

# Chemistry in your cupboard: Veet

## Introduction

Depilatory products may work either mechanically or chemically. This section explores the chemistry of hair and how hair can be removed by chemical means through dissolving the proteins that form the structure of hair. The complication of removing hair chemically is that the depilatory product needs to be able to dissolve the proteins within hair but without exerting an effect on those forming the structure of skin. Veet is an example of a depilatory product and comes in both creams and mousses and a variety of different formulations for different skin types.

## Links to the curriculum

This section contains information relevant to the following areas of your chemistry curriculum:

- Amino acids and proteins
- Bonding
- Reaction rates
- Equilibria and Le Chatelier's principle

## VEET

Depilatory products (including for example Veet®) are used to remove unwanted hair on legs and underarms, for example. Present day trends in fashion and beauty seem to demand the removal of hair from certain parts of the body. This is so much so that there was amazement when actor Julia Roberts appeared at a film premiere showing underarm hair, Figure 1.

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**Figure 1: Julia Roberts at the premiere of the film Notting Hill. Her display of underarm hair caused much comment.**

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There are different opinions about hair removal, but there is a demand for depilatory products from many women and an increasing number of men. The most common method of hair removal is, of course, shaving. However, this leaves behind a sharp edge on the end of each hair. These sharp ends lie right at the surface of the skin. As soon as the hair starts growing (within hours), these sharp edges are exposed, producing stubble which is unsightly, rough and uncomfortable, Figure 2.



**Figure 2: Shaved hair (left) and hair after chemical removal (right)**

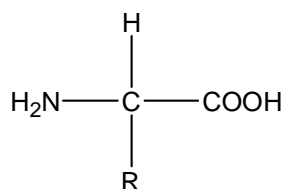
Here we look at chemical means of removing hair - these work at the surface of the skin to dissolve the protein that makes up hair, leaving rounded ends on the hair shaft, Figure 2. The result is a smoother feel for longer.

To understand how these hair proteins can be dissolved, we must first understand the chemical makeup of hair.

## The structure of hair (1 of 4)

### Amino acids, peptides and proteins

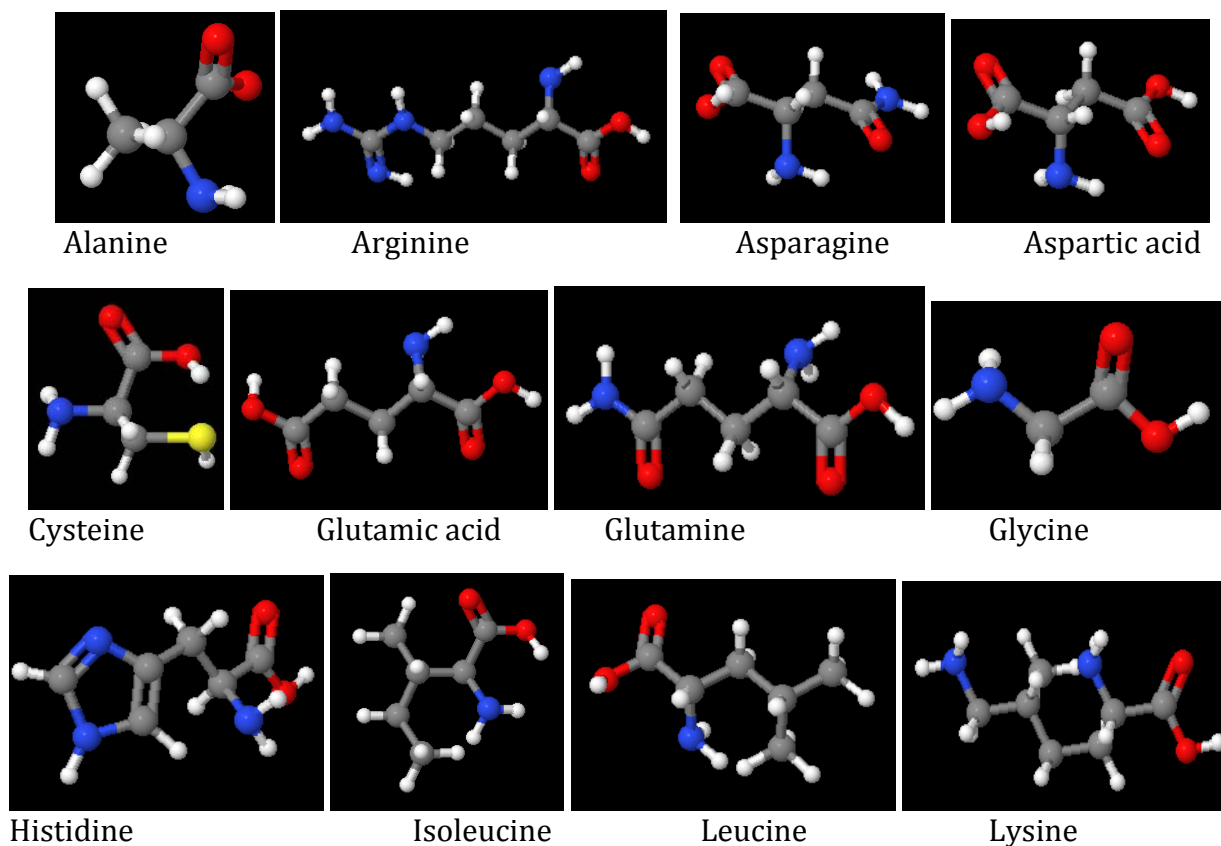
Hair is largely made up of the protein keratin. Keratin is not a single compound but a family of related compounds. Like all proteins it is a poly-amino acid. There are 20 naturally-occurring amino acids found in living things. They all have the general formula



