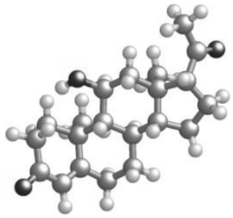

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Permanent Waves

Figure 1.
Chemistry can be beautiful.

Since ancient times, people have experimented with many ways to change the appearance of their hair. The Assyrians favoured curly hair, the Egyptians wore wigs and the Romans used curling irons. Today, it seems that people with straight hair want curls and the curly haired people covert straight hair. Now you can change the shape of your hair with permanent waving or hair straightening products, but how do these products work and what do they actually do to your hair?

Hair Structure

The part of the hair that protrudes above the skin, the part that we see, is called the *shaft*.
It looks quite simple to the naked eye, but when magnified, it reveals a complex structure. The outer layer, called the *cuticle*, consists of dead epithelial cells which overlap each other rather like the scales of a fish (**Figure 2.**). Inside the cuticle is the *cortex* which contains the protein that gives hair its strength and determines its shape as well as the pigment *melanin* that determines its colour

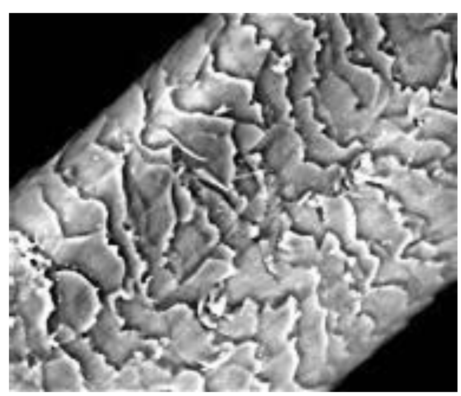

Figure 2.
Hair reveals its complex structure when investigated under a microscope.

(**Figure 3.**). Proteins are large molecules (*polymers*) that are assembled from smaller molecules called amino acids (*monomers*) (**Figure 4.** and **Figure 5.**). Your hair contains a class of protein called *keratin*. As the shaft emerges from the follicle, the keratin hardens as chemical bonds form that cross-link one protein chain to another. Three types of chemical bond are at work: *ionic*, *covalent* and *hydrogen*.

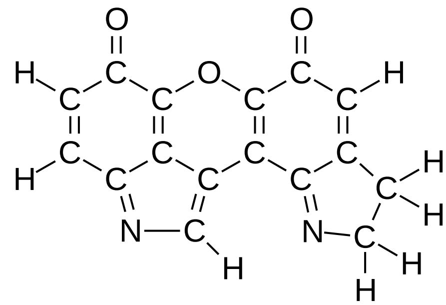

Figure 3.
The structural formula of the natural pigment *melanin*.

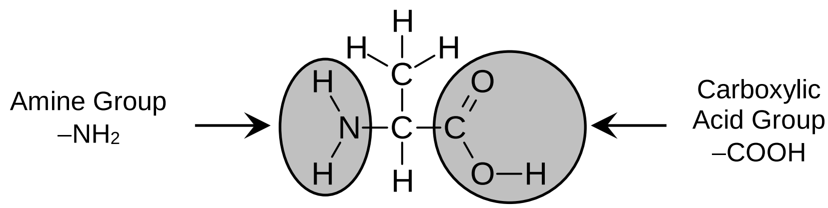

Figure 4.
The structural formula of the amino acid *alanine*.
There are 20 naturally occurring amino acids.

