Advance warning

The following items needed for activities in this unit may not already be available in your school, and may need a little time to obtain.

Activity	Item(s)	Essential/Optional	Typical quantity per experiment
EP2.2	Searle 'Canderel' tablets	Essential	1–3 tablets
	Aspartic acid	Essential	Small amounts for chromatography
	Phenylalanine	Essential	Small amounts for chromatography
EP2.5	Spearmint chewing gum	Essential	Quarter of a piece
	Caraway seeds	Essential	10 seeds
EP2.7	* Plastic coated wire (eg Radio Spares 30 × 0.25 mm strand: code RS360239 to RS360295 depending on colour)	Essential	1 m
	* 'Minit' molecular model peg type a: Ref 7–a–293 (white) to 7–a–300 (green) depending on colour	Essential	30
	* 21 cm plastic tubes: Ref 7–2–289 (red)	Essential	8
EP6.1	* Glucose test strips (such as Clinistix™ or Diastix™)	Essential	5–10
EP6.4	Potassium peroxodisulphate(VI) ($K_2S_2O_8$)	Essential	100 mg

* Current suppliers are listed on the **Salters Advanced Chemistry Web Site**.

Molecular modelling software

The model-building activities in this unit will be greatly enhanced if students also have access to molecular modelling software (see **Salters Advanced Chemistry Web Site**).

Storyline: answers to assignments

1 a i Amino acids with non-polar side-chains are
Gly Ala Val Leu Ile Phe Pro (Trp Met)

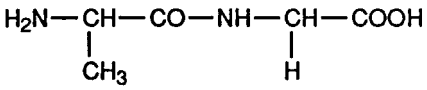
ii Amino acids with polar side-chains are
Ser Thr Cys Asp Glu Asn Gln Tyr His Lys Arg

iii Amino acids with ionisable groups on their side-chains are
Asp Glu His Lys Arg

b The side-chains in Leu and Ile cause them to be structural isomers.

c i Ser
ii Thr
iii Tyr
iv Either Asp or Glu

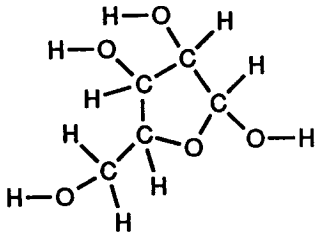
2 a



b i Ser **ii** Ala

3 a i Condensation **ii** Condensation

b



4 Only two bases are important in coding for:
Ser Leu Pro Arg Thr Val Ala Gly
Three bases are important for:
Phe Tyr Cys Trp His Glu Ile Met Asn Lys Asp Gln

5 a i Lys Lys Lys …
ii Arg Ala Arg Ala …
iii Tyr Leu Thr
b i ACC **ii** CUA or CUG

6 a GUCA
b GTCA

8 $K_c = \dfrac{[Ins_2]^3}{[Ins_6]}$ Units: $mol^2\ dm^{-6}$

Activities: notes and answers to questions

EP2.1 Investigating amines and amino acids

Safety note Information about hazardous chemicals is given on the activity sheet.

As preparation for this activity, it may help to ask students to think about how ammonia would behave in the four tests.

a Butylamine is soluble in water. It forms hydrogen bonds to water molecules.

b Butylamine solution is alkaline because of the reaction
$C_4H_9NH_2 + H_2O \rightleftharpoons C_4H_9NH_3^+ + OH^-$

c The smell of the amine is lost on addition of acid because the free amine is removed by the reaction
$C_4H_9NH_2 + H_3O^+ \rightarrow C_4H_9NH_3^+ + H_2O$

The amine is regenerated on addition of alkali
$C_4H_9NH_3^+ + OH^- \rightarrow C_4H_9NH_2 + H_2O$

d $[Cu(C_4H_9NH_2)_4(H_2O)_2]^{2+}$

e Vigorous effervescence. HCl is given off and a colourless solid is produced.
$C_4H_9NH_2 + CH_3COCl \rightarrow C_4H_9NHCOCH_3 + HCl$

f Sodium hydroxide solution hydrolyses the amide to produce butylamine.
$C_4H_9NHCOCH_3 + OH^- \rightarrow C_4H_9NH_2 + CH_3COO^-$
The moistened pH paper turns blue because of the reaction of butylamine with water in **b**.