where the side chain, R, may be a variety of groups. They are called  $\alpha$ -amino acids (or  $\alpha$  amino acids) to indicate that the  $-\text{NH}_2$  group and the  $-\text{COOH}$  group are attached to the same carbon atom. In the simplest  $\alpha$ -amino acid, glycine (systematic name aminoethanoic acid),  $\text{R} = \text{H}$ .

Amino acids are bifunctional compounds - the carboxylic group is acidic and tends to lose a proton and the amino group is basic and tends to gain one. Because of this, amino acids exist as so-called **Zwitterions**,  $^+\text{H}_3\text{NCH}(\text{R})\text{COO}^-$ . Although overall neutral zwitterions have ionic charges; this explains why amino acids are crystalline solids despite their relatively low molecular masses.

The 20 naturally-occurring amino acids can be examined in Figure 3.



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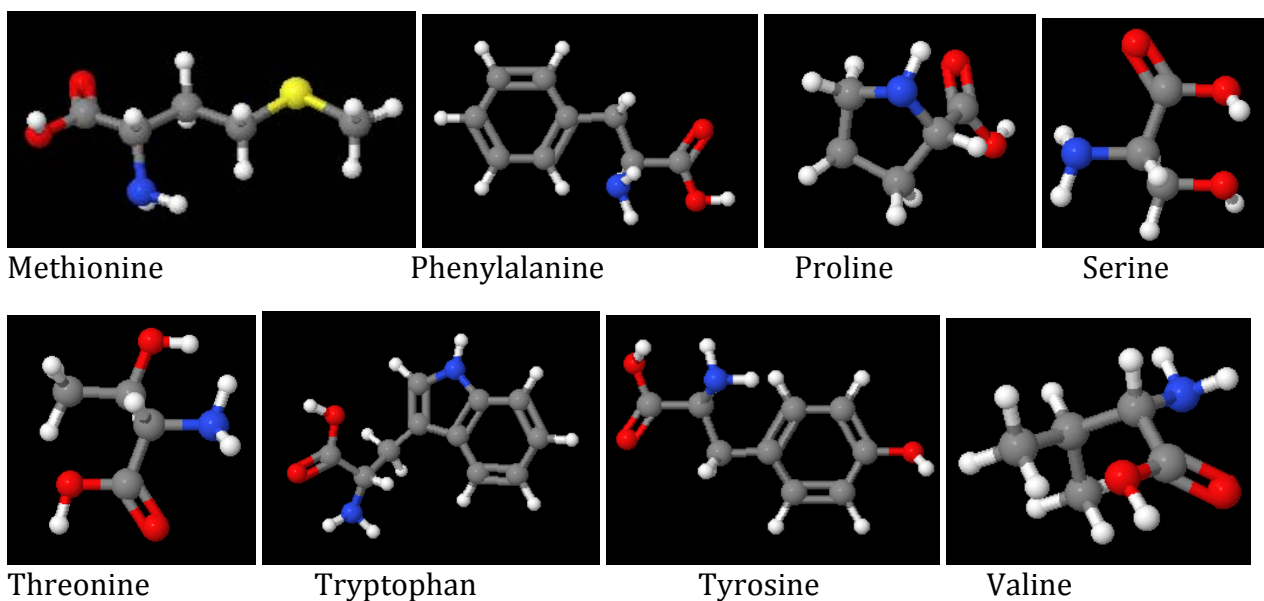


Figure 3: 3D representations of the 20 naturally-occurring amino acids

In the 3D representations, carbon atoms are coloured grey, hydrogen white, oxygen red, nitrogen blue and sulfur yellow. You may find it helpful to make a model of these amino acids using a ball and stick modelling kit such as Molymod™.

### Question 1

What is the systematic name of alanine?

### The structure of hair (2 of 4)

Two amino acids can link together with the loss of a molecule of water from the  $\text{-COOH}$  of one and the  $\text{-NH}_2$  group of the other as shown in Figure 4.

The resulting molecule, called a dipeptide, still has a  $\text{-NH}_2$  group on one end and a  $\text{-COOH}$  group on the other; similar reactions can occur with other amino acids to form tri-, tetra- and pentapeptides *etc.* The bonds linking the amino acids are called amide bonds or peptide bonds. Peptide chains more than about 50 amino acids long are usually called proteins.

