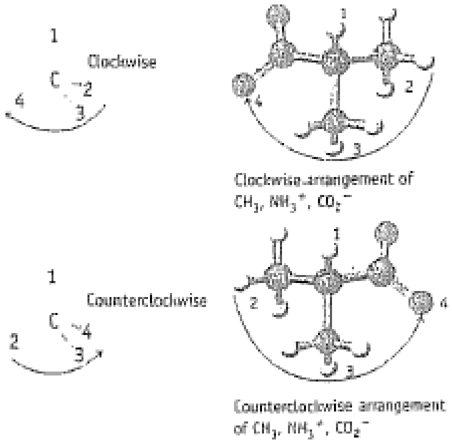
Certain molecules have the same characteristic as gloves and hands: A given structure and its mirror image - its enantiomer - cannot be superimposed. There are various ways to visualize that two enantiomers are different.

Imagine a tetrahedral carbon atom attached to four other atoms or groups, all different. For simplicity the atoms bonded to the central C atom in the amino acid alanine are shown as 1, 2, 3, and 4 in the drawing.

Sight down one of the bonds to carbon (say, the bond from atom 1 to C) in one enantiomer. The other three atoms (2, 3, and 4) will then appear in a clockwise order. In the second enantiomer, atoms 2, 3, and 4 will appear in counterclockwise order.

The handedness of seashells - Seashells are almost all right-handed. This photo shows tile egg cases for whelk shells. Each egg case is about 3 cm in diameter and about 2-3 mm thick. Each egg case is attached to a spine, and the arrangement of egg cases around the spine is right-handed.

The helical chain of DNA is like the threads of a screw. It twists to the left or it twists to the right. Here it twists to the right. If you curl your right hand around the chain, with your thumb extended, your fingers will show the direction of the twist and your thumb will point along the chain.



Enantiomers of alanine

1.2.3 Stability of Carbon Compounds

Carbon compounds are notable for their resistance to chemical change. Were this not so, far fewer compounds of carbon would be known.

Strong bonds are needed for molecules to survive in their environment. Molecular collisions in gases, liquids, and solutions often provide enough energy to break some chemical bonds, and bonds can be broken if the energy associated with photons of visible and ultraviolet light exceeds the bond energy.

Carbon - carbon bonds are relatively strong, however as are the bonds between carbon and most other atoms. The average C─C bond energy is 346 kJ/mol, the C─H bond energy is 413 kJ/mol.

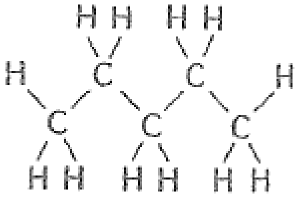
1.3 Organic Chemistry

Organic chemistry is the chemistry of carbon compounds. There is, however, a small number of carbon compounds (eg, CO, CO_2, carbonates) that are not classified as organic.

The vast number of organic compounds reflects the exceptional ability of carbon to form covalent bonds with other carbon atoms to form chains, branched chains and rings. A straight chain compounds are called aliphatic compounds and ring compounds are called cyclic compounds.

1.3.1 A straight Chain Compound – The Pentane Molecule

Each line represents one covalent bond. In pentane the 4 bonds from each carbon atom are arranged tetrahedrally in space.



In organic compounds carbon always has a valency of four. Apart from carbon, a small number of other elements are widely found in organic compounds. These are hydrogen, oxygen, nitrogen, sulphur and the halogens.

1.3.2 Formulae

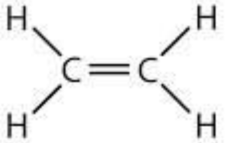
The empiral formula gives the simplest whole number ratio of atoms present.

The molecular formula gives the total number of atoms in one molecule.

The structural formula shows how the atoms are linked together in a molecule.

However we must not conclude that the structural formula gives the molecular shape.

Consider the example of ethane.

CH_2	C_2H_4	
Empirical formula	Molecular formula	Structural formula

1.3.3 Homologous series

The study of organic chemistry is greatly simplified its natural division into families or closely related compounds, each family being known as a homologous series.

In general all the compounds in a homologous series:

- Can be prepared by similar methods.
- Have similar chemical properties.
- Exhibit a gradual change in physical properties.
- Can be represented by a general formula.
- Have regularly increasing relative molecular masses.

The six lowest members of the simplest homologous series, the alkanes, are given below with their melting points and boiling points. The chemical properties of the compounds below are practically identical.

Name	Formula	Relative molecular mass	Melting point (°C)	Boiling point (°C)
Methane	CH_4	16	-183	-162
Ethane	C_2H_6	30	-172	-87
Propane	C_3H_8	44	-188	-42
Butane	C_4H_{10}	58	-135	-0,5
Pentane	C_5H_{12}	72	-130	36
Hexane	C_6H_{14}	86	-95	69

Table 1.2 The Alkanes C_nH_{2n+2}

1.3.4 Nomenclature

The alkanes are sometimes represented by R─H where R is an alkyl group.

R	Name	Number of carbon atoms
CH_3─	methyl	1
C_2H_5─	ethyl	2
C_3H_7─	propyl	3
C_4H_9─	butyl	4

Table 1.3 Alkyl groups

Other homologous series that we shall study can be considered to be derived from the alkanes by replacing one or more hydrogen atoms by other atoms or groups.

Homologous series	Compounds with 1 carbon atom	Compound with 2 carbon atoms
Alkanes	Methane CH_4	Ethane C_2H_6
Alkenes	-	Ethene C_2H_4
Alcohols	Methanol CH_3OH	Ethanol C_2H_5OH
Acids (alkaloic)	Methanoic acid HCOOH	Ethanoic acid CH_3COOH

Table 1.4 First members of some homologous series

1.4 Hydrocarbons

Hydrocarbons are compounds which contain carbon and hydrogen only. They occur abundantly in coal, petroleum and natural gas.

Saturated hydrocarbons are those in which the combining capacity of the carbon atoms is as fully used as possible in bonding with hydrogen atoms, eg the alkanes.

Unsaturated hydrocarbons are those in which the combining capacity of the carbon atoms is not fully used. Unsaturated hydrocarbons are characterized by double or triple bonds between carbon atoms, eg the alkenes.

1.4.1 Alkanes $C_n H_{2n+2}$

The alkanes form the simplest homologous series. They are found in large quantities in petroleum and natural gas. The first four members are colourless and odourless gases at room temperature. They are almost insoluble in water.

The First Four Alkanes:

CH_4	Methane
$C_2 H_6$	Ethane
$C_3 H_8$	Propane
$C_4 H_{10}$	Butane

Higher members are liquids (C_5 to C_{15}) or waxy solids (above C_{15}).

Laboratory Preparation of Alkanes

Alkanes are prepared by heating the sodium salt of an alkanoic acid with soda lime.

$$CH_3COONa(s) + NaOH(s) \longrightarrow CH_4(g) + Na_2CO_3(s)$$

Definition: Soda lime

So lime is made by adding concentrated sodium hydroxide solution to quicklime (CaO). It is a mixture of sodium and calcium hydroxides.

Note:

Because alkanes are found abundantly in natural gas and petroleum, they are not made industrially (except as by-products). On the contrary, they themselves are the important starting materials in many manufacturing processes.

Properties of Alkanes

Alkanes are characterized by their lack of reactivity. This is typical of saturated hydrocarbons. They do not react with most acids, alkalis, oxidizing agents or reducing agents. They do however:

1. Burn readily

   $$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(g)$$

   Hence they are used in very large quantities as fuels. Mixtures of alkanes with air or oxygen are generally explosive.

2. React with chlorine or bromine by substitution.
   The hydrogen atoms are replaced successively, eg chlorine with methane

   $$CH_4 \xrightarrow{Cl_2} CH_3Cl \xrightarrow{Cl_2} CH_2Cl_2 \xrightarrow{Cl_2} CHCl_3 \xrightarrow{Cl_2} CCl_4$$

   The reaction takes place smoothly if the mixture is exposed to diffuse light.

No reaction occurs in darkness; in sunlight the reaction is explosive. At each step hydrogen chloride is produced, eg.

$CH_4(g) + Cl_2(g) \longrightarrow CH_3Cl(g) + HCl(g)$ 1st step

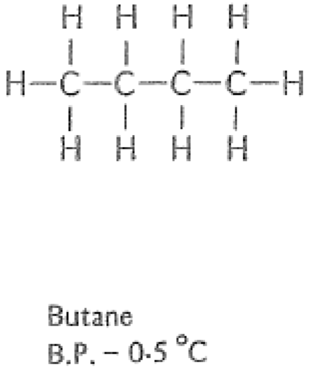
Names of the substitution products are:

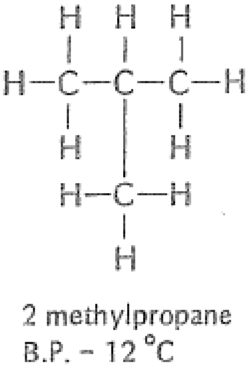
(i) CH_3Cl monochloromethane	(iii) $CHCl_3$ trichloromethane
(ii) CH_2Cl_2 cichloromethane	(iv) CCl_4 tetrachloromethane

The reaction of ethane with chlorine yields six substitution products.

Isomerism in the Alkanes

Isomers are different compounds having the same molecular formula but different structural formulae. Consider the molecular formula C4 H 10 • This represents two isomers:


Butane
B.P. – 0·5 °C


2 methylpropane
B.P. – 12 °C

⚠	**Note:** 2 methylpropane is considered to be derived from propane by replacement of one hydrogen atom on the second carbon atom (hence '2') by a methyl group.

The physical properties of such isomers differ, but their chemical properties are very similar.

There are no isomers of CH_4 , C_2H_6 or C_3H8 . It can be shown that there are 3 isomers of C_5H_{12} and 5 isomers of C_6H_{14}.

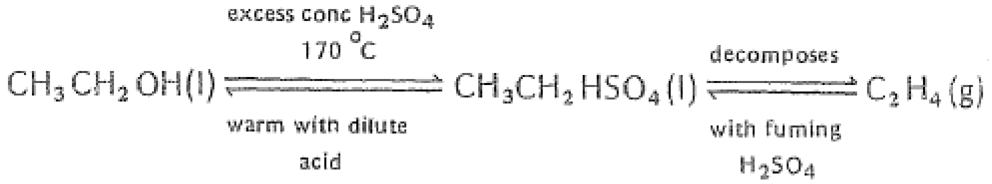
1.4.2 Alkenes C_nH_{2n}

These form a homologous series of unsaturated hydrocarbons. Each member has one double bond between carbon atoms. The three simplest members are ethene, propene and butene (**Table 1.5**).

Laboratory Preparation of Alkenes

Alkenes are prepared by the dehydration of alcohols. Thus ethene is produced when ethanol is heated with excess concentrated sulphuric(VI) acid at 170 °C.

This reaction takes place in two steps: these steps are illustrated below without using balanced equations.



$$CH_3CH_2OH(l) \underset{\text{warm with dilute acid}}{\overset{\text{excess conc } H_2SO_4 \text{ } 170\ ^{\circ}C}{\rightleftharpoons}} CH_3CH_2HSO_4(l) \underset{\text{with fuming } H_2SO_4}{\overset{\text{decomposes}}{\rightleftharpoons}} C_2H_4(g)$$

The oily liquid, ethyl hydrogen sulphate is an ester. It decomposes in the presence of hot concentrated sulphuric(V!) acid to form ethene.

The reaction can be readily reversed by reacting· e:tbene with fuming sulphuric(VI) acid. Ethyl hydrogen sulphate is produced and on warming with dilute acid it is converted into ethanol.

industrially, alkenes are obtained from the catalytic cracking of petroleum.

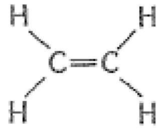
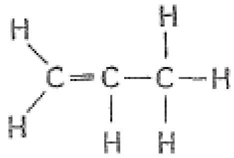
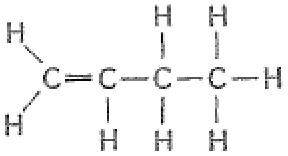
		Relative molecular mass	**Melting point (°C)**	**Boiling point (°C)**
C_2H_4	Ethene 	28	-169	-102
C_3H_6	Propene 	42	-185	-48
C_4H_8	Butene 	56	-185	-6

Table 1.5 Alkenes C_nH_{2n}

Properties of Alkenes

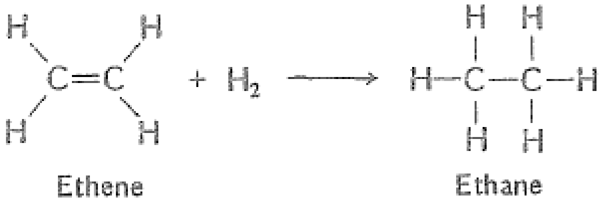
The first three members of the series are colourless gases. Higher members are liquids. They are practically insoluble in water. Ethene has a characteristic sweet smell.

1. They burn readily in air or oxygen
   Mixtures of air and alkenes are explosive in certain proportions.
   $C_2H_4(g) + 3O_2(g) \longrightarrow 2CO_2(g) + 2H_2O(g)$
2. They react readily with various reagents

In contrast to the alkanes, the alkenes react readily with a wide variety of reagents and these reactions are addition reactions.

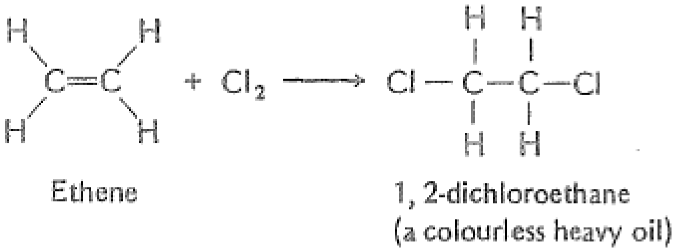
Example a

With hydrogen - when a mixture of hydrogen and ethene is passed over a catalyst of finely divided nickel at 140 °C ethane forms. This is an example of catalytic hydrogenation.



Example b

With halogens - chlorine or bromine vapour react readily with ethene. Iodine has little tendency to add to the double bond.



The product with bromine is 1, 2-dibromoethane.

Note:
The three possible positions that each chlorine atom can attach itself to a carbon atom are equivalent.

Example c

With steam - alkenes do not react with water under normal laboratory conditions. However ethanol may be prepared by the catalysed reaction between ethene and steam.

$$CH_2{=}CH_2(g) + H_2O(g) \longrightarrow CH_3CH_2OH(g)$$

The catalyst is basically phosphoric(V) acid on a siliceous support.

Ethanol is more usually prepared from ethene by reacting the alkene with fuming sulphuric (VI) acid and then warming the product (ethyl hydrogen sulphate) with dilute acid, (see *preparation of ethane*).

The halogen acids HCl, HBr and HI also react with alkenes to form addition products. Hydrogen iodide reacts most readily and hydrogen chloride least readily.

Polymerization

When heated at very high pressures (about 1 000 atmospheres) ethane polymerizes to form polyethene.

$$nCH_2{=}CH_2 \longrightarrow \underset{\text{polyethene}}{\left(CH_2-CH_2\right)_n}$$

n is quite large; up to about 1 200.

Chloroethene (CH_2=CHCl) a compound closely related to ethene, polymerizes to form polychloroethene.

$$nCH_2{=}CHCl \longrightarrow \underset{\text{polychloroethene}}{\left(CH_2-CHCl\right)_n}$$

Note:
Polyethene and polychloroethene have been known in the past as polythene and polyvinyl chloride (PVC) respectively. These names are likely to remain in common use for a long time.

Test for unsaturation

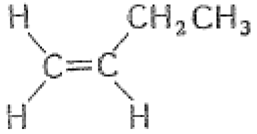
Unsaturated compounds such as the alkenes decolourize bromine water. They also turn purple alkaline potassium manganite (VII) solution firstly green (manganite (VI) ion) and then decolourize it with the formation of a brown precipitate of manganese (IV) oxide.

Note:
Alcohols also decolourize potassium manganite (VII) solution.

Isomerism in the Alkenes

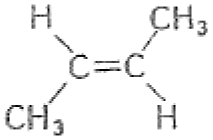
There are no isomers of C_2H_4 or C_3 H_6. However there are 4 isomers having the formula C_4H_8. These are:

(a)



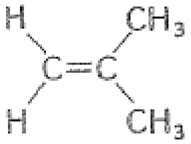
But-1-ene
B.P. – 5 °C

(b)



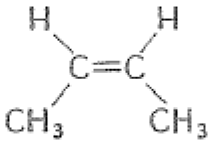
Trans but-2-ene
B.P. 2·5 °C

(c)



2-methylpropene
B.P. – 6 °C

(d)



Cis but-2-ene
B.P. 1 °C

But-1-ene and but-2-ene can be distinguished by the different positions of the double bond. The cis and trans isomers of but-2-ene come about because rotation about a double bond is not possible.

Cis-trans pairs are examples of geometrical isomers. Structure (c) is clearly a substituted propene.

All the isomers above are similar in their chemical properties.
Alcohols $C_nH_{2n-1}OH$

Alcohols can be regarded as hydroxyl derivatives of alkanes with formula R–OH.

We shall consider primary alcohols only (primary alcohols contain the grouping -CH_2OH). The four simplest members of this homologous series are given in **Table 1.6**.

Name	Formula	Melting point (°C)	Boiling point (°C)
Methanol	CH_3OH	-98	65
Ethanol	CH_3CH_2OH	-117	78
Propan-1-ol	$CH_3CH_2CH_2OH$	-127	97
Butan-1-ol	$CH_3CH_2CH_2\ CH_2OH$	-90	117

Table 1.6 Alcohols $C_nH_{2n-1}OH$

The four alcohols above are all colourless liquids. The first three are miscible with water in all proportions. Butan-1-ol dissolves to the extent of 83 g in 1 kg of water. Higher members are less soluble.

Ethanol is the ordinary alcohol found in spirits. It is produced by the fermentation of sugar by yeast. Large quantities are manufactured industrially by fermentation of molasses (from sugar cane) or of starch (from potatoes).

Methanol is one of the products of the destructive distillation of wood. Ethylated spirits is a mixture made up of about 90% raw spirit (mostly ethanol) and ·1 0% methanol.

Laboratory Preparation of Alcohols

Alcohols may be prepared by hydrolysis of esters or by the reaction of ethenes with fuming sulphuric(VI) acid. In the latter reaction the product, an alkyl hydrogen sulphate, is converted into an alcohol by warming with a dilute acid (see preparation of ethanes).

Reactions of Alcohols

1. They burn readily in air
   Mixtures of air and alcohol vapour may be explosive. Hence used as a fuel (especially in rockets).
   $$CH_3CH_2OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(g)$$

2. They react with sodium liberating hydrogen and forming an alkoxide
   $$2CH_3OH(l) + 2Na(s) \longrightarrow H_2(g) + \underset{\text{sodium methoxide}}{2CH_3ONa}$$
   The product with ethanol is sodium ethoxide.

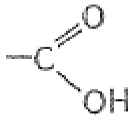
3. They are dehydrated by excess concentrated sulphuric(VI) acid at 170 °C to produce alkenes
   (See details under preparation of alkenes.)
   $$C_2H_5OH(l) \longrightarrow C_2H_4(g) + H_2O(l)$$

4. They can be readily oxidized to produce alkanoic acids
   A number of oxidizing agents may be used. A very common method is to heat the alcohol with a mixture of potassium dichromate(VI) and dilute sulphuric(VI) acid. It is important to have an excess of the oxidizing agent or else an aldehyde is produced; eg
   $$\underset{\text{ethanol}}{CH_3CH_2OH} \longrightarrow \underset{\text{ethanoic acid}}{CH_3COOH} \qquad \text{(Not a balanced equation)}$$

5. They react with carboxylic acids to form esters (See under alkanoic acids).

Alkanoic Adds C_nH_{2n+1} COOH

Each member of this homologous series has one carboxyl group. Alkanoic acids are therefore aliphatic monocarboxylic acids.



carboxyl group (often written as — COOH)

Consequently we can represent the series with the formula RCOOH. The hydrogen atom in the carboxyl group can form a hydrogen ion in aqueous solution.

Hence members of the series are monobasic acids. The four simplest members are given in the table below.

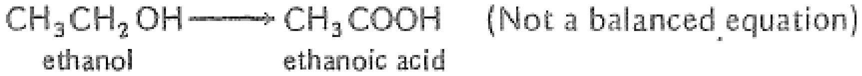
Name	**Formula**	**Melting point (°C)**	**Boiling point (°C)**
Methanoic acid	$HCOOH$	8.3	101
Ethanoic acid	CH_3COOH	17	118
Propanoic acid	CH_3CH_2COOH	-21	140
Butanoic acid	$CH_3CH_2CH_2 COOH$	-6	164

Table 1.7 Alkanoic Acids $C_nH_{2n+1C}OOH$

Lower members of the series are colourless liquids which are miscible with water in all proportions. Higher members are sparingly soluble oily liquids, and still higher ones are insoluble waxy solids. They have individual characteristic pungent smells.

Methanoic acid has a corrosive action on the skin. It occurs in the stings of ants, bees and stinging nettles. Ethanoic acid is formed by bacterial oxidation of ethanol. Vinegar, which is produced in this way, is a 6-10% aqueous solution of ethanoic acid. Butanoic add is largely responsible for the smell of rancid butter.

Laboratory Preparation of Acids
Aikanoic acids are prepared by the oxidation of primary alcohols with excess oxidizing agents (see reaction (4) of alcohols).



$$\underset{\text{ethanol}}{CH_3CH_2OH} \longrightarrow \underset{\text{ethanoic acid}}{CH_3COOH} \quad \text{(Not a balanced equation)}$$

Reactions of Alkanoic Acids

1. They are weak monobasic acids
   Hence they turn litmus red, liberate hydrogen from metals above hydrogen.

1.5 Illustrations of hybridization in chemical bonding

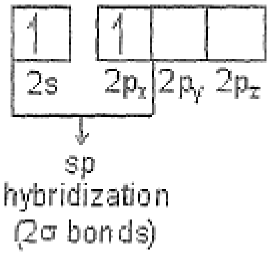
1.5.1 Beryllium Chloride (BeC_{12}):

The electronic configuration of 'Be' in ground state is $1s^2$ $2s^2$. Since there are no unpaired electrons, it undergoes excitation by promoting one of its 2s electron into empty 2p orbital.

Thus in the excited state, the electronic configuration of Be is $1s^2$ $2s^1$ $2p^1$.

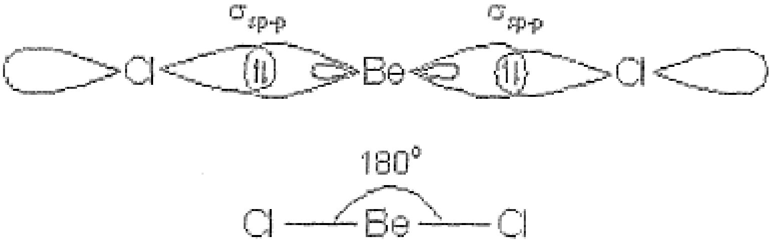
If the beryllium atom forms bonds using these pure orbitals, the molecule might be angular. However the observed shape of $BeCl_2$ is linear. To account for this, following sp hybridization was proposed.

In the excited state, the beryllium atom undergoes 'sp' hybridization by mixing a 2s and one 2p orbitals. Thus two half filled 'sp' hybrid orbitals are formed, which are arranged linearly.



These half filled sp-orbitals form two a bonds with two 'Cl' atoms.

Thus $BeCl_2$ is linear in shape with the bond angle of 180°.



1.5.2 Acetylene (C_2H_2):

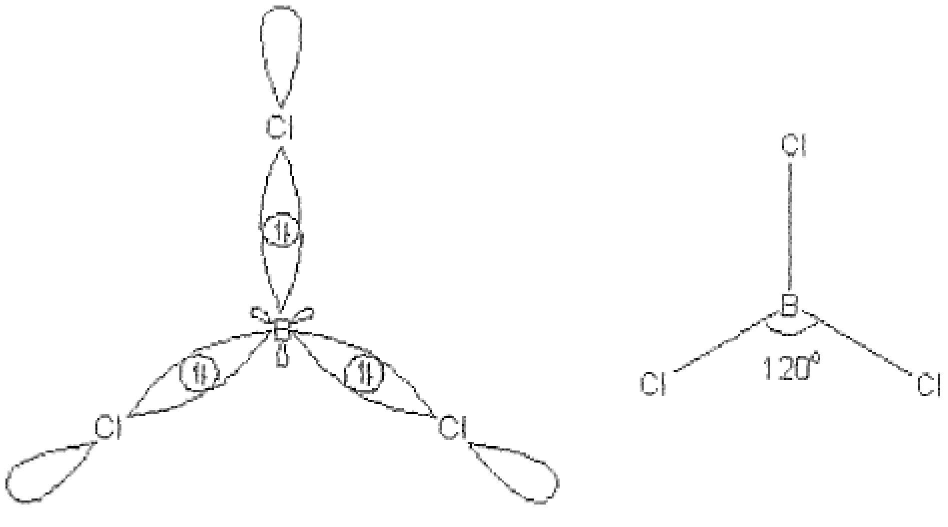
The ground state electronic configuration of 'C' is $1s^2\ 2s^2\ 2p_x^1 2p_y^1$. There are only two unpaired electrons in the ground state. However, the valency of carbon is four ie, it forms 4 bonds. In order to form four bonds, there must be four unpaired electrons.

Hence carbon promotes one of its 2s electron into the empty $2p_z$ orbital in the excited state.

Thus in the excited state, the electronic configuration of carbon is $1s^2\ 2s^1\ 2p_x^1 2p_y^1 2p_z^1$.

Each chlorine atom uses it's half filled p-orbital for the σ-bond formation.

Thus the shape of BCl_3 is trigonal planar with bond angles equal to 120°.

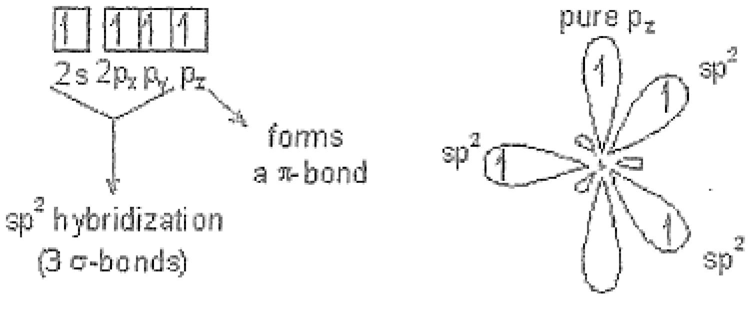


Trigonal planar structure of BCl_3

1.5.3 Ethylene (C_2H_4):

During the formation of ethylene molecule, each carbon atom undergoes sp^2 hybridization in its excited state by mixing 2s and two 2p orbitals to give three half filled sp2 hybrid orbitals oriented trigonal planar symmetry.

There is also one half filled unhybridized $2p_z$ orbital on each carbon perpendicular to the plane of sp^2 hybrid orbitals.



The carbon atoms form a $\sigma_{sp2\text{-}sp2}$ bond with each other by using sp^2 hybrid orbitals.

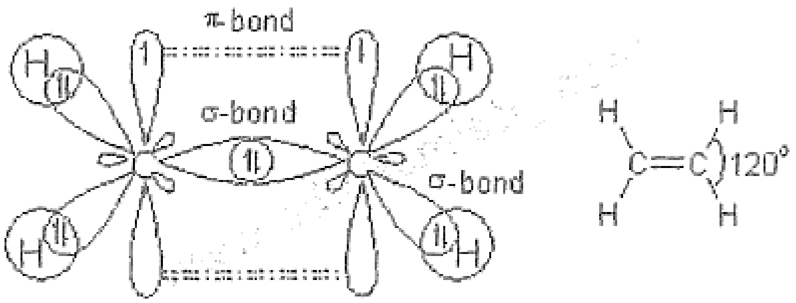
A $\pi_{p\text{-}p}$ bond is also formed between them due to lateral overlapping of unhybridized $2p_z$ orbitals.

Thus there is a double bond ($\sigma_{sp2\text{-}sp2}$ & $\pi_{p\text{-}p}$) between two carbon atoms.

Each carbon atom also forms two $\sigma_{sp2\text{-}s}$ bonds with two hydrogen atoms.

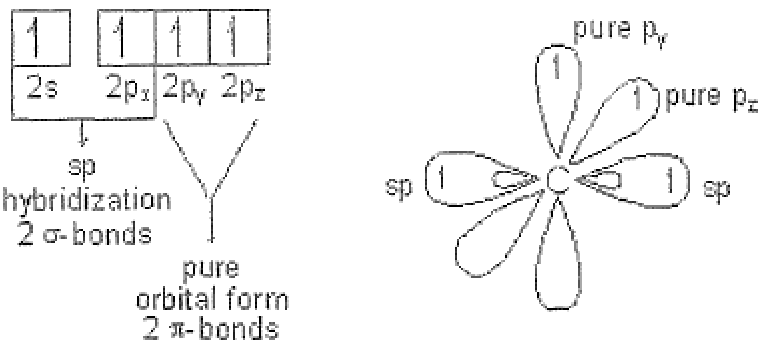
Thus ethylene molecule is planar with <HCH & <HCC bond angles equal to 120°.

All the atoms are present in one plane.



Planar structure of ethylene molecule

1.5.4 sp^3 Hybridization



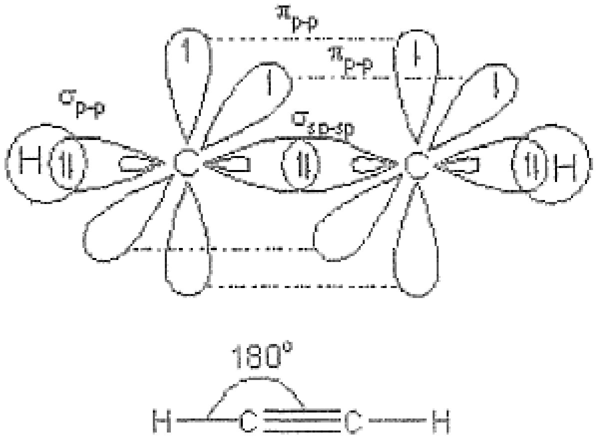
Each carbon atom undergoes 'sp' hybridization by using a 2s and one 2p orbitals in the excited state to give two half filled 'sp' orbitals, which are arranged linearly.

The two carbon atoms form a σ_{sp-sp} bond with each other by using sp-orbitals.

However there are also two unhybridized p orbitals ie, 2p$_y$ and 2p$_z$ on each carbon atom which are perpendicular to the sp hybrid orbitals. These orbitals form two π_{p-p} bonds between the two carbon atoms.

Thus a triple bond (including one σ_{sp-sp} bond & two π_{p-p} bonds) is formed between carbon atoms.

Each carbon also forms a σ_{sp-s} bond with the hydrogen atom.
Thus acetylene molecule is linear with 180° of bond angle.



Linear structure of acetylene molecule

1.5.5 sp² Hybridization

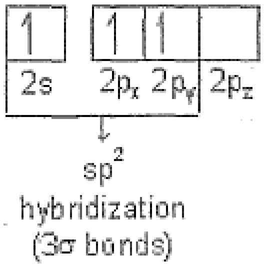
Boron trichloride (BCl_3):

The electronic configuration of 'B' in ground state is Is^2 $2s^2$ $2p^1$ with only one unpaired electron. Since the formation of three bonds with chlorine atoms require three unpaired electrons, there is promotion of one of 2s electron into the 2p sublevel by absorbing energy.

Thus Boron atom gets electronic configuration: $1s^2$ $2s^2$ $2p_x{}^1 2p_y{}^1$.

However to account for the trigonal planar shape of this BCl_3 molecule, sp^2 hybridization before bond formation was put forwarded.

In the excited state, Boron undergoes sp^2 hybridization by using a 2s and two 2p orbitals to give three half filled sp^2 hybrid orbitals which are oriented in trigonal planar symmetry.



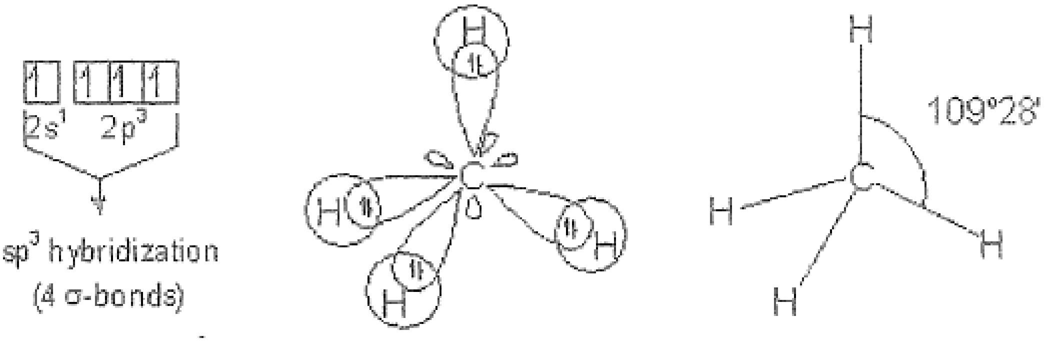
Boron forms three $\sigma_{sp\text{-}p}$ bonds with three chlorine atoms by using its half filled sp^2 hybrid orbitals.

Methane (CH_4)

During the formation of methane molecule, the carbon atom undergoes sp^3 hybridization in the excited state by mixing one '2s' and three 2p orbitals to furnish four half filled sp^3 hybrid orbitals, which are oriented in tetrahedral symmetry in space around the carbon atom.

Each of these sp^3 hybrid orbitals forms a σ_{sp3-s} bond with one hydrogen atom. Thus carbon forms four σ_{sp3-s} bonds with four hydrogen atoms.

Methane molecule is tetrahedral in shape with 109°28' bond angle.



Tetrahedral structure of methane

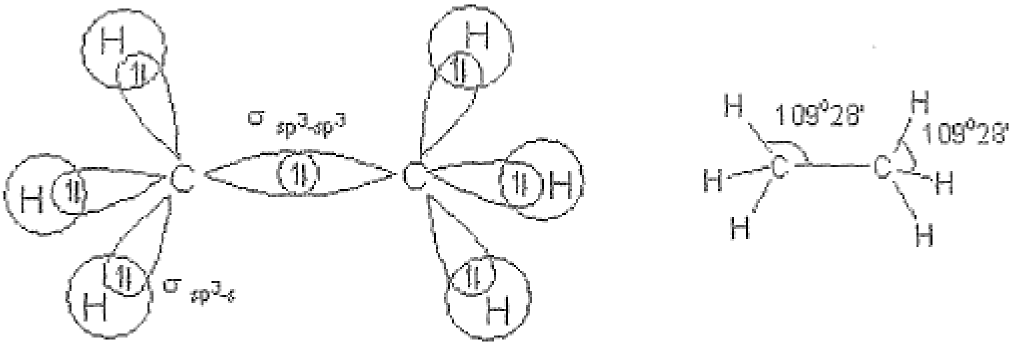
Ethane (C_2H_6):

Just like in methane molecule, each carbon atom undergoes sp^3 hybridization in the excited state to give four sp^3 hybrid orbitals in tetrahedral geometry.

The two carbon atoms form a $\sigma_{sp3-sp3}$ bond with each other due to overlapping of sp^3 hybrid orbitals along the inter-nuclear axis.

Each carbon atom also forms three σ_{sp3-s} bonds with hydrogen atoms.

Thus there is tetrahedral symmetry around each carbon with <HCH & <HCC bond angles equal to 109°28'.



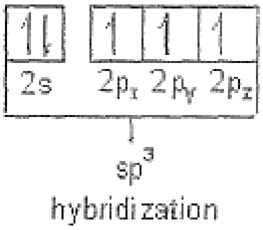
Structure of Ethane molecule

Ammonia (NH_3) :

The ground state electronic configuration of nitrogen atom is: $1s^2$ $2s^2$ $2p_x{}^1 2p_y{}^1 2p_z{}^1$. Since there are three unpaired electrons in the 2p sublevel, the nitrogen atom can form three bonds with three hydrogen atoms. This will give ammonia molecule with 90° of bond angles. However, the bond angles are reported be 107°48'.

Therefore, it was proposed that, the Nitrogen atom undergoes sp^3 hybridization of a 2s and three 2p orbitals to give four sp^3 orbitals, which are arranged in tetrahedral symmetry. It is clear that this arrangement will give more stability to the molecule due to minimization of repulsions.

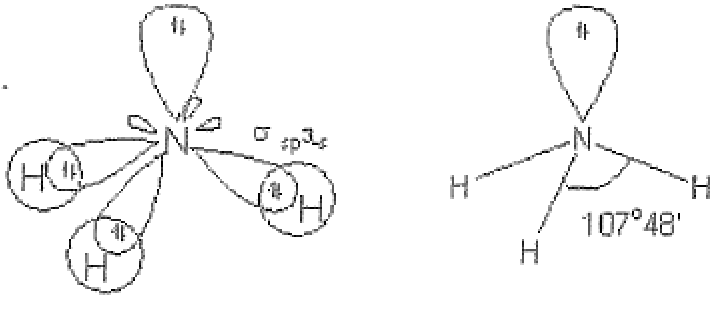
Among them three are half filled and one is full filled.



Nitrogen atom forms 3 σ_{sp3-s} bonds with three hydrogen atoms by using three half filled sp^3 hybrid orbitals. There is also a lone pair on nitrogen atom belonging to the full filled sp^3 hybrid orbital. It occupied more space than the bond pairs.

However, the <HNH bond angle is not equal to normal tetrahedral angle: 109°28'. The reported bond angle is 107°48'. The observed decrease in the bond angle is due to the repulsion caused by lone pair over the bond pairs.

That is why, ammonia molecule is trigonal pyramidal in shape with a lone pair on nitrogen atom.



Trigonal pyramidal structure of ammonia molecule

Water molecule

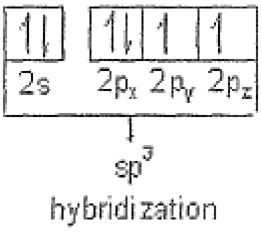
The electronic configuration of oxygen is 1s^2 2s^2 2p$_x^2$2p$_y^1$2p$_z^1$. There are two unpaired electrons in oxygen atom, which may form bonds with hydrogen atoms.

However the bond angles in the resulting molecule should be equal to 90°.

The experimental bond angles reported were equal to 104°28'. To account this, sp^3 hybridization before the bond formation was proposed.

During the formation of water molecule, the oxygen atom undergoes sp^3 hybridization by mixing a 2s and three 2p orbitals to furnish four sp^3 hybrid orbitals oriented in tetrahedral geometry.

Among them, two are half filled and the remaining two are completely filled.



Now the oxygen atom forms two $\sigma_{sp3\text{-}s}$ bonds with hydrogen atoms by using half filled hybrid orbitals.

The reported bond angle is 104°28' instead of regular tetrahedral angle: 109°28'. It is again due to repulsions caused by two lone pairs on the bond pairs.

Thus water molecule gets angular shape (V shape).

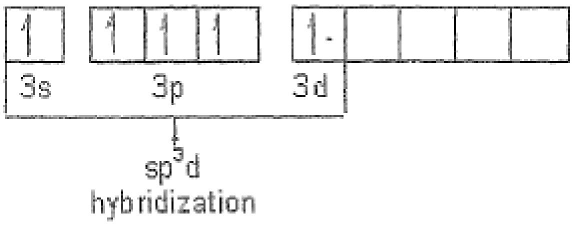
1.5.6 sp^3d Hybridization

Phosphorous pentachloride (PCl_5):

The ground state electronic configuration of phosphorus atom is: $1s^2\ 2s^22p^6\ 3s^23p_x^13p_y^13p_z^1$.

The formation of PCls molecule requires 5 unpaired electrons. Hence the phosphorus atom undergoes excitation to promote one electron from 3s orbital to one of empty 3d orbital.

Thus the electronic configuration of 'P' in the excited state is $1s^2\ 2s^2\ 2p^6\ 3s^23p_x^13p_y^3p_z^1\ 3d^1$.

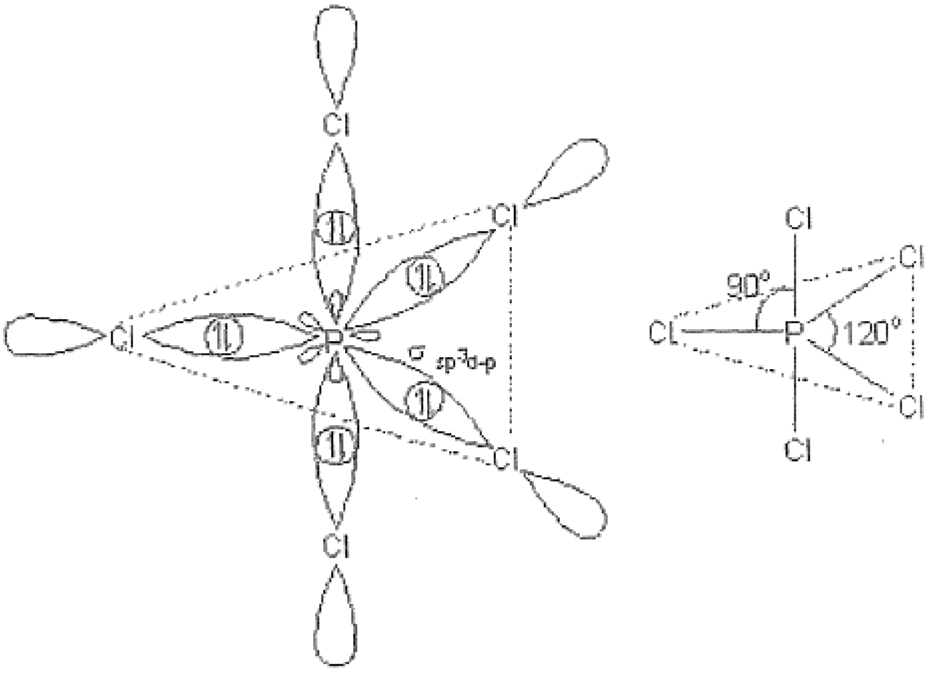


In the excited state, intermixing of a 3s, three 3p and one 3d orbitals to give five half filled sp^3d hybrid orbitals, which are arranged in trigonal bipyramidal symmetry.

ie, Three orbitals are arranged in trigonal planar symmetry, whereas the remaining two are arranged perpendicularly above and below this plane.

By using these half filled sp^3d orbitals, phosphorous forms five σ_{sp3d-p} bonds with chlorine atoms. Each chlorine atom makes use of half filled $3p_z$ orbital for the bond formation.

The shape of PCl_5 molecule is trigonal bipyramidal with 120° and 90° of <Cl - P - Ci bond angles.



Trigonal bipyramidal structure of PCl_5

1.5.7 sp^3d^2 Hybridization

Sulphur hexa fluoride (SF_6):

The electronic configuration of 'S' in ground state is $1s^2\ 2s^2 2p^6\ 3s^2\ 3p_x^2 3py^1 3p_z^1$.

In SF_6 molecule, there are six bonds formed by sulfur atom. Hence there must be 6 unpaired electrons. However there are only 2 unpaired electrons in the ground state of sulfur. Hence it promotes two electrons into two of the 3d orbitals (one from 3s and one from $3p_x$).

Thus the electronic configuration of 'S' in its 2nd excited state is $1s^2\ 2s^2\ 2p^6\ 3s^1 3p_x^1 3p_y^1 3p_z^1 3d^2$.

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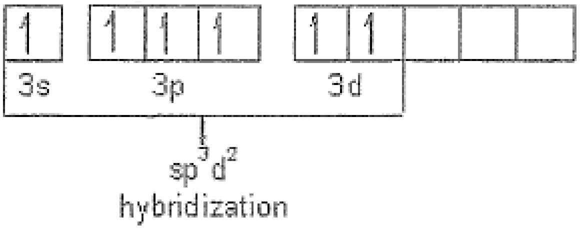
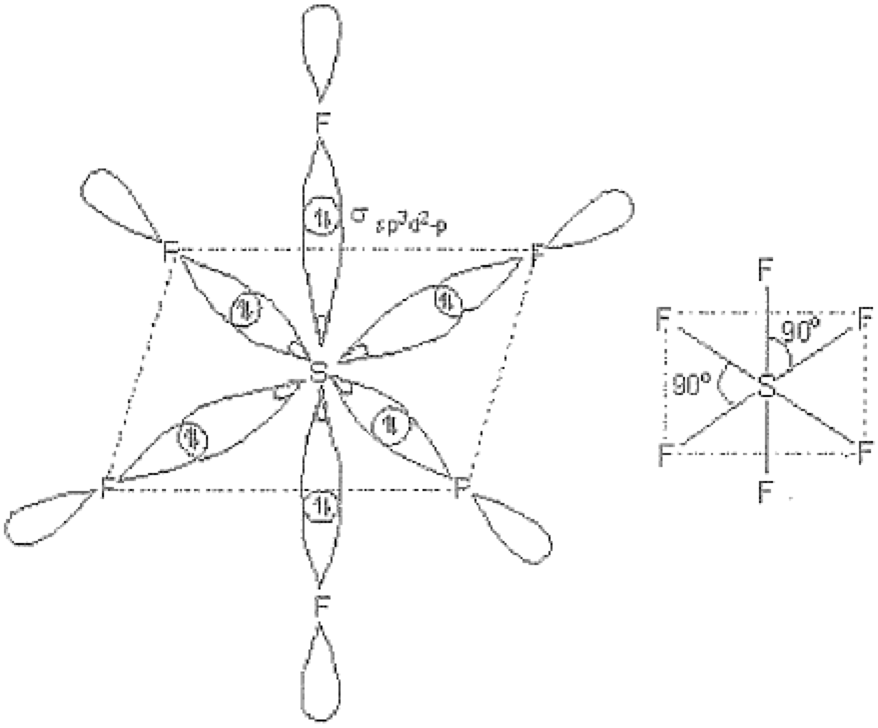


In the second excited state, sulfur under goes sp^{3}d^2 hybridization by mixing a 3s, three 3p and two 3d orbitals. Thus formed six half filled sp^{3}d^2 hybrid orbitals are arranged in octahedral symmetry.

Sulfur atom forms six $\sigma_{sp3d2-p}$ bonds with 6 fluorine atoms by using these sp^{3}d^2 orbitals. Each fluorine atom uses is half-filled 2p$_z$ orbitals for the bond formation. SF$_6$ is octahedral in shape with bond angles equal to 90°.



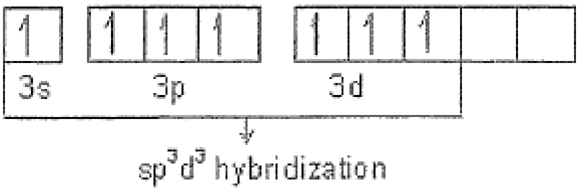
octahedral structure of sulfur hexafluoride

1.5.8 sp^{3}d^3 Hybridization

Iodine heptafluoride (IF$_7$):

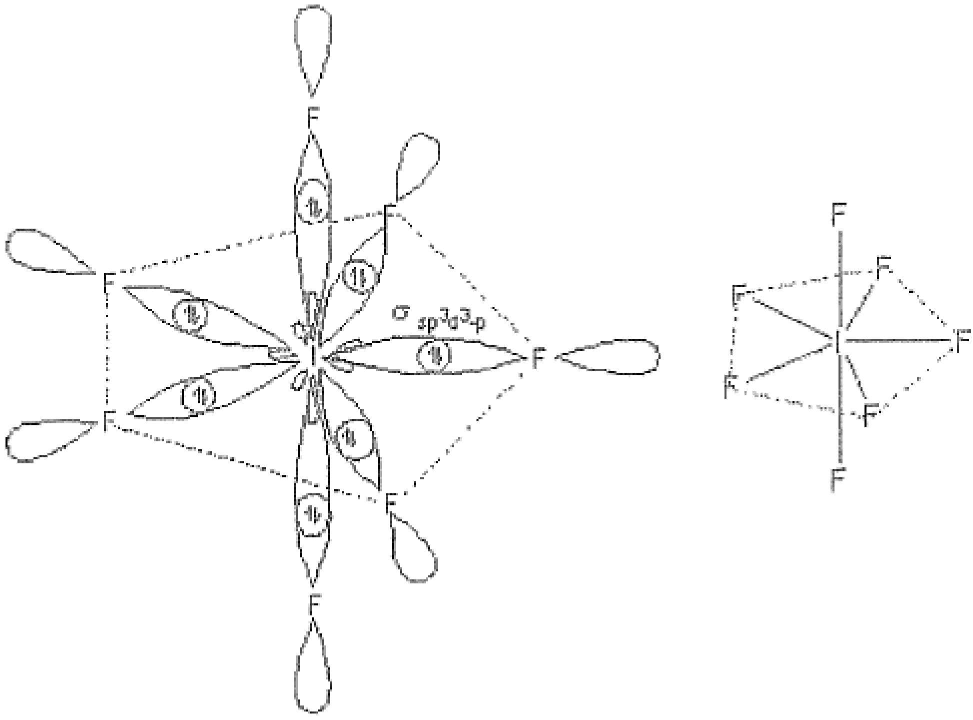
The electronic configuration of Iodine atom in the ground state is: [Kr]4d^{10}5s^2 5p^5. Since the formation of IF$_7$ requires 7 unpaired electrons, the iodine atom promotes three of its electrons (one from 5s orbital and two from 5p sublevel) into empty 5d orbitals. This state is referred to as third excited state.

The electronic configuration of Iodine in the third excited state can be written as: [Kr]4d^{10} 5s^{1}5p^{3}5d^3.



In the third excited state, iodine atom undergoes sp^{3}d^3 hybridization to give 7 half filled sp^{3}d^3 hybrid orbitals in pentagonal bipyramidal symmetry. These will form 7 $\sigma_{sp3d3-p}$ bonds with fluorine atoms.

Thus the shape of IF$_7$ is pentagonal bipyramidal. The <F-I-F bond angles in the pentagonal plane are equal to 72°, whereas two fluorine are present perpendicularly to the pentagonal plane above and below



Pentagonal bipyramidal structure of IF$_7$

< Valence bond theory & hybridization	Chemical bonding: TOC	

form two π molecular orbitals. These two π orbitals constitute two bonds. Taken together, they represent an electron distribution that is cylindrically symmetrical (like a barrel) about the axis joining the two carbon atoms.

1.5.9 The Alkanes

Methane is the first and simplest member of a family of hydrocarbons called the alkane or paraffin series, many of which occur in petroleum.

All compounds of this series are open-chain (aliphatic) compounds with the general formula C_nH_{2n+2}· All alkanes have the same characteristic type of structure, are similar in chemical properties, and show a regular gradation in most of their physical properties.

Thus, a knowledge of the chemistry of one or two representative members of the series serves to give an excellent picture of the properties and behavior of all of the rest. A few compounds in the homologous series of unbranched-chain alkanes are:

CH_4	methane
CH_3CH_3	ethane
$CH_3CH_2CH_3$	propane
$CH_3CH_2CH_2CH_3$	butane or *n*-butane
$CH_3CH_2CH_2CH_2CH_3$	pentane or *n*-pentane

The higher members of the series are named systematically with a Greek numerical prefix (hex-, hept-, oct-, etc) attached to the suffix -ane.

The prefix signifies the number of carbon atoms in the chain. For members of the series beyond propane the unbranched-chain isomers are designated in the common system of nomenclature by the abbreviation n for normal. The formula of each compound in a homologous series differs from that of the compound preceding it and following it in the series by the increment CH_2.

Although the formulas used for the alkanes may suggest that the carbon chains are straight, the tetrahedral bonding of carbon demands a zigzag arrangement. The propane molecule (**Figure 1.4**) demonstrates this geometry.

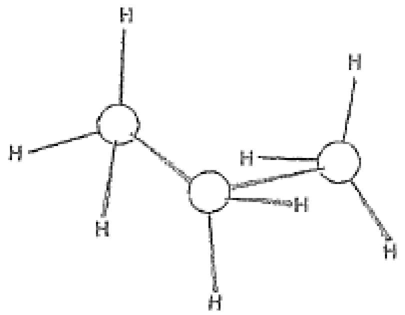


Figure 1.4 The geometry of the propane molecule.

Methane, the chief component of natural gas, may occur in the air of coal mines to the extent of 3.5 to 7 .5%. A commercial source of methane is the reduction of carbon monoxide at 250° to 300°C, with a nickel catalyst:

$$CO + 3H_2 \overset{Ni}{=} CH_4 + H_2O$$

Methane is a colorless, odorless gas that can be liquefied. Liquid methane boils at -161°C. Its extreme volatility is a consequence of the lack of attractive forces, particularly hydrogen bonding, between the symmetrical, nonpolar methane molecules.

This is in contrast to ammonia, bp -33°C, and hydrogen fluoride, bp 19°C, both of which are polar and whose molecules are associated through hydrogen bonding. It is in even more striking contrast to the physical properties of many other simple hydrides, eg, LiH, mp 680°, which is ionic in character.

Methane cannot interact effectively with water through hydrogen bonding and is therefore rather insoluble in water. Its low molecular weight leads to a gaseous density only about one-half that of air.

The five-carbon alkane, pentane, is the first liquid member of the series. The boiling points of the unbranched chain alkane family increase fairly regularly with ascending molecular weight:

Compound	Number of carbons	Bp, °C (760 mm)
pentane	5	36
hexane	6	69
heptane	7	98
octane	8	126

Table 1.8

Use of the homologous series principle in predicting properties of unknown members of the series also works quite satisfactorily with higher molecular weight members.

1.5.10 Rotation about the carbon-carbon bond in ethane

We have seen that free rotation is an important attribute of covalent single bonds. This means that there are an infinite number of relative arrangements of the hydrogen atoms in the ethane molecule as each CH_3 (methyl) group rotates about the carbon-carbon bond axis.

These different arrangements are called conformations. Two extreme conformational arrangements of ethane are pictured in **Figure 1.6**.

In the eclipsed arrangement the hydrogen atoms are closer to each other than in the staggered arrangement.

The staggered conformation is always more stable than the eclipsed, because repulsive interactions are at a minimum when the nonbonded atoms are separated by maximum distance and, other things being equal, molecules are more stable the fewer the repulsive nonbonded interactions.