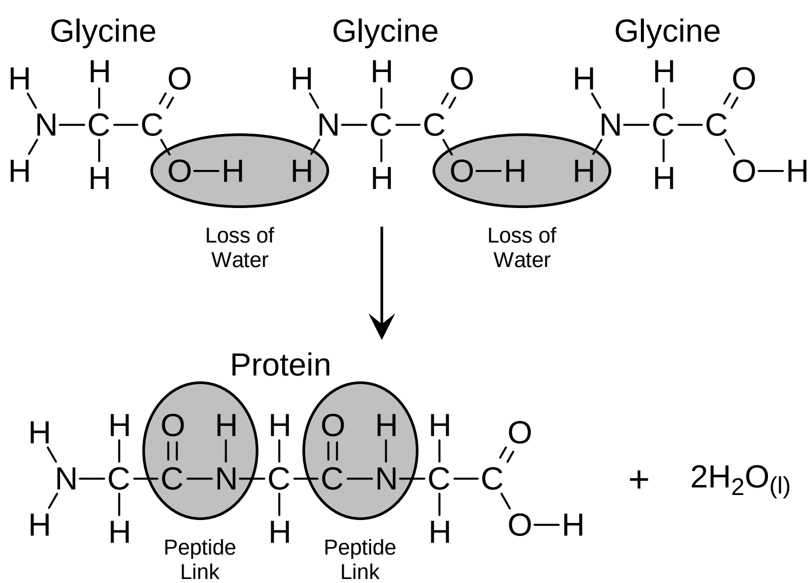

Figure 5.
The formation of a short chain protein from three amino acids.
This reaction is known as a *condensation polymerisation*.

The Zipper

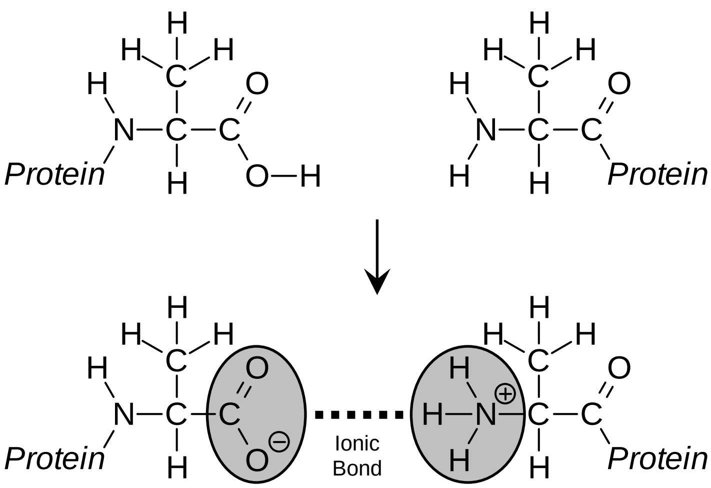

Figure 6.
The formation of an ionic bond between two protein chains.

Under the conditions usually found in hair, the carboxylic acid group and amine group on the ends of a protein chain are ionized. The –COOH group has lost a hydrogen ion (H^+) to become $–COO^-$ and the $–NH_2$ group has gained a hydrogen ion to become $–NH_3^+$ (**Figure 6.**). The attraction between the positive and negative charges pulls these ions together and forms an *ionic bond*. Note: ionic bonds are typically found in salts, such as sodium chloride, and involve many ions. When single positive and negative ions join organic molecules together, the bond is sometimes called a *salt bridge*.

Hydrogen bonds consist of attractions between weak positive and weak negative charges, in which the weak positive charge is always found on a hydrogen atom. The weak negative charge may exist on a variety of atoms, including nitrogen and oxygen (**Figure 7.**). Hydrogen bonds are weak, but there are billions of them in your hair. Hydrogen bonds can exist within the same protein chain (*intra-molecular*) as well as between different protein chains (*inter-molecular*).

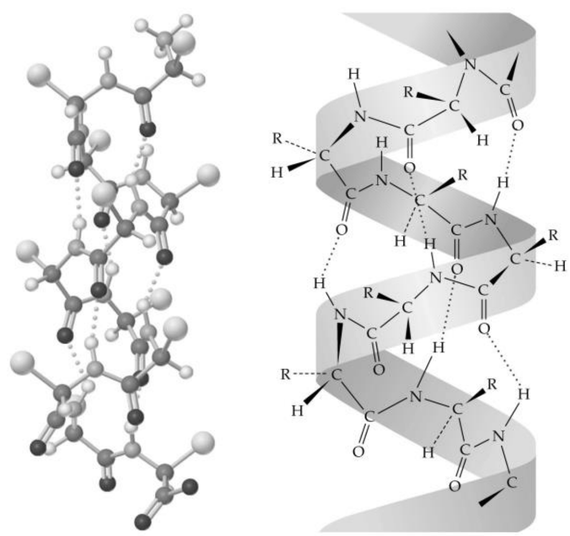

Figure 7.
This diagram shows the hydrogen bonds (dotted lines) that exist between polar regions of the keratin molecule.