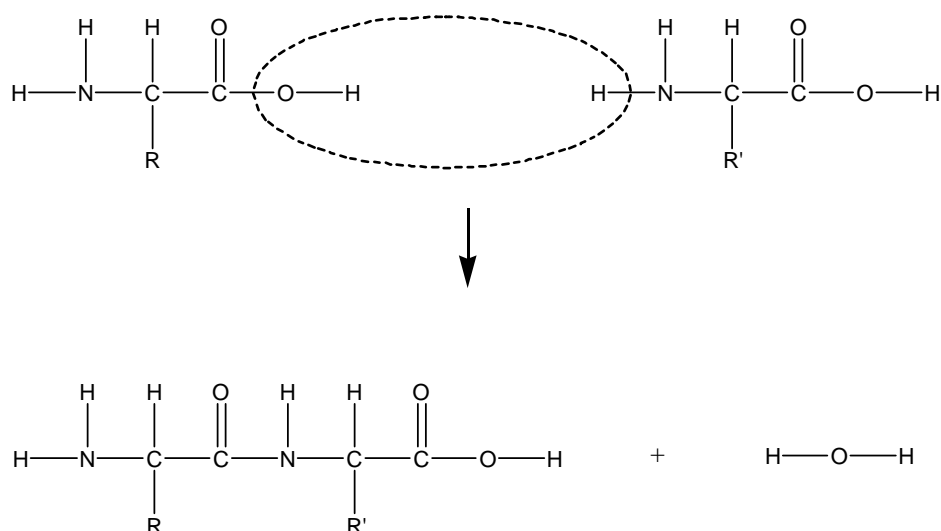


Figure 4: The formation of a dipeptide

### Question 2

Figure 4 shows the formation of a dipeptide but not how it occurs. It is actually a nucleophilic substitution reaction (also called an addition-elimination reaction).

a) Using Figure 4 as a guide, draw the displayed structural formulae (i.e. showing all atoms and all bonds) of two amino acids. Show the polarities of the  $\text{-NH}_2$  and  $\text{-COOH}$  groups by drawing  $\delta^+$  and  $\delta^-$  on the appropriate atoms and also the lone pair on the N atom.

b) Which is the most electron deficient atom of the  $\text{-COOH}$  group? Explain your answer.

c) Draw a 'curly arrow' to show the nucleophilic attack of the nitrogen atom on this carbon atom.

d) In this reaction, a molecule of water is lost. What name is given to this type of reaction?

Hair keratin, like all other proteins, consists of chains of many amino acids linked together by amide (peptide) bonds. The order of these amino acids along the chain is called the primary structure of the protein and can simply be written on a piece of paper giving the order of the three letter amino acid symbols, *e.g.* -gly-ala cys-gln-glu asp-lys-*etc.* Proteins may consist of thousands of amino acids.

Hair keratin has an unusually high proportion (up to 14%) of the amino acid cysteine (cys). We will see shortly that this is highly significant with regard to the properties of hair.

### Question 3

Hair keratin has up to 14% cysteine. What would be the proportion of cysteine (or any other amino acid) in a protein by chance if all amino acids were possible?

Remember there are 20 naturally-occurring amino acids.

### The structure of hair (3 of 4)

Proteins also have a further layer of structure – they may coil into spirals or lie alongside one another to form sheets. Two common shapes are the  $\alpha$ -helix, Figure 5, and the  $\beta$ -pleated sheet, Figure 6.

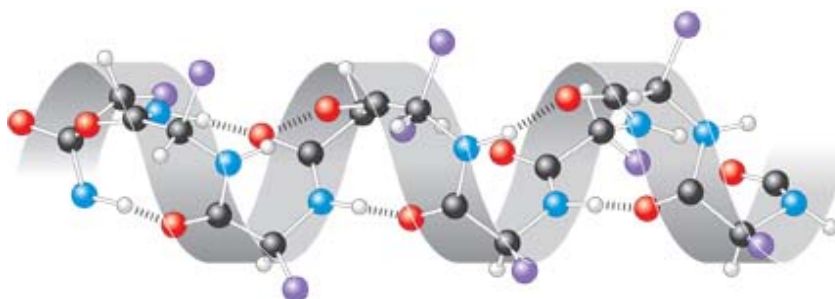


Figure 5: A protein  $\alpha$ -helix showing the hydrogen bonds

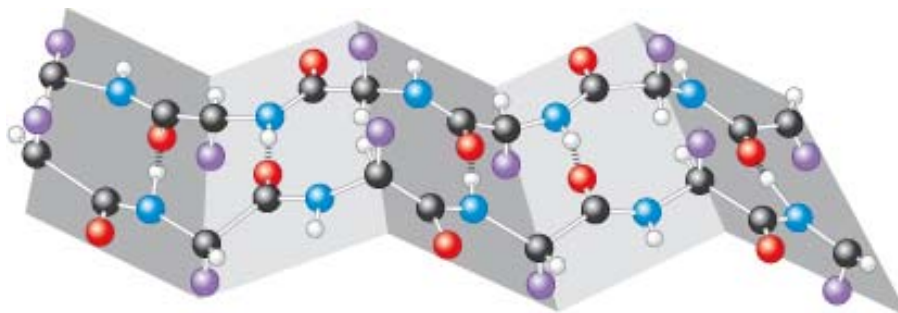


Figure 6: A  $\beta$ -pleated sheet showing the hydrogen bonds

#### Question 4

Look at Figures 5 and 6 showing protein structures. You will notice that the N-H---O hydrogen bonded system is almost linear. Explain this observation.