g Glycine is soluble in water. It is largely present as zwitterions which are solvated by water resulting in ion–dipole interactions.

h Glycine solution is close to neutral (slightly acid)

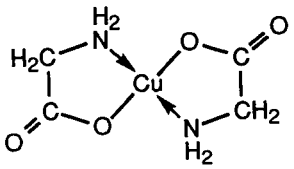
i The pH should remain fairly constant throughout the additions of acid and alkali. The theory is covered in the chemical ideas section on amino acids.

j Butylamine readily forms a dark blue insoluble complex, $[Cu(C_4H_9NH_2)_4(H_2O)_2]^{2+}\ SO_4^{2-}$
Glycine also complexes with copper ions and the solution turns dark blue. (Both the $-COO^-$ and $-NH_2$ groups can behave as ligands, though very few free $-NH_2$ groups are present in neutral solution.)

k Only butylamine reacts with ethanoyl chloride.

l Both dissolve in water although different types of interaction are involved.

m The zwitterion form of glycine is responsible for its different behaviour. There is no $-NH_2$ group with its lone pair of electrons to react with the acid chloride or the $Cu^{2+}(aq)$ ions. The zwitterion can be either a proton donor or a proton acceptor in solution. (Glycine forms the copper complex solutions when the free $-NH_2$ group is present.)

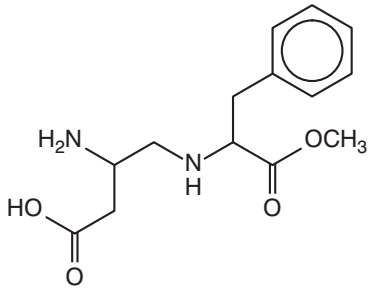


n Only relatively weak intermolecular forces (dipole–dipole forces, dipole–induced dipole forces and hydrogen bonds) between molecules of butylamine. Glycine exists as zwitterions with strong ionic forces between molecules.

EP2.2 What's in aspartame?

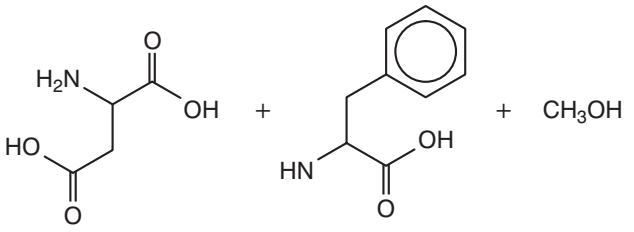
Safety note Information about hazardous chemicals is given on the activity sheet.

Check that the artificial sweetener you use contains aspartame and not saccharin. Also, avoid aspartame tablets such as Hermesetas which also contain leucine.
Peptide hydrolysis normally requires reflux for several hours with moderately concentrated acid, eg 4 mol dm^{-3}. It is possible to get adequate results after 30 minutes reflux with 4 mol dm^{-3} HCl, and after 4 hours with 1 mol dm^{-3} HCl. You can speed up the process by using two or three tablets.
It is important that hydrolysed aspartame is checked against *both* amino acids. Aspartame itself, being only a dipeptide, will travel along the paper, and could be confused with an amino acid. Also, some tablets contain phenylalanine along with the aspartame.



aspartame

acid hydrolysis



aspartic acid *phenylalanine* *methanol*

EP2.3 Using nuclear magnetic resonance (n.m.r.) spectroscopy for structure determination

Part 1: N.m.r. spectra of simple organic compounds

a ii Answers are best presented in table form:

Compound	Chemical shift	Relative number of H atoms	Type of hydrogen
Ethanol	1.2	3H	CH_3
	3.4	1H	OH
	3.7	2H	CH_2
Ethanal	2.2	3H	CH_3
	9.8	1H	CHO
Ethanoic acid	2.1	3H	CH_3
	11.8	1H	COOH

b ii A Propanal: the signal at 9.7 suggests an aldehydic **H** atom (cf Figure 2).

B Propionic acid: the signal at 12.0 suggests an **H** atom in a carboxylic acid (cf Figure 3).

C Propanone: there is only one signal, at 2.1 due to C**H**$_3$.

D Propan-1-ol: the signal at 3.2 suggests an alcohol (cf Figure 1).