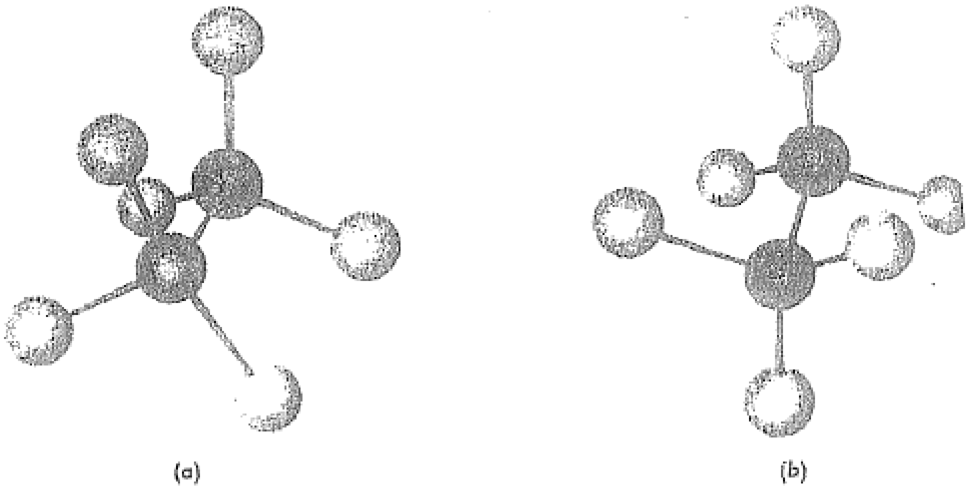


Figure 1.6 Two conformations of ethane, (a) eclipsed conformation and (b) staggered conformation

Rotation around the carbon-carbon bond is extremely rapid at room temperature. However, a small but finite activation energy is required for this rotation. At ordinary temperatures the activation energy is easily provided by thermal agitation of the molecules.

From an experimental standpoint, this means that only one ethane can be isolated because the different conformations rapidly interconvert to one another.

1.5.11 Isomerism

Careful analysis of the gaseous fraction of petroleum has revealed the presence of a second compound, in addition to butane, with the molecular formula C_4H_{10}.

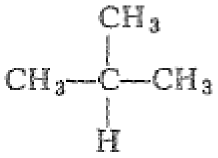
This second compound has been named isobutane (like butane). These two butanes cannot be merely different conformations for they do not interconvert, even at elevated temperatures. One can only conclude that they must have different patterns of chemical bonding.

They exhibit similar, but not identical, chemical behavior. Their physical properties are also somewhat different; eg, butane has a boiling point of + 1°C, and isobutane of -l7°C.

Study of the molecular formula C_4H_{10} leads to the prediction that there should, indeed, be two butanes because the atoms can be arranged to give two different structures:

$CH_3—CH_2—CH_2—CH_3$

butane or *n*-butane



$$\begin{array}{c} CH_3 \\ | \\ CH_3—C—CH_3 \\ | \\ H \end{array}$$

isobutane

These formulas represent molecules of two different compounds, because, although the molecules are built up of the same numbers of the same kinds of atoms, the atoms are linked together in different ways.

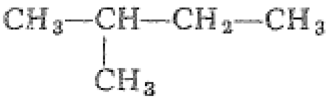
They are called isomers. Isomers always have the same molecular formulas but differ in their structures. Since the atoms in butane and isobutene are bonded at different sites, this is an example of positional isomerism.

From several lines of evidence, including the syntheses of the compounds themselves, it has been proved that butane has the unbranched and isobutane the branched structure.

Branched-chain structures are common in organic compounds. There are three pentane isomers, two of them with branched chains:

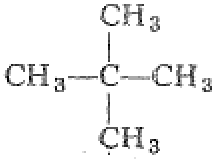
$CH_3—CH_2—CH_2—CH_2—CH_3$

pentane or *n*-pentane



$$\begin{array}{l} CH_3—CH—CH_2—CH_3 \\ | \\ CH_3 \end{array}$$

isopentane



$$\begin{array}{c} CH_3 \\ | \\ CH_3—C—CH_3 \\ | \\ CH_3 \end{array}$$

neopentane

Although the physical properties of branched-chain alkanes do not show the same smooth gradation as those of unbranched-chain alkanes, the boiling points usually decrease with increased branching. Whereas n-pentane boils at 36°, and isopentane at 28°, neopentane boils at 9.5°C.

Melting point changes can be even more dramatic, as the higher symmetry produced in branched-chain compounds sometimes provides for greater crystal forces and higher melting points; eg, the melting points of n-pentane and neopentane are - 130° and - li7°C, respectively.

The number of possible isomers increases rapidly with increasing molecular complexity. For example, thirty-five different nonanes, with molecular formula C_9H_{20}, are possible and have been synthesized.

Calculations based on a rather complex equation show that the theoretical number of possible isomers reaches 69,491,178,805,831 for the formula $C_{40}H_{82}$!

For a majority of organic compounds a simple determination of the number of each kind of atom in the molecule does not suffice to identify the substance any more than a tabulation of the number of times each letter appears on this page would tell what is written.

A knowledge of the arrangement of the various atoms within the molecule is of fundamental importance in identifying and distinguishing between organic compounds.

1.5.12 Reactions of Alkanes

As the name paraffin (little affinity) implies, the alkanes are rather unreactive chemically. At room temperature, they are inert toward strong acids, bases, and oxidizing and reducing agents. However, all saturated (containing only single bonds) hydrocarbons are attacked by oxygen at high temperatures.

If excess oxygen is present, the reaction produces carbon dioxide and water. This combustion process evolves large quantities of heat. The burning of hydrocarbon fuels is an indispensable source of heat and power in our machine age.

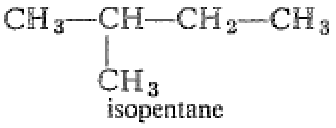
Chlorine and bromine, however, react with the paraffins even at room temperature in sunlight or in ultraviolet light, replacing one or more of the hydrogen atoms in stepwise fashion. The halogen atoms are said to substitute for the hydrogen atoms, and the reaction is called substitution.

This general type of reaction is assuming increasing industrial importance as a means for preparing other valuable organic compounds from hydrocarbons found in petroleum.

Branched-chain structures are common in organic compounds. There are three pentane isomers, two of them with branched chains:

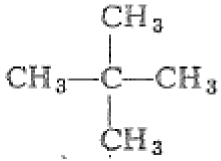
$$CH_3-CH_2-CH_2-CH_2-CH_3$$

pentane or *n*-pentane



$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-CH_3$$

isopentane



$$CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\underset{\displaystyle CH_3}{|}}{C}}}-CH_3$$

neopentane

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Chlorine and bromine, however, react with the paraffins even at room temperature in sunlight or in ultraviolet light, replacing one or more of the hydrogen atoms in stepwise fashion. The halogen atoms are said to substitute for the hydrogen atoms, and the reaction is called substitution.

This general type of reaction is assuming increasing industrial importance as a means for preparing other valuable organic compounds from hydrocarbons found in petroleum.

In methane, all four hydrogen atoms can be successively replaced by chlorine:'

$CH_4 + Cl_2 = HCl + CH_3Cl$ methyl chloride
$CH_3Cl + Cl_2 = HCl + CH_2Cl_2$ methylene chloride
$CH_2Cl_2 + Cl_2 = HCl + CHCl_3$ chloroform
$CHCl_3 + Cl_2 = HCl + CCL_4$ carbon tetrachloride

The distribution of products in the reaction mixture depends upon the temperature, the relative concentrations of methane and chlorine, and the length of the exposure to light.

Each successive replacement of a hydrogen by a chlorine atom in the, methane structure yields a compound that has a higher boiling point and density and is less inflammable than the preceding compound.

Methyl chloride is used as a local anesthetic; as a refrigerant, it has been largely displaced by the odorless, nontoxic, noninflammable Freon, CCl_2F_2.

Chloroform is a well known anesthetic and an excellent solvent for fats and oils; carbon tetrachloride is used as a fire extinguisher (Pyrene) and in dry cleaning.

Thus, by complete chlorination, methane, an explosive gas, is converted into carbon tetrachloride, a liquid fire extinguisher.

Vapor phase nitration of the paraffins at elevated temperatures yields nitroparaffins of the type of nitromethane, CH_3NO_2. The nitroparaffins are stable, nontoxic, noncorrosive liquids, which have found wide use as solvents, fuels, and synthetic intermediates.

Catalytic methods for the carefully controlled fluorination of paraffin hydrocarbons, developed during World War have led to an important class of compounds, the fluorocarbons.

Because of their extreme stability and lack of reactivity, the fluorocarbons are destined to find wide industrial application. Already they are used as lubricants, as coolants, and in the production of plastics.

1.5.14 The concept of functional groups

Much of the vast body of factual organic chemistry can be unified, systematized, classified, and even predicted on the basis of the functional group principle.

A functional group is a substituting atom or group of atoms characteristic of a particular class or homologous series of compounds.

Simple organic compounds can be classified according to their type; eg, alkanes, alkenes, alkynes, alcohols, ethers, carboxylic acids, aldehydes, ketones, amines, etc.

Each of these types of compounds contains a specific functional group which imparts to the compounds belonging to that type their general physical properties and their characteristic chemical reactivity.

An understanding of the chemistry of the various functional groups provides a framework within which almost all organic reactions can be classified.

Alkenes, such as ethylene ($CH_2=CH_2$), propene ($CH_3CH=CH_2$), and 1-butene ($CH_3CH_2CH=CH_2$), for example, all undergo certain reactions characteristic of the double bond.

Similarly, different alcohols such as ethyl alcohol (CH_3CH_2OH), *n*-propyl alcohol (CH_3CH_2 CH_2OH), and *sec*-butyl alcohol all exhibit a common set of reactions characteristic of the –OH (hydroxyl) group. Some common functional groups are shown in **Table 1.9**.

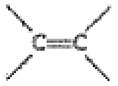
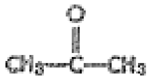
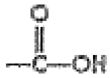
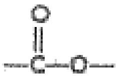
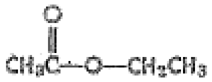
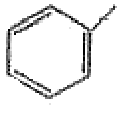
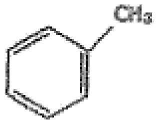
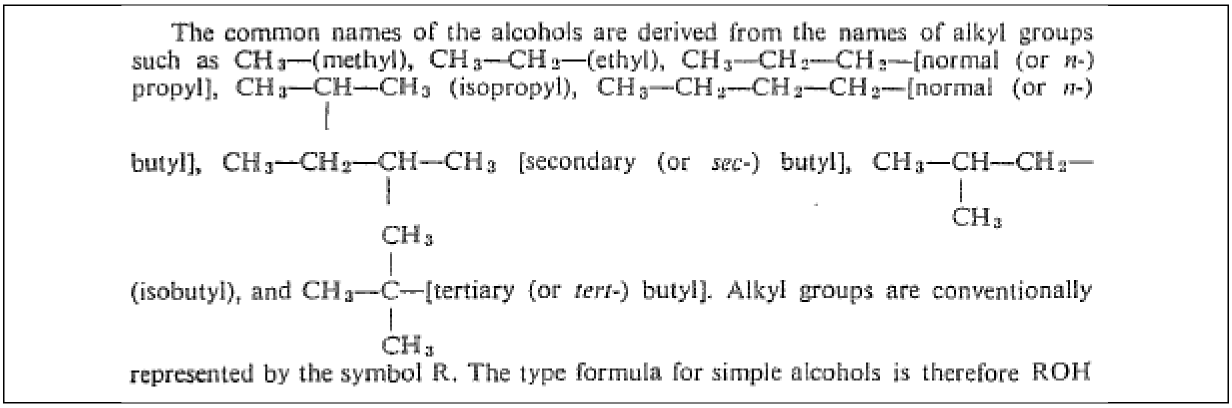
Type of compound	**Functional group**	**Example**	**Common name**
Alkene		$CH_3CH=CH_2$	propene
Alkyne	$-C\equiv C-$	$CH_3C\equiv CCH_3$	2-butyne
Alcohol	$-OH$	$CH_3CH_2CH_2CH_2OH$	*n*-butyl alcohol
Ether	$-O-$	$CH_3CH_2-O-CH_2CH_3$	ethyl ether
Aldehyde	 $-\overset{\overset{O}{\Vert}}{C}-H$	 $CH_3CH_2-\overset{\overset{O}{\Vert}}{C}-H$	propionaldehyde
Ketone	 $-\overset{\overset{O}{\Vert}}{C}-$	 $CH_3-\overset{\overset{O}{\Vert}}{C}-CH_3$	acetone
Caboxylic acid	 $-\overset{\overset{O}{\Vert}}{C}-OH$	 $CH_3CH_2-\overset{\overset{O}{\Vert}}{C}-OH$	propionic acid
Ester	 $-\overset{\overset{O}{\Vert}}{C}-O-$	 $CH_3\overset{\overset{O}{\Vert}}{C}-O-CH_2CH_3$	Ethyl acetate
Amine	$-NH_2$	 $CH_3\overset{\overset{CH_3}{\vert}}{C}HCH_2-NH_2$	isobutylamine
Nitrite	$-C\equiv N$	$CH_3CH_2-C\equiv N$	propionitrite
Arene			toluene
Halide	$-X$(F, Cl, Br, I)	 $CH_3CH_2\underset{\underset{Br}{\vert}}{C}HCH_3$	sec-butyl bromide
Nitro compound	$-NO_2$	CH_3-NO_2	nitromethane

Table 1.9 Common functional groups

Note:



The common names of the alcohols are derived from the names of alkyl groups such as CH_3—(methyl), $CH_3—CH_2$—(ethyl), $CH_3—CH_2—CH_2$—[normal (or *n*-) propyl], $CH_3—CH—CH_3$ (isopropyl), $CH_3—CH_2—CH_2—CH_2$—[normal (or *n*-) butyl], $CH_3—CH_2—CH—CH_3$ [secondary (or *sec*-) butyl], $CH_3—CH—CH_2$— (isobutyl), and $CH_3—C$—[tertiary (or *tert*-) butyl]. Alkyl groups are conventionally represented by the symbol R. The type formula for simple alcohols is therefore ROH

$$CH_3—\underset{|}{CH}—CH_3 \qquad CH_3—CH_2—\underset{\underset{CH_3}{|}}{CH}—CH_3 \qquad CH_3—\underset{\underset{CH_3}{|}}{CH}—CH_2— \qquad CH_3—\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}—$$

1.5.15 Reaction types

The five most common types of reactions which organic compounds undergo are listed in **Table 1.10**.

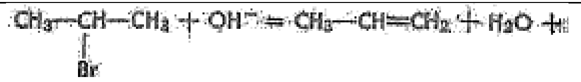
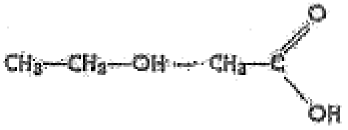
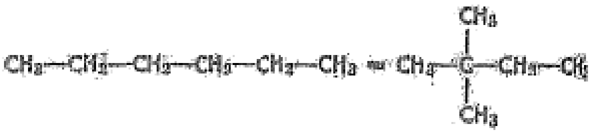
Reaction type	Example
1. Substitution	$CH_3—Cl + OH^- = CH_3—OH + Cl^-$
2. Addition	$CH_3—CH{=}CH_2 + Br_2 = CH_3—CHBr—CH_2Br$
3. Elimination	 $CH_3—\underset{\underset{Br}{|}}{CH}—CH_3 + OH^- = CH_2—CH{=}CH_2 + H_2O +$
4. Oxidation	
5. Rearrangement	 $CH_3—CH_2—CH_2—CH_2—CH_2—CH_3 = CH_3—\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}—CH_2—CH$

Table 1.10 Reaction types

1.5.16 Reaction pathways - mechanisms

One of the most fascinating and challenging subjects of contemporary research in organic chemistry is the study of the reaction pathways which a given reaction proceeds.

The detailed step-by-step description a chemical reaction is called a mechanism. An understanding of mechanisms of reactions provides a convenient means for classifying, remembering and often even predicting, reactions. As our understanding of reactions grows, so does our power to control them.

The mechanism for the chlorination of methane under ultra irradiation has been studied in detail. The overall reaction is expressed in the equation:

$$CH_4 + Cl_2 = CH_3Cl + HCl$$

The mechanism which best accounts for all the experimental facts is as follows:

Initial step $Cl_2 \xrightarrow{light} 2Cl\cdot$

Chain propagation steps $$\left\{\begin{array}{l} CH_4 + Cl\cdot \longrightarrow CH_3\cdot + HCl \\ CH_3\cdot + Cl_2 \longrightarrow CH_3Cl + Cl\cdot \end{array}\right\}$$ These steps repeat many times

Chain termination steps $$\left\{\begin{array}{l} CH_3\cdot + \cdot Cl \longrightarrow CH_3Cl \\ Cl\cdot + \cdot Cl \longrightarrow Cl_2 \\ CH_3\cdot + \cdot CH_3 \longrightarrow CH_3 - CH_3 \end{array}\right\}$$

This is an excellent example of a chain reaction, which involves a series of steps, each of which generates the reactive substance which brings about the next step.

The reactive substances in this chain reaction are the highly unstable, fleeting intermediates Cl (chlorine atom free radical) and CH_3 (methyl free radical). Any ionic, atomic, or molecular species which possesses an unpaired electron is called a free radical.

In general, any reaction in which the bonding electron pair is paired or unpaired in the making or breaking of the bond is classified as a free radical reaction. The chlorination of methane is a free radical chain reaction.

We have already discussed the carbon-carbon double bond, which is the distinguishing feature of the alkene or olefin series of hydrocarbons.

Alkenes have a lower ratio of hydrogen to carbon than the alkanes; the general molecular formula for the series is C_nH_{2n}. The alkenes have two hydrogen atoms less than the number required to saturate the valences of the carbon atoms, and hence are said to be unsaturated.

The three-carbon alkene, $CH_3–CH=CH_2$, is called propylene or propene. Propene has both a carbon-carbon double bond and a carboncarbon single bond, in addition to carbon-hydrogen bonds.

The singly bonded carbon has tetrahedral geometry (bond angles of 109,5°) and the doubly bonded carbon trigonal geometry (bond angles of 120°). This is shown diagramatically in **Figure 1.7**.

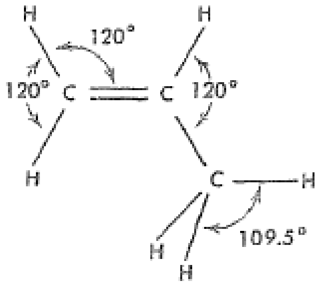
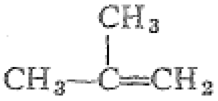


Figure 1.7 The geometry of propane

Other simple alkenes are 1-butene ($CH_3–CH_2–CH=CH_2$) and isobutylene:



$CH_3-\overset{\overset{CH_3}{|}}{C}=CH_2$

These are positional isomers.

In addition there are two different 2-butenes with the formula $CH_3–CH=CH–CH_3$. These two compounds have slightly different physical properties and undergo the same reactions characteristic of the double bond, although at somewhat different rates. The boiling points and melting points of the four isomeric butylenes are shown in **Table 2.11**.

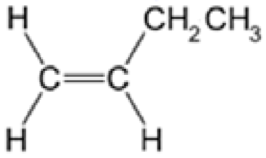
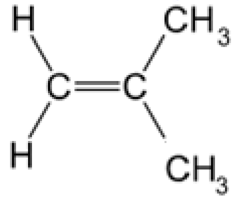
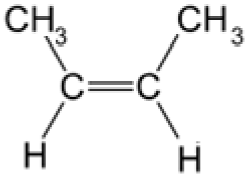
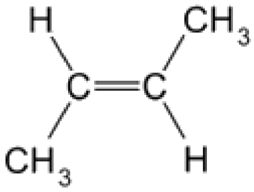
Name	**Formula**	**Bp, °C**	**Mp, °C**
1-Butene		-6	-185
Isobutylene		-7	-141
cis-2-Butene		+4	-139
trans-2-Butene		+1	-106

Table 2.11 The isomeric butylenes

The existence of two different 2-butenes results from the hindered rotation around the carbon-carbon double bond, which gives rise to a new type of isomerism.

If we examine the structure of 2-butene closely, and particularly if we use molecular models, we find that there are two different ways in which the atoms can be arranged in space.

Definition: *cis-* and *trans-*
cis- (Latin, on this side), trans- (Latin, across)

In one case, the methyl groups lie on the same side of the molecule; this isomer is called the *cis*- compound, or *cis*-2-butene.

In the second case, the methyl groups lie on opposite sides of the molecule; this isomer is called the *trans*- compound, or *trans*-2-butene. The two isomers are represented in **Figure 1.8**.

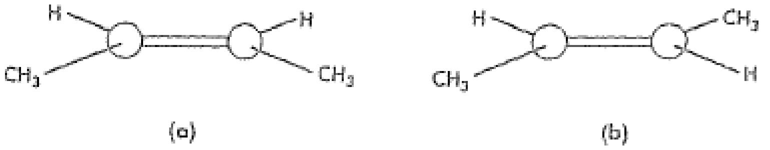


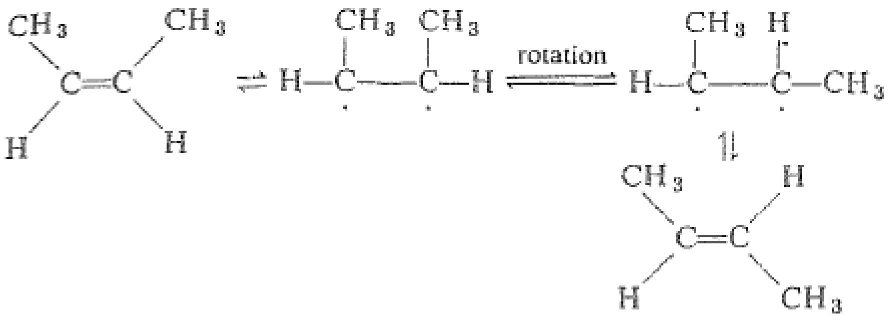
Figure 1.8 *cis*- and *trans*-2-butene a) Methyl groups on the some side, the *cis*-isomer (b) Methyl groups on opposite sides, the *trans*-isomer

The isomeric 2-butenes are called geometric isomers; one is said to have the cis-configuration, the other the trans-configuration. Isomers which differ only in the relationship of atoms in space are called stereoisomers.

Geometric isomers, such as *cis*- and *trans*-2-butene, represent one type of stereoisomers.

cis-2-Butene and *trans*-2-butene are stable relative to each other at room temperature, but interconversion of the isomers occurs at elevated temperatures.

This is attributed to the rupture of the π bond at high temperatures, with the free rotation about the carbon-carbon single bond of the resulting high-energy free radical leading to isomerization:



Geometrical or *cis-trans* isomerism can occur in alkenes only when each doubly bonded carbon atom bears two different atoms or groups of atoms. For example, there is only one 1-butene and one isobutylene.

The boiling points, melting points, and solubility behavior of the various alkenes are quite similar to those of the corresponding paraffin hydrocarbons. In general, those in the C_2 to C_4 range are gases under room conditions, those from C_5 to C_{18} are liquids, and the higher members are solids. All are nonpolar and nonhydrogen-bonding, and are essentially insoluble in water.

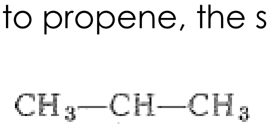
In contrast to the saturated hydrocarbons, the alkenes are highly reactive. The double bond is rather easily converted into a single bond by the addition of other molecules, giving saturated compounds. Thus ethylene, for example, adds a molecule of hydrogen in the presence of a platinum or nickel catalyst to give ethane:

$$CH_2{=}CH_2 + H_2 = CH_3{-}CH_3$$

Ethylene adds chlorine and bromine readily; with bromine, the product is ethylene bromide:

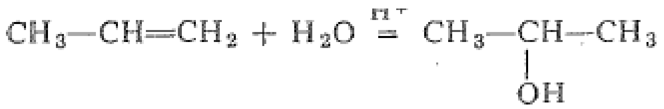
$$CH_2{=}CH_2 + Br_2 = \underset{\text{ethylene bromide}}{CH_2Br{-}CH_2Br}$$

Water adds to the carbon-carbon double bond of alkenes in the presence of an acid catalyst, such as sulfuric acid. In the acid-catalyzed addition of water to propene, the sole product is isopropyl alcohol:



$$CH_3{-}\underset{\displaystyle OH}{\underset{|}{CH}}{-}CH_3$$

No *n*-propyl alcohol, $CH_3{-}CH_2{-}CH_2OH$, is formed, even though it is perfectly stable under the conditions of the reaction:



$$CH_3—CH=CH_2 + H_2O \overset{H^+}{=} CH_3—\underset{\displaystyle OH}{\underset{|}{CH}}—CH_3$$

not

$$CH_3—CH_2—CH_2OH$$

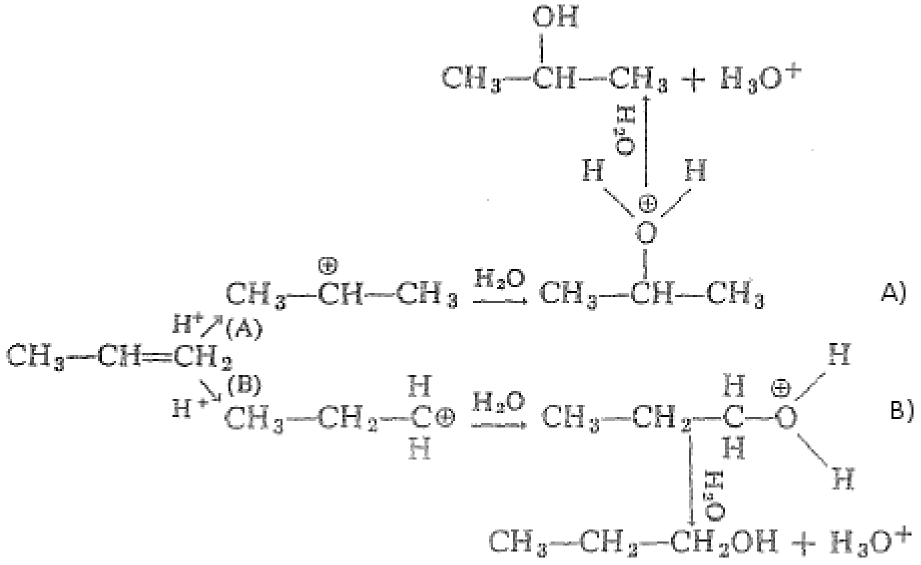
The question as to why only one of the two possible isomeric alcohol products is formed is an intriguing one. The answer lies in an understanding of the reaction mechanism.

A large body of experimental evidence supports the postulate that the acid catalyzed addition of water to an alkene is a typical electrophilic (electron-seeking) addition, in which the initial attack on the alkene made by an electrophilic (electron-seeking) species (in this case the proton).

A typical electrophilic species, such as the proton, accepts an electron pair in the Lewis acid sense. In this reaction, the π bond as the alkene is a source of an electron pair for bonding to an electron-path seeking reagent.

In other words, an alkene is, in a general sense, a Lewis base. The typical reaction of alkenes is electrophilic addition, the addition of electron-seeking or, in the general sense, acid reagents.

Now for propene, the acid-catalyzed addition of water could theoretically take either of two courses:



In each of the two proposed reaction pathways, (A) and (B), propene adds a proton from the acid catalyst to form a highly unstable, high-energy, fleeting intermediate ion bearing a positive charge on a carbon atom. Such an ion is called a carbonium ion.

It is further postulated that this first step is the slowest step (the one with the highest activation energy of the reaction sequence, and therefore, the rate-controlling step of the reaction.

In other words, the carbonium ion reacts as rapidly as it is formed. It would be entirely reasonable to assume that the reaction leading to the more stable carbonium ion-the one which can be formed with the lower activation energy-will take place preferentially.

Note:
A charge sign is often enclosed in a circle when an attempt is made to locate the charge on a particular atom (in this case the carbon atom).

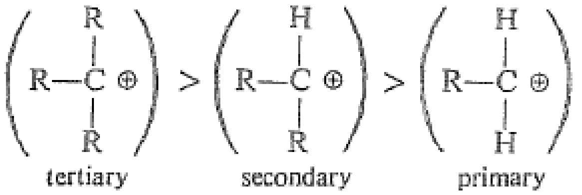
Furthermore, the course of the total reaction is determined entirely by the referential formation of one of the two possible carbonium ions, and not by the more stable product, since the addition reaction is not readily reversible under the experimental conditions used.

Therefore, once the addition of the proton to propene to form the carbonium ion has taken place, the course of the reaction is irrevocably set.

All that remains, then, is to make some judgment of the relative stabilities of the isopropyl cation, $CH_3{-}CH{-}CH_3$, versus the *n*-propyl cation, $CH_3{-}CH_2{-}CH_2$.

Abundant evidence exists pointing to the conclusion that the isopropyl cation is more stable than the *n*-propyl cation. On this basis, reaction (A), with ultimate formation of the experimentally observed product, isopropyl alcohol, would be predicted as the preferred course of reaction.

In general, carbonium ion stability is directly related to the electronic environment of the positive charge. It has been clearly established that the order of stability of carbonium ions is



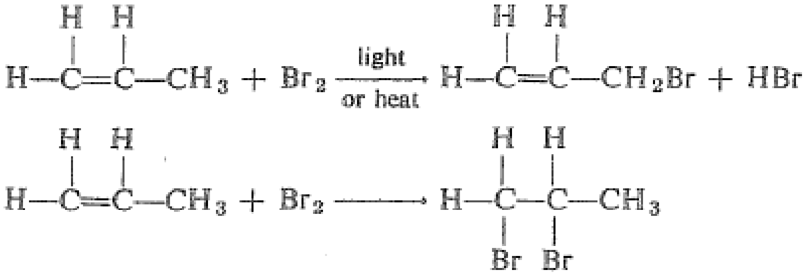
Further study of the proposed mechanism for the addition of water to propene (and, indeed, to alkenes in general) reveals that in the bond-breaking and bond-making steps, the bonding electron pairs remain paired throughout, ie, there is no pairing or unpairing of electrons, but only electron-pair sharing or unsharing.

Reactions of these types belong to the broad class called polar or ionic reactions, as distinguished from free radical reactions. In the general sense, these reactions can be considered as acid-base reactions, for in bond formation one reagent (the base) supplies both electrons of the shared pair to the electron pair acceptor (acid).

Certainly the most important reaction of alkenes takes place at the carbon-carbon double bond.

However, the alkyl groups that are present in most alkene molecules have the alkane structure and should undergo alkane reactions, such as substitution by halogen indeed, we can direct the attack of bromine on propene to substitution at the alkyl group or addition at the carbon-carbon double bond by our choice of experimental conditions.

High temperature and irradiation by ultraviolet light favor the substitution reaction. These are conditions that favor free radical formation. In the absence of light at low temperatures, the polar addition is the favored reaction:



$$\mathrm{H{-}\overset{H}{C}{=}\overset{H}{C}{-}CH_3 + Br_2 \xrightarrow[\text{or heat}]{\text{light}} H{-}\overset{H}{C}{=}\overset{H}{C}{-}CH_2Br + HBr}$$

Substitution:
free radical mechanism

$$\mathrm{H{-}\overset{H}{C}{=}\overset{H}{C}{-}CH_3 + Br_2 \longrightarrow H{-}\underset{Br}{\overset{H}{C}}{-}\underset{Br}{\overset{H}{C}}{-}CH_3}$$

Addition:
polar or ionic mechanism

1.5.17 Gasoline

In the straight distillation of petroleum, an average of less than twenty per cent of the crude oil appears in the gasoline fraction. This amount from all over the world would supply only a small fraction of the total amount required for automobiles and airplanes.

Moreover, straight run gasolines possess poor antiknock properties. As a result, three basic processes, cracking, alkylation and dimerization, and isomerization, are widely used to improve both the quality and quantity of gasoline.

Large quantities of alkenes are produced in the cracking of petroleum oils. Ethylene, a versatile synthetic intermediate in the chemist's hands, is synthesized on a large commercial scale by the vapor-phase cracking of gas oil or from natural gas.

The simplest and most widely used diolefin (alkene with two double bonds), butadiene (CH 2=CH-CH=CH2), is also an important product of petroleum cracking.

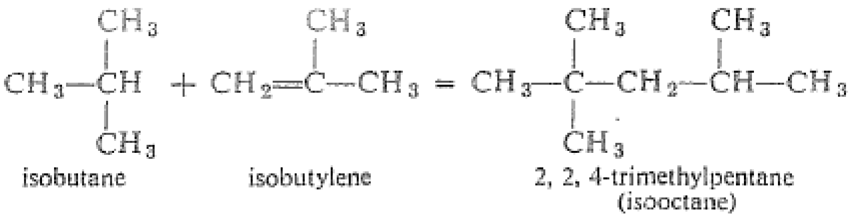
Cracking is the process by which larger and less volatile hydrocarbon molecules are broken down into a variety of smaller and more volatile ones. As is indicated by the following typical reactions that may occur in the cracking of C HH 3 0 , large amounts of olefins are formed:

$$C_{14}H_{30} = \underset{\text{an alkane}}{C_{12}H_{26}} + \underset{\text{ethylene}}{C_2H_4}$$

$$C_{14}H_{30} = \underset{\text{an alkane}}{C_{11}H_{24}} + \underset{\text{propylene}}{C_3H_6}$$

Alkylation is the reverse of cracking; it consists of the combination of low molecular weight olefins with branched paraffins to form high-quality gasoline.

The alkylation of isobutylene with isobutane, for example, produces so-called isooctane, which has an octane rating of 100. Actually, the isobutane to isobutylene:

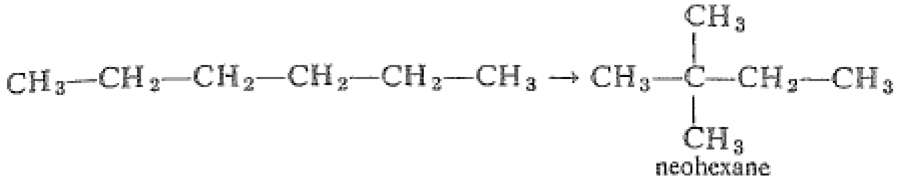


$$\underset{\text{isobutane}}{CH_3-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}H} + \underset{\text{isobutylene}}{CH_2=\overset{\overset{\displaystyle CH_3}{|}}{C}-CH_3} = \underset{\substack{\text{2, 2, 4-trimethylpentane}\\ \text{(isooctane)}}}{CH_3-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{C}H-CH_3}$$

Commercially, both thermal alkylation at high pressure and also low temperature, high-pressure catalytic alkylation with sulfuric acid or anhydrous hydrogen fluoride are employed.

Dimerization of alkenes by sulfuric or phosphoric acid can also produce high-octane fuels. Both the alkylation and dimerization reactions are thought to involve carbonium ion intermediates in their reaction pathways.

Isomerization catalysts, such as aluminum chloride and aluminum bromide, are used to rearrange or isomerize unbranched chains into branched-chain paraffins, *n*-Hexane for example, can be isomerized to neohexane:



$$CH_3-CH_2-CH_2-CH_2-CH_2-CH_3 \rightarrow \underset{\text{neohexane}}{CH_3-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CH_2-CH_3}$$

1.5.18 Alkynes

Even more highly unsaturated than the alkenes are the members of the alkyne or acetylene series. The alkynes are represented by the type formula C_nH_{2n-2}. The two carbon atoms in the simplest alkyne, acetylene (C_2H_2), are connected by a carbon-carbon triple bond.

As a consequence of the linear geometry imposed upon the alkyne H─C=C─H by the molecular orbital overlap, the two carbon and two hydrogen atoms of acetylene all lie in a straight line.

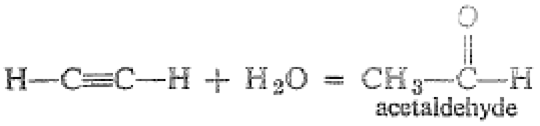
The ready availability of the four π electrons of aikynes leads to the typical addition reactions characteristic of the alkenes. Thus, acetylene can add one molecule of hydrogen chloride to form vinyl chloride, an important intermediate in the plastics industry.

The addition of a second molecule of hydrogen chloride forms 1,1-dichloroethane:

$$H{-}C{\equiv}C{-}H + HCl = \underset{\text{vinyl chloride}}{CH_2{=}CHCl}$$

$$CH_2{=}CHCl + HCl = \underset{\substack{\text{ethylidene chloride or}\\ \text{1,1-dichloroethane}}}{CH_3{-}CHCl_2}$$

Water adds to acetylene in the presence of sulfuric acid and mercuric oxide to yield acetaldehyde, an important synthetic organic intermediate:



$$H{-}C{\equiv}C{-}H + H_2O = \underset{\text{acetaldehyde}}{CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}H}$$

A characteristic reaction of acetylene is salt formation in the presence of strong bases. Acetylene and 1-alkynes (R─C≡C─H, where R is H or an alkyl group) in general behave as acids by giving up protons to strong bases. For example, acetylene reacts with amide ion in liquid ammonia to form ammonia and an acetylide salt:

$$H{-}C{\equiv}C{-}H + NH_2^{-} = \underset{\text{acetylide ion}}{H{-}C{\equiv}C{:}^{-}} + NH_3$$

Alkynes are far more acidic than alkenes and alkanes (by many orders of magnitude). This is attributed to the shift of electrons in the ≡C─H bond toward the triply bonded carbon.

Acetylene is a cheap versatile intermediate for many organic syntheses. In addition, it is widely used in the oxyacetylene torch, in. which temperatures up to 3500°C can be reached. Commercial production of acetylene is

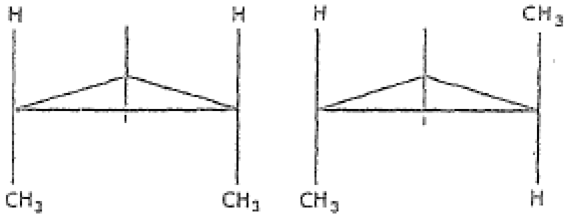
The hydrogen atoms are actually more closely crowded in the boat conformation.

There are two different spatial positions which a substituent can occupy on the chair conformation of the cyclohexane ring. The substituent (hydrogen or another group) can hold one of the six positions in the plane of the ring; these are called equatorial (equator) positions.

Alternatively, the substituent can occupy one of the six positions in which its bond axis is perpendicular to the plane of the ring; these are called axial positions.

Many experimental facts concerning the chemistry of cycloalkyl derivatives were difficult to understand and explain before the advent in 1950 of the concept of equatorial and axial substituents, which may differ significantly in their reactivities.

The substituted cycloalkanes can give rise to geometric isomerism analogous to that discussed for the alkenes. *cis*- and *trans*-isomers have been isolated in many ring systems. Examples of this stereoisomerism are shown for *cis*-1,2-dimethylcyclopropane and *trans*-1,2-dimethylcyclopropane.



cis-1,2-dimethylcyclopropane and *trans*-1,2-dimethylcyclopropane

1.5.19 Benzene and aromatic compounds

Benzene, C_6H_6, is the parent substance of the aromatic (fragrant) compounds, all of which contain as their nucleus a benzene ring, or two or more benzene rings fused together.

All aromatic compounds resemble benzene in general chemical behavior. The two major sources of aromatic compounds are petroleum and coal tar.

Aromatic compounds are extremely useful as raw materials for chemical synthesis. Benzene is an important liquid fuel and solvent, especially for rubber.

Both benzene and toluene are used for blending high-octane gasolines. Phenol (carbolic acid) is an important disinfectant.

The Structure of Benzene

The benzene molecule is a symmetrical hexagonal ring consisting of six carbon atoms in a single plane with each carbon attached to one hydrogen atom. X-ray diffraction and spectroscopic measurements show that in benzene each pair of adjacent carbon atoms are 1,397 Å apart, the six C—H bonds are 1,09 Å long, and all C—C—C and H—C—C bond angles are 120°.

In benzene, as in ethylene, the three primary bonds from each carbon involve sp^2 hybrid orbitals. One results from the overlapping of one of the hybridized sp^2 atomic orbitals with the s orbital of the adjacent hydrogen atom to form the C-H bond.

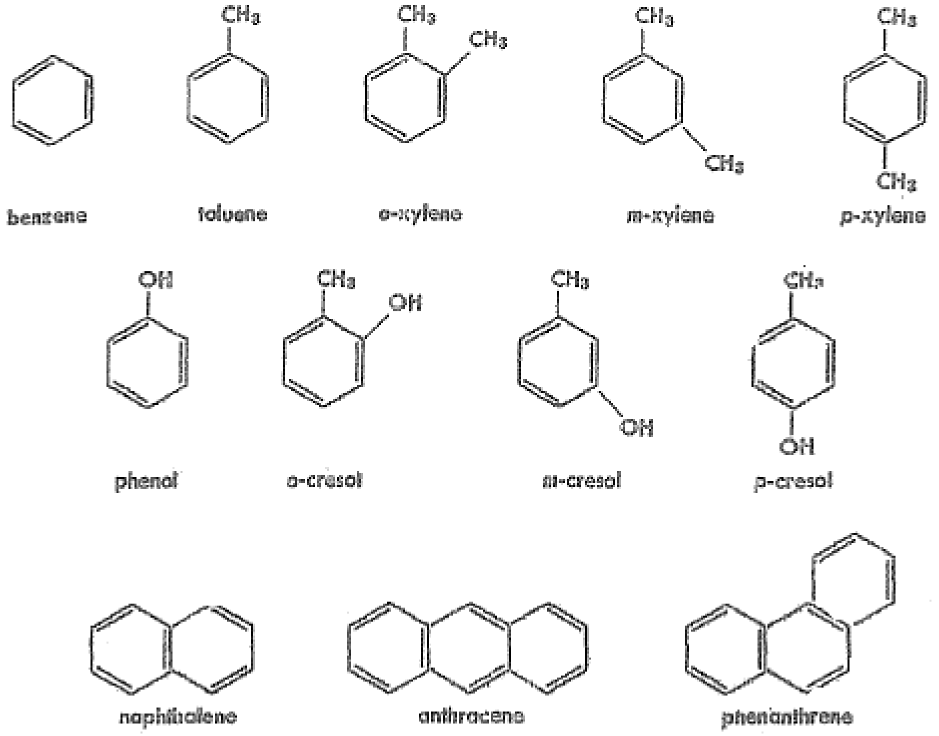


Figure 1.9 Some Aromatic compounds obtained from coal tar

Note:
The letter prefixes used in the naming of the isomeric xylenes and the isomeric cresols indicate the relative positions of the substituting groups on the ring. Adjacent positions, or compounds containing substituents in these positions, are designated as *ortho (o)*, those separated by one carbon atom as *meta (m)*, and opposite positions as *para (p)*.

The other two arise from the overlapping of each of the two remaining sp^2 atomic orbitals with an sp^2 orbital of each of two adjacent cabon atoms in the ring to form two C─C bonds.

All three σ bonds joining each carbon atom to its hydrogen atom and to the two adjacent ring carbon atoms therefore make angles of 120° with each other, and all of the four atoms involved must lie in the same plane.

Application of this orbital model picture to all of the carbon atoms in the ring predicts that all of the atoms of benzene must lie in the same plane and that all bond angles must be 120°.

These predictions are supported by the experimental evidence for the structure of benzene.

Each carbon atom in the benzene ring is then left with one *p* orbital, containing an unpaired electron, with its axis perpendicular to the plane of the benzene ring.

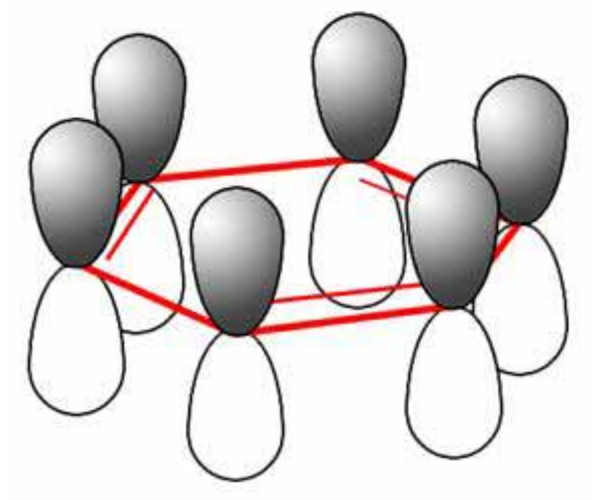


Figure 1.10 *p* atomic orbitals in benzene

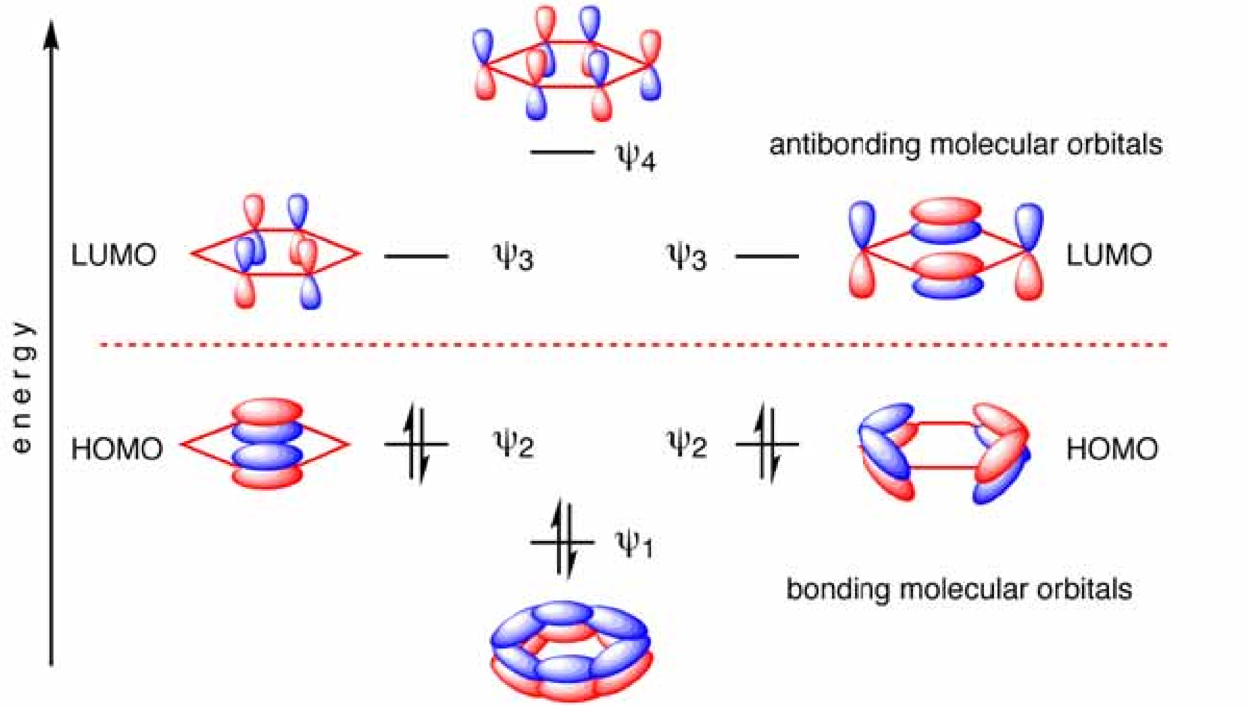
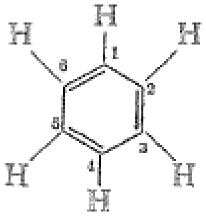


Figure 1.11 The π molecular orbital of benzene. The dashed line represents the energy of an isolated p orbital – all orbitals below this line are bonding, all above it are antibonding. Benzene has six electrons in its π system so all the bonding MOs are fully occupied.

This model, providing for a large amount of orbital overlap, can account for the relatively high stability of the benzene ring, as well as for the complete equivalence of all of the carbon-carbon bonds in the benzene ring.

How can the structure of benzene be drawn using structural formulas? One way to do this could be:

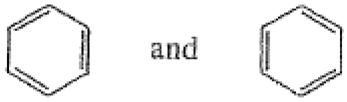


However, this picture leads to some false conclusions concerning the benzene structure. It would predict, for example, that the bonds connecting carbon atoms 1 and 2, 3 and 4, and 5 and 6, which are single bonds should be longer than the carbon-carbon double bonds between carbon 2 and 3, 4 and 5, and 1 and 6.

Note:
Recall that the length of the C─C bond is approximately 1,54 Å, and that of the C=C bond approximately 1,34 Å.

Experimental evidence shows, however, that the lengths of all the carbon-carbon bonds in benzene are 1,397 Å, intermediate between those of the C─C and C=C bonds. Clearly, one structure, as we have written it, cannot represent the structure of benzene.

August Kekule (at the University of Bonn) in 1865 proposed a solution to this problem. He suggested that there are two equivalent formulas of benzene,



in which the double bonds occupy different positions. Our current concept of benzene is based upon Kekule's formulation, but states further that some molecules can be adequately pictured only as a hybrid of two or more structural formulas. These structures are frequently called resonance structures.

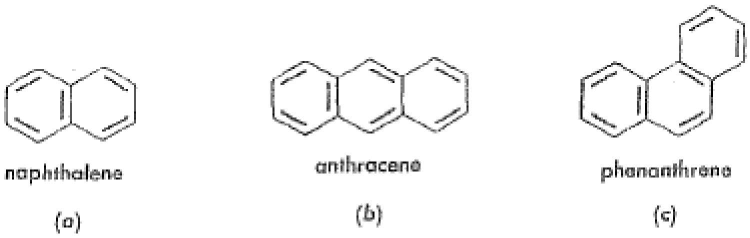


Figure 1.12 Some fused aromatic molecules

The resonance structures of benzene have the same stability or energy. Therefore, each of them contributes equally to the resonance hybrid. In general, resonance occurs when a molecule can be represented by two or more structures that differ only in the position of electrons.

Resonance structures have no physical reality or independent existence but are only hypothetical representations of molecules. Benzene is not a mixture of the two resonance structures.

Resonance structures are purely fictional. The reason that we discuss resonance at all is because of the inadequacy of our usual structural formulas in representing certain molecules.

Resonance is not an inherent property of these molecules, but only a device for picturing them. You will notice that in the case of benzene the molecular orbital view describes its structure adequately without resort to the concept of resonance.

The chemical bonding resulting from the overlap of six *p* electrons in a single cyclic π molecular orbital leads to the unusual stability associated with the benzene ring. Fused aromatic systems such as those in naphthalene, anthracene, and phenanthrene (**Figure 1.13**) also display this stability.

Cyclic molecular species not containing benzene rings but having six π electrons also show aromatic with it. The structures of some of these species are pictured in **Figure 1.13**.

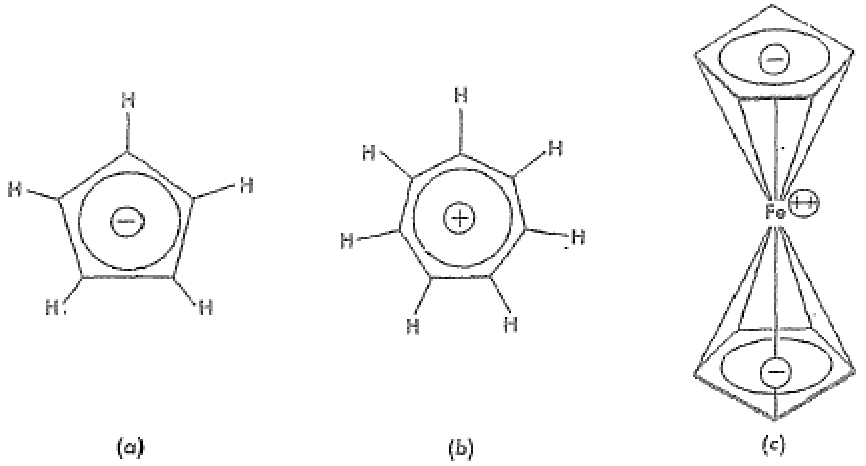


Figure 1.13 Some nonbenzenoid aromatic systems (the solid circle denotes six π-electrons (a) Cyclopentadienate anion, (b) tropylium cation, and (c) ferrocene

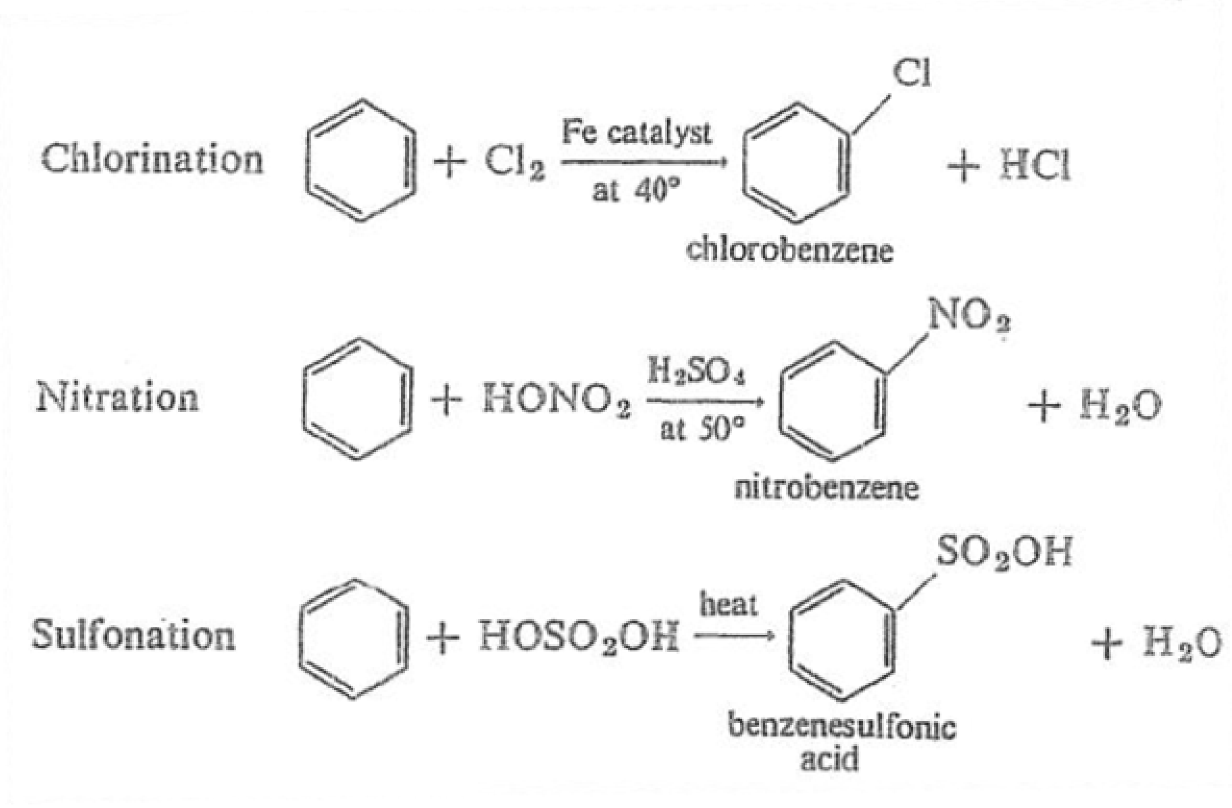
Reactions of aromatic compounds

Despite the apparent high degree of unsaturation of benzene and its derivatives, the characteristic reaction of aromatic compounds is substitution rather than addition. Because of its π electron cloud, benzene, as well as other aromatic compounds, is basic in the same sense as are the alkenes.

Addition in benzene, however, would lead to the loss of the stability associated with the completely symmetrical cyclic π electron system and the substitution of another atom or group for a hydrogen atom, however the aromatic π electron system is preserved.