This is called the **secondary structure** and it is held in place largely by hydrogen bonds between amino acids, especially between the O of the C=O and the H of the N-H groups.

#### Hydrogen bonding

Hydrogen bonds are formed by a hydrogen atom being sandwiched between two highly electronegative atoms. Only fluorine, oxygen and nitrogen are sufficiently electronegative to form hydrogen bonds and, since there is no fluorine in proteins, this just leaves oxygen and nitrogen.

One of the two electronegative atoms is covalently bonded to the hydrogen and, because of its electronegativity, pulls the shared electron pair in the bond towards itself and away from the hydrogen. This leaves the hydrogen atom with a strong partial positive

charge which means that it is strongly attracted to a lone pair of electrons on the second electronegative atom and effectively forms a second covalent bond with it.

Hydrogen bonds are only about 5% to 10% of the strength of covalent bonds but because many thousands of them may form between protein chains or different parts of the same protein chain) they are highly significant.

### Question 5

**Draw a pair of amino acids and show the hydrogen bond as a dashed line between the O of the C=O and the H of the N-H group.**

### The structure of hair (4 of 4)

#### Salt formation

Look at the structures of the amino acids. You will see that some of them have side chains (the R groups) that are acidic or basic.

### Question 6

**Look at the 20 amino acids in Figure 3.**

**List those that have**

- acidic side chains and state the type of acid in the side chain in each case.**
- basic side chains and state the type of base in the side chain in each case.**

Another type of bonding that helps to hold the secondary structure of proteins is salt formation between amino acids with acidic and basic side chains. A proton ( $\text{H}^+$  ion) is transferred from the acid to the base forming a negative ion and a positive ion - these attract one another, Figure 7.

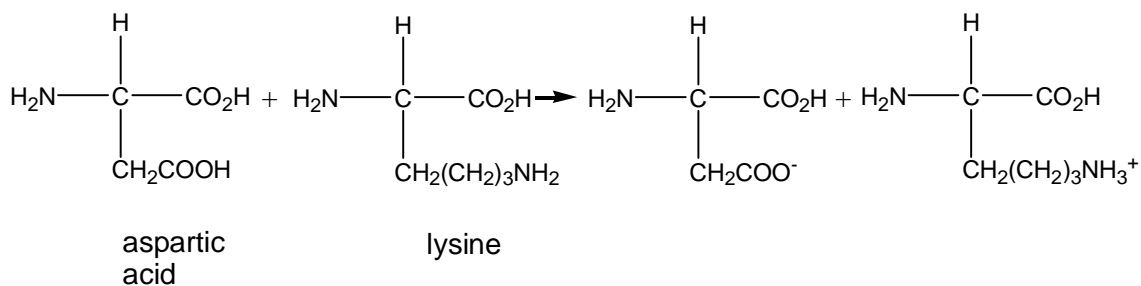


Figure 7: Salt formation

The protein keratin largely consists of an  $\alpha$ -helix. Furthermore two helices wind round each other rather like the strands of a rope. This is called the **tertiary structure** of the protein and is partly responsible for the fibrous nature of keratin. As well as hydrogen bonds and salt bonds, there is a third form of bonding that helps to hold the tertiary structure of keratin in place – sulfur-sulfur bonding.

#### Sulfur-sulfur bonding

Look at the structure of the amino acid cysteine, Figure 8.

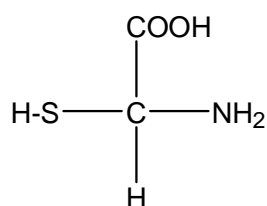


Figure 8: Structure of cysteine

You will see that its side chain has a S-H group. In certain circumstances, two cysteine molecules can link by the formation of a S-S bond between these two S-H groups. These S-S bonds are often called disulfide bridges.

The resulting 'double' amino acid is called cystine. (Take care, the two names are confusingly similar.) Forming the S-S bond involves the removal of two hydrogen atoms and so it is an oxidation process and requires an oxidising agent, represented here by [O], Figure 9.

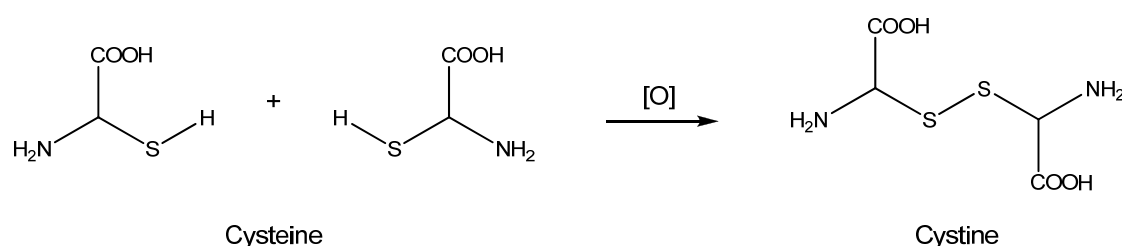


Figure 9: Disulfide bridge formation

This reaction can be reversed by using a suitable reducing agent.

