Organic Chemistry

Topic Outline

1. Naming Organic Compounds
Rules for naming alkanes, alkenes, alkynes, alcohols, etc. as per syllabus.
Naming simple isomers

5. Polymers
Addition polymers
Uses, properties & structures
Condensation polymers
Biopolymers

2. Hydrocarbons
Physical properties related to bonding.
Chemistry: saturated v. unsaturated
Substitution & addition reactions
Environmental & socioeconomic impacts

4. Organic Acids & Bases
Alcohols cf. carboxylic acids
Esters & their formation
Chemistry of fats & oils
Saponification & emulsification
Detergents   Amines & amides

3. Alcohols
Physical properties related to bonding.
Chemistry: combustion, dehydration, etc.
Oxidation of 1º, 2º & 3º alcohols   Alcohols as fuels

What is this topic about?
To keep it as simple as possible, (K.I.S.S. Principle) this topic covers:

1. Nomenclature (Naming)
What is Organic Chemistry? Concept of an "homologous series".
Naming basic organic compounds according to IUPAC rules, including simple isomers.

2. The Hydrocarbons
Physical properties relate to bonding within & between molecules. Saturated & unsaturated.
Chemical reactions: substitution in saturated types, addition reactions in unsaturated types.
Environmental & socioeconomic impacts of using hydrocarbons.

3. The Alcohols
Physical properties of alkanols related to bonding. Chemical reactions: combustion,
halogen substitution, dehydration & oxidation. Alcohols as "bio-fuels".

4. Organic Acids & Bases
Comparison of alcohols & carboxylic acids. Esterification. Names of esters. Properties.
Chemistry of fats & oils. Soap & saponification. Emulsification. Detergents. Amines & amides.

5. Polymers
Addition polymers. Uses related to properties & structures.
Condensation polymers... polyamides & polyesters. Biopolymers.

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What is "Organic Chemistry"?

The word "organic" refers to <u>living things</u>. In the early days, Chemistry was divided into 2 fields... "Organic Chemistry" referred to the chemicals in, or derived from, living things. These were generally believed to contain a "vital force" (or "life force") from which "life" arose.

"Inorganic Chemistry" was everything else in the chemical world and was lacking in "life force".

During the 19th century great progress was made in the understanding of Chemistry, including the realisation that all the complex chemicals which living things are built from, are compounds of the element <u>carbon</u> combined with (mostly) hydrogen, oxygen & nitrogen. The concept of the "vital force" was dropped and the study of Organic Chemistry became the scientific study of carbon compounds.

So "Organic Chemistry" is really "Carbon Chemistry", although (just to confuse you) the very simple compounds of carbon such as CO_2, CO or CS_2, are actually considered as "inorganic".

To confuse the issue further, in popular culture, mass media & (especially) product-marketing, "organic" has come to mean "pure", "natural", "healthy", "chemical-free", or some combination of these. Anyone who has studied the Science of Organic Chemistry finds it quite humorous to be told that we should all eat only "organic, chemical-free foods". Technically, the phrase "chemical-free substance" is an oxymoron (since all substances contain chemicals) and it is impossible to have "inorganic foods" anyway. Even the most disgusting "junk food" imaginable is in fact organic because its nutrient ingredients (no matter how heavily processed, deep-fried and adulterated) are actually carbon compounds.

Carbon Compounds

All life on Earth is based on carbon compounds, operating within an aqueous (water) environment. We have good reason to believe that, if there is life elsewhere in the Universe, it will also be carbon and water based, although the details of E.T.'s chemistry, biology and appearance cannot be predicted.

Water is the solvent without equal, and carbon is the only element capable of forming the variety of intricate and complex molecules needed to make a living organism.

Carbon rarely forms ions. The immense scope of carbon's chemistry is based on <u>covalent bonding</u>, and the key is that a carbon atom can readily form bonds with other carbon atoms, as well as (notably) hydrogen, oxygen and nitrogen atoms.

C — C
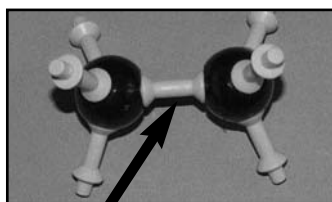
Single Bonds

A single C-C bond involves sharing one pair of electrons. Each carbon atom has 3 other bond positions available, allowing the formation of chains, rings and networks.
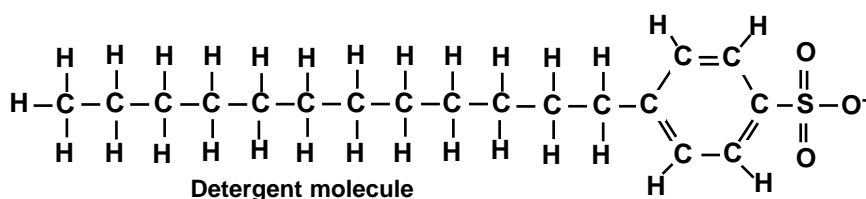
Double C=C Bonds

Carbon atoms can also share 2 pairs of electrons to form double covalent bonds between two carbon atoms, or between a carbon atom and a different atom such as oxygen.
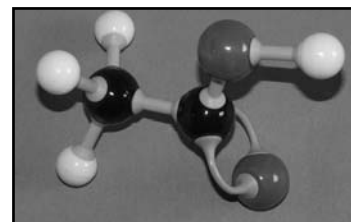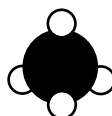
C = C

Triple Bonds

Carbon atoms can even manage to share 3 pairs of electrons.

C ≡ C
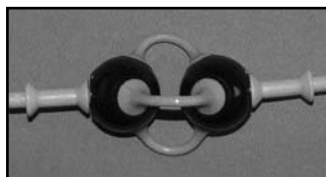
**(Before you ask:
No, carbon atoms cannot
form a quadruple bond.)**

The result is that carbon can form more possible compounds than all the other elements put together.

Organic Chemistry can involve huge, intricate, complicated molecules.

In this module we introduce the basics...

Detergent molecule

keep it simple science ®

1. Naming Organic Compounds

Your first challenge is to become familiar with the basic organic compounds, their general properties, names, molecular structures & their formulas.

Since there is such a vast number of possible carbon compounds (millions of them!!) this seems an impossible task. The key to understanding is that there are patterns. All carbon compounds can be classified in groups called "homologous series" AND there are systematic rules for naming them all.

These rules are set by the International Union of Pure and Applied Chemistry (IUPAC) and are used by scientists throughout the world. In Chemistry, everyone speaks the same language.

The Hydrocarbons

We begin with a class of organic chemicals which (as their name suggests) are composed entirely of carbon and hydrogen atoms bonded covalently.
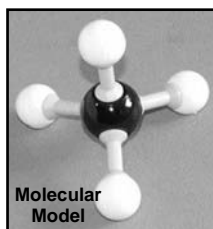
The simplest of the hydrocarbons are

The "Alkanes"

This homologous series of compounds have only carbon & hydrogen atoms and only single chemical bonds between adjacent carbon atoms.
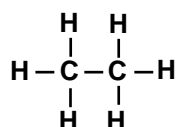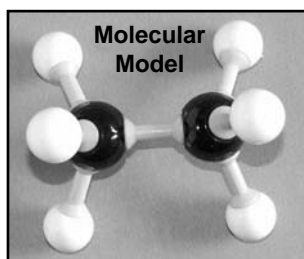
Methane

Molecular Formula CH_4

Structural Formula

$$\begin{array}{c} H \\ | \\ H-C-H \\ | \\ H \end{array}$$

Molecular Model

Ethane

Molecular Formula C_2H_6

Structural Formula

$$\begin{array}{cc} H & H \\ | & | \\ H-C-C-H \\ | & | \\ H & H \end{array}$$

Molecular Model

"Condensed Structural Formula" $CH_3\text{-}CH_3$

Propane

Molecular Formula C_3H_8

Structural Formula

$$\begin{array}{ccc} H & H & H \\ | & | & | \\ H-C-C-C-H \\ | & | & | \\ H & H & H \end{array}$$

Molecular Model
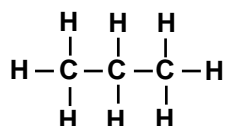
"Condensed Structural Formula" $CH_3\text{-}CH_2\text{-}CH_3$
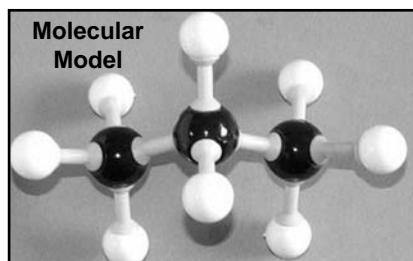
See the pattern beginning to emerge?
The Syllabus requires that you learn the first 8 compounds in this series... the "Alkanes"

Naming Alkanes

The Alkanes are just one of many "Homologous Series" of carbon compounds. An Homologous Series means a group of chemicals which form a logical series or pattern, in terms of their molecular structure. As you'll learn, they also have similar properties which also follow patterns.

You must learn the following rules for naming:

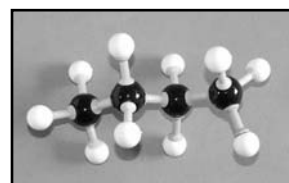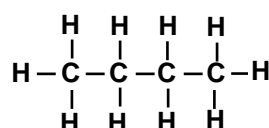| No. of Carbon Atoms		Prefix
...there are many more, but this is as far as the Syllabus expects you to learn.	1	Meth-
	2	Eth-
	3	Prop-
	4	But-
	5	Pent-
	6	Hex-
	7	Hept-
	8	Oct-

To name any ALKANE, just add "-ANE" to the appropriate prefix above.

We now continue the series...

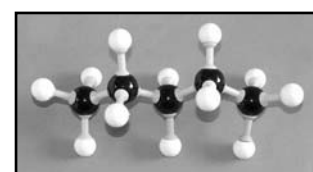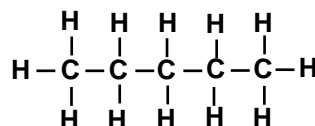### Butane

Molecular Formula C_4H_{10}

Structural Formula

$$\begin{array}{cccc} H & H & H & H \\ | & | & | & | \\ H-C-C-C-C-H \\ | & | & | & | \\ H & H & H & H \end{array}$$

"Condensed Structural Formula" $CH_3\text{-}(CH_2)_2\text{-}CH_3$

Pentane

Molecular Formula C_5H_{12}

Structural Formula

$$\begin{array}{ccccc} H & H & H & H & H \\ | & | & | & | & | \\ H-C-C-C-C-C-H \\ | & | & | & | & | \\ H & H & H & H & H \end{array}$$

"Condensed Structural Formula" $CH_3\text{-}(CH_2)_3\text{-}CH_3$

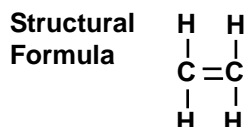| Hexane | C_6H_{14} | $CH_3\text{-}(CH_2)_4\text{-}CH_3$ |
| Heptane | C_7H_{16} | $CH_3\text{-}(CH_2)_5\text{-}CH_3$ |
| Octane | C_8H_{18} | $CH_3\text{-}(CH_2)_6\text{-}CH_3$ |

The Hydrocarbons (cont.)

The Alkenes

are also hydrocarbons, but each alkene molecule contains **one** C= C double bond.

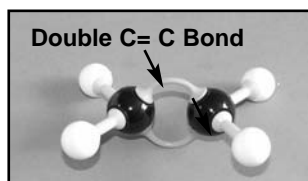Since there have to be at least 2 carbon atoms to have a double bond, the series begins with...

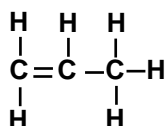### Ethene

Molecular Formula C_2H_4

Structural Formula

```
  H   H
  |   |
  C = C
  |   |
  H   H
```

To name, just add "-ENE" to the appropriate prefix.

Double C= C Bond

"Condensed Structural Formula" $CH_2=CH_2$

Propene

Molecular Formula C_3H_6

Structural Formula

```
  H   H   H
  |   |   |
  C = C — C — H
  |       |
  H       H
```


Double C= C Bond

"Condensed Structural Formula" $CH_2=CH-CH_3$
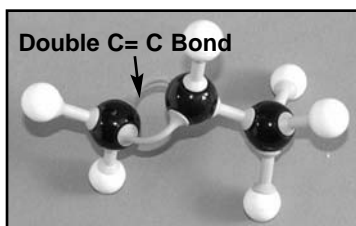
Butene

Molecular Formula C_4H_8

Structural Formula

```
  H   H   H   H
  |   |   |   |
  C = C — C — C — H
  |       |   |
  H       H   H
```


Double C= C Bond
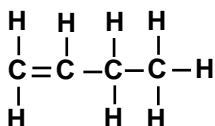
"Condensed Struct. Form." $CH_2=CH-CH_2-CH_3$
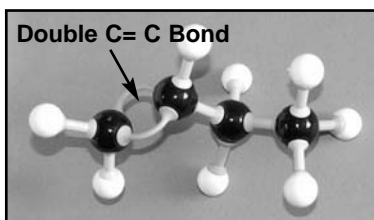
Pentene	C_5H_{10}	$CH_2=CH-(CH_2)_2-CH_3$
Hexene	C_6H_{12}	$CH_2=CH-(CH_2)_3-CH_3$
Heptene	C_7H_{14}	$CH_2=CH-(CH_2)_4-CH_3$
Octene	C_8H_{16}	$CH_2=CH-(CH_2)_5-CH_3$

... and, you guessed it...

The Alkynes

More hydrocarbons, but each alkyne molecule contains **one** C≡C triple bond.

To name, just add "-YNE" to the appropriate prefix.

Name	Molecular Formula	Cond.Struct. Formula
Ethyne	C_2H_2	$CH≡CH$
Propyne	C_3H_4	$CH≡C-CH_3$
Butyne	C_4H_6	$CH≡C-CH_2-CH_3$
Pentyne	C_5H_8	$CH≡C-(CH_2)_2-CH_3$
Hexyne	C_6H_{10}	$CH≡C-(CH_2)_3-CH_3$
Heptyne	C_7H_{12}	$CH≡C-(CH_2)_4-CH_3$
Octyne	C_8H_{14}	$CH≡C-(CH_2)_5-CH_3$

Suggested Prac Work

You may be able to use a molecular model kit to construct models of these molecules, as suggested by the photos on these pages.

This is one of the most important ways for you to "get your head around" these series of compounds.

Resist the temptation to use the kits as toys and "play Lego". Work towards **methodically** building each molecule, in turn.

Count the atoms to confirm the molecular formula.

Compare the model to the 2-D "structural formula" to get used to the conventions often used to depict these compounds.

Compare also the "condensed structural formula". These vary in the style used, but it would be best to understand how to read & interpret them.

Short-Cuts to Molecular Formulas

For each Homologous Series there is a general formula for finding any molecular formula.

Alkanes	Alkenes	Alkynes
C_nH_{2n+2}	C_nH_{2n}	C_nH_{2n-2}

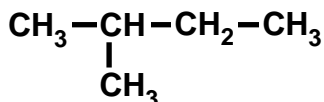where n = number of carbon atoms

Isomers

keep it simple science ®

Consider these two hydrocarbon molecules:
(shown in another variation of the "condensed structural formula")

You should build each of these with a model kit as you consider the following.

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

$$CH_3-CH-CH_2-CH_3$$
$$\qquad\quad |$$
$$\qquad\quad CH_3$$

Each of these molecules has exactly the same molecular formula: C_5H_{12}
(don't trust our word... check!)

They contain exactly the same numbers of the same atoms with exactly the same type & number of chemical bonds holding them together.

BUT THEY ARE DIFFERENT COMPOUNDS !!

Their physical & chemical properties (later) are quite similar, but NOT identical. These are NOT the same compound and therefore, they must be given different names.

Compounds like this are said to be "isomers".

> ### ISOMERS
> **have the same molecular formula, but different structures.
> They are different compounds, with different properties and must be given different names.**

So, what are they called?
The first one (you should figure out) is "pentane".

The 2nd, according to IUPAC rules is called "methylbutane". It is an isomer of pentane.

Explanation: the longest linear chain in the molecule has 4 carbon atoms joined by single bonds. Therefore, "butane" is its "backbone".

It has a -CH_3 "side-branch". This is called a "methyl-" (1-carbon) side-branch.

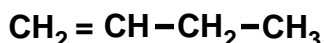**A 2-carbon side-branch (-CH_2CH_3) is "ethyl-".**

A 3-C side-branch (-$CH_2CH_2CH_3$) is "propyl-", then "butyl-", "pentyl-", and so on.

Another Example
Consider these 3 (labelled A,B,C)

A.
$$CH_3-CH-CH_2-CH_2-CH_3$$
$$\qquad\quad |$$
$$\qquad\quad CH_3$$

B.
$$CH_3-CH_2-CH-CH_2-CH_3$$
$$\qquad\qquad\quad |$$
$$\qquad\qquad\quad CH_3$$

C.
$$CH_3-CH_2-CH_2-CH-CH_3$$
$$\qquad\qquad\qquad\quad |$$
$$\qquad\qquad\qquad\quad CH_3$$

All 3 have the same formula C_6H_{14}.
You will figure out that all are isomers of hexane.

All have a 5-carbon "backbone" with a "methyl-" side-branch, so they are all "methylpentane".

To give each a unique name, we must now number the carbon atoms of the backbone and use a number to indicate the position of the side-branch.