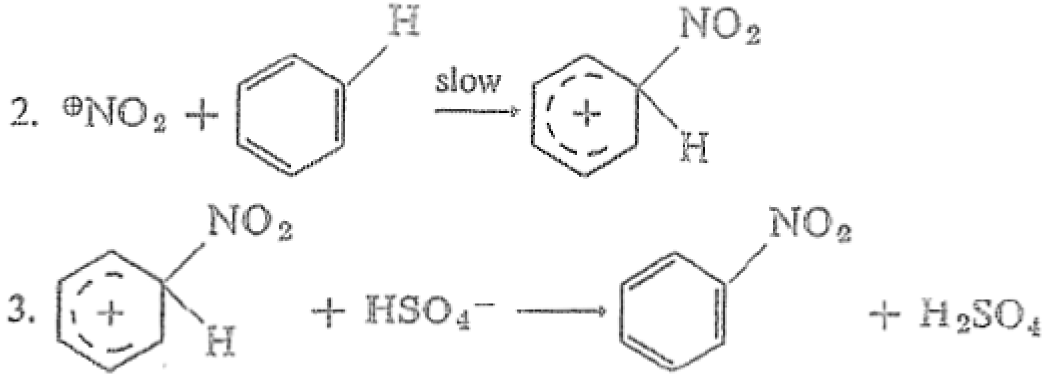
The characteristic substitution reactions of aromatic compounds is classified under the general heading of electrophilic substitution, because the attacking species is electron-pair seeking or acidic in character.

Examples of typical aromatic substitution reactions are chlorinatic nitration, and sulfonation. These reactions are illustrated for benzene:

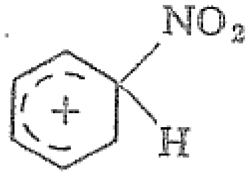


The generally accepted mechanism for the nitration of benzene is as follows:

1. $HONO_2 + 2H_2SO_4 = {}^{\oplus}NO_2 + 2HSO_4^{-} + H_3O^{+}$



In step 1, a well-established equilibrium reaction, nitric acid reacts with sulfuric acid to form the highly electrophilic nitronium ion, ${}^{+}NO_2$. It is postulated that the electrophilic nitronium ion attacks the benzene molecule in the slow and rate-controlling step 2, accepting a pair of electrons from the π electron cloud to form the high-energy carbonium ion,

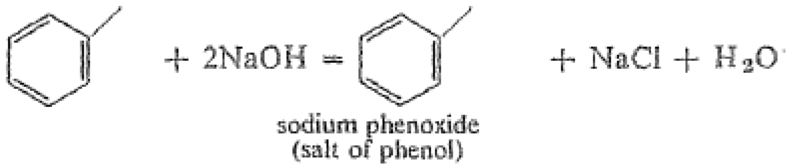


This highly unstable intermediate can be thought of as an ionic species in which the *p* orbitals from five carbon atoms overlap to form a π system which contains only four electrons.

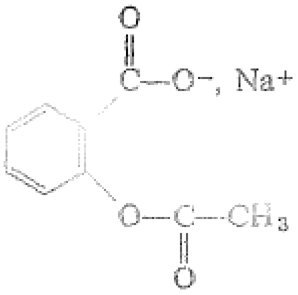
The effect of any substituent already present on the ring on the rate of further substitution on the ring and in dictating the position of further substitution can be predicted' on the basis of the relative stabilities of the various possible intermediates which can be formed.

In step 3, loss of a proton from the intermediate ion to the hydrogen sulfate ion restores the aromatic system with formation of nitrobenzene.

Chlorobenzene is used in the manufacture of the insecticide DDT. Chlorobenzene is converted to phenol, on an industrial scale, with dilute sodium hydroxide at 300°C under very high pressure, in a system of copper pipes:

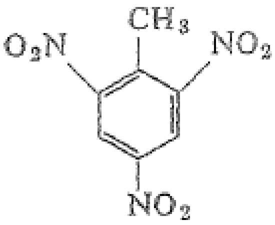


Phenol is then liberated from its sodium salt with carbon dioxide. The synthesis of aspirin utilizes phenol as a key chemical intermediate:

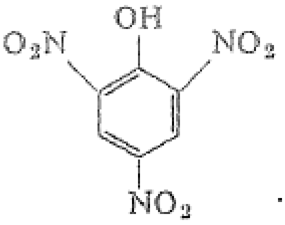


aspirin

The trinitrations of toluene and phenol give two important high explosives, trinitrotoluene (TNT) and picric acid, respectively:



trinitrotoluene



picric acid

1.5.20 Alcohols

Alcohols are characterized by the —OH (hydroxyl) functional group. The chemistry of alcohols is concerned primarily with the reactions of the C—0 and 0—H bonds associated with the OH group.

The common names of the alcohols are derived from those of the parent alkanes. Some familiar alcohols and the hydrocarbon or slkyne groups that they contain are shown in **Table 2.5**.

Formula	Name of alcohol	Alkyl group	Name of alkyl group
CH_3OH	methyl alcohol (or methanol)	$CH_3—$	methyl
CH_3CH_2OH	ethyl alcohol (or ethanol)	$CH_3CH_2—$	ethyl
$CH_3CH_2CH_2OH$	normal (or *n*-) propyl alcohol (or 1-propanol)	$CH_3CH_2CH_2—$	*n*-propyl

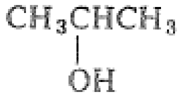
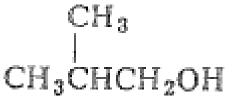
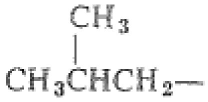
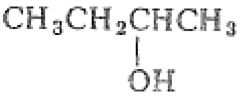
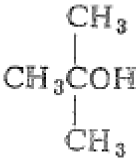
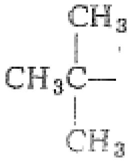
 $CH_3\underset{OH}{\underset{\vert}{C}}HCH_3$	isopropyl alcohol (or 2-propanol)	 $CH_3\underset{\vert}{C}HCH_3$	isopropyl
$CH_3CH_2CH_2CH_2OH$	*n*-butyl alcohol (or 1-butanol)	$CH_3CH_2CH_2CH_2—$	*n*-butyl
 $CH_3\overset{CH_3}{\overset{\vert}{C}}HCH_2OH$	isobutyl alcohol (or 2-methyl-1-propanol)	 $CH_3\overset{CH_3}{\overset{\vert}{C}}HCH_2—$	isobutyl
 $CH_3CH_2\underset{OH}{\underset{\vert}{C}}HCH_3$	secondary (or *sec*-) butyl alcohol (or 2-butanol)	 $CH_3CH_2\underset{\vert}{C}HCH_3$	*sec*-butyl
 $CH_3\overset{CH_3}{\overset{\vert}{\underset{CH_3}{\underset{\vert}{C}}}}OH$	tertiary (or *tert*-) butyl alcohol (or 2-rnethyl-2-propanol	 $CH_3\overset{CH_3}{\overset{\vert}{\underset{CH_3}{\underset{\vert}{C}}}}—$	*tert*-butyl

Table 2.12

Using R as the symbol for alkyl groups, we represent the general type formula for the alcohols, then, as ROH.

Because of the rather extensive hydrogen bonding between the oxygen atoms of alcohols, intermolecular association is important.

As a consequence, alcohols are considerably less volatile than the corresponding hydrocarbons, as shown in **Table 1.13**.

Alcohol	**BP, °C**	**Alkane of corresponding molecular weight**	**BP, °C**
CH_3OH	64,5	CH_3CH_3	-88,5
$CH_3CH_2CH_2CH_2OH$	118	$CH_3CH_2CH_2CH_2CH_3$	+36

Table 1.13 Boiling points of alcohols and alkanes

The lower alcohols up to lauryl alcohol, $C_{12}H_{25}OH$, are liquids with pleasant odors; the higher alcohols are solids. Lower molecular weight alcohols (up to C_5) are readily soluble in water, again because of hydrogen bonding interaction between the alcohol and water molecules.

Historically, methyl alcohol has been obtained by the destructive distillation of wood, hence the name wood alcohol. At present almost all of the production in the United States comes from the quantitative catalytic hydrogenation of carbon monoxide:

$$2H_2 + CO = CH_3OH$$

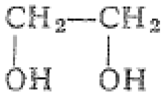
Methyl alcohol is extremely toxic when taken internally or when inhaled. Ethyl alcohol has long been produced by the bacterial fermentation of starch or molasses, hence the name grain alcohol. Large quantities are now produced by the addition of water to ethylene.

Ethyl alcohol ranks first among synthetic organic chemicals in quantity of production and in total value. It is indispensable to a host of industries, both for its own uses and as a starting material in the synthesis of other products.

Isopropyl and sec-butyl alcohols are obtained by the addition of water to the propylene and butenes produced in the cracking of petroleum.

The Weizmann process for the bacterial fermentation of starch produces large quantities of *n*-butyl alcohol. The acetate esters of these alcohols are useful as lacquer solvents.

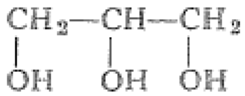
Alcohols containing two -OH groups are called dials, dihydroxy alcohols, or glycols. The simplest, and one of the most important, is ethylene glycol,



$$\begin{array}{cc} CH_2 - & CH_2 \\ | & | \\ OH & OH \end{array}$$

bp 197°C. It is obtained commercially from ethylene and is widely used as a high boiling, noncorrosive antifreeze for automobile radiators.

Most important of the trihydroxy alcohols is glycerol,



$$\begin{array}{ccc} CH_2 - & CH - & CH_2 \\ | & | & | \\ OH & OH & OH \end{array}$$

bp 290°C. It is produced as a by-product from the hydrolysis of fats and oils in soap manufacture and by chemical synthesis from propylene.

The high boiling points and marked water solubility of the polyhydroxy alcohols can be explained by the strong extensive hydrogen bonding interactions possible with these alcohols.

Alcohols do not react appreciably with water to form either hydronium or hydroxide ions; their water solutions are therefore neutral to litmus and they are classified as nonelectrolytes. Alcohols are at best weak acids, although the lower molecular weight alcohols react readily with sodium.

The product in the case of ethyl alcohol is sodium ethoxide:

$$2Na + 2CH_3CH_2OH = \underset{\text{sodium ethoxide}}{2CH_3CH_2O^-, Na^+} + H_2$$

The ethoxide ion is a strong base, stronger, in fact, than hydroxide and is frequently used as a basic catalyst in organic reactions.

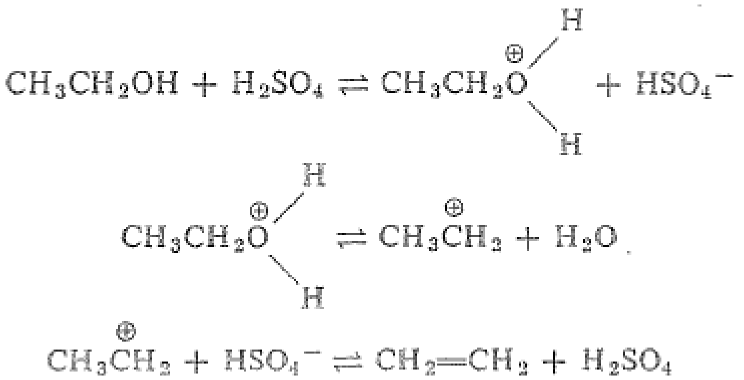
Alcohols burn in an excess of air, as do all organic compounds containing carbon, hydrogen, and oxygen, forming carbon dioxide and water.

The dehydration of alcohols in the presence of an acidic catalyst below in the class of elimination reactions. It can yield either an alkene or, by intermolecular dehydration, an ether:

$$CH_3CH_2OH \xrightarrow[180^\circ]{H_2SO_4} \underset{\text{ethylene}}{CH_2{=}CH_2} + H_2O$$

$$2CH_3CH_2OH \xrightarrow[140^\circ]{H_2SO_4} \underset{\text{ethyl ether}}{CH_3CH_2{-}O{-}CH_2CH_3} + H_2O$$

The production of ethylene from ethyl alcohol is the reverse of the acid-catalyzed addition of water to ethylene, and is thought to proceed through the same carbonium ion intermediate. For the sulfuride acid-catalyzed reaction, the postulated mechanism is

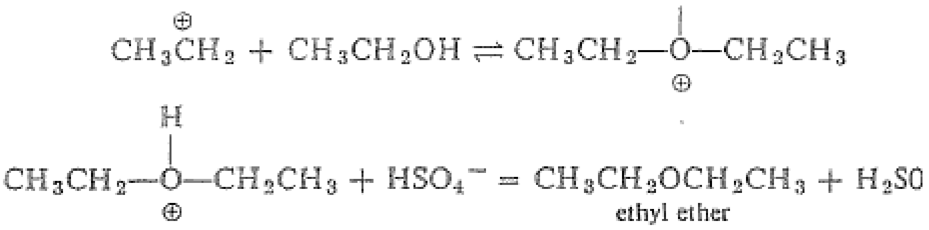


$$CH_3CH_2OH + H_2SO_4 \rightleftharpoons CH_3CH_2\overset{\oplus}{O}H_2 + HSO_4^-$$

$$CH_3CH_2\overset{\oplus}{O}H_2 \rightleftharpoons CH_3\overset{\oplus}{C}H_2 + H_2O$$

$$CH_3\overset{\oplus}{C}H_2 + HSO_4^- \rightleftharpoons CH_2{=}CH_2 + H_2SO_4$$

Reaction of the ethyl cation with additional ethyl alcohol leads to ether formation:



$$CH_3\overset{\oplus}{C}H_2 + CH_3CH_2OH \rightleftharpoons CH_3CH_2{-}\underset{\oplus}{\overset{H}{O}}{-}CH_2CH_3$$

$$CH_3CH_2{-}\underset{\oplus}{\overset{H}{O}}{-}CH_2CH_3 + HSO_4^- = \underset{\text{ethyl ether}}{CH_3CH_2OCH_2CH_3} + H_2S0$$

In practice, the reaction may be directed toward the production of either the alkene or the ether through careful control of the temperature and reagent concentration.

1.5.21 Ethers

Intermolecular elimination of a molecule of water from two molecule of alcohol produces an ether, R─0─R, where R and R' may be the same or different alkyl groups.

Lacking a hydrogen atom attached to oxygen, ether molecules are incapable of association through hydrogen bonding; hence ethers are more volatile than the isomeric alcohols.

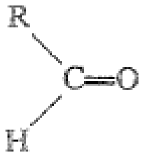
For example, methyl ether, CH_3─O─CH_3, an isomer of ethyl alcohol (both have the molecular formula C_2H_6O), is a gas. Isomers of the type of ethyl alcohol and methyl ether, which have different functional groups, are called functional isomers.

Ethyl ether is an important general anesthetic; it was first used for that purpose by Dr. Crawford W. Long of Jefferson, Georgia, in 1842, nine years before its true structure was known. Ethyl ether is an excellent solvent for organic compounds, especially oils and fats.

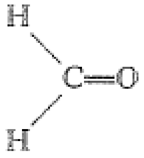
1.5.22 Aldehydes and ketones

Both aldehydes and ketones contain the

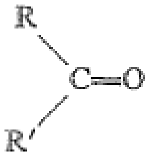
or carbonyl group. In aldehydes, the carbonyl group occurs at the end of the carbon chain; the type formula for aldehydes is therefore



where R represents an alkyl group in all but series, formaldehyde:



If the carbonyl group occurs at any carbon other than one at the end of the chain, the compound is a ketone. Hence, the type formula for ketones is



where R and R' may be the same or different alkyl groups.

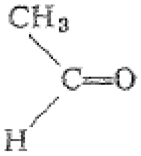
Both aldehydes and ketones are oxidation products of alcohols, from which they can be synthesized by the removal of two hydrogen atoms from the corresponding alcohol molecule. In turn, aldehydes can be easily oxidized further to carboxylic acids, whereas ketones resist further oxidation.

Mild oxidation of methyl alcohol gives formaldehyde. The oxidation is accomplished commercially by passing a mixture of methyl alcohol vapor and air over a copper or silver gauze catalyst at 500-600°C:

$$2CH_3OH + O_2 = 2HCHO + 2H_2O$$

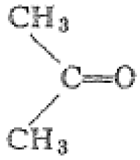
Formaldehyde is a gas (boiling point -21°C). It is widely marketed as a 37% solution ca1led formalin, which is used as a preservative for anatomical specimens and as a fumigant. The widely used plastic known as Bakelite is produced by the reaction of formaldehyde with phenol.

Acetaldehyde,



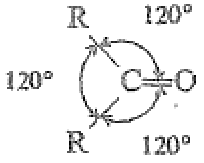
is produced commercially by the catalytic oxidation of ethyl alcohol or by the addition of water to acetylene in the presence of sulfuric acid and mercuric oxide catalysts.

Acetaldehyde is a useful starting material in the synthesis of a great variety of important compounds including *n*-butyl alcohol, acetic acid, acetone, acetic anhydride, and ethyl acetate. Acetone (dimethyl ketone),



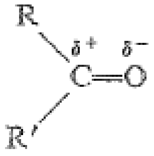
bp 56°C, is the most important of the ketones and is widely used as a commercial solvent

In aldehydes and ketons, the carbonyl carbon is joined to three other atoms by σ bonds. Since these bonds utilize sp^2 orbitals, they lie in a plane, and are 120° apart. The remaining *p* orbital of the carbon overlaps a *p* orbital of oxygen to form a π bond; the carbon and oxygen are then joined by a double bond. The carbonylcarbon, the oxygen, and the two atoms directly attached to the carbonyl carbon all lie in one plane:



Oxygen and carbon differ substantially in their relative electro-negativities, and hence the electrons in the double bond are not equally shared.

The mobile π electron cloud is polarized (displaced) strongly toward the more electronegative oxygen and away from the carbon. This polarity may be represented as follows:

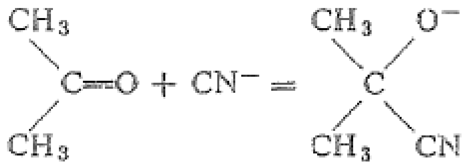


As a result, the carbonyl carbon is an electron-deficient or acidic center and is highly susceptible to attack by electron-pair donating or basic reagents. In organic chemistry, such reagents are referred to as nucleophilic (nucleus-loving) in character, and are called nucleophiles.

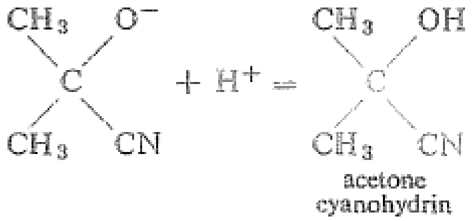
It is this susceptibility to attack by electron-donor nucleophilic reagents that dictates much of the chemistry of the carbonyl group, and therefore of the aldehydes and ketones. The characteristic reactions of the aldehydes and ketones are, like those of the alkenes, addition reactions.

The same reagents which add to carbonyl compounds do not always add to alkenes, however, since alkenes do not readily undergo nucleophilic (or basic) attack.

An example of a strong nudeophile which readily adds to the carbonyl carbon is cyanide ion. The reaction for acetone is as follows:

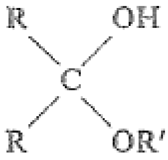


The addition reaction is consummated by transfer of a proton from the medium to form the final product, acetone cyanohydrin:

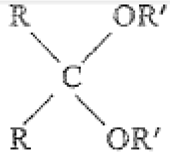


The overall reaction is addition of HCN to the carbonyl double bond, but the addition is definitely nucleophilic because the important step is the attack at the electron-deficient carbonyl carbon by the nucleophile, cyanide ion.

Alcohols, under acid catalysis, add to aldehydes and ketones to form hemiacetals:



Reaction of a second molecule of alcohol with the hemiacetal gives an acetal:



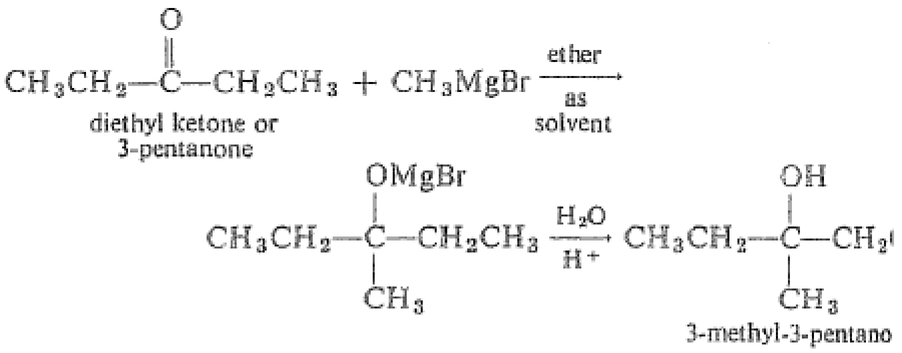
This type of reaction is of particular importance in carbohydrate chemistry. Polysaccharides, such as starch and cellulose, contain carbohydral units joined together through acetal linkages.

The formation of carbon-carbon bonds is of importance in the building of large complex organic molecules from simple ones by the methods of organic synthesis.

The carbonyl group is extremely versatile in promoting the formation of different carbon-carbon bonds. Two of the most versatile synthetic methods are the Grignard reaction and the aldol condensation.

Specific examples of these reactions are given here:

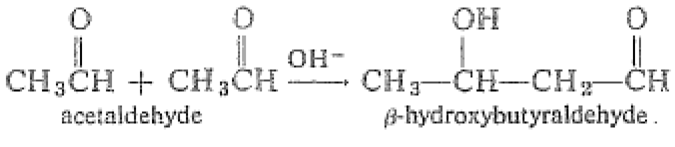
Grignard reaction



$$CH_3CH_2-\overset{\overset{O}{\|}}{C}-CH_2CH_3 + CH_3MgBr \xrightarrow[\text{solvent}]{\text{ether as}}$$

$$CH_3CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{OMgBr}{|}}{C}}-CH_2CH_3 \xrightarrow[H^+]{H_2O} CH_3CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{C}}-CH_2$$

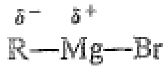
Aldol condensation



$$CH_3\overset{\overset{O}{\|}}{C}H + CH_3\overset{\overset{O}{\|}}{C}H \xrightarrow{OH^-} CH_3-\overset{\overset{OH}{|}}{C}H-CH_2-\overset{\overset{O}{\|}}{C}H$$

The Grignard reaction involves the use of an organometallic reagent, RMgBr, in which a chemical bond connects a carbon atom with the metal magnesium.

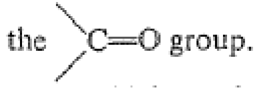
This is a highly polar bond:



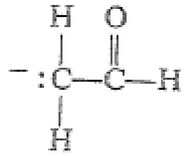
$$\overset{\delta^-}{R}—\overset{\delta^+}{Mg}—Br$$

Organometallic reagents are extremely reactive in a number of ways.

They add to the carbonyl double bond, the alkyl group acting as a strong nucleophile in attacking the electron-deficient carbon atom of



The aldol reaction demonstrates the effect that a functional group can have on nearby atoms. In acetaldehyde, the methyl hydrogens are rendered sufficiently acidic by the neighboring carbonyl group so that, in the presence of the base catalyst $^{-}$OH, a small concentration of the anion (called a carbanion) is formed.

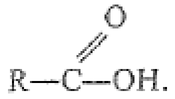


$$^{-}:\underset{H}{\overset{H}{C}}—\overset{O}{\overset{\|}{C}}—H$$

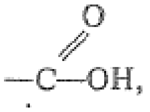
The key step in the_ aldol condensation is the attack of the highly nucleophilic carbanion at the electron-deficient carbonyl carbon of a second aldehyde molecule.

1.5.23 Carboxylic acids and their derivatives

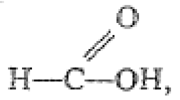
Carboxylic acids are represented by the general formula



They are characterized by the presence of a

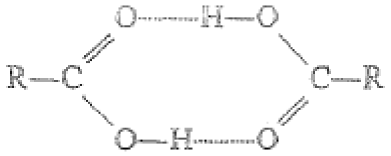


or carboxyl group, in which a carbon is linked by a double bond to an oxygen atom and by a single bond to an ─OH group. The simplest carboxylic acid is formic acid,



where the R is H. In general, the R group may be saturated or unsaturated (containing one or more multiple bonds). Both saturated and unsaturated long chain (C_{12}-C_{18}) acids are formed in the hydrolysis of the glycerol esters found in the common animal fats and animal and vegetable fatty oils. Hence the long carboxylic acids are often referred to as fatty acids.

Because of the unusually stable hydrogen bonds which they form, the molecules of the lower members of the series are associated into dimeric strcutures even in the vapor state. The general formula for such a dimer is represented as



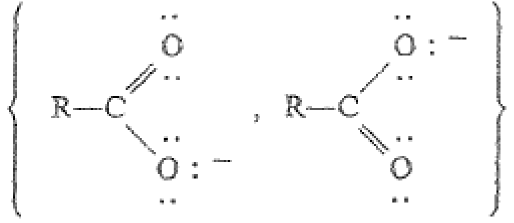
Perhaps the most interesting and characteristic property of the carboxylic acids is their acidity. They are only weakly acidic, it is true, but they are considerably stronger acids than either alcohols or water.

The lower molecular weight water-soluble acids are partially ionized in water and exist in equilibrium with the carboxylate ion and the hydronium ion:

$$RCOOH + H_2O \rightleftharpoons RCOO^- + H_3O^+$$

The K_{ac}, or acidity constant, for acetic acid at 25°C is $1,8 \times 10^5$. Higher molecular weight carboxylic acids, which are insoluble in water, are often identified by the fact that they dissolve (or form colloidal soap dispersions) in cold dilute aqueous sodium hydroxide solution:

The much stronger acidity of the carboxylic acids over that of alcohols is readily explained on the basis of the structure of carboxylate ions. A carboxylate ion is a resonance hybrid which receives contribution from two equivalent structures:



In molecular orbital terms, the *p* orbital of the carboxyl carbon in a carboxylate ion overlaps equally well with *p* orbitals from both oxygen atoms. This means, in effect, that the negative charge or electron cloud is dispersed or delocalized evenly over both oxygen atoms.

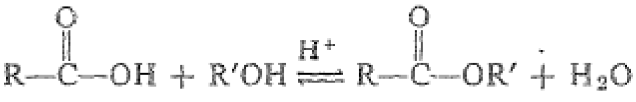
The effect of this charge dispersal is to increase significantly the stability of a carboxylate ion over an alkoxide ion (RO^-) or the hydroxide ion, where the negative charge is localized on a single oxygen atom.

As a result, a carboxylic acid tends to lose a proton more readily to form the corresponding carboxylate ion than does an alcohol to form the corresponding alkoxide ion, or water to form the hydroxide ion. This is another way of saying that carboxylic acids are stronger acids than are alcohols and water.

The K_{ac} values for fluoroacetic acid (FCH_2COOH) and chloroacetic acid ($ClCH_2COOH$) are roughly 100 times as great as that for acetic acid.

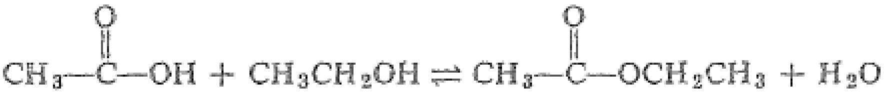
Trichloroacetic acid ($Cl_3C\ COOH$) approaches the strong mineral acids in acid strength. These facts are explained on the basis of the effect of the highly electron-withdrawing or electronegative halogen atoms in stabilizing the carboxylate ions.

Carboxylic acids react slowly with alcohols to form a class of organic compounds called esters. The reaction is catalyzed by acids:



$$R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OH + R'OH \overset{H^+}{\rightleftharpoons} R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OR' + H_2O$$

an ester



$$CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OH + CH_3CH_2OH \rightleftharpoons CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OCH_2CH_3 + H_2O$$

ethyl acetate

Esterification is a true equilibrium reaction. It is of some historical importance, as the formulation of the law of chemical equilibrium in 1867 by Guldberg and Waage was influenced by the study of esterification.

The lower molecular weight esters have pleasant odors which are at least partially responsible for the fragrance and flavor of many fruits.

The simplest carboxylic acid, formic acid, HCOOH, bp 101°C, is obtained from sodium formate, produced in the reaction between carbon monoxide and sodium hydroxide. Here carbon monoxide acts as a true acid anhydride:

$$CO + NaOH = HCOONa$$

sodium formate

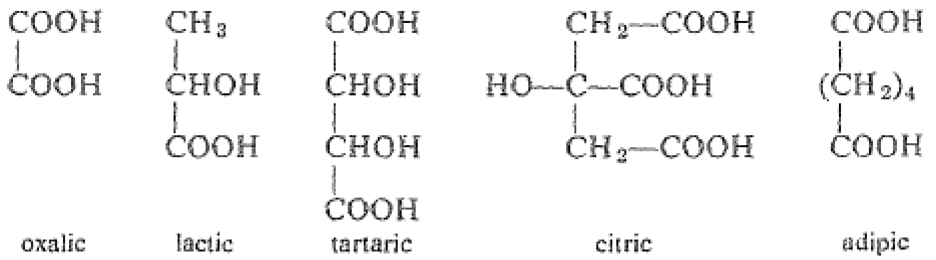
Acetic acid,

$$CH_3\overset{\overset{\displaystyle O}{/\!\!/}}{C}OH,$$

bp 118°C, is the most important organic acid in commercial use. It is readily prepared in the laboratory by oxidation of either ethyl alcohol or acetaldehyde.

Vinegar, produced by fermentative oxidation of ethyl alcohol obtained from molasses or cider, contains about 4% acetic acid.

Some important acids contain two (dicarboxylic) or three (tricarboxylic) carboxyl groups. Others, containing both carboxyl and hydroxyl groups, are called hydroxy-acids. The names and structural formulas of some of these acids are:



Lactic acid is present in sour milk; tartaric acid is the acid of grapes; and citric acid that of citrus fruits. A.dipic acid is an intermediate in the manufacture of nylon.

1.5.24 Soaps

The process of saponification or soap-making involves the hydrolysis of fats in the presence of sodium or potassium hydroxide. The sodium salts of the fatty acids palmitic, stearic, and oleic acids, shown in **Table 1.14**, are the most common constituents of ordinary soaps.

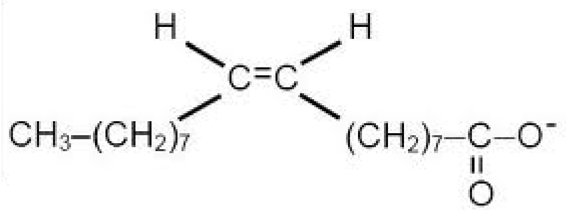
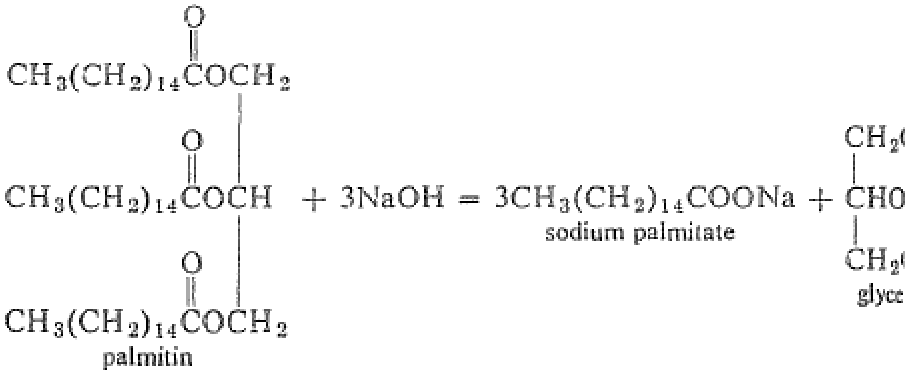
Structure	**Name**
$CH_3(CH_2)_{10}COOH$	laurice acid
$CH_3(CH_2)_{14}COOH$	palmito acid
$CH_3(CH_2)_{16}COOH$	stearic acid
	oleic acid

Table 1.14 Some fatty acids

Saponification of the fat palmitin (glyceryl palmitate) with sodium hydroxide produces the soap sodium palmitate. The fats are all esters the trihydroxy alcohol glycerol with fatty acids (triglycerides).

Most of the solid fats are glyceryl esters of saturated acids, whereas the liquid fats or fatty oils, such as cottonseed, linseed, olive, coco:1ut, and peanut oil are glyceryl esters of the unsaturated fatty acids.



Glycerol is always a by-product of soap manufacture.

Soap molecules, with their water-soluble ionic heads (carboxylate groups) and grease-solubilizing hydrocarbon tails, act as a connecting link between water and organic materials. All but very dilute soap solutions are partly colloidal, hence their adsorptive properties.

The calcium, magnesium, and iron salts of the high molecular weight fatty acids are insoluble in water and constitute the scum that is formed when ordinary soap is added to hard water.

1.5.25 Amines and amides

The amines are an important class of organic compounds in which one or more alkyl or aryl groups are substituted for the hydrogen atoms of ammonia[4].

Primary amines contain one such group; secondary, two; and tertiary, three; as illustrated for the methylamines:

ammonia | methylamine, a primary amine | dimethylamine, a secondary amine | trimethylamin a tertiary ami

As would be expected from their structures, the amines, like ammonia, are bases. They are often referred to as the "organic bases." The low molecular weight water-soluble amines are very slightly ionized and give water solutions which are basic to litmus; the high molecular weight water-insoluble amines form soluble salts with mineral acids:

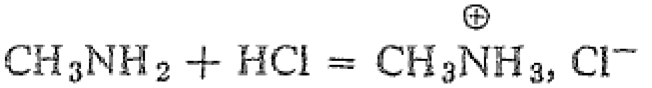
Note:
An aryl group bears the same relationship to an aromatic hydrocarbon as an alkyl group does to an aliphatic hydrocarbon. The simplest aryl group is C_6H_5—, called phenyl.

$$RNH_2 + H_2O \rightleftharpoons RNH_3^+ + OH^-$$

$$RNH_2 + HCl = RNH_4^+, Cl^-$$

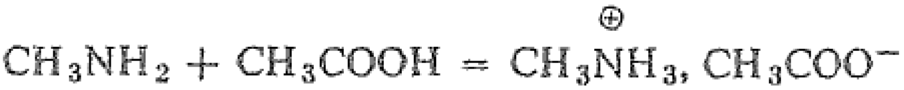
an alkylammonium chloride

Organic amines, like ammonia, react with both organic and inorganic acids to form salts:



$$CH_3NH_2 + HCl = CH_3\overset{\oplus}{NH_3}, Cl^-$$

methylammonium chloride



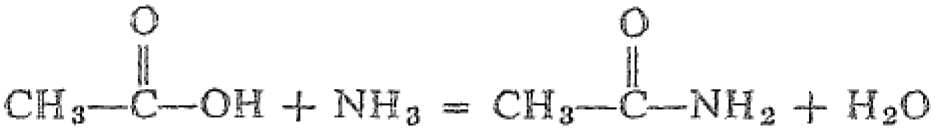
$$CH_3NH_2 + CH_3COOH = CH_3\overset{\oplus}{NH_3}, CH_3COO^-$$

methylammonium acetate

Amines are used extensively in the synthesis of medicinals. Dimethylamine is a key material in the preparation of dyes, rubber accelerators, and cleansing compounds.

Certain compounds containing two $—NH_2$ (amino) groups, the diamines, such as hexamethylenediamine, $NH_2—(CH_2)—NH_2$, are basic materials in the production of plastics and synthetic fibers.

Ammonia can be made *to* react with organic acids at elevated temperatures to produce *amides.* With acetic acid, for example, ammonia forms acetamide:



$$CH_3—\overset{\overset{O}{\|}}{C}—OH + NH_3 = CH_3—\overset{\overset{O}{\|}}{C}—NH_2 + H_2O$$

acetamide

Amides differ in formula from organic acids only by the substitution of the $-NH_2$ group for the -OH group of the acid, and they may therefore be represented by the type formula $RCONH_2$.

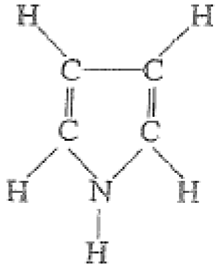
Primary and secondary amines react with acids in an analogous fashion, forming substituted amides in which one or both of the hydrogen atoms attached to the nitrogen in a simple amide are replaced by alkyl groups.

In the reaction a molecule of water is eliminated between the carboxyl group of the acid and the amino group of the amine. Proteins and nylon are complex substituted polyamides.

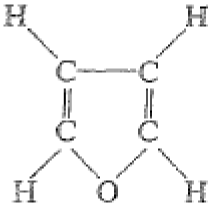
1.5.26 Heterocyclic compounds

A *heterocyclic* compound is one that contains a ring made up of more than one kind of atom. Most heterocyclic compounds are aromatic in character. Nitrogen, oxygen, and sulfur are common heteroatoms ("other" atoms) in heterocyclic compounds.

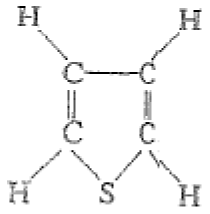
These compounds are extremely important constituents of many natural products. They undergo many of the typical aromatic substitution reactions characteristic of benzene and other aromatic compounds. Examples of some heterocyclic compounds are:



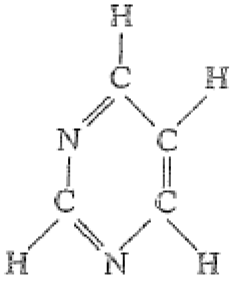
pyrrole



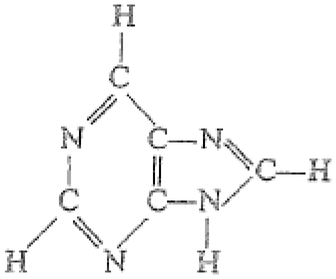
furan



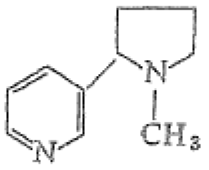
thiophene



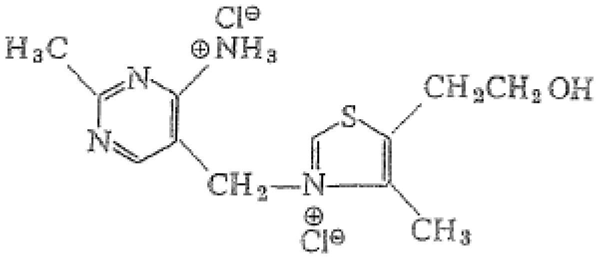
pyrimidine



purine



nicotine



thiamine
(vitamin B_1)

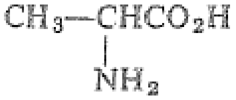
1.5.27 Amino acids

Compounds containing both a carboxyl and an amino group are amino acids. The simplest member of this series is called glycine:

$H_2N—CH_2—COOH$

glycine

Of the known isomers of amino acids !he a-amino acids, in which the amine group is bonded to the carbon atom (the so-called α-carbon atom) adjacent to the carboxyl group, are by far the most important. They are the building blocks from which proteins are made:



$$\begin{array}{l} CH_3—CHCO_2H \\ \qquad\quad | \\ \qquad\; NH_2 \end{array}$$

α-alanine
(protein constituent)

$H_2NCH_2CH_2CO_2H$

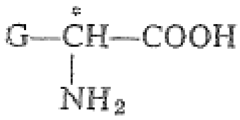
β-alanine
(not found in proteins)

Through the reaction of Ithe carboxyl group of one amino acid molecule with the amino group of another, repeating from molecule to molecule, the amino acids are capable of combining with each other to form high molecular weight proteins, which are the basic material of life.

The amino acids are products of the hydrolysis of proteins, as carried out both in the Laboratory and in the digestive process.

Optical isomers of the Amino acids

All of the a-amino acids except the simplest, glycine, may be represented by the general formula



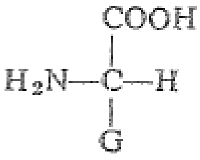
$$\mathrm{G-\underset{NH_2}{\overset{*}{C}H}-COOH}$$

where G is some organic grouping. In all these amino acids, the so-called α-carbon atom (marked by an asterisk in the general formula) is bonded to four different atoms or groups: a hydrogen atom, an amino group, a carboxyl group, and a more complex organic group, G.

A carbon atom which is attached to four different groups is called an asymmetric carbon atom, because it lacks any element of symmetry. Study of a tetrahedral figure will reveal that four different groups can be arranged at the corners of a tetrahedron in two spatially different ways.

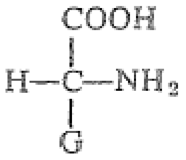
These two different spatial arrangements or configurations for an amino acid molecule, with the carbon atom at the center of the tetrahedron and the four different groups at the corners, are represented by means of molecular models and also by the corresponding tetrahedral structures in **Figure 2.10**.

Ordinary structural formulas for these two configurations are written as follows:



$$\mathrm{H_2N-\underset{G}{\overset{COOH}{C}}-H}$$

L-amino acid



$$\mathrm{H-\underset{G}{\overset{COOH}{C}}-NH_2}$$

D-amino acid

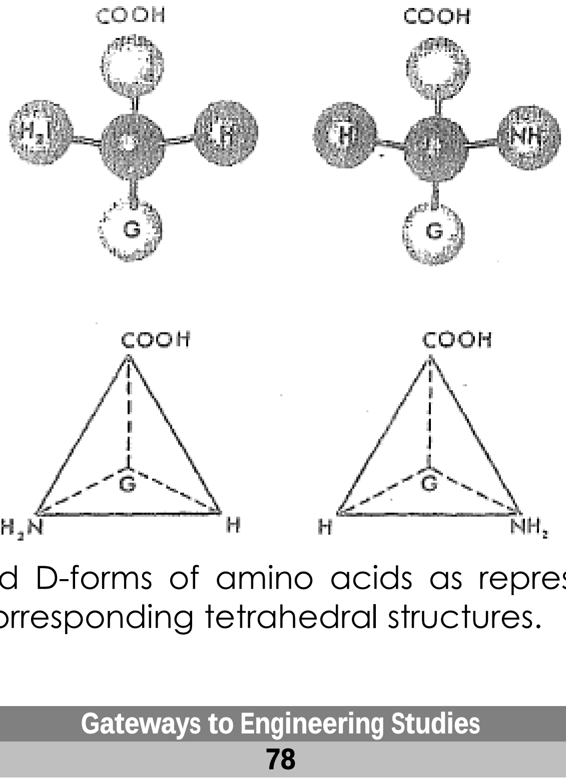


Figure 1.14 The l- and D-forms of amino acids as represented by molecular models and by the corresponding tetrahedral structures.

Study of a host of organic compounds whose molecules contain a carbon atom joined to four different groups has abundantly confirmed the conclusion reached from a consideration of their geometry, for such compounds actually do exist in two distinct forms.

As can be seen from **Figure 1.14**, the two molecular configurations are nonsuperimposable mirror images of each other; ie, they bear the same relationship to each other that the right hand bears to the left hand or the right foot to the left foot. For this reason such isomers are known as enantiomorphs or optical antipodes.

Definition: Enantiomorphs
Each of two crystalline or other geometrical forms which are mirror images of each other. (Greek enantios, opposite; and morphe, form).

Any given amino acid can be classified as belonging to the right-handed (or D, for dextro) or to the left-handed (or L, for levo) family, depending upon the configuration of its various groups in the tetrahedral structure.

Actually both the D- and L-isomers of all the common amino acids are known, but the curious fact is that only the L-amino acids occur commonly in nature. In other words, all life on our planet, so far as we know, is built up on a system of left-handed amino acids.

The physical properties of any pair of D- and L-isomers are identical except for their effects on the plane of plane-polarized light. One isomer of the pair rotates the plane of plane-polarized light to the right; the other exactly equally, but oppositely, to the left.

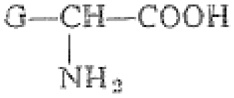
For this reason, the type of stereoisomerism represented by these isomers is called optical isomerism.

Because their chemical reactions toward other optically active compounds are different, the optical isomers behave differently in biological systems.

One may taste bitter, the other sour; one may be a violent poison for humans, whereas the other may be relatively harmless.

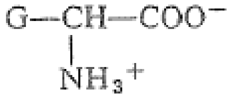
Thus a man from Mars, if his body happened to be built on a right-handed system of amino acids, would find upon visiting our planet that he could not digest or metabolize our food. He could be kept alive only on a diet containing synthetic D-amino acids. He would probably, however have this scant consolation - he would find even our most deadly virus quite harmless!

Although the α-amino acids are often formally written as:



$G-\underset{NH_2}{CH}-COOH$

they actually exist both in the crystalline state and in water solution as internal salts or double ions, called zwitterions or dipolar ions, of the type



$G-\underset{NH_3^+}{CH}-COO^-$

Some important naturally occurring α-amino acids are shown **Table 1.15**.

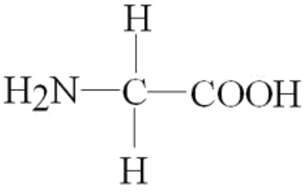
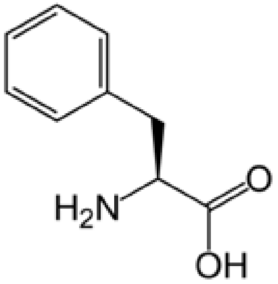
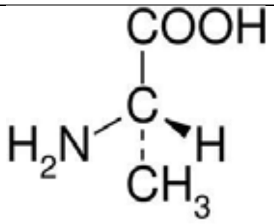
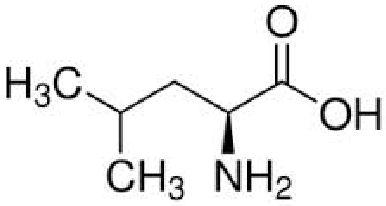
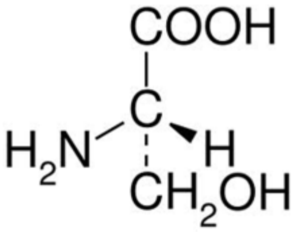
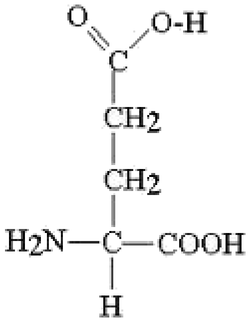
 $H_2N-\overset{H}{\underset{H}{C}}-COOH$	glycine		L-phenylalanine
	L-alanine		L-leucine
	L-serine		L-glutamic acid

Table 1.15 Some important α-Amino acids

Activity 1.1

1. Write formulas for (a) a pair of homologs, (b) a pair of isomers.
2. Write structural formulas for the isomeric hexanes (molecular formula C_6H_{14}).
3. Write formulas for the two isomeric compounds that would be obtained by the replacement of a single hydrogen atom in propane by a chlorine atom.
4. Write structural formulas for nine isomers of molecular formula C_7H_{16}; seven isomers of molecular formula $C_4H_{10}O$; fourteen isomers of molecular

formula $C_4H_{10}O_2$; eight isomers of molecular formula $C_4H_9NH_2$. Classify the various functional groups according to type.

5. Compare the volumes of oxygen required and volumes of water vapor formed in the complete combustion of I liter of ethane, 1 liter of ethylene, and 1 liter of acetylene. (Assume standard conditions throughout.) Compare the amounts of heat evolved in the three cases.
6. Represent by an equation, using structural formulas, the hydrogenation of ethylene; of acetylene.
7. What chemical reaction could be used l.o distingwsh between ethane and ethylene? Would the same test differentiate between ethylene and acetylene?
8. Assume that in a welding operation, 100 g of iron must be heated from 25° to 2500°C. Calculate the weight of ethane, of ethylene, and of acetylene that would have to be burned, assuming that in each case the water vapor and carbon dioxide formed in the reactions would also be heated to 2 500°C. Use as the heat of fusion of iron at 1 500°C, 48 cal per g, and as the average specific heats over the temperature range, for iron, 0,20 cal per g per deg; for water, 0,70 cal per g per deg; for carbon dioxide, 0,25 cal per g per deg).
9. Draw structural formulas for all of the isomers with the molecular formula C_5H_{10}. Include all positional isomers, functional isomers, and stereoisomers. (There are twelve possible isomers.)

☑ **Self-Check**		
I am able to:	**Yes**	**No**
• Describe organic compounds		
• Describe organic chemistry		
• Describe hydrocarbons		
o Alkanes		
o Alkenes		
o Alkynes		
• Describe hybridization		
If you have answered 'no' to any of the outcomes listed above, then speak to your facilitator for guidance and further development.		

Module 2

Hydrocarbons

Learning Outcomes

On the completion of this module the student must be able to:

- Describe alkanes
- Describe alkenes
- Describe alkynes

2.1 Introduction

Hydrocarbons, compounds made of carbon and hydrogen only, are classified into several subgroups: alkanes, cycloalkanes, alkenes, alkynes, and aromatic compounds (**Table 2.1**).

We begin our discussion by considering compounds that have carbon atoms with four single bonds, the alkanes and cycloalkanes.

See the General Chemistry Now CD-ROM or website: http://www.nbclearn.com/chemistry
Hydrocarbons, for a description of the classes of hydrocarbons.

Types of hydrocarbon	Characteristic features	General formula	Example
alkanes	C─C single bonds and all C atoms have four single bonds	C_nH_{2a+2}	CH_4, methane C_2H_6, ethane
cyclic alkanes	C─C single bonds and all C atoms have four single bonds	C_nH_{2a}	C_6H_{12}, cyclohexane
alkenes	C=C double bond	C_nH_{2a}	$H_2C{=}CH_2$, ethylene
alkynes	C≡C triple bond	C_nH_{2a-2}	$HC{\equiv}CH$, acetylene
aromatics	Rings with π bonding extending over several C atoms	-	Benzene, C_6H_6

Table 1.1 Some Types of Hydrocarbons

2.2 Alkanes

Alkanes have the general formula C_nH_{2a+2} with *n* having integer values (**Table2.1**). Formulas of specific compounds ran be generated from this general formula, the first four of which are CH_4 (methane), C_2H_6 (ethane), C_3H_8 (propane), and C_4H_{10} (butane) (**Figure 2.4**).

Methane has four hydrogen atoms arranged tetrahedrally around a single carbon arom. Replacing a hydrogen atom in methane by $—CH_3$ group gives ethane. If an H atom or ethane is replaced by yet another $—CH_3$ group, propane results.

Butane is derived from propane by replacing an H atom of one of the chain-ending carbon atoms with a $—CH_3$ group. In all of these compounds each C atom is attached to four other atoms, either C or H, so alkanes are often called saturated compounds.

Name	Molecular formula	State at Room Temperature
methane ethane propane butane	CH_4 C_2H_6 C_3H_8 C_4H_{10}	gas
pentane hexane heptane octane nonane decane	C_5H_{12} (pent = 5) C_6H_{14} (hex = 6) C_7H_{16} (hept = 7) C_8H_{18} (oct = 8) C_9H_{20} (non = 9) $C_{10}H_{22}$ (dec = 10)	liquid
octadecane eicosane	$C_{18}H_{38}$ (octadec = 18) $C_{20}H_{42}$ (eicos = 20)	solid

Table 2.2 Selected Hydrocarbons of the Alkane Family, C_nH_{2a+2}
(This table lists only selected alkanes. Liquid compounds with 11 to 16 carbon atoms are also known. Many solid alkanes with more than 20 carbon atoms also exit.)

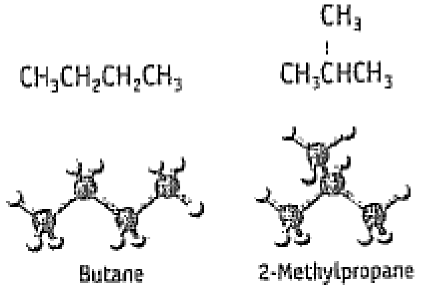
2.2.1 Structural Isomers

The formulas for alkanes do not hint at their structural diversity. Structural isomers are possible for all alkanes larger than propane. For example, there are two structural isomers for C_4H_{10} and three for C_5H_{12}.

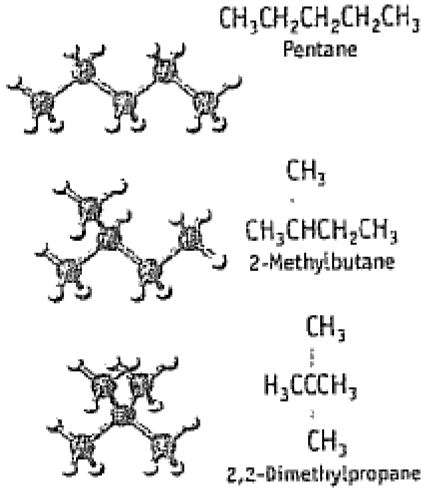
As the number of carbon atoms in an alkane increases, the number of possible structural isomers greatly increases; there are 5 isomers possible for C_6H_{14}, 9 isomers for C_7H_{16}, 18 for $CH_{10}H_{22}$ and 366,319 for $C_{20}H_{42}$.

To recognize the isomers corresponding to a given formula, keep in mind the following points:

- Each alkane is built upon a framework of tetrahedral carbon atoms, and each carbon must have four single bonds.
- An effective approach is to create a framework of carbon atoms and then fill the remaining positions around carbon with H atoms so that each C atom has four bonds.



Structural isomers of butane, C_4H_{10}.



Structural isomers of pentane, C_5H_{12}.

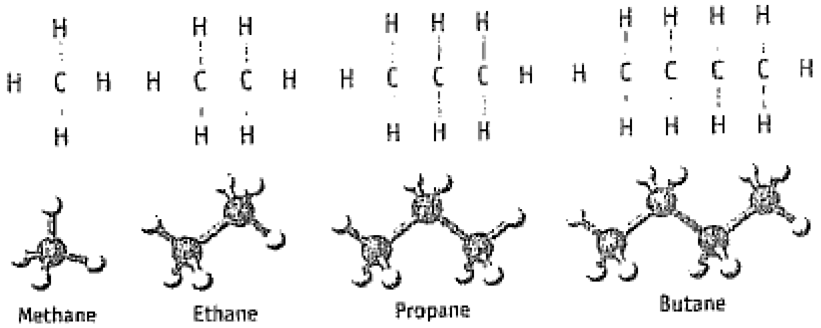


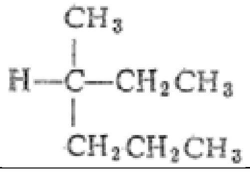
Figure 2.1 Alkanes – the lowest-molecular-weight alkanes, all gases under normal conditions are methane, ethane, propane, and butane

See the General Chemistry Now CD-ROM or website: http://www.nbclearn.com/chemistry
Explore an interactive version of **Figure 2.1** accompanied by an exercise.

Free rotation occurs around carbon-carbon single bonds. Therefore, when atoms are assembled to form the skeleton of an alkane, the emphasis is on how carbon atoms are attached to one another and not how they might lie relative to one another in the plane of the paper.

Definition: Chirality in alkanes

To be chiral, a compound must have at least one C atom attached to four different groups. Thus the C_7H_{16} isomer here is chiral.



$$H-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_2CH_2CH_3}{C}}-CH_2CH_3$$

Worked Example 2.1: Isomers of alkanes

Problem

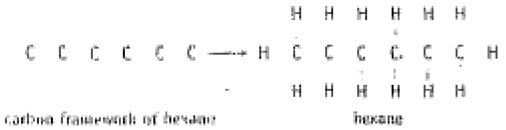
Draw structures of the five isomers of C_6H_{14}. Are any of these isomers chiral?