### Dissolving hair

Sulfur-sulfur bonds are relatively weak covalent bonds (bond energy  $266 \text{ kJ mol}^{-1}$  compared with  $347 \text{ kJ mol}^{-1}$  for C-C and  $413 \text{ kJ mol}^{-1}$  for C-H). However, they are much stronger than hydrogen bonds and can contribute significantly to holding the secondary and tertiary structures of proteins together.

As we have seen, hair keratin has an unusually high proportion of cysteine in its structure and sulfur sulfur bonds are highly significant. So the key to chemical hair removal is breaking the sulfur sulfur bonds using a suitable reducing agent.

The reagent chosen is thioglycolic acid, Figure 10, written as H-SCH<sub>2</sub>COO-H for short.



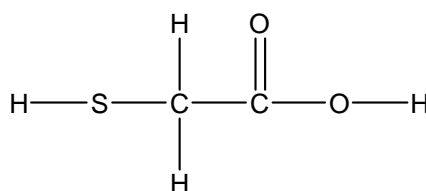


Figure 10: Thioglycollic acid

It is actually contained in the hair-removing product as potassium thioglycollate, Figure 11.

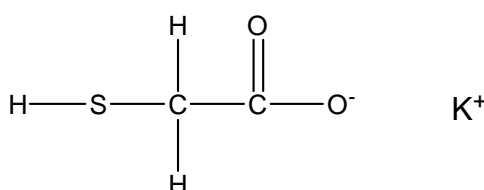
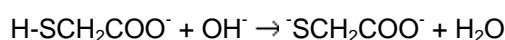


Figure 11: Potassium thioglycollate

This reacts with hydroxide ions (contained in the product as potassium hydroxide) to form a dianion



### Question 7

- The potassium ion is not drawn in the equation above. Why is this?
- What is the name for ions such as this potassium ion?
- Assuming all the species in the equation above are in aqueous solution, write the expression for  $K_c$  for this equilibrium.
- To dissolve hair most effectively we require a high concentration of the dianion. How can we bring this about? Explain your answer.
- In an aqueous solution, what can we say about the term  $[\text{H}_2\text{O}_{(l)}]_{\text{eqm}}$ ?

It is this dianion of thioglycollic acid, in which a proton ( $\text{H}^+$  ion) has been removed from both the  $-\text{COOH}$  group and the  $-\text{SH}$  group, that is the active reducing agent. To generate it we need a concentrated alkaline solution to provide  $\text{OH}^-$  ions.

### Why use thioglycollic acid? (1 of 2)

Thioglycollic acid is a reagent that you have probably not heard of. Why is this used to break the S-S bonds in cystine and why is it used in such an alkaline solution?

Cosmetic chemists have naturally carried out many experiments with different reagents at various pHs to find the best conditions for breaking the S-S bonds in cystine, Figure 12.

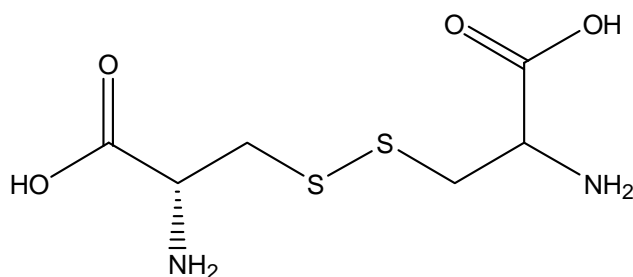


Figure 12 Structure of cysteine

The experimental set up is simple in principle. A hair fibre is wound over a hook and then clamped in place by a machine, so that it hangs vertically and the machine applies a downward force (typically a few newtons) to stretch the hair, see Figure 13. Normally hair is elastic, so when the stretching force is removed, the hair goes back to its original length (the technical term is that it 'relaxes').



Figure 13 The instrument used to assess depilatory products

### Question 8

- Suggest what properties of the bundle of hair need to be carefully controlled.
- What other factors apart from pH need to be controlled?

In the test to assess a depilatory product the hair is first stretched. Then the reagent to be tested is prepared, placed in a buffer solution to control its pH and applied to the hair. The machine adjusts the force on the hair to keep the length of the hair the same while the product works on it. As the hair becomes weaker, and wants to stretch more, then the machine reduces the applied force to maintain the hair's length. So the force applied to the hair decreases over time as the S-S bonds break. Eventually the hair itself breaks.

In effect, this procedure enables the reaction rate to be measured, because the sooner the hair breaks, the faster the reaction. The results show that the reaction appears to be first order with respect to the concentration of reagent used, and that, up to a point, it is faster at higher pH (*i.e.* more alkaline conditions).

### Question 9

**Explain what is meant by a first order reaction.**

### Why use thioglycollic acid? (2 of 2)

Typical results for the reagent ammonium thioglycollate are shown in Table 1. The concentrations of free amino acids produced from the hair protein by the reaction were measured and it was found that 63% of S-S bonds had been broken after 30 minutes of treatment with 1 mol dm<sup>-3</sup> ammonium thioglycollate at pH 7.5, for example.

pH	Relative reaction rate
8.0	1.0
9.0	3.0
9.4	4.9
9.5	4.1

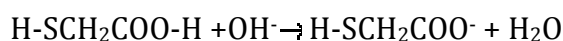
**Table 1:** The relative rates of reaction of ammonium thioglycollate with hair over a range of pHs.