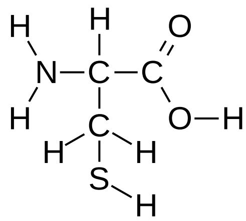

Figure 8.
The amino acid cysteine contains a thiol group, –SH.

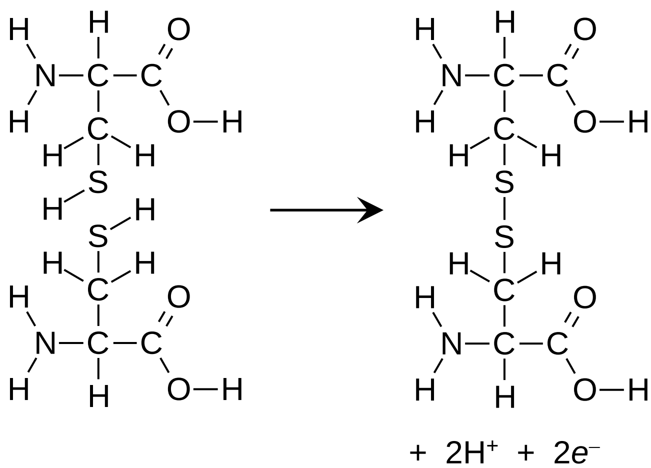

Figure 9.
The formation of a disulphide bond between two cysteine molecules.

In contrast to the ubiquitous hydrogen bonds, covalent bonds that cross-link protein chains only form at special locations where the sulphur containing amino acid called *cysteine* (**Figure 8.**) is present in both proteins.

Cysteine contains an –SH group (known as a *thiol*) that projects out from the protein backbone. Under normal conditions, hydrogen can be removed from two neighbouring –SH groups on adjacent protein chains, resulting in the formation of a covalent bond between the remaining atoms of sulphur (**Figure 9.**). As a consequence, the adjacent protein chains become cross-linked. This type of cross-link is called a *disulphide bond* and is very important when giving straight hair a permanent wave.

Unzipping the Bonds

Hair waving changes the shape of the cortex by breaking and reforming the ionic, covalent and hydrogen bonds that cross-link protein chains. Note: the bonds *within* protein chains are little affected by waving. The hydrogen bonds (**Figure 7 and Figure 10.**) are broken with water. Your hair may be 30% H_2O by weight, but it absorbs more water when you stand under the shower and this starts to break the hydrogen bonds.

Because water is polar (contains slightly positive hydrogen atoms covalently bonded to slightly negative oxygen atoms) water

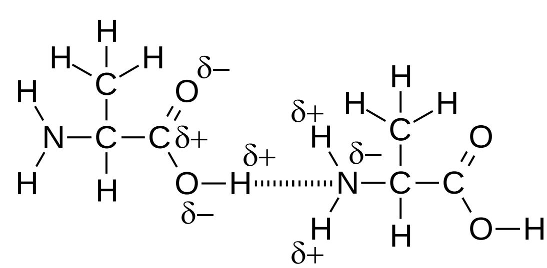

Figure 10.
Hydrogen bonds (dotted lines) between proteins arise when a hydrogen atom carrying a slight positive charge (δ+) is attracted to a nitrogen atom or oxygen atom that carries a slight negative charge (δ–).

molecules are attracted to polar regions of the protein chain where they disrupt the inter-molecular hydrogen bonds. When water penetrates the hair shaft, the slightly negative nitrogen atom of one protein chain that was originally attracted to the slightly positive hydrogen atom of another protein chain may find itself attracted to the slightly positive hydrogen atom of a water molecule instead (**Figure 11.**). The nitrogen loses its grip because it is now attached to a liquid rather than a solid. This is why hair is dampened before it is set. Wet hair swells as the hydrogen bonds are broken, and this makes it easier for other chemicals to penetrate the shaft.