Strategy

- Focus first on the different frameworks that can be built from six carbon atoms.
- Having created a carbon framework, fill hydrogen atoms into the structure so that each carbon has four bonds.

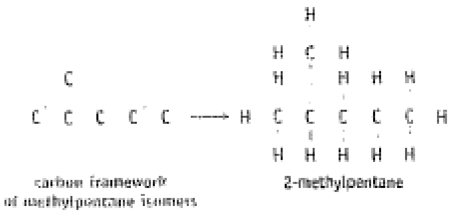
Solution

1. Placing six carbon atoms in a chain gives the framework for the first isomer. Now fill in hydrogen atoms: three on the carbons on the ends of the chain, two on each of the carbons in the middle. You have created the first isomer, hexane.

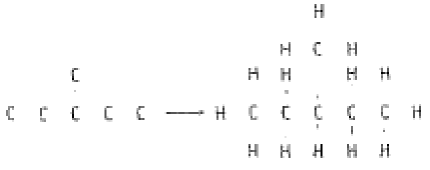


2. Draw a chain of five carbon atoms, then add the sixth carbon atom to one of the carbons in the middle of this chain. (Adding it to a carbon at the end of the chain gives a six carbon chain, the same framework drawn in 1 above.) Two different carbon frameworks can be built from the five-carbon

chain, depending on whether the sixth carbon is linked to the 2 or 3 position. For each of these frameworks, fill in the hydrogens.

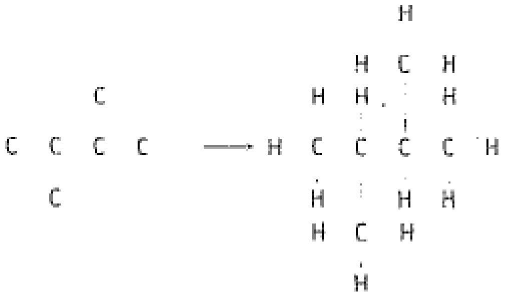


2-methylpentane

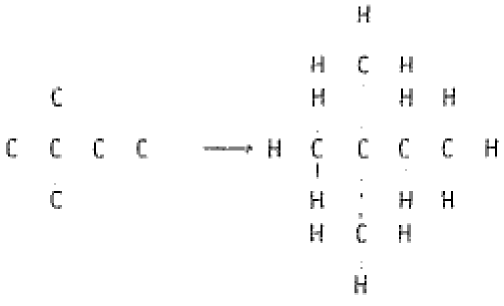


3-methylpentane

3. Draw a chain of four carbon atoms. Add in the two remaining carbons, again being careful not to extend the chain length. Two different structures are possible: one with the remaining carbon atoms each in the 2 and 3 positions, and another with both extra carbon atoms attached at the 2 position. Fill in the 14 hydrogens. You have now drawn the fourth and fifth isomers.



2,3-dimethylbutane



2,2-dimethylbutane

None of the isomers of C_6H_{14} is chiral. To be chiral, a compound must have at least one C atom with four different groups attached. This condition is not met in any of these isomers.

Comment

Should we look for structures in which the longest chain is three carbon atoms?

Try it, but you will see that it is not possible to add the three remaining carbons to a three-carbon chain without creating one of the carbon chains already drawn in a previous step.

Thus we have completed the analysis, with five isomers of this compound being identified.

Names have been given to each of these compounds.

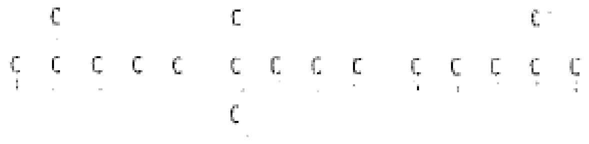
2.2.2 Naming Alkanes

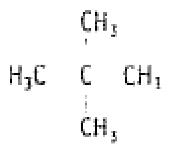
With so many possible isomers for a given alkane, chemists need a systematic way of naming them. The rules for naming alkanes and their derivatives follow:

- the names of alkanes end in "-ane".
- The names of alkanes with chains of one to ten carbon atoms are given in Table 2.2. After the first four compounds, the names are derived from Latin numbers-pentane, hexane, heptane, octane, nonane, decane - and this regular naming continues for higher alkanes.
- When naming a specific alkane, the root of the name corresponds to the longest carbon chain in the compound. One isomer of C_5H_{12} has a three carbon chain with two $-CH_3$ groups on the second C atom of the chain. Thus its name is based on propane.

Problem solving tip: Drawing Structural Formulas

An error students sometimes make is to suggest that the three carbon skeletons drawn here are different. They are, in fact, the same. All are five-carbon chains with another C atom in the 2 position. Remember that Lewis structures do not indicate the geometry of molecules.





$$\begin{array}{ccc} & CH_3 & \\ H_3C & C & CH_3 \\ & CH_3 & \end{array}$$

2,2-dimethylpropane

- Substituent groups on a hydrocarbon chain are identified by a name and the position of substitution in the carbon chain; this information precedes the root of the name. The position is indicated by a number that refers to that carbon atom to which the substituent is attached. (Numbering of the carbon atoms in a chain should begin at the end of the carbon chain that allows the substituent groups to have the lowest numbers). Both $-CH_3$ groups in 2.2-dimethylpropane are located at the 2 position.

- Names of hydrocarbon substituents, called alkyl groups, are derived from the name of the hydrocarbon. The group $-CH_3$, derived by taking a hydrogen from methane, is called the methyl group; the C_2H_3 group is the ethyl group.
- If two or more of the same substituent groups occur, the prefixes di-, tri-, and terra- are added. When different substituent groups are present, they are generally listed in alphabetical order.

Worked Example 2.2: Naming Alkanes

Problem

Give the systematic name for

$$\overset{CH_3}{CH_3CH}CH_2CH_2\overset{C_2H_5}{CH}CH_2CH_3$$

Strategy

Identify the longest carbon chain and base the name of the compound on that alkane. Identify the substituent groups on the chain and their locations. When there are two or more substituents (the groups attached to the chain), number the parent chain from the end that gives the lower number to the substituent encountered first. If the substituents are different, list them in alphabetical order.

Solution

Here the longest chain has seven C atoms, so the root of the name is heptane. There is a methyl group on C-2 and an ethyl group on C-5. Giving the substituents in alphabetic order. and numbering the chain from the end having the methyl group, the systematic name is 5-ethyl-2-methylheptane.

Systematic and Common Names

Many organic compounds are known by common names. For example, 2,2-dimethl-propane is also called neopentane. However, the IUPAC has formulated rules for systematic names, which are generally used in this book.

Definition: IUPAC

International Union Pure and Applied Chemistry

Figure 2.2 Paraffin wax and mineral oil - these common consumer products are mixtures of alkanes

2.2.3 Properties of Alkanes

Methane, ethane, propane, and butane are gases at room temperature and pressure, whereas the higher-molecular-weight compound are liquids or solids (**Table 2.2**).

An increase in melting point and boiling point with molecular weight is a general phenomenon that reflects the increased forces of attraction between molecules.

You already know about alkanes in a nonscientific context because several are common fuels. Natural gas, gasoline, kerosene, fuel oils, and lubricating oils are all mixtures of various alkanes.

White mineral oil is also a mixture of alkanes, as is paraffin wax (**Figure 2.2**).

Pure alkanes are colorless. (The colors seen in gasoline and other petroleum products are due to additives.) The gases and liquids have noticeable but not unpleasant odors. All of these substances are insoluble in water, which is typical of compounds that are nonpolar or nearly so.

Low polarity is expected for alkanes because the electronegativity of carbon (X = 2,5) and hydrogen (X = 2,2) are not greatly different.

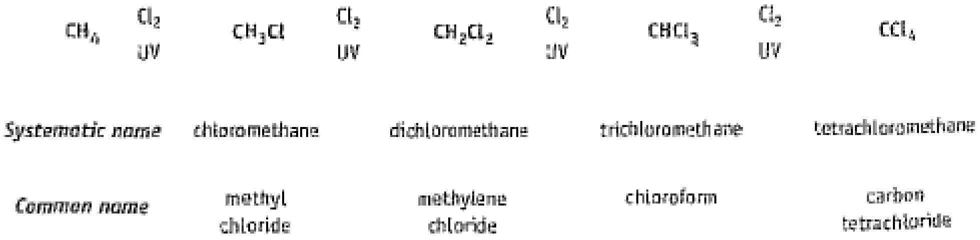
All alkanes burn readily in air to give CO_2 and H_2O in very exothermic reactions. This is, of course, the reason they are widely used as fuels.

$$CH_4(g) + 2\,O_2(g) \longrightarrow CO_2(g) + 2\,H_2O(\ell) \qquad \Delta H^\circ_{rxn} = -890.3\ kJ$$

Other than in combustion reactions, alkanes exhibit relatively low chemical reactivity.

One reaction that docs occur, however, is the replacement of the hydrogen atoms of an alkane by chlorine atoms on reaction with Cl_2. It is formally an oxidation because Cl_2 like O_2, is a strong oxidizing agent. These reactions, which can be initiated by ultraviolet radiation are free radical reactions. Highly reactive Cl atoms are formed from Cl_2 under UV radiation.

Reaction of methane with Cl_2 under these conditions proceeds in a series of steps, eventually yielding CCI commonly known as carbon tetrachloride. (HCl is the other product of these reactions.)

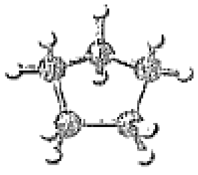


The last three compounds are used as solvents, albeit less frequently today because of their toxicity. Carbon tetrachloride was also once widely used as a dry cleaning fluid and because it does not burn, in fire extinguishers.

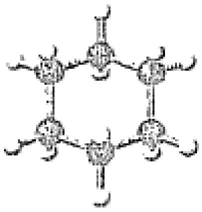
2.2.4 Cydoalkanes, C_nH_{2n}

Cycloalkanes are constructed with tetrahedral carbon atoms joined together to form a ring. For example, cyclopentane, C_5H_{10} consists of a ring of five carbon atoms. Each carbon atom is bonded to two adjacent carbon atoms and to two hydrogen atoms.

The structures of cyclopentane, C_5H_{10}, and cyclohexane, C_6H_{12}.



Cyclopentane, C_5H_{10}



Cyclohexane, C_6H_{12}

The C_5 ring is nearly planar. In contrast. the tetrahedral geometry around carbon means that the C_6 ring is decidedly puckered.

A Closer look: Flexible Molecules

Most organic molecules are flexible; that is, they can twist and bend in various ways. Few molecules better illustrate this behavior than cyclohexane.

Two structures are possible, "chair" and "boat" forms. These forms can interconvert by partial rotation of several bonds.

The more stable structure is the chair form which allows the hydrogen atoms to remain as far apart as possible. A side view of this form of cyclohexane reveals two sets of hydrogen atoms in this molecule.

Six hydrogen atoms, called the equatorial hydrogens, lie in a plane around the caring. The other six hydrogens are positioned above and below the plane and called axial hydrogens.

Flexing the ring (a rotation around the C—C single bonds) moves the hydrogen atoms between axial and equatorial environments.

Notice that the five carbon atoms fall very nearly in a plane. This is because the internal angles of a pentagon, 110°, closely match the tetrahedral angle of 109,5°. The small distortion from planarity allows hydrogen atoms on adjacent carbon atoms to be a little farther apart.

Cyclohexane has a nonpolar ring with six CH_2 groups. If the carbon atoms were in the form of a regular hexagon with all carbon atoms in one plane, the C—C—C bond angles would be 120°. To have tetrahedral bond angles of 109,5° around each C atom, the ring has to pucker. The C_6 ring is flexible, however, and exists in two interconverting forms (see **"A Closer Look: Flexible Molecules"**).

Interestingly, cyclobutane and cyclopropane are also known, although the bond angles in these species are much less than 109,5°. These compounds are examples of strained hydrocarbons, so named because an unfavorable geometry is imposed around carbon.

One of the features of strained hydrocarbons is that the C—C bonds are weaker and the molecules readily undergo ring-opening reactions that relieve the bond angle strain.

2.3 Alkenes and Alkynes

The abundance and diversity of alkanes are repeated with alkenes, hydrocarbons with one or more C=C double bonds. The presence of the double bond adds two features missing in alkanes: the possibility of geometric isomerism and increased reactivity.

The general formula for alkenes is C_nH_{2n}. The first two members of the series of alkenes are ethene, C_2H_4 (common name, ethylene), and propene, C_3H_6 (common name, propylene).

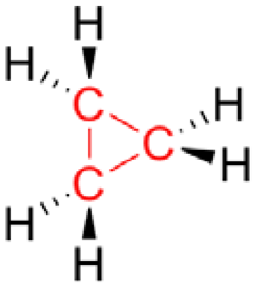
Only a single structure can be drawn for these compounds. As with alkanes, the occurrence of isomers begins with species containing four carbon atoms. Four alkene isomers have the formula C_4H_8 and each has distinct chemical and physical properties.

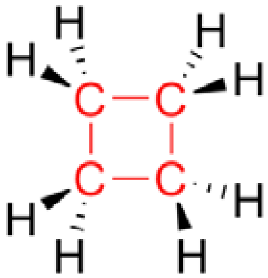
Cyclopropane and cyclobutane

Cyclopropane was at one time used general anesthetic in surgery. However its explosive nature when mixed with oxygen soon eliminated this application.

The Columbia Encyclopedia states that cyclopropane allowed the transport of more oxygen to the tissues than did other common anesthetics and also produced greater skeletal muscle relaxation.

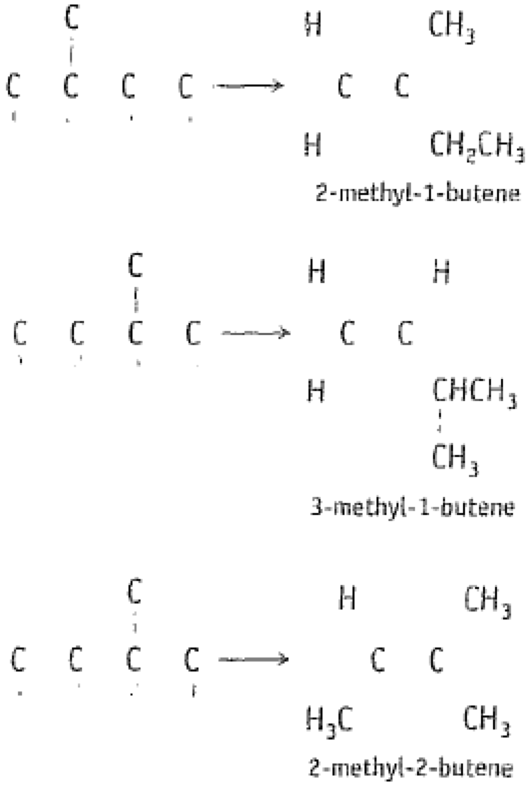
It is not irritating to the respiratory tract. Because of the low solubility of cyclopropane in the blood, postoperative recovery was usually rapid but nausea and vomiting were common.


cyclopropane


cyclobutane

Worked Example 2.3

Draw the possible four-carbon chains containing a double bond. Add the fifth carbon atom to either the 2 or 3 position. When all three possible combinations are found, fill in the hydrogen atoms. This results in three more structures:



More than one double bond can be present in a hydrocarbon. Butadiene, for example, has two double bonds and is known as a diene. Many natural products have numerous double bonds (**Figure 2.3**). There are also cyclic hydrocarbons, such as cyclohexene, with double bonds.

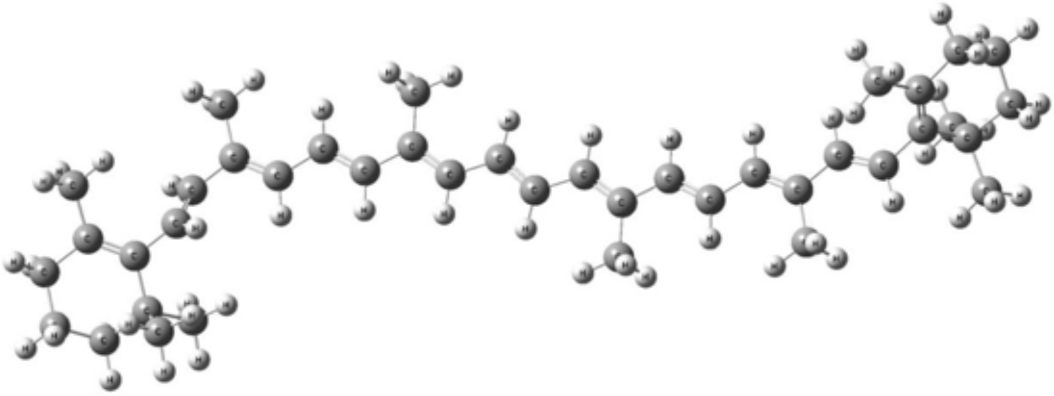
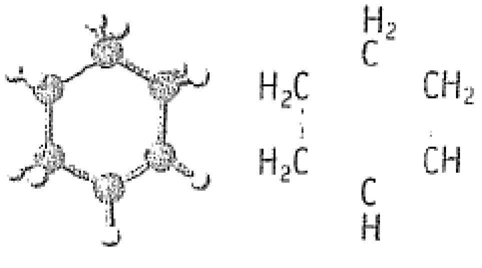


Figure 2.3 Carotene, a naturally occurring compound with 11 C=C bonds. The π electrons can be excited by visible light in the blue-violet region of the spectrum. As a result carotene appears orange-yellow to the observer.

Carotene or carotene-like molecules are partnered with chlorophyll in nature in the role of assisting in the harvesting of sunlight. Green leaves have a high concentration of carotene. In autumn, green chlorophyll molecules are destroyed and the yellows and reds of carotene and related molecules are seen.

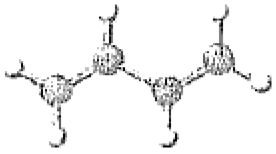
The red color of tomatoes, for example, comes from a molecule very closely related to carotene. As a tomato ripens, its chlorophyll disintegrates and the green color is replaced by the red of the carotene-like molecule.

Cycloalkenes and dienes



Cyclohexene, C_6H_{10}

$H_2C{=}CHCH{=}CH_2$



1,3-Butadiene, C_4H_6

Cyclohexene, C_6H_{10} (top) and 1,3-butadiene (C_4H_6) (bottom)

Alkynes, compounds with a carbon-carbon triple bond, have the general formula (C_nH_{2n-2}). **Table 2.3** lists alkynes that have four or fewer carbon atoms. The first member of this family is ethyne (common name, acetylene), a gas used as a fuel in metal cutting torches.

Figure 2.4 An oxy-acetylene torch. The reaction of ethyne (acetylene) with oxygen produces a very high temperature. Oxy-acetylene torches, used in welding, take advantage of this fact.

Structure	Systematic Name	Common Name	BP (°C)
$HC\equiv CH$	ethyne	acetylene	-85
$CH_3C\equiv CH$	propyne	methlacetylene	-23
$CH_3CH_2C\equiv CH$	1-butyne	ethylacetylene	9
$CH_3C\equiv CCH_3$	2-butyne	dimethylacetylene	27

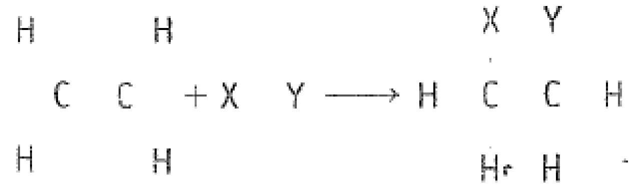
Table 2.3 Some simple alkynes C_nH_{2n-2}

2.3.1 Properties of alkenes and alkanes

Like alkanes, alkenes and alkynes are colorless. Low-molecular-weight compounds are gases, whereas compounds with higher molecular weights are liquids or solids. Alkanes, alkenes, and alkynes are also oxidized by O_2 to give CO_2 and H_2O.

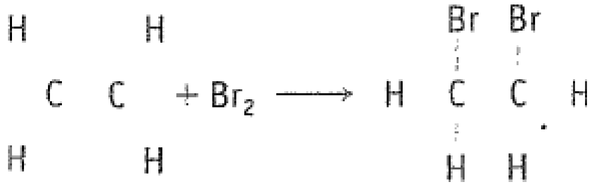
In contrast to alkanes, alkenes and alkynes have an elaborate chemistry. We gain an insight into their chemical behavior by noting that they are called unsaturated compounds. Carbon atoms are capable of bonding to a maximum of four other atoms, and they do so in alkanes and cycloalkanes.

In alkenes, however the carbon atoms linked by a double bond are bonded to only three atoms; in alkynes they bond to two atoms. It is possible to increase the number of bonds to carbon by addition reactions in which molecules with the general formula X—Y (such as hydrogen, halogens, hydrogen halides, and water) add across the carbon-carbon double bond (**Figure 2.5**). The result is a compound with four atoms bonded to carbon.



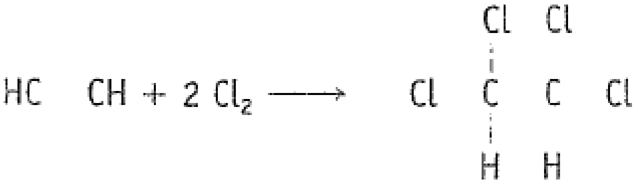
X Y = H_2, Cl_2, Br_2; H Cl, H Br, H OH, HO Cl

The products of addition reactions are substituted alkanes. For example, the addition of bromine to ethylene forms 1,2-dibromoethane.



1,2-dibromoethane

The addition of 2mol of chlorine to acetylene gives 1,1,2,2-tetrachloroethane.



1,1,2,2-tetrachloroethane

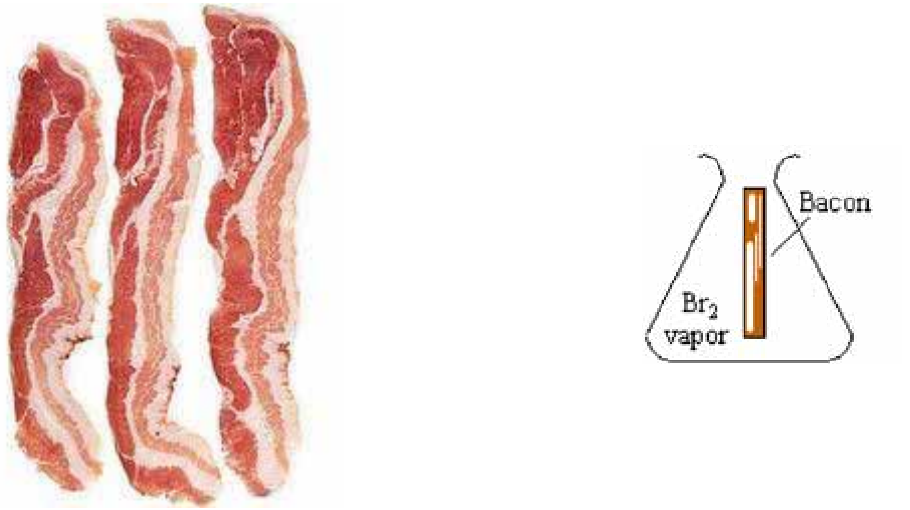


Figure 2.5 Bacon fat and addition reactions. The fat in bacon is partially unsaturated. Like other unsaturated compounds, bacon fat reacts with Br_2 in an addition reaction. Here you see the color of Br_2 vapor fade when a strip of bacon is introduced.

If the reagent added to a double bond is hydrogen (X—Y=H_2), the reaction is called hydrogenation and the product is an alkane. Hydrogenation is usually a very slow reaction, but it can be speeded up in the presence of a catalyst, often a specially prepared form of a metal, such as platinum, palladium, and rhodium.

You may have heard the term hydrogenation because certain foods contain "hydrogenated" or "partially hydrogenated" ingredients. One brand of crackers has a label that says, "Made with 100% pure vegetable shortening ... (partially hydrogenated soybean oil with hydrogenated cottonseed oil)."

One reason for hydrogenating an oil is to make it less susceptible to spoilage; another is to convert it from a liquid to a solid.

Definition: Catalysts
A substance that causes a reaction to occur at a faster rate is called a catalyst.

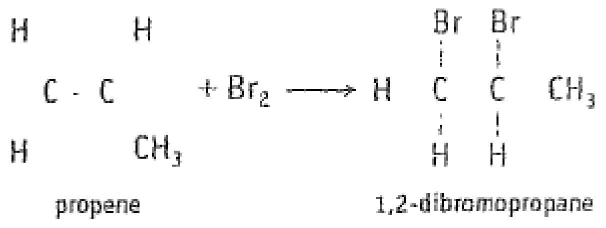
See the General Chemistry Now CD-ROM or website:
http://www.nbclearn.com/chemistry
Hydrocarbons and Addition Reactions, for a simulation and tutorial on alkene addition reactions

Worked Example 2.4 Reaction of an Alkene

Problem
Draw the structure of the compound obtained from the reaction of Br_2 with propene and name the compound.

Strategy
Bromine wilt add across the C=C double bond. The name will include the name of the carbon chain and indicate the positions of the Br atoms.

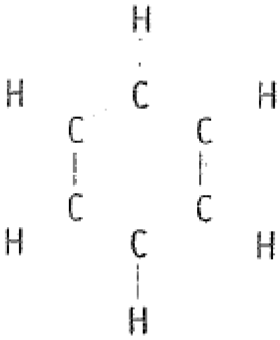
Solution



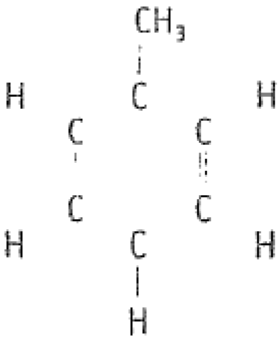
2.4 Aromatic Compounds

Benzene, C_6H_6, is a key molecule in chemistry. It is the simplest aromatic compound, one of a class of compounds so named because they have significant, and usually not unpleasant, odors. Other members of this class, which are all based on benzene, include toluene and naphthalene.

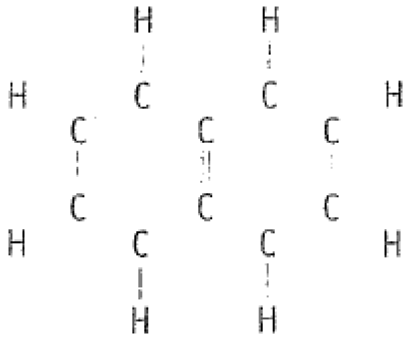
A source of many aromatic compounds is coal and the volatile substances that are released when coal is heated to a high temperature in the absence of air (**Table 2.4**).



benzene



toluene



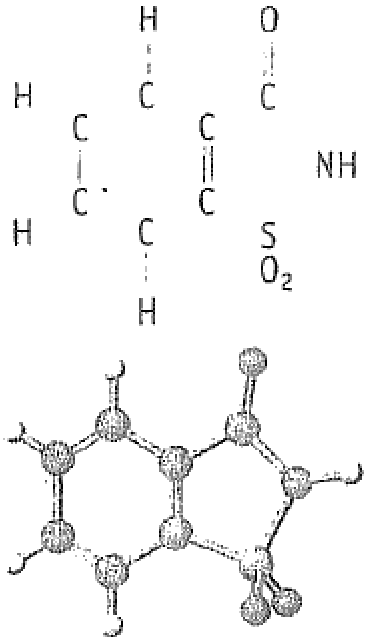
naphthalene

Benzene occupies a pivotal place in the history and practice of chemistry Michael Faraday discovered this compound in 1825 as a byproduct of illuminating gas, itself produced by heating coal.

Today, benzene is an important Industrial chemical, usually ranking among the top 25 chemicals in production annually in the United States. It is used as a solvent and is also the starting point for making thousands of different compounds by replacing the H atoms of the ring.

Toluene was originally obtained from Tolu balsam, the pleasant-smelling gum of a South American tree, Toluifera balsamum. This balsam has been used in cough syrups and perfumes. Naphthalene is an ingredient in "moth balls," although 1,4-dichlorobenzene is now more commonly used.

Aspartame and another artificial sweetener, saccharin, are also benzene derivatives.



Saccharin ($C_7H_5NO_3S$). This compound, an artificial sweetener, is a benzene derivative

Common Name	Formula	Boiling point (°C)	Melting point (°C)
benzene	C_6H_6	80	+6
toluene	$C_6H_5CH_3$	111	-95
o-xylene	$1,2C_6H_4(CH_3)_2$	144	-25
m-xylene	$1,3\text{-}C_6H_4(CH_3)_2$	139	-48
p-xylene	$1,4\text{-} C_6H_4(CH_3)_2$	138	+13
naphthalene	$C_{10}H_8$	218	+80

Table 2.4 Some Aromatic Compounds from Coal Tar

2.4.1 The Structure of Benzene

The formula of benzene suggested to 19th-century chemists that this compound should be unsaturated, but, if viewed this way, its chemistry was perplexing.

Whereas alkenes readily add Br_2, for example, benzene does not do so under similar conditions.

The benzene structural question was finally solved by August Kekulé 1829-1896). We now recognize that benzene's different reactivity relates to its structure and bonding, both of which are quite different from the structure and bonding in alkenes.

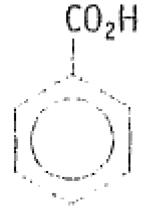
Benzene has equivalent carbon-carbon bonds, 139 pm in length, intermediate between a C─C single bond (154 pm) and a C=C double bond (134pm). The π bonds are formed by the continuous overlap of the *p* orbitals, on the six carbon atoms. Using valence bond terminology, the structure is a hybrid of two resonance structures.

Representations of benzene, C_6H_6

2.4.2 Benzene Derivatives

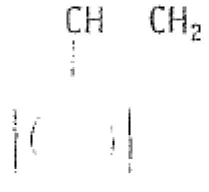
Toluene, chlorobenzene, styrene, benzoic acid, aniline, and phenol are common examples of benzene derivatives.

chlorobenzene



benzoic acid

aniline

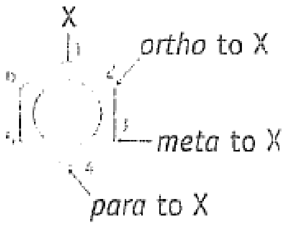


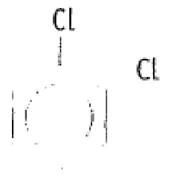
styrene

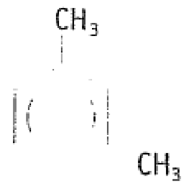
phenol

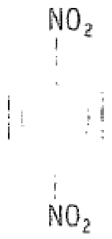
If more than one H atom of benzene is replaced, isomers can arise. Thus the systematic nomenclature for benzene derivatives involve naming substituent groups and identifying their positions on the ring numbering the six carbon atoms.

Some common names, which are based on an older naming scheme, are also regularly used. This scheme identified isomers of disubstituted benzenes with the prefixes *ortho* (*o*-, substituent groups on adjacent carbons in the benzene ring), *meta* (*m*-, substituents separated by one carbon atom), and *para* (*p*-, substituent groups on carbons on opposite sides of the ring).





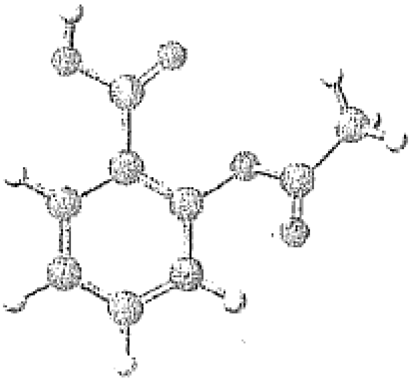


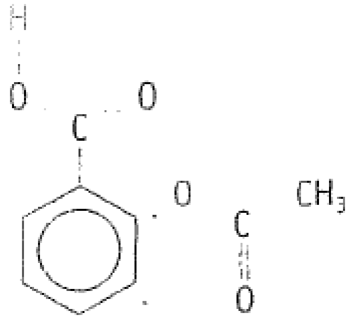


Systematic name:	1,2-dichlorobenzene	1,3-dimethylbenzene	1,4-dinitrobenzene
Common name:	*o*-dichlorobenzene	*m*-xylene	*p*-dinitrobenzene

Some products containing compounds based on benzene include sodium benzoate in soft drinks, ibuprofen in Advil and benzoyl peroxide in Oxy-10.

Aspirin, a commonly used analgesic. It is based on benzoic acid with an acetate group, O_2CCH_3, in the *ortho* position.



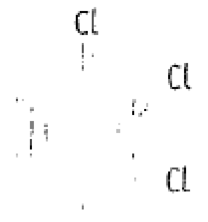


Worked Example 2.5 Isomers of substituted Benzenes

Problem
Draw and name the isomers of $C_6H_3Cl_3$.

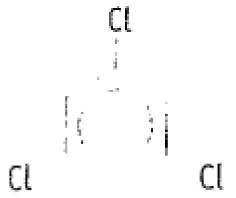
Strategy
Begin by drawing the structure of C_6H_5Cl. Place a second Cl atom on the ring in the *ortho*, *meta*, and *para* positions. Add the third Cl in one of the remaining positions.

Solution
The three isomers of $C_6H_3Cl_3$ are shown here. They are named as derivatives of benzene by specifying the number of substituent groups with the prefix "tri," the name of the substituent, and the positions of the three groups around the six-member ring.



1,2,3-trichlorobenzene

1,2,4-trichlorobenzene



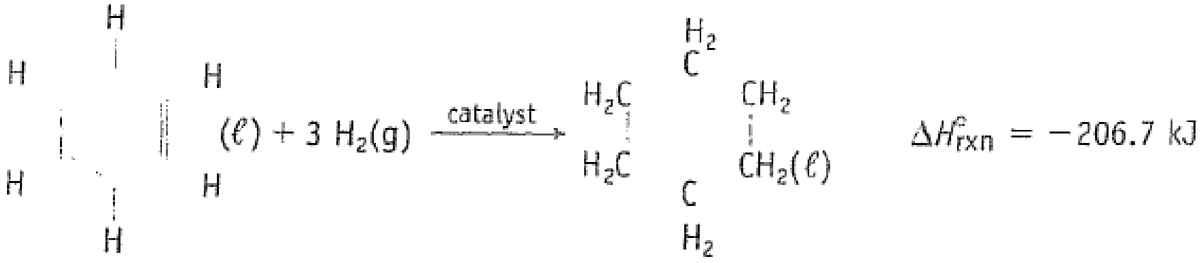
1,3,5-trichlorobenzene

2.4.3 Properties of Aromatic compounds

Benzene is a colorless liquid, and simple substituted benzenes are liquids or solids under normal conditions. The properties of aromatic compounds are typical of hydrocarbons in genera!: They are insoluble in water, soluble in nonpolar solvents, and oxidized by O_2 to form CO_2 and H_2O.

One of the most important properties of benzene and other aromatic compounds is an unusual stability that is associated with the unique π bonding in this molecule.

Because the π bonding in benzene is typically described using resonance structures; the extra stability is termed resonance stabilization. The extent of resonance stabilization in benzene is evaluated by comparing the energy evolved in the hydrogenation of benzene to form cyclohexane.



A Closer look: Petroleum Chemistry

Much of the world's current technology relies on petroleum. Burning fuels derived from petroleum provides by far the largest amount of energy in the industrial world.

Petroleum and natural gas are also the chemical raw materials used in the manufacture of plastics, rubber, pharmaceuticals, and a vast array of other compounds.

The petroleum that is pumped out of the ground is a complex mixture whose composition varies greatly depending on its source. The primary components of petroleum are always alkanes, but, to varying degrees, nitrogen and sulphur-containing compounds are also present. Aromatic compounds are present as well, but alkenes and alkynes are not.

A modern petrochemical plant

An early step in the petroleum refining process is distillation, in which the crude mixture is separated into a series of fractions based on boiling point: first a gaseous fraction (mostly alkanes with one to four carbon atoms; this fraction is often burned off), and then gasoline, kerosene, and fuel oils.

After distillation, considerable material, in the form of a semisolid, tar-like residue, remains.

The petrochemical industry seeks to maximize the amounts of the higher-valued fractions of petroleum produced and to make specific compounds for which a particular need exists. This means carrying out chemical reactions involving the raw materials on a huge scale.

One process to which petroleum is subjected is known as cracking. At very high temperatures, bond breaking or "cracking" can occur, and longer-chain hydrocarbons will fragment into smaller molecular units. These reactions are carried out in the presence of a wide array of catalysts, materials that speed up reactions and direct them toward specific products.

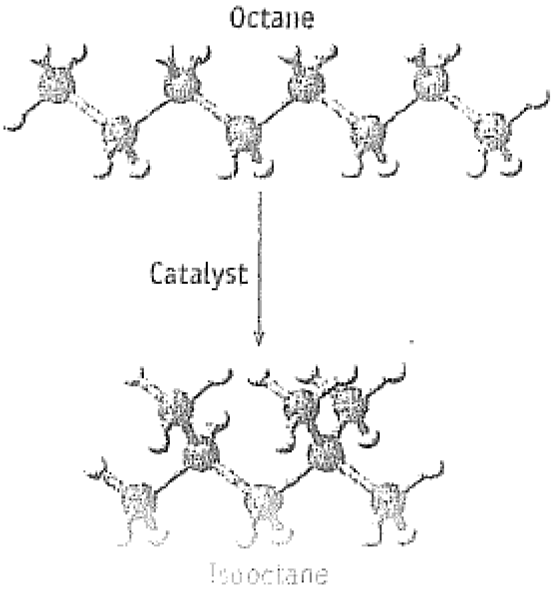
Among the important products of cracking are ethylene and other alkenes, which serve as the raw materials for the formation of materials such as polyethylene.

Cracking also produces gaseous hydrogen, a widely used raw material in the chemical industry.

Other important reactions involving petroleum are run at elevated temperatures and in the presence of specific catalysts.

Such reactions include isomerization reactions, in which the carbon skeleton of an alkane rearranges to form a new isomeric species, and reformation processes, in which smaller molecules combine to form new molecules.

Each process is directed toward achieving a specific goal, such as increasing the proportion of branched-chain hydrocarbons in gasoline to obtain higher octane ratings. A great amount of chemical research has gone into developing and understanding these highly specialized processes.



Producing gasoline. Branched hydrocarbons have a higher octane rating in gasoline. Therefore, an important process in producing gasoline is the isomerization of octane to a branched hydrocarbon such as isooctane, 2,2,4-trimethylpentane.

The hydrogenation of benzene is about 200 kJ less exothermic than the hydrogenation of three moles of ethylene. The difference is attributable to the added stability associated with π bonding in benzene.

Although aromatic compounds are unsaturated hydrocarbons, they do not undergo the addition reactions typical of alkenes and alkynes. Instead, substitution reactions occur, in which one or more hydrogen atoms are replaced by other groups.

Such reactions require a second reagent, such as H_2SO_4, $AlCl_3$ or $FeBr_3$.

Nitration: $C_6H_6(\ell) + HNO_3(\ell) \xrightarrow{H_2SO_4} C_6H_5NO_2(\ell) + H_2O(\ell)$

Alkylation: $C_6H_6(\ell) + CH_3Cl(\ell) \xrightarrow{AlCl_3} C_6H_5CH_3(\ell) + HCl(g)$

Halogenation: $C_6H_6(\ell) + Br_2(\ell) \xrightarrow{FeBr_3} C_6H_5Br(\ell) + HBr(g)$

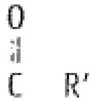
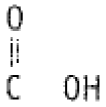
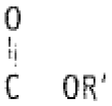
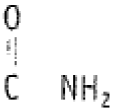
Functional Group*	General Formula*	Class of compound	Examples
F, CL, Br, I OH OR' NH_2†	RF, RCL, RBr, RI ROH ROR' RNH_2	haloalkane alcohol ether (primary) amine	CH_3CH_2Cl, chloroethane CH_3CH_2OH, ethanol $(CH_3CH_2)_2O$ diethyl ether $CH_3CH_2NH_2$, ethylamine
 $\overset{O}{\overset{\|}{C}}H$	RHCO	aldehyde	CH_3CHO, ethanol (acetaldehyde)
 $\overset{O}{\overset{\|}{C}}\ R'$	RCOR'	ketone	CH_3COCH_3, propanone (acetone)
 $\overset{O}{\overset{\|}{C}}\ OH$	RCO_2H	carboxylic acid	CH_3CO_2H, ethanoic acid (acetic acid)
 $\overset{O}{\overset{\|}{C}}\ OR'$	RCO_2R'	ester	$CH_3CO_2CH_3$ methyl acetate
 $\overset{O}{\overset{\|}{C}}\ NH_2$	$RCONH_2$	amide	CH_3CONH_2, acetamide

Table 2.5 Common Functional Groups and Derivatives of Alkanes

* R and 'R' can be the same of different hydrocarbon groups

† Secondary amines (R_2NH) and tertiary amines (R_3N) are also possible, see discussion in the text.

2.4.4 Alcohols, Ethers, and Amines

Other types of organic compounds arise as elements other than carbon and hydrogen are included in the compound. Two dements in particular, oxygen and nitrogen, add a rich dimension to carbon chemistry.

Organic chemistry organizes compounds containing elements other than carbon and hydrogen as derivatives of hydrocarbons. Formulas (and structures) are represented by substituting one or more hydrogens in a hydrocarbon molecule by a functional group.

Definition: Functional group
A functional group is an atom or group of atoms attached to a carbon atom in the hydrocarbon.

Formulas of hydrocarbon derivatives are then written as R–X, in which R is a hydrocarbon lacking a hydrogen atom, and X is the functional group that has replaced the hydrogen in the structure.

The chemical and physical properties of the hydrocarbon derivatives are a blend of the properties associated with hydrocarbons and the group that has been substituted for hydrogen.

Table 2.6 identifies some common functional groups and the families of organic compounds resulting from their attachment to a hydrocarbon.

See the General Chemistry Now CD-ROM or website: http://www.nbclearn.com/chemistry **Functional Groups**, for a description of the types of organic functional groups and for tutorials on their structures, bonding, and chemistry

Did you know? Alcohol racing fuel
Methanol, CH_30H, is used as the fuel in cars of the type that race in Indianapolis.

Alcohols and Ethers
If one of the hydrogen atoms of an alkane is replaced by a hydroxyl (–OH) group, the result is an alcohol, ROH. Methanol, CH_3OH, and ethanol, CH_3CH_2OH, are the most important alcohols, but others are also commercially important (**Table 2.6**).

Notice that several have more than one OH functional group.

Condensed formula	BP (°C)	Systematic Name	Common Name	Use
CH_3OH	65,0	methanol	methyl alcohol	fuel, gasoline additive, making formaldehyde
CH_3CH_2OH	78,5	ethanol	ethyl alcohol	beverages, gasoline additive, solvent

$CH_3CH_2CH_2OH$	97,4	1-propanol	propyl alcohol	industrial solvent
$CH_3CH(OH)CH_3$	82,4	2-propanol	isopropyl alcohol	rubbing alcohol
$HOCH_2CH_2OH$	198	1,2-ethanediol	ethylene glycol	antifreeze
$HOCH_2CH(OH)CH_2,OH$	290	1,2,3-propanetriol	glycerol (glycerin)	moisturizer in consumer products

Table 2.6 Some Important Alcohols

More than 5 x 10^8 kg of methanol is produced in the United States annually. Most of this production is used to make formaldehyde (CH_2O) and acetic acid (CH_3CO_2H), both important chemicals in their own right.

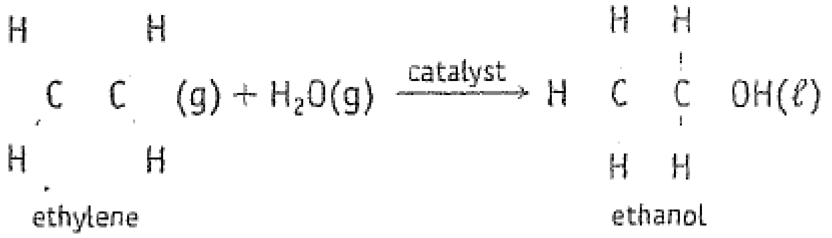
Methanol is also used as a solvent, as a de-icer in gasoline, and as a fuel in high-powered racing cars. It is found in low concentration in new wine, where it contributes to the odour or "bouquet".

Like ethanol, methanol causes intoxication, but methanol differs in being more poisonous, largely because the human body converts it to formic acid (HCO_2H) and formaldehyde (CH_2O).

These compounds attack the cells of the retina in the eye, leading to permanent blindness.

Ethanol is the "alcohol" of alcoholic beverages, in which it is formed by the anaerobic (without air) fermentation of sugar. For many years, industrial alcohol, which is used as a solvent and as a starting material for the synthesis of other compounds, was made by fermentation.

In the last several decades, however, it has become cheaper to make ethanol from petroleum byproducts - specifically by the addition of water to ethylene.



Beginning with three-carbon alcohols, structural isomers are possible. For example, 1-propanol and 2-propanol (common name, isopropyl alcohol) are different compounds (**Table 2.6**).

Ethylene glycol and glycerol are common alcohols having two and three –OH groups, respectively. Ethylene glycol is used as antifreeze in automobiles.

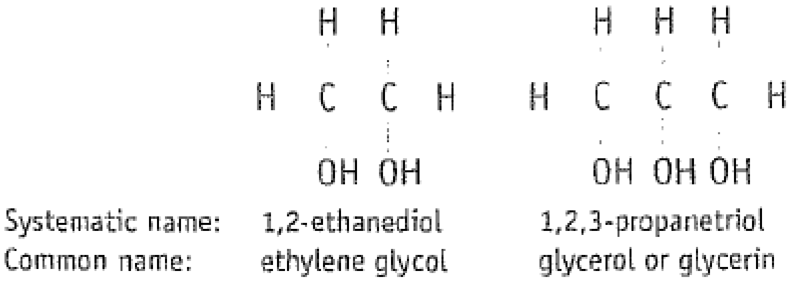
Glycerol's most common use is as a softener in soaps and lotions. It is also a raw material for the preparation of nitroglycerin (**Figure 2.6**).

Note:
Methanol, CH_3OH, is the simplest alcohol. Methanol is often called "wood alcohol" because it was originally produced by heating wood in the absence of air.

Definition: Aerobic fermentation
Aerobic fermentation (in the presence of O_2) of ethanol leads to the formation of acetic acid. This is how wine vinegar is made.

Definition: Rubbing alcohol
Common rubbing alcohol is 2-propanol, also called isopropyl alcohol.

Figure 2.6 Nitroglycerin. (a) Concentrated nitric acid and glycerin react to form an oily, highly unstable compound called nitroglycerin, $C_3H_5(ONO_2)_3$. (b) Nitroglycerin is more stable if absorbed onto an inert solid, a combination called dynamite. (c) The fortune of Alfred Nobel (1833-1896), built on the manufacture of dynamite, now funds the Nobel Prizes.



Worked Example 2.6: Structural isomers of alcohols

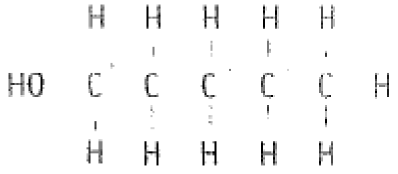
Problem
How many different alcohols are derivatives of pantane? Draw structures and name each alcohol.

Strategy

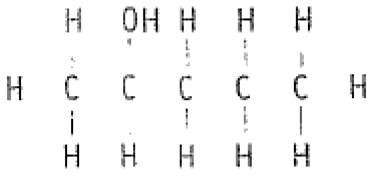
Pentane, C_5H_{12}, has a five-carbon chain. An ─OH group can replace a hydrogen atom on one of the carbon atoms. Alcohols are named as derivatives of the alkane (pentane) by replacing the "-e" at the end with "-ol" and indicating the position of the ─OH group by a numerical prefix.

Solution

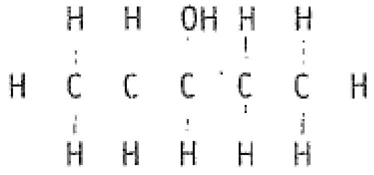
Three different alcohols are possible, depending on whether the ─OH group is placed on the first, second, or third carbon atom in the chain. (The fourth and fifth positions are identical to the second and first positions in the chain, respectively.)



1-pentanol



2-pentanol



3-pentanol

Comment

Additional structural isomers with the formula $C_5H_{11}OH$ are possible in which the longest carbon chain has three C atoms (one isomer) or four C atoms (four isomers).

2.4.5 Properties of Alcohols and Ethers

Methane, CH_4, is a gas (boiling point, -161 °C) with low solubility in water. Methanol, CH_3OH, by contrast, is a liquid that is miscible with water in all proportions.

The boiling point of methanol, 65°C, is 226°C higher than the boiling point of methane. What a difference the addition of a single atom into the structure can make in the properties of simple molecules!

Alcohols are related to water, with one of the H atoms of H_2O being replaced by an organic group. If a methyl group is substituted for one of the hydrogens of water, methanol results. Ethanol has a $─C_2H_5$ (ethyl) group, and propanol has a $–C_3H_7$ (propyl) group in place of one of the hydrogens of water.

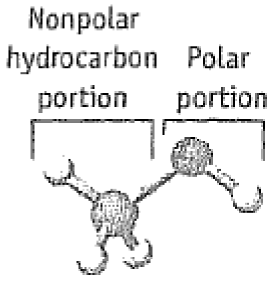
Viewing alcohols as related to water also helps in understanding the properties of alcohols.

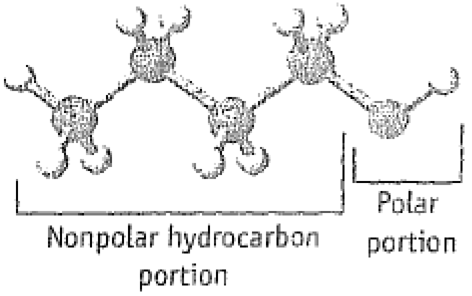
The two parts of methanol, the -CH_3 group and the -OH group, contributeto its properties. For example, methanol will burn, a property associated with hydrocarbons.

On the other hand, its boiling point is more like that of water. The temperature at which a substance boils is related to the forces of attraction between molecules, called intermolecular forces: The stronger the attractive, intermolecular forces in a sample, the higher the boiling point.

These forces are particularly strong in water, a result of the polarity of the -OH group in this molecule. Methanol is also a polar molecule, and it is the polar –OH group that leads to methanol's high boiling point. In contrast, methane is nonpolar and its low boiling point is the result of weak intermolecular forces.

It is also possible to explain the differences in the solubility of methane and methanol in water. The solubility of methanol is conferred by the polar -OH portion of the molecule. Methane, which is nonpolar, has low water solubility.





As the size of the alkyl group in an alcohol increases, the alcohol's boiling point rises, a general trend seen in families of similar compounds (see **Table 2.6**). The solubility in water in this series decreases. Methanol and ethanol are completely miscible in water whereas 1-propanol is moderately water-soluble, and 1-butanol is less soluble than 1-propanol.

With an increase in the size of the hydrocarbon group, the organic group (the nonpolar part of the molecule) has become a larger fraction of the molecule, and properties associated with non polarity begin to dominate.

Space-filling models show that in methanol, the polar and nonpolar parts of the molecule are approximately similar in size, but in 1-butanol the -OH group is less than 20% of the molecule. The molecule is less like water and more "organic."

Attaching more than one -OH group to a hydrocarbon framework has an effect that is opposite to the effect of increased hydrocarbon size.

Two -OH groups on a three-carbon framework, as found in propylene glycol, convey complete miscibility with water, in contrast to the limited solubility of 1-propanol and 2-propanol (**Figure 2.7**).

Definition: Hydrogen Bonding

The intermolecular forces of attraction of compounds with hydrogen attached to a highly electronegative atom, like O, N, or F, are so exceptional that they are accorded a special name: hydrogen bonding.

Did you know?

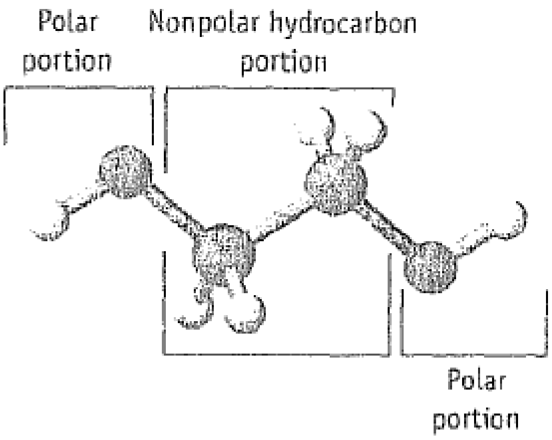
Methanol is often added to automobile gasoline tanks in the winter to prevent fuel lines from freezing. It is soluble in water and lowers the water's freezing point.

Did you know? Safe antifreeze-propylene glycol, $CH_3CHOHCH_2OH$

Most antifreeze sold today consists of about 95% ethylene glycol. Cats and dogs are attracted by the smell and taste of the compound, but it is toxic. In fact, only a few millilitres can prove fatal to a small dog or cat.

In the first stage of poisoning, an animal may appear drunk, but within 12-36 hours the kidneys stop functioning and the animal slips into a coma. To avoid accidental poisoning of domestic and wild animals, you can use propylene glycol antifreeze.

This compound affords the same antifreeze protection but is much less toxic.



Ethylene glycol is used in automobile radiators. It is soluble in water, and lowers the freezing point and raises the boiling point of the water in the cooling system

Ethylene glycol, a major component of automobile antifreeze, is completely miscible with water.

Figure 2.7 Properties and uses of methanol and ethylene glycol

Ethers have the general formula ROR'. The best known ether is diethyl ether, $CH_3CH_2OCH_2CH_3$. Lacking an -OH group, the properties of ethers are in sharp contrast to those of alcohols. Diethyl ether, for example, has a lower boiling point (34.5 °C) than ethanol, CH_3CH_2OH (78,3 °C), and is only slightly soluble in water.

See the General Chemistry Now CD-ROM or website: http://www.nbclearn.com/chemistry **Functional Groups (1): Reactions of Alcohols**, for an exercise on substitution and elimination reactions of alcohols.

2.4.6 Amines

It is often convenient to think about water and ammonia as being similar molecules: They are the simplest hydrogen compounds of adjacent second-period elements.

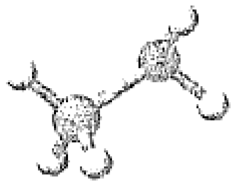
Both are polar, and they exhibit some similar chemistry, such as protonation and deprotonation.

Definition: Protonation and deprotonation
protonation (to give H_3O^+ and NH_4^+) and deprotonation (to give OH^- and $NH2^-$).

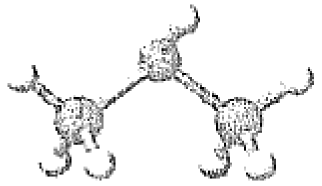
This comparison of water and ammonia can be extended to alcohols and amines. Alcohols have formulas related to water in which one hydrogen in H_2O is replaced with an organic group (R—OH). In organic amines, one or more hydrogen atoms of NH_3 are replaced with an organic group.

Amine structures are similar to ammonia's structure; that is, the geometry about the N atom is trigonal-pyramidal.