Looking at experimental results enabled cosmetic chemists to choose the best reagent and conditions – thioglycollic acid in relatively alkaline conditions has proved suitable.

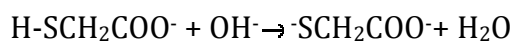
### Explaining the results

These results have been rationalised as follows

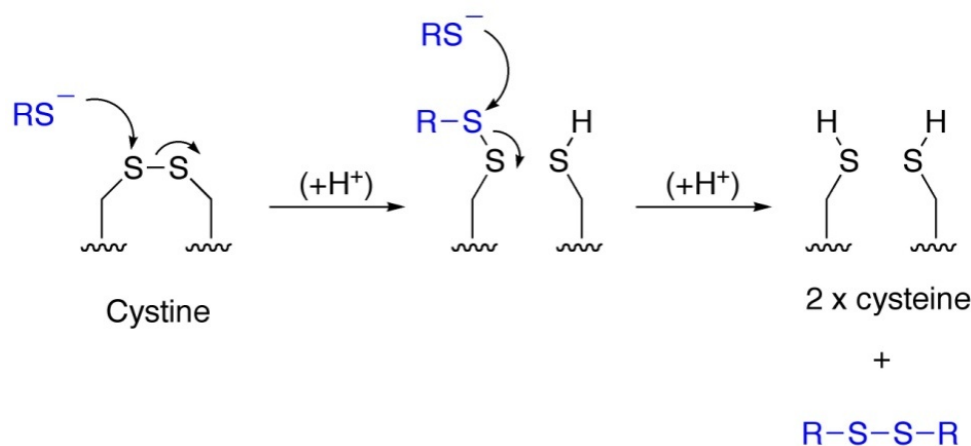
At a relatively low pH (*i.e.* fairly acidic conditions), thioglycollic acid loses a proton from its carboxylic acid group:



This reacts with hydroxide ions (contained in the product as potassium hydroxide) to form a dianion



It is the S<sup>-</sup> end of the dianion that is active in breaking the disulfide bridges. As we are only interested in this part of the molecule, we can simplify it to R'S<sup>-</sup> to save us having to write out the full structure each time. The reaction occurs in 4 stages;



**Figure 14: Mechanism of breaking the disulfide bridge in cystine**

- Nucleophilic attack by S in  $RS^-$  on one of the S atoms in cystine. This breaks the disulfide bridge in cystine and generates a new one between a cysteine molecule and the thioglycollate ion.
- The anion generated in step (a) strips a proton off water to generate a cysteine molecule.
- A second thioglycollate molecule attacks the first to break the just formed disulfide bridge and remake it between the thioglycollate molecules.
- The anion generated in step (c) strips a proton off water to generate the second cysteine molecule.

### Question 10.

**Explain why the lone pair electrons on sulfur are more available for donation than those on oxygen.**

The  $S^-$  on  $^-SCH_2COO^-$  acts as an even better nucleophile than the  $O^-$  on  $H-SCH_2COO^-$  for two reasons:

- The ion has a double negative charge
- The lone pair electrons on sulfur are more available for donation than those on oxygen.

### Application of Veet to the skin

To get a high concentration of thioglycollate anions, we need to increase the concentration of hydroxide ions. This poses a problem as  $OH^-$  ions can damage the skin. The answer to this is to minimise the time the alkaline solution is in contact with the skin.

Skin also contains proteins - including another type of keratin. Fortunately the 'soft keratin' of skin has less cysteine than the 'hard keratin' of hair (less than 5% cysteine compared with 14% for hair keratin). It therefore has fewer S-S bridges and is less susceptible to attack by thioglycollate.

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Notice that in the product a sulfur-sulfur bridge is formed between two thioglycollate ions, Figure 15.

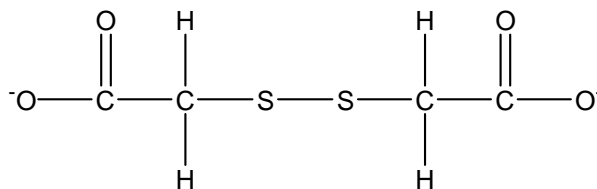


Figure 15: Disulfide bridge between two thioglycollate ions

The breaking of the sulfur-sulfur bonds loosens the links between the coiled protein chains of keratin and makes it less tightly held together.

The strongly alkaline solution has two further functions. Firstly it opens up the structure of the hair to allow the aqueous solution to penetrate and 'get at' the S-S bonds. Secondly it also affects other bonds within the keratin:

- Hydrogen bonds. These are broken because the strongly alkaline solution removes protons ( $H^+$  ions) from the  $-NH$  groups of amino acids along the protein chain so that they can no longer form hydrogen bonds (see question 3), thus 'loosening' the protein helix. In chemists' jargon, the  $-NH$  groups are 'deprotonated'.
- Salt bonds. These are disrupted by removal of  $H^+$  ions from  $-NH_3^+$  groups leaving neutral  $NH_2$  groups which are not attracted to  $-COO^-$  groups.
- Amide (peptide) bonds. Peptide bonds can be broken (hydrolysed, *i.e.* reacted with water) under alkaline conditions, thus breaking apart the protein chains themselves. In fact the keratin may be broken into strands as short as just a few peptides.