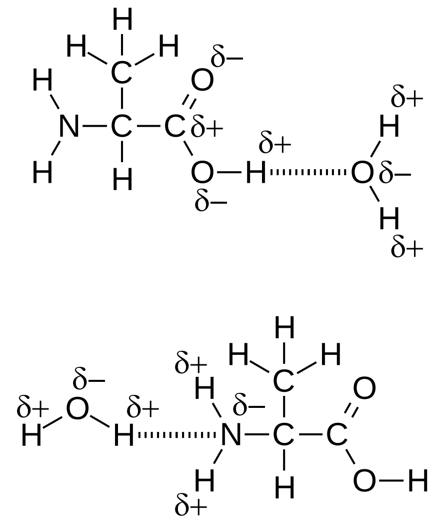

Figure 11.
Hydrogen bonds (dotted lines) between protein chains are disrupted by polar water molecules.

The ionic bonds are easily broken by acids or alkalis, though most waving solutions are alkaline. In an alkaline solution, the negative hydroxide ion (OH^-) is attracted to and reacts with the positive ammonium ion ($-NH_3^+$). During the reaction, the positive ion loses its charge. Without a positive charge to attract the negative charge, the ionic bond between the protein chains will collapse:

$$OH^- + \textit{protein}\text{–}NH_3^+ \rightarrow H_2O + \textit{protein}\text{–}NH_2$$

The remaining bonds, which pose chemists the greatest problem, are the covalent disulphide bonds. Long-lasting permanent waves did not exist until chemists synthesised a suitable reagent for breaking disulphide bonds. That reagent is ammonium thioglycolate (**Figure 12.**) the active compound in most waving solutions.

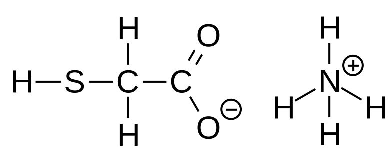

Figure 12.
Ammonium thioglycolate is the reducing agent used to break the disulphide bonds between proteins.

The alkalinity of the permanent wave solution breaks the ionic bonds, but has little effect on the disulphide bonds (**Figure 13.**) which must be broken by a *redox reaction*.

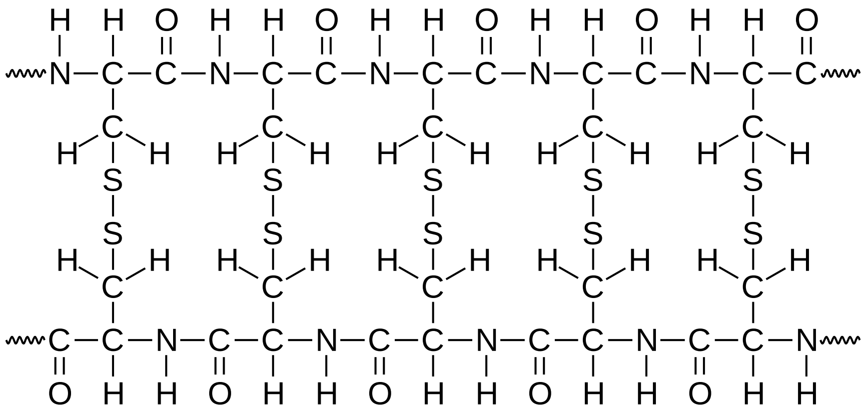

Figure 13.
The shape of the hair cannot be changed until the disulphide bonds between the protein chains have been reduced.

The reducing agent, ammonium thioglycolate, adds hydrogen (a *reduction* reaction) to the sulphur atoms that form the disulphide bonds. This breaks the main crosslink between the protein chains in the cortex of the hair.