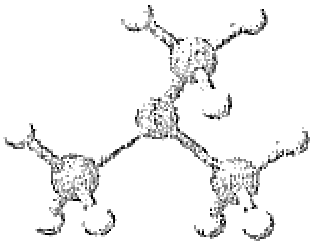
Amines are categorized based on the number of organic substituents as primary (one organic group), secondary (two organic groups), or tertiary (three organic groups). As examples, consider the three amines with methyl groups: CH_3NH_2, $(CH_3)_2NH$, and $(CH_3)_3N$.



CH_3NH_2
Primary amine
Methylamine



$(CH_3)_2NH$
Secondary amine
Dimethylamine



$(CH_3)_3N$
Tertiary amine
Trimethylamine

2.4.7 Properties of Amines

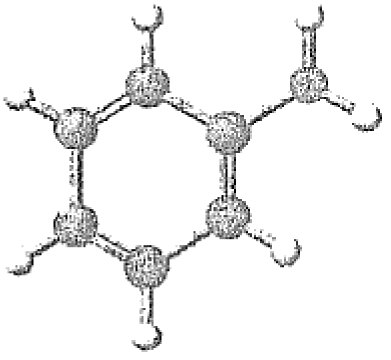
Amines usually have offensive odors. You know what the odor is if you have ever smelled decaying fish. Two appropriately named amines, putrescine and cadaverine, add to the odor of urine, rotten meat, and bad breath.

$H_2NCH_2CH_2CH_2CH_2NH_2$	$H_2NCH_2CH_2CH_2CH_2CH_2NH_2$
purescine	caddaverine
1,4-butanediamine	1,5-pentanediamine

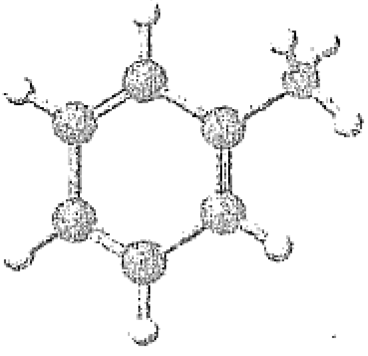
The smallest amines are water-soluble, but most amines are not. All amines are bases, however, and they react with acids to give salts, many of which are water-soluble.

As with ammonia, the reactions involve adding H^+ to the lone pair of electrons on the N atom. This is illustrated by the reaction of aniline (aminobenzene) with H_2SO_4 to give anilinium sulfate.

$$2\ C_6H_5NH_2(aq) + H_2SO_4(aq) \longrightarrow 2\ C_6H_5NH_3^+(aq) + SO_4^{2-}(aq)$$



Aniline



Anilinium ion

Recall that Perkin started with this salt in his serendipitous discovery of the dye mauve.

The facts that an amine can be protonated, and that the proton can be removed again by treating the compound with a base have practical and physiological importance.

Nicotine in cigarettes is normally found in the protonated form. (This water-soluble form is often used in insecticides.) Adding a base such as ammonia moves the H^+ ion to leave nicotine in its "free-base" form.

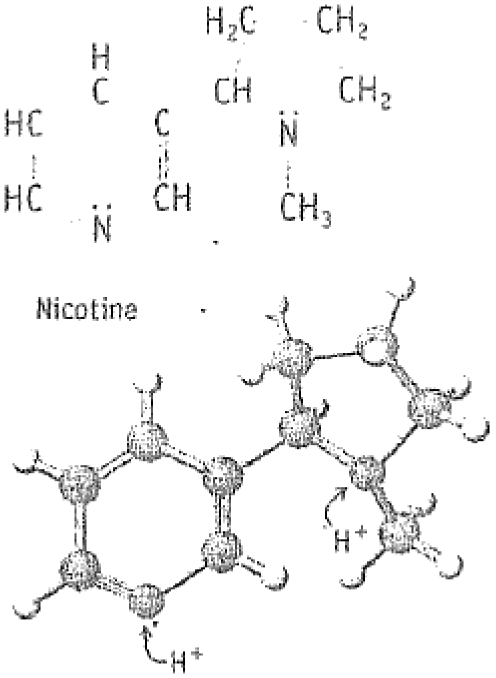
$$NicH_2^{2+}\ (aq) + 2\ NH_3(aq) \longrightarrow Nic(aq) + 2\ NH_4^+(aq)$$

In this form, nicotine is much more readily absorbed by the skin and mucous membranes, so the compound is a much more potent poison.

Note:

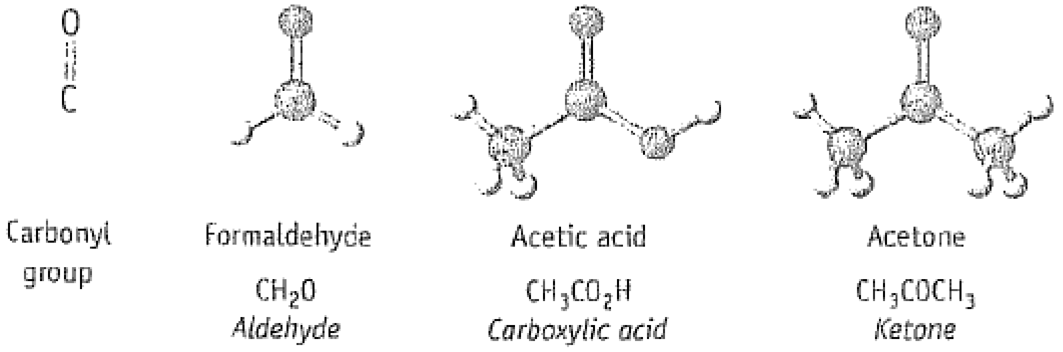
Nicotine Two nitrogen atoms in the nicotine molecule can be protonated, which is the form in which nicotine is normally found. The protons can be removed, however, by treating it with a base.

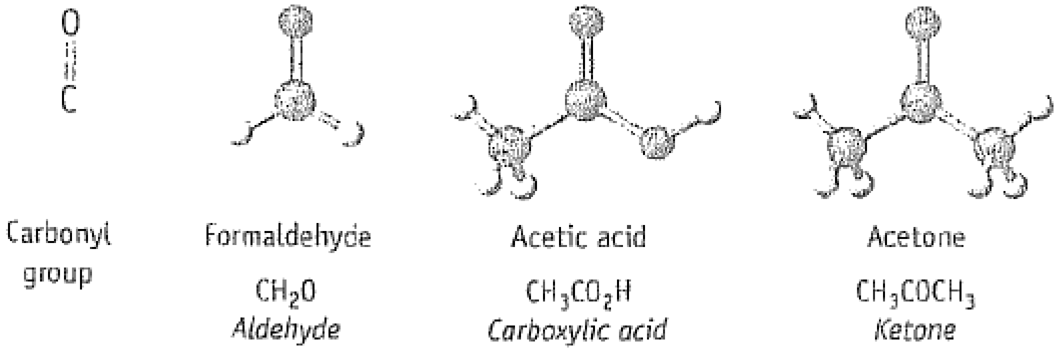
This "free-base" form is much more poisonous and addictive. See J. F. Pankow: Environmental Science & Technology, Vol 31, p. 2428, August 1997.



2.5 Compounds with a carbonyl group

Formaldehyde, acetic acid, and acetone are among the organic compounds referred to previously. These compounds have a common structural feature: Each contains a trigonal-planar carbon atom doubly bonded to an oxygen. The C=O group is called the carbonyl group, and ali of these compounds are members of a large class of compounds called carbonyl compounds.





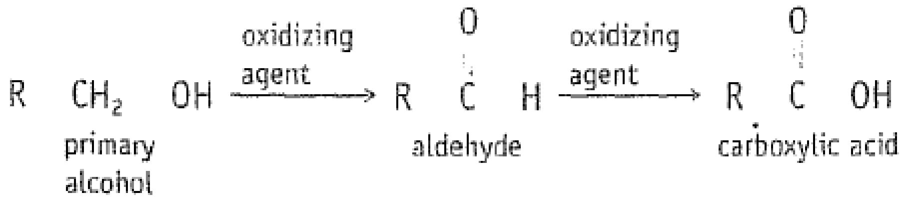
In this section, we will examine five groups of carbonyl compounds (**Table 2.5**):

- Aldehydes (RCHO) have an organic group (-R) and an H atom attached to a carbonyl group.
- Ketones (RCOR') have two -R groups attached to the carbonyl carbon; they may be the same groups, as in acetone, or different groups.
- Carboxylic acids (RCO_2H) have an -R group and an -OH group attached to the carbonyl carbon.
- Esters (RCO_2R') have-R and -OR' groups attached to the carbonyl carbon.
- Amides ($RCONR_2$, RCONHR', and $RCONH_2$) have an -R group and an amino group ($-NH_2$, -NHR, $-NR_2$) bonded to the carbonyl carbon.

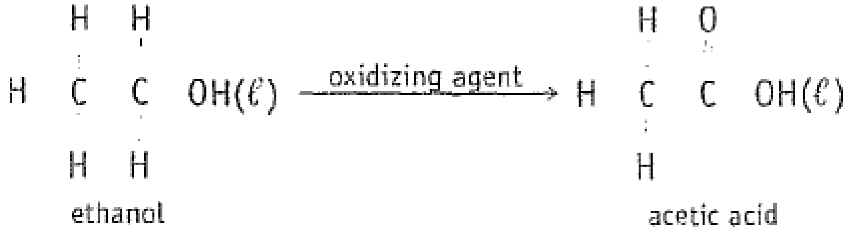
Aldehydes, ketones, and carboxylic acids-are oxidation products of alcohols and, indeed, are commonly made by this route. The product obtained through oxidation of an alcohol depends on the alcohol's structure, which is classified according to the number of carbon atoms bonded to the C atom bearing the -OH group.

Primary alcohols have one carbon and two hydrogen atoms attached, whereas secondary alcohols have two carbon atoms and one hydrogen atom attached. Tertiary alcohol have three carbon atoms attached to the C atom bearing the -OH group.

A primary alcohol is oxidized in two steps. It is first oxidized to an aldehyde and then in a second step to a carboxylic acid:



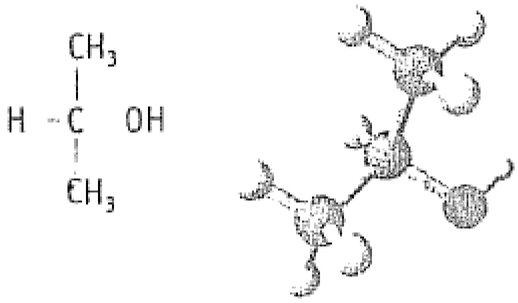
For example, the air oxidation of ethanol in wine produces \Vine vinegar, the most important ingredient of which is acetic acid.



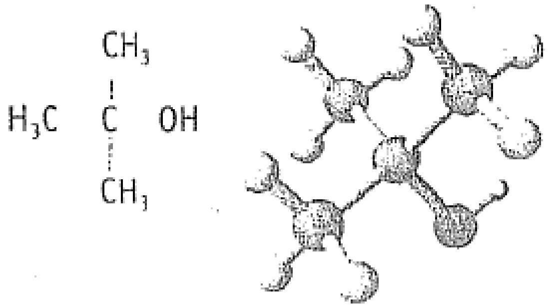
Note:

Primary alcohol: ethanol

Secondary alcohol: 2-propanol



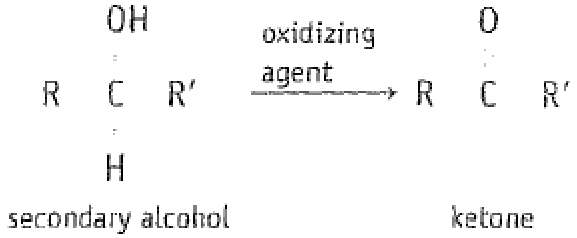
Tertiary alcohol: 2-methyl-2-propanol



Acids have a sour taste. The word "vinegar" (from the French vin aigre) means sour wine. A device to test one's breath for alcohol relies on a similar oxidation or ethanol.

Figure 2.8 Alcohol tester. This device for testing a person's breath for the presence of ethanol relies on the oxidation of the alcohol. If present, ethanol is oxidized by potassium dichromate, $K_2Cr_2O_7$, to acetaldehyde, and then to acetic acid. The yellow-orange dichromate ion is reduced to green Cr^{3+}(aq), the color change indicating that ethanol was present.

In contrast to primary alcohols, oxidation of a secondary alcohol produces a ketone:



$$R-\overset{\overset{OH}{|}}{\underset{\underset{H}{|}}{C}}-R' \xrightarrow[\text{}]{\text{oxidizing agent}} R-\overset{\overset{O}{\|}}{C}-R'$$

(R and R′ are organic groups. They may be the same or different.)

Common oxidizing agents used for these reactions are reagents such as $KMnO_4$ and $K_2Cr_2O_7$ (**Table 2.7**).

2.5.1 Aldehydes and Ketones

Aldehydes and ketones have pleasant odors and are often used in fragrances. Benzaldehyde is responsible for the odor of almonds and cherries, cinnamaldehyde is found in the bark of the cinnamon tree, and the ketone p-hydroxyphenyl-2-butanone is responsible for the odor of ripe raspberries.

Table 2.7 lists several simple aldehydes and ketones.

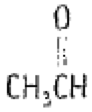
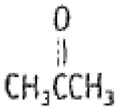
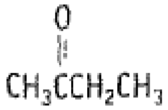
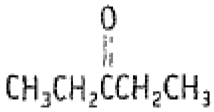
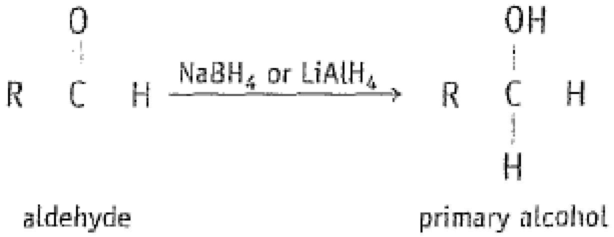
Structure	Common name	Systematic name	BP (°C)
 $H\overset{O}{\overset{\|}{C}}H$	formaldehyde	methanal	-19
 $CH_3\overset{O}{\overset{\|}{C}}H$	acetaldehyde	ethanol	20
 $CH_3\overset{O}{\overset{\|}{C}}CH_3$	acetone	propanone	56
 $CH_3\overset{O}{\overset{\|}{C}}CH_2CH_3$	methyl ethyl ketone	butanone	80
 $CH_3CH_2\overset{O}{\overset{\|}{C}}CH_2CH_3$	diethyl ketone	3-pentanone	102

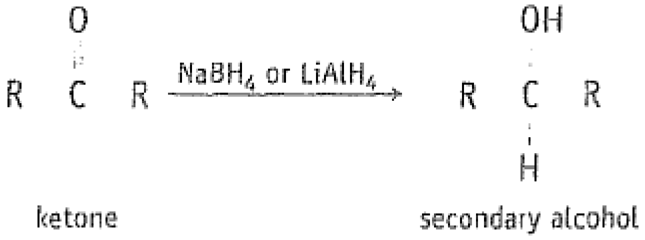
Table 2.7 Simple aldehydes and ketones

Note:
Aldehydes and odors. The odors of almonds and cinnamon are due to aldehydes, but the odor of fresh raspberries comes from a ketone.

Aldehydes and ketones are the oxidation products of primary and secondary alcohols, respectively. The reverse reactions - reduction of aldehydes to primary alcohols, and reduction of ketones to secondary alcohols - are also known.

Commonly used reagents for such reductions are $NaBH_4$ and $LiBH_4$, although H2 is used on an industrial scale.





2.5.2 Carboxylic Acids

Acetic acid is the most common and most important carboxylic acid. For many years, acetic acid was made by oxidizing ethanol produced by fermentation.

Now, however, acetic acid is generally made by combining carbon monoxide and methanol in the presence of a catalyst:

$$\underset{\text{methanol}}{CH_3OH(\ell)} + CO(g) \xrightarrow{\text{catalyst}} \underset{\text{acetic acid}}{CH_3CO_2H(\ell)}$$

About 1 billion kilograms of acetic acid is produced annually in the United States for use in plastics, synthetic fibers, and fungicides.

Many organic acids are found naturally (**Table 2.8**). Acids are recognizable by their sour taste (**Figure 2.9**) and are found in common foods: Citric acid in fruits, acetic acid in vinegar, and tartaric acid in grapes are just three examples.

Some carboxylic acids have common names derived from the source of the acid (**Table 2.8**). Because formic acid is found in ants, its name comes from the Latin word for ant (formica). Butyric acid gives rancid butter its unpleasant odor, and the name is related to the Latin word for butter (butyrum).

Figure 2.9 Acetic acid in bread. Acetic acid is produced in bread when leavened with the yeast Saccharomyces exigus. Another group of bacteria, Lacto-bacillus sanfrancisco, contribute to the flavor of sourdough bread. These bacteria metabolize the sugar maltose, excreting acetic acid and lactic acid, $CH_3CH(OH)CO_2H$, thereby giving the bread its unique sour taste.

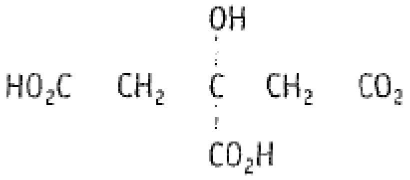
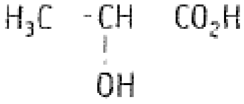
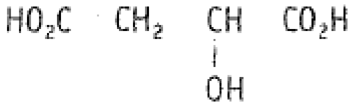
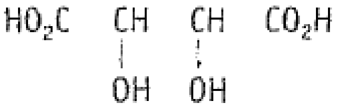
Name	Structure	Natural Source
benzoic acid	CO_2H	berries
citric acid	 $HO_2C\ \ CH_2\ \ \overset{OH}{\underset{CO_2H}{C}}\ \ CH_2\ \ CO_2$	citrus fruits
lactic acid	 $H_3C\ -\underset{OH}{CH}\ \ CO_2H$	sour milk
malic acid	 $HO_2C\ \ CH_2\ \ \underset{OH}{CH}\ \ CO_2H$	apples
oleic acid	$CH_3(CH_2)_7\ \cdot CH - CH\ \ (CH_2)_7\ \ CO_2H$	vegetable oils
oxalic acid	$HO_2C\ \ CO_2H$	rhubarb, spinach, cabbage, tomatoes
stearic acid	$CH_3(CH_2)_{16}\ \ CO_2H$	animal fats
tartaric acid	 $HO_2C\ \ \underset{OH}{CH}\ \ \underset{OH}{CH}\ \ CO_2H$	grape juice, wine

Table 2.8 Some Naturally Occurring Carboxylic Acids

The systematic names of acids (**Table 2.9**) are formed by dropping the "-e" on the name of the corresponding alkane and adding "-oic" (and the word "acid").

Because of the substantial electronegativity of oxygen, we expect the two O atoms of the carboxylic acid group to be slightly negatively charged, and the

H atom of the -OH group to be positively charged. This distribution of charges has several important implications:

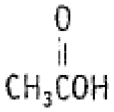
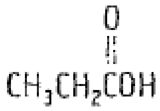
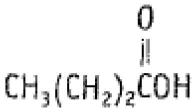
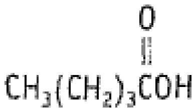
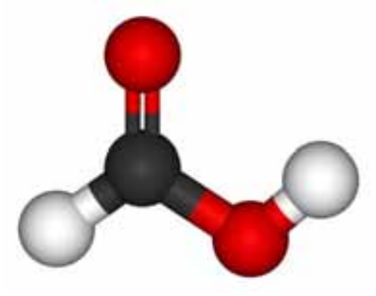
Structure	Common Name	Systematic Name	BP (°C)
 $H\overset{\overset{O}{\|}}{C}OH$	formic acid	methanoic acid	101
 $CH_3\overset{\overset{O}{\|}}{C}OH$	acetic acid	ethanoic acid	118
 $CH_3CH_2\overset{\overset{O}{\|}}{C}OH$	propionic acid	propanoic acid	141
 $CH_3(CH_2)_2\overset{\overset{O}{\|}}{C}OH$	butyric acid	butanoic acid	163
 $CH_3(CH_2)_3\overset{\overset{O}{\|}}{C}OH$	valeric acid	pentanoic acid	187

Table 2.9 Some Simple Carboxylic Acids

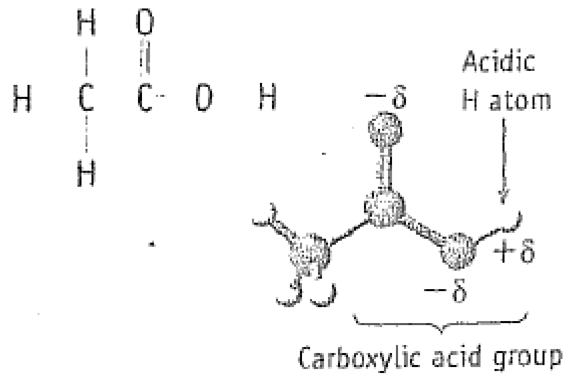
Formic acid, HCO_2H

This acid puts the sting in ant bites.



Acetic Acid

The H atom of the carboxylic acid group (–CO_2H) is the acidic proton of this and other carboxylic acids.

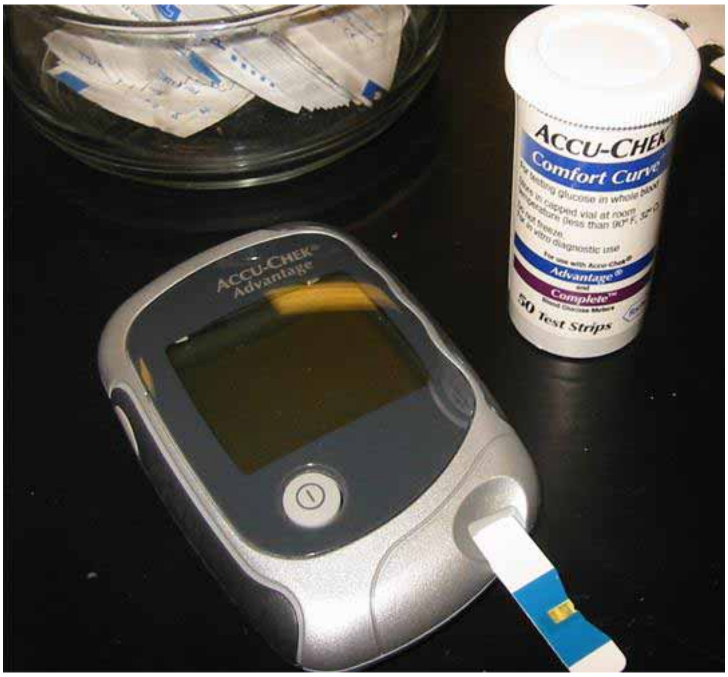


A Closer look: Glucose and Sugars

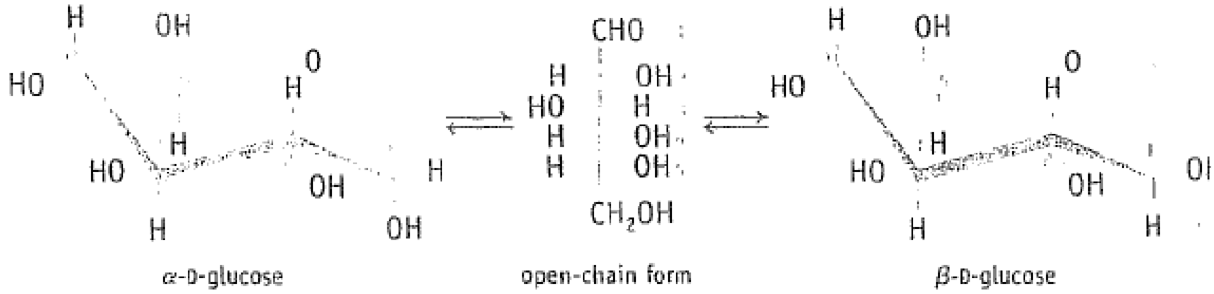
Having described alcohols and carbonyl compounds, we now pause to look at glucose, the most common, naturally occurring carbohydrate.

As their name implies, formulas of carbohydrates can be written as though they are a combination of carbon and water, $C_x(H_2O)_y$. Thus, the formula of glucose, $C_6H_{12}O_6$, is equivalent to $C_6(H_2O)_6$. This compound is a sugar, or, more accurately, a monosaccharide.

Carbohydrates are polyhydroxy aldehydes or ketones. Glucose is an interesting molecule that exists in three different isomeric forms. Two of the isomers contain six-member rings; the third isomer features a chain structure. In solution, the three forms rapidly interconvert.



Laboratory test for glucose



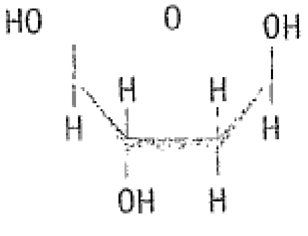
Notice that glucose is a chiral molecule.

In the chain structure, four of the carbon atoms are bonded to four different groups. In nature, glucose occurs in just one of its enantiomeric forms; thus, a solution of glucose rotates polarized light.

Knowing glucose's structure allows one to predict some of its properties. With five
polar -OH groups in the molecule, glucose is, not surprisingly, soluble in water.

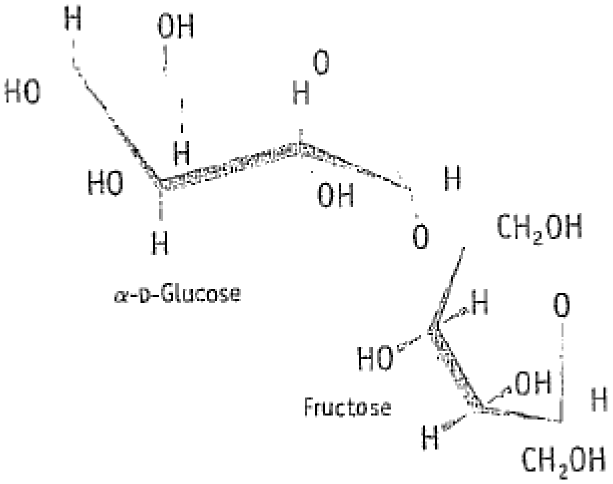
The aldehyde group is susceptible to chemical oxidation to form a carboxylic acid. Detection of glucose (in urine or blood) takes advantage of this fact; diagnostic tests for glucose involve oxidation with subsequent detection of the products.

Glucose is in a class of sugar molecules called hexoses, molecules having six carbon atoms. 2-Deoxyribose, the sugar in the backbone of the DNA molecule, is a pentose, a molecule with five carbon atoms.



deoxyribose, a pentose in the DNA backbone

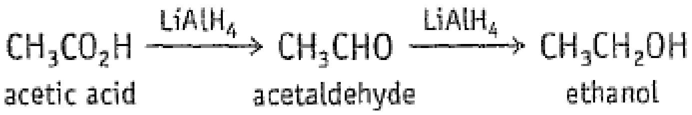
Glucose and other monosaccharides serve as the building blocks for larger carbohydrates. Sucrose, a disaccharide, is formed from a molecule of glucose and a molecule of fructose, another monosaccharide. Starch is a polymer composed of many monosaccharide units.



The structure of sucrose. Sucrose is formed from the hexoses α-D-glucose and fructose. An ether linkage is formed by loss of H20 from two ─OH groups.

- The polar acetic acid molecule dissolves readily in water, which you already know because vinegar is an aqueous solution of acetic acid. (Acids with larger organic groups are less soluble, however.)
- The hydrogen of the -OH group is the acidic hydrogen. As noted previously acetic acid is a weak acid in water, as are all other organic acids.

Carboxylic acids undergo a number of reactions. Among these is the reduction of the acid (with reagents such as LiA1H$_4$ or NaBH$_4$) first to an aldehyde and then to an alcohol. For example, acetic acid is reduced first to acetaldehyde and then to ethanol.



$$\underset{\text{acetic acid}}{CH_3CO_2H} \xrightarrow{LiAlH_4} \underset{\text{acetaldehyde}}{CH_3CHO} \xrightarrow{LiAlH_4} \underset{\text{ethanol}}{CH_3CH_2OH}$$

Chemical perspectives: Aspirin is more than 100 years old!

Aspirin is one of the most successful nonprescription drugs ever made. Americans swallow more than 50 million aspirin tablets a day, mostly for the pain-relieving (analgesic) effects of the drug. Aspirin also wards off heart disease and thrombosis (blood clots), and it has even been suggested as a possible treatment for certain cancers and for senile dementia.

Hippocrates (460-370 BC), the ancient Greek physician, recommended an infusion of willow bark to ease the pain of childbirth.

It was not until the 19th century that an Italian chemist Raffaele Piria, isolated salicylic acid, the active compound in the bark. Soon thereafter, it was found that the acid could be extracted from a wildflower, Spiraea ulmaria. It is from the name of this plant that the name “aspirin” (a + spiraea) is derived.

Hippocrates's willow bark extract, salicylic acid, is an analgesic, but it is also very irritating to the stomach lining. It was therefore an important advance when Felix Hoffmann and Henrich Dreser of Bayer Chemicals in Germany found, in 1897, that a derivative of salicylic acid, acetylsalicyclic acid, was also a useful drug and had fewer side effects. This derivative is the compound we now call “aspirin”.

Acetylsalicylic acid slowly reverts to salicylic acid and acetic acid in the presence of moisture. Indeed, if you smell the characteristic odor of acetic acid in a bottle of aspirin tablets, they are too old and should be discarded.

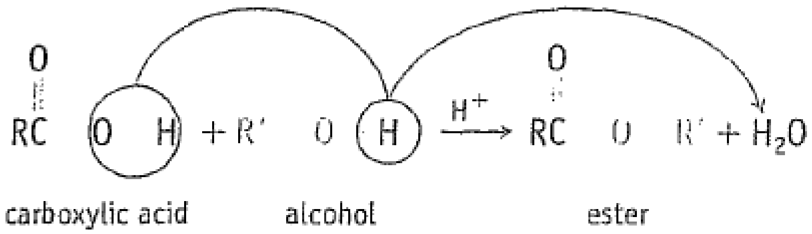
Aspirin is a component of various over-the-counter medicines, such as Anacin, Ecotrin, Excedrin, and Alka-Seltzer. The latter is a combination of aspirin with citric acid and sodium bicarbonate. Sodium bicarbonate is a base, and it reacts with the acid to produce the sodium salt of acetylsalicyclic acid, a form of aspirin tha is water-soluble and quicker-acting.

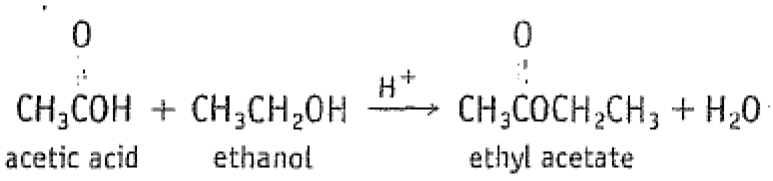
Yet another important aspect of carboxylic acid chemistry is these acids' reaction with bases to give carboxylate anions. For example, acetic acid reacts with sodium hydroxide to give sodium acetate (sodium ethanoate).

$$CH_3CO_2H(aq) + OH^-(aq) \longrightarrow CH_3CO_2^-(aq) + H_2O(\ell)$$

2.5.3 Esters

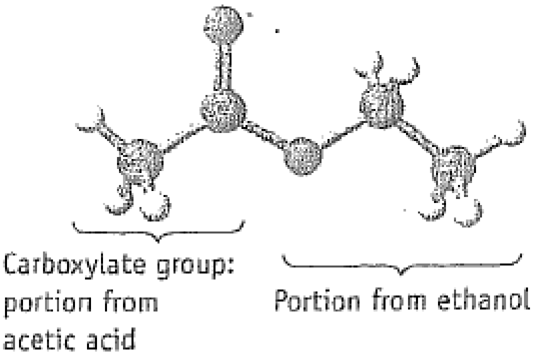
Carboxylic acids (RCO_2H) react with alcohols (R'OH) to form esters (RCO_2R') in an esterification reaction. (These reactions are generally run in the presence of strong acids because acids accelerate the reaction.)





$$CH_3\overset{O}{\overset{\|}{C}}OH + CH_3CH_2OH \xrightarrow{H^+} CH_3\overset{O}{\overset{\|}{C}}OCH_2CH_3 + H_2O$$

Table 2.10 lists a few common esters and the acid and alcohol from which they are formed. The two-part name of an ester is given by (1) the name of the hydrocarbon group from the alcohol and (2) the name of the carboxylate group derived from the acid name by replacing "-ic" with "-ate." For example, ethanol commonly called ethyl alcohol) and acetic acid combine to give the ester ethyl acetate.



Ethyl acetate, an ester

$CH_3CO_2CH_2CH_3$

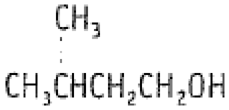
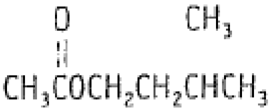
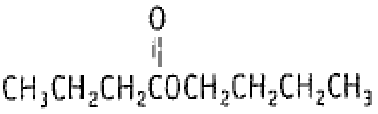
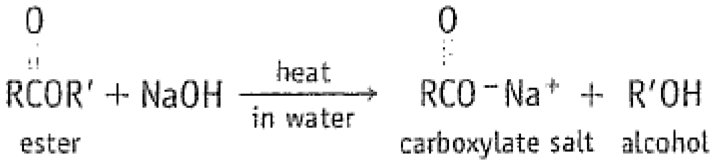
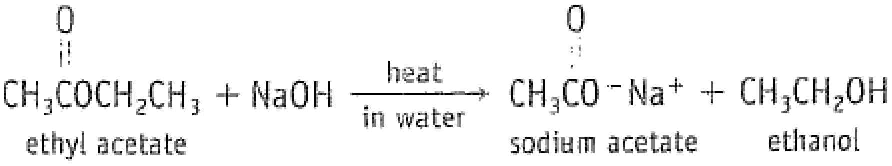
Acid	Alcohol	Ester	Odor of Ester
CH_3CO_2H acetic acid	 $CH_3\overset{\overset{\displaystyle CH_3}{\vert}}{C}HCH_2CH_2OH$ 3-methyl-1-butanol	 $CH_3\overset{\overset{\displaystyle O}{\Vert}}{C}OCH_2CH_2\overset{\overset{\displaystyle CH_3}{\vert}}{C}HCH_3$ 3-methylbutyl acetate	banana
CH_3 CH_2 CH_2CO_2H butanoic acid	$CH_3CH_2CH_2CH_2OH$ 1-butanol	 $CH_3CH_2CH_2\overset{\overset{\displaystyle O}{\Vert}}{C}OCH_2CH_2CH_2CH_3$ butyl butanoate	pineapple
CH_3 $CH_2CH_2CO_2H$ butanoic acid	 CH_2OH benzyl alcohol	 $CH_3CH_2CH_2\overset{\overset{\displaystyle O}{\Vert}}{C}OCH_2$ benzyl butanoate	rose

Table 2.10 Some Acids, Alcohols, and Their Esters

An important reaction of esters is their hydrolysis (literally, reaction with water), a reaction that is the reverse of the formation of the ester. The reaction, generally done in the presence of a base such as NaOH, produces the alcohol and a sodium salt of the carboxylic acid:

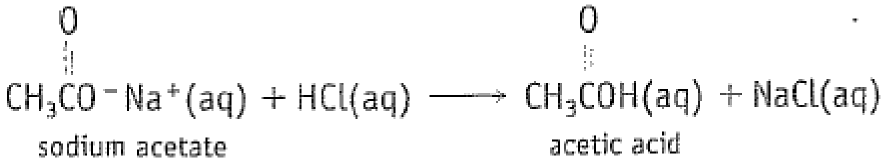


$$RC(=O)OR' + NaOH \xrightarrow[\text{in water}]{\text{heat}} RC(=O)O^-Na^+ + R'OH$$



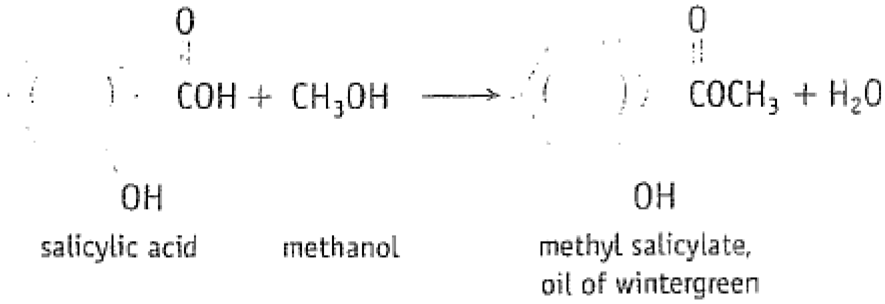
$$CH_3C(=O)OCH_2CH_3 + NaOH \xrightarrow[\text{in water}]{\text{heat}} CH_3C(=O)O^-Na^+ + CH_3CH_2OH$$

The carboxylic acid can be recovered if the sodium salt is treated with a strong acid such as HCl:



$$CH_3C(=O)O^-Na^+(aq) + HCl(aq) \longrightarrow CH_3C(=O)OH(aq) + NaCl(aq)$$

Unlike the acids from which they are derived, esters often have pleasant odors (see **Table 2.10**). Typical examples are methyl salicylate, or "oil of wintergreen," and benzyl acetate. Methyl salicylate is derived from salicylic acid, the parent compound of aspirin.



Benzyl acetate, the active component of "oil of jasmine," is formed from benzyl alcohol ($C_6H_5CH_2OH$) and acetic acid. The chemicals are inexpensive, so synthetic jasmine is a common fragrance in less expensive perfumes and toiletries.

	Did you know? Esters
Many fruits such as bananas and strawberries as well as consumer products (here perfume and oil of wintergreen) contain esters.	

Form B contains a C=N double bond, and the O and N atoms have negative and positive charges, respectively. The N atom can be assigned sp^2 hybridization, and the π bond in B arises from overlap of *p* orbitals on C and N.

The existence of a second resonance structure for an amide link explains why the carbon-nitrogen bond is relatively short, about 132 pm, a value between that of a C—N single bond (149 pm) and a C=N double bond (127 pm). In addition, restricted rotation occurs around the C=N bond, making it possible for isomeric species to exist if the two groups bonded to N are different.

Definition: Saponification
Fats and oils are esters of glycerol and long-chain acids. When reacted with a strong base (NaOH or KOH), they produce glycerol and a salt of the long-chain acid. Because this product is used as soap, the reaction is called saponification.

The amide grouping is particularly important in some synthetic polymers and in many naturally occurring compounds, especially proteins, where it is referred to as a peptide link. The compound N-acetyl-p-aminophenol, an analgesic known by the generic name acetaminophen and sold under the brand names Tylenol, Datril, and Momentum, among others, is another amide.

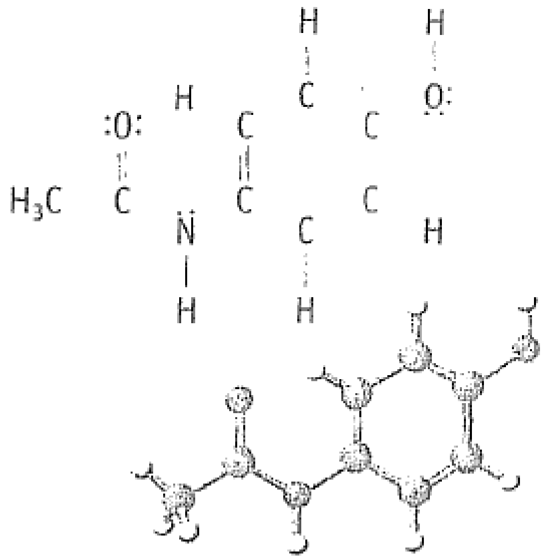
Use of this compound as an analgesic was apparently discovered by accident when a common organic compound called acetanilide (like acetaminophen but without the -OH group) was mistakenly put into a prescription for a patient.

Acetanilide acts as an analgesic, but it can be toxic. An -OH group *para* to the amide group makes the compound nontoxic, an interesting example of the relationship between molecular structure and chemical function.

See the General Chemistry Now CD-ROM or website: http://www.nbclearn.com/chemistry **Functional Groups**, for a description of the types of organic functional groups and for tutorials on their structures, bonding, and chemistry.

Did you know? Acetaminophen, *N*-acetyl-*p*-aminophenol

This analgesic is an amide. It is used in over-the-counter painkillers such as Tylenol.



Definition: Amides, peptides, and proteins

When amino acids combine, they form amide or peptide links. Polymers of amino acids are proteins. For more on amino acids and proteins, see "The Chemistry of Life: Biochemistry," pages 530-545.

Worked Example 2.7 Functional group chemistry

Problem

(a) Name the product of the reaction between ethylene and HCl.

(b) Draw the structure of the product of the reaction between propanoic acid and 1-propanol. What is the systematic name of the reaction product, and what functional group does it contain?

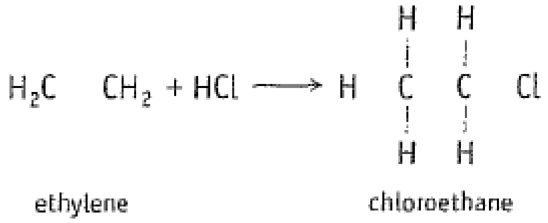
(c) What is the result of reacting 2-butanol with an oxidizing agent? Give the name and draw the structure of the reaction product.

Strategy

Ethylene is an alkene, propanoic acid is a carboxylic acid, and 2-butanol is an alcohol. Consult the discussion regarding their chemistry.

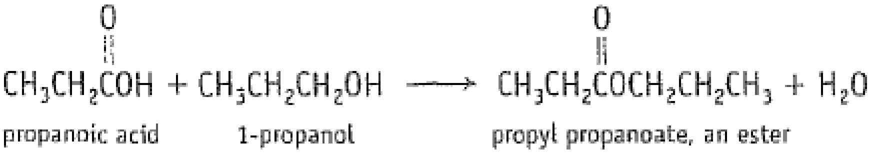
Solution

(a) HCl will add to the double bond of ethylene to produce chloroethane.



$$H_2C \quad CH_2 + HCl \longrightarrow H \; \overset{H}{\underset{H}{\overset{|}{\underset{|}{C}}}} \; \overset{H}{\underset{H}{\overset{|}{\underset{|}{C}}}} \; Cl$$

(b) Carboxylic acids such as propanoic acid react with alcohols to give esters.



$$CH_3CH_2\overset{O}{\overset{\|}{C}}OH + CH_3CH_2CH_2OH \longrightarrow CH_3CH_2\overset{O}{\overset{\|}{C}}OCH_2CH_2CH_3 + H_2O$$

(c) 2-Butanol is a secondary alcohol. Such alcohols are oxidized to ketones.

$$CH_3\overset{OH}{\overset{|}{C}}HCH_2CH_3 \xrightarrow{\text{oxidizing agent}} CH_3\overset{O}{\overset{\|}{C}}CH_2CH_3$$

2.6 Polymers

We now turn to the very large molecules known as polymers. These can be either synthetic materials or naturally occurring substances such as proteins or nucleic acids.

Although these materials have widely varying compositions, their structures and properties are understandable based on the principles developed for small molecules.

2.6.1 Classifying Polymers

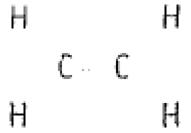
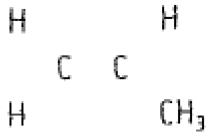
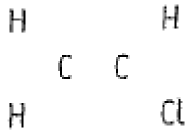
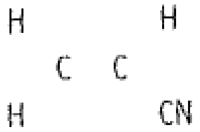
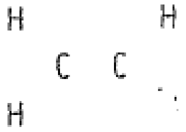
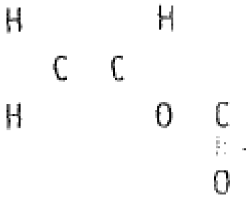
The word polymer means "many parts" (from the Greek, *poly* and *meros*). Polymers are giant molecules made by chemically joining many small molecules called monometers. Polymer molecular weights range from thousands to millions.

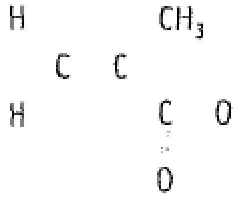
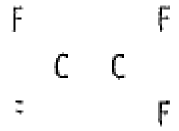
Extensive use of synthetic polymers is a fairly recent development. A few synthetic polymers (Bakelite, rayon, and celluloid) were made early in the 20th century, but most of the products with which you are familiar originated in the last 50 years.

By 1976, synthetic polymers outstripped steel as the most widely used material in the United States. The average production of synthetic polymers in the United States is approximately 150 kg per person annually.

The polymer industry classifies polymers in several different ways. One is their response to heating. Thermoplastics (such as polyethylene) soften and flow when they are heated and harden when they are cooled. Thermosetting plastics (such as Formica) are initially soft but sot to a solid when heated and cannot be resoftened.

Did you know? Biochemical Polymers
Polymer chemistry extends to biochemistry where chemists study proteins and other large molecules. See "The Chemistry of Life: Biochemistry," pages 530-545.

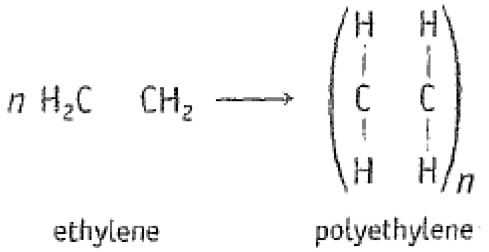
Formula	Monomer Common Name	Polymer Name (Trade Names)	Uses	US Polymer Production (Metric tons/year)*
	ethylene	Polyethylene (polythene)	squeeze bottles, bags, films, toys and molded objects, electric insulation	7 million
	propylene	polypropylene (Vectra, Herculon)	bottles, films, indoor-outdoor carpets	1,2 million
	vinyl chloride	polyvinyl chloride (PVC)	floor tile, raincoats, pipe	1,6 million
	acrylonitrile	Polyacrylonitrile (Orlan, Acrilan)	rugs, fabrics	0,5 million
	styrene	Polystyrene (Styrofoam, Styron)	food and drink coolers, building material insulation	0, 9 million
	vinyl acetate	polyvinyl acetate (PVA)	latex paint adhesives, textile coatings	200,000

	methyl methacrylate	Polyethylene methacrylate (Plexiglass, Lucite)	High-quality transparent objects, latex paints, contact lenses	200,000
	tetrafluoroethylene	Polytetrafluoroethylen (Teflon)	Gaskets, insulation, bearings, pan coatings	6,000

* One metric ton = 1000 kg

Table 2.11 Ethylene Derivatives That Undergo Addition Polymerization

The reaction can be expressed as a balanced chemical equation:



The abbreviated formula of the reaction product, $(—CH_2CH_2—)_n$, shows that polyethylene is a chain of carbon atoms, each bearing two hydrogens. The chain length for polyethylene can be very long. A polymer with a molecular weight of 1 million would contain almost 36,000 ethylene molecules linked together.

Polyethylene formed under various pressures and catalytic conditions has different properties, as a result of their different molecular structures. For example, when chromium oxide is used as a catalyst, the product is almost exclusively a linear chain (**Figure 2.12(a)**).

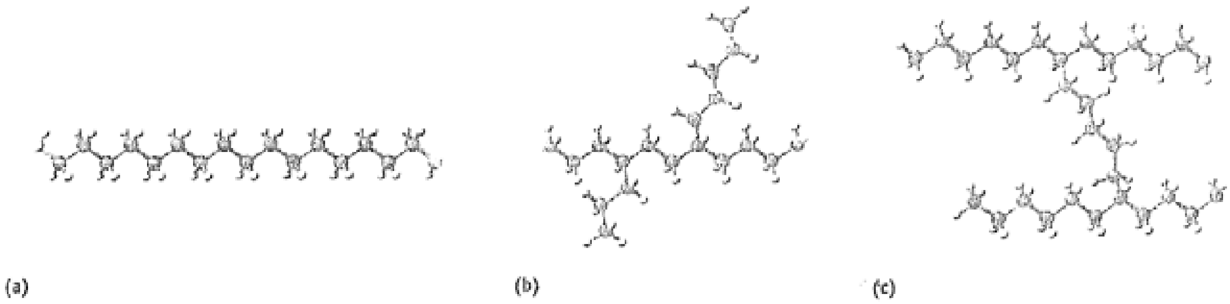


Figure 2.12 Polyethylene (a) The linear form, high-density polyethylene (HDPE). (b) Branched chains occur in low-density polyethylene (LDPE) (c) Cross-linked polyethylene (CLPE)

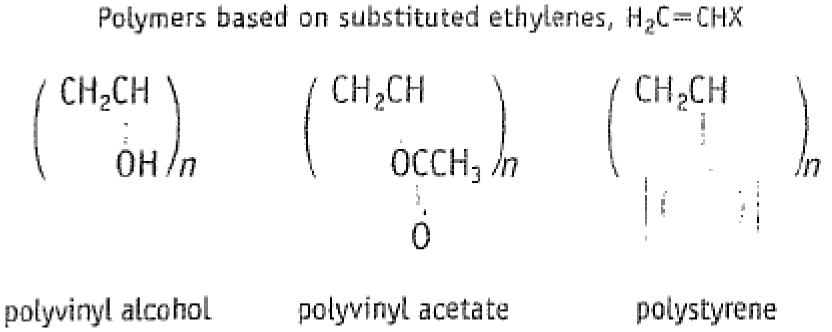
If ethylene is heated to 230°C at high pressure, however, irregular branching occurs. Still other conditions lead to cross-linked polyethylene, in which different chains are linked together (**Figure 2.12(b)** and **Figure 2.12(c)**).

The high-molecular-weight chains of linear polyethylene pack closely together and result in a material with a density of 0,97 g/cm^3. This material, referred to as high-density polyethylene (HDPE), is hard and tough, which makes it suitable for items such as milk bottles.

If the polyethylene chain contains branches, however, the chains cannot pack as closely together, and a lower-density material (0,92 g/cm^3) known as low-density polyethylene (LDPE) results. This material is softer and more flexible than HDPE. It is used in plastic wrap and sandwich bags, among other things.

Linking up the polymer chains in cross-linked polyethylene (CLPE) causes the material to be even more rigid and inflexible. Plastic bottle caps are often made of CLPE.

Polymers formed from substituted ethylenes (CH_2=CHX) have a range of properties and uses (see **Table 2.11**). Sometimes the properties are predictable based on the molecule's structure. Polymers without polar substituent groups, such as polystyrene, often dissolve in organic solvents, a property useful for some types of fabrication (**Figure 2.12**).



Polyvinyl alcohol is a polymer with little affinity for nonpolar solvents but an affinity for water, which is not surprising based on the large number of polar ─OH groups (**Figure 2.14**). Vinyl alcohol itself is not a stable compound (it isomerizes to acetaldehyde CH_3CHO), so polyvinyl alcohol cannot be made from this compound.

Instead, it is made by hydrolyzing the ester groups in polyvinyl acetate. Solubility in water or organic solvents can be a liability for polymers. The many uses of polytetrafluoroethylene [Teflon, $(─CF_2CF_2─)_n$] stem from the fact that it does not interact with water or organic solvents.

Did you know? Polyethylene film

The polymer film is produced by extruding the molten plastic through a ringlike gap and inflating the film like a balloon.

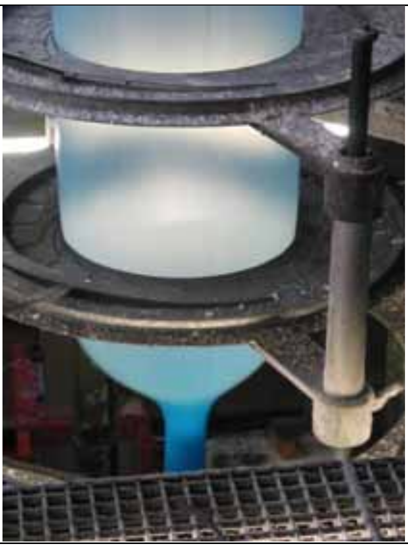
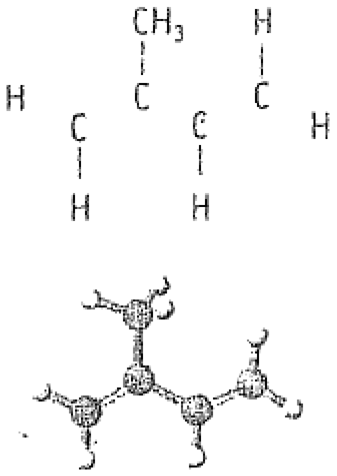


Figure 2.13 Polystyrene (a) The polymer is a clear, hard, colorless solid, but it may be more familiar as a light, foamlike material called Styrofoam. (b) Styrofoam has no polar groups and thus dissolves well in organic solvents such as acetone.

Polystyrene, with *n* = 5700, is a clear, hard, colorless solid that can be molded easily at 250°C. You are probably more familiar with the very light, foamlike material known as Styrofoam that is used widely for food and beverage containers and for home insulation (**Figure 11.13**). Styrofoam is produced by a process called "expansion molding."

Polystyrene beads containing 4% to 7% of a low-boiling liquid like pentane are placed in a mold and heated with steam or hot air. Heat causes the solvent to vaporize, creating a foam in the molten polymer that expands to fill the shape of the mold.

Figure 2.14 Slime. When baric acid, $B(OH)_3$, is added to an aqueous suspension of polyvinyl alcohol, (CH_2CHOH), the mixture becomes very viscous. This is because boric acid reacts with the –OH groups on the polymer chain, causing cross-linking to occur. (The model shows an idealized structure of a portion of the polymer.)



Isoprene, 2-methyl-1,3-butadiene.

2.6.2 Natural and synthetic rubber

Natural rubber was first introduced in Europe in 1740, but it remained a curiosity until 1823, when Charles Macintosh invented a way of using it to waterproof cotton cloth. The Mackintosh, as rain coats are still sometimes called, became popular despite major problems: Natural rubber is notably weak and is soft and tacky when warm but brittle at low temperatures.

In 1839, after five years of research on natural rubber, the American inventor Charles Goodyear (1800-1860) discovered that heating gum rubber with sulfur produces a material that is elastic, water-repellent, resilient, and no longer sticky.

Rubber is a naturally occurring polymer, the monomers of which are molecules of 2-methyl-1,3-butadiene, commonly called isoprene. In natural rubber, isoprene monomers are linked together through carbon atoms 1 and 4 - that is, through the end carbon atoms of the C_4 chain (**Figure 2.15**). This leaves a double bond between carbon atoms 2 and 3. In natural rubber, these double bonds have a *cis* configuration.

In vulcanized rubber, the material that Goodyear discovered, the polymer chains of natural rubber are cross-linked by short chains of sulfur atoms. Cross-linking helps to align the polymer chains so the material does not undergo a permanent change when stretched.

As a result, it springs back when the stress is removed. Substances that behave this way are called elastomers.