In another piece of jargon, chemists often refer to concentrated alkaline solutions as having a 'high pH'. This can be confusing at first until you remember that alkaline solutions have pHs above 7.

The overall effect of all these processes is to solublise the hair keratin.

Veet is applied to the skin as a cream or mousse, Figure 16, which is left on for a few minutes and then removed with a tool provided, usually a spatula or sponge. The physical action of the tool removes the dissolved hair from the surface of the skin. Any remaining product is then rinsed away with water.



### INGREDIENTS

Normal Skin Formula:

**Aqua, Urea, Cetearyl Alcohol, Potassium Thioglycollate, Calcium Hydroxide, Cetearth-20, PPG-15 Stearyl Ether, Magnesium Trisilicate, Potassium Hydroxide, Propylene Glycol, Lithium Magnesium Sodium Silicate, Paraffinum Liquidum, Prunus Dulcis, Acrylates Copolymer, Sodium Gluconate, Propylene Glycol Dicaprylate/Caprate, Nelumbo Nucifera Flower, Xanthan Gum, Phenoxyethanol, Methylparaben, Ethylparaban, Butylparaben, Propylparaben, Isobutylparaben, BHT, Hydrated Silica, Parfum, Linalool, Butylphenyl Methylpropional, CI 77891, CI 45380:3.**

Figure 16: Different formulation of Veet and sample ingredients

Potassium thioglycollate and potassium hydroxide are not the only ingredients, of course. Aqua is water and parfum is fragrance which is added to make the cream smell nice. Most of the other components are used to produce a cream that will dissolve the active ingredients, hold them on the skin for the requisite time and then be soluble enough to be rinsed off. Other ingredients include colours and moisturisers.

### Hair perming

The process of perming (short for 'permanent waving') of hair is based on the same chemical principles as hair removal.

Hair is placed in rollers to hold it into the required curly shape and a product containing alkaline glycollate ions, Figure 17, is applied to the hair which opens up its structure, breaks sulfur-sulfur bonds and 'loosens' the protein structure in a similar way to that described above.

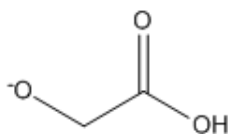
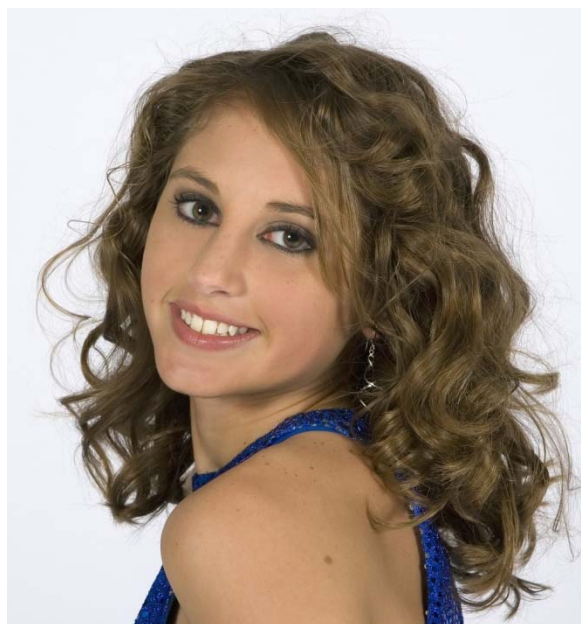


Figure 17: Structure of glycollate ion

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The difference is that an oxidising agent (usually hydrogen peroxide) is then applied to re-form the S-S bonds in new positions and 'lock' the hair permanently in its new shape, Figure 18.



**Figure 18: Permed hair is created using the same chemical principles as hair removal**

### **Further information**

Veet is sold in the UK by Reckitt Benckiser (<http://www.veet.co.uk/>). There are other depilatory products that work in a similar way.

### **Acknowledgements**

The Royal Society of Chemistry wishes to thank Chris Jones, Mike Eason and Tracey Caldwell of Reckitt Benckiser, who manufacture Veet for help in preparing this material.

The Royal Society of Chemistry gratefully acknowledges that this project was initially supported by Reckitt Benckiser in 2007. Reckitt Benckiser conducted a final review in 2013 so please note that certain information may be out of date.

## QUESTIONS AND ANSWERS

### Question 1

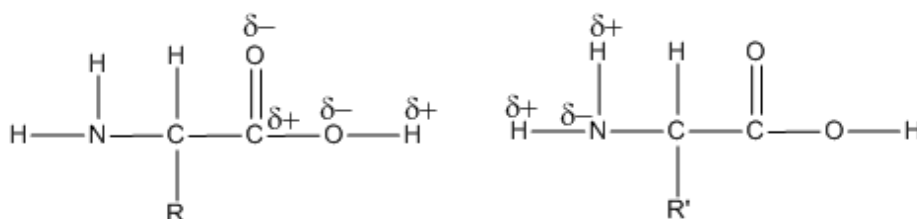
What is the systematic name of alanine?

2-aminopropanoic acid.

### Question 2

Figure 4 shows the formation of a dipeptide but not how it occurs. It is actually a nucleophilic substitution reaction (also called an addition-elimination reaction).

