Higher
Chemistry

HSN12200
Unit 2 Topic 2

Contents

Topic 2 – Natural Products

Organic Chemistry 1
Fats and Oils 1
Hardening of oils 2
Additives in margarines 2
Fats in the body 2
The Structure of Fats and Oils 2
Hydrolysis 3
Soaps 4
The Cleaning Action of Soaps and Detergents 4
Proteins 5
Reactions of amino acids 5
Chromatography 7
Other Reactions of Proteins 7
Amino Acids in Nature 7
Types of Protein 8
Enzymes 8

Topic 2 – Natural Products

Organic Chemistry

In the last two topics of this unit, the impression that carbon chemistry deals with synthetic or man-made substances might have been suggested. Nothing could be further from the truth. The traditional name for carbon chemistry is 'Organic Chemistry' and this was derived from the chemistry dealing with molecules found in living things – molecules found in nature. Another name for such molecules is biomolecules, and most organic chemistry still deals with these – the man made organic chemistry has only really developed during the 20th century.

In this topic we will meet some of the carbon molecules which are found in living systems; fats/oils and proteins.

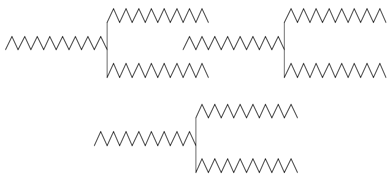
Fats and Oils

Vegetable origin	Animal origin
Soyabean oil	Whale oil
Palm oil	Cod liver oil
Olive oil	Pork fat: Lard
Castor oil	Mutton fat
Linseed oil	Beef fat

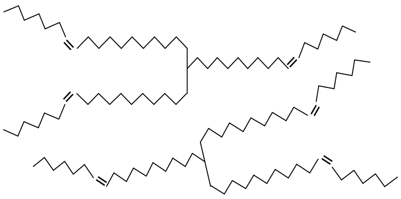
Fats and oils may be obtained from plants and animals and some examples are shown in the table. Note that the fats are mainly obtained from land animals and oils from plants and marine animals.

The main obvious difference between fats and oils is that fats are solid at room temperature and oils are liquids. There must be some difference between the two types of molecule that affects the melting points (melting points are lower for oils). The main 'chemical' difference which ties in with this is the higher level of unsaturation in oils – oil molecules contain many more C=C double bonds. This can be shown by shaking oils with bromine water – the brown colour disappears quite readily. If fats, dissolved in a suitable saturated solvent, are tested with bromine water the brown colour remains.

The diagrams and explanations below show how the presence of even just one C=C double bond can drastically alter the shape of the molecules and change the properties of the compound.



Diagrammatic representation of the structure of fat molecules



An exaggerated picture of oil molecules

The shape of both oil and fat molecules is roughly that of a tuning fork. The absence of a double bond allows the molecules to be more regularly tuning fork shaped and consequently the molecules can fit into one another. If a double bond is present then the molecules 'zigzag'; chains become distorted and cannot fit into one another.

Molecules which can pack closely together due to their regular structure have stronger Van der Waals forces between the molecules and thus higher melting points. So fats have higher melting points than oils – fats are solid at room temperature.

Marine animals that live in cold oceans often have oils because fats would be solid and could not be transported round the body.

Hardening of oils

It is possible to 'harden' oils into fats simply by reacting the double bonds with hydrogen. This is an addition reaction and changes unsaturated compounds into saturated ones. This is similar to the catalytic addition of hydrogen across the double bond in an alkene.

Margarines are made by partial hydrogenation of oils using a nickel catalyst. The degree of hydrogenation, along with different forms of refinement and blending can produce margarines with different properties.

Additives in margarines

Various ingredients are added to margarines to improve taste, appearance, saleability and health. These include:

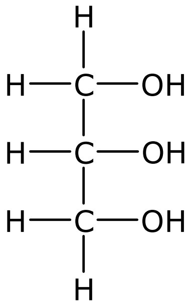
- Vitamins A and D. These are vitamins which are mainly obtained from oils and fats and which people obtained from butter. They must now be added to the butter substitutes.
- Colouring materials.
- Emulsifiers. Margarine is actually a water/oil emulsion and to keep the emulsion stable it is necessary to add emulsifying agents such as lecithin.
- Flavouring agents. These are added to enhance the 'butter' flavour of the margarines.