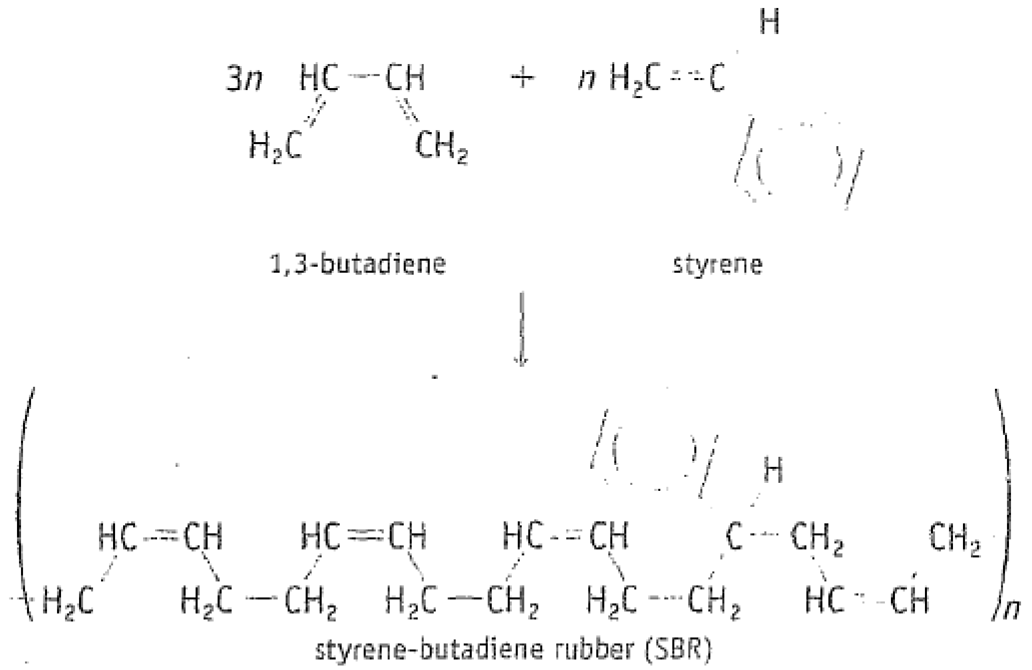
With a knowledge of the composition and structure of natural rubber, chemists began searching for ways to make synthetic rubber. When they first tried to make the polymer by linking isoprene monomers together, however, what they made was sticky and useless.

The problem was that synthesis procedures gave a mixture of *cis* and *trans* polyisoprene. In 1955, however, chemists at the Goodyear and Firestone companies discovered special catalysts to prepare the all-*cis* polymer. This synthetic materiai, which was structurally identical to natural rubber, is now manufactured cheaply.

In fact, more than 8,0 x 10^8 kg of synthetic polyisoprene is produced annually in the United States.

Other kinds of polymers have further expanded the repertoire of elastomeric materials now available. Polybutadiene, for example, is currently used in the production of tires, hoses, and belts. Some elastomers, called copolymers, are formed by polymerization of two (or more) different monomers.

A copolymer of styrene and butadiene, made with a 1:3 ratio of these raw materials, is the most important synthetic rubber now made; more than about I billion kg of styrene-butadiene rubber (SBR) is produced each year in the United States for making tires.



styrene-butadiene rubber (SBR)

And a little is left over each year to make bubble gum. The stretchiness of bubble gum once came from natural rubber, but SBR is now used to help you blow bubbles.

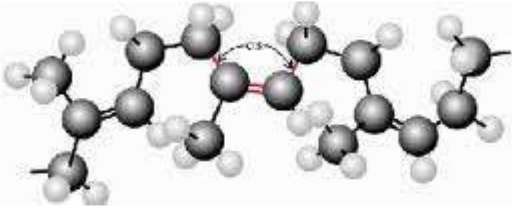


Figure 2.15 Natural rubber. The rubber that comes from the rubber tree is a natural polymer of isoprene. All the linkages of the carbon chain are *cis*. When natural rubber is heated strongly in the absence of it smells of isoprene. This observation provided a clue that rubber is composed of this building block.

2.6.3 Condensation polymers

A chemical reaction in which two molecules react by splitting out, or eliminating, a small molecule is called a condensation reaction. The reaction of an alcohol with a carboxylic acid to give an ester is an example.

A polymer can be formed in a condensation reaction if two different reactant molecules, each containing two functional groups, are used. This is one route used to make polyesters and polyamides, two important types of condensation polymers.

See the General Chemistry Now CD-ROM or website: http://www.nbclearn.com/chemistry **Synthetic Organic/Polymers**, to view an animation of condensation polyrnerization and to watch a video of the synthesis of nylon.

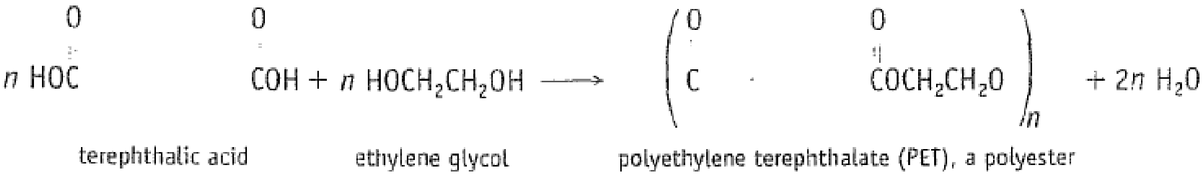
2.6.4 Polyesters

Terephthalic acid contains two carboxylic acid groups, and ethylene glycol contains two alcohol groups. When mixed, the acid and alcohol functional groups at both ends of these molecules can react to form ester linkages, splitting out water.

Did you know? Copolymer of styrene and butadiene, SBR rubber
The elasticity of bubble gum comes from SBR rubber.

Figure 2.16 Polyesters. Polyethylene terephthalate is used to make clothing and soda bottles. The two students are wearing jackets made from recycled PET soda bottles. Mylar film, another polyester, is used to make recording tape as well as balloons. Because the film has very tiny pores, Mylar can be used for helium-filled balloons; the atoms of gaseous helium move through the pores in the film very slowly.

The result is a polymer called polyethylene terephthalate (PET). The multiple ester linkages make this substance a polyester.



$$n\,\mathrm{HO\overset{O}{C}} \qquad \mathrm{\overset{O}{C}OH} + n\,\mathrm{HOCH_2CH_2OH} \longrightarrow \left(\mathrm{\overset{O}{C}} \qquad \mathrm{\overset{O}{C}OCH_2CH_2O}\right)_n + 2n\,\mathrm{H_2O}$$

Polyester textile fibers made from PET are marketed as Dacron and Terylene.

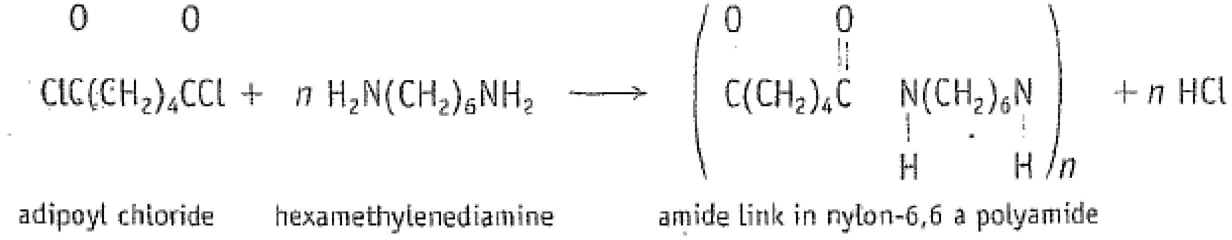
The inert, nontoxic, noninflammatory, and non-blood-clotting properties of Dacron polymers make Dacron tubing an excellent substitute for human blood vessels in heart bypass operations, and Dacron sheets are sometimes used as temporary skin for burn victims.

A polyester film, Mylar, has unusual strength and can be rolled into sheets one-thirtieth the thickness of a human hair. Magnetically coated Mylar films are used to make audio and video tapes (**Figure 2.16**).

2.6.5 Polyamides

In 1928, the DuPont Company embarked on a basic research program headed by Wallace Carothers (1896-1937). Carothers was interested in high molecular weight compounds, such as rubbers, proteins, and resins.

In 1935, his research yielded nylon-6,6 (**Figure 2.17**), a polyamide prepared from adipoyl chloride, a derivative of adipic acid, a diacid, and hexamethylenediamine, a diamine:



$$\mathrm{Cl\overset{O}{C}(CH_2)_4\overset{O}{C}Cl} + n\,\mathrm{H_2N(CH_2)_6NH_2} \longrightarrow \left(\mathrm{\overset{O}{C}(CH_2)_4\overset{O}{\overset{\|}{C}}\quad \underset{H}{\underset{|}{N}}(CH_2)_6\underset{H}{\underset{|}{N}}}\right)_n + n\,\mathrm{HCl}$$

Nylon can be extruded easily into fibers that are stronger than natural fibers and chemically more inert. The discovery of nylon jolted the American textile industry at a critical time. Natural fibers were not meeting 20th-century needs.

Silk was expensive and not durable, wool was scratchy, linen crushed easily, and cotton did not have a high-fashion image. Perhaps the most identifiable use for the new fibre was in nylon stockings. The first public sale of nylon hosiery look place on October 24, 1939, in Wilmington, Delaware (the site of DuPont's main office).

This use of nylon in commercial products ended shortly thereafter, however, with the start of World War II. All nylon was diverted to making parachutes and other military gear. It was not until about 1952 that nylon reappeared in the consumer marketplace.

Figure 2.17 Nylon-6,6. Hexamethylenediamine is dissolved in water (bottom layer), and adipoyl chloride (a derivative of adipic acid) is dissolved in hexane (top layer). The two compounds react at the interface between the layers to form nylon, which is being wound onto a stirring rod.

Figure 2.18 illustrates why nylon makes such a good fiber. To have good tensile strength (the ability to resist tearing), the polymer chains should be able to attract one another, albeit not so strongly that the plastic cannot be initially extended to form fibers.

Ordinary covalent bonds between the chains (cross-linking) would be too strong. Instead, cross-linking occurs by a somewhat weaker intermolecular force called hydrogen bonding between the hydrogens of N—H groups on one chain and the carbonyl oxygens on another chain. The polarities of the $N^{\delta-}$—$H^{\delta-}$ group and the $D^{\delta+} = O^{\delta+}$ group lead to attractive forces between the polymer chains of the desired magnitude.

Worked Example 2.8: Condensation Polymers

Problem

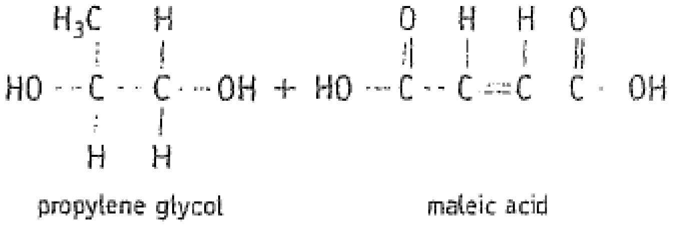
What is the repeating unit of the condensation polymer obtained by combining $HO_2CCH_2CH_2CO_2H$ (succinic acid) and $H_2NCH_2CH_2NH_2$ (1,2-ethylenediamine)?

Strategy

Recognize that the polymer wilt link the two monomer units through the amide linkage. The smallest repeating unit of the chain will contain two parts, one from the diacid and the other from the diamine.

Solution

The repeating unit of this polyamide is



See the General Chemistry Now CD-ROM or website: http://www.nbclearn.com/chemistry to explore an interactive version of **Figure 2.17** accompanied by an exercise.

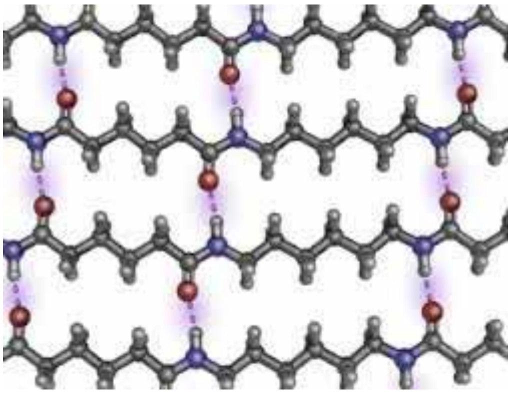
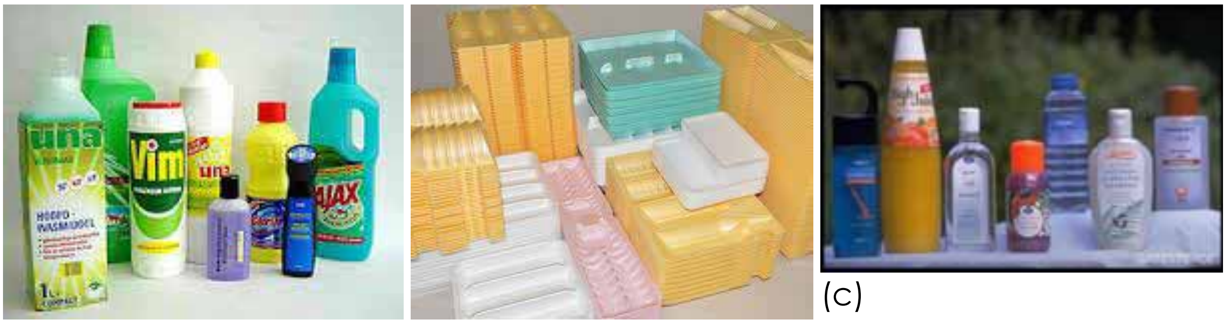


Figure 2.18 Hydrogen bonding between polyamide chains. Carbonyl oxygen atoms with a partial negative charge on one chain interact with an amine hydrogen with a partial positive charge on a neighbouring chain.



(c)

(a) (b)

Figure 2.18 Common polymer-based consumer products. (a) Packaging materials from high-density polyethylene; (b) from polystyrene; and (c) from polyvinyl chloride. Recycling information is provided on most plastics (often molded into the bottom of bottles). High-density polyethylene is designated with a "2" inside a triangular symbol and the letters "HDPE." PVC is designated with a "3" inside a triangular symbol with the letter "V" below.

Another classification scheme depends on the end use of the polymer-for example, plastics, fibers, elastomers, coatings, and adhesives.

A more chemically oriented approach to polymer classification is based on their method of synthesis. Addition polymers are made by directly adding monomer units together. Condensation polymers are made by combining monomer units and splitting out a small molecule, often water.

2.6.6 Addition Polymers

Polyethylene, polystyrene, and polyvinyl chloride (PVC) are common addition polymers (**Figure 2.18**). They are built by "adding together" simple alkenes such as ethylene (CH_2=CH_2), styrene (C_6H_5CH=CH_2), and vinyl chloride (CH_2 =CHCl).

These and other addition polymers (**Table 2.11**), all derived from alkenes, have widely varying properties and uses.

See the General Chemistry Now CD-ROM or website: http://www.nbclearn.com/chemistry **Synthetic Organic Polymers (1)**, for an animation of addition polymerization.

2.6.7 Polyethylene and Other Polyolefins

Polyethylene is by far the leader in terms of addition polymer production. Ethylene (C_2H_4), the monomer from which polyethylene is made, is a product of petroleum refining and one of the top five chemicals produced in the United States.

When ethylene is heated to between 100 and 250°C at a pressure of 1000 to 3000 atm in the presence of a Catalyst, polymers with molecular weights up to ….

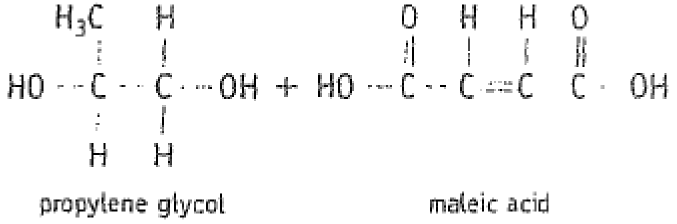
See the General Chemistry Now CD-ROM or website: http://www.nbclearn.com/chemistry see the **Homework and Goals** section.

Activity 2.1

1. Complete the following:
   (a) Draw the nine isomers having the formula C_7H_{16}. [**Hint**: There is one structure with a seven carbon chain. two structures with six-carbon chains, five structures in which the longest chain has five carbons (one is illustrated in the margin), and one structure with a four-carbon chain.]
   (b) Identify the isomers of C_7H_{16} that are chiral.
2. Name the nine isomers of C_7H_{16} in Question 1.
3. There are 17 possible alkene isomers with the formula $C_6H_{12.}$ Draw structures of the five isomers in which the longest chain has six carbon atoms and give the name of each. Which of these isomers is chiral? (There are also eight isomers in which the longest chain has five carbon atoms, and four isomers

in which the longest chain has four carbon atoms. How many can you find?)

4. Complete the following:
   (a) Draw the structure of the compound obtained from the reaction of HBr with ethylene and name the compound.
   (b) Draw the structure of the product of the reaction of Br_2 with *cis-2*-butene and name this compound
5. Aniline, $C_6H_5NH_2$, is the common name for aminobenzene. Draw a structure for ***p***-diaminobenzene, a compound used in dye manufacture. What is the systematic name for ***p***-diaminobenzene?
6. Draw the structure of 1-butanol and alcohols that are structural isomers of the compound.
7. Complete the following:
   (a) Draw the structural formula for 2-pentanone. Draw structures for a ketone and two aldehydes that are isomers of 2-pentanone, and name each of these compounds.
   (b) What is the product of the reduction of 2-pentanone with $LiBH_4$?
8. Draw the structures and name the aldehyde or ketone formed upon oxidation of the following alcohols: (a) 1-butanol, (b) 2-butanol, (c) 2-methyl-1-propanol. Are these three alcohols structural isomers?
9. Complete the following:
   (a) Name each of the following compounds and its functional group.
   (b) Name the product from the reaction of compounds 1 and 2.
   (c) What is the name and structure of the product from the oxidation of 1?
   (d) What compound could result from combining compounds 2 and 3?
   (e) What is the result of adding an acid (say HCl) to compound 3?
10. Draw the structure of the repeating unit in the condensation polymer obtained from the reaction of propylene glycol with maleic acid:



(A closely related material is combined with glass fibers [fiberglass] to make hulls for small boats and automobile panels and parts.) Is this a polyamide or a polyester?

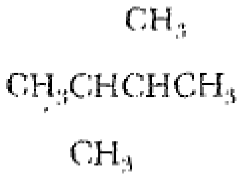
Activity 2.2

Alkanes and Cycloalkanes

1. What is the name of the straight (unbranched chain) alkane with the formula C_7H_{16}?
2. What is the molecular formula for an alkane with 12 carbon atoms? Which of the following is an alkane? Which could be a cycloalkane?

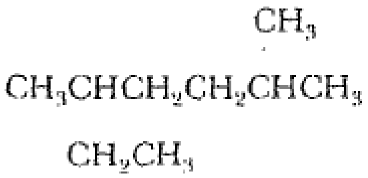
(a) C_2H_4
(b) C_5H_{10}
(c) $C_{14}H_{30}$
(d) C_7H_8

3. Isooctane, 2,2,4-trimethylpentane, is one of the possible structural isomers with the formula CHHIH· Draw the structure of this isomer, and draw and name structures of two other isomers of C_8H_{18} in which the longest carbon chain is five atoms.
   Give the systematic name for the following alkane.



$$CH_3\underset{CH_3}{CH}\overset{CH_3}{CH}CH_3$$

4. Draw a structural isomer of the compound and give its name. Draw a structural isomer of the compounds and give its names.



$$CH_3\underset{CH_2CH_3}{CH}CH_2CH_2\overset{CH_3}{CH}CH_3$$

5. Draw the structure of each of the following compound:
   (a) 2,3-climethylhexane
   (b) 2,3-dimethyloctane
   (c) 3-ethylheptane
   (d) 3-ethyl-2-methylhexane
6. Draw structures for 3-ethylpentane and 2,3-dimethylpentane.
7. Draw Lewis structures and name all possible compounds that have a seven-carbon chain with one methyl substituted group. Which of these isomers has a chiral carbon centre?
8. Draw a structure for cycloheptane. Is the seven-member ring planar? Explain your answer.
9. There are two ethylheptanes (compounds with a seven carbon chain and one ethyl substituent). Draw the structures and name these compounds. Is either isomer chiral?
10. Among the 18 structural isomers with the formula C_4H_{10} are two with a five-carbon chain having one ethyl and one methyl substituent group. Draw the structures and name these two isomers.
11. List several typical physical properties of C_4H_{10}. Predict the following physical properties of dodecane, $C_{12}H_{26}$: color, state (s, l, g), solubility in a nonpolar solvent.
12. Write balanced equations for the following reactions of alkanes.
    (a) the reaction of methane with excess chlorine
    (b) complete combustion of cyclohexane, C_6H_{12}, with excess oxygen

Alkenes and alkynes

13. Draw structures for the *cis* and *trans* isomers of 4-methyl-2-hexene.

14. What structural requirement is necessary for an alkene to have *cis* and *trans* isomers? Can *cis* and *trans* isomers exist for an alkane? For an alkyne?
15. A hydrocarbon with the formula C_5H_{10} can be either an alkene or a cycloalkane.
    (a) Draw a structure for each of the possible isomers for C_5H_{10} assuming it is an alkene. Six isomers are possible. Give the systematic name of each isomer you have drawn.
    (b) Draw a structure for a cycloalkane having the formula C_5H_{10}.
16. Five alkenes have the formula C_7H_{14} and a seven-carbon chain. Draw their structures and name them.
17. Draw the structure and give the systematic name for the products of the following reactions:
    (a) $CH_3CH{=}CH_2 + Br_2 \rightarrow$
    (b) $CH_3\ CH_2CH{=}CHCH_3 + H_2 \rightarrow$

Self-Check

I am able to:	**Yes**	**No**
• Describe alkanes		
• Describe alkenes		
• Describe alkynes		

If you have answered ‘no’ to any of the outcomes listed above, then speak to your facilitator for guidance and further development.

Module 3

Instrumentation

Learning Outcomes
On the completion of this module the student must be able to:

- Describe measurement:
    - Numbers, units and quantities
    - The International System of Units (SI)
    - Conversions factors

3.1 Introduction

Although modern analytical chemistry is dominated by sophisticated instrumentation, the roots of analytical chemistry and some of the principles used in modern instruments are from traditional techniques many of which are still used today.

3.2 Measurement

As an example of what we have just been saying, let us assume that you are faced with a specific problem. Then we can see how scientific thinking might help solve it. Suppose that you live near a large plant which manufactures cement. Smoke from the plant settles on your car and house, causing small pits in the paint. You would like to stop this air-pollution problem - but how?

As an individual you will probably have little influence, and even as part of a group of concerned citizens you may be ineffective, unless you can prove that there is a problem. Scientists have had a hand in writing most air-pollution regulations, and so you will have to employ some scientific techniques (or a scientist) to help solve your problem.

It will probably be necessary to determine how much air pollution the plant is producing. This might be done by comparing the smoke with a scale which ranges from white to gray to black, the assumption being that the darker the smoke, the more there is.

For white cement dust, however, this is much less satisfactory than for black coal smoke. A better way to determine how much pollution there is would be to measure the mass of smoke particles which could be collected near your house or car. This could be done by using a pump (such as a vacuum cleaner) to suck the polluted gas through a filter. Weighing the filter before and after such an experiment would determine what mass of smoke had been collected.

Accurate weighing is usually done with a single-pan whose principles of operation is shown in **Figure 3.1**. The empty pan is balanced by a counterweight. When an object is placed on the pan, gravitational attraction forces the pan downward.

To restore balance, a series of weights (objects of known mass) are removed from holders above the pan. The force of gravitational attraction is proportional to mass, and when the pan is balanced,
the force on it must always be the same. Therefore the mass of the object being weighed must equal that of the weights that were removed.

3.2.1 Numbers, units and quantities

If you kept a notebook or other record of your measurements, you would probably write down something like 0,0342 g to represent how much smoke had been collected.

Such a result, which describes the magnitude of some property (in this case the magnitude of the mass), is called a quantity. Notice that it consists of two parts, a number and a unit. It would be ambiguous to write just 0,0342 - you might not remember later whether that was measured in units of grams, ounces, pounds, or something else.

A quantity always behaves as though the number and the units are multiplied together. For example, we could write the quantity already obtained as 0,0342 x g. Using this simple rule of number x units, we can apply arithmetic and algebra to any quantity:

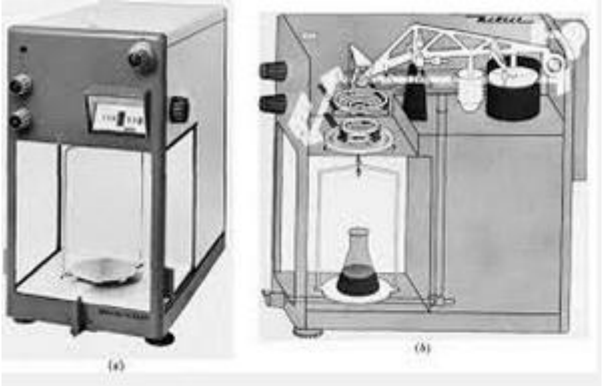


Figure 3.1 (a) Actual appearance of a modern substitution balance. (b) X-ray view showing principle of operation. When an object is placed on the balance pan, ring-shaped weights whose total mass equals that of the object are removed from holders above the pan to restore balance.

$$5\,g + 2\,g \quad = (5 + 2)\,g = 7\,g$$

$5\ g \div 2\ g = \frac{5\cancel{g}}{2\cancel{g}} =$ 2,5 (the units cancel, and so we get a pure number)

$5\ in\ x\ 2\ in = 25\ in^2$ (25 square in)

This works perfectly well as long as we do not write equations with different kinds of quantities (ie, those having units which measure different properties) on opposite sides of the equal sign. For example, applying algebra to the equation

$$5\ g\ =\ 2\ in^2$$

can lead to trouble in much the same way that dividing by zero does and should be avoided.

Notice also that whether a quantity is large or small depends on the size of the units as well as the size of the number. For example, in **Figure 3.2** the length of a metal rod has been measured with a ruler calibrated in inches and with one calibrated in centimeters.

Both results (3,50 in and 8,89 cm) are the same quantity, the length of the rod. One involves a smaller number and larger unit (3,50 in), while the other has a larger number and smaller unit. So long as we are talking about the same quantity, it is a simple matter to adjust the number to go with any units we want.

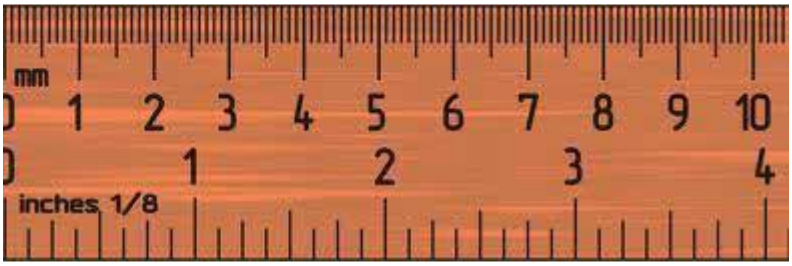


Figure 3.2 The length of a rod can be measured either in centimeters or inches. We can record the length either as 3,50 in or as 8,89 cm. In either case we are referring to the same quantity.

Worked Example 3.1

Express the length 8,89 cm in inches, given that 1 cm = 0,3937 in.

Solution

Since 1 cm and 0.3937 in are the same quantity, we can write the equation

1 cm = 0,3937 in

Dividing both sides by 1 cm, we have

$$1 = \frac{0.3937\ in}{1cm}$$

Since the right side of this equation equals one, it is called a unity factor. It can be multiplied by any quantity, leaving the quantity unchanged.

8,89 cm = 8,89 cm x 1 = 8.89 cm x 1 8,89 ~~cm~~ x $\frac{0.3937\ in}{1\cancel{cm}}$

The units centimeter cancel, yielding the result

8,89 cm = 8,89 x 0,3937 in = 3,50 in

This agrees with the direct observation made in **Figure 3.2**.

Let us return to our air-pollution problem. It has probably already occurred to you that simply measuring the mass of smoke collected is not enough. Some other variables may affect your experiment and should also be measured if the results are to be reproducible.

For example, wind direction and speed would almost certainly be important. The time of day and date when a measurement was made should be noted too. In addition you should probably specify what kind of filter you are using. Some are not fine enough to catch all the smoke particles.

Another variable which is almost always recorded is the temperature. A thermometer is easy to use, and temperature can vary a good deal outdoors, where your experiments would have to be done. In scientific work, temperatures are usually reported in degrees Celsius (°C), a scale in which the freezing point of pure water is 0°C and the normal boiling point 100°C.

In the United States, however, you would be more likely to have available a thermometer calibrated in degrees Fahrenheit (°F). The relationship between these two scales of temperature is shown in **Figure 3.3**.

More important than any of the above variables is the fact that the more air you pump through the filter, the more smoke you will collect.

Since air is a gas, it is easier to measure how much you collect in terms of volume than in terms of mass, and so you might decide to do it that way.

Running your pump until it had filled a plastic weather balloon would provide a crude, inexpensive volume measurement. Assuming the balloon to be approximately spherical, you could measure its diameter and calculate its volume from the formula.

$$V = \frac{4}{3}\pi r^3$$

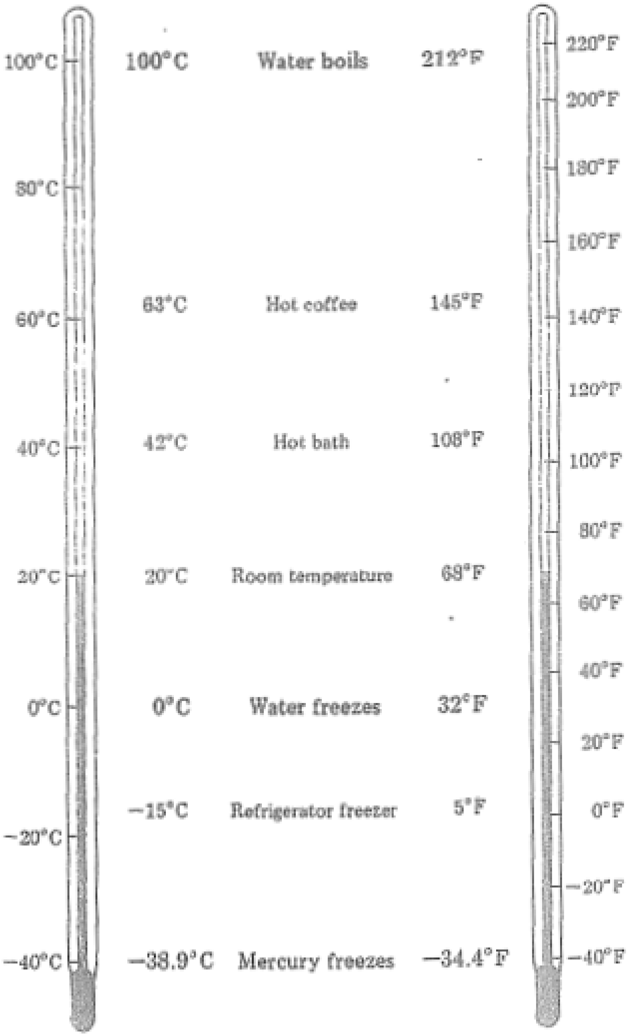


Figure 3.3 The Celsius and Fahrenheit scales compared. Temperatures in bold face are exact and easy to reproduce. Other temperatures are approximate and somewhat variable.

Worked Example 3.1

Calculate the volume of gas in a sphere whose diameter is 106 in. Express your result in cubic centimeters (cm^3).

Solution

Since the radius of a sphere is half its diameter,

$$r = \frac{1}{2}\,x\,106\,in = 53\,cm$$

We can use the same equality of quantities as in **Worked Example 3.1** to convert the radius to centimeters. When we cube the number and units, our result will be in cubic centimeters.

$$1\,cm = 0{,}3937 \text{ in}$$

$$\frac{1\,cm}{0{,}3937\,in} = 1$$

$$r =$$

Using the formula

$$V = \frac{4}{3}\pi r^3 = \frac{4}{3} \times 3{,}141\ 59 \times \left(\frac{53}{0{,}3937}cm\right)^3$$

$$= 10\ 219\ 264 \text{ cm}^3$$

You can see from **Worked Example 3.1** and **Worked Example 3.2** that two unity factors may be obtained from the equality

1 cm = 0,3937 in

We can use one of them to convert inches to centimetres and the other to convert centimetres to inches. The correct factor is always the one which results in cancellation of the units we do not want.

The result in **Worked Example 3.2** also shows that cubic centimetres are rather small units for expressing the volume of the balloon. If we used larger units, as shown in the following example, we would not need more than 10 million of them to report our answer.

Worked Example 3.3

Express the result of **Worked Example 3.2** in cubic meters, given that 1 m = 100 cm.

Solution

Again we wish to use a unity factor, and since we are trying to get rid of cubic centimetres, centimetres must be in the denominator:

$$1 \text{ cm} = 0{,}3937 \text{ in}$$

But this will not allow cancellation of *cubic* centimetres. However, note that 13 = 1. That is, we can raise a unity factor to any power, and it remains unity. Thus

$$1 = \left(\frac{1\,m}{100\,cm}\right)^3 = \frac{1\,m^3}{100^3 cm^3} = \frac{1\,m^3}{1\ 000\ 000\,cm^3}$$

and

$$\begin{aligned} 10\ 219\ 264\ \mathrm{cm}^3 &= 10\ 219\ 264\ cm^3 \times \left(\frac{1\ m}{100\ cm}\right)^3 \\ &= 10\ 219\ 264\ \cancel{cm^3} \times \frac{1\ m^3}{1\ 000\ 000\ \cancel{cm^3}} \\ &= 10{,}219\ 264\ m^3 \end{aligned}$$

3.2.2 Handling Large and Small Numbers and Units

Worked Example 3.2 illustrates a common occurrence in science-results often involve very large numbers or very small fractions. The United States used 66 500 000 000 000 000 000 J (joules) of energy in 1971, and the mass of a water molecule is 0,000 000 000 000 000 000 000 029 9 g.

Such numbers are inconvenient to write and hard. to read correctly. (We have divided the digits into groups of three to make it easier to locate the decimal point.

Spaces are used instead of commas because many countries use a comma to indicate the decimal.)

There are two ways of handling this problem. We can express a quantity in larger or smaller units, as in **Worked Example 3.3**, or we can use a better way to write small and large numbers.

The latter approach involves what is called scientific notation or exponential notation" The position of the decimal point is indicated by a power (or exponent) of 10.

For example,

$$\begin{aligned} 138 &= 13{,}8 \times 10 = 1{,}38 \times 10 \times 10 = 1{,}38 \times 102 \\ 0{,}004\ 83 &= 10 \times \frac{4{,}83}{10 \times 10 \times 10} = 4.83 \times \frac{1}{10^3} = 4{,}83 \times 10^{-3} \end{aligned}$$

A number with a negative exponent is simply the reciprocal of (one divided by) the same number with the equivalent positive exponent. Therefore decimal fractions (numbers between zero and one) may be expressed using negative powers of 10.

Numbers between 1 and 10 require no exponential part, and those larger than 10 involve positive exponents. By convention the power of 10 is chosen so that there is one digit to the left of the decimal point in the ordinary number. That is, we would usually write 5 280 as $5{,}28 \times 10^3$, not as $0{,}528 \times 10^4$ or $52{,}8 \times 10^2$.

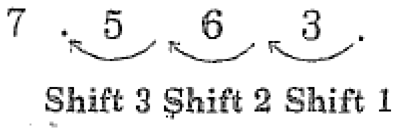
To convert a number from ordinary to scientific notation, count how many places the decimal point must be shifted to arrive at a number between 1 and 10. If these shifts are to the left, the number was large to begin with and we multiply by a large (that is, positive) power of 10. If the shift is to the right, a reciprocal (negative) power of 10 must be used.

Worked Example 3.4

Express the following numbers in scientific notation: (a) 7563; (b) 0,0156.

Solution

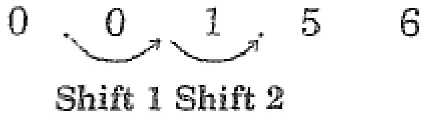
a) In this case the decimal point must be shifted left three places:



Therefore we use an exponent of *+3*:

7563 = 7,563 x 10^3

b) Shifting the decimal point two places to the right yields an between 1 and 10:



Therefore the exponent is *-2*:
0,0156 = 1,56 x 10^{-2}

When working with exponential notation, it is often necessary to add, subtract, multiply, or divide numbers. When multiplying and dividing, you must remember that multiplication corresponds to addition of exponents, and division to their subtraction.

Multiplication: $10^a \times 10^b = 10^{(a+b)}$

Division: $\frac{10^a}{10^b} = 10^{(a-b)}$

Hence:

$$(3{,}0 \times 10^5) \times (5{,}0 \times 10^3) = 15{,}0 \times 10^{(5+3)} = 15{,}0 \times 10^8$$
$$= 1{,}50 \times 10^9$$

and

$$\frac{3{,}0 \times 10^5}{5{,}0 \times 10^3} = 0{,}6 \times 10^{(5-3)} = 0{,}6 \times 10^2 = 6{,}0 \times 10$$

Worked Example 3.5

Evaluate the following, giving your answer in correct exponential notation:

a) $(3{,}89 \times 10^5) \times (1{,}09 \times 10^{-3})$ c) $\frac{5{,}0\times10^6}{3{,}98\times10^8}$

b) $(6{,}41 \times 10^{-5}) \times (2{,}72 \times 10^{-2})$ d) $\frac{7{,}53 \times10^{-3}}{8{,}57 \times 10^{-5}}$

Solution:

a) $(3{,}89 \times 10^5) \times (1{,}09 \times 10^{-3})$ $= 3{,}89 \times 1{,}09 \times 10^{5+(-3)}$
$= 4{,}24 \times 10^2$

b) $(6{,}41 \times 10^{-5}) \times (2{,}72 \times 10^{-2})$ $= 6{,}41 \times 2{,}72 \times 10^{-5+(-2)}$
$= 17{,}43 \times 10^{-7} = 1{,}743 \times 10^{-6}$

c) $\frac{5{,}0\times10^6}{3{,}98\times10^8} = \frac{5{,}0}{3{,}98} \times 10^{6-8} = 1{,}26 \times 10^{-2}$

d) $\frac{7{,}53 \times10^{-3}}{8{,}57 \times 10^{-5}}$ $=\frac{7{,}53}{8{,}57} \times 10^{-3-(-5)} = 0{,}879 \times 10^2$
$= 8{,}79 \times 10^1$

Addition and subtraction require that all numbers be converted to the same power of 10. (This corresponds to lining up the decimal points.)

Worked Example 3.6

Evaluate the following, giving your answer in scientific notation:

a) $(6{,}32 \times 10^2) - (1{,}83 \times 10^{-1})$
b) $(3{,}72 \times 10^4) + (1{,}63 \times 10^5) - (1{,}7 \times 10^3)$

Solution

First convert to the same power of 10; then add the ordinary numbers.

a) $(6{,}32 \times 10^2)$ $= 632$
$- (1{,}83 \times 10^{-1})$ $= \frac{-0{,}183}{631{,}817} = 6{,}318\,17 \times 10^2$

b) Convert all powers of 10 to 10⁴.
$3{,}72 \times 10^4$ $= 3{,}72 \times 10^4$ $= 3{,}72 \times 10^4$
$1{,}63 \times 10^5$ $= 1{,}63 \times 10 \times 10^4$ $= 16{,}3 \times 10^4$
$-1{,}7 \times 10^3$ $= -1{,}7 \times 10^{-1} \times 10^4$ $= \frac{-0{,}17\times10^4}{19{,}85\times10^4} = 1{,}985 \times 10^5$

Scientific notation is becoming more common every day. Many electronic pocket calculators use it to express numbers which otherwise would not fit into their displays.

For example, an eight-digit calculator could not display the number 6 800 000 000. The decimal point would remain fixed on the right, and the 6 and the 8 would "overflow" to the left side. Such a number is often displayed as 6.8 09, which means 6,8 x 10^9.

If you use a calculator which does not have scientific notation, we recommend that you express all numbers as powers of 10 before doing any arithmetic.

Follow the rules in the last two examples, using your calculator to do arithmetic on the ordinary numbers. You should be able to add or subtract the powers of 10 in your head.

Computers also are prone to print results in scientific notation, and they use yet another minor modification. The printed number 2.3074 E-07 means $2,3074 \times 10^{-7}$, for example.

In this case the E indicates that the number following is an exponent of 10.

3.2.3 Too Many Digits

Returning once more to our air-pollution experiment, we could express the mass of smoke collected as $3,42 \times 10^{-2}$ g and the volume of the balloon as $1,021\,926\,4 \times 10^{7}$ cm^3.

There is something strange about the second quantity, though. It contains a number which was copied directly from the display of an electronic calculator and has too many digits.

The reliability of a quantity derived from a measurement is customarily indicated by the number of significant figures (or significant digits) it contains.

For example, the three significant digits in the quantity $3,42 \times 10^{-2}$ g tell us that a balance was used on which we could distinguish $3,42 \times 10^{-2}$ g from $3,43 \times 10^{-2}$ or $3,41 \times 10^{-2}$ g.

There might be some question about the last digit, but those to the left of it are taken as completely reliable. Another way to indicate the same thing is $(3,42 \pm 0.01) \times 10^{-2}$ g. Our measurement is somewhere between $3,41 \times 10^{-2}$ and $3,43 \times 10^{-3}$ g.

As another example of choosing an appropriate number of significant digits, let us read the volume of liquid in a graduated cylinder (**Figure 3.4**).

The bottom of the meniscus lies between graduations corresponding to 38 and 39 cm^3. We can estimate that it is at 38,5 cm^3 , but the last digit might be off a bit - perhaps it looks like 38,4 or 38,6 cm^3 to you.

Since the third digit is in question, we should use three significant figures. The volume would be recorded as 38,5 cm^3.

Laboratory equipment is often calibrated similarly to this graduated cylinder - you should estimate to the nearest tenth of the smallest graduation.

In some ordinary numbers, for example, 0,001 23, zeros serve merely to locate the decimal point. They do not indicate the reliability of the measurement and therefore are not significant.

Another advantage of scientific notation is that we can assume that all digits are significant. Thus if 0,001 23 is written as 1,23 x 10^{-3}, only the 1, 2, and 3, which indicate the reliability of the measurement, are written. The decimal point is located by the power of 10.

If the rule expressed in the previous paragraph is applied to the volume of air collected in our pollution experiment, 1,021 926 4 x 10^7 cm^3 , we find that the volume has eight significant digits. This implies that it was determined to ± 1 cm^3 out of about 10 million cm^3 , a reliability which corresponds to locating a grasshopper exactly at some point along the road from Philadelphia to New York City. For experiments as crude as ours, this is not likely.

Let us see just how good the measurement was. You will recall that we calculated the volume from the diameter of the balloon, 106 in. The three significant figures imply that this might have been as large as 107 in or as small as 105 in. We can repeat the calculation with each of these quantities to see how far off the volume would be:

Figure 3.4 The level of a liquid in a graduated cylinder. The saucer-shaped surface of a liquid in a tube is called a meniscus.

$$
\begin{aligned}
r &= \tfrac{1}{2} \times 1{,}07\ in = 53{,}5\ \cancel{in} \times \frac{1\ cm}{0{,}3937\ \cancel{in}} \\
&= 135{,}890\ 27\ cm \\
V &= \tfrac{4}{3} \times 3{,}141\ 59\ \times (135{,}890\ 27\ cm)^3 \\
&= 10\ 511\ 225\ cm^3 = 1{,}051\ 122\ 5\ \times\ 10^7 cm^3
\end{aligned}
$$

Or

$$
\begin{aligned}
V &= \tfrac{4}{3} \times 3{,}141\ 59\ \times (\tfrac{1}{2} \times 105\ \cancel{in} \times \frac{1\ cm}{0{,}3937\ \cancel{in}})^3 \\
&= 9\ 932\ 759\ cm^3 = 1{,}993\ 275\ 9\ \times\ 10^7 cm^3
\end{aligned}
$$

That is, the volume is between 0,99 x 10^7 and 1,05 x 10^7 cm^3 , or (1,02 ± 0,03) x 10^7 cm^3.

We should round our result to three significant figures, for example, 1,02 x 10^7 cm^3, because the last digit, namely 2, is in question.

Note: Rules for rounding numbers

1. All digits to be rounded are removed together, not one at a time.
2. If the left-most digit to be removed is less than five, the last digit retained is not altered.
3. If the left-most digit to be removed is greater than five, the last digit retained is increased by one.
4. If the left-most digit to be removed is five and at least one of the other digits to be removed is nonzero, the last digit retained is increased by one.
5. If the left-most digit to be removed is five and all other digits to be removed are zero, the last digit retained is not altered if it is even, but is increased by one if it is odd.

The rules for rounding numbers are summarized above. Their application can be illustrated by an example.

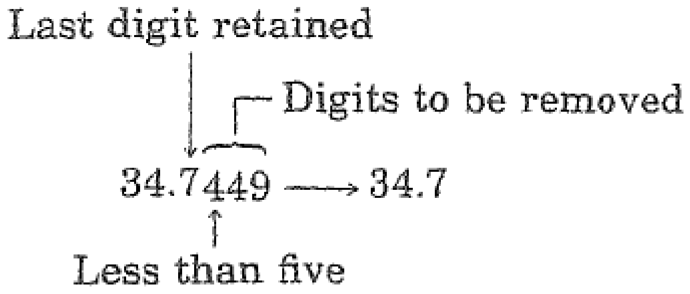
Worked Example 3.7

Round each of the numbers below to three significant figures.

a) 34,7449 b) 34,864 c) 34,754 d) 34,250 e) 34,35

Solution

a) Apply rules 1 and 2.



Note that a different result would be obtained if the digits were incorrectly rounded one at a time from the right.

b) Apply rules 1 and 3: 34,864 → 34,9
c) Apply rules 1 and 4: 34,754 → 34,8
d) Apply rules 1 and 5: 34,250 → 34,2
e) Apply rule 5: 34,35 → 34,4

To how many significant figures should we round our air-pollution results? We have already done a calculation involving multiplication and division to obtain the volume of our gas-collection balloon. It involved the following numbers:

106	Three significant figures
0,3937	Four significant figures
3,141 59	Six significant figures (we could obtain more if we wanted)
$\frac{4}{3}\ and\ \frac{1}{2}$	An infinite number of significant figures since the Integers in these fractions are exact by definition.

The result of the calculation contained three significant figures - the same as the least-reliable number. This illustrates the general rule that for multiplication and division the number of significant figures in the result is the same as in the least-reliable measurement.

Defined numbers such as $\pi, \frac{1}{2}, \frac{4}{3}, or\ 100\frac{cm}{1}m$ are assumed to have an infinite number of significant figures.

In the case of addition and subtraction, a different rule applies. Suppose, for example, that we weighed a smoke-collection filter on a relatively inaccurate balance that could only be read to the nearest 0,01 g.

After collecting a sample, the filter was reweighed on a single-pan balance to determine the mass of smoke particles.

Final mass:	2,3745 g	(coloured digits are in question)
Initial mass:	-2,32 g	
Mass of smoke:	0,0545 g	

Since the initial weighing could have been anywhere from 2,31 to 2,33 g, all three figures in the final result are in question. (It must be between 0,0445 and 0,0645 g). Thus there is but one significant digit, and the result is 0,05 g.

The rule here is that the result of addition or subtraction cannot contain more digits to the right than there are in any of the numbers added or subtracted.

⚠ Note that subtraction can drastically reduce the number of significant digits when this rule is applied.

Rounding numbers is especially important if you use an electronic calculator, since these machines usually display a large number of digits, most of which are meaningless.

The best procedure is to carry all digits to the end of the calculation (your calculator will not mind the extra work!) and then round appropriately.

Answers to subsequent calculations will be rounded according to the rules given. You may wish to go back to previous examples and round their answers correctly as well.

Worked Example 3.8

Evaluate the following expressions, rounding the answer to the appropriate number of significant figures.

a) $32{,}61\ g\ +\ 8{,}446\ g\ +\ 7{,}0\ g$
b) $0{,}136\ cm^3\ x\ 10{,}685\ g\ cm^{-3}$

Solution

a) $32{,}61\ g\ +\ 8{,}446\ g\ +\ 7{,}0\ g = 48{,}056\ g = 48{,}1\ g$ (7,0 has only one figure to the right of the decimal point.)
b) $0{,}136\ cm^3\ x\ 10{,}685\ g\ cm^{-3} = 1{,}453\ 16\ g = 1{,}45\ g.$ (0,136 has only three significant figures.)

When we suggested filling a surplus weather balloon to measure how much gas was pumped through our air-pollution collector, we mentioned that this would be a rather crude way to determine volume.

For one thing, it would not be all that simple to measure the diameter of an 8- or 9-ft sphere reliably. Using a yardstick, we would be lucky to have successive measurements agree within half an inch or so. It was for this reason that the result was reported to the nearest inch. The degree to which repeated measurements of the same quantity yield the same result is called precision.

Repetition of a highly precise measurement would yield almost identical results, whereas low precision implies numbers would differ by a significant percentage from each other.

A highly precise measurement of the diameter of our balloon could be achieved, but it would probably not be worthwhile. We have assumed a spherical shape, but this is almost certainly not exactly correct.

No matter how precisely we determine the diameter, our measurement of gas volume will be influenced by deviations from the assumed shape. When one or more of our assumptions about a measuring instrument are wrong, the accuracy of a result will be affected.

An obvious example would be a foot rule divided into 11 equal inches. Measurements employing this instrument might agree very precisely, but they would not be very accurate. An important point of a different kind is illustrated in the last two paragraphs.

A great many common words have been adopted into the language of science. Usually such an adoption is accompanied by an unambiguous scientific definition which does not appear in a normal dictionary.

Note:
Precision and accuracy are many times treated as synonyms, but in science each has a slightly different meaning.

Another example is quantity, which we have defined in terms of "number x unit."

Other English words like bulk, size, amount, and so forth, may be synonymous with quantity in everyday speech, but not in science. As you encounter other words like this, try to learn and use the scientific definition as soon as possible, and avoid confusing it with the other meanings you already know.

Even granting the crudeness of the measurements we have just described, they would be adequate to demonstrate whether or not an air pollution problem existed.

The next step would be to find a chemist or public health official who was an expert in assessing air quality, present your data, and convince that person to lend his or her skill and authority to your contention that something was wrong.

Such a person would have available equipment whose precision and accuracy were adequate for highly reliable measurements and would be able to make authoritative public statements about the extent of the air-pollution problem.

3.3 The International System of Units (SI)

The results of a scientific experiment must be communicated to be of value. This affords an opportunity for other scientists to check them. It also allows the scientific community, and sometimes the general public, to share new knowledge.

Communication, however, is not always as straightforward as it might seem. Ambiguous terminology can often turn a seemingly clear statement into a morass of misunderstanding.

As an example, consider what happened when the United States first confronted the energy crisis during 1973 and 1974. Government asked various experts to estimate and compare reserves of coal, petroleum, and natural gas which could be recovered from the earth at no more than twice current costs.

The result was an estimate of 350 billion tons of coal, 180 billion barrels of petroleum, and 1000 billion MCF of natural gas (1 MCF equals 1000 cubic feet) in the ground. Sounds simple, does it not?

Unfortunately these quantities have very little meaning when examined carefully because they are not accurately defined. For one thing, two different tons are used in United States commerce. These are the short ton (2000 lb) and the long ton (2240 lb).

Neither should be confused with the metric ton (2204,6 lb - often written tonne) which most of the rest of the world uses. With regard to barrels, a US barrel of petroleum contains 42 US gallons (that is, 35 British or imperial gallons), but a US barrel of any other liquid contains 31,5 US gallons.

Even more confusing is the term MCF, where CF stands for cubic feet and M is the roman numeral for 1000 (10^3). The capital M might well be confused with the metric system prefix which means 1 000 000 (10^6).

More importantly, since the measurement refers to gas volume, which varies with temperature and pressure, we need to know under what conditions it was made. To add a last confusing note, the word billion used in all these estimates means 1 000 000 000 (10^9) in the United States, but 1 000 000 000 000 (10^{12} - what we call a trillion) in Europe.

If in the midst of this hodgepodge, you asked, "Would it not be easier to have a single unit for mass, a single unit for volume, and express all masses or volumes in these units," you would not be the first person to have such an idea.

The main difficulty is that it is hard to get everyone to agree on a single consistent set of units. Some units are especially convenient for some tasks. For example, a yard was originally defined as the distance from a man's nose to the end of his thumb when his arm was held horizontally to one side. This made it easy to measure cloth or ribbon by holding one end to the nose and stretching an arm's length with the other hand.

Now that yardsticks, meter sticks, and other devices are readily available, the original utility of the yard is gone, but we still measure ribbon and cloth in that same unit. Many people would probably be distressed if a change were made.

Scientists are not all that different from other people - they too have favorite units - which are especially suited to certain areas of research. Nevertheless, scientists have constantly pressed for improvement and uniformity in systems of measurement.

The first such action occurred nearly 200 years ago when, in the aftermath of the French Revolution, the metric system spread over most of continental Europe and was adopted by scientists everywhere. The United States nearly followed suit, but in 1799 Thomas Jefferson was unsuccessful in persuading Congress that a system based on powers of 10 was far more convenient and would eventually become the standard of the world.

The metric system has undergone continuous evolution and improvement since its original adoption by France. Beginning in 1899, a series of international conferences have been held for the purpose of redefining and regularizing the system of units.

In 1960 the Eleventh Conference on Weights and Measures proposed major changes in the metric system and suggested a new name - the International System of Units - for the revised metric system. (The abbreviation from the French Systeme International, is commonly used.)

Scientific bodies such as the US National Bureau of Standards and the International Union of Pure and Applied Chemistry have endorsed the SI.

At the heart of the SI are the seven units listed in **Table 3.1**. All other units are derived from these seven so-called base units. For example, units for area and volume may be derived by squaring or cubing the unit for length.

Quantity measured	Name of unit	Symbol for unit
Length	meter	m
Mass	kilogram	kg
Time	second	s
Electric current	ampere	A
Temperature	kelvin	K
Amount of substance	mole	mol
Luminous intensity	candela	Cd

Table 3.1 The seven base units of the SI

Some of the base units are probably familiar to you, while others, such as the mole, candela, and kelvin, may be less so.

Rather than defining each of them now, we shall wait until later chapters when the less familiar units, as well as the quantities they are used to measure, can be described in detail.