Numbering from the left, it means that
A = "2-methylpentane"
and
B = "3-methylpentane"

Does this mean that C = "4-methylpentane"? NO !

If you build a model of A, then turn it around, you will see that you have C. A and C are the same molecule, so   C = "2-methylpentane"

You must number from either right or left so that the number(s) used are as small as possible.

$$CH_3-CH-CH_2-CH_2-CH_3$$
$$\qquad\quad |$$
$$\qquad\quad CH_3$$
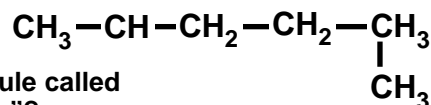
So, is this molecule called "1-methylpentane"?
Build a model and you will see that it is simply "hexane". It has NO side-branch.

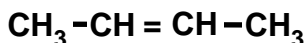**Can you also see that the example above left (methylbutane) has NO NEED for any numbers?**

Isomers of Alkenes & Alkynes

Just like the alkanes, the alkenes & alkynes can also have isomers with side-branches, and the same rules apply.

Additionally, the position of the double or triple bond may require isomer numbering, such as:
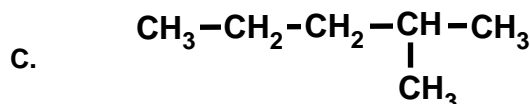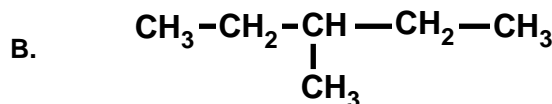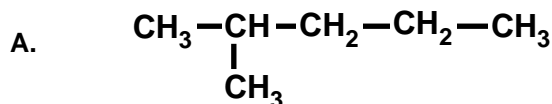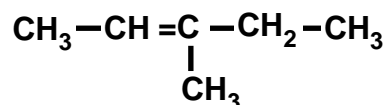
$$CH_2=CH-CH_2-CH_3 \qquad CH_3-CH=CH-CH_3$$

"butene" (number not needed if "1")   **"2-butene"**

Can you suggest a name for this isomer of hexene?

$$CH_3-CH=C-CH_2-CH_3$$
$$\qquad\qquad\quad |$$
$$\qquad\qquad\quad CH_3$$

The correct IUPAC name is "hidden" on the next page.

The Alcohols (Alkanols)

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Now you are introduced to another important homologous series... the alkanols, known commonly as "alcohols".

The alkanols contain all C-C single bonds, but on one of the carbon atoms there is an -OH group... an oxygen atom and hydrogen atom.

This is NOT a hydroxide ion (as in NaOH). It does NOT ionise in water. It is referred to as a "hydroxyl" group. You will see later that the hydroxyl group involves a polar covalent bond and that this has great significance to the physical & chemical properties of these compounds.
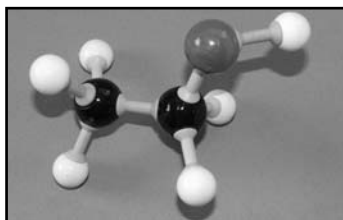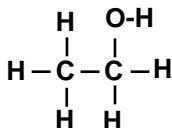
> **To name any ALKANOL**
> add "-ANOL" to the appropriate prefix.
> General Formula $C_nH_{2n+1}OH$

Methanol CH_3OH
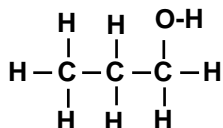(Formula could be written CH_4O, but it is usual to emphasise the -OH group)
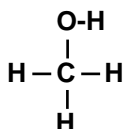
Ethanol C_2H_5OH

This is by far, the most important member of the series.

Condensed Structural Formula
CH_3-CH_2OH
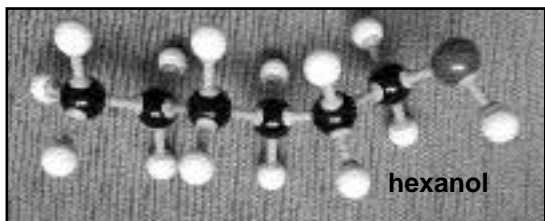
Propanol C_3H_7OH

CH_3-CH_2-CH_2OH

and then...

Butanol	C_4H_9OH	CH_3-$(CH_2)_2$-CH_2OH
Pentanol	$C_5H_{11}OH$	CH_3-$(CH_2)_3$-CH_2OH
Hexanol	$C_6H_{13}OH$	CH_3-$(CH_2)_4$-CH_2OH
Heptanol	$C_7H_{15}OH$	CH_3-$(CH_2)_5$-CH_2OH
Octanol	$C_8H_{17}OH$	CH_3-$(CH_2)_6$-CH_2OH

hexanol

From prev.page. "3-methyl-2-pentene"

Isomers of Alkanols

It is completely possible for an alkanol to have "side-branch" isomers, just like the alkanes. In that case, the same rules would apply.

However, side-branch isomers are NOT the most significant type of isomer among the alkanols. Much more important is the <u>position of the hydroxyl</u> group within the molecule. Exactly where the -OH group is, turns out to have a major influence on the chemistry of the alkanol... details later.
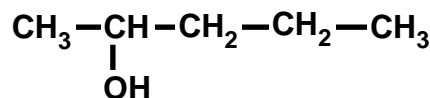
Primary (1º) Alcohols
This simply refers to alkanols in which the hydroxyl group is located on the terminal (end) carbon atom in the molecule.

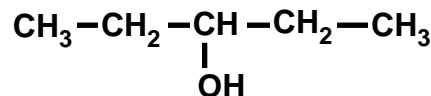All the examples at left are 1º alcohols.

Secondary (2º) Alcohols
This refers to alkanols in which the hydroxyl group is located "inside" the carbon chain on a non-terminal carbon atom.

Examples:

2-pentanol
CH_3—CH—CH_2—CH_2—CH_3
|
OH

3-pentanol
CH_3—CH_2—CH—CH_2—CH_3
|
OH

All 2º alcohols can be described in a general way by this structural formula, where R1 and R2 refer to any carbon-hydrogen chain.
R_1—CH—R_2
|
OH
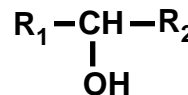
Note that the carbon atom connected to the hydroxyl group is also carrying a hydrogen atom. Compare that to the tertiary alcohols below.

Tertiary (3º) Alcohols
This refers to an alkanol with the general structure shown, right. Note that the carbon atom carrying the hydroxyl group is bonded to 3 other carbon atoms and is NOT directly bonded to a hydrogen atom. This changes the way that 3º alchols react. (later)

R_1—C—R_3 with R_2 above and OH below
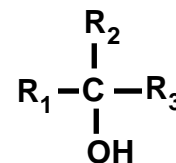
Tertiary alcohols must have a side-chain.

Example:

2-methyl-2-butanol

(sometimes written as 2-methylbutan-2-ol)

CH_3—C—CH_2—CH_3 with CH_3 above and OH below

This is also an isomer of pentanol, $C_5H_{11}OH$.

The Carboxylic Acids

This homologous series is defined by the presence of a "functional group" called the "carboxyl" group (-COOH).

The general structure of a carboxylic acid is shown, where "R" can be as simple as a single hydrogen atom (methanoic acid, at right) or it might be a long carbon-hydrogen chain, with branches, multiple double C= C bonds and other variations.

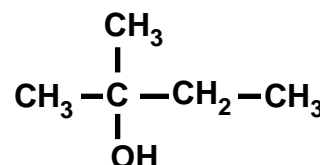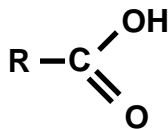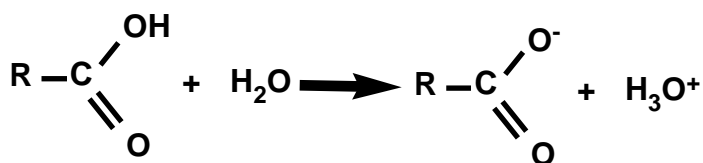The -COOH group must be on a terminal C-atom.

Because of the presence of the C= O bond attached to the same carbon atom, the O-H bond in the hydroxyl group becomes more polarised and will ionise in water forming hydronium ions.
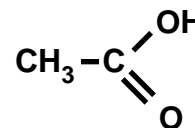
That's why they are called acids. However, they are weak acids because the degree of ionisation is typically only 1% or less.

> To name any CARBOXYLIC ACID
> add "-ANOIC ACID" to the appropriate prefix.

Methanoic acid HCOOH
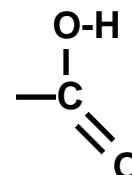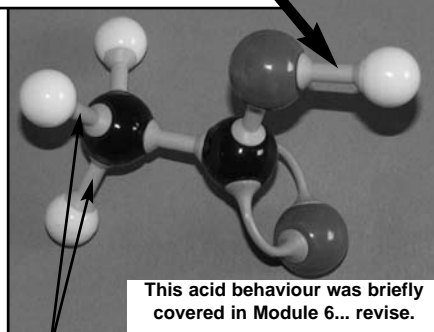(also known as "formic acid" ...research why)
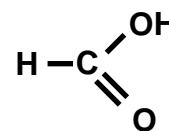
The best known member of this series is ethanoic acid CH_3COOH.

Also known as "acetic acid", it is the main ingredient in vinegar.

This bond is polar, and can ionise in water

This acid behaviour was briefly covered in Module 6... revise.

This group is usually abbreviated as "-COOH" and is always acidic.

These C-H bonds are non-polar, and never ionise.

Then follow propanoic acid (C_2H_5COOH), butanoic acid (C_3H_7COOH), pentanoic (C_4H_9COOH), hexanoic ($C_5H_{11}COOH$), and so on.

Aldehydes & Ketones

The alkanals (traditionally called "aldehydes") form an homologous series with the general structure as shown, where "R" could be as simple as a single hydrogen atom (methanal, below) or it might be a longer carbon-hydrogen chain.
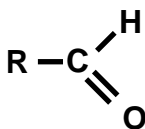
The functional group (-CHO) must occur on a terminal carbon atom. The hydrogen attached to the terminal carbon does NOT ionise to give any acidic properties.

Methanal CH_2O
(traditionally known as "formaldehyde" and famously used as a preservative.)
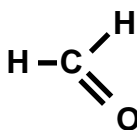
Ethanal C_2H_4O
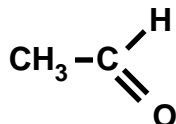
Propanal	C_3H_6O	$CH_3\text{-}CH_2\text{-}CHO$
Butanal	C_4H_8O	$CH_3\text{-}(CH_2)_2\text{-}CHO$
Pentanal	$C_5H_{10}O$	$CH_3\text{-}(CH_2)_3\text{-}CHO$
Hexanal	$C_6H_{12}O$	$CH_3\text{-}(CH_2)_4\text{-}CHO$

and so on.

The alkanones (traditionally called "ketones") form another series containing a C= O group, but it is on a carbon atom "inside" a carbon chain instead of on a terminal carbon.
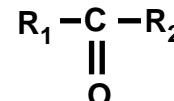
The general structure is shown, with R_1 & R_2 representing carbon-hydrogen chains.

Since the functional group (C= O) must be "inside" the carbon chain, it follows that the first member of the series must have 3 carbons and is, therefore,

propanone $CH_3\text{-}CO\text{-}CH_3$
(Traditionally called "acetone" and well known as "nail polish remover")
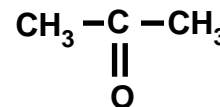
butanone $CH_3\text{-}CO\text{-}CH_2\text{-}CH_3$
Once you get to 5 or more carbon atoms, the position of the C= O group within the molecule can vary, so that isomers require numbers.

For example:
$CH_3\text{-}CO\text{-}CH_2\text{-}CH_2\text{-}CH_3$ is 2-pentanone, while
$CH_3\text{-}CH_2\text{-}CO\text{-}CH_2\text{-}CH_3$ is 3-pentanone.

You might figure out the rest with your model kit.

> Note that each aldehyde & its corresponding ketone are isomers, since both have the formula $C_nH_{2n}O$

Halogenated Compounds

"Halo-" refers to the "halogens"... the general name for the elements of group 7 of the Periodic Table; fluorine, chlorine, bromine and iodine.

Halogen atoms can readily substitute for a hydrogen atom in any organic molecule whether it is an alkane, an alcohol, carboxylic acid, alkene, or whatever. Here, we will apply the KISS Principle and cover only halogen substitution in alkanes.

The simplest example is a methane molecule with one of its hydrogens replaced by (say) a chlorine atom.

$$H-\overset{\overset{\displaystyle Cl}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-H \qquad \textbf{CH}_3\textbf{Cl}$$

\underline{chloro}methane

If, instead of chlorine, the replacement was:

• fluorine... CH_3F = \underline{fluoro}methane.
• bromine... CH_3Br = \underline{bromo}methane.
• iodine... CH_3I = \underline{iodo}methane.

What if 2, or more, hydrogens were replaced by chlorine atoms?

$$H-\overset{\overset{\displaystyle Cl}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-Cl \qquad \textbf{CH}_2\textbf{Cl}_2$$

\underline{Di}chloromethane

$$Cl-\overset{\overset{\displaystyle Cl}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-Cl \qquad \textbf{CHCl}_3$$

\underline{Tri}chloromethane

$$Cl-\overset{\overset{\displaystyle Cl}{|}}{\underset{\underset{\displaystyle Cl}{|}}{C}}-Cl \qquad \textbf{CCl}_4$$

\underline{Tetra}chloromethane

Prefixes to use for the number of halogen atoms:

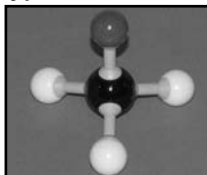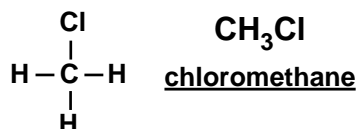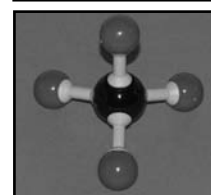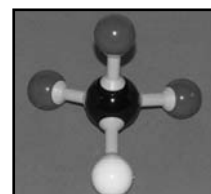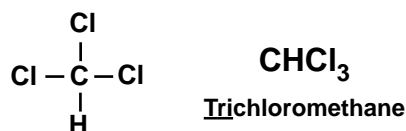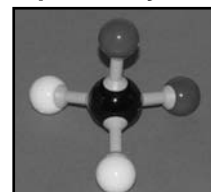|		
1 = no prefix	3 = tri	5 = penta
2 = di	4 = tetra	6 = hexa

What if there is more than one type of halogen atom substituted? They must be ordered \underline{alphabetically} by halogen name... (not by any prefixes used, though).

$$F-\overset{\overset{\displaystyle Cl}{|}}{\underset{\underset{\displaystyle F}{|}}{C}}-Br$$
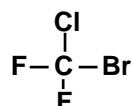
This little beauty, $CBrClF_2$ is called "\underline{bromochlorodifluoromethane}"

Isomers of Haloalkanes

When the molecule gets bigger, another variation that can occur is in the position of the various atoms.

For example, these 2 molecules are ethane, with 2 chlorines substituted in place of hydrogens.

Both Cl atoms attached to same carbon.

Cl atoms attached to different carbon atoms.
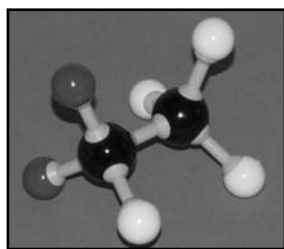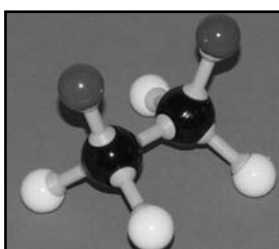
1,1-dichloroethane   **1,2-dichloroethane**

These molecules have the same molecular formula ($C_2H_4Cl_2$) but have a different structure, and are different compounds. Their m.p. & b.p., density, and other properties would be slightly different. We must give them a different name.

This is done by \underline{numbering the carbon atoms} (from whichever end gives the smallest result) and stating the position number \underline{for every halogen} atom present.

More Examples

$$C_4H_5Cl_3F_2$$
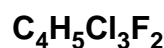
Best to number the carbons from the right.

$$H-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle F}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle Cl}{|}}{\underset{\underset{\displaystyle Cl}{|}}{C}}-\overset{\overset{\displaystyle Cl}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-F$$
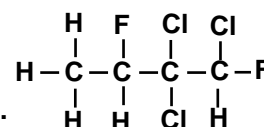
1,2,2-trichloro-1,3-difluorobutane

$$C_5H_5Br_3F_4$$
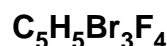
Best to number from the left.

$$F-\overset{\overset{\displaystyle F}{|}}{\underset{\underset{\displaystyle F}{|}}{C}}-\overset{\overset{\displaystyle Br}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle Br}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle Br}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-F$$
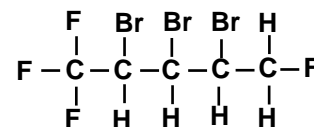
2,3,4-tribromo-1,1,1,5-tetrafluoropentane.

Now Try Worksheet 1

Where is this going next?

The syllabus requires that we keep going with the "naming thing" for a couple more homologous series. We think this is getting monotonous!

We will now switch to the study of the uses, properties & reactions of some important organic compounds.

If any of the groups we're about to ignore come up, we'll give you a quick lesson on their names \underline{at that time}.