However, the C**H** signals for **A**, **B**, **D** should be analysed to check that they confirm these identifications.

c ii

Compound	Chemical shift	Shape of signal	Relative number of H atoms	Type of hydrogen
Aminoethane	1.1	triplet	3H	CH_3
	2.7	quartet	2H	CH_2
	3.6	broad	2H	NH_2
1-Aminopropane	0.9	triplet	3H	CH_3
	1.4	multiplet	2H	CH_2
	1.8	broad	2H	NH_2
	2.7	triplet	2H	CH_2 (adjacent to NH_2)
Propanamide	1.1	triplet	3H	CH_3
	2.2	quartet	2H	CH_2
	6.2	broad	2H	NH_2

Part 2: N.m.r. spectra of other nitrogen-containing compounds

d E At 2.0 C**H**$_3$ (singlet) (adjacent to –CO–)

At 6.7 and 7.4 Two environments for each of two pairs of hydrogen atoms in an aryl ring.

Suggests structure

where X and Y are different groups.

At 9.1, 9.7 the phenol –O**H** and the amide –N**H**– groups.

Thus **E** is **2**.

F At 1.3 C**H**$_3$ (triplet)

At 3.4 N**H**$_2$ (only a single peak)

At 3.9 C**H**$_2$ (triplet) (adjacent to oxygen)

At 6.6 and 6.7, two environments for each of two pairs of hydrogen atoms in an aryl ring, a structure of

Thus **F** is **1**.

G At 2.0 C**H**$_3$ (singlet) (adjacent to –CO–)

At 6.4, 6.9, 7.0, 7.2 – four different environments for the aryl hydrogens.

At 9.3, 9.8, the phenol –O**H** and the amide –N**H** groups.

Thus **G** is **3**.

e One would expect

i.r. 1450–1650 cm^{-1}: Aryl C–H (several peaks)

1630–1700 cm^{-1}: Amide (C=O)

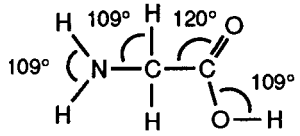
3200–3600 cm^{-1}: Phenol (–OH) (broad)

ca 3500 cm^{-1}: Amide (–NH–)

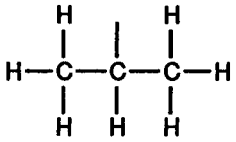
EP2.4 The shapes of α-amino acids

The model building in step **3** can be shared round members of a group to save time. If you have molecular modelling software this can be used to good effect alongside the model kits, and students can be given print-outs of say, D-alanine and L-alanine at the end of the session.

1

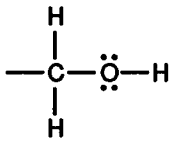


2 a



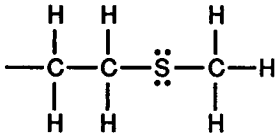
all angles 109°

b



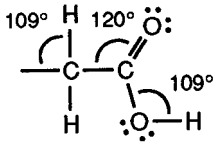
all angles 109°

c



all angles 109°

d

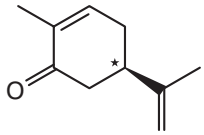


EP2.5 A testing smell

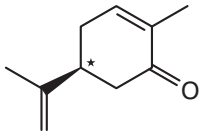
The smell of rubber bungs can mask the smell of the carvones. It is better to use plastic stoppers or clingfilm.

a Carbonyl (C=O) and alkene (C=C)

b i and **ii**



L-carvone



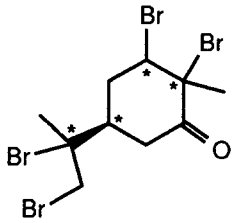
D-carvone

c i $C_{10}H_{14}O$

ii $C_{10}H_{14}OBr_4$

iii Yes, there are only differences when the other reactant is also optically active.

iv



v There are four chiral centres as shown.

d The receptors are chiral, so the enantiomers will interact differently.

EP2.7 Modelling DNA

Students gain a much better understanding of the structure of DNA if they build models of the bases and the double helix. By doing this activity they should also realise that hydrogen bonding and instantaneous dipole–induced dipole forces are important for holding the structure together.

a **i** Sugar–phosphate backbone
ii Base pairs

b The centre of the double helix is 'full'; there is no empty space. This contrasts with the traditional 'ladder' representation of DNA which gives the mistaken impression that there are large gaps between the bases.

c The helix could not be twisted more tightly because the bases are already at their closest.

d Instantaneous dipole–induced dipole bonding.

e Less twisting would take the bases further apart and the structure would lose the instantaneous dipole–induced dipole bonding. This bonding may be weak between any pair of bases, but it is significant over the whole polymer.