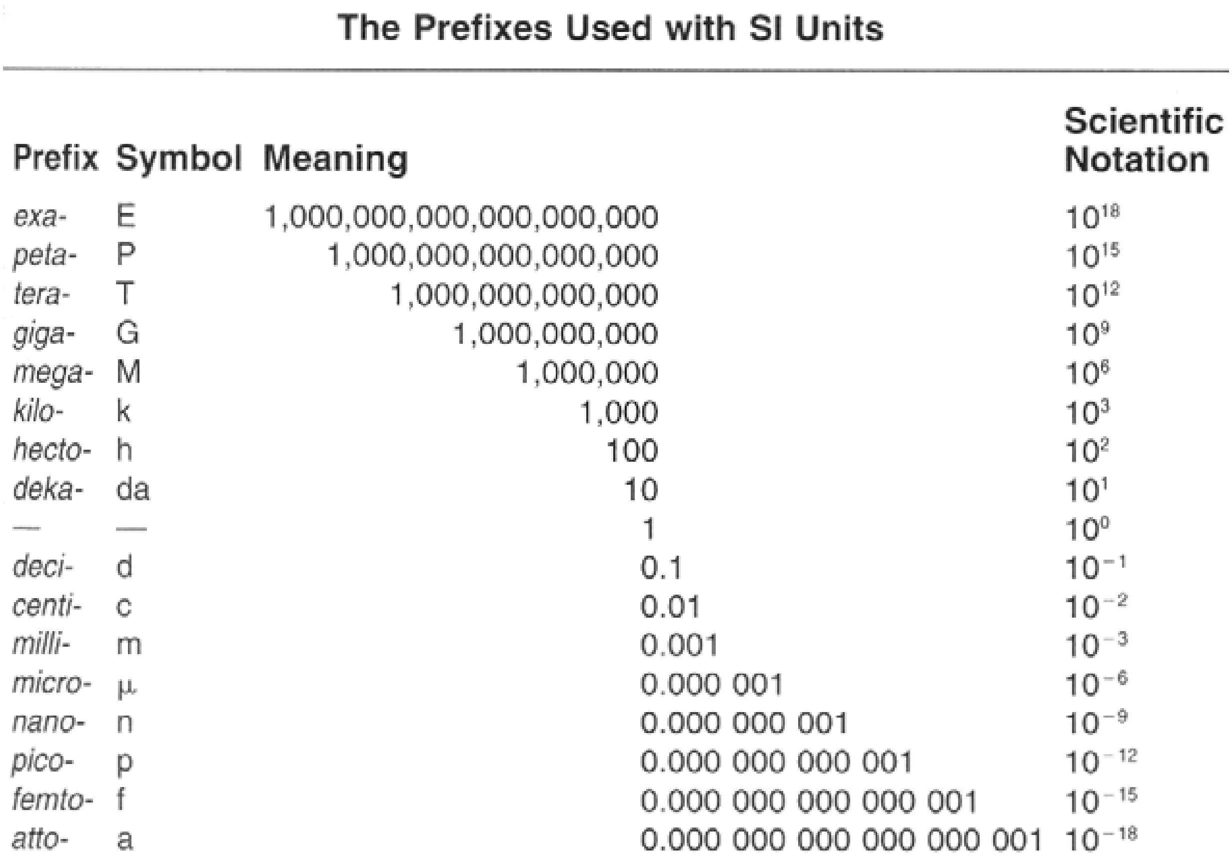
The candela, which measures the intensity of light, is not used often by chemists, and so we shall pay no further attention to it.

3.3.1 Prefixes

The SI base units are not always of convenient size for a particular measurement.

For example, the meter would be too big for reporting the thickness of this page, but rather small for the distance from Chicago to Detroit.

To overcome this obstacle the SI includes a series of prefixes, each of which represents a power of 10 (**Figure 3.5**). These allow us to reduce or enlarge the SI base units to convenient sizes.



The Prefixes Used with SI Units

Prefix	Symbol	Meaning	Scientific Notation
exa-	E	1,000,000,000,000,000,000	10^{18}
peta-	P	1,000,000,000,000,000	10^{15}
tera-	T	1,000,000,000,000	10^{12}
giga-	G	1,000,000,000	10^{9}
mega-	M	1,000,000	10^{6}
kilo-	k	1,000	10^{3}
hecto-	h	100	10^{2}
deka-	da	10	10^{1}
—	—	1	10^{0}
deci-	d	0.1	10^{-1}
centi-	c	0.01	10^{-2}
milli-	m	0.001	10^{-3}
micro-	μ	0.000 001	10^{-6}
nano-	n	0.000 000 001	10^{-9}
pico-	p	0.000 000 000 001	10^{-12}
femto-	f	0.000 000 000 000 001	10^{-15}
atto-	a	0.000 000 000 000 000 001	10^{-18}

Figure 3.6 shows how these prefixes can be applied to the meter to cover almost the entire range of lengths we might wish to measure.

One non-SI unit of length, the angstrom (Å), is convenient for chemists and will continue to be used for a limited time. Since 1 Å = 10^{-10} m (see **Figure 3.6**), the angstrom corresponds roughly to the diameters of atoms and small molecules.

Such dimensions are also conveniently expressed in picameters, 1 pm = 10^{-12} m = 0.01 Å, but the angstrom is widely used and very familiar. Therefore we will usually write atomic and molecular dimensions in both angstroms and picometers.

The SI base unit of mass, the kilogram, is unusual because it already contains a prefix. The standard kilogram is a cylinder of corrosion resistant platinum-iridium alloy which is kept at the International Bureau of Weights and Measures near Paris.

The kilogram was chosen instead of a gram because the latter would have made an inconveniently small piece of platinum-iridium and would have been difficult to handle. Also, units of force, pressure, energy, and power have been derived using the kilogram instead of the gram.

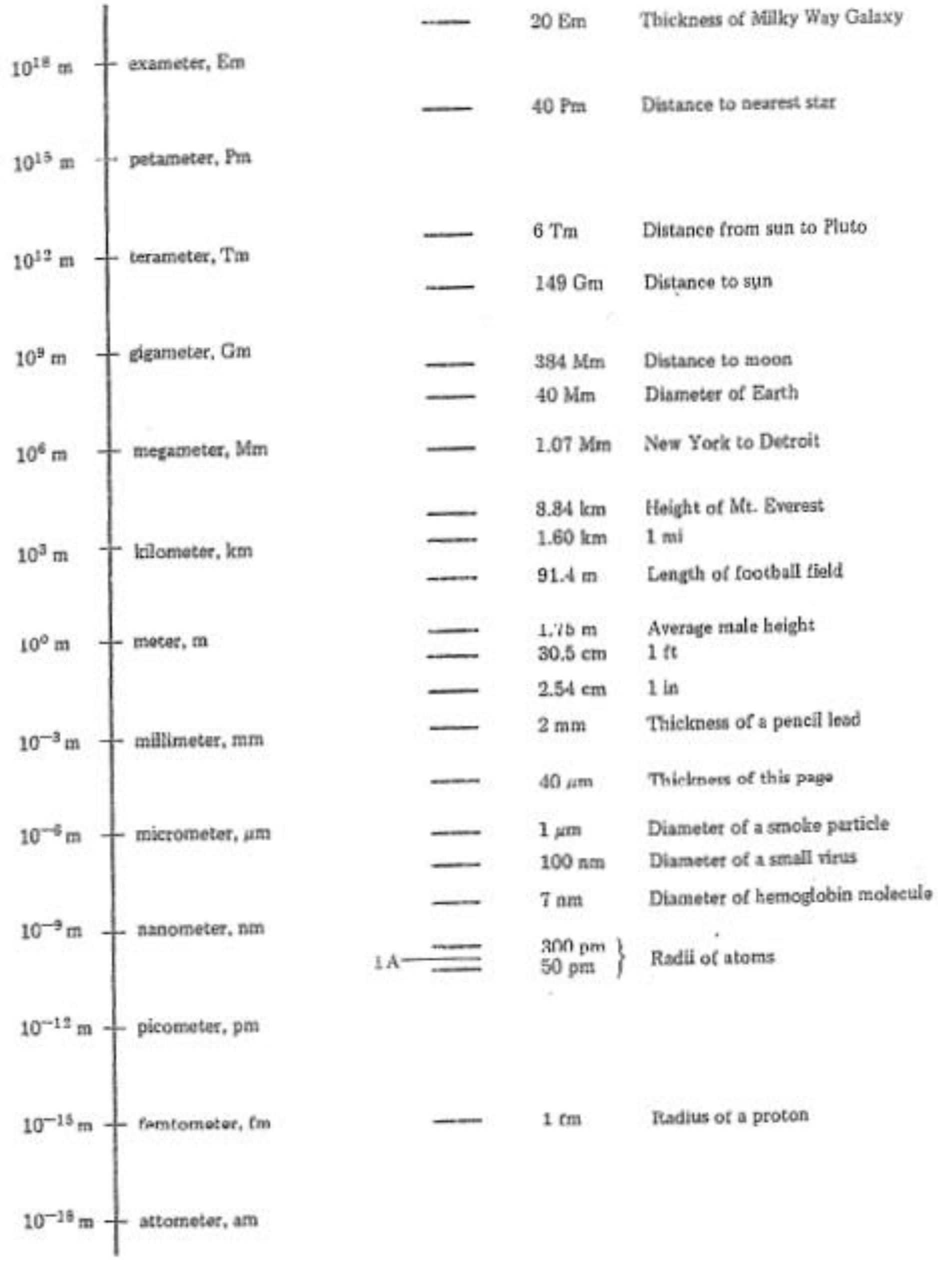


Figure 3.6 The magnitudes of some distances and lengths in the range 10^{18} through 10^{-18} m, expressed in SI units

Despite the fact that the kilogram is the SI unit of mass, the standard prefixes are applied to the gram when larger or smaller mass units are needed.

For example, the quantity 10^6 kg (1 million kilograms) can be written as 1 Gg (gigagram) but not as 1 Mkg (megakilogram). The operative rule here is that one and only one prefix should be attached to the name for a unit.

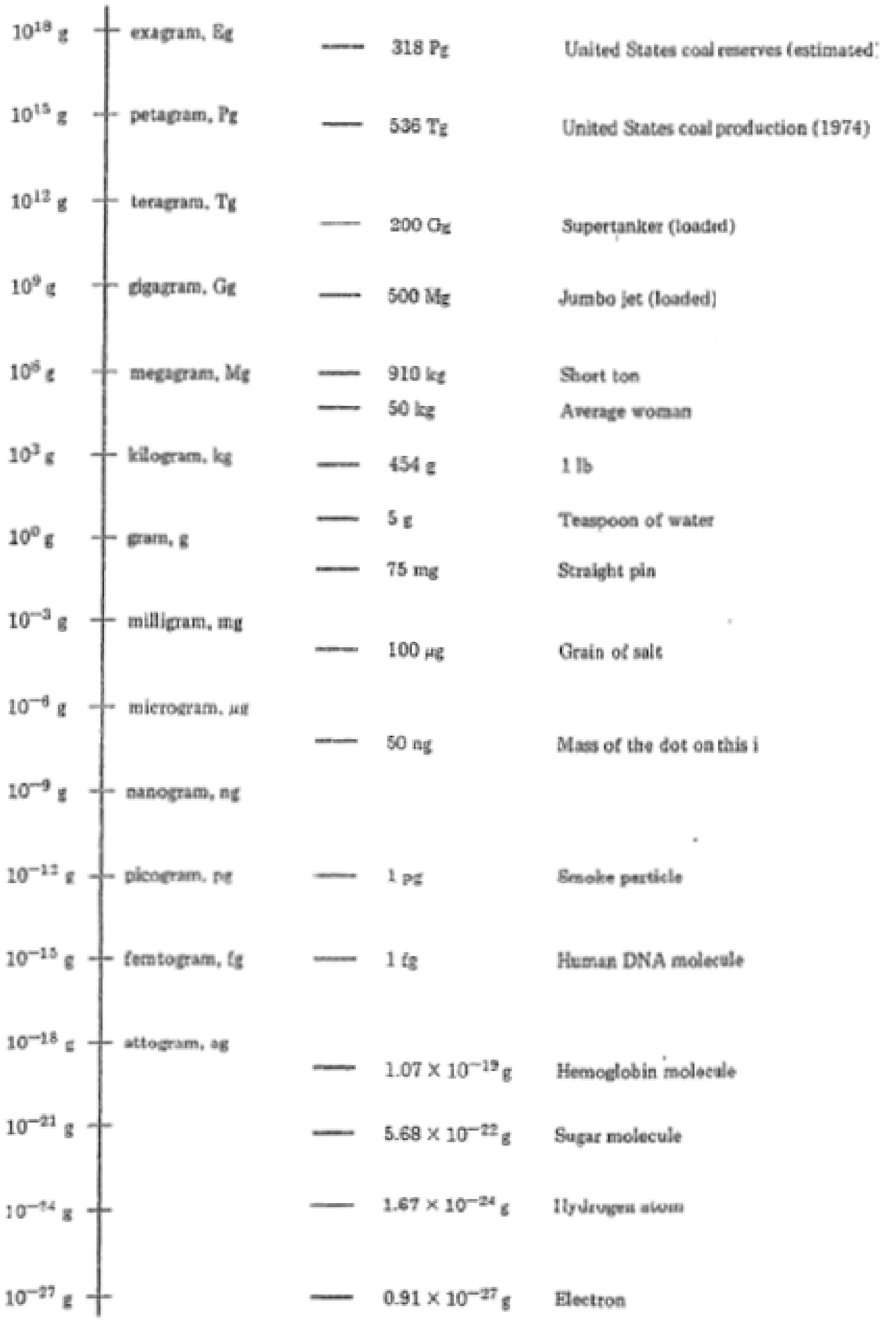


Figure 3.7 The masses of some objects in the range 10^{18} through 10^{-27} g, expressed in SI units

3.3.2 Volume

The most commonly used derived units are those of volume. As we have already seen, calculation of the volume of an object requires that a length be cubed or that three lengths be multiplied together. Thus the SI unit of volume is the cubic meter (m^3).

This is rather large for use in the chemical laboratory, and so the cubic decimeter (dm^3) or cubic centimetre (cm^3, formerly cc) are more commonly used. The relationship between these units and the cubic meter is easily shown:

1 dm = 0,1 m 1 cm = 0,01 m

Cubing both sides of each equation, we have

$1\ dm^3 = 0{,}1^3\ m^3 = 0{,}001\ m^3 = 10^{-3}\ m^3$

$1\ cm^3 = 0{,}01^3\ m^3 = 0{,}000\ 001\ m^3 = 10^{-6}\ m^3$

Note:
In the expression dm^3 the exponent includes the prefix as well as the base unit. A cubic decimetre is one-thousandth of a cubic meter, not one-tenth of a cubic meter.

Two other units of volume are commonly encountered in the chemical laboratory - the litre (l) and the millilitre (ml - one-thousandth of a litre).

The litre was originally defined as the volume of one kilogram of pure water at the temperature of its maximum density (3.98°C), but in 1964 the definition was changed.

The litre is now exactly one-thousandth of a cubic meter, that is, 1 dm^3. A millilitre is therefore exactly 1 cm^3. Because the new definition of litre altered its volume slightly, it is recommended the results of highly accurate measurements be reported in the SI units cubic decimetres or cubic centimetres, rather than in litres of millilitres.

For most situations discussed, however, the units cubic decimetre and litre, and litre, and cubic centimetre and millilitre may be used interchangeably. Thus when recording a volume obtained from laboratory glassware calibrated in millilitres, you can just as well write 24,7 cm^3 as 24,7 ml.

3.3.3 Density

The terms heavy and light are commonly used in two different ways.

We refer to weight when we say that an adult is heavier than a child. On the other hand, something else is alluded to when we say that oak is heavier than balsa wood. A small shaving of oak would obviously weigh less than a roomful of balsa wood, but oak is heavier in the sense that a piece of given size weighs more than the same-size piece of balsa.

What we are actually comparing is the mass per unit volume, that is, the density. In order to determine these densities, we might weigh a cubic centimetre of each type of wood.

If the oak sample weighed 0,71 g and the balsa 0,15 g, we could describe the density of oak as 0,71 g cm^{-3} and that of balsa as 0,15 g cm^{-3}.

Note:
The negative exponent in the units cubic centimetres indicates a reciprocal.

Thus 1 cm^{-3} = 1/cm^3 and the units for our densities could be written as $\frac{g}{cm^3}$, or g/cm^3 or g cm^{-3}. In each case the units are read as grams per cubic centimetre, the *per* indicating division.)

In general it is not necessary to weigh exactly 1 cm^3 of a material in order to determine its density. We simply measure mass and volume and divide volume into mass:

$$Density = \frac{mass}{volume} \qquad \text{or} \qquad \rho = \frac{m}{V}$$

where $\rho = density \quad m = mass \quad V = volume$

Worked Example 3.9

Calculate the density of (a) a piece of aluminium whose mass is 37,42 g and which, when submerged, increases the water level in a graduated cylinder by 13,9 ml; (b) an aluminium cylinder or mass 25,07 g, radius 0,750 m, and height 5,25 cm.

Solution:

(a) Since the submerged metal displaces its own volume,

$$Density = \rho = \frac{m}{V} = \frac{37{,}42\ g}{13{,}9\ ml} = 2{,}69\frac{g}{ml}\ or\ 2{,}69\ g\ ml^{-1}$$

(b) The volume of the cylinder must be calculated first, using the formula

$$\begin{aligned} V &= \pi r^2 h \\ &= 3{,}142 \times (0{,}750\ cm)^2 \times 5{,}25\ cm \\ &= 9{,}278\ 718\ 8\ cm^3 \\ \text{Then}\quad \rho &= \frac{m}{V} = \frac{25{,}07\ g}{9{,}278\ 718\ 8\ cm^3} \\ &= 2{,}70\ \frac{g}{cm^2}\ or\ 2{,}70\ g\ cm^{-3}\ or\ 2{,}70\ g/cm^3 \end{aligned}$$

[all acceptable alternatives]

Note:
Unlike mass or volume, the density of a substances is independent of the size of the sample.

Thus density is a property by which one substances can be distinguished from another. A sample of pure aluminium can be trimmed to any desired volume or adjusted to have any mass we choose, but its density will always be 2,70 g/cm^3 at 20°C. The densities of some common pure substances are listed in Table 3.4.

Tables and graphs are designed to provide a of information in a minimum of space. When a physical quantity (number x units) is involved, it is wasteful to keep repeating the same units. Therefore it is conventional to use pure numbers in a table or along the axes of a graph.

A pure number can be obtained from a quantity if we divided by appropriate units. For example, when divided by the units gram per cubic centimetres the density of aluminium becomes a pure number 2,70:

$$\frac{Density\ of\ aluminium}{1\ g\ cm^{-3}} = \frac{2{,}70\ \cancel{g\ cm^{-3}}}{1\ \cancel{g\ cm^{-3}}} = 2{,}70$$

Substance	**Density/g cm^{-3*}**
Helium gas	0,000 16
Dry air	0,001 185
Gasoline	0,66→0,69 (varies)
Kerosene	0,82
Benzene	0,880
Water	1,000
Carbon tetrachloride	1,595
Magnesium	1,74
Salt	2,16
Aluminium	2,70
Iron	7,87
Copper	8,96
Silver	10,5
Lead	11,34
Uranium	19,05
Gold	19,32

Table 3.2 Density of several substances at 20°C

Therefore, a column in a table or the axis of a graph is conveniently labelled in the following form:

$$\text{Quantity/units}$$

This indicates the units that must be divided into the quantity to yield the pure number in the table or on the axis. This has been done in the second column of **Table 3.2**.

3.4 Conversion factors

When we are referring to the same object or sample of material, it is often useful to be able to convert one kind of quantity into another. For example, in our discussion of fossil-fuel reserves we could define the quantities unambiguously by stating that 318 Pg (3,18 x 10^{17} g) of coal, 28,6 km^3 (2,86 x 10^{10} m^3) of petroleum, and 2,83 x 104 km^3 (2,83 x 10^{13} m^3) of natural gas (measured at normal atmospheric pressure and 15,5°C) are available.

But none of these quantities tells us what we really want to know – how much heat energy could be released by burning each of these reserves?

Only by converting the mass of coal and the volumes of petroleum and natural gas into their equivalent energies can we make a valid comparison.

When this is done, we find that the coal could release 7.2 x 1021 J, the petroleum 1,1 x 10^{21}J, and the gas 1,1 x 10^{21}J of heat energy. Thus the reserves of coal are more than three times those of the other two fuels combined.

It is for this reason that more attention is being paid to the development of new ways for using coal resources than to oil or gas.

Conversion of one kind of quantity into another is usually done with what we shall call a conversion factor. Since we have not yet discussed energy or the units (joules) in which it is measured, an example involving the more familiar quantities mass and volume will be used to illustrate the way conversion factors are employed.

The same principles apply to finding how much energy would be released by burning a fuel, and that problem will be encountered later.

Suppose we have a rectangular solid sample of gold which measures 3,04 cm x 8,14 cm x 17,3 cm. We can easily calculate that its volume is 428 cm^3, but how much is it worth?

The price of gold is about 5 dollars per gram, and so we need to know the mass rather than the volume. It is unlikely that we would have available a scale or balance which could weigh accurately such a large, heavy sample, and so we would have to determine the mass of gold equivalent to a volume of 428 cm^3.

This can be done by manipulating Eq(1.1) which defines density. If we multiply both sides by V, we obtain:

$$V \times \rho \quad = \frac{m}{\cancel{V}} \times \cancel{V} = m$$

$$m \quad = V\rho \text{ or mass = volume x density} \qquad (1.2)$$

Taking the density of gold from **Table 3.2**, we can now calculate

$$Mass \ = \ m \quad = V\rho \times 428\cancel{cm^3} \times \frac{19{,}32\ g}{1\ \cancel{cm^3}}$$

$$= 8{,}27 \times 10^3 g = 8{,}27\ kg$$

This is more than 18 lb of gold. At the price quoted above, it would be worth over 40 000 dollars!

The formula which defines density can also be used to convert the mass of a sample to the corresponding volume. If both sides of Eq(1.2) are multiplied by $1/\rho$, we have

$$\begin{aligned} \frac{1}{\rho} \times m &= V\cancel{\rho} \times \frac{1}{\cancel{\rho}} = V \\ V &= m \times \frac{1}{\rho} \end{aligned} \qquad (1.3)$$

Worked Example 3.10

Find the volume occupied by a 4,73 g sample of benzene.

Solution

According to **Table 3.2**, the density of benzene is 0,880 g cm^{-3}. Using Eq(1.3),

$$\begin{aligned} Volume = V = m\,x\,\frac{1}{\rho} &= 4.73\,\cancel{g} \times \frac{1\,cm^3}{0{,}880\,\cancel{g}} \\ &= = 5{,}38\,cm^3 \end{aligned}$$

(Note that taking the reciprocal of $\frac{0{,}880\,g}{1\,cm^3}$. Simply inverts the fraction – 1 cm^3 goes on top, and 0,880 g goes on the bottom.)

The two calculations just done show that density is a conversion factor which changes volume to mass, and the reciprocal of density is a conversion factor changing mass into volume.

This can be done because of the mathematical formula, Eq(1.1), which relates density, mass, and volume. Algebraic manipulation of this formula gave us expressions for mass and for volume [Eq(1.2) and Eq(1.3)], and we used them to solve our problems.

In practice, however, it is unnecessary to remember all three formulas or do the algebra to derive one from another. It is much easier just to manipulate the quantities involved until the result has the correct units, as shown in the following example.

Worked Example 3.11

A student weighs 98,0 g of mercury. If the density of mercury is 13,6 g/cm^3, what volume does the sample occupy?

Solution

We know that volume is related to mass through density.

Therefore

$$V = m \times conversion\,factor$$

Since the mass is in grams, we need to get rid of these units and replace them with volume units. This can be done if the reciprocal of the density is used as a conversion factor. This puts grams in the denominator so that these units cancel:

$$\begin{aligned} V &= m \times \frac{1}{\rho} \\ &= 98{,}0\,\cancel{g} \times \frac{13{,}6\,g}{1\,cm^3} = 7{,}21\,cm^3 \end{aligned}$$

If we had multiplied by the density instead of its reciprocal, the units of the result would immediately show our error:

$$V = 98{,}0\,g \times \frac{13{,}6\,g}{1cm^3} = 1333\,\frac{g^2}{cm^3}\,\text{(no cancellation)}$$

It is clear that square grams per cubic centimetre are not the units we want.

Using a conversion factor is very similar to using a unity factor – we know the factor is correct when units cancel appropriately. A conversion factor is not unity, however. Rather it is a physical quantity (or the reciprocal of a physical quantity) which is related to the two other quantities we are interconverting.

The conversion factor works because of that relationship [Eqs(1.1), (1.2), and (1.3) in the case of density, mass, and volume], not because it is equal to one.

Once we have established that a relationship exists, it is no longer necessary to memorize a mathematical formula. The units tell us whether to use the conversion factor or its reciprocal. Without such a relationship, however, mere cancellation of units does not guarantee that we are doing the right thing.

A simple way to remember relationships among quantities and conversion factors is a "road map" of the type shown below:

$$\text{Mass} \xleftrightarrow{\text{density}} \text{volume} \qquad \text{or} \qquad m \xleftrightarrow{\rho} V$$

This indicates that the mass of a particular sample of matter is related to its volume (and the volume to its mass) through the conversion factor, density.

The double arrow indicates that a conversion may be made in either direction, provided the units of the conversion factor cancel those of the quantity which was known initially. In general the road map can be written:

$$\text{First quantity} \xleftrightarrow{\text{conversion factor}} \text{second quantity}$$

As we come to more complicated problems, where several steps are required to obtain a final result, such road maps will become more useful in charting a path to the solution.

Worked Example 3.12

Black ironwood has a density of 67,24 lb/ft^3. If you had a sample whose volume was 47,3 ml, how many grams would it weigh? (1 lb = 454 g; 1 ft = 30,5 cm).

Solution

The road map

$$V \xrightarrow{\rho} m$$

tells us that the mass of the sample may be obtained from its volume using the conversion factor, density. Since millilitres and cubic centimetres are the same, we use the SI units for our calculation:

$$Mass = m = 47{,}3\ cm^3 \times \frac{67{,}24\ lb}{a\ ft^3}$$

Since the volume units are different, we need a unity factor to get them to cancel:

$$\begin{aligned} m &= 47{,}3\ cm^3 \times \left(\frac{1\ ft}{30{,}5\ cm}\right)^3 \times \frac{67{,}24\ lb}{1\ ft^3} \\ &= 47{,}3\ \cancel{cm^3} \times \frac{1\ \cancel{ft^3}}{30{,}5^3\ \cancel{cm^3}} \times \frac{67{,}24\ lb}{1\ \cancel{ft^3}} \end{aligned}$$

We now have the mass in pounds, but we want it in grams, so another unity factor is needed:

$$\begin{aligned} m &= 47{,}3\ cm^3 \times \frac{1\ \cancel{ft^3}}{30{,}5^3\ \cancel{cm^3}} \times \frac{67{,}24\ \cancel{lb}}{1\ \cancel{ft^3}} \times \frac{454\ g}{\cancel{1lb}} \\ m &= 50{,}9\ g \end{aligned}$$

In subsequent chapters we will establish a number of relationship among physical quantities. Formulas will be given which define these relationships, but we do not advocate slavish memorization and manipulation of those formulas.

Instead we recommend that you remember that a relationship exists, perhaps in terms of a road map, and then adjust the quantities involved so that the units cancel appropriately. Such an approach has the advantage that you can solve a wide variety of problems by using the same technique.

3.5 Summary

Chemistry is concerned with the composition, properties, and structure of matter, and with processes in which one substance changes into another. Chemistry does not just take place in laboratories but happens all the time, everywhere.

Consequently this subject is very important to many persons who are not called chemists. In this book we will try to provide you with a basic foundation of the facts, laws, theories, and principles currently used by chemists, as well as some examples of how chemistry can be applied in other fields. We hope that these examples will help you learn how to think "chemically" and to apply chemistry to specific problems that face you.

The behaviour of chemists and the development of science in general is based on the idea that natural events do not occur in completely unpredictable fashion. Consequently, measurements or observations made by one individual may be used by many others, provided they are communicated unambiguously.

Such communication involves reporting quantities (numbers x units) in which numbers are often written in scientific notation and rounded to indicate their reliability in terms of significant digits. In many cases scientists use ordinary words like quantity, precision, or accuracy, to which highly specific scientific definitions have been attached.

Scientific communication is also facilitated when a carefully defined, consistent set of units is used. SI units were adopted for that purpose in 1960 by an international conference, and they have been endorsed by the US National Bureau of Standards.

In the SI there are seven base units from which others are derived, making it easier to see relationships among various quantities. The sizes of base and derived units may be adjusted using prefixes which correspond to powers of 10. Thus very small or very large measurements may be reported conveniently.

When dealing with different units (such as inches and centimetres) which measure the same quantity, unity factors are used to adjust the sizes of the numbers which multiply different-sized units. In many cases it is also useful to be able to obtain one quantity (such as mass) from another (such as volume) for the same object.

If there is a known physical relationship (which can be expressed in an equation) between the quantities involved, a conversion factor (such as density or its reciprocal) may be used to interconvert the original quantities.

Correct application of a unity factor or a conversion factor can be recognized because some units will cancel, leaving a final quantity with the desired units.

Activity 3.1

When necessary, use the following equalities: 1 in = 2,540 cm; 1 lb = 453,6 g.

1. Modern single-pan analytical balances are often called substitution balances. Explain why. Why is it said that such balances have "a constant load"?
2. Fill in the blanks in the following calculations:
   a) 9,75 mm = 9,75 mm x _______ = 0,975 cm
   b) 17,28 cm = 17,28 cm x _______ in
   c) 253 cm^2 = 253 cm^2 x (________)^2 = _______ dm^2
3. Express the following quantities in the units indicated:
   a) 0,003 56 min centimetres
   b) 415 063 g in kilograms
   c) 1024 cm^2 in square meters
   d) 8,31 m^3 in cubic centimetres
   In each case use an appropriate unity factor.
4. Express the following quantities in the units indicated (use the data given at the beginning of the problems):
   a) 1 kg in pounds
   b) 1 ft in centimetres
   c) 1 mile in kilometres
   d) 1 cubic ft in cubic decimetres
   e) 1 h in seconds
   f) 1 mph in meters per second
5. Express the following temperatures in degrees Fahrenheit:
   a) 37°C b) -5°C c) 80°C
6. Express the following temperatures in degrees Celsius:
   a) 20°F b) 120°F c) -40°F
7. Which of the following equations are incorrectly written because of the omission of units or for some other reason:
   a) 7 g + 14 g = 21 c) 1,0 g = 1,0 cm^3
   b) (50 cm)^2 = 50 cm^2 d) 4,00 in = 10,16 cm
8. A cylindrical tank has a diameter of 36.0 in and a height of exactly 4ft. Using the formulas given inside the back cover and the necessary unity factors, calculate (a) the height of the tank in centimetres; (b) the circumference

of the tank in decimetres; (c) the cross-sectional area of the tank in square decimetres; (d) the volume of the tank in cubic centimetres.

9. Express the following numbers or quantities in scientific (exponential) notation:
   a) $712\ 473$
   b) $0{,}000\ 37\ \mathrm{g}$
   c) $392{,}68\ \mathrm{cm}$
   d) $3119\ \mathrm{cm}$ x $0{,}41\ \mathrm{cm}$
   e) $0{,}000\ 000\ 000\ 462\ \mathrm{m}$
   f) $\frac{327}{0{,}003\ 01}$
   g) $\frac{1644\ g}{5{,}48}$
   h) $49\ 157\ 333\ \mathrm{g}$
10. Rewrite each of the following numbers in a more conventional exponential notation:
   a 2.795E+03
   b 0.105E-05
   c 5.99 06
   Where would you find numbers written like this?
11. Evaluate each of the following expressions, giving your answer in scientific notation to the correct number of significant figures:
   a) $\frac{9{,}33 \times 10^5}{4{,}76 \times 10^{-5}}$
   b) $(32{,}7\ \times 10^3) \times (0{,}006 \times 10^{-5}$
   c) $6{,}04\ +\ (3{,}25\ \times\ 10^2)\ -\ (7{,}67\ \times\ 10^{-5})$
   d) $\frac{12{,}67 \times 10^9}{7{,}52 \times 10^6}$
12. How many significant figures are there, or should there be, in each of the following numbers or quantities?
   a) $0{,}000\ 079\ 9\ g$
   b) $42\ 000{,}0\ mm$
   c) $6{,}51\ \times\ 10^4\ mg$
   d) $\frac{1}{3}\ (12)\ (\frac{4{,}0}{0{,}7777})$
   e) $0{,}199\ \times\ 47{,}3862$
   f) $2{,}1 + 0{,}1234$
   g) $37{,}3852\ g -\ 3{,}3\ g$
   h) $\frac{120{,}6398}{1{,}2}$
13. Round each of the following numbers to four significant figures, in accordance with the rules given in **Table 3.1**:
   a) 78,9250
   b) 78,9165
   c) 78,9237
   d) 78,924 999
   e) 78,9150
   f) 78,913 762

14. Each of the following four sets of data represents repeated determinations of the same quantity. In each case state to how many significant figures the value of the quantity is known.
    a) 12,24 g, 12,25 g, 12,22 g, 12,23 g, 12,24 g
    b) 2,75 cm, 2,79 cm, 2,78 cm
    c) 0,017 25 kg, 0,019 53 kg, 0,014 49 kg
    d) 454 mm, 470 mm, 434 mm, 462 mm
15. What base SI unit accompanied by what prefix would be most convenient for describing each of the following quantities?
    a) Distance from Washington, D.C. to Paris, France
    b) Distance from Minneapolis, Minnesota to St. Paul, Minnesota
    c) Thickness of your chemistl--y textbook
    d) Mass of this page of paper
    e) Diameter of the atoms found in the molecules in this page of paper
    f) Mass of 1 gal of water
    g) Mass of the earth
16. Using appropriate exponential notation, express the following quantities in terms of SI base units:
    a) 232 pm
    b) 0,107 ag
    c) 33,4 ns
    d) 536 Gg
    e) 5,36 μA
    f) 500 Mg
17. Express the following quantities in the units indicated:
    a) 0,001 31 s in microseconds
    b) 13,5 cm^3 in cubic decimetres
    c) 0,004 97 mg in grams
    d) 0,386 mmol in moles
    e) 2,36 Å in picometres
    f) 53 pm in nanometres
    g) 1,03 g cm^{-3} in kilograms per cubic meter
    h) 3,87 mol dm^{-3} in millimoles per cubic centimetre
    Did you use unity factors in these calculations, or did you guess? How many of your guesses were wrong?
18. A metal sphere has a radius of 1,00 cm and a mass of 37,6 g.
    (a) Calculate the density of the metal.
    (b) What would be the mass of a sphere of radius 2,83 cm made from the same metal?
    (c) Assuming the metal to be pure, identify it from **Table 3.2**.
    (d) What color is the metal?
19. Using **Table 3.2**, calculate the mass of a cube of iron which is 3,00 in on a side. Express your answer in grams.
20. An irregularly shaped piece of lead weighs 119,3 g. It is dropped into a graduated cylinder containing exactly 30,0 cm^3 of water. To what volume reading will the water-level rise? (Use **Table 3.2**.)

21. If you did not previously do so, write the "road map" involved in solving Problems 18, 19, and 20.
22. The density of a metal is found to be 707,92 lb ft^{-3}. Identify this metal from **Table 3.2**.
23. Which of the following expressions are unity factors?
    a) 11,34 g cm^{-3}
    b) 2,54 cm in^{-1}
    c) 0,0936 cm^3 g^{-1}
    d) 16,4 cm^3 in^{-3}
    e) 2,20 lb kg^{-1}
    f) 3600 s h^{-1}

Self-Check

I am able to:	**Yes**	**No**
• Describe measurement:		
o Numbers, units and quantities		
o The International System of Units (SI)		
o Conversions factors		

If you have answered 'no' to any of the outcomes listed above, then speak to your facilitator for guidance and further development.

Past Examination Papers

higher education
& training

Department:
Higher Education and Training
REPUBLIC OF SOUTH AFRICA

APRIL 2013

NATIONAL CERTIFICATE

CHEMISTRY N5

(**15040015**)

22 March 2013 (X-Paper)
09:00 – 12:00

Calculators may be used.

This question paper consists of 7 pages and a periodic table.

TIME: 3 HOURS
MARKS: 100

INSTRUCTIONS AND INFORMATION

1. Answer ALL the questions.
2. Read ALL the questions carefully.
3. Number the answers according to the numbering system used in this question paper.
4. Write neatly and legibly

QUESTION 1

1.1 Give the molecular formula for 2,2,4-trimethyl pentane. (1)

1.2 When chlorine gas reacts with propane, homolytic splitting of the bond between the chlorine atoms occurs.

1.2.1 To what does the term *homolytic splitting* refer? (2)

1.2.2 What are the products called that are formed by the hemolytic splitting of the bond between the halogen atoms? (1)

1.2.3 Use the hybridisation theory to explain the orbital overlap that occurs in an ethane molecule. (3)

1.3 Nucleophiles are reactive intermediary products in chemical reactions

1.3.1 Are nucleophiles electron rich or electron deficient? (1)

1.3.2 Which of the following act as a nucleophile? Choose the answer and write only the letter (A-C) next to the question number (1.3.2) in the ANSWER BOOK. (1)

A Carbanions
B Radicals
C Carbocations

1.4 The molecular formula for a specific compound is $C_2H_4O_2$.

1.4.1 Give the empirical formula for the compound. (1)

1.4.2 Draw and name all the structural isomers for the compound (4)

1.5 Use the chlorination of propane and propene respectively to distinguish between a substitution and an addition reaction. Write down the reactions and comment on the rate of each reaction. (6)

1.6 Alkanes can be prepared from the corresponding alkenes.

1.6.1 What type of reaction is involved in the preparation of alkanes from alkenes? (1)

1.6.2 Draw the structural formula for 3,4-dimethylpent-2-ene. (2)

1.6.3 Give the IUPAC name of the main product that is formed when an alkane is prepared from 3,4-dimethylpent-2-ene. (2)

[25]

QUESTION 2

2.1 An alkene is prepared by using 2-chlorobutane in an elimination reaction.

2.1.1 Name the reactants and conditions that are needed for the reaction to occur. (3)

2.1.2 State Saytseff's rule in words. (2)

2.1.3 Apply Saytseff's rule and give the IUPAC name of the main product that is formed in this reaction. (2)

2.2 The ozonolysis of an alkene is a method for the determination of the position of a double bond in an alkene.

2.2.1 What is the unstable intermediary product called? (1)

2.2.2 Draw the structural formula of the unstable intermediary product formed when but-1-ene undergoes ozonolysis. (2)

2.2.3 Give the IUPAC name for the products formed when but-1-ene undergoes ozonolysis. (2)

2.3 What is the function of the Lindlar catalyst in the hydrogenation of an alkyne? (2)

2.4 Explain the concept *resonance* and illustrate by drawing Couper structures for the benzene molecule. (5)

2.5 What effect does resonance have on the benzene molecule? (2)

2.6 Draw the structural formulas for the following:

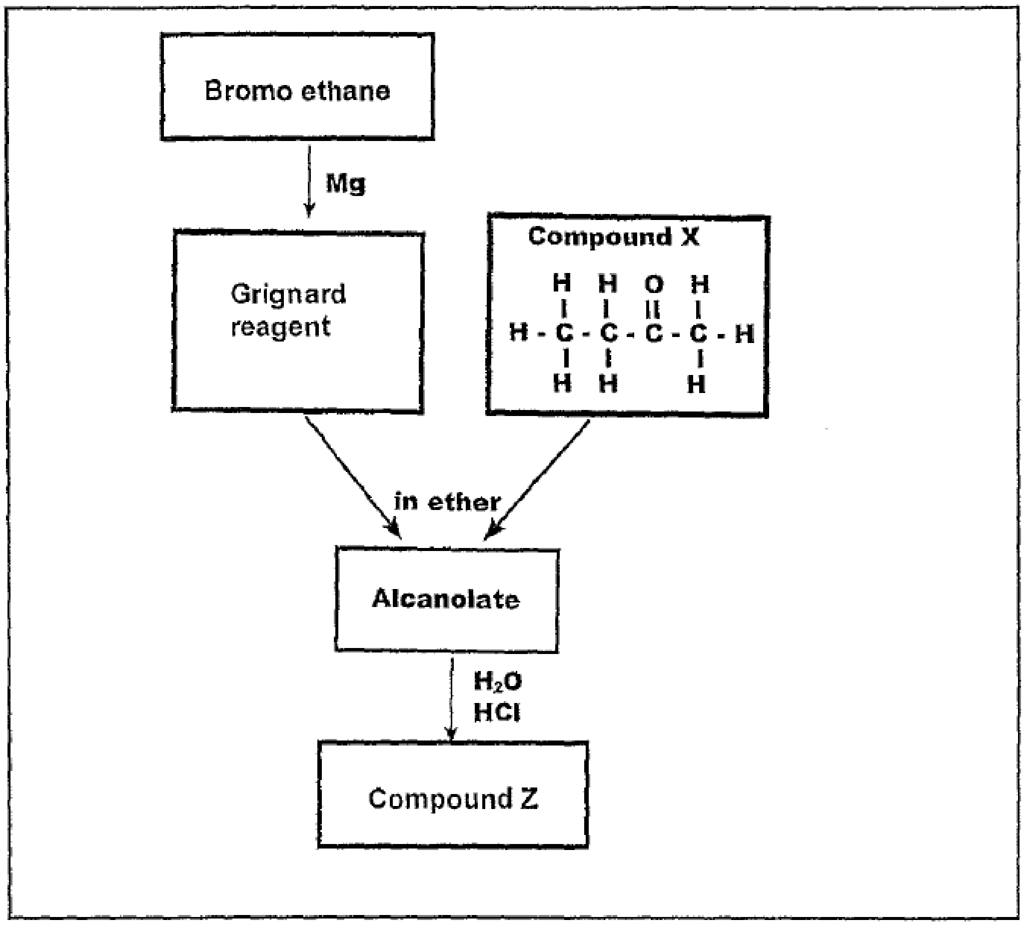
2.6.1 Phenol (2)

2.6.2 Toluene (2)

[25]

QUESTION 3

3.1 Study the following diagram:



3.1.1	Give the condensed formula for bromo ethane.	(1)
3.1.2	Draw the structural formula for the Grignard reagent that is formed.	(1)
3.1.3	To which homologous series does compound X belong?	(1)
3.1.4	Give the IUPAC name for compound X.	(1)
3.1.5	Draw the structural formula for the alkanoate that forms.	(1)
3.1.6	Draw the structural formula for compound Z.	(1)
3.1.7	Give the IUPAC name for compound Z.	(1)
3.2	Use structural formulas to write an equation for the addition of hydrogen cyanide to propanone	(4)
3.3	Alcohols can be converted to alkenes.	
3.3.1	What type of reaction is needed for the conversion?	(1)
3.3.2	Give the IUPAC name of the alkene that will form as main product when pentan-2-ol is used to prepare an alkene.	(2)

3.4 Name TWO tests that can be done to distinguish between *aldhydes* and *ketones* and indicate for each test the observations that can be made and how they can be interpreted. (4)

[25]

QUESTION 4

4.1 Discuss the acid/base characteristics of amines. (2)

4.2 How does the boiling point of ethanoic acid compare to the boiling point of ethanol? (2)

4.3 3 Two amines are structural isomers with the molecular formula C_2NH_7

4.3.1 Draw the structural formula for the T\NO isomers and give their IUPAC names. (4)

4.3.2 Classify each of the isomers as primary, secondary or tertiary. (2)

4.3.3 Which of the isomers has the highest boiling point? Explain by referring to the forces between the molecules. (3)

4.4 Name the reagents and state the conditions that are needed to prepare methyl propanoate via esterification. (4)

4.5 Consider the following process:

$$4CH_3COOH + 3LiAlH_4 \rightarrow \text{Compound A} + 4H_2 + 2LiAlO_2$$

$$\text{Compound A} + 4HCl(aq) \rightarrow 4\text{Compound B} + AlCl_3 + LiCl$$

4.5.1 What type of reaction does CH_3COOH undergo? (1)

4.5.2 Give the formula for compound A. (2)

4.5.3 Give the IUPAC name for compound B. (2)

4.6 Name the following:

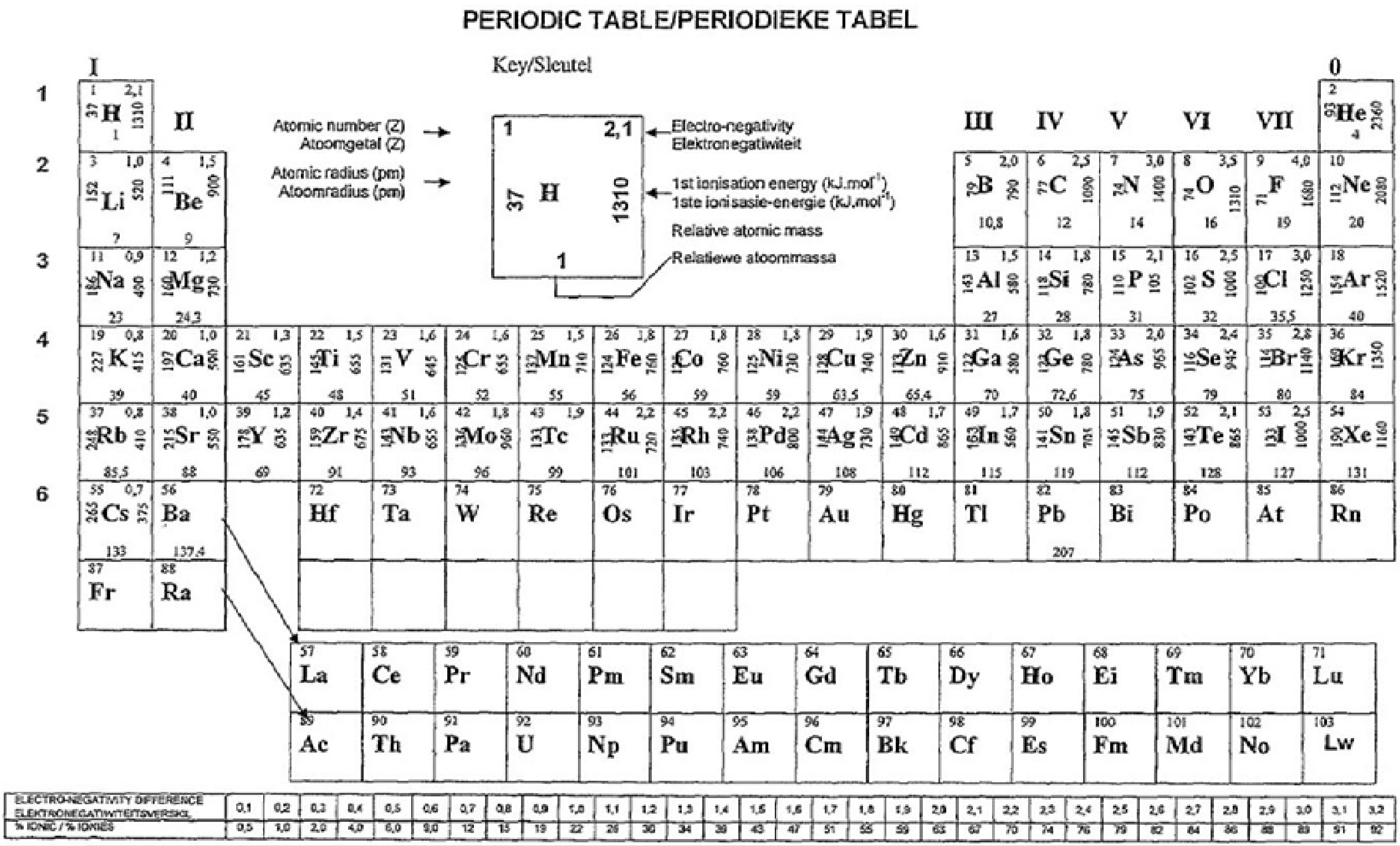
4.6.1 The product that is formed when ethane amide reacts with $LiAlH_4$ (1)

4.6.2 The product that is formed when ammonia reacts with 1-chloropropane (1)

4.6.3 The smallest amine (1)

[25]

TOTAL 100



PERIODIC TABLE/PERIODIEKE TABEL

Key/Sleutel

Atomic number (Z) Atoomgetal (Z)	1
Electro-negativity Elektronegatiwiteit	2,1
Atomic radius (pm) Atoomradius (pm)	37
	H
1st ionisation energy (kJ.mol⁻¹) 1ste ionisasie-energie (kJ.mol⁻¹)	1310
Relative atomic mass Relatiewe atoommassa	1

	I	II											III	IV	V	VI	VII	0
1	1 2,1 37 H 1310 1																	2 93 He 2360 4
2	3 1,0 152 Li 520 7	4 1,5 111 Be 900 9											5 2,0 88 B 790 10,8	6 2,5 77 C 1090 12	7 3,0 74 N 1400 14	8 3,5 74 O 1310 16	9 4,0 71 F 1680 19	10 112 Ne 2080 20
3	11 0,9 186 Na 490 23	12 1,2 160 Mg 730 24,3											13 1,5 143 Al 580 27	14 1,8 118 Si 780 28	15 2,1 110 P 105 31	16 2,5 102 S 1000 32	17 3,0 100 Cl 1250 35,5	18 154 Ar 1520 40
4	19 0,8 227 K 415 39	20 1,0 197 Ca 590 40	21 1,3 161 Sc 635 45	22 1,5 145 Ti 655 48	23 1,6 131 V 645 51	24 1,6 125 Cr 655 52	25 1,5 137 Mn 710 55	26 1,8 124 Fe 760 56	27 1,8 125 Co 760 59	28 1,8 125 Ni 730 59	29 1,9 128 Cu 740 63,5	30 1,6 133 Zn 910 65,4	31 1,6 122 Ga 580 70	32 1,8 122 Ge 780 72,6	33 2,0 121 As 965 75	34 2,4 116 Se 945 79	35 2,8 114 Br 1140 80	36 98 Kr 1350 84
5	37 0,8 248 Rb 410 85,5	38 1,0 215 Sr 550 88	39 1,2 178 Y 635 69	40 1,4 159 Zr 675 91	41 1,6 143 Nb 655 93	42 1,8 136 Mo 960 96	43 1,9 135 Tc 99	44 2,2 133 Ru 720 101	45 2,2 135 Rh 740 103	46 2,2 138 Pd 800 106	47 1,9 144 Ag 730 108	48 1,7 149 Cd 865 112	49 1,7 163 In 560 115	50 1,8 141 Sn 705 119	51 1,9 145 Sb 830 112	52 2,1 143 Te 865 128	53 2,5 133 I 1000 127	54 190 Xe 1160 131
6	55 0,7 265 Cs 375 133	56 Ba 137,4		72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb 207	83 Bi	84 Po	85 At	86 Rn
	87 Fr	88 Ra																

57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Ei	69 Tm	70 Yb	71 Lu
89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lw

ELECTRO-NEGATIVITY DIFFERENCE ELEKTRONEGATIWITEITSVERSKIL	0,1	0,2	0,3	0,4	0,5	0,6	0,7	0,8	0,9	1,0	1,1	1,2	1,3	1,4	1,5	1,6	1,7	1,8	1,9	2,0	2,1	2,2	2,3	2,4	2,5	2,6	2,7	2,8	2,9	3,0	3,1	3,2
% IONIC / % IONIES	0,5	1,0	2,0	4,0	6,0	9,0	12	15	19	22	26	30	34	39	43	47	51	55	59	63	67	70	74	76	79	82	84	86	88	89	91	92

Marking Guidelines

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Department:
Higher Education and Training
REPUBLIC OF SOUTH AFRICA

APRIL 2013

NATIONAL CERTIFICATE

CHEMISTRY N5

(15040015)

QUESTION 1

1.1 C_8H_{18} (1)

1.2.1 Atoms separate and each atom retains one bond electron. (1)

1.2.2 Radicals (3)

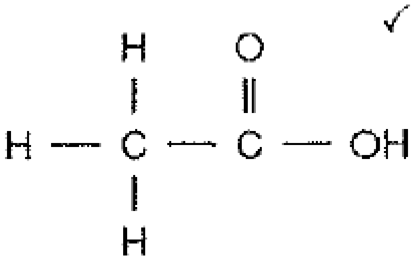
1.2.3 Every carbon atom undergoes sp^3 hybridisation

1.3.1 Electron rich (1)

1.3.2 A Carboanions (1)

1.4.1 CH_2O (1)

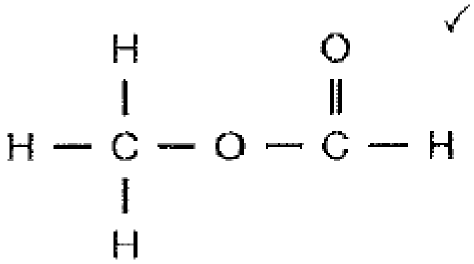
1.4.2 ✓



$$\begin{array}{ccccccc} & & H & & O & & \\ & & | & & \| & & \\ H & - & C & - & C & - & OH \\ & & | & & & & \\ & & H & & & & \end{array}$$

Ethanoic acid ✓

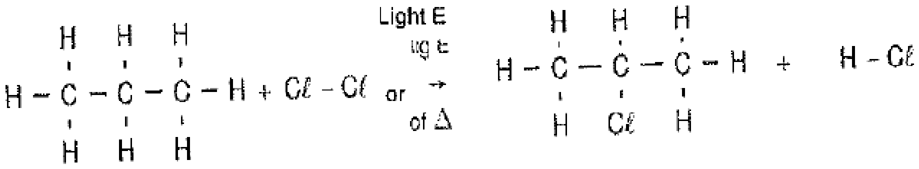
1.4.3 ✓ (4)



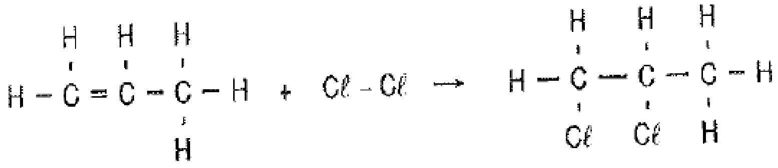
$$\begin{array}{ccccccccc} & & H & & & & O & & \\ & & | & & & & \| & & \\ H & - & C & - & O & - & C & - & H \\ & & | & & & & & & \\ & & H & & & & & & \end{array}$$

Methyl mathenoate ✓

1.5 Substitution is slow (6)

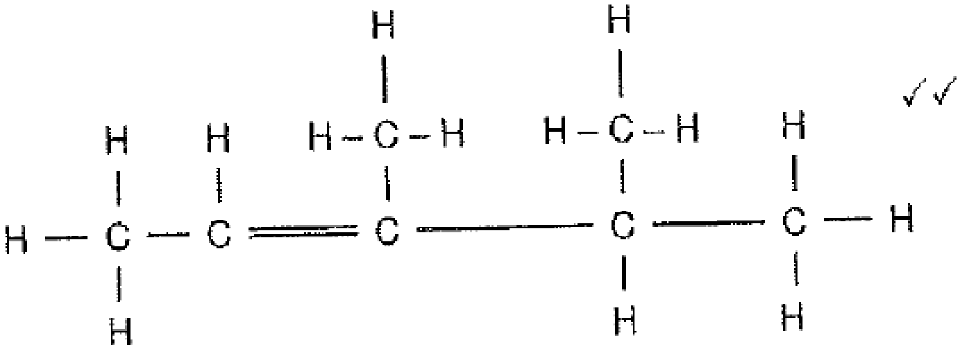


Addition is fast ✓



1.6.1 Addition (hydrogenation) (1)

1.6.2 (2)



1.6.3 3,4-dimethylpentane (2)

[25]

QUESTION 2

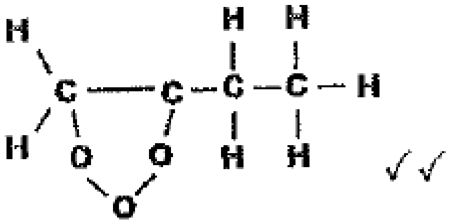
2.1.1 Heat NaOH or KOH in alcohol/water mixture (3)

2.1.2 In elimination reactions the main product is the product with the highest number of substituents on the double bond (2)

2.1.3 But-2-ene (2)

2.2.1 Ozonide (1)

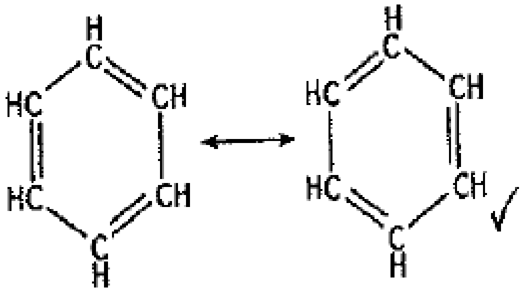
2.2.2 (2)



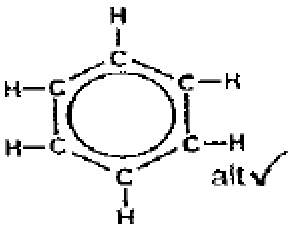
2.2.3 Methanol and propanol (2)

2.3 Limits the reaction to produce only alkenes (2)

2.4 Two different structures with alternating single and double bonds are possible (5)



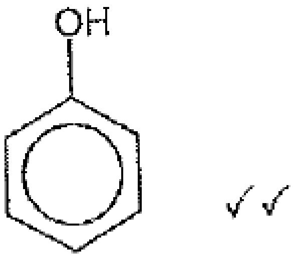
Bond length shows that benzene exists in an intermediate hybrid structure.