Fats in the body

The main dietary function of fats and oils is to provide energy. Weight for weight, they release about twice the amount of energy of carbohydrates. The difference between fats/oils in the body and carbohydrates is that fats/oils release their energy much more slowly – sugars etc. are quick burning sources of energy. Fats and oils also provide the body with some vitamins such as A, D, E and K, as these vitamins are soluble in fats/oils. In fact, margarine manufacturers are required to add some of these vitamins to their products to prevent certain vitamin deficiency problems.

The Structure of Fats and Oils

Fats and oils are actually special forms of esters where the alcohol, glycerol (propane-1,2,3-triol) has three hydroxyl groups. Because of this, glycerol is termed a 'trihydric alcohol'.



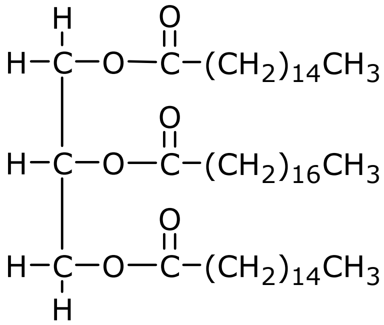
glycerol (propane-1,2,3-triol)

Each of the hydroxyl groups forms an ester linkage with a long chain carboxylic acid – these are called 'fatty acids'. The ratio of combining of glycerol molecules with fatty acid molecules is therefore 1:3.

It is in the acid chain that we find the absence or presence of the double bond – if there is a double bond the acid is called an alkenoic acid. Some examples of these acids are given below:

Palmitic acid	$CH_3(CH_2)_{14}COOH$
Stearic acid	$CH_3(CH_2)_{16}COOH$
Oleic acid	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$
Linoleic acid	$CH_3(CH_2)_3(CH_2CH{=}CH_2)_2(CH_2)_7COOH$

Note that fatty acids are saturated or unsaturated straight chain carboxylic acids with even numbers of C atoms ranging from C_4 to C_{24}, but mainly C_{16} to C_{18}. A typical fat molecule is shown below:



The fat or oil molecule is called a triglyceride. When a fat or oil is formed, the glycerol molecule can react with three different fatty acid molecules.

Any particular fat, such as beef fat, is made of a mixture of different triglycerides. So no fat or oil is a pure triglyceride.

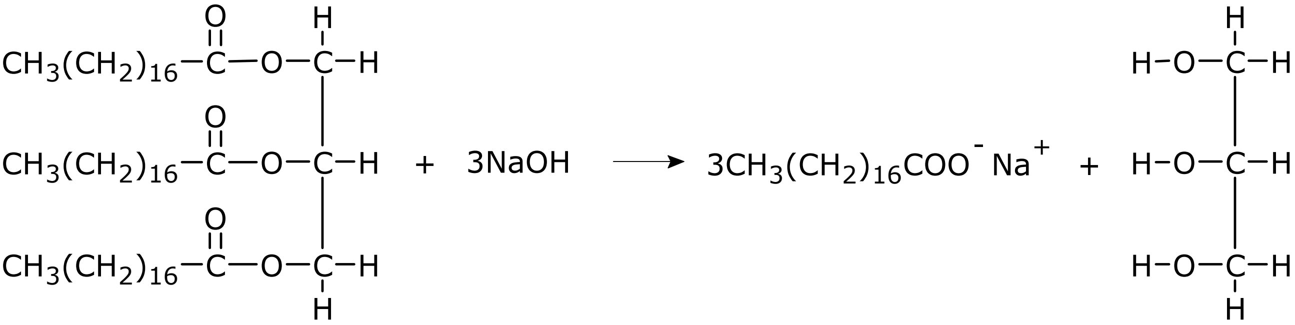
Hydrolysis

We have already seen that ester groups can undergo a hydrolysis reaction where a water molecule can be ‘reinserted’ into the ester link. This results in the alcohol and the carboxylic acid being formed.