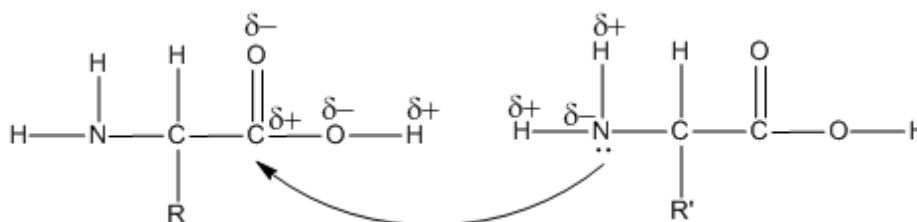
a) Using Figure 4 as a guide, draw the displayed structural formulae (*ie* showing all atoms and all bonds) of two amino acids. Show the polarities of the  $\text{-NH}_2$  and  $\text{-COOH}$  groups by drawing  $\delta^+$  and  $\delta^-$  on the appropriate atoms and also the lone pair on the N atom.



b) Which is the most electron deficient atom of the  $\text{-COOH}$  group? Explain your answer.

The most electron deficient atom is the C atom because it has two strongly electronegative  $\text{O}^{\delta-}$  atoms bonded to it.

c) Draw a 'curly arrow' to show the nucleophilic attack of the nitrogen atom on this carbon atom.



d) In this reaction, a molecule of water is lost. What name is given to this type of reaction?

A condensation or elimination reaction.

### Question 3

Hair keratin has up to 14% cysteine. What would be the proportion of cysteine (or any other amino acid) in a protein by chance if all amino acids were possible?

Remember there are 20 naturally-occurring amino acids.

5% because there are 20 amino acids, so by chance 5 out of every 100 would be cysteine.

### Question 4

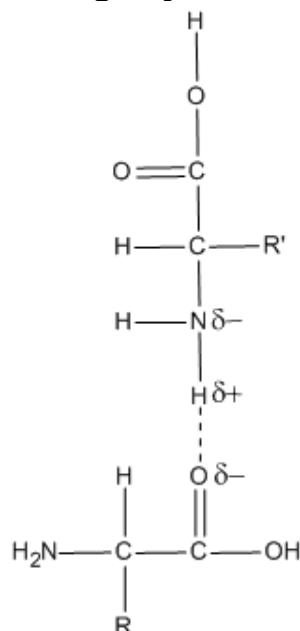
Look at Figures 5 and 6 showing protein structures. You will notice that the  $\text{N-H}\cdots\text{O}$  hydrogen bonded system is almost linear. Explain this observation.



When it is involved in hydrogen bonding, there are two electron pairs close to the hydrogen atom – the pair that forms the N-H covalent bond and the one that forms the H---O hydrogen bond. These repel each other and thus are situated 180° apart.

### Question 5

Draw a pair of amino acids and show the hydrogen bond as a dashed line between the O of the C=O and the H of the N-H group.



The hydrogen bond is shown by the dashes.

### Question 6

Look at the 20 amino acids in Figure 3.

List those that have

**a) acidic side chains and state the type of acid in the side chain in each case.**

serine, aspartic acid, glutamic acid (tyrosine has a phenolic side chain which would be a weaker acid than those above which have carboxylic acid side chains)

**b) basic side chains and state the type of base in the side chain in each case.**

tryptophan (secondary amine), histidine (secondary and tertiary amine), arginine (primary and secondary amine), lysine (primary amine).

### Question 7

**a) The potassium ion is not drawn in the equation opposite. Why is this?**

It takes no part in the reaction.

**b) What is the name for ions such as this potassium ion?**

Spectator ions.

**c) Assuming all the species in the equation above are in aqueous solution, write the expression for  $K_c$  for this equilibrium.**

$$K_c = \frac{[\text{SCH}_2\text{COO}^-(\text{aq})]_{\text{eqm}} [\text{H}_2\text{O}(\text{l})]_{\text{eqm}}}{[\text{H-SCH}_2\text{COO}^-(\text{aq})]_{\text{eqm}} [\text{OH}^-(\text{aq})]_{\text{eqm}}}$$

**d) To dissolve hair most effectively we require a high concentration of the dianion. How can we bring this about? Explain your answer.**

By increasing the concentration of  $\text{OH}^-$  ions. Le Chatelier's principle predicts that increasing  $[\text{OH}^-]$  will move the equilibrium to the right.

**e) In an aqueous solution, what can we say about the term  $[\text{H}_2\text{O}_{(l)}]_{\text{eqm}}$ ?**

It is constant.

### Question 8

**a) Suggest what properties of the bundle of hair need to be carefully controlled.**

The number of hairs in the bundle, their type, their length, their thickness, any prior treatment (e.g. bleaching), what animal they are from etc.

**b) What other factors apart from pH need to be controlled?**

Temperature, concentration of reagent etc.

### Question 9

**Explain what is mean by a first order reaction.**

A reaction whose rate is directly proportional to the concentration of the specified reactant.

### Question 10.

**Explain why the lone pair electrons on sulfur are more available for donation than those on oxygen.**

They are further from the nucleus than those on oxygen yet they feel approximately the same nuclear charge.