2. The Hydrocarbons

As you now know, "hydrocarbons" includes the alkane, alkene & alkyne homologous groups. (as well as some others we're not getting into.)

You may already know the significance of these compounds for our society:

Energy Sources
All our important liquid & gas fuels & lubricants are mixtures of hydrocarbon compounds. For example:

"Natural Gas" and L.P.G. are mostly methane.

"Bottled Gas" is usually propane or butane, or a mixture. As well as BBQ's, bottled gas is used extensively in regional areas for cooking & heating.

Petrol is a mixture of various alkanes (& some alkenes) ranging from pentane to octane, including branched-chain isomers.

Diesel fuel is a mixture of hydrocarbons with formulas from about $C_{10}H_{20}$ to about $C_{15}H_{32}$.

These fuels are the energy "backbone" of our transport systems and have traditionally been obtained from petroleum, a fossil fuel.

The use of petroleum fuels is still increasing, despite the link to climate change by global warming. Our society depends heavily on hydrocarbon fuels and ironically this may contribute to the ultimate downfall of our civilisation. But that's another story... (later)

Chemical Industry
One of our key industrial chemicals is ethene (C_2H_4), commonly called "ethylene".

More than 150 million tonnes is produced per year because it is a critical starting material for making many of our plastics and synthetic fabrics, plus many other chemical products. Most of our ethene is refined from petroleum.

Physical Properties of Hydrocarbons

As you know by now, the properties of any chemical substance are determined by the bonding within.

Alkanes and alkenes contain only 3 types of bond within the molecules:

• Single C-C bonds   **all non-polar**
• Double C= C bonds   **covalent bonds**
• C-H bonds

Therefore, you would expect these compounds to:

• have relatively low m.p. & b.p.'s   and you'd
• be insoluble in water   be correct !
• be non-conductors of electricity

To keep it simple, (K.I.S.S. principle) consider just the boiling points:

Alkane	b.p. (°C)	State 25°C	Alkene	b.p. (°C)	State 25°C
Methane	-162	gas			
Ethane	-89	gas	Ethene	-104	gas
Propane	-42	gas	Propene	-48	gas
Butane	-1	gas	Butene	-6	gas
Pentane	36	liquid	Pentene	30	liquid
Hexane	69	liquid	Hexene	64	liquid
Heptane	98	liquid	Heptene	94	liquid
Octane	126	liquid	Octene	121	liquid

More on States & Density
Alkanes with more than about 25 carbon atoms are solid at room temp. The stuff we call "wax" is a mixture of alkanes with an average of 32 carbons.

Densities are lower than water. All liquid or solid hydrocarbons float in water.

When the values for b.p. are graphed the pattern becomes obvious, and also the great similarity between the alkanes and alkenes (at least for this property).

Boiling Points rise as the molecules get larger

Can you guess what the corresponding graph for alkynes would be? Prove it!
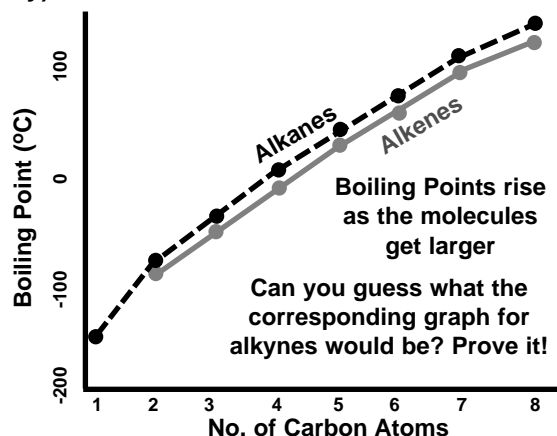
Inter-molecular Forces?
Inside each molecule ("intra-molecular") are strong, non-polar, covalent bonds.

However, the only forces between the molecules ("inter-molecular") are weak "dispersion forces", so the molecules separate from each other easily. This explains why m.p. & b.p. are generally low.

Dispersion forces arise due to transient electrical attractions from momentary imbalances of the electric charge distribution within each molecule as it vibrates & rotates. These weak forces exist within all substances, but in ionic or polar comounds they are insignificant. In hydrocarbons, that's all there is.

Dispersion forces become stronger as the size and mass of the molecule increases, which explains the pattern of the graph.

Safety Considerations

Volatility

A substance is said to be volatile if, at room temperature, it vaporises readily. A simple indicator of volatility is the boiling point, but it is not the only factor.

Obviously, the alkanes and alkenes with 4 or less carbon atoms are already gases at room temperature, but even those which are liquids are highly volatile.

Consider octane, a component of petrol. Its boiling point is a little above that of water, but it is much more volatile. At room temperature, octane (petrol) in an open container vaporises rapidly compared to water under the same conditions.

The explanation is, again, all about bonding. Water molecules tend to cling together because of the dipole-dipole attractions of hydrogen bonding. Octane molecules have only the weak "dispersion forces" holding them, and many molecules have enough energy to escape into the gas state, even at temperatures well below the boiling point.

The volatility of the alkanes and alkenes has important safety consequences.

Safety Consequences

We haven't yet looked at the chemical properties of alkanes and alkenes, but don't forget that these are fuel compounds... they contain a lot of energy, are highly inflammable, and now we find out they are highly volatile as well! DANGER, DANGER!

Natural Gas is mostly methane. It is stored in high pressure cylinders, outdoors & kept cool.

Propane & Butane are
used as bottled "BBQ gas". They are stored as pressurised liquids in pressure cylinders and used outdoors, or in well-ventilated areas only. Small amounts of "smelly" chemicals are added to gas fuels so that leaks are easily detected by smell.

Petrol, Kerosene & Diesel are highly volatile liquid
fuels. They must be stored in sealed drums or tanks, and all sparks or flames (even mobile phones) kept well away. All transfer of fuel from tank to tank (e.g. filling the car) must be done outdoors.

You will NOT be doing any practical work with these substances because of safety concerns, plus their fumes are harmful if inhaled.

Chemical Reactions of the Hydrocarbons

The fact that most of our hydrocarbons come from petroleum which formed millions of years ago, should give you a clue about their chemistry... these are (generally) stable chemicals which do not react or change readily, even though many of them seem to be large, fragile molecules.

The most important chemical reaction of the hydrocarbons (according to their human uses) is not mentioned in the syllabus for this module...

Combustion

You have studied this in the past, so this is a brief reminder. All hydrocarbons will burn by reacting with oxygen to form CO_2 and water vapour.

We will compare the combustion reactions of ethane, ethene and ethyne so you see the differences between compounds with the same number of carbon atoms.

Note the different molar quantities of oxygen required for complete combustion in each case. Less oxygen is needed if there is less hydrogen in the hydrocarbon, & slightly less energy is released. (if measured per gram of fuel) Less water is formed, per mole of fuel.

No-one uses ethene (ethylene) as a fuel because it is too valuable for making plastics, etc. Ethyne (also known as "acetylene") is used in high-temperature "oxy-acetylene torches" for welding and cutting metals.

Now compare the ethane reaction with that of octane, a component of petrol.

Octane   (kJ per gram)

$$C_8H_{18} + {}^{25}/_2\, O_2 \longrightarrow 8CO_2 + 9H_2O \qquad 47.9$$
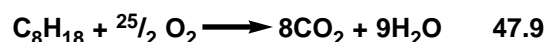
Compared to ethane, mole-for-mole this produces 4x as much CO_2, but only 3x as much water, with about 7% less energy yield per gram, although this is still high.

Undoubtably, the hydrocarbons (especially alkanes) ARE high-energy, convenient fuels. They are really useful, but we need to find alternative, renewable sources of them.

Energy release (kJ per gram)

Ethane
$$C_2H_6 + {}^{7}/_2\, O_2 \longrightarrow 2CO_2 + 3H_2O \qquad 51.8$$

Ethene
$$C_2H_4 + 3\, O_2 \longrightarrow 2CO_2 + 2H_2O \qquad 50.4$$

Ethyne
$$C_2H_2 + {}^{5}/_2\, O_2 \longrightarrow 2CO_2 + H_2O \qquad 50.0$$

Reactions of the Hydrocarbons (cont.)

ALL the hydrocarbons will undergo combustion, but (chemically) that is where their similarity ends.

In other chemical reactions, the alkanes are very different to the alkenes & alkynes. It is as if we can divide the hydrocarbons into 2 distinct chemical types... and so we do:

Saturated v. Unsaturated

The alkanes are said to be "saturated" (with hydrogen), meaning that each molecule has the maximum number of hydrogen atoms possible.

This is because all the C-C bonds are single, so every other bond position is occupied by hydrogen.

The alkenes and alkynes have at least one double (or triple) C= C bond. This reduces the number of hydrogens possible in the molecule. This condition is described as "unsaturated".

Some long-chain molecules may have multiple C= C bonds. These are said to be "polyunsaturated", a term you may have heard in relation to fat & oil molecules in our food.

Whether a hydrocarbon is saturated or unsaturated has consequences in terms of which chemical reactions (apart from combustion) each compound will undergo.

Basically, the story is:

• the C-C and C-H covalent bonds are quite stable and relatively unreactive, except for combustion,

BUT

• the C= C double (or triple) bond is much more reactive and will readily undergo a variety of chemical changes.

Halogen Substitution Reactions in (Saturated) Alkanes

One of the few reagents which will react with an alkane is one of the halogen elements... F_2, Cl_2 and Br_2. (I_2 has lower activity; doesn't react easily)

The reaction is called "substitution" because a halogen atom substitutes for a hydrogen atom.

eg CH_4 + Cl_2 ⟶ CH_3Cl + HCl
  methane   chlorine   hydrogen chloride
                  chloromethane
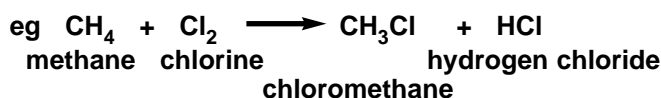
Reactions of this type can be initiated by UV light and can result in a complex mixture of different products. This is because substitution reactions proceed by a chemical process involving "free-radicals", explained below.

Step 1. Free-Radical Formation
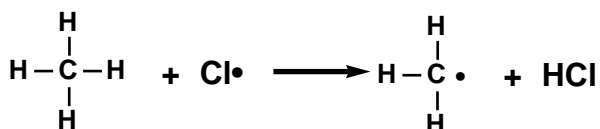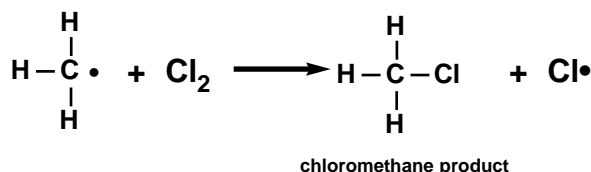
UV energy

Cl — Cl ⟶ Cl• + Cl•
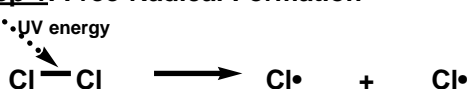
A Cl_2 molecule struck by high frequency light such as ultra-violet rays can split to form 2 unbonded single chlorine atoms.

These bare atoms are highly reactive and will "attack" almost any other substance. Highly reactive chemical species like this, with a "naked" electron are "desperate" to form a chemical bond, and are called "free-radicals".

Step 2 Free-Radical Attack

If a Cl• free-radical meets an alkane it will "steal" a hydrogen atom to form HCl:

$$H-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-H \ + \ Cl• \ \longrightarrow \ H-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}• \ + \ HCl$$

Step 3 Free-Radical Propagation

The CH_3• species is another free-radical ("methyl free-radical") and is also highly reactive.
If it bumps into a Cl_2 molecule:

$$H-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}• \ + \ Cl_2 \ \longrightarrow \ H-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-Cl \ + \ Cl•$$

chloromethane product

Can you see what is happening? Each attack by a free-radical produces yet another free-radical.

Free-radicals are propagating or "reproducing". This produces a "chain-reaction" or cascade of reactions. A mixture of an alkane with chlorine, kept in the dark, will not react. Expose it to sunlight (or certain catalysts) and there may be a sudden explosion as free-radical reactions occur!

There can be a great variety of products because a molecule that already reacted, may react again:

eg CH_3Cl + Cl_2 ⟶ CH_2Cl_2 + HCl
chloromethane + chlorine   dichloromethane + hydrogen chloride

and even:

$$H-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}• \ + \ H-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}• \ \longrightarrow \ C_2H_6$$

Two methyl free-radicals ⟶ ethane
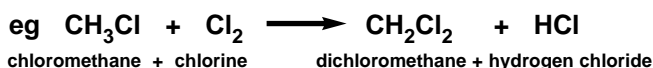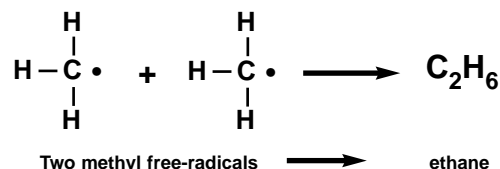
Typically, if there is an adequate supply of chlorine, the final product mixture may contain dozens of different haloalkanes, including some with longer alkane chains.

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Addition Reactions in Unsaturated Hydrocarbons

Petrochemicals

When petroleum is refined, the major products are the fuels such as petrol and diesel. However, it's not all about fuel. Our chemical industry depends on a whole range of other compounds extracted from petroleum, which are collectively called "Petrochemicals".

Petrochemicals are vital raw materials for the manufacture of
• plastics and synthetic fibres
• pigments for inks, dyes and paints
• detergents & adhesives
• cosmetics & pharmaceuticals
• explosives
        ... and much more.

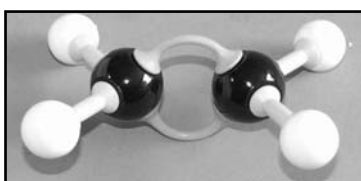One of the most important petrochemicals is

Ethene C_2H_4

Ethene is also known by its common name, "Ethylene".

We will use ethene as our prime example for the reactions following, because:

• it is one of the most useful chemicals on Earth and
• it is the smallest & simplest example of an unsaturated hydrocarbon. (KISS Principle!)

The double bond is highly reactive

X—Y
Many substances will "attack" this bond
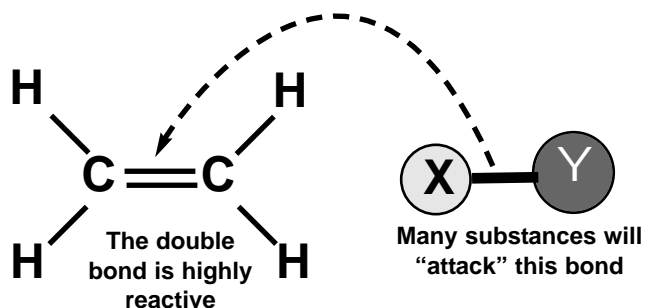
It readily "splits open" leaving a single C-C bond, and creating 2 new bond positions for other atoms/groups to attach to the molecule.

THIS IS CALLED AN "ADDITION REACTION"
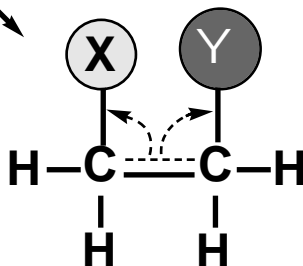
Reactions of Ethene

For each of the following you should use your molecular model kits to construct and follow the course of the reaction. Be sure you can see why these are called "addition reactions".

Reaction with Hydrogen

Ethene   +   Hydrogen ⟶ Ethane
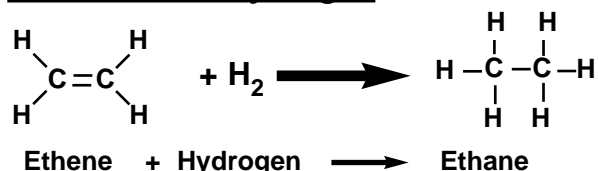
Reaction with Bromine (or any halogen)

Ethene + Bromine ⟶ 1,2-dibromoethane

Reaction with HCl

Ethene + Hydrogen Chloride ⟶ Chloroethane
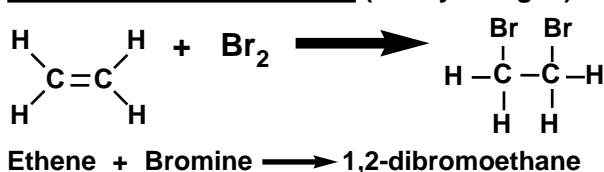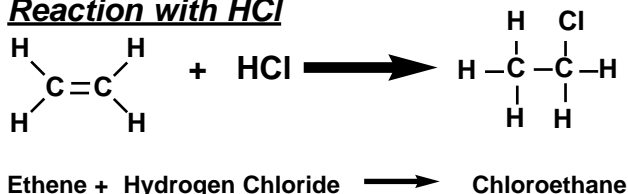
Reaction with Water

Ethene   +   Water ⟶ Ethanol
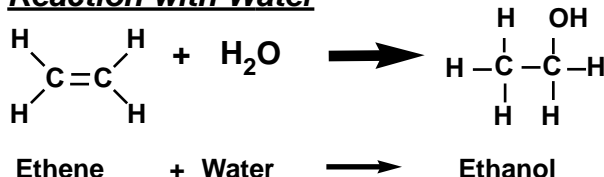
These are just a few of the possible addition reactions that can occur across the double bond.

You may be required to study these in more detail. For example, some of these require heating, some require a catalyst, etc.