It is possible to break up fat and oil molecules into the glycerol (the alcohol part) and the fatty acids by hydrolysis. This can simply be done by treatment with superheated steam. In the lab, this hydrolysis is normally done using aqueous acid or alkali. A very important example of the hydrolysis of fats and oils is in the production of soaps.

Soaps

Soaps are made from fats and oils by hydrolysing them using solutions of sodium hydroxide or potassium hydroxide. The fatty acid is formed as the sodium or potassium salts. These salts are ‘salted out’ of the reaction mixture by adding a great excess of sodium chloride and the soap can then be filtered off.

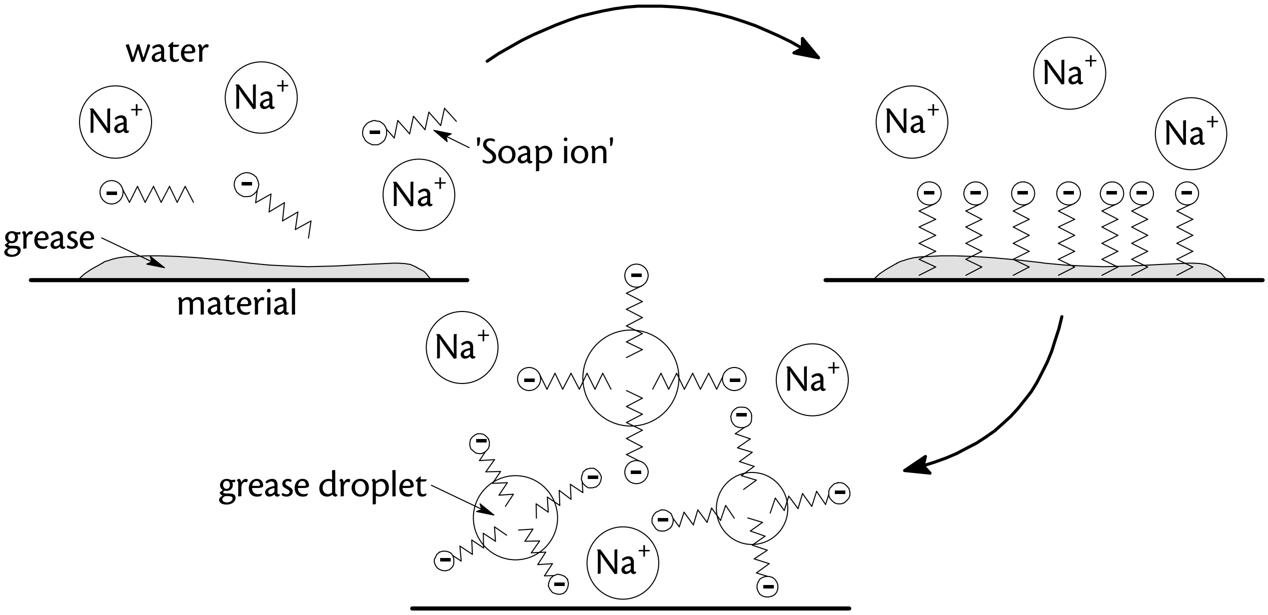


The Cleaning Action of Soaps and Detergents

Soaps and detergents are ‘emulsifying reagents’. These are simply chemicals which can make oil and water become permanently mixed to produce a stable emulsion. As most of the grime and dirt on skin, clothes and dishes tends to be trapped in oils and greases, water alone cannot rinse away the muck. If the oils/greases can be made to mix with water then it becomes easy to wash off, along with the grime. Soaps and detergents do this job in a clever way, due to the structure of the molecules:

Sodium or potassium salts of long chain fatty acids really have two quite separate parts in terms of their bonding types – a long hydrocarbon chain which is non polar and an ionic ‘head’.

Recall that non polar molecules are very insoluble in water but are soluble in non polar solvents such as oil. Ionic compounds (particularly those of the alkali metals) are generally soluble in water but not in non polar solvents. Soap molecules have two sets of solubility properties in different parts of their structure and it is this that makes soaps and detergents good emulsifying agents. The following set of diagrams show how this works.