EP2.8 Life reveals its twisted secret

This activity allows students to practise their communication skills. It also allows them to see scientists as real people, and to get an idea of how one group of them worked. Students may like to go on to read *The Double Helix* in full: J.D. Watson, *The Double Helix* 1968. With new Introduction, 1999 (Penguin Books, London).

The story of the discovery of DNA illustrates the multidisciplinary nature of this area of research. The key to the chemistry was understanding the structure of the bases and the way they hydrogen bond with each other.

EP6.1 Testing for glucose

Safety note Information about hazardous chemicals is given on the activity sheet.

In a simple experiment, the test strips could be placed in dilute acid or alkali, or in boiling water, before use to prove that these conditions deactivate the enzyme. More careful investigation might make use of solutions of different pH or water at different temperatures, and students might try to time how long a particular depth of colour takes to develop. The pH of urine is 4.8–7.5.

The enzyme has no effect on other sugars.

The use of test strips makes this activity quicker and more convenient than some other methods of studying enzyme catalysis. They can, however, be expensive for large groups. It helps to cut the test strips into thinner pieces.

EP6.2 Succinate dehydrogenase (optional extension)

Pentanedioic acid can fit onto the two marked COOH sites but the CH_2 groups are positioned differently from those in butanedioic acid. Students should predict that the substrate will bind to the enzyme but that it will be an inhibitor since it cannot be oxidised.

EP6.3 The effect of enzyme and substrate concentration on the rate of a reaction

Advance preparation

The yeast suspension must be made up and aerated for several hours before the lesson.

a and **d** The rate of reaction is greatest at $t = 0$. It falls as the reaction proceeds until it becomes zero at the end of the reaction. The rate depends on $[H_2O_2]$ which is greatest at the start of the reaction and falls to zero at the end.

b The initial rate depends on the starting concentration of hydrogen peroxide. It is high when the initial concentration of hydrogen peroxide is high.

c If the experiment has been done carefully, it should be possible to obtain a straight line showing the reaction is first order with respect to hydrogen peroxide.

e The initial rate depends on the starting concentration of enzyme. It is high when the initial concentration of hydrogen peroxide is high.

f The reaction is first order with respect to catalase.

EP6.4 Using the iodine clock method to find the order of a reaction

Safety note Information about hazardous chemicals is given in the activity sheet.

b Iodide concentrations vary from 0.5 mol dm^{-3} to 0.1 mol dm^{-3}. The corresponding times should be between about 80 s and 400 s.

c I^- is always in excess.

d 8×10^{-5} mol I_2 can be produced in each case.

e **i** 2×10^{-5} mol $S_2O_3^{2-}$
ii 1×10^{-5} mol I_2
iii 12.5% of the total reaction is studied.

g The reaction is first order with respect to iodide.

h **i** Rate $= k[I^-]\,[S_2O_8^{2-}]$ **ii** Second order
iii The value of k depends on the temperature.

$$k = \frac{\text{Rate}}{[I^-]\,[S_2O_8^{2-}]}$$

$\frac{\text{Rate}}{[I^-]}$ can be found from the gradient of the graph.

Units of k are $dm^3\ mol^{-1}\ s^{-1}$

EP6.5 Enzyme kinetics

a At high substrate concentration the process is almost zero order with respect to the substrate.

b If the first step in the mechanism were the rate determining step, the rate of the reaction would depend on [S]. (It would be first order with respect to the substrate.)

c At saturation, [ES] will be constant, and so the rate of conversion of bound substrate to unbound product (ES → P + E) remains constant. It is independent of [S], ie the reaction is zero order with respect to substrate.

d At lower substrate concentrations, the rate at which the substrate binds to the enzyme decreases as the [S] falls. Enzyme active sites will no longer be full. The stage E + S → ES eventually becomes rate determining and the reaction becomes first order with respect to substrate.

e The reaction is always first order with respect to enzyme.

f The enzyme concentration is always low compared with the substrate concentration. The concentration of ES formed depends on [E]. So the rate always depends on the enzyme concentration, no matter which step is rate determining.