For now,

Now Try Worksheet 2

The difference between the "substitution" reaction of a saturated alkane and the "addition" reactions of any unsaturated hydrocarbon, opens up a simple chemical test to tell them apart...

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Identifying Alkenes with Bromine

You may do simple experiments to learn how an alkene can be quickly and easily identified, and differentiated from an alkane.

A water solution of bromine ($Br_{2(aq)}$) has a brown colour.
If it is in contact with a liquid hydrocarbon, the water and the hydrocarbon form separate layers... they are immiscible liquids. Water, being denser, will always be at the bottom.

Bromine is actually more soluble in a hydrocarbon, so when shaken, it will dissolve into the top hydrocarbon layer, and changes colour from brown to purple.

Now this can be confusing! This switching of layers and colour change is NOT the test result you are looking for.

In an alkane (hexane is often used) the colour will change and switch layers, but it will remain coloured because no reaction occurs. (Substitution reactions with bromine require a lot of activation energy to form some free radicals.)

In an alkene (e.g. hexene) the bromine totally loses all colour because an addition reaction occurs readily at room temperature.

Before Shaking

Hexene layer

Brown "Bromine Water" layer

After Shaking

Clear Hexene layer

Clear water layer

The bromine is discoloured by any alkene.

The Reaction of Bromine with Hexene
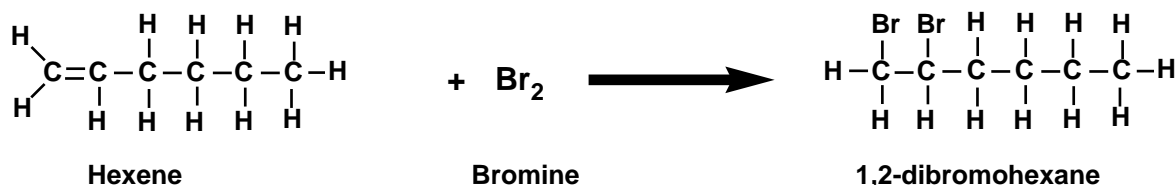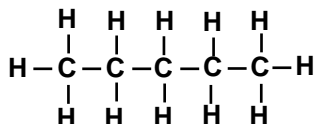

Hexene + Br₂ → 1,2-dibromohexane

Shapes of Hydrocarbon Molecules

We might draw a structural formula like this diagram, with all the carbons in a straight line.

$$H-C-C-C-C-C-H$$

However, we believe that the bonding positions around each carbon atom stay as far away from each other as possible, so in 3D the bonds point to the corners of a triangular pyramid... a tetrahedron.
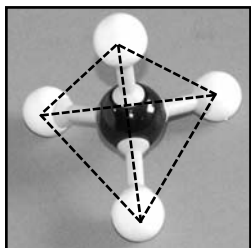
You will have seen this when building models, such as methane, shown here.

When you build longer chains, the carbons are NOT in straight lines like this,   C−C−C−C−C
but zig-zag like this.
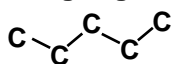
Furthermore, C-C single bonds are believed to be able to rotate around the axis of the bond, so each molecule must be a riot of movement, with atoms spinning on their bonds, vibrating internally, tumbling in space, etc.

If you build a model of (say) hexane, try twisting it around the C-C bonds in all directions... whatever the model can do, the real molecules can do, and they probably do so millions of times per second!

Effect of Double & Triple Bonds

Try building models of ethane, ethene & ethyne for comparison.

Ethane is very much a 3D molecule. With the H-atoms sticking out and able to rotate, it is like a pair of little propellers stuck back-to-back.
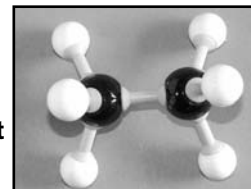
Ethene is more rigid and 2D. The double bond does NOT allow rotation and the H-atoms lie in the same flat plane.
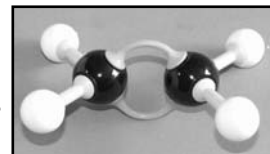
Ethyne is rigid (no rotation around the bond) and linear.
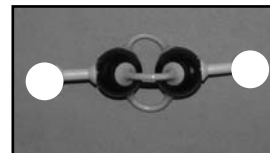
These models are thought to mimic the real molecules, so what you see is at least some indication of reality.

Try building larger models with, and without, double bonds, to see the effects on molecular shape. For interest, build this model. (alternating C-C and C= C) It's not in the syllabus, but worth finding out about.

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Environmental & Socioeconomic Impacts

The consequences of humans obtaining and using petroleum could fill many books... and have done so. What follows here is the briefest outline. It is up to you to research more detail as needed.

Obtaining Petroleum

Petroleum deposits (including Natural Gas) are the fossilised chemical remnants of ancient sea creatures. Petroleum is a complex mixture containing alkanes, alkenes and many other carbon compounds, trapped in sedimentary rocks.

Oil Well Pump, Alberta, Canada

To obtain the fuels we need, the first step is, of course, to locate the petroleum, drill down and pump it to the surface.

The next step is to separate the crude petroleum mixture into more useful "fractions". This is achieved by...

Fractional Distillation

which separates the mixture according to differences in boiling point.

Fractionating Tower in a Refinery

Simplified Schematic Diagram

Gas fraction L.P.G.

Temperature decreases up the tower

Vapours condense on collection trays...

Petrol

at different levels...

Diesel & Kerosene

according to boiling point

Heating & Fuel Oil

Lubricating Oils

Vapours rise through the tower

Vaporised Crude Oil injected

Residue: Grease & Bitumen
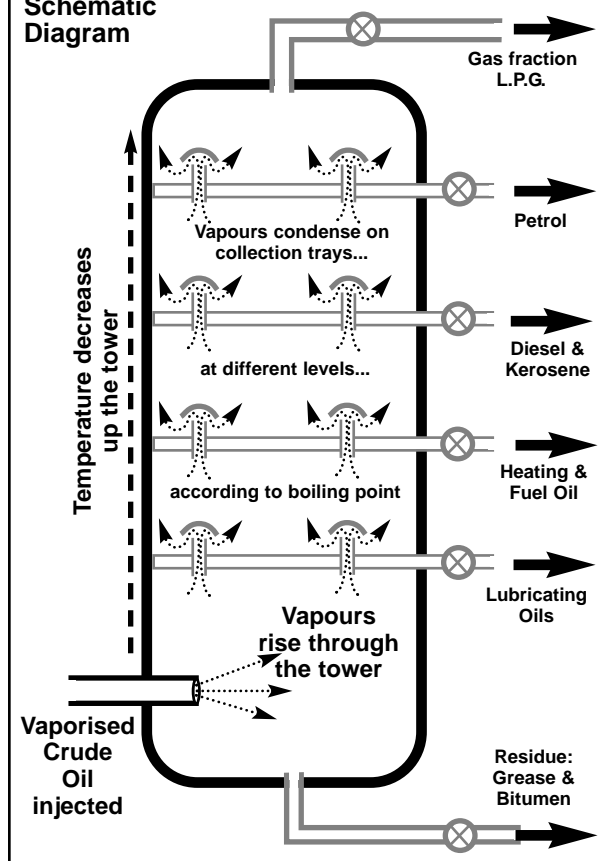
Each fraction is still a mixture. For example, petrol contains dozens of individual compounds, and the exact composition varies from place to place, and from time to time. It depends on which crude oil source is being refined, and on any adjustments made by the chemical engineers at the refinery.

Oil Refinery
Fractionating Tower

When the "fractions" are separated by fractional distillation, there is a large fraction of low-value alkanes with 15 or more carbon atoms.
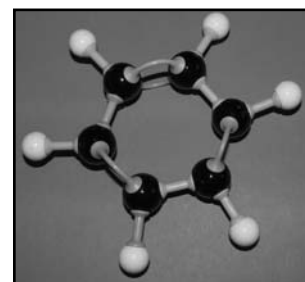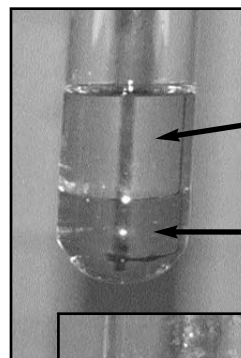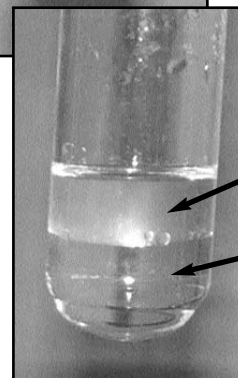e.g. pentadecane $C_{15}H_{32}$

These large molecules are broken into smaller molecules by a process called "Cracking", which can be done by simply heating ("Thermal Cracking") or by the use of a catalyst... "Cat Cracking".

When the molecule is broken into fragments, some pieces form as alkanes, but others must form as alkenes, because there are no extra hydrogen atoms to occupy the bond positions that are created.

Once "cracked", the mixture is fed back into the Fractional Distillation process. Many of the smaller molecules end up in the valuable petrol or diesel fractions. Any ethene (valuable as a major "feedstock" for plastics manufacture) formed is recovered from the gas fraction.

If you add up all the atoms in these 3 product molecules, you'll see that the total is the same

Ethene, C_2H_4

"Cracking" of $C_{15}H_{32}$ used as an example

Pentene, C_5H_{10}

Octane, C_8H_{18}
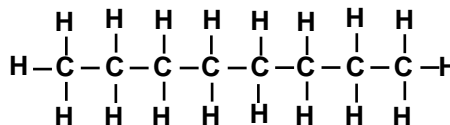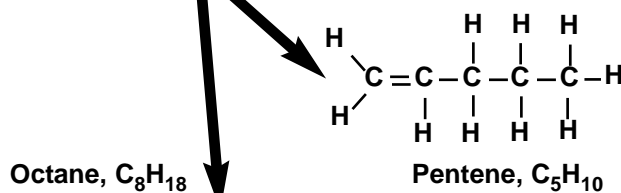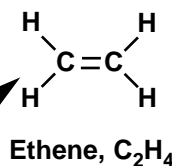
Now Try Worksheets 3 & 4

Some of the environmental impacts of obtaining petroleum have been big news whenever they occur.

However, such accidents are insignificant compared to the threat of climate change and mass extinctions which are already happening.

Burning Oil-Rig, 2010. Image by US Coast Guard

The Climate Change Debate
Simplistic Viewpoints

Many people deny that climate change is happening, and/or they refuse to believe that its cause is connected to human activities. For example, in January 2019, when extreme winter blizzards struck in parts of the northern hemisphere, the US President asked sarcastically "so, where is Global Warming when you need it?" Such simplistic ideas about this debate reveal an alarming lack of understanding of the Science.

"Global Warming" does not just mean that the weather gets warmer. The important concept is that it means that <u>more energy</u> is driving weather and climate. Yes, temperatures will rise on average, but more energy generates more wind, more storms, more extremes of weather, including occasional colder blizzards.

Our climate models predict shifts in climatic zones. Rainfall patterns will change. Areas which can now grow food, may decline. Other areas may become more productive.
This might even out eventually, but during the period of change it is likely there will be economic disruptions, vast movements of populations and possible human conflicts. (Sound familiar?)
The impacts on natural environments & extinction rates of plants & animals are already ramping-up.

Is the World Warming Up?
Apparently yes!
Since 1850, there is evidence in weather records, and in the ice cores, of a rise in average global temperature. Each of the last 3 decades has set, in turn, a new record for being the hottest decade ever recorded. All scientists agree that the average world temperature is rising.

Cause of Global Warming?
The mass media seem to have accepted that global warming is a direct result of an "enhanced greenhouse effect" due to emissions of (mainly) CO_2 from fossil fuel burning. Public opinion now generally accepts this, so that politicians are also forced to accept it, or run the risk of losing votes.

What is the Science?

Greenhouse Effect due to CO_2?
Laboratory experiments prove that CO_2 does "trap" heat, and so it can act as a "greenhouse gas".

There is clear evidence that atmospheric CO_2 levels have increased by almost 30% since 1850. The correlation with recent global warming is a very strong one.

Furthermore, we know that <u>ice core data</u> shows a strong correlation between global temperatures and CO_2 levels over the past 500,000 years or more. In this time the world has gone through a series of "ice ages" and warm "interglacials" and the CO_2 levels have changed in lock-step with these global climate changes.

For the past 20+ years, the <u>IPCC</u> (an international group of experts in many fields, commissioned by the United Nations) have reported their conclusions on 5 separate occasions. Their latest report can be summarised as:

• global warming is really happening.
• its cause is most likely due to increased CO_2 emissions from human activities.
• average global temperature are likely to rise by at least 2ºC this century. (This may be an under-estimate)
• polar regions will be affected most quickly and severely.
• sea levels WILL rise. Predictions are 0.5 - 5m by 2100.

The next IPCC report is due in 2022.

Natural Climate Cycle?
Until recently, some scientists were not convinced that the current global warming is totally due to CO_2 emissions. They pointed out that there have been major, natural fluctuations of "ice ages" and "interglacials" over the past few million years.

Since the most recent ice age ended only about 15,000 years ago, they argued that part of global warming could be due to our continuing emergence into the next interglacial.

However, the latest climate data has made it clear that Global Warming IS happening and IS mainly due to human activities.

Assessing the Predictions
Whatever its cause, the warming itself is now accepted as a fact, and scientists are continually refining the various "climate models" which allow predictions of what the impacts will be.

Everyone agrees that global warming has the potential to (at least partially) melt the ice-caps and raise sea levels. There is concensus that there will be more violent storms, and shifts in rainfall patterns.

All models agree that the effects will not be uniform: some places will be affected more than others, and some places will experience effects quite the opposite of others.

However, there is still a lot of uncertainty because the Earth's climates are so very complex. We do not yet know enough about these complexities to make perfectly accurate predictions.

Some climate factors may be very stable and self-correcting, others may reach some critical point and then undergo a major "tipping-over" change. One such factor (worthy of your research) is the possible release of vast quantities of methane from the Arctic permafrost and from the ocean floor.

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Environmental Impacts

Over the history of the Earth there have been at least 5 "Mass Extinction Events" when a large percentage (50%+) of living things died out quite suddenly. In every case, we think the cause was rapid climate change caused by meteorite impact, or episodes of massive volcanic activity.
Many scientists believe we are now entering another "Mass Extinction Event" due to human activities.

Causes of Extinction

Scientific studies have identified that the main causes of extinction of a species are: (in random order)
• Habitat loss due to deforestation, land-clearing, etc.
• Pollution   • Climate Change
• Introduction of alien species

A 2004 report in the leading journal "Nature" summarised the work of over 10,000 leading scientists. It concluded that the current extinction rate is hundreds of times higher than normal. At that rate, we can expect 10% of all species of plants and animals to disappear by 2050, and 50% by 2100.

In January 2012, 100 European researchers met in Copenhagen to discuss the latest findings. They estimated that about 30,000 species are becoming extinct each year. Many are species that we know little or nothing about.

Does it Matter?

People might worry about whales and Polar Bears, but so what if some obscure plant or insect disappears?

The problem is that every species can be connected to many others in an ecosystem. There are many complex relationships which we do not understand.

Deforestation in Central America

Extinction of one life-form breaks a connection and weakens an entire ecosystem. Like a domino effect, each extinction helps bring on the next, until the entire system may collapse.

Many ecosystems are vital to us. Ocean food chains give us millions of tonnes of food. Rainforests are the "lungs" which absorb CO_2 and produce O_2. Collapse of these systems would threaten our own survival.

There are many practical, ethical and moral reasons to be concerned about biodiversity.

Socioeconomic Impacts

Changes in Wealth & Society

In recent decades, many societies have become more affluent and politically aware. Generally speaking, these changes are good things, but affluence brings more consumption of goods, resources & energy. The emergence of a huge "middle-class" in countries such as India & China is especially notable. This social change does not help to counteract climate change.
(We mention this NOT to criticise any particular countries, but simply state the facts.)

Meanwhile, across the Middle East & N.Africa there has been political unrest and conflict for some decades. This has resulted in, not only great destruction & suffering, but movements of millions of refugees seeking greater freedom, safety & security. Who can blame them?

Food Production & Water Supply

As weather patterns shift, some areas which are now too cold, or too dry for much farming may become more productive. However, other places which now grow a lot of food, may become hotter, drier and less productive.

It may all eventually even out, but meanwhile there will be a time of disruption to food supply. The greatest worry is in Africa, where vast areas that can barely grow enough food now, seem likely to be badly affected by both lack of water and food due to climate change.

Refugees from drought & conflict, east Africa, 2011.

Human Societies & Health

Warmer average temperatures are predicted to help the spread of certain tropical diseases and parasites. These could be devastating in communities where malnutrition is more common.

Changes to food & water supplies will cause more people to become refugees and try to move elsewhere.

The movements of millions of people will inevitably bring some groups into conflict. We should expect even more regional warfare and civil unrest, especially in parts of Africa.

Wow! Can it really be true that all these things are due to humans using hydrocarbons? Well, coal is involved too, but certainly the human usage of fossil fuels is one of many direct threats to our global future. Our use of petroleum is still increasing, despite development of "green alternatives".
People travel more & buy more manufactured items which are transported world-wide. We are "addicted" to cheap energy & goods and "locked into" a global economy. Are YOU prepared to give up the benefits?

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3. The Alcohols

The structures, formulas and names for the alkanols, including 1º, 2º & 3º alcohols, were covered earlier.