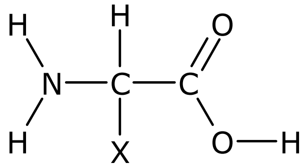


Proteins

At Standard Grade, we learned that the element nitrogen was essential in the food chain (you may wish to revise the nitrogen cycle) and its place in the food cycle is in the formation of proteins.

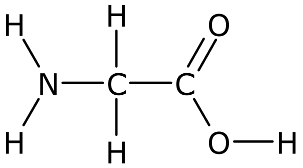
Proteins are the molecules which make up our muscle fibres, hair, nails, skin, enzymes etc. They are generally very large molecules which are made up from smaller molecules called amino acids – ie they are natural polymers.

The smaller molecules (monomers) contain two functional groups which have been met before; the amine group $-NH_2$ and the carboxyl group $-COOH$. The amino acids contain both these groups on the same molecule, and it is possible to get many isomers by altering the relative positions of the two groups on a molecule, but natural amino acids must have the two groups bonded to the same carbon atom. They are called α-amino acids

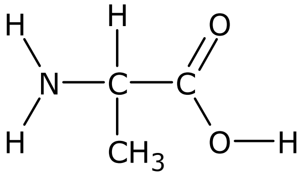


X can be H, or an alkyl group, or sometimes even groups with S, P, or other N atoms.

There are about 20 naturally occurring α-amino acids; the simplest two are glycine and alanine. Their structures and systematic names are:



aminoethanoic acid
(glycine)

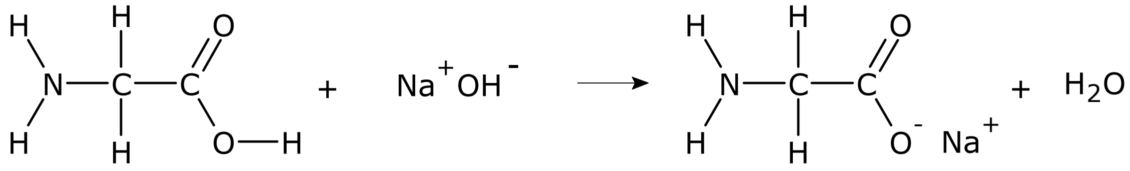


2-aminopropanoic acid
(alanine)

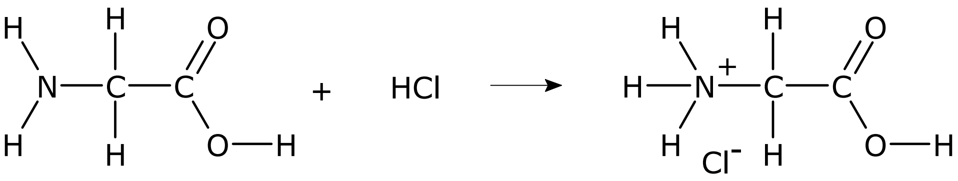
Reactions of amino acids

Amino acids have two functional groups on their molecules – the carboxyl group and the amino group, both of which have been met before. Amino acids can therefore react as acids and as bases, using either of these groups:

eg as an acid

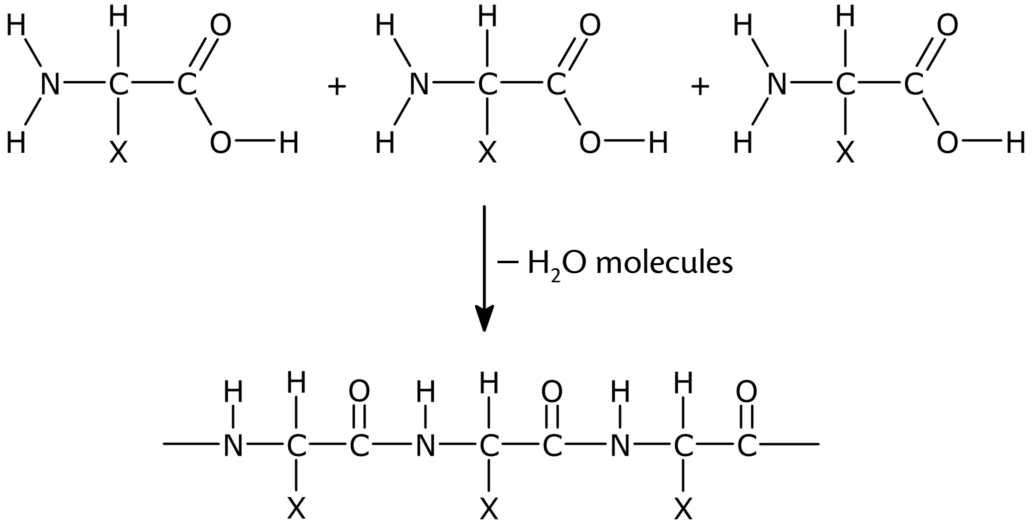


eg as a base

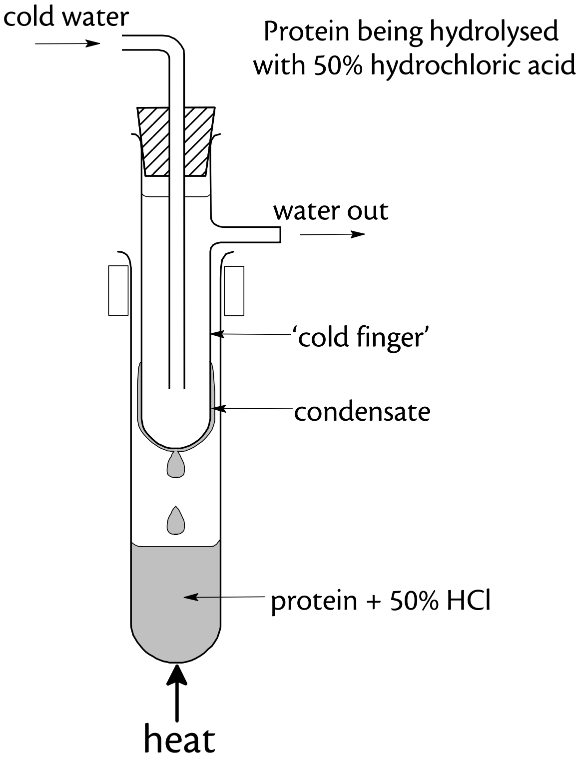


Proteins are made by the condensation of amino acid molecules to give a long string-like molecule. Proteins are therefore condensation polymers of amino acids. The link formed between the amino acids is called a peptide link (we have met the same link before in nylon and kevlar but it was referred to as the 'amide' link. In biological molecules, the term peptide has become preferred). The actual structure of a particular protein depends on the amino acids present.

The scheme below shows that the links are formed between the amino group of one molecule and the carboxyl group of an adjacent molecule.