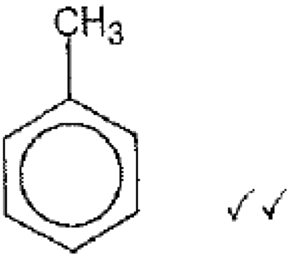
Electrons are delocalized and all bonds are equal in length.

2.5 It contributes to the stability of the benzene molecule. (2)

2.6.1 (2)



2.6.2 (2)

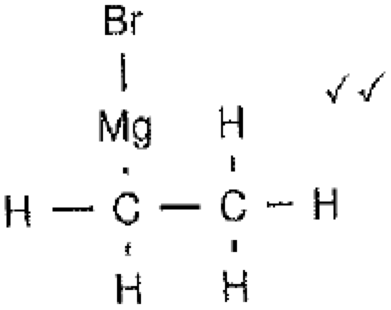


[25]

QUESTION 3

3.1.1 CH_3CH_2Br (1)

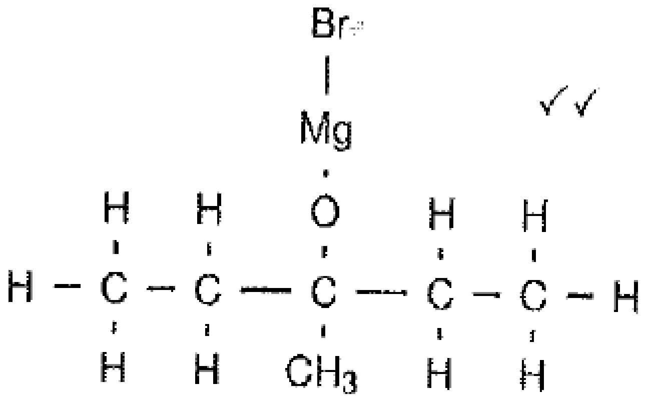
3.1.2 (1)



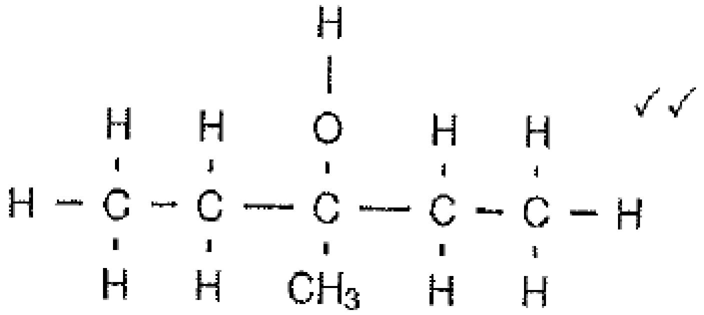
3.1.3 Ketones (1)

3.1.4 Butanone (1)

3.1.5 (1)

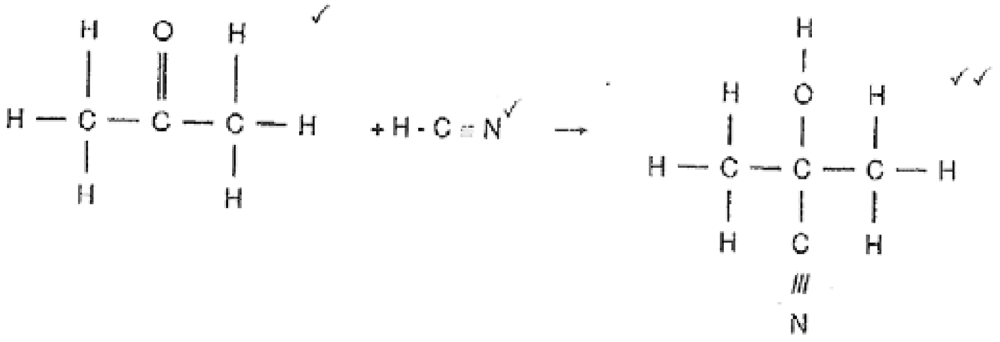


3.1.6 (1)



3.1.7 3-methylpentan-3-ol (1)

3.2 (4)



3.3.1 Elimination (dehydration) (1)

3.3.2 Pent-2-ene (2)

3.4 Tollens test (ammonia in silver nitrate): (4)
Silver mirror indicates aldehyde, none indicates ketone

Fehling solution: (Tartratokupraat (II) complex of caustic soda):
Blue solution turns red for aldehydes, not for ketones

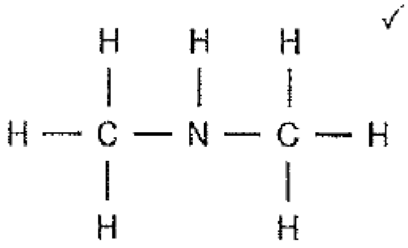
[25]

QUESTION 4

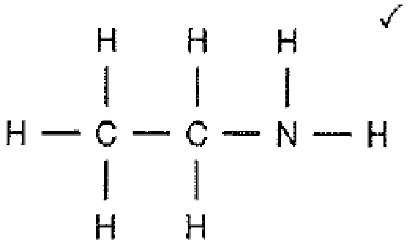
4.1 Primary and secondary amine: basic (2)
Tertiary amine: neutral

4.2 The boiling point of ethanoic acid is higher (2)

4.3.1 (4)



Dimethyl amine ✓



Ethyl amine

4.3.2 Dimethyl amine: secondary (2)
Ethyl amine: primary

4.3.3 Ethyl amine: highest boiling point (3)
More H on N, therefore more hydrogen bonds

4.4 (4)
- Methanol
- Propanoic acid
- Concentrated H_2SO_4
- Heat

4.5.1 Reduction (1)

4.5.2 Li+’(2) – $Al(OCH_2CH_3)CH_4$ (2)

4.5.3 Ethanol (2)

4.6.1 Ethyl amine (1)

4.6.2 Propyl amine (1)

4.6.3 Methyl amine (1)

[25]

TOTAL 100

Past Examination Papers

higher education
& training

Department:
Higher Education and Training
REPUBLIC OF SOUTH AFRICA

AUGUST 2012

NATIONAL CERTIFICATE

CHEMISTRY N5

(**15040015**)

22 March 2013 (X-Paper)
09:00 – 12:00

Calculators may be used.

This question paper consists of 7 pages and a periodic table.

TIME: 3 HOURS
MARKS: 100

INSTRUCTIONS AND INFORMATION

1. Answer ALL the questions.
2. Read ALL the questions carefully.
3. Number the answers according to the numbering system used in this question paper.
4. Full marks = 100%
5. Write neatly and legibly

QUESTION 1

1.1 Butane is used as fuel in a lighter.

1.1.1 Is the burning butane gas an endothermic or an exothermic reaction? Explain. (2)

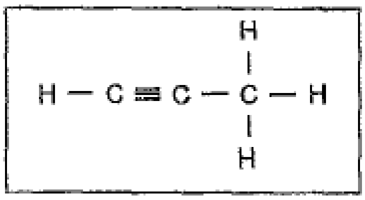
1.1.2 Write a balanced equation for the combustion reaction. (5)

1.1.3 Does butane readily dissolve in water? (1)

1.1.4 Name and draw the structural formula for a branched isomer of butane. (3)

1.1.5 Why is butane a gas at room temperature, but octane occurs as a liquid? (3)

1.2 Consider the following organic compound:



$$H - C \equiv C - \overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}} - H$$

1.2.1 Give the IUPAC name of the compound. (1)

1.2.2 Is this compound saturated or unsaturated? (1)

1.2.3 Give the general formula for the homologous series to which this compound belongs. (1)

1.2.4 Is this compound polar or non-polar? (1)

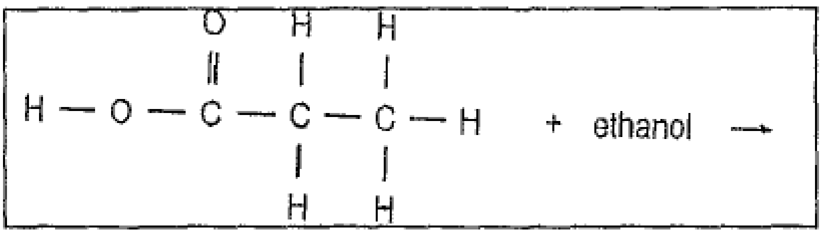
1.2.5 State Markovnikov's rule in words. (3)

1.2.6 Draw and name the main product that is formed when this compound undergoes complete hydration. (4)

[25]

QUESTION 2

2.1 Consider the following reaction of compounds A with ethanol:



$H-O-C(=O)-CH_2-CH_3$ + ethanol →

2.1.1 To which homologous series does compound A belong? (1)

2.1.2 Give the IUPAC name of compound A. (2)

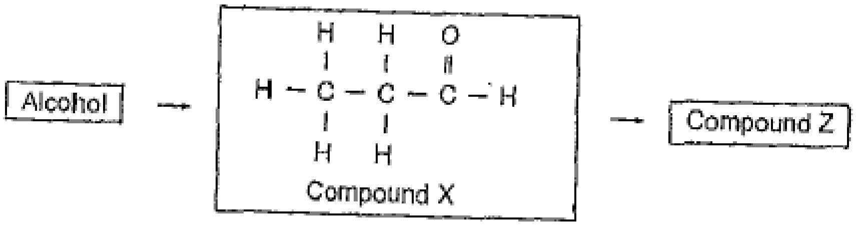
2.1.3 Draw the structural formula of ethanol. (1)

2.1.4 Give the names of the products formed in this reaction. (3)

2.1.5 Draw the structural formula of the organic product formed in this reaction (3)

2.1.6 Write an equation for the reaction of ethanol with sodium. (3)

2.2 Potassium permanganate is used to enable the following series of reactions to occur:



2.2.1 Does the alcohol readily dissolve in water? Explain. (3)

2.2.2 Give the I UPAC name of the alcohol (2)

2.2.3 Classify the alcohol as primary, secondary or tertiary. (1)

2.2.4 Write the formula for potassium permanganate. (1)

2.2.5 What is the function of the potassium permanganate in the reactions? (1)

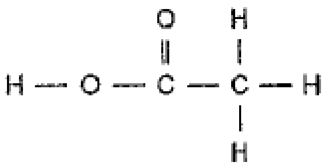
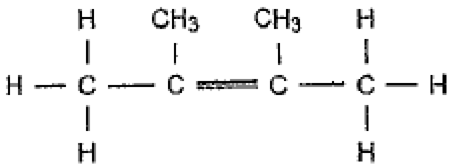
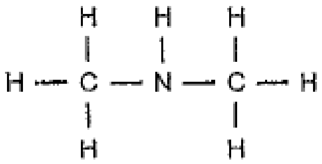
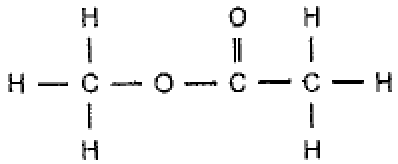
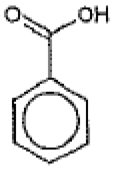
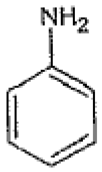
2.2.6 To which homologous series does X belong? (1)

2.2.7 To which homologous series does Z belong? (1)

2.2.8 Give the IUPAC name for compound Z. (1)

2.2.9 What type of reaction is involved in the conversion of alcohol to compound Y and to Z? (1)

2.3 The following represents formulas of organic compounds:

A  $H-O-\overset{\overset{O}{\|}}{C}-\overset{\overset{H}{\mid}}{\underset{\underset{H}{\mid}}{C}}-H$	B  $H-\overset{\overset{H}{\mid}}{\underset{\underset{H}{\mid}}{C}}-\overset{\overset{CH_3}{\mid}}{C}=\overset{\overset{CH_3}{\mid}}{C}-\overset{\overset{H}{\mid}}{\underset{\underset{H}{\mid}}{C}}-H$
C  $H-\overset{\overset{H}{\mid}}{\underset{\underset{H}{\mid}}{C}}-\overset{\overset{H}{\mid}}{N}-\overset{\overset{H}{\mid}}{\underset{\underset{H}{\mid}}{C}}-H$	D  $H-\overset{\overset{H}{\mid}}{\underset{\underset{H}{\mid}}{C}}-O-\overset{\overset{O}{\|}}{C}-\overset{\overset{H}{\mid}}{\underset{\underset{H}{\mid}}{C}}-H$
E 	F 

2.3.1 Is compound A an acid or a base? (1)

2.3.2 Is compound C an acid or a base? (1)

2.3.3 Is compound E an acid or a base? (1)

2.3.4 Give the molecular formula for compound B. (1)

2.3.5 Give the empirical formula for compound B. (1)

2.3.6 To which homologous series does compound D belong? (1)

2.3.7 To which homologous series does compound C belong? (1)

2.3.8 Give the name of compound E. (1)

2.3.9 Give the name of compound F (1)

2.3.10 Give the IUPAC name of compound C. (2)

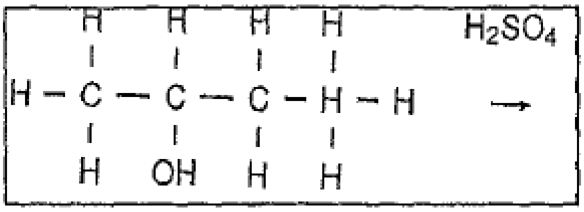
2.3.11 How many carbon atoms in compound B have sp2 hybridisation? (2)

2.3.12 Which ONE of these compounds exhibit resonance? (2)

2.3.13 Which ONE of the compounds (A to F) belongs to a homologous series that is known for pleasant fragrances? (1)

2.3.14 Which ONE of the compounds (A to F) is an unsaturated hydrocarbon? (1)

2.4



2.4.1 Is this an elimination, substitution, addition or oxidation reaction? (1)

2.4.2 Does hydrogenation, dehydrogenation, hydration or dehydration occur in this reaction? (1)

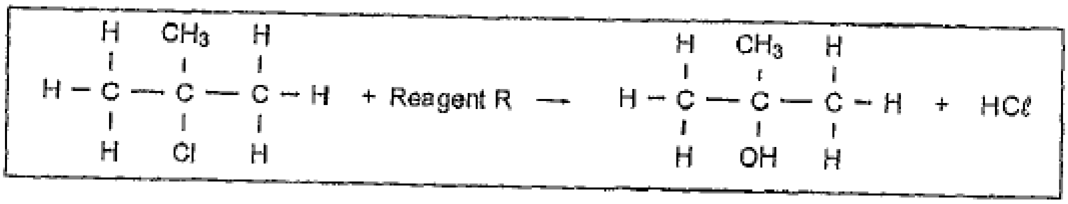
2.4.3 Draw structural formulas for the products that are formed. (4)

2.4.4 Give the IUPAC name of the organic product that is formed. (2)

[50]

QUESTION 3

3.1



3.1.1 Is this an elimination, substitution, addition or oxidation reaction? (1)

3.1.2 Give the name of reagent R. (1)

3.1.3 What is the correct IUPAC name for the organic compound that forms? (3)

3.2 2 Give ONE word/term for each of the following descriptions. Write only the word/term next to the question number (3.2.1 - 3.2.1 0) in the ANSWER BOOK.

3.2.1 The homologous group with functional group R-OH (2)

3.2.2 The homologous group with a carbonyl group on the first carbon in the chain (2)

3.2.3 The type of addition that occurs when C_2H_4 reacts with water (2)

3.2.4 Carbon atom that carries a positive charge (2)

3.2.5 Solution that is used to distinguish between ketones and aldehydes (2)

3.2.6 Saturated hydrocarbon with 12 hydrogen atoms per molecule (2)

3.2.7 The product that is formed when bromine reacts with pent-2-ene (2)

3.2.8 The smallest ketone (2)

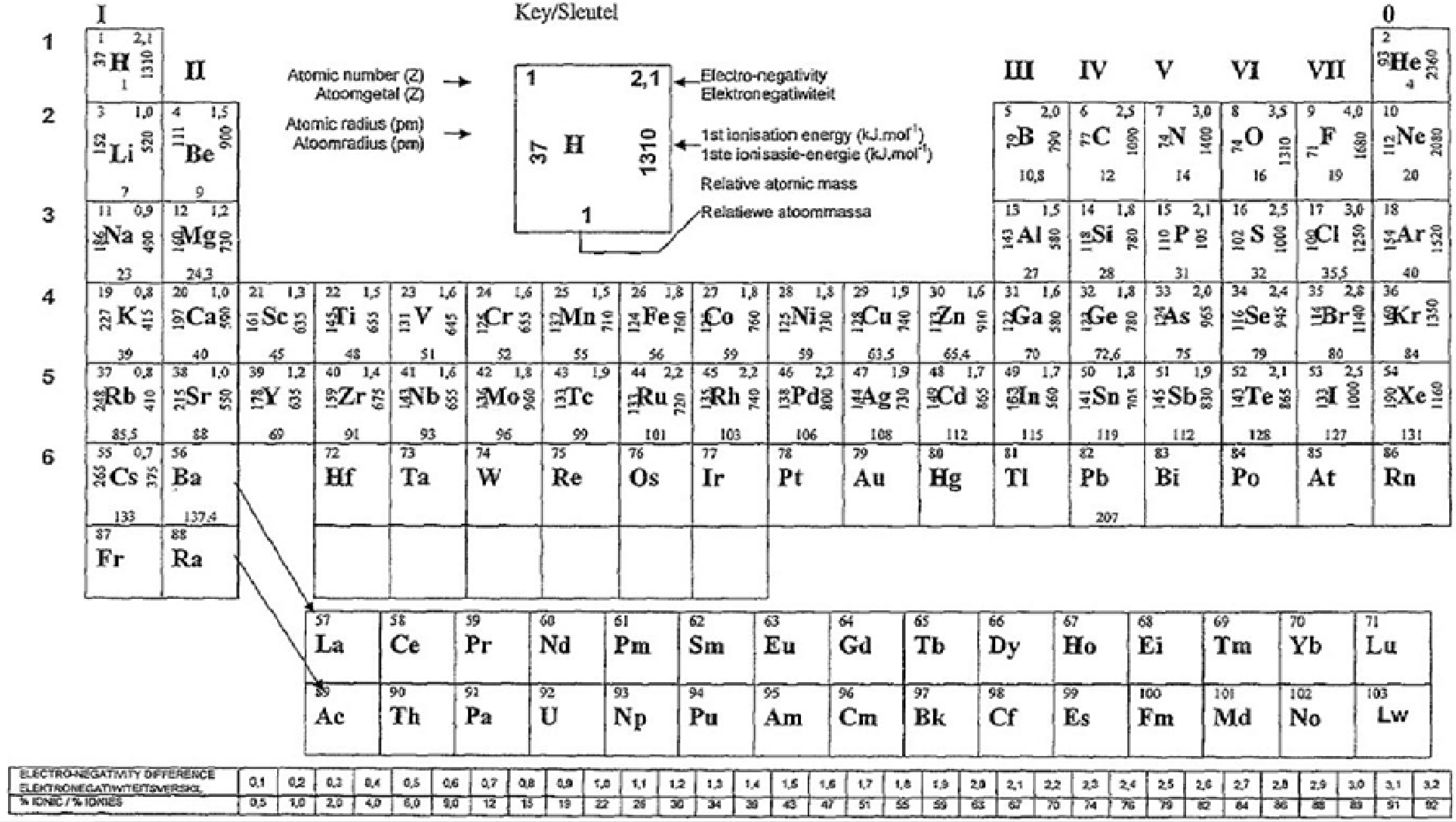
3.2.9 The type of elimination reaction necessary to change butan-2-ol to an unsaturated hydrocarbon (2)

3.2.10 The chemical process used to convert plant oils to fats (2)

[25]

TOTAL 100

PERIODIC TABLE/PERIODIEKE TABEL



Key/Sleutel

Atomic number (Z) / Atoomgetal (Z) → 1
Atomic radius (pm) / Atoomradius (pm) → 37
H
2,1 ← Electro-negativity / Elektronegatiwiteit
1310 ← 1st ionisation energy (kJ.mol⁻¹) / 1ste ionisasie-energie (kJ.mol⁻¹)
1 ← Relative atomic mass / Relatiewe atoommassa

	I	II											III	IV	V	VI	VII	0
1	1 2,1 37 H 1310 1																	2 93 He 2360 4
2	3 1,0 152 Li 520 7	4 1,5 111 Be 900 9											5 2,0 79 B 790 10,8	6 2,5 77 C 1090 12	7 3,0 74 N 1400 14	8 3,5 74 O 1310 16	9 4,0 71 F 1680 19	10 112 Ne 2080 20
3	11 0,9 186 Na 490 23	12 1,2 160 Mg 730 24,3											13 1,5 143 Al 580 27	14 1,8 118 Si 780 28	15 2,1 110 P 105 31	16 2,5 102 S 1000 32	17 3,0 100 Cl 1250 35,5	18 154 Ar 1520 40
4	19 0,8 227 K 415 39	20 1,0 197 Ca 590 40	21 1,3 161 Sc 635 45	22 1,5 145 Ti 655 48	23 1,6 131 V 645 51	24 1,6 125 Cr 655 52	25 1,5 137 Mn 710 55	26 1,8 124 Fe 760 56	27 1,8 125 Co 760 59	28 1,8 125 Ni 730 59	29 1,9 128 Cu 740 63,5	30 1,6 133 Zn 910 65,4	31 1,6 122 Ga 580 70	32 1,8 122 Ge 780 72,6	33 2,0 125 As 965 75	34 2,4 116 Se 945 79	35 2,8 114 Br 1140 80	36 189 Kr 1350 84
5	37 0,8 248 Rb 410 85,5	38 1,0 215 Sr 550 88	39 1,2 178 Y 635 69	40 1,4 159 Zr 675 91	41 1,6 143 Nb 655 93	42 1,8 136 Mo 960 96	43 1,9 135 Tc 99	44 2,2 133 Ru 720 101	45 2,2 135 Rh 740 103	46 2,2 138 Pd 800 106	47 1,9 144 Ag 730 108	48 1,7 149 Cd 865 112	49 1,7 163 In 560 115	50 1,8 141 Sn 705 119	51 1,9 145 Sb 830 112	52 2,1 143 Te 865 128	53 2,5 133 I 1000 127	54 190 Xe 1160 131
6	55 0,7 265 Cs 375 133	56 Ba 137,4		72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb 207	83 Bi	84 Po	85 At	86 Rn
	87 Fr	88 Ra																

57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Ei	69 Tm	70 Yb	71 Lu
89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lw

ELECTRO-NEGATIVITY DIFFERENCE ELEKTRONEGATIWITEITSVERSKIL	0,1	0,2	0,3	0,4	0,5	0,6	0,7	0,8	0,9	1,0	1,1	1,2	1,3	1,4	1,5	1,6	1,7	1,8	1,9	2,0	2,1	2,2	2,3	2,4	2,5	2,6	2,7	2,8	2,9	3,0	3,1	3,2
% IONIC / % IONIES	0,5	1,0	2,0	4,0	6,0	9,0	12	15	19	22	26	30	34	39	43	47	51	55	59	63	67	70	74	76	79	82	84	86	88	89	91	92

Marking Guidelines

higher education
& training

Department:
Higher Education and Training
REPUBLIC OF SOUTH AFRICA

AUGUST 2012

NATIONAL CERTIFICATE

CHEMISTRY N5

(15040015)

This marking guideline consists of 5 pages.

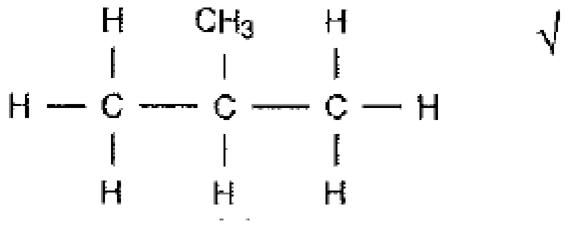
QUESTION 1

1.1.1 exothermic (2)
energy is released

1.1.2 $2C_4H_1O + 13O_2 \rightarrow 8CO_2 + 10H_2O$ balanced (5)

1.1.3 No (1)

1.1.4 (3)



Methyl propane

1.1.5 octane is a bigger molecule (3)
therefore octane's Van der Waal's Forces are stronger

1.2.1 Propyne or Prop-1-yne (1)

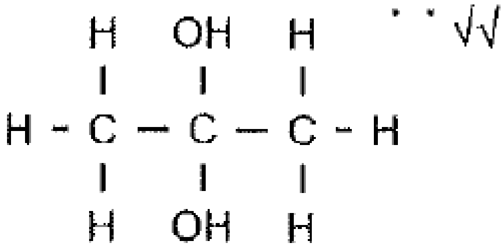
1 2.2 Unsaturated (1)

1.2.3 C_nH_{2n-2} (1)

1.2.4 Non-polar (1)

1.2.5 In the addition of a polar molecule to a carbon=carbon double bond the hydrogen attached itself to the carbon that already holds the greatest number of hydrogen atoms (3)

1.2.6 (4)



Propan-2,2-diol

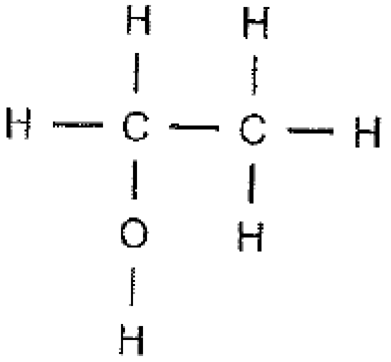
[25]

QUESTION 2

2.1.1 Carboxylic acids (1)

2.1.2 Propanoic acid (2)

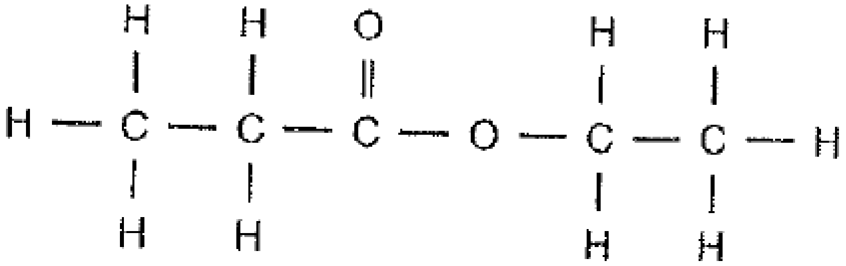
2.1.3 (1)



√

2.1.4 Ethyl propanoate (3)
Water

2.1.5 (3)



2.1.6 $2C_2H_5OH + Na\ 2C_2H_5O^- Na^+ + H_2$ (3)

2.2.1 Yes (3)
The alcohol is polar like water
Alcohol forms hydrogen bonds with water

2.2.2 propan-1-o1 (2)

2.2.3 Primary (1)

2.2.4 $KMnO_4$ (1)

2.2.5 Oxiding agent (1)

2.2.6 Aldehides (1)

2.2.7 Carboxylic acid (1)

2.2.8 Propanoic acid (1)

2.2.9 Oxidation (1)

2.3.1 Acid (1)

2.3.2 Base (1)

2.3.3 Acid (1)

2.3.4 C_6H_{14} (1)

2.3.5 CH_2 (1)

2.3.6 Ester (1)

2.3.7 Amine (1)

2.3.8 Bensonic acid (1)

2.3.9 Analine (1)

2.3.10 Dimethyl amine (2)

2.3.11 2 (2)

2.3.12 E and F (2)

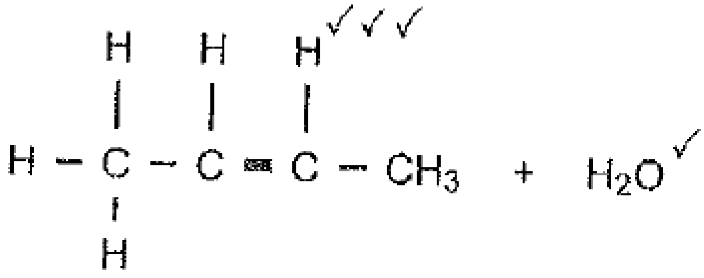
2.3.13 B (1)

2.3.14 D (1)

2.4.1 Substitution (1)

2.4.2 Dehydration (1)

2.4.3 (4)



$$H-\overset{H}{\underset{H}{C}}-\overset{H}{C}=\overset{H^{\checkmark\checkmark\checkmark}}{C}-CH_3 \quad + \quad H_2O^{\checkmark}$$

2.4.4 But-2-ene (2)

[50]

QUESTION 3

3.1.1 Addition

3.1.2 Water (1)

3.1.3 2-methylpropan-2-ol (3)

3.2.1 Alcohols (2)

3.2.2	Aldehyde	(2)
3.2.3	Hydration	(2)
3.2.4	Carbonium ion	(2)
3.2.2	Pentane	
3.2.3	2,3-dibromopentane	
3.2.4	Garbonium ion	
3.2.5	Fehlings or Tollens-reagent	(2)
3.2.6	Pentate	(2)
3.2.7	2,3-dibromopentane	(2)
3.2.8	Propanone, propan-2-one or acetone	(2)
3.2.9	Dehydration	(2)
3.2.10	Hydrogenation	(2)

[25]

TOTAL 100

Past Examination Papers

higher education
& training

Department:
Higher Education and Training
REPUBLIC OF SOUTH AFRICA

APRIL 2012

NATIONAL CERTIFICATE

CHEMISTRY N5

(15040015)

22 March 2013 (X-Paper)
09:00 – 12:00

Calculators may be used.

This question paper consists of 8 pages and a periodic table.

TIME: 3 HOURS
MARKS: 100

INSTRUCTIONS AND INFORMATION

1. Answer ALL the questions.
2. Read ALL the questions carefully.
3. Number the answers according to the numbering system used in this question paper.
4. Full marks = 100%
5. Write neatly and legibly

QUESTION 1

Give ONE word/term for each of the following descriptions. Write only the word/term next to the question number (1.1 -1.10) in the ANSWER BOOK.

1.1 The homologous series with functional group R-OH (2)

1.2 The type of reaction that occurs when C2H4 reacts with bromine (2)

1.3 C_5H_{10} (2)

1.4 Saturated hydrocarbon with eight hydrogen atoms per molecule (2)

1.5 $CH_3CHCHCH_3$ (2)

1.6 The product that is formed when bromine reacts with propene (2)

1.7 The carboxylic acid that is used to prepare ethyl methanoate (2)

1.8 A structural isomer of methyl propane (2)

1.9 The organic product that is formed when propanoic acid reacts with methanol (2)

1.10 The smallest carboxylic acid (2)

[20]

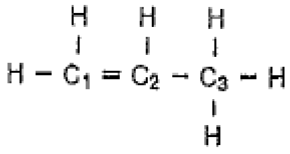
QUESTION 2

Various options are given as possible answers to the following questions. Write only the letter (A- D) next to the question number (2.1 - 2.5) in the ANSWER BOOK.

2.1 C_4H_{10} has a· ... boiling point than C_3H_8 as a result of the strength of the ... between the molecules. (2)

A higher, covalent bonds
B higher, Van der Waals Forces
C lower, covalent bonds
D lower, Van der Waals Forces

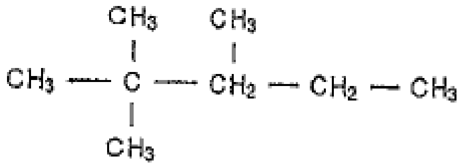
2.2 The type of hybridisations of the carbon atoms in the following compound are … (2)



A C_1 sp^3, C_2 sp^3 and C_3 sp^2
B C_1 sp^2, C_2 sp^2 and C_3 spa

C C_1 sp^3, C_2 sp^2 and C_3 spa
D C_1 sp^2, C_2 sp^3 and C_3 sp^2

2.3 What is the correct IUPAC name for the following compound? (2)



$$CH_3 - \overset{CH_3}{\underset{CH_3}{C}} - \overset{CH_3}{CH_2} - CH_2 - CH_3$$

A 2,3-trimethyl propane
B 2,2,3-trimethyl propane
C 2,3-trimethyl pentane
D 2,2,3-trimethyl pentane

2.4 A certain gas mixture readily removes the colour from a bromine solution in the absence of sunlight. The mixture probably contains ... (2)
A methane.
B ethene.
C methyl propane.

2.5 Which ONE of the following compounds has a low boiling point and does not dissolve readily in water? (2)
A $CH_3CH_2CH_2OH$
B CH_3CH_2COOH
C $CH_3CH_2CH_3$
D CH_3OCOCH_3

[10]

QUESTION 3

3.1 Draw and give the UIPAC names of TWO structural isomers of $C_2H_4O_2$. (4)

3.2 A carbonium ion can be formed during heterolysis.

3.2.1 Explain what a *carbonium* is. (2)

3.2.2 What does the term *heterolysis* refer to? (2)

3.3 Use structural formulas to write an equation for the dehydrohalogenation of 2-chloropropane. (5)

3.4 Each of the following represents the formula of an organic compound:
A C_4H_6
B $CH_3CHOHCH_3$
C C_2H_4
D BrCH2CH2Br
E CH_3CH_2COOH

3.4.1 What is the general formula of the class of compounds represented by A? (1)

3.4.2 Give the IUPAC names of each of the compounds. (5)

3.4.3 Write a balanced equation for the reaction that occurs when compound A is ignited in excess oxygen. (3)

3.4.4 To which homologous series does B belong? (1)

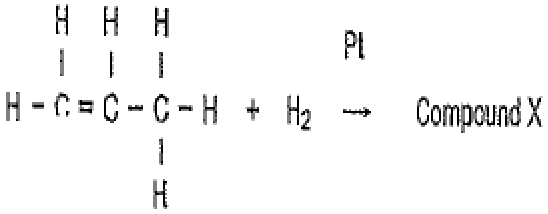
3.4.5 What type of reaction is involved in the conversion of C to D? (1)

3.4.6 Name the homologous series to which E belongs. (1)

[25]

QUESTION 4

4.1 Consider the following reaction:



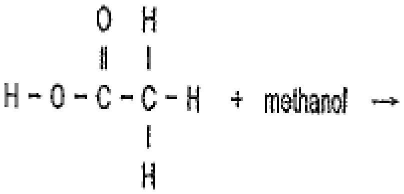
$$H-\overset{H}{\overset{|}{C}}=\overset{H}{\overset{|}{C}}-\underset{H}{\underset{|}{\overset{H}{\overset{|}{C}}}}-H + H_2 \xrightarrow{Pt} \text{Compound X}$$

4.1.1 Is this an elimination, substitution, addition or oxidation reaction? (1)

4.1.2 Give the IUPAC name of the organic reactant in this reaction. (2)

4.1.3 Draw the structural formula for compound X. (2)

4.2



$$H-O-\overset{O}{\overset{\|}{C}}-\underset{H}{\underset{|}{\overset{H}{\overset{|}{C}}}}-H + \text{methanol} \rightarrow$$

4.2.1 To which homologous series does compound A belong? (1)

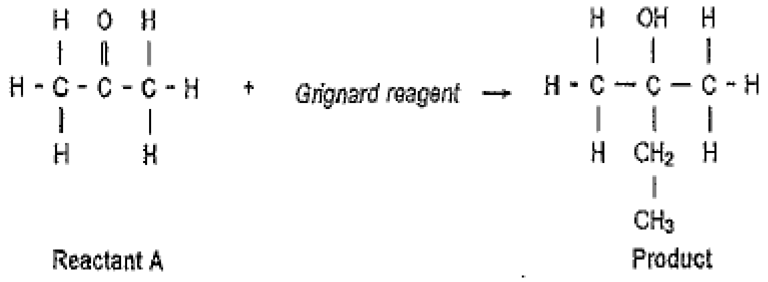
4.2.2 Give the IUPAC name of compound A. (1)

4.2.3 Draw the structural formula of methanol. (1)

4.2.4 Give the names of the products formed in this reaction. (3)

4.2.5 Draw the structural formula of the organic product formed in this reaction. (3)

4.3 Consider the following reaction in which a Grignard reagent is used:

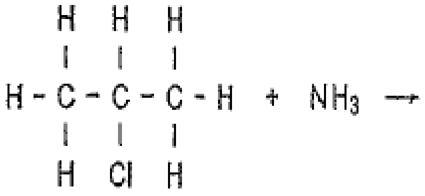


4.3.1 Give the IUPAC name for the reactant A that is displayed in the equation. (2)

4.3.2 Give the IUPAC name for the product that is displayed in the equation. (2)

4.3.3 Draw the structural formula for the Grignard reagent that is used in the reaction. (2)

4.4 Consider the following reaction:



4.4.1 Is this an elimination, substitution, addition or oxidation reaction? (1)

4.4.2 Use structural formulas to write down the products that form in the reaction. (3)

4.4.3 To which homologous series does the organic product belong? (1)

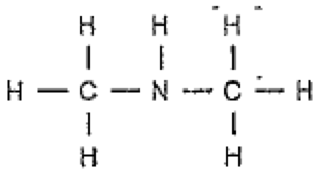
[25]

QUESTION 5

5.1 Markovnikov's rule is relevant to many reactions of organic compounds.State Markovnikov's rule in words. (2)

5.2 Name the type of reaction necessary to change butan-2-ol to an unsaturated hydrocarbon. (2)

5.3 Consider the following organic compound:



5.3.1 Give the IUPAC name of the compound. (4)

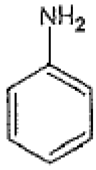
5.3.2 Are the molecules of this compound polar? (2)

5.3.3 Can this compound readily dissolve in water? (3)

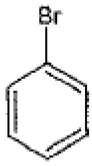
5.3.4 Is this compound and acid or a base? (4)

5.4 Consider the following organic compounds:

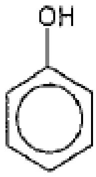
A



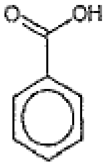
B



C



D



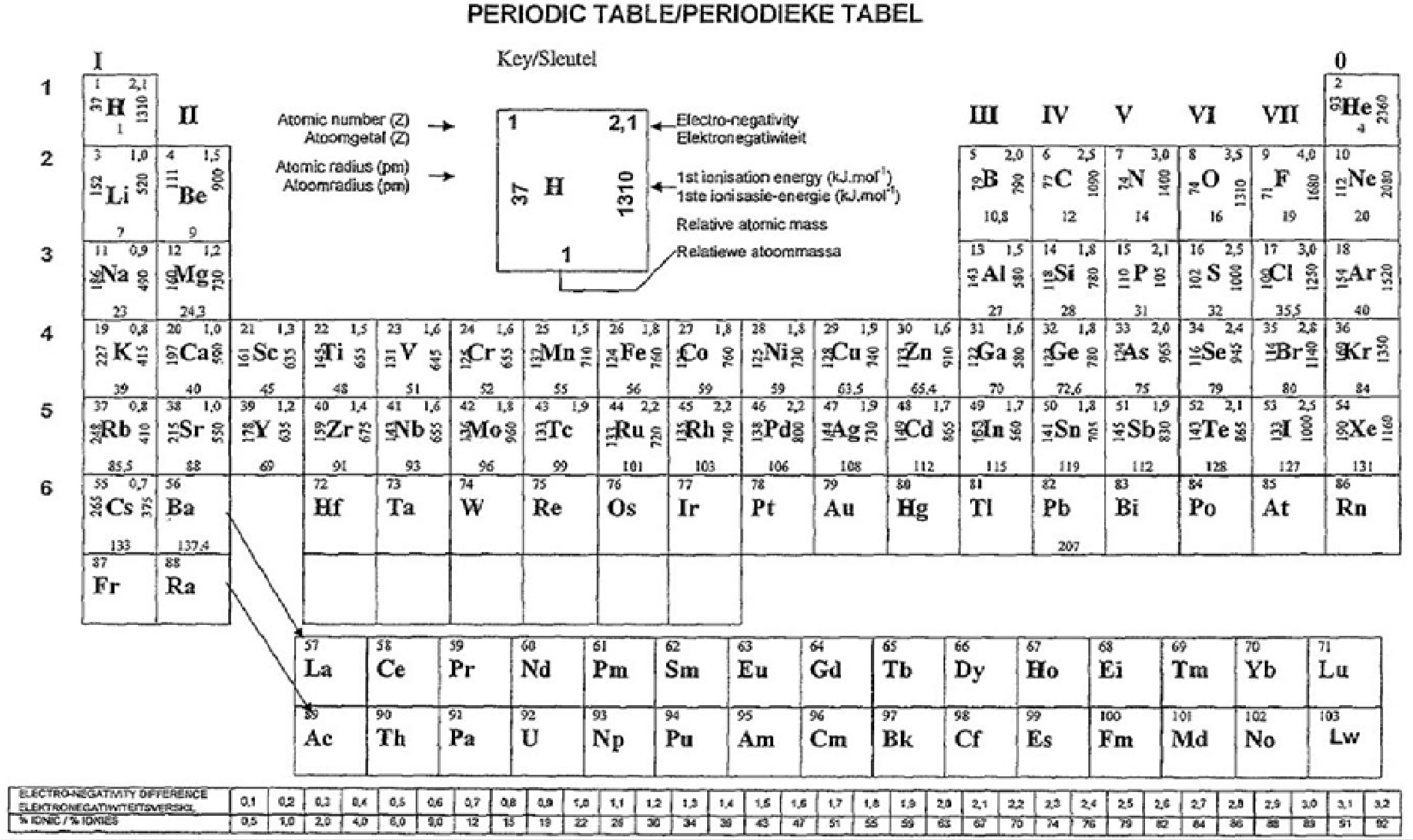
5.4.1 Give the names of compounds A to D (1)

5.4.2 To which homologous series do these compounds belong? (2)

5.5 Explain the concept *resonance* and illustrate by drawing Couper structures for the benzene molecule. (2)

[20]

TOTAL 100



PERIODIC TABLE/PERIODIEKE TABEL

Key/Sleutel

Atomic number (Z) / Atoomgetal (Z) → 1

Atomic radius (pm) / Atoomradius (pm) → 37

2,1 ← Electro-negativity / Elektronegatiwiteit

1310 ← 1st ionisation energy (kJ.mol⁻¹) / 1ste ionisasie-energie (kJ.mol⁻¹)

H

1 ← Relative atomic mass / Relatiewe atoommassa

	I	II											III	IV	V	VI	VII	0
1	1 2,1 37 H 1310 1																	2 93 He 2360 4
2	3 1,0 152 Li 520 7	4 1,5 111 Be 900 9											5 2,0 79 B 790 10,8	6 2,5 77 C 1090 12	7 3,0 74 N 1400 14	8 3,5 74 O 1310 16	9 4,0 71 F 1680 19	10 112 Ne 2080 20
3	11 0,9 186 Na 490 23	12 1,2 160 Mg 730 24,3											13 1,5 143 Al 580 27	14 1,8 118 Si 780 28	15 2,1 110 P 105 31	16 2,5 102 S 1000 32	17 3,0 100 Cl 1250 35,5	18 154 Ar 1520 40
4	19 0,8 227 K 415 39	20 1,0 197 Ca 590 40	21 1,3 161 Sc 635 45	22 1,5 145 Ti 655 48	23 1,6 131 V 645 51	24 1,6 125 Cr 655 52	25 1,5 137 Mn 710 55	26 1,8 124 Fe 760 56	27 1,8 125 Co 760 59	28 1,8 125 Ni 730 59	29 1,9 128 Cu 740 63,5	30 1,6 133 Zn 910 65,4	31 1,6 122 Ga 580 70	32 1,8 123 Ge 780 72,6	33 2,0 125 As 965 75	34 2,4 116 Se 945 79	35 2,8 114 Br 1140 80	36 189 Kr 1350 84
5	37 0,8 248 Rb 410 85,5	38 1,0 215 Sr 550 88	39 1,2 178 Y 635 69	40 1,4 159 Zr 675 91	41 1,6 143 Nb 655 93	42 1,8 136 Mo 960 96	43 1,9 135 Tc 99	44 2,2 133 Ru 720 101	45 2,2 135 Rh 740 103	46 2,2 138 Pd 800 106	47 1,9 144 Ag 730 108	48 1,7 149 Cd 865 112	49 1,7 163 In 560 115	50 1,8 141 Sn 705 119	51 1,9 145 Sb 830 112	52 2,1 143 Te 865 128	53 2,5 133 I 1000 127	54 190 Xe 1160 131
6	55 0,7 265 Cs 375 133	56 Ba 137,4		72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb 207	83 Bi	84 Po	85 At	86 Rn
	87 Fr	88 Ra																

57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Ei	69 Tm	70 Yb	71 Lu
89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lw

ELECTRO-NEGATIVITY DIFFERENCE ELEKTRONEGATIWITEITSVERSKIL	0,1	0,2	0,3	0,4	0,5	0,6	0,7	0,8	0,9	1,0	1,1	1,2	1,3	1,4	1,5	1,6	1,7	1,8	1,9	2,0	2,1	2,2	2,3	2,4	2,5	2,6	2,7	2,8	2,9	3,0	3,1	3,2
% IONIC / % IONIES	0,5	1,0	2,0	4,0	6,0	9,0	12	15	19	22	26	30	34	39	43	47	51	55	59	63	67	70	74	76	79	82	84	86	88	89	91	92

Marking Guidelines

higher education
& training

Department:
Higher Education and Training
REPUBLIC OF SOUTH AFRICA

APRIL 2012

NATIONAL CERTIFICATE

CHEMISTRY N5

(15040015)

This marking guideline consists of 5 pages

QUESTION 1

1.1 Alcohols (2)

1.2 Addition or halogenation (2)

1.3 Pentene (2)

1.4 Propane (2)

1.5 but-2-ene (2)

1.6 1 ,2-dibromopropane (2)

1.7 metanoic acid (2)

1.8 butan (2)

1.9 methylpropanoate (2)

1.10 methanoic acid/formic acid (2)

[20]

QUESTION 2

2.1 b (2)

2.2 b (2)

2.3 d (2)

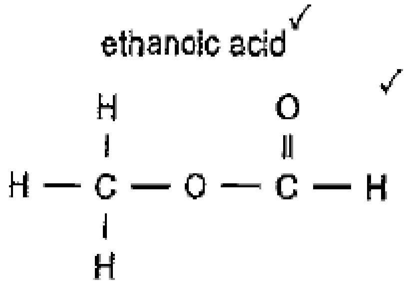
2.4 b (2)

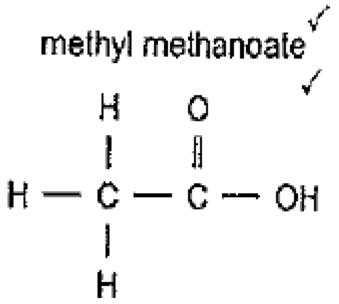
2.5 C (2)

[10]

QUESTION 3

3.1 (4)

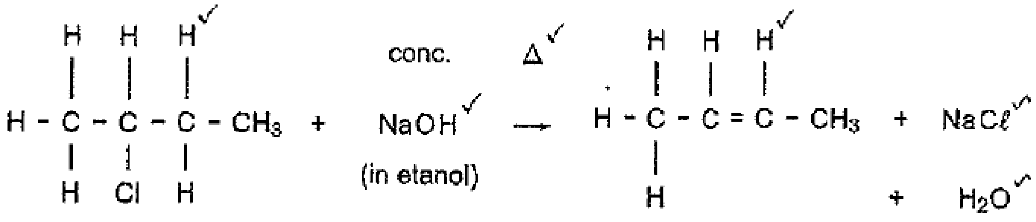




3.2.1 Carbon atom that carries a positive charge. (2)

3.2.2 Atoms separate and one atom retain both bond electrons. (2)

3.3 (5)



$$H-\underset{H}{\overset{H}{C}}-\underset{Cl}{\overset{H}{C}}-\underset{H}{\overset{H^{\checkmark}}{C}}-CH_3 + \underset{\text{(in etanol)}}{\overset{\text{conc.}}{NaOH^{\checkmark}}} \xrightarrow{\Delta^{\checkmark}} H-\underset{H}{\overset{H}{C}}-\overset{H}{C}=\overset{H^{\checkmark}}{C}-CH_3 + NaC\ell^{\checkmark} + H_2O^{\checkmark}$$

3.4.1 $C_nH_{2n}^{-2}$ (1)

3.4.2 (5)
A Butyne
B Propan-2-ol
C Ethene
D 1 ,2-dibromo-ethane
E Propanoic acid

3.4.3 $2C_4H_6 + 9O_2 \rightarrow 8CO_2 + 6H_2O$ + energy balanced (3)

3.4.4 Alcohols (1)

3.4.5 Addition (1)

3.4.6 Carboxylic acids (1)

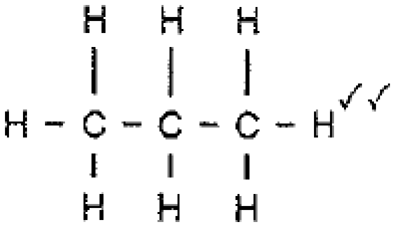
[25]

QUESTION 4

4.1.1 Addition (1)

4.1.2 Prop-1-ene (2)

4.1.3 (2)

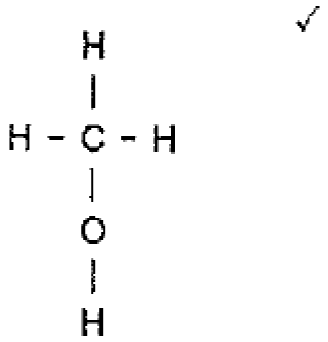


$$H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-H^{\checkmark\checkmark}$$

4.2.1 carboxylic acids (1)

4.2.2 Ethanoic acid (1)

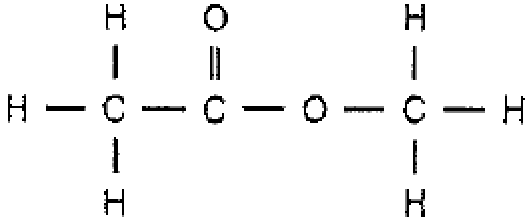
4.2.3 (1)



$$\begin{array}{ccccc} & & H & & \\ & & | & & \\ H & - & C & - & H \\ & & | & & \\ & & O & & \\ & & | & & \\ & & H & & \end{array} \checkmark$$

4.2.4 Methyl ethanoate (3)
Water

4.2.5 (3)

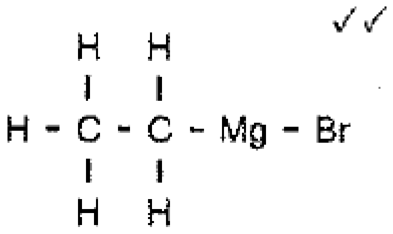


$$\begin{array}{ccccccccccc} & & H & & O & & & & H & & \\ & & | & & \| & & & & | & & \\ H & — & C & — & C & — & O & — & C & — & H \\ & & | & & & & & & | & & \\ & & H & & & & & & H & & \end{array}$$

4.3.1 Propan-2-one (2)

4.3.2 2-methyl-butan-2-ol (2)

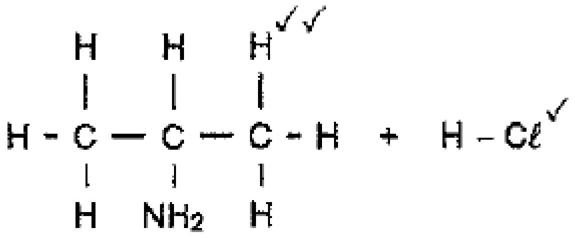
4.3.3 (2)



$$\begin{array}{ccccccccc} & & H & & H & & & & \\ & & | & & | & & & & \\ H & - & C & - & C & - & Mg & - & Br \\ & & | & & | & & & & \\ & & H & & H & & & & \end{array} \checkmark\checkmark$$

4.4.1 Substitution (1)

4.4.2 (3)



$$\begin{array}{cccccccccc} & & H & & H & & H^{\checkmark\checkmark} & & & \\ & & | & & | & & | & & & \\ H & - & C & — & C & — & C & - & H & + \quad H-C\ell^{\checkmark} \\ & & | & & | & & | & & & \\ & & H & & NH_2 & & H & & & \end{array}$$

4.4.3 Amines (1)

[25]

QUESTION 5

5.1 In the addition of a polar molecule to a carbon = carbon double bond the hydrogen attaches itself to the carbon that already holds the greatest umber of hydrogen atoms. (2)

5.2 Elimination or dehydration (2)

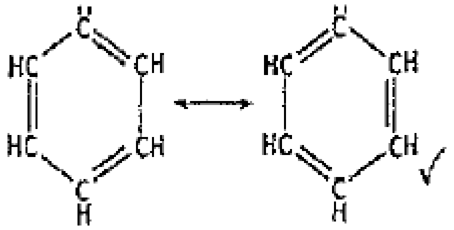
5.3.1 Dimethyl amine (4)

5.3.2 (2)
Yes
5.3.3 (3)
Yes
5.3.4 (4)
Base
5.4

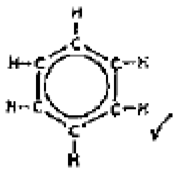
5.4.1 A Analine (1)
B Bromobenzene
C Phenol
D Benzoic acid

5.4.2 Arenes or armomats (2)

5.5 Two different structures with alternating single and double bonds are possible. (2)



Bondlength show that Benzene exits in an intermediate hybrid structure.
Electrons are delocalized and all bonds equal in length.



[20]

TOTAL 100

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This book, with its modular competence-based approach, is aimed at assisting facilitators and learners alike. With its comprehensive understanding of the engineering construction environment, it assists them to achieve the outcomes set for course.

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