Physical Properties of Alkanols

What a difference that oxygen atom makes!

Polar Covalent Bond — creates electric charge dipole

$\delta-$ $\delta+$

Non-Polar Covalent Bonds

Ethanol

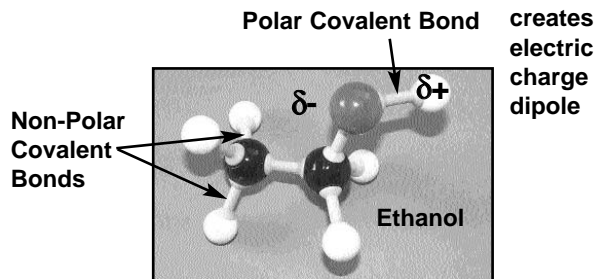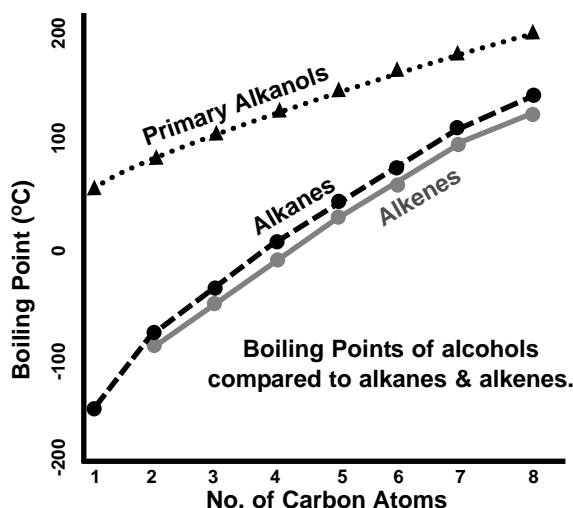The polar covalent bond in the -OH group creates a charge dipole, and strong <u>hydrogen bonding</u> exists between the molecules.

This results in <u>mp's and b.p's being much higher</u> than the corresponding alkanes. The first 8 alkanols are all liquids at room temperature. (none are gases)

Boiling Point (ºC)

Primary Alkanols

Alkanes

Alkenes

No. of Carbon Atoms

Boiling Points of alcohols compared to alkanes & alkenes.

The smaller alkanols are <u>soluble and fully miscible</u> in water, because they can form hydrogen bonds with water molecules. The larger ones become less soluble as the non-polar hydrocarbon chain grows longer.

The alkanols (especially ethanol) are <u>excellent solvents</u>, able to dissolve many water-soluble (polar) solutes, but also able to dissolve many non-polar substances which do not dissolve well in water. This is why ethanol is widely used in industry to dissolve reagents, pharmaceuticals and food chemicals. Around the home "methylated spirit" is used as a cleaning agent... it dissolves things that won't wash off easily with water.

(Methylated Spirit, or "metho" is about 95% ethanol, 5% water with small amounts of additives to make it distasteful to discourage anyone from drinking it)

Alkanols are inflammable, and can be <u>used as fuels</u>, although their energy content is not as high as the corresponding alkanes. (More on that later)

Ethanol is, of course, the alcohol in beer, wine and spirits. These are made by the process of <u>fermentation</u> (below) carried out by living microbes, especially yeast, which is a single-celled fungus organism.

You should be aware that, despite our society's acceptance of the consumption of alcohol as a social drug, all the <u>alcohols are toxic</u>. Our bodies can tolerate ethanol in small doses, but others such as methanol or propanol, are quite dangerous and potentially lethal.

Prac Work   *Fermentation*

You may have carried out an experiment to ferment sugar to ethanol.

The photo shows a typical laboratory set-up. The flask contains sugar & yeast in water. Temp. should be kept at about 25ºC.

<u>Overall reaction</u>
Glucose ⟶ Ethanol + Carbon dioxide
$C_6H_{12}O_{6(aq)} \longrightarrow 2\ C_2H_5OH_{(aq)} + 2\ CO_{2(g)}$
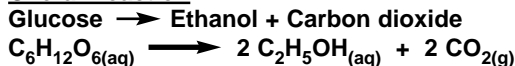
You might weigh the flask before, and after, several days of fermentation. It will <u>lose mass</u> due to the loss of CO_2 gas.

You will also observe bubbling in the flask over several days, and the limewater would rapidly go "milky" proving that the gas produced is CO_2.

When the bubbling subsides, the contents of the flask may have the yeasty, alcohol smell of beer.

You may have even distilled your brew to collect ethanol, as described at right.

Any gas produced bubbles through a beaker of limewater

Fermentation

Distillation

Electric heating. NO FLAMES !!
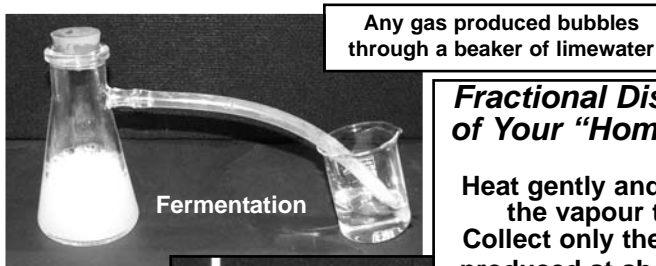
Fractional Distillation of Your "Home-Brew"

Heat gently and monitor the vapour temp. Collect only the fraction produced at about 80ºC.

<u>To test your distillate</u>: pour a few drops into a watch glass and ignite carefully in a darkened room or fume-cupboard. If it burns with a blue flame, your distillate is 80-90% ethanol.
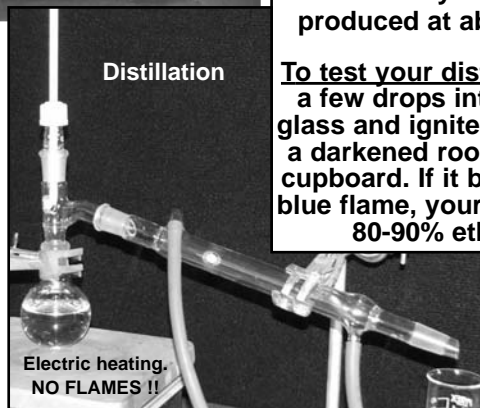
Chemistry of the Alkanols

Combustion

You are reminded (from Module 4) of the equation for the combustion of ethanol:

$$C_2H_5OH_{(g)} + 3O_{2(g)} \longrightarrow 2CO_{2(g)} + 3H_2O_{(g)}$$

(The tricky part is balancing... be careful balancing the oxygen atoms, noting that there is already 1 oxygen atom on the left side in the ethanol molecule.)

All the smaller alkanols burn well and can be used as fuels. Ethanol is added to petrol (at 10%) as an "extender" and as a token attempt to reduce greenhouse gas emissions. This is discussed later in this section.

Enthalpy of Combustion

The Syllabus requires you to measure the enthalpy of combustion for a range of alcohols.

This was covered previously in Module 4.

Our description of a simple experiment is repeated below.

This technique is notoriously <u>inaccurate</u>, (the answer you get may be very wrong) but in the case of comparing the heats of combustion of different alcohols, what is important is to achieve some <u>reliability</u> in your results.

Prac Work: Measuring ΔH_c of Alcohols

You may be able to carry out experiments to measure and calculate values for the Heat of Combustion of several alcohol fuels. A typical school experimental set-up is shown:
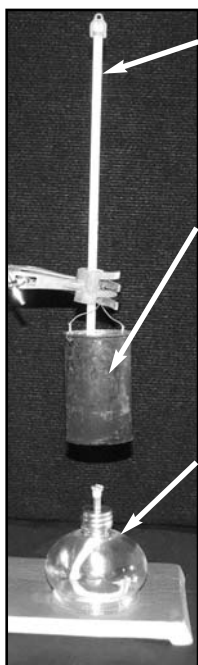
Thermometer measures temp. change in water.

Metal can holds a measured quantity of water. It acts as a <u>calorimeter</u>, absorbing heat released by the fuel.

"Spirit burner" burns an alcohol fuel using a wick.
Burner is weighed before and after to measure the mass of fuel used.

Typical results using Ethanol

Mass of ethanol burnt = 0.80g   Mass of water in metal can = 100g
Starting temperature of water = 16°C   Final temperature of water = 42°C
$\Delta T = 26°C$

Analysis of Results

Heat absorbed by water in the calorimeter:
    $Q = m.c.\Delta T$ = 0.100 x 4,183 x 26 = 10,876 J $\cong$ 11 kJ
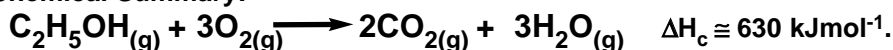This is the heat absorbed by the water for 0.80g of ethanol burnt.

$\therefore$ Heat of Combustion <u>per gram</u> = 11 / 0.80 = 13.75 kJ/g

MM(ethanol) = 46.1g
$\therefore$ Molar Heat of Combustion = 13.75 x 46.1 $\cong$ 630 kJmol^{-1}.

Chemical Summary:
$$C_2H_5OH_{(g)} + 3O_{2(g)} \longrightarrow 2CO_{2(g)} + 3H_2O_{(g)} \quad \Delta H_c \cong 630 \text{ kJmol}^{-1}.$$

Hopefully, you might be able to repeat this activity with several different alcohols.

Discussion

Firstly, those of you paying attention will have spotted that our chemical summary is not correct! The states given for the ethanol and for the water vapour are a correct description of what happened in the experiment, but are incorrect for the formal definition of "Heat of Combustion". (Revise in Mod.4)

What about the value obtained? The "text book value" of ΔH_c (ethanol) = 1367 kJmol^{-1}. Typically, in a school experiment, values of only about half, or less, are obtained. Why?

The analysis of results assumes that all the heat released by the burning fuel is absorbed by the water in the "calorimeter". However, this calorimeter is very primitive and inefficient. A lot of (most of?) the heat of the fuel can escape into the surroundings, and therefore does not get measured. Accuracy can be improved by using a larger can, wind baffles, insulation, etc., but will always give results well below "text" values.

To improve <u>reliability</u> you must ensure that every detail (eg distance from burner to tin can, time of heating, etc.) is the same from one trial to the next. This way, the results may be inaccurate, but will be <u>consisently wrong</u> from one trial to the next, which allows valid comparisons from one alcohol to another.

If you wish to find out how scientists obtain accurate measurements of combustion energies, research "Bomb Calorimeter".
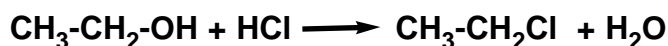
Chemistry of the Alkanols (cont.)

Substitution with HX

"HX" is a chemical shorthand for hydrogen bonded to one of the halogen elements. "HX" might mean HF, HCl, HBr or HI. Most commonly it refers to HCl, hydrochloric acid.
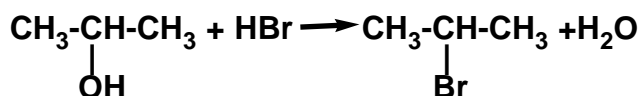
Concentrated HCl will react with an alcohol to produce chloroethane.

$$ethanol + HCl \longrightarrow chloroethane + water$$

$$CH_3\text{-}CH_2\text{-}OH + HCl \longrightarrow CH_3\text{-}CH_2Cl + H_2O$$

This reaction is described as "substitution", but it does NOT proceed (like halogen-substitution in an alkane) via the formation of free-radicals. Free-radical reactions can take a variety of directions and produce a mixture of many different products.

This substitution cleanly replaces the -OH group with the halogen, without variations.

A 2º alcohol such as 2-propanol would react:

$$2\text{-propanol} + HBr \longrightarrow 2\text{-bromopropane} + water$$

$$CH_3\text{-CH-}CH_3 + HBr \longrightarrow CH_3\text{-CH-}CH_3 + H_2O$$
$$\quad\quad |\qquad\qquad\qquad\qquad |$$
$$\quad\quad OH\qquad\qquad\qquad\quad Br$$

You might use molecular models to clarify these.

Oxidation

If necessary, you should revise the concepts of "REDOX" chemistry, covered in Module 3.

In your REDOX Data Sheet, you will find two strong oxidising agents (near the bottom) of interest here.
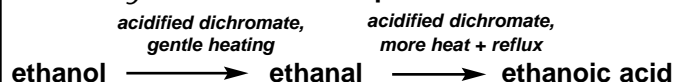
$Cr_2O_7^{2-}$ is the "dichromate ion".

MnO_4^- is the "permanganate ion".

Both these ions are used in the form of salts of potassium: $K_2Cr_2O_7$ & $KMnO_4$

You might see from the half-equations in the Data Sheet that these ions need to be acidified. Then they act as strong oxidising agents. One of the things they will attack is an alcohol.

Primary Alcohol example

acidified dichromate, gentle heating   *acidified dichromate, more heat + reflux*

$$ethanol \longrightarrow ethanal \longrightarrow ethanoic acid$$

$$CH_3CH_2OH \longrightarrow CH_3CHO \longrightarrow CH_3COOH$$

A 1º alcohol is oxidised to an <u>aldehyde</u>. This can be further oxidised to the <u>carboxylic acid</u>.

As the reaction proceeds, the $Cr_2O_7^{2-}$ may change colour. This can be a useful "indicator" for the reaction.
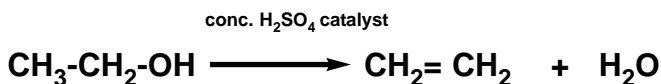
Dehydration Reaction

You previously saw that ethene can be converted to ethanol by an <u>Addition Reaction</u> across the double bond. You may have used molecular model kits to help visualise this reaction. The reaction is facilitated by dilute sulfuric acid, which acts as a catalyst.

dilute H_2SO_4 catalyst

$$CH_2= CH_2 + H_2O \longrightarrow CH_3\text{-}CH_2\text{-}OH$$
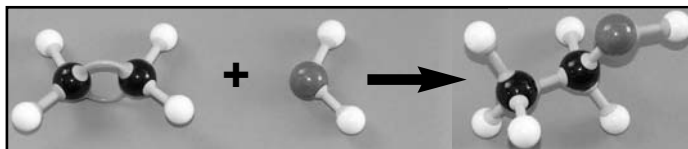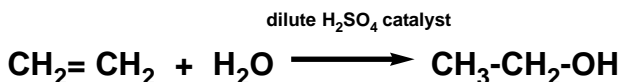
Ethanol to Ethene

The reverse reaction is also possible:

conc. H_2SO_4 catalyst

$$CH_3\text{-}CH_2\text{-}OH \longrightarrow CH_2= CH_2 + H_2O$$

Once again a catalyst is needed to make the reaction run at a practical rate for an industrial process. The same catalyst, sulfuric acid is used, but in concentrated (not dilute) form.
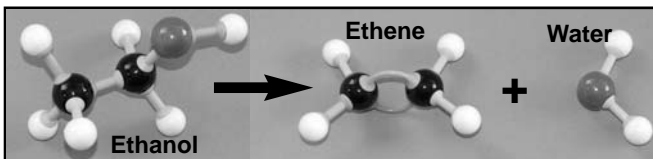
The reaction is called "<u>dehydration</u>" because water is removed from the molecule.

The significance of this reaction is that ethanol can be made from plant materials by fermentation, a process that is renewable and sustainable. Making ethylene (ethene) by dehydration of ethanol would result in a major chemical resource being available without needing petrochemicals.

Secondary Alcohol example

acidified dichromate, heat + reflux

$$2\text{-propanol} \longrightarrow propanone$$

$$CH_3\text{-CH-}CH_3 \longrightarrow CH_3\text{-C-}CH_3$$
$$\quad |\qquad\qquad\qquad\qquad ||$$
$$\quad OH\qquad\qquad\qquad\quad O$$
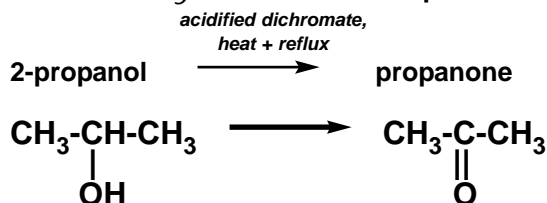
A 2º alcohol is oxidised to a ketone.

Tertiary Alcohol

acidified dichromate

$$2\text{-methyl-2-butanol} \longrightarrow NO\ REACTION$$

$$\qquad CH_3$$
$$\qquad |$$
$$CH_3-C-CH_2-CH_3$$
$$\qquad |$$
$$\qquad OH$$

Tertiary alcohols do NOT react.
These differences are useful for identifying an alcohol as either 1º, 2º or 3º.
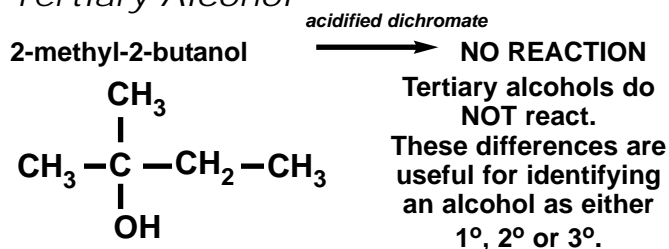
Alcohols As Fuels
(and other issues)

Ethanol to Replace Petrol?

Using the process of fermentation, followed by distillation, ethanol can be manufactured on an industrial scale from either sugar or corn starch.

High-yielding oil crops can be grown to produce alternative "bio-diesel" fuel for heavy transport.

The use of these alternative "bio-fuels" is to try to reduce CO_2 emissions from fossil fuels and reduce our dependance on them.