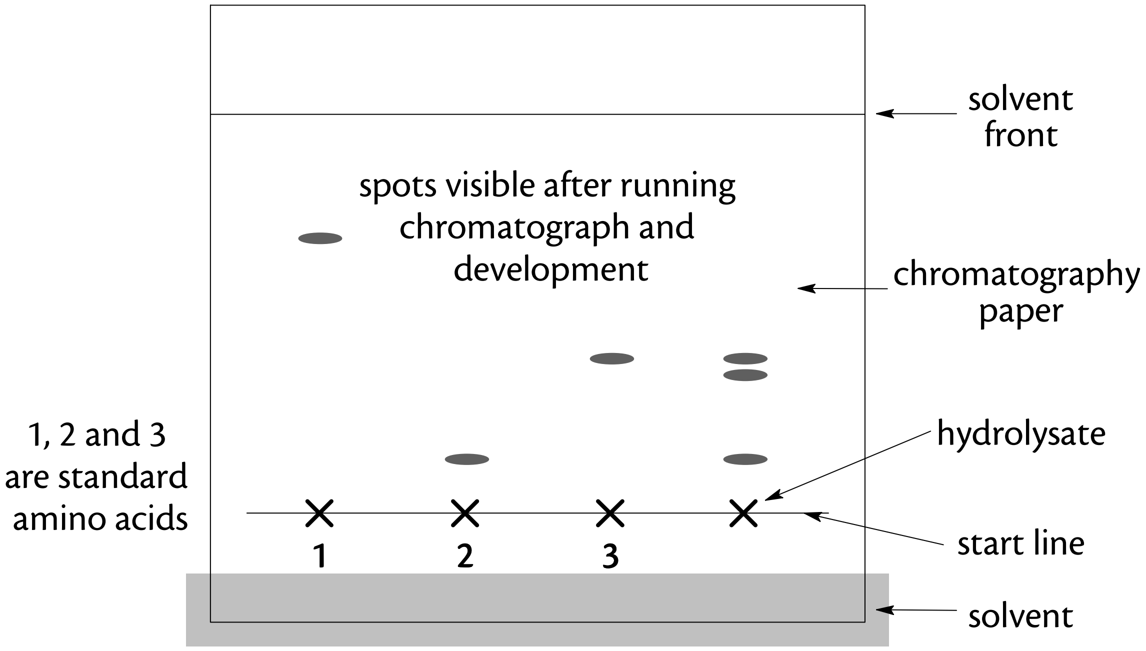


Proteins have very large molecular mass due to their being made from several thousand amino acid molecules. They can be broken back down to their constituent amino acids by hydrolysis (just as all condensation polymers can!) In the lab, this can be done by 'refluxing' the protein with fairly concentrated hydrochloric acid. The apparatus below shows how this can be done simply. In the stomach, enzymes more efficiently hydrolyse the proteins into the amino acids.



Chromatography

The amino acids produced by the breakdown of proteins can be identified by using the technique of chromatography. This has been studied at Standard Grade level. The diagram below shows the result of running a simple chromatogram of a hydrolysed protein. Note that, unlike the pigments in inks, amino acids are colourless and invisible so the spots on the paper must be 'developed' using a special solution.



Other Reactions of Proteins

Proteins are nitrogen containing compounds and this can be shown by heating the protein with a strong alkali. Soda lime is normally used for this and if the protein is ground up with soda lime and gently heated in a test tube alkaline gases are given off – this can be shown using damp pH paper, which turns blue. Note that this test does not confirm that a substance is a protein, only that it contains nitrogen!

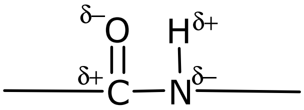
Amino Acids in Nature

The number of possible amino acid structures is very great, but nature only uses 26 different structures. Protein molecules normally consist of several thousand amino acids condensed together so the permutations are endless! (Hence the huge variety of protein structures.) The bodies of living things cleverly build up proteins specific to the bodies' needs from the supply of amino acids in the diet. Some amino acids can actually be made in the body given the correct materials. Some, however, must be present in our diet and these are called 'essential amino acids'. The absence of even one of these essential amino acids from our diet can cause serious dietary deficiencies – remember it takes only the lack of one amino acid to prevent the formation of a protein which it contains! If the body cannot produce it and it is not present in our diet then the protein can't be made. In many Asian and African countries, the people live on a highly restricted vegetarian diet and the availability of all the essential amino acids is limited – protein deficiency diseases such as kwashiorkor affect many people as a result.

Types of Protein

Proteins in the body perform a vast range of jobs. As a result of this, they can exist in a range of sizes and shapes.

We have seen that the amino acids are joined by peptide links:

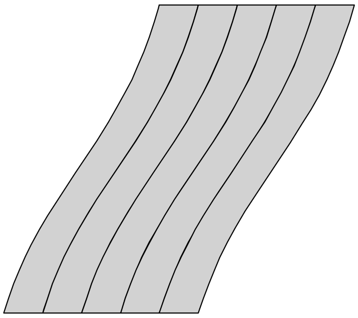


These polar peptide links can hydrogen bond (an intermolecular force) with each other in the same chain to produce a helix structure or in different chains to produce a sheet structure. These helices or sheets can then be folded to give fibrous or globular proteins.