The sulphur atoms of the disulphide bonds are *reduced* (gain of hydrogen / gain of electrons):

$$\textit{protein}^1\text{–S–S–}\textit{protein}^2 + 2H^+ + 2e^- \rightarrow \textit{protein}^1\text{–S–H} + \text{H–S–}\textit{protein}^2$$

The thioglycolate ion is *oxidised* (loss of hydrogen / loss of electrons):

$$^-OOCCH_2S\text{–}H + H\text{–}SCH_2COO^- \rightarrow {}^-OOCCH_2S\text{–}SCH_2COO^- + 2H^+ + 2e^-$$

Combining these two balanced chemical equations and cancelling the $2H^+$ and $2e^-$ on either side of the arrow gives the overall balanced chemical equation for the redox reaction:

$$\begin{array}{ccc} \textit{protein}^1\text{–S–S–}\textit{protein}^2 & & \textit{protein}^1\text{–S–H} + \text{H–S–}\textit{protein}^2 \\ + {}^-OOCCH_2S\text{–}H + H\text{–}SCH_2COO^- & \rightarrow & + {}^-OOCCH_2S\text{–}SCH_2COO^- \end{array}$$

Once the disulphide bonds between the protein chains have been broken, the protein chains can be pulled past each other (**Figure 14.**). This allows the hair to be reshaped.

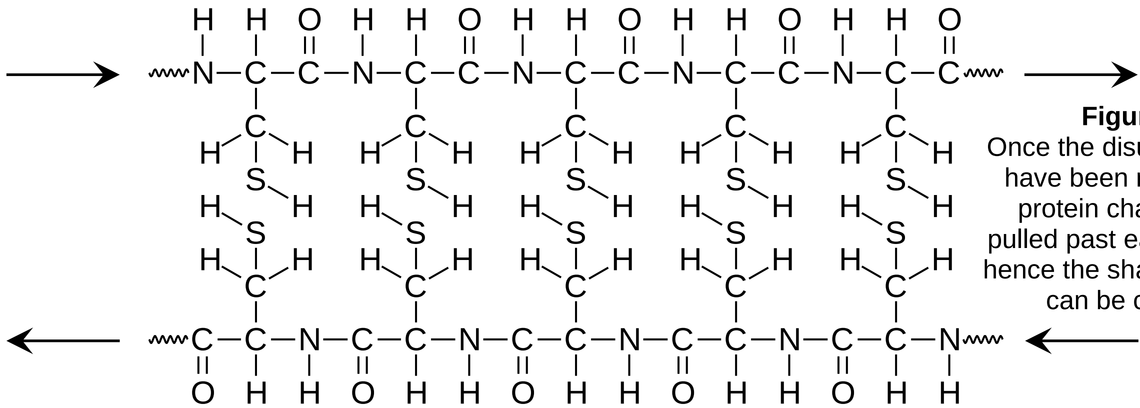

Figure 14.
Once the disulphide bonds have been reduced, the protein chains can be pulled past each other and hence the shape of the hair can be changed.

The pH of the waving solution is 8.0 to 9.5. The alkalinity causes the cuticle of the hair to open and allows the solution to penetrate more rapidly than acid perms. Unfortunately, the solution of ammonium thioglycolate and ammonium hydroxide combine to produce the acrid scent of ammonia and the rotten egg smell that is typical of sulphur containing compounds.

It's Enough to Curl Your Hair

After the chemical action of the waving solution, physical action changes the shape of the hair. The hair is smoothly wrapped around curlers. Because the crosslinks between protein chains have been broken, the hair assumes the shape of the curler (**Figure 15**). Now it is time to reverse the first redox reaction.