(Bio-fuels also release CO_2, but this is equal to the amount absorbed by the growing plants. Therefore, these fuels are claimed to be "carbon-neutral". If you do some research on this, you will find that such claims may be "optimistic" with current methods.)

Ethanol can be added to petrol in mixtures up to about 10-20% and burnt in car engines without any modifications needed, and with only a slight loss of engine performance.

This use of ethanol as an "extender" to conserve petrol and help reduce emissions, has been around for years, so 10% ethanol fuel is now common.

Sounds good so far, but the concern is about the amount of arable land required to grow the crops for bio-fuel. It can be calculated that, to totally replace petroleum fuels with bio-fuels would require up to 75% of all the farm land in the world!

This is obviously not a viable way to go.

(Note: Australian ethanol production uses only wastes from the sugar industry.)

Pro's & Con's of Ethanol Fuel

Advantages
- **Ethanol is a renewable fuel, when made from plant chemicals.**
- **The technology is already known and proven.**
- **It is (theoretically) "Greenhouse-friendly".**
- **It can be mixed with petrol up to about 20% and used without any modifications to existing engines.**

This, however, is only part of the story...

Disadvantages & Difficulties
- **To totally replace petrol with ethanol up to 75% of agricultural land would have to be dedicated to growing crops to supply the ethanol industry. The attempt by Brazil to do exactly this in the 1980's was an economic failure, and disrupted a lot of their food production farming to make way for "ethanol farming".**

- **The current technology for ethanol production requires massive amounts of energy for the distillation process. Currently fossil fuels are used for heating and transport, and so the process is not as renewable, nor "Greenhouse-friendly" as first thought.**

- **To run vehicles on pure ethanol fuel requires a total new engine design to allow for the fact that ethanol tends to be corrosive, has a different energy content, ignition temperature and burn characteristics. The cost of the change-over, to both manufacturers and car-owners makes this unlikely to happen.**

Future Bio-Fuels

Because of the "Fuel v. Food" controversy, the European Union has declared that "1st generation bio-fuels" (those which require crops growing on arable land) will be banned by 2030. Research has been underway for years to develop the next generation of biofuels. There are several promising directions being investigated:

Using Agricultural Waste
Every year, millions of tonnes of plant wastes are produced (stems, husks, etc) from our food plants. Using genetically modified micro-organisms, (GMO's) it should be possible to break these wastes down to a material which could then be fermented to produce ethanol, etc. without reducing the land available for food.

Using Non-Arable Land
Some research projects are aimed at using non-arable land, such as salt water ponds in deserts, to grow GM algae (or other GMO's) to produce sugars or oils for bio-fuel. Promising, but not yet commercially available.

Electric Cars?
Recent developments in light-weight storage batteries have seen great improvements in electric cars. However, if these are re-charged using coal-generated power, we are not much better off environmentally. As renewable electricity systems (solar, wind, etc.) continue to grow and dependance on coal declines, it may be that we can wean ourselves off petrol, to the electric car.

However, that seems unlikely to happen for heavy transport. Trucks, trains, ships & aircraft may depend on petroleum for some time yet.
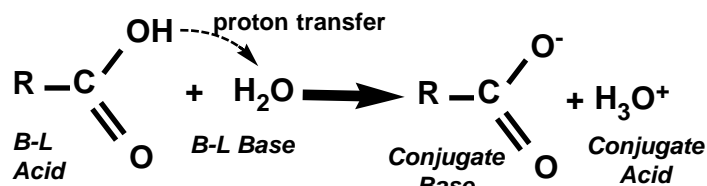
Now Try Worksheets 5 & 6

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4. Organic Acids & Bases

The names & structures of the underlined carboxylic acid homologous group were covered earlier.

This diagram is a reminder of why these compounds are considered acids. In water...

proton transfer

$R-C \overset{OH}{\underset{O}{}}$ + H_2O $\longrightarrow$ $R-C \overset{O^-}{\underset{O}{}}$ + H_3O^+

B-L Acid — B-L Base — Conjugate Base — Conjugate Acid

## Comparison of Physical Properties: Alcohols cf. Carboxylic Acids

You learnt previously how the alkanol "hydroxyl group" (-OH) contains a polar bond, and how this causes the properties of the alkanols to be quite different to those of the corresponding alkanes.

Polarity of the alkanol functional group

$$\overset{\delta-}{R-O} \overset{\delta+}{-H}$$
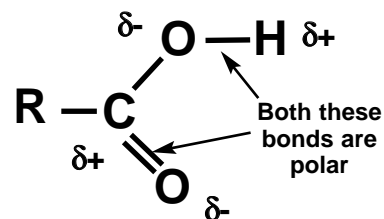
This bond is polar
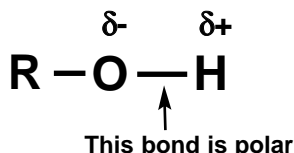
In an alkanol, the dipoles result in hydrogen bonding between molecules.

For example, in ethanol the molecules are attracted by their dipole charges and form a hydrogen bond.
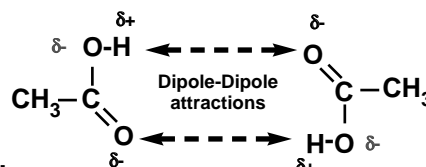
Hydrogen bond

δ- O-H δ+ $\longleftrightarrow$ δ- O-H δ+
CH_3-CH_2 — CH_3-CH_2
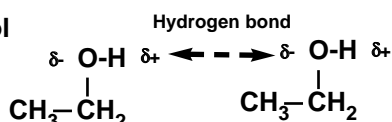
Now, compare the COOH functional group of the carboxylic acids:

Both these bonds are polar

Because of the presence of another underlined electronegative oxygen atom, there are two sets of dipoles on the molecule.

So, for example, in ethanoic acid...

each pair of molecules has 2 sets of dipoles, so twice as many H-bonds can form.

Dipole-Dipole attractions

You already know that the alkanols have much higher m.p's & b.p's than the corresponding alkanes, because of the hydrogen bonding between molecules.

The m.p's & b.p's of the carboxylic acids are higher still, due to the presence of extra dipole-dipole attractions.

For comparison:

	Ethane	Ethanol	Ethanoic acid
Boiling Pt (°C)	-89	+78	+118

The polarity of the molecules also explains why, in both homologous series, the smaller alcohols AND carboxylic acid are all soluble in water because they form hydrogen bonds with water molecules. In both series, the larger molecules become less soluble in water and more "fatty" or "waxy" as the hydrocarbon chain becomes longer.
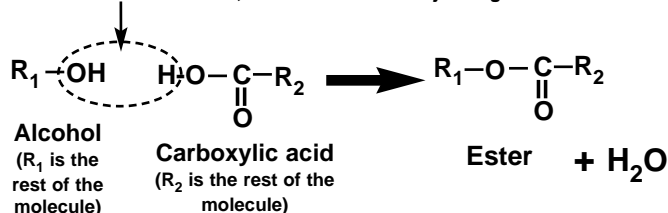
Carboxylic Acids + Alcohols = Esters

"Esters" are a group of organic compounds formed by the reaction between an alcohol & a carboxylic acid.
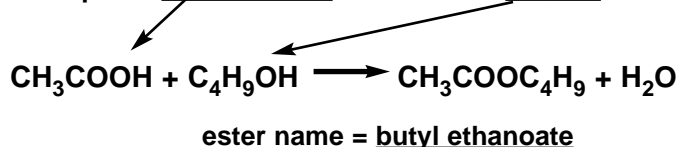
The reaction to form an ester is described as a "condensation" because it produces a water molecule, but it is so widespread in nature, and so important, that it rates its own name, "esterification".

The reaction can be visualised as follows:

These atoms form water, and the 2 molecules join together

R_1-OH $H-O-C-R_2$ $\longrightarrow$ $R_1-O-C-R_2$ + H_2O

Alcohol (R_1 is the rest of the molecule) — Carboxylic acid (R_2 is the rest of the molecule) — Ester + H_2O

Example: If underlined ethanoic acid reacted with underlined butanol:

$$CH_3COOH + C_4H_9OH \longrightarrow CH_3COOC_4H_9 + H_2O$$

ester name = butyl ethanoate

You should use a molecular kit to visualise structure.

Remnant of CH_3COOH — Remnant of C_4H_9OH
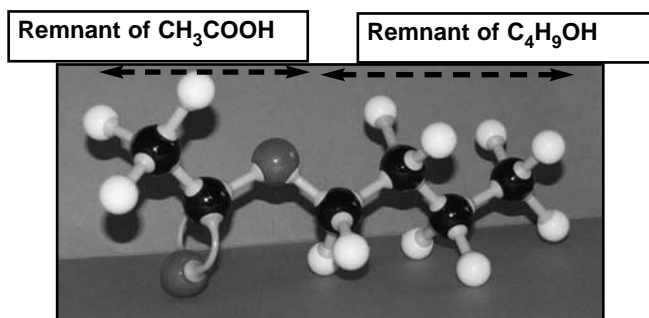
Naming an Ester

Alcohol name first.
Drop-off "-ANOL", and add "-YL".
In the example at left, "butanol" becomes "butyl".

Acid name second.
Drop-off "-IC ACID", and add "-ATE"
In our example, "ethanoic acid" becomes "ethanoate" (the same as the ion from this acid).

The name of the ester is "butyl ethanoate"

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The Esters (cont.)

All esters contain this chemical "functional group" inside the molecule, with hydrocarbon chains on either side.
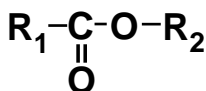
$$R_1-\underset{\underset{O}{\|}}{C}-O-R_2$$

The zone around the oxygen atoms is polar, but both ends of the molecule are non-polar.

Because of this, esters generally have <u>low solubility</u> in water (some exceptions), and have lower mp's & bp's than the alcohol & carb.acid they come from.

Esters are <u>volatile</u> with a <u>strong odour</u>... often sweet and fruity. This is their "job"; to give the smells and flavours to many foods and perfumes.
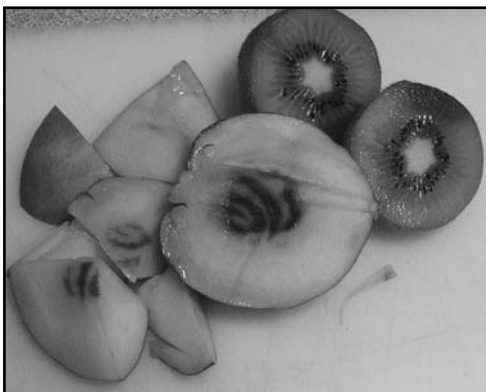
The delicious smell and taste of ripe fruit is largely due to natural esters

---

Practical Work: *Making an Ester*

You may make an ester in the laboratory using a process known as <u>Reflux</u>.

A simple laboratory reflux set-up is shown.

The reflux condenser is open to the atmosphere at the top.

This is vital to avoid any dangerous build-up of pressure which would occur in a sealed flask.

Volatile chemical vapours rise, but are condensed and drip back into the flask... "reflux".

The reaction flask is heated to speed up the otherwise very slow reaction. Note that the mixture must NOT be heated by a bunsen flame because the mixture could ignite and explode.

Electrical Heating Element
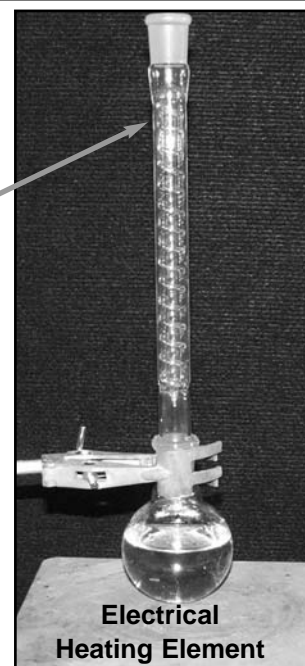
As well as a <u>carboxylic acid</u> and an <u>alcohol</u>, it is usual to add the <u>catalyst</u>, concentrated <u>sulfuric acid</u>, H_2SO_4.

$$\text{carboxylic acid + alkanol} \underset{}{\overset{\text{conc. } H_2SO_4}{\rightleftharpoons}} \text{ester + water}$$

As well as speeding the reaction up, the H_2SO_4 catalyst also absorbs the water product. This has the effect of shifting the equilibrium to the right (according to Le Chatelier's Principle) and increasing the yield of the ester.

Occurrence of Esters

Esters occur widely in nature, especially in fruits and flowers. They are largely responsible for the smell & taste of many foods.

There may be a complex mixture of esters and other compounds which give the complete smell of (say) a ripe strawberry, but there's always an ester giving the main smell and taste sensation.

Some examples:
<u>Strawberry</u>   ethyl butanoate, $C_3H_7COOC_2H_5$

<u>Orange</u>   octyl ethanoate, $CH_3COOC_8H_{17}$

Notice that the "remnant" of the alcohol comes first in the name, but last in the formula.

Fats & Oils are Esters, Too

Esters made from very long chain carboxylic acids (the "fatty acids"), are used by all living things as high-energy foods and energy storage chemicals.

We call them fats or oils, depending on their melting point.

We study them next, plus some useful chemicals derived from them.

Now Try Worksheets 7 & 8

Chemistry of Fats & Oils

Triglycerides

"Triglyceride" is the general name given to a compound made from 3 molecules of "fatty acid" joined to a "glycerol" molecule. This joining-together is actually esterification.

"Fatty Acids" are the long-chain carboxylic acids, with 12 or more C-atoms.

Example below is an 18-carbon fatty acid called stearic acid, $CH_3(CH_2)_{16}COOH$
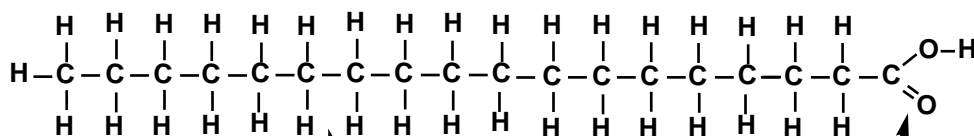
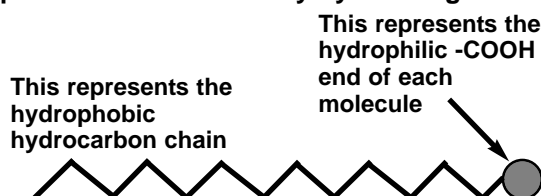This long, non-polar, hydrocarbon section is "hydrophobic" (="water-hating")

Note these properties... they become important later.

The -COOH group is polar and "hydrophilic" (="water-loving")
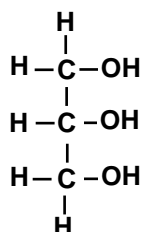
There are many different fatty acids;
• some have more (or fewer) carbon atoms.
• some have one or more double (C= C) bonds.
  (and less hydrogen atoms)

To keep it simple (K.I.S.S!) all the fatty acids can be represented schematically by the diagram below.

This represents the hydrophilic -COOH end of each molecule

This represents the hydrophobic hydrocarbon chain

Triglycerides are esters in which 3 fatty acids are bonded to a glycerol molecule.

Schematically, it can be depicted as follows:

Glycerol

3 fatty acids

This is what we call "fat" or "oil".

Glycerol is a "triple alcohol" molecule containing 3 hydroxyl (OH) groups. Its systematic name is "propane-1,2,3-triol".

Structural Formula

Schematic Diagram

Fats v. Oils?

"Fats" are simply triglycerides which are solid at room temperature (like beef fat), while oils are liquid at room temperature (like olive oil). The difference is simply the melting point. This in turn is due to the different fatty acids in the triglyceride... animal fats tend to contain "saturated" fatty acids (all single C-C bonds like stearic acid above) while the vegetable oils often contain "unsaturated" fatty acids containing many double C=C bonds and less hydrogen.
Fewer H-atoms tends to lower the melting point.

Properties of Fats & Oils (Triglycerides)

All pretty obvious really !

Fats & oils are soft, greasy substances which taste great when heated to about 300ºC and used to cook slivers of potato, which are then sprinkled with crystalline sodium chloride. Good chemistry that!

All the triglycerides are completely insoluble in water because their long, non-polar hydrocarbon chains have no affinity with polar water molecules.

They have lower density than water and, when mixed, will float on top.

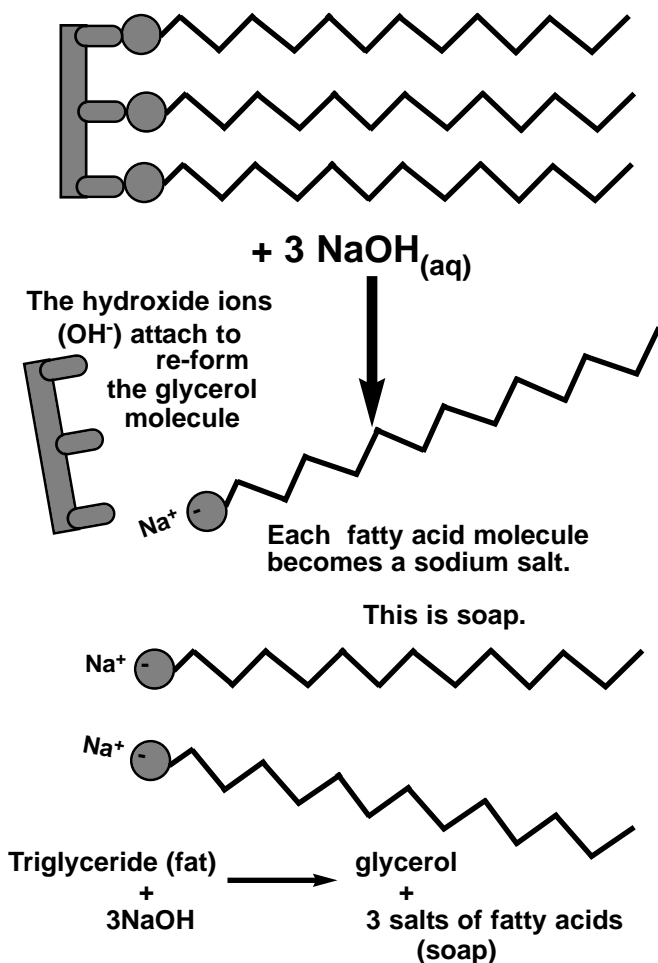Without any mobile charges within, they are non-conductors of electricity.