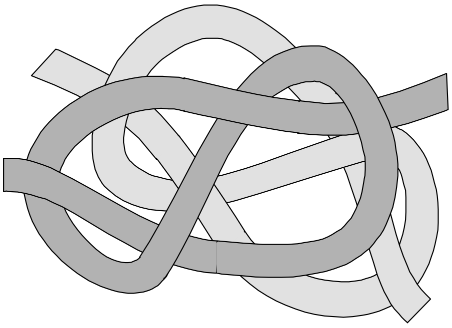
Fibrous proteins are the ones which form the structural materials in animal tissues – eg skin, muscle, hair, nails.

Globular proteins tend to have spiral chains folded and twisted round into more compact units and are generally the ones which are involved in the chemistry of metabolic regulation within the living systems. For example, enzymes (more of which later), hormones (eg insulin for the control of blood sugar levels) and haemoglobin for the transport of oxygen within the bloodstream are globular proteins.

The following diagram shows examples of these two types of protein.



fibrous protein



globular protein

Enzymes

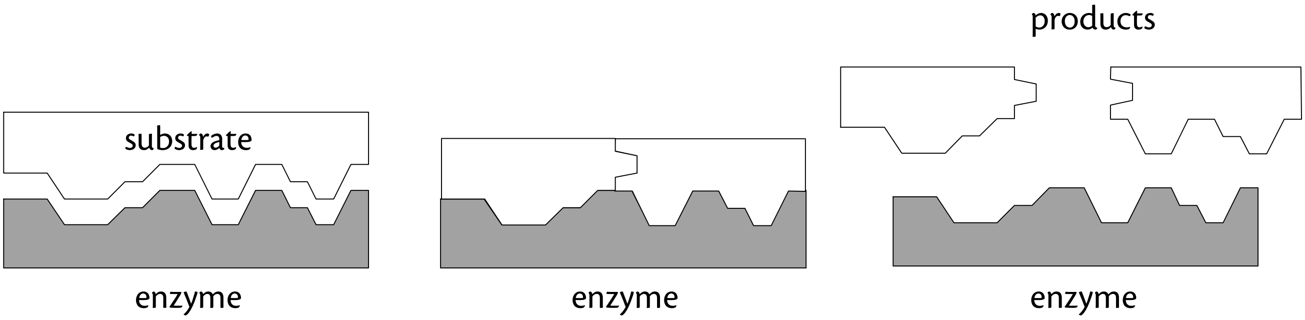
Enzymes are proteins. They are important natural substances in the bodies of all living things. Enzymes are natural catalysts and without them, the biochemical reactions which happen in all living things would not take place. All enzymes are totally protein in their structure but some need another part (called a co-enzyme) before they can function.

Enzymes are said to be specific. This means that each enzyme only catalyses one reaction – the enzyme diastase can only break down molecules of starch to glucose in the mouth and stomach but can have nothing to do with the breakdown of proteins for example.

Some chemical processes involve a sequence of reactions each stage of which requires a different enzyme. The production of ethanol from starch in fermentation for example:

$$\text{starch} \xrightarrow{\text{amylase}} \text{maltose} \xrightarrow{\text{maltase}} \text{glucose} \xrightarrow{\text{zymase}} \text{ethanol} + CO_2$$

The scheme below shows how enzymes are thought to work; the ‘lock and key’ principle.



The specificity of enzymes is therefore due to their molecular shapes. Different proteins can have different shapes so can interact with different molecules. The 3D shapes of the molecules are influenced by the presence of hydrogen bonds between the chains. Enzymes are most active within certain narrow temperature and pH ranges. The protein structure of the enzyme is permanently altered at high temperature or low pH conditions as the hydrogen bonds are broken. This is called ‘denaturing’ the protein – eg. cooking an egg – once the egg is cooked it can never become ‘uncooked’. How easily the protein is denatured depends on how susceptible the enzyme is to pH and temperature. Note that in denaturing, that covalent bonds are not broken.