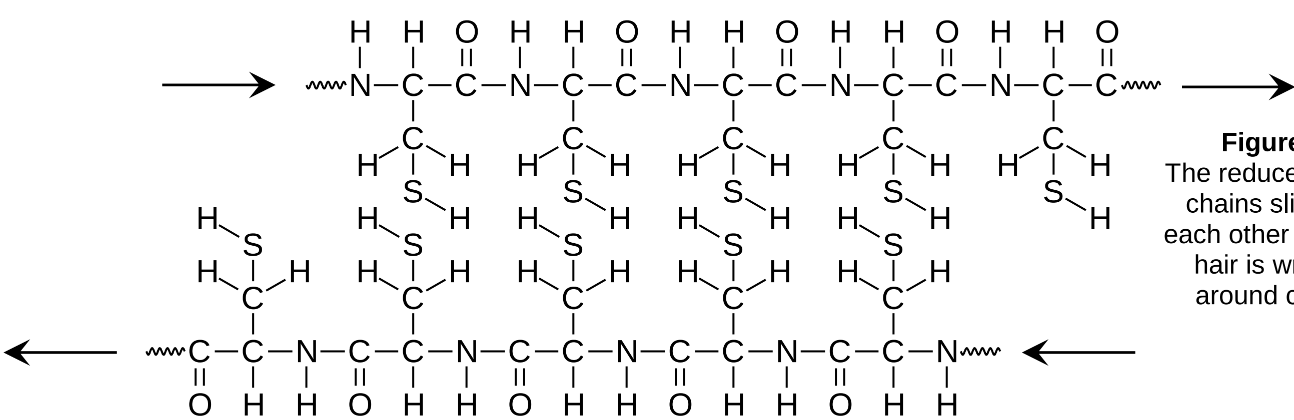

Figure 15.
The reduced protein chains slide past each other when the hair is wrapped around curlers.

The rest of the process involves another redox reaction. First, all of the ammonium thioglycolate solution is washed out of the hair with warm water. Next, a so-called *neutralising agent*, usually *hydrogen peroxide* (formula – H_2O_2) is applied. The hydrogen peroxide molecules go to the –SH groups of the protein chain and remove the hydrogen atoms (an *oxidation* reaction) to form water.

The sulphur atoms of the disulphide bonds are *oxidised* (loss of hydrogen / loss of electrons):

$$protein^1\text{–S–H} + \text{H–S–}protein^2 \rightarrow protein^1\text{–S–S–}protein^2 + 2H^+ + 2e^-$$

The oxygen of the hydrogen peroxide is *reduced* (gain of hydrogen / gain of electrons):

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$$

Combining these two balanced chemical equations and cancelling the $2H^+$ and $2e^-$ on either side of the arrow gives the overall balanced chemical equation for the redox reaction:

$$protein^1\text{–S–H} + \text{H–S–}protein^2 + H_2O_2 \rightarrow protein^1\text{–S–S–}protein^2 + 2H_2O$$

As the sulphur is oxidised, the disulphide bonds that cross-link the protein chains are reformed (**Figure 16.**).

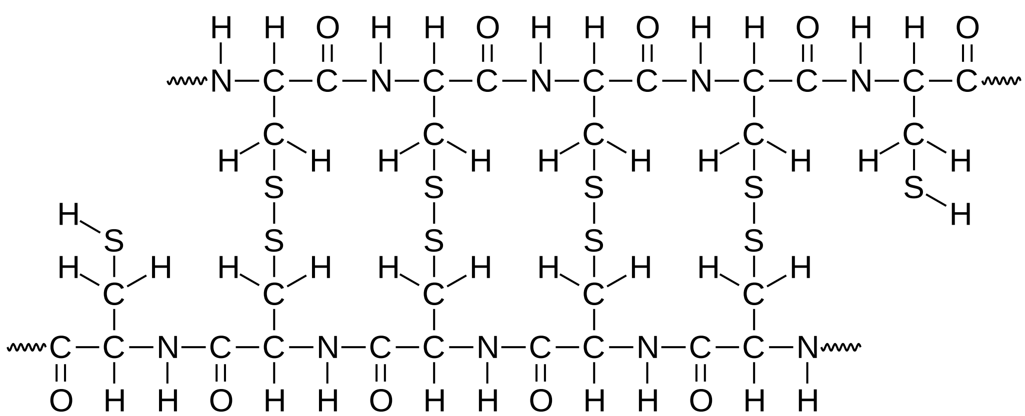

Figure 16.
The protein chains cannot slide past each other once the disulphide bonds have reformed between them. The curls and waves that have been applied to the hair's shape are now permanent.

Zipping Up

The neutralising agent is then washed out of the hair. As the hair dries, the hydrogen bonds and ionic bonds reform. The hair is strong again, but with a different shape imposed on it because the various chemical bonds have been rearrange into different positions.

Adapted from *ChemMatters* published by the *American Chemical Society* (April 1993).