Overall, their physical properties are similar to the larger members of the alkanes. This should not be surprising.

However, one of their chemical reactions may surprise (and intrigue) you...

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Saponification = to make Soap

The making of soap involves reacting a triglyceride with a strong base such as NaOH. It can be depicted schematically as follows:

+ 3 NaOH$_{(aq)}$

The hydroxide ions (OH⁻) attach to re-form the glycerol molecule

Na⁺ -

Each fatty acid molecule becomes a sodium salt.

This is soap.

Na⁺ -

Na⁺ -

Triglyceride (fat) → glycerol
+   +
3NaOH   3 salts of fatty acids
                          (soap)

If the fatty acid was stearic acid, $CH_3(CH_2)_{16}COOH$, then the soap molecule would be sodium stearate, $CH_3(CH_2)_{16}COO^-Na^+$.

Prac Work: **_Saponification_**

You may have carried out a simple experiment in the laboratory to make some soap from vegetable oil and NaOH. (Strong base... use risk analysis & safety precautions!)

Simply mixing the ingredients in hot water, then stirring or shaking for a few minutes is enough to make the soap.

Adding some salt and allowing the mixture to cool is usually effective in causing a layer of soap to separate into a solid layer on top. This is best washed to remove NaOH residues before handling.

This is how soap has been made for thousands of years.

Your crude cake of soap can be tested by shaking a piece in warm water to see it "lather" and form a soapy foam.

Any fat or oil can be used to make a soap. Traditionally, animal fats from meat wastes and scraps were used. Tallow (from beef) and lard (from pork) have been the main sources of soap for centuries. Whale oil was used extensively well into the 20th century.

In the modern industry, vegetable oils are mostly used because they can be more reliably supplied in large quantities at consistent quality and price. They also have a better "marketing appeal". The main oils used include palm, olive, coconut and soybean oil.
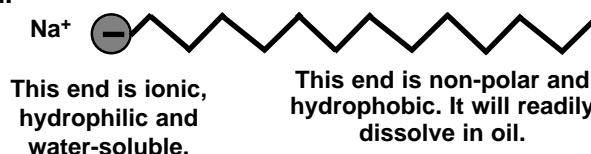
Soap as an Emulsifier

The reason that soap works for washing and cleaning is that it is able to emulsify fats in water... it is an emulsifier.

You need to realise that water by itself will often not wash away "dirt" because usually there is some fatty material in the "dirt". This is not water soluble, and tends to cling to skin and fabrics and resist being simply rinsed away.

As you know, when water and oil are mixed, they rapidly separate with the oil forming a layer on top. This is because oils (triglycerides) are large, non-polar molecules which are immiscible with water.
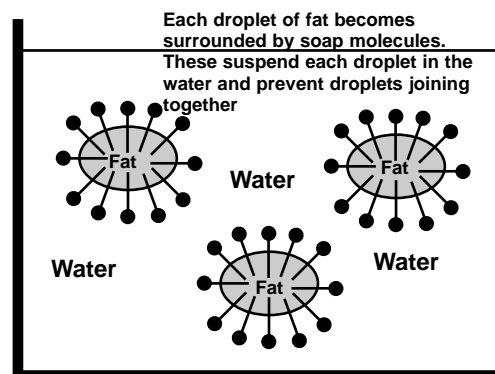
However, if water, oil and soap are mixed and agitated, the oil becomes broken up into tiny droplets which remain mixed into the water, and tend to separate more slowly, or not at all. Why?

Remember that soap is the sodium salt of a fatty acid.

Na⁺ −

This end is ionic, hydrophilic and water-soluble.

This end is non-polar and hydrophobic. It will readily dissolve in oil.

If each soap molecule is represented by ——● then what happens when soap emulsifies fat is shown in this diagram.

Notice how the non-polar end of each soap molecule dissolves in the fat droplet, with the ionic, hydrophilic end sticking out into the water.

Each droplet of fat becomes surrounded by soap molecules. These suspend each droplet in the water and prevent droplets joining together

Fat   Water   Fat

Water   Water

Fat

Each tiny droplet of fat remains suspended in the water. Droplets cannot join together & float on top. Eventually they are rinsed down the drain.
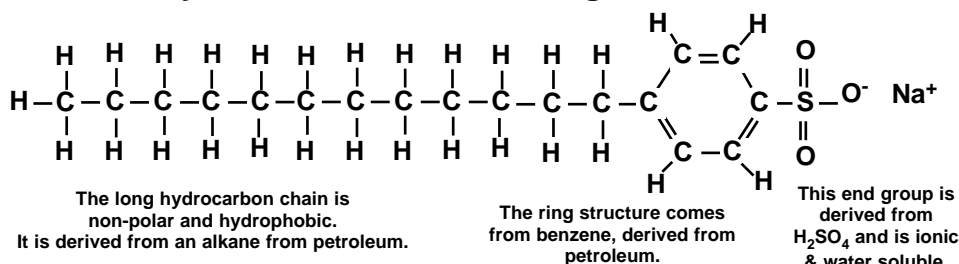
Detergents

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®

Detergents are "artificial soaps". They were first invented during the 1940's and have largely replaced soap in many cleaning roles because they are more powerful as emulsifiers, can be made to have various properties suitable for specialist tasks, and work well in a wider variety of applications.

Chemistry & Molecular Structure

There are many different detergents, but one of the most common types has a structure as shown. Note the basic similiarity (in general terms) to a soap molecule, but also the differences in detail.

Sodium Alkylbenzene Sulfonate Detergent Molecule

The long hydrocarbon chain is non-polar and hydrophobic.
It is derived from an alkane from petroleum.

The ring structure comes from benzene, derived from petroleum.

This end group is derived from H_2SO_4 and is ionic & water soluble.

The molecule can be represented as:

SO_3^- Na$^+$

This molecule acts very efficiently to emulsify fats into water, so that greasy "dirt" is cleaned off or washed away.

Definition of an Emulsion

What exactly is an emulsion anyway?

Two liquids which will not dissolve in each other and always separate when mixed together are said to be "immiscible"... like water and oil.

An emulsion is when 2 immiscible liquids are combined so that they form a stable, uniform mixture which does not separate.

It is NOT a solution. The molecules are not intimately associated at all. In an emulsion, one of the liquids is broken up into tiny, microscopic droplets which are spread uniformly throughout the other liquid.

To achieve an emulsion, a 3rd chemical (the "emulsifier") is required to keep the droplets dispersed, and stop them joining together.

For each pair of immiscible liquids there are 2 possible types of emulsion.
For example, with cosmetic creams:
A sorbolene (or "vanishing cream") is an emulsion where the oil phase is dispersed in the water.

A "cold cream" is an emulsion where the water phase is dispersed in the oil.
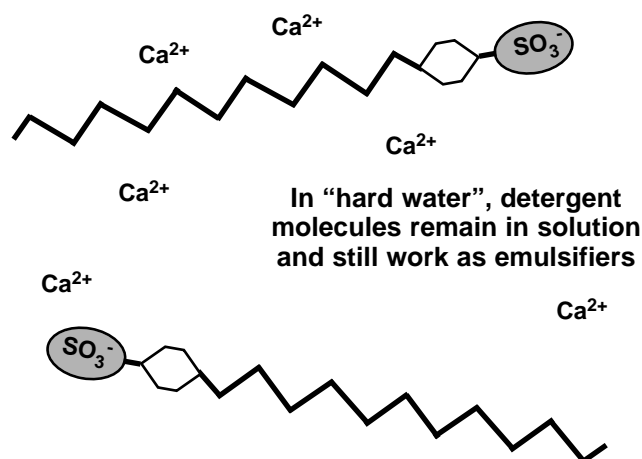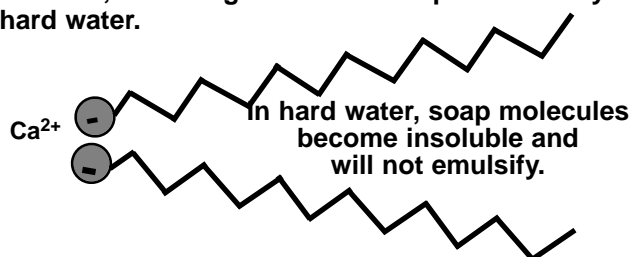

Effect of "Hard Water"

Some water supplies contain significant concentrations of Ca^{2+} and/or Mg^{2+} ions. This water tends to cause mineral deposits to build up in pipes and kettles and so has come to be called "hard water".

Apart from clogging up water pipes, hard water has one other major problem... soap will not work in hard water.

If you attempt to use soap in hard water, it will not lather, and a greasy "scum" forms. It does not cause emulsification and will not clean anything.

The problem is that Ca^{2+} or Mg^{2+} ions will combine with the fatty acid ions to form an insoluble compound. The molecules precipitate and cling together forming the "scum".

An important characteristic of detergents is that their ion (alkyl-benzene sulfonate ion) remains in solution, so detergents will work quite normally in hard water.

Ca^{2+}

In hard water, soap molecules become insoluble and will not emulsify.

Ca^{2+} Ca^{2+} SO_3^-

Ca^{2+}

Ca^{2+}

In "hard water", detergent molecules remain in solution and still work as emulsifiers

Ca^{2+}

Ca^{2+}

SO_3^-

This is one of the reasons that detergents have mostly taken over from soap as cleaning products.

You can test this effect yourself by trying to produce a soap lather in seawater, or bore water. Then try with some dishwashing detergent or hair shampoo... big difference!
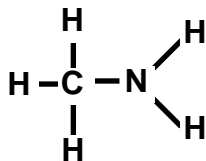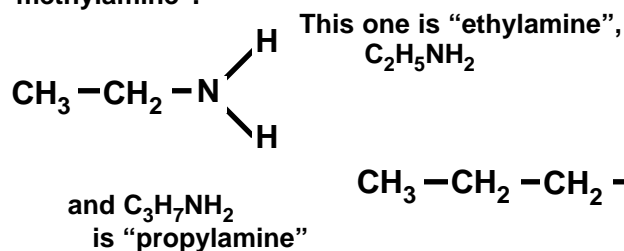
Now Try Worksheet 9

Amines

If you follow a logical progression from the earlier homologous series, the amines can be thought of as typical hydrocarbon chains with a nitrogen-hydrogen (-NH_2 "amine") group attached.

The simplest amine has this structure and its formula is written CH_3NH_2.

$$H - C - N \begin{smallmatrix} H \\ \\ H \end{smallmatrix}$$

You might logically name this as "methanamine", but the standard IUPAC name is "methylamine".

This one is "ethylamine", $C_2H_5NH_2$

$$CH_3 - CH_2 - N \begin{smallmatrix} H \\ \\ H \end{smallmatrix}$$

and $C_3H_7NH_2$ is "propylamine"

$$CH_3 - CH_2 - CH_2 - N \begin{smallmatrix} H \\ \\ H \end{smallmatrix}$$

The reason for this naming pattern is to emphasise the importance of the -NH_2 group. Instead of thinking "Oh, that's methane with NH_2 attached", the name "methylamine" tells you "this is an amine structure with a methyl group attached".
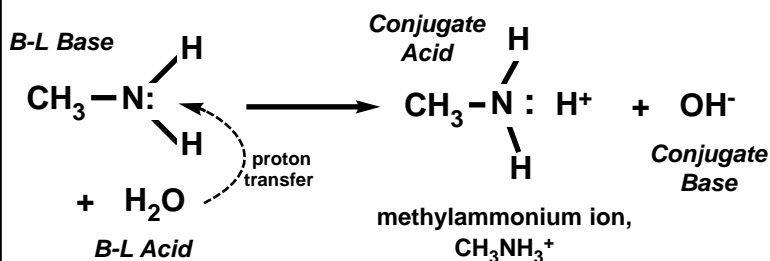
You need to understand that the amine group is derived from ammonia, NH_3.

Ammonia is chemically (you will recall) a base, because in water:

proton transfer

$$NH_3 + H_2O \longrightarrow NH_4^+ + OH^-$$
ammonium ion
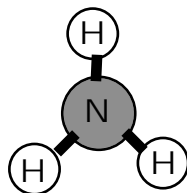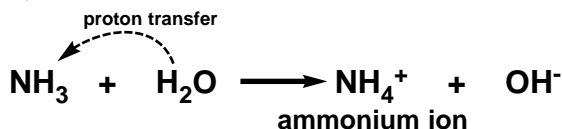
This is made possible because the nitrogen atom in NH_3 has an unshared pair of electrons. It can accept an extra proton (H+ ion) which bonds with the spare electron pair, forming the ammonium ion, NH_4^+.

Similarly, an amine compound can do the same. We use the simplest amine, methylamine, as the example:

B-L Base

Conjugate Acid

$$CH_3 - N: \begin{smallmatrix} H \\ \\ H \end{smallmatrix} \longrightarrow CH_3 - N:H^+ + OH^-$$

proton transfer

+ H_2O

Conjugate Base

B-L Acid

methylammonium ion, $CH_3NH_3^+$

In fact, the amines are slightly stronger bases than ammonia itself, although still classified as "weak".

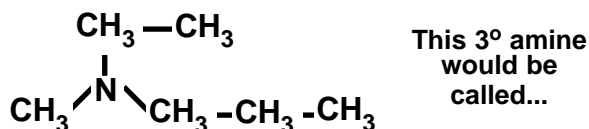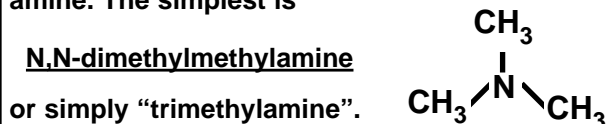## *Primary, Secondary, Tertiary Amines*

Now that you are thinking in terms of adding hydrocarbon bits onto ammonia, then you will appreciate that all preceding examples have been "1º amines" which have just one C_nH_{2n+1} group attached.

A "2º amine" has 2 such groups attached to the ammonia structure. The structure shown would be N-methylmethylamine,

$$CH_3 - N \begin{smallmatrix} H \\ \\ CH_3 \end{smallmatrix}$$
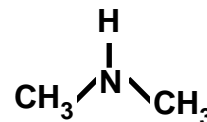
where the "N" indicates that another methyl group is attached to the nitrogen atom. This compound is also known as "dimethylamine".

And (as you were about to guess) if there are 3 groups attached to the N-atom this is a tertiary amine. The simplest is

N,N-dimethylmethylamine

or simply "trimethylamine".

$$CH_3 - N \begin{smallmatrix} CH_3 \\ \\ CH_3 \end{smallmatrix}$$

$$CH_3 - N \begin{smallmatrix} CH_3 - CH_3 \\ \\ CH_3 - CH_3 - CH_3 \end{smallmatrix}$$

This 3º amine would be called...

N-ethyl-N-methylpropylamine.

(Propyl chain is longest, so it has priority in the amine name. Ethyl side-branch comes before methyl side-branch alphabetically.)

Physical Properties of Amines

The -NH_2 group is polar, so hydrogen bonds form between molecules. This means that mp's & bp's are much higher than corresponding alkanes. However, nitrogen is less electronegative than oxygen, so the polarity is lower than in the corresponding alcohols.

	Ethane	Ethanol	Eth.acid	Ethylamine
bp(ºC)	-89	+78	+118	+17

Small amines are soluble in water, but solubility decreases rapidly as the hydrocarbon chains get bigger. Solubility also declines rapidly in 2º and 3º amines.

Amines are volatile and their vapours smell distinctly of ammonia. Some amines smell "fishy"... in fact the characteristic smell of fish, especially if it is a bit "off", is due to trimethylamine.

Now Try Worksheet 10

keep it simple science ®

Amides

| This is another homologous series which we deliberately ignored previously. |

Recall that:

carboxylic + alcohol ⟶ ester + water
acid

Well, similarly:

carboxylic + amine ⟶ amide + water
acid

Once again the reaction can be described as a "condensation" because water is produced.

These form water

$R_1 - C$ OH + H N $- R_2$
‖
O
carboxylic acid   **amine**
H

$R_1 - C - N - R_2$ + H_2O
‖ |
amide O H
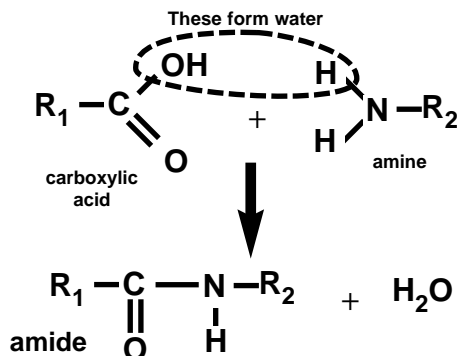
For example, if <u>butanoic acid</u> (C_3H_7COOH) reacted with <u>ethylamine</u> ($C_2H_5NH_2$):
(we have turned the amine formula around to make the reaction clearer)

$C_3H_7COOH + NH_2C_2H_5$ ⟶ H_2O
+ $C_3H_7CO.NHC_2H_5$
N-ethylbutanamide
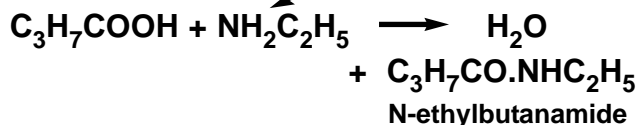
Notice that the name begins with reference to the amine and ends with the acid's name, modified with "amide". So "N-ethylbutan~~oic acid~~ + amide".

This reaction is very important in Biology; this is how <u>amino acids</u> join together to form <u>proteins</u>.

Later in this module you will see that some of our important plastics are made by this "amide reaction".

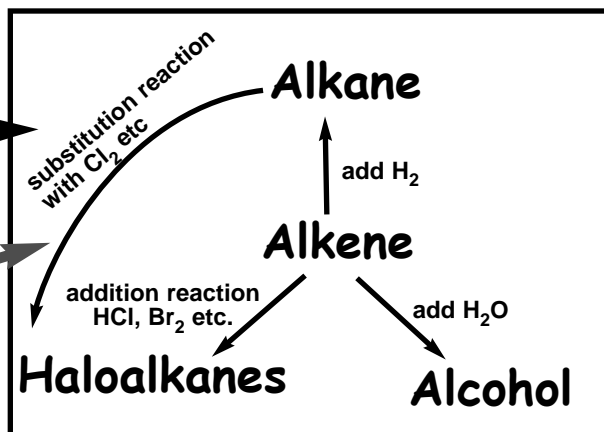| After This, Try Worksheet 11 |

Reaction Pathway Flowcharts

If, by now, you are feeling a little overwhelmed by the number of different homologous series of organic chemicals and all their different reactions, the following may help... BUT you have to do it yourself !

Begin with small notebook pages, or separate sheets.

Summarise all the reactions studied for one group of chemicals (say, the hydrocarbons) as a simple flow-chart on one sheet: example shown.

Do the same for another group such as the alcohols.

Look for connections

Alkane
substitution reaction with Cl_2 etc
add H_2
Alkene
addition reaction HCl, Br_2 etc.   add H_2O
Haloalkanes   **Alcohol**

Haloalkanes
subst. HX
Aldehyde ⟵ **Alcohol**
oxidations   dehydration
Ketone
react with carb.acid   **Alkene**
Carb.acid
Ester

Continue to do this for all the groups we have covered, then look for connections and overlaps.

Move your little sheets around to see how they connect to each other. You may have to re-draw each one into a better structure so they connect in a better way.

As your diagrams get better connected, merge them onto a larger page or a chart. Add details such as reagents & catalysts needed for each reaction. Add example equations for each reaction type.
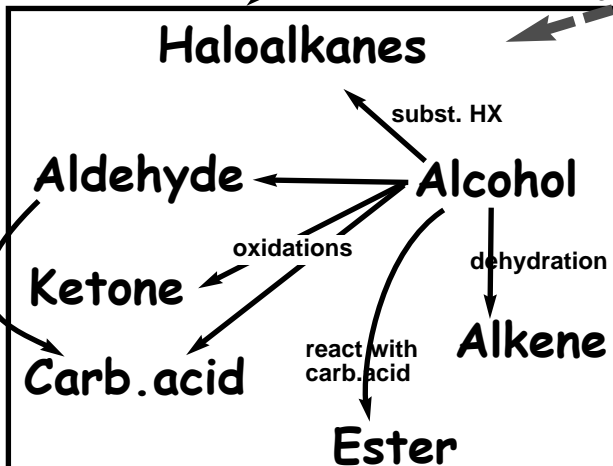
You'll end up with a very useful summary & study guide. More importantly, by doing this you will learn and understand lots more about Organic Chemistry.   Have Fun !

| If you need some help, or need to cheat, search for "flowcharts of organic chem reactions" on the internet. |

® keep it simple science

5. Polymers

Polymers are large molecules made by joining together many small molecules, called monomers. ("poly" = many, "mono" = one, "mer" = unit)

Many of the important molecules in living cells are polymers, for example:

• starch is a polymer of many glucose molecules.
• proteins are polymers of amino acids.
• DNA is a polymer of nucleotides, sugar and phosphate.

Many common, widely used substances are manufactured polymers, including all the different plastics and synthetic fibres such as nylon.

Ethylene is the starting chemical ("feedstock") in the manufacture of many polymers.
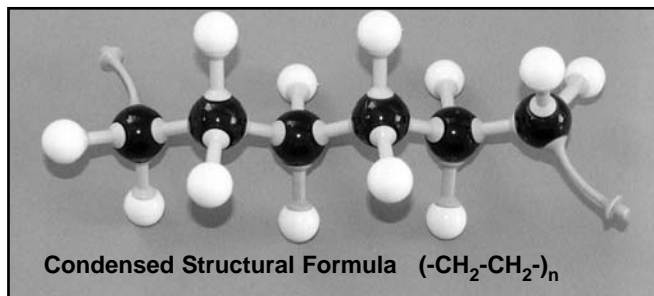
Addition Polymerisation of Ethene

You should recall that ethene (ethylene) can carry out addition reactions with bromine, water, etc., by "opening-up" its double bond. Under the right conditions and with an appropriate catalyst, many ethylene molecules can react with each other by the same mechanism.

You may have used molecular models to help visualise the process.

$CH_2=CH_2$ $CH_2=CH_2$ $CH_2=CH_2$
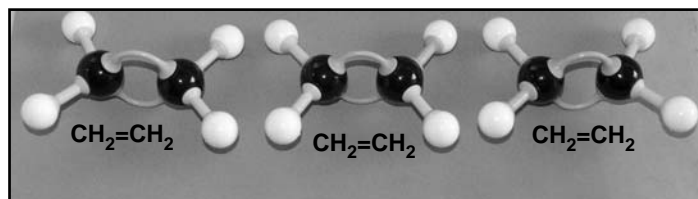
The result is that the ethylene monomers join together by addition reactions across the double bond. This is an "Addition Polymerisation" process and results in a polymer called "Polyethene", or "Polyethylene", also known by the trade name "Polythene".

Condensed Structural Formula $(-CH_2-CH_2-)_n$

> **Addition Polymerisation is an Addition Reaction across a double C= C bond which joins monomers to make a polymer. Polymers can be named by adding "poly-" as a prefix to the monomer name.**

Industrial Production of Polyethene

More polyethene is manufactured than all other plastics put together... it is one of the most used synthetic materials in our world. There are basically two different production methods, which produce two different forms of polyethene.

Low Density Polyethene

If the monomer ethene is treated with
• high pressure (over 1,000 atmospheres)
• high temperature (300ºC)
• an "initiator" chemical
addition polymerisation occurs, with about 2,000 monomers joining to form each "super-molecule" of polymer. In this case, the initiator chemical also causes the polymer molecules to have side-branches.
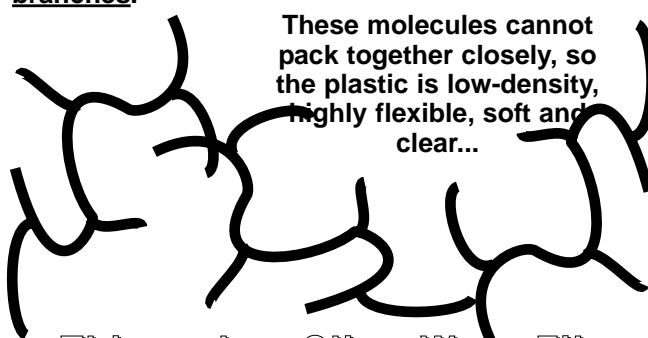
These molecules cannot pack together closely, so the plastic is low-density, highly flexible, soft and clear...
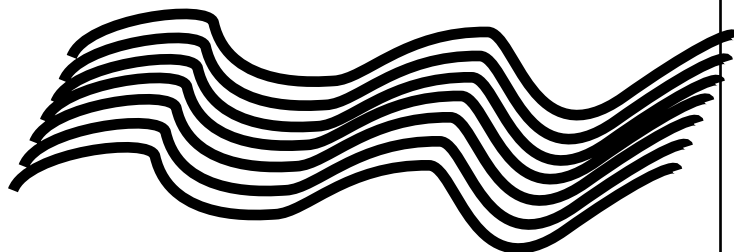
This makes Cling-Wrap Film & Plastic Bags.

High Density Polyethene

is manufactured
• at lower pressure (2-3 atmospheres)
• at lower temperature (about 60ºC)
• with a complex catalyst

This time there are no side-branches. The long polymer molecules can pack together forming a higher-density, harder plastic used for toys, plastic utensils, and tough, "crinkly" carry bags.

As with all materials, the uses of these plastics is closely linked to the properties they have, and their properties are controlled by their chemical and molecular structure and bonding.
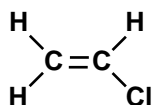
This idea is taken further on the next page.

Addition Polymers (cont.)

Other Addition Polymers

The compound chloroethene is an ethene molecule with one hydrogen atom replaced by a chlorine.

Chloroethene is also known by its common name "vinyl chloride"

Since this molecule contains a double bond, it can undergo addition polymerisation to form "polyvinylchloride" or PVC.

$(-CH_2-CHCl-)_n$
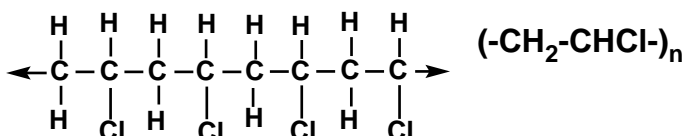
If one of the hydrogen atoms of an ethene molecule is replaced by the ring-shaped "benzene" group, the compound has the technical name "ethenylbenzene", but is commonly known as "styrene".

This structure is commonly abbreviated as

Benzene ring
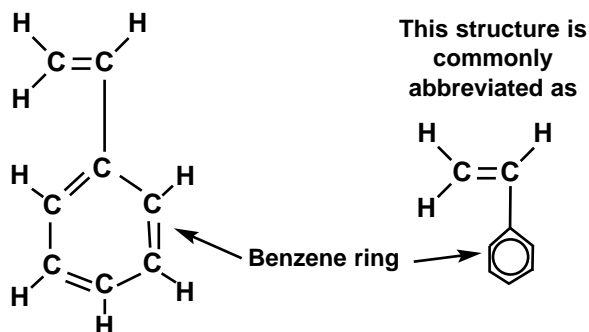
If this undergoes addition polymerisation, the polymer is "polystyrene", so familiar in insulation, hot-drink cups, bean-bag filling, etc.

Polystyrene $(-CH_2-CH(C_6H_5)-)_n$
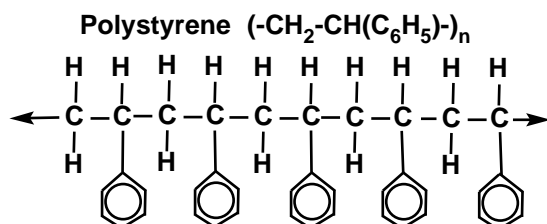
Tetrafluoroethene is the monomer which produces an addition polymer called "polytetrafluoroethene", abbreviated PTFE.
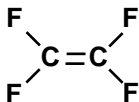
This plastic is better know as "teflon". (TM trademark) The strength of the C-F bonds give teflon one of the lowest known ratings for friction. It is so "slick" that a gecko lizard (which can run vertically up a pane of window glass) cannot climb it.

It is also highly resistant to chemical attack, so it has many applications (beyond "non-stick" cookware) in medicine, electronics and industry.

Uses, Properties & Structure

The molecular structure and bonding of each plastic determines its properties, and the properties determine what uses the material is best suited for.

To keep it simple (K.I.S.S. Principle) we will compare just 3 of the plastics mentioned so far.

In low-density polyethene, the molecules are long, non-polar, branched chains (diagram previous page). Being non-polar (so only weak dispersion forces operate) and unable to get close together, each molecule can bend and twist easily.

So, the plastic is soft and very flexible. It is perfect for cling-wrap film, sandwich bags and as the plastic lining in milk or juice cartons.

In PVC, the chlorine atoms more than double the mass of each monomer. Since dispersion forces increase with molecular weight, it means that the polymer molecules attract each other more strongly. Each molecule is held in place more, so the entire substance is harder and less flexible.

PVC is a tougher, more rigid plastic. This makes it ideal for drainage pipes, guttering and electrical conduit pipes.

In polystyrene, the compact benzene side group is almost twice the mass of a chlorine atom, so the molecules are even heavier and dispersion forces stronger. Polystyrene is a hard, tough, rigid plastic, often used for making handles for cookware and hand-tools such as hammers or chisels.

Note that the more familiar use of polystyrene is in light-weight "foam-plastic" for insulation, hot-cups and packaging. In this form it has been injected with gas to make it very light and "fluffy".

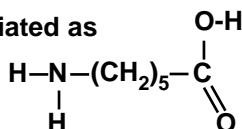The plastic itself is hard and rigid.

keep it simple science ®
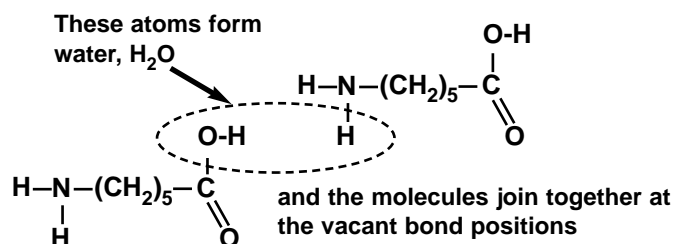
Condensation Polymers

There is another way that polymers can form.
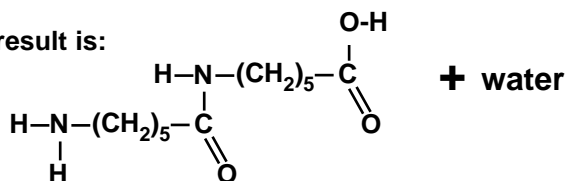For example, the monomer "6-aminohexanoic acid" has the structure

NH₂ "amine" group

$$H-N-C-C-C-C-C-C \quad \text{COOH acid group}$$
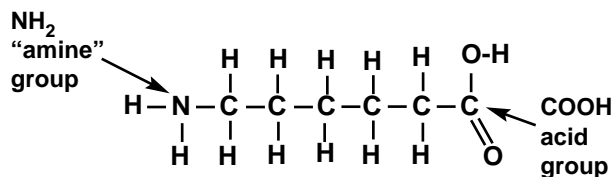
This can be abbreviated as

$$H-N-(CH_2)_5-C \quad \overset{O-H}{\underset{O}{}}$$

Two of these molecules can join together as follows

These atoms form water, H₂O

and the molecules join together at the vacant bond positions

You can see it is an "amide condensation" reaction.

The result is:

$$H-N-(CH_2)_5-C \quad + \text{ water}$$

Each molecule can join to another at each end, so many monomers can join in long chains... a polymer is formed.

The example above results in the polymer we call "nylon", widely used in fabrics and clothing.

Remember that the reaction
carboxylic + alcohol ⟶ ester + water
acid
    is also a "condensation" reaction.

Therefore, if you begin with a monomer with a structure   HO─R─COOH

it can react at each end by "ester condensation" to form a polymer we call a "polyester". These are widely used to make fabrics, carpets, etc.

Condensation Polymers are formed when monomer molecules join together in either an "amide condensation" or an "ester condensation". As well as all the synthetic fibres, many biologically important macro-molecules are condensation polymers.

Biopolymers

The word "biopolymer" refers to those naturally occurring polymers made by living things, such as proteins, starch and cellulose.

Humans have used these polymers for thousands of years. e.g. cellulose is a polymer of the sugar glucose which forms the cell walls of all plant cells. Humans use cellulose fibres (in cotton and linen) for clothing fabrics and for nearly 100 years have been using chemically-modified versions of it. For example, "rayon" is a synthetic fibre made from chemically-modified cellulose.

Research has been going on for many years on ways to get living things to grow polymers with properties more like those of the useful petrochemical-based plastics.

A lot of the research has centred around the polymer "polyhydroxybutyrate" (PHB) which has properties not too different from polyethene. It was discovered 80 years ago that PHB can be made by a species of bacteria, _Bacillus magaterium_.

In recent years, the Monsanto company has used Genetic Engineering (GE) to transfer the genes for PHB production from bacteria into corn plants. The crop is grown, harvested and can be eaten as usual, but the stalks and leaves are also harvested for their PHB content, which is as high as 20% of the dry weight.

Analysis
• PHB has properties which make it suitable to replace some plastics for packaging, but it tends to be brittle, and extra breakages must be accepted.

• PHB has the major advantage of being biodegradable, but this also limits its range of uses, since it can rot and disintegrate during use.

• There is resistance from farmers and consumers regarding the use of GE plants.

• The production of PHB is not yet as cheap as using petrochemical plastics.

Conclusion
PHB grown in corn has potential, but is unlikely to become widely used yet.

**Now Try
Worksheets 12 & 13**